A Textbook of
Chemical Engineering Thermodynamics

SECOND EDITION

K.V. NARAYANAN
Former Professor and Head
Department of Chemical Engineering
and
Former Principal
Government Engineering College
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A TEXTBOOK OF CHEMICAL ENGINEERING THERMODYNAMICS, Second Edition
K.V. Narayanan

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Preface

The main concern of the author while writing the first edition of *A Textbook of Chemical Engineering Thermodynamics* was to provide a student-friendly book on the subject of thermodynamics which was considered by many in the academic circles, as a difficult subject consisting of abstract and difficult-to-conceptualize ideas, principles and variables. Within a very short period after its publication, the book received wide acceptance among the faculty and students of Chemical Engineering and related disciplines. This prompted the author to bring out this second edition retaining the basic structure, sequence, philosophy and style of presentation.

Several changes and corrections were made in previous reprints of the first edition based on readers' feedback. Suggestions have also been made to include more number of worked-out examples illustrating the applications of the laws of thermodynamics. Therefore, in this edition, worked-out examples have been added in almost all Chapters to make the abstract concepts of thermodynamics more clear to the readers. More than 25 such worked-out numerical examples and a few exercise problems are incorporated in the new edition. The Chapter on Phase Equilibria is revised recognizing the importance that the Equations of State Approach and vaporization equilibrium constants for solving vapour-liquid-equilibrium problems have attained recently due to the increased use of simulation packages in the design of process units. More than 90 **GATE questions** with answers have been added to the Appendix in Objective Type Questions on Chemical Engineering Thermodynamics, taking the total number of such questions to 236, which will definitely be a boon to the candidates preparing for competitive examinations.

The author believes that with the improvements made, the second edition will retain the strength of the first edition that so many people have appreciated and commented. Many Universities have accepted the earlier edition as a textbook or reference book for their course study in Chemical Engineering or related branches of Engineering, such as Biotechnology and Biochemical Engineering Petroleum Engineering, Fire and Safety Engineering, Electrochemical Engineering, Polymer Scienc and Engineering, Environmental Engineering etc. The author is grateful to all the academicians who have shown interest in the book and the faculties who have come forward with valuable suggestions for improvement and hope their continued patronage for the present work as well. He would also like to acknowledge the valuable service of the editorial and marketing team at PHI Learning, Delhi for making the work a commendable success.

The author is also grateful to the readers for their interest and hope that they will continue to make suggestions for improvement of the book.

K.V. NARAYANAN

Preface to the First Edition

The field of chemical engineering is conventionally classified into two broad categories: the *unit operations* and the *unit processes*. The former involves physical transformation and the latter chemical changes. The chemical engineer, whether he is concerned with the unit operations or with the unit processes has to evaluate the energy requirements for initiating these transformations, study the energy changes involved in such processes, and determine the extent to which these transformations can be carried out. The science of thermodynamics deals exactly with these problems and a strong foundation in thermodynamics is therefore a *must* for the success of a chemical engineer in his professional life.

Chemical engineering thermodynamics is one of the core courses in the undergraduate chemical engineering curriculum. In this course, more emphasis is given to the treatment of properties of solutions, phase equilibria and chemical reaction equilibria, all coming under the realm of ‘chemical thermodynamics’ rather than on the thermodynamic analysis of heat engines and heat-power cycles. The conventional textbooks on thermodynamics are, therefore, inadequate to meet these requirements. Hence the need for a book on thermodynamics that deals exclusively with the theory and applications of chemical engineering thermodynamics.

During the several years of my experience in teaching thermodynamics to the undergraduate students, I have come across students who have strong ‘likes’ and ‘dislikes’ toward the subject. Unfortunately, the latter frequently outnumber the former. The seemingly abstract nature of thermodynamic principles is only partly to blame for this scenario. The major reason is the dearth of student-friendly textbooks that help the student in providing a sound basis and act as catalysts for going deeper into the subject. An unwilling student should not be compelled to studying the vast subject of thermodynamics, without giving him or her a proper orientation. These inadequacies of the existing books on the subject have been kept in mind while writing this book. An earnest attempt has been made to eliminate avoidable rigour and intricacies that usually make the subject dry. Instead, the book tries to provide a firm foundation in the theory through the application of the fundamentals to solve practically important problems.

This book is intended to serve as a textbook for the undergraduate students in chemical engineering and other related branches of engineering such as polymer engineering, petroleum engineering, and safety and environmental engineering. Numerical examples given under each section would help the student gain a better insight into the theory. In this text, only SI units used. Review questions at the end of the chapters would help the student check his/her understanding of the topics discussed in each chapter before going to the next. Each chapter is provided with a number of exercise problems, and answers to all of them are given at the end of the book. A number of objective-type questions are included in the Appendix: ‘An Aptitude Test in Chemical Engineering Thermodynamics’. The studen would find these very helpful in preparing for competitive examinations. Most of the questions presented in this section are taken from earlier Graduate Aptitude Test in Engineering (GATE) question papers.

This book is the outgrowth of the several lectures I have delivered to the chemical engineerin students in the Government Engineering College, Thrissur. The response from the students who benefitted from these lectures was a major source of inspiration for writing this book. Valuable help and suggestions at various stages in its evolution have contributed towards bringing it out in the present form. My colleagues at the Government Engineering Colleges at Thrissur and Calicu provided a helpful environment for undertaking this work and I am very grateful towards all of them. I recall with gratitude the stimulating experience I spent at IIT Madras during my research work under Prof. M.S. Ananth, which contributed much in sustaining my interest in the subject of thermodynamics. I am thankful to the Director of Technical Education, Kerala and the Government of Kerala for granting me permission to publish the book. And my special thanks are due to my wife Lakshmi for her suggestions for improving the quality and content of the book as also for the cooperation in accommodating the lengthy hours that I spent during the preparation of the manuscript. Thanks are also due to my daughter Aparna for her patience and understanding even when I could not attend to her due to my preoccupation in this book-writing project.

Comments, constructive criticism and suggestions for improving the quality of the book would be gratefully accepted.

K.V. NARAYANAN

1

Introduction and Basic Concepts

The science of thermodynamics deals with energy and its transformation. It tells us about the direction in which changes take place in nature. It also determines the conditions under which a proposed change attains a state of equilibrium—a state in which no further change is possible under the given conditions. Original thermodynamic formulae were applied to a limited class of processes such as those occurring in heat engines. Thermodynamic analysis is now applied to a wide variety of problems covering both physical and biological sciences. Thermodynamics finds extensive applications in chemical engineering. The field of chemical engineering is commonly divided into two: *unit operations* and *unit processes*. The former involves only physical transformation such as gas absorption, distillation, heat transfer, and filtration, whereas the latter consists of the combination of the physical changes with chemical processes such as oxidation, nitration, and catalysis. In chemical processes, like the synthesis of ammonia from a mixture of nitrogen and hydrogen, thermodynamics enables us to determine the maximum yield of ammonia obtained under given conditions of temperature and pressure. In a unit operation like distillation, it predicts the minimum reflux ratio provided in the fractionation column to achieve a specified separation. The fundamental problems that a chemical engineer encounters, whether they are related to unit operations or to unit processes, involve two basic aspects of a change—the equilibrium and the rate of change. The strength and limitations of thermodynamics will become obvious when we try to find answers to these problems.

1.1 SCOPE AND LIMITATIONS OF THERMODYNAMICS

The heat and work effects accompanying a physical or chemical process can be accurately predicted using thermodynamic calculations. What is the maximum work obtained from a specified change in the state of the system? Or, what is the minimum work required to effect a certain change in the system? What is the efficiency with which work is produced when a certain fuel is burned in a steam engine? The answers to these questions are readily provided by thermodynamics.

Thermodynamics sets certain limits to the various processes occurring in nature. It also helps us to determine *a priori* whether a proposed process is possible or not. Since it deals with the direction of change and equilibrium, it enables one to calculate the equilibrium conditions for both physical and chemical changes. For example, thermodynamics can predict the equilibrium yield in a chemical reaction and also gives insight into the driving force for the change under the given conditions of temperature and pressure. The equilibrium yield gives the engineer an ultimate value that he strives to attain by trying improvements in the process. Attempts to cross these limits have all been futile as is evident from the history of the evolution of blast furnace technology for iron making.

In the blast furnaces, iron is produced by reduction of iron oxide by carbon monoxide.

$$\mathrm{Fe_2O_3 + 3CO} \ \square\ \mathrm{2Fe + 3CO_2}$$

In the early years of the development of blast furnace technology, the presence of carbon monoxide in the effluent gases was thought to be due to insufficient contact time in the furnace. To improve the time of contact of coal with the ore, furnaces as tall as 30 to 40 m were built, but the conversion could not be improved. The concept of equilibrium conversion was not recognised at that time. Later, with the application of thermodynamics to chemical reaction equilibrium, it became clear that in a chemical reaction conversions above the equilibrium value could never be attained in practice. Apart from predicting the equilibrium yield, thermodynamics also helps us to derive information on the possible side reactions and methods of eliminating undesired products. It can also help us in selecting the optimum conditions for the reaction such as the temperature, pressure, concentration of reactants, etc.

Though thermodynamics can tell us whether a chemical reaction is possible or not, it cannot say whether a possible reaction will actually occur or not. The rate of any process may be written as the ratio of the driving force to resistance. Thermodynamics can tell us about the driving force, but resistance to flow of energy or material introduces questions of mechanisms that are outside its scope. Consequently, it cannot say at what rate the system approaches equilibrium. That is, thermodynamics cannot predict whether a specified change will take place in a reasonable period of time or not. As an example, consider the unit operation of gas absorption. The driving force for the absorption of a gas in a liquid, the energy requirements, the minimum amount of absorbing liquid required, etc., could be determined from thermodynamic considerations. But the rate of absorption is influenced by many other factors that are alien to thermodynamics. Thermodynamics can predict the minimum work required in a process, but the actual work requirement can be determined only if we know the losses like friction that are unavoidable.

Not withstanding these limitations, thermodynamics remains a powerful and universal tool with the engineer. It enables us to calculate the maximum amount of work a given fuel can produce in a steam engine, the maximum efficiency of a turbine or a refrigerator and the maximum yield in a given chemical reaction. It also helps us in establishing the optimum range of temperatures and pressures that are to be used in a chemical or physical process and it guides us in the choice of solvent to be used in such separation operations as gas absorption and liquid extraction.

1.2 DEFINITIONS AND FUNDAMENTAL CONCEPTS

1.2.1 Systems and Processes

System. In thermodynamics, a substance or group of substances in which we have special interest is called a *system*. It is that part of the universe which is set apart for our special consideration. It may be a reaction vessel, a distillation column, or a heat engine.

Process. The changes taking place within the system is referred to as a *process*. Thus, hydrocarbon fuel and oxygen in a combustion chamber constitute the system and the combustion of fuel to form water and carbon dioxide constitutes a process.

Surroundings. The part of the universe outside the system and separated from the system by boundaries is called *surroundings*. The boundaries may be either physical or imaginary; they may be rigid or movable. For practical reasons, the surroundings are usually restricted to that portion of the universe which is in the immediate vicinity of the system and are affected by changes occurring in the system. For example, when the steam condensing in a shell-and-tube heat exchanger is treated as the system, the cooling water to which the latent heat of vaporisation is transferred may be treated as the surroundings.

1.2.2 Homogeneous and Heterogeneous Systems

Homogeneous system. This system is also called a *phase*. Here the properties are the same throughout or the properties vary smoothly without showing any surface of discontinuity. Liquid water in a beaker and a column of dust-free air above the earth's surface are examples of homogeneous system.

Heterogeneous system. This is a system which consists of two or more distinct homogeneous regions or phases. There is a sudden change in properties at the phase boundaries. A liquid mixture of benzene and water forms a heterogeneous system made up of two immiscible liquid phases. Water and water vapour taken in a closed container is another example of a heterogeneous system. Systems consisting of only gases and vapours are always homogeneous. With liquids, two phases are common, and with solids any number of different phases are possible.

1.2.3 Closed and Open Systems

Closed system and open system. Systems that can exchange energy with the surroundings but which cannot transfer matter across the boundaries are known as *closed systems. Open systems,* on the other hand, can exchange both energy and matter with their environment. In a multiphase system, each phase is open since material is free to enter and leave each phase, although the system as a whole may be closed to the flow of matter. A batch reactor is a closed system while a tubular flow reactor is an open system. Cyclical processes, like power and refrigeration cycles are closed systems when considered as a whole, whereas each component of the cycle such as compressor, pump, and heat exchanger is open.

Isolated system. This is a system, which is totally unaffected by the changes in its environment. Neither energy nor matter can cross the boundaries of an isolated system. A closed system is *thermally isolated*, when the enclosing walls are impervious to the flow of heat; it is *mechanically isolated*, when enclosed by rigid walls, and is *completely isolated,* when neither material nor energy in any form can be added to it or removed from it. A perfectly isolated system is an ideal concept that cannot be attained in practice. The system and surroundings considered together constitute an isolated system. Thus, the universe can be treated as an isolated system.

1.2.4 State and Properties

Certain specifications such as pressure, volume, and temperature are necessary to define the conditions of a given system. The condition defined by such specifications is called the *state* of the system. The variables used to define the state are called the *state functions* or the *properties* of the system. The minimum number of such variables required to represent the state uniquely depend on the number of phases constituting the system and the number of distinct chemical species present in the system (see the phase rule). The properties generally used to represent the state of a homogeneous system consisting of a single substance are the pressure, the volume, and the temperature. However, any one of these three properties depends upon the other two. Thus, if two properties, say, pressure and the temperature are specified, all other physical properties, e.g. density, viscosity, refractive index are thereby definitely fixed. Thus, thermodynamic properties serve to define the state of a system completely.

1.2.5 Intensive and Extensive Properties

The *extensive properties* depend on the quantity (or extent) of matter specified in the system. Mass and volume are extensive properties. The total value of any extensive property is the sum of the values of the property of individual components into which the system can be subdivided. An *intensive property* is independent of the size of the system. Pressure, temperature, specific volume, density, etc., are intensive properties. Some intensive properties are derived from the extensive properties by specifying the unit amount of the substance concerned. Examples are specific volume, specific heat, and density. Heat capacity is an extensive property, while specific heat is an intensive property. As the intensive properties are independent of the amount of the substance, they describe specific characteristics of a substance in a given state.

1.2.6 State and Path Functions

State functions. Properties of a substance describe its present state and do not give a record of its previous history. They are *state functions* in the sense that they are fixed for a particular state of the system and do not in any way depend upon the past history or the path by which the state was arrived at. When a system is considered in two different states, the difference in property between the two states depends solely upon those states themselves and not upon the manner in which the system changes from one state to the other. For example, DM, the change in some property M of the system as it changes from state 1 to state 2, is always the same regardless of the process by which the change is brought about. For a cyclic process, the initial and final states are the same and the change in the property DM will be zero.

Path functions. The values of heat and work accompanying a given change in state vary with the path from the initial to the final state. For example, some mass of hydrocarbon may be completely burnt in air at constant volume in a combustion chamber. All the energy lost by the system appears as heat, no work being done. In contrast, a large part of the energy of the hydrocarbon-air system is converted to mechanical work and only the remainder into heat in an internal combustion engine. It means that the heat and work involved in a given change of state are not to be determined solely by the initial and final states; they also depend on the manner in which the change is carried out. Heat and work are therefore not thermodynamic properties of the system. They are properties of the process and are called *path functions*.

1.3 FORCE, PRESSURE AND ENERGY

1.3.1 Force

According to Newton's second law of motion, the force acting on a body is directly proportional to the time rate of change of momentum. For a body of constant mass, Newton's law reduces to

$F = cma$

where F is the force, m is the mass of the body, a is the acceleration, and c is a proportionality constant. In the SI system, the constant c is unity and we have

$F = ma$ (1.1)

When a body of mass 1 kg is accelerated by 1 m/s^2, the force acting on the body is 1 kg m/s^2, which is designated as 1 newton or (1 N).

EXAMPLE **1.1** A man circling the earth in a spaceship weighed 300 N at a location where the local gravitational acceleration was 4.5 m/s^2. Calculate the mass of the man and his weight on the earth where the gravitational acceleration is 9.81 m/s^2.

Solution Force is equal to the product of mass and acceleration, i.e.

$F = ma$

or

$300 = m \square 4.5$

Therefore,

$$m = \frac{300}{4.5} = 66.67 \text{ kg}$$

The weight on the earth is the force acting on the object on the earth.

$F = 66.67 \square 9.81 = 654$ N

1.3.2 Pressure

Pressure is defined as the normal component of the force per unit area exerted by the fluid on a real or imaginary boundary. The unit of pressure in the SI system is newton per square metre (N/m^2), also called the pascal (Pa). A multiple of pascal, called the bar*,* is also used as a unit of pressure.

1 bar = 10^5 Pa = 10^5 N/m^2

The pressure exerted by the atmosphere is called the *atmospheric pressure* and it varies with location and elevation on the earth's surface. One standard atmospheric pressure abbreviated as atm is used in all system of units as an empirical unit of pressure. It is the average pressure exerted by the earth's atmosphere at sea level. Pressure is sometimes expressed in terms of the height of the column of mercury, which it will support at a temperature of 273 K in a standard gravitational field. At standard atmospheric pressure this height is 0.76 m (760 mm or 760 torr) with density of mercury taken as $13.5951 \square 10^3$ kg/m^3.

1 standard atmosphere (atm) = 1.01325 bar = $1.01325 \square 10^5$ Pa

= $1.01325 \square 10^5$ N/m^2 = 760 mm Hg

EXAMPLE **1.2** A special manometer fluid has a specific gravity of 2.95 and is used to measure a pressure of 1.15 bar at a location where the barometric pressure is 760 mm Hg. What height will the manometer fluid indicate?

Solution If h is the height of the manometer fluid, the mass of the fluid is

$$m = h\rho A$$

where ρ is the density of the liquid and A is the area of cross-section of the column of liquid. The force exerted by the fluid is

$$F = ma = h\rho Ag$$

where g is the acceleration due to gravity.
The pressure exerted by the fluid is

$$\frac{F}{A} = h\rho g$$

This should be equal to the difference in pressures between the two ends of the manometer (ΔP) when the manometer indicates a steady reading.

$$\Delta P = h\rho g \qquad (1.2)$$

Here,

$$\Delta P = P_1 - P_2$$

$$P_1 = 1.15 \text{ bar} = 1.15 \times 10^5 \text{ N/m}^2$$

$$P_2 = 760 \text{ mm Hg} = 1.01325 \text{ bar} = 1.01325 \times 10^5 \text{ N/m}^2$$

$$\Delta P = 1.15 \times 10^5 - 1.01325 \times 10^5 = 0.13675 \times 10^5 \text{ N/m}^2$$

Therefore,

$$0.13675 \times 10^5 = h\rho g = h(2.95 \times 10^3) \times 9.8067$$

Thus,

$$h = \frac{0.13675 \times 10^5}{(2.95 \times 10^3) \times 9.8067} = 0.4727 \text{ m} = 472.7 \text{ mm}$$

1.3.3 Energy

Work. Energy is expended in the form of work when a force acts through a distance. Thus,

$$dW = F\,dZ \qquad (1.3)$$

where W is the work done, F is the force acting, and Z is the displacement. The unit of work in the SI system is N m (newton metre) or J (joule).

Let us consider the expansion or compression work in a cylinder, an important quantity in engineering thermodynamics. Assume that a gas is confined in a cylinder and let the pressure of the gas be P and volume V. If the surface area of the piston exposed to the gas is A, the force acting on the piston is

$$F = PA \qquad (1.4)$$

The displacement of the piston in the direction of the force dZ is related to the change in volume dV of the gas as

$$dZ = \frac{dV}{A} \qquad (1.5)$$

Substituting Eqs. (1.4) and (1.5) in Eq. (1.3), we get

$$dW = P\,dV \qquad (1.6)$$

If the volume of the gas changes from the initial value V_1 to the final value V_2, Eq. (1.6) may be readily integrated to get the work done on the face of the piston:

$$W = \int_{V_1}^{V_2} P\,dV \qquad (1.7)$$

The pressure–volume history of the gas undergoing the change in state is illustrated on the P-V diagram of Fig. 1.1. The integral of the Eq. (1.7) is given by the area under the curve between the limits V_1 and V_2. The area, and hence the work done in the compression or expansion of the gas depend on the shape of the PV curve, thus establishing that the work done in a process is a path function.

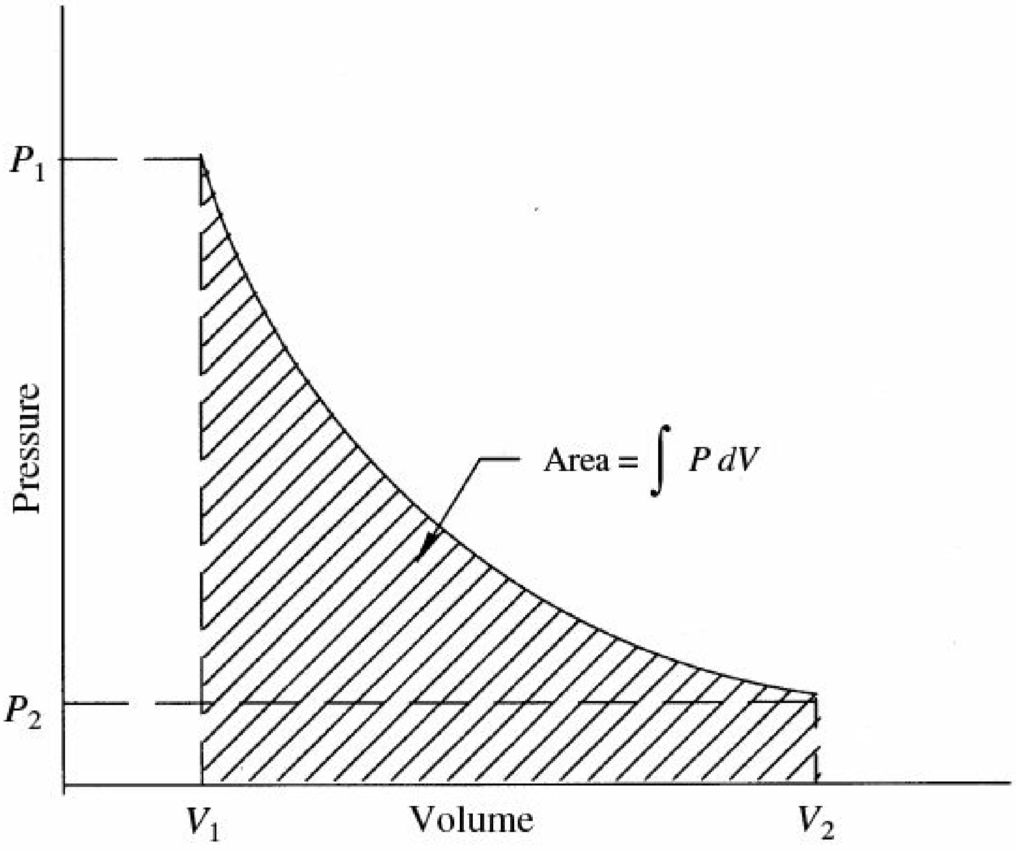


Fig. 1.1 Work of expansion on the P-V diagram.

Heat. It is that quantity which is transferred between bodies due to the difference in temperatures existing between them. In the early years of the development of the science of thermodynamics, this quantity was thought of as a substance called calorie. Heat is now recognised as a form of energy that cannot be stored as such within the system. Heat is manifest only during a change of state of the system; it is energy in transit, like work. Heat exchanged in a process depends on the way in which the process is carried out, as pointed out earlier. Therefore, just as work, heat is a path function. And like work, it is expressed in joules. Two other units used for heat are the calorie and the BTU (the British thermal unit).

1 calorie = 4.1868 J; 1 BTU = 1055.04 J

Energy. It is a quantity that can be stored within the system and can be exchanged between the system and the surroundings. The exchange of energy occurs either as heat or as work. Heat and work are called energy in transit; they cannot be stored within the system. Energy possessed by the system due to its position above some arbitrary reference plane is referred to as its potential energy (PE). If mass m is at an elevation z above the ground, the potential energy of the mass is

$$\text{PE} = mgz \qquad (1.8)$$

where g is the acceleration due to gravity. The energy possessed by the body by virtue of its motion is called its kinetic energy (KE). If a body of mass m is moving at a velocity u, the kinetic energy of the body is

$$\text{KE} = \frac{1}{2} mu^2 \qquad (1.9)$$

As is obvious, the kinetic energy and potential energy are not thermodynamic properties of the system. They do not change with change in the temperature or pressure of the body. In contrast, the internal energy, which a system possesses by virtue of the molecular configuration and motion of molecules, is a thermodynamic property of the system. Internal energy will be discussed in detail in Chapter 2. The unit of energy in SI system is joule (J).

$$1 \text{ J} = 1 \text{ N m} = 1 \text{ kg m}^2/\text{s}^2$$

Power. It is defined as the time rate of doing work. Its unit in the SI system is J/s, commonly designated as W (watts). In engineering calculations, power is sometimes expressed as horsepower (hp). Hence, 1 hp = 745.7 W.

***EXAMPLE* 1.3** The potential energy of a body of mass 10.0 kg is 1.5 kJ. What is the height of the body from the ground? If a body of mass 10 kg is moving at a velocity of 50 m/s, what is its kinetic energy?

Solution The potential energy (PE) is given by Eq. (1.8).

$$\text{PE} = mgz$$

$$1.5 \square 10^3 = 10 \square 9.8067 \square z$$

$$z = 15.3 \text{ m}$$

Thus the elevation z = 15.3 m.

Kinetic energy (KE) is given by Eq. (1.9).

$$\text{KE} = \frac{1}{2} mu^2 = \frac{1}{2} \times 10 \times (50)^2 = 12500 \text{ N m} = 12.5 \text{ kJ}$$

***EXAMPLE*1.4** A man whose weight is 600 N takes 2 min for climbing up a staircase. What is the power developed in him, if the staircase is made up of 20 stairs each 0.18 m in height?

Solution Total vertical displacement = 20 □ 0.18 = 3.6 m

Work done = Force □ Displacement = 600 □ 3.6 = 2160 N m (= 2160 J)

Power developed = Work done/Time

$$= \frac{2160}{2 \times 60} = 18 \text{ J/s } (=18 \text{ W})$$

***EXAMPLE* 1.5** Nitrogen gas is confined in a cylinder and the pressure of the gas is maintained by a weight placed on the piston. The mass of the piston and the weight together is 50 kg. The acceleration due to gravity is 9.81 m/s^2 and the atmospheric pressure is 1.01325 bar. Assume frictionless piston. Determine:

(a) The force exerted by the atmosphere, the piston, and the weight on the gas if the piston is 100 mm in diameter.

(b) The pressure of the gas.

(c) If the gas is allowed to expand pushing up the piston and the weight by 400 mm, what is the work done by the gas in J?

(d) What is the change in the potential energy of the piston and the weight after the expansion in part (c)?

Solution

(a) Force exerted by the atmosphere = Pressure ☐ Area

$$= 1.01325 \square 10^5 \square \frac{\pi}{4} \square (100 \square 10^{-3})^2$$

$$= 795.805 \text{ N}$$

Force exerted by the piston and weight = $m \square g = 50 \square 9.81 = 490.5$ N

Total force acting on the gas = 795.805 + 490.5 = 1286.305 N

(b) Pressure = Force/Area = $\frac{1286.305}{(\pi/4) \times (100 \times 10^{-3})^2} = 1.6378 \square 10^5$ N/m^2 (=1.6378 bar)

(c) Work done = Force ☐ Displacement = $1286.305 \square (400 \square 10^{-3}) = 514.5$ J

(d) Change in the potential energy, D(PE) = mgD$z = 50 \square 9.81 \square (400 \square 10^{-3}) = 196.2$ J

***EXAMPLE* 1.6** A spherical balloon of diameter 0.5 m contains a gas at 1 bar and 300 K. The gas is heated and the balloon is allowed to expand. The pressure inside the balloon is found to vary linearly with the diameter. What would be the work done by the gas when the pressure inside reaches 5 bar?

Solution Since the pressure varies linearly with the diameter of the balloon,

$$P/D = \text{constant}$$

where P is the pressure inside the balloon and D is the diameter. Since these are respectively, $1 \square 10^5$ N/m^2 and 0.5 m initially, $P/D = 2 \square 10^5$ or $P = 2 \square 10^5 D$. As the final pressure is $5 \square 10^5$ N/m^2, the final diameter would be $5 \square 10^5/2 \square 10^5 = 2.5$ m.

$$\text{Work done} = \int P\,dV = \int (2 \times 10^5\,D)\; d\;(\pi/6)\,D^3$$

That is,

$$W = (2 \times 10^5)\,\frac{\pi}{2}\int_{0.5}^{2.5} D^3\,dD = \frac{\pi}{4} \times 10^5\,(2.5^4 - 0.5^4)$$

$$= 30.6305 \times 10^5 \text{ N m} = 30.6305 \times 10^5 \text{ J}$$

1.4 EQUILIBRIUM STATE AND THE PHASE RULE

1.4.1 Steady State

The distinction between steady state and the equilibrium state must be clear at the outset. A system, which is interacting with the surroundings, is said to have attained a *steady-state condition* when the properties at a specified location in the system do not vary with time. Consider the walls of a furnace, the inside surface of which is exposed to hot combustion gases and the outside surface to the atmospheric air. Heat transfer occurs from the inside of the furnace to the outside and the temperature at a specified location in the wall varies with time. When the wall has attained steady state with respect to heat transfer, the temperature at any given point remains constant and does not vary with time. However, the temperatures at different points in the wall would be different. It is obvious that a system in the steady state exchanges mass, heat, or work with the surroundings, even when exhibiting time invariance for the properties.

1.4.2 Equilibrium State

A system is said to be in a state of equilibrium if the properties are uniform throughout and they do not vary with time. By properties we mean the properties on a macroscopic scale and do not exclude the probability of individual molecules having different values for the properties. A system is in *thermal equilibrium*, when no heat exchange occurs between various points within the system and the temperature is uniform throughout. In a system which is in *mechanical equilibrium*, the pressure is uniform. Even under the conditions of uniform temperature and pressure, transfer of mass may occur between the various phases constituting the system, or chemical reaction may occur between the various components present in the system. In a system, which is in a state of *thermodynamic equilibrium*, in addition to the absence of heat and work exchange, there would be no mass transfer between the phases, no diffusion of mass within the phase, and no chemical reaction between the constituents. A state of equilibrium implies, therefore, a state at rest. Since all such changes are caused by driving forces of some kind, the state of equilibrium may also be treated as the one in which all forces are in exact balance. The state of equilibrium will be retained by the system after any small, but short mechanical disturbance in the external conditions.

1.4.3 Phase Rule

The concept of equilibrium is important in thermodynamics, because, properties have any real meaning only in the equilibrium state. The state of an equilibrium system consisting of a pure fluid is uniquely determined by specifying any two intensive variables, as observed earlier.

Thus, when we say that CO_2 gas is contained in a vessel at a pressure of 2 bar and temperature of 300 K, the intensive state of the system is completely determined. The number of independent variables necessary to define the state of equilibrium uniquely is known as the *number of degrees of freedom*. This number will be different for different equilibrium states. For example, for water and water vapour in thermodynamic equilibrium, only one independent variable needs to be specified to define the state uniquely. The number of degrees of freedom in this case is just one. That is, when we say that this system is at a pressure of one standard atmosphere, the temperature gets automatically specified as 373 K, the normal boiling point of water. Thus, the specification of pressure determines the temperature and all other intensive thermodynamic properties of the system. In fact, there exists a definite relationship between the number of degrees of freedom (F), the number of distinct chemical species constituting the system (C) and the number of phases present at equilibrium (π). This is given by the Gibbs phase rule,

$$F = C - \pi + 2$$

The phase rule will be discussed in detail in Chapters 8 and 9.

1.5 TEMPERATURE AND ZEROTH LAW OF THERMODYNAMICS

1.5.1 Zeroth Law

Let a body A be brought in thermal contact with another body B. Heat flows from one to the other and eventually thermal equilibrium is established between A and B. If another body C is also in thermal equilibrium with B, then it is experimentally observed that A and C are also in thermal equilibrium. This observation although appears as frivolous, cannot be explained using known scientific principles. Hence, it has come to be accepted as a law of nature. It is known as the *zeroth law of thermodynamics*, as it precedes the first and second laws in the logical hierarchy of thermodynamic principles. It may be stated thus: *If body A is in thermal equilibrium with B and B is in thermal equilibrium with C, then C is also in thermal equilibrium with A.*

1.5.2 Temperature

The temperature measures the degree of *hotness* or *coldness* of a body. Since the physiological sensation of hotness or coldness does not give a quantitative measure of the temperature, we should device some methods for defining and measuring it. The zeroth law of thermodynamics forms the basis for the measurement of temperature. When two bodies are in thermal equilibrium, we say that the temperatures of both the bodies are equal. The zeroth law allows us to build thermometers which are devices that indicate the change in temperatures by the changes in some physical properties of the thermometer fluid. Such properties are called the thermometric properties. Commonly used thermometric properties include:

1. Volume of gases and liquids (thermometers)
2. Pressure of gases at constant volume (constant-volume gas thermometers)
3. Electrical resistance of solids (thermistors)
4. Electromotive forces of two dissimilar metals (thermocouples)
5. Intensity of radiation (pyrometers)

Suppose the body B in the previous illustration is a glass capillary filled with mercury, which we may call a thermometer. When it is in thermal equilibrium with body *A*, it has a certain height for the mercury column in the capillary that depends on the temperature of *A*. If the thermometer, when brought in contact with body *C,* indicates the same height for the column of mercury, we say that the bodies *A* and *C* are at the same temperature. To assign numerical values to the temperature, there should be some reference states, the temperatures of which are known. The reference states chosen are the ice point and the normal boiling point of water. In the Celsius scale of temperature, these reference states are arbitrarily assigned values 0°C and 100°C, respectively. The interval between these two reference points is divided into 100 equal parts and each part is designated as one degree Celsius.

In the above method of temperature measurement, we have utilised the relative expansion of the glass and mercury, with temperature as the thermometric property. The variation of the thermometric property used for temperature measurement should be linear with temperature; otherwise, different thermometers will indicate same readings only at the fixed points. To circumvent this difficulty, a temperature scale that does not depend on the nature of the thermometric fluid is desired. The ideal gas thermometer provides, in a sense, such an absolute temperature scale.

1.5.3 Ideal Gas Temperature Scale

A detailed discussion of ideal gas is given in Chapter 3. Here it suffices to treat an *ideal gas* as one in which the distance between the molecules is so large that the inter-molecular forces are negligible and the volume occupied by the molecules is only a negligible fraction of the total volume. It follows from kinetic theory that for such a fluid the product of pressure and volume varies linearly with temperature. This is stated mathematically by the ideal gas equation

$PV = RT$, where R is a constant known as the ideal gas constant and V is the molar volume of the gas. All real gases behave ideally as pressure is reduced to zero. Thus, regardless of the nature of gas, the PV product approaches the same value at a given temperature for all gases, as P tends to zero. Thus, the quantity PV can be used as a thermometric property to measure the temperature, regardless of the nature of the substance. Suppose, a low-pressure gas is confined in a constant-volume gas thermometer as shown in Fig. 1.2. It is brought into contact with the system whose temperature is to be measured. By raising or lowering the tube containing mercury, the volume of the gas in the bulb can be maintained constant at the level M indicated in the figure.

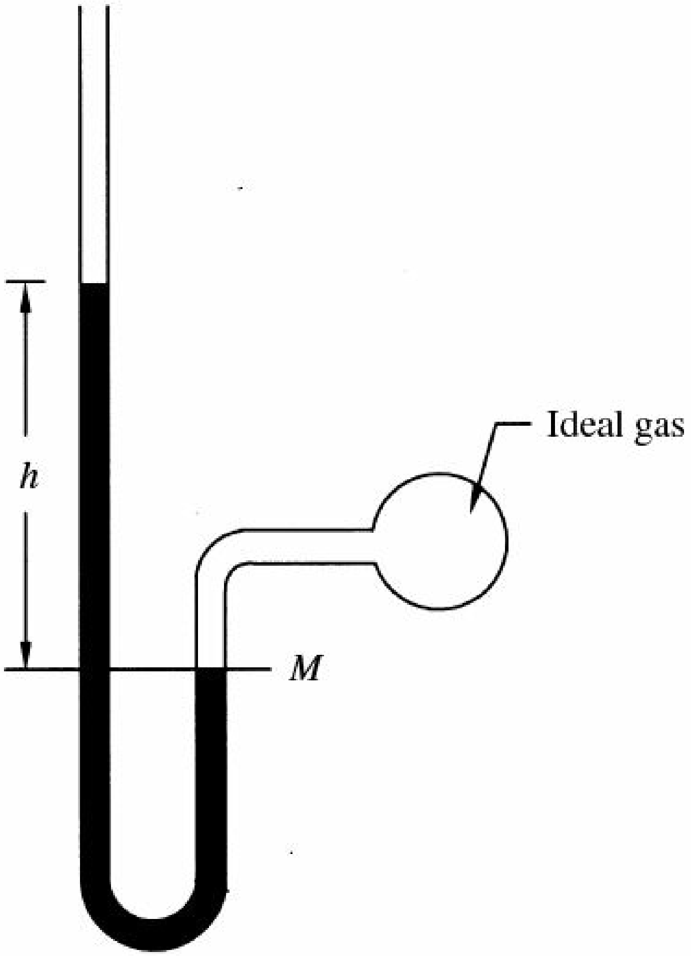


Fig. 1.2 Constant-volume gas thermometer.

The height h of the mercury column indicates the pressure P of the gas. If the thermometer is now brought into contact with a system at the reference state, and the pressure P^* measured, then

$$\frac{T}{T^*} = \frac{PV}{(PV)^*}$$

Since the volume is maintained constant, this equation leads to

$$\frac{T}{T^*} = \frac{P}{P^*}$$

The reference temperature chosen is the triple point of water, i.e. the temperature at which the solid, liquid, and vapour phases of water coexist in equilibrium and it is assigned a value of 273.16 K. Here, K is the abbreviation for degree Kelvin, the SI unit for temperature. Thus, by bringing th thermometer in contact with the system and by measuring the pressure P of the gas, the temperature T is given by

$$T = T^* \frac{P}{P^*} = 273.16 \frac{P}{P^*}$$

where P^* is the pressure indicated by the thermometer in equilibrium with the triple state of water.

The temperature scale based on this principle is referred to as the ideal gas temperature scale. The temperature indicated by this scale is found to be identical to the *absolute thermodynamic temperature* that follows from the second law of thermodynamics which will be discussed in Chapter 4. Hence, the ideal-gas temperature has been accepted as an absolute temperature.

The triple-point temperature of water is found to be 0. 01 K higher than the ice point of water, the latter in Celsius scale being 0∞C. Thus, to convert the temperature measured in ∞C to the absolute temperature in K, we use:

$$T\ (\text{K}) = t\ (\infty\text{C}) + 273.15$$

where T is in K and t is in ∞C.

In the FPS system of units the Fahrenheit scale is used to measure temperature. On this scale, the ic point is assigned a temperature 32∞F and the normal boiling point of water a temperature 212∞F. The interval between these two fixed points is divided into 180 equal parts, each part indicating one degree Fahrenheit. The relationship between the temperature in degree Celsius and degree Fahrenhei is:

$$t\ (\infty\text{F}) = 1.8t\ (\infty\text{C}) + 32$$

The absolute scale that corresponds to the Fahrenheit scale is called the *Rankine scale*. The temperature in degree Fahrenheit (t) is related to the temperature in degree Rankine (T) as:

$$T\ (\text{R}) = t\ (\infty\text{F}) + 459.67$$

The Rankine scale is related to the Kelvin scale by

$$T\ (\text{R}) = 1.8T\ (\text{K})$$

1.6 HEAT RESERVOIRS AND HEAT ENGINES

1.6.1 Heat Reservoir

A thermal reservoir is a sufficiently large system in stable equilibrium from which finite amount of heat can be transferred without any change in its temperature. A heat source is a high temperature reservoir (HTR) from which heat is transferred and heat sink is a low temperature reservoir (LTR) tc which heat is transferred.

1.6.2 Heat Engine

A heat engine is a thermodynamic system operating in a cycle to which heat is transferred and from which work is extracted. The *thermal efficiency* of a heat engine is defined as the ratio of work output to the heat input.

Figure 1.3 shows an engine that receives heat Q_1, delivers work W and rejects heat Q_2 to the sink. The thermal efficiency (h) of the engine is defined as the ratio of work output (W) to the heat supplied (Q_1).

$$\eta = \frac{W}{Q_1} \qquad (1.10)$$

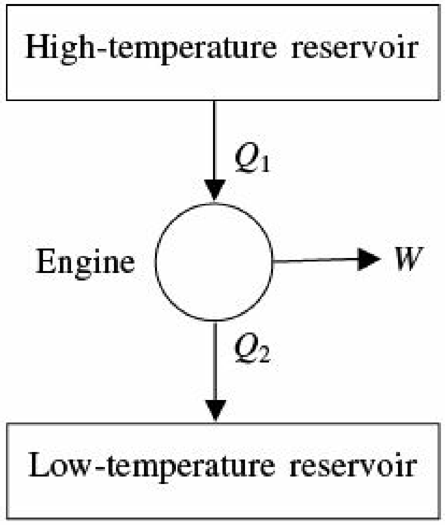


Fig. 1.3 Schematic representation of a heat engine.

1.6.3 Heat Pump

A *heat pump* is a thermodynamic system operating in a cycle that removes heat from a low temperature body and delivers it to a high temperature body. External energy in the form of work is necessary to accomplish this. Figure 1.4 shows a heat pump which receives heat Q_2 from the sink and delivers heat Q_1 to the high temperature reservoir utilising external work W. The coefficient of performance (COP) of heat pump is defined depending upon the primary purpose for which it is used. When used as a refrigerator, the primary purpose is the removal of heat from a low temperature system. The COP of a refrigerator is the ratio of heat transferred from low temperature reservoir (Q_2) to the work-input (W). For refrigerator,

$$\eta = \frac{Q_2}{W} \tag{1.11}$$

When the heat output by the pump is our primary concern, the COP is defined as the ratio of heat rejected (Q_1) to the work-input (W). For heat pump,

$$\eta = \frac{Q_1}{W} \tag{1.12}$$

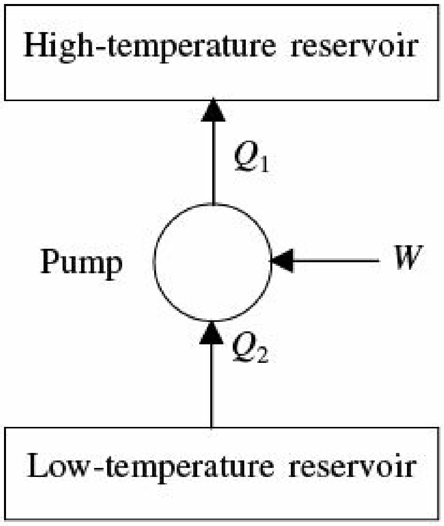


Fig. 1.4 Schematic representation of a heat pump.

1.7 REVERSIBLE AND IRREVERSIBLE PROCESSES

Processes occur when there exists a driving force for a change of state between the parts of the system or between the system and the surroundings. If this driving force is finite, the process is *irreversible* and if it is infinitesimal in magnitude, the process is *reversible*.

All spontaneous processes occurring in nature are irreversible. They cannot be reversed without the use of external energy. If the system undergoing an irreversible process were to be brought back to its initial state, the surroundings would have to undergo some change through heat or work interactions. In short, as a result of the processes in the forward and reverse directions, if changes remain in the surroundings or in the system itself, the process would be irreversible. The free expansion of a gas is a highly irreversible process. When a gas at a high pressure is expanded by passing through a valve, it undergoes an irreversible change, because it cannot be compressed back to the original pressure without resort to energy from an external source like, say, a compressor. The natural processes like diffusion of a solute from a concentrated solution to a dilute one, the transfer of heat from a hot body to a cold body, rusting of iron in the presence of atmospheric oxygen, mixing of two pure gases, are all irreversible.

In contrast, the direction of a reversible process can be changed by an infinitesimal change in the forces acting on the system. A system undergoing a reversible process can be brought back to its original state, leaving no change in the surroundings. Consider water and water vapour in equilibrium contained in a cylinder provided with a frictionless piston. The external force on the piston is kept equal to the force due to the vapour pressure of water at the given temperature. By increasing the force acting on the piston by an infinitesimally small amount, the vapour will condense; and decreasing it slightly will make water to vaporise. The process is very close to a reversible process as the work required to condense a certain amount of water vapour would be equal to that required to vaporise the same quantity of water.

As another example of a reversible process consider the chemical reaction occurring in a galvanic cell in which the electrodes made of zinc and platinum are immersed in an aqueous solution of hydrochloric acid. The following reaction occurs:

$$\mathrm{Zn} + 2\mathrm{HCl} \ \square\ \mathrm{ZnCl_2} + \mathrm{H_2}$$

The electrodes are connected through an external circuit to a potentiometer. The system is in equilibrium when the applied potential difference is balanced by the e.m.f. produced by the cell. By increasing or decreasing the potential difference slightly, the reaction can be carried out in the forward or reverse direction. Similarly, heat transfer between two bodies may be made nearly reversible by bringing down the temperature difference between them to a very small value.

We see that in a reversible process the driving and opposing forces are in exact balance so that by increasing or decreasing the forces by an infinitesimal amount, the process can be made to reverse the direction. Since the driving force differs from the opposing force by not more than a differential amount, it takes an infinite time for a reversible process to go to completion. Since we engineers would like to carry out the processes in a finite time, reversible processes are never attained in practice. Although such processes never occur in nature, they may be regarded as the limit of realisable processes.

If all naturally occurring processes are irreversible, then why should we introduce the concept of reversible processes? The answer to this question can be provided by considering a simple example. A gas at high pressure is confined in a piston–cylinder arrangement. The piston is held in position by placing a suitable weight *W* over it. The pressure of the gas is balanced by the atmospheric pressure and the weight of the piston that includes the weight placed on it. Assume that the piston and cylinder neither absorb nor transmit heat and that the piston moves within the cylinder without friction. Now, suppose that the mass *W* is removed by sliding it into a compartment on the side. Due to the force imbalance, the piston rises up as indicated in Fig. 1.5.

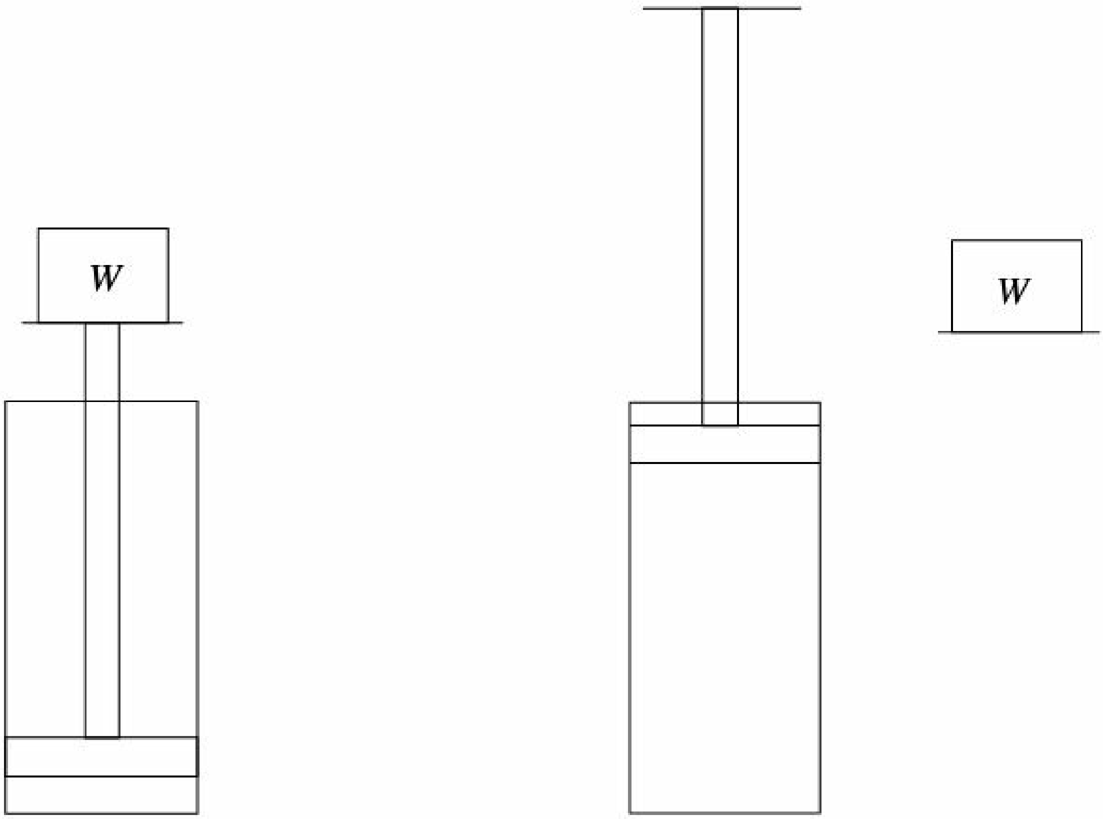


Fig. 1.5 Irreversible expansion of a gas.

The work done by the gas on expansion against the atmosphere is not available for restoring the gas to its initial state. If the gas returns to its original state, work would be done on the system, in which case, the surroundings undergoes some change. Therefore, the process is clearly an irreversible one. On the other hand, if the weight is raised to a higher level due to the expansion of the gas, the potential energy of the surroundings would increase and by utilising the increment in the potential energy, the state of the system can be restored. But, this is not happening here, because the weight removed from the piston is at the same level as it was before the expansion of the gas. It can be easily shown that the work appearing in the surroundings by the irreversible expansion of the gas cannot be measured as

$$W = \int P\,dV$$

The work of expansion done by the gas against the atmosphere is measured as the product of the force and the displacement of the piston. If F is the force acting downwards and dz is the displacement of the piston, then the work done against the atmosphere is $w = \int F\,dz$. When the force acting downwards and the gas pressure are in exact balance, $F = PA$, where A is the area of the piston and the work done by the gas against the atmosphere is $\int PA\,dz = \int P\,dV$. Here, dV is the increase in volume due to expansion. Once the weight W is removed from the piston, the forces are out of balance; that is, the force exerted by the gas and the downward force are not equal. In this case, it is incorrect, if the work appearing in the surroundings is evaluated as $\int P\,dV$. It is only for a reversible process, the forces are always in exact balance and the work done by the system is evaluated from the properties of the system. Thus $W = \int P\,dV$ is applicable only for a reversible process. The calculation of work appearing in the surroundings using the properties of the system is possible only if the process is reversible.

The above process can be carried out reversibly if the weight on the piston is replaced by infinitely large number of fine particles together weighing W. Refer Fig. 1.6. If the particles were removed one at a time, the pressure of the gas would never be out of balance with the downward forces. When the entire weight is removed from the piston, the potential energy of the surroundings is increased, as is evident from the height of the pile obtained on the side. The system does maximum useful work on the surroundings. The weights can be replaced one by one on the piston and the piston can be made to retrace its path without using any extra energy from the surroundings. This is a reversible process, as the process can be reversed at any instant by an infinitesimally small increase in the downward forces and the original state of the system is restored without any change in the surroundings. The work done by the gas during expansion can be calculated from the properties of the gas as $\int P\,dV$. It may also be noted that the reversible work is the maximum work obtainable if the process is expansion of the gas and the minimum work required if the process is compression.

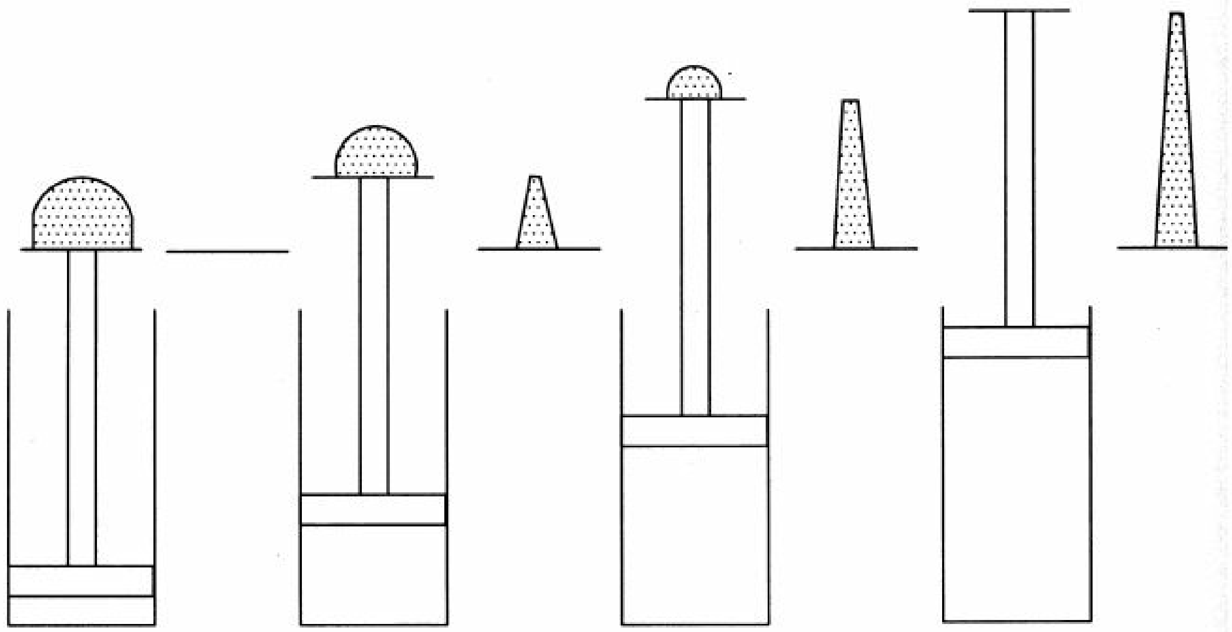


Fig. 1.6 Simulation of reversible expansion of a gas.

In the above process, we have assumed a frictionless piston. Though friction between the walls of the cylinder and the piston can be reduced in practice, it can never be completely eliminated. In the presence of friction, the work done by the gas in expanding from a high pressure to a lower value will be greater than the work appearing in the surroundings by the amount needed to overcome the effect of friction. In a similar manner, more work would have to be done by the surroundings to restore the system to the original state than that resulted from the forward process. It means that the presence of friction, however small it may be, eliminates the chances of achieving a reversible process in actual practice. Friction is not the only factor that causes irreversibility. Processes involving dissipative effects such as fluid flow, convective heat transfer, etc., can never be carried out reversibly. Reversible process is an idealised concept introduced in thermodynamics to compare the performance of actual processes. It represents a limiting case that can be approached, but never attained.

In conclusion, we may summarise the characteristics of a reversible process as follows:

1. In a reversible process, the driving and opposing forces are in exact balance, and an infinitesimal change in the external conditions would cause a reversal in the direction of the process.
2. For reversible process to occur, friction, turbulence, and other dissipative effects should be absent.
3. It takes an infinite time for its completion.
4. A reversible process occurring in a work-producing machine delivers the maximum amount of work and that occurring in a work-requiring machine requires the minimum amount of work.
5. A reversible process is an idealised and imaginary concept and may be used for the comparison of the performance of actual systems and for indicating the efficiency of processes.

EXAMPLE **1.7** Two kilograms of CO_2 gas is contained in a piston–cylinder assembly at a pressure of 6.5 bar and a temperature of 300 K. The piston has a mass of 5000 kg and a surface area of 1 m^2. The friction of the piston on the walls is significant and cannot be ignored. The atmospheric pressure is 1.01325 bar. The latch holding the piston in position is suddenly removed and the gas is allowed to expand. The expansion is arrested when the volume is double the original volume. Determine the work appearing in the surroundings. Will it be the same as the work done by the gas?

Solution The initial volume of the gas is evaluated assuming that the gas follows the ideal gas equation, $PV = nRT$.

Number of moles of the gas n = Mass/Molecular Weight = 2/44 = 0.0455 kmol

Initial volume, $V = nRT/P = 0.0455 \square (8.314 \square 10^3) \square 300/6.5 \square 10^5 = 0.1746 \text{ m}^3$

Final volume $= 2V = 0.3492 \text{ m}^3$

Change in the volume, $\text{D}V = 2V - V = 0.1746 \text{ m}^3$

Pressure on the surroundings = Atmospheric pressure + Pressure due to the weight of the piston

$= 1.01325 \square 10^5 + 5000 \square 9.8067$

$= 1.50359 \square 10^5 \text{ N/m}^2$

Work done on the surroundings $= P\text{D}V = (1.50359 \square 10^5) \square 0.1746 = 0.2625 \square 10^5$ J

Since the pressure of the gas is changing continuously, the work done by the gas cannot be evaluated as $\int P\,dV$. This work would be greater than the work appearing in the surroundings because of the irreversible nature of the process.

***EXAMPLE* 1.8** A gas which occupies a volume of 0.2 m^3 at a pressure of 1 bar is expanded to a final pressure of 7.0 bar. The pressure of the gas varies according to the relation $P = 1200\ V + b$, where P is in kPa, V is in m^3 and b is a constant. Calculate the work done by the gas.

Solution Initial conditions are P_1 = 1 bar = 100 kPa and $V_1 = 0.2 \text{ m}^3$.

The pressure and volume of the gas are related by

$$P = 1200\ V + b$$

Therefore,

$$P_1 = 1200\ V_1 + b$$

$$100 = 1200 \square 0.2 + b$$

or

$$b = -140 \text{ kPa}$$

Therefore, the pressure-volume relationship is $P = 1200\ V - 140$

The final pressure P_2 = 7.0 bar = 700 kPa. Therefore, the final volume V_2 is given by

$$700 = 1200\ V_2 - 140$$

or

$$V_2 = 0.7 \text{ m}^3$$

The work done by the gas is given by

$$W = \int_{V_1}^{V_2} p dV = \int_{0.2}^{0.7} (1200V - 140)\, dV = \frac{1200}{2}(0.7^2 - 0.2^2) - 140(0.7 - 0.2) = 200 \text{ kJ}$$

200 kJ of work is done by the gas during the expansion.

SUMMARY

Thermodynamics deals with energy and its transformation. The heat and work effects accompanying a process can be accurately predicted by thermodynamics. It imposes certain restrictions to all naturally occurring processes. The limits set by thermodynamics, such as the equilibrium yield in a chemical reaction, are the best that can be attained in a given situation. An important limitation of thermodynamics is its inability to predict the mechanisms of changes and hence, the rate of the process. An attempt is made in this chapter to introduce certain basic concepts that are frequently employed in any thermodynamic analysis. The classification of systems as closed and open is based on whether matter can be exchanged between the system and the surroundings or not. The properties are classified as intensive and extensive on the basis of their dependence on the quantity of matter involved. Thermodynamic quantities are classified as path functions and state functions, based on whether they are dependent on the past history of the system or not. Heat and work were defined and were shown as examples of path functions. The SI units used for measuring some other thermodynamic quantities such as force, energy, temperature, and pressure were also given along with their definitions. The principle of measurement of temperature is based on the zeroth law of thermodynamics. An ideal-gas thermometer can be used to measure the absolute temperature, independent of the thermometer fluid.

The equilibrium state is one in which all forces are exactly balanced and any tendency for changes on a macroscopic scale is absent. The minimum number of intensive properties required to define such a state was provided by the phase rule, which links this number to the number of components and the number of phases constituting the system. All naturally occurring processes were shown to be irreversible. A system undergoing a reversible process can be brought back to its original state without any changes in the surroundings. Reversible process is an idealised concept that can be used for comparing the performance of actual processes.

REVIEW QUESTIONS

1. Can thermodynamics help us to determine the maximum yield of a specified product in a chemical reaction?
2. Using thermodynamic principles, can you determine the rate of a chemical reaction? Why?
3. It is suggested that by increasing the size of the furnace and thereby providing sufficient reaction time, the CO content in the effluent gases leaving a blast furnace can be reduced to zero. Comment on this suggestion.
4. Distinguish between system and surroundings.
5. What do you understand by homogeneous system and heterogeneous system? Is the system consisting of an equimolar mixture of water and benzene at room temperature and pressure, homogeneous or heterogeneous?

6. Distinguish between closed system and open system. Say whether the following systems are closed or open:

(a) A tubular reactor
(b) A batch reactor
(c) Individual phases in a multiphase system.

7. How would you define extensive and intensive properties? State whether the following properties are intensive or extensive: (a) volume, (b) density, (c) specific volume, (d) heat capacity, (e) specific heat, (f) potential energy, (g) pressure, (h) temperature.

8. Distinguish between state function and path functions with examples. A cyclic process may be defined as the one in which after a series of changes, the system is brought back to its initial conditions. What would be the change in a state function in a cyclic process?

9. Why don't we treat the potential energy and kinetic energy of a system as its thermodynamic properties?

10. What is zeroth law of thermodynamics? How is it helpful in measuring temperature?

11. Is it true that the temperature indicated by different devices would be the same only at the fixed points used for calibrating them? Why?

12. What is the importance of the ideal-gas temperature scale?

13. How are the efficiency of a heat engine and the COP of a heat pump defined?

14. What do you understand by thermal reservoirs?

15. Distinguish between steady state and equilibrium state.

16. The work done by the gas during expansion can be calculated from the properties of the gas as $\int P\,dV$. Is it applicable to irreversible processes?

17. 'A reversible process is never attained in practice. It can only be approached.' What are the factors that make this statement true?

18. What do you mean by the number of degrees of freedom? What is the number of degrees of freedom when a binary liquid mixture is in equilibrium with its vapour?

EXERCISES

(In all the following problems, unless otherwise specified, take the gravitational acceleration to be 9.80671 m/s^2.)

1.1 A man circling the earth in a spaceship weighed 300 N at a location where the local gravitational acceleration was 3.35 m/s^2. Calculate the mass of the man and his weight on the earth, where the gravitational acceleration is 9.81 m/s^2.

1.2 If a man weighs 600 N at a place where the local acceleration due to gravity is 9.81 m/s^2, what would be his weight on the moon, where the acceleration due to gravity is 1.67 m/s^2?

1.3 A special manometer fluid has a specific gravity of 3.65 and is used to measure a pressure of 1.25 bar at a location where the barometric pressure is 760 mm Hg. What height will the manometer fluid register?

1.4 A mercury manometer used for pressure measurement indicates 500 mm. The density of mercury is $13.56 \square 10^3$ kg/m^3 and acceleration due to gravity is 9.81 m/s^2. Express the pressure indicated in bar.

1.5 What is the pressure exerted on a skin diver who has descended to 20 m below the surface of the sea, if the atmospheric pressure is 1 bar at the sea level and the specific gravity of the sea water is 1.03?

1.6 A mercury manometer used to measure pressure inside a vessel indicates 400 mm. One end of the manometer is exposed to the atmosphere. The atmospheric pressure is 1.01325 bar. Density of mercury is $13.56 \square 10^3$ kg/m^3 and $g = 9.81$ m/s^2. What is the absolute pressure in the vessel in N/m^2?

1.7 The potential energy of a body of mass 20 kg is 3.5 kJ. What is the height of the body from the ground? If a body of mass 20 kg is moving at a velocity of 50 m/s, what is its kinetic energy?

1.8 A car having a mass of 1200 kg is running at a speed of 60 km/h. What is the kinetic energy of the car in kJ? What is the work to be done to bring the car to a stop?

1.9 A body of mass 50 kg is lifted through a distance of 15 m. What is the work done? If it took 2 min for lifting the mass, calculate the power.

1.10 A man whose weight is 700 N takes 2.5 min for climbing up a staircase. What is the power developed in him, if the staircase is made up of 20 stairs each 0.18 m in height?

1.11 The steam supplied to an engine liberates 5000 J of heat. If the engine efficiency is only 40 per cent, to what height a body of mass 10 kg can be lifted using the work output from the engine?

1.12 Nitrogen gas is confined in a cylinder and the pressure of the gas is maintained by a weight placed on the piston. The mass of the piston and the weight together is 100 kg. The acceleration due to gravity is 9.81 m/s^2 and the atmospheric pressure is 1.01325 bar. Assume frictionless piston. Determine:

(a) The force exerted by the atmosphere, the piston and the weight on the gas if the piston is 200 mm in diameter.

(b) The pressure of the gas.

(c) If the gas is allowed to expand pushing up the piston and the weight by 500 mm, what is the work done by the gas in kJ?

(d) What is the change in the potential energy of the piston and the weight after the expansion in part (c)?

1.13 A spherical balloon of diameter 0.5 m contains a gas at 1 bar and 300 K. The gas is heated and the balloon is allowed to expand. The pressure inside the balloon is directly proportional to the square of the diameter. What would be the work done by the gas when the pressure inside reaches 5 bar?

1.14 A body of mass 20 kg is dropped from a height of 15 m. What is the potential energy of the body at the time of its release? Assume that the potential energy gets converted into kinetic energy when the body strikes the ground. At what velocity does it strike the ground?

1.15 A balloon which was originally empty is being filled with hydrogen from a cylinder at a constant temperature of 300 K. The atmospheric pressure is 1.01325 bar. What is the work done by the balloon–cylinder system when the balloon attains a spherical shape

6 m in diameter?

1.16 Five kilograms of CO_2 gas is contained in a piston–cylinder assembly at a pressure of 7.5 bar and a temperature of 300 K. The piston has a mass of 6000 kg and a surface area of 1 m^2. The friction of the piston on the walls is significant and cannot be ignored. The atmospheric pressure is 1.01325 bar. The latch holding the piston in position is suddenly removed and the gas is allowed to expand. The expansion is arrested when the volume is double the original volume. Determine the work done in the surroundings.

2

First Law of Thermodynamics

2.1 GENERAL STATEMENTS OF FIRST LAW OF THERMODYNAMICS

The idea of designing an engine that would produce mechanical work continuously without drawing energy from external sources and without undergoing a change had been a great fascination for scientists and engineers. The failure to construct such a perpetual motion machine (PMM) formed the basis for the law of conservation of energy (H. von Helmholtz, 1847). The fundamental implication of this law is that *“although energy may be converted from one form to another, it cannot be created or destroyed”*. Whenever a quantity of one form of energy is produced, an exactly equivalent amount of another kind must be used-up.

When the law of conservation of energy was proposed, heat was not considered to be a form of energy. It was a series of experiments conducted by Joule between 1843 and 1847 that established heat as a form of energy. A known quantity of water taken in an insulated container was agitated by means of a paddle wheel. The resulting temperature rise was noted. It was found that an exact proportionality existed between the amount of work expended on the water and the rise in temperature. The same proportionality was obtained by the following different methods of transforming work into heat:

1. The mechanical work was converted to electricity and the electric current was passed through coils immersed in water.
2. A gas confined in a cylinder immersed in water was compressed mechanically.
3. Two metal pieces immersed in water were rubbed against each other by mechanical work.

The use of a given amount of work on a quantity of adiabatically enclosed water gave the same temperature rise regardless of the way in which the process was carried out. Joule’s experiments established a quantitative relationship between heat and work thus rejecting the earlier theory that treated heat as a substance. The recognition that heat and internal energy are forms of energy led to their inclusion in the law of conservation of energy along with work, potential energy, and kinetic energy and the law came to be known as *first law of thermodynamics*.

The first law of thermodynamics is a generalisation based on our experiences like the failure to construct a perpetual motion machine, the constancy of mechanical equivalent of heat, etc. It is stated in a number of ways, but precisely it means that *energy is indestructible.* Any loss or gain of energy by the system must be exactly equivalent to the gain or loss of energy of the surroundings. For an isolated system—a combination of the system and the surroundings—the total energy therefore, remains constant, although it may be changed from one form to another. The universe can be treated as an isolated system and therefore we can say, *“the energy of the universe is conserved”*.

2.2 FIRST LAW OF THERMODYNAMICS FOR CYCLIC PROCESS

Consider a static system undergoing a cycle of changes. Work is done on the system by forces acting from the surroundings, or vice versa, and heat is transferred between the system and the surroundings during the process. Then, according to the first law of thermodynamics, the algebraic summation of all work effects exactly equals the summation of all heat effects. Let Q denote the heat added to the system and W the work done by the system (Q is negative when heat is rejected by the system and W is negative when work is done on the system) and if both are measured in consistent units,

$$\Sigma W = \Sigma Q$$

If the units chosen for heat and work are different, the above equation can be written as

$$\Sigma W = J \Sigma Q$$

J is the mechanical equivalent of heat if the work is mechanical, and electrical equivalent of heat if the work is electrical.

2.3 INTERNAL ENERGY

Heat and work represent energy in transit. Energy exchange between the system and the surroundings occurs either as heat or as work. Heat and work are thus external effects of changes occurring within the system or are external manifestations of stored energy. What happens to the state of the system after heat is supplied to it and before work is extracted from it? The system undergoes a change because energy gets stored within it. The energy stored in the system by virtue of the configuration and motion of the molecules constituting the system is called its *internal energy*. It is a definite property of the system and is denoted by U.

The energy due to the mass motion of the system as a whole (the kinetic energy), and that due to its external position in a gravitational, electrical, or magnetic field (the potential energy) are not included in the internal energy, U, as these forms of energy are not properties of the system. The molecules constituting the system possess kinetic energy of translation, rotation, and vibration. They also possess potential energy due to the forces of attraction existing among them. These molecular potential and kinetic energies contribute to the internal energy of the system. The addition of heat to the system results in the increase of its molecular kinetic energy and thus increases the internal energy of the system.

A given system under a given set of conditions has a definite internal energy. In a cyclic process, the internal energy of the system after a series of changes remains the same as it was before. The heat and work involved in a non-cyclic process are not equal. Consequently, some energy gets stored in the system or some stored energy gets removed from the system during a non-cyclic process. These changes in the stored energy are measured as the change in the internal energy of the system. It should be borne in mind that it is impossible to measure the total internal energy of a substance and therefore absolute values of internal energy are not known. This is not a serious limitation because it is the changes in internal energy and not the absolute values that are usually needed in thermodynamic analysis.

It can be shown that internal energy is a thermodynamic property of the system and is solely determined by the thermodynamic state and not by the path by which that state was arrived at.

Consider a system undergoing a series of changes from state 1 to state 2 along path a as shown in Fig. 2.1. Let the initial conditions be restored along path b. If the surroundings remain unchanged, the change in internal energy (ΔU) along path a must be exactly equal but opposite in sign to that along path b. On the other hand, if ΔU along path b were less than that along path a, there would be a *residuum* of energy resulting from this cyclic operation. Energy would have been created without loss of an equivalent amount of another kind, or in short, a PMM would have been possible. As this is contrary to the first law, the energy changes along paths a and b should be numerically equal. By the same reasoning, it can be shown that $\mathrm{D}U$ along paths c and d also should be numerically equal but opposite in sign to $\mathrm{D}U$ along path a. Here, paths b, c, and d are different routes for changing the state of the system from state 2 to state 1. This means that the internal energy change accompanying a given change of state depends only on the end states and not on the path followed; that is, internal energy is a state function.

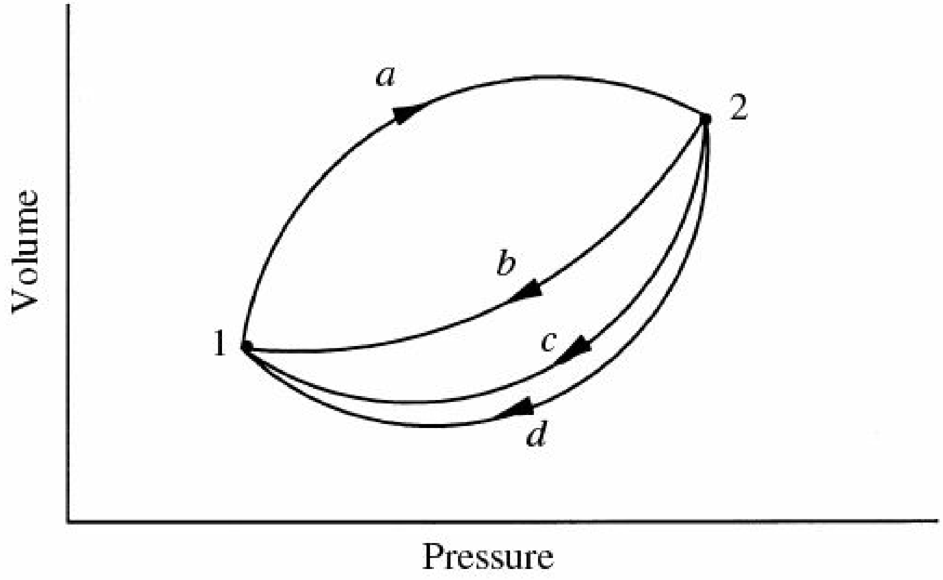


Fig. 2.1 Internal energy is a state function.

2.4 FIRST LAW OF THERMODYNAMICS FOR NON-FLOW PROCESS

The first law of thermodynamics requires that the change in the total energy of the system be compensated by an equal but opposite change in the total energy of the surroundings, so that, there is no net change in the energy in any process. The change in the total energy of the surroundings occurs only through the exchange of heat or work with the system. Then the change in the total energy of the surroundings, $(\mathrm{D}E)_{\mathrm{sur}}$, must be equal to the energy transferred to or from it as heat and work. Since Q is the heat transferred to the system and W is the work extracted from it during the process,

$$(\mathrm{D}E)_{\mathrm{sur}} = -Q + W \qquad (2.1)$$

For a closed system undergoing only changes in the kinetic, potential, and internal energies, the total energy change of the system $(\mathrm{D}E)_{\mathrm{sys}}$ is given by

$$(\mathrm{D}E)_{\mathrm{sys}} = \mathrm{D}(KE) + \mathrm{D}(PE) + \mathrm{D}U \qquad (2.2)$$

Since $(\mathrm{D}E)_{\mathrm{sys}} = -(\mathrm{D}E)_{\mathrm{sur}}$, we can combine Eqs. (2.1) and (2.2) as follows.

$$\mathrm{D}(KE) + \mathrm{D}(PE) + \mathrm{D}U = Q - W \qquad (2.3)$$

In the above equations $\mathrm{D}(KE)$ and $\mathrm{D}(PE)$ denote changes in kinetic energy and potential energy respectively. Equation (2.3) means that the total energy change in a closed system is equal to the heat added to the system minus the work done by the system. For a steady-state non-flow process in which there are no changes in the kinetic energy and potential energy, the above equation simplifies to

$$\boxed{\Delta U = Q - W} \tag{2.4}$$

For differential changes in the thermodynamic state of a closed system, Eq. (2.4) can be written as

$$\boxed{dU = dQ - dW} \tag{2.5}$$

Equations (2.4) and (2.5) are the mathematical statements of first law of thermodynamics for non-flow processes.

***EXAMPLE* 2.1** A system consisting of some fluid is stirred in a tank. The rate of work done on the system by the stirrer is 2.25 hp. The heat generated due to stirring is dissipated to the surroundings. If the heat transferred to the surroundings is 3400 kJ/h, determine the change in internal energy

Solution The work done on the system can be obtained as:

$$-W = 2.25\text{ hp} = 2.25(745.7) = 1677.825\text{ W} = 1677.825\text{ J/s}$$

Heat transferred to the surroundings is

$$-Q = 3400\text{ kJ/h} = 3400 \times 10^3/3600 = 944.444\text{ J/s}$$

By Eq. (2.4),

$$\Delta U = Q - W = -944.444 - (-1677.825) = 733.381\text{ J/s}$$

The internal energy of the system increases by 733.381 J in one second.

***EXAMPLE* 2.2** Iron filings are contained in a cylinder in an atmosphere of oxygen. It combines with oxygen according to the following reaction.

$$2\text{ Fe} + (3/2)\text{ O}_2 \rightarrow \text{Fe}_2\text{O}_3$$

The pressure inside the cylinder is maintained at 101 kPa. The temperature is kept constant at 298 K by removing heat. For 2 mol iron reacted, calculate Q, W, and ΔU given that 831.08 kJ of heat is liberated in the process.

Solution The heat liberated when 2 mol iron reacts with oxygen is 831.08×10^3 J. Therefore,

$$Q = -831.08 \times 10^3\text{ J}$$

Neglecting the volume occupied by the solids, the volume change accompanying the process is equal to the change in the volume of oxygen. Assuming ideal gas behaviour for the gas,

$$P\Delta V = (\Delta n)\,RT$$

where ΔV is the volume change and Δn, the increase in the number of moles accompanying the reaction. Here $\Delta n = -1.5$. Therefore, the work done by the system,

$$W = P\Delta V = (\Delta n)RT = -1.5\,RT = -1.5(8.314)\,298 = -3716.4\text{ J}$$

The change in the internal energy is

$$\Delta U = Q - W = -831.08 \times 10^3 - (-3716.4) = -827.364 \times 10^3\text{ J}$$

***EXAMPLE* 2.3** A car riding downhill at a speed of 20 m/s was applied brake when it was at a height of 30 m vertically above the bottom of a hill. When the car comes to a halt at the bottom of the hill, how much energy as heat must be dissipated by the brakes, if wind and other frictional effects are neglected? The car weighed 1400 kg.

Solution The first law of thermodynamics is given by Eq. (2.3):

$$D(KE) + D(PE) + DU = Q - W$$

Here $D(KE)$ and $D(PE)$ are the changes in kinetic energy and potential energy of the car respectively.

The kinetic energy of the car is (1/2) mu^2 and the potential energy is mgz. The kinetic energy and potential energy of the car when it comes to a stop at the bottom are both equal to zero. Therefore, the changes in kinetic energy and potential energy are the negative of their respective initial values. Noting that m is the mass, u is the velocity and z is the elevation above the bottom of the hill,

$$D(KE) = -(1/2)\,mu^2, = -(1/2)\,1400\,(20^2) = -2.8 \square 10^5 \text{ J}$$

$$D(PE) = -mgz, = -1400\,(9.81)\,30 = -4.12 \square 10^5 \text{ J}$$

Therefore,

$$Q = (-2.8 \square 10^5) + (-4.12 \square 10^5) = -6.92 \square 10^5 \text{ J}$$

Hence, heat dissipated by the brakes = $6.92 \square 10^5$ J.

***EXAMPLE* 2.4** A system consisting of a gas confined in a cylinder is undergoing the following series of processes before it is brought back to the initial conditions:

Step 1: A constant pressure process when it receives 50 J of work and gives up 25 J of heat.
Step 2: A constant volume process when it receives 75 J of heat.
Step 3: An adiabatic process. (*Note:* In adiabatic process there is no heat exchange between system and surroundings.)

Determine the change in internal energy during each step and the work done during the adiabatic process.

Solution The process is shown in Fig. 2.2. Step AB is a constant pressure process.

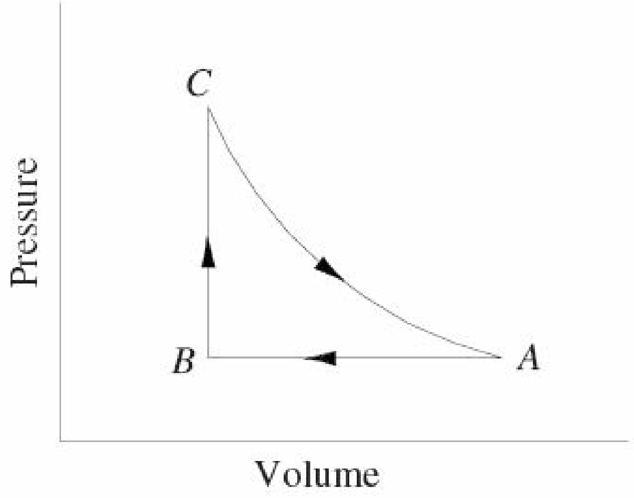


Fig. 2.2 Illustration of processes in Example 2.4.

Internal energy change for this step is calculated as

$$(DU)_{AB} = Q_{AB} - W_{AB} = -25 + 50 = 25 \text{ J}$$

During step *BC*, no work is done, as it is a constant volume process. Change in internal energy is

$$(\mathrm{D}U)_{BC} = Q_{BC} = 75 \text{ J}$$

Step *CA* being an adiabatic process, $Q_{CA} = 0$. Therefore,

$$(\mathrm{D}U)_{CA} = -W_{CA}$$

For a cyclic process, the net change in internal energy is zero. That is,

$$(\mathrm{D}U)_{AB} + (\mathrm{D}U)_{BC} + (\mathrm{D}U)_{CA} = 0$$

$$(\mathrm{D}U)_{CA} = -[(\mathrm{D}U)_{AB} + (\mathrm{D}U)_{BC}] = -(25 + 75) = -100 \text{ J}$$

Therefore, W_{CA}, the work done during the adiabatic process $= -(\mathrm{D}U)_{CA} = 100$ J.

***EXAMPLE* 2.5** A gas is undergoing a change of state from *A* to *B* along path *ACB* in which the total heat supplied to the system is 80 J and the work done by the system is 30 J (Fig. 2.3). The cycle is completed by bringing the system back to the initial state along the curved path *BA* for which work of 40 J is done on the system.

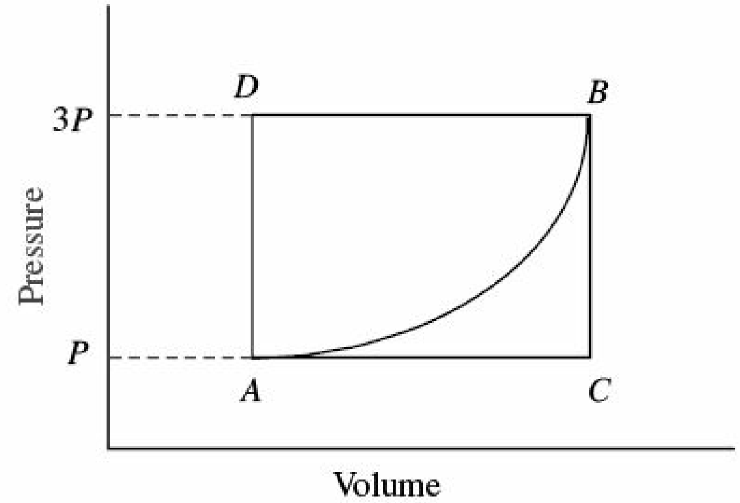


Fig. 2.3 Change of state of gas along different routes in Example 2.5.

Determine the following:

(a) The heat transferred if the initial process were carried out along path *ADB* as shown in the figure.

(b) The heat quantity involved in the process *AD* and *DB*, if the internal energy of the system at state *D* is greater than that at state *A* by 40 J.

(c) The heat supplied or removed in the process along path *BA*.

Solution For the process occurring along *ACB*, $Q = 80$ J, $W = 30$ J. Q is positive since heat is supplied to the system and W is positive since work is done by the system.

The first law of thermodynamics gives

$$\mathrm{D}U = Q - W$$

Therefore, the change in internal energy for the process *ACB* is

$$\mathrm{D}U = 80 - 30 = 50 \text{ J}$$

(a) Internal energy being a state function, for the process occurring along path *ADB* also

$\Delta U = 50$ J. The work done is calculated as pressure times the change in volume. Since the volume change is zero for process *AD* and the pressure for process *DB* is three times that of process *AC*, the work done along *ADB* will be 3 times the work done along path *ACB*. Therefore, $W = 3 \times 30 = 90$ J. Heat involved is calculated as

$$Q = \Delta U + W = 50 + 90 = 140 \text{ J}$$

That is, 140 J of heat is supplied to the system.

(b) No work is involved in process *AD* since it is a constant volume process. The change in internal energy in process *AD* is given to be $\Delta U = 40$ J. Therefore, heat involved in this process is

$$Q = \Delta U + W = 40 + 0 = 40 \text{ J (Heat is supplied to the system.)}$$

Change in internal energy between states *B* and *A* is calculated to be 50 J. Now,

$$\Delta U_{AB} = \Delta U_{AD} + \Delta U_{DB}$$

or

$$\Delta U_{DA} = \Delta U_{AB} - U_{AB} = 50 - 40 = 10 \text{ J}$$

Work done by the system in process *DA* is 3 times the work done along path *AC* = 90 J. Therefore, heat quantity involved is

$$Q = \Delta U + W = 10 + 90 = 100 \text{ J (Heat is supplied to the system.)}$$

(c) For the return path along *BA*, $W = -40$ J, $\Delta U = -50$ J (negative of the change in internal energy for the process from *A* to *B*.)

$$Q = \Delta U + W = -50 - 40 = -90 \text{ J (Heat is given out by the system.)}$$

***EXAMPLE*2.6** A rigid tank is divided into two equal parts by a partition. Initially one of the partitions is filled with 10 kg water at 300.15 K and 101.3 kPa and the other part is evacuated. The partition is then removed and the water is allowed to fill the entire tank. The water attains the temperature of 300.15 K by exchanging heat with the surroundings. From steam tables, the specific volume of saturated water and water vapour at 300.15 K are found to be 1.003×10^{-3} m^3/kg and 38.81 m^3/kg, respectively and the internal energy values of saturated liquid and saturated vapour are 113.1 and 2412.6 kJ/kg, respectively. Determine (a) the volume of the tank, (b) the final pressure in the tank and (c) the heat transferred.

Solution (a) The saturation temperature of water at 101.3 kPa is 373.15 K. Initially, at 300.15 K and 101.3 kPa, water is a subcooled liquid. Assuming that the specific volume of water at this condition is the same as the specific volume of saturated water at 300.15 K, we can take the specific volume of water at this condition to be 1.003×10^{-3} m^3/kg. Therefore, 10 kg water occupies a volume of $1.003 \times 10^{-3} \times 10 = 1.003 \times 10^{-2}$ m^3. Since water occupies half the volume of the container, volume of the container = $2 \times 1.003 \times 10^{-2}$ m^3 = 2.006×10^{-2} m^3.

(b) Assume that the tank and the water contained in it constitute the system. It is a closed system and when the partition is removed, no work is done as the boundary of the system is rigid. In the final state, 10 kg water occupies a volume of 2.006×10^{-2} m^3 at a temperature

of 300.15 K. Specific volume of water at this condition is $2.006 \square 10^{-3}$ m^3/kg. Since the specific volume of saturated liquid and saturated vapour are, respectively, $1.003 \square 10^{-3}$ m^3/kg and 38.81 m^3/kg, water in the final state is a mixture of saturated liquid and saturated vapour. When saturated liquid and vapour phases coexist at equilibrium at 300.15 K, the pressure should be the saturation pressure at this temperature.
Therefore, the final pressure attained is 3.564 kPa.
(c) Let x be the fraction of the mixture that is vapour. Then

$$1.003 \times 10^{-3} + x(38.81 - 1.003 \times 10^{-3}) = 2.006 \times 10^{-3}$$

or

$$x = \frac{2.006 \times 10^{-3} - 1.003 \times 10^{-3}}{38.81 - 1.003 \times 10^{-3}} = 2.6 \times 10^{-5}$$

The first law of thermodynamics written for a closed system is

$$\Delta U = Q - W$$

Since no work is exchanged between the system and the surroundings, $W = 0$ and the first law leads to $Q = \text{D}U$. The heat transferred is equal to the change in internal energy.
Internal energy of water initially is $U_1 = 113.1$ kJ/kg.
Internal energy in the final state is $U_2 = U_l + x(U_v - U_l)$, where U_l and U_v are the internal energy of saturated liquid and saturated vapour, respectively, at 300.15 K. It is given that U_l and U_v are, respectively, 113.1 and 2412.6 kJ/kg. Therefore,

$$U_2 = 113.1 + 2.6 \square 10^{-5}(2412 - 113.1)\ 113.16 \text{ kJ/kg}$$

$$\text{D}U = U_2 - U_1 = 113.16 - 113.1 = 0.05 \text{ kJ/kg}$$

For 10 kg water total change in internal energy is $\text{D}U = 0.5$ kJ.
It means that 0.5 kJ heat is transferred during the process.

2.5 ENTHALPY

For a system kept at constant volume in which no work of expansion or any other kind of work is done, the change in internal energy is equal to the heat supplied to it. When the system is free to change its volume against a constant external pressure, the change in internal energy is no longer equal to the energy supplied as heat. In effect, a part of the energy supplied is utilised by the system for occupying a new volume; the energy thus utilised is equal to the work required to ‘push’ the surroundings against a constant pressure. Consequently, $\text{D}U < Q$. However, the heat supplied at constant pressure can be measured as the change in another thermodynamic property of the system which we call the *enthalpy*. Enthalpy is denoted by H and is perhaps the most widely used of all thermodynamic functions. It is defined as

$$H = U + PV \qquad (2.6)$$

Here U is the internal energy of the system, P the absolute pressure and V the volume of the system.

Since U, P, and V are all state functions, any combination of them also must be a state function. Enthalpy is, therefore, a state function.

The product, PV, in Eq. (2.6) represents the work that must have been done against an environmental pressure P to create a volume V occupied by the system, or rather, the energy that the system possesses because of it occupying a space. Thus, enthalpy may be treated as 'total energy', because it includes both the intrinsic energy it possesses (U) and the energy due to the expansion possibilities of the system (PV). In differential form, Eq. (2.6) can be written as

$$dH = dU + d(PV) \qquad (2.7)$$

Since all the terms in Eq. (2.7) are state functions, it can be readily integrated to give

$$\Delta H = \Delta U + \Delta(PV) \qquad (2.8)$$

Equation (2.8) is applicable for any finite change occurring in the system.

We can show that the change in enthalpy for a mechanically reversible, non-flow process at constant pressure is equal to the heat supplied. Equation (2.7) can be expanded as

$$dH = dU + P\,dV + V\,dP \qquad (2.9)$$

Substituting Eq. (2.5) into Eq. (2.9), we get

$$dH = dQ - dW + P\,dV + V\,dP$$

Noting that $dW = P\,dV$ for a reversible non-flow process and $V\,dP = 0$ for constant pressure process, the above equation simplifies to

$$dH = dQ \text{ (for constant pressure process)} \qquad (2.10)$$

That is, when a system is heated at constant pressure, and only expansion work occurs, the change in enthalpy is equal to the heat supplied. On the other hand, for a process occurring at constant volume, work of expansion is zero and Eq. (2.5) reveals that the change in internal energy is equal to the heat supplied.

$$dU = dQ \text{ (for constant volume process)} \qquad (2.11)$$

***EXAMPLE* 2.7** Calculate ΔU and ΔH in kJ for 1 kmol water, as it is vaporised at the constant temperature of 373 K and constant pressure of 101.3 kPa. The specific volumes of liquid and vapour at these conditions are 1.04×10^{-3} and 1.675 m^3/kmol respectively; 1030 kJ of heat is added to water for this change.

Solution The expansion work done by the system during vaporisation is

$$W = P\Delta V = 101.3 \times 10^3\,(1.675 - 0.00104) \times 10^{-3} = 169.57 \text{ kJ}$$

$$Q = 1.03 \times 10^3 \text{ kJ}$$

$$\Delta U = Q - W = 860.43 \text{ kJ}$$

$$\Delta H = \Delta U + \Delta(PV)$$

For constant pressure process, this becomes

$$\Delta H = \Delta U + P\Delta(V) = 1.03 \times 10^3 \text{ kJ}$$

***EXAMPLE* 2.8** Liquid CO_2 at 233 K has a vapour pressure of 1.005×10^3 kPa and a specific volume of 0.9×10^{-3} m^3/kg. Assume that CO_2 is a saturated liquid at these conditions and its enthalpy is zero. Latent heat of vaporisation of CO_2 is 320.5 kJ/kg and the specific volume of saturated vapour is 38.2×10^{-3} m^3/kg. Calculate the internal energy of saturated liquid, and internal energy and enthalpy of saturated vapour.

Solution The internal energy of saturated liquid is obtained as

$$U_L = H_L - PV_L$$

where H_L is the enthalpy of saturated liquid and V_L is its specific volume.

$$U_L = 0 - (1.005 \times 10^3)(0.9 \times 10^{-3}) = -\,0.9045 \text{ kJ/kg}$$

Denoting the latent heat of vaporisation by ΔH_V, we get

$$H_V = H_L + \Delta H_V = 0 + 320.5 = 320.5 \text{ kJ/kg}$$

$$U_V = H_V - PV_V = 320.5 - (1.005 \times 10^3)\,(38.2 \times 10^{-3}) = 282.11 \text{ kJ/kg}$$

***EXAMPLE* 2.9** An electric current of 0.5 A from a 12 V supply is passed for 5 minutes through a resistance in thermal contact with saturated water at 1 atm. As a result, 0.798 g of water is vaporised. Assuming that the water vapour behaves ideally, calculate the molar internal energy change and enthalpy change during this process.

Solution The electrical energy supplied to the heater enters the water as heat. Since the vaporisation is occurring at constant pressure, the heat supplied to the water equals the change in its enthalpy, Eq. (2.10).

The electric energy supplied $= 0.5(12)\,(5 \times 60)/(10^3) = 1.8$ kJ

$$\Delta H = 1.8/0.798 \text{ kJ/g} = 1.8/(0.798/18) = 41 \text{ kJ/mol}$$

Referring to Eq. (2.9), for constant pressure process,

$$\Delta H = \Delta U + P\Delta V$$

Assuming the molar volume of saturated liquid to be negligible compared to that of saturated vapour, ΔV is approximately equal to the molar volume of the vapour. Since vapour behaves ideally, $P\Delta V = RT$, where R is the ideal gas constant. Therefore,

$$\Delta U = \Delta H - RT = 41 - (8.314 \times 10^{-3})\,373 = 37.9 \text{ kJ/mol}$$

***EXAMPLE*2.10** A piston–cylinder device contains 0.1 kg of saturated water vapour that is maintained at a constant pressure of 400 kPa. Heat is supplied by means of a resistance heater provided within the cylinder. A current of 0.2 A from a 230-V source is passed continuously for 10 min. Heat loss from the system is estimated to be 15.41 kJ. Making use of steam tables, determine the final temperature of the steam.

Solution Heat supplied by means of the electric heater:

$$VI \times t = 230 \times 0.2 \times 10 \times 60 = 27600 \text{ J} = 27.6 \text{ kJ}$$

Heat lost from the system = 15.41 kJ

Net heat supplied, $Q = -15.41 + 27.6 = 12.19$ kJ.

In a constant pressure process, the heat supplied goes to increase the enthalpy of the system. That is, $Q = \Delta H = 12.19$ kJ.

The enthalpy of 0.1 kg of water vapour increases by 12.19 kJ or for unit mass the change in enthalpy is

$$\Delta H = \frac{12.19}{0.1} = 121.9 \text{ kJ/kg}$$

Initially the system consists of saturated water vapour at 400 kPa. From steam tables (saturated steam), the enthalpy at this condition is $(H_1) = 2738.6$ kJ/kg.

Since the enthalpy increase $\Delta H = 121.9$ kJ/kg, enthalpy in the final state is

$$H_2 = H_1 + \Delta H = 2738.6 + 121.9 = 2860.5 \text{ kJ/kg.}$$

The enthalpy of superheated steam at 400 kPa is 2860.5 kJ/kg. From the tables of properties o superheated steam, the temperature of steam is found to be 473.15 K.

2.6 FIRST LAW OF THERMODYNAMICS FOR FLOW PROCESS

The steady-state flow through an equipment is of considerable importance industrially, as material flow through equipment such as pumps, fans, compressors, turbines, nozzles, heat exchangers, reactors, etc. The term *steady state* requires that the conditions at all points in the apparatus are independent of time. For this to be true, there should be no accumulation or depletion of material or energy within the equipment and all rates must be constant. The total mass flow rates at all points along the path of the fluid must be the same.

Consider an idealised flow system as shown in Fig. 2.4. A fluid is flowing through the apparatus from section 1 to section 2. The velocity, specific volume, pressure, and height above the datum are represented by u, V, P, and Z respectively. The suffix 1 indicates conditions at section 1 and suffix 2 the conditions at section 2. Heat Q is added per unit mass of the fluid by means of the heat exchanger and shaft work W_S is extracted by means of a turbine or any other suitable device.

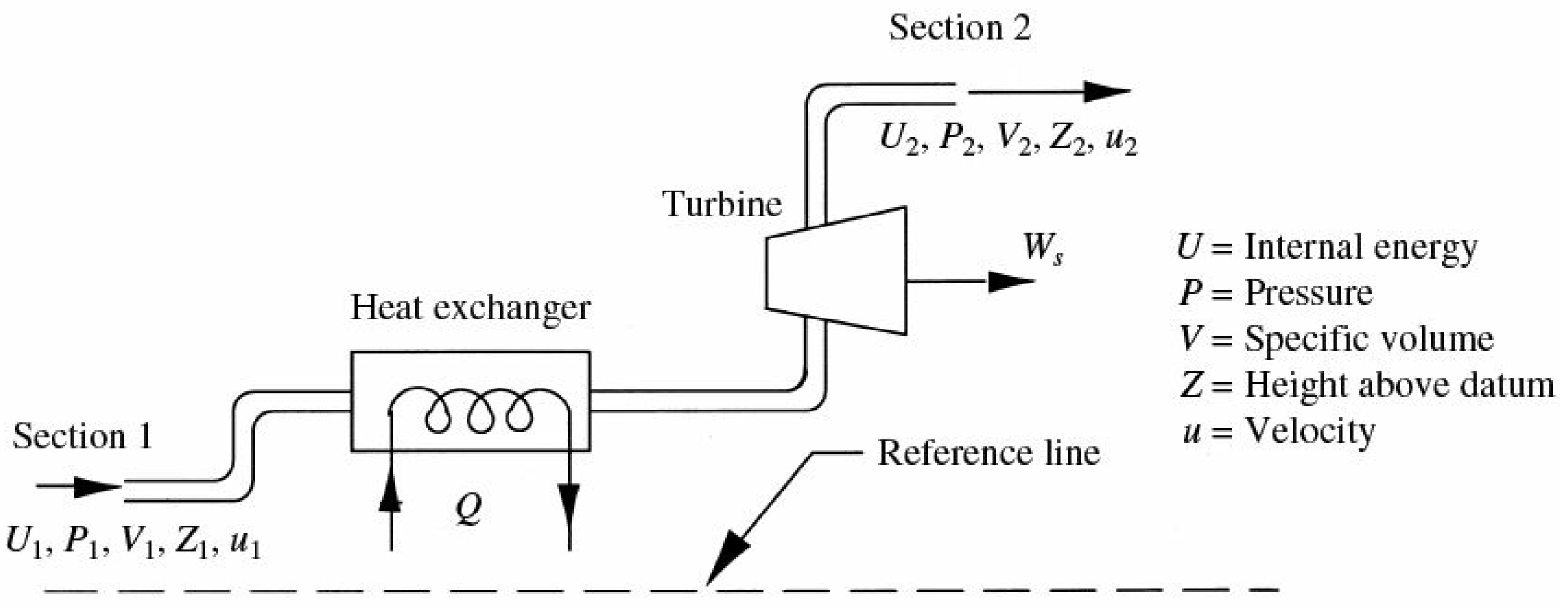


Fig. 2.4 Steady-state flow process.

According to the first law of thermodynamics, the total energy with which the fluid is entering at section 1 plus the energy imparted to the fluid while it is in the system must be equal to the total energy with which the fluid is leaving the system at section 2.

The contributions to the total energy at section 1 are:

Internal energy: Each unit mass of the fluid brings with it a certain amount of internal energy U_1. The incoming internal energy is mU_1.

Potential energy: The fluid has a potential energy above the reference plane equal to the work done against gravity in raising it to a height Z_1. The potential energy of the fluid at section 1 is mgz_1.

Kinetic energy: It is due to the velocity of the fluid and at section 1, its value is $(1/2)mu_1^2$.

Entrance work: A mass of fluid entering the system is being pushed by the fluid behind it by a certain force. This force multiplied by the distance through which the force acts is equal to the *flow energy* or *entrance work*. The force acting on the fluid equals the product of the pressure and the cross-sectional area of the tube. Since a unit mass of the fluid at pressure P_1 occupies a volume V_1, the distance through which the force acts in order to move the fluid into the system is equal to V_1/A, where A is the cross-sectional area of the tube. This work which is equal to P_1V_1 for unit mass of the fluid is done by the flowing fluid and therefore is called 'flow energy'. The flow energy at section 1 is mP_1V_1.

Total energy at section 1 = $mU_1 + mgZ_1 + (1/2)mu_1^2 + mP_1V_1$

The energy at section 2 is also made up of similar quantities. The force at section 1 does work on the system, while at section 2, it is in the opposite direction and represents work done by the system on the surroundings.

Total energy at section 2 = $mU_2 + mgZ_2 + (1/2)mu_2^2 + mP_2V_2$

The energy imparted to the fluid within the system is determined by knowing the amount of heat exchanged between the system and the surroundings and the total work done by the system or work done on the system. That is,

Total energy imparted to the fluid is = $mQ - mW_s$

Combining the preceding three results, we see that for unit mass of fluid the energy balance gives

$$U_1 + gZ_1 + P_1V_1 + \frac{1}{2}u_1^2 + Q - W_s = U_2 + gZ_2 + P_2V_2 + \frac{1}{2}u_2^2$$

or

$$DU + D(PV) + gDZ + \frac{1}{2}Du^2 = Q - W_s \qquad (2.12)$$

Substituting Eq. (2.8) into Eq. (2.12), we get

$$\boxed{\Delta H + g\Delta Z + \frac{1}{2}\Delta u^2 = Q - W_s} \tag{2.13}$$

Equation (2.13) is the mathematical statement of first law of thermodynamics for flow processes and can be used for solving problems involving flow of fluids, power required for pumps, and compressors, etc. For most applications in thermodynamics, the kinetic energy and potential energy terms in Eq. (2.13) are negligibly small compared with the other terms so that the equation can be written as

$$\boxed{\Delta H = Q - W_s} \tag{2.14}$$

This equation is analogous to Eq. (2.4) developed for non-flow processes.

***EXAMPLE* 2.11** A steam turbine using steam at 1368 kPa and 645 K and discharging saturated steam at 137 kPa is used to generate power for certain chemical plant. The turbine acts adiabatically and the feed and discharge velocities may be considered equal. Determine the theoretical horsepower developed by the turbine if it uses 1650 kg steam per hour. From the steam tables, enthalpy of superheated steam at 1368 kPa and 645 K = 3200 kJ/kg and enthalpy of saturated steam at 137 kPa = 2690 kJ/kg.

Solution Refer Eq. (2.13). Since the process is adiabatic, $Q = 0$. Assuming that the inlet and discharge of the turbine are at the same level, $\Delta Z = 0$. Feed and discharge velocities being equal, $\Delta u^2 = 0$. Equation (2.13) reduces to

$$W_S = -\Delta H = -(H_2 - H_1) = H_1 - H_2 = 3200 - 2690 = 510 \text{ kJ/kg}$$

Since the steam consumption rate is 1650 kg/h,

$$\text{work done by the turbine} = (510 \times 10^3)\ 1650/3600 = 233750 \text{ J/s}$$
$$= 233750/745.7 = 313.46 \text{ hp}$$

***EXAMPLE* 2.12** A liquid mixture containing 50 mol percent each of benzene and toluene at 313 K is to be continuously flash vaporised so that 60 mol percent of the feed is vaporised. The residual liquid product contains 35 mol percent benzene. If the enthalpies per mole of feed, distillate and the residue are respectively 5, 30 and 2 kJ/mol, calculate the heat added in kJ per mole of vapour product.

Solution Basis: 1 mol vapour product.

The vapour produced being 60 percent of the feed, feed = 1/0.6 = 1.667 mol and the residue is 1.667 – 1.00 = 0.667 mol.

The process is represented as shown in Fig. 2.5. Let F be the moles of the feed which is being flash vaporized in unit time, D be the moles of vapour produced and W be the moles of liquid produced in unit time.

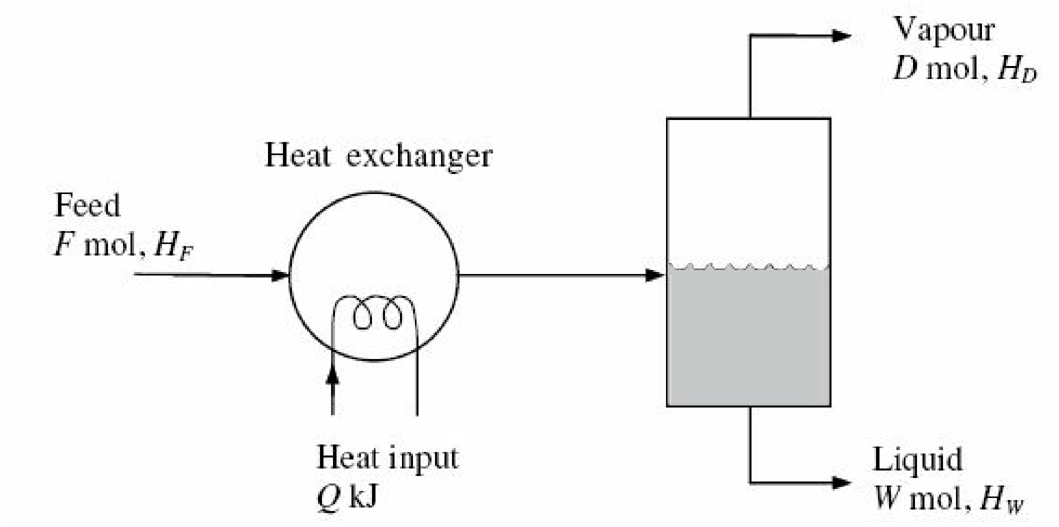


Fig. 2.5 Flash vaporisation process in Example 2.12.

Here $F = 1.667$ mol, $D = 1$ mol and $W = 0.667$ mol.
The first law applicable for the system is given by Eq. (2.14).

$$\Delta H = Q - W_S$$

Since no work is exchanged between the system and the surroundings, $W_S = 0$ and Eq. (2.14) reduces to

$$Q = \Delta H$$

where Q is the heat added and ΔH is the change in enthalpy.
Denoting the enthalpy of the vapour by H_D, enthalpy of the liquid by H_L and enthalpy of the feed by H_F, the change in enthalpy is

$$\Delta H = DH_D + WH_W - FH_F$$

Here, $H_D = 30$ kJ/mol, $H_W = 2$ kJ/mol and $H_F = 5$ kJ/mol.
Therefore,

$$\Delta H = DH_D + WH_W - FH_F$$

$$= 1 \times 30 + 0.667 \times 2 - 1.667 \times 5 = 23.0 \text{ kJ}$$

Since $Q = \Delta H$, the heat supplied = 23.0 kJ/mol product.

***EXAMPLE* 2.13** Water at 368 K is pumped from a storage tank at the rate of 25 m^3/h. The motor for the pump supplies work at the rate of 2 hp. The water passes through a heat exchanger, where it gives up heat at the rate of 42000 kJ/min and is delivered to a second storage tank at an elevation of 20 m above the first tank. What is the temperature of the water delivered to the second storage tank? Assume that the enthalpy of water is zero at 273 K and the specific heat of water is constant at 4.2 kJ/kg K.

Solution

The mass flow rate of water = 25×10^3 kg/h

Work done per kg of water pumped = $2(745.7 \times 10^{-3})\ 3600/(25 \times 10^3) = 0.2148$ kJ/kg

$$\text{Heat given out per kg of fluid} = (42000)\ 60/(25 \ \square\ 10^3) = 100.8 \text{ kJ/kg}$$

$$\text{Change in potential energy, } \mathrm{D}(PE) = mg\mathrm{D}Z = 20\ (9.81)10^{-3} = 0.1962 \text{ kJ/kg}$$

Here, $Q = -\ 100.8$ kJ/kg and $W_S = -\ 0.2148$ kJ/kg. Assume that there is no change in the kinetic energy of water. Substituting these in Eq. (2.13),

$$\mathrm{D}H = -\ 100.8 + 0.2148 - 0.1962 = -\ 100.78 \text{ kJ/kg}$$

$$H_2 - H_1 = -\ 100.78 \text{ kJ/kg}$$

Therefore,

$$H_2 = H_1 - 100.78 \text{ kJ/kg}$$

But,

$$H_1 = C_P(T - T_0) = 4.2\ (368 - 273) = 399 \text{ kJ/kg}$$

Hence,

$$H_2 = 399 - 100.78 = 298.22 \text{ kJ/kg}$$

Let T be the temperature of water at the second storage tank. Then,

$$4.2\ (T - 273) = 298.22$$

or

$$T = 298.22/4.2 + 273 = 344.0 \text{ K}$$

***EXAMPLE* 2.14** Water is flowing in a straight horizontal insulated pipe of 25 mm i.d. There is no device present for adding or removing energy as work. The upstream velocity is 10 m/s. The water flows in a section where the diameter is suddenly increased. (a) What is the change in enthalpy if the downstream diameter is 50 mm? (b) What is the maximum enthalpy change for a sudden enlargement in pipe?

Solution Since Q and W_S are both equal to zero, Eq. (2.13) becomes

$$\Delta H + \frac{1}{2}\Delta u^2 = 0$$

Thus

$$\Delta H = -\frac{1}{2}\Delta u^2 = \frac{1}{2}(u_1^2 - u_2^2)$$

(a) Since $A_1u_1 = A_2u_2$, where A_1 and A_2 are the upstream and downstream cross-sectional areas of the pipe respectively, we see that

$$u_2 = \frac{A_1}{A_2}u_1 = \frac{D_1^2}{D_2^2}u_1 = \frac{25^2}{50^2}10 = 2.5 \text{ m/s}$$

Therefore,

$$\Delta H = (1/2)\,(10^2 - 2.5^2) = 46.88 \text{ J/kg}$$

(b) When the enthalpy change is maximum, $(1/2)\,(u_1^2 - u_2^2)$ is maximum, i.e. $u_2 = 0$ for a given upstream velocity u_1. Therefore,

$$(\Delta H)_{\max} = (1/2)\,u_1^2 = (1/2)\,10^2 = 50 \text{ J/kg}$$

***EXAMPLE*2.15** Steam at 1800 kPa and 673.15 K steadily enters a nozzle at a rate of 5 kg/s and leaves the nozzle at 1400 kPa with a velocity of 300 m/s. The inlet area of the nozzle is 0.02 m^2. Heat losses from the nozzle per unit mass of the steam are estimated to be 3.3 kJ/kg. Determine the exit temperature of the steam.

Solution: A nozzle is a device for converting thermal or mechanical energy into kinetic energy by changing the cross-sectional area available for flow (see Chapter 5). Flow through a nozzle is schematically represented in Fig. 2.6.

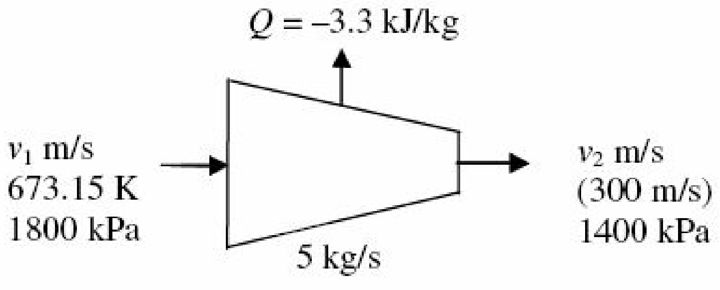


Fig. 2.6 Flow through nozzle in Example 2.15.

The first law of thermodynamics for a steady flow process is given by

$$\mathrm{D}H + \mathrm{D}KE + \mathrm{D}PE = Q - W_S \qquad \text{(i)}$$

Here $\mathrm{D}PE = 0$, since the inlet and exit of the nozzle are assumed to be at the same level.
$W_S = 0$, since no work is exchanged between the system and the surroundings.

$Q = -3.3$ kJ/kg (negative because, heat is lost)

$\Delta KE = \frac{1}{2}(v_2^2 - v_1^2)$, where v_1 and v_2 are the velocities of steam at the inlet and exit of the nozzle. The velocity of steam at the inlet (v_1) can be calculated knowing the mass rate $\dot{m}$, area of nozzle at the inlet (A_1) and the specific volume of steam (V_1).

$$\dot{m} = v_1 \times A_1 \times \rho_1 = v_1 \times A_1 \times \frac{1}{V_1}$$

Here $\dot{m} = 5$ kg/s, $A_1 = 0.02$ m^2. Specific volume V_1 is determined from superheated steam property tables corresponding to $P = 1800$ kPa and $T = 673.15$ K. $V_1 = 0.16847$ m^3/kg.

$$\dot{m} = v_1 \times A_1 \times \frac{1}{V_1}$$

$$5 = v_1 \times 0.02 \times \frac{1}{0.16847}$$

which gives $v_1 = 42.12$ m/s

$$v_2 = 300 \text{ m/s (given).}$$

$$\Delta KE = \frac{1}{2}(v_2^2 - v_1^2) = \frac{1}{2}(300^2 - 42.12^2) = 44113 \text{ J/kg} = 44.113 \text{ kJ/kg}$$

Enthalpy at the inlet of the nozzle $H_1 = 3250.9$ kJ/kg (from superheated steam tables).

$$\Delta H = H_2 - H_1 = H_2 - 3250.9$$

where H_2 is the enthalpy of steam at the nozzle exit.

Substituting ΔKE and ΔH into Eq. (i) and noting that $\Delta PE = 0$ and $W_s = 0$, we get

$$H_2 - 3250.9 + 44.113 = -3.3$$

or

$$H_2 = 3250.9 - 44.113 - 3.3 = 3203.5 \text{ kJ/kg}$$

Since the exit steam is at 1400 kPa, the temperature of superheated steam having enthalpy of 3203.5 kJ/kg at 1400 kPa is found to be 648.15 K from steam tables.

Temperature of exit steam = 648.15 K.

2.7 HEAT CAPACITY

The *heat capacity* of a substance is the quantity of heat to be supplied to effect a temperature rise of one degree. Thus

$$dQ = C\,dT$$

where C is known as heat capacity of the substance. Heat capacity of unit mass of a substance is also known as *specific heat* of the substance. The heat capacity depends on the way in which heat is supplied. When heat is supplied to a system at constant volume, the system is unable to do any work and the quantity of heat required is given by

$dQ = C_V\, dT$ (constant volume) (2.15)

where C_V is known as the *heat capacity at constant volume*. Thus,

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \tag{2.16}$$

According to Eq. (2.5), for a constant volume process $dU = dQ$, so that we can write Eq. (2.16) as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{2.17}$$

If heat is supplied to a substance at constant pressure, it is free to expand doing work against the constant pressure. A part of the heat supplied to the system is utilised for the work of expansion and more heat will be required to raise the temperature than that required in a constant volume process for the same temperature change. The amount of heat required is related to the temperature rise as

$dQ = C_P\, dT$ (constant pressure) (2.18)

where C_P is called the *heat capacity at constant pressure*. Thus,

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \tag{2.19}$$

For a constant pressure process, Eq. (2.5) becomes

$dU = dQ - P\, dV$

or $dQ = dU + P\, dV = dH$ (constant pressure)

Equation (2.19) may be written as

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{2.20}$$

Since for a given temperature change, the heat required is more in a constant pressure process than that in a constant volume process, $C_P > C_V$. However, the difference between C_P and C_V for solids and liquids are very small compared to that for gases, as the change in volume of solids and liquids during heating is not very significant.

Equations (2.17) and (2.20) give

$dU = C_V\, dT$ (constant volume) (2.21)

$dH = C_P\, dT$ (constant pressure) (2.22)

For a constant volume process, change in the internal energy is given by Eq. (2.21). Since internal energy is a state function, Eq. (2.21) should give the change in internal energy in any process, provided the initial and final volume are the same irrespective of the path along which this change is

brought about. However, Eq. (2.15) gives the heat required only for a process where the volume undergoes no change. Similarly, the change in enthalpy in a constant pressure process or a process in which the initial and final pressures are the same, can be evaluated by Eq. (2.22) whereas
Eq. (2.18) determines the heat supplied in a true isobaric process only.

***EXAMPLE* 2.16** Hydrogenation of an oil is carried out in a reactor at a pressure of 136.8 kPa and a temperature of 453 K. The hydrogen gas at 293 K is heated to 453 K by passing through a coil where it experiences a pressure drop of 300 kPa. Hydrogen behaves like an ideal gas and its heat capacity at constant pressure is 29.4 kJ/kmol. Neglecting kinetic energy effects determine the heat transfer rate in the coils per 1000 kg hydrogen.

Solution The hydrogen gas at the inlet of the coils is at $T = 293$ K and $P = 300 + 136.8 = 436.8$ kPa and the hydrogen at the exit is at $T = 453$ K and $P = 136.8$ kPa. It is assumed that there is no pressure drop between the coil exit and the reactor.

Neglecting the kinetic and potential energy changes the general first law equation, Eq. (2.13), reveals that the heat supplied is equal to the change in enthalpy of the gas. The enthalpy being a state function change in enthalpy can be calculated by assuming the actual process to be occurring through a number of steps. Let us assume that in step 1, the pressure of the gas is being reduced from 436.8 kPa to 136.8 kPa isothermally at 293 K, and in step 2, the gas is heated from 293 K to 453 K at a constant pressure of 136.8 kPa.

The enthalpy of an ideal gas is dependent only on temperature. Thus, $\mathrm{D}H$ for step 1 = 0. For step 2,

$$\mathrm{D}H = mC_P\,\mathrm{D}T = (1000/2.02)\ 29.4\ (453 - 293) = 2328.7 \text{ kJ}$$

Heat transferred in the coils,

$$Q = \mathrm{D}H = 0 + 2328.7 = 2328.7 \text{ kJ}$$

***EXAMPLE* 2.17** Heat is transferred to 10 kg of air which is initially at 100 kPa and 300 K until its temperature reaches 600 K. Determine the change in internal energy, the change in enthalpy, the heat supplied, and the work done in the following processes:

(a) Constant volume process
(b) Constant pressure process.

Assume that air is an ideal gas for which the P-V-T relationship is $PV = nRT$, where n is the number of moles of the gas and R is the ideal gas constant. $R = 8.314$ kJ/kmol K. Take $C_P = 29.099$ kJ/kmol K, $C_V = 20.785$ kJ/kmol K and molecular weight of air = 29.

Solution Number of moles of the gas = 10/29 = 0.3448 kmol. $P_1 = 100$ kPa, $T_1 = 300$ K.

Hence,

$$V_1 = nRT_1/P_1 = 0.3448\ (8.314)\ 300/100 = 8.6\ \text{m}^3$$

(a) $$V_2 = 8.6\ \text{m}^3, \qquad T_2 = 600\ \text{K}$$

Change in internal energy:

$$\Delta U = n\int C_V\, dT = (0.3448)\ 20.785(600 - 300) = 2150\ \text{kJ}$$

Heat supplied:

$$Q = \Delta U = 2150\ \text{kJ}$$

Work done:

$$W = Q - \Delta U = 0$$

Change in enthalpy:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR\Delta T = 2150 + (0.3448)\ 8.314\ (600 - 300) = 3010\ \text{kJ}$$

(b) $$P_2 = 100\ \text{kPa}, \qquad T_2 = 600\ \text{K}$$

Change in enthalpy:

$$\Delta H = n\int C_P\, dT = (0.3448)\ 29.099(600 - 300) = 3010\ \text{kJ}$$

Heat supplied:

$$Q = \Delta H = 3010\ \text{kJ}$$

Change in internal energy:

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - nR\Delta T = 3010 - (0.3448)\ 8.314\ (600 - 300) = 2150\ \text{kJ}$$

Work done:

$$W = Q - \Delta U = 860\ \text{kJ}$$

[The work done may also be calculated as

$$W = P\Delta V = P(V_2 - V_1)$$

$$V_2 = nRT_2/P = 0.3448\ (8.314)\ 600/100 = 17.2\ \text{m}^3$$

Therefore,

$$W = 100\ (17.2 - 8.6) = 860\ \text{kJ}]$$

***EXAMPLE* 2.18** The P-V-T behaviour of nitrogen is represented by the ideal gas equation $PV = nRT$, where n is the number of moles of the gas and R the ideal gas constant ($R = 8.314$ kJ/kmol K). The heat capacities of the gas are $C_V = 20.8$ and $C_P = 29.1$ kJ/kmol K. The gas initially at 10 bar and 280 K is undergoing a change of state to the final condition of 1 bar and 340 K. Determine the change in internal energy and the change in enthalpy.

Solution Take a basis of 1 kmol ideal gas. The initial conditions of the gas are represented by suffix

1 and the final conditions by suffix 2. $P_1 = 10$ bar, $T_1 = 280$ K. Therefore,

$$V_1 = nRT_1/P_1 = 8.314\ (280)/1000 = 2.328\ \text{m}^3$$

$P_2 = 1$ bar, $T_2 = 340$ K, Therefore,

$$V_2 = nRT_2/P_2 = 8.314\ (340)/100 = 28.268\ \text{m}^3$$

Since the changes in the state functions depend only on the terminal conditions and not on the path followed, we can assume that the actual change is carried out in different steps for which ΔH and ΔU are easily evaluated. Since the changes in U and H along a constant volume and constant pressure paths are easily calculated using C_V and C_P, we may assume that the proposed change in state is occurring along the following two-step process:

1. *A constant volume process in which the pressure is reduced to the final value* P_2 *and the temperature gets reduced to* T□.

Let P□ and V□ denote the pressure and volume of the system after this step. Then

P□ $= P_2$, V□ $= V_1$

T□ $=$ P□V□$/nR = 100\ (2.328)/8.314 = 28$ K

For this constant volume process,

$$\Delta U = C_V \Delta T = 20.8(28 - 280) = -\ 5241.6\ \text{kJ}$$

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + V\Delta P = -\ 5241.6 + 2.328(100 - 1000) = -\ 7336.8\ \text{kJ}$$

$$W = 0$$

$$Q = \Delta U = -\ 5241.6\ \text{kJ}$$

2. *A constant pressure process in which the gas is heated to the final temperature* T_2 *and the final volume* V_2.

For this constant pressure process,

$$\Delta H = C_P \Delta T = 29.1(340 - 28) = 9079.2\ \text{kJ}$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P\Delta V = 9079.2 - 100\ (28.268 - 2.328) = 6485.2\ \text{kJ}$$

$$Q = \Delta H = 9079.2\ \text{kJ}$$

$$W = Q - \Delta U = 9079.2 - 6485.2 = 2594\ \text{kJ}$$

For the actual process, the changes in U and H are obtained as the sum of the respective values in the two-step process.

$$\Delta U = -\ 5241.6 + 6485.2 = 1243.6\ \text{kJ}$$

$$\Delta H = -\ 7336.8 + 9079.2 = 1742.4\ \text{kJ}$$

SUMMARY

The essence of the first law of thermodynamics is contained in the statement: “The energy of the universe is conserved” (Section 2.1). Mathematical expressions for the first law were developed for a static system undergoing a cycle of changes (Section 2.2), for a non-flow process (Section 2.4), and for a flow process (Section 2.6). The internal energy U is a thermodynamic property arising by virtue of the configuration and motion of the molecules constituting the system (Section 2.3). Enthalpy H is defined as the sum of the internal energy that the system possesses and the product PV, the latter being the energy of the system by virtue of it occupying a space (Section 2.5). It was shown that for a cyclic process, the difference between the algebraic summation of all the heat effects and the summation of all the work effects is zero, whereas for non-flow processes, in general, the difference between the heat supplied to the system and the work done by the system is equal to the change in its internal energy. The application of the first law of thermodynamics to the steady-state flow through an equipment, in which the changes in the kinetic and potential energies were negligible, revealed that the difference between the heat and work effects accompanying the process could be measured by the enthalpy change in the process.

Section 2.7 was devoted to the definitions of two very important thermodynamic properties used for the determination of the heat requirements in a process: the heat capacities at constant pressure and at constant volume, C_P and C_V, respectively. The heat requirement under the constant volume restriction is different from that in a constant pressure process, since in the latter, a part of the heat supplied is utilised for maintaining the pressure and is not available for increasing the temperature (Section 2.7).

REVIEW QUESTIONS

1. What is the significance of Joule's experiments in the formulation of the first law of thermodynamics?
2. "Energy can neither be created nor be destroyed". How does this statement lead to the statement "The energy of the universe is conserved"?
3. What do you mean by a cyclic process? State and explain the first law for a cyclic process.
4. Distinguish between internal energy, kinetic energy, and potential energy of a system.
5. What is the change in internal energy in a cyclic process? What is it in a static non-flow process?
6. Prove that the internal energy is a state function.
7. What is enthalpy of a system? How is it related to the internal energy?
8. Prove that the heat supplied is equal to the change in internal energy for a constant volume process and the change in enthalpy for a constant pressure process.
9. What is meant by 'entrance work' in flow systems?
10. How do you state mathematically the first law of thermodynamics that can be used for solving steady-state fluid flow problems?
11. Why is the specific heat at constant pressure, C_P, always greater than that at constant volume, C_V?
12. For all processes, where the initial and final pressures are the same, $dQ = dH = C_P\,dT$. Do you agree? If not, why?

2.1 Water is being heated in a closed container provided with a paddle agitator. 50 kJ of heat is supplied and 10 kJ lost to the surroundings. The work done by the paddle-wheel is 750 N m. What is the change in internal energy of the contents of the vessel?

2.2 An insulated rigid tank is divided into two equal parts by a partition. Initially, one part contains 5 kg of an ideal gas at 1 MPa and 400 K and the other part is evacuated. The partition is now removed and the gas expands into the entire tank. Determine the final temperature and pressure in the tank.

2.3 An elevator with a mass of 2500 kg rest at a level of 7.5 m above the base of the elevator shaft. It is raised to 75 m when the cable holding it breaks. It falls freely to the base where it is brought to rest by a strong spring. Assume that the acceleration due to gravity is 9.81 m/s^2. Neglecting the effect of friction, Calculate: (a) The potential energy of the elevator in its initial position. (b) The potential energy of the elevator in its highest position. (c) The work done in raising the elevator. (d) The kinetic energy and velocity of the elevator just before it strikes the spring. (e) The potential energy of the spring when the elevator rests on it.

2.4 Consider 1 kg of water in a waterfall which is flowing down from a height of 100 m. At the bottom of the fall it joins a river the downstream velocity of which may be assumed negligible. Neglecting any energy exchange between the water and the surroundings, calculate: (a) The potential energy at the top of the falls. (b) The kinetic energy just before the water strikes the bottom. (c) The change in temperature of the water when it enters the river.

2.5 A 10 g lead ball at 300 K is dropped from a height of 10 m. Calculate: (a) the kinetic energy and speed of the ball as it reaches the ground and (b) the temperature rise of the ball if all its kinetic energy is transformed into internal energy as the ball is suddenly stopped after 10 m, given that the specific heat of lead is 125.6 J/kg K and its volume change is negligible.

2.6 A mixture of saturated steam and saturated water is contained in a rigid tank of volume 0.1 m^3 at a pressure of 2 bar. The liquid occupies 10% of the total volume. How much heat must be added in order that the tank contains only saturated steam? What will be the pressure in the tank? The specific volumes of saturated liquid and saturated vapour are 1.061×10^{-3} m^3/kg and 0.8857 m^3/kg respectively. The internal energy of saturated liquid and saturated vapour are respectively 504.5 kJ/kg and 2529.5 kJ/kg.

2.7 Iron reacts with hydrochloric acid at 300 K according to

$$FeS\ (s) + 2HCl\ (aq) \rightarrow FeCl_2\ (aq) + H_2\ (g)$$

Determine the work done when 0.1 kg iron reacts with HCl in (a) a closed vessel, (b) an open vessel.

2.8 A vessel of volume 1 m^3 initially contains one per cent by volume saturated liquid water and the rest saturated vapour at 1 bar. How much heat is to be supplied so that the vessel gets filled with vapour? Take data from steam tables.

2.9 Liquid water at 373 K and 101.3 kPa has an internal energy of 420 kJ/kg on an arbitrary basis The specific volume at these conditions is 1.04×10^{-3} m^3/kg. The water is brought to the vapour state at 473 K and 700 kPa. At this condition, its specific volume is 0.3 m^3/kg and its enthalpy is 2844 kJ/kg. Calculate the enthalpy of the liquid and the changes in internal energy and enthalpy accompanying the vaporisation process.

2.10 A sample of 10 g of liquid benzene at its boiling point is vaporised using a 12 V, 0.5 A electric supply. The normal boiling point and latent heat of vaporisation of benzene are 353.2 K and $30.8 \square 10^3$ kJ/kmol respectively. Determine: (a) the change in internal energy, (b) the time required for complete vaporisation.

2.11 A cylinder fitted with a piston has a volume 0.1 m^3 and contains 0.5 kg of steam at 500 kPa. How much heat is to be supplied to bring the temperature of the steam to 823 K keeping the pressure constant? What is the work done in the process?

2.12 A 5-kg saturated liquid water contained in a piston-cylinder arrangement at 200 kPa is heated by passing a current of 8 A through an electric resistance heater kept within the cylinder for 46 min. Water is stirred by a paddle wheel which does a work of 500 kJ. If one-half of the liquid is evaporated at constant pressure, what is the voltage of the electric source?

2.13 A steam boiler of volume 2.3 m^3 initially contained 1.7 m^3 liquid water in equilibrium with 0.6 m^3 of vapour at 100 kPa. The boiler is heated keeping the inlet and discharge valves closed. The relief valve is set to lift when the pressure in the boiler reaches 5500 kPa. Determine the amount of heat supplied to the contents in the boiler before the relief valve lifts.

2.14 A gas expands from an initial volume of 0.2 m^3 to a final volume of 0.4 m^3 in a reversible steady flow process. During the process, the pressure varies with the volume as

$$P = 5 \square 10^5\, V + 7 \square 10^4$$

where P is in N/m^2 and V is in m^3. The inlet line is 4 m below the outlet line and the gas enters with a negligible velocity. The internal energy of the gas decreases by 30 kJ during the process. Determine the heat transferred.

2.15 A trial run on a steam turbine power plant gave the following results

Entrance to boiler	*Exit of turbine*
Mass flow rate = 3600 kg/h	Velocity of steam = 25 m/s
Enthalpy of water = 850 kJ/kg	Elevation above datum = 0
Elevation above datum = 4.3 m	Enthalpy of steam = 2625 kJ/kg
Velocity of water = 5 m/s	

Determine the power developed by the turbine if the heat added in the boiler is 2100 kJ/s.

2.16 The work required for compressing a gas from an initial condition of 100 kPa and 300 K to a final pressure of 300 kPa is found to be 280 kJ/kg of the gas. The compressed gas is admitted to a nozzle where its velocity is increased to 700 m/s. If the gas enters the compressor with negligible velocity and leaves the nozzle at 100 kPa and 300 K, what is the heat removed during compression?

2.17 In a test of water-jacketed air compressor, it was found that the shaft work required to drive the compressor was 150 kJ/kg air compressed. The enthalpy of air leaving the compressor was found to be greater than that of the air entering the compressor by 80 kJ/kg and the heat removed by the cooling water was 100 kJ/kg of air. Determine the amount of energy that must have been dissipated as heat to the atmosphere from the bearings, cylinder walls, etc.

2.18 Water at 200 kPa and 355 K (H = 343.3 kJ/kg) enters a straight horizontal pipe at a velocity 3 m/s where it is heated by flue gases from the outside. Steam leaves the system at 100 kPa and 423 K (H = 2776.3 kJ/kg) at a velocity of 200 m/s. How much heat must have been supplied per kg of water flowing?

2.19 A steam-jet ejector is used to entrain saturated water vapour at 25 kPa (H = 2618.2 kJ/kg) leaving an evaporator, by high pressure saturated steam at 1000 kPa (2778.1 kJ/kg). It is estimated that with every kg of high-pressure steam 0.75 kg of the vapour from the evaporator can be entrained. If the mixed stream leaving the ejector is at 100 kPa what is its temperature?

2.20 Air at 80 kPa, 300 K, and 250 m/s enters a diffuser at a rate of 2.5 kg/s and leaves at 320 K. The exit area of the diffuser is 0.04 m^2. The air is estimated to lose heat at a rate of 20 kJ/s during this process. Assume air to be an ideal gas with average molecular weight of 29 and average heat capacity, C_P of 1.0068×10^3 J/kg K under the stated conditions. Determine (a) the exit velocity and (b) the exit pressure of the air.

2.21 Superheated steam at 2 MPa and 673 K is expanded to a pressure 15 kPa in an adiabatic turbine, the power output of which is 5 MW. The steam enters at a velocity of 50 m/s and leaves at 180 m/s as a two-phase mixture consisting of 90% vapour. The inlet and exit of the turbine are at elevations of 10 m and 6 m from the datum. Determine the work done per unit mass of the steam flowing through the turbine and the mass flow rate of the steam.

2.22 A compressor receives air at 101.3 kPa at a steady rate of 0.5 kg/s and delivers at 700 kPa. At the inlet, the velocity and specific volume of air are 6 m/s and 0.83 m^3/kg, respectively and those at the exit are 4 m/s and 0.15 m^3/kg, respectively. The internal energy of compressed air is greater than that of inlet air by 90 kJ/kg. Heat is removed from the cylinder at a rate of 60 W by the circulating cooling water. Determine the power required to drive the compressor.

2.23 Turbines in a hydroelectric power plant receive water from a 100-m high dam, generate power and discharge water through a 6-m diameter pipe at a velocity of 15 m/s into a river below the dam. Assume that the dam and the surroundings are at the same temperature. What is the power output from the plant?

2.24 A pump which supplies water at the rate of 200 cubic metre per hour is driven by a 20-kWh electric motor having an efficiency of 80%. The pressures at the inlet and exit of the pump are 100 and 316 kPa, respectively and the potential energy change across the pump is negligible. The inlet and exit pipes are of the same diameters. Determine the mechanical efficiency of the pump.

2.25 The turbine in a hydroelectric power plant receives water at a rate of 120 m^3/s from an elevation of 150 m. If the combined efficiency of the turbine-generator system is 80%, determine the power output from the plant in MW. Neglect frictional losses in the piping.

2.26 Oil flows at a rate of 1000 kg/min from an open reservoir at the top of a hill 400 m in height to another reservoir at the bottom of the hill. Heat is supplied to the oil on its way at the rate 1800 kJ/min and work is supplied by a 1 hp pump. Take the mean specific heat of oil to be 3.35 kJ/kg K. Determine the temperature change of the oil.

2.27 A gas initially at 100 bar is undergoing a reversible process in which its pressure gets doubled at a constant volume of 0.5 m^3. If the total internal energy (U□) of the gas in kJ is related to the pressure P in bar and total volume (V□) in m^3 according to U□ = 2.0 PV□, calculate the change in enthalpy and the heat supplied.

2.28 (a) Three kilo mole nitrogen gas (C_P = 29.1 kJ/kmol K and C_V = 20.8 kJ/kmol K) at 350 K is taken in a rigid container and is heated to 550 K. How much heat must be supplied, if the mass of the vessel is 100 kg and its specific heat is 0.5 kJ/kg K?

(b) Two kilo mole nitrogen is taken in a piston/cylinder arrangement at 500 K. Determine the quantity of heat extracted from the gas to cool it to 350 K at constant pressure if the heat capacity of the container is negligible.

2.29 An insulated rigid container contains air at 5 bar and 375 K. The volume of the container is 1 m^3. Air may be assumed to behave as an ideal gas so that the P-V-T relationship is $PV = nRT$, where R = 8.314 kJ/kmol K. The specific heat C_V of air is 20.785 kJ/kmol K. The temperature of the air is increased by a rotating paddle wheel. Calculate the work done to raise the temperature of the air to 425 K.

2.30 Assume that the P-V-T relationship for nitrogen gas can be approximated by the ideal gas equation $PV = nRT$, where R = 8.314 kJ/kmol K. The heat capacities are C_V = 20.786 kJ/kmol K and C_P = 29.1 kJ/kmol K. Nitrogen which was initially at 1 bar and 280 K, is compressed to 5 bar and 280 K by two different reversible processes:

(a) Cooling at constant pressure followed by heating at constant volume

(b) Heating at constant volume followed by cooling at constant pressure.

For each of the above paths, determine the conditions at the intermediate state and DU, DH, Q and W.

2.31 One kilo mole of a gas for which $PV = nRT$, where R = 8.314 kJ/kmol K is originally at 300 K and 1 bar. It is then heated at constant pressure to a temperature of 400 K and compressed isothermally to a volume equal to its initial volume. Assume that C_P = 30 kJ/kmol K. Find DU, DH, Q and W.

3

P-V-T Behaviour and Heat Effects

3.1 P-V-T BEHAVIOUR OF PURE FLUIDS

The thermodynamic state of a pure fluid can be described in terms of two independent properties. Consider the thermodynamic state of a one component system, for example, water, which is represented in Fig. 3.1 as a function of pressure and volume. The figure shows the variation in molar volume with pressure at various constant temperatures. Assume that the initial state of the system is represented by point *a*. The change in volume of water with pressure at a constant temperature T_1 is along the isotherm *a-b-d-e*. Since liquid water is almost incompressible, the reduction in pressure for the change of state from *a* to *b* produces only negligible increase in volume. When point *b* is reached, vaporisation begins and this results in a rapid increase in volume. From *b* to *d*, the two phases, liquid and vapour, are in equilibrium. The temperature and pressure remain constant during the phase change as indicated by the horizontal portion of the isotherm *b-d*. The saturated liquid state is represented by point *b* and the saturated vapour state by point *d*. The relative amounts of the vapour and liquid phases in equilibrium change with continued vaporisation, and at point *d*, the entire liquid has been vaporised. The vapour and liquid coexisting in equilibrium are called *saturated phases*. Points along the horizontal line

b-d represent all possible mixtures of liquid and vapour, with point *b* representing saturated liquid state (100% liquid) and point *d* saturated vapour state (100% vapour). The pressure at which the liquid and vapour phases coexist in equilibrium is called the *saturation pressure,* and the temperature corresponding to this pressure is called the *saturation temperature*. Further reduction in pressure increases the volume of the system along the curve *d-e*. When the pressure over the system is brought down to a value less than the saturation pressure at constant temperature or when the temperature is increased above the saturation temperature at constant pressure, the vapour gets superheated.

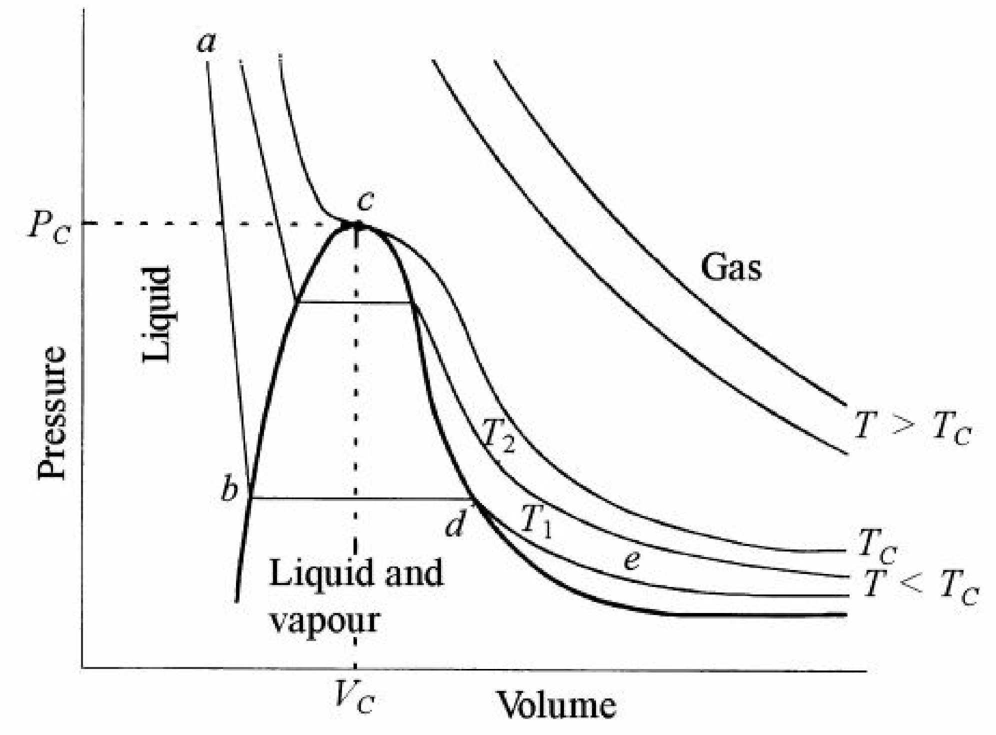


Fig. 3.1 *P-V-T* behaviour of pure fluids (e.g. water).

We see that the *P-V* isotherm has two discontinuities in its slope at points *b* and *d*. The isotherm at a higher temperature T_2 will be similar to that at temperature T_1, but the length of the horizontal section joining the saturated liquid and vapour phases will be smaller. The locus of the saturated phases is represented by the dome-shaped curve *b-c-d*. The area under this dome represents the two-phase region, the area to the left of curve *a-c* is the liquid region, and the area to the right of curve *c-d* is the vapour region.

When the temperature of the system is increased to T_C, the critical temperature, the discontinuities in the isotherm disappear indicating that, at the critical temperature, the saturated liquid and saturated vapour phases become indistinguishable. The liquid state changes to vapour state without any discontinuity at the critical point represented by point *c* in the figure. The properties of the substance at the critical point are known as *critical properties*. The critical properties of water are $T_C = 647.3$ K, $P_C = 220.5$ bar and $V_C = 56 \times 10^{-6}$ m^3/mol. The critical temperature and critical pressure represent the highest temperature and pressure respectively, at which a pure material can exist in vapour–liquid equilibrium. If the temperature is less than the critical temperature, the substance to the right of the saturated vapour line is called a *vapour* and, if the temperature is above the critical temperature, the substance is called a *gas*. A vapour can be condensed to a liquid by compression at constant temperature or by cooling at constant pressure whereas a gas can be condensed by a reduction of temperature at constant pressure only. It cannot be condensed by compression at constant temperature. If the temperature and pressure are greater than T_C and P_C respectively, the substance is in the *fluid region* and it can neither be condensed by any of the above methods nor can it be vaporised by reduction in pressure as is possible with liquids. The substance in this state is neither a gas nor a liquid.

The phase behaviour of pure fluids can be represented on *PT* diagram as in Fig. 3.2, which includes the solid region also. Consider unit mass of ice at pressure and temperature corresponding to point *p* in the figure. When it is heated at constant pressure, the temperature increases and at point q ice starts to melt. The temperature corresponding to point q is the fusion temperature. The fusion line represents the state of the system at which the solid is in equilibrium with the liquid. If transfer of heat is continued, the temperature remains constant till the entire solid is liquefied. The fusion temperature is a function of the pressure only. If heating is continued, the substance enters the liquid region, and when it attains the temperature corresponding to point r lying on the vaporisation curve, the liquid begins to vaporise. When all liquid has been vaporised, temperature increases along the line r-s in the vapour region. Heating beyond the critical temperature T_C takes the substance into the gas region.

The fusion curve and the vaporisation curve meet at the triple point where the three phases coexist in equilibrium. According to the phase rule, the triple point is invariant. For water at the triple point, $T = 273.16$ K and $P = 6.1 \square 10^{-3}$ bar. If the pressure of the system is below the triple point pressure, the heating of the solid results in *sublimation*, i.e. the transformation of solid directly into vapour. The sublimation curve in Fig. 3.2 represents the state of the system in which the vapour is in equilibrium with solid. It may be noted that the fusion curve extends up to infinity whereas the vaporisation curve terminates at the critical point.

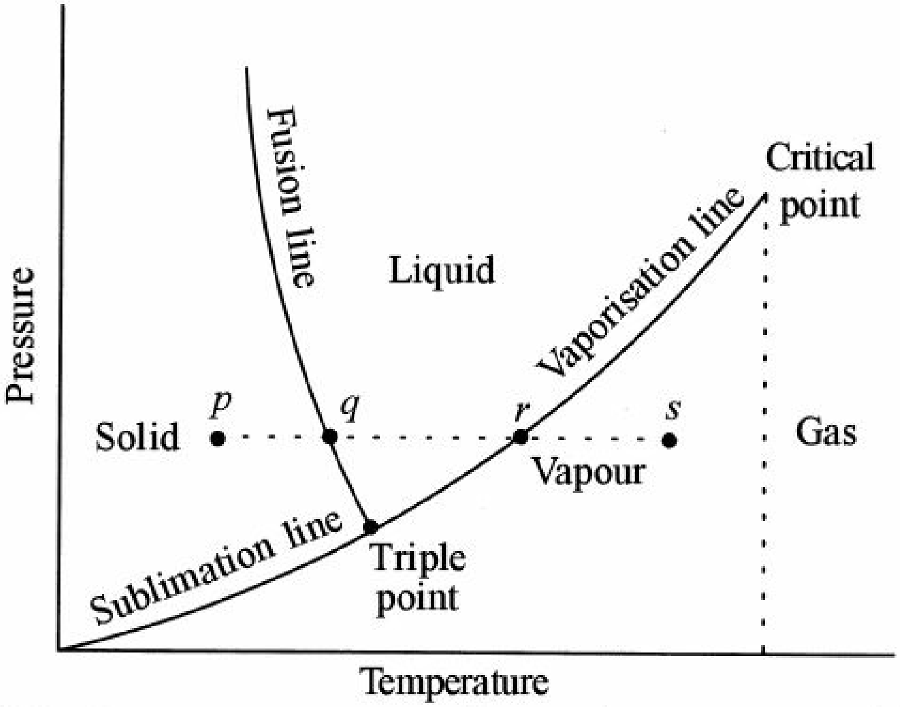


Fig. 3.2 Pressure-temperature diagram for a pure material.

3.2 EQUATIONS OF STATE AND THE CONCEPT OF IDEAL GAS

The thermodynamic state of a single homogeneous fluid may be specified by properties such as pressure, temperature, and volume. An equation of state is a functional relationship between these three variables and it may be written as

$$f(P, V, T) = 0 \qquad (3.1)$$

The most simple equation of state is the one applicable for ideal gases.

On a molecular level, an ideal gas may be treated as the one for which (a) the size of the molecules is very small compared to the distance between them so that the volume of the molecules is negligible in comparison with the total volume of the gas and (b) the intermolecular forces are negligibly small.

Thermodynamics characterises an ideal gas as the one for which the following properties are applicable:

1. For one mole of an ideal gas the equation of state is given by

$$PV = RT \qquad (3.2)$$

where R is known as the ideal gas constant. Its value is 8.314 J/mol K.

2. The internal energy of an ideal gas depends only on temperature. It is independent of pressure and volume.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 = \left(\frac{\partial U}{\partial P}\right)_T \qquad (3.3)$$

The increase in temperature of an ideal gas results in increased kinetic activity of the molecules, which is manifested as an increase in its internal energy. When the gas is compressed at constant temperature, it will offer no resistance and consequently results in no change in its energy, as there are no intermolecular forces to overcome.

3. The Joule-Thomson coefficient (m) is zero for an ideal gas.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = 0 \qquad (3.4)$$

The Joule-Thomson coefficient is defined as the change in temperature resulting from the expansion of a gas between two constant pressures under adiabatic condition and with no exchange of work with the surroundings. The adiabatic condition ($Q = 0$) and no exchange of work ($W = 0$) ensure that the enthalpy H is constant ($dH = dQ - dW$) during Joule-Thomson expansion. Hence, the Joule-Thomson coefficient is denoted by $(\partial T/\partial P)_H$.

Gases, like hydrogen, helium, nitrogen, and oxygen at room temperatures, follow the perfect gas law very closely and they can be treated as ideal gases. However, the only state at which the real gases follow ideal behaviour is at zero pressure. For engineering purposes, all gases in the neighbourhood of atmospheric pressure are treated as ideal.

***EXAMPLE* 3.1** Assuming air to behave as ideal gas, calculate the molar volume of air at 350 K and 1 bar.

Solution Temperature $T = 350$ K and pressure $P = 1$ bar $= 10^5$ N/m^2. According to Eq. (3.2), one mole of air at the stated conditions will have a volume V, where

$$V = \frac{RT}{P} = \frac{8.314 \times 350}{1 \times 10^5} = 2.91 \times 10^{-2}\ \text{m}^3$$

Thus, the molar volume of air at 350 K and 1 bar = 2.91 □ 10^{-2} m^3/mol.

3.3 PROCESSES INVOLVING IDEAL GASES

3.3.1 Constant Volume Process

From the general mathematical statement of the first law of thermodynamics for nonflow process [see Eq. (2.5)],

$$dU = dQ - dW$$

Consider one mole of an ideal gas undergoing a constant volume process. Since the volume remains constant, there is no work of expansion and $dW = 0$; the heat supplied is equal to the product of heat capacity and rise in temperature, i.e. $dQ = C_V\, dT$. C_V is the heat capacity at constant volume. It is the heat required to increase the temperature of unit mass of a substance by unity when the volume of the substance undergoes no change. Substituting these two results into Eq. (2.5), we get

$$\boxed{dU = dQ = C_V\, dT} \qquad (3.5)$$

Equation (3.5) is applicable to all gases, whether ideal or real, provided the process occurs at constant volume. But it can be shown that for ideal gases the change in internal energy is always given by

$$\boxed{dU = C_V\, dT} \qquad (3.6)$$

irrespective of how the process is carried out. This is a consequence of the property of the ideal gas that its internal energy is a function of temperature alone. Consider the change of state of an ideal gas from state 1 at which the temperature is T_1, to state 2 at which the temperature is T_2. The internal energy in the initial state is U_1 and that in the final state it is U_2. These are determined by specifying the temperatures T_1 and T_2 respectively. When the gas is undergoing a constant volume process between state 1 and state 2, the change in internal energy according to Eq. (3.5) is

$$DU = U_2 - U_1 = \int C_V\, dT$$

Now consider any other process occurring between the same temperature limits T_1 and T_2. Internal energy being a state function, the change in its value depends only on the terminal conditions. However, for ideal gases, U depends only on the temperature of the gas, and the temperatures at the initial and final states of this process, are the same as those in the constant volume process. Therefore, the change in internal energy in this process is $U_2 - U_1$, same as that resulted in the constant volume process. It means that the internal energy change in any process involving an ideal gas is given by Eq. (3.6). However, since the heat interaction in a process depends on the way in which the process is carried out, Eq. (3.5) is applicable only for a process satisfying the constant-volume restriction.

It can be shown that C_V for an ideal gas is independent of pressure and volume and depends on temperature only. The same is true for C_P also. These will be proved in Chapter 6.

3.3.2 Constant Pressure Process

Consider the reversible expansion of an ideal gas in a cylinder. The pressure inside the cylinder is kept constant at P by maintaining a constant force over the piston. The heat supplied is the product of heat capacity and rise in temperature: $dQ = C_P\, dT$, where C_P is the heat capacity at constant pressure. The work involved is the work of expansion done against the surrounding atmosphere, which, for a reversible process is given by $dW = P\,dV$. Substituting these expressions for dQ and dW into Eq. (2.5), we get the mathematical statement of the first law of thermodynamics in the following form.

$$dU = C_P\,dT - P\,dV$$

or

$$dU + P\,dV = C_P\,dT \qquad (3.7)$$

Enthalpy is defined as $H = U + PV$. For a constant pressure process, the change in enthalpy is

$$dH = dU + P\,dV$$

Equation (3.7) can now be rewritten as

$$dH = C_P\,dT \qquad (3.8)$$

Thus, for the process occurring at constant pressure, we have the following general result applicable for all gases whether ideal or not.

$$dH = dQ = C_P\,dT \qquad (3.9)$$

Since for an ideal gas, $H = U + PV = U + RT$, and U is a function of temperature only, the enthalpy of an ideal gas depends only on temperature. Assume that the gas is initially at temperature T_1 and let its enthalpy be H_1. As long as the temperature is constant at T_1, the enthalpy is constant, irrespective of the pressure. Let the gas expand under constant pressure to a final state where the temperature is T_2 and enthalpy is H_2. According to Eq. (3.9), the change in enthalpy is

$$\Delta H = H_2 - H_1 = \int C_P\,dT \qquad (3.10)$$

If the change occurred along any path other than the constant pressure path, but, between the same terminal temperatures, the enthalpy change should be the same: $\Delta H = H_2 - H_1$. For constant pressure path, this is shown to be equal to $\int C_P\,dT$. Therefore, for any process occurring between the same temperature levels, the change in enthalpy is $\int C_P\,dT$. In general, for an ideal gas,

$$\boxed{dH = C_P\,dT} \qquad (3.11)$$

However, it should be noted that $dQ = C_P\,dT$ is applicable only for an isobaric process.

***EXAMPLE* 3.2** Show that $C_P - C_V = R$ for an ideal gas.

Solution Enthalpy is defined as

$$H = U + PV$$

Therefore,

$$dH = dU + d(PV)$$

For ideal gas, $PV = RT$, and hence,

$$dH = dU + R\,dT$$

Substituting Eqs. (3.6) and (3.11) into the above equation, we obtain

$C_P\,dT = C_V\,dT + R\,dT$

Rearranging this equation, we get

$$\boxed{C_P - C_V = R} \tag{3.12}$$

3.3.3 Constant Temperature Process

Internal energy of an ideal gas will change only if the temperature changes. In an isothermal process involving an ideal gas, the change in internal energy and the change in enthalpy would be zero. Put $dU = 0$ in Eq. (2.5), so that

$dW = dQ$ (3.13)

The above equation can be integrated to determine the heat and work effects in an isothermal process involving ideal gases.

$Q = W = \int P\,dV$

Since $P = RT/V$, the above equation gives

$$Q = W = RT \ln \frac{V_2}{V_1} \tag{3.14}$$

where V_1 and V_2 are the initial and final volumes of the gas in an isothermal process. Let P_1 and P_2 be the pressures in the initial and final states, respectively. Then the ideal gas equation leads to the following relation:

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \tag{3.15}$$

Substituting Eq. (3.15) into Eq. (3.14), the latter can be modified as

$$\boxed{Q = W = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2}} \tag{3.16}$$

3.3.4 Adiabatic Process

In an *adiabatic process,* there is no heat interaction between the system and the surroundings. dQ is zero in Eq. (2.5) so that we have

$dU = -\,dW = -\,P\,dV$ (3.17)

for an adiabatic reversible process. Later in this section it is shown that, in an adiabatic process the pressure and volume are related as PV^g = constant, where g = C_P/C_V, which is assumed constant for an ideal gas. It is already proved that $C_P - C_V = R$, a constant. If the ratio and the difference between two quantities are constant then the quantities themselves should be constant. Therefore, the assumption of constant g implies that both C_P and C_V are constant. For the common monatomic and diatomic gases at low temperatures and pressures, it is found that the assumption of constant heat capacities introduces no serious error.

Using Eq. (3.6) in Eq. (3.17), we see that

$$dW = P\,dV = -C_V\,dT \tag{3.18}$$

By the ideal gas equation, $P = RT/V$ and Eq. (3.18) yields

$$-\frac{R}{C_V}\frac{dV}{V} = \frac{dT}{T} \tag{3.19}$$

Since $C_P - C_V = R$,

$$\frac{R}{C_V} = \frac{C_P}{C_V} - 1 = \gamma - 1 \tag{3.20}$$

Using Eq. (3.20), Eq. (3.19) can be rewritten as

$$-(\gamma - 1)\frac{dV}{V} = \frac{dT}{T} \tag{3.21}$$

Let the pressure, volume, and temperature are respectively P_1, V_1, and T_1 in the initial state of the gas and P_2, V_2 and T_2 respectively be the corresponding values in the final state after the adiabatic process. Equation (3.21) on integration between the initial and final conditions gives

$$\ln\frac{T_2}{T_1} = (\gamma - 1)\ln\frac{V_1}{V_2}$$

which on rearrangement leads to the following relation between temperature and volume in an adiabatic operation:

$$\boxed{\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}} \tag{3.22}$$

Using the perfect gas law, the ratio of volumes can be eliminated from Eq. (3.22) in favour of the ratio of pressures.

$$\frac{V_1}{V_2} = \frac{P_2}{P_1}\frac{T_1}{T_2}$$

The resulting expression, Eq. (3.23), is the relationship between pressure and temperature in an adiabatic process involving ideal gases.

$$\boxed{\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma - 1)/\gamma}} \tag{3.23}$$

Compare Eq. (3.22) with Eq. (3.23). Then

$$\frac{V_1}{V_2} = \left(\frac{P_2}{P_1}\right)^{1/\gamma}$$

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

or

$$\boxed{PV^{\gamma} = \text{constant}} \tag{3.24}$$

The work done in the adiabatic process is given by Eq. (3.18). Since C_V is constant, Eq. (3.18) can be readily integrated.

$$\boxed{W = C_V(T_1 - T_2)} \tag{3.25}$$

Equation (3.20) can be used to eliminate C_V from this equation in terms of γ.

$$W = \frac{RT_1 - RT_2}{\gamma - 1} = \frac{P_1V_1 - P_2V_2}{\gamma - 1} \tag{3.26}$$

Equation (3.26) gives the work done in an adiabatic process involving ideal gas. This can be put into a more useful form as follows:

$$W = \frac{P_1V_1}{\gamma - 1}\left(1 - \frac{P_2}{P_1}\frac{V_2}{V_1}\right) = \frac{P_1V_1}{\gamma - 1}\left[1 - \frac{P_2}{P_1}\left(\frac{P_1}{P_2}\right)^{1/\gamma}\right]$$

That is,

$$W = \frac{P_1V_1}{\gamma - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{(\gamma - 1)/\gamma}\right] \tag{3.27}$$

3.3.5 Polytropic Process

In a *polytropic process,* the relationship between pressure and volume is assumed to be PV^n = constant, where n is a constant. If $n = 0$, the process is isobaric; if $n = 1$, the process become isothermal; and if n = □, the process is isochoric (constant volume). If n = g, the process is an adiabatic process. Generally the value of n lies between 1 and g, indicating that the process lies between isothermal and adiabatic. In this case, the heat and work involved in the process are to be calculated using the first law of thermodynamics and the relationships applicable for ideal gases. Equations (2.5), (3.6) and (3.11) may be used for this purpose along with the expression $dW = PdV$ which gives the work of expansion in any reversible process.

$$dU = dQ - dW \tag{2.5}$$

$$dU = C_V\,dT \tag{3.6}$$

$$dH = C_P\,dT \tag{3.11}$$

***EXAMPLE* 3.3** An ideal gas is undergoing a series of three operations: The gas is heated at constant volume from 300 K and 1 bar to a pressure of 2 bar. It is expanded in a reversible adiabatic process to a pressure of 1 bar. It is cooled at constant pressure of 1 bar to 300 K. Determine the heat and work effects for each step. Assume $C_P = 29.3$ kJ/kmol K.

Solution The difference between C_P and C_V of an ideal gas is equal to R, the ideal gas constant. Hence C_V is given by

$$C_V = C_P - R = 29.3 - 8.314 = 20.986 \text{ kJ/kmol K}$$

Step 1: Volume remains constant. Therefore, work done is zero and heat supplied is $C_V(T_2 - T_1)$. Also, $T_2/T_1 = P_2/P_1 = 2$; That is,

T_2 = 2 □ 300 = 600 K

where T_2 is the final temperature attained. Heat supplied is

$$20.986 \square (600 - 300) = 6295.8 \text{ kJ/kmol}$$

Step 2: The process is adiabatic. Therefore, heat supplied is zero. The work done is given by Eq (3.25) as

$$W = C_V (T_1 - T_2)$$

where T_1 and T_2 are the initial and final temperatures in the adiabatic process which are related to the initial and final pressures by Eq. (3.23):

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma - 1)/\gamma}$$

Therefore,

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{(\gamma - 1)/\gamma} = 600 \times \left(\frac{1}{2}\right)^{0.4/1.4} = 492.2 \text{ K}$$

$$W = 20.986\ (600 - 492.2) = 2262.3 \text{ kJ/kmol}$$

Since W is positive, work is done by the system.

Step 3: The process is isobaric. Heat supplied is calculated as

$$C_P (T_2 - T_1) = 29.3\ (300 - 492.2) = -\ 5631.5 \text{ kJ/kmol}$$

(Heat is given out by the system).

$$DU = C_V (T_2 - T_1) = 20.896(300 - 492.2) = -\ 4016.2 \text{ kJ/kmol}$$

First law states that $DU = Q - W$. Hence,

$$W = Q - DU = -\ 5631.5 + 4016.2 = -\ 1615.3 \text{ kJ/kmol}$$

So, work is done on the system.

***EXAMPLE* 3.4** Calculate the change in internal energy, change in enthalpy, work done, and the heat supplied in the following processes:

(a) An ideal gas is expanded from 5 bar to 4 bar isothermally at 600 K.

(b) An ideal gas contained in a vessel of 0.1 m^3 capacity is initially at 1 bar and 298 K. It is heated at constant volume to 400 K.

(Assume that $C_P = 30$ J/mol K.)

Solution (a) Since the internal energy and enthalpy of ideal gas depend only on temperature, in an isothermal process, they remain constant. $DU = DH = 0$. Equation (3.16) is used to calculate the work done and heat supplied.

$$Q = W = RT \ln \frac{P_1}{P_2} = 8.314 \square 600 \square \ln \frac{5}{4} = 1113.13 \text{ kJ/kmol}$$

(b) Number of moles of the gas is

$n = PV/RT = (1 \square 10^5)\ 0.1/(8.314 \square 298) = 4.04$ mol

$C_V = C_P - R = 30 - 8.314 = 21.686$ J/mol K

$\mathrm{D}U = C_V(T_2 - T_1) = 21.686\ (400 - 298) = 2212$ J/mol $= 2212\ (4.04) = 8936$ J

$\mathrm{D}H = C_P\ (T_2 - T_1) = 30(400 - 298) = 3060$ J/mol $= 3060(4.04) = 12362$ J

Being a constant volume process, $W = 0$, and

$Q = \mathrm{D}U + W = \mathrm{D}U = 8936$ J

***EXAMPLE* 3.5** Twenty kilograms of air is compressed from 1 bar, 300 K to 5 bar in a single stage compressor. The process is polytropic with $n = 1.25$. The specific heat of air at constant pressure in kJ/kmol K is:

$C_P = 27.4528 + 6.1839 \square 10^{-3}\ T - 8.9932 \square 10^{-7}\ T^2$

Determine:

(a) The work done by the compressor per cycle and
(b) The amount of heat transferred to the surroundings.

Solution Molecular weight of air may be taken as 29. Dividing the mass of air by the molecular weight, the number of moles can be determined.

$$\text{Number of moles of air} = 20/29 = 0.69 \text{ kmol}$$

Initial volume of air is

$$nRT/P = (0.69 \times 10^3)\ 8.314\ (300)/(1 \times 10^5) = 17.21 \text{ m}^3$$

The pressure and volume in a polytropic process are related as

$$P_1V_1^n = P_2V_2^n$$

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)^{1/n} = 17.21\left(\frac{1}{5}\right)^{1/1.25} = 4.75 \text{ m}^3$$

(a) Work done:

$$W = \int P\,dV = \int C\,\frac{dV}{V^n}$$

where C is a constant such that $PV^n = C$.

$$W = \frac{C}{1-n}\left(V_2^{-n+1} - V_1^{-n+1}\right) = -\frac{C(4.75^{-0.25} - 17.21^{-0.25})}{0.25} = -\,0.7456\,C$$

$$C = P_1V_1^n = (1.0 \times 10^5)\ 17.21^{1.25} = 3.5028 \times 10^6$$

Therefore,

$$W = -0.7456\ (3.5028 \square 10^{6}) = -2.612 \square 10^{6}\ \text{J}$$

That is, 2612 kJ of work is required by the compressor.

(b) Amount of heat:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$T_2 = T_1 \frac{P_2}{P_1} \frac{V_2}{V_1} = 300 \times \frac{5}{1} \times \frac{4.75}{17.21} = 414\ \text{K}$$

The actual process is occurring along a polytropic path from the initial state at which the conditions are $P = 1$ bar, $V = 17.21$ m^3 and $T = 300$ K to the final state where $P = 5$ bar, $V = 4.75$ m^3, and $T = 414$ K. This process may be assumed to occur in two steps:

1. A constant temperature process at 300 K whereby the pressure is increased from 1 bar to 5 bar,
2. A constant pressure process at 5 bar by which the temperature is increased from 300 K to 414 K.

The change in the internal energy for the actual process is equal to the sum of the internal energy changes in these two steps. The step 1 being an isothermal process D$U = 0$. For step 2,

$$\Delta U = \int C_V\, dT$$

Thus, the change in the internal energy of the actual process is

$$\Delta U = \int C_V dT = \int (C_P - R)\, dT = \int_{300}^{414} (27.4528 + 6.1839 \times 10^{-3} T - 8.9932 \times 10^{-7} T^2 - 8.314)\, dT$$

$$\Delta U = 19.1388\ (414 - 300) + (1/2)\ (6.1839 \times 10^{-3})\ (414^2 - 300^2) - (1/3)\ (8.9932 \times 10^{-7})\ (414^3 - 300^3)$$

$$= 2420.3\ \text{J/mol}$$

$$= 2420.3\ (0.69 \times 10^3)\ \text{J} = 1670\ \text{kJ}$$

The heat supplied:

$$Q = \Delta U + W = 1670 - 2612 = -942\ \text{kJ}$$

This means that heat is liberated in an amount equal to 942 kJ.

3.4 EQUATIONS OF STATE FOR REAL GASES

Perfect gas law is inadequate to explain the behaviour of real gases. For real gases to behave ideally, the molecular interactions should be negligible. At low molar volumes or high pressures, molecules come very close to each other and molecular interactions cannot be neglected. The perfect gas law may be viewed as an approximation to describe the behaviour of real gases at ordinary pressures or as the limiting behaviour of real gases at low pressures. Many equations of state have been proposed to explain the actual behaviour of gases.

3.4.1 Limiting Conditions

An equation of state, in general, should satisfy certain limiting conditions. They are:

1. All equations reduce to the ideal gas equation at low pressures. That is,

$PV = RT$ as P □ 0

2. The slope of the PV isotherm against P may be equal to, greater than, or less than zero as pressure tends to zero. This is true for the slope of the compressibility factor versus P curve also. That is, either

$$\left[\frac{\partial(PV)}{\partial P}\right]_T \le 0 \quad \text{as } P \to 0$$

or

$$\left[\frac{\partial(PV)}{\partial P}\right]_T \ge 0 \quad \text{as } P \to 0$$

3. The P-V curve at constant temperature should exhibit a point of inflection at the critical point.

$$\left(\frac{\partial P}{\partial V}\right)_{T_C} = 0\,; \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_C} = 0 \tag{3.28}$$

4. The P-T curves are linear except at very high densities.

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

This relation is exact as $T \to \infty$ and is approximate at other conditions. However, at high densities,

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V < 0$$

This inequality means that the P-T curves are convex upward from the T-axis. A few of the commonly used equations of state are discussed in the following sections.

3.4.2 van der Waals Equation

van der Waals proposed the following equation to explain the P-V-T behaviour of real gases.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where a and b are called *van der Waals constants*. This equation is cubic in volume and below the critical temperature, there are three real roots. The largest is the vapour volume and the smallest the liquid volume. The intermediate root has no physical significance. When P is the saturation pressure, the smallest and the largest roots correspond to molar volumes of saturated liquid and saturated vapour respectively.

The perfect gas equation fails to explain the P-V-T behaviour of real gases as the volume occupied by the molecules of a real gas and the forces of interaction between them are not negligible as in an ideal gas. van der Waals equation takes into account these two features of a real gas by incorporating certain correction factors in the pressure and volume terms of the ideal gas equation. In order to find a correction term to compensate for the attractive forces between molecules, consider the forces of attraction on a molecule hitting the wall of the container. When the molecule hits the wall it experiences a net attractive force towards the surrounding molecules, thereby, reducing the pressure that would have been exerted by the molecule on the wall in the absence of intermolecular attraction. This attractive force is directly related to the number of molecules per unit volume and the frequency of molecular collision, the latter in turn being proportional to the number of molecules per unit volume. In short, the net attractive force is proportional to $1/V^2$ where V is the molar volume of the gas. The actual pressure, P, of the gas is less than the ideal pressure calculated by kinetic theory by a/V^2, where a is a constant. Or, the pressure term in the ideal gas equation should be replaced by $P + (a/V^2)$.

The centres of two identical molecules are at a distance equal to the molecular diameter at the instant of their collision with each other. The molecular separation at collision cannot be smaller than this distance. Since each molecule is surrounded by a forbidden volume that cannot be penetrated by another molecule, the effective volume of the gas will be less than the actual volume. The volume term in the ideal gas equation is replaced by $V - b$, where b indicates the forbidden volume per mole of the gas. Equation (3.29) results by incorporating these corrections to P and V terms in the ideal gas equation $PV = RT$.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{3.29}$$

The constants in the van der Waals equation can be evaluated utilising the limiting condition [Eq. (3.28)] to be obeyed by any equation of state. Applying this criterion in Eq. (3.29), we get

$$V_C = 3\,b; \quad T_C = \frac{8\,a}{27\,Rb}; \quad P_C = \frac{RT_C}{2b} - \frac{a}{9b^2}$$

The last two identities can be solved to get the van der Waals constants as

$$a = \frac{27\,R^2\,T_C^2}{64\,P_C}; \quad b = \frac{RT_C}{8\,P_C} \tag{3.30}$$

***EXAMPLE* 3.6** One kilo mol CO_2 occupies a volume of 0.381 m^3 at 313 K. Compare the pressures given by

(a) Ideal gas equation

(b) van der Waals equation

Take the van der Waals constants to be $a = 0.365$ Nm^4/mol^2 and $b = 4.28$ □ 10^{-5} m^3/mol.

Solution The molar volume of CO_2 is

$$V = 0.381 \text{ □ } 10^{-3} \text{ m}^3\text{ /mol}$$

(a) Ideal gas equation: $P = RT/V = 8.314\ (313)/(0.381$ □ $10^{-3}) = 68.30$ □ 10^5 N/m^2 = 68.30 bar

(b) van der Waals equation: Equation (3.29) may be rearranged as

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$= \frac{8.314\ (313)}{(0.381 \times 10^{-3}) - (0.428 \times 10^{-4})} - \frac{0.365}{(0.381 \times 10^{-3})^2}$$

$$= 51.8 \times 10^5 \text{ N/m}^2 = 51.8 \text{ bar}$$

***EXAMPLE* 3.7** Calculate the volume occupied by one mole of oxygen at 300 K and 100 bar using

(a) The ideal gas law

(b) The van der Waals equation.

Take $a = 0.1378$ N m^4/mol^2 and $b = 3.18$ □ 10^{-5} m^3/mol.

Solution (a) Using the ideal gas equation,

$$V = RT/P = 8.314\ (300)/(1 \text{ □ } 10^7) = 0.249 \text{ □ } 10^{-3} \text{ m}^3$$

(b) Volume can be determined using Eq. (3.29) by a trial and error procedure. Assume a value for V and evaluate the left hand side of the van der Waals equation. If the value assumed is the correct one, D in the following equation will be zero.

$$\left(P + \frac{a}{V^2}\right)(V - b) - RT = \Delta$$

Otherwise, repeat the calculation till D becomes equal to zero. The ideal gas volume may be chosen for the first trial. The results of a few such calculations are given below:

V, m^3	0.22 □ 10^{-3}	0.24 □ 10^{-3}	0.23 □ 10^{-3}
D	–76	+ 85.9	4

The molar volume of oxygen by the van der Waals equation ≈ 0.23 □ 10^{-3} m^3/mol.

3.4.3 Redlich–Kwong Equation

The Redlich–Kwong equation (1949) is a two-parameter equation of state widely used in engineering calculations.

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)} \tag{3.31}$$

The constants *a* and *b* are evaluated using the limiting condition Eq. (3.28), as we have evaluated the van der Waals constants using Eq. (3.28).

$$a = \frac{0.4278\,R^2T_C^{2.5}}{P_C}; \qquad b = \frac{0.0867\,RT_C}{P_C} \tag{3.32}$$

3.4.4 Redlich–Kwong–Soave Equation

Soave (1972) proposed a modification to the Redlich–Kwong equation. The Soave modification is given below:

$$P = \frac{RT}{V-b} - \frac{a'(T)}{V(V+b)} \tag{3.33}$$

where *a*□(*T*) = *a*a, where *a* and *b* are constants similar to the constants in Eq. (3.31) with the only change that the exponent of T_C is 2 instead of 2.5 in Eq. (3.32). a depends on the temperature and the acentric factor.

[*Note:* For simple fluids, it has been observed that at temperature equal to 7/10 of the critical temperature, the reduced vapour pressure closely follows the following empirical result:

$$\frac{P^S}{P_C} = \frac{1}{10} \text{ at } \frac{T}{T_C} = 0.7$$

where P^S is the vapour pressure. Pitzer defined the acentric factor in terms of the reduced vapour pressure at a reduced temperature of 0.7 as

$$\omega = -\,1.00 - \log\left(\frac{P^S}{P_C}\right)_{T_R\,=0.7} \tag{3.34}$$

For simple fluids, the acentric factor = 0; for more complex fluids, the acentric factor > 0. The acentric factors are listed in standard references. See, e.g. Prausnitz, J.M.,*Molecular Thermodynamics of Fluid Phase Equilibria,* Prentice Hall Inc., 1986].

3.4.5 Peng–Robinson Equation

Proposed in 1976, the equation is developed on the same lines as Eq. (3.33).

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)+b(V-b)} \tag{3.35}$$

where *a*, *b* are constants and a is a function of reduced temperature T_r and acentric factor w.

3.4.6 Benedict–Webb–Rubin Equation

This equation of state was proposed in 1940. Being a multi-parameter model it is complex, but, more accurate than the cubic equations of state discussed above. Despite its complexity, it is widely used in petroleum and natural gas industries for determining the thermodynamic properties of light hydrocarbons and their mixtures.

$$P = \frac{RT}{V} + \frac{B_0RT - A_0 - C_0/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{V^3T^2}\left(1 + \frac{\gamma}{V^2}\right) \exp\frac{-\gamma}{V^2} \qquad (3.36)$$

where A_0, B_0, C_0, a, b, c, a and g are constants.

3.4.7 Virial Equation

It has been observed experimentally that the product PV for a gas or vapour along an isotherm is almost constant and it equals RT, as pressure tends to zero or volume tends to infinity. This suggests the possibility of expressing PV/RT as a power series in P or $1/V$. The ratio PV/RT, which is the ratio of the volume of a real gas (V) to the volume if the gas behaved ideally at the stated temperature and pressure (RT/P) is called the *compressibility factor* and is denoted by Z. Virial equations express the compressibility factor of a gas or vapour as a power series expansion in
P or $1/V$.

$$Z = \frac{PV}{RT} = 1 + B'P + C'P^2 + D'P^3 + \ldots \qquad (3.37)$$

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \qquad (3.38)$$

Equations (3.37) and (3.38) are known as *virial equations* and the constants B, C, D and B□, C□, D□ are known as *virial coefficients*. B and B□ are called *second virial coefficients*; C and C□ are called *third virial coefficients,* and so on. For a given gas, these coefficients are functions of temperature only. The virial equation finds its greatest application at low to moderate pressures where it can be truncated after the second term without much error. Because it can be derived from kinetic theory, it has got a sound theoretical basis and is free from arbitrary assumptions. This feature makes virial equations distinct from other equations of state. The coefficients also can be given physical interpretation. The virial coefficients account for the molecular interactions. The second virial coefficients take into account deviations from ideal behaviour which results from interactions between two molecules. The third virial coefficients take into account the deviations from ideal behaviour that results from the interactions of three molecules, and so on.
The two sets of virial coefficients are related as:

$$B' = \frac{B}{RT}, \quad C' = \frac{C - B^2}{(RT)^2}$$

***EXAMPLE* 3.8** Find the second and third virial coefficients of the van der Waals equation when expressed in the form of Eq. (3.38).

Solution The van der Waals equation [Eq. (3.29)] can be expanded as

$$PV = RT - \frac{a}{V} + Pb + \frac{ab}{V^2} \tag{3.39}$$

Equation (3.29) gives P as

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{3.40}$$

Replace P from the right hand side of Eq. (3.39) using Eq. (3.40). Noting that $a = RT$, the resulting equation may be written as

$$Z = 1 + \frac{b}{V - b} - \frac{1}{V}$$

which, on rearrangement gives

$$Z = 1 + \frac{b}{V}\left(1 - \frac{b}{V}\right)^{-1} - \frac{1}{V} \tag{3.41}$$

Since

$$\left(1 - \frac{b}{V}\right)^{-1} = 1 + \frac{b}{V} + \frac{b^2}{V^2} + \ldots$$

Equation (3.41) may be simplified as

$$Z = 1 + (b - 1)\frac{1}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \ldots$$

Comparing Eq. (3.38) with the preceding equation, we see that

$$B = b - 1, \qquad C = b^2, \qquad D = b^3$$

and so on.

***EXAMPLE* 3.9** Calculate the compressibility factor and molar volume for methanol vapour at 500 K and 10 bar by using the following equations. Experimental values of virial coefficients are, $B = -2.19 \square 10^{-4}$ m^3/mol; $C = -1.73 \square 10^{-8}$ m^6/mol^2. The critical temperature and pressure of methanol are 512.6 K and 81 bar.

(a) Truncated form of virial equation, Eq. (3.38)

(b) Redlich–Kwong equation.

Solution (a) The virial equation truncated to three terms is

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

which can be rearranged as

$$V = \frac{RT}{P}\left(1 + \frac{B}{V} + \frac{C}{V^2}\right)$$

$$= 4.157 \times 10^{-3}\left(1 - \frac{2.19 \times 10^{-4}}{V} - \frac{1.73 \times 10^{-8}}{V^2}\right) \tag{i}$$

Volume is determined by trial. Use the ideal gas volume,

$V = RT/P = 4.157 \square 10^{-3}$ m^3

as the initial guess value. Put this on the right-hand side of Eq. (i). Then V on the left-hand side is $3.934 \square 10^{-3}$ m^3. Since the volumes are different, the calculations are repeated with a new value of V.

For $V = 3.934 \square 10^{-3}$ on the right-hand side, V on the left-hand side $= 3.921 \square 10^{-3}$ m^3 and for $V = 3.921 \square 10^{-3}$ on the right-hand side, V on the left-hand side $= 3.920 \square 10^{-3}$ m^3. Since for $V = 3.92 \square 10^{-3}$ m^3, both sides gave the same result, this value may be accepted as the molar volume of methanol. The compressibility factor may now be evaluated as

$Z = PV/RT = 0.943$

(b) The constants in the Redlich–Kwong equation are evaluated first.

$$a = \frac{0.4278\, R^2 T_C^{2.5}}{P_C}; \qquad b = \frac{0.0867\, RT_C}{P_C}$$

$$T_C = 512.6 \text{ K}, \qquad P_C = 81 \text{ bar} = 81 \times 10^5 \text{ N/m}^2$$

Therefore, $a = 21.7181$ Nm^{4}K$^{0.5}$/mol^2 and $b = 4.5617 \times 10^{-5}$ m^3/mol. The Redlich–Kwong equation can be rearranged as

$$V = \frac{RT}{P} + b - \frac{a(V - b)}{T^{0.5}\, PV(V + b)}$$

$$= \frac{8.314 \times 500}{10^6} + 4.5617 \times 10^{-5} - \frac{21.7181(V - 4.5617 \times 10^{-5})}{500^{0.5}\,(10^6)\, V(V + 4.5617 \times 10^{-5})}$$

$$= 4.2026 \times 10^{-3} - 9.7126 \times 10^{-7}\,\frac{V - 4.5617 \times 10^{-5}}{V(V + 4.5617 \times 10^{-5})}$$

Assume values for V, starting with the ideal gas volume, on the right-hand side of this equation.

Calculate V. The calculations are continued until the difference between the assumed and calculated values is very small.

Put $V = 4.157 \square 10^{-3}$ m^3 (ideal gas volume). Then, calculated volume = $3.974 \square 10^{-3}$ m^3

Put $V = 3.974 \square 10^{-3}$ m^3. Then, calculated volume = $3.964 \square 10^{-3}$ m^3

Put $V = 3.964 \square 10^{-3}$ m^3. Then, calculated volume = $3.963 \square 10^{-3}$ m^3

We see that by the third trial, the difference between the calculated and assumed values has almost vanished. Therefore,

$V = 3.963 \square 10^{-3}$ m^3 and $Z = 0.953$

3.5 COMPRESSIBILITY CHARTS

As pointed out earlier, the compressibility factor measures the deviation of a real gas from ideal behaviour. It is defined as $Z = PV/RT$. It is the ratio of the volume of a real gas at a set of specified temperature and pressure to the volume occupied by the gas at the same temperature and pressure if it were an ideal gas. The compressibility factor of a perfect gas has a value of unity at all conditions. Since a real gas behaves ideally as pressure is reduced, the compressibility factor of a real gas approaches unity as the pressure is reduced to zero.

$$\lim_{P \to 0} Z = 1$$

Figure 3.3 schematically shows a plot of compressibility factor of nitrogen at 273 K and carbon dioxide at 323 K plotted against pressure. The compressibility factor may be less than or more than unity depending on the temperature and pressure of the gas.

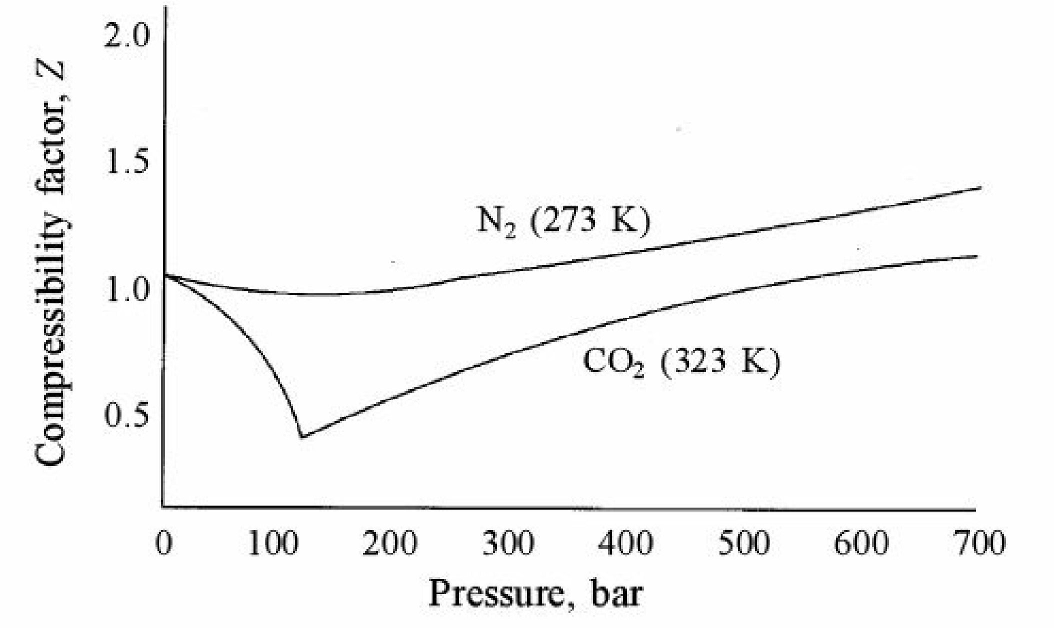


Fig. 3.3 Compressibility factor versus pressure.

3.5.1 Principle of Corresponding States

Compressibility charts as shown in Fig. 3.3 can be drawn for different substances. The use of such charts for practical applications is very cumbersome and they serve little useful purpose when compared with a generalised chart applicable for all gases. In fact, such generalised compressibility charts are made correlating the P-V-T behaviour of all fluids, based on the principle of corresponding states. This principle states that *all gases when compared at the same reduced temperature and the reduced pressure, have approximately the same compressibility factor and all deviate from the ideal behaviour to the same extent.*

The critical properties are used as basis for setting up a scale for comparing the properties of substances. The reduced variables are obtained by dividing the actual variables by the corresponding critical constants. Thus the reduced pressure $P_r = P/P_C$, the reduced temperature $T_r = T/T_C$, and the reduced volume $V_r = V/V_C$. Any two gases have the same reduced properties if they depart from the corresponding critical points by the same degree. Accordingly, methane (T_C = 191 K, P_C = 46 bar) at temperature of 382 K and pressure of 69 bar is expected to have the same compressibility factor as nitrogen (T_C = 126 K, P_C = 34 bar) at a temperature of

252 K and a pressure of 51 bar. This is, because both gases at the specified temperature and pressure have the same reduced properties ($T_r = 2$, $P_r = 1.5$) or they are removed from the respective critical states by the same extent. The compressibility factor of any single component substance is thus a function of only two properties, usually the reduced temperature and reduced pressure. The *principle of corresponding states* can be stated mathematically as

$$Z = f(T_r, P_r) \qquad (3.42)$$

It is to be noted that this principle is only an approximation and works the best for gases composed of spherical molecules; for non-spherical or polar molecules it fails. Its significance is that it enables one to coordinate the properties of a range of gases to a single diagram such as the generalised compressibility chart discussed below.

3.5.2 Generalised Compressibility Charts

The generalised compressibility chart (Fig. 3.4) is constructed based on the principle of corresponding states. On these charts, the compressibility factor, Z, is plotted as a function of reduced temperature and reduced pressure. The generalised compressibility charts provide one of the best means of expressing the deviation from ideal behaviour. When precise equation of state is not available, these charts provide a convenient method for the evaluation of compressibility factor. The average deviation of the values from the experimental results is within 5%.

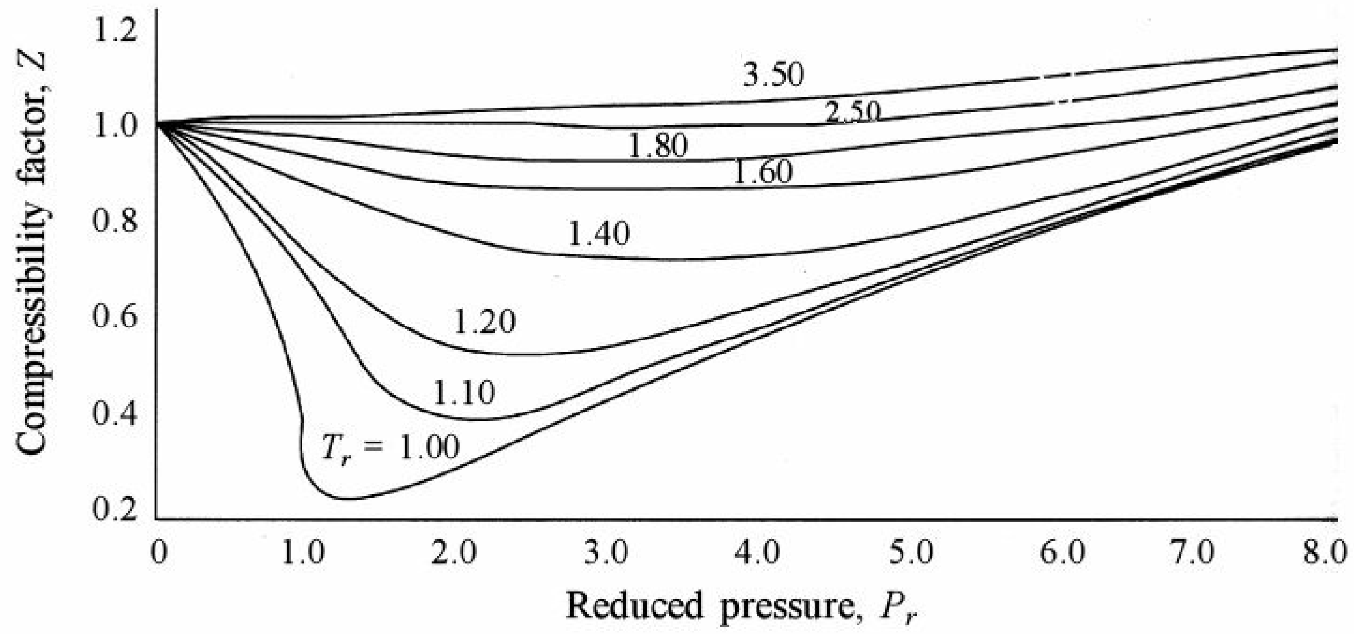


Fig. 3.4 Generalised compressibility chart.

3.6 HEAT EFFECTS ACCOMPANYING CHEMICAL REACTIONS

Energy changes are involved in the course of a chemical reaction where heat is either absorbed or evolved. The reactions in which heat is absorbed are called *endothermic reactions* and those in which heat is evolved are called *exothermic reactions*. Knowledge of the heat effects accompanying chemical reactions and the influence of the operating parameters on these energy changes is essential for the proper design and operation of reaction vessels.

3.6.1 The Standard Heat of Reaction

By *heat of reaction* we mean the change in enthalpy of the system for the reaction proceeding at constant temperature. It is the difference between the enthalpy of products and the enthalpy of reactants and is denoted by ΔH. Thus, positive values of ΔH indicate increase in the enthalpy and therefore represent endothermic reactions, and, negative values of ΔH mean decrease in enthalpy and so exothermic reactions.

The *standard heat of reaction* at a temperature T is the enthalpy change accompanying a reaction when both the reactants and products are at their standard states at temperature T. It is represented by the symbol ΔH_T^0, the superscript '0' indicates that the heat of reaction refers to the standard conditions. By convention, the standard heats of reaction are reported at a temperature of 298 K and are represented by ΔH_{298}^0. A standard state is determined by specifying the pressure, composition, and the state of aggregation, or the physical state of the species. The standard state pressure is 1 standard atmosphere by convention. The choice of 1 bar as the standard state pressure is now widely accepted. The species are assumed to be pure components in the standard state. The physical state of the components are: for gases, the pure substances in the ideal gas state at 1 bar; for solids and liquids, the pure substances in the solid or liquid state respectively at 1 bar.

Consider the reaction:

$$2\,C\,(s) + O_2\,(g) \rightarrow 2\,CO\,(g); \quad \Delta H_{298}^0 = -221.2\ \text{kJ}$$

The above equation means that 2 mol solid carbon reacts with 1 mol gaseous oxygen both at their standard state of 1 bar giving 2 mol gaseous carbon monoxide, also at the standard state of 1 bar, the temperature being kept constant at 298 K. During this reaction 221.2 kJ of heat is liberated. The heat evolved or absorbed in a chemical reaction corresponds to the stoichiometric numbers of the reacting species as written in the chemical equation. For example, when the reaction is written as follows the standard heat of reaction is just half of the value in the previous equation.

$$\text{C (s)} + \frac{1}{2}\ \text{O}_2\text{ (g)} \rightarrow \text{CO (g)}; \qquad \Delta H^0_{298} = -\,110.6\ \text{kJ}$$

3.6.2 The Standard Heat of Combustion

When the reaction under consideration is a combustion reaction, the heat of reaction is known as *heat of combustion*. Or, the 'heat of combustion of a substance' is the heat of reaction when a substance is oxidised with molecular oxygen. The *standard heat of combustion* at temperature *T* is the enthalpy change when the substance at its standard state and temperature *T* undergoes combustion, yielding products also at their standard state and temperature *T*. The standard heat of combustion of liquid acetaldehyde at 298 K, $\Delta H^0_{C,\,298}$, is – 1168.12 kJ/kmol. The heat of combustion is usually expressed per mole of substance reacted.

$$\text{CH}_3\text{CHO (1)} + \frac{5}{2}\text{O}_2\text{ (g)} \ \square\ 2\text{CO}_2\text{ (g)} + 2\text{H}_2\text{O (1)}; \quad \Delta H^0_{C,\,298} = -\,1168.12\ \text{kJ}$$

The negative of the heat of combustion of a fuel is sometimes referred to as its heating value. This is the energy exchanged with the surroundings when unit mass of fuel is burnt in oxygen. The heat of combustion of a fuel is a negative quantity, whereas the heating value is positive. When water formed during combustion is in the liquid state, the energy liberated will be more than the energy liberated when the combustion products contain water in the vapour-state. The heating value in the former case is known as *gross heating value,* and that in the latter is known as *net heating value*.

3.6.3 The Standard Heat of Formation

The change in enthalpy accompanying the formation of 1 mol of a substance from the constituent elements is termed the *heat of formation*. When the reactants and products are at their standard states, the heat of formation is called *standard heat of formation*. The standard heat of formation of carbon monoxide gas at 298 K, $\Delta H^0_{f,\,298}$, is – 110.6 kJ/mol. The standard heat of formation at 298 K for methyl chloride is –82 kJ.

$$\text{C (s)} + \frac{3}{2}\text{H}_2\text{ (g)} + \frac{1}{2}\text{Cl}_2\text{ (g)} \rightarrow \text{CH}_3\text{Cl (g)}; \qquad \Delta H^0_{f,\,298} = -82\ \text{kJ}$$

3.6.4 Hess's Law of Constant Heat Summation

Heat of reaction represents the difference between enthalpy of products and enthalpy of reactants. Enthalpy, as we know, is a state function and the heat of reaction, therefore, depends only on the initial and final states, no matter how the change from this initial to the final state is achieved. *The net heat evolved or absorbed in a chemical reaction is the same whether the reaction takes place in a* *single step or in a series of steps.* This is known as *Hess's law*. Hess's law permits us to treat all thermochemical equations as algebraic equations. Using this, we can calculate the heat of formation of a compound from a series of reactions not involving the direct formation of the compound from its elements. For example, the heat of formation of a compound can be calculated, if the heat of combustion data of all the species involved in the formation reaction are known. Similarly, if the data on the heat of formation of all the substances taking part in a chemical reaction are available, the heat of reaction may be readily calculated. The standard heats of formation of elements are taken as zero.

It can be shown that the standard heat of reaction is the difference between the algebraic sum of the standard heat of formation of products and that of the reactants.

$$\Delta H^0 = \sum_{\text{Products}} \Delta H_f^0 - \sum_{\text{Reactants}} \Delta H_f^0 \tag{3.43}$$

The heat of reaction may be calculated from heat of combustion data in a similar manner.

$$\Delta H^0 = \sum_{\text{Reactants}} \Delta H_C^0 - \sum_{\text{Products}} \Delta H_C^0 \tag{3.44}$$

***EXAMPLE* 3.10** Calculate the heat of formation of methane gas from the following heat of combustion data:

(a) CH_4 (g) + $2O_2$ (g) ☐ CO_2 (g) + $2H_2O$ (l); ΔH^0_{298} = – 890.94 kJ

(b) C (s) + O_2 (g) ☐ CO_2 (g); ΔH^0_{298} = – 393.78 kJ

(c) H_2 (g) + $\frac{1}{2}$ O_2 (g) ☐ H_2O (l); ΔH^0_{298} = – 286.03 kJ

Solution Consider the operation: Eq. (c) ☐ 2 + Eq. (b) – Eq. (a). This gives

C (s) + $2H_2$ (g) ☐ CH_4 (g); ΔH_f^0 = – 2 ☐ 286.03 + (– 393.78) – (– 890.94) = – 74.9 kJ

The above equation represents the formation of methane gas from the elements. The heat of formation is –74.9 kJ/mol.

The heat of formation may be obtained directly by using Eq. (3.44) as well. Sum of the heat of combustion of reactants is

$$-393.78 + 2\,(-286.03)\text{ kJ} = -965.84\text{ kJ}$$

Sum of the heat of combustion of products is –890.94 kJ. By Eq. (3.44),

$$\Delta H_f^0 = -965.84 + 890.94 = -74.9\text{ kJ}$$

***EXAMPLE* 3.11** Using Hess's law, calculate the heat of formation of chloroform ($CHCl_3$) with the following given data:

(a) $CHCl_3$ (g) + $\frac{1}{2}$ O_2 (g) + H_2O (l) ☐ CO_2 (g) + 3 HCl (g); ΔH^0_{298} = – 509.93 kJ

(b) H_2 (g) + $\frac{1}{2}$ O_2 (g) ☐ H_2O (l); ΔH^0_{298} = – 296.03 kJ

(c) C (s) + O_2 (g) □ CO_2 (g); ΔH^0_{298} = – 393.78 kJ

(d) $\frac{1}{2}$ H_2 (g) + $\frac{1}{2}$ Cl_2 (g) □ HCl (g); ΔH^0_{298} = – 167.57 kJ

Solution Apply the following operation:

$$\text{Eq. (c)} + 3 \times \text{Eq. (d)} - \text{Eq. (a)} - \text{Eq. (b)}$$

The following equation results

$$C + \frac{1}{2} H_2 + \frac{3}{2} Cl_2 \rightarrow CHCl_3;\quad \Delta H^0_{f,\,298} = ?$$

Accordingly, the heat of formation would be

$$-393.78 + 3(-167.57) + 509.93 + 296.03 = -90.53 \text{ kJ/mol}$$

3.6.5 Effect of Temperature on Standard Heat of Reaction

Consider the reaction

$aA + bB$ □ $lL + mM$

Here, *a, b, l, m* are called stoichiometric coefficients. This reaction may be written as

$lL + mM - aA - bB = 0$

in which – *a,* – *b, l, m* are called stoichiometric numbers. Denoting the stoichiometric numbers of the species taking part in a chemical reaction by n_i, a chemical reaction in general may be represented by

$$\sum_i \nu_i A_i = 0 \qquad (3.45)$$

Here n_i is positive for products and negative for the reactants. For a chemical reaction represented by such general equation, how would you determine the standard heat of reaction at temperature T if the standard heat of reaction is given at temperature T_1? The actual reaction occurring at temperature T, for which the standard heat of reaction is ΔH^0_T, may be treated as occurring in three steps as depicted in Fig. 3.5.

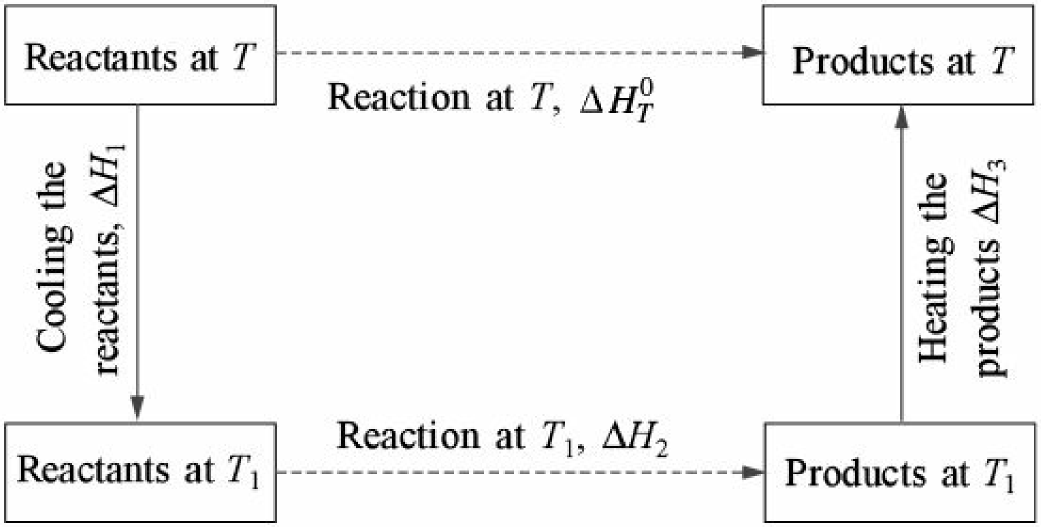


Fig. 3.5 Effect of temperature on heat of reaction.

The reactants are cooled from temperature T to T_1. The enthalpy change for this step is

$$\Delta H_1 = \sum_{\text{Reactants}} \int_T^{T_1} n_i C_{P,i}\, dT = \sum_{\text{Reactants}} \int_{T_1}^{T} \nu_i C_{P,i}\, dT \tag{3.46}$$

The reaction is allowed to occur at temperature T_1. The enthalpy change is

$$\Delta H_2 = \Delta H_{T_1}^0 \tag{3.47}$$

The temperature of the products is raised from T_1 to T in this step. The enthalpy change is

$$\Delta H_3 = \sum_{\text{Products}} \int_{T_1}^{T} n_i C_{P,i}\, dT = \sum_{\text{Products}} \int_{T_1}^{T} \nu_i C_{P,i}\, dT \tag{3.48}$$

The standard heat of reaction at temperature T, is obtained by adding the preceding three equations.

$$\begin{aligned}\Delta H_T^0 &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= \sum_{\text{Reactants}} \int_{T_1}^{T} \nu_i C_{P,i}\, dT + \Delta H_{T_1}^0 + \sum_{\text{Products}} \int_{T_1}^{T} \nu_i C_{P,i}\, dT\end{aligned}$$

The above result can be written as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^{T} \left(\sum_i \nu_i C_{P,i} \right) dT \tag{3.49}$$

The summation in the above equation is overall species taking part in the reaction. Let the heat capacity of the substances be represented by the following equation.

$$C_P = \alpha + \beta T + \gamma T^2 \qquad (3.50)$$

Utilising Eq. (3.50), Eq. (3.49) can be written as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^{T} \Delta\ C_P\ dT \qquad (3.51)$$

where

$$\Delta C_P = \Delta\alpha + (\Delta\beta)T + (\Delta\gamma)\ T^2 \qquad (3.52)$$

and

$$\Delta\alpha = \Sigma\ \nu_i\alpha, \quad \Delta\beta = \Sigma\ \nu_i\beta, \quad \text{and} \quad \Delta\gamma = \Sigma\ \nu_i\gamma \qquad (3.53)$$

Equation (3.51) may be expanded as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \Delta\alpha(T - T_1) + \frac{1}{2}\Delta\beta\,(T^2 - T_1^2) + \frac{1}{3}\Delta\gamma\,(T^3 - T_1^3)$$

The constants appearing in the above equation can be grouped together to a single constant $\Delta H'$, so that we have

$$\Delta H_T^0 = \Delta H' + \Delta\alpha T + \frac{\Delta\beta}{2}T^2 + \frac{\Delta\gamma}{3}T^3 \qquad (3.54)$$

The constant $\Delta H'$ in the above equation can be evaluated if the heat of reaction at a single temperature is known. Equation (3.54) can now be used for the evaluation of the standard heat of reaction at any temperature T.

***EXAMPLE* 3.12** The heat of reaction at 300 K and one atmosphere pressure for the following gas-phase reaction:

$$A + 3B \rightarrow C$$

is –200 kJ per mol of A converted. Data on the molar heat capacity at constant pressure (kJ/mol K) for the various components are: C_P for $A = -1.7 \times 10^{-3} + 3.4 \times 10^{-4}\ T$, where T is in K, C_P for $B = 0.03$ and C_P for $C = 0.1$. Calculate the heat of reaction at 500 K and at a pressure of 100 kPa.

Solution Assume that the reactants initially at 500 K are cooled to 300 K (enthalpy change $= \Delta H_1$). The reaction is then allowed to take place at 300 K (heat of reaction $= \Delta H_{300}^0$). The products of the reaction are heated to 500 K (enthalpy change $= \Delta H_2$).

$$\Delta H^0_{500} = \Delta H_1 + \Delta H^0_{300} + \Delta H_2 \qquad \text{(i)}$$

Basis: 1 mol *A* supplied. Reactants are assumed to be in the stoichiometric proportions.

$$\Delta H_1 = \int_{500}^{300} (-1.7 \times 10^{-3} + 3.4 \times 10^{-4} T)\, dT + 3\,(0.03)\,(300 - 500) = -44.86 \text{ kJ}$$

$$\Delta H^0_{300} = -200 \text{ kJ}$$

$$\Delta H_2 = 1 \times 0.1 \times (500 - 300) = 20 \text{ kJ}$$

By Eq. (i),

$$\Delta H^0_{500} = -44.86 - 200 + 20 = -224.86 \text{ kJ}$$

***EXAMPLE* 3.13** Pure CO is mixed with 100% excess air and burnt. Only 80% of the CO burns. Th reactants are at 373 K and the products are at 573 K. Calculate the amount of heat added or remove per kmol of CO fed to the reactor.

Mean molal specific heats between 298 K and *T* K in kJ/kmol K are:

Gas	*T* = 373 K	*T* = 573 K
CO	29.22	30.61
CO_2	—	43.77
O_2	29.84	30.99
N_2	29.17	29.66

Standard heats of formation at 298 K in kJ/mol are CO = –110.524 and CO_2 = –393.514.

Solution Basis: 1 kmol CO fed to the reactor.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

Oxygen theoretically required = 0.5 kmol; oxygen supplied = 1 kmol. Since air is 21% oxygen and 79% nitrogen, the air supplied contains 79/21 = 3.76 kmol nitrogen. Since 80% of the CO is converted, the product stream consists of 0.2 kmol CO, 0.8 kmol CO_2, 0.6 kmol oxygen and 3.76 kmol nitrogen.

The amount of heat added or removed (ΔH) can be computed as

$$\Delta H = \Delta H_1 + \Delta H^0_{298} + \Delta H_2$$

where ΔH_1 is the enthalpy of cooling the reactants from 373 K to 298 K, ΔH_2 is the enthalpy of heating the products from 298 K to 573 K and ΔH^0_{298} is the standard heat of reaction at 298 K. Enthalpy of cooling the reactants from 373 K to 298 K.

$$\Delta H_1 = (1 \times 29.22 + 1 \times 29.84 + 3.76 \times 29.17)(298 - 373) = -12655.4 \text{ kJ}$$

Standard heat of reaction at 298 K = ΔH^0_{298} = (Sum of the heat of formation of products – Sum of the heat of formation of reactants) × 0.8 = $(-393.514 \times 10^3 + 110.524 \times 10^3) \times 0.8 = -226.392 \times 10^3$ kJ.

Enthalpy of heating the products from 298 K to 573 K:

$$\Delta H_2 = (0.2 \times 30.61 + 0.8 \times 43.77 + 0.6 \times 30.99 + 3.76 \times 29.66)(573 - 298) = 47094.7 \text{ kJ}$$

The enthalpy change during the actual reaction:

$$\Delta H = \Delta H_1 + \Delta H^0_{298} + \Delta H_2 = -12655.4 - 226392 + 47094.7 = -191953 \text{ kJ}$$

Therefore, heat to be removed per mole of CO fed to the reactor = 191953 kJ.

***EXAMPLE* 3.14** For the following reaction the standard heat of reaction at 298 K is –164.987 kJ.

$$CO_2 \text{ (g)} + 4 H_2 \text{ (g)} \square 2 H_2O \text{ (g)} + CH_4 \text{ (g)}$$

The constants in the heat capacity (J/mol K) equation, Eq. (3.50), are given below:

	a	b	g
CO_2	26.75	$42.26 \square 10^{-3}$	$-14.25 \square 10^{-6}$
H_2	26.88	$4.35 \square 10^{-3}$	$-0.33 \square 10^{-6}$
H_2O	29.16	$14.49 \square 10^{-3}$	$-2.02 \square 10^{-6}$
CH_4	13.41	$77.03 \square 10^{-3}$	$-18.74 \square 10^{-6}$

Calculate the standard heat of reaction at 773 K.

Solution Equation (3.54) relates the heat of reaction to temperature.

$$Da = 2 \square 29.16 + 13.41 - 26.75 - 4 \square 26.88 = -62.54$$

$$\mathrm{D}b = (2 \square 14.49 + 77.03 - 42.26 - 4 \square 4.35) \square 10^{-3} = 46.35 \square 10^{-3}$$

$$\mathrm{D}g = (-2 \square 2.02 - 18.74 + 14.25 + 4 \square 0.33) \square 10^{-6} = -7.21 \square 10^{-6}$$

Equation (3.54) gives

$$\Delta H_T^0 = \Delta H' - 62.54\,T + \frac{46.35 \times 10^{-3}}{2} T^2 - \frac{7.21 \times 10^{-6}}{3} T^3$$

At $T = 298$ K and $\Delta H_T^0 = -164.987 \times 10^3$ J, the above equation gives $\Delta H' = -148345$ J, so that

$$\Delta H_T^0 = -148345 - 62.54\,T + 23.175 \times 10^{-3}\,T^2 - 2.403 \times 10^{-6}\,T^3$$

Putting $T = 773$ K in this equation, we get $\Delta H_{773}^0 = -183950$ J $= -183.950$ kJ.

***EXAMPLE* 3.15** Pure CO is mixed with 100 per cent excess air and completely burned at constant pressure. The reactants are originally at 400 K. Determine the heat added or removed if the products leave at 600 K. The standard heat of reaction at 298 K is 283.028 kJ per mol CO burned. The mean specific heats applicable in the temperature range of this problem are 29.10, 29.70, 29.10, and 41.45 J/mol K respectively for CO, O_2, N_2, and CO_2 respectively.

Solution Basis: 1 mol CO reacted.

$$CO + \frac{1}{2} O_2 \rightarrow CO_2$$

Oxygen theoretically required = 0.5 mol

Oxygen supplied = 1 mol (100 per cent excess)

Nitrogen in the air supplied = 1 □ 79/21 = 3.76 mol

Let $\mathrm{D}H_1$ be the enthalpy of cooling the reactants from 400 K to 298 K. The reactants stream contains 1 mol oxygen, 3.76 mol nitrogen, and 1 mol CO.

$$\mathrm{D}H_1 = (1 \square 29.70 + 3.76 \square 29.10 + 1 \square 29.10)(298 - 400) = -17.158 \text{ kJ}$$

Let $\mathrm{D}H_2$ be the enthalpy of heating the products from 298 K to 600 K. The product stream contains 1 mol CO_2, 0.5 mol oxygen, and 3.76 mol nitrogen.

$$\mathrm{D}H_2 = (1 \square 41.45 + 3.76 \square 29.10 + 0.5 \square 29.70)(600 - 298) = 50.046 \text{ kJ}$$

$$\mathrm{D}H = \mathrm{D}H_1 + \Delta H_{298}^0 + \mathrm{D}H_2 = -17.158 - 283.028 + 50.046 = -250.14 \text{ kJ}$$

Heat removed = 250.14 kJ.

3.6.6 Temperature of Reaction

A reaction is termed an *adiabatic reaction* if there is no heat interaction between the reaction mixture and the surroundings. If the reaction is exothermic, the heat liberated during the reaction will be utilised to increase the enthalpy of the products, as no heat is removed to maintain the temperature constant. The products get heated up and the temperature attained is termed the *temperature of the* *reaction*. When a fuel is burned in air or oxygen under adiabatic conditions the temperature attained by the system is known as the *adiabatic flame temperature.* The maximum adiabatic flame temperature is attained when the fuel is burned in theoretically required amount of pure oxygen. The adiabatic flame temperature attained when the fuel is burned in air or excess oxygen, is less than the theoretical maximum flame temperature attained in oxygen.

Denoting as before, the enthalpy of cooling the reactants from temperature T_1 to 298 K by ΔH_1 and the enthalpy of heating the products from 298 to T, the adiabatic flame temperature, by ΔH_2, we can write

$$\Delta H = \Delta H_1 + \Delta H^0_{298} + \Delta H_2$$

Here ΔH is the difference between the enthalpy of products and the enthalpy of reactants, or simply, the heat added or removed during the reaction. For an adiabatic reaction, this quantity is zero, and therefore,

$$\Delta H_2 = -\Delta H_1 - \Delta H^0_{298} \qquad (3.55)$$

Equation (3.55) may be used to evaluate the temperature attained in an adiabatic reaction.

***EXAMPLE* 3.16** Calculate the theoretical flame temperature for CO when burned with 100% excess air when both the reactants are at 373 K. The heat capacities (J/mol K) may be assumed constant a 29.23 for CO, 34.83 for O_2, 33.03 for N_2, and 53.59 for CO_2. The standard heat of combustion at 298 K is – 283.178 kJ/mol CO.

Solution Basis: 1 mol CO.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

Reactants:

$$O_2 = 1 \text{ mol}; N_2 = 3.76 \text{ mol}; CO = 1 \text{ mol}$$

Products:

$$O_2 = 0.5 \text{ mol}; N_2 = 3.76 \text{ mol}; CO_2 = 1 \text{ mol}$$

$$\Delta H_1 = (1 \times 34.83 + 3.76 \times 33.03 + 1 \times 29.23)(298 - 373) = -14119 \text{ J}$$

$$\Delta H_2 = (0.5 \times 34.83 + 3.76 \times 33.03 + 1 \times 53.59)(T - 298) = 195.20\,T - 58169$$

where T is the adiabatic flame temperature.

Using Eq. (3.55), we get

$$195.20\,T - 58169 = 14119 + 283178$$

Solving this, we get the theoretical flame temperature as $T = 1821$ K.

***EXAMPLE*3.17** Dry methane is burned with dry air. Both are at 298 K initially. The flame temperature is 1600 K. If complete combustion is assumed, how much excess air is being used? The reaction is

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The standard heat of reaction is –8.028 □ 10^5 J/mol of methane reacted. Mean molal specific heats of gases between 298 K and 1600 K are in J/mol K:

CO_2 = 51.66; H_2O = 40.45; O_2 = 34.01 and N_2 = 32.21

Solution For a basis of one mole of methane, let x be the moles of oxygen supplied. Nitrogen in the air supplied is $x(79/21)$ mol.

The products of combustion consist of:

CO_2 : 1 mol, H_2O : 2 mol, O_2 : $x - 2$ mol, N_2 : $x(79/21)$ mol.

For adiabatic combustion reaction,

$$\Delta H_1 + \Delta H^0_{298} + \Delta H_2 = 0$$

Since the reactants are initially at the temperature of reaction (298 K), DH_1 = 0 and the above equation reduces to

$$\Delta H^0_{298} + \Delta H_2 = 0 \qquad \text{(i)}$$

ΔH_2 is the enthalpy of heating the products of the reaction from 298 K to 1600 K.

$$\Delta H_2 = \left(1 \times 51.66 + 2 \times 40.45 + (x-2) \times 34.01 + x \times 32.21 \times \frac{79}{21}\right)(1600 - 298)$$

$$= 20.204 \times 10^4 x + 8.4031 \times 10^4$$

The heat of reaction at 298 K,

$$\Delta H^0_{298} = -8.028 \times 10^5 \text{ J}$$

Substituting ΔH^0_{298} and ΔH_2 in Eq. (i), we obtain

$$20.204 \times 10^4 x + 8.4031 \times 10^4 - 8.028 \times 10^5 = 0$$

Therefore, $x = 3.56$ mol.

Oxygen theoretically required = 2 mol. Oxygen supplied = 3.56 mol

Percent excess of air supplied = $\dfrac{3.56 - 2}{2} \times 100 = 78.00\%$

***EXAMPLE* 3.18** A feed at 1298 K, consisting of flue gas (CO_2, O_2 and N_2) and air, is passed through a bed of pure carbon. The two reactions that occur both go to completion.

$$CO_2(g) + C(s) \rightarrow 2CO(g),\ \Delta H^0_R \text{ at 298 K} = 170 \text{ kJ/mol}$$

$$O_2(g) + 2C(s) \rightarrow 2CO(g),\ \Delta H^0_R \text{ at 298 K} = -220.4 \text{ kJ/mol}$$

The combustion is adiabatic and the product gases exit at 1298 K. Calculate the required moles of CO_2 per mole of oxygen in the feed stream, so that the net heat generated is zero and the bed temperature remains at 1298 K. The mean molal heat capacities (kJ/mol K) are 0.02 for C, 0.03 for O_2, 0.03 for CO and 0.05 for CO_2.

Solution Let x mol CO_2 be present per mol of oxygen in the feed stream. x mol CO_2 reacts according to the first reaction producing 2 mol CO and 1 mol O_2 reacts according to the second reaction producing 2 mol CO. Therefore, the products of reaction contains $2x + 2$ mol CO.

Enthalpy of cooling the reactants from 1298 K to 298 K,

$$\mathrm{D}H_1 = [x \square 0.05 + 1 \square 0.03 + (x + 2) \square 0.02]\,(298 - 1298)$$

$$= -\,(70x + 70)\ \text{kJ}$$

As the enthalpy of heating the nitrogen present in the reactant stream and the enthalpy of cooling the nitrogen in the product stream are equal and they would cancel in an energy balance, they are not included in the calculations.

Standard heat of reaction at 298 K = ΔH^0_{298} = $170\,x - 220.4$ kJ

Enthalpy of heating the products from 298 K to 1298 K:

$$\mathrm{D}H_1 = [(2x + 2) \square 0.03]\,(1298 - 298)$$

$$= (60x + 60)\ \text{kJ}$$

The enthalpy change during the actual reaction:

$$\Delta H_1 + \Delta H^0_{298} + \Delta H_2 = 0$$

$$-70 - 70x + 170x - 220.4 + 60 + 60x = 0$$

Therefore, $x = 1.44$ mol or 1.44 mol CO_2 should be present per each mol of oxygen.

SUMMARY

The general *P-V-T* behaviour of fluids, the physical significance of the triple point and the critical point and the process of fusion, sublimation and vaporisation were discussed with the help of a *PV* diagram and a *PT* diagram for a pure fluid (Section 3.1). An equation of state is the functional relationship between pressure, volume, and temperature of the fluid. The most simple of such equations ($PV = RT$) is obeyed by ideal gases. The salient features of an ideal gas were described from microscopic as well as macroscopic points of view (Section 3.2). The heat and work involved in various processes with ideal gases, such as the constant volume process, the constant pressure process, the isothermal process, the adiabatic process, and the polytropic process were derived (Section 3.3). The changes in the internal energy (U) and the enthalpy (H) of an ideal gas are given by $dU = C_V\,dT$ and $dH = C_P\,dT$, irrespective of how the process is carried out. It was also shown that for ideal gases, U and H are functions of temperature alone.

For engineering calculations, many gases can be assumed to behave ideally under atmospheric conditions. However, the only state at which the real gases follow ideal behaviour in the true sense of the term, is at zero pressure. Several equations of state were proposed to explain the behaviour of real gases. Though they differ widely, there are certain limiting conditions that are to be satisfied by all equations of state (Section 3.4). The compressibility factor, defined as $Z = PV/RT$, is a measure of the deviation of real gases from the ideal gas behaviour. The generalised compressibility charts provide a convenient means for the estimation of the thermodynamic properties in the absence of experimental data. These charts are based on the principle of corresponding states: all gases when compared at the same reduced temperature and the reduced pressure, have approximately the same compressibility factor and all deviate from the ideal behaviour to the same extent (Section 3.5).

The role of thermochemistry in the design and analysis of chemical processes is very important. The enthalpy changes involved in chemical reactions, the influence of temperature on these and the methods for the evaluation of the heat of reaction were discussed in Section 3.6. It was also established that the maximum adiabatic flame temperature is attained when a fuel is burned with the theoretical requirement of pure oxygen. The ideas presented here will be used extensively in the analysis of chemical reaction equilibria in Chapter 9.

REVIEW QUESTIONS

1. What do you mean by the saturation pressure and the saturation temperature of a substance?

2. What is the difference between a vapour and a gas?

3. Explain the physical significance of the triple point and the critical point.

4. In a microscopic sense, what are the two characteristics of an ideal gas? How do these features explain the dependency of the internal energy of an ideal gas on temperature alone?

5. Do you agree that for ideal gases, $dU = C_V\,dT$ and $dH = C_P\,dT$ for all processes irrespective of their nature?

6. How is the temperature of an ideal gas related to pressure and volume in an adiabatic process?

7. What is the expression for the work done in an adiabatic process in terms of the pressure ratio?

8. What do you understand by an equation of state? What are the limiting conditions to be satisfied by such equations?

9. van der Waals equation results when the ideal gas equation is corrected to include the effect of the molecular interaction and the volume of molecules. What are these correction terms?

10. How do you relate the van der Waals constants to the critical properties?

11. What do you mean by acentric factor?

12. How do you explain the physical significance of the virial coefficients?

13. How is the compressibility factor defined?

14. What is the principle of corresponding states?

15. Define: (a) The heat of reaction, (b) The standard heat of reaction, (c) The standard heat of formation, and (d) The standard heat of combustion.

16. How is the standard heat of reaction evaluated using (a) The standard heat of formation and (b) The standard heat of combustion of the various components?

17. How is the Hess's law of constant heat summation useful in thermochemical calculations?

18. If the standard heat of reaction at one temperature is known, how would you evaluate the standard heat of reaction at any other temperature?

19. What is the adiabatic flame temperature? How is it estimated? What influence does excess air have on its value?

EXERCISES

3.1 Sulphur dioxide is circulated as the refrigerant in a small refrigerator. SO_2 gas at a pressure of 5 bar and temperature 340 K is to be cooled at constant volume of 0.142 m^3, to 293 K as part of the refrigeration cycle. Calculate (a) The heat liberated, (b) The work done by the gas on cooling, (c) The final pressure attained on cooling and (d) The change in enthalpy. Sulphur dioxide may be treated as an ideal gas. The specific heat (J/mol K) is found to vary with temperature (K) according to

$$C_P = 25.736 + 5.796 \square\ 10^{-2}\ T - 3.8112 \square\ 10^{-5}\ T^2 + 8.612 \square\ 10^{-9}\ T^3$$

3.2 Ten kilograms of an equimolar mixture of CO and H_2 at 1500 K and 1 bar is cooled at constant pressure to 350 K. Assume that the gases are ideal. Determine: (a) the heat given off during cooling, (b) the change in internal energy, (c) the work done on the gas.

The specific heats in J/mol K are as follows:

$$C_{P,H_2} = 29.086 - 8.3694 \square\ 10^{-4}\ T + 2.0130 \square\ 10^{-6}\ T^2$$

$$C_{P,CO} = 26.553 + 7.6882 \square\ 10^{-3}\ T - 1.1727 \square\ 10^{-6}\ T^2$$

3.3 CO_2 is sold commercially in steel containers at 60 bar. The gas is leaking through the outlet valve slowly so that the temperature may be assumed constant at the room temperature of 300 K.

(a) What is the work done in the expansion of 10 kg of this gas from 60 bar to 1 bar?
(b) If the temperature were constant at 290 K, would there be any difference in the work done?
(c) What are the changes in enthalpy in both the above cases?

3.4 An ideal gas is compressed adiabatically from 1.5 bar, 338 K to 9 bar. The process is reversible, and g = 1.23 is constant over the entire range of conditions. Calculate:

(a) The temperature at the end of compression
(b) The work of compression
(c) The heat transferred
(d) The change in internal energy
(e) The change in enthalpy

3.5 An ideal gas undergoes the following reversible processes:

(a) From an initial state of 343 K and 1 bar it is compressed adiabatically to 423 K.
(b) It is then cooled to 343 K at constant pressure.
(c) Finally, it is expanded to its original state isothermally.

Calculate D*U*, D*H*, *W* and *Q* for each step as well as for the entire cycle. Assume $C_V = (3/2)\ R$.

3.6 Air, initially at 389 K and 8 bar is expanded reversibly and isothermally to such a pressure that when it is cooled to 278 K at constant volume, its pressure is 2 bar. Assume air to be an ideal gas with C_P = 29.3 J/mol K. Calculate the work, heat transferred, changes in internal energies, and changes in enthalpies.

3.7 Methane is stored in a tank of capacity $5.7 \square\ 10^{-2}\ m^3$ at a pressure of 15 bar and 294 K. The gas is allowed to flow from the tank through a partially opened valve to a gas holder where the pressure is constant at 1.15 bar. When the pressure in the tank dropped to 5 bar, what would be the mass of methane removed under the following conditions?

(a) If the process took place slowly so that the temperature was constant.
(b) If the process took place so rapidly that the heat transferred was negligible.

Methane behaves as ideal gas with g = 1.4.

3.8 A rigid non-conducting tank with a volume of 4 m^3 is divided into two equal parts by a membrane. On one side of the membrane, the tank contained gas *A* at 5 bar and 350 K and on the other side a gas *B* at 10 bar and 450 K. *A* and *B* are ideal gases with C_V values $(5/2)R$ and $(7/2)R$ respectively. The membrane is suddenly ruptured and the gases get mixed. What are the final temperature and pressure?

3.9 One cubic metre of an ideal gas at 600 K and 20 bar expands to ten times its initial volume as follows:

(a) By a reversible, isothermal process
(b) By a reversible, adiabatic process
(c) By an irreversible, adiabatic process in which the expansion is against a restraining pressure of 1 bar.

If $C_P = 21$ J/mol K, calculate the final temperature, pressure, and the work done by the gas.

3.10 Estimate the molar volume of CO_2 at 500 K and 100 bar using van der Waals equation. The van der Waals constants are 0.364 m^4 N/mol^2 and $4.267 \square 10^{-5}$ m^3/mol.

3.11 Calculate the molar volume of ammonia at 373 K and 10 bar using (a) the van der Waals equation and (b) the Redlich–Kwong equation, given that the critical temperature is 405.5 K and the critical pressure is 112.8 bar.

3.12 Use the Redlich–Kwong equation to calculate the pressure of 0.5 kg gaseous ammonia contained in a vessel of 0.03 m^3 at a constant temperature of 338 K. The critical temperature and pressure are 405.5 K and 112.8 bar respectively.

3.13 Calculate the pressure developed by 1 kmol gaseous ammonia contained in a vessel of 0.6 m^3 capacity at a constant temperature of 473 K by the following methods:

(a) Using the ideal gas equation
(b) Using the van der Waals equation given that

$$a = 0.4233 \text{ N m}^4/\text{mol}^2; \qquad b = 3.73 \square 10^{-5} \text{ m}^3/\text{mol}$$

(c) Using the Redlich–Kwong equation given that $P_C = 112.8$ bar; $T_C = 405.5$ K.

3.14 Determine the van der Waals constants and the molar volume of ethane at the critical point, given that the critical temperature and pressure are respectively 305.2 K and 49.4 bar.

3.15 Using the Redlich–Kwong equation calculate the molal volumes of saturated liquid and saturated vapour of methyl chloride at 333 K. The saturation pressure of methyl chloride at 333 K is 13.76 bar. The critical temperature and pressure are respectively 416.3 K and 66.8 bar.

3.16 Using the virial equation calculate the molar volume and compressibility factor of isopropanol vapour at 473 K and 10 bar. The virial coefficients are:

$$B = -3.88 \square 10^{-4} \text{ m}^3/\text{mol}; \qquad C = -2.6 \square 10^{-8} \text{ m}^6/\text{mol}^2$$

3.17 Determine the molar volume of gaseous methane at 300 K and 600 bar by the following methods:

(a) Using the ideal gas equation
(b) Using the van der Waals equation given that

$a = 0.2285$ N m^4/mol^2; $b = 4.27 \square 10^{-5}$ m^3/mol

(c) Using the Redlich–Kwong equation given that $T_C = 191.1$ K and $P_C = 46.4$ bar.

3.18 An empirical equation $PV^{d} = C$, where C is constant, is used to relate P and V of any reversible process. Show that for an ideal gas this equation leads to

$$W = \frac{RT_1}{\delta - 1}\left[1 - \left(\frac{P_2}{P_1}\right)^{\frac{\delta - 1}{\delta}}\right]$$

Show that in the case of an isothermal process when $\delta = 1$, the above equation reduces to

$$W = RT \ln \frac{P_1}{P_2}$$

3.19 Heat of combustion of solid carbon and gaseous CO are respectively–393.78 kJ/mol and –283.18 kJ/mol. Determine the heat of formation of CO.

3.20 Using Hess's law evaluate the heat of formation of solid $CaCO_3$. The following data are available:

(a) Ca (s) + $\frac{1}{2}$ O_2 (g) □ CaO (s); $\Delta H^0_{298} = -635.77$ kJ

(b) C (s) + O_2 (g) □ CO_2 (g); $\Delta H^0_{298} = -393.77$ kJ

(c) CaO (s) + CO_2 (g) □ $CaCO_3$ (s); $\Delta H^0_{298} = -178.15$ kJ

3.21 Calculate the standard heat of reaction for the following reaction:

2 FeS_2 (s) + $\frac{11}{2}$ O_2 (g) □ Fe_2O_3 (s) + 4 SO_2 (g)

The standard heat of formation at 298 K are –178.02 kJ/mol for FeS_2 (s), –822.71 kJ/mol for Fe_2O_3 (s) and –297.10 kJ/mol for SO_2 (g).

3.22 The standard heat of combustion of benzene at 298 K is – 3269.5 kJ/mol when burnt completely to CO_2 and liquid water. The standard heat of combustion of hydrogen to liquid water is –286.04 kJ/mol and that of carbon to carbon dioxide is – 393.78 kJ/mol. Calculate the standard heat of formation of liquid benzene.

3.23 The standard heat of reaction at 298 K for the following reaction is – 42.433 kJ.

C_2H_4 (g) + H_2O (g) □ C_2H_5OH (g)

Calculate the heat of reaction at 400 K. The constants in the heat capacity equation

$$C_P = a + bT + gT^2$$

are as given below: (C_P is in J/mol K and T in K).

	a	b	g
C_2H_4	11.85	119.75 □ 10^{-3}	– 36.53 □ 10^{-6}
H_2O	30.38	9.62 □ 10^{-3}	+ 1.19 □ 10^{-6}
C_2H_5OH	29.27	166.39 □ 10^{-3}	– 49.93 □ 10^{-6}

3.24 The standard heat of combustion of graphite at 298 K is – 393.778 kJ/mol. Determine the heat o combustion at 800 K. The heat capacities in J/mol K are:

$$\text{Carbon: } 11.19 + 1.096 \times 10^{-2}\, T - \frac{4.894 \times 10^5}{T^2}$$

$$\text{Oxygen: } 34.62 + 1.08 \times 10^{-3}\, T - \frac{7.859 \times 10^5}{T^2}$$

$$\text{Carbon dioxide: } 43.29 + 1.147 \times 10^{-2}\, T - \frac{8.185 \times 10^5}{T^2}$$

3.25 Calculate the heat of combustion of methane at 800 K given that the heat of combustion at 298 K is – 802.861 kJ/mol and the mean heat capacity in the temperature range from 298 K to 800 K are 41.868 J/mol K, 30.563 J/mol K, 41.449 J/mol K, and 34.332 J/mol Kfor methane, oxygen, CO_2 and water vapour respectively.

3.26 Ammonia is synthesised according to the following reaction:

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3; \quad \Delta H^0_{298} = -\,46.222 \text{ kJ}$$

The specific heats of the components are represented by

$C_P = a + bT + gT^2$

where C_P is in J/mol K and the constants a, b and g are:

	a	b	g
N_2	27.31	5.2335 □ 10^{-3}	– 4.1868 □ 10^{-9}
H_2	29.09	– 8.374 □ 10^{-4}	+ 2.0139 □ 10^{-6}
NH_3	25.48	36.89 □ 10^{-3}	– 6.305 □ 10^{-6}

Express the heat of reaction as function of temperature.

3.27 Calculate the heat of the following gas-phase reaction

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O; \quad \Delta H^0_{298} = -\,242 \text{ kJ}$$

if the reactants are at 473 K and the product is at 993 K. The specific heats C_P = a + bT + gT^2 J/mol K may be evaluated using the data given below:

	a	b	g
H_2	29.09	– 8.374 □ 10^{-4}	2.0139 □ 10^{-6}
O_2	25.74	12.987 □ 10^{-3}	– 3.864 □ 10^{-6}
H_2O	30.38	9.621 □ 10^{-3}	– 1.185 □ 10^{-6}

3.28 Carbon monoxide (CO) at 1000 K is burned with air at 800 K in 90% excess air. The products of combustion leave the reaction chamber at 1250 K. Calculate the heat evolved in the reaction chamber per kmol of CO burned. The standard heat of reaction at 298 K is –283.028 kJ/mol CO. The mean specific heat applicable in the temperature range of this problem are 29.38, 49.91, 33.13, and 31.43 J/mol K for CO, CO_2, O_2, and N_2 respectively.

3.29 Hydrochloric acid is produced from chlorine according to

$Cl_2 + H_2O$ □ 2 HCl + $\frac{1}{2}$ O_2

The standard heats of formation at 298 K are –241.82, – 92.307 kJ/mol for water vapour and hydrochloric acid respectively. The reaction is to be carried out at 500 K with saturated steam at 500 K and chlorine gas at 500 K entering the reactor with a ratio of 3 mol steam per mol of chlorine gas. Determine the amount of heat to be added or to be removed per kmol of acid obtained if the reaction goes to completion and the products leave at 500 K. Mean specific heats of chlorine gas, oxygen, HCl, and water vapour may be taken as 35.0, 33.0, 40.0, and 25.0 J/mol K respectively, and enthalpy of saturated water vapour at 298 K and 500 K are 2547 kJ/kg and 2801 kJ/kg respectively.**3.30** Calculate the theoretical flame temperature for a gas containing 25% CO and 75% N_2 when burned with 80% excess air, when both the reactants are at 298 K. The standard heat of formation are –393. 70 kJ/mol for CO_2 and –110.00 kJ/mol for CO. The mean molar specific heats in J/mol K are

T, K	CO_2	O_2	N_2
800	45.43	31.59	30.31
1000	47.56	32.37	30.64
1200	49.35	33.02	31.22
1400	50.82	33.60	31.77
1600	51.99	34.05	32.25
1800	53.18	34.40	32.65

3.31 Calculate the theoretical flame temperature of a gas mixture consisting of 20% CO and 80% N_2 when burned with 100% excess air, both air and gas initially being at 298 K. The standard heat of reaction at 298 K is –283.178 J/mol CO. The heat capacity in J/mol K are given by $C_P = a + bT + gT^2$, where

	a	b	g
CO_2	26.54	42.45 □ 10^{-3}	– 14.298 □ 10^{-6}

O_2	25.61	$13.26 \square 10^{-3}$	$-4.208 \square 10^{-6}$
N_2	27.03	$5.815 \square 10^{-3}$	$-0.289 \square 10^{-6}$

3.32 0.5 mol hydrogen at 300 K, 2 mol nitrogen and oxygen present in the ratio of 3:1, and 0.3 mol of CO are mixed. The nitrogen–oxygen mixture was initially present at 400 K and the initia temperature of CO was 500 K. Fifty per cent of the CO present reacts. If the final temperature o the system raises to 1200 K under adiabatic conditions, and if the standard heat of formation o CO_2 is two times that of CO, calculate the standard heat of formation of CO_2. The mean heat capacities in J/mol K are 32.5 for O_2, 31.1 for N_2, 29.0 for H_2, 31.0 for CO, and 49.0 for CO_2.

3.33 Calculate the standard heat of reaction at 800 K for the combustion of pentane gas, given tha the mean heat capacities in J/mol K are 247 for C_5H_{12}, 33.62 for O_2, 52.32 for CO_2, and 38.49 for H_2O. The standard heat of combustion at 298 K is –3271.71 kJ/mol.

3.34 An internal combustion engine uses octane as fuel. The air and fuel vapour mixture enter the engine at 298 K. Twenty per cent excess air is supplied. Seventy-five per cent of the carbon present in the fuel is converted to CO_2 and the rest to CO, and the combustion products leave the engine at 800 K, calculate the energy transferred as heat to the engine per kg fuel burned. The mean heat capacities in J/mol K are 32.5 for O_2, 31.1 for N_2,

31.0 for CO, 50.0 for H_2O, and 49.0 for CO_2. The heat of formation of CO_2, CO, and H_2O at 298 K are –393.509, –110.525, and –241.818 kJ/mol respectively. Heat of formation of octane is –208.75 kJ/mol.

3.35 Calculate the maximum flame temperature attained when methane is burned with theoretical air when both fuel and air are at 298 K initially. The mean heat capacities in J/mol K are 62.75 for CO_2, 52.96 for H_2O, 38.67 for O_2, 37.13 for N_2. The standard heat of combustion o methane at 298 K is –802.625 kJ/mol.

3.36 Calculate the standard heat of reaction at 298 K for the following reaction:

$$4\,HCl\,(g) + O_2\,(g) \square 2\,H_2O\,(g) + 2\,Cl_2\,(g)$$

The standard heats of formation arE –92.307 kJ/mol for HCl (g) and –241.818 kJ/mol for H_2O (g).

3.37 Hydrocarbon fuels can be produced from methanol by the following reaction:

$$6\,CH_3OH\,(g) \square C_6H_{12}\,(g) + 6\,H_2O\,(g)$$

Compare the standard heat of combustion of 6 mol CH_3OH (g) at 298 K with the standard heat of combustion of C_6H_{12} (g) at 298 K, products in both the cases being CO_2 (g) and H_2O (g).

3.38 Methanol is synthesised according to the following reaction:

$$CO\,(g) + 2\,H_2\,(g) \square CH_3OH\,(g)$$

The standard heats of formation at 298 K are –110.125 kJ/mol for CO and –200.660 kJ/mol for methanol. The specific heats (J/mol K) are given by:

$$C_P\,(CH_3OH) = 19.382 + 101.564 \square 10^{-3}T - 28.683 \square 10^{-6}T^2$$

$Cp\,(\mathrm{CO}) = 28.068 + 4.631 \square 10^{-3}T - 2.5773 \square 10^{4}T^{-2}$

$Cp\,(\mathrm{H_2}) = 27.012 + 3.509 \square 10^{-3}T + 6.9006 \square 10^{4}T^{-2}$

(a) Calculate the standard heat of reaction at 1073 K.
(b) Express the heat of reaction as a function of temperature.

3.39 Methane is burned with 20% excess air; both methane and air being at 298 K. The standard heat of combustion of methane at 298 K is – 802.625 kJ. The heat capacities in J/mol K are:

$Cp\,(\mathrm{CH_4}) = 14.150 + 75.499 \square 10^{-3}T - 17.9915 \square 10^{-6}\,T^{2}$

$Cp\,(\mathrm{O_2}) = 30.255 + 4.207 \square 10^{-3}T - 1.8873 \square 10^{5}T^{-2}$

$Cp\,(\mathrm{N_2}) = 27.270 + 4.930 \square 10^{-3}T + 3.3256 \square 10^{4}T^{-2}$

$Cp\,(\mathrm{CO_2}) = 45.369 + 8.688 \square 10^{-3}T + 9.6193 \square 10^{5}T^{-2}$

$Cp\,(\mathrm{H_2O}) = 28.850 + 12.055 \square 10^{-3}T + 1.006 \square 10^{5}T^{-2}$

Calculate the adiabatic flame temperature attained.

3.40 Carbon monoxide reacts with water vapour to form carbon dioxide and hydrogen.

$\mathrm{CO\,(g) + H_2O\,(g) \square CO_2\,(g) + H_2\,(g)};\ \Delta H^{0}_{298} = -41.190$ kJ

The reactants are at 298 K and in stoichiometric proportions. Seventyfive per cent of CO is converted in the reaction. The products leave the reaction chamber at 800 K. The mean heat capacities in J/mol K are 30.35 for CO, 45.64 for CO_2, 36.00 for water vapour, and 29.30 for hydrogen. Determine the quantity of heat to be added or removed in the reaction chamber per 1000 kg of hydrogen produced.

3.41 Calculate the standard heat of the following reaction at 298 K:

$\mathrm{C_5H_{12}\,(g) + 8\,O_2\,(g) \square 5\,CO_2\,(g) + 6\,H_2O\,(l)}$

The standard heats of formation are as follows:

$\mathrm{CO_2}$ (g) = – 393.509 kJ , $\mathrm{H_2O}$ (g) = –241.818 kJ, $\mathrm{C_5H_{12}}$ (g) = –146.76 kJ

The latent heat of vaporisation of water at 298 K = 43.967 kJ/mol.

3.42 A gas mixture consisting of 20% ethane and 80% oxygen at 298 K is burned completely after diluting it with double the volume of CO_2 at the same temperature 298 K. The mean heat capacities in J/mol K are 54.56 for CO_2, 43.02 for water vapour, and 35.52 for oxygen. The standard heat of reaction of ethane at 298 K is –1478 kJ/mol. Determine the theoretical flame temperature.

4

Second Law of Thermodynamics

4.1 LIMITATIONS OF THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics deals with energy changes involved in a process. But, it alone cannot answer many questions related to transformation of energy. The first law specifies only this: if energy is produced during a process, it must be compensated with a loss of an exactly equal quantity, so that the total energy before and after the process are the same. It helps us to determine the energy changes involved in a process, but it cannot tell us whether a proposed change would actually occur or not. If it occurs, what is the direction of the change and what are the conditions of equilibrium under which the system undergoes no further change?

The major limitation of the first law of thermodynamics is, therefore, its inability to deal with the direction of the process and the extent of change. Also, according to the first law, all forms of energy are quantitatively equivalent and they are just additive terms in an energy balance. It fails to recognise the qualitative differences between various forms of energy. This difference is apparent when we attempt to convert heat into work by means of a heat engine. Before we embark on the detailed study of the second law of thermodynamics, a discussion on these limitations is quite in order.

4.1.1 Direction of Change

We have seen that the first law of thermodynamics deals with the amount of energy in different forms that are involved in various spontaneous processes, but it is not concerned with the 'direction of change'. For example, when water on the top of a mountain runs to the bottom as a stream or as a waterfall, the initial potential energy of water is converted to the kinetic energy and the first law of thermodynamics is satisfied, because, the total energy remains unchanged. It would equally be satisfied in the reverse process in which the water flows upwards spontaneously. The first law doesn't suggest the impossibility of water flowing upwards spontaneously. However, such an occurrence is contrary to our experience.

Now, let us consider another example. When two bodies at different temperatures are brought into contact, heat energy flows from the body at high temperature to that at low temperature spontaneously. Heat energy will never flow from a lower temperature level to a higher temperature level without applying external work. According to the first law, the energy gained by the cold body should be equal to the energy lost by the hot body. Again, there is nothing in the first law that predicts that the transfer of heat must always be from the hot to the cold body. The first law would be satisfied equally well if the transfer of energy took place in the reverse direction, but such a transfer never happens in nature. Similarly, we never observe a mixture of gases made up of two or more components spontaneously separating into its constituents. Though such a process is against our experience, it would not be inconsistent with the first law of thermodynamics as long as no net change in the total energy is involved. Thus, it is clear that apart from the first law, but complementary to it, there should be some principle to deal with the spontaneous processes and their direction.

The inadequacy of the first law of thermodynamics to explain our general experience with spontaneous processes or tendency to change led to the development of the second law of thermodynamics, which deals with the direction of change. With the help of the tools provided by the second law, we can find answers to many problems that are not answered by the first law. For a chemical reaction occurring from a given initial state of reactants to a given final state of products, the first law can be utilised to estimate the heat of reaction and the effect of temperature and pressure on it. But, will the reaction proceed spontaneously? What is the equilibrium point at which no further change occurs? How is the equilibrium affected by the operating conditions? What is the maximum work available from a process? What is the minimum work required to carry out a process? What is the maximum efficiency with which a process could be carried out? Such questions are answered by the second law of thermodynamics, usually in combination with the first law.

4.1.2 Qualitative Difference between Heat and Work

Another limitation of the first law of thermodynamics is that it does not take into account the difference in quality between heat and work. When we treat heat and work as additive terms in an energy balance, we are in fact ignoring the intrinsic difference between them. It is true that, in the application of the first law this difference is not going to affect our calculations. However when we consider converting heat energy to other forms of energy, the qualitative difference between heat and work would be obvious. It is possible to convert one form of work to another (such as electrical to mechanical) with almost 100 per cent efficiency, provided, the irreversibilities in the apparatus are eliminated. But the efficiency of converting energy transferred to a system as heat into any of the forms of work is limited to very low values. This leads us to the conclusion that heat is a less versatile or more degraded form of energy compared to the other forms of energy or work can be termed energy of a higher quality than heat. During the conversion of heat into work, a portion of the energy becomes *unavailable*, that is, not capable of being transformed into useful form.

The difference between the quality of heat and other forms of energy are accounted for in the second law of thermodynamics. When we say that heat flows always from a higher to a lower temperature we are assigning a characteristic quality as well as quantity to heat, the quality being represented by temperature. We know that the efficiency of a thermal power plant increases as the temperature of the steam in the boiler increases. In the transformation of heat to work, the increase in the efficiency that results from the increase in the temperature of the source clearly establishes the connection between the temperature and the quality of heat.

4.2 GENERAL STATEMENTS OF THE SECOND LAW THERMODYNAMICS

The second law of thermodynamics is just the generalisation of our experiences with spontaneous processes and can be stated in a number of ways:

1. Heat cannot by itself pass from a cold to a hot body.
2. All spontaneous processes are, to some extent, irreversible and are accompanied by a degradation of energy.
3. Every system, when left to itself, will on the average, change toward a system of maximum probability.

4. *Kelvin–Planck statement.* It is impossible to construct an engine that, operating continuously (in a cycle), will produce no effect other than the transfer of heat from a single thermal reservoir at a uniform temperature and the performance of an equal amount of work. This statement implies that at least two thermal reservoirs of different temperatures are necessary for a heat engine to operate. This is because only part of the heat transferred to the engine from a high temperature reservoir is converted to work; the rest is rejected to a low temperature reservoir. Further, the statement implies that no heat engine can have 100% efficiency because heat cannot be completely converted to work. The word ‘continuous’ in the Kelvin–Planck statement has an important implication. Consider the isothermal expansion of an ideal gas. The change in internal energy, ΔU, is zero in this process. This means that the heat absorbed by the gas is completely converted to work. Though it may appear to contradict the second law, in fact, it is not so. What the second law requires is that there should be no change in the system or in the surroundings other than the complete conversion of heat into work. Here, the pressure of the gas has decreased and the process cannot be carried out continuously. The pressure of the gas would soon become equal to that of the surroundings, and further expansion would be impossible. The continuous conversion of heat to work is possible only in a cyclic process. But, in the cyclic process, energy from the surroundings is utilised in the form of work, in order to compress the gas back to its original pressure.
5. *Clausius statement.* It is impossible to construct a heat pump that, operating continuously, will produce no effect other than the transfer of heat from a lower temperature body to a higher temperature one. In other words, any process, which consists solely in the transfer of heat from one temperature to a higher one, is impossible. It means that energy in the form of work must be supplied to the heat pump in order to transfer heat from a cold body to a hot body. Therefore, the coefficient of performance of a heat pump can never be infinity.

4.2.1 The Equivalence of the Kelvin and Clausius Statements

All the statements of the second law are equivalent and mean the same thing. Any device that violates any one of these statements will violate all other statements. Figure 4.1 shows an engine, which violates Kelvin–Planck statement by absorbing heat from a single thermal reservoir and producing an equivalent amount of work. The work output of this engine ($W = Q_1$) is used to drive a heat pump which transfers an amount of heat Q_2 from a low temperature reservoir and an amount ($Q_1 + Q_2$) to a high temperature reservoir. The combined system shown by the dotted lines in the figure then act as heat pump which transfers an amount of heat Q_2 from a lower temperature to a higher temperature reservoir without using any external work. This is a violation of Clausius statement.

Now consider a heat pump, which violates the Clausius statement, by absorbing heat Q_2 from a low temperature reservoir and transferring it to a high temperature reservoir (Fig. 4.2). Let a heat engine work between these two reservoirs by absorbing heat Q_1 ($Q_1 > Q_2$) delivering work W ($W = Q_1 - Q_2$) and rejecting heat Q_2 to the low temperature reservoir. Since this process does not affect the low-temperature reservoir, the net effect is a heat engine operating with a single thermal reservoir absorbing heat $Q_1 - Q_2$ and converting it completely to work. This is a violation of the Kelvin–Planck statement.

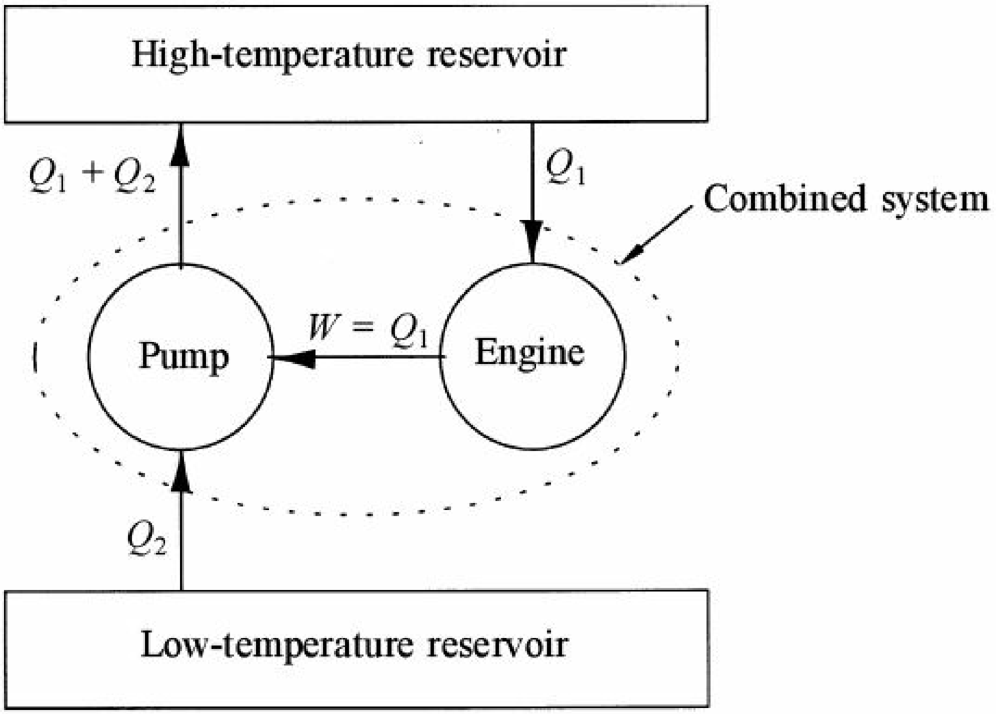


Fig. 4.1 A heat engine that violates the Kelvin–Planck, statement.

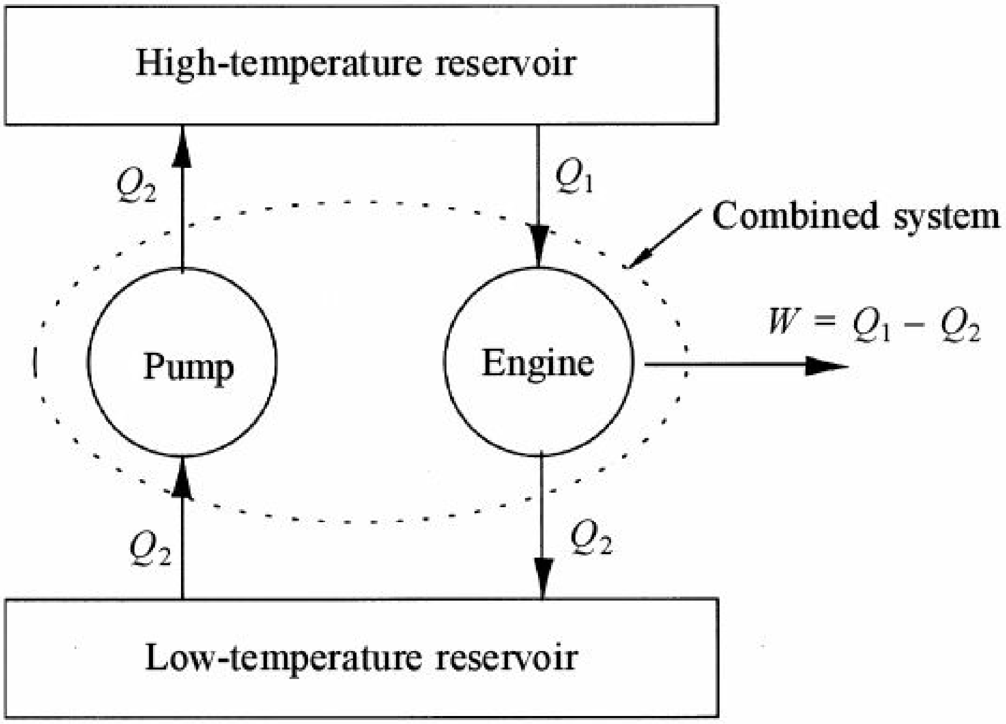


Fig. 4.2 A heat pump that violates the Clausius statement.

4.3 ENTROPY

4.3.1 Why the Concept of Entropy?

The second law of thermodynamics states that all spontaneous processes are, to some extent, irreversible and are accompanied by a degradation of energy. It also means that it is impossible for any self-acting machine to transfer energy from a given state to a higher state of availability. To make these statements quantitative there is required some function that always changes in a certain way during a spontaneous process and therefore, will characterise such a change. Internal energy was defined to give quantitative significance to the first law. Internal energy does not change in any characteristic way in a spontaneous process, and it does not help in any way in the development of the second law. The function that is fundamental in the development of the second law is *entropy*, which means transformability (change) in Greek, introduced by Clausius in 1851. Later in this chapter, we will show that the second law of thermodynamics necessitates that all spontaneous processes result in an increase in the entropy and no process is possible that results in a decrease in entropy.

Consider an imaginary process for gas separation as illustrated in Fig. 4.3. Assuming that the gases behave ideally, the change in the internal energy, $\Delta U = 0$. On the basis of the first law, the process is not an impossible one. With the aid of the entropy function it can readily be shown that the imagined process is impossible, because, it would involve a net decrease in entropy of the system with no corresponding increase in the entropy of the surroundings.

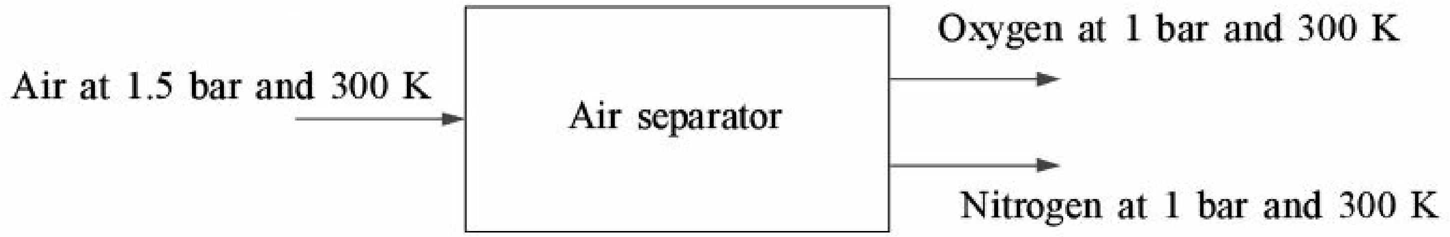


Fig. 4.3 A process that is permitted by the first law, but that violates the second law.

We have seen that although there is an exact quantitative equivalence among the different forms of energy, there is a marked difference in the availability of these forms for useful work. Heat represents the least 'available' form of energy and transformation of other forms into heat represents a degradation of energy. Entropy is the thermodynamic property, which serves as a measure of the unavailability or degradation of energy. An increase in unavailability of the total energy of a system is quantitatively expressed by a corresponding increase in its entropy. Entropy, being an intrinsic property of matter, is not affected by the external position of the body or its motion relative to other bodies. The entropy of unit mass of water at the top of the mountain is equal to the entropy of the same amount of water at the bottom of the falls, if the temperature and pressure are the same. Similarly, the entropy of unit mass of water in the flowing stream will be equal to the entropy of water in a stagnant pool, provided that the conditions such as the temperature and pressure are the same in both the cases. The entropy of a system is affected only by the nature of matter under consideration and by the state in which it exists.

4.3.2 Entropy and Heat

As noted above, the entropy is a measure of the unavailability of the internal energy. Among the various forms, heat is the least available form of energy. Whenever a certain form of energy gets transformed to heat the total energy gets degraded with a corresponding increase in the entropy of the system. Consider 1 kg of water at the top of a mountain of height about 426.8 m. At this position, water possesses a potential energy of nearly 4.187 kJ. When the water falls and strikes the river at the bottom, all its potential energy gets converted to thermal energy with a consequent temperature rise of water by approximately 1 K. This process results in a degradation of total energy. If not, we could have reversed the process and raised the water to its initial position by cooling it by 1 K. This degradation of energy is measured by a net increase in the entropy. In this case, the increase in entropy was due to the degeneration of mechanical energy into heat. In general, an increase in entropy results from the addition of heat into the system through the degradation of energy in any form or, by the direct supply of heat to the system. In short, *the entropy of the system is increased by the addition of heat through any mechanism or from any source.* The increase in entropy is proportional to the heat exchanged but not equal to it, since, it is necessary to consider the temperature of the system when the heat is transferred.

4.3.3 Entropy and Temperature

The amount of heat added to a system is only a partial measure of the magnitude of its entropy increase. It also depends upon the temperature of the system to which heat is added. Consider a system consisting of a weight and two separate reservoirs, one at temperature T_h and the other at a lower temperature T_c. The weight is first allowed to fall to the high-temperature reservoir, transferring to it certain quantity of heat in the process. The heat so transferred is then made to flow into the reservoir at T_c. These two irreversible processes result in a net increase in entropy which would be the same as the increase in entropy that would result if the weight were allowed to fall directly to the reservoir at T_c. This is so, because, the initial and the final conditions are the same in both cases. Entropy, as will be shown later, is a thermodynamic property that depends only on the terminal states and not on the path followed. Therefore, the change in entropy would be the same in both cases. In the first instance, it is the sum of two contributions: one, the entropy change that resulted by the dropping of the weight to the hot reservoir; and the other by the transfer of heat to the cold reservoir. Since, these two together equal the entropy change resulted by the dropping of the weight to the cold reservoir, we can conclude that the change in entropy due to the lowering of weight to a reservoir at a high temperature is less than that resulted when the weight was lowered to the reservoir at a low temperature. It means that the transfer of energy to a low temperature leads to a greater degradation than that resulted by the transfer of the same quantity to a higher temperature. The greater the degradation of the energy, the greater would be the irreversibility of the process. Entropy, being a thermodynamic function, used to measure the degree of degradation or the extent of irreversibility, should therefore, be related not to Q, but to Q/T, where Q is the heat received by the reservoir and T is its temperature.

In conclusion, *the transfer of heat within an isolated system to a region of lower temperature increases the unavailability of energy and the entropy of the system. The addition of heat to a system at a lower temperature leads to a greater degradation of energy than that resulted by the addition at a higher temperature.*

4.3.4 Entropy and the Nature of the Process

We have seen that a quantitative description for entropy should take into account the heat transferred and the temperature level at which it is transferred. In addition, in order to complete the definition of entropy, the nature of the process should also be specified. For example, a gas may be expanded freely to a lower pressure within a closed system, which is completely isolated from the surroundings thermally and mechanically. This is an irreversible process resulting in degradation of energy of the system and consequently an increase in its entropy. However, no heat is added, no work is done, and for an ideal gas, the process is isothermal. How is then the increase in entropy for this process measured? Consider an engine operating within the system that continuously converts the work done into heat by means of friction. In this case, heat is added to the system by degradation of mechanical work. The amount of heat added increases with the efficiency of the engine, and reaches a maximum when the engine operates reversibly. But the change in entropy (being a state function) accompanying a process, is dependent only on the initial and final states and not on the path. So, when we take the amount of heat transferred to measure the increase in entropy through the term Q/T, the nature of the process should be specified. The logical choice, thus, is the maximum possible degradation of higher forms of energy into heat, which is possible only in a reversible process. Entropy change should therefore be measured as Q_R/T, where Q_R is the heat transferred when the process is occurring reversibly.

To summarise, the quantitative definition of entropy requires the following specifications:

1. The amount of heat transferred.
2. The temperature level at which the transfer occurs
3. The nature of the process, whether reversible or irreversible.

To comply with these requirements, we define entropy change in a process as

$$\boxed{dS = \frac{dQ_R}{T}} \tag{4.1}$$

In Eq. (4.1), S denotes the entropy, Q the heat transferred, T the absolute temperature, and the suffix R indicates the reversibility of the process.

4.4 THE CARNOT PRINCIPLE

Nicolas Sadi Carnot (1824) introduced the concept of cyclic operations and was among the first to study the principles of the second law of thermodynamics. He devised a classical ideal cycle named after him that formed the basis for the mathematical statement of second law of thermodynamics.

The *Carnot cycle* consists of an alternate series of two reversible isothermal processes and two reversible adiabatic processes as shown in Fig. 4.4.

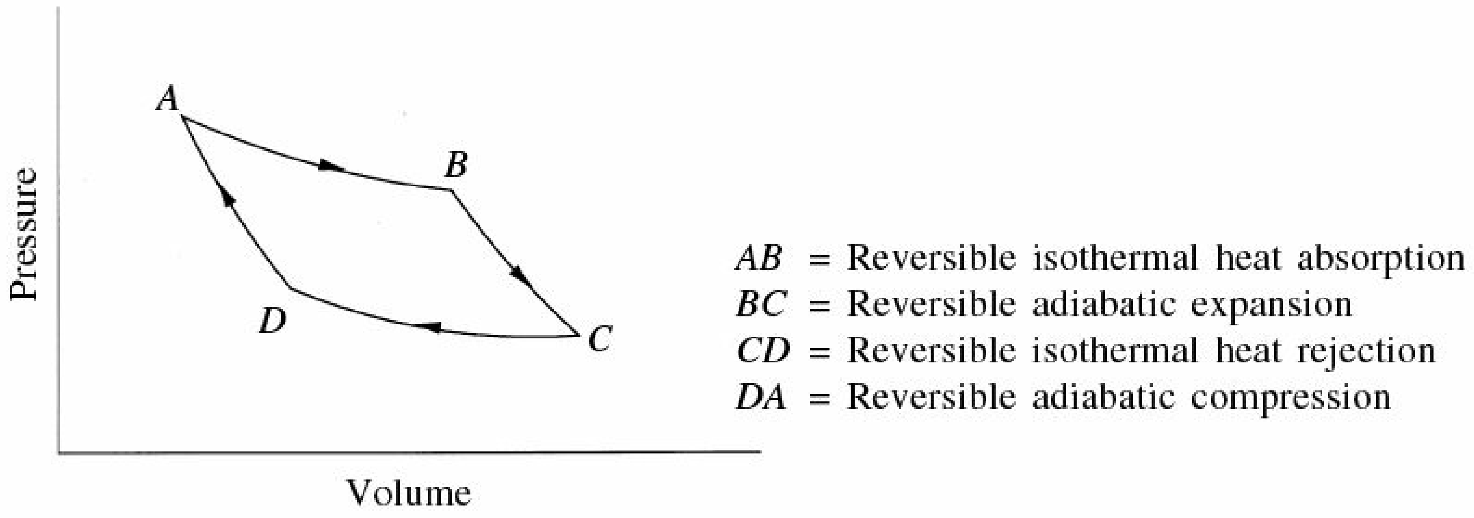


Fig. 4.4 *P-V* diagram for the Carnot cycle.

During the process *AB*, heat is transferred reversibly and isothermally to the working substance from the high-temperature reservoir (HTR) at temperature T_1 and the system performs an amount of work which is given by the area under the curve *AB* on the *PV* diagram. During the reversible adiabatic expansion (*BC*), the temperature of the system decreases from T_1 to T_2. The area under the curve *BC* gives the net work obtained from this step. During process *CD*, the system rejects heat Q_2 to a low-temperature reservoir (LTR) at a constant temperature T_2. The area on the *PV* diagram under the curve *CD* is the net work done on the system during this step. The final step is a reversible adiabatic compression (*DA*) during which the temperature rises from T_2 to T_1 and the original conditions are restored to the system. The area under the curve *DA* is the work done on the system for this change. The enclosed area *ABCD* represents the net work delivered by the engine.

The *Carnot principle* involves the following two propositions.

1. No heat engine operating in a cycle between two constant temperature reservoirs can be more efficient than a reversible engine working between the same two reservoirs.
2. All reversible engines working between two constant temperature reservoirs have the same efficiency irrespective of the working substance, and this efficiency is dependent only on the temperature levels.

The first proposition can be easily verified by considering a reversible engine (*R*) and an irreversible engine (*I*) operating between two heat reservoirs as shown in Fig. 4.5. Assume that the irreversible engine is more efficient than the reversible one. Let the work output of both the engines be *W*. Since, the efficiency is defined as the ratio of the work output to the heat input, then for engine *I*, both the heat absorbed $Q_{1,I}$ and the heat rejected $Q_{2,I}$ are less than the corresponding values $Q_{1,R}$ and $Q_{2,R}$ for the reversible engine.

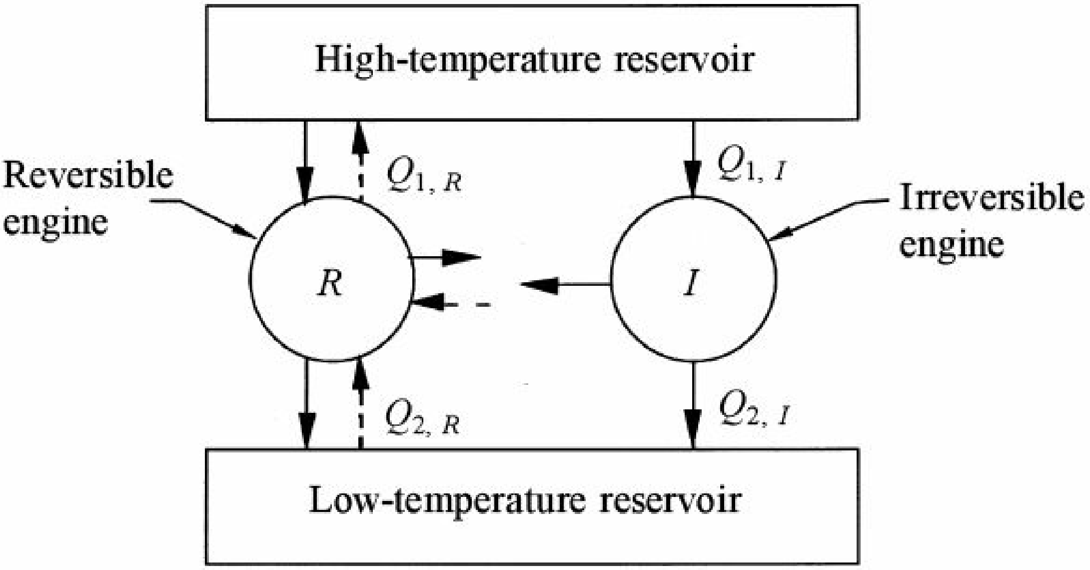


Fig. 4.5 The proof of Carnot's principle.

Since the reversible engine can be operated as a heat pump as shown by the dotted arrows in Fig. 4.5, the work output from engine (*I*) can be utilised to pump heat $Q_{2,R}$ from the LTR, thereby, rejecting heat $Q_{1,R}$ to the HTR. The net effect of the combined system would be the transfer of heat ($Q_{2,R} - Q_{2,I}$) from a cold body to the hot one without the aid of an external agency. As this is a violation of the second law of thermodynamics, an irreversible engine cannot be more efficient than a reversible one.

To prove the second proposition, assume that the irreversible engine (*I*) in Fig. 4.5 be replaced by a reversible engine (*R*□). Let this engine be more efficient than the engine *R*. By reasoning on the same lines as in the preceding paragraph, we can show that the engine *R* can be reversed to run as a heat pump, producing a net effect of transfer of energy from a lower to a higher temperature without any work. Since this is contrary to the second law, *R*□ cannot be more efficient than *R* and vice versa. This means that neither *R* nor *R*□ can be more efficient than each other, i.e., both must have same efficiency. Since, no restrictions were placed on the working fluid in the engine, this efficiency is independent of the working substance and depends only on the temperature levels between which the system is operating.

Denoting the efficiency of the Carnot engine by h,

h = $f(T_1, T_2)$

Since the efficiency is defined as the ratio of W to Q_1, and W by the first law of thermodynamics is equal to $Q_1 - Q_2$, we can write the above equation as

$$\frac{Q_1 - Q_2}{Q_1} = f(T_1, T_2) \tag{4.2}$$

or

$$\frac{Q_2}{Q_1} = \phi(T_1, T_2) \tag{4.3}$$

Equation (4.3) means that the ratio of heat rejected to the heat absorbed by a reversible engine is a function only of the temperatures of the heat source and sink.

4.4.1 Thermodynamic Temperature Scale

The fact that the efficiency of a Carnot engine is independent of the working fluid enables us to define a universal scale of temperature independent of the individual properties of the thermometric substance and of the arbitrary nature of the method of measurement. Lord Kelvin proposed an absolute thermodynamic scale of temperature such that the functional relationship in Eq. (4.3) could be written as

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \tag{4.4}$$

Equation (4.4) means that if an ideal Carnot engine be constructed and Q_1 and Q_2 are measured, their ratio would be the ratio of the absolute thermodynamic temperature of the heat source to that of the sink. The choice of the function $f(T_1, T_2)$ as T_1/T_2 is arbitrary. We could have chosen this function as equal to T_2/T_1, or exp $(T_1 - T_2)$ instead of T_1/T_2. But the present choice is found to be convenient, because by this choice, the absolute temperature coincides with the temperature in the ideal gas equation. The unit of absolute temperature is defined by choosing a single fixed point, the triple point of water as $T_t = 273.16$ K. If a heat engine has a heat source at this temperature, the temperature of the cold sink—the object, whose temperature we want to measure—can be found by measuring Q_1 and

Q_2 and using

$$T_2 = \frac{Q_2}{Q_1} \times T_1$$

With the above choice of the thermodynamic temperature, the efficiency (η) of an ideal Carnot engine, Eq. (4.2), becomes

$$\boxed{\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}} \tag{4.5}$$

and Eq. (4.3) becomes

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

The absolute zero or the zero of the thermodynamic temperature scale is the value of T_2 at which the Carnot efficiency becomes equal to unity. Equation (4.5) gives the maximum efficiency of a heat engine operating between two thermal reservoirs at thermodynamic temperatures T_1 and T_2. In the following section, we consider the efficiency of an ideal Carnot engine using an ideal gas as the working fluid and show that the thermodynamic temperature and the ideal gas temperature are the same.

4.4.2 Ideal Gas as the Carnot Engine Working Substance

Consider an ideal Carnot engine cycle as depicted in Fig. 4.4 with an ideal gas as the working substance. Let P_A, P_B, P_C and P_D denote the pressures of the gas at the various states represented by points *A*, *B*, *C* and *D* respectively. The isothermal expansion step *AB* and isothermal compression step *CD* are carried out at constant temperatures T_1 and T_2 respectively. The net work done by the engine

$$W_{\text{net}} = W_{AB} + W_{BC} + W_{CD} + W_{DA} \tag{4.6}$$

The work done during the reversible adiabatic operations *BC* and *DA* are equal to $-\Delta U$. It follows from the first law, Eq. (2.4), $\Delta U = Q - W$, in which $Q = 0$

$$W_{BC} = -\Delta U_{BC} = -\int_{T_1}^{T_2} C_V \, dT \tag{4.7}$$

$$W_{DA} = -\Delta U_{DA} = -\int_{T_2}^{T_1} C_V \, dT \tag{4.8}$$

Equations (4.7) and (4.8) reveal that W_{BC} and W_{DA} are numerically equal and opposite in sign so that they cancel each other in Eq. (4.6). Therefore,

$$W_{\text{net}} = W_{AB} + W_{CD} \tag{4.9}$$

The change in internal energy in an isothermal process involving ideal gases = 0. Therefore, $W = Q$. The work done and the heat absorbed (Q_1) during the isothermal expansion AB are given by

$$W_{AB} = Q_1 = RT_1 \ln \frac{P_A}{P_B} \tag{4.10}$$

The work done during the isothermal compression *CD* is given by

$$W_{CD} = RT_2 \ln \frac{P_C}{P_D} \tag{4.11}$$

Substituting Eqs. (4.10) and (4.11) into Eq. (4.9), we get

$$W_{\text{net}} = RT_1 \ln \frac{P_A}{P_B} + RT_2 \ln \frac{P_C}{P_D} \tag{4.12}$$

Equations (4.10) and (4.12) lead to the following equation for the efficiency of the engine:

$$\eta = \frac{W_{\text{net}}}{Q_1} = \frac{RT_1 \ln(P_A/P_B) + RT_2 \ln(P_C/P_D)}{RT_1 \ln(P_A/P_B)} = 1 + \frac{T_2 \ln(P_C/P_D)}{T_1 \ln(P_A/P_B)} \tag{4.13}$$

For the adiabatic processes *BC* and *DA,* the temperatures and pressures are interrelated as given below.

$$\frac{T_1}{T_2} = \left(\frac{P_A}{P_D}\right)^{(\gamma-1)/\gamma} \quad \text{for process } DA \tag{4.14}$$

$$\frac{T_1}{T_2} = \left(\frac{P_B}{P_C}\right)^{(\gamma-1)/\gamma} \quad \text{for process } BC \tag{4.15}$$

Comparing Eqs. (4.14) and (4.15), we see that

$$\frac{P_A}{P_B} = \frac{P_D}{P_C} \tag{4.16}$$

Substituting Eq. (4.16) into Eq. (4.13), we get

$$\eta = 1 - \frac{T_2}{T_1} = \frac{(T_1 - T_2)}{T_1} \tag{4.17}$$

By the first law of thermodynamics $W_{\text{net}} = Q_1 - Q_2$. Therefore, Eq. (4.17) can be written as

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \tag{4.18}$$

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Comparison of Eq. (4.18) with Eq. (4.5) shows that the ideal gas temperature and the absolut thermodynamic temperature are identical.

***EXAMPLE*4.1** A heat engine operates between a heat source at 700 K and a heat sink at 300 K. What is the maximum efficiency of the engine?

Solution The efficiency of a Carnot engine operating between two temperature levels T_1 and T_2 is given by Eq. (4.17). This is the maximum efficiency that can be expected of any heat engine. Therefore, the theoretical efficiency of the given engine is

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{700 - 300}{700} = 0.57$$

***EXAMPLE* 4.2** From a reservoir at 600 K, 1000 J of heat is transferred to an engine that operates o the Carnot cycle. The engine rejects heat to a reservoir at 300 K. Determine the thermal efficiency o the cycle and the work done by the engine.

Solution The efficiency of an ideal Carnot engine is given by Eq. (4.5).

$$\eta = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} = \frac{600 - 300}{600} = 0.5$$

The efficiency of the engine is 50%.

$W = 0.5\, Q_1 = 0.5$ □ $1000 = 500$ J

The work done by the engine = 500 J.

EXAMPLE4.3 It is required to freeze 1 kg water at 273 K by means of a refrigeration machine which operates in the surroundings at 300 K. The latent heat of fusion of ice at 273 K is 334.11 kJ/kg. Determine:

(a) The minimum amount of work required
(b) The heat given up to the surroundings.

Solution The work required will be minimum for an ideal Carnot machine acting as a refrigerator. The coefficient of performance (COP) of such a machine is given by the relation

$$\text{COP} = \frac{Q_2}{W} = \frac{T_2}{T_1 - T_2} \tag{4.19}$$

Here, Q_2 is the heat absorbed at a temperature T_2, and T_1 is the temperature of the surroundings to which heat is given up. For freezing 1 kg water, the heat to be removed is 334.11 kJ, i.e. $Q_2 = 334.11$ kJ.

(a) From Eq. (4.19),

$$W = \frac{Q_2(T_1 - T_2)}{T_2} = 334.11\, \frac{300 - 273}{273} = 33.04 \text{ kJ}$$

(b) Since $W = Q_1 - Q_2$,

$$Q_1 = W + Q_2 = 33.04 + 334.11 = 367.15 \text{ kJ}$$

EXAMPLE4.4 An inventor claims to have developed a refrigeration unit which maintains the refrigerated space at 270 K while operating in a room where the temperature is 300 K and which has a coefficient of performance of 9.5. How do you evaluate his claim?

Solution The coefficient of performance of an ideal refrigerating machine is given by Eq. (4.19).

$$\text{COP} = \frac{Q_2}{W} = \frac{T_2}{T_1 - T_2}$$

Here $T_1 = 300$ K and $T_2 = 270$ K. Therefore,

$$\text{COP} = \frac{Q_2}{W} = \frac{T_2}{T_1 - T_2} = \frac{270}{300 - 270} = 9.0$$

No machine operating between 270 K and 300 K can have a COP greater than 9.0. Hence, the inventor’s claim of a COP of 9.5 is unacceptable.

***EXAMPLE* 4.5** A new engine is claimed to be having a power output of 4.5 hp while receiving a heat input of 6.25 kW and working between the source and sink temperature limits of 1000 K and 500 K. Determine the efficiency of the proposed engine. Is the claim for the engine admissible?

Solution The work output of the proposed engine is 4.5 □ 745.7 = 3355.65 W and the heat input is 6250 W. The efficiency of the proposed engine is, therefore,

$$3355.65/6250 = 0.537$$

The maximum efficiency of an engine working between the temperature limits 1000 K and 500 K is the Carnot efficiency. Thus, the maximum efficiency is

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{1000 - 500}{1000} = 0.50$$

No engine can have an efficiency greater than this value. Hence the claim of the proposed engine is impossible.

4.5 ENTROPY—A STATE FUNCTION

Equation (4.18) can be rearranged as

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

where Q_1 is the heat absorbed and Q_2 is the heat rejected by the system. The heat absorbed by the system is positive and heat rejected is negative as per the sign convention we have adopted so that the above equation should be written as

$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2} \tag{4.20}$$

or

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{4.21}$$

Equation (4.21) means that the sum of the quantities Q_1/T_1 and Q_2/T_2 for a reversible heat engine is zero. Any reversible cyclic operation like the one represented on the *P*-*V* diagram in Fig. 4.6 may be regarded as made up of a large number of imaginary Carnot cycles and for each such cycle we can write equation similar to Eq. (4.21) as

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0 \tag{4.22}$$

where dQ_1 and dQ_2 are the heat absorbed and heat rejected respectively during one such an imaginary cycle.

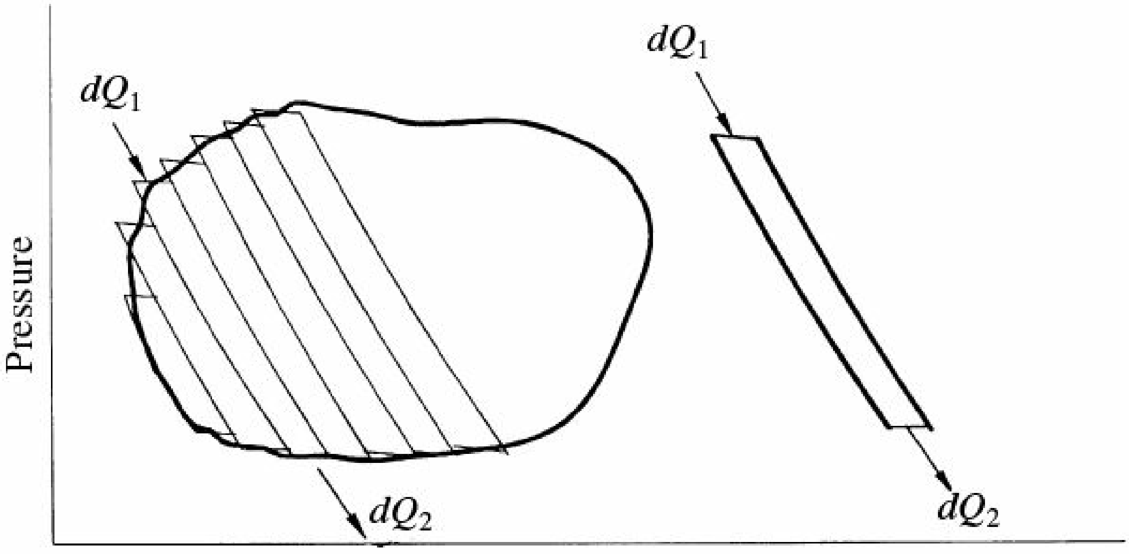


Fig. 4.6 A reversible cycle divided into a number of Carnot's cycles.

Combining all such equations that are written for the separate Carnot cycles into which the original reversible cycle is divided, we get

$$\oint \frac{dQ_R}{T} = 0 \tag{4.23}$$

where the subscript R refers to the reversible process and the cyclic integral limits the equation to the cyclic operation. We have defined entropy change in a process by Eq. (4.1). Substituting Eq. (4.1) into Eq. (4.23) we see that

$$\oint dS = (\Delta S)_{\text{cycle}} = 0 \tag{4.24}$$

where S is the entropy of the system. We have characterised the thermodynamic property of a system as a quantity that undergoes no net change in a cyclic operation. Equation (4.24) means that the entropy change DS for the cyclic operation is equal to zero; or, in short, entropy S as defined by Eq. (4.1) is a thermodynamic property of the system. It reveals an interesting fact: *whereas the heat transferred in a process is a path function, the ratio of the heat transferred to the temperature at which it is transferred is a state function.*

4.6 CALCULATION OF ENTROPY CHANGES

The entropy change as defined by Eq. (4.1), accompanying a process is applicable for a reversible process. In practice, processes are never carried out reversibly. Entropy being a state function depends only on the end states. The entropy change in an irreversible process occurring between any two states would be the same as the entropy change in a reversible process occurring between them, the latter being evaluated by Eq. (4.1). Thus, the entropy change in any irreversible process can be evaluated by devising an imaginary reversible process for accomplishing the same change and calculating the entropy change in the latter.

If the process involves only the direct transfer of heat or the degradation of higher forms of energy into heat, the restriction of reversibility in Eq. (4.1) may be ignored. Thus, entropy change due to the addition of heat can always be calculated by Eq. (4.1), whether the transfer is accomplished reversibly or irreversibly. Similarly, for processes involving the changes in the relative position or movements of matter (as in the case of a falling object) the heat added, even if the process is highly irreversible, measures the entropy change. However, if a process is irreversible because of a finite difference in another driving force, such as pressure, calculation of entropy change is done by devising a reversible process for accomplishing the change. Thus, we see that in the evaluation of entropy changes, the reversibility restriction is to be strictly followed only for processes involving changes in the intrinsic state of the matter.

4.6.1 Phase Change

The entropy change in phase transitions like fusion, vaporisation, or transition from one crystalline form to another can be evaluated from the values of the latent heat of phase change and the temperature at which the change is carried out. The phase changes can be treated as changes occurring reversibly at constant temperature. For example, the entropy of vaporisation ΔS_V is found out as

$$\boxed{\Delta S_V = \frac{\Delta H_V}{T}} \tag{4.25}$$

***EXAMPLE* 4.6** Calculate the entropy of evaporation of dry saturated steam at 500 kPa.
Data: From the steam tables, latent heat of vaporisation, ΔH_V = 2106 kJ/kg; Saturation temperature of steam = 425 K.

Solution By Eq. (4.25), entropy change accompanying vaporisation is ΔS_V = 2106/425 = 4.96 kJ/kg K

4.6.2 Processes involving Ideal Gases

For a differential change in the thermodynamic state of a closed system, the first law of thermodynamics [Eq. (2.5)] can be written as

$$dQ = dU + dW$$

When the process is reversible and the work involved is only work of expansion ($P\,dV$), the above equation can be modified as

$$dQ_R = dU + P\,dV$$

Since this infinitesimal change in the state of the system can be assumed to occur at constant temperature T, the entropy change by Eq. (4.1) is

$$dS = \frac{dU + P\,dV}{T} \tag{4.26}$$

For an ideal gas, $dU = C_V\,dT$ and $P = RT/V$.

$$dS = \frac{C_V\,dT + RT\,(dV/V)}{T} = C_V\,\frac{dT}{T} + R\frac{dV}{V}$$

Assuming that C_V is independent of temperature, this equation can be integrated for a finite change from state 1 to state 2 giving for one mole of an ideal gas,

$$\boxed{\Delta S = C_V \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}} \tag{4.27}$$

where the suffixes 1 and 2 indicate the properties of the gas at state 1 and state 2 respectively. Equation (4.27) can be used for the evaluation of entropy change accompanying the change in states of ideal gases. It can be put in another form also. We know that for ideal gases,

$$C_V = C_P - R \tag{4.28}$$

and

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}\,\frac{T_2}{T_1} \tag{4.29}$$

Substituting Eqs. (4.28) and (4.29) into Eq. (4.27), we obtain the following:

$$\boxed{\Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}} \tag{4.30}$$

Referring to Eqs. (4.27) and (4.30), we see that for constant volume process

$$\boxed{\Delta S = C_V \ln \frac{T_2}{T_1}} \tag{4.31}$$

For constant pressure process, we have

$$\boxed{\Delta S = C_P \ln \frac{T_2}{T_1}} \tag{4.32}$$

For an isothermal process, we obtain

$$\boxed{\Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}} \tag{4.33}$$

Though the above equations are derived on the premise that the processes are reversible, they can be used for irreversible processes occurring between the same terminal conditions as well. This is because the change in entropy depends only on the end states and not on the history of the system.

***EXAMPLE* 4.7** Determine the change in entropy when 2 kg of a gas at 277 K is heated at constant volume to a temperature of 368 K. Take the specific heat at constant volume = 1.42 kJ/kg K.

Solution Entropy change accompanying a constant volume process is given by Eq. (4.31). For $m = 2$ kg,

$$\Delta S = mC_V \ln \frac{T_2}{T_1} = 2.0(1.42) \ln \frac{368}{277} = 0.8067 \text{ kJ/K}$$

***EXAMPLE* 4.8** Calculate the entropy change when 1 kmol of an ideal gas at 300 K and 10 bar expands through a throttle to a pressure of 1 bar, both pressures being maintained constant during the process by suitable means.

Solution During throttling enthalpy is unchanged. For an ideal gas enthalpy being a function of temperature alone, the temperature remains unchanged during the process. Therefore, entropy change accompanying the process can be computed by Eq. (4.33).

$$\Delta S = R \ln \frac{P_1}{P_2} = 8.314 \ln \frac{10}{1} = 19.14 \text{ kJ/kmol K}$$

***EXAMPLE* 4.9** What is the change in entropy when 1 kmol of an ideal gas at 335 K and 10 bar is expanded irreversibly to 300 K and 1 bar? $C_P = 29.3$ kJ/kmol K.

Solution The entropy change in this process is given by Eq. (4.30)

$$\Delta S = C_P \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$= (29.3) \ln \frac{300}{335} - 8.314 \ln \frac{1}{10} = 15.91 \text{ kJ/kmol K}$$

4.6.3 Adiabatic Mixing Process

When two substances at different temperatures are mixed together adiabatically, both will attain an intermediate temperature, say, T. The change in entropy of each is calculated as

$$\Delta S = \int \frac{dQ_R}{T} = \int_{T_1}^{T} C_P \frac{dT}{T} \tag{4.34}$$

where T_1 denotes its initial temperature. The total entropy change is then obtained by adding the individual changes. Equation (4.34) can be used for the calculation of change in entropy in processes like mixing of two fluid streams or quenching of metallic bodies in liquids.

***EXAMPLE* 4.10** Ten kilograms water at 375 K is mixed adiabatically with 30 kg water at 275 K. What is the change in entropy? Assume that the specific heat of water is 4.2 kJ/kg K and is independent of temperature.

Solution Let T be the final temperature attained by the system. Then the heat balance gives

$$10(375 - T) = 30(T - 275)$$

Solving this, $T = 300$ K. Let ΔS_1 be the change in entropy of the hot water and let ΔS_2 be that of cold water. Then by Eq. (4.34),

$$\Delta S_1 = 10 \times 4.2 \times \ln \frac{300}{375} = -9.37 \text{ kJ/K}$$

$$\Delta S_2 = 30 \times 4.2 \times \ln \frac{300}{275} = 10.96 \text{ kJ/K}$$

The total entropy change is

$$\Delta S = \Delta S_1 + \Delta S_2 = 1.59 \text{ kJ/K}$$

***EXAMPLE* 4.11** A steel casting at a temperature 725 K and weighing 35 kg is quenched in 150 kg oil at 275 K. If there are no heat losses, determine the change in entropy. The specific heat (C_P) of steel is 0.88 kJ/kg K and that of oil is 2.5 kJ/kg K.

Solution Let T be the final temperature attained by the system. Then the heat balance gives

$$35(0.88)\,(725 - T) = 150(2.5)\,(T - 275)$$

where T is the final temperature attained by the system. Solving this, we get, $T = 309.15$ K. Let ΔS_1 be the change in entropy of the casting and let ΔS_2 be that of oil. Then,

$$\Delta S_1 = 35 \times 0.88 \times \ln \frac{309.15}{725} = -26.25 \text{ kJ/K}$$

$$\Delta S_2 = 150 \times 2.5 \times \ln \frac{309.15}{275} = 43.90 \text{ kJ/K}$$

The entropy change of the casting and oil together is

$$-26.25 + 43.90 \text{ kJ/K} = 17.65 \text{ kJ/K}$$

4.6.4 Isothermal Mixing of Ideal Gases

Consider a mixture of two or more ideal gases at pressure P and temperature T. Let the mole fraction of the components in the mixture be represented by x_i. The entropy change resulting from the irreversible process of mixing of ideal gases in their pure state at temperature T and pressure P to form the mixture at the same temperature and pressure can be computed by the following equation, the proof of which is provided in Chapter 7 [see Eq. (7.122)].

$$\Delta S = -R \sum x_i \ln x_i \qquad (4.35)$$

Gibbs paradox. When two distinct intermingling ideal gases are mixed, the resulting entropy change is given by Eq. (4.35). For an equimolar mixture, the entropy change is,

$$\Delta S = -R\,(0.5 \ln 0.5 + 0.5 \ln 0.5) = -R \ln 0.5 = R \ln 2.0$$

This is true as long as the gases are different, no matter how nearly identical they are. But, when the gases are the same, the change in entropy on mixing should be zero. This curious result is known as the *Gibb's paradox*.

EXAMPLE **4.12** Assuming that air is a mixture of 21% oxygen and 79% nitrogen by volume, calculate entropy of 1 kmol air relative to pure oxygen and nitrogen, all at the same temperature and pressure.

Solution According to Eq. (4.35), entropy change accompanying the process of mixing pure oxygen and nitrogen to form 1 kmol air is

$$\Delta S = -8.314(0.21 \ln 0.21 + 0.79 \ln 0.79) = 4.27 \text{ kJ/kmol K}$$

This value represents entropy of 1 kmol air relative to pure components.

4.6.5 Chemical Reactions

The entropy changes accompanying chemical reactions are evaluated through the use of absolute entropies of the various components taking part in the reaction. Let S_P denote the sum of the entropies of the reactants and S_R denotes that of the products. Then the entropy change accompanying the reaction is given by

$$\Delta S = S_P - S_R \qquad (4.36)$$

EXAMPLE **4.13** Calculate the entropy change for the following gas phase reaction occurring at 1 bar and 298 K.

$$CO + \frac{1}{2} O_2 = CO_2;\ \Delta H = -2.8318 \times 10^5 \text{ J/mol}$$

The absolute entropies of CO, oxygen and CO_2 are respectively 198 J/mol K, 205.2 kJ/kmol K and 213.8 J/kmol K. Can you calculate the entropy change as the ratio of heat of reaction to the temperature of the reaction? Why?

Solution Refer Eq. (4.36). The reactants are CO and oxygen. The product is CO_2.

$$S_P = 213.8 \text{ J/K},\ S_R = 198 + 0.5 \times 205.2 = 300.6 \text{ J/K}$$

$$\Delta S = 213.8 - 300.6 = -86.8 \text{ J/K}$$

Since the reaction is highly irreversible, entropy change cannot be calculated as the ratio of heat of reaction to the temperature.

$$\Delta S \neq \left(\frac{\Delta H}{T} = \frac{-2.8318 \times 10^5}{298} = -950.27 \text{ J/K} \right)$$

The heat of reaction ($-\Delta H$) is the heat liberated when the reaction occurred irreversibly. If the reaction were carried out reversibly, for example, in an electrolytic cell with the generation of electric energy, the heat liberated would be ($-T\Delta S$). Therefore, the difference between these two represents the heat loss because of the irreversible nature of the process, or the heat that could have been utilised for the production of useful work like electrical energy. Thus the energy available for useful work is

$$2.8318 \square 10^5 - 298 \square 86.8 = 2.57314 \square 10^5 \text{ J}$$

4.7 CLAUSIUS INEQUALITY

The Carnot principle states that a reversible heat engine is more efficient than an irreversible engine. The efficiency of a reversible engine is given by Eq. (4.17)

$$\eta = 1 - \frac{T_2}{T_1} = \frac{T_1 - T_2}{T_1}$$

Now consider an irreversible engine operating between the same thermal reservoirs. Let dQ_1 be the heat absorbed and dQ_2 be the heat rejected by the engine. The efficiency of the engine is

$$\eta = \frac{dQ_1 - dQ_2}{dQ_1} = 1 - \frac{dQ_2}{dQ_1} \tag{4.37}$$

Then, by Carnot principle,

$$1 - \frac{dQ_2}{dQ_1} < 1 - \frac{T_2}{T_1} \tag{4.38}$$

which means

$$-\frac{dQ_2}{dQ_1} < -\frac{T_2}{T_1}$$

or

$$\frac{dQ_1}{T_1} - \frac{dQ_2}{T_2} < 0$$

Adopting the sign convention that the heat rejected dQ_2 is negative, the preceding relation gives

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} < 0 \tag{4.39}$$

An irreversible cyclic operation can be divided into a number of heat engine cycles involving infinitesimally small heat interactions, as we have done in Fig. 4.6 for the case of a reversible cyclic operation. For each such cycle, it is possible to write equations analogous to Eq. (4.39) so that the net result would be

$$\oint \frac{dQ}{T} < 0 \tag{4.40}$$

where T is the temperature of the thermal reservoir. Combining Eq. (4.23) for the reversible cyclic operation with Eq. (4.40) for the irreversible process, we get

$$\boxed{\oint \frac{dQ}{T} \le 0} \tag{4.41}$$

which is known as *Clausius inequality*. It states that *in a cyclic operation, the sum of the dQ/T terms around a complete cycle is less than or equal to zero depending on whether the process is irreversible or reversible.*

***EXAMPLE* 4.14** Using Clausius inequality show that the change in entropy in a process is related to the heat interaction as

$$dS \ge \frac{dQ}{T}$$

where the greater than sign refers to an irreversible process and equal to sign refers to a reversible process.

Solution Consider a reversible process between states *A* and *B* as illustrated in the *P-V* diagram (Fig. 4.7).

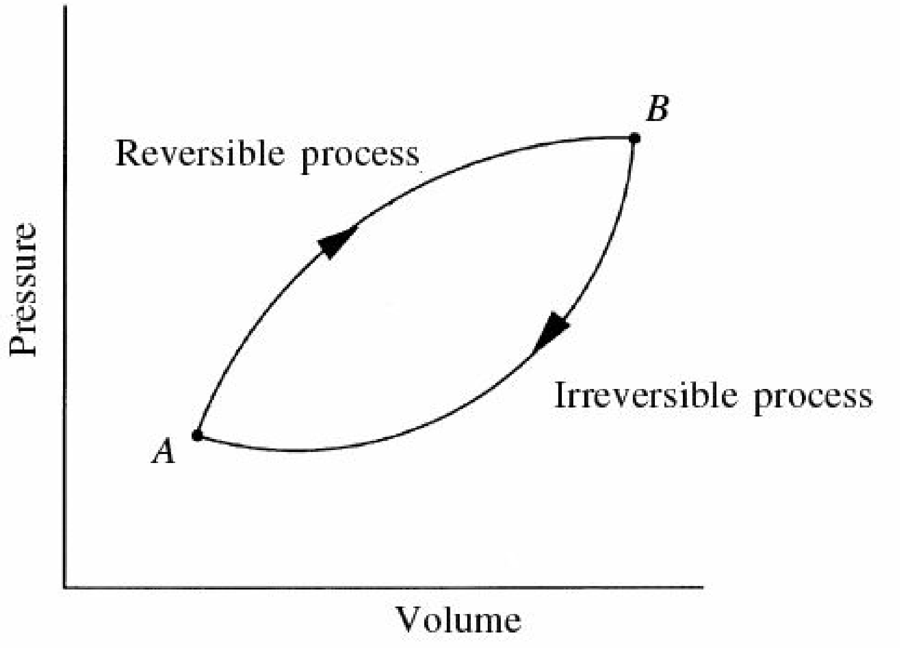


Fig. 4.7 *P-V* diagram for the process in Example 4.12.

For this process, the change in entropy by Eq. (4.1) is

$$\Delta S_{AB} = \int_{AB} \frac{dQ}{T} \tag{4.42}$$

where dQ is the heat change involved in this step. Assume that the system is brought back to the initial condition along an irreversible path *BA*. The system has undergone a complete cycle of operations. Entropy being a state property, net change in entropy is zero for the cycle. That is

$$\Delta S_{AB} + \Delta S_{BA} = 0$$

Since the cycle as a whole is irreversible, Eq. (4.41) gives

$$\int_{AB} \frac{dQ}{T} + \int_{BA} \frac{dQ}{T} < 0$$

Using Eq. (4.42) in the above inequality

$$\Delta S_{AB} + \int_{BA} \frac{dQ}{T} < 0$$

This inequality can be written in another form

$$-\Delta S_{BA} + \int_{BA} \frac{dQ}{T} < 0 \tag{4.43}$$

where ΔS_{BA} represents the entropy change along the reversible path from *B* to *A*. Equation (4.43) can be rewritten as

$$\Delta S_{BA} > \int_{BA} \frac{dQ}{T}$$

The entropy change for the processes occurring along a reversible path and an irreversible path between the same end states *A* and *B* should be the same. The left-hand side of the preceding equation therefore represents the entropy change along the irreversible path *BA* also, which, according to the equation is greater than the sum of the dQ/T terms along the path. However, the change in entropy along the reversible path can always be computed as equal to the sum of the dQ/T terms. In short,

$$\Delta S \geq \int \frac{dQ}{T}$$

We can put the above relation into the following general form for an infinitesimal change in the state of the system.

$$\boxed{dS \geq \frac{dQ}{T}} \tag{4.44}$$

The inequality in Eq. (4.44) refers to an irreversible process and the equality to a reversible process.

4.8 MATHEMATICAL STATEMENT OF THE SECOND LAW OF THERMODYNAMICS

Entropy is a property of the system that determines the direction of change. In this section, we show that all spontaneous processes are accompanied by an increase in the entropy, and for reversible processes, entropy doesn't change.

First, let us consider the entropy change in a closed adiabatic system. Referring to Fig. 4.8, the path *AB* may be treated as an irreversible adiabatic operation. That is, the curve *AB* is the pressure-volume relationship of a spontaneous process occurring in a closed system for which there is no net heat interaction.

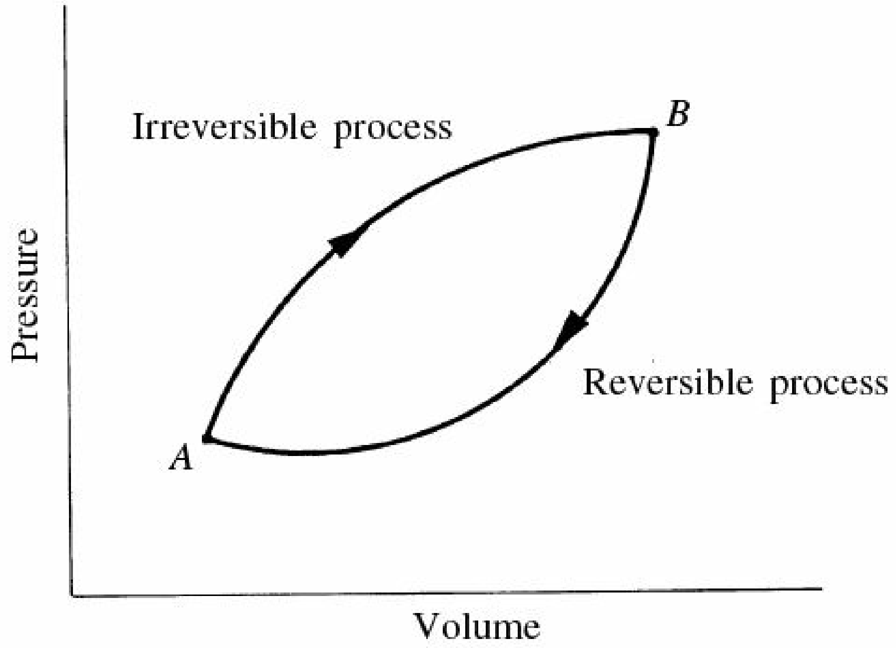


Fig. 4.8 All spontaneous processes result in increase of entropy.

The work associated with this process is W_{AB}. Let the system be brought back to the original condition along the reversible path *BA*. Let Q_{BA} and W_{BA} be the heat and work associated with this process. In the combination of these two processes the system has undergone a cycle of changes so that the overall energy and entropy changes must be zero. Since $\mathrm{D}U$ is zero, the first law of thermodynamics demands that the net heat interaction must be equal to the net work interaction. That is,

$$Q_{BA} = W_{AB} + W_{BA}$$

If Q_{BA} were positive, the above equation would mean that the system receives heat and converts it completely to work, which would be a violation of the second law of thermodynamics. The second law therefore requires that Q_{BA} be either negative or zero. Q_{BA} and the net work cannot be zero, as these would then correspond to a reversible cyclic process. But the cycle is irreversible. Therefore, Q_{BA} is negative and since the entropy change $\mathrm{D}S_{BA}$ for the reversible step can be calculated as the ratio of heat transferred to the temperature,

$$\mathrm{D}S_{BA} < 0$$

Or, the process *BA* is accompanied by a decrease in entropy. As the entropy change for the cycle as a whole is zero, the entropy change along path *AB* must be positive.

$$\Delta S_{AB} > 0 \qquad (4.45)$$

Thus, we see that a spontaneous process occurring in a closed adiabatic system is accompanied by an increase in entropy. For a reversible process occurring in a closed adiabatic system the entropy change must be zero, as there is no heat exchange. An isolated system is a closed adiabatic system. Therefore we can conclude that the entropy change of an isolated system in any process must be equal to or greater than zero.

$$\boxed{\Delta S \text{ (isolated system)} \geq 0} \qquad (4.46)$$

As pointed out in Chapter 1, the isolated system can be treated as one made up of the system and its surroundings. Therefore, Eq. (4.46) can be written as

$$(\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}} \geq 0 \qquad (4.47)$$

As a spontaneous process occurring in a closed adiabatic system is accompanied by an increase in entropy, for such a system it can be said that entropy is that property of the system that determines the direction of change. The processes for which entropy changes are positive are possible, and processes for which these are negative are impossible.

The validity of the above equations can be verified for a process in which an amount of heat Q is transferred from a heat source at temperature T_1 to a heat sink at T_2. The change in entropy of the heat source is $-Q/T_1$ and that of the heat sink is Q/T_2. The entropy change of the heat source and sink add up to give the following result.

$$(\Delta S)_{\text{total}} = -\frac{Q}{T_1} + \frac{Q}{T_2} = Q\,\frac{T_1 - T_2}{T_1 T_2} \qquad (4.48)$$

If the quantity Q is positive and if the transfer of heat is carried out irreversibly as is the case when there exists a finite difference in the temperatures of the source and the sink, $(\Delta S)_{\text{total}}$ would be positive. The process can be made reversible by lowering the temperature T_1 to a value only slightly greater than T_2. In this case, the $(\Delta S)_{\text{total}}$ approaches zero and for a true reversible process the value becomes equal to zero. Thus, we see that the Eq. (4.47) provides a general result of universal validity which can be restated as

$$\boxed{(\Delta S)_{\text{total}} \geq 0} \qquad (4.49)$$

Equations (4.46) and (4.49) are the *general mathematical statements of second law of thermodynamics*. These statements apply to the total change in entropy; in an irreversible process, a decrease in entropy may occur either in the system or in the surroundings. These statements require only that the sum of the entropy changes of the system and the surroundings together be positive in an irreversible process like the isothermal expansion of a gas. If the same expansion were carried out reversibly, the increase in the entropy of the gas will be compensated by a decrease in the entropy of the surroundings that results because of the withdrawal of heat. If this heat exchange also were accomplished reversibly, the net change in entropy would be zero. Equation (4.49) is also known as *the principle of increase in entropy*.

The principle of increase in entropy with reference to an isolated system means that the only processes that can occur in an isolated system are those that have an increase in entropy associated with them. The universe is a perfect example of an isolated system and all naturally occurring processes in the universe are accompanied by an increase in entropy and are irreversible. Hence we can say that the *entropy of the universe goes on increasing*. The statements for the first and second laws of thermodynamics can now be combined: *The energy of the universe is conserved whereas the entropy is increasing.*

***EXAMPLE* 4.15** One kilogram of superheated steam at 1.5 MPa and 523 K (H = 2923.5 kJ/kg S = 6.71 kJ/kg K) is contained in a piston-cylinder assembly. The unit is kept at ambient conditions of 300 K and the steam condenses to saturated liquid (H = 845 kJ/kg S = 2.32 kJ/kg K) at constant pressure. Calculate the change in entropy and check whether the process is reversible or not.

Solution The change in entropy of steam is the difference between the entropy of the condensate and entropy of superheated steam. That is,

Change in entropy of steam = 2.32 – 6.71 = – 4.39 kJ/kg K

At constant pressure, the change in enthalpy is equal to the heat supplied. Thus, the heat given out by steam during condensation,

$$Q = -\text{D}H = 2923.5 - 845 = 2078.5 \text{ kJ/kg}$$

Change in entropy of the surroundings is

$$\frac{Q}{T} = \frac{2078.5}{300} = 6.93 \text{ kJ/kg}$$

Therefore, $(\text{D}S)_{\text{total}}$ = 2.54 kJ/kg

Since $(\text{D}S)_{\text{total}}$ is positive, the process is irreversible.

***EXAMPLE* 4.16** Two compartments each of 1 m^3 capacity are connected by a valve and insulated from the surroundings and from each other. One compartment contains saturated steam at 683.6 kPa and the other contains steam at the same temperature but at a pressure of 101.3 kPa. The valve is opened and the pressure is allowed to equalise. Determine the change in entropy of the system consisting of the two vessels. Comment on the irreversibility of the process.

Solution From steam tables, the enthalpy, entropy, specific volume and internal energy of saturated steam at 683.6 kPa (T_S = 437.2 K) are 2761 kJ/kg, 6.7133 kJ/kg K, $278.9 \square 10^{-3}$ m^3/kg and 2570.4 kJ/kg respectively. For superheated steam at 101.3 kPa and 437.2 K, these values are 2804 kJ/kg 7.6712 kJ/kg K, 1976.2 m^3/kg and 2603.3 kJ/kg respectively.

Mass of saturated steam:

$$1.0/(278.9 \square 10^{-3}) = 3.5855 \text{ kg}$$

Mass of superheated steam:

$$1.0/(1976.2 \square 10^{-3}) = 0.5060 \text{ kg}$$

Mass of the system:

$$3.5855 + 0.5060 = 4.0915 \text{ kg}$$

Specific volume of the system:

$2.0/4.0915 = 0.4888\ m^3/kg$

Since no heat exchange and work interaction between the system and the surroundings occur during the mixing process, according to the first law of thermodynamics, the internal energy after mixing remains the same as that before mixing. The internal energy of saturated steam is

$2570.4 \square 3.5855 = 9216.2$ kJ

The internal energy of superheated steam is

$2603.3 \square 0.5060 = 1317.3$ kJ

Therefore, the specific internal energy of the system is

$(9216.2 + 1317.3)/4.0915 = 2574.5$ kJ/kg

The internal energy and specific volume of the system after mixing are now known. They are $U = 2574.5$ kJ/kg and $V = 0.4888\ m^3/kg$. These determine the state of the system. By interpolation of the data from steam tables we get the pressure = 400 kPa and temperature = 437 K and the specific entropy of the system = 6.9992 kJ/kg K.

Initial entropy = $(6.7133 \square 3.5855 + 7.6712 \square 0.5060) = 27.9522$ kJ/K

Final entropy = $6.9992 \square 4.0915 = 28.6372$ kJ/K

Change in entropy = 0.6850 kJ/K

As the surroundings are unaffected, the above value represents the total entropy change. Since it is positive, the process is irreversible.

***EXAMPLE* 4.17** Two perfectly insulated tanks each of capacity 1 m^3 are connected by means of a small pipeline fitted with a valve. The first tank contains an ideal gas at 300 K and 200 kPa and the second one is completely evacuated. The valve is opened and the pressure and temperature are equalised. Determine the change in total entropy.

Solution Using the ideal gas equation, the number of moles of the gas is determined.

$$\text{Quantity of gas} = \frac{PV}{RT} = \frac{200 \times 1}{8.314 \times 300} = 0.0802 \text{ kmol}$$

The system, which, in this case, is the gas contained in the vessels, exchanges no heat and work with the surroundings. By the first law DU = 0. The internal energy of an ideal gas depends only on temperature and therefore temperature after mixing is the same as that before mixing. Thus we have, Final conditions:

$T = 300$ K, $V = 2\ m^3$ and $P = 100$ kPa

Initial conditions:

$T = 300$ K, $V = 1\ m^3$ and $P = 200$ kPa

Equation (4.33) can be used to evaluate the entropy change.

D$S = R \ln \frac{2}{1} = 5.7628$ kJ/kmol K $= 0.0802 \square 5.7628 = 0.4622$ kJ/K

Entropy of the surroundings does not change. Hence, the change in total entropy = 0.4622 kJ/K.

***EXAMPLE* 4.18** Oil at 500 K is to be cooled at a rate of 5000 kg/h in a counter-current exchanger using cold water available at 295 K. A temperature approach of 10 K is to be main-tained at both ends of the exchanger. The specific heats of oil and water are respectively 3.2 and 4.2 kJ/kg K. Determine the total entropy change in the process.

Solution Assume that the oil is cooled to the minimum permissible temperature. Then the inlet and exit temperature of the oil are 500 K and 305 K. The inlet and exit temperature of the water are 295 K and 490 K. The mass flow rate *m* of water can be determined by an enthalpy balance.

$$m \times 4.2 \times (490 - 295) = 5000 \times 3.2 \times (500 - 305)$$

Solving this, we get $m = 3809.5$ kg/h. Entropy change of oil and water can be calculated by

$$\Delta S = mC_P \ln \frac{T_2}{T_1}$$

where T_2 and T_1 are the final and the initial temperature of the fluid, respectively.

$$(\Delta S)_{\text{oil}} = 5000 \times 3.2 \times \ln \frac{305}{500} = -\ 7908.7 \text{ kJ/K}$$

$$(\Delta S)_{\text{water}} = 3809.5 \times 4.2 \times \ln \frac{490}{295} = 8118.8 \text{ kJ/K}$$

$$\text{Total entropy change} = 8118.8 - 7908.7 = 210.1 \text{ kJ/K}$$

4.9 ENTROPY AND IRREVERSIBILITY

The total increase in entropy associated with an actual process is a measure of the loss in capacity of the system and surroundings as a whole to do work. In other words, the increase in entropy accompanying a spontaneous process is a measure of lost work.

Consider an irreversible process in which a quantity of heat Q is transferred from a source at a temperature T_1 to a sink at a lower temperature T_2. The change in total entropy in this process is given by Eq. (4.48).

$$(\Delta S)_{\text{total}} = -\frac{Q}{T_1} + \frac{Q}{T_2} = Q\,\frac{T_1 - T_2}{T_1 T_2}$$

Now consider a reversible heat engine operating between the same thermal reservoirs receiving the same quantity of heat Q. The efficiency of such an engine is given by Eq. (4.17)

$$\eta = \frac{T_1 - T_2}{T_1}$$

The work output of the engine can be calculated as the product of the efficiency and the heat input.

$$W = Q\,\frac{T_1 - T_2}{T_1} \tag{4.50}$$

This is the work which would have resulted had the heat transfer process been reversible, but which was lost because of the irreversible nature of the process. Equation (4.50) can be modified as

$$W = T_2 Q\,\frac{T_1 - T_2}{T_1 T_2} \tag{4.51}$$

Equation (4.51) can be combined with Eq. (4.48) to give

$$W_{\text{lost}} = T_2(\Delta S)_{\text{total}} \tag{4.52}$$

Equation (4.52) gives a physical meaning to the total entropy change in an irreversible process. The product of total entropy change and the temperature of the heat sink gives the quantity of heat that is wasted or degraded in an irreversible process. A reversible engine which receives heat Q_1 from the reservoir at temperature T_1 would perform some work rejecting a part of it, say Q_2, to a heat sink at temperature T_2. The heat rejected in the case of an irreversible engine which receives the same amount of heat would be greater by an amount equal to $T_2(\Delta S)_{\text{total}}$. Thus

$T_2(\Delta S)_{\text{total}}$ represents heat taken in at a higher temperature that would have been available for doing work had the process been reversible, but that was lost because of the irreversibility of the actual process.

Though Eq. (4.52) is developed for a heat transfer process, it can be shown that it is applicable to any process. We can generalise the equation into the following form

$$W_{\text{lost}} = T_0(\Delta S)_{\text{total}} \tag{4.53}$$

T_0 is the temperature of the surroundings. In practice, it is approximately equal to the temperature of the atmosphere. The lower the value of T_0, the lesser the work loss due to irreversibility of the process. But, the lowest practicable temperature is that of the atmosphere. To maintain the temperature of a heat sink below that of the atmosphere, work is needed, and this work would be more than that is gained by lowering T_0.

***EXAMPLE* 4.19** Evaluate the loss in capacity for doing work when the steel casting in Example 4.11 is quenched in oil.

Solution Refer Example 4.11. The change in entropy of the casting is

$$\Delta S_1 = -26.25 \text{ kJ/K}$$

The change in entropy of the oil is

$$DS_2 = 43.90 \text{ kJ/K}$$

The total entropy change is

$$(DS)_{\text{total}} = DS_1 + DS_2 = 17.65 \text{ kJ/K}$$

The loss in capacity for doing work is

$$T_0\, DS = 275 \,\square\, 17.65 = 4853.75 \text{ kJ}$$

This is the net work, which would have been accomplished if all the changes resulting from the process had been carried out reversibly.

EXAMPLE **4.20** Hydrocarbon oil is to be cooled from 425 K to 340 K at a rate of 5000 kg/h in a parallel flow heat exchanger. Cooling water at a rate of 10,000 kg/h at 295 K is available. The mean specific heats of the oil and water are respectively 2.5 kJ/kg K and 4.2 kJ/kg K.

(a) Determine the total change in entropy. Is the process reversible?

(b) If a reversible Carnot engine is to be operated receiving the heat from the oil and rejecting the heat to the surroundings at 295 K, how much work would be available?

Solution The exit temperature of water is obtained by an energy balance. Assuming no heat loss, the energy balance gives

$$5000 \,\square\, 2.5 \,\square\, (425 - 340) = 10000 \,\square\, 4.2 \,\square\, (T - 295)$$

where T is the exit temperature of cooling water. Solving this, we get $T = 320.3$ K.

(a) The change in entropy of oil:

$$5000 \times 2.5 \times \ln \frac{340}{425} = -2789.3 \text{ kJ/K}$$

Change in entropy of water:

$$10000 \times 4.2 \times \ln \frac{320.3}{295} = 3455.9 \text{ kJ/K}$$

Total entropy change is

$$(\Delta S)_{\text{oil}} + (\Delta S)_{\text{water}} = 3455.9 - 2789.3 = 666.6 \text{ kJ/K}$$

Since this is positive, the process is irreversible.

(b) The heat given out by the oil on cooling,

$$Q = 5000 \times 2.5 \times (425 - 340) = 1.0625 \times 10^6 \text{ kJ/h}$$

The heat rejected Q_2 to the surroundings at T_0 by the Carnot engine is given by

$$\frac{Q_2}{Q} = \frac{T_0}{T}$$

i.e.

$$Q_2 = T_0(Q/T) = -T_0\Delta S$$

where ΔS is the change in entropy of the oil. The work output of the engine would be

$$Q - Q_2 = 1.0625 \times 10^6 - 295 \times 2789.3 = 2.39657 \times 10^5 \text{ kJ}$$

4.10 STATISTICAL EXPLANATION FOR ENTROPY

To understand the physical meaning of entropy, the relationship between entropy and probability should be made clear. All spontaneous processes are in the direction of maximum probability and, as we have shown in the preceding sections, they are accompanied by an increase in entropy. For example, consider the spontaneous process of mixing of the two pure gases *A* and *B* in a container. The pure gases, which were initially separated by a membrane, are allowed to mix together. The most probable state in which the system exists is the 'mixed-up' state, and the chances for one part of the vessel being occupied by pure *A* and the other part by pure *B* are very remote. This concept may be illustrated by a large number of white and black balls shaken together in a box. The most probable average arrangement is a uniform distribution of black and white balls and a compartment of the box being occupied by balls of only one colour is hardly observed. We see that the most probable state in which a system can exist is that having the least orderly arrangement. That is, in the most probable state of the system the molecules are distributed with greatest randomness. The second law of thermodynamics in its most general form can be stated thus: *every system, which is left to itself, will, on the average, change towards a condition of maximum probability.*

All spontaneous processes occur in the direction from order to disorder and chaos, and an increase in entropy is associated with all these processes. Thus entropy may be looked upon as a measure of randomness which is a minimum in systems with an orderly arrangement. Consider, for example, the diffusion of one gas into another. The molecules of the gases, which were initially separated, have mixed in a random manner. The spontaneous conduction of heat along a metallic bar results in a random distribution of the kinetic energy of the molecules. The rejection of heat from a system though decreases the disorder of the molecules, an equivalent or greater amount of disorder results in the environment. It is therefore reasonable to postulate a relationship between the entropy of the system and the randomness or degree of disorder in the given state.

The concept of entropy as a measure of randomness is also helpful in predicting qualitatively whether a proposed process is accompanied by an increase or decrease in entropy, from a consideration of randomness or disorder in the initial and final states. Similarly, knowledge of the entropy change often provides information concerning structural changes accompanying a given process. To illustrate this, consider a substance undergoing a change of phase from solid to liquid. The process involves an increase in entropy as well as an increase of disorder. In general, the greater the increase of disorder accompanying a process, the greater is the increase in entropy.

Boltzmann (1896) put forward the statistical definition of entropy by the following relation.

$$S = k \ln \mathrm{W} \qquad (4.54)$$

In this equation, k is the Boltzmann constant and the quantity W is the number of different ways in which the energy of the system can be achieved by rearranging the atoms or molecules among their available states.

4.11 THIRD LAW OF THERMODYNAMICS

We have seen in the previous section that the more completely a system is shuffled the greater is its entropy. Entropy is a measure of the randomness of molecular arrangement of a system. An orderly or unmixed configuration results in low entropy. It is natural therefore, to expect a substance to have zero entropy when it reaches a state in which all randomness have disappeared. A perfect crystalline substance at the absolute zero of temperature would meet this requirement and should have zero entropy. Using the experimental data on the heat capacity of perfect crystalline substances at very low temperatures their entropy at 0 K was calculated and it was shown that they all have same entropy values at this temperature. These observations lead to the postulate of the third law of thermodynamics: *The absolute entropy is zero for a perfect crystalline substance at absolute zero of temperatures.*

In comparison with internal energy and enthalpy, which are calculated relative to an arbitrary reference state, entropy is a reference property and is absolute, as are pressure, volume and temperature. Third law of thermodynamics can be utilised to calculate the absolute entropy of substances at a given temperature by assigning the value zero for entropy of the crystalline form of the substance at absolute zero. This is done by measuring the heat capacity at different temperatures and the latent heats of phase transition that the substance must have undergone to arrive at the present state from the initial state of absolute zero of temperature. For example, let the melting point of the substance be T_f and the boiling point be T_b. The entropy at T, where T is above the boiling point may be evaluated as

$$S = \int_0^{T_f} \frac{C_{PS}\,dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{C_{PL}\,dT}{T} + \frac{\Delta H_V}{T_b} + \int_{T_b}^{T} \frac{C_{PG}\,dT}{T} \qquad (4.55)$$

where C_{PS}, C_{PL} and C_{PG} are the specific heats of solid, liquid and gas respectively, and DH_f and DH_V are the latent heats of fusion and vaporisation respectively. The main difficulty in using the above equation is with regards to the measurement of heat capacity at very low temperatures.

***EXAMPLE* 4.21** It is known that the molar heat capacity of a substance at low temperatures can be approximated by the relation $C_P = aT^3$, where a is a constant. Determine the molar entropy of a metal at 10 K if the molar heat capacity at this temperature is 0.45 J/mol K.

Solution The entropy of the solid at 10 K is evaluated using the first integral in Eq. (4.55)

$$S = \int_0^T C_P \frac{dT}{T} = \int_0^T aT^3 \frac{dT}{T} = \frac{1}{3} aT^3$$

At temperature T, $C_P = aT^3$. Therefore,

$$S = C_P/3 = 0.45/3 = 0.15 \text{ J/mol K}$$

***EXAMPLE* 4.22** Calculate the absolute entropy of water vapour at 473 K and 101.3 kPa above 273 K base temperature. Compare this with the value reported in steam tables (S = 7.829 kJ/kg K). The average heat capacity of water = 4.2 kJ/kg K and that of water vapour between 373 K and 473 K = 1.9 kJ/kg K. The latent heat of vaporisation at 373 K = 2257 kJ/kg.

Solution Equation (4.55) is reduced to the following form for the present purpose.

$$S = \int_{T_f}^{T_b} C_{PL} \frac{dT}{T} + \frac{\Delta H_V}{T_b} + \int_{T_b}^{T} C_{PG} \frac{dT}{T}$$

$$= \int_{273}^{373} 4.2 \frac{dT}{T} + \frac{2257}{373} + \int_{373}^{473} 1.9 \frac{dT}{T} = 4.2 \ln \frac{373}{273} + 6.051 + 1.9 \ln \frac{473}{373}$$

S = 7.813 kJ/kg K and it compares favourably with the value reported in the steam tables: S = 7.829 kJ/kg K.

SUMMARY

The first law of thermodynamics is concerned with the amount of energy in different forms that are involved in various spontaneous processes. But, it fails to explain the direction and extent of such processes. Though heat can be treated as a form of energy there is a marked qualitative difference between heat and other forms of energy. Because of these inadequacies of the first law in explaining the naturally occurring processes, the second law of thermodynamics was proposed, which can be stated in a number of ways. To give a mathematical expression for the second law, the concept of entropy was introduced. Entropy was shown to be a thermodynamic property of the system, which serves as a measure of the unavailability or the degradation of energy. An increase in the unavailability of the total energy of a system is quantitatively expressed by a corresponding increase in its entropy. It is defined by

$$dS = \frac{dQ_R}{T}$$

The Carnot principle and the concept of the thermodynamic temperature were explained in Section 4.4. The Carnot engine was shown to have the maximum efficiency among all engines operating between any two given temperature limits. This efficiency is a function of only the reservoir temperatures and is independent of the working fluid. This led to the relationship

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

which formed the basis of the thermodynamic temperature scale. The ideal gas temperature and the thermodynamic temperature were shown to be the same. In Section 4.6, methods for calculating the change in entropy for some typical processes were examined. The Clausius inequality states that in a cyclic operation, the sum of the dQ/T terms around the cycle is less than or equal to zero. The Clausius inequality lead to the following generalisation for any given process:

$$dS \geq \frac{dQ}{T}$$

The general mathematical statement (Section 4.8) of the second law is provided by

D*S* (isolated system) ≥ 0

This statement means that all naturally occurring processes in the universe are accompanied by an increase in entropy and all are irreversible. This increase in the entropy is a measure of the irreversibility (Section 4.9). The relationship between entropy and probability was highlighted in Section 4.10 by providing a statistical explanation for entropy. As a consequence of this direct link between entropy and 'disorder', a perfect crystalline substance may be thought of as having zero entropy at absolute zero of temperature. The third law of thermodynamics (Section 4.11) was shown to be nothing but a generalisation of this observation.

REVIEW QUESTIONS

1. What are the limitations of the first law of thermodynamics?

2. Give the Kelvin–Planck statement and the Clausius statement of the second law of thermodynamics and show that they are equivalent.

3. Establish with examples why the concept of entropy is essential to explain the direction of spontaneous processes.

4. How do you explain the qualitative difference between heat and other forms of energy?

5. "The addition of heat to a system at lower temperature results in greater degradation of energy than the addition to a higher temperature". Do you agree? Justify your answer.

6. Give the mathematical definition of entropy and explain the terms involved.

7. "Entropy of a rotating flywheel is the same as that of the flywheel at rest." Do you agree? Substantiate your answer.

8. What are Carnot propositions?

9. Prove that a Carnot engine has the maximum efficiency and that the efficiency is independent of the working fluid.

10. How does the concept of thermodynamic temperature follow from the Carnot principle?

11. Is it possible to obtain zero temperature on the absolute thermodynamic temperature scale? Why?

12. How would you prove that the thermodynamic temperature and ideal gas temperature are identical?

13. How is entropy change in an irreversible process determined?

14. What is the general equation for evaluating the change in entropy of an ideal gas which is undergoing a change of state?

15. What is the Gibb's paradox in relation to the entropy change in the isothermal mixing of ideal gases?

16. Can you determine the entropy change in a chemical reaction as the ratio of the heat of reaction to the temperature of the reaction? Why?

17. State and prove the Clausius inequality.

18. State mathematically the principle of the increase in entropy and hence show that "the entropy of the universe is increasing".

19. "The second law of thermodynamics is the law of conservation of total entropy for a reversible process". Do you agree?

20. How would the increase in entropy be used as a measure of the irreversibility of a process?

21. How is the entropy and probability interrelated?

22. "A knowledge of the entropy change provides information concerning the structural changes accompanying a process". Comment on this.

23. State the third law of thermodynamics. How does it follow from the statistical explanation for entropy?

EXERCISES

4.1 Calculate the minimum work required to produce 10 kg ice cubes from water initially at 273 K. Assume that the surroundings are at 300 K. The latent heat of fusion of water at 273 K = 333.5 kJ/kg.

4.2 A 800 MW thermal power plant uses steam at 600 K and discards heat to a river at 295 K. Determine the heat discarded to the river if the thermal efficiency of the plant is 70 per cent of the maximum possible value.

4.3 The overhead vapour from a distillation column is taken to a condenser where it is condensed by heat exchange with cooling water that enters at 300 K and leaves at 310 K. The vapour can be treated as pure water vapour at 101.3 kPa. Its flow rate is 5000 kg/h. It is condensed and subcooled to 345 K. If the condenser were replaced by a reversible engine calculate the following:

(a) The work output of the engine

(b) The per cent reduction in the cooling water circulation rate when the condenser is replaced with Carnot engine.

4.4 A reversible refrigerator absorbs heat from water at 273 K in order to produce ice at the same temperature and rejects heat to the surroundings at 300 K. The work requirement of the refrigerator is to be met by a reversible heat engine operating between a heat source at 425 K and surroundings at 300 K. For each kilo joule of heat received by the engine, calculate:

(a) The heat removed from water

(b) The heat rejected to the surroundings.

4.5 An inventor claims to have developed a heat pump with a COP of 6 which maintains the cold space at 250 K when operating in a surrounding temperature of 310 K. Would you agree with his claim?

4.6 An engine using hot spring water at 330 K as the heat source receives 420 kJ and is said to reject 335 kJ to melting ice at 273 K. Comment on the engine efficiency.

4.7 An inventor claims to have developed a refrigerating machine which maintains the refrigerated space at 267 K while operating in a room at 300 K. If the COP claimed is 8.5, how would you evaluate his claim?

4.8 One mole of an ideal gas is compressed isothermally at 400 K from an initial pressure of 1 bar to a final pressure of 10 bar. The work required for this irreversible process is 20 per cent more than that required for a reversible compression. The heat liberated during compression is absorbed by a heat reservoir at 300 K. Determine:

(a) The entropy change of the gas
(b) The entropy change of the reservoir
(c) The total entropy change.

4.9 Three moles hydrogen and 1 mol nitrogen, both at 10 bar and 373 K are separately admitted, mixed and then heated to 773 K in a heat exchanger with a corresponding increase in pressure. Calculate the entropy change in the process. Assume $C_V = 21$ J/mol K for the mixture.

4.10 Ten kilogram of water (the system) is heated from 290 K to 340 K under the following conditions:

(a) Using saturated steam at 10 bar
(b) Using saturated steam at 5 bar
(c) Using superheated steam at 5 bar and 513 K
(d) Using 10 kg water at 340 K in a counter-current exchanger.

Assume that the condensate is not subcooled. In each case calculate the entropy change of the system, the entropy change of the surroundings and the total entropy change and compare them.

4.11 An ideal gas at 300 K and 10 bar enters an apparatus, which is thermally and mechanically insulated from the surroundings. The gas leaves the apparatus in two streams in equal quantities. One stream is at 360 K and 1 bar and the other is at 240 K and 1 bar. The heat capacity of the gas is 30 kJ/kmol K. Determine the total entropy change. Is the process thermodynamically possible?

4.12 An ideal gas at 420 K and 5 bar enters a steady-flow system and leaves at 298 K and 1 bar. Heat is exchanged with the surroundings at 298 K. The mean specific heat of the gas is 30 kJ/kmol K. Assuming reversible operation, determine the work extracted from each kilo mole of gas flowing through the system.

4.13 Oil of specific heat 3.2 kJ/kg K is cooled from 495 K to 315 K at a rate of 5000 kg/h by exchanging heat with a large thermal reservoir at a constant temperature of 300 K. What is the lost work in the process?

4.14 It has been suggested that a building could be heated by a refrigeration engine operating in a Carnot cycle. The engine takes heat from the outside at 280 K and delivers heat to the building at 295 K. How much work would have to be done for every kilo joule heat delivered to the building?

4.15 An inventor claims to have developed an engine that produces 1200 kJ of work while receiving 1000 kJ of heat from a single heat reservoir. Such an engine would violate both the first and second laws of thermodynamics. Do you agree? Why?

4.16 Calculate the molal entropy of fusion and vaporisation of ethyl alcohol which melts at 158.8 K and boils at 351.5 K. The latent heat of fusion and vaporisation are 108 kJ/kg and 855 kJ/kg respectively.

4.17 Air at an initial condition of 1.4 bar, 295 K, and 0.3 m^3 is compressed to a pressure of 4.5 bar whereby its volume is reduced to 0.12 m^3. Calculate the change in the molal entropy of the gas in this process. Take the specific heat at constant volume of air to be 20.52 kJ/kmol K.

4.18 A block of copper at a temperature of 825 K and weighing 5 kg is dropped into 50 kg water at 300 K. If there are no heat losses what is the change in entropy of (a) copper, (b) water, and (c) copper and water both considered together? C_P of copper is 0.4 kJ/kg K and that of water is 4.2 kJ/kg K.

4.19 A refrigerator is to be used to maintain the temperature of certain storage space at 250 K. The compressor is rated at 250 W and the cooling duty is estimated to be 5 □ 10^4 kJ per day. Determine the fraction of the time the compressor runs if the refrigerator is used in

(a) a cold country where the ambient temperature is 290 K and

(b) a tropical country where the ambient temperature 310 K.

4.20 How much work must be done in order to cool the air in an otherwise empty room of dimensions 5.0 m □ 5.0 m □ 3.0 m from 303 K to 295 K when the ambient temperature is (a) 293 K (b) 303 K? Take specific heat of air to be 29 kJ/kmol K and density to be 1.2 kg/m^3.

4.21 Liquid helium is produced from its saturated vapour at 4.2 K. The latent heat of vaporisation of helium at this temperature is 83.3 kJ/kmol. Calculate the minimum work required to produce liquid helium if the ambient temperature is 305 K.

4.22 A heat engine absorbs 260 kJ of heat from a source at 325 K and yields a work output of 72 kJ rejecting 100 kJ of heat to a reservoir at 300 K and 88 kJ of heat to another reservoir at 275 K Does this engine violate the laws of thermodynamics?

4.23 The heat capacity of chloroform in the range 240 K to 330 K is given by

$$C_P = 91.47 + 7.5 \square 10^{-2}\, T$$

where C_P is in J/mol K and T in K. Calculate the change in molar entropy of chloroform when it is heated from 273 K to 300 K.

4.24 One kilogram of saturated liquid water at 100 kPa is mixed with 5 kg of superheated steam at 100 kPa and 573 K in an insulated container. Assuming that the pressure remains constant during mixing, calculate the entropy generation due to the mixing process.

4.25 In a heat exchanger, air is heated from 293 K to 353 K by means of a second air stream which enters the exchanger at 423 K. The molar flow rates of both the streams are equal and the specific heat of air is 29.3 kJ/kmol K.

(a) Calculate the entropy change of both the streams and the total entropy change.

(b) Repeat the above calculations if the cooler air temperature is raised to 393 K. Why could this be achieved only in a counter-current system?

4.26 A cylinder of free volume 0.283 m^3 is divided into two compartments by a piston. Initially the piston is at one end and the cylinder contains 1 kg steam at 423 K. Air from a supply main at 1400 kPa and 288 K is then admitted slowly via a throttle valve to the other side of the piston. Estimate the temperature of the air when pressure equilibrium is attained. Neglect any heat loss from the cylinder and assume no heat transfer across the piston. State clearly the assumptions made. $C_V = 21$ J/mol K for air.

4.27 One kilo mole of water is heated at the constant pressure of 1400 kPa from a temperature of 294 K to the boiling point and then completely vaporised at this pressure. What portion of the heat transferred is unavailable for transformation to work in a heat engine assuming that the temperature of the heat sink is 283 K? Boiling point of water at 1400 kPa = 468 K. Latent heat of vaporisation = 1960 kJ/kg.

4.28 What is the increase in unavailable energy for the conditions in Exercise 4.27, if the heat is transferred from a furnace at 1480 K?

4.29 Determine the entropy of the mixture of two ideal gases *A* and *B* in the proportion 1 : 2. If this mixture is expanded through a throttle from pressure 500 kPa to 100 kPa what is the entropy change of the universe?

4.30 Oil with a heat capacity of 3.2 kJ/kg K is to be cooled from 495 K to 315 K at a rate of 5000 kg/h. An unlimited supply of cooling water at a constant temperature of 303 K is available. Determine the lost work in the process and the thermodynamic efficiency of the process.

4.31 A hot hydrocarbon oil (C_P = 2.512 kJ/kg K) is cooled from 422 K to 339 K in a heat exchanger at the rate of 2500 kg/h. Cooling water at the rate of 5000 kg/h enters the exchanger at 294 K. Assume that there is no heat loss in the exchanger.

(a) What is the change in entropy of the oil?

(b) What is the total change in entropy?

(c) How much work could be obtained if the cooling of the oil were carried out by a reversible Carnot engine rejecting heat to a sink at 294 K?

4.32 (a) Nitrogen gas (C_P = 30 kJ/kmol K) at 1 bar and 300 K is to be compressed to 10 bar and 450 K at a rate of 5000 kg/h. Cooling water (C_P = 4.1868 kJ/kg K) enters the compressor at 300 K at the rate of 7500 kg/h and leaves at 320 K. Determine the power required by the compressor.

(b) For the same conditions of nitrogen as in the previous part, determine the minimum power required by the compressor. The rate of circulation and the inlet temperature of cooling water remain the same as above.

4.33 Calculate the change in entropy when one gram of ice at 273 K is converted into steam at 373 K. Latent heat of fusion of ice = 336 J/g, latent heat of vaporisation = 2268 J/g and the mean specific heat of water between 273 K and 373 K = 4.2 J/g K.

5

Some Applications of the Laws of Thermodynamics

Engineers would be able to devise methods for improving the efficiency of a process by proper application of laws of thermodynamics. This chapter deals with the thermodynamic analysis of some typical industrial processes using the first and the second laws of thermodynamics. The first section deals with the general energy balance equations and their application to some important fluid flow problems. Refrigeration and liquefaction processes are discussed next, with emphasis on the thermodynamic cycles rather than on the equipment used. In the last sections, the thermodynamic analysis of various power cycles that are commonly used in steam-power plants, internal combustion engines and gas turbines are discussed.

5.1 FLOW PROCESSES

Thermodynamics can be used to find solutions to many fluid flow problems. Some of the basic equations in fluid mechanics are developed using the first and second laws of thermodynamics. However, questions that are related to the mechanism of flow, such as the loss of heat due to friction are not within the scope of thermodynamics. In order to facilitate the application of thermodynamic principles to flow process, we assume that the flow is unidirectional and the fluid properties do not change in the direction perpendicular to the direction of flow. By the latter idealisation, we mean that the properties at any point in the flow system are average values applicable for the entire cross-section.

5.1.1 Continuity Equation

For a control volume (see Fig. 5.1), the law of conservation of mass may be written as:

$$\begin{array}{l}\text{Rate of accumulation of mass}\\ \text{within the control volume}\end{array} + \begin{array}{l}\text{Net rate of mass out}\\ \text{by the flowing streams}\end{array} = 0$$

Mathematically, the above relation can be represented as

$$\boxed{\frac{dm}{dt} + \Delta(\rho u A) = 0} \tag{5.1}$$

where r is the average fluid density, A is the fluid cross-sectional area and u is the average fluid velocity. Equation (5.1) is known as the continuity equation. For steady-state flow process, there is no accumulation of mass within the control volume, and the equation reduces to

$$\boxed{\Delta(\rho u A) = 0} \tag{5.2}$$

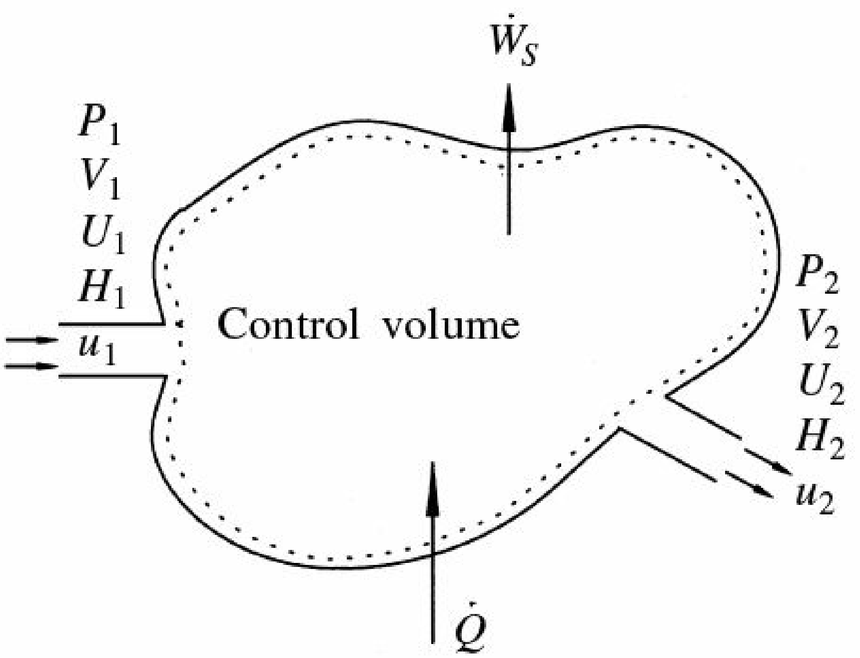


Fig. 5.1 Energy balance for a control volume.

Denoting the conditions at the entrance to the control volume by subscript 1 and the conditions at the exit by subscript 2, Eq. (5.2) may be re-written as

$$r_1 u_1 A_1 = r_2 u_2 A_2$$

5.1.2 Energy Equation

The law of conservation of energy for a control volume is given by

$$\begin{array}{c}\text{Rate of accumulation of energy}\\ \text{within the control volume}\end{array} + \begin{array}{c}\text{Net rate of energy out}\\ \text{by the flowing streams}\end{array} = \dot{Q} - \dot{W}$$

where $\dot{Q}$ and $\dot{W}$ are the rate at which heat is supplied to the fluid and the rate at which shaft work is done by the fluid respectively.

Rate of accumulation of energy is dU^t/dt, where U^t is the total internal energy within the control volume. The total energy of the fluid stream is the sum of its kinetic energy (*KE*), potential energy (*PE*), and internal energy (*IE*). The law of conservation of energy can now be expressed as

$$\frac{dU^t}{dt} + \Delta(KE) + \Delta(PE) + \Delta(IE) = \dot{Q} - \dot{W} \tag{5.3}$$

In Eq. (5.3), the symbol Δ represents the difference between exit and entrance streams.

$$\Delta\,(KE) + \Delta\,(PE) + \Delta\,(IE) = \Delta\left[\dot{m}\left(\frac{u^2}{2} + gZ + U\right)\right] \tag{5.4}$$

where $\dot{m}$ is the mass flow rate and Z is the height above a reference plane. The work rate $\dot{W}$ is made up of two parts—the shaft work $\dot{W}_S$ and the flow-work, the latter being the product of the pressure and the volume of the fluid. The flow work is equal to $\Delta[\dot{m}(PV)]$ and it is the net work done by the fluid in pushing it into and out of the control volume.

$$\dot{W} = \dot{W}_S + \Delta[\dot{m}(PV)] \tag{5.5}$$

Substituting Eqs. (5.4) and (5.5) in Eq. (5.3) and noting that $H = U + PV$, the energy equation becomes

$$\frac{dU^t}{dt} + \Delta\left[\dot{m}\left(\frac{u^2}{2} + gZ + H\right)\right] = \dot{Q} - \dot{W}_S \tag{5.6}$$

For steady-state flow process, there is no accumulation of energy within the control volume, and Eq. (5.6) reduces to

$$\Delta\left[\dot{m}\left(\frac{u^2}{2} + gZ + H\right)\right] = \dot{Q} - \dot{W}_S \tag{5.7}$$

For flow systems where the kinetic and potential energy changes are negligible, Eq. (5.7) can be further simplified to

$$\Delta \dot{m}H = \dot{Q} - \dot{W}_S \tag{5.8}$$

If the fluid enters and leaves the control volume in a single stream, the mass rate of flow remains the same at the entrance and exit. Then Eq. (5.7) becomes

$$\boxed{\Delta\left(\frac{u^2}{2} + gZ + H\right) = Q - W_S} \tag{5.9}$$

This equation is known as the *total energy balance*. For the case, where changes in kinetic and potential energies are negligible, Eq. (5.9) becomes

$$\Delta H = Q - W_S \tag{5.10}$$

In both Eqs. (5.9) and (5.10), $Q = (\dot{Q}/\dot{m})$ and $W_S = (\dot{W}_S/\dot{m})$.

The 'total energy balance' considers only the input and output from the system. For fluid mechanics calculations, it is customary to express this equation in the form of mechanical energy balance. The mechanical energy balance takes irreversible effects, such as, fluid friction also into account. Equation (5.9) may be put in the following form:

$$\frac{\Delta u^2}{2} + g\Delta Z + \Delta H = Q - W_S \tag{5.11}$$

From the definition of enthalpy of a fluid [see Eq. (2.9)], we get

$$dH = dU + PdV + VdP \tag{5.12}$$

Using the first law of thermodynamics [see Eq. (2.5)],

$$dU = dQ - dW \tag{5.13}$$

For a reversible process, the work done by the fluid is

$$dW = P\,dV$$

Substituting this into Eq. (5.13) and combining the resulting equation with Eq. (5.12), we get

$$dH = dQ + V\,dP \tag{5.14}$$

Integrate Eq. (5.14) between the entrance and exit of the control volume. Then,

$$\Delta H = Q + \int_{P_1}^{P_2} V\,dP \tag{5.15}$$

Using this relation, Eq. (5.11) can be modified to the following form:

$$-W_S = \frac{\Delta u^2}{2} + g\Delta Z + \int_{P_1}^{P_2} V\,dP \tag{5.16}$$

If the changes in kinetic and potential energies are negligible, the shaft work is given by

$$\boxed{W_S = -\int_{P_1}^{P_2} V\,dP} \tag{5.17}$$

The above equations are developed assuming reversible processes. On including the work lost due to the irreversibilities, Eq. (5.16) takes the following form:

$$\boxed{\frac{\Delta u^2}{2} + g\Delta Z + \int_{P_1}^{P_2} V\,dP + W_S + F = 0} \tag{5.18}$$

Here, F represents the lost work due to friction or mechanical energy dissipated to heat due to irreversibilities in the system. Equation (5.18) is known as the *mechanical energy balance*.

Bernoulli's equation. Bernoulli's equation is a special form of the mechanical energy balance applicable only to non-viscous incompressible fluids, which do not exchange shaft work with the surroundings. For non-viscous fluids, $F = 0$. The integral in Eq. (5.18) can be evaluated if the functional relationship between pressure and volume is known. For incompressible fluids, volume is independent of pressure, and hence

$$\int_{P_1}^{P_2} V\,dP = V\Delta P = \frac{\Delta P}{\rho} \tag{5.19}$$

where r is the density of the fluid. Since no shaft work is exchanged, $W_S = 0$. Using these simplifications, Eq. (5.18) can be written as

$$\frac{\Delta u^2}{2} + g\Delta Z + \frac{\Delta P}{\rho} = 0 \tag{5.20}$$

$$\boxed{\frac{u^2}{2} + gZ + \frac{P}{\rho} = \text{constant}} \tag{5.21}$$

Equation (5.21) is known as *Bernoulli's equation*.

***EXAMPLE*5.1** Water flowing upward through a vertical pipe enters a reducer with a velocity of 1 m/s. The diameters at the entrance and exit of the reducer are 0.2 m and 0.1 m respectively. If the pressure at the entrance to the section is 105 kPa, what is the pressure at the exit given that the entrance and exit are 5 m apart?

Solution The continuity equation is given as $r_1 u_1 A_1 = r_2 u_2 A_2$. Since, the density of water remains constant,

$$u_1 A_1 = u_2 A_2$$

where u_1 and A_1 are velocity and area of cross-section at entrance (section 1) and u_2 and A_2 are the corresponding values at exit (section 2).

$$\frac{\pi}{4}(0.2)^2 \times 1 = \frac{\pi}{4}(0.1)^2 \times u_2$$

Therefore, $u_2 = 4$ m/s.

Apply Bernoulli's equation [Eq. (5.20)] between sections 1 and 2. Then,

$$\frac{\Delta u^2}{2} + g\Delta Z + \frac{\Delta P}{\rho} = 0$$

$$\frac{4^2 - 1^2}{2} + 9.81 \times 5 + \frac{(P_2 - 105) \times 10^3}{1000} = 0$$

Thus, $P_2 = 48.45$ kPa.

***EXAMPLE* 5.2** A valve on a well-insulated steam pipe carrying saturated steam at 1000 kPa is found leaking. The temperature of the steam escaping from the leak is measured to be 398 K. Determine the quality of steam flowing through the pipe.

The following data are taken from the steam tables: Enthalpy of saturated vapour at 1000 kPa = 2778 kJ/kg; Enthalpy of saturated liquid at 1000 kPa = 763 kJ/kg; Enthalpy of superheated steam at 398 K and 101.3 kPa = 2726 kJ/kg.

Solution Assuming that the kinetic and potential energy changes are negligible, Eq. (5.10) may be used.

$$DH = Q - W_S$$

Let the section 1 be taken at a point in the pipe and x be the fraction of steam that is liquid. The enthalpy of steam at this section is equal to the sum of the enthalpies of x kg saturated liquid and $(1 - x)$ kg saturated vapour. That is,

$$H_1 = x(763) + (1 - x)2778$$

Let the section 2 be taken at a point in the steam issuing from the leak in the valve. The steam issues to the atmosphere where the pressure is 101.3 kPa and its temperature is 398 K. For superheated steam at this condition enthalpy is $H_2 = 2726$ kJ/kg.

Between sections 1 and 2 no work is done and no heat is exchanged. Therefore, Q and W_S are zero. Equation (5.10) reduces to

$$\Delta H = H_2 - H_1 = 0$$

$$2726 - x(763) - (1 - x)2778 = 0$$

Thus $x = 0.026$. That is, the steam contains 2.6% liquid.

***EXAMPLE*5.3** An evacuated tank is being filled by a gas from a constant pressure line through a valve. (a) Show that in the absence of heat transfer, the internal energy of the gas in the tank at the end of the process is equal to the enthalpy of the gas admitted. (b) Show that if the gas is assumed to be ideal gas, the final temperature attained by the contents of the tank is independent of the quantity of the gas admitted.

Solution (a) The energy equation for the control volume

$$\frac{dU^t}{dt} + \Delta\left[\dot{m}\left(\frac{u^2}{2} + gZ + H\right)\right] = \dot{Q} - \dot{W}_S \qquad \text{[refer to Eq. (5.6)]}$$

can be simplified to the following form neglecting the kinetic and potential energy changes.

$$\frac{dU^t}{dt} + \Delta[\dot{m}H] = \dot{Q} - \dot{W}_S$$

Knowing that $\dot{m} = \dfrac{dm}{dt}$, $\dot{Q} = \dfrac{dQ}{dt}$ and $\dot{W}_S = \dfrac{dW_S}{dt}$, the above equation can be multiplied by dt so that we get

$$dU^t + H\,dm = dQ - dW_S$$

Integration gives

$$\Delta U^t + \Delta(H\,m) = Q - W_S \tag{5.6a}$$

The first term on the left represents the change in the total internal energy within the control volume and the second term represents the net enthalpy transport by the flowing streams.

The increase in the total internal energy of the tank contents is

$$\Delta U^t = m_2U_2 - m_1U_1$$

$$\Delta[Hm] = H_em_e - H_im_i \qquad (5.6b)$$

where m_1 is the mass of gas initially present in the tank and m_2 is the mass after the tank is filled, m_i

is the mass of gas entering the control volume (inlet stream) and m_e is the mass of gas leaving the control volume (exit stream). Since initially the tank is evacuated, $m_1 = 0$.

$$m_2 = m_1 + (m_i - m_e)$$

Here $m_e = 0$; therefore, $m_2 = m_i$.

Substituting these in Eq. (5.6b), we get

$$\Delta U^t = m_2 U_2$$

$$\Delta[H\,m] = -\,H_i m_i$$

Substituting the above values into Eq. (5.6a) and noting that $Q = 0$, $W_s = 0$, we get

$$m_2 U_2 - m_i H_i = 0$$

$$U_2 = H_i \qquad (5.6c)$$

The internal energy of the gas in the tank is equal to the enthalpy of the gas entering the tank.

(b) If the gas is ideal, H_i in Eq. (5.6c) can be written as

$$H_i = U_i + P_i V_i = U_i + RT_i$$

where U_i is the internal energy of the gas admitted and T_i is its temperature. Equation (5.6c) now simplifies as

$$U_2 - U_i = RT_i \qquad (5.6d)$$

Assuming constant heat capacity C_V, the change in internal energy of the ideal gas is

$$U_2 - U_i = C_V (T_2 - T_i)$$

Substituting this in Eq. (5.6d), we get

$$C_V (T_2 - T_i) = RT_i$$

which can be rewritten as

$$T_2 - T_i = \frac{R}{C_V} T_i = \frac{C_P - C_V}{C_V} T_i = (\gamma - 1) T_i$$

or

$$T_2 = \gamma\, T_i$$

This means that when an evacuated tank is being filled by an ideal gas from a constant pressure line, the temperature attained by the gas in the tank is independent of the amount of gas admitted in the absence of heat transfer.

***EXAMPLE*5.4** A rigid, insulated tank that is initially evacuated is connected through a valve to a supply line that carries steam at 1.2 MPa and 673 K. Now the valve is opened, and steam is allowec to flow slowly into the tank until the pressure reaches 1.2 MPa, at which point the valve is closed. Determine the final temperature of the steam in the tank.

Solution Equation (5.6a) can be written as

$$m_2U_2 - m_1U_1 + H_em_e - H_im_i = Q - W_S$$

m_1 is the mass of steam initially present in the tank = 0.

m_e is the mass of steam leaving the control volume or mass of exit steam from the tank = 0.

m_2 is the final mass of steam present in the tank = mass of steam admitted = m_i.

Since no work is exchanged, and no heat is transferred, $Q = W_S = 0$.

Using these results, Eq. (5.6a) becomes

$$U_2 = H_i$$

U_2 is the internal energy of steam in the tank and H_i is the enthalpy of steam in the supply line, that is the enthalpy of superheated steam at 1.2 MPa and 673 K. From steam tables, the enthalpy of steam at 1.2 MPa and 673 K (= H_i) = 3260.7 kJ/kg.

Therefore, internal energy of steam in the tank = U_2 = 3260.7 kJ/kg. Since the pressure in the tank is to be 1.2 MPa, the condition of steam is (P = 1.2 MPa, U = 3260.7 kJ/kg). The temperature of steam satisfying these conditions is read from steam table. T = 853 K.

***EXAMPLE* 5.5** A rigid tank of volume 0.1 m^3 initially contains a refrigerant at 283 K. Sixty percent by mass of the refrigerant in the tank is vapour and the rest is liquid. The tank is connected through a valve to a pipeline which carries the same refrigerant at 403 K and 1 MPa. The valve is opened and the refrigerant is allowed to enter the tank till the pressure in the tank reaches 1.017 MPa at which the contents of the vessel is entirely saturated vapour. Now the valve is closed. Determine:

(a) The mass of refrigerant admitted

(b) The heat transferred

Data: Saturation pressure at 283 K = 415.8 kPa, saturation temperature at 1.017 MPa = 313 K Specific volumes of saturated liquid and vapour at 283 K are, respectively, $7.94 \square 10^{-4}$ m^3/kg, and $4.945 \square 10^{-2}$ m^3/kg, specific volume of saturated vapour at 313 K = 0.02 m^3/kg. Enthalpy of saturated liquid at 283 K = 213.58 kJ/kg, enthalpy of saturated vapour at 283 K = 404.23 kJ/kg enthalpy of saturated vapour at 313 K = 419.821 kJ/kg and enthalpy of superheated vapour at 403 K and 1 MPa = 514.69 kJ/kg.

Solution The energy balance for the system is

$$\text{D}U^t + \text{D}(H\,m) = Q - W_S$$

$$\text{D}U^t = m_2U_2 - m_1U_1$$

where U_1 and U_2 are the initial and final internal energies of the contents of the tank and m_1 and m_2 are the mass of the material in the tank before and after steam is allowed to enter the vessel.

$$\text{D}(H\,m) = m_eH_e - m_iH_i$$

where m_i and m_e are, respectively, the mass of material entering and leaving the control volume, and H_i and H_e are the enthalpies of the respective streams.

Q is the heat supplied and W_s is the work done. Since no work is done and no material is leaving the control volume, $W_S = 0$ and $m_e = 0$. Also,

$$m_2 = m_1 + m_i$$

The energy balance for the present case reduces to the following form:

$$m_2U_2 - m_1U_1 - m_iH_i = Q \qquad (5.6e)$$

(a) Mass of refrigerant initially present is m_1 kg. Sixty per cent by mass of the refrigerant initially present in the tank is saturated vapour and 40% is saturated liquid at the saturation temperature of 283 K. Specific volumes of saturated liquid and vapour at 283 K are, respectively, $7.94 \square 10^{-4}$ m^3/kg, and 4.945×10^{-2} m^3/kg. Since 0.4 m_1 kg liquid and 0.6 m_1 kg vapour together occupy a volume of 0.1 m^3,

$$0.4\, m_1 \square 7.94 \square 10^{-4} + 0.6\, m_1 \square 4.945 \square 10^{-2} = 0.1$$

or

$$m_1 = 3.3347 \text{ kg}$$

In the final state, m_2 kg of saturated vapour at 1.017 MPa occupies a volume of 0.1 m^3. Since the saturation temperature corresponding to 1.017 MPa is given to be 313 K, the final temperature of the refrigerant in the tank is 313 K. The specific volume of saturated vapour at 313 K is given to be 0.02 m^3/kg. Therefore,

$$m_2 \square 0.02 = 0.1$$

or

$$m_2 = 5.0 \text{ kg}$$

The mass of refrigerant admitted = $m_i = m_2 - m_1 = 5.0 - 3.3347 = 1.6653$ kg.

(b) The internal energy of the initial mass in the tank is $U_1 = 0.4 \square U_l + 0.6 \square U_v$, where U_l and U_v are the internal energies of saturated liquid and saturated vapour at 283 K. These can be calculated from the given enthalpy and specific volume using the relation $U = H - PV$. The saturation values at 283 K are:

$$U_l = 213.58 - 415.8 \square 7.94 \square 10^{-4} = 213.25 \text{ kJ/kg}$$

$$U_v = 404.23 - 415.8 \square 4.945 \square 10^{-2} = 383.67 \text{ kJ/kg}$$

Therefore,

$$U_1 = 0.4 \square U_l + 0.6 \square U_v = 0.4 \square 213.25 + 0.6 \square 383.67 = 315.50 \text{ kJ/kg}$$

Similarly, the internal energy of the final state can be evaluated as

$$U_2 = 419.821 - 1.017 \square 10^3 \square 0.02 = 399.48 \text{ kJ/kg}$$

H_i is the enthalpy of the refrigerant admitted into the tank. Since the refrigerant in the supply line is at 403 K and 1 MPa,

$$H_i = 514.69 \text{ kJ/kg}$$

Now the heat transferred is calculated.

$$Q = m_2U_2 - m_1U_1 - m_iH_i$$

$$Q = 5.0 \;\square\; 399.48 - 3.3347 \;\square\; 315.50 - 1.6653 \;\square\; 514.69 = 88.19 \text{ kJ}$$

***EXAMPLE* 5.6** An ideal gas (molecular weight = 29, g =1.4) is contained in a tank of volume 1 m^3 at 10 MPa and 400 K. The gas is discharged into the surrounding atmosphere by opening a valve. The valve is closed when the pressure inside the tank falls to 5 MPa. If the surrounding atmosphere is at 101.3 kPa, determine the temperature of the gas in the tank and the mass of gas discharged.

Solution Equation (5.6a) can be written as

$$m_2U_2 - m_1U_1 + H_em_e - H_im_i = Q - W_S$$

Here, $m_i = 0$, since no material is admitted into the control volume. $Q = 0$ and $W_S = 0$. Also $m_e = m_1 - m_2$. Therefore, Eq. (5.6a) reduces to

$$m_2U_2 - m_1U_1 + H_em_e = 0 \qquad (5.6f)$$

$$m_2U_2 - m_1U_1 + (m_1 - m_2)H_e = 0$$

$$m_1 = \frac{P_1V_1}{RT_1} = \frac{10000 \times 1}{400\,R} = \frac{25}{R}$$

$$m_2 = \frac{P_2V_2}{RT_2} = \frac{5000 \times 1}{RT_2}$$

where T_2 is the final temperature of the gas in the tank.

Using these values in Eq. (5.6f) and also noting that the internal energy and enthalpies of ideal gas are functions only of temperature, we get

$$m_2 C_V T_2 - m_1 C_V T_1 + (m_1 - m_2)\, C_P \frac{T_1 + T_2}{2}$$

$$\frac{5000}{RT_2} C_V T_2 - \frac{25}{R} C_V T_1 + \left(\frac{25}{R} - \frac{5000}{RT_2}\right) C_P \left(\frac{T_1 + T_2}{2}\right) = 0$$

Mutiplying all the terms in the above equation by R/C_V, we get

$$5000 - 25T_1 + \left(25 - \frac{5000}{T_2}\right)\gamma \left(\frac{T_1 + T_2}{2}\right) = 0$$

$$5000 - 25 \times 400 + \left(25 - \frac{5000}{T_2}\right) \times 1.4 \times \left(\frac{400 + T_2}{2}\right) = 0$$

This equation is solved for T_2. The final temperature of the gas in the tank, $T_2 = 328.9$ K.

Mass of gas discharged is $m_1 - m_2$

$$m_1 - m_2 = \frac{25}{R} - \frac{5000}{RT_2} = \frac{25}{8.314} - \frac{5000}{8.314 \times 328.9} = 1.1785 \text{ kmol}$$

Mass of gas discharged = 1.1785 × 29 = 34.18 kg.

5.1.3 Flow in Pipes

Pressure drop. The pressure drop accompanying the steady-state flow of a fluid through a straight pipe is evaluated from the mechanical energy balance [Eq. (5.18)] expressed in differential form:

$$u\,du + g\,dZ + V\,dP + dW_S + dF = 0 \qquad (5.22)$$

The friction term is usually expressed in terms of the flow geometry, dynamics of flow and a dimensionless friction factor f, known as the *Fanning friction factor.*

$$dF = \frac{2fu^2}{D}\,dL \qquad (5.23)$$

In Eq. (5.23), D and L are the length and diameter of the pipe respectively.

Maximum velocity. The maximum velocity attainable in pipe flow can be determined using thermodynamic principles. The total energy balance [Eq. (5.11)] may be put in differential form as follows:

$$\frac{du^2}{2} + g\,dZ + dH = dQ - dW_S$$

Assuming isentropic flow and neglecting potential energy changes, this equation can be simplified as

$$\frac{du^2}{2} + dH = 0$$

or

$$dH = -u\,du \tag{5.24}$$

For flow through closed conduits of uniform cross-section, the equation of continuity [Eq. (5.2)] may be put in differential form as $d(u\rho) = 0$, or

$$u\,d\rho + \rho\,du = 0 \qquad \text{and} \qquad du = -u\frac{d\rho}{\rho} \tag{5.25}$$

Substitute Eq. (5.25) into Eq. (5.24). The result is

$$dH = u^2\frac{d\rho}{\rho} \tag{5.26}$$

Noting that $dQ = T\,dS$ for a reversible process, Eq. (5.14) may be written as

$$dH = T\,dS + V\,dP \tag{5.27}$$

Compare Eq. (5.26) with Eq. (5.27).

$$T\,dS = u^2\frac{d\rho}{\rho} - V\,dP = u^2\frac{d\rho}{\rho} - \frac{dP}{\rho} \tag{5.28}$$

Equation (5.28) may be written in the following form:

$$\rho T\,dS = u^2\,d\rho - dP \tag{5.29}$$

For flow of gas through a pipe of uniform cross-section, since the flow is in the direction of decrease in pressure ($dP < 0$), the specific volume increases or density decreases (dr < 0) in the flow direction. The first term on the right is negative and the second term is positive. At a particular pressure, these two contributions to the entropy change will be equal in magnitude so that $dS = 0$. The maximum velocity is attained by the gas at this condition and it can be evaluated as:

$u_{\max}^2$ dr $- dP = 0$ for constant S

$$u_{\max}^2 = \left(\frac{\partial P}{\partial \rho}\right)_S \tag{5.30}$$

The speed of sound in a fluid is evaluated as the square root of the derivative on the right-hand side of Eq. (5.30). Therefore, , where c is the sonic velocity. Thus, we see that the maximum fluid velocity attained in a pipe of uniform cross-section is equal to the speed of sound in the fluid.

5.1.4 Flow through Nozzles

A *nozzle* is a device for converting thermal or mechanical energy into kinetic energy. This is achieved by changing the cross-sectional area available for flow. Nozzles find application in turbines, ejectors, diffusers, etc. In the analysis of flow through nozzles presented below, it is assumed that the flow is isentropic.

Relation between A and u. Let us first see the relationship between cross-sectional area and velocity of the fluid through a pipe of varying cross-section. Equation (5.2), the equation of continuity, expressed in differential form is given below:

$$d(u\rho A) = 0$$

This equation may be put into the following form:

$$(\rho A)\, du + u\, d(\rho A) = 0$$

or

$$du = -\frac{u}{\rho A}\, d(\rho A) \tag{5.31}$$

The mechanical energy balance [Eq. (5.18)] may be put in differential form as given below:

$$u\, du + g\, dZ + V\, dP + dW_S + dF = 0$$

For frictionless flow ($dF = 0$) with no work exchange ($dW_S = 0$), and neglecting change in potential energy ($dZ = 0$), the above equation gives

$$u\, du + V\, dP = 0$$

Noting that $V = 1/\rho$, the above equation may be written as

$$dP = -\rho u\, du \tag{5.32}$$

Combining Eqs. (5.31) and (5.32) we get the following results:

$$dP = \frac{u^2}{A}\, d(\rho A) = \frac{u^2}{A}\, (\rho\, dA + A\, d\rho)$$

$$\frac{dP}{d\rho} = \frac{\rho u^2}{A}\left(\frac{dA}{d\rho}\right) + u^2 \tag{5.33}$$

Because of our assumption of isentropic flow, $(dP/d\rho)$ in the above equation may be replaced by $(\partial P/\partial \rho)_S$ which was shown to be equal to c^2, where c is the sonic velocity. Also, $d\rho$ can be replaced by dP/c^2. The resulting equation can be rearranged as

$$\frac{dA}{A} = \frac{dP}{\rho u^2}\left(1 - \frac{u^2}{c^2}\right) \tag{5.34}$$

The ratio of actual velocity to the speed of sound is known as the *Mach number* and is denoted by **M**. Equation (5.34) may now be written as

$$\frac{dA}{dP} = \frac{A}{\rho u^2}(1 - \mathbf{M}^2) \tag{5.35}$$

Using Eq. (5.32), ***dP*** may be eliminated from the above equation.

$$\boxed{\frac{dA}{du} = \frac{A}{u}(\mathbf{M}^2 - 1)} \tag{5.36}$$

For subsonic velocity of the gas $\mathbf{M} < 1$ and $(dA/du) < 0$. For supersonic velocity, $\mathbf{M} > 1$ and $(dA/du) > 0$. For sonic velocity, $\mathbf{M} = 1$ and $(dA/du) = 0$. Equation (5.36), therefore, means that if the gas is to be accelerated continuously from subsonic to supersonic velocity, the area of cross- section for flow should first decrease ($dA < 0$), then remain constant ($dA = 0$), and finally increase ($dA > 0$). This principle is used for increasing the velocity of gases beyond Mach number unity in the converging–diverging nozzles (Fig. 5.2).

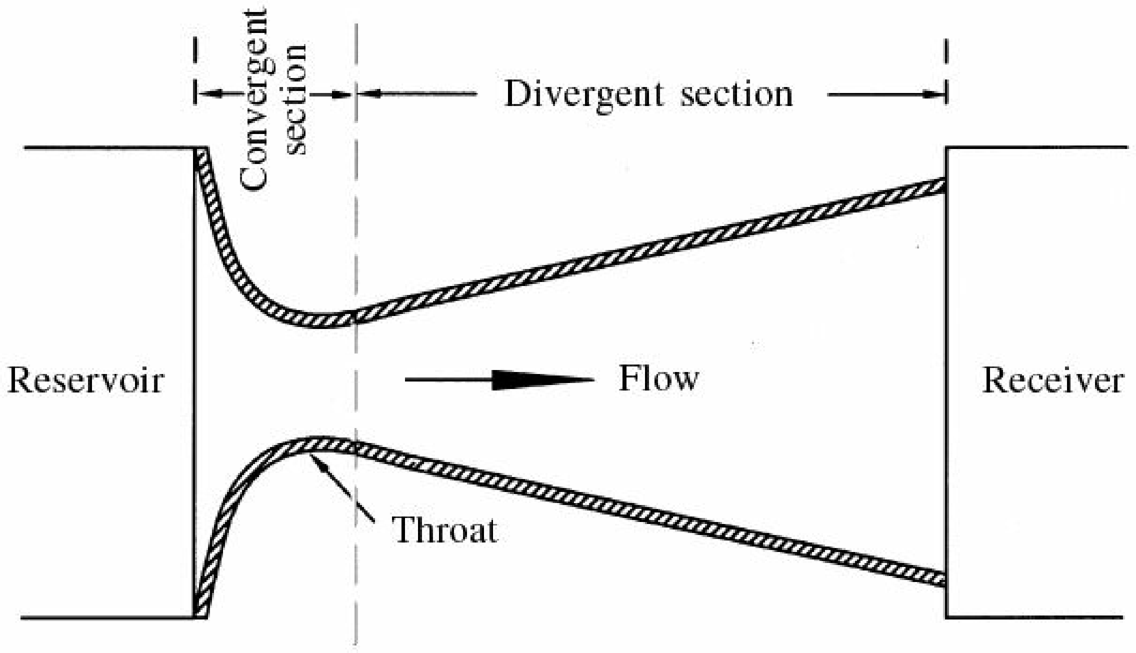


Fig. 5.2 The convergent-divergent nozzle.

Velocity at the throat. It is clear that the maximum velocity attained by the gas in the converging section of the converging-diverging nozzle is the sonic velocity. Therefore, referring to Eq. (5.30), we see that the *velocity at the throat* is given by

$$u_{\text{throat}}^2 = \left(\frac{\partial P}{\partial \rho}\right)_S \tag{5.37}$$

Critical pressure ratio. The relationship between pressure and velocity in a nozzle is given by Eq. (5.32), which may be put in the following form:

$$d\frac{u^2}{2} = -\frac{dP}{\rho} = -V\,dP \tag{5.38}$$

At the inlet to the nozzle, let $u = 0$ and $P = P_0$, and at any plane normal to the flow within the nozzle, let the velocity and pressure be u and P respectively. Assuming isentropic flow of ideal gases, the pressure and volume are related as PV^γ = constant. Substituting this in Eq. (5.38) and integrating, we get

$$u^2 = \frac{2\gamma P_0 V_0}{\gamma - 1}\left[1 - \left(\frac{P}{P_0}\right)^{(\gamma-1)/\gamma}\right] \tag{5.39}$$

The subscript ‘0’ in the above equation denotes the condition at the inlet to the nozzle. Since $PV^\gamma = P/\rho^\gamma$ = constant for isentropic expansion of ideal gases,

$$\left(\frac{\partial P}{\partial \rho}\right)_S = \gamma\frac{P}{\rho} = \gamma PV \tag{5.40}$$

Comparing this with Eq. (5.37), we obtain

$$u_{\text{throat}}^2 = \gamma PV \tag{5.41}$$

Suppose that the nozzle is connected between a reservoir at pressure P_0 and a receiver at pressure P_r. Flow through the nozzle occurs when P_r is less than P_0 and the velocity of the fluid at the throat is maximum. On further reduction of the receiver pressure, the flow rate and the velocity through the nozzle increases. A limiting value is attained when the velocity at the throat becomes sonic. The pressure at the throat at this condition is P_C, the critical pressure. The critical pressure ratio P_C/P_0, is the pressure ratio P/P_0 at which the velocity of the fluid at the throat becomes the sonic velocity. Substituting $u = u_{\text{throat}}$ in Eq. (5.39) and using Eq. (5.41), we get:

$$\boxed{\frac{P_C}{P_0} = \left(\frac{2}{\gamma + 1}\right)^{\gamma/(\gamma-1)}} \tag{5.42}$$

where the ratio P_C/P_0 is the *critical pressure ratio*. This depends only on g, the ratio of specific heats. Reduction of the receiver pressure below that corresponding to the critical condition, the throat will not affect the flow rate through the nozzle.

The maximum velocity attainable in a converging nozzle is the velocity of sound and it is attained when the pressure ratio reaches the critical value. Therefore, a converging nozzle can discharge a fluid at constant flow rate to a region of variable pressure, independent of the down stream pressure. The pressure ratio, provided it is less than the critical value, will not affect the flow rate through the nozzle. In a converging-diverging nozzle, if the sonic velocity is not attained in the throat because of insufficient pressure drop, the diverging section acts as a diffuser, which increases the pressure and reduces the velocity. Therefore, the purpose of the divergent section is to reduce velocity and regain pressure if the flow is subsonic, and increase velocity and obtain Mach numbers greater than unity if flow is supersonic.

***EXAMPLE* 5.7** Steam at 600 kPa and 573 K (H = 3062 kJ/kg) enters a nozzle at a rate of 10 kg/s and discharges it at 100 kPa and 473 K (H = 2875 kJ/kg). Heat loss to the surroundings is estimated to be 100 kW. Assuming that the inlet velocity of steam is negligible, determine the discharge velocity.

Solution The total energy balance [Eq. (5.9)] is used for solving this problem.

$$\Delta\left(\frac{1}{2}u^2 + gZ + H\right) = Q - W_S$$

Neglecting change in potential energy and putting $W_S = 0$, the equation reduces to

$$\Delta\left(\frac{1}{2}u^2 + H\right) = Q$$

$$Q = -100 \text{ kJ/s} = -100/10 = -10 \text{ kJ/kg of steam}$$

$$\Delta H = 2875 - 3062 = -187 \text{ kJ/kg}$$

Therefore,

$$\frac{\Delta u^2}{2} = -10 + 187 = 177 \text{ kJ/kg} = 177000 \text{ J/kg}$$

$$\frac{u_2^2}{2} - \frac{u_1^2}{2} = 177000$$

But, $u_1 = 0$. Thus, $u_2 = 595$ m/s.

***EXAMPLE* 5.8** Air at 600 K and 2000 kPa enters a convergent-divergent nozzle whose throat area is one-half that of the discharge of the divergent section. Assuming g = 1.4 for air, determine the following:

(a) The pressure, temperature, velocity, and density at the throat when the Mach number is 0.8 at the throat.

(b) The critical pressure corresponding to the reservoir condition.

Solution (a) Mach number **M** is given as $\mathbf{M}^2 = u^2/c^2$. Thus, $u^2 = c^2\mathbf{M}^2$, and using Eq. (5.40),

$$u^2 = \mathbf{M}^2 \text{g} PV$$

Substituting this in Eq. (5.39) and rearranging, we get

$$\mathbf{M}^2 = \frac{2}{\gamma - 1}\left[\left(\frac{P_0}{P}\right)^{(\gamma-1)/\gamma} - 1\right]$$

The pressure ratio is obtained by writing the above equation in the following form:

$$\frac{P}{P_0} = \frac{1}{\left(1 + \frac{\gamma - 1}{2}\mathbf{M}^2\right)^{\gamma/(\gamma-1)}}$$

For $\mathbf{M} = 0.8$ and $P_0 = 2000$ kPa, the pressure at the throat is

$$P = \frac{2000}{\left(1 + 0.2 \times 0.8^2\right)^{1.4/0.4}} = 1312 \text{ kPa}$$

The velocity at the throat may be evaluated using Eq. (5.39):

$$u^2 = \frac{2\gamma P_0 V_0}{\gamma - 1}\left[1 - \left(\frac{P}{P_0}\right)^{(\gamma-1)/\gamma}\right]$$

where

$$P/P_0 = 1312/2000 = 0.656$$

$$P_0 V_0 = RT_0/M = 8314(600)/29 = 172014 \text{ m}^2/\text{s}^2$$

where M is the molecular weight of air. Substituting these in Eq. (5.39),

$u = 369.7$ m/s

Equation (3.23) relates the temperature and the pressure in an adiabatic process.

$$\frac{T}{T_0} = \left(\frac{P}{P_0}\right)^{(\gamma-1)/\gamma}$$

Temperature at the throat:

$$T = 600(0.656)^{0.4/1.4} = 532 \text{ K}$$

Since $PV^\gamma = P/\rho^\gamma$ = constant, we can write

$$\frac{P}{P_0} = \left(\frac{\rho}{\rho_0}\right)^{\gamma}$$

where ρ is the density at a point where the pressure is P and ρ_0 is the density at the inlet to the nozzle. Therefore,

$$\rho = \rho_0 \left(\frac{P}{P_0}\right)^{1/\gamma}$$

$$\rho_0 = \frac{1}{V_0} = \frac{P_0 M}{RT_0} = \frac{2000 \times 29}{8.314 \times 600} = 11.627 \text{ kg/m}^3$$

Using the preceding equation for ρ, the density at the throat is

$$\rho = 11.627(0.656)^{1/1.4} = 8.604 \text{ kg/m}^3$$

(b) Using Eq. (5.42), the critical pressure is evaluated as

$$\frac{P_C}{P_0} = \left(\frac{2}{\gamma + 1}\right)^{\gamma/(\gamma-1)}$$

$$P_C = 2000(2/2.4)^{1.4/0.4} = 1056.6 \text{ kPa}$$

5.1.5 Ejectors

Ejectors or *jet pumps* are devices which employ the momentum and kinetic energy of a high velocity stream to entrain and compress a second gas or vapour stream. Steam-jet ejectors are used for pumping large volumes of vapour and gas at low pressures. See Fig. 5.3.

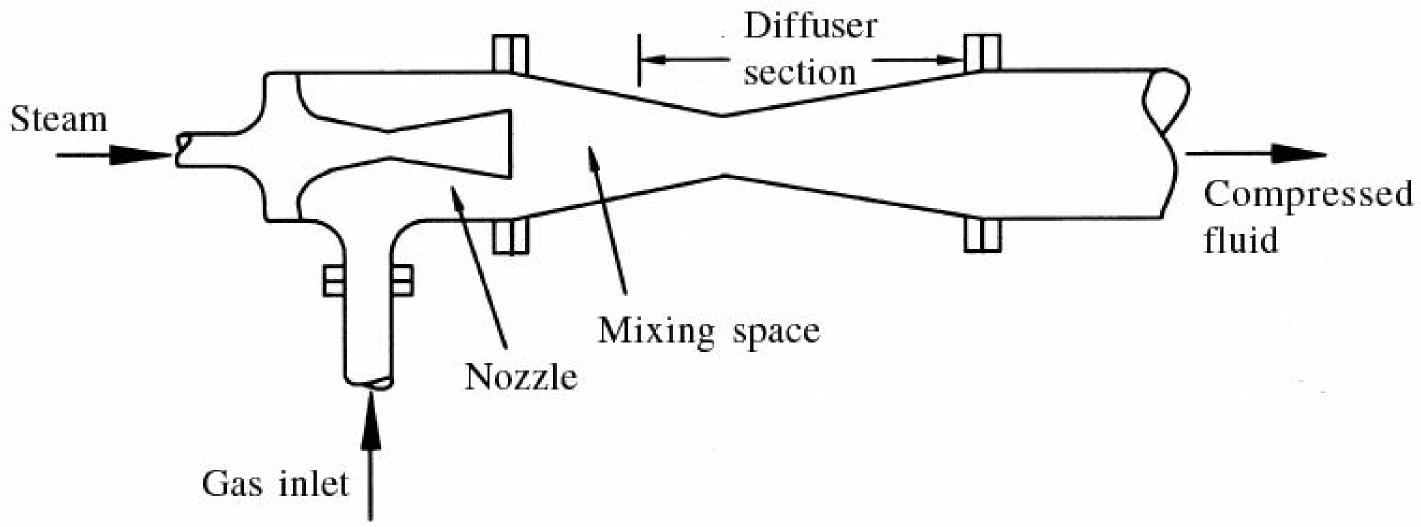


Fig. 5.3 Steam-jet ejector.

An ejector consists of the following parts:

1. A nozzle for accelerating the primary fluid
2. A fluid suction for accelerating the secondary fluid before its entrainment
3. A mixing section, where the secondary fluid is further accelerated and primary fluid is decelerated
4. A diffuser section for decelerating the combined stream of primary and secondary fluids with consequent increase in pressure.

Steam (primary fluid) is first expanded by passing through a nozzle, where it attains supersonic velocity. Due to the high velocity of the steam entering the mixing space, a low-pressure region is created there and as a result the steam transfers some of its momentum to the gas or vapour (secondary fluid) entering through the gas inlet. In the diffuser section, the mixed stream is decelerated and it gets compressed, the work of compression being derived at the expense of its kinetic energy. The compressed gas leaving the ejector is discharged directly to atmosphere or it can be sent to a water-cooled condenser. The latter option is employed in multi-stage ejectors to reduce the quantity of steam handled in the successive stages.

An exhaustive thermodynamic analysis of the ejector performance requires application of the equations of continuity, momentum, and energy to various component parts. The overall efficiency of an ejector is the ratio of work of isentropic compression of the secondary fluid from the suction to the discharge pressure, divided by the work of isentropic expansion of the primary fluid from its initial to the discharge pressure.

5.1.6 Throttling Process (Joule–Thomson Expansion)

Throttling process, also known as *Joule–Thomson expansion*, is a steady-state steady-flow process across a restriction, which results in a reduction in pressure for the fluid. The flow through a partially opened valve or a porous plug is a typical example of throttling process. The throttling process may be treated as an adiabatic operation, because the expansion takes place in a very short time within a very small region, so that the heat exchange between the system and the surroundings is negligible. As no mechanisms are present for extracting work, the process is a highly irreversible one.

Since the kinetic and potential energy changes are negligible, we can use Eq. (5.10) to describe the throttling process. Since $dQ = 0$ and $dW_S = 0$, this equation reduces to $dH = 0$. That is, Joule–Thomson expansion is an isenthalpic process. The temperature of the gas changes as a result of this expansion. The change in temperature resulting from the throttling operation is known as the Joule–Thomson coefficient μ, which is defined as

$$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H} \tag{5.43}$$

During expansion ΔP is negative. Therefore, a positive value of Joule–Thomson coefficient means that ΔT is negative and the gas cools on throttling. On the other hand, a negative Joule–Thomson coefficient means that throttling results in an increase in temperature. Joule–Thomson coefficient of a gas can be determined using the pressure-volume-temperature relationship. This is discussed in detail in the next chapter [see Eq. (6.70)]. It is sufficient here to note that, at any given pressure, the Joule–Thomson coefficient is positive only within a temperature range, that is between the upper and lower *inversion temperatures*. Only within these temperatures a gas cools on throttling. For a perfect gas, enthalpy being a function of temperature alone, throttling, which is essentially a constant enthalpy process, produces no temperature change. That is, the Joule–Thomson coefficient of ideal gas is zero. This is true for any gas whose volume varies linearly with temperature at a given pressure (see Exercise 6.30). For real gases, however, above a certain pressure the throttling process always results in cooling. For nitrogen, this pressure is found to be about 375 bar.

Joule–Thomson liquefaction process is explained in Section 5.3.2.

5.1.7 Compressors

Compressors may be of reciprocating type or turbo type. The *reciprocating type* compressors are used for developing high pressure-ratios, whereas *turbo type* compressors are preferred for high volumetric rate. The general energy equations are applicable for both types.

Adiabatic compression. For *adiabatic compression* of gases under negligible changes in kinetic and potential energies, Eq. (5.9) reduces to

$$W_S = -\Delta H$$

The minimum shaft work required for compressing a gas adiabatically from a given initial state to a given discharge pressure is the isentropic work which is given as

$$\boxed{W_S \text{ (isentropic)} = -\Delta H_S} \tag{5.44}$$

where ΔH_S is the enthalpy change accompanying the isentropic compression. The ratio of this isentropic work to the actual work required for compression is the compressor efficiency.

$$\eta = \frac{W_S \text{ (isentropic)}}{W_S \text{ (actual)}} \tag{5.45}$$

Equation (5.17) can also be used to evaluate the shaft work required for developing a given pressure ratio in a reversible operation.

$$W_S = -\int_{P_1}^{P_2} V\,dP \tag{5.17}$$

For an ideal gas undergoing isentropic compression, using the relation PV^γ = constant [see Eq. (3.24)], Eq. (5.17) can be readily integrated.

$$PV^\gamma = \text{constant} = P_1 V_1^\gamma$$

$$V = V_1 \left(\frac{P_1}{P} \right)^{1/\gamma}$$

Using this relation, V in Eq. (5.17) may be replaced and the resulting equation is integrated.

$$\boxed{W_S = \frac{\gamma}{\gamma - 1} P_1 V_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma - 1)/\gamma} \right] = \frac{\gamma}{\gamma - 1} RT_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma - 1)/\gamma} \right]} \tag{5.46}$$

The work required for compressing an ideal gas may be written in terms of the initial and final temperatures as well. For an ideal gas, $\Delta H = C_P \Delta T$. Equation (5.44) gives

$$W_S = -\Delta H = C_P(T_1 - T_2) \tag{5.47}$$

The work computed by Eq. (5.46) or by Eq. (5.47) provides the value for the numerator in Eq. (5.45).

Isothermal compression. For reversible isothermal compression of a gas, Eq. (5.10) becomes

$$W_S = Q - \Delta H$$

Since $Q = T\Delta S$ under this condition, we have

$$W_S = T\Delta S - \Delta H \tag{5.48}$$

If the gas is ideal $\Delta H = 0$, because, the enthalpy of ideal gas depends only on temperature. Also,

$$\Delta S = R \ln \frac{P_1}{P_2}$$

For ideal gases, Eq. (5.48) therefore simplifies to

$$\boxed{W_S = RT \ln \frac{P_1}{P_2} = RT \ln \frac{V_2}{V_1}} \tag{5.49}$$

Equation (5.49) gives the shaft work required in isothermal compression of ideal gases. The same result is obtained from Eq. (5.17) also by replacing V by RT/P.

Multi-stage compression. The reversible isothermal and adiabatic paths for the compression of an ideal gas from an initial pressure P_1 to a final pressure P_2 is shown in Fig. 5.4.

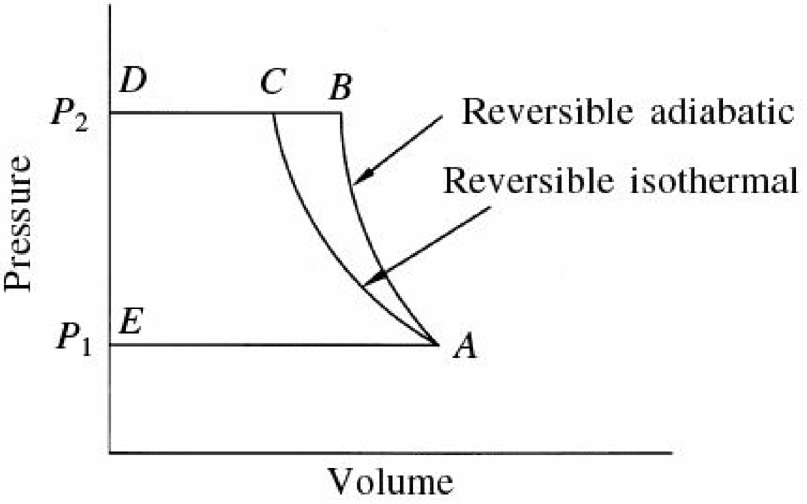


Fig. 5.4 Adiabatic and isothermal compression on a *P-V* diagram.

The area bounded by the curves, the pressure axis, and the horizontal lines drawn at $P = P_1$ and $P = P_2$ gives the integral $\int V\,dP$ evaluated between limits P_1 and P_2, which, by Eq. (5.17), is the shaft work required. From Fig. 5.4, it is evident that compression along the isothermal path requires less work compared to the adiabatic path. The actual compression takes place along a path intermediate to these two limiting paths. However, the isothermal path can be approached in practice by compressing the gas in stages with inter-stage cooling at constant pressure. In Fig. 5.5, it is shown that the compression of gas from pressure P_1 to pressure P_2 achieved in three adiabatic steps.

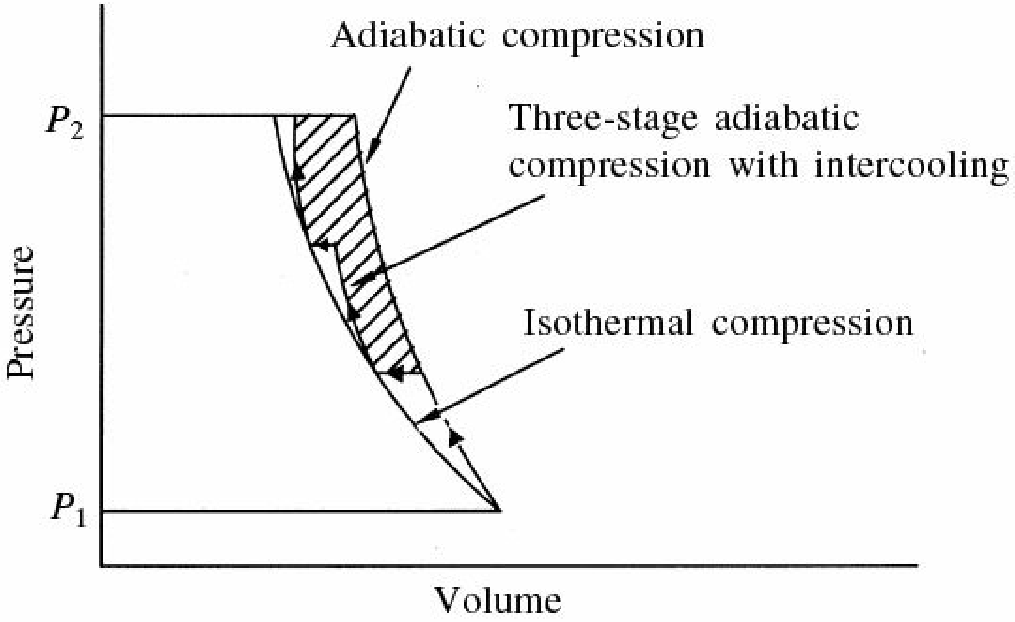


Fig. 5.5 *P-V* diagram of a three-stage adiabatic compression with interstage cooling.

After the first and second stages the gas is cooled to the original temperature at constant pressure. The actual path traced by the gas is shown with arrows and it is very close to the isothermal path for compressing the gas between the same pressure limits. The shaded area in Fig. 5.5 is the saving in the work required for compressing the gas from pressure P_1 to pressure P_2 by using a three stage compressor with inter-stage cooling over the work required in a single-stage compressor employing the same compression ratio.

Because of mechanical difficulties, a compression ratio greater than 5 cannot be attained in a single-stage reciprocating compressor. Multi-stage compressors are used to develop high compression ratios. The main advantage of this compression is that it allows inter-stage cooling and thereby an isothermal operation is closely approached. This results in reduction in the work done for compression.

The work requirement in a multi-stage compressor is the sum of the work requirements for the individual stages. For a two-stage compressor in which an ideal gas is compressed from pressure P_1 to P□ in the first stage and cooled to the initial temperature T_1 before it is sent to the second stage for the final compression to a pressure P_2, the total work required according to Eq. (5.46) is

$$W_S = \frac{\gamma}{\gamma - 1} RT_1 \left[1 - \left(\frac{P'}{P_1} \right)^{(\gamma - 1)/\gamma} + 1 - \left(\frac{P_2}{P'} \right)^{(\gamma - 1)/\gamma} \right] \tag{5.50}$$

For a multi-stage compressor with n stages, if the compression ratios in all the stages are equal and are denoted by r, then the total work required may be written as

$$W_S = \frac{n\gamma}{\gamma - 1} RT_1 \left[1 - (r)^{(\gamma - 1)/\gamma}\right] \tag{5.51}$$

In writing Eq. (5.51) it is assumed that after each stage, the temperature of the gas is brought down to the initial value. It can be shown that for the minimum total work in a multi-stage compressor, the pressure ratios in all the stages are equal and are given by

$$r = \left(\frac{P_2}{P_1} \right)^{1/n}$$

where P_2/P_1 is the overall pressure ratio.

_EXAMPLE_5.9 Show that in a two-stage reciprocating compressor, the minimum total work results when the pressure ratios in each stage are equal and are given by the square root of the over-all pressure ratio.

Solution The total work required when the initial and final pressures are P_1 and P_2 respectively and the intermediate pressure is given by Eq. (5.50)

$$\boxed{W_S = \frac{\gamma}{\gamma - 1} RT_1 \left[1 - \left(\frac{P'}{P_1} \right)^{(\gamma-1)/\gamma} + 1 - \left(\frac{P_2}{P'} \right)^{(\gamma-1)/\gamma} \right]}$$

To determine the pressure P', for which the total work is minimum, differentiate the above equation with respect to P' and equate the derivative (dW_S/dP') to zero.

$$\frac{dW_S}{dP'} = \frac{\gamma}{\gamma - 1} RT_1 \left[-\frac{\gamma - 1}{\gamma} \left(\frac{1}{P_1} \right)^{(\gamma-1)/\gamma} (P')^{-1/\gamma} + \frac{\gamma - 1}{\gamma} (P_2)^{(\gamma-1)/\gamma} (P')^{(1-2\gamma)/\gamma} \right] = 0$$

On simplification, we get

$$P' = (P_1 P_2)^{1/2} \tag{5.52}$$

Divide Eq. (5.52) by P_1. Then we get

$$\frac{P'}{P_1} = \left(\frac{P_2}{P_1} \right)^{1/2} \tag{5.53}$$

Similarly, we get

$$\frac{P_2}{P'} = \left(\frac{P_2}{P_1} \right)^{1/2} \tag{5.54}$$

Equations (5.53) and (5.54) reveal that for minimum total work in a two-stage compressor, the pressure ratios in both stages are equal and they are equal to the square root of the over-all pressure ratio.

***EXAMPLE* 5.10** What is the effect of ‘clearance’ on the work and theoretical volumetric efficiency of a single-stage reciprocating compressor?

Solution The *P-V* diagram of a single-stage reciprocating compressor is shown in Fig. 5.6.
Here 1–2 is the compression stroke, 2–3 the discharge stroke, 3–4 the expansion stroke and
4–1 the suction (intake) stroke. At the end of the discharge stroke, a volume V_3 of the high-pressure gas remains entrapped within the cylinder. This volume is known as the *clearance volume*. During the expansion stroke, the pressure of this gas is reduced and the volume increased to V_4. During the suction stroke, the volume of gas sucked in is equal to $V_1 - V_4$, which is the *intake volume* of the compressor. The volume swept through by the piston after discharge of the compressed gas is the *displacement volume* and is equal to $V_1 - V_3$. The ratio of clearance volume to displacement volume is called the *clearance* and is denoted by *c*. The *theoretical volumetric efficiency* is the ratio of the intake volume to the displacement volume. Thus we have,

$$\text{Clearance } c = \frac{V_3}{V_1 - V_3}$$

$$\text{Theoretical volumetric efficiency} = \frac{V_1 - V_4}{V_1 - V_3}$$

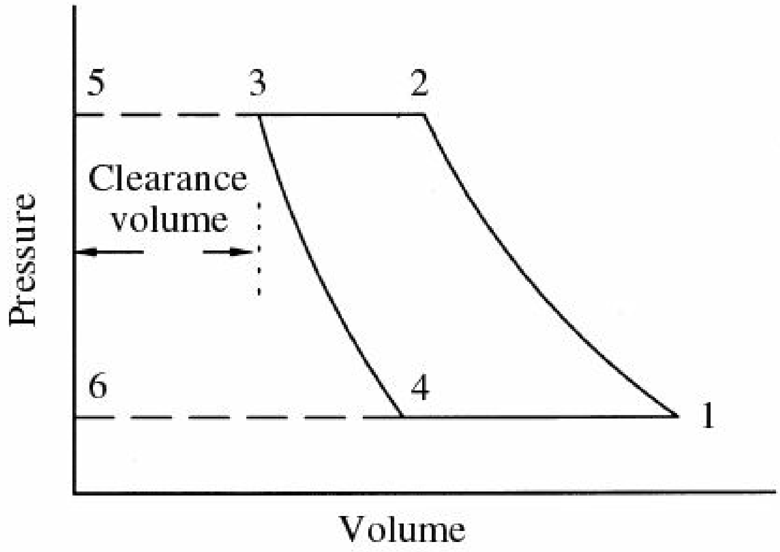


Fig. 5.6 Effect of clearance on the work of a single-stage compression.

The work required for compressing an ideal gas in a reversible adiabatic process from pressure P_1 to pressure P_2 is given by Eq. (5.46)

$$W_S = \frac{\gamma}{\gamma - 1} P_1 V_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma - 1)/\gamma} \right]$$

On the *P*-*V* diagram, it is given by the area 1–2–5–6. This is the work required by a compressor with no clearance. The work of expansion is given by the area 4–3–5–6 as well as by the equation

$$W_S = \frac{\gamma}{\gamma - 1} P_1 V_4 \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma - 1)/\gamma} \right]$$

The net work required is given by the area 1–2–3–4, which is the difference between the areas 1–2–5–6 and 4–3–5–6. The net work required by the compressor is, therefore,

$$W_S = \frac{\gamma}{\gamma - 1} P_1 (V_1 - V_4) \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma - 1)/\gamma} \right]$$

It means that, if we use the actual intake volume of the gas in Eq. (5.46), the work required fo compressors with clearance will be the same as that for compressors without clearance. To be precise, the clearance has no effect on the work of compression.

Theoretical volumetric efficiency

Theoretical volumetric efficiency

$$= \frac{V_1 - V_4}{V_1 - V_3} = \frac{(V_1 - V_3) + (V_3 - V_4)}{V_1 - V_3} = \frac{V_1 - V_3}{V_1 - V_3} + \frac{V_3}{V_1 - V_3} - \frac{V_4}{V_1 - V_3}$$

As the expansion process is reversible adiabatic, the pressure and volume are related as

$$V_4 = V_3\left(\frac{P_2}{P_1}\right)^{1/\gamma}$$

Substitute this relation in the expression for volumetric efficiency. The resulting expression simplifies to

$$\text{Theoretical volumetric efficiency} = \frac{V_1 - V_4}{V_1 - V_3} = 1 + c - c\left(\frac{P_2}{P_1}\right)^{1/\gamma}$$

***EXAMPLE* 5.11** Carbon dioxide at 1 bar and 300 K is to be compressed to a pressure of 10 bar in a single-stage compressor at a rate of 100 m^3/h. Assuming that CO_2 behaves as an ideal gas, calculate the temperature of the gas after compression and the work required. Take g = 1.3.

Solution For ideal gas, the work of compression is given by Eq. (5.46)

$$W_S = \frac{\gamma}{\gamma - 1} P_1 V_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \right]$$

$$= \frac{1.3}{0.3} \times 10^5 \times \frac{100}{3600} \times (1 - 10^{0.3/1.3}) = -8.44 \text{ kW}$$

The work required is 8.44 kW.
[*Note:* Work required may be calculated using the second expression of Eq. (5.46) also.

$$W_S = \frac{\gamma}{\gamma - 1} RT_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} \right]$$

$$= \frac{1.3}{0.3} \times 8.314 \times 300 \times (1 - 10^{0.3/1.3}) = -7579.3 \text{ kJ/kmol}$$

Number of moles of the gas compressed is given by

$$PV/RT = (1 \times 10^5)\ 100/(8.314 \times 10^3 \times 300 \times 3600) = 1.114 \times 10^{-3} \text{ kmol/s}$$

Therefore, the required work is

$$-W_S = 7579.3\ (1.114 \ \square\ 10^{-3}) = 8.44 \text{ kW]}$$

Temperature and pressure in adiabatic compression are interrelated.

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma} = 300 \times 10^{0.3/1.3} = 510.4 \text{ K}$$

***EXAMPLE* 5.12** Consider the compression of air (molecular weight = 29) from 10^5 Pa at 300 K to 3.6 □ 10^6 Pa in ideal two-stage compressor with intercooling. Assume that the temperature of air leaving the intercooler is also 300 K and that the optimum interstage pressure is used. The compressor is water jacketted and the polytropic exponent n is 1.30 for both stages. Determine the work of compression per kg of air.

Solution By Eq. (5.54), the optimum interstage pressure in a two-stage compressor is the geometric mean of the initial and final pressures. That is,

$$P' = \sqrt{P_1 P_2} = (10^5 \times 3.6 \times 10^6)^{0.5} = 6 \times 10^5 \text{ Pa}$$

For polytropic compression, the formula for evaluating the work of compression per mol of gas is similar to Eq. (5.51).

$$W_S = \frac{Nn}{n-1} RT_1 \left[1 - (r)^{(n-1)/n}\right]$$

where N is the number of stages and n is the polytropic exponent. Here $N = 2$ and $n = 1.3$. The compression ratio is

$$r = \frac{P'}{P_1} = 6$$

Therefore,

$$W_S = \frac{2 \times 1.3}{0.3} \times 8.314 \times 300\,[\,1 - 6^{0.3/1.3}\,] = -11069.2 \text{ kJ/kmol}$$

The work of compression per kg of air = (1/29) × 11069.2 = 358.2 kJ.

***EXAMPLE*5.13** Saturated steam at 100 kPa is compressed adiabatically to 500 kPa. The compression efficiency is 80%. Determine the work required to run the compressor and the temperature of the exhaust steam.

Solution From steam tables, the following properties of the steam entering the compressor are taken: Temperature, T_1 = 372.8 K; Enthalpy, H_1 = 2675.5 kJ/kg; Entropy, S_1 = 7.3594 kJ/kg K.

For isentropic compression, $S_2 = S_1$ = 7.3594 kJ/kg K.

Temperature T_2 (= 545.74 K) of superheated steam at 500 kPa having entropy of 7.3594 kJ/kg K is obtained from steam tables by interpolation. Enthalpy of superheated steam at 500 kPa and 545.74 K, H_2 = 3008 kJ/kg. The change in enthalpy of steam in isentropic compression is

$$H_2 - H_1 = 3008 - 2675.5 = 332.5 \text{ kJ/kg}$$

From Eq. (5.44),

$$W_S \text{ (isentropic)} = -\Delta H_S = -332.5 \text{ kJ/kg}$$

Since the compression efficiency is only 80%,

$$W_S \text{ (actual)} = -332.5/0.8 = -415.6 \text{ kJ/kg}$$

Therefore, the work required for compression is 415.6 kJ per kg of steam admitted to the compressor. The actual change in the enthalpy of steam is

$$\Delta H = \frac{\Delta H_S}{\eta} = \frac{332.5}{0.8} = 415.6 \text{ kJ/kg}$$

Therefore, the actual enthalpy of steam leaving the compressor is

$$2675.5 + 415.6 = 3091.1 \text{ kJ/kg}$$

The temperature of superheated steam at 500 kPa and having enthalpy of 3091.1 kJ/kg that leaves the compressor is obtained from steam tables by interpolation. That is, $T = 586$ K.

5.2 REFRIGERATION

Refrigeration is the process of producing and maintaining a temperature below that of the surrounding atmosphere. Refrigeration processes find wide applications in chemical process industries. The process is used in manufacturing synthetic rubber, textiles, chlorine, plastics, hydrogen fluoride, etc. Refrigeration is used to remove heat of chemical reactions and to liquefy process gases for gas separation by distillation and condensation. Liquefaction processes for the production of pure gases such as oxygen and nitrogen from air and liquefaction and storage of natural gases employ refrigeration principles. Separation of volatile hydrocarbons in petroleum industries, separation of gasoline from natural gas, solvent recovery, crystallisation of salts from solutions, manufacture of ice, treatment, transport and preservation of food and beverages, etc., are some other important applications of refrigeration operation. Apart from its widespread use in the air-conditioning of houses and buildings and in domestic refrigerators, refrigeration is also used in the air-conditioning of plant areas as in the manufacture of rayon, photographic film, gelatine, etc.

Refrigeration implies production of low temperature by continually absorbing heat at a low level and rejecting it at a high level. Since heat cannot flow from a body at low temperature to one at a higher temperature spontaneously, external work is required to achieve refrigeration. Thus, refrigeration is essentially an operation involving the pumping of heat from one temperature to a higher temperature. In mechanical refrigeration, which is the most commonly used method for commercial applications, the low temperature is produced by the evaporation of a liquid whose properties are, such that, at the pressure of evaporation, the saturation temperature is low. The evaporated liquid is then returned to its original state for continuous operation. The complete series of processes that the working fluid—the refrigerant—undergoes, constitute a refrigeration cycle. A typical refrigeration cycle includes evaporation of the liquid refrigerant, compression of the refrigerant vapour, condensation of the vapour into liquid, and finally expansion of the liquid.

5.2.1 Coefficient of Performance (COP)

Refer Fig. 5.7, which represents schematically the refrigeration process. Let Q_2 be the heat that is absorbed at a low temperature T_2 and Q_1 be the heat rejected at high temperature T_1. By first law of thermodynamics, the external work required to bring about this transfer is

$$W = Q_1 - Q_2$$

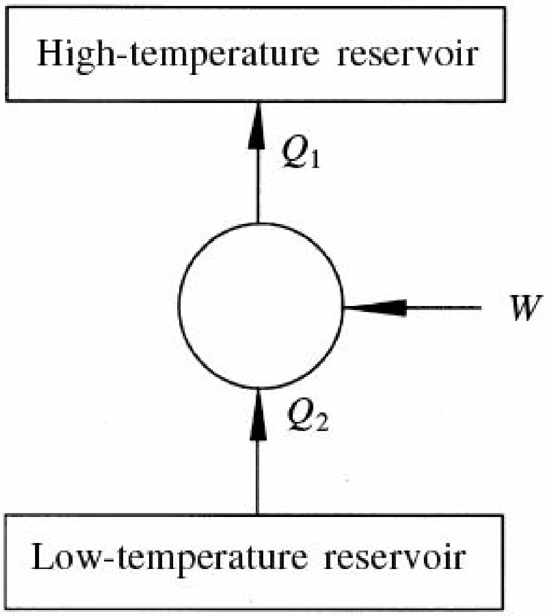


Fig. 5.7 Schematic representation of a refrigeration cycle.

The *efficiency* or *coefficient of performance* (COP) of a refrigerator is defined as the quantity of heat absorbed at the low temperature per unit of work.

$$\boxed{\text{COP} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}} \tag{5.55}$$

5.2.2 Refrigerator Capacity

The *refrigerator capacity* determines the rate of circulation of the refrigerant, which in turn, decides the design and size of the various units such as condenser, compressor, evaporator, and the expansion devices. The capacity is sometimes measured in ton of refrigeration. One ton is defined as the heat absorption at the rate of 12000 BTU per hour (One BTU is the amount of heat required to raise the temperature of one pound, i.e. 0.4536 kg of water by one degree Fahrenheit, or (1/1.8) K. Thus, 1 BTU = 1.055 kJ). This rate corresponds to the rate of heat removal that is required to freeze 1 ton of water in a day originally at 273 K. One ton of refrigeration is equivalent to a refrigeration rate of 12660 kJ/h in SI units.

5.2.3 Carnot Cycle

The *Carnot cycle* can be used as a model of the ideal refrigeration cycle, because, of all the refrigerators operating between the same two thermal reservoirs, the maximum COP is attained by the one based on Carnot cycle. The Carnot refrigeration cycle is depicted in Fig. 5.8(a).

It consists of the following steps: reversible adiabatic compression (*AB*), isothermal heat rejection (*BC*), reversible adiabatic expansion (*CD*) and isothermal heat absorption (*DA*). During the isothermal heat absorption (*DA*), an amount of heat Q_2 is absorbed at low temperature level T_2. The area *ADXY* on the *T-S* diagram [Fig. 5.8(b)] represents the heat absorbed. It is equal to T_2DS, where DS is the change in entropy of the fluid due to the heat absorption. Heat rejected at higher temperature T_1 is equal to Q_1 and is represented by the area *BCXY*. It is equal to T_1DS. The external work done for this transfer of heat against a temperature gradient is given by $W = Q_1 - Q_2$, which is the enclosed area *ABCD* in Fig. 5.8(b).

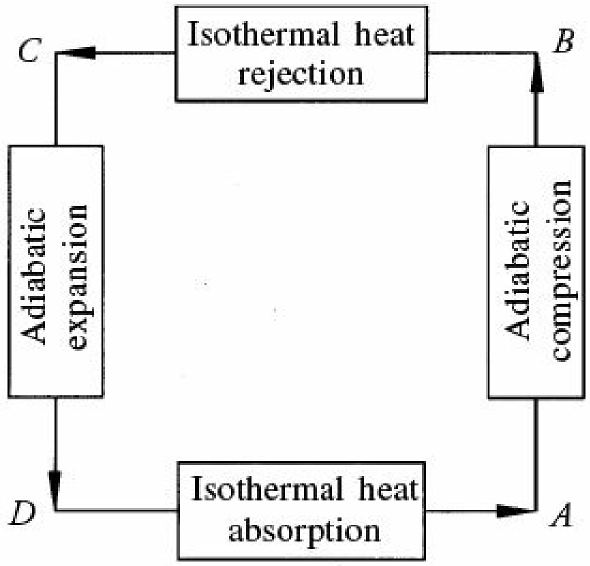


Fig. 5.8(a) Components of a Carnot cycle.

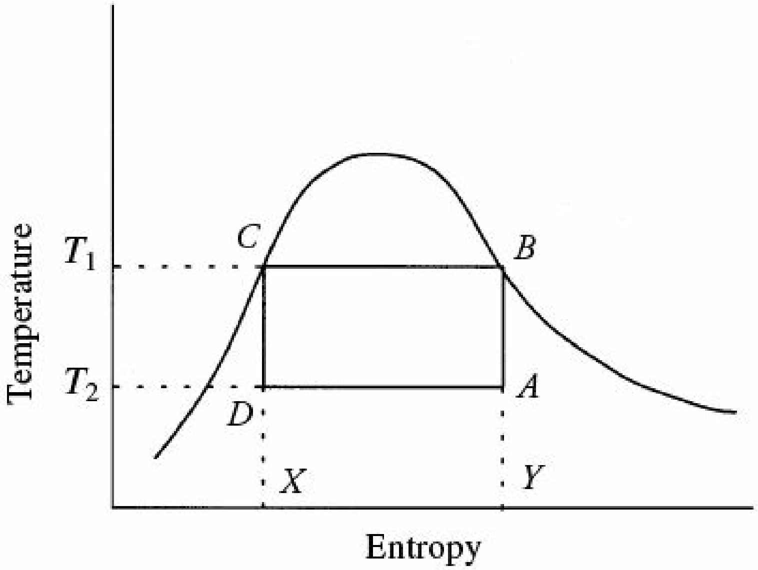


Fig. 5.8(b) *T-S* diagram of the Carnot cycle.

The coefficient of performance of the Carnot cycle is,

$$\text{COP} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2 \Delta S}{(T_1 - T_2)\Delta S} = \boxed{\frac{T_2}{T_1 - T_2}} \tag{5.56}$$

We note that the coefficient of performance of the Carnot refrigeration cycle depends only on the temperature levels between which the machine operates and is independent of the working fluid. Equation (5.56) establishes the optimum performance that can be expected of any refrigerating machine operating between given temperature limits. Equation (5.56) on rearrangement gives

$$\boxed{W = Q_2 \frac{T_1 - T_2}{T_2}} \tag{5.57}$$

which is the minimum work required for transferring heat Q_2 from a low temperature T_2 to a higher temperature T_1. It is impossible to construct a refrigeration machine that will pump heat with less expenditure of work than that given by Eq. (5.57). Because of the inherent irreversibilities in any practical process, the COP of an actual machine will be less than that given by Eq. (5.56) and the work required for transfer of a given quantity of heat will be more than that given by Eq. (5.57). However, these equations can be used as a standard for comparison of the actual processes and suggest possible improvement in such processes. Equation (5.57) indicates that the work input increases with decrease in the temperature of the refrigerator or with increase in the temperature of the heat receiver and is independent of the refrigerant. It may be noted here that even in the actual cycles, the influence of the working fluid on the work input per unit of refrigeration is quite insignificant.

Limitations. A refrigeration machine operating on the Carnot cycle cannot be achieved in practice. Carnot cycle demands reversible operation, and it is difficult to eliminate all irreversibilities in an actual operation. Isothermal heat interactions at the heat absorption and the heat rejection stages, which proceed at very slow rates necessitate large heat transfer areas. A temperature difference between the refrigerant and the reservoirs in the heat absorption and heat rejection stages is necessary, in order to have a finite rate of heat transfer. If the heat absorption is achieved by the evaporation of a refrigerant then the possibility of the input stream to the compressor containing liquid cannot be overruled. This may lead to severe erosion problems in the compressor. Apart from these, the work output of an expansion engine or a turbine used for reversible expansion is normally very small whereas their costs are prohibitively high.

***EXAMPLE*5.14** To maintain the temperature of a solution at 261 K, 1000 kJ of heat per minute is continuously removed from it. The surrounding temperature is 288 K. What is the least amount o power necessary to accomplish this?

Solution Using Eq. (5.57),

$$W = Q_2 \frac{T_1 - T_2}{T_2} = 1000 \frac{288 - 261}{261} = 103.45 \text{ kJ/min} = \frac{103.45 \times 1000}{746 \times 60} = 2.31 \text{ hp}$$

***EXAMPLE* 5.15** A refrigeration machine operating at a condenser temperature of 290 K needs 1 kW of power per ton of refrigeration. Determine the following:

(a) The coefficient of performance

(b) The heat rejected to the condenser

(c) The lowest temperature that can be maintained.

Solution (a) 1 Ton of refrigeration = 12660 kJ/h = 3516.67 W

That is $Q_2 = 3516.67$ W; $W = 1000$. Therefore, COP = $Q_2/W = 3516.67/1000 = 3.52$

(b) The heat rejected, $Q_1 = Q_2 + W = 3516.67 + 1000 = 4516.67$ W = 4.52 kW

(c) Let T_2 is the lowest possible temperature in the refrigerator, then

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$T_2 = T_1 \frac{Q_2}{Q_1} = 290 \times \frac{3516.67}{4516.67} = 225.8 \text{ K}$$

5.2.4 Vapour-compression Cycle

The actual refrigeration cycles are less efficient than the ideal Carnot cycle, because of the presence of the inevitable irreversible effects, such as friction, imperfect heat insulation, and because of the finite temperature difference that is maintained for a reasonably good rate of heat transfer in the refrigerator and the condenser. In the vapour-compression cycle shown in Fig. 5.9(a), the refrigerant vapour is compressed (*AB*) to such a pressure that the available cooling water can condense the vapour in a condenser (*BC*) operated at this pressure which is maintained constant. The vapour, during condensation rejects heat to the cooling medium. By passing through a throttling valve, the pressure of the liquid leaving the condenser is reduced (*CD*) to the pressure maintained in the evaporator. The liquid then evaporates (*DA*), absorbing heat at constant temperature T_2. The vapour thus produced enters the compressor, and the cycle is repeated. The process is represented on the *T-S* diagram as shown in Fig. 5.9(b). The liquid portion of the refrigerant leaving the throttling valve is vaporised at constant pressure P_2 and constant temperature T_2 in the refrigerator. The vapour leaving the refrigerator is saturated (*A*). It is possible that the vapour leaving the refrigerator may get slightly superheated or may be slightly unsaturated. On adiabatic compression, the vapour gets super heated (*B*) and this vapour enters the condenser at pressure P_1. The reversible adiabatic compression is an isentropic process and is represented by the vertical line *AB*. In the condenser, the vapour is first cooled and the superheat is removed from the vapour, as shown by the line *BE*, and then it is condensed at constant temperature T_2. The saturated liquid (*C*) leaving the condenser is expanded by throttling. The throttling is a constant enthalpy process and is represented by the curve *CD*. Throttling results in the partial vaporisation of the liquid, and the point (*D*) representing the mixture leaving the valve lies in the two-phase region. Figure 5.9(c) shows the vapour-compression cycle on a pressure-enthalpy diagram.

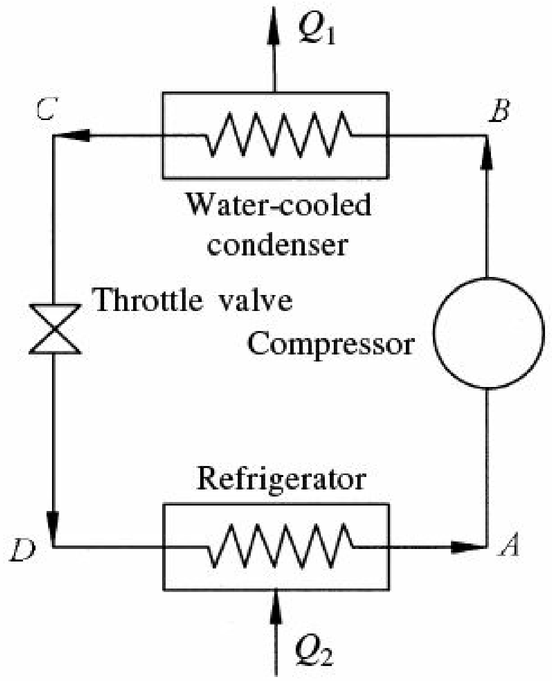


Fig. 5.9(a) Components of an ordinary vapour-compression cycle.

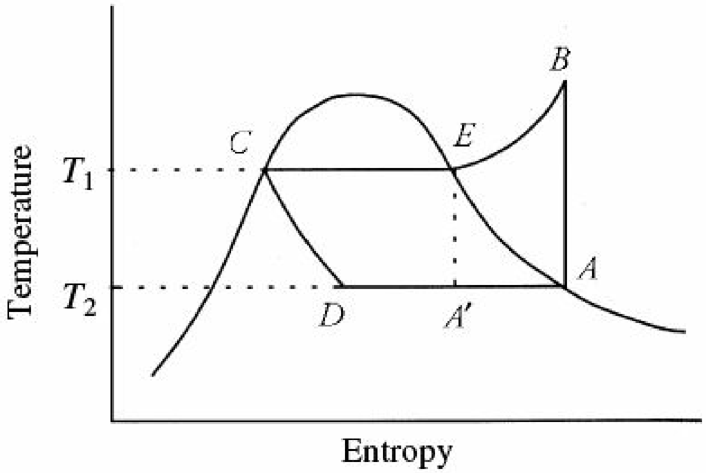


Fig. 5.9(b) *T-S* diagram of the ordinary vapour-compression cycle.

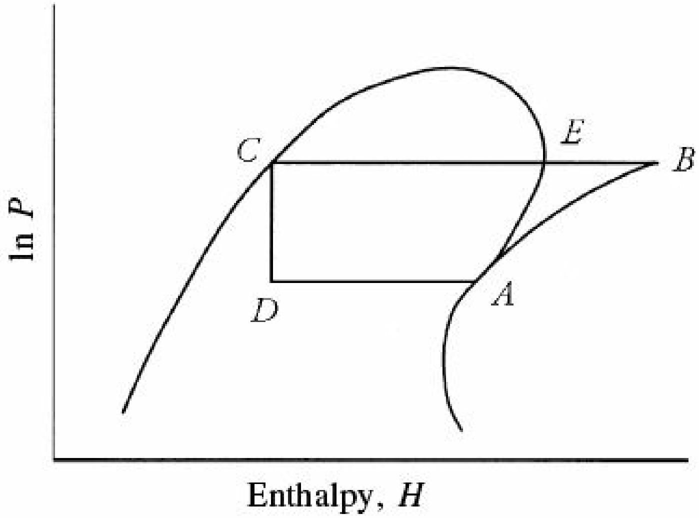


Fig. 5.9(c) *P-H* diagram of a vapour-compression cycle.

As the heat absorption in the refrigerator occurs at constant pressure, the heat absorbed during vaporisation is equal to the change in the enthalpy of the refrigerant.

$$Q_2 = H_A - H_D \qquad (5.58)$$

The heat rejected is

$$Q_1 = H_B - H_C \qquad (5.59)$$

Since the work required, $W = Q_1 - Q_2$, and $H_D = H_C$ (the process *CD* is isenthalpic), we have

$$W = H_B - H_A \qquad (5.60)$$

The coefficient of performance is

$$\boxed{\text{COP} = \frac{Q_2}{W} = \frac{H_A - H_D}{H_B - H_A}} \qquad (5.61)$$

If the rate of heat absorption is specified, the rate of circulation of the refrigerant ($\dot{m}$) can be easily evaluated.

$$\dot{m}(H_A - H_D) = Q_2 \qquad (5.62)$$

For a refrigerator rated at 1 ton (Q_2 = 12660 kJ/h), the rate of circulation in kg/h may be evaluated by

$$\dot{m} = \frac{12660}{H_A - H_D} \qquad (5.63)$$

where H_A and H_D are in kJ/kg.

The vapour leaving the compressor is superheated at the condenser pressure P_1. Its temperature is greater than the saturation temperature T_1. Also, the throttling process is highly irreversible. Because of these two reasons, the ordinary vapour-compression cycle presented above, is less efficient than the Carnot cycle. By allowing the evaporation to proceed up to point A□ in Fig. 5.9(b), and compressing the resultant vapour–liquid mixture adiabatically to saturation at pressure P_1 (process *A*□*E* in the figure) the first difficulty can be overcome. But the practical gain in such an operation is only very small in comparison with the operational difficulties associated with the compression of a two-phase mixture. If the expansion process (*CD*) were carried out in an expansion engine instead of throttling, the irreversibilities can be minimised to a great extent. This is what is done in an expansion-engine vapour-compression cycle illustrated in Figs. 5.10(a) and (b). Here, the expansion is isentropic and hence *CD* is a vertical line on the *T-S* diagram.

The heat absorbed and heat rejected during this cycle are respectively Q_2 and Q_1, which are given by $Q_2 = H_A - H_D$ and $Q_1 = H_B - H_C$.

The work input $W = Q_1 - Q_2$. Hence,

$$\text{COP} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{H_A - H_D}{(H_B - H_C) - (H_A - H_D)} \tag{5.64}$$

As the expansion engine operating on a two-phase mixture is expensive, this cycle is preferred only for large installations. Because of their simplicity and low cost, the throttle valves are preferred over turbines in small installations.

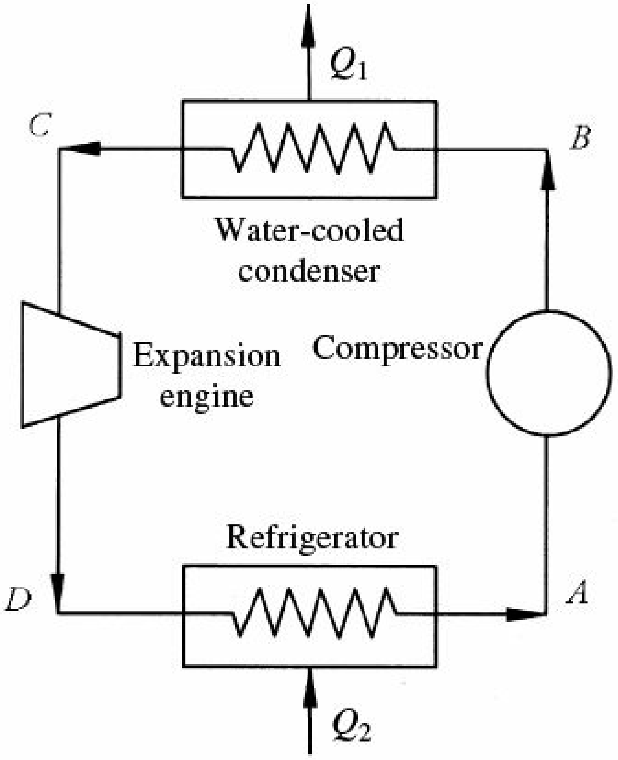


Fig. 5.10(a) Components of an expansion engine vapour-compression cycle.

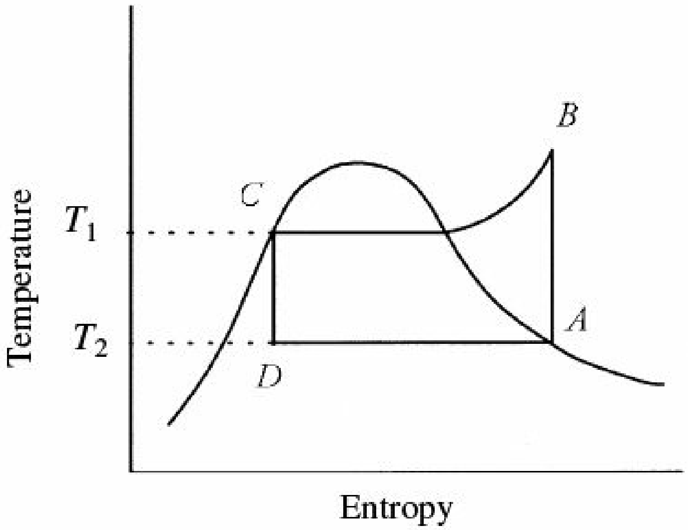


Fig. 5.10(b) *T-S* diagram of the expansion engine vapour-compression cycle.

***EXAMPLE* 5.16** A vapour compression refrigeration system with ammonia as the working fluid is to operate between 266 K and 300 K. Determine the following:

(a) COP, given that the enthalpy of saturated vapour at 266 K = 656 kJ/kg and enthalpy of superheated vapour leaving the compressor = 724 kJ/kg, enthalpy of saturated liquid at 300 K = 144 kJ/kg.

(b) COP, if a temperature approach of 5 K is necessary in the evaporator and condenser, and the efficiency of the compressor is 75%. Enthalpy of saturated vapour at 261 K = 652 kJ/kg and the enthalpy of superheated vapour entering the condenser = 758 kJ/kg, enthalpy of saturated liquid at 305 K = 159 kJ/kg.

(c) The COP of an ideal Carnot refrigerator.

Solution (a) $H_A = 656$, $H_B = 724$, and $H_C = H_D = 144$. Using Eq. (5.61),

$$\text{COP} = \frac{H_A - H_D}{H_B - H_A} = \frac{656 - 144}{724 - 656} = 7.53$$

(b) $H_A = 652$, $H_B = 758$, and $H_C = H_D = 159$, then

$$\text{COP} = \frac{H_A - H_D}{H_B - H_A} \times \eta = \frac{652 - 159}{(758 - 652) \times 1/0.75} = 3.49$$

(c) For Carnot cycle, COP is given by Eq. (5.56)

$$\text{COP} = \frac{T_2}{T_1 - T_2} = \frac{266}{300 - 266} = 7.8$$

***EXAMPLE*5.17** A vapour-compression cycle using ammonia as refrigerant is employed in an ice manufacturing plant. Cooling water at 288 K enters the condenser at a rate of 0.25 kg/s and leaves at 300 K. Ammonia at 294 K condenses at a rate of 0.50 kg/minute. Enthalpy of liquid ammonia at 294 K is 281.5 kJ/kg. The compressor efficiency is 90%. Saturated ammonia vapour at 258 K and enthalpy of 1426 kJ/kg enters the compressor. What is the power requirement of the compressor and refrigeration capacity in tons?

Solution Since heat is rejected at constant pressure in the condenser, we have

$$Q_1 = \dot{m}_c C_P \Delta T$$

where $\dot{m}_c$ is the cooling water circulation rate and ΔT is the temperature rise of the water.

$$Q_1 = 0.25 \times 4.2 \times 12 = 12.6 \text{ kJ/s}$$

Heat absorbed and work required are evaluated as

$$Q_2 = \dot{m}(H_A - H_D) = \frac{0.50}{60}(1426 - 281.5) = 9.5375 \text{ kJ/s}$$

$$W = Q_1 - Q_2 = 12.6 - 9.5375 = 3.0625 \text{ kJ/s}$$

Power requirement of the compressor:

$$3.0625/0.9 = 3.4028 \text{ kW} = 4.56 \text{ hp}$$

Refrigerator capacity:

$$9.5375 \times 3600 \text{ kJ/h} = 9.5375 \times 3600/12660 = 2.71 \text{ ton}$$

***EXAMPLE*5.18** An expansion engine vapour-compression machine rated at 10 ton is used to maintain the temperature of a cold storage at 261 K. The cooling water is available at 293 K. A 5-K approach is necessary in the condenser as well as in the evaporator. The saturation pressure, enthalpy, and entropy of saturated vapour at 256 K are 1.62 bar, 181 kJ/kg and 0.714 kJ/kg K respectively. The saturation pressure, enthalpy, and entropy of saturated liquid at 298 K are 6.79 bar, 62 kJ/kg, and 0.231 kJ/kg K respectively. The enthalpy of superheated vapour leaving the compressor at a pressure of 6.79 bar with entropy 0.714 kJ/kg K is 206 kJ/kg. Calculate the COP an the refrigerant circulation rate.

Solution Allowing a 5-K approach in the condenser and in the evaporator, T_1 = 298 K and T_2 = 256 K.

Using Eq. (5.64), the COP is evaluated as

$$\text{COP} = \frac{H_A - H_D}{(H_B - H_C) - (H_A - H_D)}$$

The enthalpy H_D in this equation is to be determined first. Referring to Fig. 5.11 we can see that the ratio of the line lengths, *DA*/*FA*, measures the fraction of the mixture at *D*, that is liquid.

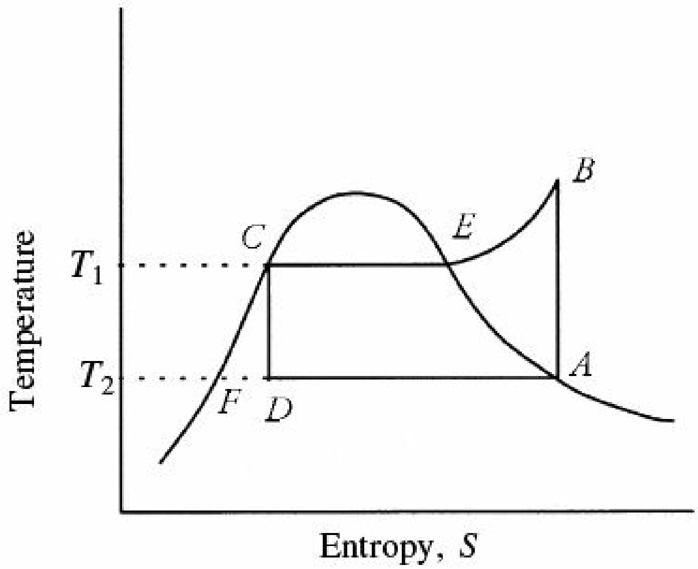


Fig. 5.11 *T-S* diagram of the vapour-compression cycle in Example 5.13.

$$x = \frac{DA}{FA} = \frac{H_A - H_D}{H_A - H_F} = \frac{H_A - H_D}{\Delta H_V}$$

where DH_V is the heat of vaporisation at 1.62 bar. Similarly, we can write, using the entropy of vaporisation DS_V,

$$x = \frac{DA}{FA} = \frac{S_A - S_D}{S_A - S_F} = \frac{S_A - S_D}{\Delta S_V}$$

Eliminate x from the preceding two equations and rearrange the result using the relation ΔS for a phase change = $\Delta H/T$, we get

$$\frac{H_A - H_D}{S_A - S_D} = \frac{\Delta H_V}{\Delta S_V} = T_2$$

$$H_D = H_A - T_2(S_A - S_D)$$

Since the expansion process CD is reversible adiabatic, $S_D = S_C$, so that

$$H_D = H_A - T_2(S_A - S_C) = 181 - 256(0.714 - 0.231) = 57.4 \text{ kJ/kg}$$

It is given that $H_A = 181$, $H_B = 206$, and $H_C = 62$. Substituting these values in Eq. (5.64), we get COP = 6.06.

Equation (5.63) is used to calculate the refrigerant circulation rate.

$$\dot{m} = \frac{12660 \times 10}{H_A - H_D} = \frac{12660 \times 10}{181 - 57.4} = 1024.3 \text{ kg/h}$$

5.2.5 Choice of Refrigerant

Today a number of refrigerants have been developed and are in use. Among them, the halogenated hydrocarbons such as Freon-12 find wide application. They have the advantages that they are non-toxic, non-flammable, and non-explosive. Methyl chloride, carbon dioxide, sulphur dioxide, propane, and ammonia are other commonly used refrigerants. The important properties of a refrigerant are as follows.

1. *Boiling temperature:* It is necessary that the operating pressure be maintained above atmospheric to avoid air and moisture leaks into the system. The normal boiling point of the refrigerant should, therefore, be lower than the desired temperature levels in the refrigerator.

2. *Freezing point:* The freezing point of the refrigerant should be well below the minimum temperature at which the system is operated.

3. *Critical temperature and pressure:* The critical temperature and pressure of the refrigerant should be above the operating system temperature and pressure. If the operating temperature is above the critical temperature, it is impossible to condense the gas by compressing it to high pressures.

4. *Condenser and evaporator pressures:* The condenser pressure should not be very high. If pressure is very high, the cost of equipment and the cost of operation would be excessive. If the evaporator pressure is excessively low, the compression ratio would be abnormally high. If the refrigerant has sub-atmospheric vapour pressures at the temperature in the refrigerator coils, the possibility of contamination by leaks cannot be overruled.

5. *Specific volume:* Specific volume of the vapour determines the size of the compressor. Low suction volumes are desirable for reciprocating compressors and high suction volumes for centrifugal compressors.

6. *Latent heat:* A high latent heat of vaporisation of the refrigerant is desired, because it results in high refrigerating effect per unit weight of the refrigerant and low rate of circulation of the refrigerant.

7. *Specific heat of liquid:* If the specific heat of the refrigerant liquid is unduly high, large quantity of heat would have to be removed to cool the hot liquid entering the evaporator to bring its temperature down to the saturation value. Therefore, low specific heat of the liquid refrigerant is preferred.

8. *Molecular weight:* Molecular weight of the refrigerant affects the compressor size because the specific volume of the vapour is directly related to it. A high-molecular weight refrigerant gives high specific volumes for the vapour, which is preferred for centrifugal compressors, whereas for reciprocating compressors a low molecular weight for the refrigerant is advantageous.

9. *Safety aspects:* Refrigerants are grouped according to toxicity and flammability. Halogenated hydrocarbons are relatively non-flammable, non-toxic, and non-explosive. These belong to group 1. Group 2 refrigerants are either toxic or flammable. Examples are methyl chloride and sulphur dioxide. The highly flammable and explosive refrigerants like propane, propylene, ethane, ethylene, methane, etc., fall into group 3.

10. *Other desirable properties:* Normally, a refrigerant would be in use for a very long period. Consequently, the chemical stability of the refrigerant is another important criterion in the choice of a proper refrigerant. They should also be non-corrosive, should have low viscosity and high thermal conductivity.

We see that the choice of refrigerant is limited to relatively few fluids, as it is necessary that they should have a vapour pressure above the atmospheric pressure at the evaporator temperature and the vapour pressure should not be excessively high at the condenser temperature.

5.2.6 Air-refrigeration Cycle

The air-refrigeration cycle is illustrated in Fig. 5.12. Here, the working fluid is air, which undergoes no phase change in the unit. The air is compressed adiabatically to a pressure P_1 and temperature T_1 in the compressor (*AB*). In the cooler, it is then cooled at constant pressure P_1 (*BC*). The air at pressure P_1 is expanded in an engine or a turbine to a pressure P_2, which, in an ideal case, is equal to the pressure of air at the compressor intake (*CD*). The work output of the expander contributes a part of the work requirement of the compressor. The gas leaving the expander is passed through the refrigerator, where it absorbs heat at constant pressure P_2 (*DA*). The gas leaving the refrigerator enters the compressor, and the cycle is repeated.

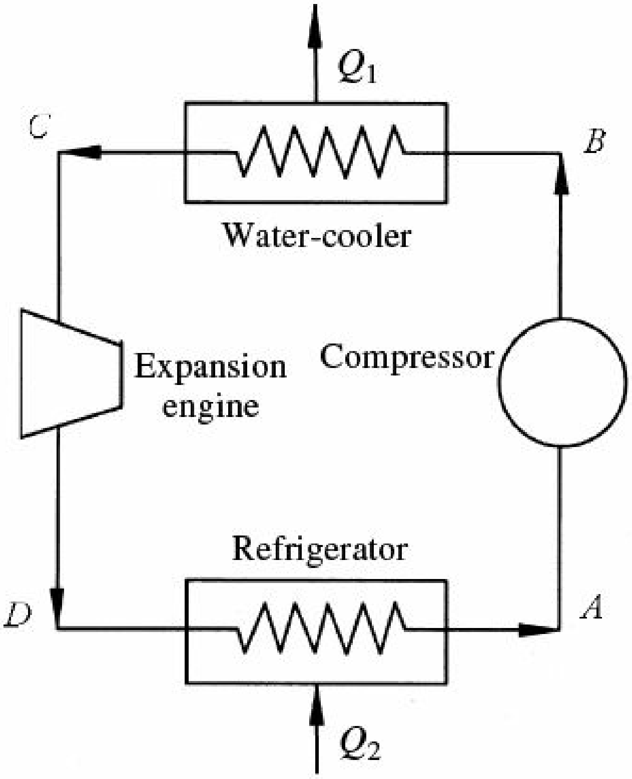


Fig. 5.12(a) Components of an air-refrigeration cycle.

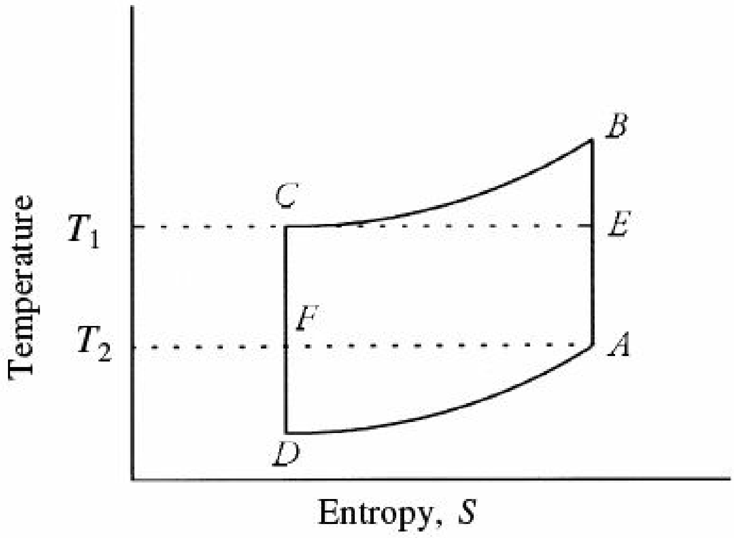


Fig. 5.12(b) Air-refrigeration cycle on *T-S* diagram.

On the *T-S* diagram, T_1 is the temperature of the cooling water and T_2 is the temperature to be maintained in the refrigerator. The area under the curve *DA* down to the *S*-axis is the heat absorbed in the refrigerator and the enclosed area *ABCD* is the work required for the removal of heat. It can be easily shown that, an ideal Carnot refrigerator operating between temperature levels T_1 and T_2 removes greater amount of heat with less work than an air-refrigeration machine.

Let the rate of air circulation be $\dot{m}$. Assume that the heat capacity of air remains constant during the cycle. Then, heat absorbed is

$$Q_2 = \dot{m}C_P(T_A - T_D)$$

and the heat rejected is

$$Q_1 = \dot{m}C_P(T_B - T_C)$$

The net work required is

$$W = Q_1 - Q_2 = \dot{m}C_P\,[(T_B - T_C) - (T_A - T_D)]$$

The coefficient of performance of an air-refrigeration machine is

$$\text{COP} = \frac{Q_2}{W} = \frac{T_A - T_D}{(T_B - T_C) - (T_A - T_D)} \tag{5.65}$$

The initial and final temperatures of the fluid undergoing adiabatic process are related to the initial and final pressures [see Eq. (3.23)].

$$\frac{T_B}{T_A} = \left(\frac{P_1}{P_2}\right)^{(\gamma-1)/\gamma} = \frac{T_C}{T_D} \tag{5.66}$$

Using Eq. (5.66), we can write

$$T_B - T_C = (T_A - T_D)\left(\frac{P_1}{P_2}\right)^{(\gamma-1)/\gamma} \tag{5.67}$$

Substitute Eq. (5.67) into Eq. (5.65)

$$\text{COP} = \frac{1}{(P_1/P_2)^{(\gamma-1)/\gamma} - 1} = \frac{T_A}{T_B - T_A} \tag{5.68}$$

The main advantage of the air-refrigeration cycles is that the air is available at no cost. Majority of the commonly used refrigerants possess certain undesirable properties like corrosiveness, explosiveness, toxicity, and flammability. Compared to these, air is harmless. In spite of all these, the air refrigeration processes are rarely used now. They are replaced by the vapour-compression processes. The disadvantages of the air cycles are their low efficiencies, large heat transfer surfaces required, and large quantity of air to be circulated through the unit. Since, the heat transfer in the refrigerator and the cooler occurs through air-films, which offer very high resistance to heat transfer, large temperature difference would be necessary between the air and the refrigerator as well as between the air and the cooler. For any specified refrigeration requirement, this would lead to an increase in the difference between the temperature of air in the cooler and that in the refrigerator, which, in turn, leads to low efficiencies. Also, since the specific heat of air is low, relatively large quantity of air is circulated through the unit in order to achieve an appreciable amount of refrigeration.

***EXAMPLE* 5.19** An air-refrigeration machine rated at 10 ton is used to maintain the temperature of a cold room at 261 K when the cooling water is available at 293 K. The machine operates between pressures of 1.013 bar and 4.052 bar. Assume a 5-K approach in the cooler and the refrigerator. The specific heat of air may be taken as 1.008 kJ/kg K and g = 1.4. Calculate the COP and air-circulation rate.

Solution Refer Fig. 5.12. The temperature of the air leaving the refrigerator is

$$T_A (= T_2) = 261 - 5 = 256 \text{ K}$$

The temperature of the air leaving the cooler is

$$T_C (= T_1) = 293 + 5 = 298 \text{ K}$$

Use Eq. (5.66) to determine temperature T_B;

$$T_B = T_A \left(\frac{P_1}{P_2} \right)^{(\gamma - 1)/\gamma} = 256(4)^{0.4/1.4} = 380.4 \text{ K}$$

Similarly, T_D = 200.5 K. Using Eq. (5.68),

$$\text{COP} = 256/(380.4 - 256) = 2.06$$

Equation (5.65) may also be used to determine the COP.

To find the air-circulation rate, consider the energy balance in the refrigerator.

$$\dot{m} C_P (T_A - T_D) = 10 \times 12660$$

$$\dot{m} = \frac{10 \times 12660}{1.008 \times (256 - 200.5)} = 2263 \text{ kg/h}$$

5.2.7 Absorption Refrigeration

In a vapour-compression cycle, external work is required to run the compressor. The ultimate source of this work is normally a heat engine, which absorbs heat from a high-temperature source and rejects part of it to a heat sink, the difference is transformed to work. The net effect is, a part of the heat that is absorbed from a high temperature source by a heat engine is utilised in a vapour-compression refrigeration system for pumping heat from a low temperature region to a high temperature region. Then a question may naturally arise, why should we not use this heat directly in a refrigeration system without converting it into work by means of a heat engine? An *absorption refrigeration* unit uses the heat absorbed from a high-temperature source directly for achieving the necessary refrigeration.

The principle behind absorption refrigeration is illustrated in Fig. 5.13. For a refrigeration rate of Q_2 kJ/h, the minimum work required when the refrigerator and the condenser are at temperatures T_2 and T_1 respectively is given by Eq. (5.56)

$$W = Q_2 \frac{T_1 - T_2}{T_2} \tag{5.69}$$

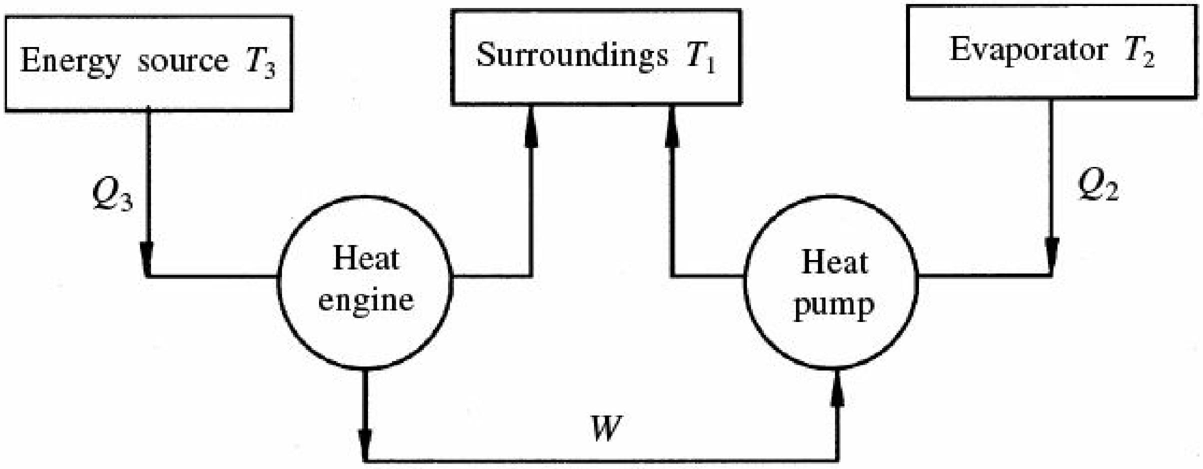


Fig. 5.13 The principle of absorption refrigeration.

In order to deliver a work equal to W, a heat engine operating between a high-temperature source at T_3 and the surroundings at T_1 should absorb a quantity of heat Q_3, where

$$Q_3 = W \frac{T_3}{T_3 - T_1} \tag{5.70}$$

Substituting Eq. (5.69) into Eq. (5.70) we get

$$Q_3 = Q_2 \frac{T_1 - T_2}{T_2} \frac{T_3}{T_3 - T_1} \tag{5.71}$$

Equation (5.71) gives the amount of heat from a high temperature source required to obtain a refrigeration capacity of Q_2. The ratio (Q_2/Q_3), which is the refrigeration obtained per unit quantity of high temperature heat, is known as the *efficiency of an absorption refrigeration cycle.*

$$\boxed{\frac{Q_2}{Q_3} = \frac{T_3 - T_1}{T_3} \frac{T_2}{T_1 - T_2}} \tag{5.72}$$

Equation (5.72) represents the ideal case, because, both the heat engine and the refrigerator were assumed to operate on the Carnot cycle. Actual efficiency will be less than the value given by this equation. For example, consider a heat source of saturated steam at 1 bar (T_3 = 373 K), surroundings at 300 K (T_1) and a refrigerator space at 260 K (T_2). Using Eq. (5.72), we get the efficiency to be 1.27. For the actual absorption refrigerator, the efficiency would be roughly only one-third of this value.

The compressor in the vapour-compression unit is replaced by an absorber-regenerator combination as shown in Fig. 5.14. Heat is liberated when the refrigerant vapour is absorbed in a non-volatile solvent. A typical absorption refrigeration cycle for moderate temperature applications uses water as the refrigerant and lithium bromide solution as the absorbent. For lower temperatures, ammonia is used as the absorbent and water as the solvent. The heat liberated during absorption is discarded to the surroundings at temperature T_1. The liquid leaving the absorber is a solution of the refrigerant in a relatively non-volatile solvent. It is pumped through a heat exchanger as shown in the figure. The temperature and pressure of the solution increase when the liquid reaches the regenerator. Regeneration of the refrigerant is achieved by evaporating it from the solution and the heat required for this is absorbed from the source at T_3. Low-pressure steam is usually used as the source. The regenerated absorbent liquid, which is almost free of the refrigerant, is cooled by passing through the heat exchanger. The heat given off by the solvent is utilised to raise the temperature of the solution leaving the absorber. The solvent is recycled to the absorber.

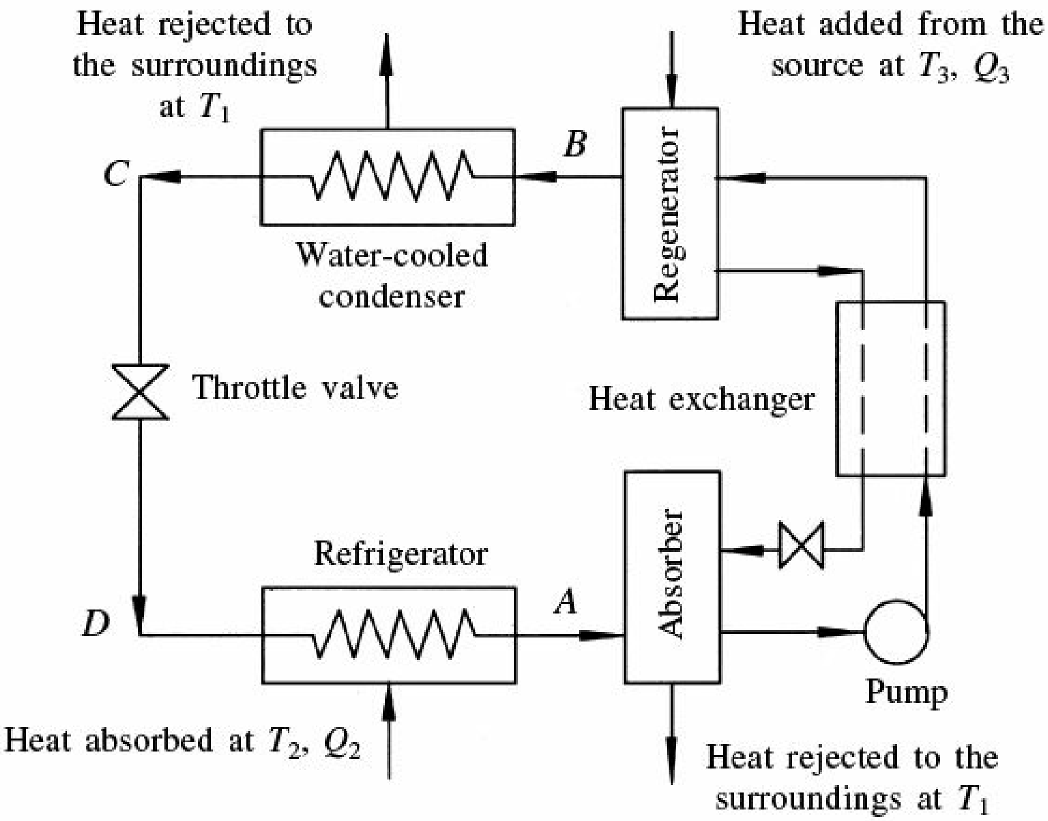


Fig. 5.14 Absorption refrigeration cycle.

5.2.8 Heat Pumps

A *heat pump* is a refrigerator operating in reverse order. Here, work is done to pump heat from a cold reservoir such as a river or the surrounding land into a hot sink such as the inside of a house. Heat pumps are used to heat houses and commercial buildings during the winter and cool them during the summer. During winter, the liquid refrigerant is allowed to evaporate in coils kept in the outside air. Heat is absorbed from the low-temperature source and the liquid gets vaporised during this stage. The vapour is then compressed to such a pressure that it can be condensed at a high temperature. In the condenser, the heat is transferred to cooling water or air which is used for heating the houses. By reversing the flow of the refrigerant, the same unit can be used to absorb heat from the rooms and reject it to the outside air during summer.

The coefficient of performance of a heat pump used for winter heating can be defined as the ratio of heat rejected to the high-temperature sink to the work required for the transfer. COP is Q_1/W. Compare this with the COP of the refrigerator. In the refrigerator, the quantity of prime interest being the heat absorbed at low temperature, the COP is defined as Q_2/W. A refrigerator with a COP of 3 will absorb three units of heat using one unit of work and deliver 4 units of heat to the rooms. Therefore, the COP of this machine when working as a heat pump is 4. The effectiveness of a hea pump for winter heating should be judged by comparing the cost of its operation with the cost of the conventional heating methods employing combustion of fuels.

***EXAMPLE* 5.20** Show that a 1-kW heat pump working between an indoor temperature of 300 K and an outside temperature of 290 K is equivalent to a 30-kW heater.

Solution The heat absorbed can be determined assuming a Carnot cycle.

$$\frac{Q_2}{W} = \frac{T_2}{T_1 - T_2} = \frac{290}{10} = 29$$

Let the net work input be 1 kJ. Then heat absorbed, $Q_2 = 29$ kJ. The heat rejected is

$$Q_1 = Q_2 + W = 29 + 1 = 30 \text{ kJ}$$

That is, a 1-kW pump if operated reversibly, is equivalent to a 30-kW heater.

***EXAMPLE*5.21** A heat pump is used to maintain the temperature inside a building at 295 K by pumping heat from the outside air at 275 K. The unit has an overall efficiency of 25%. The pump is driven electrically and the electric power is generated by the combustion of certain fuel gas. The heat of combustion of the fuel is 890.9 kJ/mol. It is estimated that only 33% of the heat of combustion of the fuel is converted into electricity. Determine the amount of fuel burned for delivering 1000 MJ of heat to the building.

Solution $Q_1 = 10^6$ kJ. The coefficient of performance of the heat pump is

$$\frac{Q_1}{W} = \frac{T_1}{T_1 - T_2} = \frac{295}{295 - 275} = 14.75$$

Therefore, work required to deliver 10^6 kJ of heat is

$10^6/14.75 = 6.78 \times 10^4$ kJ

Since the engine efficiency is only 25%, the actual amount of electrical energy to be supplied is

$6.78 \times 10^4/0.25 = 27.12 \times 10^4$ kJ

Since the efficiency of conversion of heat of combustion to electricity is 33%, the heat energy required as heat of combustion is

$27.12 \times 10^4/0.33 = 82.18 \times 10^4$ kJ

Number of moles of fuel burned is

$82.18 \times 10^4/890.9 = 922.5$ mol = 0.9225 kmol

5.3 LIQUEFACTION PROCESSES

Gas liquefaction has gained wide acceptability in recent years. Liquefaction processes make the task of storage, handling, and transportation of gases simple. In addition to the benefits such as the reduction of storage space and transportation costs achieved by liquefaction process in general, gas liquefaction is widely used for separation of gaseous mixtures into their component parts. Air liquefaction and separation are used to produce liquid oxygen and nitrogen widely used in missile and rocket development and low-temperature refrigeration. The developments in the space research have led to a manifold increase in the use of liquid helium. Liquid hydrogen finds application in nuclear weapons development and rocket propulsion.

There are three general methods of engineering importance for liquefaction of gases:

1. Vaporisation of a liquid
2. Joule–Thomson expansion
3. Expansion of gas in an engine delivering external work.

5.3.1 Vaporisation of Liquid

This method can be used to reach liquid–air temperatures by employing a series of liquids of different boiling points. The liquid of the lowest boiling point absorbs heat from the system to be refrigerated, and delivers this heat to the next higher boiling liquid in a condenser–boiler combination. Finally, the fluid of the highest boiling point is condensed by cooling (by air or water) thus discharging the heat to the atmosphere. This method has been used for liquefaction of air and natural gas. The lowest temperature that can be attained by this method is 63 K, the triple point of nitrogen.

5.3.2 Free Expansion

For liquefaction of the gas by this method, the initial pressure of the gas should be raised to such a high value that on Joule–Thomson expansion, which is an isenthalpic operation, the constant enthalpy lines cut into the two-phase region as shown in Fig. 5.15. Otherwise, no liquefaction is possible by Joule–Thomson expansion. For example, the gas at an initial state such as the one represented by a point *A* in this figure, cannot be liquefied by throttling.

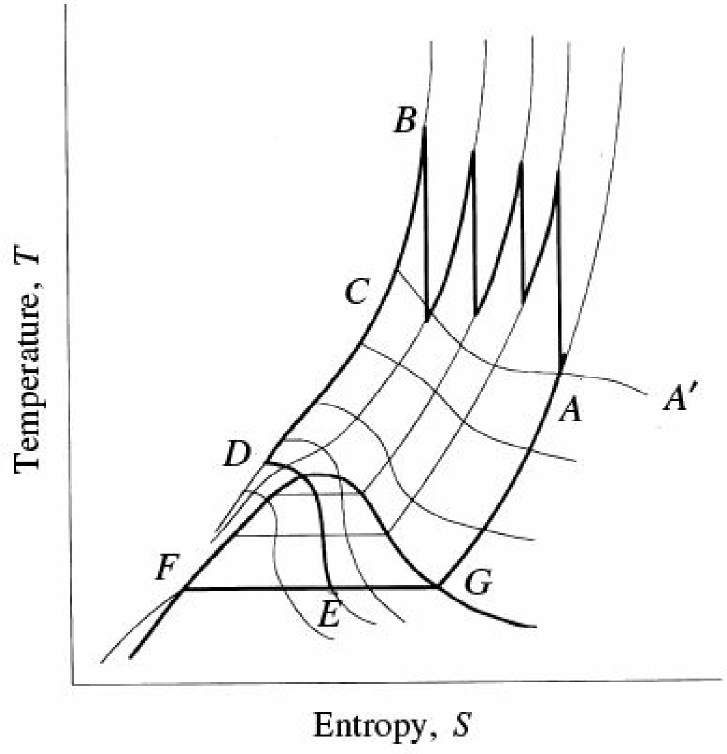


Fig. 5.15 *T-S* diagram of a simple Joule–Thomson liquefaction process.

The Linde process for gas liquefaction works on the principle of Joule–Thomson expansion. It can be used for liquefaction of gases that cool on Joule–Thomson expansion, that is, for gases that possess a positive Joule–Thomson coefficient. (The Joule–Thomson coefficient and its dependence on other thermodynamic variables are discussed in detail in Section 6.4.12.) Most gases have a positive Joule–Thomson coefficient at ordinary conditions, hydrogen and helium being exceptions. Even hydrogen and helium have positive coefficients below 100 K and 20 K respectively. The Linde process for liquefaction of air is shown in Fig. 5.16.

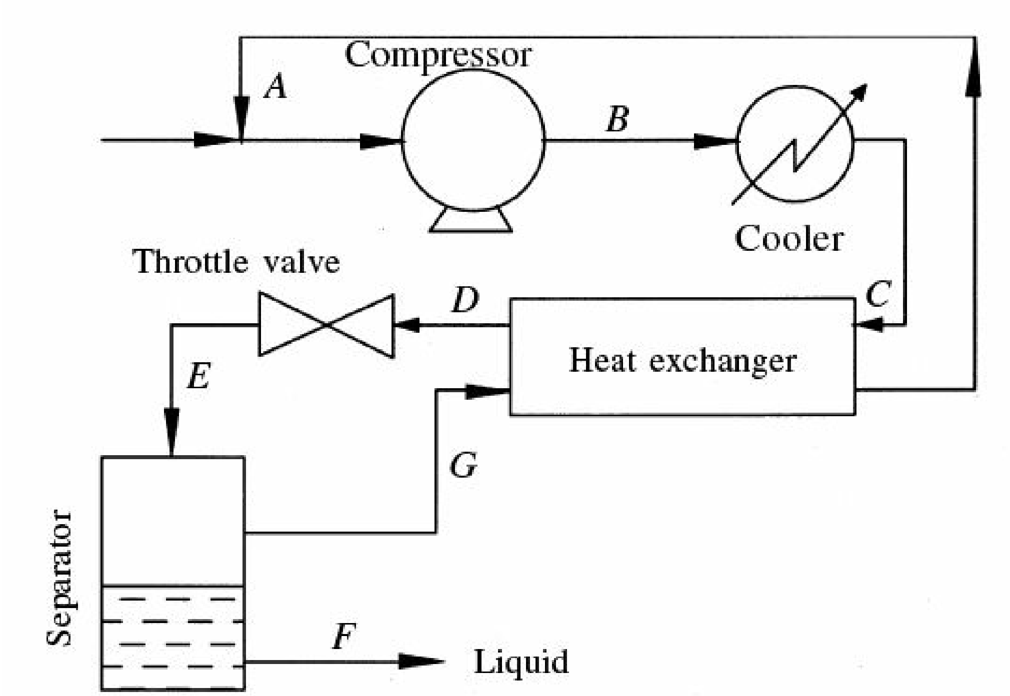


Fig. 5.16 The Linde process for gas-liquefaction.

The temperature of the air at the upstream side of the throttle valve is reduced to a sufficiently low value (e.g. 170 K at 100 bar) so that the constant enthalpy lines cut into the two-phase region. The cooling of air is achieved by passing it counter-currently to the unliquefied part of the air leaving the throttling valve. Fresh air and the unliquefied air form the input to the compressor. Air leaving the compressor is cooled by ambient air or by cooling water and subsequently by counter-current heat exchange with the recycled air. In the throttling valve, a fraction of the gas is liquefied. By applying the first law, it can be shown that the fraction x of the liquefied air is given by

$$H_C = xH_F + (1 - x)H_A$$

or

$$x = \frac{H_C - H_A}{H_F - H_A} \tag{5.73}$$

5.3.3 Isentropic Expansion

The Claude process for gas liquefaction utilises isentropic expansion of a compressed gas. The throttle valve, in Fig. 5.16, will be replaced by an expansion turbine. The process can be followed on the *T-S* diagram as shown in Fig. 5.17.

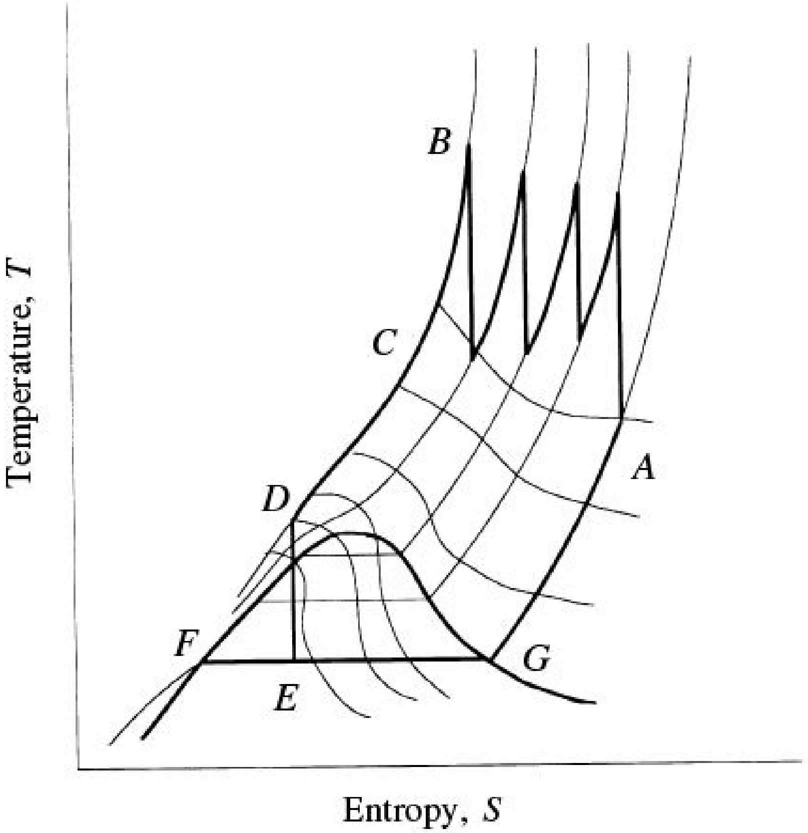


Fig. 5.17 *T-S* diagram for Claude process for gas liquefaction.

The vertical line *DE* represents the isentropic expansion. The fraction of gas liquefied can be determined as follows.

An energy balance around the heat exchanger, turbine, and the separator gives

$$xH_C = (1 - x)H_A + xH_F + W_S \qquad (5.74)$$

where W_S is the work delivered by the turbine. If the turbine operates adiabatically, the shaft work W_S is equal to the decrease in enthalpy of the gas during expansion.

$$W_S = H_D - H_E \qquad (5.75)$$

The fraction of the gas liquefied in an isentropic expansion is clearly greater than that in a free expansion. However, since the turbine is to be operated with a two-phase mixture, the isentropic expansion process has certain practical difficulties. To overcome these, only a portion of the gas leaving the compressor may be expanded isentropically. The remaining portion is cooled in a heat exchanger before it is expanded in a throttle valve. The saturated gas leaving the turbine is used to cool the portion of the gas that is throttled. In this way, the inlet stream to the valve can be cooled to a very low temperature, which will result in greater liquefaction.

The cost of power is an important consideration in the commercialisation of a liquefaction process, and hence, it is essential that the *thermodynamic efficiency* of the process is known. This is defined as the ratio of the minimum reversible work for the given process to the actual work. This can be evaluated as the product of two other efficiencies, viz., the *cycle efficiency* and *practical efficiency*.

$$\text{Cycle efficiency} = \frac{\text{Reversible work for the process}}{\text{Theoretical work for ideal operation}} \tag{5.76}$$

$$\text{Practical efficiency} = \frac{\text{Theoretical work for ideal operation}}{\text{Actual work for the cycle}} \tag{5.77}$$

The reversible work is the least possible amount of work that is necessary to effect a given change in the state of the system. It is given by the second law of thermodynamics as

$$-W = \Delta H - T_0 \Delta S \tag{5.78}$$

where T_0 is the temperature of the heat sink to which heat may be rejected in large quantities. The reversible work depends only on the initial and final states of the system and is independent of the cycle. The theoretical work for ideal operation—the quantity in the denominator of Eq. (5.76)—is evaluated as the work required by the given cycle if it is operated after eliminating all irreversible effects. The practical efficiency takes into account the imperfections of the equipment used in the cycle.

***EXAMPLE* 5.22** Steam at 2.54 bar is expanded to produce superheated steam at 1 bar and 385 K. Determine the fraction of liquid in the inlet stream and the temperature of the stream if

(a) The expansion is isenthalpic

(b) The expansion is isentropic.

The following data are taken from steam tables:

Enthalpy of saturated vapour at 2.54 bar = 2717 kJ/kg; enthalpy of saturated liquid at 2.54 bar = 538 kJ/kg; entropy of saturated vapour at 2.54 bar = 7.05 kJ/kg K; entropy of saturated liquid at 2.54 bar =1.61 kJ/kg K; enthalpy of superheated steam at 1 bar and 385 K = 2700 kJ/kg. Entropy of superheated steam at 1 bar and 385 K = 7.42 kJ/kg K.

Solution Let the fraction of the inlet stream, which is liquid be x.

(a) Enthalpy balance around the throttle valve:

$$x(538) + (1 - x)2717 = 2700$$

Therefore, $x = 0.008$ and temperature = 401 K (from the steam tables).

(b) The process being isentropic, entropy of inlet steam = entropy of steam leaving the turbine = 7.42 kJ/kg K. Since, the entropy of saturated vapour at the inlet pressure is 7.05 kJ/kg K, which is less than the entropy of steam leaving the turbine, the inlet steam is superheated. Therefore, $x = 0$; temperature of superheated steam having entropy of 7.42 kJ/kg K = 478 K.

***EXAMPLE* 5.23** Linde process is used for air liquefaction. The high-pressure gas leaving the compressor is at 120 bar and is cooled to 306 K (516 kJ/kg) before it is sent through the heat exchanger where it exchanges heat with low pressure gas leaving the separator at 2 bar. A 14 K approach is desired at the hot end of the exchanger so that the low-pressure gas leaving the exchanger is at 292 K (526 kJ/kg). Enthalpy of saturated liquid and saturated vapour at 2 bar are 121 kJ/kg and 314 kJ/kg, respectively. Determine:

(a) The fraction of the air liquefied during expansion

(b) Temperature of the air on the high-pressure side of the throttle valve.

Solution Refer Fig. 5.15.

$H_C = 516$ kJ/kg; $H_A = 526$ kJ/kg; $H_F = 121$ kJ/kg; $H_G = 314$ kJ/kg

(a) Using Eq. (5.73), we get the fraction of the liquefied air

$$x = \frac{H_C - H_A}{H_F - H_A} = \frac{516 - 526}{121 - 526} = 0.025$$

(b) Take an enthalpy balance around the heat exchanger. Assume no heat loss, then we get

$$H_C - H_D = (1 - x)(H_A - H_G)$$

$$516 - H_D = (1 - 0.025)(526 - 314)$$

Therefore, $H_D = 309$ kJ/kg. H_D is the enthalpy of air on the high-pressure (120 bar) side of the throttle valve. Temperature (=167 K) of this air is determined from *T-S* diagram for air. (For *T-S* diagram of air, see Perry and Chilton: *Chemical Engineers Handbook.*) Therefore, the temperature of air on the upstream side of the valve is 167 K.

5.4 THE STEAM-POWER PLANT

Steam-power plants operate on a closed cycle. The working fluid undergoes a series of operations and returns to the initial state. The thermodynamic analysis of steam power plants is done by comparing the performance of the actual cycles with certain idealised cycles. In the following sections, we discuss these ideal steam-power cycles with a view to suggest methods for the evaluation of their thermal efficiencies and point out how the actual cycles deviate from these ideal cycles. Though the working fluid considered is water, the discussion is applicable for vapour-power cycles in general.

5.4.1 Rankine Cycle

The components of a *Rankine cycle*, also known as the *standard vapour-power cycle* are shown in Fig. 5.18.

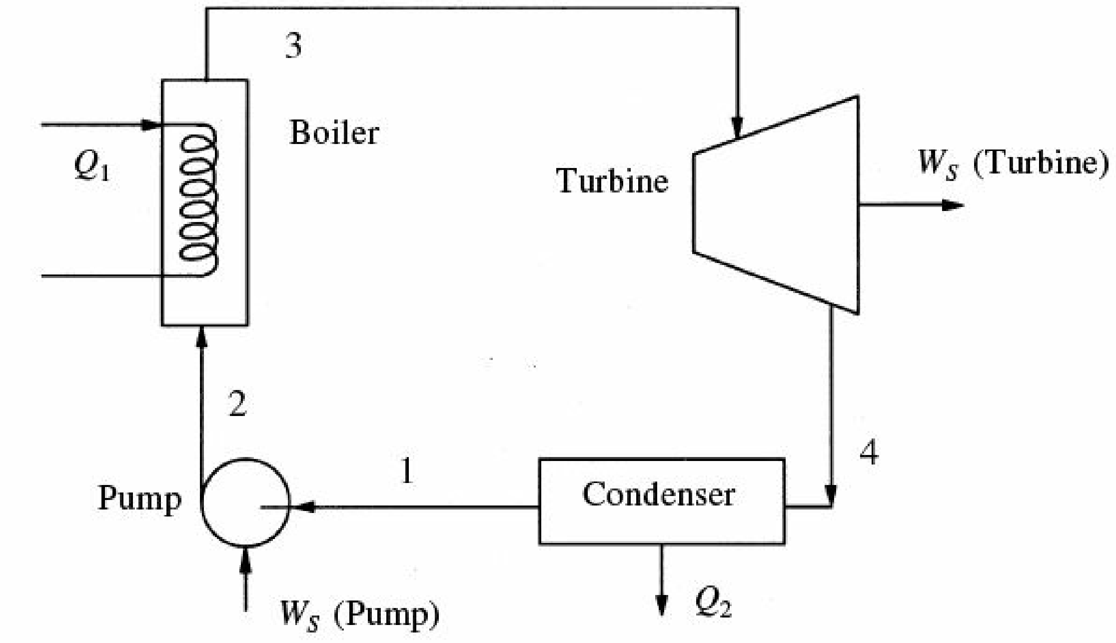


Fig. 5.18 Rankine cycle.

Water at low temperature and pressure is compressed isentropically to the boiler pressure by the feed pump (1–2). In the boiler, heat is supplied to the water at constant pressure, whereby, its temperature rises to the saturation temperature corresponding to the pressure in the boiler. Further supply of heat results in the evaporation of water and in superheating the vapour, thus produced (2–3). The superheated vapour at the elevated pressure is then allowed to expand isentropically in a turbine to the condenser pressure (3–4). In the condenser, the low-pressure exhaust steam from the turbine gives out its heat to the cooling water at constant pressure (4–1). The saturated liquid water leaving the condenser then enters the feed pump and the cycle is repeated.

The cycle is represented on a *T-S* diagram, as illustrated in Fig. 5.19(a). Let Q_1 be the heat absorbed at constant pressure in the boiler and Q_2 be the heat rejected at constant pressure to the cooling water in the condenser, both correspond to unit mass of the working fluid. Then,

$$Q_1 = H_3 - H_2, \qquad Q_2 = H_4 - H_1$$

$$\boxed{\text{Net work obtained per unit mass of water} = (H_3 - H_2) - (H_4 - H_1)} \tag{5.79}$$

$$\boxed{\text{Efficiency of the Rankine cycle, } \eta = \frac{W_{\text{net}}}{Q_1} = \frac{(H_3 - H_2) - (H_4 - H_1)}{H_3 - H_2}} \tag{5.80}$$

In Fig. 5.19(b), is shown the *T-S* diagram of a Carnot engine operating between the same average temperature levels. A Carnot cycle, as discussed earlier, consists of two reversible adiabatic operations and two reversible isothermal operations. Comparing the preceding figures, it can be readily concluded that the efficiency of the Rankine cycle is less than that of a Carnot cycle operating between the same thermal reservoirs. A question that may arise naturally is that, why should we use the Rankine cycle as the ideal cycle for assessing the performance of actual cycles, rather than a Carnot cycle? One of the reasons for this is the practical difficulty associated with the operation of the turbine and the feed pump with a mixture of liquid and vapour. A turbine that operates with an input of saturated steam and discharges a mixture of vapour and liquid may lead to severe erosion problems. Also, it is difficult to operate a pump, which takes in a two-phase mixture and discharges a saturated liquid. The Rankine cycle is free from these problems and is, therefore, accepted as a model for the actual vapour-power cycle.

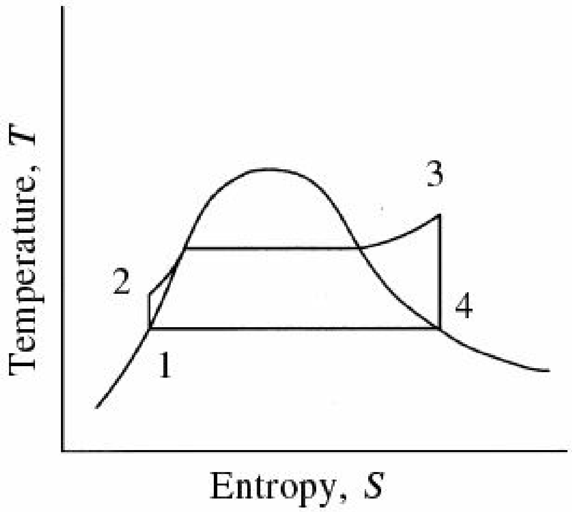


Fig. 5.19(a) The Rankine cycle on a T-S diagram.

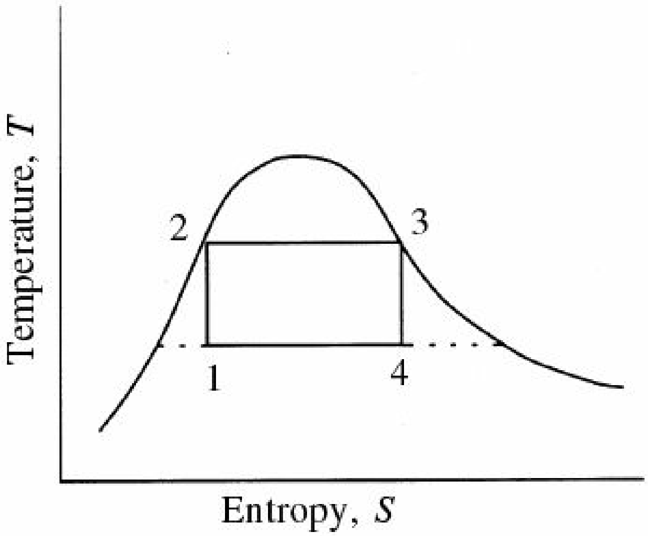


Fig. 5.19(b) Ideal Carnot cycle on the T-S diagram.

***EXAMPLE* 5.24** In a 1-MW steam power plant, superheated steam at 2800 kPa and 598 K enters the turbine and it is expanded to the condenser pressure of 5 kPa. Assuming an isentropic turbine efficiency of 85% and an isentropic pump efficiency of 80%, determine the following:

(a) The ideal Rankine cycle efficiency for the stated conditions

(b) The thermal efficiency of the plant

(c) The rate of steam production

The following data are taken from the steam tables:

Specific volume of saturated liquid at 5 kPa is $1.005 \square 10^{-3}$ m^3/kg.

State of water	*Enthalpy*	*Entropy*
	(kJ/kg)	(kJ/kg K)
Saturated liquid at 5 kPa	138	0.4764
Saturated vapour at 5 kPa	2562	8.3951
Superheated steam at 2800 kPa and 598 K	3063	6.6875

Solution (a) Refer Fig. 5.19(b) and consider the feed water pump. The work required by the pump operating isentropically is given by

$$W_S = -\int_{P_1}^{P_2} V\,dP = H_2 - H_1 \tag{5.17}$$

Since the saturated liquid entering the pump is incompressible,

$$-W_S = V(P_2 - P_1) = 1.005 \times 10^{-3} \times (2800 - 5) \times 10^3 = 2.809 \times 10^3 \text{ J/kg} = 2.809 \text{ kJ/kg}$$

Therefore,

$$H_2 = H_1 + 2.809 = 138 + 2.809 = 140.809 \text{ kJ/kg}$$

$H_3 = 3063$ kJ/kg and $S_3 = 6.6875$ kJ/kg K. To determine the enthalpy of steam leaving the turbine, its quality should be known. For this, consider the isentropic expansion in the turbine.

$$S_4 = S_3 = 6.6875 \text{ kJ/kg K}$$

$$S_4 = S_l + x(S_v - S_l) = 0.4764 + x(8.3951 - 0.4764)$$

where x is the fraction of steam that is vapour. $x = 0.784$.

$$H_4 = H_l + x(H_v - H_l) = 138 + 0.784\,(2562 - 138) = 2038 \text{ kJ/kg}$$

The efficiency of ideal Rankine cycle is given by Eq. (5.80):

$$\eta = \frac{W_{\text{net}}}{Q_1} = \frac{(H_3 - H_2) - (H_4 - H_1)}{H_3 - H_2}$$

$$= \frac{(3063 - 140.81) - (2038 - 138)}{3063 - 140.81} = 0.35 = 35\%$$

(b) The actual work requirement in the pump will be greater than that in an ideal isentropic process. As the efficiency is 80%, the actual required work is

$2.809/0.8 = 3.5$ kJ/kg $= H_2' - H_1$

Hence the enthalpy of water leaving the feed water pump is

$H_2' = H_1 + 3.5 = 138 + 3.5 = 141.5$ kJ/kg

The work output of the turbine in isentropic expansion is

$(H_3 - H_4) = 3063 - 2038 = 1025$ kJ/kg

Since the efficiency is 85%, the actual work output is

0.85 □ 1025 kJ/kg = 871 kJ/kg $= H_3 - H_4'$

Therefore, the actual enthalpy of steam leaving the turbine is

$H_4' = H_3 - 871 = 3063 - 871 = 2192$ kJ/kg

The efficiency of the actual cycle is

$$\text{Efficiency } \eta = \frac{W_{\text{net}}}{Q_1} = \frac{(H_3 - H_2') - (H_4' - H_1)}{H_3 - H_2'} = \frac{(3063 - 141.5) - (2192 - 138)}{3063 - 141.5} = 0.297$$

The actual efficiency is 29.7%.

(c) Net work output is

W_{net} = h □ Q_1 = 0.297 □ (3063 – 141.5) = 868 kJ/kg

That is, 1 kg of steam expanding in the turbine will deliver a net work of 868 kJ. For the rated capacity of the plant, the work output = 1000 kJ/s = 3.6 □ 10^6 kJ/h. Therefore, steam produced in the boiler = 3.6 □ 10^6/868 = 4147.5 kg/h.

5.4.2 Reheat Cycle

The efficiency of Rankine cycle can be improved by increasing the pressure in the boiler. However, this will lead to an increase in the proportion of the liquid in the exhaust from the turbine. This problem is circumvented in a reheat cycle. The *reheat cycle* uses high pressure during the absorption of heat, yet eliminates the presence of excessive moisture in the discharge from the turbine. The cycle is presented in Fig. 5.20.

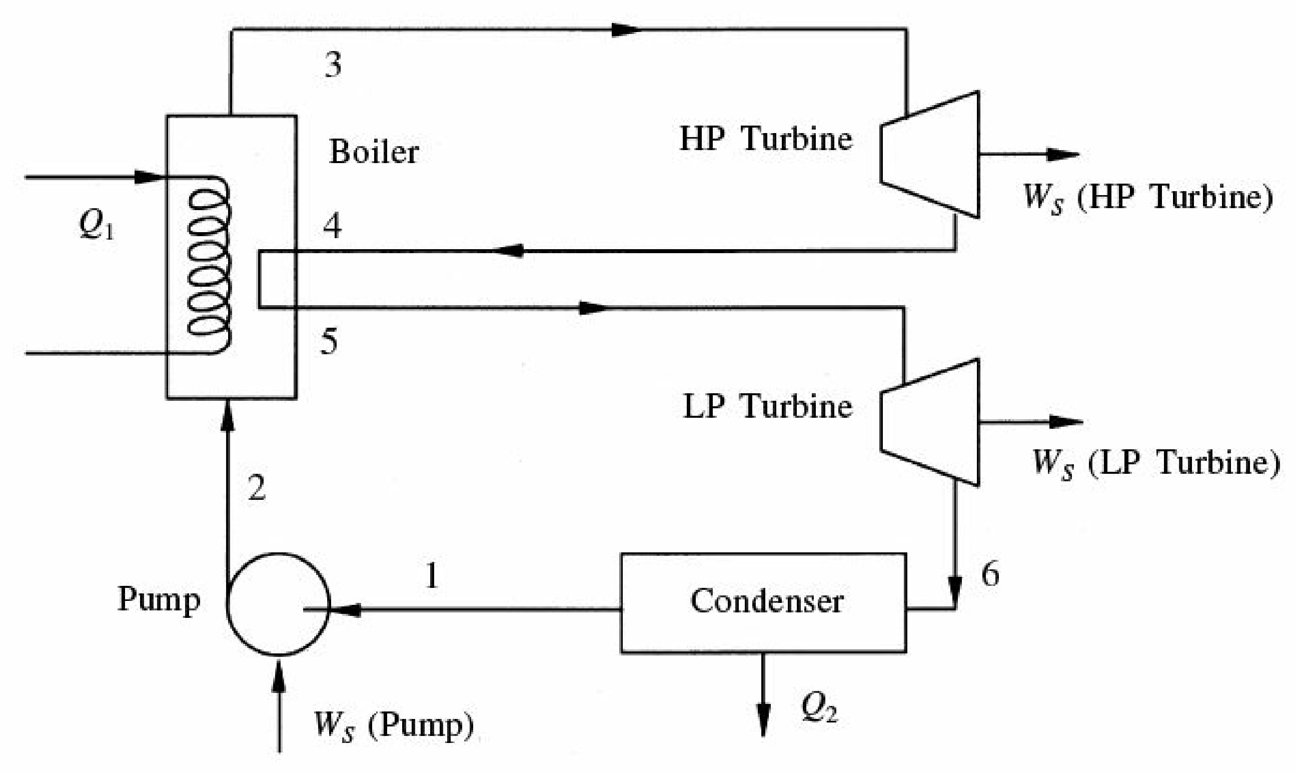


Fig. 5.20 Reheat cycle.

The superheated steam leaving the boiler is admitted to a high-pressure turbine, and after expansion is returned to the boiler for reheating. It is heated to a high temperature in the boiler, and then sent to a low-pressure turbine where it is expanded to the condenser pressure. The *T-S* diagram for the reheat cycle is shown in Fig. 5.21.

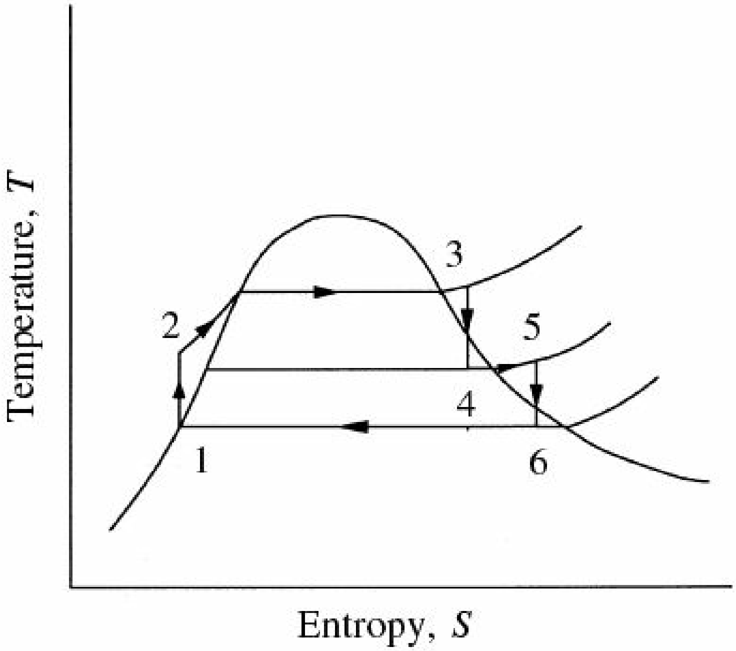


Fig. 5.21 The reheat cycle on *T-S* diagram.

Total heat absorbed by the fluid = $(H_3 - H_2) + (H_5 - H_4)$

Heat rejected by the fluid = $(H_6 - H_1)$

Net work obtained = Heat absorbed – Heat rejected = $(H_3 - H_2) + (H_5 - H_4) - (H_6 - H_1)$ (5.81)

$$\text{Efficiency } \eta = \frac{\text{Net work}}{\text{Heat input}} = \frac{(H_3 - H_2) + (H_5 - H_4) - (H_6 - H_1)}{(H_3 - H_2) + (H_5 - H_4)} \tag{5.82}$$

The net work obtained may also be determined as the sum of the work output from the high-pressure and low-pressure turbines minus the work input to the feed water pump. Since, the turbines and the pump act isentropically, $W_S = -\Delta H$ and

$$\text{Net work output} = (H_3 - H_4) + (H_5 - H_6) - (H_2 - H_1) \tag{5.83}$$

The right side in Eq. (5.83) gives the same value as the numerator on the right side of Eq. (5.82).

***EXAMPLE* 5.25** Superheated steam at 7600 kPa and 673 K enters a high-pressure turbine in a 1 MW steam power plant employing steam reheat cycle, where it is expanded to a pressure of 1400 kPa. The exhaust steam is reheated to 658 K and sent to the low-pressure turbine, where it is expanded to 5 kPa. Assume isentropic expansion in the turbine and isentropic compression in the feed water pump. Determine:

(a) The work output for the high-pressure and low-pressure turbines.
(b) The thermal efficiency of the cycle.
(c) The rate of steam circulation.

The following data are taken from steam tables:

Specific volume of saturated liquid at 5 kPa = 1.005 □ 10^{-3} m^3/kg.

State of water	*Enthalpy* (kJ/kg)	*Entropy* (kJ/kg K)
Saturated liquid at 5 kPa	138	0.4764
Saturated vapour at 5 kPa	2562	8.3951
Saturated liquid at 1400 kPa	830	2.2842
Saturated vapour at 1400 kPa	2790	6.4693
Superheated steam at 1400 kPa and 658 K	3226	7.2558
Superheated steam at 7600 kPa and 673 K	3150	6.4022

Solution (a) The work output of high-pressure turbine is $H_3 - H_4$. Here, H_3 = 3150 kJ/kg. To determine H_4, the enthalpy of steam leaving the high-pressure turbine, its quality should be known. Let the fraction of steam in the vapour state be x. Then the entropy at 4 is

$$S_4 = 2.2842 + x(6.4693 - 2.2842)$$

As the expansion process is isentropic,

$$S_4 = S_3 = 6.4022 \text{ kJ/kg K}$$

Therefore,

$$S_4 = 2.2842 + x(6.4693 - 2.2842) = 6.4022$$

Solving this we get, $x = 0.984$

$$H_4 = 830 + 0.984(2790 - 830) = 2759 \text{ kJ/kg}$$

[*Note*: The *HS* diagram, also known as the *Mollier diagram*, may also be used to determine the values of the enthalpy and entropy of steam at various conditions. Mollier diagram will be discussed in detail in Chapter 6.]

The work output of the high-pressure turbine = 3150 – 2759 = 391 kJ/kg

Similarly,

$$S_6 = 0.4764 + x(8.3951 - 0.4764) = S_5 = 7.2558 \text{ kJ/kg K}$$

Thus, $x = 0.856$ and

$$H_6 = 138 + 0.856(2562 - 138) = 2213 \text{ kJ/kg}$$

The work output from the low-pressure turbine is

$$H_5 - H_6 = 3226 - 2213 = 1013 \text{ kJ/kg}$$

(b)

$$\text{Efficiency } \eta = \frac{\text{Net work}}{\text{Heat input}} = \frac{(H_3 - H_2) + (H_5 - H_4) - (H_6 - H_1)}{(H_3 - H_2) + (H_5 - H_4)} \tag{5.82}$$

Work output of the feed water pump,

$$-W_S = H_2 - H_1 = \int_{P_1}^{P_2} V\,dP = V(P_2 - P_1)$$

or

$H_2 - H_1 = 1.005 \square 10^{-3} \square (7600 - 5) \square 10^3 = 7633$ J/kg = 7.633 kJ/kg

Since,
$H_1 = 138$ kJ/kg

$H_2 = H_1 + 7.633 = 138 + 7.633 = 145.6$ kJ/kg

$$\eta = \frac{(H_3 - H_2) + (H_5 - H_4) - (H_6 - H_1)}{(H_3 - H_2) + (H_5 - H_4)}$$

$$= \frac{(3150 - 145.6) + (3226 - 2759) - (2213 - 138)}{(3150 - 145.6) + (3226 - 2759)} = 0.402$$

Thermal efficiency is 40.2%.

(c) The net work output is given by the numerator of Eq. (5.82), $W_{\text{net}} = 1396.4$ kJ/kg. The rate of circulation of steam for 1000 kW of net work output = 1000 □ 3600/1396.4 = 2578.1 kg/h.

5.4.3 Regenerative Cycle

In the Rankine cycle, the feed water enters the boiler in a sub-cooled state corresponding to the pressure in the boiler and it is heated to the saturation temperature before vaporisation begins. But the heating medium in the boiler is at a very high temperature. Because of this large difference between the temperature of the heating medium and that of the feed water, the heat interaction in the boiler is a highly irreversible process. The process can be carried out more or less reversibly, if the water from the condenser rather than being pumped directly to the boiler, is first heated by steam extracted from various stages of expansion in the turbine. The heating process thus approaches a reversible isothermal heat interaction process. In this way, the thermal efficiency of the Rankine cycle could be greatly improved. The Rankine cycle modified in this manner is known as the *regenerative cycle*. A regenerative cycle with a single feed heater is shown in Fig. 5.22.

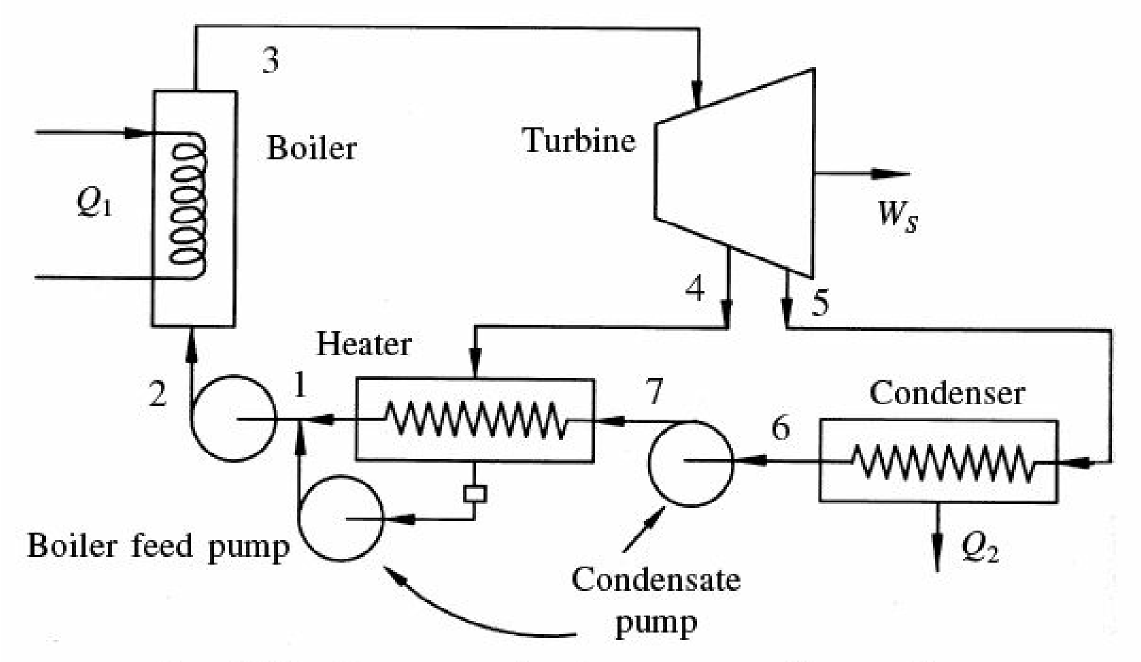


Fig. 5.22 Components of a regenerative cycle.

The *T-S* diagram of an ideal regenerative cycle is presented in Fig. 5.23. Assume that 1 kg of superheated steam (3) enters the high-pressure side of the turbine. Let m kg of the steam is extracted from certain point in the turbine (3–4) and the remaining $(1 - m)$ kg steam be allowed to expand to the condenser pressure (3–5). The extracted steam is admitted to the feed water heater where it releases its latent heat (4–1). This heat is transferred to the feed water leaving the condenser (7–1) that is being pumped by the condensate pump (6–7). Under ideal conditions, the temperature of the m kg of condensed steam that is withdrawn through the steam trap and that of the $(1 - m)$ kg feed water which gets heated on its passage through the heater, are the same (1). These two streams are mixed together and the combined stream is pumped to the boiler pressure (1–2). The latent heat of vaporisation and the superheat required by the steam are supplied in the boiler (2–3) and the cycle is repeated.

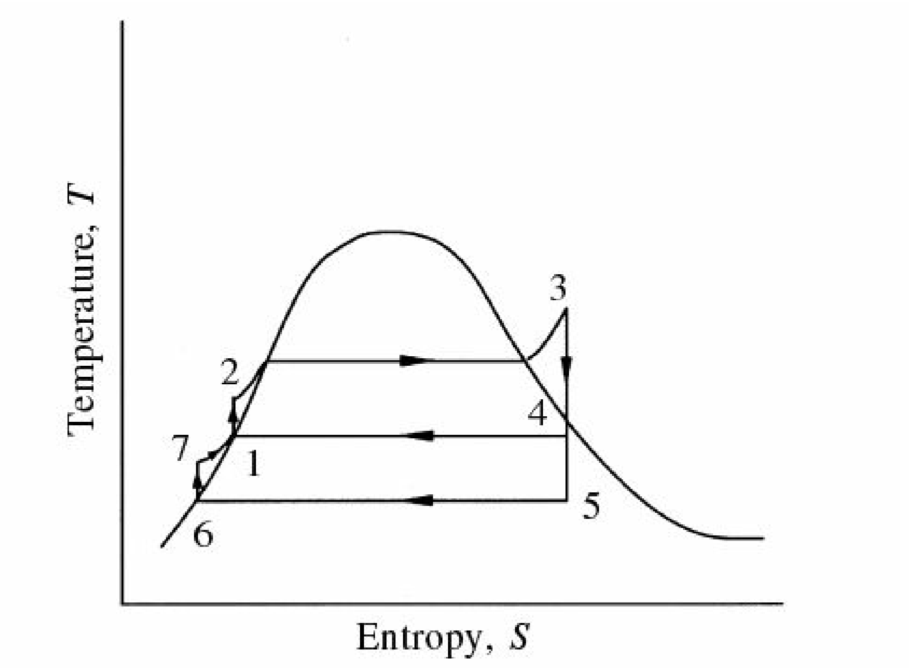


Fig. 5.23 The regenerative cycle on *T-S* diagram.

Heat supplied in the boiler = $Q_1 = H_3 - H_2$

Heat rejected in the condenser = $Q_2 = (1 - m)(H_5 - H_6)$

The net work obtained = $W_{\text{net}} = Q_1 - Q_2 = (H_3 - H_2) - (1 - m)(H_5 - H_6)$ (5.84)

$$\boxed{\text{Thermal efficiency } \eta = \frac{W_{\text{net}}}{Q_1} = \frac{(H_3 - H_2) - (1 - m)(H_5 - H_6)}{H_3 - H_2}} \tag{5.85}$$

***EXAMPLE*5.26** Superheated steam at 2800 kPa and 598 K enters the high-pressure side of the turbine in a steam power plant. A fraction of the steam is withdrawn from a point in the turbine at a pressure of 275 kPa and is sent to the feed water heater operated at 275 kPa and the remaining steam is expanded to the condenser pressure of 5 kPa. Assume that the expansion in the turbine and the compression in the boiler feed water pump are isentropic and that the power required by the condensate pump is negligible. Determine the fraction of steam withdrawn from the turbine and the thermal efficiency of the cycle.

Specific volume of saturated liquid at 275 kPa =1.070 ☐ 10^{-3} m^3/kg

State of water	*Enthalpy*	*Entropy*

	(kJ/kg)	(kJ/kg K)
Saturated liquid at 5 kPa	138	0.4764
Saturated vapour at 5 kPa	2562	8.3951
Saturated liquid at 275 kPa	549	1.6408
Saturated vapour at 275 kPa	2721	7.0209
Superheated steam at 2800 kPa and 598 K	3063	6.6875

Solution Refer to Fig. 5.23. Take an energy balance around the feed water heater. Let m be the fraction of steam extracted from the turbine.

$$m(H_4 - H_1) = (1 - m)(H_1 - H_7)$$

As the power input to the condensate pump is negligible, $H_7 = H_6$, the enthalpy of saturated liquid at 5 kPa = 138 kJ/kg. H_1 = 549 kPa. To determine the enthalpy H_4, the quality of steam is to be determined first. We know that,

$$S_4 = S_3 = 1.6408 + x(7.0209 - 1.6408) = 6.6875$$

Solving this, $x = 0.938$.

$$H_4 = 549 + 0.938(2721 - 549) = 2586 \text{ kJ/kg}$$

Substituting these values in the energy balance equation,

$$m(2586 - 549) = (1 - m)(549 - 138)$$

Solving this we get, $m = 0.168$. That is, the fraction of steam extracted = 0.168. The work input to the feed water pump is

$$H_2 - H_1 = V(P_2 - P_1) = 1.070 \square 10^{-3} (2800 - 275) \square 10^3 \square 10^{-3} = 2.702 \text{ kJ/kg}$$

Since, $H_1 = 549$ kJ/kg,

$$H_2 = 549 + 2.702 = 551.702 \text{ kJ/kg}$$

Considering the isentropic expansion in the turbine,

$$S_5 = S_3 = 6.6875 = 0.4764 + x(8.3951 - 0.4764)$$

Solving this we get, $x = 0.784$ so that,

$$H_5 = 138 + 0.784(2562 - 138) = 2038 \text{ kJ/kg}$$

Thermal efficiency is given by Eq. (5.85)

$$\eta = \frac{(H_3 - H_2) - (1 - m)(H_5 - H_6)}{H_3 - H_2} = \frac{(3063 - 551.7) - (1 - 0.168)(2038 - 138)}{3063 - 551.7} = 0.371$$

Thermal efficiency is 37.1%.

5.5 INTERNAL COMBUSTION ENGINES

The steam power plants and internal combustion engines are broadly designated as heat engines, because in both, the chemical energy of a fuel is converted into heat energy, which is utilised to perform mechanical work. *Internal combustion engine* differs from steam power plants such that the former operates on open cycles whereas the latter on closed cycles. In internal combustion engines, the working fluid which is a mixture of air and fuel is burned inside the engine and after a series of processes which results in the production of mechanical work, the combustion products are discarded. The working fluid does not undergo a cycle of changes in an internal combustion engine, as does the steam in a steam power plant. However, the engine operates on a closed mechanical cycle. The internal combustion engines involve no transfer of heat through surfaces, which restrict the temperature and pressure, as is the case with the boiler of the steam power plants. The high temperatures and the absence of heat transfer surfaces are the main advantages of internal combustion engines over steam power generation systems.

The thermodynamic analysis of internal combustion engine is made possible by devising ideal closed cycles with air as the working fluid and by comparing the performance of actual cycles with these ideal air-standard cycles. The assumptions involved in this approach are:

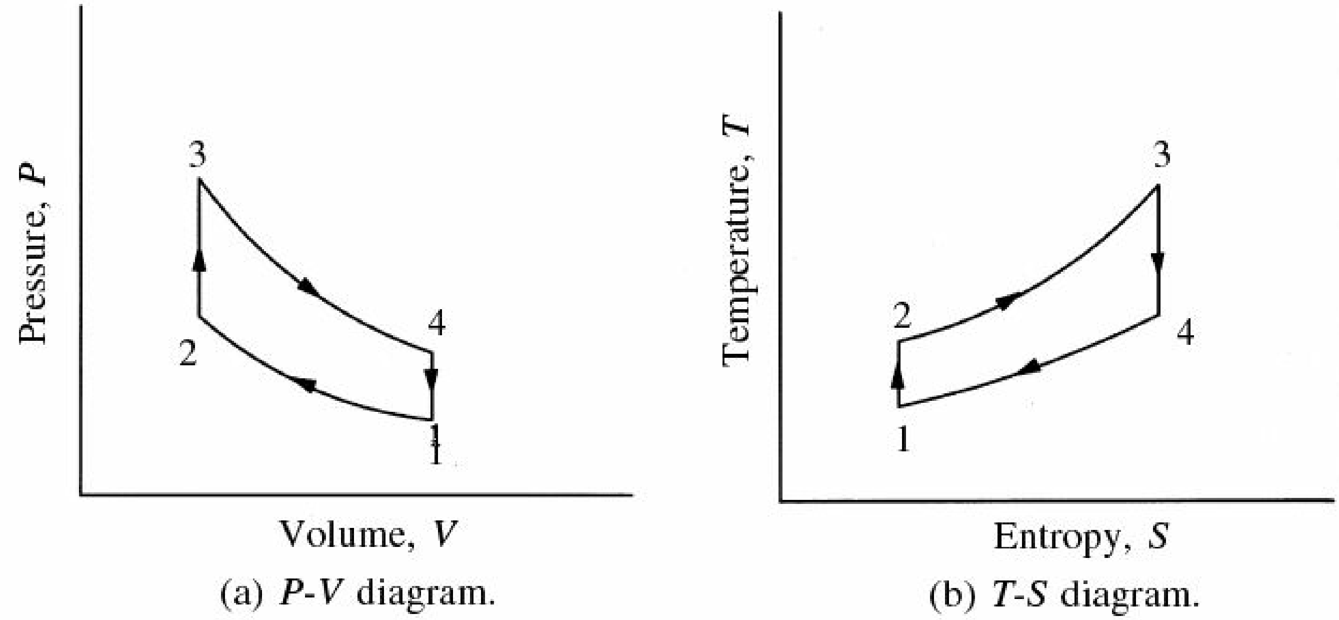
1. The working fluid is a fixed mass of air and it undergoes no chemical change. Air is assumed to behave as an ideal gas.
2. The combustion process in the actual cycle is replaced by a heat transfer process in the ideal cycle. Heat is assumed to be transferred from an external heat source.
3. The exhaust stroke in the actual engine is replaced by a heat rejection step in the ideal cycle. Heat is assumed to be transferred to the surroundings.
4. The air is assumed to have constant specific heat and all the processes are internally reversible.

The Otto cycle and the Diesel cycle are the two important air-standard cycles used for the analysis o internal combustion engines.

5.5.1 Otto Cycle

The *P-V* and *T-S* diagram of the air-standard Otto cycle are shown in Fig. 5.24. The cycle is characterised by the following processes:

1. *Process 1–2:* A given mass of air, assumed an ideal gas, is compressed isentropically during the inward stroke of the piston. As a result, the temperature of the gas increases from T_1 to T_2.



(a) *P-V* diagram. (b) *T-S* diagram.

Fig. 5.24 The Otto cycle on *P-V* and *T-S* diagrams.

2. *Process 2–3:* Heat (Q_1) is supplied to the system at constant volume by allowing the system to come in contact with a high-temperature reservoir. The heat transfer results in the increase in temperature from T_2 to T_3. It also increases the pressure and entropy of the fluid. (In actual engines, this process is achieved approximately by igniting the compressed gas by means of a spark. The combustion of the fuel/air mixture occurs so rapidly that it may be approximated by a constant volume process).

3. *Process 3–4:* The air is expanded isentropically during the outward stroke of the piston. Both the pressure and temperature decrease during this process. Temperature decreases from T_3 to T_4 during this step. (In actual engines, the products of combustion at very high pressure and temperature expand approximately adiabatically during this step.)

4. *Process 4–1:* Heat (Q_2) is transferred from the system reversibly, at constant volume to a low-temperature reservoir. The temperature, pressure, and entropy of the system decrease during this stage. (In actual engine, during the corresponding process the exhaust valve opens and the pressure falls rapidly at nearly constant volume.)

Heat absorbed, $Q_1 = mC_V(T_3 - T_2)$

Heat rejected, $Q_2 = mC_V(T_4 - T_1)$

The thermal efficiency of the cycle, $\eta = \frac{W_{\text{net}}}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$ (5.86)

The thermal efficiency can be expressed in terms of the compression ratio also. The temperature and volume in an isentropic process are related as given by Eq. (3.22).

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}, \quad \frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{\gamma - 1}$$

As processes 2–3 and 4–1 occur at constant volume, $V_4 = V_1$ and $V_3 = V_2$. It follows that,

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} = r^{\gamma - 1}$$

where r is the compression ratio defined as

$$r = \frac{V_1}{V_2} = \frac{V_4}{V_3}$$

We now have,

$$T_1 = \frac{T_2}{r^{\gamma - 1}} \quad \text{and} \quad T_4 = \frac{T_3}{r^{\gamma - 1}} \tag{5.87}$$

Substituting Eq. (5.87) into Eq. (5.86), we get the expression for thermal efficiency in terms of the compression ratio.

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2} = 1 - \frac{T_3 - T_2}{T_3 - T_2}\left(\frac{1}{r}\right)^{\gamma - 1} = \boxed{1 - \left(\frac{1}{r}\right)^{\gamma - 1}} \tag{5.88}$$

We see that the thermal efficiency of an Otto engine depends on the compression ratio and the ratio of specific heats, g. For a specified value of g, the efficiency increases with increase in compression ratio; the increase is rapid at low values of r, but slow at high values of r. The upper limit of the compression ratio is set by the ignition temperature of the fuel. If the compression ratio exceeds this limit, the temperature of the fuel-air mixture exceeds the ignition temperature, resulting in uncontrolled combustion of the fuel-air mixture, a condition known as *knocking*.

***EXAMPLE* 5.27** The compression ratio in an air-standard Otto cycle is 8. The temperature and pressure at the beginning of the compression stroke are 290 K and 100 kPa. Heat transferred per cycle is 450 kJ/kg of air. The specific heat of air are C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K. Determine the following:

(a) The pressure and temperature of air at the end of each process
(b) The thermal efficiency
(c) The work done by kg of air
(d) The mean effective pressure.

Solution (a) The cycle is represented in Fig. 5.24. $P_1 = 100$ kPa and $T_1 = 290$ K. The volume of 1 kg of air at this condition is V_1. It is evaluated using the ideal gas equation

$$V_1 = \frac{nRT_1}{P_1} = \frac{1 \times 8314 \times 290}{29 \times 10^5} = 0.8314 \text{ m}^3$$

Conditions at state 2: $r = 8$; Therefore, $V_2 = V_1/8 = 0.1039$ m^3. $C_P = 1.005$ kJ/kg K and $C_V = 0.718$ kJ/kg K. Therefore,

$$\gamma = \frac{C_P}{C_V} = 1.4$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = r^{\gamma-1} = 8^{0.4} = 2.297, \text{ therefore, } T_2 = 2.297 \times 290 = 666.2 \text{ K}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma} = 8^{1.4} = 18.38 \text{ , therefore, } P_2 = 18.38 \times 100 = 1838 \text{ kPa}$$

Conditions at 3: 2–3 is a constant volume process. $V_3 = V_2 = 0.1039$ m^3.
Heat supplied is obtained as

$$Q_1 = C_V(T_3 - T_2)$$

$$450 = 0.718\,(T_3 - T_2)$$

$$T_3 = 450/0.718 + 666.2 = 1292.9 \text{ K}$$

$$\frac{P_3}{P_2} = \frac{T_3}{T_2} = \frac{1292.9}{666.2} = 1.9407$$

This gives

$$P_3 = 1838 \times 1.9407 = 3567 \text{ kPa}$$

Conditions at 4:

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{\gamma-1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = 8^{0.4} = 2.297$$

$$T_4 = 1292.9/2.297 = 562.9 \text{ K}$$

$$\frac{P_3}{P_4} = \left(\frac{V_4}{V_3}\right)^{\gamma} = 8^{1.4} = 18.38$$

$$P_4 = 3567/18.38 = 194 \text{ kPa}$$

Heat rejected during the constant volume process 4–1 is

$Q_2 = C_V(T_4 - T_1) = 0.718 \square (562.9 - 290) = 195.9$ kJ/kg

(b) Thermal efficiency is calculated using Eq. (5.88).

$$\eta = 1 - \left(\frac{1}{r}\right)^{\gamma - 1} = 1 - (1/8)^{0.4} = 0.565$$

(*Note:* The efficiency may also be calculated as

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{450 - 195.9}{450} = 0.565)$$

(c) Work done is equal to

$$Q_1 - Q_2 = 450 - 195.9 = 254.1 \text{ kJ/kg}$$

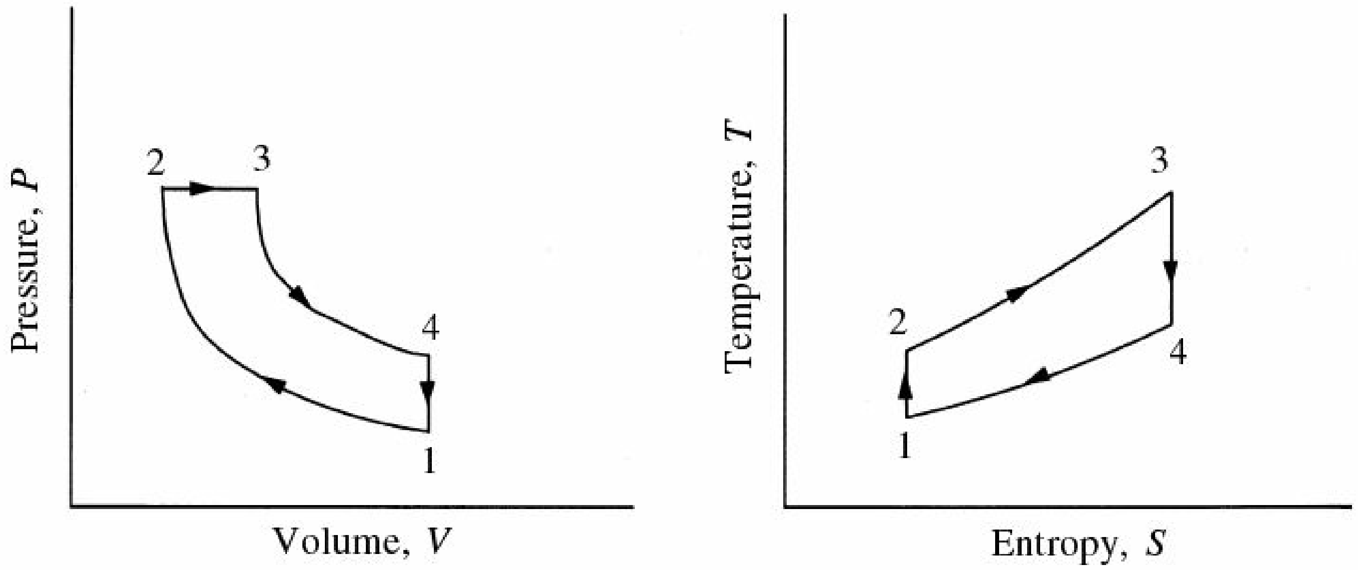
(d) Mean effective pressure, P_m is found such that the product of the mean effective pressure and the piston stroke gives the net work.

$$P_m \times (0.8314 - 0.1039) = 254.1$$

$$P_m = 349.3 \text{ kPa}$$

5.5.2 Diesel Cycle

The *P-V* and *T-S* diagram of the air-standard Diesel cycle are shown in Fig. 5.25. The Diesel engines differ from the Otto engines, insofar as in the former, the temperature at the end of compression, exceeds the fuel ignition temperature and the combustion of fuel occur spontaneously. The *Diesel cycle* consists of the following processes:



(a) *P-V* diagram. (b) *T-S* diagram.

Fig. 5.25 The Diesel cycle on *P-V* and *T-S* diagrams.

1. *Process 1–2:* Air assumed to behave as an ideal gas, is compressed isentropically to a high temperature and pressure. The temperature of the gas increases from T_1 to T_2.

2. *Process 2–3:* Heat Q_1 is supplied to the fluid at constant pressure. The temperature increases to T_3. (In actual engines, this is accomplished by injecting the fuel to the hot compressed air at the end of the compression stroke. The fuel ignites spontaneously and the piston starts moving outward slowly.)

3. *Process 3–4:* The gas undergoes an isentropic expansion by which the pressure and temperature of the gas decrease. The temperature attained after the expansion process is T_4.

4. *Process 4–1:* Heat Q_2 is rejected at constant volume thus decreasing the temperature and pressure of the gas further. (In actual engines, during the corresponding stage, the discharge port opens and the combustion products are exhausted.)

Heat absorbed $Q_1 = mC_P(T_3 - T_2)$

Heat rejected $Q_2 = mC_V(T_4 - T_1)$

Thermal efficiency is obtained as

$$\eta = \frac{W_{\text{net}}}{Q_1} = 1 - \frac{Q_2}{Q_1} = \boxed{1 - \frac{1}{\gamma}\frac{(T_4 - T_1)}{(T_3 - T_2)}} \qquad (5.89)$$

In Eq. (5.89), γ = ratio of specific heats, C_P/C_V. The ratio of the volumes at the beginning and at the end of the compression stroke is called the *compression ratio* and it is denoted by r. Therefore, $r = V_1/V_2$. The ratio of volumes at the end and beginning of the constant pressure heat addition process is called the *cut-off ratio* and it is denoted by r_c. Thus, $r_c = V_3/V_2$.

For the isentropic compression step 1–2, $T_2/T_1 = (V_1/V_2)^{\gamma-1} = r^{\gamma-1}$, so that

$$T_2 = T_1 r^{\gamma-1} \qquad (5.90)$$

For the constant pressure process 2–3, $T_3/T_2 = V_3/V_2 = r_c$, so that

$$T_3 = T_2 r_c = T_1 r_c r^{\gamma-1} \tag{5.91}$$

For the isentropic expansion step 3–4,

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{\gamma-1} = \left(\frac{V_4}{V_2} \times \frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{V_1}{V_2} \times \frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{r}{r_c}\right)^{\gamma-1}$$

Hence,

$$T_4 = T_3 \left(\frac{r_c}{r}\right)^{\gamma-1} = T_1 r_c^{\gamma} \tag{5.92}$$

Substituting Eqs. (5.90)–(5.92) in Eq. (5.89) and simplifying the result, we get the expression for thermal efficiency as

$$\boxed{\eta = 1 - \frac{1}{\gamma}\,\frac{1}{r^{\gamma-1}}\left(\frac{r_c^{\gamma} - 1}{r_c - 1}\right)} \tag{5.93}$$

For the same compression ratio *r*, the Otto cycle is more efficient than the Diesel cycle. However, in Diesel engine, it is possible to achieve a compression ratio higher than that attainable in an Otto engine, which in turn, results in high efficiencies.

***EXAMPLE* 5.28** A Diesel engine operates with a compression ratio of 15. The pressure and temperature at the beginning of the compression stroke are 100 kPa and 300 K. Heat is transferred at the rate of 500 kJ/kg of the working fluid per cycle. Determine:

(a) The pressure and temperature at each stage of the cycle
(b) The work done per kg air
(c) The thermal efficiency
(d) The mean effective pressure

Take the specific heats of air as $C_P = 1.005$ kJ/kg K and $C_V = 0.718$ kJ/kg K.

Solution The cycle is illustrated in Fig. 5.25.

(a) Here, $r = 15$, $T_1 = 300$ K, $P_1 = 100$ kPa, and g = $C_P/C_V = 1.4$.

Isentropic compression 1–2:

$$V_1 = \frac{RT}{MP} = \frac{8314 \times 300}{29 \times 10^5} = 0.86 \text{ m}^3/\text{kg}$$

Therefore,

$$\frac{T_2}{T_1} = r^{\gamma-1} = 15^{0.4} = 2.954$$

$$T_2 = 886.2 \text{ K}$$

Also,

$$\frac{V_1}{V_2} = r = 15$$

Therefore,

$$V_2 = 0.86/15 = 0.0573 \text{ m}^3$$

Finally,

$$\frac{P_2}{P_1} = r^{\gamma} = 15^{1.4} = 44.3126$$

Thus,

$$P_2 = 4431.3 \text{ kPa}$$

Constant pressure heat addition 2–3:

$$Q_1 = C_P(T_3 - T_2) = 1.005(T_3 - 886.2)$$

Since Q_1 is 500 kJ, the above result leads to $T_3 = 1383.7$ K. Also,

$$\frac{V_3}{V_2} = \frac{T_3}{T_2}; \qquad \frac{V_3}{0.0573} = \frac{1383.7}{886.2}$$

This gives $V_3 = 0.0895 \text{ m}^3/\text{kg}$.

$$P_3 = P_2 = 4431.3 \text{ kPa}$$

Isentropic expansion 3–4:

$V_4 = V_1 = 0.86 \text{ m}^3/\text{kg}$

$$\frac{T_3}{T_4} = \left(\frac{V_4}{V_3}\right)^{\gamma-1} = \left(\frac{0.86}{0.0895}\right)^{0.4} = 2.4721$$

Therefore, $T_4 = 559.8$ K.

$$\frac{P_4}{P_3} = \left(\frac{V_3}{V_4}\right)^{\gamma} = \left(\frac{0.0895}{0.86}\right)^{1.4} = 0.0421$$

Thus $P_4 = 186.54$ kPa.

Constant volume heat rejection, 4–1: Heat rejected is calculated as

$$Q_2 = C_V (T_4 - T_1) = 0.718(559.8 - 300) = 186.54 \text{ kJ/kg}$$

(b) Net work done per cycle per kg air is

$$W_{\text{net}} = Q_1 - Q_2 = 500 - 186.54 = 313.46 \text{ kJ/kg}$$

(c) Thermal efficiency is

$$\eta = \frac{W_{\text{net}}}{Q_1} = \frac{313.46}{500} = 0.627$$

[*Note:* Thermal efficiency may be calculated using Eq. (5.93) also.

$$\eta = 1 - \frac{1}{\gamma}\frac{1}{r^{\gamma-1}}\left(\frac{r_c^{\gamma} - 1}{r_c - 1}\right)$$

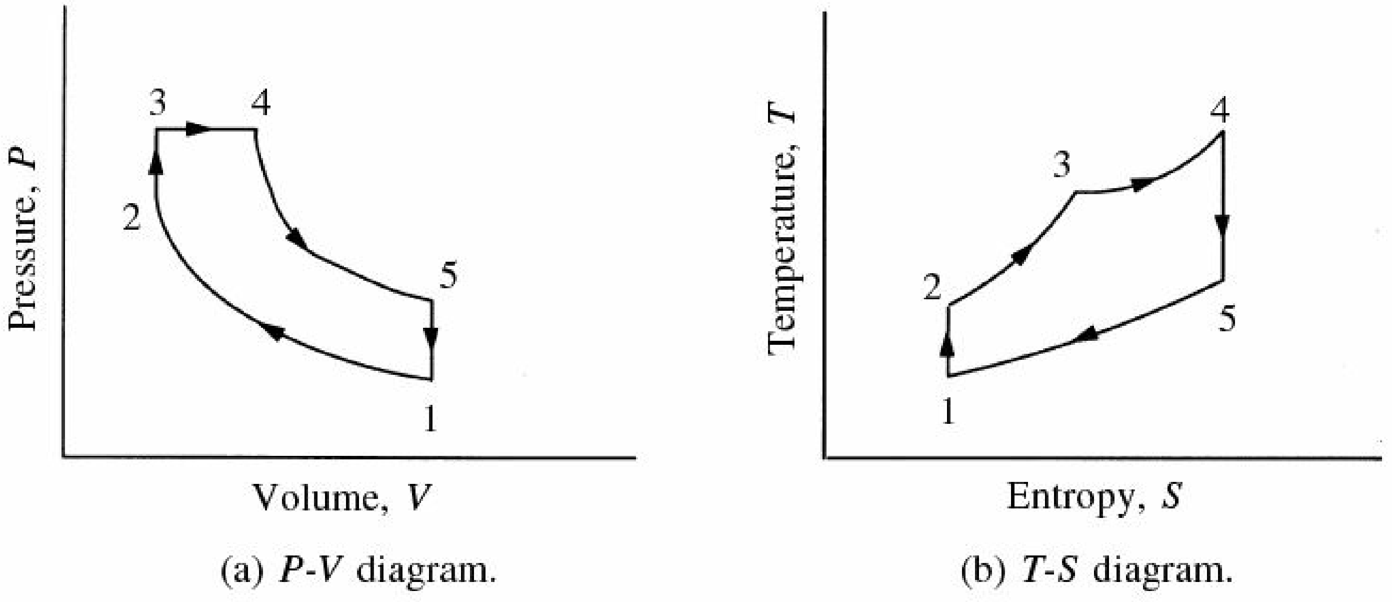
Here, the cut-off ratio $r_c = V_3/V_2 = 0.0895/0.0573 = 1.562$.]

(d) The mean effective pressure is

$$P_m = \frac{W_{\text{net}}}{V_1 - V_2} = \frac{313.46}{0.86 - 0.0573} = 390.5 \text{ kPa}$$

5.5.3 Dual Cycle

In an ideal Otto cycle, the heat is supplied during a constant volume process. It requires that the combustion of the fuel is instantaneous and occurs so rapidly that the change in volume is negligible. In contrast, in the air-standard ‘Diesel cycle’, the heat is supplied during a constant pressure process. It necessitates the combustion process to occur very slowly. Both these ideal situations are not achievable in practice, and hence the combustion process is neither a constant volume process nor a constant pressure process. An air-standard *dual cycle* is a compromise between an ideal Otto cycle and an ideal Diesel cycle. The *P-V* and *T-S* diagrams for a dual cycle are shown in Fig. 5.26.



(a) *P-V* diagram. (b) *T-S* diagram.

Fig. 5.26 The dual cycle on *P-V* and *T-S* diagrams.

In dual cycle, heat transfer is assumed to occur first at constant volume and then at constant pressure. Referring to the figure, the heat supplied is obtained as

$$Q_1 = mC_V(T_3 - T_2) + mC_P(T_4 - T_3)$$

The heat rejected is given by

$$Q_2 = mC_V(T_5 - T_1)$$

The thermal efficiency is

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_V(T_5 - T_1)}{C_V(T_3 - T_2) + C_P(T_4 - T_3)} = \boxed{1 - \frac{(T_5 - T_1)}{(T_3 - T_2) + \gamma(T_4 - T_3)}} \tag{5.94}$$

5.6 GAS-TURBINE POWER PLANT

An open-cycle gas-turbine power plant is schematically illustrated in Figs. 5.27(a) and (b). The compressor discharges air into a combustion chamber where it is heated by combustion of fuel. The mixture of air and combustion gases is then expanded in a turbine. A part of the power output from the turbine is used to run the compressor and the rest is available as useful work. The expanded gas may be discharged to the atmosphere, or may be used to preheat the air discharged from the compressor. In closed-cycle operation, the working fluid after expansion is recycled to the compressor through an exhaust-gas cooler. Heat is supplied by a heat transfer process.

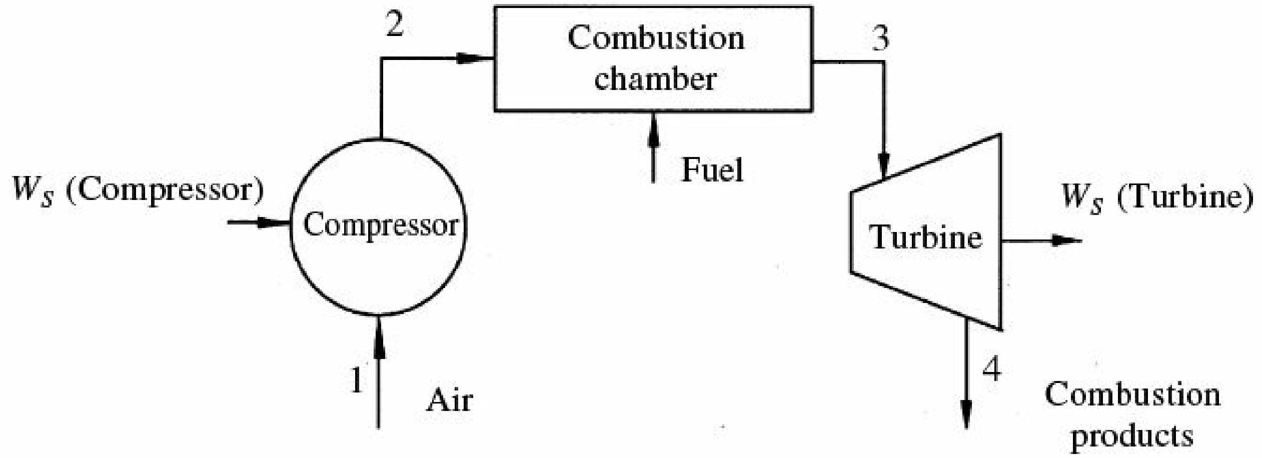


Fig. 5.27(a) The open cycle gas-turbine power plant.

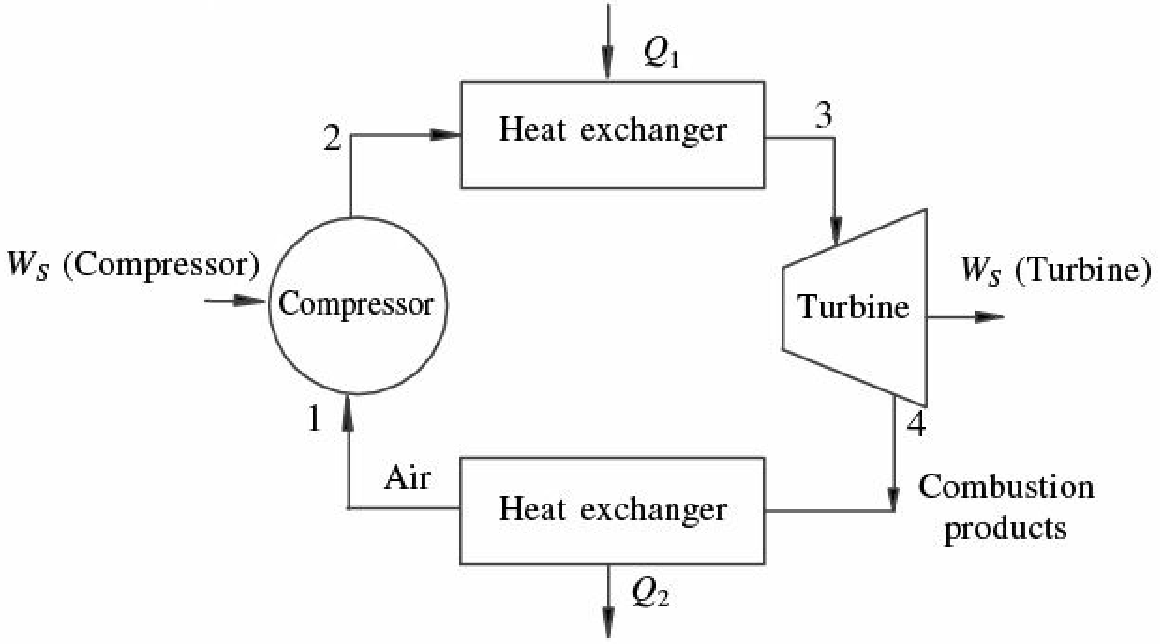
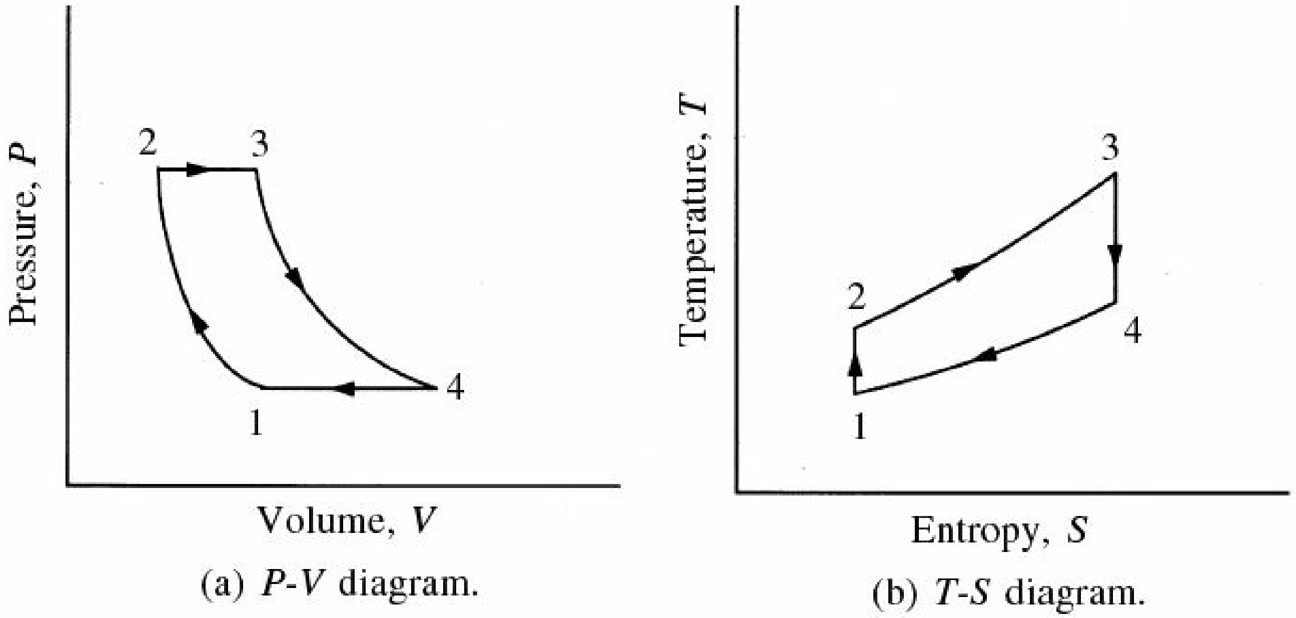


Fig. 5.27(b) The closed cycle gas-turbine power plant.

5.6.1 Brayton Cycle

The ideal air-standard *gas-turbine* cycle is known as the *Brayton cycle*. The *P-V* diagram and the *T-S* diagram of the Brayton cycle are given in Fig. 5.28.



(a) *P-V* diagram.

(b) *T-S* diagram.

Fig. 5.28 The Brayton cycle on *P-V* and *T-S* diagrams.

The ideal cycle includes an isentropic compression (1–2), a constant-pressure heating (2–3), an isentropic expansion (3–4), and a constant-pressure cooling (4–1).

The heat supplied is

$$Q_1 = mC_P(T_3 - T_2)$$

The heat rejected is

$$Q_2 = mC_P(T_4 - T_1)$$

The thermal efficiency is evaluated as

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \tag{5.95}$$

Denoting the pressure ratio for the turbine by r,

$$r = \frac{P_2}{P_1} = \frac{P_3}{P_4} \tag{5.96}$$

For isentropic processes 1–2 and 3–4 we get

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\gamma/(\gamma - 1)} \quad \text{and} \quad \frac{P_3}{P_4} = \left(\frac{T_3}{T_4}\right)^{\gamma/(\gamma - 1)} \tag{5.97}$$

Comparison of Eq. (5.96) and Eq. (5.97) shows that

$$\frac{T_2}{T_1} = \frac{T_3}{T_4} = (r)^{(\gamma - 1)/\gamma} \tag{5.98}$$

From Eq. (5.98) we get

$$\frac{T_3 - T_2}{T_4 - T_1} = (r)^{(\gamma - 1)/\gamma} \tag{5.99}$$

Substituting Eq. (5.99) into Eq. (5.95) the thermal efficiency is obtained as

$$\boxed{\eta = 1 - \left(\frac{1}{r}\right)^{(\gamma - 1)/\gamma}} \tag{5.100}$$

The thermal efficiency of the air-standard Brayton cycle therefore increases by increasing the pressure ratio. Also from Eq. (5.95), we see that the higher the temperature of the combustion gases entering the turbine (T_3), the greater the work produced per kg of fuel burned. However, the strength of the turbine blades sets a limit to the maximum temperature of the gas that can be employed.

***EXAMPLE*5.29** In an air-standard Brayton cycle, the temperature and pressure of air entering the compressor are 300 K and 100 kPa. The maximum pressure and temperature in the cycle are 500 kPa and 1200 K. Assuming air to be an ideal gas with constant specific heats C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K, determine:

(a) The pressure and temperature at each point in the cycle
(b) The work required by the compressor
(c) The work done by the turbine
(d) The thermal efficiency.

Solution (a) $P_1 = P_4 = 100$ kPa; $P_2 = P_3 = 500$ kPa; $T_1 = 300$ K and $T_3 = 1200$ K; g $= C_P/C_V = 1.4$.

Isentropic compression 1–2:

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\gamma/(\gamma - 1)} = \left(\frac{T_2}{300}\right)^{1.4/0.4} = \frac{500}{100}$$

This gives $T_2 = 475.1$ K.

Isentropic expansion 3–4:

$$\frac{P_3}{P_4} = \left(\frac{T_3}{T_4}\right)^{\gamma/(\gamma - 1)} = \left(\frac{1200}{T_4}\right)^{1.4/0.4} = \frac{500}{100}$$

This gives $T_4 = 757.7$ K.

(b) The work required by the compressor is

$$-W_S = H_2 - H_1 = mC_P(T_2 - T_1) = 1.005(475.1 - 300) = 176 \text{ kJ/kg}$$

(c) The work done by the turbine is

$$W_S = H_3 - H_4 = mC_P(T_3 - T_4) = 1.005(1200 - 757.7) = 444.5 \text{ kJ/kg}$$

(d) Thermal efficiency

$$\eta = 1 - \left(\frac{1}{r}\right)^{(\gamma-1)/\gamma} = 1 - \left(\frac{P_1}{P_2}\right)^{0.4/1.4} = 1 - \left(\frac{100}{500}\right)^{0.2857} = 0.3686$$

[*Note:* Thermal efficiency may be calculated by another way also.

The heat supplied is

$$Q_1 = mC_P (T_3 - T_2) = 728.5 \text{ kJ/kg}$$

$$\eta = \frac{W_{\text{net}}}{Q_1} = \frac{W_{\text{turbine}} - W_{\text{compressor}}}{Q_1} = \frac{444.5 - 176}{728.5} = 0.3686]$$

SUMMARY

Through the application of first and second laws of thermodynamics, attempts were made in Section 5.1 to find solutions to some fluid flow problems. The continuity equation, the total energy balance equation, and the mechanical energy balance equation were derived and the Bernoulli equation was deduced. These are applied to some practically important cases such as the flow through pipes, nozzles, and ejectors. Thus it was shown that for flow through straight pipes of uniform cross-section, the maximum fluid velocity attained is equal to the speed of sound in the fluid. For isentropic flow through nozzles, if the gas is to be accelerated continuously from subsonic to supersonic velocity, the area of cross-section for flow should first decrease, then remain constant and finally increase, thus establishing the thermodynamic basis of the convergent-divergent nozzles. A brief description of the throttling process and the definition of the Joule–Thomson coefficient was also provided. Equations for calculating the work of isothermal and adiabatic compression were also formulated. The isothermal path for compression for which the work requirement is less than that for the adiabatic path, can be approached by multi-stage compression with interstage cooling. Also, for minimum total work in a multi-stage compressor, the pressure ratios in all the stages should be equal.

Four important refrigeration cycles, the Carnot cycle, the vapour-compression cycle, the air-refrigeration cycle, and the absorption refrigeration cycles were analysed for their coefficients of performance, and their relative merits and demerits were discussed in Section 5.2. The vapour compression cycle employing an expansion engine gives higher COP, but are not recommended for small-scale applications. An absorption refrigeration system uses, for achieving refrigeration, the heat absorbed from a high-temperature source directly without converting it into work by means of a heat engine, as is done in a vapour-compression cycle. A thermodynamic analysis of the Linde process employing free-expansion and the Claude process employing isentropic expansion for air-liquefaction revealed that the fraction of air liquefied in an isentropic expansion was greater than that in a free-expansion. However, the isentropic expansion process has practical difficulties that are associated with the operation of the turbine with a two-phase mixture (Section 5.3).

The thermodynamic analysis of steam-power plants was done by comparing the performance of the actual cycles with certain idealised cycles. The ideal cycles considered were the Rankine cycle, the reheat cycle, and the regenerative cycle. Equations for evaluating their thermal efficiencies were developed. The thermal efficiency of the Rankine cycle can be improved in the regenerative cycle by heating the water leaving the condenser before being sent to the boiler, by steam extracted from various stages of expansion in the turbine (Section 5.4). The Otto cycle and the Diesel cycle are the two important air-standard cycles used for the analysis of internal combustion engines. The thermal efficiency of the Otto cycle depends on the compression ratio and the ratio of specific heats. For the same compression ratio, the Otto cycle is more efficient than the Diesel cycle. However, in a Diesel engine a compression ratio higher than that is permissible in an Otto engine, may be employed and hence high efficiencies may be achieved. The dual cycle was found to be a compromise between the Otto cycle and the Diesel cycle (Section 5.5).

REVIEW QUESTIONS

1. Derive the total energy balance for a flow system and deduce the mechanical energy balance equation.
2. Derive the Bernoulli's equation and list out the assumptions involved.
3. Show that the maximum fluid velocity attainable for flow through a pipe of uniform cross-section is equal to the sonic velocity.
4. Define Mach number. How is it important in establishing the relation between the velocity and the area of cross-section for flow through nozzles?
5. What is the critical pressure for flow through nozzles? "A converging nozzle can discharge a fluid at constant flow-rate to a region of variable pressure independent of the down stream pressure." Explain.
6. Flow of a fluid through a well-insulated partially opened valve results in throttling. Prove that a throttling expansion is an isenthalpic operation.
7. What is Joule–Thomson coefficient? If a gas cools on throttling, will it be positive or negative?
8. What are the Joule–Thomson inversion temperatures?
9. How is the minimum work in an adiabatic compressor related to the decrease in enthalpy of the fluid?
10. Why is inter-stage cooling necessary in a multi-stage compression?
11. For minimum total work in a multi-stage compression, what can you say about the pressure ratios in different stages?
12. How does the clearance affect the work of adiabatic compression?
13. What is COP of a refrigerator? What do you know about the work required per ton of refrigeration by a Carnot refrigerating unit in comparison with other cycles?
14. What are the practical limitations of a Carnot cycle for refrigeration and how are these overcome in a vapour-compression cycle?
15. With the help of a *T-S* diagram, deduce expressions for the COP of the vapour-compression cycles.
16. Why is throttling used in practical refrigerators in place of turbine?
17. What are the desirable properties of a refrigerant?
18. How is the COP of an air cycle related to the compression ratio? What are the advantages and disadvantages of air-refrigeration machines?
19. What is the basic principle behind the absorption refrigeration systems?

20. Explain the working principle of a heat pump.

21. What are the three general methods available for gas liquefaction? Why is it necessary that a gas be compressed to a high pressure before it is subjected to liquefaction by throttling?

22. Compare the Linde process with the Claude process for air liquefaction.

23. How is the Rankine cycle practically superior to the Carnot cycle as an ideal steam-power cycle? Why is it advantageous to use superheat in the Rankine cycle?

24. How could the efficiency of the Rankine cycle be improved in (a) reheat cycle
(b) regenerative cycle?

25. What simplifications are inherent in using the air-standard cycles for assessing the performance of internal combustion engines?

26. What are the factors that affect the thermal efficiency of Otto cycle?

27. What are the major differences between the Otto cycle and Diesel cycle for IC engines.

28. "An air-standard dual cycle may be treated as a compromise between the Otto cycle and the Diesel cycle". Justify.

29. What is the effect of the pressure ratio on the thermal efficiency of the Brayton cycle?

EXERCISES

5.1 A 50-mm diameter horizontal jet of water strikes a vertical plane. If the horizontal force needed to support the plane is 360 N, what is the velocity of the jet?

5.2 Wet steam containing 5% by weight of liquid at a pressure of 500 kPa is mixed at a rate of 1 kg/s with superheated steam at 500 kPa and 473 K (H = 2855 kJ/kg) to obtain dry saturated steam at 500 kPa (H_l = 640 kJ/kg; H_V = 2749 kJ/kg). Determine the rate of addition of superheated steam if mixing is done adiabatically.

5.3 An ideal gas with heat capacity C_P = 29.7 kJ/kmol K flows steadily through a long capillary tube at 5 bar and 350 K and leaves at 2 bar. What is its exit temperature?

5.4 3600 kg/h of superheated steam at 200 kPa and 673 K enters a turbine with a velocity of 100 m/s. The inlet to the turbine is at an elevation of 10 m and the exit is at an elevation of 3 m. The steam leaves the turbine at a velocity of 150 m/s and is 98% dry at a pressure of 10 kPa. What is the power output of the turbine if the energy loss from it is estimated to be 40000 kJ/h?

5.5 A tank has a volume of 3 m^3 and contains 1400 kg liquid water in equilibrium with its vapour, which fills the remainder of the tank. The temperature and pressure are 505 K and 2902 kPa respectively (enthalpy of saturated vapour = 2802 kJ/kg; enthalpy of saturated liquid = 1000 kJ/kg; specific volume of saturated liquid = $1.213 \square 10^{-3}$ m^3/kg; specific volume of saturated vapour = $68.89 \square 10^{-3}$ m^3/kg). A quantity of 1000 kg water at
340 K (H = 280 kJ/kg) is to be pumped into the tank without removing any steam. How much heat must be added during this process, if the pressure and temperature in the tank remain at their initial values?

5.6 A turbine is fed with steam at 78 bar and 698 K (enthalpy = 3213 kJ/kg) at a rate of
1000 kg/h. Saturated steam at 5 bar (H = 2749 kJ/kg) is withdrawn from one point in the turbine

at a rate of 250 kg/h. The remaining steam leaves the turbine saturated at 1 bar ($H = 2676$ kJ/kg). Determine the power output from the turbine, if it operates adiabatically?

5.7 A tank contains 1 kg steam at a pressure of 2100 kPa and a temperature of 648 K (enthalpy and specific volume are 3192 kJ/kg and 137.76 ☐ 10^{-3} m^3/kg). It is connected through a valve to a vertical cylinder containing a frictionless piston. The piston is loaded with a weight such that a pressure of 700 kPa is necessary to support it. Initially the piston is at the bottom of the cylinder. The valve is opened slightly, so that steam flows into the cylinder until the pressure is uniform throughout the system. The final temperature of steam in the tank is found to be 513 K (enthalpy and specific volume of the superheated steam at 700 kPa and 513 K are 2933 kJ/kg and 329.23 ☐ 10^{-3} m^3/kg). Calculate the temperature of steam in the cylinder, if no heat is transferred from the steam to the surroundings.

5.8 A well-insulated closed tank has a volume of 70 m^3. Initially it contains 23000 kg water distributed between liquid and vapour phases at 300 K. Saturated steam at 1100 kPa is admitted to the tank until the pressure reaches 700 kPa. Determine the amount of steam added.

5.9 An evacuated tank is connected to a pipe carrying steam at 1400 kPa and 598 K (enthalpy = 3097 kJ/kg) through a valve. The valve is opened and the tank is filled with steam until the pressure is 1400 kPa, and then the valve is closed. Assume that the process is adiabatic and the kinetic and potential energies are negligible. Determine the final temperature of the steam.

5.10 A tank of volume 0.3 m^3 initially contains saturated steam at 345 kPa. It is connected to a pipeline carrying steam at 1400 kPa and 598 K through a valve. The valve is then opened and steam from the line flows into the tank till the pressure is equal to 1400 kPa. Calculate the mass of steam that flows into the tank.

5.11 A rigid and insulated tank of volume 1 m^3 initially contains air at 300 K and 10 bar. A valve is opened and the gas is discharged until the mass of air in the tank is reduced by half. Determine the temperature and pressure of the gas left in the tank.

5.12 An insulated rigid tank is initially evacuated and kept in a room. The atmospheric air in the room is at 101.3 kPa and 300 K. A valve is opened and air is allowed to enter the tank. The valve is closed when the pressure in the tank reaches 101.3 kPa. The air can be assumed to be an ideal gas with constant specific heats. What is the final temperature of the air in the tank?

5.13 A rigid insulated tank of volume 1 m^3 contains an ideal gas (molecular weight = 29, g = 1.4) at a pressure of 200 kPa and temperature 400 K. The tank is connected to a pipe-line carrying the same gas at 5 MPa and 650 K through a valve. The valve is opened and the gas is allowed to enter the tank till the pressure reaches 5 MPa. Determine
(a) the temperature attained by the gas in the tank and (b) the amount of gas admitted into the tank.

5.14 A rigid tank 0.1 m^3 in volume initially contains saturated water vapour at 425 K. The tank is connected by a valve to a supply line that carries steam at 1400 kPa and 523 K. Now the valve is opened and steam is allowed to enter the tank. Heat transfer takes place with the surroundings such that the temperature in the tank remains constant at 425 K at all times. The valve is closed when it is observed that one-half of the volume of the tank is occupied by liquid water. Specific volume of saturated liquid and saturated vapour at 425 K are $1.093 \square 10^{-3}$ and 0.3749 m^3/kg, respectively. Internal energy of saturated liquid and saturated vapour at 425 K are 639.7 and 2561.2 kJ/kg, respectively. Enthalpy of superheated steam at 1400 kPa and 523 K is 2927.2 kJ/kg. Determine (a) the amount of steam that has entered the tank, and (b) the heat transferred.

5.15 A rigid tank of volume 1 m^3 initially contains equal volumes of water and water vapour at 523 K. Water is discharged as saturated liquid from the bottom of the tank at a constant flow rate by opening a valve. The contents in the tank are kept at the constant temperature of 523 K by transfer of heat. The valve is closed when one half of the initial mass has been discharged. Determine the quality (mass fraction of vapour) of the vapour-liquid mixture left in the tank and the heat transferred.

5.16 An ideal gas confined in a piston-cylinder assembly at a pressure of 101.3 kPa and 300 K occupies a volume of 0.015 m^3 initially. The cylinder is connected through a valve to a pipeline through which the same gas is flowing at steady state at a pressure of 700 kPa and 400 K. The valve is opened and the gas is admitted into the cylinder keeping the pressure inside constant at 101.3 kPa. The valve is closed when the volume of gas in the cylinder has become double the original volume. Assume the specific heat at constant pressure and constant volume are, respectively, 29.4 and 21 kJ/kmol K. Determine the final temperature of the gas in the cylinder.

5.17 Air, assumed to be an ideal gas with molar heat capacity C_P = 30 kJ/kmol K, is flowing through a pipe of diameter 0.15 m at a rate of 0.3 m^3/s at 100 kPa and 300 K before entering a compressor. A cooler removes heat from the compressed gas at a rate of 75.0 kJ/s. The gas at 315 K and 550 kPa is then carried away through a pipe of diameter 0.03 m. What is the power input to the compressor?

5.18 A pump is used to transfer a solution of density 1200 kg/m^3 from a mixing vessel to a storage tank through a pipe of diameter 0.08 m at velocity 1 m/s. The level difference between the liquid in the mixing vessel and the storage tank is 20 m. Both tanks are open to the atmosphere. Frictional loss is estimated to be 300 W. Determine the pressure increase over the pump. What is the power input to the pump?

5.19 A pump is used to transfer a solution of density 1250 kg/m^3 at a rate of 12 m^3/h from an open storage tank to the top of an absorption tower which is operated at a pressure of 500 kPa. The pump discharges into the tower through openings equivalent in area to a $25 \square 10^{-3}$ m pipe. The point of discharge is 30 m above the level of solution in the tank. The pump intake is through a pipe of diameter $50 \square 10^{-3}$ m which extends to a depth of 2 m below the level of solution in the tank. The friction head in the suction line is estimated to be 1.5 m of water and that in the discharge line is 10 m of water. If the efficiency of the pump is 70%, what is the power input to the pump? What pressures will be indicated by the pressure gauges at the inlet and exit of the pump?

5.20 Steam at 700 kPa and 553 K enters a nozzle with negligible velocity and discharges at a pressure of 475 kPa. Determine:

(a) The exit velocity

(b) The cross-sectional area at the nozzle exit for a flow rate of 0.5 kg/s.

5.21 Steam at 1400 kPa and 598 K enters a convergent-divergent nozzle with negligible velocity. The nozzle may be assumed to act isentropically. The cross-sectional area at the throat is 6.5 □ 10^{-4} m^2. Determine the state of the steam at the discharge end of the nozzle if the pressure there is 350 kPa. What is the mass flow rate of the steam?

5.22 Calculate the maximum Mach number at the discharge of the divergent section of the convergent-divergent nozzle under the conditions given in Example 5.4, assuming that supersonic velocity is realised in the nozzle.

5.23 Air expands through a nozzle from a negligible initial velocity to a final velocity of 350 m/s. What is the temperature drop of air, if air is assumed an ideal gas with $C_P = (7/2)R$?

5.24 Steam at 6000 kPa and 773 K enters a converging-diverging nozzle and discharges to a constant pressure region at 2000 kPa. If the expansion in the nozzle is isentropic, determine the velocity and temperature of the discharge steam.

5.25 Steam at 700 kPa and 573 K enters a nozzle with a velocity 30 m/s. The nozzle operates isentropically. Determine the area of cross-section at a point in the nozzle where the pressure is 400 kPa, as a fraction of the inlet area. Take the necessary data from the steam tables.

5.26 Steam at 700 kPa and 573 K enters a nozzle with a velocity 30 m/s. The nozzle operates isentropically and the steam may be assumed to behave as an ideal gas with g = 1.3. Determine:

(a) The critical pressure ratio and the velocity at the throat.

(b) The discharge pressure, if the Mach number at the discharge is 2.

5.27 A wind tunnel is fed with air through a nozzle at a Mach number 1.5 and temperature 300 K. The diameter of the discharge end of the diverging section of the nozzle is 0.15 m. Assume air to be an ideal gas with C_P = 30 kJ/mol K. Calculate the temperature and pressure of the air fed to the nozzle.

5.28 Discuss the effect of clearance on the work required and on the volumetric efficiency of a multi-stage adiabatic compressor.

5.29 Saturated steam at 175 kPa is compressed adiabatically to 650 kPa in a centrifugal compressor at a rate of 1.5 kg/s. The compressor efficiency is 75%. What is the power requirement of the compressor and what are the enthalpy and entropy of steam leaving the compressor?

5.30 A single-stage compressor is used to compress 1500 m^3/h of ammonia gas at 255 K and 100 kPa to 550 kPa. The isentropic compression efficiency is 75% and volumetric efficiency is 85%. Calculate:

(a) The power required for compression

(b) Piston displacement in m^3/s.

(Refer Perry and Chilton, *Chemical Engineer's Handbook* for the *T-S* diagram of ammonia.)

5.31 A single-stage compressor is used to compress 800 m^3/h of carbon dioxide measured at 288

K and 1 bar from its initial state of 0.5 bar and 300 K to a final pressure of 1.5 bar. A volumetric efficiency of 75% and a compression efficiency of 85% may be assumed. Assuming adiabatic compression, calculate the power required for driving the compressor, the piston displacement in m^3/s, and the discharge temperature.

5.32 A two-stage compressor is used to compress 800 m^3/h of carbon dioxide measured at 288 K and 1 bar from its initial state of 0.5 bar and 300 K to a pressure of 1.5 bar with inter-cooling to 300 K. A compression efficiency of 85% may be assumed in each stage. Calculate the power required to run the compressor and the discharge temperature.

5.33 Determine the coefficient of performance of an ideal Carnot engine operating between a low temperature 280 K and surrounding temperature 300 K.

5.34 The work output from a Carnot engine operating between two thermal reservoirs at 500 K and 300 K respectively, is utilised by a Carnot refrigeration machine for absorbing heat at the rate of 4 kJ/s from a cold room at 270 K and discarding heat to the surroundings at 300 K. Determine the quantity of heat absorbed by the engine at 500 K. If the COP of the refrigerator and the efficiency of the engine are two-third of the ideal values, what is the quantity of heat absorbed by the engine at 500 K?

5.35 The work output of an ideal Carnot engine operating between two thermal reservoirs, one at 1000 K and the other at 300 K is utilised to drive the compressor of a vapour-compression refrigeration unit working on Freon-12. The heat rejected by the engine is 30 kW. The refrigerator operates between 240 K and 300 K. The enthalpy of saturated Freon-12 liquid at 300 K = 61.9 kJ/kg, the enthalpy of saturated Freon-12 vapour at 240 K = 172.8 kJ/kg. Determine the COP, the refrigerator capacity, and the circulation rate of the refrigerant.

5.36 An ordinary vapour-compression cycle uses steam as the working fluid. The steam leaves the condenser at 303 K and is evaporating at 278 K. The enthalpy of saturated vapour at 278 K is 2510.6 kJ/kg and the enthalpy of saturated liquid at 303 K is 125.78 kJ/kg. Calculate the circulation rate for a refrigeration load of 1000 MJ/h.

5.37 A vapour-compression refrigerator employing Freon-12 works between pressure limits of 182.5 kPa and 960.6 kPa. The heat transfer from the condenser is found to be 72 kJ per minute and the heat absorbed in the evaporator is 3200 kJ/h. The refrigerant vapour leaves the evaporator in the saturated state. Calculate:

(a) The refrigerant flow rate through the system in kg per minute
(b) The energy input to the compressor and
(c) The COP of the system.

The enthalpy of saturated vapour at 182.5 kPa = 181.2 kJ/kg and the enthalpy of saturated liquid at 960.6 kPa = 76.2 kJ/kg.

5.38 Ammonia is being used in an ordinary vapour-compression machine rated at 5 ton. The evaporator is at 273 K and the condenser is at 303 K. The saturation pressures of ammonia corresponding to these temperatures are 4.29 bar and 11.67 bar respectively. The allowable temperature rise for cooling water in the condenser is 10 K. The enthalpy of saturated liquid and vapour at 273 K are 168 kJ/kg and 1300 kJ/kg respectively. The enthalpy of saturated liquid and vapour at 303 K are 300 and 1327 kJ/kg respectively. The enthalpy of superheated vapour leaving the compressor at 11.67 bar is 1445 kJ/kg. Determine the following:

(a) The theoretical minimum horse power to drive the unit
(b) The refrigerant circulation rate
(c) The cooling water circulation rate
(d) The coefficient of performance

5.39 A standard vapour-compression refrigeration unit using ammonia produces a refrigeration equivalent to 210 kJ/minute. The unit operates between a condenser temperature of 308 K and a refrigerator temperature of 258 K. Assuming that the compression process is reversible adiabatic and the vapour leaves the refrigerator saturated, calculate the COP and the ammonia circulation rate. The following data are available:

T (K)	P^S (bar)	H_L (kJ/kg)	H_V (kJ/kg)
308	12.05	324	1474
258	2.44	113	1430

The enthalpy of vapour leaving the compressor is 1650 kJ/kg.

5.40 A refrigerator with Freon-12 as refrigerant operates with an evaporator temperature of 248 K (P = 1.2 bar, S = 0.7130 kJ/kg K, H = 176.22 kJ/kg) and a condensation temperature of 298 K (P = 6.4 bar, S = 0.224 kJ/kg K, H = 59.17 kJ/kg). The saturated liquid leaving the condenser is passed through an expansion valve and an evaporator. The vapour leaving the evaporator is saturated.

(a) If the refrigerator is rated at 1.5 ton, what is the circulation rate of Freon-12?
(b) By how much the circulation rate would be reduced, if the throttle valve were replaced by a turbine?
(c) The liquid leaving the condenser is passed through a counter-current heat exchanger where it gives off its heat to the vapour leaving the evaporator. The liquid leaving the condenser is at 298 K and the vapour leaving the evaporator is at 248 K. In the exchanger the vapour gets heated to 292 K (P = 1.2 bar, H = 203.53 kJ/kg, S = 0.8164 kJ/kg K). What would be the circulation rate of Freon-12?
(d) What is the COP in each of the above cases?

Enthalpy of superheated vapour at 6.4 bar and having an entropy 0.7130 kJ/kg K = 204.69 kJ/kg. Enthalpy of superheated vapour at 6.4 bar and having an entropy 0.8164 kJ/kg K = 241.90 kJ/kg. Enthalpy and entropy of superheated vapour at P = 1.2 bar and T = 248 K are 203.53 kJ/kg K and 0.8164 kJ/kg K respectively.

5.41 A refrigerating machine using ammonia as the refrigerant is employed for producing 500 kg/h of ice from water. Ammonia boils at 266 K and condenses at 293 K. The water in the condenser gets heated from 283 K to 288 K. Calculate the theoretical minimum power of the compressor and the rate of circulation of cooling water. The latent heat of fusion of water is 339.1 kJ/kg.

5.42 A refrigeration system requires 1 kW of power for a refrigeration rate of 3 kJ/s. Determine:

(a) The coefficient of performance

  (b) The heat rejected by the system
  (c) The lowest temperature that the system can maintain if the heat is rejected at 308 K.

5.43 An ideal vapour-compression unit with Freon-12 as refrigerant operates between an evaporator temperature of 243 K and a condenser temperature of 308 K. If the power input to the compressor is 50 kW, what is the refrigeration capacity (in tons) of refrigeration? The enthalpy of saturated liquid Freon-12 at 308 K is 69.55 kJ/kg. The enthalpy of saturated vapour at 243 K is 174.2 kJ/kg. The enthalpy of superheated vapour leaving the compressor is 200 kJ/kg.

5.44 A cold room is to be maintained at 261 K using an air-refrigeration system which should absorb 1000 kJ/minute. Cooling water is available at 293 K. Air leaves the compressor at 506.5 kPa and later expanded to 101.3 kPa. Assume air to behave as an ideal gas and calculate COP and power requirements. Take $C_P = 1.008$ kJ/kg K and $g = 1.4$.

5.45 A heat pump is used for heating the inside of a building in the winter and for air-conditioning in the summer. The average winter temperatures are 278 K outside and 293 K inside. The average summer temperatures are 303 K outside and 299 K inside. A 5 K temperature approach is allowed in all cases. Determine the work required in both cases as a fraction of heat input assuming ideal cycle.

5.46 Nitrogen at 200 K and 200 bar is expanded reversibly through an adiabatic turbine to saturation and is then allowed to pass through a throttle valve to a pressure of 1 bar.

  (a) What percentage of the gas is liquefied?
  (b) The gas leaving the separator is passed through a heat exchanger kept between the turbine and the valve for cooling the high-pressure stream to the valve. A 5 K approach is desired at the hot end of this exchanger. Determine the per cent of nitrogen liquefied.

(Refer Perry and Chilton: *Chemical Engineer's Handbook* for enthalpy data of nitrogen.)

5.47 Air is to be liquefied in a Linde-liquefaction system. The air enters the throttle valve at 300 K and 100 bar and is expanded there to 1 bar. The flow rate of air is 85 m^3/h at a temperature of 289 K and pressure of 1 bar. Assume no heat losses, zero temperature difference at the warm end of the exchanger, and adiabatic compression. Determine:

  (a) The rate of production of liquid in kg/h and the fraction of air liquefied
  (b) The rate of production of liquid and the fraction of air liquefied if a heat loss of 2.5 kJ/kg and a temperature approach of 15 K are to be accounted.

5.48 The low-pressure side of the throttle valve in the Linde process for the liquefaction of methane is maintained at 1 bar (the enthalpy of saturated liquid and vapour at 1 bar are 285 kJ/kg and 797 kJ/kg respectively). The gas leaves the compressor at 60 bar and 300 K ($H = 1140$ kJ/kg). The uncondensed gases are passed through the heat exchanger where it gets heated to 295 K ($H = 1189$ kJ/kg). Determine:

  (a) The fraction of the gas liquefied
  (b) The temperature of the gas at the high-pressure side of the valve.

5.49 In the Linde process for liquefaction, air is compressed from a pressure of 1 bar to 200 bar. Air at a rate of 200 kg/h is treated. The air entering the compressor is at 298 K ($H = 510$ kJ/kg) and that leaving it is cooled to 298 K ($H = 474$ kJ/kg). The air is throttled to a pressure of 1 bar. The enthalpy of saturated liquid at 1 bar is 92 kJ/kg. Heat loss from the unit is estimated to be 8.3 kJ/kg of air. Determine:

(a) The rate of liquefaction
(b) The power requirement.

5.50 An ideal regenerative cycle operates with steam supplied at 2800 kPa and 773 K and condenser pressure of 5 kPa. Extraction points provided are at 350 kPa and 75 kPa, one closed and the other open. Neglecting pump work, calculate the thermal efficiency of the plant.

5.51 In a steam power plant operating on the Rankine cycle, the turbine is supplied wit superheated steam at 2600 kPa and 573 K. The steam leaving the turbine containing 93% vapou is sent to a condenser operated at 13.6 kPa. The feed water pump takes in water at 13.0 kPa an 319 K and delivers water to the boiler at 2900 kPa. Superheated steam as it leaves the boiler i at 2800 kPa and 598 K. Determine the following for kg steam flowing through the plant:

(a) Pump work
(b) Turbine work
(c) Heat transfer in the line between boiler and turbine
(d) Heat transfer in boiler
(e) Heat transfer in condenser.

5.52 In a steam power plant, steam is supplied to the high-pressure turbine at 2800 kPa and 648 K It is expanded to 558 kPa and sent to the boiler where it is heated to 558 kPa and 648 K. It i then expanded to a final pressure of 2.5 kPa in the low-pressure turbine. Determine:

(a) The ideal reheat cycle efficiency
(b) The ideal Rankine cycle efficiency in the absence of reheating.

5.53 A steam turbine power plant operates on a regenerative cycle. Steam enters the turbine at 3500 kPa and 710 K. A fraction of the steam is extracted at 211 kPa and sent to an open heater and the remainder is condensed at 7 kPa. Neglecting pump work, determine the thermal efficiency.

5.54 In a steam power plant of the regenerative type, steam is supplied to the turbine at 2800 kPa and 648 K. The condenser is operated at 7 kPa. The steam is extracted from the turbine at 68 kPa and 81.5 kPa and sent separately to two closed heaters. Determine the thermal efficiency o the cycle.

5.55 The turbine of a 1-MW steam power plant is supplied with superheated steam at 3000 kPa and 573 K, where it is expanded to the condenser pressure of 5 kPa. The isentropic efficiency o the turbine is 85%. The saturated liquid leaving the condenser is pumped to the boiler pressure by means of the feed water pump, the thermodynamic efficiency of which is 80%. Determine:

(a) The efficiency of the ideal Rankine cycle
(b) Thermal efficiency of the cycle
(c) The rate of production of steam.

5.56 The high-pressure turbine of a steam power plant is supplied with superheated steam at 3000 kPa and 773 K. After expansion to 600 kPa, the exhaust steam is returned to the boiler to heat i to 773 K and 600 kPa. It then enters the low-pressure turbine and expanded to 5 kPa. Th exhaust steam leaving the turbine is taken to a condenser operated at 5 kPa. The saturated liquid leaving the condenser is pumped to the boiler pressure by means of feed water pump. The isentropic efficiency of the turbine is 0.85 and that of the pump is 0.7. What is the thermal efficiency of the plant?

5.57 Superheated steam at 3000 kPa and 573 K is supplied to the turbine of a steam power plant operating on the regenerative cycle. A fraction of the steam at 400 kPa is extracted from the turbine and is sent to the feed water-heater and the remainder is expanded to the condenser pressure of 10 kPa and admitted to the condenser. The saturated liquid leaving the condenser is pumped to a pressure of 400 kPa and enters the heater where it exchanges heat with the extracted steam. The exit streams leaving the heater are combined together and pumped to the boiler. Determine the thermal efficiency of the cycle.

5.58 A thermal power plant operating on Rankine cycle is rated at 1 MW. Superheated steam at 5000 kPa and 673 K enters the turbine where it is expanded to the condenser pressure of 7 kPa. The saturated liquid leaving the condenser is pumped to the boiler pressure, the isentropic efficiency of the pump being 75%. The isentropic efficiency of the turbine is 80%. Determine:

(a) Thermal efficiency of the plant
(b) The rate of production of steam.

5.59 An 80-MW steam power plant is operated on Rankine cycle. The turbine is fed with superheated steam at 8600 kPa and 773 K where it is expanded to the condenser pressure of 10 kPa. The saturated liquid leaving the condenser is pumped to the boiler. The isentropic efficiencies of both the pump and the turbine are 75%. Determine:

(a) The thermal efficiency of an ideal Rankine cycle for the stated conditions
(b) Thermal efficiency of the cycle
(c) Rate of production of steam
(d) Rate of heat input in the boiler and the condenser.

5.60 Superheated steam enters the turbine of a steam power plant operating on regenerative cycle at 4100 kPa and 700 K. After expansion to 404 kPa, some of the steam is extracted from the turbine for the purpose of heating the feed water in an open feed water heater. The pressure in the feed water heater is 404 kPa and the water leaving it is saturated liquid at 404 kPa. The steam not extracted is expanded to a pressure of 7 kPa. What is the thermal efficiency of the cycle?

5.61 It is desired to determine the effect of turbine inlet pressure on the performance of a Rankine cycle. Steam enters the turbine at 650 K and exhausts at 14 kPa. Calculate the cycle thermal efficiency and moisture content of steam leaving the turbine for the turbine inlet pressure of 700 kPa, 3500 kPa, 7000 kPa and 14000 kPa.

5.62 It is desired to study the effect of turbine inlet temperature on the performance of an ideal Rankine cycle. Steam enters the turbine at 3500 kPa and exhausts at 14 kPa. Calculate the cycle thermal efficiency and moisture content of the steam leaving the turbine for the inlet temperatures of 573 K, 623 K, 873 K and 923 K.

5.63 An air-standard Otto cycle operates with a compression ratio of 8 and a maximum temperature per cycle of 1400 K. If the temperature and pressure at the beginning of compression stroke are 300 K and 100 kPa respectively, determine the following assuming air to be an ideal gas with constant specific heats C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K:

(a) The heat supplied

(b) The work produced
(c) The thermal efficiency.

5.64 Determine the thermal efficiency and the work output per kg of air of an air-standard Otto cycle with a compression ratio of 8. The temperature and pressure at the beginning of compression stroke are 300 K and 100 kPa. Heat supplied to the engine is 2000 kJ/kg. Assume air as an ideal gas with C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K.

5.65 For an air-standard Otto cycle the temperature and pressure at the beginning of compression stroke are 310 K and 100 kPa respectively. The maximum temperature and pressure permitted are 3000 K and 7000 kPa respectively. Assuming air as an ideal gas with C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K, determine

(a) The compression ratio
(b) The thermal efficiency
(c) The net work output from the engine.

5.66 In an air-standard Otto cycle, the work output per kg air is 1000 kJ and the temperature at the end of heat addition is 3500 K and that at the end of compression process is 800 K. Determine the compression ratio of the engine assuming air as an ideal gas with C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K.

5.67 In an air-standard Diesel cycle, the temperature, pressure, and volume at the beginning of the compression stroke are respectively 300 K, 100 kPa, and 0.05 m^3. The pressure at the end of compression stroke is 4000 kPa and the heat supplied is 500 kJ/kg. Assuming air as an ideal gas with C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K, determine:

(a) The compression ratio
(b) The cut-off ratio
(c) The work done per cycle
(d) The thermal efficiency.

5.68 An air-standard Otto cycle operates on 5 kg of air with a compression ratio of 10. If the temperature and pressure at the beginning of compression stroke are 310 K and 80 kPa and the heat supplied is 500 kJ, determine the following, assuming air to be an ideal gas with constant specific heats of C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K.

(a) The pressure and temperature for each step in the process
(b) The net work output
(c) The thermal efficiency.

5.69 Compare the thermal efficiency of an Otto cycle of compression ratio 8 and operating with air (g =1.4) with that of an air-standard Diesel cycle of the same compression ratio and a cut-off ratio of 2. How does the comparison change if the cut-off ratio is 3?

5.70 A 6-cylinder reciprocating engine operates on air-standard Diesel cycle, each cylinder having 115 mm bore and 125 mm stroke and a speed of 2000 rpm. The temperature and pressure at the beginning of compression stroke are 300 K and 100 kPa respectively and the maximum temperature permitted is 1650 K. The clearance volume is one-eighth of the stroke volume. Assume air as an ideal gas with C_P = 1.005 kJ/kg K and C_V =

0.718 kJ/kg K. Calculate:

(a) The compression ratio
(b) The temperature and pressure after compression
(c) The thermal efficiency
(d) The power output from the engine.

5.71 For an air-standard Diesel cycle, the temperature and pressure at the beginning of the compression stroke are 325 K and 100 kPa. The pressure after compression is 4000 kPa. The heat supplied is 600 kJ/kg of air. Assume air as an ideal gas with C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K. Determine

(a) The compression ratio
(b) The cut-off ratio
(c) The work output
(d) The thermal efficiency.

5.72 In an air-standard Diesel cycle, the pressure and temperature at the beginning of the compression stroke are 100 kPa and 295 K respectively, and the heat supplied is 1500 J/mol, what are the compression ratio and the expansion ratio of the cycle if the pressure at the end of combustion step is 400 kPa. Assume air to be an ideal gas with $C_P = (7/2)R$ and $C_V = (5/2)R$.

5.73 An air-standard Diesel cycle operates with a compression ratio of 16. If the temperature and pressure at the beginning of compression stroke are 310 K and 100 kPa and the heat supplied is accompanied by an increase in entropy of 1.2 kJ/kg K determine the following, assuming air to be an ideal gas with constant specific heats of C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K.

(a) The maximum temperature
(b) The cut-off ratio
(c) The heat supplied
(d) The thermal efficiency.

5.74 In an air-standard Diesel cycle operating with 5 kg air, the temperature and pressure at the beginning of compression stroke are 310 K and 80 kPa. The heat rejected per cycle is 4000 kJ and the maximum temperature per cycle is 3000 K. If the efficiency of the cycle is 60 per cent determine the compression ratio assuming air to be an ideal gas with constant specific heats of C_P = 1.005 kJ/kg K and C_V = 0.718 kJ/kg K.

5.75 An air-standard Diesel cycle has an initial pressure and temperature of 100 kPa and 300 K. The compression ratio is 14. Temperature at the end of heat supply is 1980 K. The specific heat ratios are 1.37, 1.34, and 1.31 respectively for the compression, heat supply, and expansion processes. Determine:

(a) The thermal efficiency
(b) The work output from the cycle per kg air
(c) The entropy change for the heat supply process.

5.76 In an air-standard Diesel cycle, the compression ratio is 16 and the cut-off ratio is 3. The conditions at the beginning of the compression stroke are 100 kPa and 300 K. Assuming air as an ideal gas with $C_P = 1.005$ kJ/kg K and $C_V = 0.718$ kJ/kg K, determine the following:

(a) The heat supplied
(b) The net work output
(c) The thermal efficiency.

5.77 In air-standard dual cycle, the temperature and pressure at the start of the compression stroke are 300 K and 100 kPa. The compression ratio is 15 and the maximum temperature is 3000 K The maximum pressure is 7000 kPa. Determine:

(a) The work done per kg air
(b) The heat supplied.

Assume air to be an ideal gas with $C_P = 1.005$ kJ/kg K and $C_V = 0.718$ kJ/kg K.

5.78 In a gas-turbine cycle, the air enters the compressor at 100 kPa and 300 K and leaves at 500 kPa. The maximum temperature is 1200 K. Assume a compressor efficiency of 80 per cent, a turbine efficiency of 85 per cent and a pressure drop between the compressor and turbine of 15 kPa. Take $C_P = 1.005$ kJ/kg K and $C_V = 0.718$ kJ/kg K. Determine:

(a) The compressor work
(b) The turbine work
(c) The cycle efficiency.

5.79 In an air-standard gas-turbine cycle with a pressure ratio of 8, the temperature and pressure of the air entering the compressor are 300 K and 100 kPa. The permissible maximum temperature is 1300 K. Determine:

(a) The temperature and pressure at each point in the cycle
(b) The compressor work
(c) The turbine work
(d) The thermal efficiency.

5.80 A gas-turbine power plant operates with a pressure ratio of 6. The temperature of the air entering the compressor is 300 K and the maximum permissible temperature in the turbine is 1100 K. Determine:

(a) The efficiency of an ideal gas-turbine cycle if g = 1.4,
(b) The thermal efficiency of the power plant if the compressor and the turbine operate adiabatically but reversibly with efficiencies 83 per cent and 86 per cent respectively.

5.81 The pressure ratio across the compressor of an air-standard Brayton cycle is 4. The conditions of air at the beginning of the compression stroke are 290 K and 100 kPa.
The maximum temperature in the cycle is 1100 K. Assume constant specific heats
$C_P = 1.005$ kJ/kg K and $C_V = 0.718$ kJ/kg K. The rate of airflow is 10 kg/s. Determine:

(a) The compressor work
(b) The turbine work
(c) The thermal efficiency of the cycle
(d) The mean effective pressure, if this cycle were utilised for a reciprocating machine.

5.82 A stationary gas-turbine power plant operates on the ideal Brayton cycle and delivers 20,000 hp to an electric generator. The maximum temperature and pressure are 1100 K and 420 kPa respectively and the minimum temperature and pressure are 290 K and 100 kPa.

(a) What is the power output of the turbine?
(b) What fraction of the output of the turbine is used to drive the compressor?
(c) What is the rate of circulation of air in kg/s?

5.83 The compressor of a gas-turbine power plant operating on Brayton cycle is supplied with air at 300 K and 100 kPa. The temperature of air at the inlet to the turbine is 900 K. The pressure ratio is 4. The pressure drop in the combustion chamber is 10 kPa and that in the exit line from the turbine is 5 kPa. Determine:

(a) The temperature and pressure at each point
(b) The thermal efficiency of the cycle.

6

Thermodynamic Properties of Pure Fluids

Determination of thermodynamic properties of a fluid that cannot be measured directly necessitates relating such properties to measurable quantities. In this chapter some new thermodynamic functions are introduced and the equations giving the interrelationships between various thermodynamic properties are discussed. These equations are derived using the method of partial derivatives. The method of Jacobians for the systematic derivation of thermodynamic relations is also presented and the method is illustrated with some typical examples. Relationships formulated in this chapter would be useful in evaluating numerical values of all types of thermodynamic properties which, in turn, are necessary for the practical calculations like the evaluation of the heat and work requirements in industrially important processes. Using these relations, the thermodynamic properties of pure fluids can be evaluated from the measurable quantities like pressure-volume-temperature relationship, heat capacity data and coefficients of expansion and compressibility.

6.1 CLASSIFICATION OF THERMODYNAMIC PROPERTIES

Thermodynamic properties of fluids can be classified into three broad groups: the reference properties, the energy properties and the derived properties.

6.1.1 Reference Properties

Also known as *primary properties*, these properties are the ones that are used to define the state of the system. They have absolute values, as against energy properties, which are measured relative to some arbitrary reference state. Examples of reference properties are temperature, pressure, volume, and entropy. Of these, temperature and pressure are intensive, and volume and entropy are extensive. In addition to these, in dealing with the solutions, the composition is also treated as a reference property.

6.1.2 Energy Properties

The four energy properties are the internal energy (U), enthalpy (H), the Helmholtz free energy (A), and the Gibbs free energy (G). All are extensive thermodynamic properties and are known relative to some reference state. These are referred to as energy properties, because, the changes in these thermodynamic functions indicate useful work under certain conditions of restraint.

6.1.3 Derived Properties

These are partial derivatives of energy properties or the reference properties. Examples include specific heat (C), coefficient of expansion (b), Joule–Thomson coefficient (m), and coefficient of compressibility (κ).

Among the four energy properties, the internal energy and enthalpy were introduced in earlier chapters. In the following sections, the Helmholtz work function and the Gibbs free energy are defined. Both these functions involve entropy in their definition and in many cases it is convenient to work with these properties rather than the entropy itself.

6.2 WORK FUNCTION (HELMHOLTZ FREE ENERGY)

The Helmholtz free energy (A) of a system is defined as

$$A = U - TS \qquad (6.1)$$

where U, T, and S are the internal energy, temperature, and entropy of the system respectively. Since U, T, and S are characteristic of the system and depend only on its thermodynamic state, Helmholtz free energy is a state function. Since U and S are both extensive, A also is an extensive property.

To understand the physical significance of the work function, consider an isothermal reversible change occurring from state 1 to state 2. Then from Eq. (6.1), the change in the work function accompanying this process is

$$\Delta A = \Delta U - T\Delta S \qquad (6.2)$$

ΔA, ΔU, and ΔS denote the changes in the work function, the internal energy and the entropy respectively of the system during the process. Since the process is reversible, the heat absorbed $Q_R = T\Delta S$, and Eq. (6.2) can be written as

$$\Delta A = \Delta U - Q_R \qquad (6.3)$$

According to the first law of thermodynamics for a closed system,

$$\Delta U = Q - W \qquad (6.4)$$

Substituting this result in Eq. (6.3), we get

$$\Delta A = -W_R$$

or

$$W_R = -\Delta A \qquad (6.5)$$

The right-hand side of Eq. (6.5) is the decrease in the work function. The equation therefore means that the decrease in the work function accompanying a process at constant temperature is equal to the reversible work done by the system during the process. Since the reversible work is the maximum work obtainable from any change in state, the decrease in the work function in an isothermal process is a measure of the maximum work available from a given change of state. In any actual isothermal process, the work done by the system would be less than the decrease in the Helmholtz free energy, but the maximum work that can be done by the system is equal to $-\Delta A$ in the limit of a reversible process.

Consider an irreversible chemical reaction in which zinc reacts with dilute sulphuric acid producing zinc sulphate and hydrogen at constant temperature and pressure. No work, other than the small amount done against the atmosphere by the evolved hydrogen, is available from this process. The same reaction may be carried out reversibly in a galvanic cell in which an electrode made of zinc is connected through an external circuit to another electrode of hydrogen in contact with a platinised electrode. The electrical energy now produced can be utilised to run a device such as an electric motor. If at every instant the external electric system is made to exert such a large counter e.m.f., that, when infinitesimally increased, would force current in the opposite direction, thus reversing the reaction. The decrease in the work function in this process would be equal to the total work done by the system, which include both the electrical work and the work of expansion.

Helmholtz free energy being a state function, $-\Delta A$ would be the same for reversible as well as for irreversible process occurring between the same end states. But, whereas in the former it represents the maximum work obtained, in the latter, it represents the maximum work which would have resulted, had all irreversibilities been eliminated. It should also be noted that any change in state, isothermal or otherwise, is accompanied by a definite change in the work function, but it is only for an isothermal process that this change is a measure of the maximum work.

6.3 GIBBS FREE ENERGY

For the process in which zinc metal is allowed to react with dilute acid reversibly in a galvanic cell, we have seen that the decrease in Helmholtz free energy determines the maximum work, which includes the electrical energy, and the work of expansion resulting from the reaction. The maximum 'useful work', which in this case, is the amount of electrical energy produced, is given by the decrease in another thermodynamic property known as the *Gibbs free energy*. It is denoted by G, and like the work function, makes use of entropy in its definition.

$$G = H - TS \qquad (6.6)$$

Like the work function A, Gibbs free energy G is a single valued function of the thermodynamic state of the system and is an extensive property. It is widely used in the study of phase equilibria and chemical reaction equilibria. Since by definition, enthalpy $H = U + PV$, Eq. (6.6) can be written as

$$G = (U + PV) - TS = A + PV \qquad (6.7)$$

Equation (6.7) reveals that A is related to G in the same way as U is related to H

The physical significance of the Gibbs free energy function can be made clear if we consider a reversible process at constant temperature and pressure. Equation (6.7) gives ΔG, the change in free energy for a finite change in the state of the system as

$$\Delta G = \Delta A + \Delta(PV) \qquad (6.8)$$

We have already seen that $\Delta A = -W_R$ for a reversible process at constant temperature. For a constant pressure process, $\Delta(PV) = P(\Delta V)$. Therefore, Eq. (6.8) becomes

$$\Delta G = -W_R + P\Delta V$$

or

$$-\Delta G = W_R - P\Delta V \qquad (6.9)$$

W_R represents the total reversible work obtainable from a given change of state, which includes in addition to work of expansion, other forms of work such as electrical and surface work. Thus, we see that the decrease in Gibbs free energy in a process occurring at constant temperature and pressure is the maximum work other than the work of expansion available from the process, or the maximum 'net work', W'_R, obtainable from the process.

$$W'_R = -\Delta G \qquad (6.10)$$

It is because of the fact that the change in Gibbs function G measures the net useful work, it is known as the '*free energy*'.

For the electrochemical cell that we have considered earlier, the total work obtained (W_R) includes electrical work and the work done against the constant pressure of the atmosphere ($P\Delta V$). The latter work is always done whether the process is reversible or irreversible. Thus, the maximum electrical work that could be done by the system undergoing a given change in state is less than the total maximum work, $-\Delta A$, by the expansion work and is measured by the decrease in the Gibbs free energy, $-\Delta G$.

The value of ΔG in any process is quite definite, no matter under what conditions the process is carried out, but only when the temperature and pressure are constant the free energy change would represent the maximum net work available from the given change in state.

6.4 RELATIONSHIPS AMONG THERMODYNAMIC PROPERTIES

The method of partial derivatives is used here to develop the important thermodynamic relationships. The major thrust of this section is to express thermodynamic properties in terms of measurable quantities.

6.4.1 Exact Differential Equations

Let z be a single-valued continuous function of two independent variables x and y.

$$z = f(x, y)$$

Then the total differential of z can be written in terms of its partial derivatives with respect to independent variables x and y as

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad (6.11)$$

A differential equation of this type is termed an exact differential equation. The value of $\int dz$ between the two end-conditions depends only on the values of z at these conditions, i.e.

$$\int_1^2 dz = z_2 - z_1$$

This value is independent of the path followed in bringing about the change from the initial condition 1 to final condition 2. The thermodynamic properties, in general, possess these characteristics of the function z. For example, the work function or the free energy can be regarded as single valued functions of the thermodynamic state, and dA and dG can be treated as exact differentials. Equation (6.11) can be written as

$$dz = M\,dx + N\,dy \qquad (6.12)$$

where $M = (\partial z/\partial x)_y$ and $N = (\partial z/\partial y)_x$.

Also, we can write

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$\frac{\partial^2 z}{\partial y\, \partial x} = \frac{\partial^2 z}{\partial x\, \partial y} \tag{6.13}$$

A property of exact differential equation that we will be using frequently is shown by Eq. (6.13).

6.4.2 Fundamental Property Relations

The differentials of energy properties form the basis for the derivation of a large number of equations relating thermodynamic properties. These are developed below for systems of constant mass and composition in which the only external force is the pressure and the process occurring is reversible. The first law for non-flow process is provided by Eq. (2.5) as $dU = dQ - dW$. For the present case, the heat and work terms are related to the properties of the system as $dQ = T\, dS$ and $dW = P\, dV$, so that Eq. (2.5) becomes

$$\boxed{dU = T\, dS - P\, dV} \tag{6.14}$$

Equation (6.14) can be treated as the combined statement of first and second laws of thermodynamics for reversible processes.

Using the definition of enthalpy (i.e. $H = U + PV$), the differential of H is

$$dH = dU + P\, dV + V\, dP \tag{6.15}$$

Combining this with Eq. (6.14), we get

$$\boxed{dH = T\, dS + V\, dP} \tag{6.16}$$

In a similar way, starting from the definition of Helmholtz free energy, Eq. (6.1), and Gibbs free energy, Eq. (6.6), the following relationships can also be derived.

$$\boxed{dA = -S\, dT - P\, dV} \tag{6.17}$$

$$\boxed{dG = -S\, dT + V\, dP} \tag{6.18}$$

Equations (6.14), (6.16), (6.17), and (6.18) are the fundamental differential equations which express the energy properties in terms of the four reference properties P, V, T, and S. It can be seen that each of the energy properties is functionally related to a special pair of variables. For example, Eq. (6.18) shows that

$G = f(P, T)$

Thus P and T are the *canonical variables* or special variables for Gibbs free energy G. Canonical variables for the work function are V and T.

6.4.3 Maxwell’s Equations

Maxwell's equations are helpful in replacing unmeasurable quantities appearing in thermodynamic equations by measurable quantities. Using these relations, the partial derivatives of entropy with respect to pressure and volume are expressed as derivatives possessing easily identifiable physical meaning. Each of the four Maxwell's equations is derived from the exact differential equations of the four energy properties.

Consider the exact differential of internal energy, i.e. Eq. (6.14). At constant volume, it becomes

$$\left(\frac{\partial U}{\partial S}\right)_V = T$$

Differentiating the above with respect to volume at constant S

$$\frac{\partial^2 U}{\partial V\,\partial S} = \left(\frac{\partial T}{\partial V}\right)_S \tag{6.19}$$

At constant entropy, Eq. (6.14) reduces to

$$\left(\frac{\partial U}{\partial V}\right)_S = -P$$

Differentiating this with respect to S at constant V

$$\frac{\partial^2 U}{\partial S\,\partial V} = -\left(\frac{\partial P}{\partial S}\right)_V \tag{6.20}$$

Comparing Eq. (6.19) with Eq. (6.20) and utilising the properties of exact differential equations given by Eq. (6.13), we get

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \tag{6.21}$$

This is the first of the four Maxwell's equations. The remaining three equations are obtained in a similar way starting from Eqs. (6.16), (6.17), and (6.18). The results are given below.

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \tag{6.22}$$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T} \tag{6.23}$$

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \tag{6.24}$$

Mnemonic diagram. A square drawn with the diagonal arrows pointing upwards is shown in Fig. 6.1. The sides of the squares are labelled with the energy properties in alphabetical order (A, G, H, and U) starting with the topside. The corners are labelled with the canonical variables oi the energy properties in such a way that each energy property is flanked by its canonical variables.

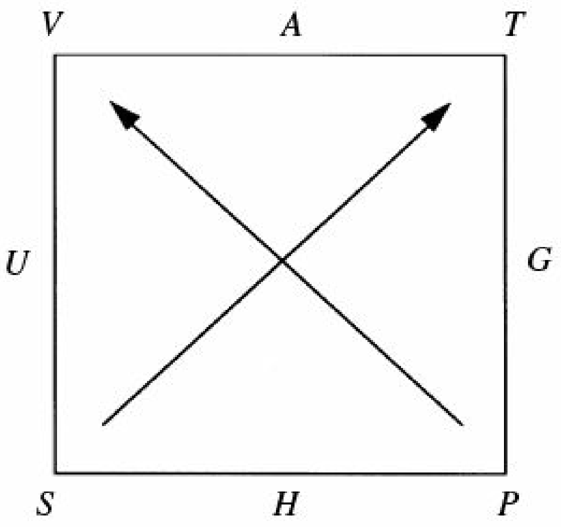


Fig. 6.1 Mnemonic diagram for thermodynamic property relations.

The above diagram can be used as a convenient tool for writing the differential equations for the energy properties as well as the Maxwell's equations. The differential equations contain the differentials of its natural variables and their coefficients. The differentials are obtained from the variables adjacent to the energy property under consideration, and the coefficients are obtained from the variables that are diametrically opposite to these variables. The sign of the coefficient is to be decided from the direction in which the arrows are pointing. If the arrow is pointing away from the canonical variable, the coefficient is positive and if the arrow is pointing towards the canonical variable, the coefficient is negative. For example, dU is written in terms of its canonical variables dS and dV. The coefficients are respectively T and P which are diametrically opposite to S and V. Since the arrow is pointing away from S and towards V the sign of T is positive and that of P is negative. Therefore, $dU = T\,dS - P\,dV$. To get Maxwell's equations, Fig. 6.1 is thus used: Consider, for illustration, the topside of the square. The partial derivative formed by the canonical variables is $(\partial T/\partial V)$. The suffix to be used is the variable that is diametrically opposite to the first variable, i.e. S. Then one of the partial derivatives in the desired relation is $(\partial T/\partial V)_S$. The other derivative is obtained from the opposite side of the square in a similar way. This is $(\partial P/\partial S)_V$. Since the direction of arrows being opposite, i.e. towards T and away from P, the sign of the derivatives will be opposite. Therefore,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{6.21}$$

***EXAMPLE* 6.1** The molar volume of an organic liquid at 300 K and 1 bar is 0.1 m^3/kmol and its coefficient of expansion is 1.25 ☐ 10^{-3} K^{-1}. What would be the change in entropy if the pressure is increased to 20 bar at 300 K? What assumption is involved in the solution?

Solution The coefficient of volume expansion is defined as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Since, this is equal to $1.25 \times 10^{-3}\ \mathrm{K}^{-1}$,

$$\left(\frac{\partial V}{\partial T}\right)_P = 1.25 \times 10^{-3} V = 1.25 \times 10^{-4}\ \mathrm{m}^3/\mathrm{kmol\ K}$$

Consider Maxwell's relation Eq. (6.24), which gives

$$dS = -\left(\frac{\partial V}{\partial T}\right)_P dP$$

The change in entropy is

$$DS = -1.25 \square 10^{-4} (P_2 - P_1) = -1.25 \square 10^{-4} (20.0 - 1.0) \square 10^5 = -237.5\ \mathrm{J/kmol\ K}$$

It is assumed that the derivative $(\partial V/\partial T)_P$ is constant in the pressure range 1 to 20 bar.

6.4.4 Clapeyron Equation

The *Clapeyron equation* predicts the dependence of equilibrium pressure on temperature when two phases of a given substance coexist. It is given by

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} \qquad (6.25)$$

where DH and DV are the enthalpy and volume change accompanying a phase change. It can be derived from Maxwell's relation Eq. (6.23), which is applicable to any closed, homogeneous or heterogeneous system in equilibrium, with an external pressure. Consider a single component system containing two phases, say liquid and vapour, in thermodynamic equilibrium. By the phase rule, the system is univariant, i.e. only one intensive parameter can be varied independently. The equilibrium pressure (for the present case, the vapour pressure), is dependent on temperature only and is independent of volume. Thus, the partial derivative $(\partial P/\partial T)_V$ in Eq. (6.23) can be replaced by (dP/dT) without the constant volume restriction. Moreover, $(\partial S/\partial V)_T = DS/DV$, where DS is the entropy change when a given quantity of the substance is transferred from one phase to the other at constant temperature and DV is the accompanying volume change. (DS/DV) is a constant at a given temperature, for both DS and DV are extensive quantities that are proportional to the amount of material transferred. As we are dealing with equilibrium and therefore with a reversible process, $DS = Q/T = DH/T$, where DH is the change in enthalpy during the phase change or the latent heat of phase change. Substituting these into Eq. (6.23) we get the Clapeyron equation, Eq. (6.25):

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$

Clapeyron equation may be used for various purposes. It can be used to calculate the heat of vaporisation, if the variation of vapour pressure with temperature is known. Alternatively, if the heat of vaporisation is available, it is possible to predict the vapour pressure variation with temperature. [*Note:* An alternative derivation for the Clapeyron equation is provided in Chapter 8. See Example 8.3.]

Clausius-Clapeyron equation. If the temperature is not too near the critical point, the volume of the liquid is small in comparison with the volume of vapour. The volume change accompanying vaporisation $\Delta V = V_G - V_L$ is therefore approximately equal to V_G, the molar volume of vapour. Equation (6.25) now becomes

$$\frac{dP}{dT} = \frac{\Delta H}{T V_G} \tag{6.26}$$

The vapour pressures in regions well below the critical point is relatively small so that the vapour can be assumed to behave as an ideal gas. The molar volume, V_G, can now be replaced by RT/P^S so that Eq. (6.26) becomes

$$\frac{dP^S}{dT} = P^S \frac{\Delta H}{RT^2}$$

or

$$\frac{d \ln P^S}{dT} = \frac{\Delta H}{RT^2} \tag{6.27}$$

This result is known as *Clausius-Clapeyron equation*. Assuming that the heat of vaporisation remains constant in the temperature range T_1 to T_2, Eq. (6.27) can be integrated to give the following equation.

$$\ln \frac{P_2^S}{P_1^S} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{6.28}$$

P_2^S and P_1^S are the saturation pressures at temperatures T_2 and T_1 respectively.

***EXAMPLE* 6.2** Calculate the vapour pressure of water at 363 K, if the vapour pressure at 373 K is 101.3 kPa. The mean heat of vaporisation in this temperature range is 2275 kJ/kg.

Solution Refer Eq. (6.28). $T_1 = 363$ K; $T_2 = 373$ K; $P_2^S = 101.3$ kPa; $\Delta H = 2275 \times 18$ kJ/kmol; $R = 8.314$ kJ/kmol K.

Substituting the values in Eq. (6.28), we get

$$\ln \frac{101.3}{P_1^S} = \frac{2275 \times 18}{8.314}\left(\frac{1}{363} - \frac{1}{373}\right) = 0.3638$$

$$P_1^S = 70.41 \text{ kPa}$$

***EXAMPLE* 6.3** Mercury has a density of 13.69 □ 10^3 kg/m^3 in the liquid state and 14.193 □ 10^3 kg/m^3 in the solid state, both measured at the melting point of 234.33 K at 1 bar. If the heat of fusion of mercury is 9.7876 kJ/kg, what is the melting point of mercury at 10 bar?

Solution The Clapeyron equation [Eq. (6.25)], can be rearranged as:

$$\frac{dT}{T} = \frac{\Delta V}{\Delta H}\, dP$$

Assuming that $\Delta V/\Delta H$ remains constant, the above equation can be integrated as

$$\ln \frac{T_2}{T_1} = \frac{\Delta V}{\Delta H}(P_2 - P_1)$$

Here, $T_1 = 234.33$ K, $P_1 = 1$ bar, $P_2 = 10$ bar, $\Delta H = 9.7876$ kJ/kg, we can obtain T_2 as below.

$\Delta V = V_L - V_S$, where V_L is the specific volume of liquid mercury and V_S is the specific volume of solid mercury. Then

$$\Delta V = \frac{10^{-3}}{13.69} - \frac{10^{-3}}{14.193} = 2.5888 \times 10^{-6} \text{ m}^3/\text{kg}$$

$$\ln \frac{T_2}{234.33} = \frac{2.5888 \times 10^{-6}}{9.7876}(10 - 1) \times 10^2 = 2.3805 \times 10^{-4}$$

The melting point of mercury at 10 bar, $T_2 = 234.39$ K.

6.4.5 Entropy–Heat Capacity Relationships

Maxwell's equations provide the partial derivatives of entropy with pressure or volume. The partial derivatives of entropy with temperature are provided by the entropy–heat capacity relationships.

The specific heats at constant pressure (C_P) and constant volume (C_V) are discussed in Section 2.7. These are defined as under,

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \tag{6.29}$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \tag{6.30}$$

Since $dQ = T\,dS$ for reversible process Eqs. (6.29) and (6.30) can be written as

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P, \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

which on rearrangement give the following relationships.

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \tag{6.31}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \tag{6.32}$$

An important use of Eqs. (6.31) and (6.32) is in the determination of entropy change of a system at constant pressure or at constant volume respectively, for a specified change in temperature. Equation (6.31) on integration gives

$$\Delta S = \int C_P \frac{dT}{T}$$

If C_P is independent of temperature, the above equation can be written as

$$\Delta S = C_P \ln \frac{T_2}{T_1} \tag{6.33}$$

If C_P varies with temperature, the required integration can be performed analytically provided C_P is expressed as a function of temperature. In the absence of such a relationship, graphical integration will give the desired result. In the graphical method, the values of C_P/T are plotted against T (or, C_P against $\ln T$) and the area under the curve between T_1 and T_2 (or, between $\ln T_1$ and $\ln T_2$) will give D*S*.

***EXAMPLE* 6.4** Determine the increase in entropy of solid magnesium when the temperature is increased from 300 K to 800 K at atmospheric pressure. The heat capacity is given by the following relation

$$C_P = 26.04 + 5.586 \,\square\, 10^{-3}\, T + 28.476 \,\square\, 10^{4}\, T^{-2}$$

where C_P is in J/mol K and temperature in K.

Solution Equation (6.31) on integration gives

$$\Delta S = \int C_P \frac{dT}{T} = \int_{300}^{800} \left(\frac{26.04}{T} + 5.586 \times 10^{-3} + 28.476 \times 10^{4} T^{-3} \right) dT$$

$$= 25.55 + 2.793 + 1.360 = 29.693 \text{ J/mol K}$$

6.4.6 Differential Equations for Entropy

The state of a pure homogeneous fluid is uniquely determined by specifying any two thermodynamic properties. Choosing temperature and pressure as variables, other properties like entropy are related to them as $S = f(P, T)$. The total differential of S is

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT \tag{6.34}$$

Substituting Eqs. (6.24) and (6.31) into the above

$$\boxed{dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP} \tag{6.35}$$

If entropy were treated as function of temperature and volume, then $S = f(V, T)$ and

$$dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT \tag{6.36}$$

Substituting Eqs. (6.23) and (6.32) into Eq. (6.36), we get

$$\boxed{dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV} \tag{6.37}$$

The partial derivative $(\partial P/\partial T)_V$ appearing in Eq. (6.37) can be expressed in terms of $(\partial V/\partial T)_P$ and $(\partial V/\partial P)_T$ which, in turn, are related to the coefficient of volume expansion and compressibility of the substance respectively. This is done as below.

Let the volume V be expressed as a function of P and T. $V = f(P, T)$. Then the total differential of V can be written as

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

At constant volume, $dV = 0$ so that the above equation becomes

$$\left(\frac{\partial V}{\partial P}\right)_T dP = -\left(\frac{\partial V}{\partial T}\right)_P dT \quad \text{(at constant volume)}$$

This on rearrangement gives

$$\left(\frac{\partial P}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} = -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T \tag{6.38}$$

When Eq. (6.38) is substituted into Eq. (6.37), we get the differential equation for entropy as below.

$$\boxed{dS = \frac{C_V}{T}\,dT - \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\,dV} \tag{6.39}$$

6.4.7 Modified Equations for U and H

Changes in the internal energy and enthalpy can now be expressed in terms of changes in measurable quantities like pressure, volume, temperature, and specific heat of the fluid. Equations (6.14) and (6.16) give the differentials of internal energy and enthalpy respectively. Modified equations for U and H would result when Eq. (6.35) or Eq. (6.39) is substituted into Eqs. (6.14) and (6.16). Rewriting Eq. (6.14) using Eq. (6.39), we get

$$dU = T\left[\frac{C_V}{T}\,dT - \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\,dV\right] - P\,dV$$

This can be rearranged as

$$\boxed{dU = C_V dT - \left[P + T\,\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\right] dV} \tag{6.40}$$

Rewriting Eq. (6.16) using Eq. (6.35), the following modified equation results:

$$\boxed{dH = C_P\,dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP} \tag{6.41}$$

It is also possible to write *dU* in terms of *dP* and *dT* by substituting Eq. (6.35) into Eq. (6.14) and *dH* in terms of *dV* and *dT* by substituting Eq. (6.39) into Eq. (6.16). The results are as follows:

$$\boxed{dU = C_P\,dT - \left[P\,dV + T\left(\frac{\partial V}{\partial T}\right)_P dP\right]} \tag{6.42}$$

$$\boxed{dH = C_V\,dT + \left[V\,dP - T\,\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\,dV\right]} \tag{6.43}$$

***EXAMPLE* 6.5** Develop equations for evaluating the change in internal energy and change in enthalpy for process involving ideal gases.

Solution Equations (6.40) and (6.41) are used for evaluating *dU* and *dH*.

$$dU = C_V\, dT - \left[P + T\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\right] dV$$

$$dH = C_P\, dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

For one mole of an ideal gas, $PV = RT$, and therefore,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}, \quad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

Substituting these into Eqs. (6.40) and (6.41), we get

$$dU = C_V dT - \left[P - T\frac{R/P}{(RT/P^2)}\right] dV = C_V\, dT$$

$$dH = C_P\, dT + \left[V - T\left(\frac{R}{P}\right)\right] dP = C_P\, dT$$

The preceding two equations indicate that the internal energy and enthalpy of an ideal gas are functions of temperature alone, and for isothermal process there would be no change in these properties.

***EXAMPLE* 6.6** The equation of state of a certain substance is given by the expression $V = RT/P - C/T^3$, and the specific heat is given by the relation $C_P = A + BT$ where A, B, and C are constants. Derive expressions for changes in internal energy, enthalpy and entropy for

(a) an isothermal process

(b) an isobaric process.

Solution Since $V = RT/P - C/T^3$,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{3C}{T^4}, \qquad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

(a) *Isothermal process: dT* = 0. Equation (6.42) reduces to

$$dU = -\left[P dV + T\left(\frac{\partial V}{\partial T}\right)_P dP\right] = -\left[P d\left(\frac{RT}{P} - \frac{C}{T^3}\right) + T\left(\frac{R}{P} + \frac{3C}{T^4}\right)_P dP\right] = -\frac{3C}{T^3} dP$$

This is the change in internal energy.

Equation (6.41) gives the change in enthalpy

$$dH = \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP = \left[\frac{RT}{P} - \frac{C}{T^3} - T\left(\frac{R}{P} + \frac{3C}{T^4}\right)\right] dP = -\frac{4C}{T^3} dP$$

Using Eq. (6.35), we have the change in the entropy

$$dS = -\left(\frac{R}{P} + \frac{3C}{T^4}\right) dP$$

(b) *Isobaric process: dP* = 0. Equation (6.42) reduces to $dU = C_P\, dT - P\, dV$. Since

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

we get the change in the internal energy as

$$dU = (A + BT)\, dT - P\left(\frac{\partial V}{\partial T}\right)_P dT = \left[(A + BT) - P\left(\frac{R}{P} + \frac{3C}{T^4}\right)\right] dT = (A - R + BT - 3PCT^{-4})\, dT$$

From Eq. (6.41), change in the enthalpy is

$$dH = C_P\, dT = (A + BT)\, dT$$

From Eq. (6.35), change in the entropy is

$$dS = \frac{C_P}{T} dT = \left(\frac{A}{T} + B\right) dT$$

6.4.8 Effect of Temperature, Pressure and Volume on U, H and S

The most useful relations for the estimation of various thermodynamic properties of a fluid in a given state are those which give the effect of temperature and pressure on entropy and enthalpy. The partial derivatives representing these effects are given below in terms of measurable quantities, although these effects are contained in the equations developed in previous sections.

The effects of pressure and temperature on entropy are given by the Maxwell's equation, Eq. (6.24), and the heat capacity relation, Eq. (6.31), respectively. They are reproduced below.

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{6.24}$$

$$\left(\frac{dS}{dT}\right)_P = \frac{C_P}{T} \tag{6.31}$$

The effects of temperature and volume on internal energy are obtained from Eq. (6.40), which reduces to the following forms under constant volume and constant temperature restrictions.

$$dU = C_V\,dT \qquad \text{(at constant volume)} \tag{6.44}$$

$$dU = -\left[P + T\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\right] dV \qquad \text{(at constant temperature)} \tag{6.45}$$

Equations (6.44) and (6.45) may be written as partial derivatives as follows:

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \tag{6.46}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left[P + T\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\right] = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{6.47}$$

The second identity in Eq. (6.47) follows from Eq. (6.38).

Equations to predict the variation of enthalpy with temperature and pressure are derived from Eq. (6.41) under the constraints of constant pressure and constant temperature. At constant pressure, Eq. (6.41) gives

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \tag{6.48}$$

At constant temperature Eq. (6.41) becomes

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{6.49}$$

The method of calculation of entropy and enthalpy of a fluid in a given thermodynamic state using Eqs. (6.24), (6.31), (6.48) and (6.49) is explained below. Other thermodynamic properties easily follow from these values. It is assumed that the following data are available.

1. The pressure-volume-temperature relationship for the fluid either as an equation of state or as a tabulated experimental result.
2. The heat capacity C_{P0} at pressure P_0 and temperature T_0.
3. The enthalpy H_0 and entropy S_0 at temperature T_0 and pressure P_0.

Assume that the properties are to be evaluated at temperature T and pressure P. This state is represented by point B in Fig. 6.2.

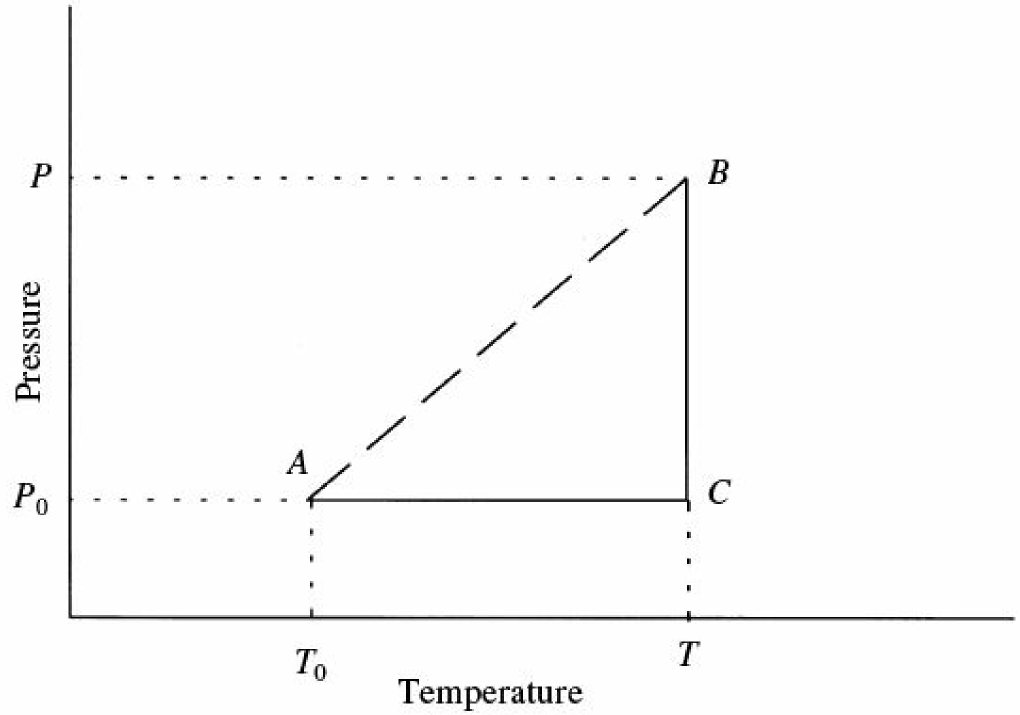


Fig. 6.2 Evaluation of enthalpy and entropy as functions of temperature and pressure.

The entropy (S_0) and enthalpy (H_0) are known at temperature T_0 and pressure P_0, the fluid in this state being represented by point A in Fig. 6.2. Since S and H are state functions, DS and DH for the fluid will be the same when it undergoes a change of state from state A to state B, as the DS and DH calculated for any process occurring between states A and B. We can, for convenience, devise a two-step process for bringing about this change so that the enthalpy and entropy changes in these separate steps are easily evaluated. During process AC the fluid is heated from T_0 to T at constant pressure P_0 (step 1) and during the process CB the fluid is compressed from pressure P_0 to P at constant temperature T (step 2). DS and DH for these steps are evaluated thus:

Step 1: Let H□ and S□ be the enthalpy and entropy at point C. Then by Eqs. (6.48) and (6.31), we get

$$H' - H_0 = \int_{T_0}^{T} C_{P0}\, dT, \qquad S' - S_0 = \int_{T_0}^{T} \frac{C_{P0}}{T}\, dT$$

Since H_0 and S_0 are known, H□ and S□ are readily evaluated by these equations.

Step 2: For process CB, the enthalpy and entropy changes are obtained from Eqs. (6.49) and (6.24) respectively.

$$H - H' = \int_{P_0}^{P} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP \tag{6.50}$$

$$S - S' = -\int_{P_0}^{P} \left(\frac{\partial V}{\partial T}\right)_P dP \tag{6.51}$$

Using the values of *H*□ and *S*□ obtained in step 1 the enthalpy (*H*) and entropy (*S*) at point *B* are calculated.

The integrals appearing in the preceding two equations are evaluated using the *P-V-T* data. If the data are available in the form of an equation of state, the derivative $(\partial V/\partial T)_P$ is obtained by differentiation, and the integration is performed analytically. Instead, if the *P-V-T* data are available as a tabulated result, the integration has to be performed graphically. This is done by plotting *V* against *T* for various constant pressures and measuring the slopes at temperature *T*. These slopes give the partial derivative $(\partial V/\partial T)_P$. These are then plotted against *P*, and the area under the curve between pressure P_0 and *P* is found out which gives the integral in Eq. (6.51). For evaluating the enthalpy, the whole terms within the brackets in Eq. (6.50) are plotted against *P* and the area is determined as before.

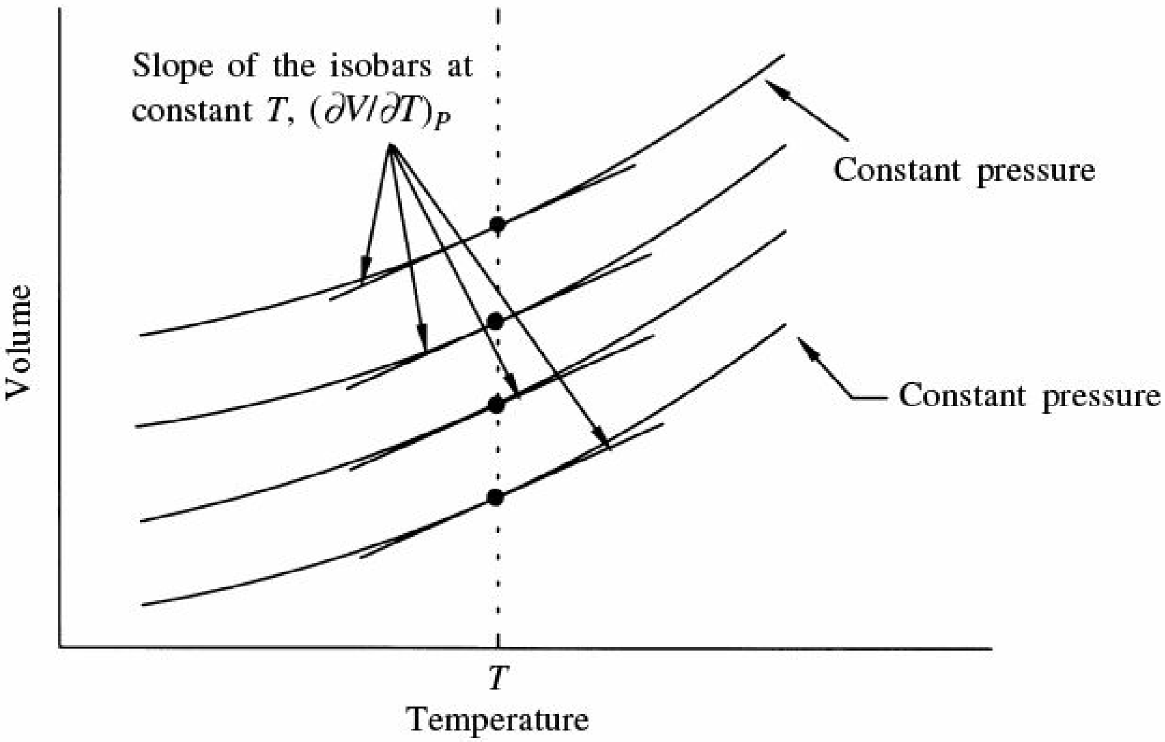


Fig. 6.3 Evaluation of the integral in Eqs. (6.50) and (6.51) using *V-T* curves.

***EXAMPLE* 6.7** Calculate the internal energy, enthalpy, entropy and free energy for one mole of nitrogen at 773 K and 100 bar assuming that nitrogen behaves as an ideal gas. The molal heat capacity of nitrogen at 1 bar is given as $C_P = 27.3 + 4.2$ □ $10^{-3}T$, where *T* is in K and C_P is in J/mol K. Enthalpy of nitrogen is zero at 273 K and 1 bar. The entropy of nitrogen is 192.4 J/molK at 298 K and 1 bar.

Solution Assume that the nitrogen is initially at 273 K and 1 bar for evaluation of enthalpy, and at 298 K and 1 bar for evaluation of entropy. Let the gas undergo a change of state in two steps. First, a constant pressure process at 1 bar when its temperature is increased to 773 K. Secondly, a constant temperature process at 773 K when the pressure of the gas increases to 100 bar.

Step 1:

$$\Delta H = \int_{273}^{773} C_{P0}\, dT = \int_{273}^{773} (27.3 + 4.2 \times 10^{-3}T)\, dT = 14.748 \times 10^{3} \text{ J/mol}$$

$$\Delta S = \int_{298}^{773} \frac{C_{P0}}{T}\, dT = \int_{298}^{773} 27.3\,\frac{dT}{T} + 4.2 \times 10^{-3}\, dT = 28.02 \text{ J/mol K}$$

Let H' and S' be the enthalpy and entropy values after step 1. Then

$$H' = H_0 + \Delta H = 0 + 14.748 \times 10^{3} \text{ J/mol.}$$

$$S' = S_0 + \Delta S = 192.4 + 28.02 = 220.42 \text{ J/mol K}$$

Step 2:

$$\Delta H = \int_{1}^{100} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP \text{ and } \Delta S = -\int_{1}^{100} \left(\frac{\partial V}{\partial T}\right)_P dP$$

Since nitrogen behaves as ideal gas,

$$V = RT/P, \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}, V - T\left(\frac{\partial V}{\partial T}\right)_P = V - \frac{RT}{P} = 0$$

Therefore,

$$\Delta H = 0$$

$$\Delta S = -\int_{1}^{100} R\,\frac{dP}{P} = -8.314 \ln 100 = -38.29 \text{ J/mol K}$$

Enthalpy:

$$H = H' + \Delta H = H' = 14.748 \times 10^{3} \text{ J/mol}$$

Entropy:

$$S = S' + \Delta S = 220.42 - 38.29 = 182.13 \text{ J/mol K}$$

Internal energy:

$$U = H - PV = H - RT = 14.748 \times 10^{3} - 8.314 \times 773 = 8.321 \times 10^{3} \text{ J/mol}$$

Gibbs free energy:

$$G = H - TS = 14.748 \times 10^{3} - 773 \times 182.13 = -126.038 \times 10^{3} \text{ J/mol}$$

***EXAMPLE* 6.8** Calculate the change in internal energy of 25 kmol of CO_2 gas when it is isothermally expanded from 1.0132 □ 10^4 kPa to 1.0132 □ 10^2 kPa at 373 K. Assume CO_2 to obey

$$\left(P + \frac{365}{V^2}\right)(V - 0.043) = RT$$

Solution The change in internal energy in an isothermal process is given by Eq. (6.47):

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Here,

$$P = \frac{RT}{V - 0.043} - \frac{365}{V^2} \tag{i}$$

Therefore,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - 0.043} \tag{ii}$$

Substituting Eqs. (i) and (ii) in Eq. (6.47),

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V - 0.043} - P = \frac{RT}{V - 0.043} - \frac{RT}{V - 0.043} + \frac{365}{V^2} = \frac{365}{V^2} \tag{iii}$$

Integrating Eq. (iii), we get

$$\Delta U = 365 \int_{V_1}^{V_2} \frac{dV}{V^2} \tag{iv}$$

Here V_1 is the initial volume of the gas which is evaluated from the equation of state.

$$\left(1.0132 \times 10^4 + \frac{365}{V_1^2}\right)(V_1 \;\; - 0.043) = 8.314 \times 373$$

Solving this, we get,

$$V_1 = 0.215 \text{ m}^3$$

Similarly, V_2 is the final volume of the gas after expansion.

$$\left(1.0132 \times 10^2 + \frac{365}{V_2^2}\right)(V_2 \;\; - 0.043) = 8.314 \times 373$$

Solving this, we get,

$$V_2 = 30.53 \text{ m}^3$$

Substituting the integration limits in Eq. (iv), we get for 25 kmol of CO_2,

$$\Delta U = 25 \times 365 \int_{0.215}^{30.53} \frac{dV}{V^2} = -25 \times 365 \times \left(\frac{1}{30.53} - \frac{1}{0.215}\right) = 42143 \text{ kJ}$$

***EXAMPLE* 6.9** A gas obeys the equation of state $P(V - B) = RT + (AP^2)/T$, where A and B are constants. The mean specific heat (C_P) at atmospheric pressure is 33.6 J/mol K. If

$A = 1.0$ □ 10^{-3} m^3 K/(bar) mol; $B = 8.0$ □ 10^{-5} m^3/mol

calculate

(a) The entropy change when the state of the gas is changed from state 1 (4 bar, 300 K) to state 2 (12 bar, 400 K).

(b) The mean heat capacity at 12 bar.

Solution (a) The proposed change is assumed to take place in three steps in series as illustrated in Fig. 6.4.

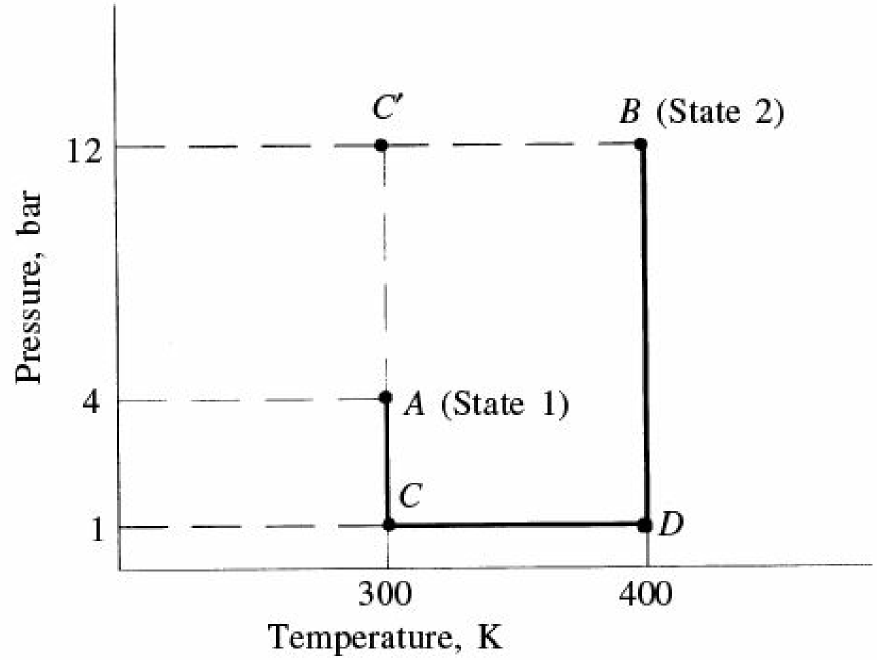


Fig. 6.4 Changes in the state of the gas in Example 6.8.

Step 1: Process *AC*, isothermal at 300 K

Step 2: Process *CD*, isobaric at 1 bar.

Step 3: Process *DB*, isothermal at 400 K

Since the equation of state is

$$P(V - B) = RT + (AP^2)/T$$

differentiation yields,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} - \frac{AP}{T^2}$$

For step 1,

$$\Delta S = -\int_4^1 \left(\frac{\partial V}{\partial T}\right)_P dP = \int_1^4 \left(\frac{R}{P} - \frac{AP}{T^2}\right) dP$$

Noting that $R = 8.314 \times 10^{-5}$ m^3 (bar)/mol K, the above equation gives

$$\Delta S = 8.314 \times 10^{-5} \ln 4 - \frac{1 \times 15 \times 10^{-3}}{2 \times 300^2} = 11.52 \times 10^{-5} \text{ m}^3 \text{ (bar)/mol K} = 11.52 \text{ J/mol K}$$

For step 2,

$$\Delta S = \int_{300}^{400} \frac{C_{P0}}{T}\, dT = 33.6 \ln \frac{400}{300} = 9.67 \text{ J/mol K}$$

For step 3,

$$\Delta S = -\int_{1}^{12} \left(\frac{\partial V}{\partial T}\right)_P dP = -\int_{1}^{12} \left(\frac{R}{P} - \frac{AP}{T^2}\right) dP = -R \ln \frac{12}{1} + \frac{1.0 \times 10^{-3}\,(12^2 - 1^2)}{2 \times 400^2}$$

$= -20.6 \times 10^{-5}$ m^3 (bar)/mol K = – 20.6 J/mol K

Therefore, the change in entropy for the actual process = 11.52 + 9.67 – 20.6 = 0.59 J/mol K.

(b) If the change in state is brought about by a two-step process: first, along path *AC′* (constant temperature) and then along path *C′B* (constant pressure), the total change in entropy will be same as in part (a).

$$\Delta S = -\int_{4}^{12} \left(\frac{R}{P} - \frac{AP}{T^2}\right) dP + C_{Pm} \int_{300}^{400} \frac{dT}{T} = 0.59 \text{ J/mol K} = 0.59 \times 10^{-5} \text{m}^3 \text{ (bar)/mol K}$$

Substituting the values, we get

$$-9.063 \times 10^{-5} + 0.2877\, C_{Pm} = 0.59 \times 10^{-5} \text{ m}^3 \text{ (bar)/mol K}$$

$$C_{Pm} = 33.55 \times 10^{-5} \text{ m}^3 \text{ (bar)/mol K} = 33.55 \text{ J/mol K}$$

6.4.9 Relationship between C_P and C_V

We have seen that the partial derivatives of entropy with respect to temperature are related to the specific heats as given by Eqs. (6.31) and (6.32).

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}, \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

Equation (6.35) gives the total differential of S as

$$dS = \frac{C_P}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

Dividing by dT and imposing the constant volume restriction, the above equation becomes

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_P}{T} - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \tag{6.52}$$

Substitute Eq. (6.32) into Eq. (6.52) so that

$$\frac{C_V}{T} = \frac{C_P}{T} - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

which can be rearranged as

$$\boxed{C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V} \tag{6.53}$$

Equation (6.38) can be used to replace $(\partial P/\partial T)_V$ from this equation. The resulting equation is

$$\boxed{C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T} \tag{6.54}$$

If the P-V-T behaviour of the fluid is known either as an equation of state or as a graphical result, Eq. (6.54) can be used to evaluate the difference between C_P and C_V over wide ranges of temperature and pressure.

Equation (6.54) can be written in terms of coefficient of volume expansion (b) and coefficient of compressibility (k) which are defined as below.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

which means that $(\partial V/\partial T)_P = \beta V$ and $(\partial V/\partial P)_T = -\kappa V$. Using these in Eq. (6.54) the following equation results:

$$\boxed{C_P - C_V = \frac{\beta^2 V T}{\kappa}} \tag{6.55}$$

Equation (6.55) is the most convenient form for the calculation of $C_P - C_V$ of solids and liquids.

Equations (6.54) and (6.55) are particularly valuable because most of the laws developed under statistical thermodynamics on specific heat deal with C_V, though these are rarely determined experimentally. These equations provide useful tools for calculating C_V from experimentally determined values of C_P.

***EXAMPLE* 6.10** Show that for ideal gases $C_P - C_V = R$.

Solution For ideal gases, $PV = RT$, or $V = RT/P$. Also,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}, \qquad P = \frac{RT}{V}, \qquad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2}$$

Substituting these into Eq. (6.54), we obtain

$$C_P - C_V = T\left(\frac{R}{P}\right)^2\left(\frac{RT}{V^2}\right) = R$$

***EXAMPLE* 6.11** The coefficient of compressibility and coefficient of volume expansion of mercury at 273 K and 1 bar are 3.9 ☐ 10^{-6} $(\text{bar})^{-1}$ and 1.8 ☐ 10^{-4} K^{-1} respectively. Calculate C_V for mercury given that $C_P = 0.14$ kJ/kg K and density = 13.596 ☐ 10^3 kg/m^3.

Solution Using Eq. (6.55),

$$C_P - C_V = \frac{(1.8 \times 10^{-4})^2\,(13.596 \times 10^3)^{-1}\,273}{3.9 \times 10^{-6}} = 16.68 \times 10^{-5}\,\frac{\text{m}^3\,(\text{bar})}{\text{kg K}} = 16.68\ \text{J/kg K}$$

Therefore,

$$C_V = 0.14 \times 10^3 - 16.68 = 123.32\ \text{J/kg K}$$

***EXAMPLE* 6.12** Show that for a gas obeying van der Waals equation of state,

$$C_P - C_V = \frac{R}{1 - 2a(V-b)^2/(RTV^3)}$$

where a and b are van der Waals constants.

Solution The van der Waals equation is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{3.29}$$

Differentiate Eq. (3.29) with respect to V at constant T

$$(V - b)\left[\left(\frac{\partial P}{\partial V}\right)_T - \frac{2a}{V^3}\right] + P + \frac{a}{V^2} = 0$$

This equation can be rearranged using Eq. (3.29) as

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{2a(V - b)^2 - RTV^3}{V^3(V - b)^2} \tag{6.56}$$

Differentiating Eq. (3.29) with respect to T at constant P, we obtain

$$(V - b)\left[-\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P\right] + \left(P + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P = R$$

The above equation can be rearranged to give

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{-R(V - b)V^3}{2a(V - b)^2 - RTV^3} \tag{6.57}$$

Substituting Eqs. (6.56) and (6.57) into Eq. (6.54), we get the following result:

$$C_P - C_V = \frac{R}{1 - 2a(V - b)^2/(RTV^3)}$$

6.4.10 Ratio of Heat Capacities

Combining Eqs. (6.31) and (6.32) we see that

$$\frac{C_P}{C_V} = \frac{(\partial S/\partial T)_P}{(\partial S/\partial T)_V} \tag{6.58}$$

In order to express this ratio in terms of P-V-T data, let us assume that $S = f(P, T)$ so that

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT$$

At constant entropy, $dS = 0$. That is,

$$\left(\frac{\partial S}{\partial P}\right)_T dP_S + \left(\frac{\partial S}{\partial T}\right)_P dT_S = 0$$

$$\left(\frac{\partial S}{\partial P}\right)_T dP_S = -\left(\frac{\partial S}{\partial T}\right)_P dT_S$$

Rearranging this equation we get

$$\left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_S$$

By assuming $S = f(V, T)$ and proceeding as above, we can show that

$$\left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_S$$

Substituting the partial derivatives given by the preceding two equations into Eq. (6.58), we see that

$$\frac{C_P}{C_V} = \frac{(\partial S/\partial P)_T\ (\partial P/\partial T)_S}{(\partial S/\partial V)_T\ (\partial V/\partial T)_S} = \left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial V}\right)_S \tag{6.59}$$

It is to be noted that it is impossible to write the ratio of heat capacities in terms of *P-V-T* data alone; entropy appears in at least one of the partial derivatives.

6.4.11 Effect of Pressure and Volume on C_P and C_V

The change in entropy with changes in temperature and pressure is given by Eq. (6.35).

$$dS = \frac{C_P}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

The above equation reduces to the Maxwell's equation, Eq. (6.24), under constant temperature (i.e. when $dT = 0$) and the heat capacity relation, Eq. (6.31), under constant pressure (i.e. when $dP = 0$).

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{6.24}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \tag{6.31}$$

Differentiate Eq. (6.24) with respect to temperature, keeping the pressure constant and Eq. (6.31) with respect to pressure keeping the temperature constant. This results in Eqs. (6.60) and (6.61) respectively.

$$\frac{\partial^2 S}{\partial T\partial P} = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{6.60}$$

$$\frac{\partial^2 S}{\partial P\partial T} = \left(\frac{\partial C_P/T}{\partial P}\right)_T = \frac{1}{T}\left(\frac{\partial C_P}{\partial P}\right)_T \tag{6.61}$$

Compare Eq. (6.60) with Eq. (6.61). The right-hand sides of these equations are equal. That is,

$$\boxed{\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P} \tag{6.62}$$

As $(\partial C_P/\partial P)_T$ can be written as $(\partial C_P/\partial V)_T\,(\partial V/\partial P)_T$, Eq. (6.62) becomes

$$\boxed{\left(\frac{\partial C_P}{\partial V}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P\left(\frac{\partial P}{\partial V}\right)_T} \tag{6.63}$$

Equations (6.62) and (6.63) represent the effect of pressure and volume on C_P.

The following two equations that give the effect of pressure and volume on C_V can be derived in a manner similar to that used for the derivation of Eqs. (6.62) and (6.63)

$$\boxed{\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V} \tag{6.64}$$

$$\boxed{\left(\frac{\partial C_V}{\partial P}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V\left(\frac{\partial V}{\partial P}\right)_T} \tag{6.65}$$

Equations (6.62)–(6.65) hold good for any homogeneous substance; however, they are usually applied to gases.

***EXAMPLE* 6.13** Show that C_P and C_V of ideal gases are independent of pressure and volume.

Solution Since $PV = RT$,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}, \quad \left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}, \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$$

On substituting these results into Eqs. (6.62)–(6.65), we see that

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left(\frac{\partial C_P}{\partial V}\right)_T = \left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial C_V}{\partial P}\right)_T = 0$$

This means that, for ideal gases C_P and C_V depend only on temperature.

***EXAMPLE* 6.14** A certain gas is found to obey the following equation of state.

$$V = \frac{RT}{P} - \frac{C}{T^2} + \frac{D}{T^3}$$

(a) Develop a relation to predict the effect of pressure on C_P

(b) What is $C_P - C_V$?

Solution Equation (6.62) gives the effect of pressure on C_P. The partial derivatives in this equation are evaluated first.

$$V = \frac{RT}{P} - \frac{C}{T^2} + \frac{D}{T^3}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{2C}{T^3} - \frac{3D}{T^4}, \qquad \left(\frac{\partial^2 V}{\partial T^2}\right)_P = -\frac{6C}{T^4} + \frac{12D}{T^5}, \qquad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2}$$

(a) Substituting these results in Eq. (6.62),

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{6C}{T^3} - \frac{12D}{T^4}$$

(b) Substituting the necessary partial derivatives in Eq. (6.54), we get

$$C_P - C_V = \left(\frac{1}{P} + \frac{2C}{RT^3} - \frac{3D}{RT^4}\right)^2 RP^2$$

***EXAMPLE* 6.15** A gas obeys the relation $P(V - b) = RT$ and has a constant C_V. Show that

(a) U is a function of temperature alone

(b) g is constant

(c) $P(V - b)^{g}$ is constant for a reversible adiabatic process.

Solution (a) To prove that U depends only on temperature, it is enough to show that U does not change with P or V at constant T. Consider Eq. (6.40). At constant temperature this equation can be simplified to

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left[P + T\,\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\right] = T\left(\frac{\partial P}{\partial T}\right)_V - P \tag{6.66}$$

Since the equation of state is $P(V - b) = RT$,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

Substituting this in Eq. (6.66),

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad (6.67)$$

Since

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

and as is evident from the equation of state, $(\partial P/\partial V)_T \neq 0$, we have

$$\left(\frac{\partial U}{\partial P}\right)_T = 0 \qquad (6.68)$$

Equations (6.67) and (6.68) together mean that U depends only on T

(b) Equation (6.54) gives $C_P - C_V$ as

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

Here

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}, \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V - b)^2}$$

Thus

$$C_P - C_V = -T\left(\frac{R}{P}\right)^2 \left(-\frac{RT}{(V - b)^2}\right) = R, \text{ a constant}$$

It is given that C_V is constant. Therefore, C_P and hence, $\gamma = C_P/C_V$ are also constant.

(c) Here

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}, \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

Consider S as a function of P and V. That is, $S = f(P, V)$

$$dS = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

At constant S, we have

$$\left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV = 0$$

Rearranging this, we get

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{(\partial S/\partial V)_P}{(\partial S/\partial P)_V} = -\frac{(\partial S/\partial T)_P(\partial T/\partial V)_P}{(\partial S/\partial T)_V(\partial T/\partial P)_V} = -\frac{C_P}{C_V} \times \frac{(\partial T/\partial V)_P}{(\partial T/\partial P)_V} = -\gamma\frac{P/R}{(V-b)/R} = -\gamma\frac{P}{V-b}$$

This can be written as

$$\frac{dP}{P} = -\gamma\frac{dV}{V-b}$$

$$d \ln P = -d \ln (V-b)^{\gamma}$$

or

$$d \ln P(V-b)^{\gamma} = 0$$

i.e.

$$P(V-b)^{\gamma} = C$$

where C is a constant.

6.4.12 Joule–Thomson Coefficient

As discussed in Section 5.3, the Joule–Thomson expansion is employed for cooling and liquefying o gases. It involves adiabatic throttling of a gas. The enthalpy remains constant during the process. The *Joule–Thomson coefficient* (m) is the fall in temperature associated with a unit decrease in pressure under this condition.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \tag{6.69}$$

Generally, a gas cools on throttling, so that the Joule–Thomson coefficient is positive. However, it may take negative values if the temperature increases with the expansion of the gas.

The gas, which is initially at a state represented by the point P in Fig. 6.5, is undergoing Joule–Thomson expansion. It will experience a rise in temperature till the point Q is reached, and thereafter the temperature decreases with further decrease in pressure. The slope of the isenthalp is equal to the Joule–Thomson coefficient as per the defining relation Eq. (6.69). It is positive only in the regior where pressure is less than that at Q and is zero at point Q, where the isenthalp exhibits a maximum. The locus of the maximum in the isenthalp curves forms the *Joule–Thomson inversion curve* as shown in the figure. To the left of this, m is positive and to the right it is negative. Figure 6.6 shows the complete range of a typical Joule–Thomson inversion curve.

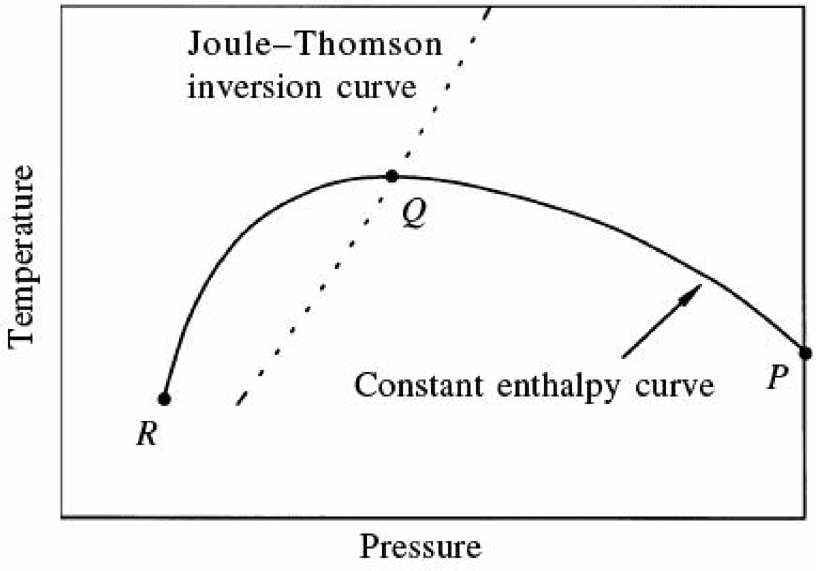


Fig. 6.5 Variation of Joule–Thomson coefficient with the state of the gas.

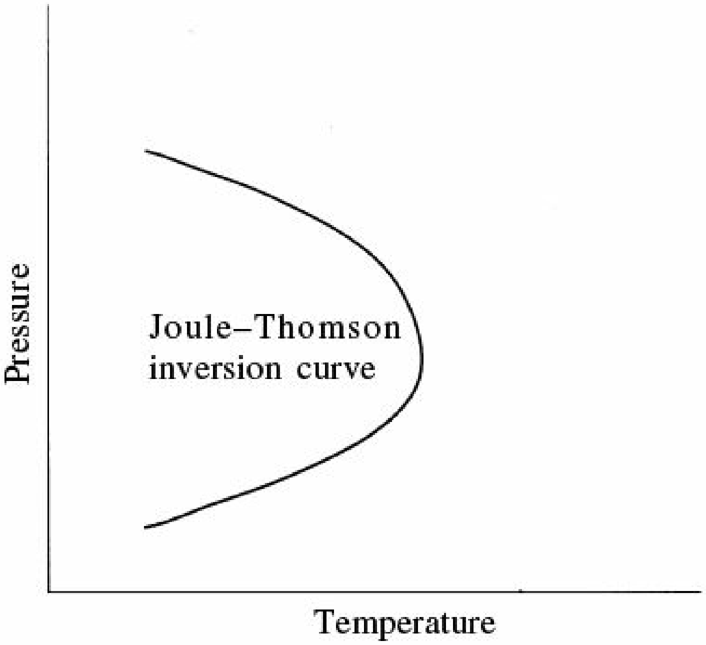


Fig. 6.6 A typical Joule–Thomson inversion curve.

The region bounded by this curve and the temperature axis indicates the conditions under which the gas would cool on Joule–Thomson expansion, whereas in the region outside this curve throttling process results in increase in temperature.

The Joule–Thomson coefficient may be calculated from the P-V-T behaviour and specific heat data as detailed below. The modified differential of enthalpy [Eq. (6.41)] may be taken as the starting point.

$$dH = C_P\, dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP \tag{6.41}$$

As noted above, for Joule–Thomson expansion $dH = 0$. Imposing this condition on Eq. (6.41) we get

$$C_P\, dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP = 0$$

or

$$\left(\frac{\partial T}{\partial P}\right)_H = \mu = \frac{T(\partial V/\partial T)_P - V}{C_P}$$

$$\boxed{\mu C_P = T\left(\frac{\partial V}{\partial T}\right)_P - V} \tag{6.70}$$

***EXAMPLE* 6.16** Show that the Joule–Thomson coefficient is zero for ideal gases.

Solution For ideal gases, $(\partial V/\partial T)_P = R/P$. The right-hand side of Eq. (6.70) therefore becomes zero, which means that the Joule–Thomson coefficient (m) is zero.

***EXAMPLE* 6.17** Prove that the reversible adiabatic expansion of a gas always results in a temperature decrease. Prove also that this decrease in temperature is greater than that resulting from Joule–Thomson expansion between the same initial and final pressures.

Solution For a reversible adiabatic process $dS = 0$ and Eq. (6.35) reduces to the following form.

$$\frac{C_P}{T}\, dT - \left(\frac{\partial V}{\partial T}\right)_P dP = 0$$

This can be rearranged as

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P \tag{6.71}$$

Since the volume of a gas increases with increase in temperature, $(\partial V/\partial T)_P > 0$, which means that $(\partial T/\partial P)_S > 0$. That is, the temperature decreases with decrease in pressure in a reversible adiabatic process. Eliminate $(\partial V/\partial T)_P$ in Eq. (6.70) by substituting into it Eq. (6.71).

$$\mu = \left(\frac{\partial T}{\partial P}\right)_S - \frac{V}{C_P}$$

Since V/C_P is always positive, $\mu < (\partial T/\partial P)_S$. That is, the Joule–Thomson coefficient is less than the temperature drop in a reversible adiabatic expansion.

6.4.13 Gibbs–Helmholtz Equation

The Gibbs–Helmholtz equation provides the effect of temperature on Gibbs free energy. Consider Eq (6.18).

$$dG = -S\,dT + V\,dP \qquad (6.18)$$

At constant pressure, the above equation reduces to

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{6.72}$$

Even though this equation gives the effect of temperature on G it will be convenient for practical calculations to replace S in terms of measurable quantities. This can be done as follows.

Noting that $d(u/v) = (v\,du - u\,dv)/v^2$, the derivative of G/T can be written as

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{T(\partial G/\partial T)_P - G}{T^2}$$

Use Eq. (6.72) to eliminate $(\partial G/\partial T)_P$ from the above equation.

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{-TS - G}{T^2}$$

Since by definition, $G = H - TS$, the above equation can be simplified as

$$\boxed{\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}} \tag{6.73}$$

Equation (6.73) is known as *Gibbs–Helmholtz equation* and it finds wide application in the analysis of chemical reaction equilibria. Integration of Eq. (6.73) yields

$$\frac{G}{T} = -\int \frac{H}{T^2}\,dT + G' \tag{6.74}$$

where G' is a constant of integration. The enthalpy of a substance can be written as

$$H = \int C_P\,dT + H'$$

where H□ is a constant of integration whose value is known by the choice of reference state at which enthalpy is arbitrarily set equal to zero. Expressing C_P as a power function of T as

$C_P = a + bT + cT^2$, $H = H$□ $+ aT + (1/2)\,bT^2 + (1/3)\,cT^3$. Substituting these in Eq. (6.74), we get

$$
\begin{aligned}
G &= H' - aT\ln T - \frac{b}{2}T^2 - \frac{c}{6}T^3 + G'T \\
&= H - aT - \frac{b}{2}T^2 - \frac{c}{3}T^3 - aT\ln T - \frac{b}{2}T^2 - \frac{c}{6}T^3 + G'T \\
&= H - aT\ln T - bT^2 - \frac{c}{2}T^3 + IT \qquad (6.75)
\end{aligned}
$$

In Eq. (6.75), I (=G□ $- a$) is a constant which should be evaluated first for applying it for the calculation of G.

6.5 METHOD OF JACOBIANS

Jacobians are determinants, the elements of which are partial derivatives. The method of Jacobians can be used as a very powerful but simple tool for deriving the relationships between thermodynamic properties. In the earlier sections we have developed these relationships through partial derivatives. All these relations may be derived using the method of Jacobians. Here we discuss the method in general, and derive a few typical equations which were derived in previous sections using the method of partial derivatives.

6.5.1 Properties of Jacobians

Let us consider three variables, x, y and z, each of which is a function of the independent variables u and v. Then,

$x = x(u, v)$, $y = y(u, v)$, $z = z(u, v)$

The Jacobian of x and y, denoted by $[x, y]/[u, v]$, is defined as,

$$
\frac{[x, y]}{[u, v]} = \begin{bmatrix} \left(\frac{\partial x}{\partial u}\right)_v & \left(\frac{\partial y}{\partial u}\right)_v \\ \left(\frac{\partial x}{\partial v}\right)_u & \left(\frac{\partial y}{\partial v}\right)_u \end{bmatrix} = \left(\frac{\partial x}{\partial u}\right)_v \left(\frac{\partial y}{\partial v}\right)_u - \left(\frac{\partial x}{\partial v}\right)_u \left(\frac{\partial y}{\partial u}\right)_v \qquad (6.76)
$$

The following are some of the properties of the Jacobians that are useful in the derivation of thermodynamic relationships.

Property 1:
$$[x, y] = -[y, x] \tag{6.77}$$

Property 2:
$$[x, x] = 0 \tag{6.78}$$

Property 3:
$$[\alpha x, \beta y] = \alpha\beta[x, y] \tag{6.79}$$

Property 4: In Jacobian notation, the partial derivative $(\partial y/\partial x)_z$ can be expressed as

$$\left(\frac{\partial y}{\partial x}\right)_z = \frac{[y, z]}{[x, z]} \tag{6.80}$$

Property 5:
$$\frac{[x, y]}{[u, v]} = \frac{[x, y]/[s, t]}{[u, v]/[s, t]} \tag{6.81}$$

Property 6: The exact differential equation, $dz = M\,dx + N\,dy$, in terms of Jacobians becomes

$$[z, u] = M[x, u] + N[y, u] \tag{6.82}$$

Property 7: The exact differential equation, $dz = M\,dx + N\,dy$, may be put in another form as

$$dz = \frac{[z, y]}{[x, y]}\,dx + \frac{[z, x]}{[y, x]}\,dy \tag{6.83}$$

The properties 1–5 can be easily verified by writing the Jacobians as determinants and expanding them. To verify property 6 consider the total differential:

$$dz = M\,dx + N\,dy \tag{6.84}$$

Divide this by dv, keeping u constant we get,

$$\left(\frac{\partial z}{\partial v}\right)_u = M\left(\frac{\partial x}{\partial v}\right)_u + N\left(\frac{\partial y}{\partial v}\right)_u$$

Using the property 4, the partial derivatives in the above equation may be eliminated in favour of the Jacobians as:

$$\frac{[z, u]}{[v, u]} = M\frac{[x, u]}{[v, u]} + N\frac{[y, u]}{[v, u]}$$

The above result can be written in simplified notation as in Eq. (6.82). Noting that in Eq. (6.84),

$$M = \left(\frac{\partial z}{\partial x}\right)_y, \qquad N = \left(\frac{\partial z}{\partial y}\right)_x$$

and using the property 4, Eq. (6.83) can also be easily verified.

Another relationship among Jacobians which is found to be extremely useful in the derivation of thermodynamic relations may be developed as follows. Divide Eq. (6.83) by dv, keeping u constant and express the result in terms of Jacobians.

$$\left(\frac{\partial z}{\partial v}\right)_u = \frac{[z, y]}{[x, y]}\left(\frac{\partial x}{\partial v}\right)_u + \frac{[z, x]}{[y, x]}\left(\frac{\partial y}{\partial v}\right)_u$$

$$\frac{[z, u]}{[v, u]} = \frac{[z, y]}{[x, y]}\frac{[x, u]}{[v, u]} + \frac{[z, x]}{[y, x]}\frac{[y, u]}{[v, u]}$$

That is,

$$[z, u]\,[x, y] = [z, y]\,[x, u] - [z, x]\,[y, u]$$

or

$$[x, u]\,[y, z] + [y, u]\,[z, x] + [z, u]\,[x, y] = 0 \qquad (6.85)$$

6.5.2 Thermodynamic Relations through the Method of Jacobians

Fundamental property relations. Consider the differentials of the energy properties that were developed in section 6.4.2. They are given by Eqs. (6.14) and (6.16)–(6.18). Using property 6, these equations may be expressed in terms of the Jacobians Eqs. (6.86)–(6.89) respectively, as:

$$[U, w] = T[S, w] - P[V, w] \qquad (6.86)$$

$$[H, w] = T[S, w] + V[P, w] \qquad (6.87)$$

$$[A, w] = -S[T, w] - P[V, w] \qquad (6.88)$$

$$[G, w] = -S[T, w] + V[P, w] \qquad (6.89)$$

In Eqs. (6.86)–(6.89), w stands for any thermodynamic property other than the energy property.

Maxwell's equations. It can be shown that all Maxwell's equations can be expressed as

$$[P, V] = [T, S]$$

For example, consider Maxwell's equation, Eq. (6.23)

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad (6.23)$$

Using property 4, Eq. (6.80), the partial derivatives in Eq. (6.23) may be replaced by the Jacobians.

$$\frac{[P, V]}{[T, V]} = \frac{[S, T]}{[V, T]}$$

Using the property 1, this becomes

$$\frac{[P, V]}{[T, V]} = -\frac{[S, T]}{[T, V]}$$

so that

$$[P, V] = -[S, T]$$

or

$$\boxed{[P, V] = [T, S]} \tag{6.90}$$

Heat capacities C_P and C_V. The heat capacities were defined by Eqs. (6.31) and (6.32)

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}, \quad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

Replacing the partial derivatives in favour of the Jacobians using the property 4, we get

$$\boxed{C_P = T\frac{[S, P]}{[T, P]}} \tag{6.91}$$

$$\boxed{C_V = T\frac{[S, V]}{[T, V]}} \tag{6.92}$$

Coefficients of expansion and compressibility. The volume coefficient of expansion (b) and coefficient of isothermal compressibility (k) are two other measurable quantities like heat capacities at constant pressure and constant volume. They are defined as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \qquad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

In terms of Jacobians these become

$$\boxed{\beta = \frac{1}{V}\frac{[V, P]}{[T, P]}} \tag{6.93}$$

$$\boxed{\kappa = -\frac{1}{V}\frac{[V, T]}{[P, T]} = \frac{1}{V}\frac{[V, T]}{[T, P]}} \tag{6.94}$$

Hence, we see that all thermodynamic properties can be expressed in terms of measurable quantities by the method of Jacobians. If the equations contain energy properties U, H, A or G, they may be eliminated in terms of the reference properties P, V, T and S. Fundamental property relations in terms of Jacobians, Eqs. (6.86)–(6.89) may be used for this purpose. To eliminate entropy S, Maxwell's relations, Eq. (6.90), or the heat capacity relations Eq. (6.91) or Eq. (6.92) may be used. By introducing wherever possible, b, the volume coefficient of expansion, and k, the coefficient of isothermal compressibility, the resulting relationships get fully expressed in terms of measurable quantities. A few examples would be helpful to illustrate the method.

***EXAMPLE* 6.18** Derive the following by the method of Jacobians:

$$\text{(a)}\ dS = \frac{C_P}{T}\,dT - \left(\frac{\partial V}{\partial T}\right)_P dP \tag{6.35}$$

$$\text{(b)}\ dS = \frac{C_V}{T}\,dT - \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\,dV \tag{6.39}$$

Solution (a) If entropy were treated as function of temperature and pressure, then

$$S = f(P, T)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \tag{6.34}$$

In Jacobian notation, Eq. (6.34) becomes

$$dS = \frac{[S, P]}{[T, P]}\,dT + \frac{[S, T]}{[P, T]}\,dP \tag{6.95}$$

From the heat capacity relation, Eq. (6.91), we have

$$\frac{[S, P]}{[T, P]} = \frac{C_P}{T} \tag{6.96}$$

and from the Maxwell's equation, Eq. (6.90), and using the property 1 of Jacobians, we get

$$\frac{[S, T]}{[P, T]} = -\frac{[T, S]}{[P, T]} = -\frac{[P, V]}{[P, T]} = -\frac{[V, P]}{[T, P]} \tag{6.97}$$

By Eq. (6.80),

$$\frac{[V, P]}{[T, P]} = \left(\frac{\partial V}{\partial T}\right)_P \tag{6.98}$$

Substituting Eqs. (6.96)–(6.98) into Eq. (6.95), we get

$$dS = \frac{C_P}{T}\, dT - \left(\frac{\partial V}{\partial T}\right)_P dP \tag{6.35}$$

It may also be noted that the Jacobian on the left-hand side of Eq. (6.98) is equal to $V\beta$ by Eq. (6.93), so that Eq. (6.95) may also be written as

$$dS = \frac{C_P}{T}\, dT - \beta V\, dP \tag{6.99}$$

(b) If entropy were treated as function of temperature and volume, then $S = f(V, T)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \tag{6.36}$$

In Jacobian notation,

$$dS = \frac{[S, V]}{[T, V]}\, dT + \frac{[S, T]}{[V, T]}\, dV \tag{6.100}$$

By Eq. (6.92),

$$\frac{[S, V]}{[T, V]} = \frac{C_V}{T} \tag{6.101}$$

By Maxwell's equation, $[P, V] = [T, S]$. Therefore,

$$\frac{[S, T]}{[V, T]} = \frac{[V, P]}{[V, T]} \tag{6.102}$$

Using Eq. (6.81), Eq. (6.102) may be written as

$$\frac{[S, T]}{[V, T]} = \frac{[V, P]}{[V, T]} = \frac{[V, P]/[T, P]}{[V, T]/[T, P]} = -\frac{[V, P]/[T, P]}{[V, T]/[P, T]} = -\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T} \tag{6.103}$$

Substituting Eqs. (6.101) and (6.103) into Eq. (6.100), we get

$$dS = \frac{C_V}{T}\,dT - \frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\,dV \tag{6.39}$$

We can use Eqs. (6.93) and (6.94) to write Eq. (6.103) in the following form.

$$\frac{[S, T]}{[V, T]} = -\frac{[V, P]/[T, P]}{[V, T]/[P, T]} = \frac{\beta}{\kappa}$$

Using this, Eq. (6.100) may be written as

$$dS = \frac{C_V}{T}\,dT + \frac{\beta}{\kappa}\,dV \tag{6.104}$$

***EXAMPLE* 6.19** Derive the following relation between C_P and C_V using the method of Jacobians:

$$C_P - C_V = \frac{\beta^2 VT}{\kappa} \tag{6.55}$$

Solution The heat capacity at constant pressure is given by Eq. (6.91) and heat capacity at constant volume by Eq. (6.92).

$$C_P = T\,\frac{[S, P]}{[T, P]} \tag{6.91}$$

$$C_V = T\,\frac{[S, V]}{[T, V]} \tag{6.92}$$

The relationship between Jacobians $[S, P]$ and $[S, V]$ may be obtained using Eq. (6.85).

$$[x, u]\,[y, z] + [y, u]\,[z, x] + [z, u]\,[x, y] = 0$$

Put $x = S$, $y = P$, $z = V$, and $u = T$ in the above equation.

$$[S, T]\,[P, V] + [P, T]\,[V, S] + [V, T]\,[S, P] = 0$$

On rearrangement, we get

$$[S, P] = -\frac{[S, T]\,[P, V] + [P, T]\,[V, S]}{[V, T]} = \frac{[P, T]\,[S, V] - [S, T]\,[P, V]}{[V, T]}$$

or

$$\frac{[S, P]}{[T, P]} = \frac{[P, T]\,[S, V] - [S, T]\,[P, V]}{[T, P]\,[V, T]} = -\frac{[S, V]}{[V, T]} - \frac{[S, T]\,[P, V]}{[T, P]\,[V, T]}$$

The above result can be modified as

$$\frac{[S, P]}{[T, P]} = \frac{[S, V]}{[T, V]} - \frac{[T, S]\,[P, V]}{[T, P]\,[T, V]} \tag{6.105}$$

From Eqs. (6.91) and (6.92) we see that

$$C_P - C_V = T\left[\frac{[S, P]}{[T, P]} - \frac{[S, V]}{[T, V]}\right] \tag{6.106}$$

Substituting Eq. (6.105) into Eq. (6.106), we obtain

$$C_P - C_V = -T\frac{[T, S]\,[P, V]}{[T, P]\,[T, V]} \tag{6.107}$$

Using Maxwell's equation, Eq. (6.107) can be written as

$$C_P - C_V = T\frac{[V, P]\,[P, V]}{[T, P]\,[T, V]} \tag{6.108}$$

Equation (6.108), when expressed in terms of partial derivatives, gives Eq. (6.53).

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \tag{6.53}$$

Multiplying the numerator and denominator of the right-hand side of Eq. (6.108) by $[T, P]$, we get

$$C_P - C_V = T\frac{[V, P]}{[T, P]}\,\frac{[T, P]}{[T, V]}\,\frac{[P, V]}{[T, P]} = -T\frac{[V, P]}{[T, P]}\,\frac{[T, P]}{[T, V]}\,\frac{[V, P]}{[T, P]} \tag{6.109}$$

In terms of partial derivatives, the above result gives

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \tag{6.54}$$

Substituting Eqs. (6.93) and (6.94) into Eq. (6.109), we get

$$C_P - C_V = \frac{\beta^2 VT}{\kappa} \tag{6.55}$$

***EXAMPLE* 6.20** Using the method of Jacobians show that

$$\left(\frac{\partial H}{\partial V}\right)_T = -\frac{1}{\kappa} + T\left(\frac{\partial P}{\partial T}\right)_V$$

Solution The differential equation for enthalpy in Jacobian notation is given as

$$[H, w] = T[S, w] + V[P, w] \qquad (6.87)$$

Let $w = T$. Then

$$[H, T] = T[S, T] + V[P, T] \qquad (6.110)$$

The property 2 of Jacobians permits us to express the $(\partial H/\partial V)_T$ as

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{[H, T]}{[V, T]} \tag{6.111}$$

Substitute Eq. (6.110) into Eq. (6.111). Then

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{[H, T]}{[V, T]} = \frac{T[S, T] + V[P, T]}{[V, T]} \tag{6.112}$$

Using the Maxwell's equation, Eq. (6.112) becomes

$$\left(\frac{\partial H}{\partial V}\right)_T = \frac{T[V, P] + V[P, T]}{[V, T]} = T\frac{[V, P]}{[V, T]} + V\frac{[P, T]}{[V, T]}$$

Substitute Eq. (6.94) and eliminate the Jacobian in terms of the partial derivative to get

$$\left(\frac{\partial H}{\partial V}\right)_T = -\frac{1}{\kappa} + T\left(\frac{\partial P}{\partial T}\right)_V \tag{6.113}$$

***EXAMPLE* 6.21** Using the method of Jacobians, derive a relationship for the Joule–Thomsor coefficient in terms of measurable quantities.

Solution By definition, the Joule–Thomson coefficient is $\mu = (\partial T/\partial P)_H$. In Jacobian form,

$$\mu = \frac{[T, H]}{[P, H]} \tag{6.114}$$

Using Eq. (6.87),

$$[H, T] = T[S, T] + V[P, T]$$

$$[H, P] = T[S, P] + V[P, P] = T[S, P]$$

Substituting these in Eq. (6.114), we get

$$\mu = \frac{[H, T]}{[H, P]} = \frac{T[S, T] + V[P, T]}{T[S, P]} \tag{6.115}$$

Using Eqs. (6.90) and (6.91), Eq. (6.115) becomes

$$\mu = \frac{T[V, P] + V[P, T]}{C_P[T, P]} = \frac{T(\partial V/\partial T)_P - V}{C_P} \tag{6.116}$$

Equation (6.116) may be rearranged as

$$C_P\mu = T\left(\frac{\partial V}{\partial T}\right)_P - V \tag{6.70}$$

6.6 FUGACITY

The concept of *fugacity* was introduced by G.N. Lewis (1901) and is widely used in solution thermodynamics to represent the behaviour of real gases. The name fugacity is derived from the Latin for 'fleetness' or the 'escaping tendency'. It has been used extensively in the study of phase and chemical reaction equilibria involving gases at high pressures. Though the 'fugacity' is mainly applied to mixtures, the present discussion is limited to pure gases.

For an infinitesimal reversible change occurring in the system under isothermal conditions, Eq. (6.18) reduces to

$$dG = V\,dP$$

For one mole of an ideal gas V in the above equation may be replaced by RT/P, so that

$$dG = RT\frac{dP}{P} = RT\,d(\ln P) \tag{6.117}$$

Equation (6.117) is applicable only to ideal gases. If, however, we represent the influence of pressure on Gibbs free energy of real gases by a similar relationship, then the true pressure in the above equation should be replaced by an 'effective' pressure, which we call fugacity f of the gas. The following equation, thus, provides the partial definition of fugacity.

$$dG = RT\,d(\ln f) \tag{6.118}$$

Equation (6.118) is satisfied by all gases whether ideal or real. Integration of this equation gives

$$G = RT \ln f + C \qquad (6.119)$$

where C is a constant of integration that depends upon the temperature and nature of the gas. Fugacity has the same dimension as pressure, usually atmosphere or bar.

6.6.1 Standard State for Fugacity

Consider the molar free energies of a gas in two states both at the same temperature. Let G_1 and G_2 be the free energies and f_1 and f_2 be the corresponding fugacities in these states. By Eq. (6.119), the change in free energy is

$$\Delta G = G_2 - G_1 = RT \ln \frac{f_2}{f_1} \qquad (6.120)$$

The free energy change can be experimentally measured and by the above equation the measured free energy change gives the ratio of fugacities f_2/f_1. The fugacity in any state can be evaluated if the fugacity is assigned a specific value in a particular reference state.

For an ideal gas integration of Eq. (6.117) gives the free energy change as

$$\Delta G = G_2 - G_1 = RT \ln \frac{P_2}{P_1} \qquad (6.121)$$

Whereas Eq. (6.121) is applicable only to ideal gases, Eq. (6.120) is valid for all fluids, ideal or real. It follows that in the case of ideal gases, $f_2/f_1 = P_2/P_1$, or fugacity is directly proportional to pressure. The proportionality constant is chosen to be unity for convenience. That is, $f/P = 1$ or $f = P$, for ideal gases. The fugacity is always equal to the pressure for an ideal gas. However, for real gases, fugacity and pressure are not proportional to one another, and f/P is not constant. As the pressure of the gas is reduced, the behaviour of the real gas approaches that of an ideal gas. That is, at very low pressures, the fugacity of a real gas should be the same as its pressure. So the gas at a very low pressure P^0 is chosen as the reference state and it is postulated that the ratio of fugacity to pressure at this state is unity. Thus the definition of fugacity is completed by stating that

$$\boxed{\lim_{P \to 0} \frac{f}{P} = 1 \quad \text{or} \quad \frac{f}{P} \to 1 \quad \text{as } P \to 0} \qquad (6.122)$$

Thus, the standard state of a real gas is a hypothetical state in which the gas is at a pressure P^0 where it behaves perfectly. By this choice, the standard state has the simple properties of an ideal gas. If the standard state were chosen as the one for which f is equal to say, 1 bar, the standard state of different gases would have different and complex properties. If the standard state chosen were the gas at zero pressure, the free energy would have become – □ at the standard state. The choice of the hypothetical standard state standardises the interaction between the particles by setting them to zero. Since all intermolecular forces are absent in the standard state chosen, the differences in the standard free energies of different gases arise solely from the internal structure and properties of the molecules, and not from the way they interact with each other.

Equation (6.122), which sets the fugacity of the real gas equal to its pressure at low pressures, permits the evaluation of absolute values for fugacities at various pressures. It is this property that makes fugacity a widely accepted thermodynamic property in practical calculations.

6.6.2 Fugacity Coefficient

The ratio of fugacity to pressure is referred to as *fugacity coefficient* and is denoted by f. It is dimensionless and depends on nature of the gas, the pressure, and the temperature. Integrating Eq. (6.118) between pressures P and P^0,

$$G - G^0 = RT \ln \frac{f}{f^0} \tag{6.123}$$

Since $f^0 = P^0$ and $f = \phi P$, we can write the above equation as

$$G = G^0 + RT \ln \frac{P}{P^0} + RT \ln \phi \tag{6.124}$$

For ideal gases, by Eq. (6.120), $G = G^0 + RT \ln P/P^0$. Combining this result with Eq. (6.124) we see that the free energy of a real gas = free energy of an ideal gas + RT ln f. The quantity RT ln f, therefore, expresses the entire effect of intermolecular interaction.

Since all gases becomes ideal as pressure approaches zero, we can say that

$f \square P$ as $P \square 0$

f □ 1 as $P \square 0$

6.6.3 Effect of Temperature and Pressure on Fugacity

In Eq. (6.123), G^0 and f^0 refer to the molar free energy and fugacity respectively at a very low pressure where the gas behaves ideally. This equation can be rearranged as

$$R \ln \frac{f}{f^0} = \frac{G}{T} - \frac{G^0}{T}$$

Differentiate this with respect to temperature at constant pressure.

$$R\left[\left(\frac{\partial \ln f}{\partial T}\right)_P - \left(\frac{\partial \ln f^0}{\partial T}\right)_P\right] = \left(\frac{\partial (G/T)}{\partial T}\right)_P - \left(\frac{\partial (G^0/T)}{\partial T}\right)_P$$

Substituting the Gibbs–Helmholtz equation, Eq. (6.73), into the above result and observing that f^0 is equal to the pressure and is independent of temperature, we get

$$\boxed{\left(\frac{\partial \ln f}{\partial T}\right)_P = \frac{H^0 - H}{RT^2}} \tag{6.125}$$

H is the molar enthalpy of the gas at the given pressure and H^0 is the enthalpy at a very low pressure.

$H^0 - H$ can be treated as the increase of enthalpy accompanying the expansion of the gas from pressure P to zero pressure at constant temperature. Equation (6.125) indicates the *effect of temperature on the fugacity*.

The effect of pressure on fugacity is evident from the defining equation for fugacity [Eq. (6.118)].

$$dG = V\,dP = RT\,d(\ln f) \qquad (6.118)$$

which on rearrangement gives:

$$\boxed{\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{V}{RT}} \qquad (6.126)$$

6.6.4 Determination of Fugacity of Pure Gases

Using compressibility factor, Z. The *compressibility factor Z* of a real gas is the ratio of its volume to the volume of an ideal gas at the same temperature and pressure.

$$Z = \frac{PV}{RT} \quad \text{or} \quad \frac{V}{RT} = \frac{Z}{P}$$

Introducing this in Eq. (6.126) and rearranging, the following result is obtained.

$$d(\ln f) = \frac{V}{RT}\,dP = \frac{Z}{P}\,dP$$

The above result, as such, is of not much use for the determination of fugacity, because as $P \to 0$, $Z/P \to \infty$. This difficulty can be overcome if we add and subtract dP/P on the right-hand side of the preceding equation.

$$d(\ln f) = \frac{dP}{P} + (Z - 1)\frac{dP}{P} = d\,(\ln P) + (Z - 1)\frac{dP}{P}$$

$$d\left(\ln \frac{f}{P}\right) = (Z - 1)\frac{dP}{P}$$

When this is integrated between 0 and P we get

$$\boxed{\ln \frac{f}{P} = \int_0^P \left(\frac{Z - 1}{P}\right) dP} \qquad (6.127)$$

As $(Z - 1)/P$ is finite as pressure approaches zero, there is no difficulty in using Eq. (6.127) for the evaluation of f. The values of the compressibility factor, Z, from zero pressure to pressure P are calculated from the volume of the gas at the corresponding pressures. The integral in Eq. (6.127) is found out graphically by plotting $(Z - 1)/P$ against P.

***EXAMPLE* 6.22** Derive an expression for the fugacity coefficient of a gas obeying the equation of state $P(V - b) = RT$ and estimate the fugacity of ammonia at 10 bar and 298 K, given that $b = 3.707 \square 10^{-5}$ m^3/mol.

Solution Since, $P(V - b) = RT$, we have,

$$PV = RT + Pb, \qquad Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

Equation (6.127) becomes

$$\ln \frac{f}{P} = \ln \phi = \int_0^P \frac{b}{RT}\, dP = \frac{Pb}{RT}$$

where ϕ is the fugacity coefficient. For ammonia at 10 bar and 298 K,

$$\ln \frac{f}{10} = \ln \frac{(3.707 \times 10^{-5})\,(10 \times 10^{5})}{8.314 \times 298} = 0.015$$

Therefore, fugacity $f = 10.151$ bar.

Using generalised charts. Using Eq. (6.127) in reduced form, a generalised chart similar to the generalised compressibility chart can be prepared for predicting the fugacity of gases.

$$\ln \frac{f}{P} = \int_0^{P_r} \frac{Z - 1}{P_r}\, dP_r \qquad (6.128)$$

The integral in Eq. (6.128) is evaluated graphically at constant temperature by taking compressibility factors from the isotherms on the generalised compressibility chart. The fugacity coefficient is then plotted against reduced pressure (P_r) for various constant reduced temperature (T_r) values. This provides a generalised chart for fugacity of all gases as shown in Fig. 6.7.

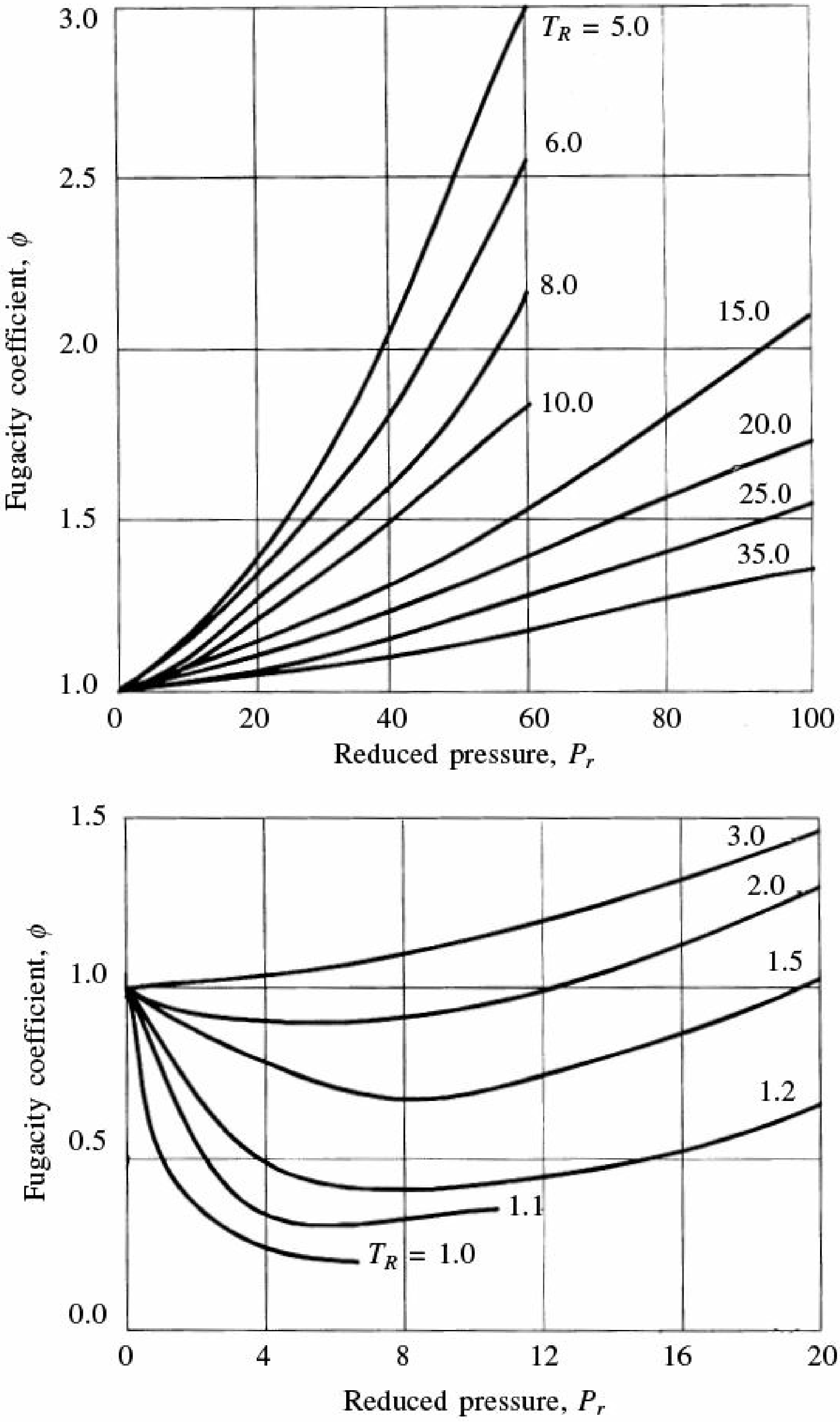


Fig. 6.7 Fugacity coefficient as function of reduced temperature and pressure (generalised chart for fugacity coefficient).

If experimental volumetric data are not available, this chart can be used for approximate calculation of fugacity, provided the critical temperature and pressure are known. The accuracy of the results depends upon how closely the generalised compressibility charts predicts the actual *P-V-T* behaviour of gases.

Using residual volumes. Equation (6.118) relates the fugacity of the gas to the molar volume V at temperature T and pressure P

$dG = V\,dP = RT\,d(\ln f)$ (6.118)

The residual volume a is defined as the difference between V and the volume occupied by one mole of an ideal gas at the same temperature and pressure.

$$\alpha = V - \frac{RT}{P}$$

Substitution of this in Eq. (6.118) gives

$$d(\ln f) = \left(\frac{\alpha}{RT} + \frac{1}{P}\right) dP$$

$$d\left(\ln \frac{f}{P}\right) = \frac{\alpha}{RT}\, dP \tag{6.129}$$

This result is integrated between a very low pressure and the given pressure P. At low pressures, $f/P = 1$ and the required integral is

$$\ln\left(\frac{f}{P}\right) = \frac{1}{RT} \int_0^P \alpha\, dP \tag{6.130}$$

To find f, the residual volume a derived from experimentally determined values of molar volumes at different pressures are plotted against P. Refer Fig. 6.8. The area under the curve between pressures 0 and P is equal to the integral in Eq. (6.130).

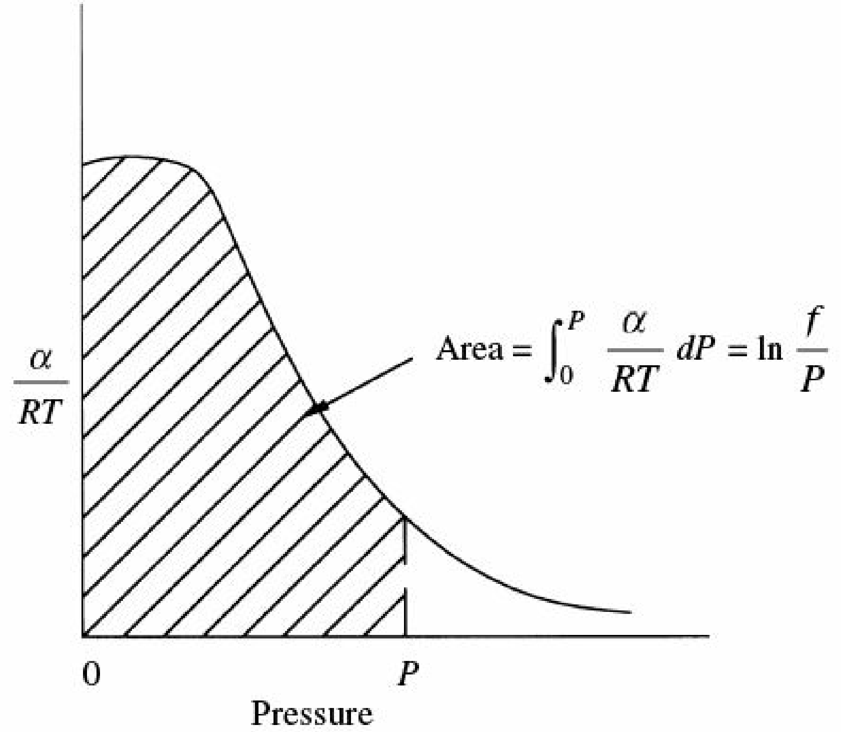


Fig. 6.8 Determination of fugacity by residual volume method.

***EXAMPLE* 6.23** From the *P-V-T* data for a gas it is found that $\int_0^{50} \alpha\, dP$ = – 556.61 J/mol. Find the fugacity of the gas at 50 bar and 300 K.

Solution Using Eq. (6.130), we obtain

$$\ln\frac{f}{50} = -\frac{556.61}{8.314\times 300} = -0.2232, \text{ therefore } f = 40 \text{ bar}$$

Using equations of state. We have seen that Eq. (6.118) defines fugacity as

$dG = V\,dP = RT\,d\,(\ln f)$

On integrating this between pressure P^0 where fugacity is f^0 and pressure P where fugacity is f, we get the following result.

$$\ln\frac{f}{f^0} = \frac{1}{RT}\int_{P^0}^{P} V\,dP \tag{6.131}$$

If an analytical equation of state is available, and if it can be put in a form in which *V* is expressed explicitly as a function of *P*, the integral in Eq. (6.131) can be readily evaluated. On the other hand, if *P* is expressed as a function of *V*, the integral is determined by integration by parts. We can use the following identity for this purpose:

$$\int V\,dP = PV - \int P\,dV \tag{6.132}$$

Then the integral in Eq. (6.131) becomes

$$\int_{P^0}^{P} V\,dP = PV - P^0V^0 - \int_{V^0}^{V} P\,dV \tag{6.133}$$

where V^0 is volume of the gas at pressure P^0. Since the gas behaves ideally under this condition, $P^0V^0 = RT$ and Eq. (6.133) becomes

$$\int_{P^0}^{P} V\,dP = PV - RT - \int_{V^0}^{V} P\,dV \tag{6.134}$$

Equation (6.134) can be used for evaluating the integral in Eq. (6.131).

***EXAMPLE* 6.24** Find the fugacity coefficient at 1 bar, 5 bar, and 10 bar for a gas that follows the equation of state $PV = RT(1 - 0.00513\,P)$, where P is pressure in bar.

Solution According to Eq. (6.118),

$$RT\,d(\ln f) = V\,dP = RT\left(\frac{1}{P} - 0.00513\right)dP = RT\,(d\ln P - 0.00513\,dP)$$

Therefore,

$$d\ln\frac{f}{P} = -0.00513\,dP \quad\text{or}\quad \ln\phi = -0.00513\int_0^P dP = -0.00513\,P$$

This gives the fugacity coefficient as 0.995 at 1 bar, 0.975 at 5 bar and 0.950 at 10 bar.

***EXAMPLE* 6.25** Show that the fugacity of a gas obeying the van der Waals equation of state is given by

$$\ln f = \frac{b}{V-b} - \frac{2a}{RTV} + \ln\frac{RT}{V-b}$$

where a and b are *van der Waals constants*.

Solution The van der Waals equation [Eq. (3.29)] can be written in the following form:

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \tag{6.135}$$

Substituting Eq. (6.134) into Eq. (6.131), we get

$$\ln \frac{f}{P^0} = \frac{1}{RT}\left(PV - RT - \int_{V^0}^{V} P\,dV\right) \tag{6.136}$$

Rearranging Eq. (6.135), we get

$$PV - RT = \frac{RTb}{V - b} - \frac{a}{V} \tag{6.137}$$

Integrating Eq. (6.135), we get

$$\int_{V^0}^{V} P\,dV = \int_{V^0}^{V} \frac{RT}{V - b}\,dV - \int_{V^0}^{V} \frac{a}{V^2}\,dV = RT \ln \frac{V - b}{V^0 - b} + \frac{a}{V} - \frac{a}{V^0}$$

Since V^0 is very large compared to b, $V^0 - b$ □ V^0. Further, V^0 can be replaced by RT/P^0 as V^0 is the volume of a gas at a very low pressure P^0 at which ideal gas equations are obeyed by the gas. Also, as V^0 is very large, a/V^0 can be neglected. With these simplifications, the above equation becomes

$$\int_{V^0}^{V} P\,dV = RT \ln \frac{(V - b)P^0}{RT} + \frac{a}{V} = RT \ln P^0 + RT \ln \frac{V - b}{RT} + \frac{a}{V} \tag{6.138}$$

Substituting results (6.137) and (6.138) into Eq. (6.136)

$$\ln \frac{f}{P^0} = \frac{1}{RT}\left(\frac{RTb}{V - b} - \frac{a}{V} - RT \ln P^0 - RT \ln \frac{V - b}{RT} - \frac{a}{V}\right)$$

$$\ln f = \frac{b}{V - b} - \frac{2a}{RTV} + \ln \frac{RT}{V - b} \tag{6.139}$$

***EXAMPLE* 6.26** Calculate the fugacity of pure ethylene at 100 bar and 373 K. The van der Waals constants are $a = 0.453$ J m^3/mol^2, $b = 0.571$ □ 10^{-4} m^3/mol, molar volume at 100 bar and 373 K = 2.072 □ 10^{-4} m^3/mol.

Solution Substitute $a = 0.453$, $b = 0.571$ □ 10^{-4}, $V = 2.072$ □ 10^{-4}, $R = 8.314$, and $T = 373$ into Eq. (6.139). Note that $RT/(V - b)$ be multiplied by 10^{-5} for dimensional consistency.
Thus we get $\ln f = 4.3$ and $f = 73.7$ bar.

Using values of enthalpy and entropy. Equation (6.123) indicates the free energy change between the given state where free energy and fugacity are G and f respectively, and a standard state where the free energy and fugacity are G^0 and f^0 respectively. By the definition of free energy, $G = H$

– TS, and $G^0 = H^0 – TS^0$, where H^0 and S^0 are the enthalpy and entropy values at the standard state. Using these, Eq. (6.123) becomes

$$(H - H^0) - T(S - S^0) = RT \ln \frac{f}{f^0}$$

$$\ln \frac{f}{f^0} = \frac{1}{RT} [(H - H^0) - T(S - S^0)] \tag{6.140}$$

Assuming that the gas behaves ideally at the reference state, $f^0 = P^0$, the pressure at the standard state. The fugacity can be calculated using the values of H, H^0, S and S^0 in Eq. (6.140)

***EXAMPLE* 6.27** Determine the fugacity and fugacity coefficient of steam at 623 K and 1000 kPa using enthalpy and entropy values from steam tables. Assume that steam behaves ideally at 101.3 kPa.

Data from steam tables: At 1000 kPa and 623 K, $H = 3159$ kJ/kg; $S = 7.3$ kJ/kg K. At 101.3 kPa and 623 K, $H = 3176$ kJ/kg; $S = 8.38$ kJ/kg K.

Solution Since steam behaves ideally at 101.3 kPa, fugacity at this pressure = 101.3 kPa. Using Eq (6.140),

$$\ln \frac{f}{101.3} = \frac{1}{(8.314/18) \times 623} [(3159 - 3176) - 623(7.3 - 8.38)] = 2.279$$

$$f = 9.76691 \times 101.3 = 989.4 \text{ kPa} = 9.89 \text{ bar}$$

Approximate method for estimation. Experimental evidences suggest that at moderate pressures, the value of PV for any gas is a linear function of its pressure at constant temperature. The functional relationship between PV and P may be written as $PV = RT + kP$, where k is a constant. The residual volume a, by definition is a $= V – RT/P = k$. It means that the residual volume a is constant and is independent of pressure. Substituting this result in Eq. (6.130),

$$\ln \left(\frac{f}{P}\right) = \frac{1}{RT} \int_0^P \alpha \, dP \tag{6.130}$$

$$\ln \frac{f}{P} = \frac{\alpha P}{RT} \tag{6.141}$$

At moderate pressures, f/P is close to unity and therefore, ln (f/P) □ (f/P) – 1. (*Note:* When x approaches unity, ln x is approximately equal to $x – 1$). Equation (6.141) can be modified as

$$\frac{f}{P} - 1 = \frac{\alpha P}{RT}$$

$$f = \left(1 + \frac{\alpha P}{RT}\right) P = P + \left(V - \frac{RT}{P}\right) \frac{P^2}{RT} = \frac{VP^2}{RT}$$

$$f = \frac{VP^2}{RT} \tag{6.142}$$

Equation (6.142) can be used to determine the approximate value of the fugacity of a gas from its pressure and molar volume.

***EXAMPLE* 6.28** The density of gaseous ammonia at 473 K and 50 bar is 24.3 kg/m^3. Estimate its fugacity.

Solution The molar volume of ammonia under the given conditions is

$V = 17/(24.3 \square 1000)$ m^3/kmol

Pressure, $P = 50 \square 10^5$ N/m^2

Using Eq. (6.142), we get

$$f = \frac{17(50 \times 10^5)^2}{24.3(8.314)\,473(1000)} = 44.4745 \times 10^5 \text{ N/m}^2 = 44.4745 \text{ bar}$$

6.6.5 Fugacities of Solids and Liquids

Every solid or liquid has a definite vapour pressure although it may be immeasurably small, in some cases. At this pressure, the solid (or the liquid) will be in equilibrium with its vapour. When two phases of a substance are in thermodynamic equilibrium, the molar free energies in both phases should be equal. This follows from the criterion of phase equilibrium, which will be discussed in detail in Chapter 8. By this criterion the molar free energy of the liquid (or the solid) in equilibrium with its vapour is equal to the molar free energy of the vapour. That is, $G^L = G^V$ and $G^S = G^V$, where the superscripts L, S and V refer to liquid, solid and gas respectively. Since the molar free energy is related to the fugacity as $G = RT \ln f + C$, where C is constant that depends only on temperature, it follows that

$$f^L = f^V, f^S = f^V \tag{6.143}$$

Equation (6.143) means that the fugacity of solid (or liquid) is equal to the fugacity of the vapour with which it is in equilibrium, provided that the reference state is taken to be the same in each case. If the vapour pressure is not very high, the fugacity of the vapour would be equal to the vapour pressure; hence, the fugacity of a liquid (or a solid) is approximately equal to its vapour pressure.

If the vapour pressure is very high and the vapour cannot be treated as ideal gas its fugacity is related to the saturation pressure as in Eq. (6.142)

$$f^{\text{sat}} = \frac{VP^{S^2}}{RT} \qquad (6.142)$$

P^S is the saturation pressure of the gas and f^{sat} is the saturation fugacity. The latter should in turn be equal to the fugacity of solid or liquid at the desired temperature and the saturation pressure, by Eq. (6.143). Since, $RT\,d(\ln f) = V\,dP$ and the liquid can be assumed to be incompressible, the fugacity of the liquid at any other pressure P is readily obtained as

$$\ln \frac{f}{f^{\text{sat}}} = \frac{V}{RT}(P - P^S) \qquad (6.144)$$

where V is the molar volume of the liquid.

***EXAMPLE* 6.29** Calculate the fugacity of liquid water at 303 K and 10 bar if the saturation pressure at 303 K is 4.241 kPa and the specific volume of liquid water at 303 K is 1.004 □ 10^{-3} m^3/kg.

Solution The molar volume is

$$V = 1.004 \times 10^{-6} \times 18 = 18.072 \times 10^{-6}\ \text{m}^3/\text{mol}$$

Assuming that the vapour behaves as an ideal gas, we have

$$P^S = 4.241\ \text{kPa} = 0.0424\ \text{bar} = f^{\text{sat}}$$

Using Eq. (6.144),

$$\ln \frac{f}{f^{\text{sat}}} = \frac{18.072 \times 10^{-6}}{8.314 \times 303}(10 - .0424) \times 10^5 = 7.1435 \times 10^{-3}$$

Therefore, $f = 0.0427$ bar.

***EXAMPLE* 6.30** Calculate the fugacity of n-butane in the liquid state at 350 K and 60 bar. The vapour pressure of n-butane at 350 K is 9.35 bar. The molar volume of saturated liquid at 350 K is 0.1072 □ 10^{-3} m^3/mol. The fugacity coefficient for the saturated vapour at 350 K is 0.834.

Solution The fugacity of saturated vapour at 350 K = 0.834 □ 9.35 = 7.798 bar. Therefore, fugacity of saturated liquid at 350 K = 7.798 bar = f^{sat}. Using Eq. (6.144),

$$\ln \frac{f}{f^{\text{sat}}} = \frac{0.1072 \times 10^{-3}}{8.314 \times 350}(60 - 9.35) \times 10^5 = 0.18659$$

Thus the fugacity of the liquid at 60 bar and 350 K, $f = 9.4$ bar.

6.7 ACTIVITY

The vapour pressures of relatively non-volatile solids and liquids may be extremely low, so, an experimental determination of their fugacity is impractical. When dealing with such substances, it would be convenient to work with another function called *activity* rather than with fugacity itself. ‘Activity’ is, in fact, relative fugacity and is defined as the ratio of fugacity to fugacity in the standard state. It finds wide application in the study of homogeneous chemical reaction equilibria involving solids and liquids. Activity is denoted by the letter a, where

$$a = \frac{f}{f^0} \tag{6.145}$$

The standard state at which fugacity is f^0 is chosen arbitrarily, but the temperature in the standard state is the same as the temperature in the given conditions. For gases, the standard state fugacity is chosen by convenience to be unity, and therefore, fugacity and activity are numerically equal.

The change in the free energy accompanying the process in which the substance is undergoing a change of state from the standard state to the given conditions is related to the activity of the substance as

$$\Delta G = RT \ln \frac{f}{f^0} = RT \ln a \tag{6.146}$$

Since $dG = V\,dP - S\,dT$, the change in the free energy when the substance is compressed isothermally is given by

$$\Delta G = \int V\,dP \tag{6.147}$$

Assuming that the substance is incompressible between the standard state pressure P^0 and the given pressure P, Eq. (6.147) can be integrated as

$$\Delta G = V(P - P^0) \tag{6.148}$$

The assumption of constant V is a good approximation and will not introduce much error for solids and liquids up to very high pressures, provided the temperature is well below the critical value. Comparison of Eqs. (6.146) and (6.148) shows that

$$\ln a = \frac{V}{RT}(P - P^0) \tag{6.149}$$

The concept of activity is particularly useful in the study of solutions. The commonly used standard states and their properties are discussed in detail in Chapter 7.

***EXAMPLE* 6.31** Determine the activity of solid magnesium (MW = 24.32) at 300 K and 10 bar if the reference state is 300 K and 1 bar. The density of magnesium at 300 K is 1.745 ☐ 10^3 kg/m^3 and is assumed constant over this pressure range.

Solution Using Eq. (6.149), we obtain

$$\ln a = \frac{24.32 \times (10 - 1) \times 10^5}{1.745 \times 10^6 \times 8.314 \times 300} = 5.029 \times 10^{-3}$$

Therefore, $a = 1.00504$.

6.7.1 Effect of Pressure and Temperature on Activity

From Eq. (6.146) we see that,

$$\Delta G = G - G^0 = RT \ln a$$

$$R \ln a = \frac{G}{T} - \frac{G^0}{T} \tag{6.150}$$

Differentiating with respect to T at constant pressure,

$$R\left(\frac{\partial \ln a}{\partial T}\right)_P = \left(\frac{\partial (G/T)}{\partial T}\right)_P - \left(\frac{\partial (G^0/T)}{\partial T}\right)_P \tag{6.151}$$

Using Gibbs–Helmholtz equation [Eq. (6.73)] in the above equation, we see that

$$\left(\frac{\partial \ln a}{\partial T}\right)_P = \frac{H^0 - H}{RT^2} \tag{6.152}$$

Equation (6.152) predicts the effect of temperature on activity. Combining Eqs. (6.146) and (6.147) we get, for constant temperature,

$$RT\, d \ln a = V\, dP \tag{6.153}$$

$$\left(\frac{\partial \ln a}{\partial P}\right)_T = \frac{V}{RT} \tag{6.154}$$

Equation (6.154) predicts the effect of pressure on activity.

6.8 DEPARTURE FUNCTIONS AND GENERALISED CHARTS

The methods for the evaluation of thermodynamic properties from experimental P-V-T data or analytical equations of state were discussed earlier. If these data are not available or if very accurate values of the properties are not required, rough estimate of the thermodynamic properties can be made through the use of *departure functions* or *residual properties*. The residual properties are defined as the difference between the thermodynamic property at the specified temperature and pressure and the property that the substance would have exhibited at the same temperature and pressure, had it been an ideal gas. Representing the properties in the ideal gas state with the superscript *id,* the residual enthalpy (H^R) and residual entropy (S^R) are defined as

$$H^R = H - H^{\text{id}} \tag{6.155}$$

$$S^R = S - S^{\text{id}} \tag{6.156}$$

H^R and S^R are also known as *enthalpy departure* and *entropy departure*, respectively. These represent hypothetical property changes because a gas cannot be both real and ideal at a given P and T.

Equations (6.155) and (6.156) are differentiated with respect to pressure to get the following results.

$$\left(\frac{\partial H^R}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - \left(\frac{\partial H^{\text{id}}}{\partial P}\right)_T \tag{6.157}$$

$$\left(\frac{\partial S^R}{\partial P}\right)_T = \left(\frac{\partial S}{\partial P}\right)_T - \left(\frac{\partial S^{\text{id}}}{\partial P}\right)_T \tag{6.158}$$

We have already seen that the entropy and enthalpy vary with pressure as

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{6.24}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P \tag{6.49}$$

For ideal gas $V = RT/P$; therefore,

$$\left(\frac{\partial H^{\text{id}}}{\partial P}\right)_T = 0, \quad \left(\frac{\partial S^{\text{id}}}{\partial P}\right)_T = -\frac{R}{P} \tag{6.159}$$

The molar volume $V = ZRT/P$, where Z is the compressibility factor. Then

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{ZR}{P} + \frac{RT}{P}\left(\frac{\partial Z}{\partial T}\right)_P = \frac{R}{P}\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_P\right] \tag{6.160}$$

Substituting Eq. (6.160) into Eqs. (6.49) and (6.24), the following equations are obtained:

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{RT^2}{P}\left(\frac{\partial Z}{\partial T}\right)_P \tag{6.161}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\frac{R}{P}\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_P\right] \tag{6.162}$$

Equations (6.157) and (6.158) can now be written as

$$\left(\frac{\partial H^R}{\partial P}\right)_T = -\frac{RT^2}{P}\left(\frac{\partial Z}{\partial T}\right)_P \tag{6.163}$$

$$\left(\frac{\partial S^R}{\partial P}\right)_T = -\frac{R}{P}(Z-1) - \frac{RT}{P}\left(\frac{\partial Z}{\partial T}\right)_P \tag{6.164}$$

Integrating these equations for an isothermal change from pressure $P = 0$, where $H^R = 0$ and $S^R = 0$, to pressure P,

$$H^R = -RT^2 \int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \tag{6.165}$$

$$S^R = -R \int_0^P \left[(Z-1)\frac{dP}{P} + T\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}\right] \tag{6.166}$$

The values of Z and $(\partial Z/\partial T)_P$ are calculated directly from the experimental P-V-T data and the integrals in the preceding two equations are evaluated by numerical or graphical methods. Analytical integration is possible when Z is expressed as an equation of state. Thus, H^R and S^R and all other residual properties are readily evaluated. We see that there exists a direct connection between the experimental data and the residual properties, which makes the latter a very valuable tool for evaluation of thermodynamic properties.

Once the residual enthalpy and entropy are known, the enthalpy and entropy of the gas can be calculated using Eqs. (6.155) and (6.156). The enthalpy and entropy of the ideal gas at pressure P and temperature T for use in these equations can be determined by an arbitrary choice of the reference state at pressure P^0 and temperature T^0 where the enthalpy and entropy values are H^0 and S^0 respectively.

$$H^{\mathrm{id}} = H^0 + \int_{T_0}^{T} C_P^{\mathrm{id}}\, dT \tag{6.167}$$

$$S^{\mathrm{id}} = S^0 + \int_{T_0}^{T} C_P^{\mathrm{id}} \frac{dT}{T} - R \ln \frac{P}{P^0} \tag{6.168}$$

Equations (6.165) and (6.166) can be put into a reduced form noting that $P = P_C P_r$, $T = T_C T_r$, $dP = P_C\, dP_r$ and $dT = T_C\, dT_r$

$$\frac{H^R}{RT_C} = -\, T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} \tag{6.169}$$

$$\frac{S^R}{R} = -\int_0^{P_r} \left[(Z - 1) + T_r \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \right] \frac{dP_r}{P_r} \tag{6.170}$$

Z and $(\partial Z/\partial T_r)_P$ required for the evaluation of the integral in the above equations can be obtained from the generalised compressibility charts. The H^R/RT_C or the S^R/R values thus calculated are plotted against reduced pressure with reduced temperature as parameter to give the generalised enthalpy departure chart and the entropy departure chart, respectively. [See Hougen O.A., K.M Watson and R.A. Ragatz, *Chemical Process Principles*, Part II.]

It is observed that the uncertainty in Z taken from the generalised compressibility chart is only around 2.5 per cent. However, a greater uncertainty is expected in the reduced residual properties as their calculation involves the derivatives of Z.

6.9 THERMODYNAMIC DIAGRAMS

Thermodynamic properties of pure fluids or mixtures of constant composition are determined when any two properties are specified. Thermodynamic diagrams provide these properties in terms of two independent variables. Various combinations of these independent variables give rise to different type of thermodynamic diagrams. These diagrams find wide applications in computation of thermodynamic properties and thermodynamic analysis of processes. We have already used the *T-S* diagrams in the analysis of refrigeration cycles and the vapour-power cycles in Chapter 5.

6.9.1 Types of Diagrams

***P-H* diagram.** In a *P-H* diagram the pressure *P* (or, ln *P*) is the *Y*-axis and enthalpy *H* is the *X*-axis. The general appearance of a *P-H* diagram is shown in Fig. 6.9. This chart is particularly used for calculating the heat loads and temperature changes in refrigeration systems. The refrigeration cycles have both constant pressure (evaporators and condensers) and constant enthalpy (throttling valve) processes and the *P-H* diagrams are very useful in analysing them. The dome-shaped envelope encloses the two-phase region. Within the envelope, horizontal lines of constant pressure and constant temperature are shown. Temperature lines are nearly vertical in the liquid-phase region; are horizontal in the two-phase region and drop steeply in the vapour-phase region. The constant entropy lines are shown as continuous lines in the vapour as well as in the two-phase region. Constant volume lines show a point of inflection as they cross from the vapour-phase region to the two-phase region. Figure 6.9 also shows lines of constant quality (x).

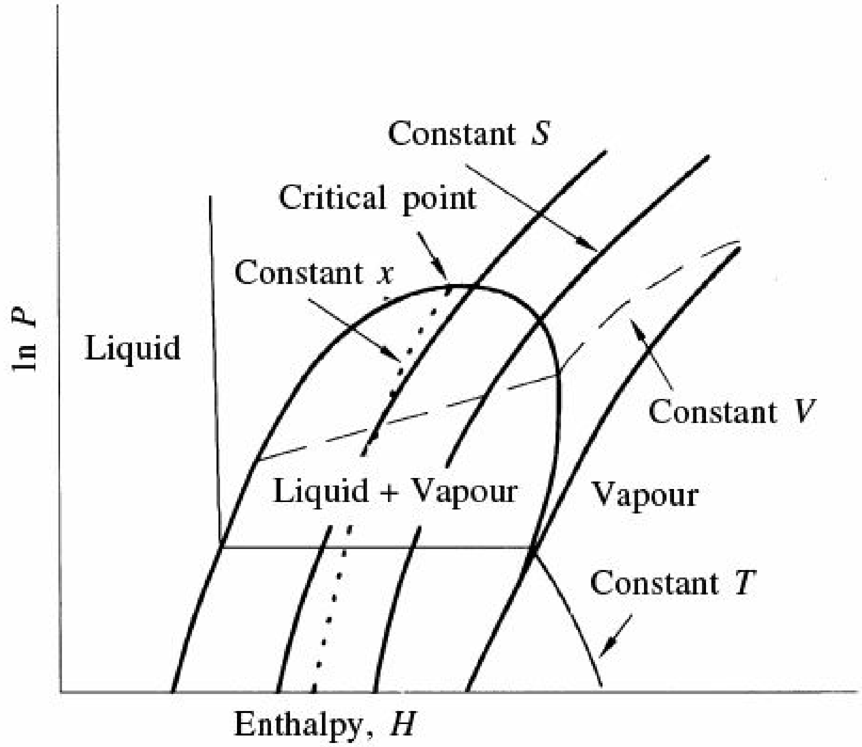


Fig. 6.9 *P-H* diagram.

***H-T* diagram.** Enthalpy H forms the Y-axis and temperature T is the X-axis. A typical H-T diagram is shown in Fig. 6.10. These are useful in the calculations in throttling processes as well as in the constant pressure flow processes.

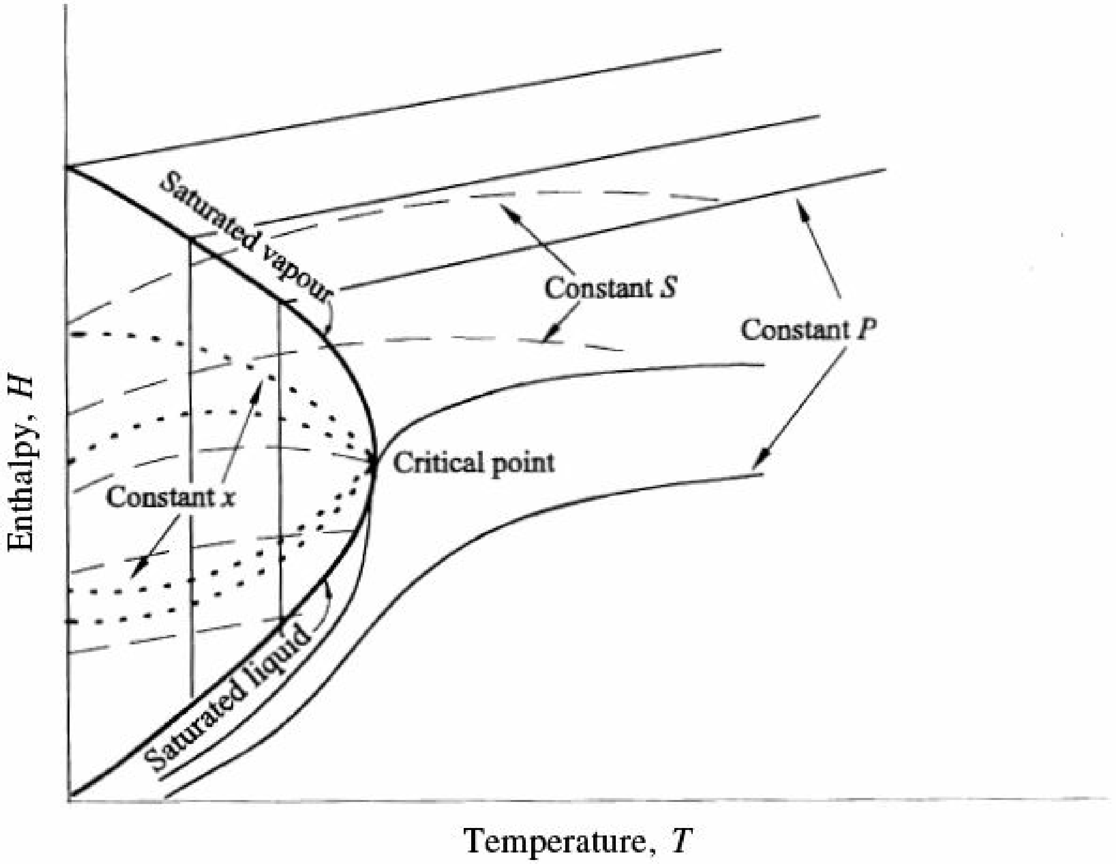


Fig. 6.10 *H-T* diagram.

The vertical distance between the saturated vapour curve and the saturated liquid curve gives the heat of vaporisation at a particular temperature and pressure.

***T-S* diagram.** A typical *T-S* diagram is shown in Fig. 6.11. These are useful in following the temperature changes in isentropic processes. A reversible adiabatic process is essentially isentropic and would be represented by a vertical line on the *T-S* diagram. In the case of turbines and compressors, a vertical line drawn from the initial pressure to the final pressure shows the path followed by the fluid undergoing reversible adiabatic operation. Horizontal lines of constant pressure, lines of constant enthalpy, and constant quality are drawn within the two-phase region. The former two lines are drawn in the liquid-phase and vapour-phase regions as well. The horizontal distance between the saturation curves is λ/T, where λ is the heat of vaporisation at temperature T.

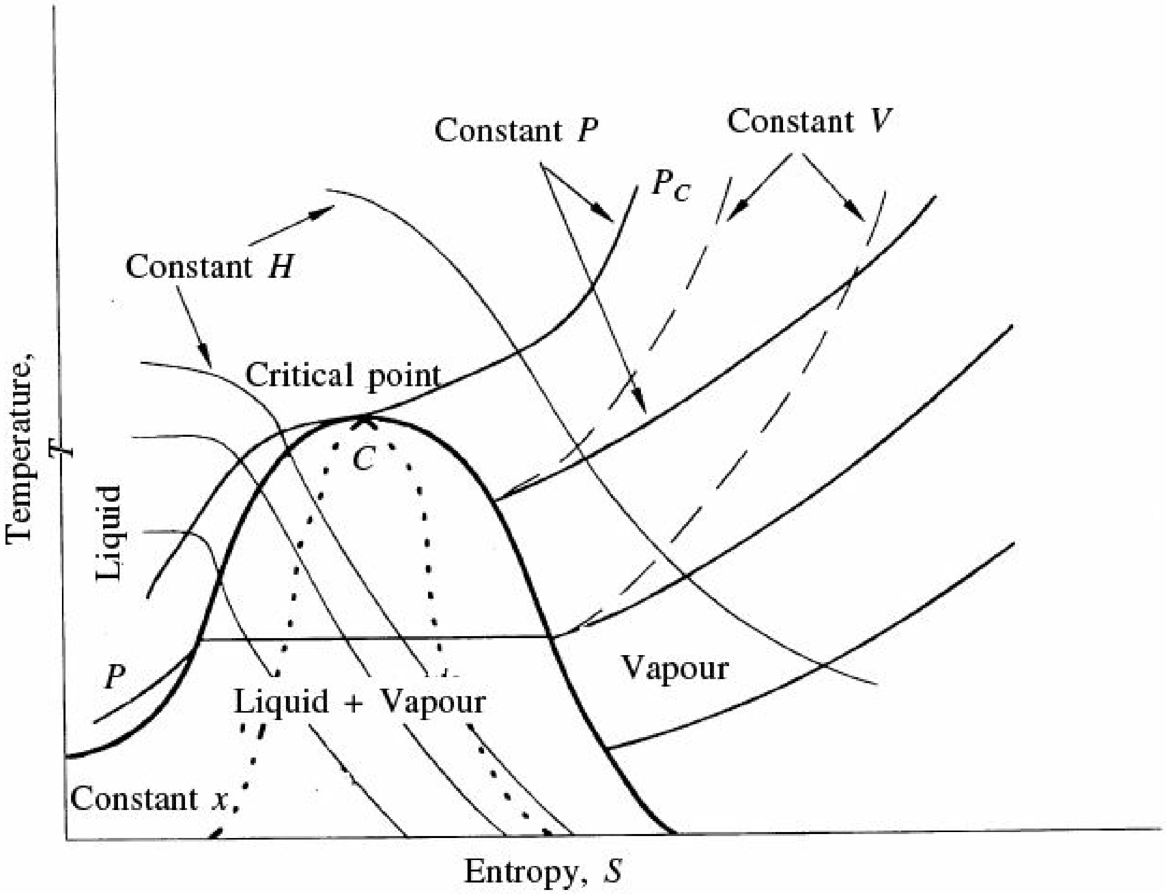


Fig. 6.11 *T-S* diagram.

***H-S diagram* (*the Mollier diagram*).** Figure 6.12 shows the enthalpy-entropy chart, popularly known as the Mollier diagram.

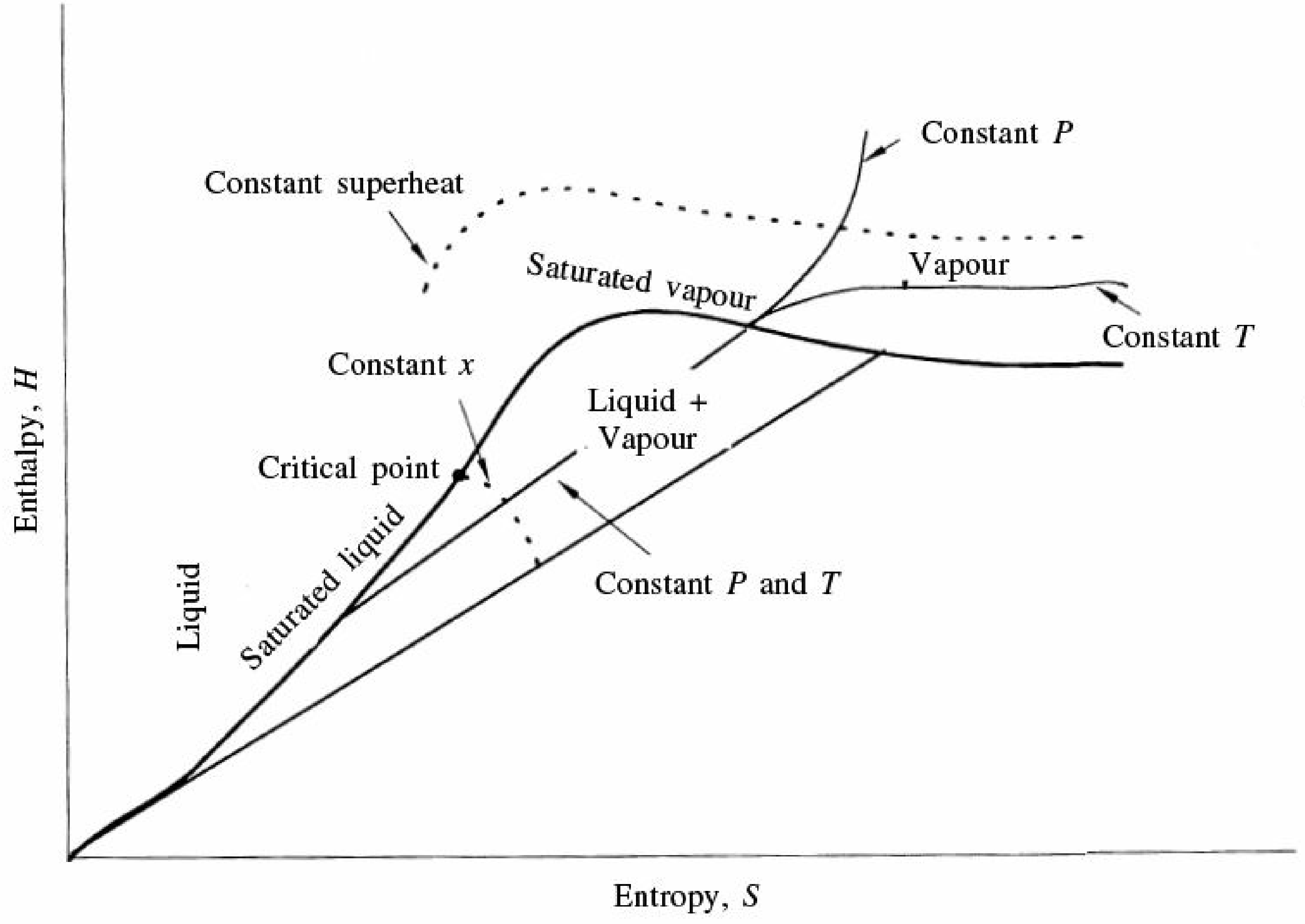


Fig. 6.12 *H-S* diagram (Mollier diagram).

The energy requirements in flow processes, in general, and the temperature changes involved in isentropic and isenthalpic processes are easily determined using these charts. The lines of constant temperature and pressure shown within the two-phase region, separate in the vapour region into pressure lines that rise continuously and temperature lines that drop and eventually become horizontal. Lines of constant quality are also shown in the two-phase region.

6.9.2 Construction of Thermodynamic Diagrams

Thermodynamic charts are prepared by first calculating the ideal gas properties by the standard methods, followed by measuring the enthalpy and entropy departures to correct for pressure. The departure functions are obtained from the generalised charts for departure functions. The critical pressure, temperature and an expression for ideal gas heat capacity as a function of temperature are the additional required data. The construction of *T-H* and *T-S* diagrams is discussed below.

Construction of T-H diagram. Here we discuss how the enthalpy is calculated as function of pressure at three temperatures. The temperatures chosen are T_0, T and T_C. T_0 is a reference or base temperature; T is any temperature below the critical temperature and T_C is the critical temperature. Properties below T_0 are not generally required for practical calculations. For the present calculations we assume that the substance exist as saturated liquid at the base temperature. The saturation pressure is denoted by P_0. In Fig. 6.13, the point A represents the system at the reference state.

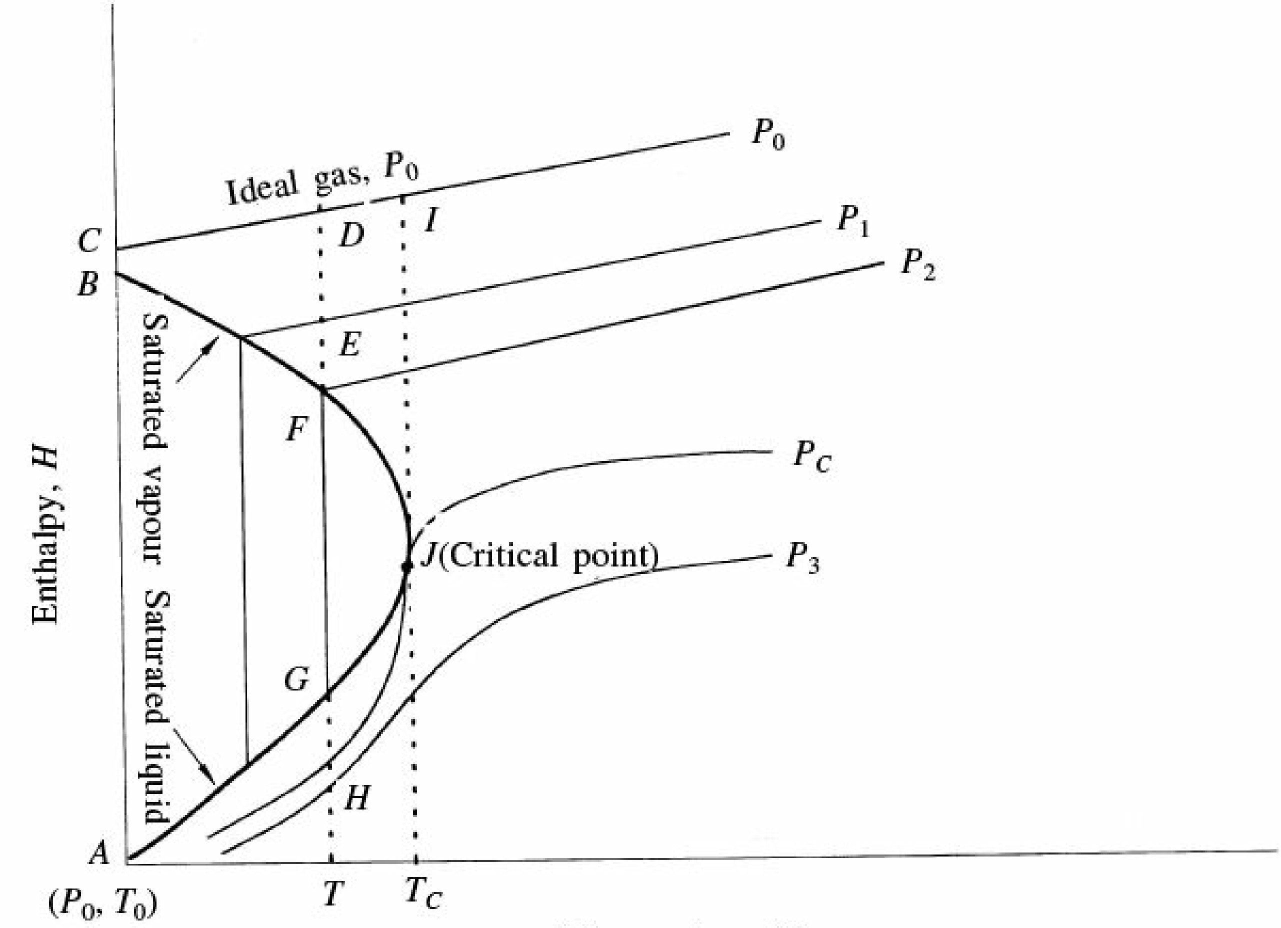


Fig. 6.13 Construction of *T-H* diagram.

The various steps in the calculations are given below:

1. Enthalpy H_A at point A is assumed to be zero.
2. Enthalpy at point B, $H_B = H_A + l_0$, where the heat of vaporisation at temperature T_0 and pressure P_0 is determined from experimental data or using the enthalpy departure charts. If the latter is used, $\lambda_0 = H_V^R - H_L^R$, where H_V^R and H_L^R are the residual enthalpies of saturated vapour and saturated liquid respectively at $P_r = P_0/P_C$ and $T_r = T_0/T_C$.
3. The enthalpy H_C at point $C = H_B - H_C^R$ where $H_C^R = H_B - H_C$, the residual enthalpy at $P_r = P_0/P_C$ and $T_r = T_0/T_C$.
4. The enthalpy at D is calculated using ideal gas heat capacity C□$_P$, which is independent of pressure.

$$H_D = H_C + \int_{T_0}^{T} C'_P \, dT$$

5. The point E represents the condition of the gas at any pressure, say P_1 and temperature T above the dew point. $H_E = H_D + (H_E - H_D) = H_D + H_E^R$, where H_E^R is the residual enthalpy at $P_r = P_1/P_C$ and $T_r = T/T_C$ and is evaluated from the generalised charts.
6. Point F represents condition of the gas at saturation pressure P_2 and temperature T. The residual

enthalpy determined at $P_r = P_2/P_C$ and $T_r = T/T_C$ gives H_F^R. The enthalpy at F, $H_F = H_F^R + H_D$.

7. Point G has the same reduced properties as point F. $H_G - H_D$ is obtained from the liquid line of the two-phase envelope of the generalised enthalpy departure chart. Let this be H_G^R. The enthalpy at G, $H_G = H_G^R - H_D$.
8. For any pressure above the bubble point pressure, say P_3, the enthalpy departure function, $H_H^R = H_H - H_D$, where H_H^R is the residual enthalpy corresponding to $P_r = P_3/P_C$ and $T_r = T/T_C$. Therefore, $H_H = H_H^R + H_D$.
9. Point I represents the ideal gas state at temperature T_C. Enthalpy at I, $H_I = H_D + \int_{T_C}^{T} C_P' \, dT$.
10. Critical conditions are indicated by point J. The enthalpy departure function H_J^R is obtained at $P_r = T_r = 1$. The enthalpy at J, $H_J = H_I + H_J^R$. The enthalpy at any temperature and pressure can be calculated in this way and the T-H diagram can be constructed.

Construction of T-S diagram. The T-S diagram (refer Fig. 6.14.) is constructed in a similar way as a T-H diagram, with additional steps for calculating the effect of pressure on entropy of an ideal gas.

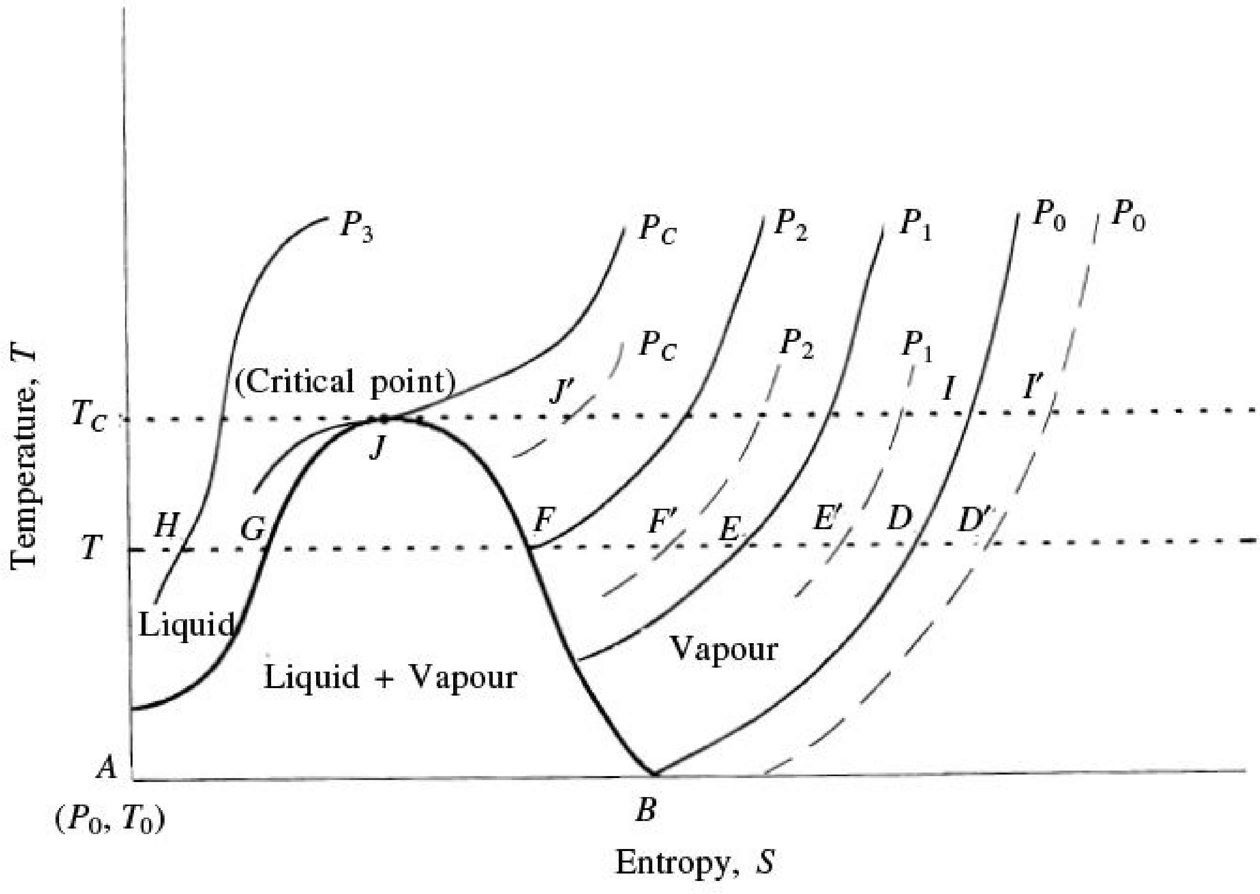


Fig. 6.14 Construction of T-S diagram.

1. Point A represents the entropy of the saturated liquid at the reference temperature, T_0.

2. Point B represents the entropy of the saturated gas at T_0 and P_0. $S_B = S_A + l_0/T$.

3. The entropy S_C of the ideal gas at T_0 and P_0 is obtained as $S_C = S_B - S_C^R$, where S_C^R is the entropy correction taken from the generalised charts at $T_r = T_0/T_C$ and $P_r = P_0/P_C$.

[*Note:* In obtaining the pressure correction for entropy, two corrections must be made; one for change in pressure under ideal behaviour and the other for departure from ideal behaviour at the given T and P. For ideal behaviour, one isothermal line suffices for enthalpies, whereas for entropies, a different line is required for each pressure.]

4. The entropy $S_{D\square}$ is the entropy of ideal gas at T and P_0 represented by point $D\square$. The entropy $S_{D\square}$ is obtained as $S_{D\square} = S_C + \int_{T_0}^{T} (C'_P/T)\,dT$. The entropy at D, $S_D = S_{D\square} + S_D^R$, where S_D^R is the residual entropy at $T_r = T_0/T_C$ and $P_r = P_0/P_C$.

5. The entropy of the gas at any pressure P_1 (below saturation) and temperature T is obtained by first making a pressure correction to get $S_{E\square}$ and then correcting for departure from ideality. Thus, $S_{E\square} = S_{D\square} - R \ln P_1/P_0$ and $S_E = S_{E\square} + S_E^R$. Here, S_E^R is the entropy departure evaluated at $T_r = T/T_C$ and $P_r = P_1/P_C$.

6. $S_{F\square} = S_{D\square} - R \ln P_2/P_0$ and $S_F = S_{F\square} + S_F^R$. The residual entropy in this equation is the entropy of saturated vapour at T and P_2.

7. $S_G = S_F - l/T$.

8. $S_{H\square} = S_{D\square} - R \ln P_3/P_0$ and $S_H = S_{H\square} + S_H^R$.

9 . $S_{I\square} = S_C + \int_{T_0}^{T_C} (C'_P/T)\,dT$ and $S_I = S_{I\square} + S_I^R$, the residual entropy in this equation being evaluated at $T_r = 1$ and $P_r = P_0/P_C$.

10. $S_{J\square} = S_{I\square} - R \ln P_C/P_0$ and $S_H = S_{J\square} + S_J^R$, where the entropy departure function is evaluated at $T_r = P_r = 1$.

Calculations on these lines can be carried out for the construction of the entire *T-S* diagram.

SUMMARY

This chapter discusses the evaluation of the thermodynamic properties of pure fluids using measurable quantities like the pressure-volume-temperature relationship, the heat capacity data, and the coefficients of expansion and compressibility. In addition to the internal energy and the enthalpy introduced in the earlier chapters, two more energy properties, both involving entropy in their definitions, were introduced in this chapter. They are the Helmholtz free energy (A) and the Gibbs free energy (G). It was proved that the decrease in A in an isothermal process is a measure of the maximum work available from a given change of state, whereas the decrease in G in a process occurring at constant temperature and pressure is the maximum work other than the work of expansion available from the process.

The total differentials of the four energy properties are used for the development of the Maxwell's equations. These equations help us to eliminate unmeasurable quantities like the partial derivatives of entropy with respect to the pressure or volume appearing in the thermodynamic relations, in terms of measurable quantities. More so, the partial derivatives of the entropy with respect to temperature, which are related to C_P and C_V through their definitions, were used extensively in this chapter for the formulation of some important thermodynamic relationships. These include the Clapeyron equation [Eqs. (6.25) and (6.28)], equations to measure the change in entropy using the *P*-*V*-*T* and specific heat data [Eqs. (6.35), (6.37) and (6.39)], equation for evaluating the difference between C_P and C_V in terms of isothermal compressibility and coefficient of volume expansion of the fluid [Eq. (6.55)], equation for the Joule–Thomson coefficient in terms of measurable quantities [Eq. (6.70)], the Gibbs–Helmholtz equation [Eq. (6.73)] to predict the effect of temperature on Gibbs free energy, etc.

The method of Jacobians was shown to be a very powerful tool for deriving the relationships between thermodynamic properties (Section 6.5). In terms of Jacobians, it was shown that the Maxwell's equations could be written as $[P, V] = [T, S]$. Several relationships were derived to illustrate the power of the method of Jacobians.

The change in the free energy of an ideal gas in an isothermal process is measured by the relation, $dG = RT\, d(\ln P)$. The concept of fugacity was introduced so that the free energy change of any fluid could be measured as $dG = RT\, d(\ln f)$. The fugacity was discussed with emphasis on pure gases. The effect of temperature and pressure on fugacity and the methods for the estimation of fugacity were also described. When dealing with non-volatile liquids or solids, it was found that it is convenient to work with the function known as the activity, rather than the fugacity. A brief discussion of the activity of pure substances in this chapter (Section 6.7) forms the basis for an exhaustive study on the properties of mixtures in Chapter 7. The enthalpy and entropy departures were discussed in Section 6.8 with a view to their application in making rough estimates of the thermodynamic properties of fluids in the absence of experimental *P*-*V*-*T* data or an analytical equations of state. These functions were found to be very valuable in the construction of various thermodynamic diagrams (Section 6.9).

REVIEW QUESTIONS

1. Differentiate between reference properties, energy properties, and derived properties.
2. Define Helmholtz free energy, and prove that at constant temperature the decrease in work function measures the maximum work available from a given change of state.
3. Define Gibbs free energy, and show that at constant temperature and pressure the decrease in the Gibbs free energy measures the maximum net work available from a given change of state.
4. What are the fundamental differential equations for the energy properties? List the canonical variables for *U*, *H*, *A,* and *G*.
5. What are the Maxwell's equations and what is their importance in establishing relationships between thermodynamic properties?
6. How would you obtain the Clapeyron equation from Maxwell's equations? What are the assumptions involved in the derivation of Clausius–Clapeyron equation from the Clapeyron equation?
7. How are the definitions of C_P and C_V useful in eliminating the partial derivatives of entropy

with respect to temperature from thermodynamic property relationships?

8. Derive the equations for change in entropy of a fluid in terms of the *P*-*V*-*T*-relationship and specific heat data.

9. How would you formulate the general equations for changes in enthalpy and internal energy in terms of measurable quantities? Predict the effect of temperature and pressure on *U* and *H* using these equations.

10. What are the steps involved in the calculation of the entropy and enthalpy of a fluid at temperature *T* and pressure *P*? What additional data are required for this calculation?

11. Show that the difference between C_P and C_V can be expressed in terms of the coefficient of volume expansion and the coefficient of compressibility. What would be $C_P - C_V$ for (a) Ideal gas and (b) van der Waals gas?

12. Show that C_P and C_V of an ideal gas depend on temperature alone.

13. How is Joule–Thomson coefficient evaluated from *P*-*V*-*T*-information? Prove that an ideal gas will not undergo any temperature change on throttling.

14. What is the importance of the Gibbs–Helmholtz equation? How would you obtain an equation for the free energy as a function of temperature using the Gibbs–Helmholtz equation?

15. Define fugacity, and show that the fugacity and pressure are identical for ideal gases. What is the standard state for fugacity for a real gas?

16. The free energy of a real gas can be thought of as the sum of the free energy of an ideal gas at the same conditions of the gas and the contribution due to the intermolecular interaction. How is the latter contribution represented in terms of the fugacity coefficient?

17. Explain any three methods for estimating the fugacity of a pure gas.

18. How is a rough estimate of fugacity of a gas made from its pressure and molar volume?

19. How would you estimate the fugacity of a liquid at pressure *P* and temperature *T,* if its molar volume and saturation pressure are given?

20. What is meant by the activity of a pure fluid? How would you estimate the activity of an incompressible substance?

21. What do you mean by enthalpy and entropy departures? How are they important in the evaluation of thermodynamic properties?

22. What are the different types of thermodynamic diagrams? List their respective fields of application.

23. Using the generalised charts for departure functions, explain the method of construction of any two thermodynamic diagrams.

EXERCISES

6.1 Show that

(a) $$C_P = T\frac{(\partial V/\partial T)_P}{(\partial T/\partial P)_S}$$

(b) $$dH = C_P\,dT + \left[V - \frac{(C_P - C_V)\kappa}{\beta}\right] dP$$

(c) $$T\left(\frac{\partial P}{\partial T}\right)_V - P = \left(\frac{\partial U}{\partial V}\right)_T$$

(d) $$\left(\frac{\partial U}{\partial P}\right)_T = -\left[T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T\right]$$

6.2 Maxwell's equation can be used to evaluate the latent heat of vaporisation of a pure substance. Choose the appropriate equation and explain the method to estimate the latent heat of vaporisation as a function of temperature using the vapour pressure data.

6.3 Show that for a gas obeying the van der Waals equation $(\partial C_V/\partial V)_T = 0$.

6.4 A gas is found to obey the equation of state $P(V - b) = RT$. Show that its C_P doesn't change with changes in pressure at constant temperature.

6.5 Define Joule–Thomson coefficient and explain how it could be used for determining the heat capacity of gases.

6.6 Show that

$$\mu = \frac{RT^2}{PC_P}\left(\frac{\partial Z}{\partial T}\right)_P$$

where Z is the compressibility factor. 'The Joule–Thomson coefficient is negative at pressures greater than about $9P_C$, where P_C is the critical pressure.' Justify.

6.7 Show that for a gas obeying the equation of state $PV(1 - bP) = RT$,

(a) $$\Delta G = RT \ln \frac{P_2(1 - bP_1)}{P_1(1 - bP_2)}$$

(b) $$\Delta A = RT \ln \frac{P_2(1 - bP_1)}{P_1(1 - bP_2)} - \frac{RT}{(1 - bP_2)} + \frac{RT}{(1 - bP_1)}$$

6.8 With the help of Maxwell equations prove that the specific heats of ideal gases are functions of temperature only.

6.9 Using the method of Jacobians derive a relationship for the ratio of heat capacities C_P and C_V.

Show that the slope of P-V diagram for a reversible adiabatic process is γ times that for a reversible isothermal process.

6.10 Using the method of Jacobians show that

(a) $\left(\dfrac{\partial H}{\partial S}\right)_V = T\left(1 + \dfrac{V\beta}{C_V\,\kappa}\right)$

(b) $\left(\dfrac{\partial G}{\partial V}\right)_T = -\dfrac{1}{\kappa}$

(c) $\left(\dfrac{\partial H}{\partial S}\right)_T = T - \dfrac{1}{\beta}$

(d) $\left(\dfrac{\partial P}{\partial T}\right)_V = \dfrac{\beta}{\kappa}$

(e) $-\left(\dfrac{\partial P}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V\left(\dfrac{\partial T}{\partial V}\right)_P$

(f) $\kappa_S = \kappa - \dfrac{VT\beta^2}{C_P}$, where $\kappa_S = -(1/V)\,(\partial V/\partial P)_S$, the adiabatic compressibility.

(g) $\left(\dfrac{\partial U}{\partial V}\right)_T = T\left(\dfrac{\partial P}{\partial T}\right)_V - P$

(h) $C_P = \dfrac{T(\partial V/\partial T)_P}{(\partial T/\partial P)_S}$

(i) $\left(\dfrac{\partial P}{\partial V}\right)_H = \dfrac{C_P}{\beta^2 V^2 T - C_P V\kappa - V^2\beta}$

6.11 A pure gas flowing at a low rate through a well-insulated horizontal pipe at high pressure is throttled to a slightly lower pressure. The gas obeys the equation of state $P(V - b) = RT$, where b is a positive constant. Does the gas temperature rise or fall by throttling?

6.12 The following relationship between fugacity and pressure has been proposed: $f = P + aP^2$, where a is a function of temperature only. Find an equation of state for the gas conforming to this relation. Is the equation of state realistic? Explain.

6.13 Derive an expression for fugacity coefficient of a gas obeying the following equation of state

$$P = \frac{RT}{V - b}\,\frac{a}{T^{0.5}\,(V + b)V}$$

where a and b are empirical constants.

6.14 Using the generalised compressibility factor method, explain how you would make a generalised condition of enthalpy departure for a range of pressures.

6.15 Describe the T-S diagram of a pure fluid. Given the equation of state or the generalised compressibility charts, explain how you would construct the *T-S* diagram. Give the relevant thermodynamic relations and the reference states used. What additional data are necessary?

6.16 The melting point of benzene is found to increase from 278.5 K to 278.78 K, when the external pressure is increased by 100 bar. Heat of fusion of benzene is 128 kJ/kg. What is the change in volume per kg accompanying the fusion of benzene?

6.17 Carbon tetrachloride boils at 349.75 K at 1 bar. Its latent heat of vaporisation is 194.8 kJ/kg. What would be the boiling point of carbon tetrachloride at 2 bar?

6.18 The variation of vapour pressure of benzene with temperature is given in the table below.

T, K	280.6	288.4	299.1	315.2	333.6	353.1
P, bar □ 10^2	5.33	8.00	13.30	26.70	53.33	100

Estimate the latent heat of vaporisation of benzene and its vapour pressure at 393 K.

Is it possible to approximate the vapour pressure as an exponential function of temperature? Does the Clapeyron equation suggest such an approximation?

6.19 If the pressure inside a pressure cooker is 200 kPa, what is the boiling point of water inside it? The normal boiling point of water is 373 K and the latent heat of vaporisation of water is 2257 kJ/kg at 373 K.

6.20 The vapour pressure and molar volume of water as function of temperature are given below:

T, K	490	500	510
P^S, kPa	2181	2637	3163
V_G, m^3/kg	91.50 □ 10^{-3}	75.85 □ 10^{-3}	63.23 □ 10^{-3}
V_L, m^3/kg	1.18 □ 10^{-3}	1.20 □ 10^{-3}	1.22 □ 10^{-3}

Calculate the latent heat of vaporisation of water at 500 K using (a) Clapeyron equation; (b) Clausius–Clapeyron equation.

6.21 (a) Prove the following, where m is the Joule–Thomson coefficient.

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -\mu\left(\frac{\partial C_P}{\partial T}\right)_P - C_P\left(\frac{\partial \mu}{\partial T}\right)_P$$

(b) If m = – 0.1975 + 138/T – 319 P/T^2 K/bar, and C_P = 6.557 + 6.1477 □ 10^{-2} T – 2.148 □ 10^{-7} T^2 kJ/kmol K, evaluate the derivative $(\partial C_P/\partial P)_T$ at 1 bar and 333 K when T is in K and P is in bar.

6.22 The volume coefficient of expansion of water at 373 K is 7.8 □ 10^{-4} K^{-1}. Calculate the change in entropy when the pressure is increased from 1 bar to 100 bar. At 373 K, density of water is 958 kg/m^3.

6.23 Calculate the change in enthalpy, entropy and internal energy when 1 mol liquid water at 273 K and 1 bar is converted into steam at 473 K and 3 bar. List the assumptions used.

Data: At 1 bar the specific heat of steam is $C_P = 37.002 - 8.00 \square 10^{-3} T + 9.24 \square 10^{-6} T^2$, where C_P is in kJ/kmol and T is in K. Enthalpy of vaporisation at 373 K = 40.6 kJ/kmol.

6.24 Calculate the change in internal energy, enthalpy, entropy and free energy when one kmol hydrogen gas at 300 K and 1 bar is heated and compressed to 500 K and 100 bar. The entropy of hydrogen in the initial state is 131.5 kJ/kmol K. Enthalpy at 273 K may be taken to be zero Assume $C_P = 27.3 + 4.2 \square 10^{-3} T$ at 1 bar where C_P is in kJ/kmol K and T is in K. Hydrogen may be treated as ideal gas.

6.25 Calculate the enthalpy and entropy of isobutane vapour at 360 K and 15.6 bar from the following data:

Enthalpy and entropy for saturated liquid at 290 K are both zero. The average specific heat of isobutane liquid between 290 K and 295 K is 2.34 kJ/kg K. The heat ofvaporisation at 295 K is 335 kJ/kg. The vapour pressure of isobutane is 3.1 bar at 295 K The specific heat of the gas at 3.1 bar varies with temperature as given below:

T, K	295	310	328	345	360
C_P, kJ/kg K	1.806	1.806	1.777	1.806	1.856

The specific volumes of gaseous isobutane in m^3/kg are as follows:

P, bar	310 K	328 K	345 K	360 K	378 K
2.7	0.151	0.160	0.169	0.179	0.188
4.1	0.096	0.103	0.110	0.116	0.122
6.8	–	0.057	0.062	0.066	0.070
10.2	–	–	0.037	0.041	0.044
13.6	–	–	–	0.028	0.031
15.6	–	–	–	0.023	0.026

6.26 Calculate $C_P - C_V$ for CO_2 at 1 bar and 273 K given that the van der Waals constants for CO_2 are $a = 0.365$ J m^3/mol^2 and $b = 42.8 \square 10^{-6}$ m^3/mol.

6.27 Calculate the C_P of CO_2 gas at 100 bar and 373 K given that C_P at 1 bar and 373 K is 40.6 J/mol K. The van der Waals constants are $a = 0.365$ J m^3/mol^2 and $b = 42.8 \square 10^{-6}$ m^3/mol.

[*Hint*:
$$\Delta C_P = -\int_1^{100} T(\partial^2 V/\partial T^2)_P \, dP$$

Assume various values of P and find $(\partial^2 V/\partial T^2)_P$ in each case. Plot $-T(\partial^2 V/\partial T^2)_P$ against P and find the area under the curve between $P = 1$ and $P = 100$ bar. The area thus determined equals DC_P].

6.28 Wet steam at 20 bar is throttled to a pressure of 1.5 bar and a temperature of 411 K. What was the initial quality of steam? Take the data from the steam tables.

6.29 Calculate $(\partial U/\partial P)_T$, $(\partial H/\partial P)_T$ and m of a substance at 298 K and 1 bar, if the following data are given:

$C_P = 138$ kJ/kmol K, $V = 0.09$ m^3/kmol, $(\partial V/\partial T)_P = 9.0 \square 10^{-8}$ m^3/kmol K and $(\partial V/\partial P)_T = -9.0 \square 10^{-9}$ m^3/kmol bar.

6.30 Show that for any gas whose volume varies linearly with temperature at a given pressure, the Joule–Thomson coefficient is zero.

6.31 At 200 K, the compressibility factor of oxygen varies with pressure as given below. Evaluate the fugacity of oxygen at this temperature and 100 bar.

P, bar	1.00	4.00	7.00	10.00	40.00	70.00	100.00
Z	0.99701	0.98796	0.97880	0.96956	0.8734	0.7764	0.6871

6.32 (a) Calculate the fugacity of CO at 50 bar and 400 bar, if the following data are applicable a 273 K.

P, bar	25	50	100	200	400	800	1000
Z	0.9890	0.9792	0.9741	1.0196	1.2482	1.8057	2.0819

(b) Using the values of *Z* at 50 and 400 bar, calculate the van der Waals constants for CO. From these determine the fugacities at these pressures and compare the results with the previous ones.

6.33 Calculate the fugacity of methane gas at 322 K and 55 bar, given that the critical constants are 190.7 K and 46.4 bar.

6.34 Calculate the fugacity of nitrogen at 800 bar from the following data at 273 K.

P, bar	50	100	200	400	800	1000
PV/*RT*	0.9846	0.9846	1.0365	1.2557	1.7959	2.0641

6.35 Find the per cent increase in the fugacity of gaseous oxygen per degree rise in temperature in the neighbourhood of 298 K and 200 bar, if under these conditions, the Joule–Thomson heat is 1457 J/mol. (Joule–Thomson heat = $H_0 - H$.)

6.36 Estimate the fugacity of gaseous propane at 12 bar and 310 K using the following data.

P, bar	1.7	3.4	6.8	10.2	11.7	13.6	34
V, m^3/kg	0.3313	0.1609	0.0754	0.0468	0.0382	0.021	– 0.00207

Also compute the fugacity of propane at 310 K and 70 bar given that the vapour pressure o propane at 310 K is 13 bar.

6.37 The experimental pressure–volume data for benzene at 675 K from a very low pressures up to about 75 bar may be approximated by the equation $V = 0.0561(1/P - 0.0046)$, where *V* is in m^3/mol and pressure *P* is in bar. What is the fugacity of benzene at 1 bar and 675 K?

6.38 In the previous problem what is the fugacity of benzene at 75 bar and 675 K assuming that the fugacity of benzene at 1 bar is unity?

6.39 (a) The compressibility of a gas may be represented by $PV/RT = A + BP + CP^2 + DP^3$, where A, B, C and D are functions of temperature and P is measured in bar. Derive an expression for fugacity as a function of pressure at a given temperature.

(b) Evaluate the fugacity of nitrogen at 273 K and 300 bar, given that at 273 K the constants in the equation of state given in part (a) are $A = 1.00$, $B = -5.314$ □ 10^{-4}, $C = 4.276$ □ 10^{-6} and $D = -3.292$ □ 10^{-9}.

6.40 (a) Find an expression for the fugacity coefficient of a gas that obeys the equation of state

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

(b) Use the result in part (a) to estimate the fugacity of argon at 1.00 bar and 273 K if the constants B and C are respectively -21.13 □ 10^{-6} m^3/mol and 1054 □ 10^{-12} m^6(mol)$^{-2}$.

6.41 Derive an expression for fugacity coefficient of a gas obeying the equation of state $z = a + bP + cP^2$, where P is in bar. Determine fugacity of oxygen at 293 K and 100 bar, given that $a = 1.0$; $b = -0.753$ □ 10^{-3}, and $c = 0.15$ □ 10^{-5}.

7

Properties of Solutions

We have seen in Chapter 6 that the thermodynamic properties of homogeneous pure substances depend only on the state of the system. The relationships developed for pure fluids are not applicable to solutions and need modification. The thermodynamic properties of solutions and heterogeneous systems consisting of more than one phase are influenced by the addition and removal of matter. The term solution includes homogeneous mixtures of two or more components in the gas, liquid or solid phase. The pressure, temperature and the amount of various constituents present determine the extensive state of a solution; and pressure, temperature and composition determine the intensive state. In this chapter, we discuss how the thermodynamic properties of a solution are determined and introduce certain concepts that are essential to the study of phase equilibria and chemical reaction equilibria.

7.1 PARTIAL MOLAR PROPERTIES

The properties of a solution are not additive properties of its components. For example, the volume of a solution is not the sum of the volumes of the pure components constituting the solution. It means that when a substance becomes part of a solution it loses its identity. But it still contributes to the property of the solution as is evident from the fact that by changing the amount of substance, the solution property also changes. Thus we need a new set of concepts that enable us to apply thermodynamics to solutions of variable composition. In this connection, the concept of partial molar properties is of great use. The term partial molar property is used to designate the property of a component when it is in admixture with one or many components. To be more precise, the *partial molar property* of a particular component in a mixture measures the contribution of that component to the mixture property. If M^t is the total value of any extensive thermodynamic property of a solution, the partial molar property $\bar{M}_i$ of the component i in the solution is defined as

$$\bar{M}_i = \left(\frac{\partial nM}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \left(\frac{\partial M^t}{\partial n_i}\right)_{T,P,n_{j\neq i}} \tag{7.1}$$

In Eq. (7.1), n is the total number of moles and M is the molar property of the solution. n_i denotes the number of moles of component i in solution, so that $n = \Sigma n_i$.

In general, any partial molar property $\bar{M}_i$ is the increase, in the property M^t of the solution resulting from the addition at constant temperature and pressure, of one mole of that substance to such a large quantity of the system that its composition remains virtually unchanged. It is an intensive property and its value depends only on the composition at the given temperature and pressure. The subscript $n_{j\neq i}$ indicates that the number of moles of all components in the solution other than the number of moles of *i* are kept constant.

7.1.1 Physical Meaning of Partial Molar Properties

To understand the *physical meaning* of partial molar properties let us consider the partial molar volume, the simplest partial molar property to visualise. It is the contribution that a component in the solution makes to the total volume. Consider an open beaker containing a huge volume of water. Assume that one mole of water is added to it. The volume increases by $18 \square 10^{-6}$ m^3, which is the molar volume of pure water. If the same amount of water is added to a large amount of pure ethanol taken in the beaker, the increase in volume will be approximately $14 \square 10^{-6}$ m^3, which is the partial molar volume of water in pure ethanol. The difference in the increase in volumes can be explained thus: the volume occupied by a given number of water molecules depends on the molecules surrounding them. When water is mixed with a large volume of alcohol, there is so much alcohol present that each water molecule is surrounded by pure ethanol. Consequently, the packing of the molecules would be different from that in pure water, and the molecules occupy lesser volume.

If one mole water is added to an equimolar mixture of alcohol and water, the increase in volume of the solution would be different from that resulted when the same quantity were added to pure alcohol. The partial molar properties of the components of a mixture vary with composition because the environment of each type of molecule changes as the composition changes. The intermolecular forces also get changed resulting in the changes in the thermodynamic properties of solutions with compositions. The variation of partial molar volumes with concentration is shown in Fig. 7.1 for ethanol (*E*) – water (*W*) system.

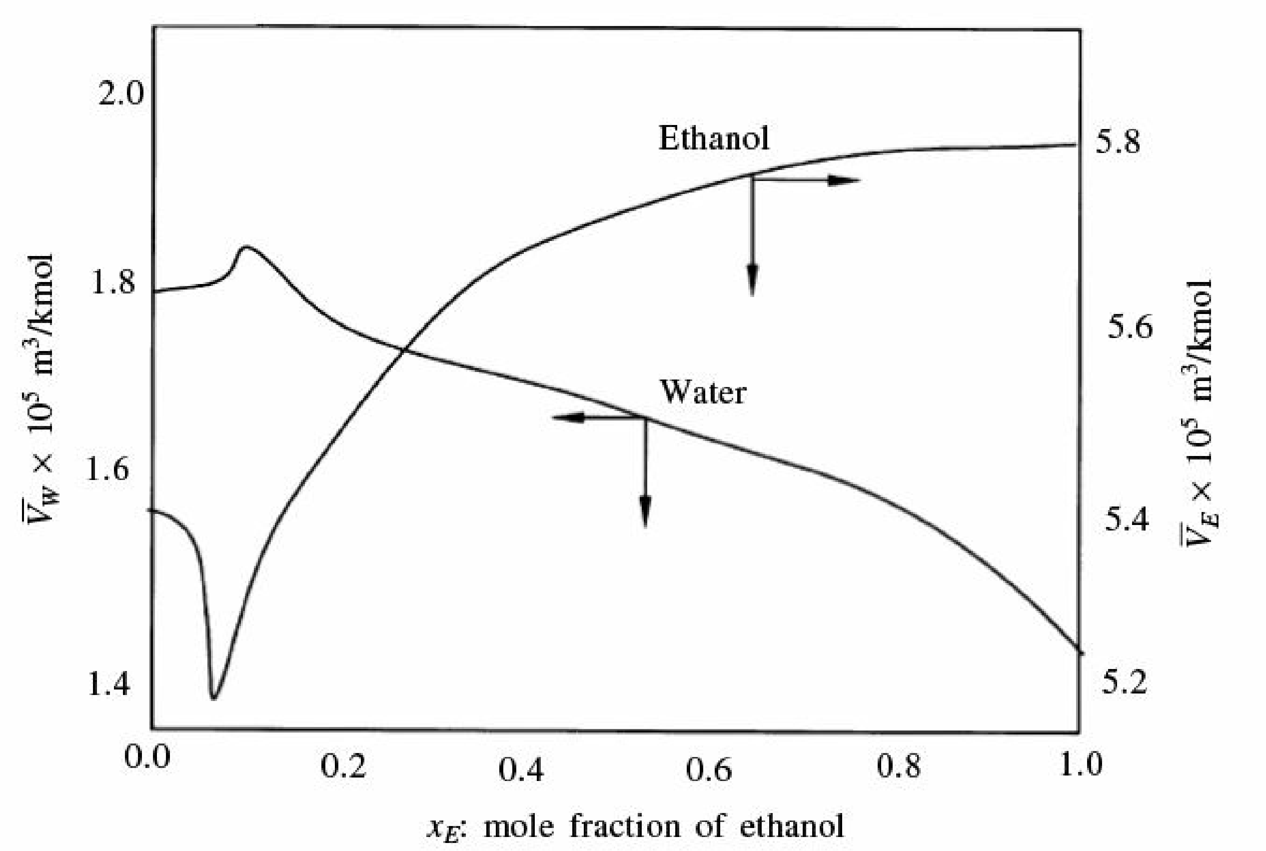


Fig. 7.1 Partial molar volumes in alcohol-water mixture.

We have seen that the effective molar volume of water added to the ethanol–water solution, i.e. the partial molar volume $\overline{V}_W$ in the solution is less than the molar volume V_W of pure water at the same temperature and pressure. To be specific, when pure water is added to an ethanol water solution of volume V^t and allowed sufficient time for heat exchange so that temperature remains the same as that before addition, the increase in volume of the solution DV^t П D$n_W V_W$, where Dn_W is the moles of water added. The increase in volume is given by

$$\Delta V^t = \Delta n_W \overline{V}_W \tag{7.2}$$

Equation (7.2) can be written as

$$\overline{V}_W = \frac{\Delta V^t}{\Delta n_W} \tag{7.3}$$

In this process, a finite drop of water was added which may cause a finite change in composition. If $\overline{V}_W$ were to represent a property of the solution, it must be based on data for the solution at this composition. For an infinitesimal amount of water added, Eq. (7.3) becomes

$$\overline{V}_W = \lim_{\Delta n_W \to 0} \frac{\Delta V^t}{\Delta n_W} = \left(\frac{\partial V^t}{\partial n_W} \right)$$

Since temperature, pressure and number of moles of alcohol are kept constant during addition of water,

$$\overline{V}_W = \left(\frac{\partial V^t}{\partial n_W} \right)_{T,P,n_E} \tag{7.4}$$

where n_E represents the number of moles of alcohol present in the solution.

In general, the partial molar volume $\overline{V}_i$ of component i is defined as

$$\overline{V}_i = \left(\frac{\partial V^t}{\partial n_i} \right)_{T,\,P,\,n_{j \neq i}} \tag{7.5}$$

and it denotes the incremental change in mixture volume which occurs when a small quantity of component i is added at constant pressure and temperature. The amount of i added is so small that no detectable change in composition occurs. While the molar volume is always positive, the partial molar volume may even be negative. The partial molar volume of $MgSO_4$ in water at infinite dilution (i.e. in the limit of zero concentration) is –1.4 □ 10^{-6} m^3/mol which means that the addition of one mole of $MgSO_4$ to a large volume of water results in a decrease in volume of 1.4 □ 10^{-6} m^3. The contraction may be due to the breaking up and subsequent collapse of the open structure of water as the ions become hydrated.

Though different from molar properties of the pure components, to get a physical picture of the concept of partial molar properties, we can treat them as the molar properties of the components in solution. However, it is to be borne in mind that the components of a solution are intimately intermixed and cannot have individual properties of their own. The partial molar properties in fact, represent the contribution of individual components constituting the solution to the total solution property as described in the following section.

7.1.2 Partial Molar Properties and Properties of Solution

Consider any thermodynamic *extensive* property (such as volume, free energy, heat capacity, etc.), its value for a homogeneous system being completely determined by the temperature, pressure and the amounts of various constituents present. Let M be the molar property of a solution and M^t be the total property. Then, $M^t = nM$, where n is $n_1 + n_2 + n_3 + \dots$. Here, n_1, n_2, n_3, . . . are the number of moles of the respective components 1, 2, 3, . . . of the system. The solution property is a function represented by

$$M^t = f(P, T, n_1, n_2, \dots, n_i, \dots) \qquad (7.6)$$

If there is a small change in the pressure, temperature and the amounts of various constituents, then

$$dM^t = \left(\frac{\partial M^t}{\partial P}\right)_{T,N} dP + \left(\frac{\partial M^t}{\partial T}\right)_{P,N} dT + \left(\frac{\partial M^t}{\partial n_1}\right)_{P,T,n_2,} dn_1 + \cdots + \left(\frac{\partial M^t}{\partial n_i}\right)_{P,T,n_{j \neq i}} dn_i + \cdots \qquad (7.7)$$

The subscript N in the first two partial derivatives indicate that the number of moles is kept constant, and the subscript $n_{j\neq i}$ indicates that the number of moles of all components other than that of component i is kept constant.

At constant temperature and pressure, dP and dT are zero, so that Eq. (7.7) reduces to

$$dM^t = \sum_{i=1}^{n} \left(\frac{\partial M^t}{\partial n_i}\right)_{P,T,n_{j \neq i}} dn_i \qquad (7.8)$$

The partial derivatives appearing on the right-hand side are, by Eq. (7.1), the partial molar properties $\overline{M}_i$. That is, at constant temperature and pressure,

$$dM^t = \sum_{i=1}^{n} \overline{M}_i \, dn_i \qquad (7.9)$$

It is evident that the partial molar properties $\overline{M}_i$ are not extensive properties, but are intensive properties of the solution. They depend, therefore, not upon the total amount of each constituent, but only upon the composition, or the relative amounts of the constituents. If we add several constituents simultaneously to a given solution at constant temperature and pressure, keeping the ratio of the various constituents constant, the partial molar properties are not changed. Then, the change in property

$$dM^t = \overline{M}_1 dn_1 + \overline{M}_2 dn_2 + \cdots = (\overline{M}_1 x_1 + \overline{M}_2 x_2 + \cdots)\, dn \tag{7.10}$$

where x_i represents mole fraction of component i in the solution. Integration of Eq. (7.10) yields

$$M^t = (\overline{M}_1 x_1 + \overline{M}_2 x_2 + \cdots)\, n = \overline{M}_1 n_1 + \overline{M}_2 n_2 + \cdots \tag{7.11}$$

Therefore, M^t, the total property of the solution, is the sum of the partial molar properties of the constituents each weighted according to its number of moles. That is,

$$M^t = \Sigma\, n_i \overline{M}_i \tag{7.12}$$

This equation along with Eq. (7.9), which can be written in the following form serves as the relationship between partial molar properties and total solution property.

$$dM^t = \Sigma\, \overline{M}_i\, dn_i \tag{7.13}$$

For one mole of the solution it can be easily shown (see Example 7.1) that

$$M = \Sigma\, x_i \overline{M}_i \tag{7.14}$$

$$dM = \Sigma\, \overline{M}_i\, dx_i \tag{7.15}$$

Thus the molar volume V of a solution made up of components 1, 2, . . . can be written as

$$V = x_1 \overline{V}_1 + x_2 \overline{V}_2 + \cdots$$

We see that the partial molar property $\overline{M}_i$ of any constituent may be regarded as the contribution of one mole of that constituent to the total value of the property under the specified conditions. In other words, the partial molar properties may be treated exactly as though they represent the molar properties of the components in the solution.

***EXAMPLE* 7.1** Give an alternative derivation for Eqs. (7.12) and (7.14) starting from Eq. (7.9)

Solution Equation (7.9) gives

$$dM^t = \Sigma\, \overline{M}_i\, dn_i$$

Using $x_i n = n_i$, $d(x_i n) = n\, dx_i + x_i\, dn$ and $dM^t = d(nM) = n\, dM + M\, dn$, where M, as pointed out earlier, is the molar property. Equation (7.9) becomes

$$n\, dM + M\, dn = \Sigma\, \overline{M}_i (x_i\, dn + n\, dx_i)$$

On rearranging the above result, we get

$$(M - \Sigma\, \overline{M}_i x_i)\, dn = (\Sigma\, \overline{M}_i\, dx_i - dM)\, n$$

n represents the total amount of various constituents and *dn* the changes in the total number of moles. One is free to choose any value for *n* as well as *dn*. In short, *n* and *dn* can be independently changed. For all possible values of *n* and *dn*, the above equation is to be satisfied. This is possible only if the terms in brackets reduce to zero.

$$M - \Sigma\, x_i \overline{M}_i = 0 \qquad \text{or} \qquad M = \Sigma\, x_i \overline{M}_i \tag{7.14}$$

$$\Sigma\, \overline{M}_i\; dx_i - dM = 0 \qquad \text{or} \qquad dM = \Sigma\, \overline{M}_i\; dx_i \tag{7.15}$$

Multiplying Eq. (7.14) by n, we get

$$nM = M^t = \Sigma\, n_i \overline{M}_i \tag{7.12}$$

***EXAMPLE* 7.2** Will it be possible to prepare 0.1 m^3 of alcohol-water solution by mixing 0.03 m^3 alcohol with 0.07 m^3 pure water? If not possible, what volume should have been mixed in order to prepare a mixture of the same strength and of the required volume? Density of ethanol and water are 789 and 997 kg/m^3 respectively. The partial molar volumes of ethanol and water at the desired compositions are: Ethanol = 53.6 □ 10^{-6} m^3/mol; water = 18 □ 10^{-6} m^3/mol.

Solution Let us first find out the number of moles of ethanol and water mixed and their mole fractions in the resultant mixture.

Moles of ethanol in the solution = (0.03 □ 789 □ 10^3)/46 = 514.57 mol
Moles of water in the solution = (0.07 □ 997 □ 10^3)/18 = 3877.22 mol
Mole fraction of ethanol desired = 514.57/(514.57 + 3877.22) = 0.1172
Mole fraction of water = 1 – 0.1172 = 0.8828

Actual volume of solution is

514.57 □ 53.6 □ 10^{-6} + 3877.22 □ 18 □ 10^{-6} = (0.02758 + 0.06979) = 0.09737 m^3

That is, by mixing 0.03 m^3 alcohol with 0.07 m^3 water, we would get only 0.09737 m^3 of solution. To prepare 0.1 m^3 of solution the volumes to be mixed are:

Ethanol = (0.03/0.09737) □ 0.1 = 0.03081 m^3 and Water = (0.07/0.09737) □ 0.1 = 0.07189 m^3

***EXAMPLE* 7.3** A 30 per cent by mole methanol-water solution is to be prepared. How many cubic metres of pure methanol (molar volume, 40.727 □ 10^{-6} m^3/mol) and pure water (molar volume, 18.068 □ 10^{-6} m^3/mol) are to be mixed to prepare 2 m^3 of the desired solution? The partial molar volumes of methanol and water in a 30 per cent solution are 38.632 □ 10^{-6} m^3/mol and 17.765 □ 10^{-6} m^3/mol, respectively.

Solution Molar volume of the desired solution is

$V = x_1\overline{V}_1 + x_2\overline{V}_2$ = (0.3 □ 38.632 □ 10^{-6} + 0.7 □ 17.765 □ 10^{-6}) = 24.0251 □ 10^{-6} m^3/mol

Therefore, 2 m^3 of the desired solution contains

$2/(24.0251 \times 10^{-6}) = 83.2463 \times 10^3$ mol

Number of moles of methanol in 2 m^3 of solution = $83.2463 \times 10^3 \times 0.3 = 24.9739 \times 10^3$ mol

Number of moles of water in 2 m^3 of solution = $83.2463 \times 10^3 \times 0.7 = 58.2724 \times 10^3$ mol

Volume of methanol to be taken = $24.9739 \times 10^3 \times 40.727 \times 10^{-6}$ m^3 = 1.0171 m^3

Volume of water to be taken = $58.2724 \times 10^3 \times 18.068 \times 10^{-6}$ m^3 = 1.0529 m^3

***EXAMPLE* 7.4** Laboratory alcohol containing 96% alcohol and 4% water is to be diluted to a solution containing 56% alcohol and 44% water. All percentages are on weight basis. The partial specific volumes are as follows: In 96% alcohol solution, $\overline{V}_W = 0.816 \times 10^{-3}$ m^3/kg, $\overline{V}_E = 1.273 \times 10^{-3}$ m^3/kg. In 56% alcohol solution, $\overline{V}_W = 0.953 \times 10^{-3}$ m^3/kg, $\overline{V}_E = 1.243 \times 10^{-3}$ m^3/kg. The density of water may be taken as 0.997×10^3 kg/m^3.

(a) How much water should be added to 2×10^{-3} m^3 of the laboratory alcohol?
(b) What is the volume of the dilute alcohol obtained?

Solution Basis: 2×10^{-3} m^3 laboratory alcohol.

1 kg laboratory alcohol $\equiv (0.96 \times 1.273 + 0.04 \times 0.816) \times 10^{-3} = 1.255 \times 10^{-3}$ m^3

2×10^{-3} m^3 of laboratory alcohol $\equiv 2 \times 10^{-3}/(1.255 \times 10^{-3}) = 1.594$ kg

(a) Let the mass of water added be *m* kg. Taking an alcohol balance, we get

$$1.594 \times 0.96 = (m + 1.594)\ 0.56$$

Thus mass of water added is,

$$m = (1.594 \times 0.96)/0.56 - 1.594 = 1.1386 \text{ kg}$$

and volume of water added is

$$1.1386/(0.997 \times 10^3) = 1.142 \times 10^{-3} \text{ m}^3$$

(b)
Mass of dilute alcohol obtained = 1.594 + 1.1386 = 2.7326 kg

Specific volume of 56% alcohol = $(0.56 \times 1.243 + 0.44 \times 0.953) \times 10^{-3} = 1.115 \times 10^{-3}$ m^3/kg
Therefore,

Volume of dilute alcohol obtained = $1.115 \times 10^{-3} \times 2.7326 = 3.0468 \times 10^{-3}$ m^3

7.1.3 Determination of Partial Molar Properties

***Method* 1 (*Analytical*).** If the volume of a solution is known as a function of its composition, the partial molar volume of a constituent may be found by partial differentiation with respect to the amount of that constituent.

$$\overline{V}_i = \left(\frac{\partial V^t}{\partial n_i}\right)_{P,T,n_j}$$

***Method* 2 (*Graphical*).** Let V^t, the volume of the solution containing a fixed amount of one of the constituents (say, n_1) is known for several values of the amount of other constituent (say, n_2). We may plot V^t against n_2. See Fig. 7.2. The slope of the tangent to the curve is $(\partial V^t/\partial n_2)_{P,T,n1}$ which, by definition is $\overline{V}_2$, the partial molar volume of component 2. The volume of solution is assumed so large that no significant change in composition occurs when n_2 is changed. This method has limitation of not yielding values of $\overline{V}_1$ directly. Also, it is not advisable to use this method for determination of $\overline{V}_2$ when n_2 is large compared to n_1. The method of tangent intercepts is free from such limitations and is therefore preferred for the determination of partial molar properties.

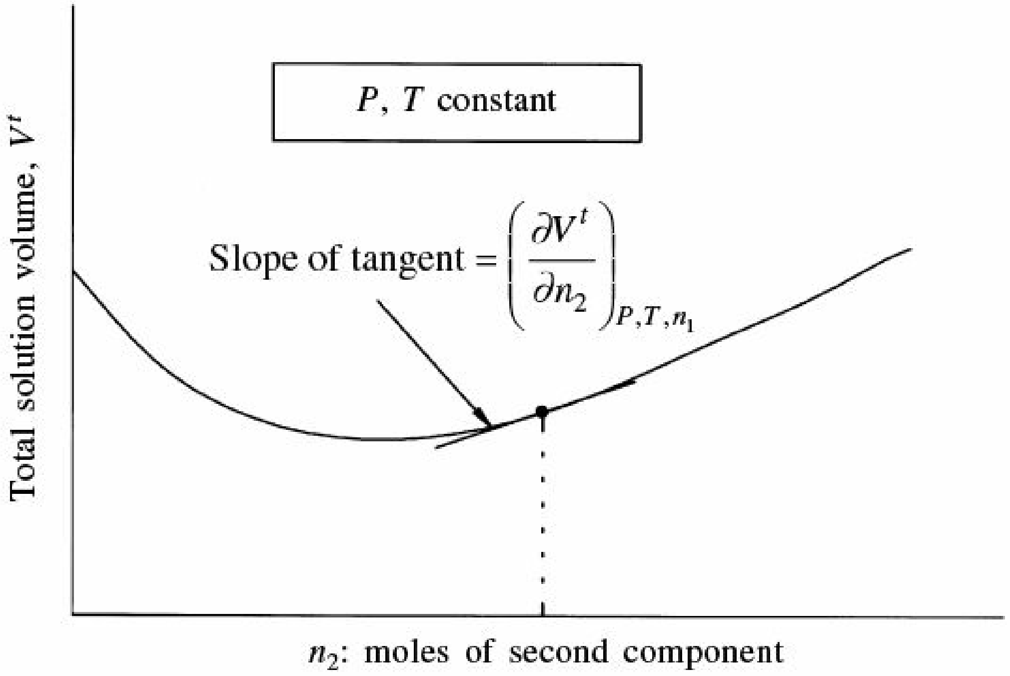


Fig. 7.2 Determination of partial molar properties by Method 2.

***Method* 3 (*The tangent-intercept method*).** This is also a graphical method widely used for the determination of partial molar properties of both components in a binary solution. The molar volume V is plotted against mole fraction of one of the components (say, x_2, the mole fraction of component 2). To determine the partial molar volumes, draw the tangent to the curve at the desired mole fraction. The intercept that this tangent makes with the vertical axis at $x_2 = 1$ gives $\overline{V}_2$ and the intercept on the vertical axis at $x_2 = 0$ (or $x_1 = 1$) gives $\overline{V}_1$. In Fig. 7.3, $BD = \overline{V}_2$ and $AC = \overline{V}_1$.

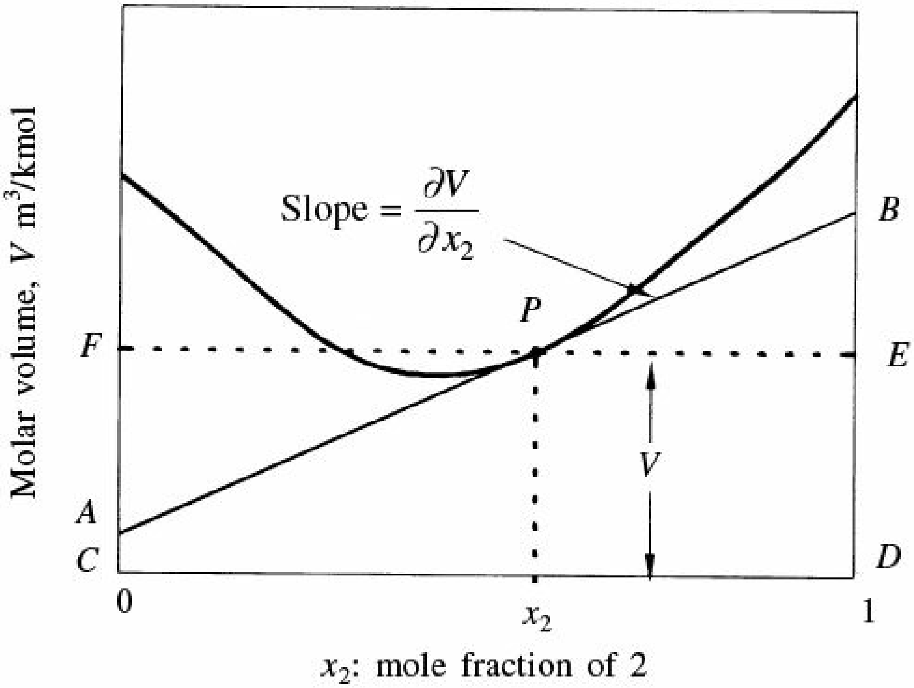


Fig. 7.3 The method of tangent-intercepts for the determination of partial molar properties.

To prove this result, consider a binary solution containing n_1 moles of component 1 and n_2 moles of component 2. Let the total volume be V^t and let V be the molar volume. Then

$$V^t = nV = (n_1 + n_2)\, V \tag{7.16}$$

Differentiating Eq. (7.16) with respect to n_1, keeping n_2, T and P constant

$$\left(\frac{\partial V^t}{\partial n_1}\right)_{T,\,P,\,n_2} = \bar{V}_1 = V + (n_1 + n_2)\left(\frac{\partial V}{\partial n_1}\right)_{n_2} \tag{7.17}$$

The mole fraction x_2 is given by

$$x_2 = \frac{n_2}{n_1 + n_2} \tag{7.18}$$

Differentiating Eq. (7.18) with respect to n_1 keeping n_2 constant, we get

$$\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} = -\frac{n_2}{(n_1 + n_2)^2} = -\frac{x_2}{n_1 + n_2}$$

which can be rearranged as

$$\frac{n_1 + n_2}{dn_1} = -\frac{x_2}{dx_2} \tag{7.19}$$

Equation (7.19) can be substituted into Eq. (7.17) to yield the following:

$$\overline{V}_1 = V - x_2 \frac{\partial V}{\partial x_2} \tag{7.20}$$

Similarly it can be shown that

$$\overline{V}_2 = V - x_1 \frac{\partial V}{\partial x_1} \tag{7.21}$$

Since, for a binary solution, $x_1 = 1 - x_2$ and $dx_1 = -dx_2$, Eq. (7.21) can be put in another form:

$$\overline{V}_2 = V + (1 - x_2)\frac{\partial V}{\partial x_2} \tag{7.22}$$

In Fig. 7.3, the length *BD* = *BE* + *ED*, where *BE* is the slope of the tangent at *P* times the length *PE*. That is,

$$BE = (1 - x_2)\ (\partial V/\partial x_2)$$

and *ED* = *V*, the molar volume at the mole fraction x_2. Thus

$$BD = V + (1 - x_2)\ (\partial V/\partial x_2)$$

which, by Eq. (7.22) is $\overline{V}_2$. Similarly, the length

$$AC = FC - FA = V - x_2\ (\partial V/\partial x_2) = \overline{V}_1$$

The above methods are applicable for the determination of various other partial molar properties also. Of the various mixture properties, only the volume can be determined absolutely. For the determination of other properties like $\overline{G}_i, \overline{H}_i$, etc., it becomes necessary to work with property changes on mixing (discussed later in this chapter) like D*G*, D*H*, etc. The method of tangent intercept for the determination of, say $\overline{G}_1$ and $\overline{G}_2$, requires the plot of D*G* per mole versus x_2.

***EXAMPLE* 7.5** At 300 K and 1 bar, the volumetric data for a liquid mixture of benzene and cyclohexane are represented by $V = 109.4 \square 10^{-6} - 16.8 \square 10^{-6}x - 2.64 \square 10^{-6}x^2$, where *x* is the mole fraction of benzene and *V* has the units of m^3/mol. Find expressions for the partial molar volumes of benzene and cyclohexane.

Solution The molar volume of the solution as a function of composition is given:

$$V = 109.4 \square 10^{-6} - 16.8 \square 10^{-6}x_1 - 2.64 \square 10^{-6}x_1^2 \tag{7.23}$$

where x_1 = mole fraction of component 1 (in this case, benzene). By Eq. (7.20),

$$\overline{V_1} = V - x_2 \frac{\partial V}{\partial x_2} \tag{7.24}$$

$$\overline{V_1} = V + (1 - x_1) \frac{\partial V}{\partial x_1} \tag{7.25}$$

Differentiating Eq. (7.23), we get

$$\frac{\partial V}{\partial x_1} = -16.8 \times 10^{-6} - 5.28 \times 10^{-6} x_1$$

Substitute this in Eq. (7.25), we get

$$\begin{aligned}\overline{V_1} &= 109.4 \times 10^{-6} - 16.8 \times 10^{-6}x_1 - 2.64 \times 10^{-6}x_1^2 + (1 - x_1)(-16.8 \times 10^{-6} - 5.28 \times 10^{-6}x_1) \\ &= 92.6 \times 10^{-6} - 5.28 \times 10^{-6}x_1 + 2.64 \times 10^{-6}x_1^2\end{aligned}$$

Using Eq. (7.21), $\overline{V_2}$ can be found out.

$$\overline{V_2} = V - x_1 \frac{\partial V}{\partial x_1}$$

$$\begin{aligned}\overline{V_2} &= 109.4 \times 10^{-6} - 16.8 \times 10^{-6}x_1 - 2.64 \times 10^{-6}x_1^2 - x_1(-16.8 \times 10^{-6} - 5.28 \times 10^{-6}x_1) \\ &= 109.4 \times 10^{-6} + 2.64 \times 10^{-6}x_1^2\end{aligned}$$

The partial molar volume of benzene:

$$\overline{V_1} = 92.6 \times 10^{-6} - 5.28 \times 10^{-6}x_1 + 2.64 \times 10^{-6}x_1^2$$

The partial molar volume of cyclohexane:

$$\overline{V_2} = 109.4 \times 10^{-6} + 2.64 \times 10^{-6}x_1^2$$

***EXAMPLE* 7.6** The enthalpy at 300 K and 1 bar of a binary liquid mixture is

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2)$$

where H is in J/mol. For the stated temperature and pressure, determine:

(a) Expressions for $\overline{H_1}$ and $\overline{H_2}$ in terms of x_1

(b) Numerical values for the pure component enthalpies H_1 and H_2

(c) Numerical values for the partial molar enthalpies at infinite dilution $\overline{H}_1^{\infty}$ and $\overline{H}_2^{\infty}$.

Solution The molar enthalpy of the solution as function of concentrations of the constituents is given:

$$H = 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) \tag{7.26}$$

(a) Differentiating Eq. (7.26), we get

$$\frac{\partial H}{\partial x_1} = 400 + 600\,\frac{\partial x_2}{\partial x_1} + x_1 x_2\left(40 + 20\,\frac{\partial x_2}{\partial x_1}\right) + (40\,x_1 + 20\,x_2)\left(x_1\,\frac{\partial x_2}{\partial x_1} + x_2\right)$$

Since $x_1 = 1 - x_2$, $dx_1 = -\,dx_2$ and $\partial x_2/\partial x_1 = -1$, the above equation simplifies to

$$\frac{\partial H}{\partial x_1} = 400 - 600 + x_1 x_2(40 - 20) + (40x_1 + 20x_2)\,(x_2 - x_1) = -\,200 + 40x_1x_2 - 40x_1^2 + 20x_2^2$$

$$\overline{H}_1 = H + (1 - x_1)\,\frac{\partial H}{\partial x_1}$$

$$= 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) + (1 - x_1)\,(-\,200 + 40x_1x_2 - 40x_1^2 + 20x_2^2)$$

$$= 420 - 60\,x_1^2 + 40\,x_1^3 \qquad (7.27)$$

$$\overline{H}_2 = H - x_1\,\frac{\partial H}{\partial x_1}$$

$$= 400x_1 + 600x_2 + x_1x_2(40x_1 + 20x_2) - x_1(-\,200 + 40x_1x_2 - 40x_1^2 + 20x_2^2)$$

$$= 600 + 40x_1^3 \qquad (7.28)$$

(b) $H_1 = \overline{H}_1$ when $x_1 = 1$. Using Eq. (7.27), we get,

$$H_1 = 420 - 60 + 40 = 400 \text{ J/mol}$$

$H_2 = \overline{H}_2$ when $x_2 = 1$ or $x_1 = 0$. Using Eq. (7.28), $\overline{H}_2 = 600$ J/mol

[Alternatively, $H_1 = H$, when $x_1 = 1$, $x_2 = 0$. $H_1 = 400$ J/mol, using Eq. (7.25) $H_2 = H$, when $x_1 = 0$, $x_2 = 1 = 600$ J/mol using Eq. (7.23).]

(c) $\overline{H}_1^\infty = \overline{H}_1$ as $x_1 \to 0$ and $\overline{H}_2^\infty = \overline{H}_2$ as $x_2 \to 0$ (or $x_1 \to 1$)

Put $x_1 = 0$ in Eq. (7.27). $\overline{H}_1^\infty = 420$ J/mol

Put $x_1 = 1$ in Eq. (7.28). $\overline{H}_2^\infty = 640$ J/mol

***EXAMPLE* 7.7** The volume of an aqueous solution of NaCl at 298 K was measured for a series o molalities (moles of solute per kg of solvent) and it was found that the volume varies with molality according to the following expression.

$$V = 1.003 \square 10^{-3} + 0.1662 \square 10^{-4}m + 0.177 \square 10^{-5}m^{1.5} + 0.12 \square 10^{-6}m^2$$

where m is the molality and V is in m^3. Calculate the partial molar volumes of the components at m = 0.1 mol/kg.

Solution The partial molar volume of NaCl:

$$\overline{V}_1 = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} = \left(\frac{\partial V}{\partial m}\right)_{n_2}$$

$$V = 1.003 \times 10^{-3} + 0.1662 \times 10^{-4} m + 0.177 \times 10^{-5} m^{1.5} + 0.12 \times 10^{-6} m^2 \qquad (7.29)$$

Differentiating Eq. (7.29) with reference to m,

$$\begin{aligned}\overline{V}_1 &= 0.1662 \times 10^{-4} + 0.177 \times 1.5 \times 10^{-5} m^{0.5} + 0.12 \times 2 \times 10^{-6} m \\ &= 0.1662 \times 10^{-4} + 0.2655 \times 10^{-5} m^{0.5} + 0.24 \times 10^{-6} m\end{aligned}$$

Substituting $m = 0.1$, this equation gives $\overline{V}_1 = 0.1748 \times 10^{-4}$ m^3/mol. Substituting $m = 0.1$ in Eq. (7.29), $V = 1.0047 \times 10^{-3} m^3$. But,

$$V = n_1\overline{V}_1 + n_2\overline{V}_2 = m\overline{V}_1 + \frac{1000}{18}\overline{V}_2$$

Rearranging this equation and substituting the values, we find

$$\overline{V}_2 = (1.0047 \times 10^{-3} - 0.1 \times 0.1748 \times 10^{-4}) \times \frac{18}{1000} = 18.05 \times 10^{-6} \text{ m}^3/\text{mol}$$

Partial molar volume of water = 18.05 □ 10^{-6} m^3/mol

Partial molar volume of NaCl = 17.48 □ 10^{-6} m^3/mol

7.2 CHEMICAL POTENTIAL

The *chemical potential*, denoted by the symbol m, is a widely used thermodynamic property. It is used as an index of chemical equilibrium in the same manner as temperature and pressure are used as indices of thermal and mechanical equilibrium. The chemical potential m$_i$ of component *i* in a solution is the same as its partial molar free energy in the solution, $\overline{G}_i$. That is, chemical potential of a component *i* in a solution can be defined as

$$\mu_i = \overline{G}_i = \left(\frac{\partial G^t}{\partial n_i}\right)_{T,P,n_j} \qquad (7.30)$$

The total free energy G^t of a solution is a function of pressure, temperature and number of moles of various components.

$$G^t = f(P, T, n_1, n_2, \ldots, n_i, \ldots) \qquad (7.31)$$

The total differential dG^t is

$$dG^t = \left(\frac{\partial G^t}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G^t}{\partial T}\right)_{P,N} dT + \Sigma \left(\frac{\partial G^t}{\partial n_i}\right)_{P,T,n_{j\neq i}} dn_i \tag{7.32}$$

Then using Eq. (7.30),

$$dG^t = \left(\frac{\partial G^t}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G^t}{\partial T}\right)_{P,N} dT + \Sigma \mu_i \, dn_i \tag{7.33}$$

We have shown that for a closed system, when there is no change in the amount of various constituents,

$dG = V\,dP - S\,dT$ (6.18)

Considering the total properties of the system,

$dG^t = V^t\,dP - S^t\,dT$

from which, it follows that

$$\left(\frac{\partial G^t}{\partial T}\right)_{P,N} = -S^t, \quad \left(\frac{\partial G^t}{\partial P}\right)_{T,N} = V^t \tag{7.34}$$

Equation (7.33) can be written as

$$\boxed{dG^t = V^t\,dP - S^t\,dT + \Sigma \mu_i\,dn_i} \tag{7.35}$$

This is the fundamental relationship for changes in the free energy of a solution. At constant temperature and pressure, the change in the free energy is due entirely to the changes in the number of moles and is given by

$$\boxed{dG^t_{T,P} = \Sigma \mu_i\,dn_i} \tag{7.36}$$

By reasoning analogous to that used in the derivation of Eq. (7.12), we have, at constant temperature and pressure,

$G^t = \Sigma \mu_i n_i$

For a binary solution, the molar free energy of the solution is

$G = x_1\mu_1 + x_2\mu_2$

The chemical potential of a component is thus seen to be the contribution of that component to the Gibbs free energy of the solution. The chemical potential is an important property of solution extensively used in the study of phase and chemical equilibria.

7.2.1 Effect of Temperature and Pressure on Chemical Potential

Effect of temperature. Consider Eqs. (7.30) and (7.34). Differentiate Eq. (7.30) with respect to temperature. Then

$$\left[\frac{\partial \mu_i}{\partial T}\right]_{P,N} = \frac{\partial^2 G^t}{\partial T\, \partial n_i} \tag{7.37}$$

Differentiating Eq. (7.34) with respect to n_i, we get

$$-\left[\frac{\partial S^t}{\partial n_i}\right]_{P,T,n_j} = \frac{\partial^2 G^t}{\partial n_i\, \partial T} \tag{7.38}$$

Equations (7.37) and (7.38) imply that

$$\left[\frac{\partial \mu_i}{\partial T}\right]_{P,N} = -\left[\frac{\partial S^t}{\partial n_i}\right]_{P,T,n_j} = -\bar{S}_i \tag{7.39}$$

where $\bar{S}_i$ is the partial molar entropy of the component i in the solution. This result, though gives the variation of chemical potential with temperature, can be put in a more useful form [compare with Eq. (6.73)] as follows: Since

$$G = H - TS, \qquad \bar{G}_i = \bar{H}_i - T\bar{S}_i, \qquad \mu_i = \bar{H}_i - T\bar{S}_i$$

we can write

$$-\bar{S}_i = \frac{\mu_i - \bar{H}_i}{T} \tag{7.40}$$

We know that

$$\left[\frac{\partial(\mu_i/T)}{\partial T}\right]_{P,N} = \frac{T(\partial\mu_i/\partial T) - \mu_i}{T^2}$$

Substituting Eqs. (7.39) and (7.40) into the above equation, we get,

$$\left[\frac{\partial(\mu_i/T)}{\partial T}\right]_{P,N} = -\frac{\bar{H}_i}{T^2} \tag{7.41}$$

Equation (7.41) predicts the effect of temperature on chemical potential.

Effect of pressure. Equations (7.30) and (7.34) are further differentiated to develop equations that predict the effect of pressure on chemical potential. Differentiating Eq. (7.30) with respect to pressure, we obtain

$$\left[\frac{\partial \mu_i}{\partial P}\right]_{T,N} = \frac{\partial^2 G^t}{\partial P\, \partial n_i} \tag{7.42}$$

Differentiating Eq. (7.34) with respect to n_i,

$$\frac{\partial^2 G^t}{\partial n_i\, \partial P} = \left[\frac{\partial V^t}{\partial n_i}\right]_{P,T,n_{j \neq i}} = \bar{V}_i \tag{7.43}$$

Compare Eq. (7.42) with Eq. (7.43)

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \bar{V}_i \tag{7.44}$$

The rate of change of chemical potential with pressure is thus equal to the partial molar volume of the constituent.

***EXAMPLE* 7.8** Prove the alternative definition of chemical potential that $m_i = (\partial U/\partial n_i)_{S, V, nj}$.

Solution The internal energy of a system may be expressed as a function of thermodynamic state and moles of the components like the Gibb's free energy. For the present purpose, it is convenient to express it as

$$U^t = f(S^t, V^t, n_1, n_2, \ldots, n_i, \ldots)$$

which gives

$$dU^t = \left(\frac{\partial U^t}{\partial S^t}\right)_{V,N} dS^t + \left(\frac{\partial U^t}{\partial V^t}\right)_{S,N} dV^t + \Sigma \left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j \neq i}} dn_i \tag{7.45}$$

Since $dU = T\, dS - P\, dV$ for a closed system,

$$\left(\frac{\partial U^t}{\partial S^t}\right)_{V,N} = T; \quad \left(\frac{\partial U^t}{\partial V^t}\right)_{S,N} = -P \tag{7.46}$$

Combining these with Eq. (7.45)

$$dU^t = T\, dS^t - P\, dV^t + \Sigma \left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j \neq i}} dn_i \tag{7.47}$$

But, we know that

$$G = H - TS = U + PV - TS$$

so that

$$dG = dU + P\, dV + V\, dP - T\, dS - S\, dT$$

The change in the total free energy at constant temperature and pressure is therefore,

$$dG^t_{T,P} = dU^t + P\,dV^t - T\,dS^t \tag{7.48}$$

Combining Eqs. (7.47) and (7.48)

$$dG^t_{T,P} = \Sigma\left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i \tag{7.49}$$

Compare Eq. (7.49) with Eq. (7.36). We now have

$$\Sigma\,\mu_i\,dn_i = \Sigma\left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}} dn_i$$

Since dn_1, dn_2, etc., are independent of one another, it follows that

$$\boxed{\mu_i = \left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}}} \tag{7.50}$$

Equation (7.50) is an *alternative definition of chemical potential*. But it should be understood that $(\partial U^t/\partial n_i)_{S,V,nj\sqcap i}$ is not partial molar internal energy, for it refers to constant entropy and volume and not to constant temperature and pressure. Partial molar internal energy is not equal to chemical potential.

***EXAMPLE* 7.9** Show that for an ideal gas,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \frac{RT}{P}$$

Solution For a mixture of ideal gases,

$$V^t = (n_1 + n_2 + \ldots)\,\frac{RT}{P}$$

where n_1, n_2, etc., are the moles of various constituents. Differentiating this with respect to n_i, we get

$$\left(\frac{\partial V^t}{\partial n_i}\right)_{P,T,n_{j\neq i}} = \bar{V}_i = \frac{RT}{P_i}$$

By Eq. (7.44),

$$\left(\frac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i = \frac{RT}{P}$$

7.3 FUGACITY IN SOLUTIONS

The concept of fugacity was discussed in Chapter 6 with reference to pure substances. It was pointed out that *fugacity* is a useful concept in dealing with mixtures. For pure fluids, the definition of fugacity is provided by Eq. (6.118) and (6.122):

$$dG = RT\, d(\ln f)$$

$$\lim_{P \to 0} \frac{f}{P} = 1$$

The fugacity of a component i in a solution (gaseous, liquid or solid) is defined analogously by

$$d\mu_i = RT\, d(\ln \bar{f}_i) \tag{7.51}$$

$$\lim_{P \to 0} \frac{\bar{f}_i}{\bar{p}_i} = 1 \tag{7.52}$$

Here μ_i is the chemical potential, $\bar{f}_i$ the fugacity and $\bar{p}_i$ is the partial pressure of component i in the solution. For an ideal gas mixture, the fugacity of a component is equal to its partial pressure. All gaseous mixtures behave ideally on approaching zero pressure. The partial pressure is defined as product of total pressure and mole fraction of $i(y_i)$ in the mixture.

$$\bar{p}_i = y_i P \tag{7.53}$$

7.3.1 Fugacity in Gaseous Solutions

The fugacity of a component i in a gaseous solution is given by Eq. (7.51). Equation (7.44) gives the effect of pressure on chemical potential.

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \overline{V}_i$$

where $\overline{V}_i$ is the partial molar volume of the component in the solution. Rearranging this equation

$$d\mu_i = \overline{V}_i \, dP \tag{7.54}$$

Compare Eq. (7.54) with Eq. (7.51). We get

$$RT \, d(\ln \bar{f}_i) = \overline{V}_i \, dP \tag{7.55}$$

$$d(\ln \bar{f}_i) = \frac{\overline{V}_i}{RT} \, dP$$

Subtracting $d(\ln \bar{p}_i)$, where $\bar{p}_i$ is the partial pressure of component i in the gas mixture, from both sides,

$$d\left(\ln \frac{\bar{f}_i}{\bar{p}_i}\right) = \frac{1}{RT}\left[\overline{V}_i \, dP - RT \, d(\ln \bar{p}_i)\right] \tag{7.56}$$

Since $\bar{p}_i = y_i P$, where y_i is the mole fraction,

$$d(\ln \bar{p}_i) = d(\ln P) + d(\ln y_i)$$

At constant composition, $d(\ln y_i) = 0$, so that the above equation reduces to

$$d(\ln \bar{p}_i) = d(\ln P) = \frac{dP}{P}$$

Substituting this in Eq. (7.56) we obtain,

$$d\left(\ln \frac{\bar{f}_i}{\bar{p}_i}\right) = \frac{1}{RT}\left(\overline{V}_i - \frac{RT}{P}\right) dP$$

As $P \to 0$, $\bar{f}_i = \bar{p}_i$, and the above equation can be readily integrated to give

$$\left(\ln \frac{\bar{f}_i}{\bar{p}_i}\right) = \ln \bar{\phi}_i = \frac{1}{RT} \int_0^P \left(\overline{V}_i - \frac{RT}{P}\right) dP \tag{7.57}$$

where $\bar{\phi}_i$ denotes the *fugacity coefficient* of a component in solution.

$$\bar{\phi}_i = \frac{\bar{f}_i}{\bar{p}_i} = \frac{\bar{f}_i}{y_i P} \tag{7.58}$$

For a mixture of ideal gases, we have the following simple equation of state:

$PV^t = (n_1 + n_2 + n_3 + \ldots)\, RT$

$$\boxed{\bar{V}_i = \left(\frac{\partial V^t}{\partial n_i}\right)_{T,P,n_j} = \frac{RT}{P}}$$

Substituting this into Eq. (7.57), it follows that

$$\bar{f}_i = \bar{p}_i = y_i P \tag{7.59}$$

which states that the fugacity of a component in a mixture of ideal gases is equal to the partial pressure of that component in the mixture. However, this is not true for real gases. Equation (7.57) provides the means for computing fugacities in the real gaseous solution. But this requires the evaluation of $\bar{V}_i$ as a function of pressure, which in turn requires the knowledge of how the solution volume varies with composition at each pressure. These types of data are rarely available, and hence rigorous calculation of fugacities in gaseous mixtures using Eq. (7.57) is rarely done.

7.3.2 Lewis–Randall Rule

As the calculation of fugacity in a mixture of gases through the general equation [Eq. (7.57)] is very difficult, we devise a model for mixtures known as the *ideal solution model* the fugacity of which can be easily evaluated. The fugacity in actual solution is then determined by taking into account the deviation of the actual solution from this ideal model behaviour. As an ideal gaseous solution we can consider a gas mixture formed without any volume change on mixing the components. A gas mixture that follows the Amagat's law is an ideal gaseous solution. For such solutions, the volume of the mixture is a linear function of the mole numbers at a fixed temperature and pressure. That is,

$$V^t = \Sigma\, n_i V_i \qquad (7.60)$$

where V_i is the molar volume of pure i at the same temperature and pressure. For such ideal solutions,

$$\bar{V}_i = \left(\frac{\partial V^t}{\partial n_i}\right)_{T,P,n_j} = V_i \tag{7.61}$$

Note that the right-hand side of Eq. (7.57) reduces to the same result as that given by Eq. (6.128) where the residual volume for the pure component is given by $\alpha = V_i - RT/P$. That is, for pure components at a temperature T and pressure P,

$$\ln \frac{f_i}{P} = \frac{1}{RT} \int_0^P \left(V_i - \frac{RT}{P} \right) dP \tag{7.62}$$

and for component i in a gas mixture at the same temperature and pressure,

$$\ln \frac{\bar{f}_i}{\bar{p}_i} = \frac{1}{RT} \int_0^P \left(\bar{V}_i - \frac{RT}{P} \right) dP \tag{7.63}$$

Subtracting Eq. (7.62) from Eq. (7.63),

$$\ln \frac{\bar{f}_i P}{f_i \bar{p}_i} = \frac{1}{RT} \int_0^P (\bar{V}_i - V_i)\, dP \tag{7.64}$$

Since $\bar{p}_i = y_i P$, we can simplify the above equation to the following form:

$$\ln \frac{\bar{f}_i}{y_i f_i} = \frac{1}{RT} \int_0^P (\bar{V}_i - V_i)\, dP$$

On substitution of Eq. (7.61), in the preceding equation, we get,

$$\ln \frac{\bar{f}_i}{y_i f_i} = 0 \quad \text{or} \quad \bar{f}_i = y_i f_i \tag{7.65}$$

which is commonly known as *Lewis–Randall* rule or *Lewis fugacity rule*. It states that fugacity of a component in an ideal solution is directly proportional to the mole fraction of the component in the solution. In Eq. (7.65), $\bar{f}_i$ is the fugacity of the species i in an ideal gaseous solution, and f_i is the fugacity of pure i evaluated at the temperature and pressure of the mixture. Thus, we have now, $\bar{f}_i = y_i f_i$ for ideal gaseous solution and, $\bar{f}_i = \bar{p}_i = y_i P$ for ideal (perfect) gases.

For a gas mixture to behave as an ideal solution, it requires only that the molar volume in the pure state and the partial molar volume in the solution be the same, or $\bar{V}_i = V_i$. For the mixture to be an ideal gas it requires that $\bar{V}_i = V_i = RT/P$, which means that the molar volumes of all the components are the same whether in the mixture or in the pure state. For ideal solutions, the volumes of components may differ from one another. In short, the concept of an ideal gaseous solution is less restrictive than that of a mixture of ideal gases.

The Lewis–Randall rule is a simple equation and is therefore widely used for evaluating fugacities of components in gas mixtures. It allows the fugacity of a component in the mixture to be calculated without any information about the solution except its composition. However, it is not reliable because of the severe simplification inherent in Amagat's law of additive volumes. But at high pressures it is often a very good assumption, because, at liquid like densities, fluids tend to mix with little or no change in volume (J.M. Prausnitz et al., 1986). Lewis fugacity rule is valid for systems where the intermolecular forces in the mixture are similar to those in the pure state. Thus, it can be said that this rule is valid

1. At low pressures when the gas phase behaves ideally
2. At any pressure if the component is present in excess
3. If the physical properties of the components are nearly the same
4. At moderate and high pressures, the Lewis–Randall rule will give incorrect results if the molecular properties of the components are widely different and the component under consideration is not present in excess.

7.3.3 Fugacities in Liquid Solutions

Calculation of fugacity of a component in a liquid solution using Eq. (7.57) is not practical because the volumetric data at constant temperature and composition are rarely available. These data are required for the integration over the entire range of pressures from the ideal gas state to the pressure of the solution including the two-phase region. For calculation of fugacities in liquid solutions, another approach is used. We define an ideal solution whose fugacity can be easily calculated knowing its composition and measure the departure from ideal behaviour for the real solution. A quantitative measure of the deviation from ideality is provided by the function known as the *activity coefficient* which will be discussed in Section 7.6.

7.3.4 Ideal Solutions and Raoult's Law

A solution in which the partial molar volumes of the components are the same as their molar volumes in the pure state is called an *ideal solution*. There is no volume change when the components are mixed together to form an ideal solution. That is, for an ideal solution $V = \Sigma\, x_i \bar{V}_i = \Sigma\, x_i V_i$, where V is the molar volume of the solution, V_i and $\bar{V}_i$ are the molar volume and partial molar volume respectively of the component *i,* and x_i is the mole fraction of component *i* in the solution. If a mixture of two liquids is to behave ideally, theoretical considerations reveal that the two types of molecules must be similar. The environment of any molecule and hence the force acting on it is then not appreciably different from that existing in the pure state. We have shown that for ideal gaseous solutions, the Lewis–Randall rule is applicable which states that fugacity of each constituent is directly proportional to the number of moles of the constituent in the solution. The Lewis–Randall rule is applicable to ideal liquid solutions also. It can be written as

$$\bar{f}_i = x_i f_i \qquad (7.66)$$

where $\bar{f}_i$ is the fugacity of component *i* in the solution, f_i is the fugacity of *i* in the pure state, and x_i is the mole fraction of component *i* in the solution.

While the ideal solution model is adequate for many gas mixtures for reasonable temperature and pressure, the same is not true for the case of liquid solutions. Very few solutions follow Eq. (7.66) over the entire composition range. Ideal liquid solution behaviour is often approximated by solutions comprised of molecules not too different in size and chemical nature. Thus a mixture of isomers (e.g. *ortho*-, *meta*- and *para*-xylene), adjacent members of homologous series of organic compounds (e.g. *n*-hexane and *n*-heptane, ethanol and propanol, benzene and toluene, ethyl bromide and ethyl iodide) etc., are expected to form ideal solutions.

Raoult's Law. The criterion of phase equilibria permit us to replace the liquid phase fugacities $\bar{f}_i$

and f_i with fugacities in the gas phase with which the liquid is in equilibrium. Thus, $\bar{f}_i^L = \bar{f}_i^V$ under equilibrium. Here superscripts V and L refer to the vapour phase and the liquid phase respectively. Thus, fugacity $\bar{f}_i$ in Eq. (7.66) is equal to the fugacity of constituent i in the vapour phase. If the vapour phase is assumed to be ideal gas, which is true if the pressure is not too high, the vapour phase fugacity $\bar{f}_i^V$ is the same as partial pressure $\bar{p}_i$ of component i in the vapour. If the liquid phase is pure i, the fugacity of pure i in the vapour phase can be replaced with the vapour pressure P_i^S. Under these conditions the Lewis–Randall rule, Eq. (7.66), becomes

$$\bar{p}_i = x_i P_i^S \tag{7.67}$$

This expression is known as Raoult's Law. This is a simplified form of the Lewis–Randall rule Whereas the Lewis–Randall rule is obeyed by all ideal solutions, the Raoult's law is applicable to ideal solutions if the vapour phase with which it is in equilibrium is an ideal gas.

Raoult's law provides a very simple expression for calculating the fugacity of a component in the liquid mixture which is the same as the partial pressure of the component in the vapour. It says that the partial pressure is directly proportional to the mole fraction in the liquid solution. Ideal solutions which conform to Raoult's law over the entire range of concentrations are rare. A frequently cited example for ideal solutions is mixtures of optical isomers of organic compounds. Raoult's law applies as fair approximation to mixtures of hydrocarbons showing a reasonable similarity in molecular structure such as are encountered in petroleum industry. In most other cases Raoult's law applies only over a limited concentration range.

7.4 HENRY'S LAW AND DILUTE SOLUTIONS

Solutions conforming to Raoult's law over the entire concentration range are rare as pointed out earlier. A solution, any of whose components does not obey Raoult's law is designated as *non-ideal solution*. Even non-ideal solutions exhibit a common form of ideal behaviour over a limited concentration range where the fugacity $\bar{f}_i$ (or, the partial pressure $\bar{p}_i$) is directly proportional to the concentration in the liquid. This behaviour is exhibited by the constituent as its mole fraction approaches zero, and is generalised by *Henry's law*.

$$\bar{f}_i = x_i K_i \tag{7.68}$$

$$\bar{p}_i = x_i K_i \tag{7.69}$$

Often, the solute portion of the non-ideal liquid solution can be assumed to follow Henry's law. $\bar{p}_i$ is the partial pressure of the solute over the solution, x_i is its mole fraction in the solution and K_i is a proportionality constant known as Henry's law constant. K_i may be greater or less than P_i^S, the vapour pressure of the solute at the temperature and total pressure in question. When K_i and P_i^S are equal, Henry's law and Raoult's law are identical. Henry's law may be thought of as a general rule of which Raoult's law is a special case. Henry's law is obeyed in all solutions by the solute at extremely low concentrations. Essentially all liquids will obey Henry's law close to mole fraction zero, but many will deviate from the law above 0.01–0.02 mole fraction. And almost all liquids deviate above 0.1 mole fraction. But in some exceptional cases, Henry's law is found to be obeyed quite well up to $x_i = 0.5$.

For ideal solutions, the partial fugacity (or partial pressure) of a component is proportional to its mole fraction. For a real solution it has been found experimentally that as the mole fraction of the component approaches unity, its fugacity approximates to the value for an ideal solution, though at lower mole fractions, the behaviour departs markedly from ideal behaviour.

In Fig. 7.4, the fugacity curve becomes asymptotic to the straight line showing ideal behaviour as mole fraction approaches unity. In a dilute solution, the component present in larger proportions designated as solvent, obeys Raoult's law even though it may depart from ideal solution behaviour in a more concentrated solution. As the mole fraction of the solute—the component present in smaller proportions—approaches zero, it will conform to the ideal behaviour predicted by Henry's law. Thus, we can generalise by saying that *the solute in a dilute solution obeys Henry's law and the solvent obeys Raoult's law*. It can be shown that over the range of compositions where the solvent obeys Raoult's law, the solute obeys Henry's law (see Example 7.15).

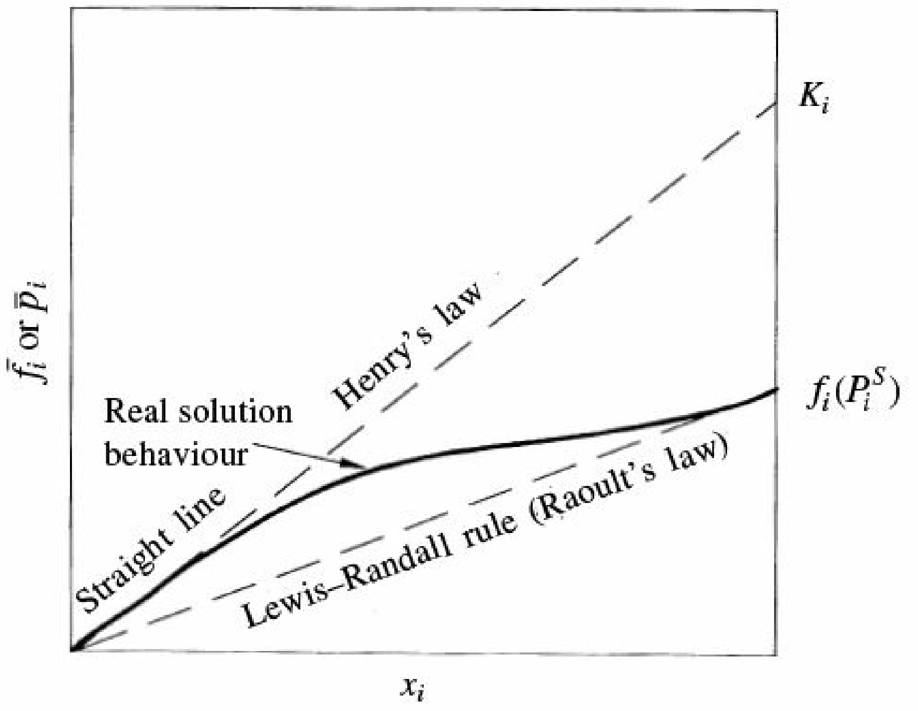


Fig. 7.4 Fugacity (partial pressure) versus concentration of real solutions.

7.4.1 Ideal Behaviour of Real Solutions

The ideal behaviour exhibited by non-ideal solutions can be summarised by the following mathematical statements.

$$\lim_{x_i \to 1} \frac{\bar{f}_i}{x_i} = f_i \qquad \text{[Lewis–Randall rule]} \tag{7.70}$$

$$\lim_{x_i \to 0} \frac{\bar{f}_i}{x_i} = K_i \qquad \text{[Henry's law]} \tag{7.71}$$

7.4.2 Henry's Law and Gas Solubility

Since the solubility of the gases in liquids is usually very low, the mole fraction of a gas in a saturated liquid solution is very small. The solute gas obeys Henry's law and therefore its fugacity (or the partial pressure) would be directly proportional to its mole fraction, the proportionality constant being the Henry's law constant [Eq. (7.69)]. In other words, the mole fraction or the solubility of the gas in the liquid is proportional to the partial pressure of the gas over the liquid as given by

$$x_i = \frac{\bar{p}_i}{K_i} \tag{7.72}$$

where K_i is the Henry's law constant.

***EXAMPLE* 7.10** The Henry's law constant for oxygen in water at 298 K is $4.4 \square 10^4$ bar. Estimate the solubility of oxygen in water at 298 K for a partial pressure of oxygen at 0.25 bar.

Solution Equation (7.72) gives the solubility of a gas in liquid in terms of its mole fraction. Substituting the values $K_i = 4.4 \square 10^4$ bar, and $\bar{p}_i = 0.25$ bar in Eq. (7.72) we get $x_i = 0.0568 \square 10^{-4}$. For very dilute solutions, we can write

$$x_{\mathrm{O}_2} = \frac{\text{Moles of oxygen}}{\text{Moles of oxygen + moles of water}} \approx \frac{\text{Moles of oxygen}}{\text{Moles of water}}$$

Therefore, the solubility of oxygen is $0.0568 \square 10^{-4}$ moles per mole of water. In mass units, it can be written as

$$0.0568 \square 10^{-4} \square 32 \square 1/18 = 0.101 \square 10^{-4} \text{ kg oxygen per kg water}$$

***EXAMPLE* 7.11** The partial pressure of acetone (*A*) and chloroform (*B*) were measured at 298 K and are reported below:

x_B	0	0.2	0.4	0.6	0.8	1.0
, bar	0.457	0.355	0.243	0.134	0.049	0
, bar	0	0.046	0.108	0.187	0.288	0.386

(a) Confirm that the mixture conforms to Raoult's law for the component present in excess and Henry's law for the minor component.

(b) Determine the Henry's law constants.

Solution The partial pressures are plotted against mole fraction x_A as shown in Fig. 7.5.

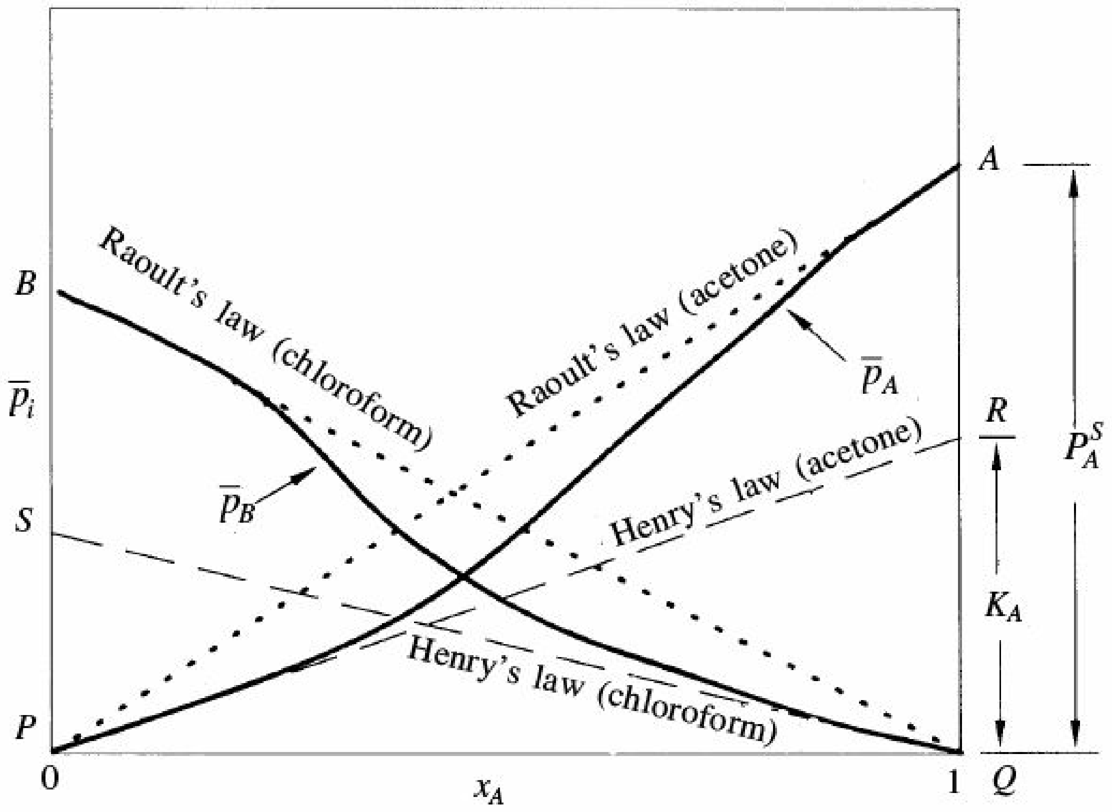


Fig. 7.5 Partial pressure versus mole fraction data for Example 7.11.

From the data given, it can be seen that P_A^S = 0.457 and P_B^S = 0.386 bar. The dotted line representing the ideal behaviour (Raoult's law) of component *A* is drawn by joining the origin and (x = 1, p = 0.457) by a straight line. Raoult's law for component *B* is also drawn. The dotted lines *PA* and *QB* represent the ideal behaviour. The Henry's law line *PR* is drawn tangential to the curve $\bar{p}_A$ versus x_A as x_A tends to 0 and the line *QS* is drawn tangential to the $\bar{p}_B$ versus x_A curve as x_A tends to 1.

(a) We see that the partial pressure curve for component *A* coincides with the Raoult's law line in the region where mole fraction of component *A* approaches unity and in this region, the partial pressure of component *B* coincides with the Henry's law line. Thus, in the region where Raoult's law is obeyed by *A*, Henry's law is obeyed by *B,* and vice versa.

(b) The slopes of the Henry's law line *PR* gives K_A, the Henry's law constant for *A*. K_A = 0.23 bar. Similarly slope of *QS* is K_B. K_B = 0.217 bar.

7.5 ACTIVITY IN SOLUTIONS

The activity with reference to pure substance was defined [see Eq. (6.145)] and the concept was discussed in Chapter 6. The *activity* of a component in a solution can be defined in a similar way. It is the ratio of fugacity of a component in the solution in a given condition to the fugacity of that component in the standard state. It is denoted by a_i.

$$a_i = \frac{\bar{f}_i}{f_i^0} \tag{7.73}$$

Since the fugacities are related to the chemical potential as

$$\mu_i = RT \ln \bar{f}_i + C, \qquad \mu_i^0 = RT \ln f_i^0 + C$$

it follows that

$$\Delta\mu_i = RT \ln \frac{\bar{f}_i}{f_i^0} = RT \ln a_i \tag{7.74}$$

$\Delta\mu_i = \mu_i - \mu_i^0$ is the increase in the chemical potential of species *i* when it is brought into solution from its standard state.

The concept of activity plays an important role in solution thermodynamics because activity can be related to compositions directly. For example, let the standard state for a substance be the pure component at the temperature and pressure of the solution. Then the activity of that component becomes equal to its mole fraction in the case of ideal solutions and is a strong function of mole fraction in the case of real solutions.

$$a_i = \frac{\bar{f}_i}{f_i^0} = \frac{\bar{f}_i}{f_i}$$

For ideal solutions as $\bar{f}_i = x_i f_i$, the activity $a_i = x_i$. For real solutions, the activity can be shown to be equal to the product of activity coefficient and mole fraction. The activity coefficient is discussed later in this chapter.

The term activity is a ratio without dimensions. It is a widely used function in solution thermodynamics, particularly in dealing with property changes of mixing. The relationship between property change of mixing and activity is discussed later in this chapter.

7.5.1 Selection of Standard States

The numerical values of activity depend upon the choice of the standard state, this choice being based largely on experimental convenience and reproducibility. For all such standard states, the temperature is the same as the temperature of the solution under study and it is not a fixed value. Following are the commonly accepted standard states:

Gases. Two standard states are common:

1. The pure component gas in its ideal state at 1 bar. At this state, the fugacity is unity if expressed in bar. The activity becomes

   $$a_i = \frac{\bar{f}_i}{f_i^0} = \frac{\bar{f}_i}{1} = \bar{f}_i$$

   That is, the activity of a component in a mixture of gases is equal to its fugacity, numerically. If the mixture behaves as an ideal gas at the given conditions the activity and partial pressure are the same. This standard state is used in the study of chemical reaction equilibrium.
2. The pure component gas at the pressure of the system. With this choice the activity of each component in ideal gas solution becomes equal to its mole fraction.

   $$a_i = \frac{\bar{f}_i}{f_i^0} = \frac{\bar{f}_i}{f_i} = \frac{x_i f_i}{f_i} = x_i$$

This standard state becomes hypothetical at temperatures where the total pressure exceeds the saturation pressure of the component gas in the pure state. Vapour–liquid equilibrium studies conventionally use this standard state.

Liquids. Two standard states are common for liquids also.

1. The pure component liquid at a pressure of 1 bar. This state is hypothetical if the vapour pressure of the pure liquid exceeds 1 bar.
2. The pure liquid at the pressure of the system. This state becomes hypothetical at temperatures above the critical or saturation temperature of the pure liquid. This standard state is used in vapour–liquid equilibrium studies.

Solids. The standard state chosen for solid is usually the pure component in the solid state at a pressure of 1 bar.

7.6 ACTIVITY COEFFICIENTS

We have already seen that the concept of ideal solution enables us to calculate the fugacity of a component in the liquid solution from the knowledge of its concentration in the solution and its fugacity in the pure state. The calculation of fugacity of a component in a real solution should take into account the degree of departure from ideal behaviour. *Activity coefficients* measure the extent to which the real solution departs from ideality. Activity coefficient of the component *i* in solution is denoted by g_i and is defined by the following relationship.

$$\bar{f}_i = \gamma_i x_i f_i^0 \tag{7.75}$$

where f_i^0 is the fugacity in the standard state. For ideal solutions $g_i = 1$, and we have

$$\bar{f}_i = x_i f_i^0 \tag{7.76}$$

which is same as the Lewis–Randall rule [Eq. (7.66)] with the pure liquid at the system pressure as the standard state.

Two types of ideal behaviour are observed; the first conforms to Lewis–Randall rule (or Raoult's law) in which case $f_i^0 = f_i$, the fugacity of the pure species at the system pressure and the second type conforms to an ideal dilute solution behaviour (the Henry's law), in which case $f_i^0 = K_i$, the Henry's law constant. Depending upon the standard states on which they are based, the activity coefficients can take different numerical values. For the standard state in the sense of Lewis–Randall rule or Raoult's law,

$$\bar{f}_i = \gamma_i x_i f_i \tag{7.77}$$

$$\gamma_i = \frac{\bar{f}_i}{x_i f_i} = \frac{a_i}{x_i} \tag{7.78}$$

$$a_i = \gamma_i x_i \tag{7.79}$$

where a_i is the activity of *i* in the solution. Equation (7.77) is, in fact, Lewis fugacity rule modified by the factor g_i to correct for deviation from ideality. This equation should reduce to Raoult's law as x approaches unity and to Henry's law as x approaches zero. For this to be possible, g must equal unity as mole fraction approaches unity (Raoult's law region) and K_i/f_i, as mole fraction, approaches zero (Henry's law region). In terms of partial pressures, Eq. (7.77) may well be written as

$$\bar{p}_i = \gamma_i x_i P_i^S \tag{7.80}$$

If the hypothetical state, where the pure component fugacity = Henry's law constant, is chosen as the standard state, we get,

$$\bar{f}_i = \gamma'_i x_i K_i \tag{7.81}$$

$$\bar{p}_i = \gamma'_i x_i K_i \tag{7.82}$$

Then the activity coefficient approaches unity as x approaches zero. In Eqs. (7.81) and (7.82), γ'_i is the activity coefficient referred to infinite dilution.

When activity coefficients are defined with reference to an ideal solution in the sense of Raoult's law, then for each component *i,*

g_i □ 1 as x_i □ 1

On the other hand, if activity coefficients are defined with reference to an ideal dilute solution, then

g_1 □ 1 as x_1 □ 1 (solvent)

γ'_2 □ 1 as x_2 □ 0 (solute)

Activity coefficients with reference to ideal dilute solution would be useful when dealing with liquid mixtures that cannot exist over the entire composition range as happens, for example, in a liquid mixture containing gaseous solute. If the critical temperature of the solute is lower than the temperature of the mixture, then a liquid phase cannot exist as x_2 □ 1, and the relations based on an ideal mixture in the sense of Raoult's law can be used only by introducing a hypothetical standard state for component 2. However, relations based on an ideal dilute solution eliminate this difficulty.

Activity coefficients are very strong functions of concentration of solution. The variation of g with x over the entire range of composition is usually complex, but can often be roughly approximated in binary solutions by the empirical equations such as the one proposed by Porter:

$$\ln \gamma_1 = bx_2^2, \quad \ln \gamma_2 = bx_1^2$$

where b is an empirical constant. These relationships apply best when the components are not too dissimilar in structure and polarity.

7.6.1 Effect of Pressure on Activity Coefficients

The effect of pressure on fugacity was derived in Chapter 6 [Eq. (6.126)].

$$\left(\frac{\partial \ln f_i}{\partial P}\right)_T = \frac{V_i}{RT}$$

Here f_i is the fugacity of pure i and V_i is its molar volume. In a similar way it can be shown that, $\bar{f}_i$, the fugacity of i in solution varies with pressure according to

$$\left(\frac{\partial \ln \bar{f}_i}{\partial P}\right)_T = \frac{\bar{V}_i}{RT} \tag{7.83}$$

Combining Eq. (6.126) with Eq. (7.83), we get

$$\left(\frac{\partial \ln \bar{f}_i/f_i}{\partial P}\right)_T = \frac{\bar{V}_i - V_i}{RT} \tag{7.84}$$

According to Eq. (7.77) $\bar{f}_i/f_i = \gamma_i x_i$, so that Eq. (7.84) can be written as

$$\left(\frac{\partial \ln \gamma_i x_i}{\partial P}\right)_T = \frac{\bar{V}_i - V_i}{RT} \tag{7.85}$$

As the mole fraction x_i is independent of pressure $(\partial \ln x_i/\partial P) = 0$, and hence

$$\left(\frac{\partial \ln \gamma_i}{\partial P}\right)_T = \frac{\bar{V}_i - V_i}{RT} \tag{7.86}$$

The molar volumes $\bar{V}_i$ and V_i correspond to the particular phase under consideration. For liquid solutions, the effect of pressure on activity coefficients is negligible at pressures below atmospheric. For gaseous mixtures, activity coefficients are nearly unity at reduced pressures below 0.8.

7.6.2 Effect of Temperature on Activity Coefficients

The effect of temperature on fugacity of a pure substance was given by Eq. (6.125) as

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_P = \frac{H_i^0 - H_i}{RT^2}$$

Similarly, for the substance in the solution

$$\left(\frac{\partial \ln \bar{f}_i}{\partial T}\right)_P = \frac{H_i^0 - \bar{H}_i}{RT^2} \tag{7.87}$$

Combining the above two equations, and noting that $\bar{f}_i/f_i = \gamma_i x_i$, where x_i is independent of temperature,

$$\left(\frac{\partial \ln \gamma_i}{\partial T}\right)_P = \frac{H_i - \bar{H}_i}{RT^2} \tag{7.88}$$

Equation (7.88) gives the effect of temperature on activity coefficients. The term ($\bar{H}_i$ – H_i) is the partial heat of mixing of component *i* from its pure state to the solution of given composition both in the same state of aggregation and pressure. For gaseous mixtures, this term is negligible at low pressures.

***EXAMPLE* 7.12** The partial pressures of acetone (*A*) and chloroform (*B*) were measured at 298 K and are reported below:

x_A	0	0.2	0.4	0.6	0.8	1.0
, bar	0	0.049	0.134	0.243	0.355	0.457
, bar	0.386	0.288	0.187	0.108	0.046	0

Calculate the activity and activity coefficient of chloroform in acetone at 298 K,

(a) Based on the standard state as per Lewis–Randall rule

(b) Based on Henry's law.

Solution The Henry's law constant was determined in Example 7.11. K_B = 0.217 bar. The vapour pressure of pure chloroform, P_B^S = 0.386 bar. The activity was defined by Eq. (7.73) and activity coefficient by Eq. (7.75). Combining these two we get,

$$a_i = g_i x_i$$

Based on the Lewis–Randall rule, the activity,

$$a_i = \frac{\bar{p}_i}{P_i^S} \tag{7.89}$$

Based on the Henry's law, the activity,

$$a_i' = \frac{\bar{p}_i}{K_i} \tag{7.90}$$

The activity coefficient based on the Lewis–Randall rule is

$$\gamma_i = \frac{\bar{f}_i}{f_i^0 x_i} = \frac{a_i}{x_i} \tag{7.91}$$

The activity coefficient based on the Henry's law is

$$\gamma_i' = \frac{\bar{f}_i}{K_i x_i} = \frac{a_i'}{x_i} \tag{7.92}$$

The above equations are used to calculate the activity and activity coefficients for different concentrations. A sample calculation is provided below for the second set where

$x_A = 0.2$, $x_B = 0.8$, $\bar{p}_A = 0.049$ bar, $\bar{p}_B = 0.288$ bar, $K_B = 0.217$ bar, $P_B^S = 0.386$ bar

(a) For the standard state referred to the Lewis–Randall rule:

$$a_B = \frac{\bar{p}_B}{P_B^S} = \frac{0.288}{0.386} = 0.75$$

$$\gamma_B = \frac{a_B}{x_B} = \frac{0.75}{0.8} = 0.94$$

(b) For the standard state referred to the Henry's law:

$$a_B' = \frac{\bar{p}_B}{K_B} = \frac{0.288}{0.217} = 1.33$$

$$\gamma_B' = \frac{a_B'}{x_B} = \frac{1.33}{0.8} = 1.66$$

The above calculations are repeated for other concentrations and the results are given below:

x_B	0	0.2	0.4	0.6	0.8	1.0
a	0	0.12	0.28	0.48	0.75	1.0
a□	0	0.21	0.50	0.86	1.33	1.78
g		0.60	0.70	0.80	0.94	1.0
g□	1.0	1.05	1.25	1.43	1.66	1.78

***EXAMPLE* 7.13** The fugacity of component 1 in binary liquid mixture of components 1 and 2 at 298 K and 20 bar is given by

$$\bar{f}_1 = 50\,x_1 - 80\,x_1^2 + 40\,x_1^3$$

where $\bar{f}_1$ is in bar and x_1 is the mole fraction of component 1. Determine:

(a) The fugacity f_1 of pure component 1

(b) The fugacity coefficient f_1

(c) The Henry's law constant K_1

(d) The activity coefficient g_1.

Solution (a) When the mole fraction approaches unity, the fugacity of a component in the solution becomes equal to the fugacity of the pure component. That is,

$f_1 = \bar{f}_1$ when $x_1 = 1$. Therefore, $f_1 = 50 - 80 + 40 = 10$ bar

(b)

$$\phi_1 = f_1/P = 10/20 = 0.5$$

(c) By Eq. (7.71), the Henry's law constant is

$$K_1 = \lim_{x_1 \to 0} \frac{\bar{f}_1}{x_1} = \lim_{x_1 \to 0} (50 - 80\, x_1 + 40\, x_1^2) = 50 \text{ bar}$$

(d)

$$\gamma_1 = \frac{\bar{f}_1}{x_1 f_1} = \frac{50\, x_1 - 80\, x_1^2 + 40\, x_1^3}{10\, x_1} = 5 - 8\, x_1 + 4\, x_1^2$$

7.7 GIBBS–DUHEM EQUATIONS

In a mixture, the partial molar properties of the components are related to one another by one of the most useful equations in thermodynamics, the Gibbs–Duhem equations. It tells us how the partial molar properties change with compositions at constant temperature and pressure.

We have seen that at constant temperature and pressure, the property M^t of the solution is the sum of the partial molar properties of the constituents, each weighted according to the number of moles of the respective constituents.

$$M^t = \Sigma n_i \overline{M}_i \tag{7.12}$$

The total derivative dM^t gives the change in the property of the solution at constant T and P.

$$dM^t = \Sigma n_i \, d\overline{M}_i + \Sigma \overline{M}_i \, dn_i \tag{7.93}$$

where M is the molar value of the property of the solution M^t. But, since $M^t = f(T, P, n_1, n_2, \ldots)$, at constant T and P we have Eq. (7.13), which gives

$$dM^t = \Sigma \overline{M}_i \, dn_i \tag{7.13}$$

Comparing Eq. (7.93) with Eq. (7.13) we get the important result,

$$\Sigma n_i \, d\overline{M}_i = 0 \tag{7.94}$$

This result is the general form of the *Gibbs–Duhem equation*. If the property under consideration is the Gibbs free energy of the solution, then the above equation becomes

$$\Sigma n_i \, d\mu_i = 0 \tag{7.95}$$

Dividing throughout by n, the total number of moles in the solution, we get

$$\Sigma x_i \, d\mu_i = 0 \tag{7.96}$$

Here x_i is the mole fraction of component i in the solution and μ_i is the chemical potential of the component.

Other forms of Gibbs–Duhem equation. Consider a binary solution made up of components 1 and 2 whose mole fractions in the solution are x_1 and x_2 respectively. Equation (7.96) can be written as

$$x_1 \, d\mu_1 + x_2 \, d\mu_2 = 0 \tag{7.97}$$

where μ_1 and μ_2 are the chemical potentials of components 1 and 2 respectively. This can be rearranged as

$$x_1 \, d\mu_1 = -x_2 \, d\mu_2$$

Dividing by dx_1 and noting that $dx_1 = -dx_2$ in binary mixtures, the above result gives

$$\boxed{x_1 \frac{\partial \mu_1}{\partial x_1} = x_2 \frac{\partial \mu_2}{\partial x_2}} \tag{7.98}$$

Introducing the relationship between chemical potential and the fugacity [Eq. (7.51)] into the above, we get

$$\boxed{x_1 \frac{\partial \ln \bar{f}_1}{\partial x_1} = x_2 \frac{\partial \ln \bar{f}_2}{\partial x_2}} \tag{7.99}$$

Since activity $a_i = \bar{f}_i / f_i^0$, fugacities in Eq. (7.99) may be replaced in terms of activity as

$$x_1 \frac{\partial \ln (a_1 f_1^0)}{\partial x_1} = x_2 \frac{\partial \ln (a_2 f_2^0)}{\partial x_2}$$

Since f_i^0, the fugacity in the standard state, is independent of the composition of the solution,

$$\frac{\partial \ln (f_i^0)}{\partial x_i} = 0$$

Thus the Gibbs–Duhem equation in terms of activity is

$$\boxed{x_1 \frac{\partial \ln a_1}{\partial x_1} = x_2 \frac{\partial \ln a_2}{\partial x_2}} \tag{7.100}$$

By Eq. (7.79), $a_i = \gamma_i x_i$. Substitute this into Eq. (7.100) and thus the most important and widely used form of the Gibbs–Duhem equation, that involving the activity coefficients, is obtained.

$$x_1 \frac{\partial \ln \gamma_1 x_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2 x_2}{\partial x_2}$$

$$x_1 \frac{\partial \ln \gamma_1}{\partial x_1} + x_1 \frac{\partial \ln x_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2} + x_2 \frac{\partial \ln x_2}{\partial x_2}$$

The second terms on both sides of the above equation vanish, as they are equal to unity. Therefore,

$$\boxed{x_1 \frac{\partial \ln \gamma_1}{\partial x_1} = x_2 \frac{\partial \ln \gamma_2}{\partial x_2}} \tag{7.101}$$

As the activity coefficients directly measure the departure from the ideal solution behaviour, Eq. (7.101) is the most useful form of the *Gibbs–Duhem equation*.

The various forms of Gibbs–Duhem equations are rigorous thermodynamic relations that are valid fo conditions of constant temperature and pressure. They tell us that the partial molar proper-ties of a mixture cannot change independently; in a binary mixture, if the partial molar property of one of the component increases, the partial molar properties of the other should decrease.

Gibbs–Duhem equations find wide applications in solution thermodynamics. These include:

(a) In the absence of complete experimental data on the properties of the solution, Gibbs–Duhe equations may be used to calculate additional properties. For example, if experimental data are available for the activity coefficient of one of the components in a binary solution over certain concentration range, the activity coefficient of the other component over the same composition range can be estimated using Gibbs–Duhem equations. This is particularly useful wherever the volatilities of the two components differ markedly. The measurements usually give the activity coefficient of the more volatile component whereas that of the less volatile component is calculated using Eq. (7.101). Thermodynamic properties of some high-boiling liquids (e.g. polymers) dissolved in a volatile liquid (say, benzene) can be computed by measuring the partial pressure of the latter in the solution.

(b) Thermodynamic consistency of experimental data can be tested using Gibbs–Duhem equations. If the data on the partial molar property of each component measured directly in experiments satisfy the Gibbs–Duhem equation, it is likely that they are reliable, but if they do not satisfy the Gibbs–Duhem equation, it is certain that they are incorrect.

(c) Gibbs–Duhem equations can be used for the calculation of partial pressure from isothermal total pressure data. Suppose that in an experimental investigation of vapour–liquid equilibrium, the total pressures are measured as a function of composition of one of the phases (usually the liquid phase) and the composition of the other phase is not measured. The Gibbs–Duhem equation facilitates the calculation of the composition of other phase thereby reducing the experimental work considerably.

(d) Partial pressure data can be obtained from isobaric boiling point data using Gibbs–Duhem equations. The isobaric *T*-*x* data can be easily converted to *x*-*y* data.

In the sections that follow the application of Gibbs-Duhem equation is illustrated in the derivation of the relationship between Henry's law and Raoult's law for a real solution (see Example 7.15), in proving the essential criterion that the vapour and liquid compositions are the same for an azeotropic mixture (see Example 8.11) etc.

***EXAMPLE* 7.14** Show that in a binary solution, if the molar volume of one of the components increases with concentration, the molar volume of the other must decrease.

Solution When Eq. (7.94) is written for one mole of the solution with *M* replaced by *V*, we get

$$\Sigma x_i \, d\overline{V}_i = 0$$

For a binary solution,

$$x_1 \, d\overline{V}_1 + x_2 \, d\overline{V}_2 = 0$$

This is rearranged as

$$d\overline{V}_1 = -\frac{x_2}{x_1} \, d\overline{V}_2$$

It means that if $d\overline{V}_1$ is positive, $d\overline{V}_2$ must be negative. That is, if partial molar volume of component 1 increases the partial molar volume of component 2 must decrease.

***EXAMPLE* 7.15** Prove that if Henry's law is obeyed by component 1 in a binary solution over certain concentration range, Lewis–Randall rule (Raoult's law) will be obeyed by component 2 over the same concentration range.

Solution Equation (7.99) gives Gibbs–Duhem equations in terms of fugacities

$$x_1 \frac{\partial \ln \bar{f}_1}{\partial x_1} = x_2 \frac{\partial \ln \bar{f}_2}{\partial x_2}$$

Since $dx_2 = -dx_1$, Eq. (7.99) becomes

$$x_1 \, \partial \ln \bar{f}_1 = -x_2 \, \partial \ln \bar{f}_2$$

$$d \ln \bar{f}_2 = -\frac{x_1}{x_2} \, d \ln \bar{f}_1 \tag{7.102}$$

If component 1 obeys Henry's law, we can write $\bar{f}_1 = K_1 x_1$ and hence Eq. (7.102) gives

$$d \ln \bar{f}_2 = -\frac{x_1}{x_2} \, d \ln (K_1 x_1) = -\frac{x_1}{x_2} \frac{K_1 \, dx_1}{K_1 \, x_1} = -\frac{dx_1}{x_2} = \frac{dx_2}{x_2} = d \ln x_2$$

Integrating this equation, we get

$$\ln \bar{f}_2 = \ln x_2 + C \tag{7.103}$$

where C is a constant of integration.

Since $\bar{f}_2 = f_2$ when $x_2 = 1$, $C = \ln f_2$ and Eq. (7.103) becomes

$$\ln \frac{\bar{f}_2}{f_2} = \ln x_2$$

or

$$\bar{f}_2 = x_2 f_2$$

which is the Lewis–Randall rule for component 2.

In Fig. 7.6, Henry's law applies to component 1 in a binary system over the range 0 to x_1'. Lewis–Randall rule will be applicable to component 2 over the same composition range.

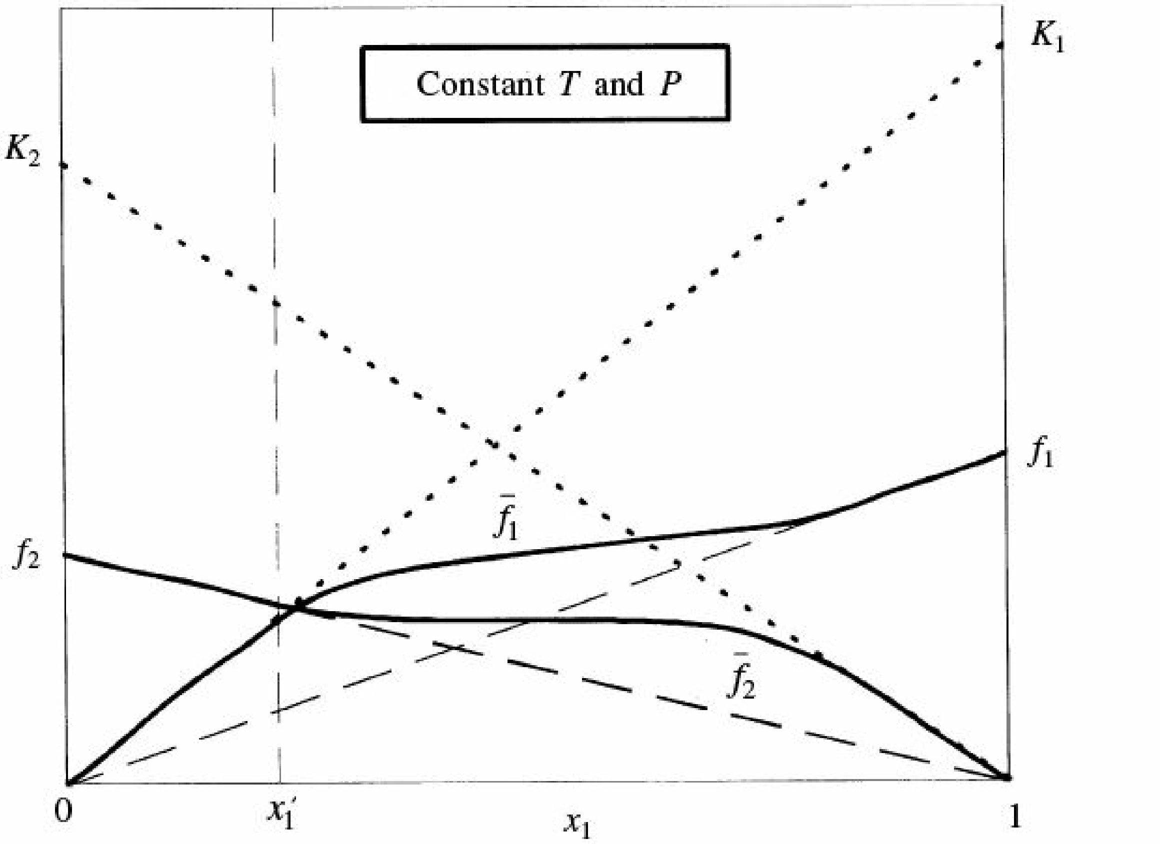


Fig. 7.6 Plot of fugacity versus mole fraction for Example 7.15.

***EXAMPLE* 7.16** The activity coefficient of component 1 in a binary solution is given by

$$\ln \gamma_1 = ax_2^2 + bx_2^3 + cx_2^4$$

where *a, b, c* are constants independent of concentrations. Obtain an expression for g_2 in terms of x_1.

Solution Using the Gibbs–Duhem equation [Eq. (7.101)], we get

$$x_2 \frac{\partial \ln \gamma_2}{\partial x_2} = -x_1 \frac{\partial \ln \gamma_1}{\partial x_2} = -x_1 (2ax_2 + 3bx_2^2 + 4cx_2^3)$$

which may be rewritten as

$$\frac{\partial \ln \gamma_2}{\partial x_2} = -x_1 (2a + 3bx_2 + 4cx_2^2)$$

Replacing x_2 in the preceding equation by $(1 - x_1)$, we get

$$\frac{\partial \ln \gamma_2}{\partial x_1} = -x_1 (2a + 3b + 4c) + x_1^2 (-3b - 8c) + x_1^3(4c)$$

Integrating the above equation,

$$\ln \gamma_2 = \int [x_1(2a + 3b + 4c) + x_1^2 (-3b - 8c) + x_1^3 (4c)]\, dx_1 + C'$$

where $C□$ is a constant of integration. Integrating and using the boundary condition that when $x_2 = 1$ (or $x_1 = 0$), $\gamma_2 = 1$ we get $C□ = 0$. Therefore, we get the required expression:

$$\ln \gamma_2 = [a + (3/2)\, b + 2c]\, x_1^2 - [b + (8/3)\, c]\, x_1^3 + c x_1^4$$

The above example illustrates how the activity coefficient of one of the species in a binary mixture can be evaluated if the activity coefficient of the other is known as an analytical equation in x. Now, suppose that γ_1 is determined experimentally and is reported as a function of x in a tabular form. How is γ_2 evaluated? Rearrange Gibbs–Duhem equation, Eq. (7.101) in the form

$$d \ln \gamma_2 = -\frac{x_1}{x_2}\, d \ln \gamma_1 \tag{7.104}$$

Integrating the above equation, we obtain

$$\ln \gamma_2 = -\int \frac{x_1}{x_2}\, d\,(\ln \gamma_1) + C \tag{7.105}$$

When $x_1 = 0$, $\ln \gamma_2 = 0$ and hence, $C = 0$. As a result,

$$\ln \gamma_2 = -\int_{(\ln \gamma_1)\text{ at } x_1 = 0}^{(\ln \gamma_1)\text{ at } x_1} \frac{x_1}{x_2}\, d\,(\ln \gamma_1) \tag{7.106}$$

The integral in Eq. (7.106) is to be evaluated graphically. For this, plot a graph taking x_1/x_2 along the y-axis and $\ln \gamma_1$ on the x-axis. The area under the curve from $\ln \gamma_1$ at $x_1 = 0$ to the $\ln \gamma_1$ value at the desired concentration x_1 will give the integral in Eq. (7.106). The negative of this is the value of $\ln \gamma_2$ at x_1.

7.8 PROPERTY CHANGES OF MIXING

We know that the molar volume of an ideal solution is simply the average of the molar volumes of the pure components, each weighted according to its mole fraction. That is, $V = \Sigma\, x_i V_i$ for ideal solutions. If such a relation could be written for all extensive thermodynamic properties of a solution, then

$$M = \Sigma\, x_i M_i \tag{7.107}$$

where M is the molar property of the solution, M_i and x_i are the molar property of pure i and its mole fraction respectively. But Eq. (7.107) is not true even for ideal solutions when the property under consideration is entropy or entropy related functions like free energy. For non-ideal solutions, this equation cannot be used for the estimation of thermodynamic properties unless we apply a correction term ΔM, known as the *property change of mixing*. Thus, in general, when thermodynamic properties of a solution, whether ideal or real, are evaluated from the pure component properties the equation used should be

$$M = \sum x_i M_i + \Delta M \qquad (7.108)$$

In Eq. (7.108), ΔM is the difference in the property of the solution M and sum of the properties of the pure components that make it up, all at the same temperature and pressure as the solution. Thus

$$\Delta M = M - \sum x_i M_i \qquad (7.109)$$

Replacing M in Eq. (7.108) by the molar volume V,

$$V = \sum x_i V_i + \Delta V$$

where ΔV is the volume change on mixing. $\Delta V = 0$, for ideal solutions.

A more general definition of ΔM can be written as

$$\Delta M = M - \sum x_i M_i^0 \qquad (7.110)$$

where M_i^0 is the molar property of pure i in a specified standard state. If the component exists in the pure form in the same state of aggregation as the solution and at the temperature and pressure as the solution, then $M_i^0 = M_i$. For example, if all components exist in the pure state as stable liquids at the temperature and pressure of the solution, $V_i^0 = V_i$ and $\Delta V = V - \sum x_i V_i$. Here, ΔV is the volume change of mixing when one mole of the solution is formed at constant temperature and pressure from the pure liquid constituents.

Property change of mixing is a function of temperature and pressure like any other thermodynamic property of solution and its value depends on the standard state specified for the components. Comparison of Eq. (7.14), which relates the properties of the solution to the partial molar properties of the constituent species, with Eq. (7.108) yields

$$\Delta M = \sum x_i (\overline{M}_i - M_i^0) \qquad (7.111)$$

The quantity $\overline{M}_i - M_i^0$ can be treated as the change in the property of component i when one mole of pure i in its standard state is brought to the solution of given composition at the same temperature and pressure. Using Eq. (7.111), the volume change of mixing and free energy change of mixing can be written as

$$\Delta V = \sum x_i (\overline{V}_i - V_i^0) \qquad (7.112)$$

$$\Delta G = \sum x_i (\overline{G}_i - G_i^0) \qquad (7.113)$$

7.8.1 Activity and Property Change of Mixing

***Free energy change of mixing,* ΔG.** Using the definition of fugacity, Eq. (6.118), the change in the free energy of a substance when it is brought from its standard state to the solution, can be written as

$$\bar{G}_i - G_i^0 = RT \ln \frac{\bar{f}_i}{f_i^0} = RT \ln a_i \tag{7.114}$$

Substitute this into Eq. (7.113). The result is

$$\frac{\Delta G}{RT} = \Sigma\, x_i \ln a_i \tag{7.115}$$

***Volume change of mixing*, D*V*.** The partial molar free energy (the chemical potential) varies with pressure as

$$\left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,x} = \bar{V}_i \tag{7.44}$$

Similarly for pure substance, we have

$$\left(\frac{\partial G_i^0}{\partial P}\right)_T = V_i^0$$

$\bar{V}_i$ and V_i^0 are the partial molar volume and molar volume of component *i* in the standard state respectively. Replacing $\bar{V}_i$ and V_i^0 in Eq. (7.112) in terms of $\bar{G}_i$ and G_i^0 using the preceding two relations, we get

$$\Delta V = \Sigma\, x_i \left[\frac{\partial(\bar{G}_i - G_i^0)}{\partial P}\right]_{T,x}$$

Using the result of Eq. (7.114) into the above equation, we get

$$\Delta V = RT\, \Sigma\, x_i \left[\frac{\partial \ln a_i}{\partial P}\right]_{T,x} \tag{7.116}$$

Equation (7.116) can be rewritten in the form

$$\frac{P\Delta V}{RT} = \Sigma\, x_i \left[\frac{\partial \ln a_i}{\partial \ln P}\right]_{T,x} \tag{7.117}$$

***Enthalpy change of mixing*, D*H*.** The Gibbs–Helmholtz equation [see Eqs. (6.73) and (7.41) relates the free energy of the substance in the pure state or in the solution to the corresponding enthalpies of the substance as

$$\left[\frac{\partial (G_i^0/T)}{\partial T}\right]_P = -\frac{H_i^0}{T^2} \tag{6.73}$$

$$\left[\frac{\partial (\bar{G}_i/T)}{\partial T}\right]_{P,x} = -\frac{\bar{H}_i}{T^2} \tag{7.41}$$

The enthalpy of mixing

$$\Delta H = \Sigma x_i (\bar{H}_i - H_i^0) \tag{7.118}$$

Using Eqs. (6.73) and (7.41) in the above,

$$\Delta H = -T^2 \Sigma x_i \left[\frac{\partial}{\partial T}\left(\frac{\bar{G}_i - G_i^0}{T}\right)\right]_{P,x}$$

Substituting Eq. (7.114) into this, we get

$$\Delta H = -T^2 R \Sigma x_i \left[\frac{\partial}{\partial T} \ln a_i\right]_{P,x}$$

$$\frac{\Delta H}{RT} = -\Sigma x_i \left[\frac{\partial \ln a_i}{\partial \ln T}\right]_{P,x} \tag{7.119}$$

***Entropy change of mixing*, D*S*.** The partial molar entropy $\bar{S}_i$ and molar entropy of component *i* in the standard state S_i^0 are related to the free energy of *i* in the solution and free energy of pure *i* as given below.

$$\left[\frac{\partial G_i}{\partial T}\right]_P = -S_i \tag{6.72}$$

$$\left[\frac{\partial \bar{G}_i}{\partial T}\right]_{P,x} = -\bar{S}_i \tag{7.39}$$

Entropy of mixing is defined as

$$\Delta S = \Sigma\, x_i(\bar{S}_i - S_i^0)$$

Substitute Eqs. (6.72) and (7.39) into this. Then

$$\Delta S = -\Sigma\, x_i \left[\frac{\partial(\bar{G}_i - G_i^0)}{\partial T}\right]_{P,x}$$

Use Eq. (7.114) in the above result.

$$\Delta S = -R\,\Sigma\, x_i \left[\frac{\partial(T \ln a_i)}{\partial T}\right]_{P,x}$$

$$\frac{\Delta S}{R} = -\Sigma\, x_i \left[\frac{\partial \ln a_i}{\partial \ln T}\right]_{P,x} - \Sigma\, x_i \ln a_i \tag{7.120}$$

Equations (7.115), (7.117), (7.119) and (7.120) reveal that all property changes of mixing can be written in terms of activity of the components in solution.

7.8.2 Property Changes of Mixing for Ideal Solutions

For ideal solutions fugacity is given by Lewis–Randall rule, $\bar{f}_i = x_i f_i$. With reference to the pure component standard state, the activity is given as $a_i = \bar{f}_i / f_i = x_i$. Replacing a_i with x_i in the results in the previous section and noting that the concentration is independent of pressure and temperature, we have the following results for the property changes of mixing of ideal solutions.

$$\Delta G = RT\,\Sigma\, x_i \ln x_i \tag{7.121}$$

$$\Delta V = 0$$

$$\Delta H = 0$$

$$\Delta S = -R\,\Sigma\, x_i \ln x_i \tag{7.122}$$

Thus, we see that the volume change of mixing, and enthalpy change of mixing of ideal solution are zero. This is true for internal energy change and heat capacity change of mixing as well. But, the free energy change of mixing and entropy change of mixing are not zero. As an ideal gas is a special case of an ideal solution, the above equations are applicable for ideal gas mixtures also.

7.9 HEAT EFFECTS OF MIXING PROCESSES

Since the energy of interaction between like molecules is different from that between unlike molecules, the energy of a solution is different from the sum of the energies of its constituents. This difference between the energy of the solution and the energy of the constituents leads to the absorption and evolution of heat during the mixing process. The *heat of mixing*, ΔH (or the enthalpy change of mixing), is the enthalpy change when pure species are mixed at constant pressure and temperature to form one mole (or unit mass) of solution. For binary mixtures,

$$\Delta H = H - (x_1 H_1 + x_2 H_2) \qquad (7.123)$$

Knowing the enthalpies of the pure constituents H_1 and H_2 and the heat of mixing at the given concentration, the enthalpy of the solution can be computed as

$$H = (x_1 H_1 + x_2 H_2) + \Delta H \qquad (7.124)$$

When solids or gases are dissolved in liquids, the accompanying enthalpy change is usually measured as heats of solution, which is defined as the enthalpy change when one mole of the solute dissolves in the liquid. Thus

$$\Delta H_S = \frac{\Delta H}{x_1} \qquad (7.125)$$

where ΔH_S is the heat of solution per mole of solute (component 1). When the constituents are all liquids and solutions of all proportions are possible, the heat effect is usually termed as heat of mixing. Figures 7.7 and 7.8 illustrate the two types of presentation of heat of mixing.

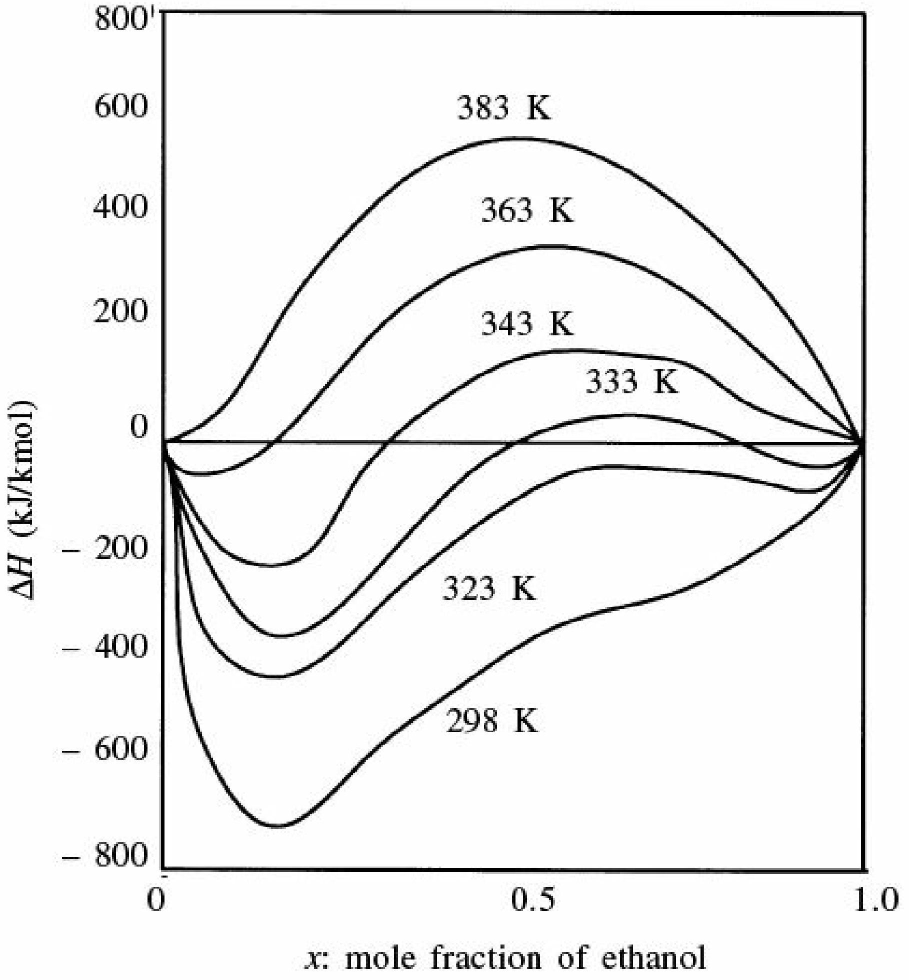


Fig. 7.7 Heat of mixing for ethanol–water solution.

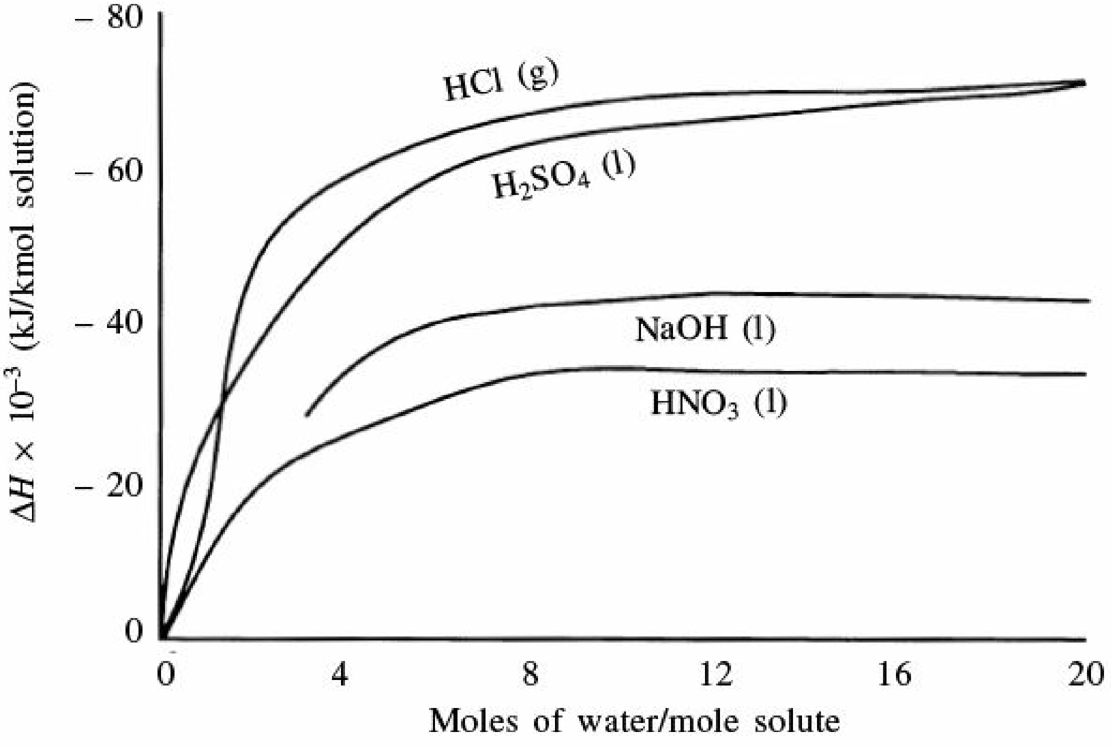


Fig. 7.8 Heats of solution at 298 K.

In Fig. 7.7, the heat of mixing of ethanol–water is shown from which it is clear that mixing process at lower temperatures and concentration of ethanol is exothermic and at higher temperatures and high concentrations it is endothermic. In Fig. 7.8, heats of solution of various substances in water are plotted with moles of water per mole of solute as abscissa.

Using the heat of mixing at one temperature and heat capacity data of pure species and the solution, the heat of mixing at any temperature can be calculated. The method of calculation is similar to the one employed for the calculation of standard heat of reaction at any temperature from the values at 298 K.

***EXAMPLE* 7.17** The enthalpy change of mixing for a binary liquid solution at 298 K and 1 bar is given by the equation D$H = x_1x_2(40x_1 + 20x_2)$, where D$H$ is in J/mol and x_1 and x_2 are the mole fractions of components 1 and 2 respectively. The enthalpies of the pure liquids at the same temperature and pressure are 400 and 600 J/mol respectively. Determine numerical values of the partial molar enthalpies at infinite dilution $\overline{H}_1^\infty$ and $\overline{H}_2^\infty$ at 298 K and 1 bar.

Solution Refer Eqs. (7.20) and (7.21) and replace V by H.

$$\overline{H}_1 = H - x_2 \frac{\partial H}{\partial x_2}, \quad \overline{H}_2 = H - x_1 \frac{\partial H}{\partial x_1}$$

Enthalpy change of mixing ΔH can be treated as a molar property, so that

$$\overline{\Delta H_1} = \Delta H - x_2 \frac{\partial \Delta H}{\partial x_2} \tag{7.126}$$

$$\overline{\Delta H_2} = \Delta H - x_1 \frac{\partial \Delta H}{\partial x_1} = \Delta H + (1 - x_2) \frac{\partial \Delta H}{\partial x_2} \tag{7.127}$$

Here $\Delta H = x_1x_2 (40x_1 + 20x_2)$. Therefore,

$$\frac{\partial \Delta H}{\partial x_2} = 40x_1^2 - 20x_2^2 - 40x_1x_2 \tag{7.128}$$

From Eqs. (7.126) and (7.128),

$$\overline{\Delta H_1} = 20(1 - x_1)^2 (2x_1 + 1) \tag{7.129}$$

Using Eqs. (7.127) and (7.128),

$$\overline{\Delta H_2} = 40x_1^3 \tag{7.130}$$

$$\overline{\Delta H_1}^\infty = \overline{\Delta H_1} \qquad \text{as } x_1 \to 0$$

Put $x_1 = 0$ in Eq. (7.129). Then $\overline{\Delta H_1}^{\infty} = 20$ J/mol.

But $\overline{\Delta H_1}^{\infty} = \overline{H_1}^{\infty} - H_1$. Therefore,

$$\overline{H_1}^{\infty} = \overline{\Delta H_1}^{\infty} + H_1 = 20 + 400 = 420 \text{ J/mol}$$

$$\overline{\Delta H_2}^{\infty} = \overline{\Delta H_2} \qquad \text{as } x_1 \to 1$$

Put $x_1 = 1$ in Eq. (7.130).

$$\overline{\Delta H_2}^{\infty} = \overline{H_2}^{\infty} - H_2 = 40 \text{ J/mol}$$

As $H_2 = 600$ J/mol, $\overline{H_2}^{\infty} = 640$ J/mol.

***EXAMPLE* 7.18** At 300 K and 1 bar, the volumetric data for a liquid mixture of benzene and cyclohexane are represented by $V = 109.4 \square 10^{-6} - 16.8 \square 10^{-6}x - 2.64 \square 10^{-6}x^2$, where x is the mole fraction of benzene and V has the units of m^3/mol. Determine the expression for volume change of mixing for the standard state based on Lewis–Randall rule.

Solution The expressions for the partial molar volumes of benzene (1) and cyclohexane (2) were derived in Example 7.5. They are

Partial molar volume of benzene:

$$\overline{V_1} = 92.6 \times 10^{-6} - 5.28 \times 10^{-6}x_1 + 2.64 \times 10^{-6}x_1^2$$

Partial molar volume of cyclohexane:

$$\overline{V_2} = 109.4 \times 10^{-6} + 2.64 \times 10^{-6}x_1^2$$

$V_1 = V$ at $x_1 = 1$ and $V_2 = V$ at $x_1 = 0$. Therefore,

$$V_1 = 89.96 \times 10^{-6} \text{ m}^3\text{/mol}; \qquad V_2 = 109.4 \times 10^{-6} \text{ m}^3\text{/mol}$$

For pure liquid standard state, Eq. (7.112) is

$$\Delta V = \Sigma x_i (\overline{V_i} - V_i) = x_1 (\overline{V_1} - V_1) + x_2 (\overline{V_2} - V_2)$$

Substituting the expressions for $\overline{V_1}$ and $\overline{V_2}$ and the values of V_1 and V_2 into the above equation and simplifying, we get

$$\Delta V = 2.64 \times 10^{-6}x_1x_2$$

***EXAMPLE* 7.19** A vessel is divided into two compartments. One contains 100 moles nitrogen at 298 K and 1 bar and the other contains 100 moles of oxygen at the same conditions. The barrier separating them is removed and the gases are allowed to reach equilibrium under adiabatic conditions. What is the change in entropy of the contents of the vessel?

Solution As the gases are ideal, the temperature and pressure before and after mixing will be the same. For one mole of the mixture the change in entropy on its formation from pure components is given by Eq. (7.122).

$$\Delta S = -R \sum x_i \ln x_i$$

Since $x_i = 0.5$,

$$\Delta S = -R \ln 0.5 = 8.314 \times \ln 2 = 5.763 \text{ J/mol K}$$

For 200 moles of the mixture, $\Delta S = 1152.57$ J/K

***EXAMPLE* 7.20** The heat of formation of LiCl is – 408.610 kJ/mol at 298 K. The heat of solution fo 1 mol LiCl in 12 moles water is –33.614 kJ at 298 K. Calculate the heat of formation of LiCl in 1 moles water at 298 K.

Solution The chemical reaction of formation of LiCl and the physical change of dissolution of LiCl i water can be represented by the following:

$$\text{Li} + \frac{1}{2}\text{Cl}_2 \rightarrow \text{LiCl}; \qquad \Delta H^0 = -408.610 \text{ kJ}$$

$$\text{LiCl} + 12\text{H}_2\text{O} \rightarrow \text{LiCl (12H}_2\text{O)}; \qquad \Delta H_S = -33.614 \text{ kJ}$$

Adding these two equations, we get

$$\text{Li} + \frac{1}{2}\text{Cl}_2 + 12\text{H}_2\text{O} \rightarrow \text{LiCl (12H}_2\text{O)}; \qquad \Delta H^0_{298} = -442.224 \text{ kJ}$$

***EXAMPLE* 7.21** A container is divided into two compartments. One contains 3.0 moles hydrogen at 298 K and 1.0 bar and the other contains 1.0 mol nitrogen at 298 K and 3.0 bar. Calculate the free energy of mixing when the partition is removed.

Solution Assume that the gases behave ideally. The volume occupied by hydrogen is

$(nRT)/P = 3RT$

Volume occupied by nitrogen is

$(nRT)/P = RT/3$

Therefore, the total volume occupied after the partition is removed is

$3RT + RT/3 = (10/3)RT$

The final pressure attained by the mixture is

$$\frac{nRT}{V} = \frac{4RT}{(10/3)RT} = 1.2 \text{ bar}$$

It is assumed that the process is taking place in two steps. In the first, the individual gases are separately brought to the final pressure at constant temperature and in the second, the gases are mixed at constant pressure and temperature. For the first step, the change in free energy is due to change in the pressure and is equal to

$$\Delta G\,(1) = RT\,\ln \frac{P_2}{P_1} = RT\left(3.0\ln\frac{1.2}{1.0} + 1.0\ln\frac{1.2}{3.0}\right) = -0.38\,RT$$

The free energy of mixing for the second step is given by Eq. (7.121)

$$\Delta G(2) = nRT\,\Sigma\, x_i \ln x_i = 4.0RT\,(0.25 \ln 0.25 + 0.75 \ln 0.75) = -2.25RT$$

The total free energy change is

$$\Delta G = \Delta G(1) + \Delta G(2) = -2.63RT = -6.52 \text{ kJ}$$

***EXAMPLE* 7.22** Calculate the mean heat capacity of a 20 mole per cent solution of alcohol in water at 298 K, given the following:

Heat capacity of water: 4.18 □ 10^3 J/kg K; Heat capacity of ethanol: 2.18 □ 10^3 J/kg K; Heat of mixing for 20 mole per cent ethanol–water at 298 K: – 758 J/mol; Heat of mixing for 20% (mole) ethanol–water at 323 K: – 415 J/mol. Assume that the heat capacities of pure liquids are constant between 298 and 523 K.

Solution The enthalpy change when 0.8 moles of water and 0.2 moles of ethanol both at 323 K are mixed together is given by the heat of mixing at 323 K which is equal to – 415 J/mol of solution. 0.8 mol water at 323 K + 0.2 mol ethanol at 323 K □ 1.0 mole 20 per cent ethanol–water; DH = – 415 J/mol. This change can be assumed to be taking place in four steps as detailed below:

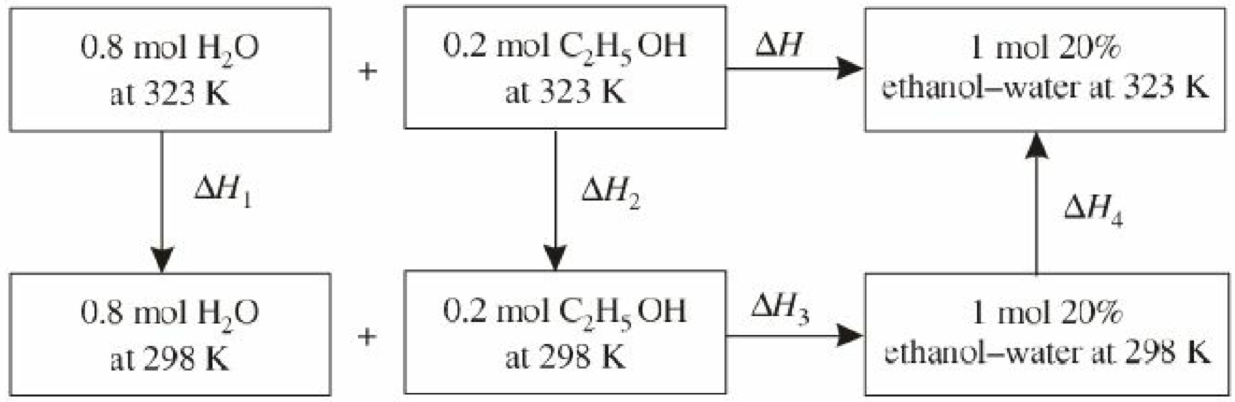


Fig. 7.9 The four steps involved in the process described in Example 7.22.

Step 1: 0.8 mol water is cooled from 323 K to 298 K. Let DH (1) be the enthalpy of cooling. Then

DH(1) = 0.8 □ 18 □ 4.18 □ (298 – 323) = – 1504.8 J

Step 2: 0.2 mol ethanol is cooled from 323 K to 298 K. Let DH(2) be the enthalpy of cooling.

DH(2) = 0.2 □ 46 □ 2.58 □ (298 – 323) = – 593.4 J

Step 3: 0.8 mol water and 0.2 mol ethanol at 298 K are mixed together. Heat of mixing is

DH(3) = –758 J/mol

Step 4: 20 per cent ethanol–water solution is heated to 323 K. The enthalpy of heating is

DH(4) = C_{Pm}(323 – 298)

where C_{Pm} is the mean specific heat of solution.

$$\mathrm{D}H = \mathrm{D}H(1) + \mathrm{D}H(2) + \mathrm{D}H(3) + \mathrm{D}H(4)$$

$$-415 = -1504.8 - 593.4 - 758 + C_{Pm}(323 - 298)$$

Thus the mean heat capacity of a 20 per cent solution is $C_{Pm} = 97.65$ J/mol K

***EXAMPLE* 7.23** What temperature will be attained when a 20% mole ethanol–water mixture is adiabatically formed from the pure liquids at 298 K? Heat of mixing for 20% mole ethanol–water at 298 K: –758 J/mol. The mean heat capacity of a 20% mole solution of alcohol in water at 298 K: 97.65 J/mol K.

Solution The adiabatic mixing process involves no change in enthalpy or $\mathrm{D}H = 0$. It means the temperature of the solution will increase or decrease on mixing depending upon whether heat is absorbed or evolved during the process. Let T be the temperature attained by the solution on mixing. Then its enthalpy above 298 K is $C_{Pm}(T - 298)$, where C_{Pm} is its mean heat capacity. The temperature T can be evaluated by assuming that the process is occuring in steps as shown in Fig. 7.10.

$$\mathrm{D}H = \mathrm{D}H_S + C_{Pm}(T - 298)$$

$$0 = -758 + 97.65(T - 298)$$

Therefore, $T = 305.8$ K.

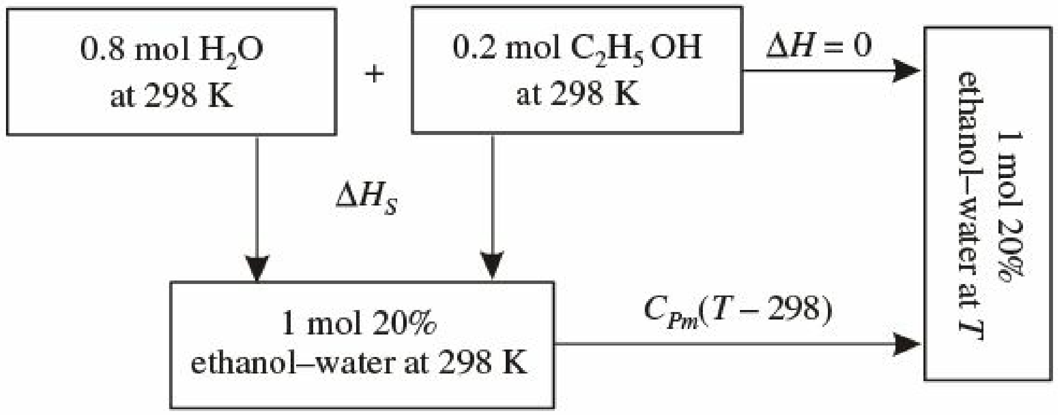


Fig. 7.10 Adiabatic mixing process described in Example 7.23.

7.10 EXCESS PROPERTIES

The difference between the property of a real solution and that of an ideal solution is important in chemical thermodynamics, especially in the treatment of phase equilibria. The *excess property,* M^E, is defined as the difference between an actual property and the property that would be calculated for the same temperature, pressure and composition by the equations for an ideal solution.

$$M^E = M - M^{\mathrm{id}} \qquad (7.131)$$

M is the molar property of the solution and M^{id} is the property of an ideal solution under the same conditions.

The excess property change of mixing is defined in a similar manner.

$$\Delta M^E = \Delta M - \Delta M^{\text{id}} \qquad (7.132)$$

ΔM^E is the excess property change of mixing, ΔM and ΔM^{id} are the property changes of mixing for a real solution and an ideal solution respectively, both under the same conditions. As

$$\Delta M = M - \Sigma x_i M_i^0, \ \Delta M^{\text{id}} = M^{\text{id}} - \Sigma x_i M_i^0$$

Equation (7.132) can be written as

$$\Delta M^E = M - M^{\text{id}} \qquad (7.133)$$

Compare Eq. (7.131) with Eq. (7.133). We see that

$$\Delta M^E = M^E \qquad (7.134)$$

Equation (7.134) means that the excess property change of mixing and the excess property are the same.

Let us consider the excess volume V^E of a solution.

$$V^E = \Delta V^E = \Delta V - \Delta V^{\text{id}}$$

Since ideal solution involves no volume change of mixing, $\Delta V^{\text{id}} = 0$. Therefore, the excess volume of a solution and the volume change of mixing ΔV are the same. The same is true for some other extensive thermodynamic properties like enthalpy, internal energy, heat capacity, etc. Excess properties in these cases do not represent new thermodynamic properties. However, for entropy and entropy related functions, the excess properties are different from property changes of mixing and they represent new and useful quantities.

Excess functions indicate the deviations from ideal solution behaviour and are easily related to activity coefficients. Excess functions may be positive or negative; when the excess Gibbs free energy of a solution is positive the solution is said to exhibit positive deviation from ideality, whereas if it is less than zero, the deviation from ideality is negative.

The definition of partial molar excess functions is analogous to that of partial molar thermodynamic properties [see Eq. (7.1)].

$$\overline{M}_i^E = \left(\frac{\partial n M^E}{\partial n_i} \right)_{T,P,n_j} \qquad (7.135)$$

$\overline{M_i^E}$ is the partial molar excess property of component *i*. Therefore, analogous to Eq. (7.132) we can write,

$$M^E = \Sigma x_i \overline{M}_i^E \qquad (7.136)$$

Equation (7.136) says that the molar excess property M^E of a solution is the average of the partial molar excess property of each component weighted according to its mole fractions.

7.10.1 Excess Gibbs Free Energy

For phase equilibrium studies the most useful excess property is the partial molar excess Gibbs free energy which can be directly related to the activity coefficient. Excess Gibbs free energy is defined as

$$G^E = G - G^{\mathrm{id}} \qquad (7.137)$$

Using Eq. (7.136), we can write the excess Gibbs free energy as

$$G^E = \Sigma x_i \mu_i^E \tag{7.138}$$

where μ_i^E is the excess chemical potential or excess partial molar free energy of component *i*. But,

$$\mu_i^E = \mu_i - \mu_i^{\mathrm{id}} = \Delta\mu_i - \Delta\mu_i^{\mathrm{id}} \tag{7.139}$$

$\Delta\mu_i$, the change in chemical potential for component *i* when it is transferred from its standard state to the solution at the same temperature and pressure is related to its fugacity in the solution, as

$$\Delta\mu_i = RT \ln \frac{\bar{f}_i}{f_i^0} \tag{7.140}$$

$\bar{f}_i$ is the fugacity of component *i* in solution and f_i^0 is the fugacity in the standard state. Similarly, if the component becomes part of an ideal solution at the same conditions,

$$\Delta\mu_i^{\mathrm{id}} = RT \ln \frac{\bar{f}_i^{\mathrm{id}}}{f_i^0} \tag{7.141}$$

Since fugacity in an ideal solution is $\bar{f}_i^{\mathrm{id}} = x_i f_i^0$, Eq. (7.141) can be written as

$$\Delta\mu_i^{\mathrm{id}} = RT \ln x_i \tag{7.142}$$

In Eq. (7.140) the fugacity $\bar{f}_i$ is related to x_i,, □$_i$ and f_i^0 as $\bar{f}_i = x_i \gamma_i f_i^0$, so that Eq. (7.140) becomes

$$\mathrm{Dm}_i = RT \ln x_i \mathrm{g}_i \qquad (7.143)$$

Substituting Eq. (7.142) and Eq. (7.143) into Eq. (7.139), the result is

$$\boxed{\mu_i^E = RT \ln \gamma_i} \tag{7.144}$$

Because of this simple relationship between activity coefficient and excess chemical potential it becomes possible to express the activity coefficient as a function of composition.

From Eq. (7.138), we see that the molar excess Gibbs free energy of a solution is simply,

$$G^E = RT \, \Sigma \, x_i \ln \gamma_i \tag{7.145}$$

Since $\mu_i^E = \overline{G}_i^E$, the partial molar free energy of a component *i* in the solution, the above equation can be put in the form of Eq. (7.135)

$$\boxed{\ln \gamma_i = \frac{\mu_i^E}{RT} = \left[\frac{\partial (nG^E/RT)}{\partial n_i}\right]_{T,P,n_j}} \tag{7.146}$$

***EXAMPLE* 7.24** The two-suffix-Margules equation is the simplest expression for excess Gibbs free energy that is obeyed by chemically similar materials.

$$G^E = Ax_1x_2 \qquad (7.147)$$

where A is an empirical constant independent of composition. Derive the expressions for the activity coefficients that result from this expression.

Solution Write Eq. (7.146) for components 1 and 2. Then

$$\ln \gamma_1 = \left[\frac{\partial(nG^E/RT)}{\partial n_1}\right]_{T,P,n_2}, \qquad \ln \gamma_2 = \left[\frac{\partial(nG^E/RT)}{\partial n_2}\right]_{T,P,n_1}$$

Since $G^E = Ax_1x_2 = A(n_1/n)\,(n_2/n)$,

$$nG^E = A\frac{n_1n_2}{n} \qquad (7.148)$$

Differentiating Eq. (7.148) with respect to n_1, keeping n_2 constant, we get

$$RT \ln \gamma_1 = An_2\left(\frac{n - n_1}{n^2}\right) = A x_2^2$$

Differentiating Eq. (7.148) with respect to n_2, keeping n_1 constant, we get

$$RT \ln \gamma_2 = Ax_1^2$$

The desired expressions for activity coefficient are

$$\ln \gamma_1 = \frac{A}{RT}x_2^2, \qquad \ln \gamma_2 = \frac{A}{RT}x_1^2$$

Figure 7.11 shows the plot of ln γ_1, ln γ_2 and G^E/RT against composition.

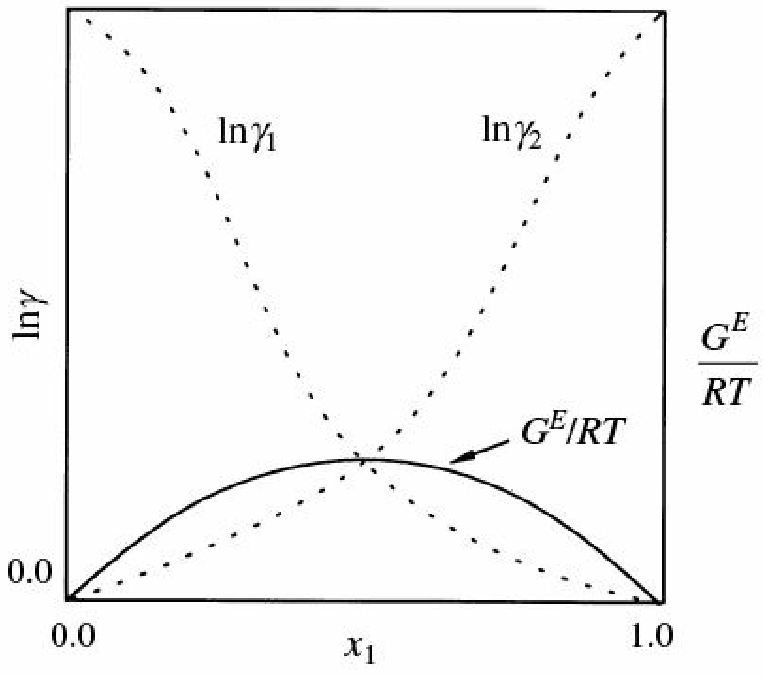


Fig. 7.11 Activity coefficient for Example 7.24.

SUMMARY

A proper understanding of the thermodynamic properties of solutions is essential for the analysis of many chemical engineering problems such as the phase equilibria and chemical reaction equilibria. New concepts were found necessary to deal with the solutions, the concept of partial molar properties being the most important among them. The general definition of partial molar property was given by Eq. (7.1). The partial molar property of a substance in a solution is an intensive property strongly dependent on the concentration. It gives the increase, in the property of the solution resulting from the addition at constant temperature and pressure, of one mole of the substance, to such a large quantity of the system that its composition remains virtually unchanged. The method of tangent intercepts was found to be most suitable for the determination of partial molar properties. The partial molar free energy of a substance was designated as its chemical potential. It is the contribution that the component makes towards the total free energy of the solution. It is a widely used thermodynamic property and serves as an index of chemical equilibrium in the same manner as temperature and pressure are used as indices of thermal and mechanical equilibrium.

The concept of fugacity introduced in Chapter 6 was extended to take care of mixtures through Eqs. (7.51) and (7.52). For the evaluation of fugacity of mixtures, data on the variation of the solution volume with composition at different pressures is necessary [Eq. (6.57)]. Since such data are scarce, the fugacity in the solution is to be evaluated by devising an ideal solution model and by measuring the extent to which the real solutions deviate from it. The Lewis–Randall rule allows the fugacity of a component in the mixture to be calculated without any information about the solution except its composition. It states that the fugacity of a component in an ideal solution is directly proportional to the mole fraction of the component in the solution [Eq. (7.65)]. For ideal liquid solutions, if the vapour phase with which it is in equilibrium is assumed to behave as an ideal gas, the Lewis–Randall rule may be simplified to the Raoult’s law [Eq. (7.67)]. The Raoult’s law states that the partial pressure of a component in the vapour phase is directly proportional to the mole fraction of that component in the liquid, which is in equilibrium with the vapour. Even for non-ideal solutions, the fugacity (or the partial pressure) was found to be directly proportional to the mole fraction in the liquid as the mole fraction approaches zero (Henry’s law). Often, the solute portion of a dilute non-ideal liquid solution can be assumed to follow the Henry’s law and the solvent portion, the Raoult’s law. The activity of a component in a solution (Section 7.6) can be related to compositions directly and hence plays an important role in solution thermodynamics. Activity coefficients (Section 7.6) measure the extent to which real solutions deviate from ideal behaviour. Two types of ideal behaviour are observed; one conforming to the Lewis–Randall rule and the other conforming to the Henry’s law, thus giving rise to two types of activity coefficients.

In Section 7.7, the Gibbs–Duhem equations were developed relating the partial molar properties of the components to one another. They tell us that the partial molar properties of a mixture cannot change independently; in a binary mixture, if the partial molar property of one of the component increases, that of the other should decrease. Various forms of the Gibbs–Duhem equations applicable for binary solutions were also developed.

The property changes of mixing were defined (Section 7.8) as the difference in the property of the solution and the sum of the properties of the pure components constituting the solution, all at the same temperature and pressure as the solution. The property changes were presented in terms of the activity of the constituents as shown by Eq. (7.115) for the free energy, Eq. (7.117) for the volume, Eq.

(7.119) for the enthalpy and Eq. (7.120) for the entropy change on mixing. The difference between the energy of the solution and the energy of the constituents leads to absorption and evolution of heat during the mixing process. The heat effects of mixing process were dealt with in detail in Section 7.9. The excess property (Section 7.10) was defined as the difference between an actual property and the property that could be calculated for the same temperature, pressure and composition by the equations for an ideal solution. For phase equilibrium studies the most useful excess property is the partial molar excess Gibbs free energy which can be directly related to the activity coefficient. A simple relationship was shown to exist between activity coefficient and excess chemical potential which makes it possible to express the activity coefficient as a function of the composition.

REVIEW QUESTIONS

1. Distinguish between molar volume and partial molar volume. Does the partial molar volume of a substance vary with the concentration of the substance in the solution?
2. Express the partial molar property as the partial derivative of the total property of the solution. Is it an intensive property or an extensive property?
3. How are the partial molar volumes of the constituents of a binary mixture related to their mole fractions of the constituents and the molar volume of the solution? Explain how these equations are useful for the determination of partial molar volumes by the tangent-intercept method.
4. Define chemical potential. What is its physical significance?
5. Chemical potential can be equated to the partial derivatives of *U*, *A*, *H* or *S* under certain constraints. However, it cannot be treated as the partial molar internal energy, partial molar enthalpy, etc. Explain.
6. Show that the rate of change of chemical potential of a substance with pressure is equal to its partial molar volume in the solution.
7. What are the characteristics of an ideal solution? What is Lewis–Randall rule?
8. “The concept of an ideal gaseous solution is less restrictive than the concept of an ideal gas mixture.” Explain.
9. State Raoult’s law. Show that it is a simplified form of the Lewis–Randall rule.
10. State Henry’s law and show that the Raoult’s law is a special case of the Henry’s law.
11. Given the Henry’s law constant, how would you determine the solubility of a gas in a liquid?
12. Define activity and show that the activity and mole fraction in an ideal solution are identical.
13. The activities in a gas mixture may be numerically equal to the fugacities or the mole fractions in the mixture. Explain.
14. Define activity coefficient. How do you distinguish between the activity coefficient based on the Lewis–Randall rule and that based on the ideal dilute solution?
15. Do the activity coefficients vary with composition or not? What is the effect of temperature and pressure on the activity coefficient?
16. Discuss the Gibbs–Duhem equation and its various forms. What are the major fields of application of the Gibb’s Duhem equations?
17. What do you mean by property changes of mixing? How are these related to the activities of the

components in the mixture?

18. "All property changes of mixing are zero for ideal solutions". Do you agree? Explain.

19. Define excess property. Under what circumstance the property change of mixing and the excess properties are identical?

20. How is the activity coefficient related to the excess free energy?

EXERCISES

7.1 Prove the following:

(a)
$$\mu_i = \left(\frac{\partial H^t}{\partial n_i}\right)_{P,S,n_j}$$

(b)
$$\mu_i = \left(\frac{\partial A^t}{\partial n_i}\right)_{T,V,n_j}$$

(c)
$$\mu_i = -T\left(\frac{\partial S^t}{\partial n_i}\right)_{U,V,n_j}$$

7.2 Discuss the method for the calculation of entropy of solutions.

7.3 Discuss the variable pressure and variable temperature modifications of Gibbs–Duhem equations.

7.4 Derive an expression for partial molar volumes $\overline{V}_1$ and $\overline{V}_2$ using the following relation for the molar volume of the binary liquid mixture of components 1 and 2.

$$V = x_1 V_1 + x_2 V_2 + x_1 x_2 [B + C(x_2 - x_1)]$$

where x_1 and x_2 are the mole fractions and V_1 and V_2 are the molar volumes in the pure state.

7.5 Describe schematically an experimental technique for the determination of volume change and enthalpy change on mixing.

7.6 The activity coefficients in a binary mixture based on the Lewis–Randall rule standard state are given by

$$\ln \gamma_1 = A x_2^2; \qquad \ln \gamma_2 = A x_1^2$$

Derive expressions for activity coefficients based on Henry's law in terms of composition.

7.7 Show that the Henry's law constant varies with pressure as

$$\left(\frac{\partial \ln K_2}{\partial P}\right)_T = \frac{\overline{V}_2^\infty}{RT}$$

where $\overline{V}_2^\infty$ is the partial molar volume of the solute at infinite dilution.

7.8 The enthalpy of a binary liquid mixture containing components 1 and 2 at 298 K and 1.0 bar is given by

$$H = 400x_1 + 600x_2 + x_1 x_2 (40x_1 + 4x_2)$$

where H is in J/mol. Determine

(a) Pure component enthalpies

(b) Partial molar enthalpies.

7.9 The volume of a mixture of two organic liquids 1 and 2 is given by

$$V = 110.0 - 17x_1 - 2.5x_1^2$$

where V is the volume in m^3/mol at 1.0 bar and 300 K. Find the expressions for $\overline{V_1}, \overline{V_2}$ and ΔV.

7.10 If the partial molar volumes of species 1 in a binary liquid solution at constant temperature and pressure is given by

$$\overline{V_1} = V_1 + \alpha x_2^2$$

derive the equat3ion for $\overline{V_2}$. What equation for V is consistent with this?

7.11 The molar enthalpy of a binary mixture is given by

$$H = x_1(a_1 + b_1x_1) + x_2(a_2 + b_2x_2)$$

Derive an expression for $\overline{H_1}$.

7.12 Using the method of tangent intercepts plot the partial molar volume of HNO_3 in aqueous solution at 293 K using the following data where w is the mass percentage of HNO_3.

w	2.162	10.98	20.80	30.00	39.20	51.68	62.64	71.57	82.33	93.4	99.60
r □ 10^{-3}, kg/m^3	1.01	1.06	1.12	1.18	1.24	1.32	1.38	1.42	1.46	1.49	1.51

7.13 On addition of chloroform to acetone at 298 K, the volume of the mixture varies with composition as follows:

x	0	0.194	0.385	0.559	0.788	0.889	1.000
V □ 10^3, m^3/kmol	73.99	75.29	76.50	77.55	79.08	79.82	80.67

where x is the mole fraction of chloroform. Determine the partial molar volumes of the components and plot against x.

7.14 The partial molar volumes of acetone and chloroform in a mixture in which mole fraction of acetone is 0.5307 are 74.166 □ 10^{-6} m^3/mol and 80.235 □ 10^{-6} m^3/mol respectively. What is the volume of 1 kg of the solution?

7.15 The volume of a solution formed from $MgSO_4$ and 1.0 kg of water fits the expression

$$V = 1.00121 \square 10^{-3} + 34.69 \square 10^{-6}(m - 0.070)^2$$

where m is the molality of the solution. Calculate the partial molar volume of the salt and solvent when $m = 0.05$ mol/kg.

7.16 Calculate the partial molar volumes of methanol and water in a 40 per cent (mol) methanol solution given the following data at 1 bar and 298 K. (x = mole fraction of methanol)

x	0	0.114	0.197	0.249	0.495	0.692	0.785	0.892	1.0
V □ 10^3, m^3/mol	0.0181	0.0203	0.0219	0.023	0.0283	0.0329	0.0352	0.0379	0.0407

7.17 The standard enthalpy of formation of HCl (in kJ/mol) from the elements at 298 K are given below:

n_W	1.0	2.0	3.0	4.0	5.0	6.0	8.0	10.0	50.0	100.0	□
	92.66	119.0	141.67	149.73	156.96	158.81	161.16	162.42	166.22	166.79	205.9

Calculate the partial molar enthalpies of HCl and water in a solution containing 10 kmol HCl/m^3 of solution.

7.18 The following table gives the molality and density of aqueous solutions of KCl at 298 K. Determine the partial molar volume of KCl at $m = 0.3$.

m, mol/kg	0.0	0.1668	0.2740	0.3885	0.6840	0.9472
r, kg/m^3	997.07	100.49	100.980	101.271	102.797	103.927

7.19 Calculate the concentration of nitrogen in water exposed to air at 298 K and 1 bar if Henry's law constant for nitrogen in water is 8.68 □ 10^4 bar at this temperature.
Express the result in moles of nitrogen per kg water (*Hint*: Air is 79 per cent nitrogen by volume).

7.20 The partial pressure of methyl chloride in a mixture varies with its mole fraction at 298 K as detailed below:

x	0.0005	0.0009	0.0019	0.0024
, bar	0.27	0.48	0.99	1.24

Estimate the Henry's law constant of methyl chloride.

7.21 Two moles of hydrogen at 298 K and 2.0 bar and 4.0 moles of nitrogen at 298 K and 3.0 bar are mixed together. What is the free energy change on mixing and what would be the value had the pressures been identical initially?

7.22 Calculate the activity and activity coefficient of acetone based on Lewis–Randall rule and Henry's law for the data given in Example 7.12.

7.23 The activity coefficient data for a binary solution at fixed temperature and pressure are correlated as

$$\ln \gamma_1 = x_2^2(0.5 + 2x_1), \quad \ln \gamma_2 = x_1^2(1.5 - 2x_2)$$

Do these equations satisfy Gibbs–Duhem equations?

7.24 In a binary mixture, the activity coefficient g$_1$ of component 1, in the entire range of composition, is given by

$$R \ln \gamma_1 = Ax_2^2 + Bx_2^3$$

where *R*, *A* and *B* are constants. Derive expression for the activity coefficient of component 2.

7.25 For a mixture of acetic acid and toluene containing 0.486 mole fraction toluene, the partial pressures of acetic acid and toluene are found to be 0.118 bar and 0.174 bar respectively at 343 K. The vapour pressures of pure components at this temperature are 0.269 bar and 0.181 bar for toluene and acetic acid respectively. The Henry's law constant for acetic acid is 0.55 bar.

Calculate the activity and activity coefficient for acetic acid in the mixture

(a) Based on Lewis–Randall rule

(b) Based on Henry's law.

7.26 Calculate the activity and activity coefficients for toluene for the conditions in Exercise 7.24 assuming pure liquid standard state.

7.27 Partial pressure of ammonia in aqueous solutions at 273 K varies with concentration as:

x	0.05	0.10	0.15	0.50	1.00
, bar	0.0179	0.0358	0.062	1.334	4.293

Calculate

(a) The activity coefficient of ammonia in 10 mole per cent solution using pure liquid standard state

(b) The Henry's law constant if the system obeys Henry's law.

7.28 The activity coefficient of *n*-propyl alcohol in a mixture of water (*A*) and alcohol (*B*) at 298 K referred to the pure liquid standard state is given below:

x_B	0	0.01	0.02	0.05	0.10	0.20
g_B	12.5	12.3	11.6	9.92	6.05	3.12

Find g_A in the solution containing 10 per cent (mole) *n*-propyl alcohol.

7.29 The activity coefficient of thallium in amalgams at 293 K are given below.

x_2	0	0.00326	0.01675	0.04856	0.0986	0.168	0.2701	0.424
g_2	1.0	1.042	1.231	1.776	2.811	4.321	6.196	7.707

Determine the activity coefficient of mercury (component 1) at various compositions.

7.30 A vessel is divided into two parts. One part contains 2 mol nitrogen gas at 353 K and 40 bar and the other contains 3 mol argon gas at 423 K and 15 bar. If the gases are allowed to mix adiabatically by removing the partition determine the change in entropy. Assume that the gases are ideal and C_V is equal to 5/2 *R* for nitrogen and 3/2 *R* for argon.

7.31 A stream of nitrogen flowing at the rate of 7000 kg/h and a stream of hydrogen flowing at the rate of 1500 kg/h mix adiabatically in a steady flow process. If the gases are ideal and are at the same temperature and pressure, what is the rate of entropy increase in kJ/h K as a result of the process?

7.32 The molar volume of a binary liquid mixture is given by

$$90 \;\square\; 10^{-3}x_1 + 50 \;\square\; 10^{-3}x_2 + x_1x_2(6 \;\square\; 10^{-3}x_1 + 9 \;\square\; 10^{-3}x_2)$$

Obtain expressions for $\overline{V_1}$ and $\overline{V_2}$ and show that they satisfy Gibbs–Duhem equations.

7.33 Water at a rate of 54 □ 10^3 kg/h and $Cu(NO_3)_2$ ◇ $6H_2O$ at a rate of 64.8 □ 10^3 kg/h are mixed together in a tank. The solution is then passed through a heat exchanger to bring the temperature to 298 K, same as the temperature of the components before mixing. Determine the rate of heat transfer in the exchanger. The following data are available. Heat of formation at 298

K of $Cu(NO_3)_2$ is –302.9 kJ and that of $Cu(NO_3)_2$ ◇ $6H_2O$ is –2110.8 kJ. The heat of solution of $Cu(NO_3)_2$ ◇ nH_2O at 298 K is – 47.84 kJ per mol salt and is independent of *n*.

7.34 If pure liquid H_2SO_4 is added to pure water both at 300 K to form a 20 per cent (weight) solution, what is the final temperature of the solution? The heat of solution of sulphuric acid in water is H_2SO_4 (21.8 H_2O) = –70 □ 10^3 kJ/kmol of sulphuric acid. Standard heat of formation of water = – 286 kJ/mol. Mean heat capacity of sulphuric acid may be taken from *Chemical Engineer's Handbook.*

7.35 LiCl □ H_2O (c) is dissolved isothermally in enough water to form a solution containing 5 mol of water per mole of LiCl. What is the heat effect? The following enthalpies of formation are given:

LiCl (c) = – 409.05 kJ, LiCl◇H_2O (c) = – 713.054 kJ

LiCl ($5H_2O$) = – 437.232 kJ, H_2O (l) = – 286.03 kJ

7.36 Calculate the heat effects when 1.0 kmol of water is added to a solution containing 1.0 kmol sulphuric acid and 3.0 kmol of water. The process is isothermal and occurs at 298 K. *Data:* Heat of mixing for H_2SO_4 ($3H_2O$) = – 49,000 kJ per kmol H_2SO_4. Heat of mixing for H_2SO_4 ($4H_2O$) = – 54,100 kJ per kmol H_2SO_4.

7.37 A single effect evaporator is used to concentrate a 15% (weight) solution of LiCl in water to 40%. The feed enters the evaporator at 298 K at the rate of 2 kg/s. The normal boiling point of a 40% LiCl solution is 405 K and its specific heat is 2.72 kJ/kg K. For what heat transfer rate in kJ/h, should the evaporator be designed? The heat of solution of LiCl in water per mole of LiC at 298 K are:

DH_S for LiCl(13.35 H_2O) = – 33.8 kJ, for LiCl (3.53 H_2O) = – 23.26 kJ. Enthalpy of superheated steam at 405 K, 1 bar = 2740.3 kJ/kg. Enthalpy of water at 298 K = 104.8 kJ/kg Molecular weight of LiCl = 42.39.

7.38 The excess Gibbs free energy of solutions of methyl cyclohexane (MCH) and tetrahydrofuran (THF) at 303 K are correlated as

$$G^E = RTx(1 - x)[0.4587 - 0.1077(2x - 1) + 0.0191(2x - 1)^2]$$

where *x* is the mole fraction of methyl cyclohexane. Calculate the Gibbs free energy change on mixing when 1 mol MCH and 3 mol THF are mixed.

7.39 Derive the relation between the excess Gibbs free energy of a solution based on the Lewis–Randall rule and that based on the asymmetric treatment (Lewis–Randall rule for solvent and Henry's law for solute) of solution ideality.

7.40 The excess enthalpy of a solution is given by

$$H^E = x_1x_2(40x_1 + 20x_2) \text{ J/mol}$$

Determine expressions for $\overline{H}_1^E$ and $\overline{H}_2^E$ as functions of x_1.

7.41 Given that

$$M^E = x_1x_2[A + B(x_1 - x_2) + C(x_1 - x_2)^2]$$

derive expressions for $\overline{M}_1^E$ and $\overline{M}_2^E$. What are the limiting values for $\overline{M}_1^E$ and $\overline{M}_2^E$ and M^E/x_1x_2 as x_1 □ 0 and x_1 □ 1?

7.42 The excess Gibbs free energy is given by

$$G^E/RT = -\,3x_1x_2(0.4x_1 + 0.5x_2)$$

Find expressions for $\ln g_1$ and $\ln g_2$.

7.43 Do the following equations satisfy Gibbs–Duhem equations?

$$\ln \gamma_1 = Ax_2^2 + Bx_2^2\,(3x_1 - x_2), \qquad \ln \gamma_2 = Ax_1^2 + Bx_1^2(x_1 - 3x_2)$$

Find expressions for G^E/RT.

7.44 The excess volume (m^3/kmol) of a binary liquid mixture is given by

$$V^E = 0.01\, x_1x_2(3x_1 + 5x_2)$$

at 298 K and 1 bar. Determine $\overline{V}_1$ and $\overline{V}_2$ for an equimolar mixture of components 1 and 2 given that $V_1 = 0.12$ m^3/kmol and $V_2 = 0.15$ m^3/kmol.

8

Phase Equilibria

A system is said to be in a state of *equilibrium* if it shows no tendency to depart from that state either by energy transfer through the mechanism of heat and work or by mass transfer across the phase boundary. Since a change of state is caused by a driving force, we can describe a system at equilibrium as one in which there are no driving forces for energy or mass transfer. That is, for a system in a state of equilibrium, all forces are in exact balance. It may be noted here that the state of equilibrium is different from a steady state condition. Under *steady state* there exist net fluxes for material or energy transfer across a plane surface placed anywhere in the system. Under equilibrium the net flux is zero.

Transfer of material or energy across phase boundaries occurs till equilibrium is established between the phases. In our daily experience, we come across a number of processes in which materials are transferred from one phase to another. During breathing we take oxygen from the air through the lungs and dissolve it in the blood. During the preparation of tea or coffee we extract the soluble components in the powder into boiling water. Dilute aqueous solution of alcohol is concentrated by distillation in which a vapour rich in alcohol is produced from the boiling solution. The phase equilibrium thermodynamics is of fundamental importance in many branches of science, whether physical or biological. It is particularly important in chemical engineering, because majority of manufacturing processes involve transfer of mass between phases either during the preparation of the raw materials or during the purification of the finished products. Gas–liquid absorption, distillation, liquid–liquid extraction, leaching, adsorption, etc., are some of the important separation techniques employing mass transfer between phases. In addition to these, many industrial chemical reactions are carried out under conditions where more than one phase exist. A good foundation in phase equilibrium thermodynamics is essential for the analysis and design of these processes.

In this chapter due emphasis is given to the development of the relationship between the various properties of the system such as pressure, temperature and composition when a state of equilibrium is attained between the various phases constituting the system. The temperature–pressure-composition relationships in multiphase system at equilibrium form the basis for the quantitative treatment of all separation processes. The two types of phase equilibrium problems that are frequently encountered are:

1. The determination of composition of phases which exist in equilibrium at a known temperature and pressure
2. The determination of conditions of temperature and pressure required to obtain equilibrium between phases of specified compositions.

The present chapter tries to provide solutions to these problems.

8.1 CRITERIA OF PHASE EQUILIBRIUM

Consider a homogeneous closed system in a state of internal equilibrium. The criteria of internal thermal and mechanical equilibrium are that the temperature and pressure be uniform throughout the system. For a system to be in thermodynamic equilibrium, additional criteria are to be satisfied. Consider a closed system consisting of two phases of a binary solution, for example, the vapour and liquid phases of an alcohol–water solution. The requirement of uniformity of temperature and pressure does not preclude the possibility of transfer of mass between the phases. If the system is in thermodynamic equilibrium, mass transfer also should not occur. It means that additional criteria are necessary for establishing the state of thermodynamic equilibrium.

A system can interact with the surroundings reversibly or irreversibly. In the *reversible process,* a state of equilibrium is maintained throughout the process. So it can be treated as a process connecting a series of equilibrium states. The driving forces are only infinitesimal in magnitude and the process can be reversed by an infinitesimal change (either increase or decrease) in the potential for the system or the surroundings. The *irreversible process,* in contrast, occurs with a finite driving force, and it can not be reversed by infinitesimal changes in the external conditions. However, all irreversible processes tend towards a state of equilibrium. We have shown in Chapter 4 under ‘Clausius inequality’,

$$dS \geq \frac{dQ}{T} \tag{4.44}$$

In this equation, the equality sign refers to a reversible process which can be treated as a succession of equilibrium states and the inequality refers to the entropy change for a spontaneous process whose ultimate result would be an equilibrium state. The first law of thermodynamics expressed mathematically by Eq. (2.5) can be rewritten as

$$dQ = dU + dW \qquad (8.1)$$

Substituting Eq. (8.1) into Eq. (4.44), we get

$$T\,dS \geq dU + dW$$

$$dU \square T\,dS - dW \qquad (8.2)$$

dW in Eq. (8.2) may be replaced by $P\,dV$ so that

$$dU \square T\,dS - P\,dV \qquad (8.3)$$

Equation (8.3) is valid for cases where external pressure is the only force and the work is, therefore, the work of expansion only. By this, we exclude other effects like those due to gravitational and electromagnetic fields and surface and tensile forces. Equation (8.3) can be treated as the combined statement of the first and second law of thermodynamics applied to a closed system which interact with its surroundings through heat transfer and work of volume displacement. This equation is utilised for deriving the criteria of equilibrium under various sets of constraints, each set corresponding to a physically realistic or commonly encountered situation. These different criteria are discussed now.

Constant U and V. An isolated system does not exchange mass, heat or work with the surroundings. In Eq. (8.1), $dQ = 0$, $dW = 0$ and hence $dU = 0$. A well-insulated vessel of constant volume would closely approximate this behaviour. Thus in Eq. (8.3) $dU = 0$ and $dV = 0$ so that

$$\boxed{dS_{U,V} \geq 0} \tag{8.4}$$

The entropy is constant in a reversible process and increases in a spontaneous process occurring in a system of constant U and V. Since an irreversible process leads the system to an equilibrium state, the entropy is maximum at equilibrium when no further spontaneous processes are possible.

Constant T and V. Helmholtz free energy is defined by Eq. (6.1).

$$A = U - TS$$

Rearranging Eq. (6.1), we get

$$U = A + TS$$

$$dU = dA + T\,dS + S\,dT$$

Substitute this result in Eq. (8.3) and rearrange the resulting expression to the following form

$$dA \,\square\, -P\,dV - S\,dT \qquad (8.5)$$

Under the restriction of constant temperature and volume, the latter implying no work, the equation simplifies to

$$\boxed{dA_{T,V} \le 0} \qquad (8.6)$$

Equation (8.6) means that the spontaneous process occurring at constant temperature and volume is accompanied by a decrease in the work function and consequently, in a state of thermodynamic equilibrium under these conditions the Helmholtz free energy or the work function is a minimum.

Constant P and T. Equation (6.6) defines Gibbs free energy as

$$G = H - TS$$

Since $H = U + PV$ we can write Eq. (6.6) as

$$G = U + PV - TS$$

Taking the differentials

$$dG = dU + P\,dV + V\,dP - T\,dS - S\,dT$$

rearranging these as

$$dU = dG - P\,dV - V\,dP + T\,dS + S\,dT$$

and combining this result with Eq. (8.3), we obtain

$$dG \,\square\, V\,dP - S\,dT \qquad (8.7)$$

At constant temperature and pressure, Eq. (8.7) reduces to

$$\boxed{dG_{T,P} \le 0} \qquad (8.8)$$

Equation (8.8) means that the free energy either decreases or remains unaltered depending upon whether the process is spontaneous or reversible. It implies that for a system in equilibrium at a given temperature and pressure the free energy must be minimum.

Since most chemical reactions and many physical changes are carried out under conditions of constant temperature and pressure, Eq. (8.8) is the commonly used criterion of thermodynamic equilibrium. It also provides a very convenient and simple test for the feasibility of a proposed process. No process is possible which results in an increase in the Gibbs free energy of the system, because according to Eq. (8.8) the Gibbs free energy always decreases in a spontaneous process and in the limit of the reversible process, the free energy doesn't change at all.

In the equilibrium state, differential variations can occur in the system at constant temperature and pressure without producing any change in the Gibbs function. Thus, the equality in Eq. (8.8) can be used as the general criterion of equilibrium or as a thermodynamic statement that characterises the equilibrium state.

$$dG = 0 \text{ (at constant } T \text{ and } P\text{)} \qquad (8.9)$$

To apply this criterion for phase equilibrium problems we need formulate an expression for dG as function of the number of moles of the components in various phases and set it equal to zero. This equation along with the mass conservation equations provides the solutions to phase equilibrium problems.

8.2 CRITERION OF STABILITY

It can be shown that the criterion of equilibrium [Eq. (8.8)] can be used to formulate the criterion of stability for a binary mixture. When two pure liquids at a given temperature T and pressure P are mixed together, the resulting mixture should have a lower free energy at the same temperature and pressure. This is because the mixed state is an equilibrium state or stable state compared to the unmixed state. The molar free energy of the mixture is thus less than the sum of the molar free energies of the constituents for all possible concentrations. That is,

$$G - \Sigma x_i G_i < 0 \qquad (8.10)$$

The left-hand side in the above equation is the free energy change on mixing ΔG. Therefore,

$$\Delta G < 0 \qquad (8.11)$$

When the free energy change on mixing ΔG is plotted against x_1 —the mole fraction of constituent 1 in the binary mixture—the resulting curve is one of the two types shown in Fig. 8.1. The upper curve is for a binary mixture, which is miscible for the entire concentration range. Assume that the points A and B represent two binary mixtures of composition x_A and x_B respectively. Points on the dotted line AB represent the composition as well as ΔG of the mixture of two phases obtained when solutions represented by the points A and B are mixed together. Since the line AB is above the solid curve that represents the free energy of the miscible solution, the free energy of the mixture in the miscible state is the minimum and the mixture exists as a single homogeneous phase. However, this argument is not valid for the lower curve in Fig. 8.1. The dotted line MN represents the free energy of the two-phase mixture obtained when two binary mixtures of composition x_M and x_N, respectively, are mixed together. It lies below the ΔG curve of the homogeneous solution. Any point on the line MN represents the ΔG that would result for systems consisting of two phases of mole fraction x_M and x_N. Thus, when the system moves from the solid curve to the dotted line MN, there is a decrease in the free energy. That is, the system attains stability when it moves from a homogeneous to a heterogeneous state. Therefore, for mixtures of composition between points M and N, the equilibrium or stable state consists of two immiscible phases. We see that the second derivative of ΔG with respect to x_1 is always positive for stable liquid phase and if it becomes zero or negative, phase separation occurs. The criterion of stability is that *at constant temperature and pressure the free energy change on mixing* ΔG*, its first and second derivatives are all continuous functions of the concentration x and*

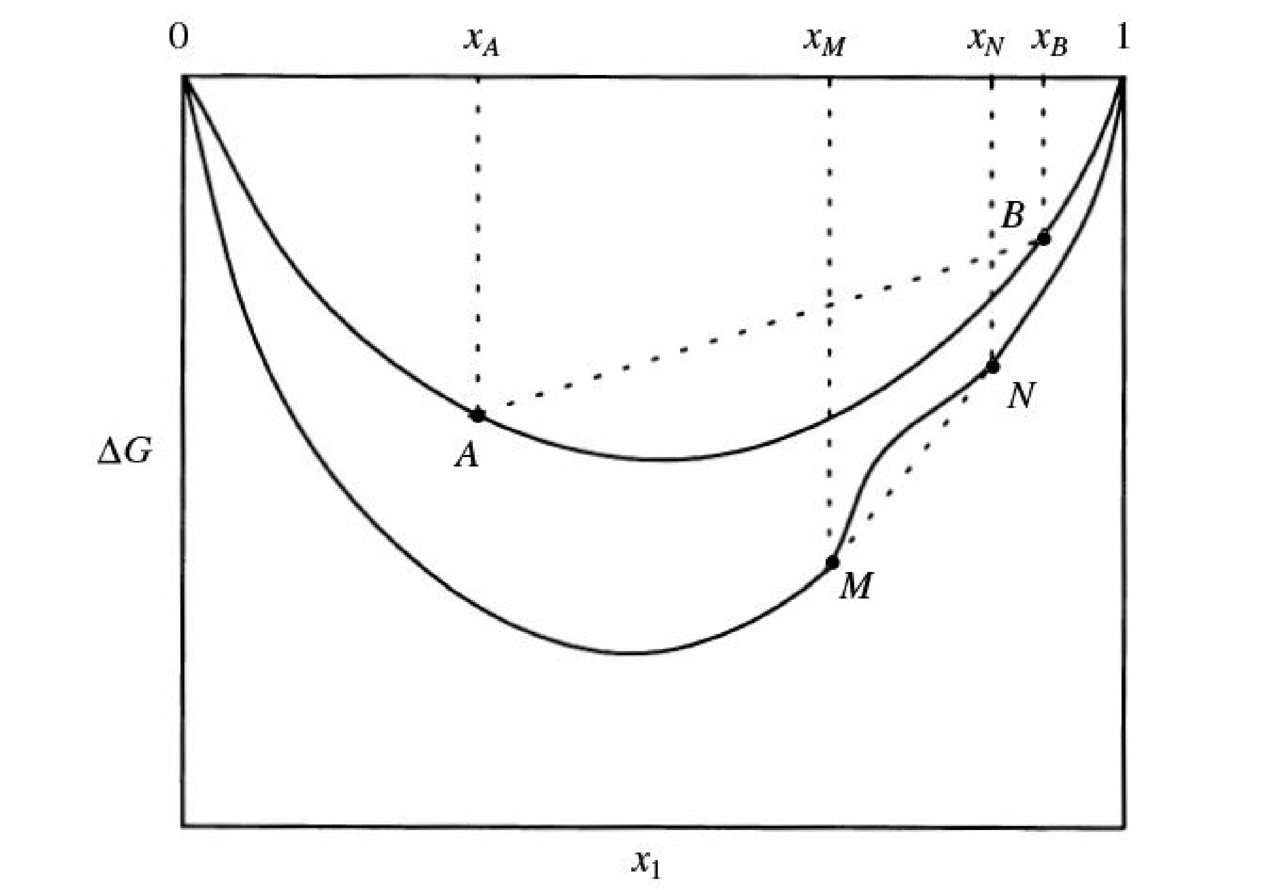


Fig. 8.1 Free energy of mixing plotted as a function of composition.

$$\frac{d^2\Delta G}{dx_1^2} > 0 \qquad \text{(at constant } T \text{ and } P) \tag{8.12}$$

***EXAMPLE* 8.1** Show that for a stable liquid phase, the fugacity of each component in a binary mixture always increases with increase in concentration at constant temperature and pressure.

Solution The excess free energy of mixing was defined in Chapter 7. It was shown there that

$$\Delta G^E = \Delta G - \Delta G^{\text{id}}$$

$$\Delta G^E = G^E = RT\,\Sigma\, x_i \ln \gamma_i$$

$$\Delta G^{\text{id}} = RT\,\Sigma\, x_i \ln x_i$$

Combining these three equations we find that

$$\Delta G = RT\,\Sigma\, x_i \ln(\gamma_i x_i)$$

$$\frac{\Delta G}{RT} = \Sigma\, x_i \ln(\gamma_i x_i) = x_1 \ln(\gamma_1 x_1) + x_2 \ln(\gamma_2 x_2)$$

Differentiating this with respect to x_1,

$$\frac{d}{dx_1}\left(\frac{\Delta G}{RT}\right)=\frac{d}{dx_1}\,[x_1\,\ln(\gamma_1 x_1)+x_2\,\ln(\gamma_2 x_2)]=\ln(x_1\gamma_1)-\ln(x_2\gamma_2)+x_1\,\frac{\partial\ln\gamma_1}{\partial x_1}+x_2\,\frac{\partial\ln\gamma_2}{\partial x_1}\quad(8.13)$$

By Gibbs–Duhem equations,

$$x_1\frac{\partial\ln\gamma_1}{\partial x_1}=x_2\frac{\partial\ln\gamma_2}{\partial x_2}=-x_2\frac{\partial\ln\gamma_2}{\partial x_1}$$

When this is substituted into Eq. (8.13), we get

$$\frac{d}{dx_1}\left(\frac{\Delta G}{RT}\right)=\ln(\gamma_1 x_1)-\ln(\gamma_2 x_2)\quad(8.14)$$

Activity coefficients are defined as [see Eq. (7.77)],

$$\gamma_1=\frac{\bar{f}_1}{x_1 f_1},\qquad \gamma_2=\frac{\bar{f}_2}{x_2 f_2}$$

where $\bar{f}_1$ and $\bar{f}_2$ are the fugacities of components in solution and f_1 and f_2 are the fugacities of pure components. Substituting these into Eq. (8.14), we get

$$\frac{d}{dx_1}\left(\frac{\Delta G}{RT}\right)=\ln\frac{\bar{f}_1}{f_1}-\ln\frac{\bar{f}_2}{f_2}\quad(8.15)$$

Differentiating Eq. (8.14) again with respect to x_1 and noting that fugacities of pure components are independent of concentration, we get

$$\frac{d^2}{dx_1^2}\left(\frac{\Delta G}{RT}\right) = \frac{d}{dx_1}\ln \bar{f}_1 - \frac{d}{dx_1}\ln \bar{f}_2 \tag{8.16}$$

According to Gibbs–Duhem equations, the fugacities in a binary mixture are interrelated as indicated below.

$$x_1 \frac{\partial \ln \bar{f}_1}{\partial x_1} = x_2 \frac{\partial \ln \bar{f}_2}{\partial x_2} = -\, x_2 \frac{\partial \ln \bar{f}_2}{\partial x_1}$$

Therefore,

$$\frac{d}{dx_1}\ln \bar{f}_2 = -\frac{x_1}{x_2}\frac{d \ln \bar{f}_1}{dx_1}$$

Using this equation, Eq. (8.16) can be written as

$$\frac{d^2}{dx_1^2}\left(\frac{\Delta G}{RT}\right) = \frac{d}{dx_1}\ln \bar{f}_1 + \frac{x_1}{x_2}\frac{d}{dx_1}\ln \bar{f}_1 = \frac{1}{x_2}\frac{d}{dx_1}\ln \bar{f}_1$$

$$\frac{d^2 \Delta G}{dx_1^2} = \frac{RT}{x_2}\frac{d}{dx_1}\ln \bar{f}_1$$

Equation (8.12) reveals that the left-hand side of the above equation is greater than zero. Therefore,

$$\frac{RT}{x_2}\frac{d}{dx_1}\ln \bar{f}_1 > 0$$

$$\frac{d}{dx_1}\ln \bar{f}_1 > 0$$

In a similar way, we can show that

$$\frac{d}{dx_2}\ln \bar{f}_2 > 0$$

The last two equations imply that fugacity of components in a stable solution always increase with increase in concentration.

8.3 PHASE EQUILIBRIA IN SINGLE-COMPONENT SYSTEMS

Consider the thermodynamic equilibrium in a system consisting of two or more phases of a single substance. Though the individual phases can exchange mass with each other and are therefore open, the system as a whole is closed. As an example, we can treat the equilibrium between vapour and liquid phases of a single substance at a constant temperature and pressure. Applying the criterion of equilibrium [see Eqs. (8.8) and (8.9)] to this closed system,

$$dG = 0$$

$$dG^a + dG^b = 0 \qquad (8.17)$$

where the dG^a and dG^b are the changes in free energies of the phases '*a*' and '*b*' respectively. Since each phase is open, the change in its free energy may be due to the changes in temperature, pressure and the number of moles of the components that constitute the phase. Equation (7.35) expresses this mathematically as

$$dG = V\,dP - S\,dT + \Sigma \overline{G}_i\,dn_i$$

Applying this equation to the phases '*a*' and '*b*', we can write

$$dG^a = V^a\,dP^a - S^a\,dT^a + G^a\,dn^a,\ dG^b = V^b\,dP^b - S^b\,dT^b + G^b\,dn^b$$

At constant temperature and pressure,

$$dG^a = G^a\,dn^a,\ dG^b = G^b\,dn^b \qquad (8.18)$$

As the system as a whole is closed,

$$dn^a + dn^b = 0, \text{ or } dn^a = -\,dn^b \qquad (8.19)$$

Substituting Eqs. (8.18) and (8.19) into Eq. (8.17), we get

$$(G^a - G^b)dn^a = 0 \qquad (8.20)$$

Equation (8.20) means that

$$G^a = G^b \qquad (8.21)$$

Whenever two phases of the same substance are in equilibrium under a given temperature and pressure, the molar free energy is the same in each phase.

We can verify the above result easily by considering the example of boiling water. As long as both phases are present, an appreciable transfer of material from one phase to the other at constant temperature and pressure would not disturb the equilibrium. The change in the free energy for the equilibrium process (or reversible process) of evaporating a mole of liquid water is

$$\Delta G = \Delta H - T\Delta S \qquad (8.22)$$

As pressure is constant, $\Delta H = Q$, and the process being reversible, $Q = T\Delta S$. Equation (8.22) gives

$$\Delta G = 0$$

For vaporisation of 1 mol of liquid, $\Delta G = G^V - G^L$, where G^L and G^V are the molar free energy of water in the liquid and vapour states at the given T and P. Therefore, under equilibrium

$$G^V = G^L \qquad (8.23)$$

As the molar free energies are related to the fugacity of the substance by

$$G = RT \ln f + C$$

Equation (8.21) can be expressed in terms of fugacity of the phases.

$$f^a = f^b \qquad (8.24)$$

where f^a and f^b are the fugacities in phases a and b respectively. It is convenient to work with fugacities of substances as these have absolute values in contrast to free energies, which are usually expressed as differences.

The above conclusions can be extended to three phases, which is the maximum number of phases that can coexist under equilibrium in a system of one component.

***EXAMPLE* 8.2** Using the criterion of phase equilibrium, show that the change in entropy during phase changes can be calculated from the latent heat of phase change and the absolute temperature as $DS = DH/T$.

Solution Suppose that two phases *a* and *b* are in equilibrium. Using the definition of free energy [Eq. (6.6)],

$$G^a = H^a - TS^a, \ G^b = H^b - TS^b$$

Here, *H* and *S* denote the enthalpy and entropy of the substance. Substituting these results in Eq. (8.21),

$$H^a - TS^a = H^b - TS^b$$

This equation can be rearranged as,

$$S^b - S^a = \frac{H^b - H^a}{T}$$

The left-hand side of the above equation is the entropy change accompanying the phase change of one mole of the substance (DS), and the numerator on the right-hand side represents the enthalpy change for the phase change of one mole of the substance or the latent heat of phase change (DH). That is,

$$\Delta S = \frac{\Delta H}{T}$$

***EXAMPLE* 8.3** Deduce the Clapeyron equation using the criterion of equilibrium, Eq. (8.9).

Solution In Chapter 6 we have derived the Clapeyron equation, Eq. (6.25), using Maxwell’s relations.

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

The criterion of equilibrium provides an alternate route for its derivation. Consider any two phases *a* and *b* of the same substance under equilibrium. Since G^a and G^b are both functions of temperature and pressure, and these functional relationships are different for different phases, the two phases can coexist only at such values of the temperature and pressure that $G^a = G^b$. If the temperature and pressure are altered infinitesimally without disturbing the equilibrium, the change in the free energy must be the same in each phase.

$$dG^a = dG^b \qquad (8.25)$$

In a phase change there is no work other than the work of expansion, so that

$$dG = V\,dP - S\,dT$$

Using this in Eq. (8.25),

$$V^a\,dP - S^a\,dT = V^b\,dP - S^b\,dT \qquad (8.26)$$

V and S are the molar volume and molar entropy of the fluid with the superscript representing the phase for which the properties correspond to. Equation (8.26) can be rearranged to the following form.

$$\frac{dP}{dT} = \frac{S^a - S^b}{V^a - V^b} = \frac{\Delta S}{\Delta V} \tag{8.27}$$

In the above equation, ΔS and ΔV are the entropy change and volume change respectively, accompanying the phase change. Since the transition between phases is occurring reversibly, the entropy change can be evaluated if the latent heat of phase change is known.

$$\Delta S = \frac{\Delta H}{T} \tag{8.28}$$

where ΔH is the latent heat for the phase change. Substituting Eq. (8.28) into Eq. (8.27) the Clapeyron equation results.

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{8.29}$$

This relation gives the increase in pressure that is necessary to maintain the equilibrium between phases for a pure substance when the temperature is increased. By using the following simplifications Eq. (8.29) can be modified to yield the Clausius–Clapeyron equation applicable for vapour–liquid equilibria.

1. The latent heat of vaporisation is constant and independent of temperature.
2. The molar volume of liquid is negligible compared to that of vapour.
3. The vapour behaves as ideal gas.

The Clausius–Clapeyron equation was derived [Eq. (6.28)] in Chapter 6 and is reproduced below.

$$\ln \frac{P_2^S}{P_1^S} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8.30}$$

where P_1^S and P_2^S are the vapour pressures at temperatures T_1 and T_2 respectively.

8.4 PHASE EQUILIBRIA IN MULTICOMPONENT SYSTEMS

The criterion of equal molar free energy [Eq. (8.21)] is applicable for equilibrium between phases of a single component. This criterion needs modification when dealing with heterogeneous multicomponent systems. A heterogeneous closed system is made up of two or more phases with each phase behaving as open system within the overall closed system. Because each phase consists of two or more components in different proportions, it is necessary that the criterion of multicomponent phase equilibrium be developed in terms of partial molar free energies or the chemical potentials of the components. The criteria of thermal and mechanical equilibrium are, as discussed earlier, the uniformity of temperature and pressure. For the system to be in equilibrium with respect to mass transfer, the driving force for mass transfer—the chemical potential—must have uniform values for each component in all phases. This criterion of internal equilibrium is derived in the following paragraphs.

Consider a heterogeneous system consisting of π phases indicated by the letters, α, β, γ, ..., π. The various components that constitute the system are 1, 2, 3, ..., C. The symbol μ_i^κ denotes the chemical potential of component 'i' in phase 'κ'. Suppose that small amounts of various components are transferred from one phase to another, the system being in equilibrium and the temperature and pressure kept constant. Since the system as a whole is closed, the proposed transfer should satisfy the following criterion.

$$dG = 0 \text{ (at constant } T \text{ and } P) \qquad (8.9)$$

The free energy change in a multicomponent system is given by Eq. (7.35) as

$$dG = V\,dP - S\,dT + \Sigma\,\mu_i\,dn_i$$

At constant temperature and pressure, the above equation becomes

$$dG = \Sigma\,\mu_i\,dn_i$$

Substitute this into Eq. (8.9) to get

$$\Sigma\,\mu_i\,dn_i = 0 \qquad (8.31)$$

Let dn_i^κ denote the increase in the number of moles of component i in phase κ. Equation (8.31) may then be written as

$$\sum_{i=1}^{C} \sum_{\kappa=\alpha}^{\pi} \mu_i^\kappa\,dn_i^\kappa = 0$$

Expanding this equation, we get

$$\begin{aligned}
&\mu_1^\alpha\,dn_1^\alpha + \mu_1^\beta\,dn_1^\beta + \ldots + \mu_1^\pi\,dn_1^\pi + \\
&\mu_2^\alpha\,dn_2^\alpha + \mu_2^\beta\,dn_2^\beta + \ldots + \mu_2^\pi\,dn_2^\pi + \\
&\quad\vdots \qquad\quad \vdots \qquad\qquad\quad \vdots \\
&\mu_C^\alpha\,dn_C^\alpha + \mu_C^\beta\,dn_C^\beta + \ldots + \mu_C^\pi\,dn_C^\pi = 0
\end{aligned} \qquad (8.32)$$

Since the system as a whole is closed, it should satisfy the mass conservation equation given below.

$$\begin{aligned}
&dn_1^\alpha + dn_1^\beta + \ldots + dn_1^\pi = 0 \\
&dn_2^\alpha + dn_2^\beta + \ldots + dn_2^\pi = 0 \\
&\quad\vdots \qquad \vdots \qquad\qquad \vdots \\
&dn_C^\alpha + dn_C^\beta + \ldots + dn_C^\pi = 0
\end{aligned} \qquad (8.33)$$

The variations in the number of moles dn_i are independent of each other. However, they are subject to the constraints imposed by Eq. (8.33). For all possible variations dn_i^κ, Eq. (8.32) is to be satisfied. This is possible only if

$$\begin{aligned}\mu_1^\alpha &= \mu_1^\beta = \ldots = \mu_1^\pi \\ \mu_2^\alpha &= \mu_2^\beta = \ldots = \mu_2^\pi \\ \vdots \quad & \quad \vdots \qquad\quad \vdots \\ \mu_C^\alpha &= \mu_C^\beta = \ldots = \mu_C^\pi\end{aligned} \tag{8.34}$$

Equation (8.34) means that *when a system consisting of several components distributed between various phases is in thermodynamic equilibrium at a definite temperature and pressure, the chemical potential of each component is the same in all the phases*. If they are different, the component for which such a difference exists will show a tendency to pass from the region of higher to the region of lower chemical potential. Thus the equality of chemical potential along with the requirement of uniformity of temperature and pressure serves as the general criterion of thermodynamic equilibrium in a closed heterogeneous multicomponent system. In short, we can write

$$\boxed{\begin{array}{ll} T = \text{constant}; & P = \text{constant} \\ \mu_i^\alpha = \mu_i^\beta = \ldots = \mu_i^\pi & \text{for} \quad i = 1, 2, 3, \ldots, C \end{array}} \tag{8.35}$$

Since the chemical potential is related to fugacity as

$$\mu_i = RT \ln \bar{f}_i + C$$

where C is a constant, an alternative and equally general criterion of equilibrium can be written in terms of fugacities as

$$\boxed{\begin{array}{ll} T = \text{constant}; & P = \text{constant} \\ \bar{f}_i^\alpha = \bar{f}_i^\beta = \ldots = \bar{f}_i^\pi & \text{for} \quad i = 1, 2, 3, \ldots, C \end{array}} \tag{8.36}$$

Fugacity is a more useful property than chemical potential for defining equilibrium since it can be expressed in absolute values, whereas chemical potential can be expressed only relative to some arbitrary reference state. Equation (8.36) is therefore widely used for the solution of phase equilibrium problems.

***EXAMPLE* 8.4** Using the criterion of phase equilibrium show that the osmotic pressure over an ideal solution can be evaluated as

$$P_{\text{osmotic}} = \frac{RTx_A}{V_B}$$

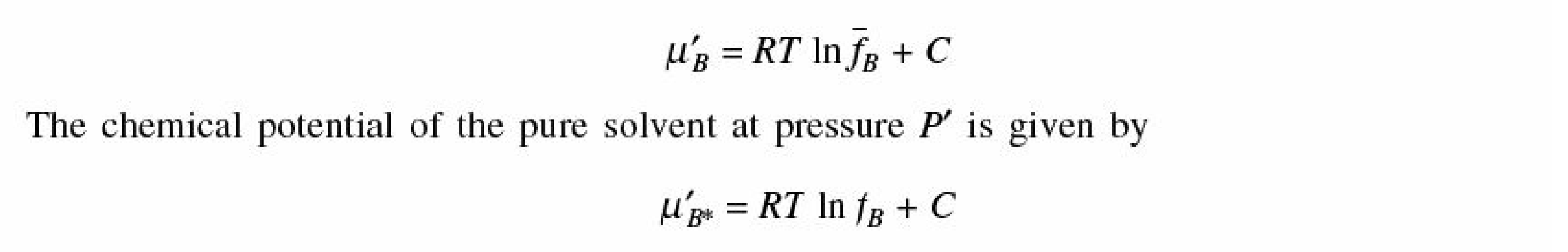
where x_A is the mole fraction of solute and V_B is the molar volume of the solvent.

Solution Consider a vessel which is divided into two compartments by a semi-permeable membrane. Pure solvent (say, water) is taken in one of the compartments and a solution (say, sucrose in water) is taken in the other. Let T be the temperatures on both sides of the membrane and P be the pressure. While the membrane is impermeable to the flow of the solute, it permits the flow of solvent into the solution. This phenomenon of a solvent diffusing through a membrane which is permeable to it, but is impermeable to the solute, is known as *osmosis*.

Osmosis is caused by the difference in the chemical potentials of the solvent on the two sides of the membrane. At a given pressure, the chemical potential of a pure solvent is greater than that of the solvent in the solution. By increasing the pressure at the solution side of the membrane, the chemical potential of the solvent in the solution can be increased. When the pressure is increased to P' keeping the temperature constant, the chemical potential of the solvent in the solution would become equal to that of the pure solvent at pressure P, and the diffusion would stop. If the pressure is increased above P', the direction of diffusion would be reversed. In that event, the solvent would diffuse from the solution to the pure solvent. This process is known as *reverse osmosis*. The excess pressure $P' - P$ to be applied over the solution at constant temperature to arrest the process of osmosis is known as the *osmotic pressure*. Thus, osmotic pressure is

$$P_{\text{osmotic}} = P' - P$$

Let the mole fraction of the solutes constituting the solution be represented by x_A and the mole fraction of the solvent be represented by x_B. Let μ'_B denotes the chemical potential of the solvent at pressure P'. Equation (7.51) relates the chemical potential of a component in a solution to its fugacity. Thus

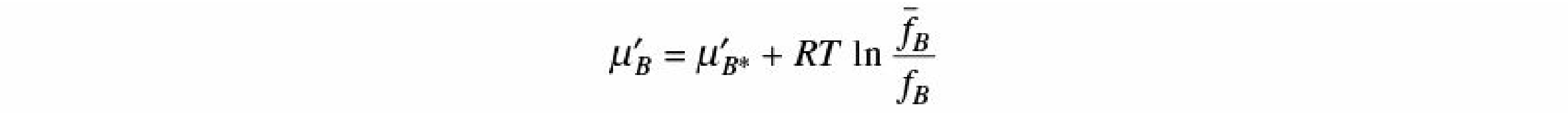


$$\mu'_B = RT \ln \bar{f}_B + C$$

The chemical potential of the pure solvent at pressure P' is given by

$$\mu'_{B*} = RT \ln f_B + C$$

Combining the preceding two equations, we get



$$\mu'_B = \mu'_{B*} + RT \ln \frac{\bar{f}_B}{f_B}$$

In this equation, μ'_{B*} is the chemical potential of pure solvent at pressure P', f_B is its fugacity and $\bar{f}_B$ is its fugacity in the solution. Since the solution is ideal, the above equation may be simplified utilising the Lewis–Randall rule which relates f_B and that $\bar{f}_B$ as $\bar{f}_B = x_B.f_B$. Now we get the following result for the chemical potential of the solvent in the solution at pressure P'.

$$\mu'_B = \mu'_{B*} + RT \ln x_B$$

Under equilibrium this should be equal to the chemical potential of the solvent in the pure state at pressure P which may be denoted by μ_{B*}. That is

$$\mu'_{B*} + RT \ln x_B = \mu_{B*}$$

Rearranging this, we obtain

$$\mu'_{B*} - \mu_{B*} = -RT \ln x_B$$

The left-hand-side of this equation involves the chemical potentials of pure B at pressures P and P'. Since the temperature is constant, we can use Eq. (6.18) to replace the chemical potential in terms of the pressure and volume. Equation (6.18) leads to $dG = d\mu = V\,dP$. Thus

$$\int_P^{P'} V\,dP = -RT \ln x_B$$

Since volume of a liquid is not affected by change in pressure, the integral in this equation can be easily determined in terms of the molar volume V_B. Thus

$$V_B\,(P\square - P) = -RT \ln x_B$$

Noting the definition of the osmotic pressure, the preceding equation may be written as

$$P_{\text{osmotic}} = -\frac{RT \ln x_B}{V_B} = -\frac{RT \ln (1 - x_A)}{V_B}$$

For small values of x_A, we can use the approximation $\ln (1 - x_A) = -x_A$. Thus we get

$$P_{\text{osmotic}} = \frac{RT\,x_A}{V_B}$$

8.5 PHASE RULE FOR NON-REACTING SYSTEMS

The essence of a phase equilibrium problem is to express quantitatively the relationship between the variables that describe the state of equilibrium of two or more homogeneous phases, which are free to interchange energy and matter. For a homogeneous phase at equilibrium the intensive properties are the same everywhere. In phase equilibrium studies, the intensive properties of interest are pressure, temperature, density and composition.

The phase rule allows us to determine the *number of degrees of freedom*, denoted by F, which are the number of independent variables that must be arbitrarily fixed so as to establish uniquely the intensive state of the system. The phase rule was developed by J. Willard Gibbs (1875). The commonly used phase rule variables are the temperature, pressure and composition. By specifying these, the intensive state of the system at equilibrium is uniquely established. However, all these variables may not be independent. The phase rule gives the number of variables from this set, which when arbitrarily specified, would establish the remaining variables at fixed values. Thus, by degrees of freedom, we mean the number of intensive properties that can be varied without changing the number of phases or the number of components in any phase.

Consider a homogeneous phase of a pure substance like water contained in a beaker, or carbon dioxide gas confined in a cylinder. The state of the system is determined whenever two properties are set at definite values. Here, the number of degrees of freedom is two. This number is not necessarily two for more complex systems. For example, a mixture of steam and liquid water in equilibrium at 101.3 kPa can exist only at 373.15 K. It is impossible to change the temperature without also changing the pressure, if the liquid and vapour are to continue to exist in equilibrium. The number of degrees of freedom in this case is only one, for we can exercise independent control over only one variable, either the temperature or the pressure, and not both. It is evident that there is a connection between the number of degrees of freedom (F), the number of phases in equilibrium (p), and the number of components constituting the system (C). The phase rule gives the relationship between these three quantities. It states that

$$F = C - \mathsf{p} + 2 \qquad (8.37)$$

The phase rule can be derived using the equilibrium criteria Eq. (8.35). Consider a heterogeneous system consisting of C components distributed between p phases. The composition of a phase containing C components is determined by specifying $C - 1$ concentration terms. This is because if the mole fractions of all but one of the components in a mixture are known, the mole fraction of the remaining component is the difference between one and the sum of the $C - 1$ concentration values. Since there are p phases, the number of concentration variables required to define the state of the system is $\mathsf{p}(C - 1)$. Recognising that the temperature and pressure are also to be specified,

$$\text{Total number of variables} = \mathsf{p}(C - 1) + 2 \qquad (8.38)$$

If the system under consideration were not in internal equilibrium, the number of degrees of freedom would have been that given by Eq. (8.38). The fact that the system is in thermodynamic equilibrium implies that the system obeys the principle of equality of chemical potential [Eq. (8.35)]. Therefore, all concentrations are not independent. The concentrations of a component in the different phases are interrelated such that its chemical potential is the same in all phases. For any component there exist ($\mathsf{p} - 1$) equations connecting the concentration in the p phases. Since there are C components, there are $C(\mathsf{p} - 1)$ independent equations which automatically fixes $C(\mathsf{p} - 1)$ of the possible variables in Eq. (8.38). Therefore,

$$\text{Number of variables that are not independent} = C(\mathsf{p} - 1) \qquad (8.39)$$

The number of degrees of freedom F, which is equal to the number of variables that are independent, and hence must be arbitrarily fixed to define the system completely is obtained as the difference between Eqs. (8.38) and Eq. (8.39).

$$F = \mathsf{p}(C - 1) + 2 - C(\mathsf{p} - 1)$$

$$F = C - \mathsf{p} + 2 \qquad (8.40)$$

Equation (8.40) is the *phase rule* derived by Gibbs. It may be noted that if a particular component is absent from any phase, the number of composition variables is reduced correspondingly. At the same time, there will be a similar decrease in the number of independent equations. The result is that Eq. (8.40) is valid even if all the components are not present in every phase.

The number C, which stands for the number of components, to be used in Eq. (8.40) is the least number of independent chemical compounds from which the system can be created. This becomes important in dealing with systems involving chemical reactions. For example, if a system consisting of methanol, hydrogen and carbon monoxide is at equilibrium, the number of components is only one as the chemical reaction $CO + 2H_2$ □ CH_3OH occurs in the system. The phase rule for the reacting system is discussed in Chapter 9.

As an example of the application of the phase rule, consider the homogeneous system of a single substance. Here, $C = 1$, $p = 1$, and therefore, $F = 2$ (bivariant). Two variables, say, temperature and pressure are to be specified to define the state of the system. Consider a two-phase system, for example, pure liquid water in equilibrium with its vapour. Here, $C = 1$, $p = 2$ and $F = 1$ (univariant). One intensive property, either pressure or temperature but not both, may be varied freely. If, solid is also present in the system, $p = 3$ and F becomes zero (invariant). In this case, no intensive property can be varied, and the specification that three phases are in equilibrium, fixes the temperature and pressure. The triple point of water is at 273.16 K and 618 Pa and that of carbon dioxide is at 216.55 K and 523.9 kPa. For a binary liquid mixture of alcohol and water in equilibrium with its vapour, $C = 2$, $p = 2$ and $F = 2$. Two intensive properties may be freely varied. For example, both temperature and pressure may be varied freely over restricted ranges in composition of the phases, but all three variables cannot be independently changed. If the composition of the liquid and the pressure are specified, the boiling temperature and the equilibrium vapour composition are automatically fixed. A liquid mixture of benzene and toluene containing 39% benzene is in equilibrium with its vapour at 100 kPa. This determines the equilibrium temperature as 368 K and the composition of the vapour in equilibrium as 61.2% benzene.

8.6 DUHEM'S THEOREM

The state of a system is completely determined when both the intensive as well as the extensive state of the system is fixed. The phase rule gives the number of independent intensive variables to be specified to define the intensive state of the system uniquely. It does not deal with the extensive state of the system. By extensive state we mean the amount (or the mass) of the various phases present and the total properties of the system. The Duhem's theorem helps in establishing the extensive state of the system. It states that *for any closed system formed initially from the given masses of prescribed chemical species, the equilibrium state is completely determined when any two independent variables are fixed.*

In addition to the phase rule variables, the mass of each phase should be known to define the state of the system completely. Therefore, the total number of variables = $p(C - 1) + 2 + p$, where the last term is the number of terms representing the mass of various phases. Since the system is closed, and is formed from specified amounts of the chemical species present, a material balance equation can be written for each of the C components present in the system. The total number of equations connecting the variables will thus be more than the corresponding number in the phase rule by C, the number of material balance equations. This is equal to $C(p - 1) + C$. The difference between the number of variables and the number of equations is therefore two indicating that only two independent variables need be fixed to define the state of the system completely. These may be either intensive or extensive. If $F < 2$, at least one extensive variable must be fixed for complete determination of the system. For example, for water and water vapour in equilibrium, since the number of degrees of freedom is one, the intensive state of the system is specified by fixing either the pressure or the temperature. But the total properties can be evaluated only if the amount of liquid or vapour is also specified. However, for a binary mixture, say, water and alcohol, in vapour–liquid equilibrium, since the number of degrees of freedom is two, no additional specifications are needed to predict the amount of liquid and vapour present in equilibrium, provided, we know the amounts of the components from which the system is formed. Duhem’s theorem is applicable to reacting systems as well (see Chapter 9).

8.7 VAPOUR–LIQUID EQUILIBRIA

The vapour-liquid equilibrium (VLE) data are essential for many engineering calculations, especially in the design and analysis of separation operations such as distillation, absorption, etc. Thermodynamics provides a system of equations relating the necessary experimental data and the unknown vapour-liquid equilibrium compositions, temperature and pressure.

The conditions of equilibrium [Eq. (8.36)] require that the fugacity of a component in the liquid phase be equal to that in the vapour phase. That is,

$$\bar{f}_i^L = \bar{f}_i^V \qquad \text{for} \quad i = 1, 2, 3, \ldots, C \tag{8.41}$$

where, $\bar{f}_i$ represents the fugacity of component *i* in the solution and the superscripts *V* and *L* represent the vapour and liquid phases, respectively. Using this equation, the problem of determining the composition of the liquid and vapour phases in equilibrium is quite simple: it is necessary only to evaluate the compositions so that the fugacity of each component be the same in both phases. For example, for a binary mixture of ethanol and water in vapour-liquid equilibrium, at a definite temperature and pressure, the mole fractions in the liquid and vapour must be such that the fugacity of ethanol is the same in both phases. That is, $\bar{f}_E^L = \bar{f}_E^V$. Here, $\bar{f}_E$ is the fugacity of ethanol in the mixture. To evaluate quantitatively the equilibrium compositions, the fugacity of a component should be expressed in terms of its mole fraction in the mixture. Using the definition of activity coefficient, the fugacity of a substance in the vapour phase can be written in terms of its mole fraction y_i in the mixture, the fugacity of pure *i* as a vapour at the system temperature and pressure.

$$\bar{f}_i^V = \gamma_i^V \, y_i f_i^V \tag{8.42}$$

If the stable state for *i* at *T* and *P* is not a vapour, evaluating f_i^V requires the introduction of a hypothetical state. The use of the concept of fugacity coefficient helps to overcome this difficulty. The fugacity of a component in a gas mixture can be written as

$$\bar{f}_i^V = y_i \, \bar{\phi}_i^V P \tag{8.43}$$

where $\bar{\phi}_i^V$ is the fugacity coefficient of *i* in the mixture. The fugacity coefficient $\bar{\phi}_i^V$ may be evaluated from an equation of state for the mixture.

For the liquid phase, the fugacity of a component can be expressed as the product of its mole fraction x_i in the solution, the activity coefficient γ^L_i and the fugacity of the component in the standard state.

$$\bar{f}_i^L = x_i \gamma_i^L f_i^0 \tag{8.44a}$$

Alternatively, the fugacity in the liquid phase for component i can also be expressed in terms of the fugacity coefficient in the liquid phase ($\bar{\phi}_i^L$), the concentration x_i and the pressure.

$$\bar{f}_i^L = x_i \bar{\phi}_i^L P \tag{8.44b}$$

Combining Eqs. (8.43) and (8.44b), we get

$$y_i \bar{\phi}_i^V P = x_i \bar{\phi}_i^L P$$

or

$$y_i \bar{\phi}_i^V = x_i \bar{\phi}_i^L \tag{8.45}$$

Substituting Eqs. (8.43) and (8.44a) into Eq. (8.41), we get

$$y_i \bar{\phi}_i^V P = \gamma_i^L x_i f_i^0 \tag{8.46}$$

Equations (8.45) and (8.46) are the fundamental relationships for estimating the vapour–liquid equilibrium by two different approaches—the equations of state approach and *the activity coefficient model approach*. Equation (8.45) forms the basis of estimating VLE by the*equation of state approach,* which will be discussed under Section 8.12.1.

Equation (8.46) is the fundamental relationship in the study of vapour–liquid equilibrium based on activity coefficient model for the liquid phase fugacity. The liquid-phase activity coefficients in Eq. (8.46) can be estimated by any of the models described in the following sections. Estimation of the vapour–liquid equilibria using activity coefficients is useful when polar components are present in the system. For most substances at low pressures, $\bar{\phi}_i^V$ can be assumed to be unity. If the pressure is very high, $\bar{\phi}_i^V$ must be evaluated using an equation of state. Using the activity coefficient approach, the vapour–liquid equilibrium problems may be attacked, by dividing them into the following grouping for convenience.

Case 1: Ideal gas-phase, ideal liquid solution. For mixtures of ideal gases, $\bar{\phi}_i^V$ = 1. For ideal liquid solutions, at low pressures, γ^L_i = 1, and the fugacity f_i^0 is equal to the saturation pressure of pure liquid P_i^S at the temperature of interest. Equation (8.46) becomes

$$y_i P = x_i P_i^S \tag{8.47}$$

Case 2: Low-pressure VLE problems If the liquid phase is not an ideal solution so that $\gamma \neq 1$, but the pressure is low enough that the assumption of ideal gas behaviour for the gas phase would not introduce any significant errors in practical calculations, Eq. (8.46) can be simplified as

$$y_i P = \gamma_i^L x_i P_i^S \tag{8.48}$$

Case 3: High-pressure VLE problems In the general case where ideal behaviour cannot be assumed for the gas and liquid phases, the fugacity coefficient $\bar{\phi}_i^V$ and the activity coefficient γ^L_i

should first be determined for solving vapour–liquid equilibrium problems using Eq. (8.46). These are normally complex functions of temperature, pressure and compositions and can be written as

$$\bar{\phi}_i^V = F'(T, P, y_1, y_2, \ldots, y_{n-1})$$

$$\gamma_i^L = F''(T, P, x_1, x_2, \ldots, x_{n-1})$$

The fugacity in the reference state f_i^0 is the fugacity of pure i at the same T, P and state of aggregation as the mixture. To calculate this, it is convenient to determine first the fugacity of pure i in the liquid state at T under its equilibrium vapour pressure P_i^S and then apply a correction term for the fact that $P \neq P_i^S$. The fugacity of the liquid under its equilibrium vapour pressure is equal to the vapour pressure times the fugacity coefficient ϕ_i^S. The fugacity coefficient ϕ_i^S is the ratio of the fugacity of the component i under its saturation conditions to the saturation pressure of the substance and tends to unity if the vapour behaves as an ideal gas. Using Eq. (6.31), we can write

$$\ln \frac{f_i^0}{\phi_i^S P_i^S} = \frac{1}{RT} \int_{P_i^S}^{P} V_i \, dP$$

Here the liquid phase molar volume V_i can be assumed not to change appreciably with pressure so that the above equation can be written as

$$\ln \frac{f_i^0}{\phi_i^S P_i^S} = \frac{V_i}{RT} (P - P_i^S)$$

Therefore,

$$f_i^0 = \phi_i^S P_i^S \exp\left[\frac{V_i(P - P_i^S)}{RT}\right]$$

This result is substituted into Eq. (8.46).

$$y_i \bar{\phi}_i^V P = \gamma_i^L x_i \phi_i^S P_i^S \exp\left[\frac{V_i(P - P_i^S)}{RT}\right] \tag{8.49}$$

The exponential in the above equation is known as the *Poynting correction* and it is approximately unity when pressure is low. Also at low pressures when the gas behaves ideally, $\bar{\phi}_i^V = \phi_i^S = 1$ and the above equation reduces to Eq. (8.48).

8.8 PHASE DIAGRAMS FOR BINARY SOLUTIONS

8.8.1 Constant-pressure Equilibria

Consider a binary system made up of components A and B. Component A is assumed to be more volatile than B, i.e. the vapour pressure of A is greater than that of B at any given temperature. For a binary liquid mixture in equilibrium with its vapour, according to the Gibbs Phase rule, the number of degrees of freedom is two. When the pressure is fixed, only one variable, say liquid phase composition, can be changed independently and other properties such as the temperature and the vapour phase compositions get uniquely determined. Vapour–liquid equilibrium data at constant pressure are usually represented by means of either the temperature-composition diagrams (the *T-x-y* diagrams or the boiling point diagrams) or the distribution diagrams (*x-y* diagrams or equilibrium curves).

Boiling-point diagram. The boiling point diagrams are plots of temperature as ordinate against composition of liquid and vapour as abscissa. The composition of liquid is usually indicated by the mole fraction of more volatile component in the liquid, x, and the composition of the vapour is indicated by the mole fraction of the more volatile component in the vapour, y. Therefore, the boiling point diagrams are also called *T-x-y* diagrams. The upper curve in Fig. 8.2 gives the temperature versus vapour composition (y), and is known as the 'dew-point curve'. The lower curve in the figure is temperature versus liquid composition (x), also called the 'bubble-point curve'. Below the bubble-point curve the mixture is subcooled liquid and above the dew-point curve the mixture is superheated vapour. Between the bubble-point and dew-point curves the mixture cannot exist as a single phase, it spontaneously separates into saturated liquid and vapour phases that are in equilibrium.

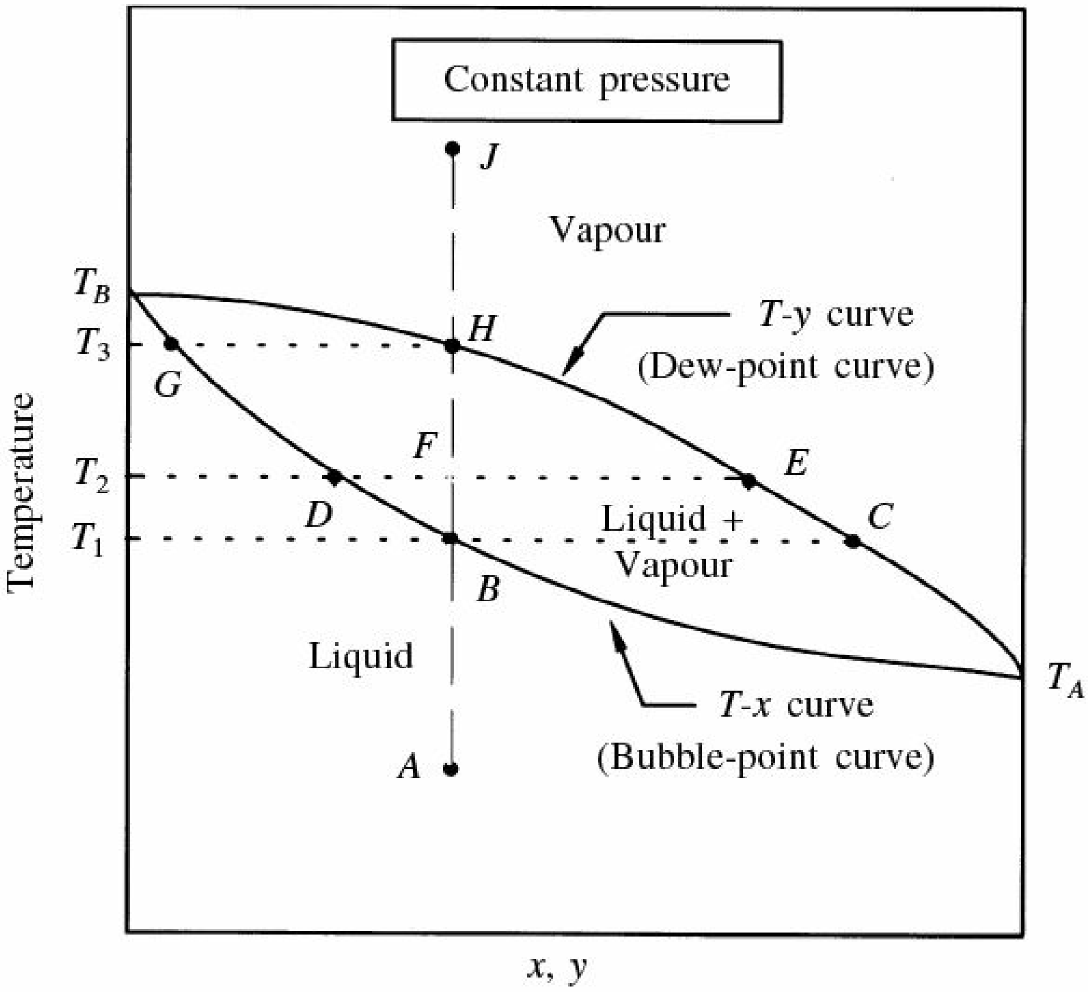


Fig. 8.2 *T-x-y* diagram (boiling-point diagram).

To make these points clearer, consider a mixture whose temperature and composition (x_1) are such that it is represented by point *A* in Fig. 8.2. Since the point *A* lies below the bubble-point curve, the solution is entirely liquid. The mixture is taken in a closed container and the pressure over the system is maintained at a constant value by a piston. The mixture is heated slowly so that its temperature increases along the vertical line passing through point *A* till point *B* on the bubble-point curve is reached. The temperature T_1 corresponding to point *B*, is the bubble point of the original mixture. The first bubble of the vapour is produced at this temperature and it will have the composition (y_1) represented by point *C* on the upper curve. The vapour is richer in the more volatile component. Therefore $y_1 > x_1$, and the dew-point curve lies above the bubble-point curve. The mixtures at points *B* and *C* are the liquid and vapour at equilibrium at the system pressure and temperature T_1. Since both are at the same temperature, they can be joined by a horizontal line *BC*, known as a 'tie line'. Further heating will result in the vaporisation of more liquid, and at temperature T_2 the system will consist of saturated liquid represented by point *D* and saturated vapour represented by point *E*, which are in equilibrium. Since the vapour formed is not removed from the system, the overall composition of the combined mixture of liquid and vapour will be same as x_1, the composition of the original mixture. However, the relative amounts of the liquid and the vapour change as the temperature is changed.

These relative amounts are given by the ratio in which the point representing the combined mixture (in this case, point *F*) divides the tie line *DE*. By material balance consideration, it can be easily verified that

$$\frac{\text{Amount of liquid}}{\text{Amount of vapour}} = \frac{\text{Line } EF}{\text{Line } DF}$$

If heating is continued, eventually a temperature T_3 is reached when almost all liquid is vaporised. The last drop of liquid getting vaporised at this temperature has a composition denoted by point *G* and the equilibrium vapour has the composition at *H* same as the original mixture. Temperature T_3 is the dew point of the original mixture. The mixture temperature increases along the vertical line *HJ* on further heating. On cooling the superheated mixture at point *J*, the first drop of condensate appears when the temperature drops to T_3, the dew point of the mixture and the composition of the liquid is given by point *G*.

We have seen that the mixture at point *A* has vaporised over a temperature range from T_1 (the bubble point) to T_3 (the dew point), unlike a pure substance, which vaporises at a single temperature known as the boiling point of the substance. For a solution, the term 'boiling point' has no meaning, because, at a given pressure the temperature during vaporisation of a solution varies from the bubble point to the dew point.

Equilibrium diagram. The vapour–liquid equilibrium data at constant pressure can be represented on a x versus y plot or an equilibrium distribution diagram. If the vapour composition is taken as the ordinate and the liquid composition is taken as the abscissa, a tie line such as line *BC* on the boiling point diagram gives rise to a point such as point *P* on the distribution diagram (Fig. 8.3). Since the vapour is richer in the more volatile component, the curve lies above the diagonal on which $x = y$.

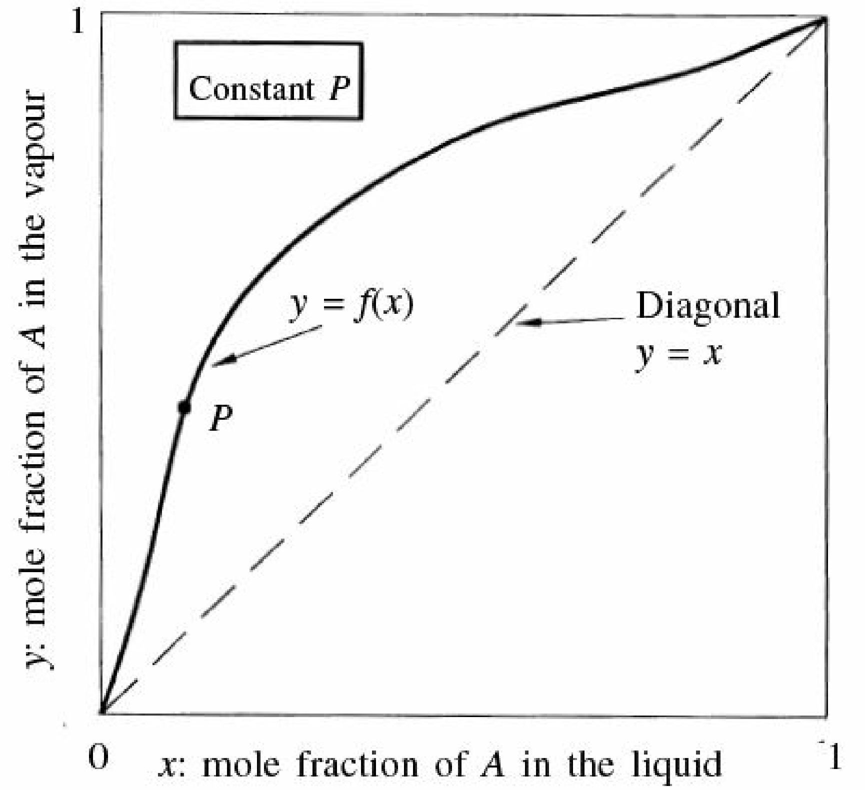


Fig. 8.3 *x-y* diagram (Equilibrium distribution diagram).

A liquid–vapour equilibrium curve very close to the diagonal means that the composition of the vapour is not much different from the composition of the liquid with which it is in equilibrium; when the curve coincides with the diagonal, x and y are equal.

Effect of pressure on VLE. On the boiling point diagram the temperatures corresponding to $x = 0$ and $x = 1$ are the boiling points of pure substances B and A respectively. The boiling points of pure substances increase with pressure. This is true for the bubble and dew points of a mixture of given composition. Consequently the boiling point diagrams at higher pressures will be above the boiling point diagrams at lower pressures as shown in Fig. 8.4. Since the relative volatility decreases as pressure is increased, the closed loop formed by the dew-point and bubble-point curves become narrow at high pressures. Figure 8.5 indicates the effect of pressure on the distribution diagram. In Fig. 8.4, P_3 is the *critical pressure* for component A and above this pressure, the looped curves are shorter.

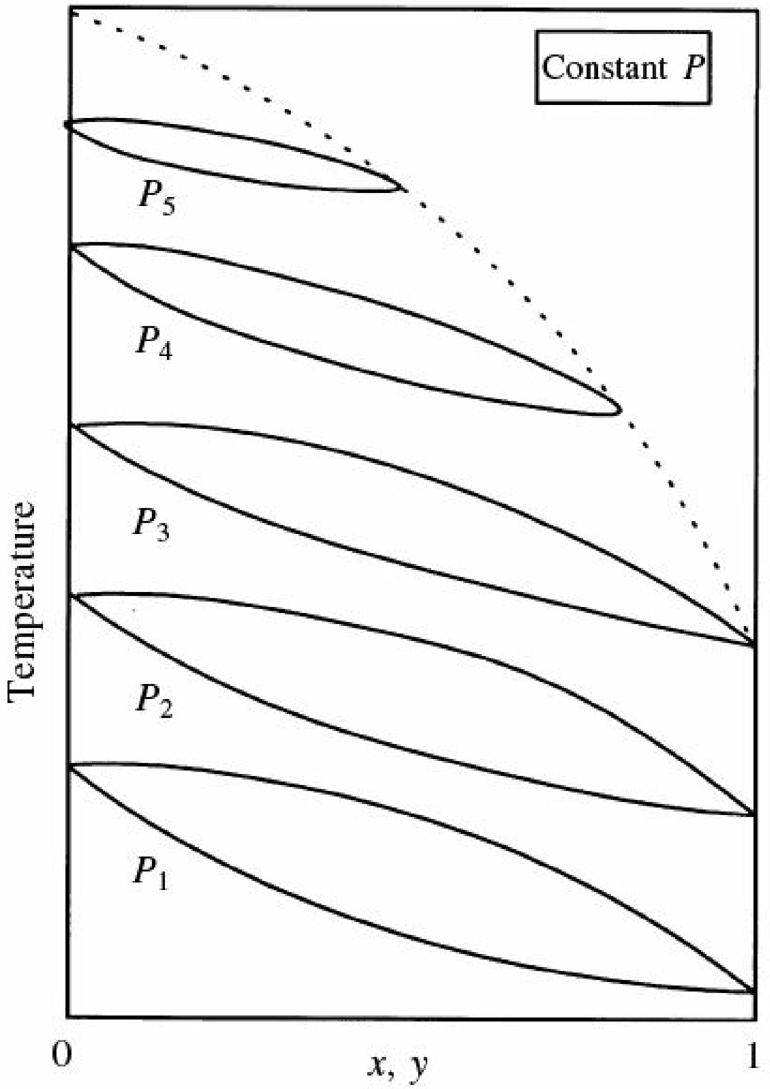


Fig. 8.4 Effect of increasing pressure on *T*-*x*-*y* diagram.

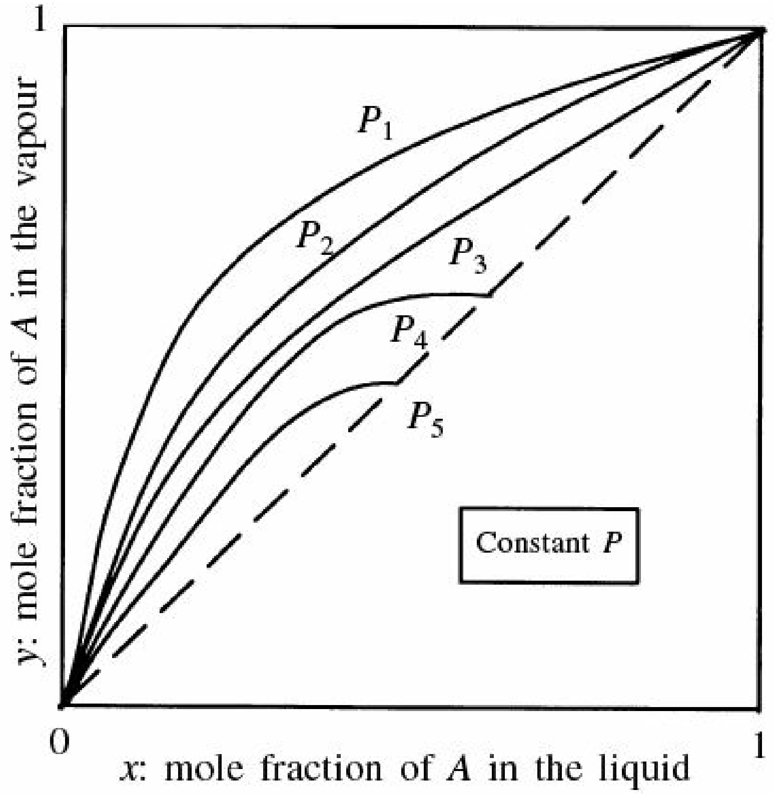


Fig. 8.5 Effect of varying the pressure on the equilibrium diagram.

8.8.2 Constant-temperature Equilibria

Vapour–liquid equilibrium data at constant temperature are represented by means of *P*-*x*-*y* diagrams; Fig. 8.6 shows a typical *P*-*x*-*y* diagram.

The pressure at $x = 0$ is the vapour pressure of pure $B(P_B^S)$ and the pressure at $x = 1$ is the vapour pressure of pure $A(P_A^S)$. Since component *A* is assumed to be more volatile, $P_A^S > P_B^S$ and therefore, the *P*-*x*-*y* diagram slopes upwards as shown in the figure. The *P*-*y* curve lies below the *P*-*x* curve so that for any given pressure, $y > x$. A solution lying above the *P*-*x* curve is in the liquid region and that lying below the *P*-*y* curve is in the vapour region. In between *P*-*x* and *P*-*y* curves the solution is a mixture of saturated liquid and vapour. A horizontal line such as *AB* connects the liquid and vapour phases in equilibrium and is therefore, a tie line. Assume that a liquid mixture whose conditions may be represented by the point *C* in Fig. 8.6, is taken in a closed container. When the pressure over this system is reduced at constant temperature, the first bubble of vapour forms at point *D*, and vaporisation goes to completion at point *E*. Further reduction in pressure leads to the production of superheated vapour represented by point *F*. The effect of temperature on *P*-*x*-*y* diagram is shown in Fig. 8.6(b). When the temperature is less than the critical temperature of both components, the looped curve such as the one shown at the bottom of Fig. 8.6(b) results. The other two curves refer to temperatures greater than the critical temperature of *A*.

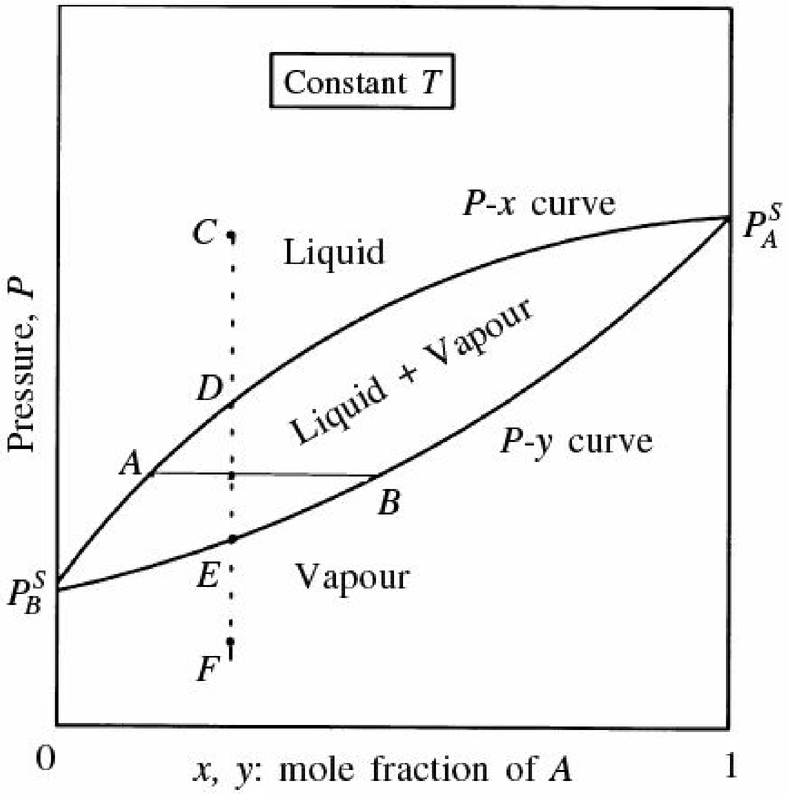


Fig. 8.6(a) *P-x-y* diagram.

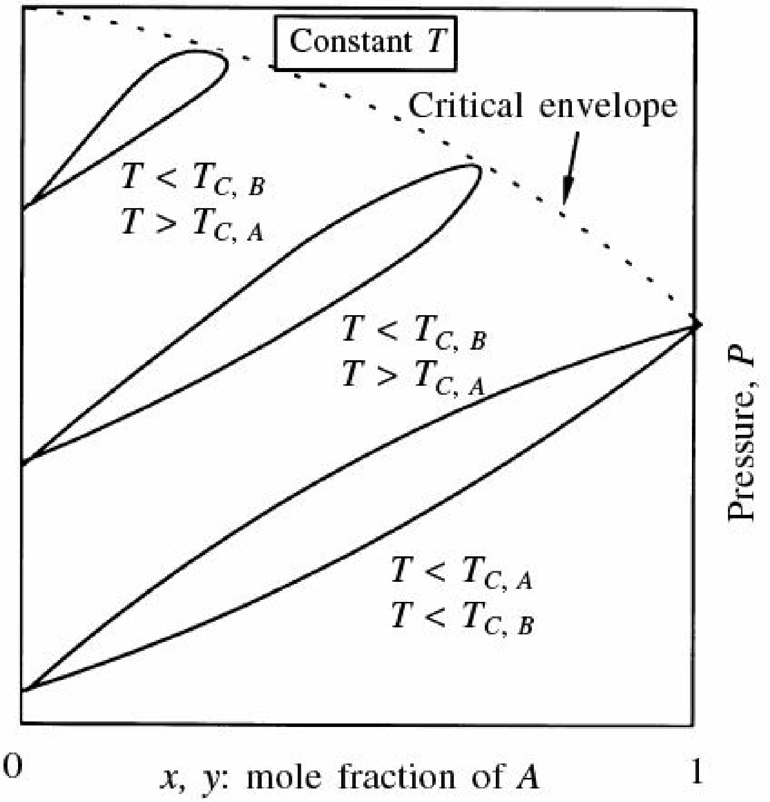


Fig. 8.6(b) Effect of temperature on *P-x-y* diagram near the critical point.

8.9 VAPOUR–LIQUID EQUILIBRIA IN IDEAL SOLUTIONS

It is possible to determine the vapour–liquid equilibrium (VLE) data of certain systems from the vapour pressures of pure components constituting the system. If the liquid phase is an ideal solution and the vapour behaves as an ideal gas, the VLE data can be estimated easily without resorting to direct experimentation. A solution conforming to the ideal behaviour has the following characteristics, all interrelated.

1. The components are chemically similar. The average intermolecular forces of attraction and repulsion in the pure state and in the solution are of approximately the same order of magnitude.
2. There is no volume change on mixing ($\Delta V = 0$) or the volume of the solution varies linearly with composition.
3. There is neither absorption nor evolution of heat on mixing the constituents that form an ideal solution ($\Delta H = 0$); that is, there is no temperature change on mixing.
4. The components in an ideal solution obey Raoult's law, which states that the partial pressure in the vapour in equilibrium with a liquid is directly proportional to the concentration in the liquid. That is, $\bar{p}_i = x_i P_i^S$, where $\bar{p}_i$ is the partial pressure of component i and x_i is its mole fraction in the liquid. P_i^S is the vapour pressure of pure i. This criterion also implies that the total vapour pressure over an ideal solution is a linear function of its composition.

For an experimental test of an ideal solution, the last criterion is the safest one to use. For example, the solution formed by two chemically dissimilar materials like benzene and ethyl alcohol should definitely be non-ideal. It is found that for an equimolar mixture of benzene and ethyl alcohol, there is no change in volume during mixing at room temperature. This peculiar behaviour is because of the fact that when this solution is formed from its constituents, there is increase in volume up to certain concentration and thereafter the volume decreases as shown in Fig. 8.7. When the solution volume is plotted against the composition, the curve will intersect the broken line representing the volume of an ideal solution at a particular concentration represented in the figure by point *P*.

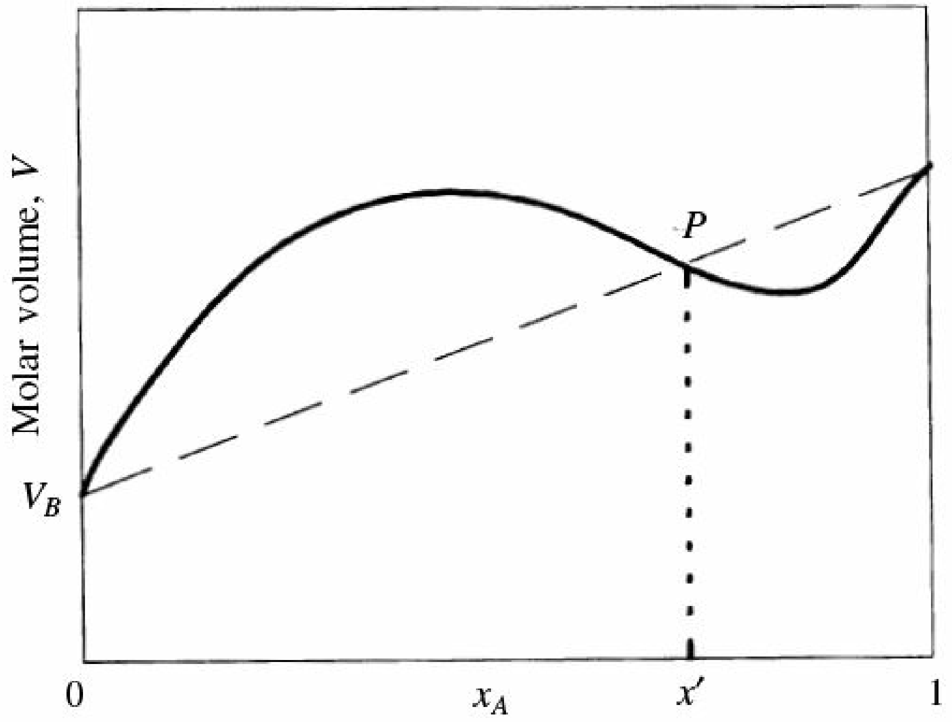


Fig. 8.7 A real solution with no volume change of mixing at point *P*.

If the volume were measured for the concentration of the solution corresponding to point *P*, no change in volume would be observed. This may be the case for enthalpy change of mixing also at some particular composition. The conclusion to be drawn is that negligible volume change or temperature change for one particular composition of the mixture is not a safe criterion of an ideal solution. If these are to be used as the tests for ideal behaviour, then these tests should be done for more than one concentration of the solution. In contrast, the criterion that the total vapour pressure over an ideal solution varies linearly with composition is safe and reliable.

It should be understood that there exists no ideal solution in the strict sense of the word; but actual mixtures approach ideality as a limit. Ideality requires that the molecules of the constituents are similar in size, structure and chemical nature; only optical isomers of organic compounds meet these requirements. Thus a mixture of *ortho*-, *meta*- and *para*-xylene conforms very closely to the ideal solution behaviour. Practically, adjacent or nearly adjacent members of the homologous series of organic compounds can be expected to form ideal solutions. Thus mixtures of benzene and toluene, *n*-octane and *n*-hexane, ethyl alcohol and propyl alcohol, acetone and acetonitrile, paraffin hydrocarbons in paraffin oils, etc., can be treated as ideal solutions in engineering calculations.

Consider an ideal binary solution made up of component 1 and component 2. We have shown in Chapter 7 that all ideal solutions obey Lewis–Randall rule.

$$\bar{f}_i = x_i f_i \tag{7.66}$$

Here $\bar{f}_i$ is the fugacity of the component i in the liquid and f_i is the fugacity of pure i. Using the criterion of equilibrium $\bar{f}_i^L = \bar{f}_i^V$ and noting that if pressure is not too high, the vapour would not depart too greatly from ideal gas behaviour, it is possible to write

$$\bar{p}_i = x_i P_i^S \tag{7.67}$$

This is the mathematical statement of Raoult's law. Here $\bar{p}_i$ is the partial pressure and P_i^S is the vapour pressure in the pure state for component i. Writing Eq. (7.67) for component 1 and component 2 in the solution we get

$$\bar{p}_1 = x_1 P_1^S, \quad \bar{p}_2 = x_2 P_2^S \tag{8.50}$$

The total pressure P is the sum of the partial pressures and, therefore,

$$P = x_1 P_1^S + x_2 P_2^S = x_1 P_1^S + (1 - x_1) P_2^S$$

This on rearrangement gives

$$P = P_2^S + (P_1^S - P_2^S)\, x_1 \tag{8.51}$$

Equation (8.51) shows that at a given temperature, the total pressure over an ideal solution is a linear function of composition thus establishing the fourth criteria given above. When the partial pressures and total pressure are plotted against mole fraction x_1, we get according to Eq. (8.50) and Eq. (8.51) the straight lines shown in Fig. 8.8. The broken lines give the partial pressures and the continuous line gives the total pressure.

The *P*-*x*-*y* diagram can be easily constructed. At any fixed temperature, the total pressure can be calculated using Eq. (8.51) for various x values ranging from 0 to 1. The corresponding equilibrium vapour phase compositions are obtained by applying Dalton's law according to which the partial pressure in the vapour is equal to the mole fraction in the vapour (y) times the total pressure (P). That is

$$\bar{p}_1 = y_1 P, \qquad \bar{p}_2 = y_2 P \tag{8.52}$$

Combining Eqs. (8.50) and (8.52), we see that

$$y_1 P = x_1 P_1^S \tag{8.53}$$

Equation (8.53) can be rearranged as

$$y_1 = x_1 \frac{P_1^S}{P} \tag{8.54}$$

Thus Eq. (8.51) is used to calculate the total pressure at given x and Eq. (8.54) is used to calculate the corresponding equilibrium vapour phase composition y. The *P*-*x*-*y* diagram can now be plotted as shown in the Fig. 8.8.

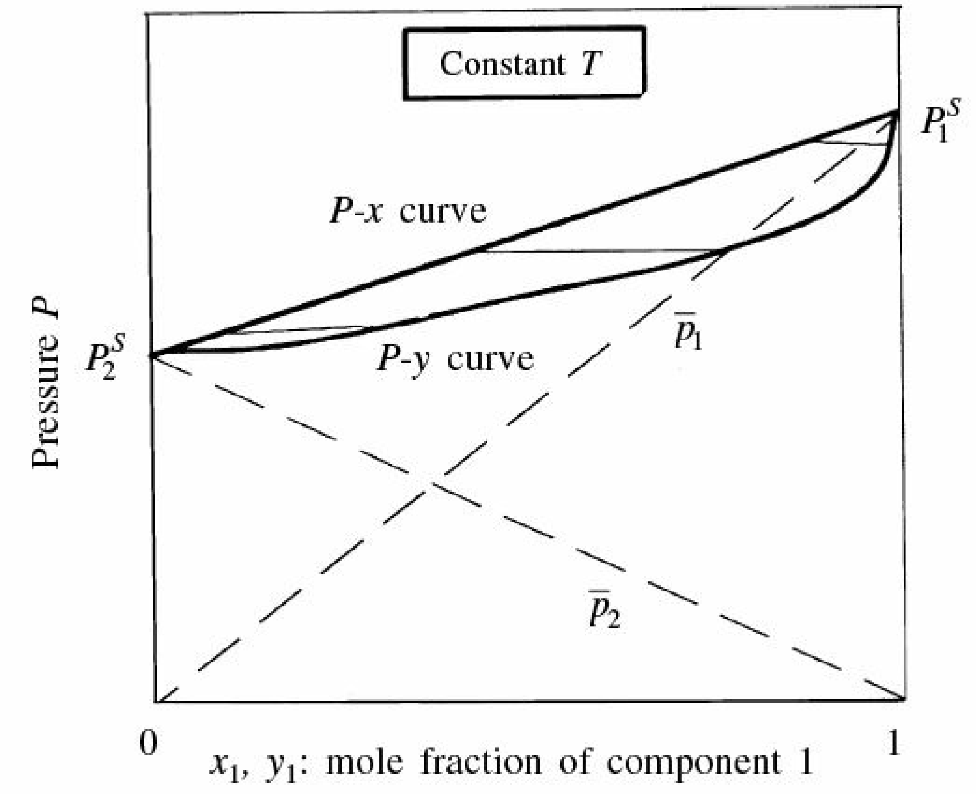


Fig. 8.8 Pressures over ideal solution.

To prepare the *T*-*x*-*y* diagrams at a given total pressure *P* we can again use Eqs. (8.51) and (8.54). Assume temperatures lying between the boiling points of pure liquids at the given pressure. For the temperature assumed, find the vapour pressures of the pure liquids and calculate *x* from Eq. (8.51). Use these in Eq. (8.54) and calculate the vapour composition *y*. Instead, if we attempt to find the equilibrium temperature for the solution of known concentration *x*, the temperature may be estimated by trial, such that the sum of the partial pressures is equal to the given total pressure. Once the temperature is thus known, the vapour phase composition is determined as before. The *T*-*x* curve is the lower curve in the figure and is called the bubble-point curve. The *T*-*y* curve is the upper curve and is called the dew-point curve.

The *y*-*x* diagram is also prepared from the constant total pressure data. It can be constructed from the boiling point diagram by drawing horizontal tie lines. The intersections of these lines with the bubble-point curve give *x* and the intersections with the dew-point curve give *y*. Figure 8.10 shows a typical equilibrium diagram.

There is an approximate method for the construction of the equilibrium diagram, and it is based on the assumption that the ratio of vapour pressures of the components is independent of temperature. This assumption may not introduce much error, as it is possible that the vapour pressures of both components vary with temperature and these variations are to the same extent that their ratio remains unaltered. Thus

$$\alpha = \frac{P_1^S}{P_2^S}, \text{ a constant}$$

The quantity α is designated as the relative volatility of the system.

From Eq. (8.54),

$$y_1 = x_1 \frac{P_1^S}{P}, \qquad y_2 = x_2 \frac{P_2^S}{P}$$

Taking the ratio of the above two equations and noting that $y_2 = 1 - y_1$ and $x_2 = 1 - x_1$ we get

$$\frac{y_1}{1 - y_1} = \frac{x_1}{1 - x_1} \frac{P_1^S}{P_2^S} = \alpha \frac{x_1}{1 - x_1}$$

which can be written in the following form.

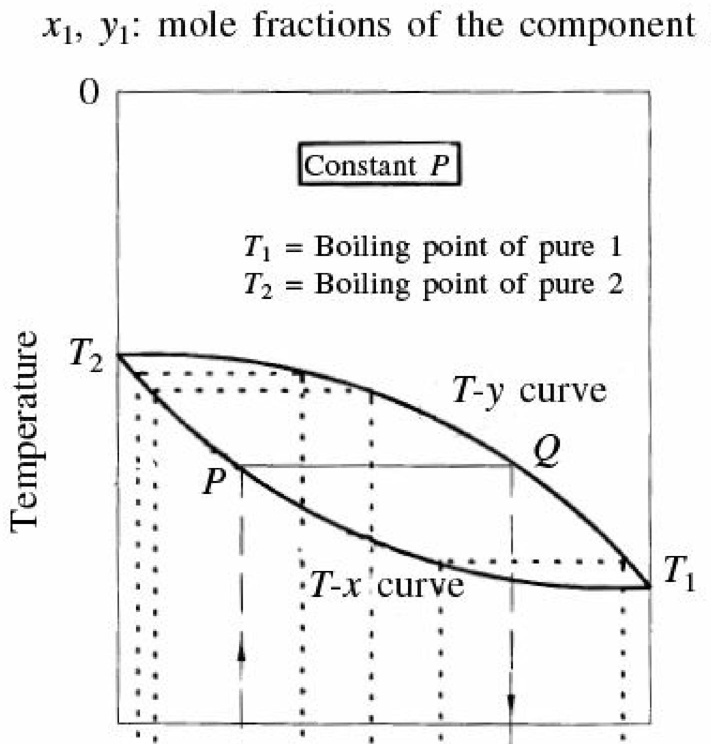


Fig. 8.9 *T-x-y* diagram of an ideal solution.

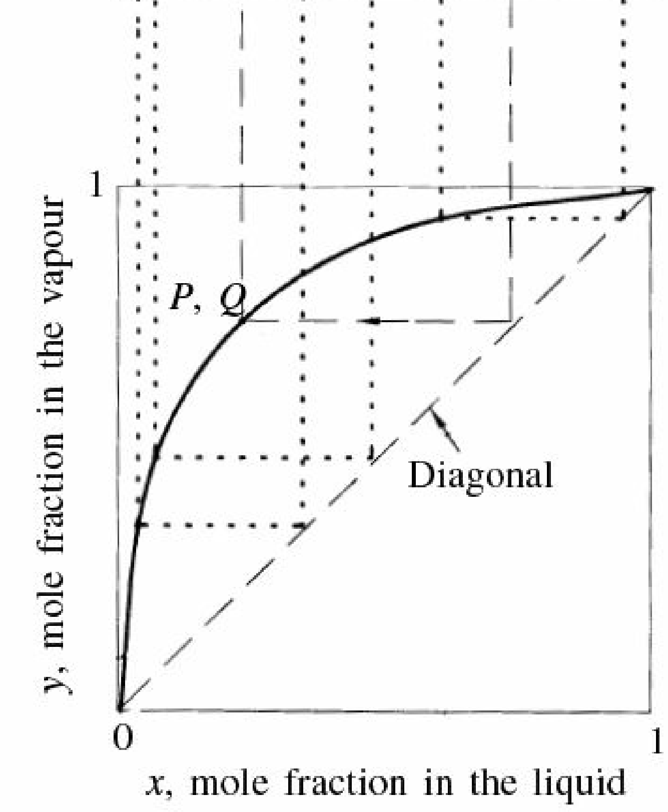


Fig. 8.10 Equilibrium diagram.

$$y_1 = \frac{\alpha x_1}{1 + (\alpha - 1)\, x_1} \tag{8.55}$$

Although Eq. (8.55) is not exact over a wide range of temperatures, the effect of variation in α is so small that an average α value can be used in Eq. (8.55) and the whole *y*-*x* data required for the preparation of the equilibrium curve can be evaluated.

***EXAMPLE* 8.5** Prove that if Raoult's law is valid for one constituent of a binary solution over the whole concentration range, it must also apply to the other constituent.

Solution Assume that Raoult's law is obeyed by component 1 in a binary mixture. Then

$$\bar{p}_1 = x_1 P_1^S$$

As pointed out earlier, Raoult's law is obeyed by ideal solutions when the vapour phase behaves as an ideal gas whereas Lewis–Randall rule is obeyed by ideal solutions irrespective of whether the gas phase is ideal or not. So for component 1, we can write

$$\bar{f}_1 = x_1 f_1$$

Differentiating this equation and noting that f_1 is constant at the given conditions

$$d(\ln \bar{f}_1) = d(\ln x_1)$$

which on rearrangement gives

$$\frac{d(\ln \bar{f}_1)}{d(\ln x_1)} = 1 \tag{8.56}$$

Gibbs–Duhem equation relates fugacities of components in a binary mixture as

$$x_1 \frac{d(\ln \bar{f}_1)}{dx_1} = x_2 \frac{d(\ln \bar{f}_2)}{dx_2}$$

which on rearrangement gives

$$\frac{d(\ln \bar{f}_1)}{d(\ln x_1)} = \frac{d(\ln \bar{f}_2)}{d(\ln x_2)} \tag{8.57}$$

This equation is sometimes referred to as *Duhem–Margules equation.* Comparing Eq. (8.56) with Eq. (8.57) we see that

$$\frac{d(\ln \bar{f}_2)}{d(\ln x_2)} = 1$$

i.e.

$$d(\ln \bar{f}_2) = d(\ln x_2)$$

Noting that $\bar{f}_2 = f_2$ when $x_2 = 1$ the above equation can be integrated.

$$\int_{f_2}^{\bar{f}_2} d(\ln \bar{f}_2) = \int_1^{x_2} d(\ln x_2)$$

$$\ln \frac{\bar{f}_2}{f_2} = \ln \frac{x_2}{1}$$

or

$$\frac{\bar{f}_2}{f_2} = x_2$$

That is, $\bar{f}_2 = x_2 f_2$, which is the Lewis–Randall rule for component 2. If the vapour is an ideal gas, this can be equally written as

$$\bar{p}_2 = x_2 P_2^S$$

This is Raoult's law for component 2. The conclusion to be drawn from the above derivation is that if Raoult's law is applicable to one of the constituents of a liquid mixture at all concentrations, it must be applicable to the other constituent as well.

***EXAMPLE* 8.6** *n*-Heptane and toluene form ideal solution. At 373 K, their vapour pressures are 106 and 74 kPa respectively. Determine the composition of the liquid and vapour in equilibrium at 373 K and 101.3 kPa.

Solution Refer Eq. (8.51). Then,

$$P_1^S = 106; \ P_2^S = 74, \quad P = 101.3$$

$$101.3 = 74 + (106 - 74)x$$

where x is the mole fraction of heptane in the liquid. On solving this, we get $x = 0.853$

From Eq. (8.54),

$y = 0.853$ □ $106/101.3 = 0.893$

The liquid and the vapour at the given conditions contain respectively 85.3% (mol) and 89.3% (mol) heptane.

***EXAMPLE* 8.7** An equimolar solution of benzene and toluene is totally evaporated at a constant temperature of 363 K. At this temperature, the vapour pressures of benzene and toluene are 135.4 and 54 kPa respectively. What are the pressures at the beginning and at the end of the vaporisation process?

Solution Put $x = 0.5$ in Eq. (8.51). Then $P = 94.7$ kPa. This is the pressure at the beginning of vaporisation. Equation (8.51) can be written as

$$x = \frac{P - P_2^S}{P_1^S - P_2^S}$$

Substitute this in Eq. (8.54). Then,

$$y = \frac{P - P_2^S}{P_1^S - P_2^S} \times \frac{P_1^S}{P}$$

On rearranging this equation, we get

$$P = \frac{P_1^S P_2^S}{P_1^S - y(P_1^S - P_2^S)}$$

Put $y = 0.5$ in this. Thus, we get $P = 77.2$ kPa. (This is the pressure at the end of vaporisation).

***EXAMPLE* 8.8** A mixture of A and B conforms closely to Raoult's law. The pure component vapour pressures P_A^S and P_B^S in kPa at T K are given by

$$\ln P_A^S = 14.27 - \frac{2945}{T - 49}$$

$$\ln P_B^S = 14.20 - \frac{2973}{T - 64}$$

If the bubble point of a certain mixture of A and B is 349 K at a total pressure of 80 kPa, find the composition of the first vapour that forms.

Solution At 349 K, the vapour pressures of the pure components are:

$$\ln P_A^S = 14.27 - \frac{2945}{349 - 49} = 4.4533. \qquad P_A^S = 85.9128 \text{ kPa}$$

$$\ln P_B^S = 14.20 - \frac{2973}{349 - 64} = 3.7684. \qquad P_B^S = 43.3116 \text{ kPa}$$

At a given temperature and pressure, the composition of the liquid and vapour phases in equilibrium is calculated using Eqs. (8.51) and (8.54), respectively. The composition of the vapour so calculated at the bubble-point temperature is the composition of the first vapour produced from a liquid on boiling.

Using Eq. (8.51),

Using Eq. (8.51),

$$x_A = \frac{P - P_B^S}{P_A^S - P_B^S} = \frac{80 - 43.3116}{85.9128 - 43.3116} = 0.8612$$

and using Eq. (8.54),

$$y_A = \frac{x_A P_A^S}{P} = 0.9249$$

The vapour formed contains 92.5% A.

***EXAMPLE* 8.9** The vapour pressures of acetone (1) and acetonitrile (2) can be evaluated by the Antoine equations

$$\ln P_1^S = 14.5463 - \frac{2940.46}{T - 35.93}$$

$$\ln P_2^S = 14.2724 - \frac{2945.47}{T - 49.15}$$

where T is in K and P is in kPa. Assuming that the solutions formed by these are ideal, calculate

(a) x_1 and y_1 at 327 K and 65 kPa

(b) T and y_1 at 65 kPa and $x_1 = 0.4$

(c) P and y_1 at 327 K and $x_1 = 0.4$

(d) T and x_1 at 65 kPa and $y_1 = 0.4$

(e) P and x_1 at 327 K and $y_1 = 0.4$

(f) The fraction of the system that is liquid and the composition of the liquid and vapour in equilibrium at 327 K and 65 kPa when the overall composition of the system is 70 mole per cent acetone.

Solution (a) From the Antoine equations, at 327 K,

$$\ln P_1^S = 14.5463 - \frac{2940.46}{327 - 35.93} = 4.4441, \quad P_1^S = 85.12 \text{ kPa}$$

$$\ln P_2^S = 14.2724 - \frac{2945.47}{327 - 49.15} = 3.6715, \quad P_2^S = 39.31 \text{ kPa}$$

Using Eq. (8.51),

$$65 = 39.31 + x_1(85.12 - 39.31) \qquad x_1 = 0.5608$$

Using Eq. (8.54),

$$y_1 = 0.5608 \times 85.12/65 = 0.7344$$

(b) Equation (8.51) can be written as

$$65 = P_2^S + 0.4\,(P_1^S - P_2^S)$$

The temperature is to be determined by trial so that this equation is satisfied. Assume T = 340 K. Antoine equations give P_1^S = 131.1 kPa and P_2^S = 63.14 kPa. Therefore,

$$P_2^S + 0.4\,(P_1^S - P_2^S) = 90.32 \text{ kPa} > 65 \text{ kPa}$$

Assume T = 330 K. At this temperature P_1^S = 94.36 kPa and P_2^S = 44.02 kPa. Thus,

$$P_2^S + 0.4\,(P_1^S - P_2^S) = 64.15 \text{ kPa} < 65 \text{ kPa}$$

Assume T = 330.4 K. P_1^S = 95.65 kPa and P_2^S = 44.68 kPa. Thus,

$$P_2^S + 0.4\,(P_1^S - P_2^S) = 65.07 \text{ kPa}$$

Thus, equilibrium temperature, T = 330.4 K. Using Eq. (8.54),

$$y_1 = 0.4 \times 95.65/65 = 0.5886$$

(c) At 327 K, we have P_1^S = 85.12 kPa and P_2^S = 39.31 kPa. Here x_1 = 0.4. Using these values in Eq. (8.51), we get P = 57.63 kPa. Using Eq. (8.54)

$$y_1 = 0.4 \square 85.12/57.63 = 0.5908$$

(d) Equation (8.51) can be written as

$$x_1 = \frac{P - P_2^S}{P_1^S - P_2^S}$$

When this is substituted into Eq. (8.54), we get

$$y_1 = \frac{P_1^S}{P} \times \frac{P - P_2^S}{P_1^S - P_2^S}$$

Here y_1 = 0.4 and P = 65. Therefore,

$$\frac{P_1^S}{65} \times \frac{65 - P_2^S}{P_1^S - P_2^S} = 0.4$$

Assume a temperature and calculate the vapour pressures using Antoine equations. Substitute the vapour pressure values in the above equation. See whether the Left-hand side = 0.4. This is repeated till the left-hand side of the above equation becomes equal to 0.4.

At T = 334 K, P_1^S = 107.91 kPa and P_2^S = 51.01 kPa.

$$\frac{P_1^S}{65} \times \frac{65 - P_2^S}{P_1^S - P_2^S} = 0.408$$

As this is very close to the required value of 0.4, $T = 334$ K.

Using Eq. (8.54), we get

$$x_1 = \frac{y_1 P}{P_1^S} = \frac{0.4 \times 65}{107.91} = 0.241$$

(e) At 327 K, we have $P_1^S = 85.12$ kPa and $P_2^S = 39.31$ kPa. Here $y_1 = 0.4$

Equation (8.54) relates *y* to *x*. When *P* in Eq. (8.54) is eliminated using Eq. (8.51) we get

$$y_1 = \frac{x_1 P_1^S}{P_2^S + x_1 (P_1^S - P_2^S)}$$

This can be rearranged to the following form.

$$x_1 = \frac{y_1 P_2^S}{P_1^S - y_1 (P_1^S - P_2^S)}$$

Substituting the given values, we get $x_1 = 0.2354$.

From Eq. (8.54),

$$P = \frac{x_1 P_1^S}{y_1} = \frac{0.2354 \times 85.12}{0.4} = 50.09 \text{ kPa}$$

(f) The composition of the vapour and liquid in equilibrium at $P = 65$ kPa and $T = 327$ K were determined in part (a). They are $x_1 = 0.5608$ and $y_1 = 0.7344$. Let *f* be the fraction of the mixture that is liquid. Then an acetone balance gives

1 ☐ 0.7 = *f* ☐ 0.5608 + (1 – *f*) ☐ 0.7344

Solving this, we get *f* = 0.1982. That is, 19.82% (mol) of the given mixture is liquid.

***EXAMPLE* 8.10** Mixtures of *n*-Heptane (*A*) and *n*-Octane (*B*) are expected to behave ideally. The total pressure over the system is 101.3 kPa. Using the vapour pressure data given below,

(a) Construct the boiling point diagram and

(b) The equilibrium diagram and

(c) Deduce an equation for the equilibrium diagram using an arithmetic average a value.

T, K	371.4	378	383	388	393	398.6
P^S_A, kPa	101.3	125.3	140.0	160.0	179.9	205.3
P^S_B, kPa	44.4	55.6	64.5	74.8	86.6	101.3

Solution *Sample calculation:* Consider the second set of data. $T = 378$ K; $P^S_A = 125.3$ kPa; $P^S_B =$

55.6 kPa.

Using Eq. (8.51),

$$101.3 = 55.6 + x_A(125.3 - 55.6)$$

Therefore, $x_A = 0.656$.

Using Eq. (8.54), we see

$$y_A = 0.656 \square 125.3/101.3 = 0.811$$

Relative volatility is

$$\mathsf{a} = P^S{}_A/P^S{}_B = 125.3/55.6 = 2.25$$

These calculations are repeated for other temperatures. The results are tabulated below:

T, K	371.4	378	383	388	393	398.6
x_A	1.000	0.656	0.487	0.312	0.157	0
y_A	1.000	0.811	0.674	0.492	0.279	0
a	2.28	2.25	2.17	2.14	2.08	2.02

(a) Plot of T versus x and y gives the boiling point diagram

(b) Plot of y against x gives the equilibrium diagram

(c) The average of the last row gives a = 2.16. Use this value of a in Eq. (8.55) to get the equation for the equilibrium curve.

$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A} = \frac{2.16\, x_A}{1 + 1.16\, x_A}$$

8.10 NON-IDEAL SOLUTIONS

We have seen that the partial pressure of a component in an ideal solution varies linearly with concentration in the solution. If the solution behaves ideally, the different molecules should be chemically similar. In that case, the molecules of a particular substance, when brought into solution with other components, would not experience any difference in the environment surrounding them from that existed in their pure state. The intermolecular forces in the pure state of the substance and that in the solution would then be approximately of the same order of magnitude. Therefore, the fugacity (or the partial pressure) of a substance, which is a measure of the tendency of the substance to escape from the solution, is not affected by the properties of the other components in the solution. It depends only on the number of molecules of the substance present, or its concentration. In short, the components in an ideal solution obey Raoult’s law. But for non-ideal solutions, the partial pressures do not vary linearly with composition, as shown in Fig. 8.11 for the case of carbon disulphide–acetone system.

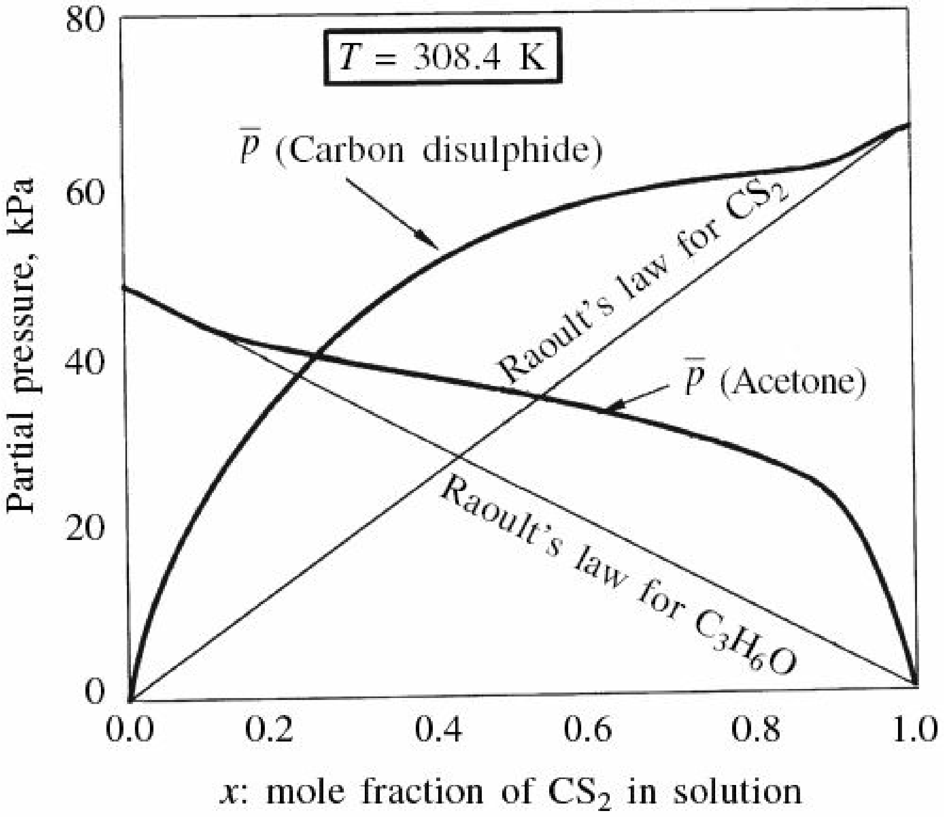


Fig. 8.11 Partial pressure over non-ideal solution.

The non-ideal behaviour of liquid mixtures arises due to the dissimilarity among molecules. The dissimilarities arise from the difference in the molecular structure or from the difference in the molecular weight. The non-ideal behaviour of light hydrocarbons such as methane, ethylene, etc., in mixtures of heavier paraffin or crude oil is due to the difference in the molecular weights. In contrast, it is a type of intermolecular attraction called hydrogen bonding, that is responsible for the non-ideal behaviour resulting from the difference in the molecular structure. Molecules, which contain atoms such as oxygen, chlorine, fluorine or nitrogen, tend to be polar. When the electrons in the bonds between these atoms and hydrogen are not equally shared, a dipole is created. The electrons tend to be closer to the larger atoms, which become negatively charged compared to hydrogen which becomes the positive end of the dipole. In a solution of polar substances, the molecules tend to arrange themselves so that the charge deficiency of the hydrogen atoms is compensated by an intermolecular bond with a 'donor' or negatively charged atom. These hydrogen bonds have energies of the order of several kJ/mol. Because of hydrogen bonding, bimolecular complexes between like or unlike molecules are formed, and even chain-like or three-dimensional aggregates between a large number of molecules are sometimes formed. The formation or destruction of hydrogen bonding during mixing leads to very large heat effects and drastic changes in the thermodynamic properties.

Non-ideal behaviour falls into one of the following two types: *positive deviation from ideality and negative deviation from ideality*. The positive deviation from ideality results when the actual partial pressure of each constituent is greater than it should be if Raoult's law were obeyed. Solutions in which intermolecular forces between like molecules are stronger than those between unlike molecules, show appreciable positive deviation from ideality. On mixing the constituents which form a solution exhibiting positive deviation from ideality, there is an absorption of heat. This can be proved easily if we recognise the experimental observation that most solutions tend to exhibit ideal behaviour as temperature is increased. For a solution showing positive deviation, $\bar{f}_i/f_i$ for each component is greater than its mole fraction x_i, and as temperature is increased it becomes equal to x_i, because the solution tends to ideality as temperature is increased. It means that for a system of given composition for which deviation from Raoult's law is positive, the ratio $\bar{f}_i/f_i$ decreases with increasing temperature. That is

$$\left(\frac{\partial \ln (\bar{f}_i/f_i)}{\partial T}\right)_P < 0 \tag{8.58}$$

The effect of temperature on fugacity was given by Eq. (6.125):

$$\left(\frac{\partial \ln f_i}{\partial T}\right)_P = \frac{H^0 - H_i}{RT^2}$$

Using Eqs. (6.125) and (7.87), Eq. (8.58) becomes

$$\left(\frac{\partial \ln (\bar{f}_i/f_i)}{\partial T}\right)_P = \frac{H_i - \bar{H}_i}{RT^2} \tag{8.59}$$

Comparing Eq. (8.58) with Eq. (8.59) we see that $(H_i - \bar{H}_i)/RT^2 < 0$, which means $\bar{H}_i > H_i$. The total enthalpy of the solution is $\Sigma n_i \bar{H}_i$, whereas the enthalpy of the system before mixing is S $n_i H_i$. Since the former is greater than the latter, there is absorption of heat during mixing. Examples of solutions showing positive deviation from ideality are oxygen–nitrogen, ethanol–ethyl ether, water–ethanol, carbon disulphide–acetone, benzene–cyclohexane, acetonitrile–benzene, *n*-hexane–nitroethane, etc.

For solutions exhibiting negative deviation from ideal behaviour, the partial pressures are less than those given by Raoult's law. By a derivation similar to the one presented in the preceding paragraph, it can be shown that when solutions showing negative deviation are formed from pure constituents there is evolution of heat. At the molecular level, appreciable negative deviation reflects stronger intermolecular forces between unlike than between like pairs of molecules. Examples are chloroform–ethyl ether, chloroform–benzene, hydrochloric acid–water, phenol–cyclohexanol, chloroform–acetone, etc.

The general nature of the vapour pressure curves showing positive and negative deviation are shown in Fig. 8.12. Figures 8.12(a) and (b) refer to constant temperature conditions. The uppermost curves give the total vapour pressure as function of liquid composition. The corresponding curves, as a function of the vapour composition lie below it, so that the vapour is rich in the more volatile component.

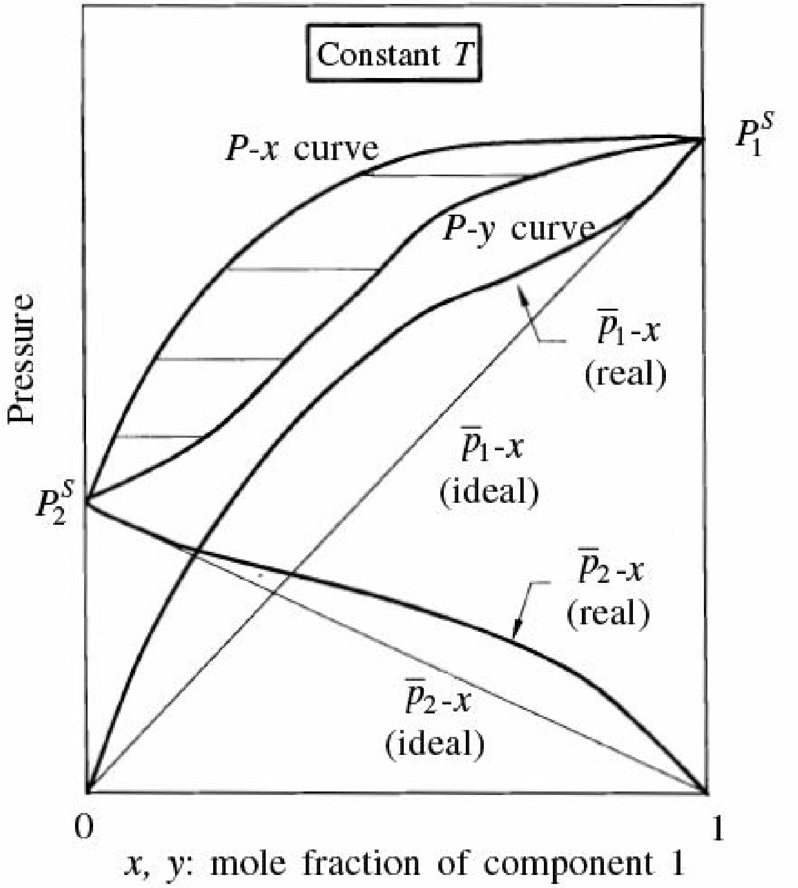


Fig. 8.12(a) Positive deviation from ideality.

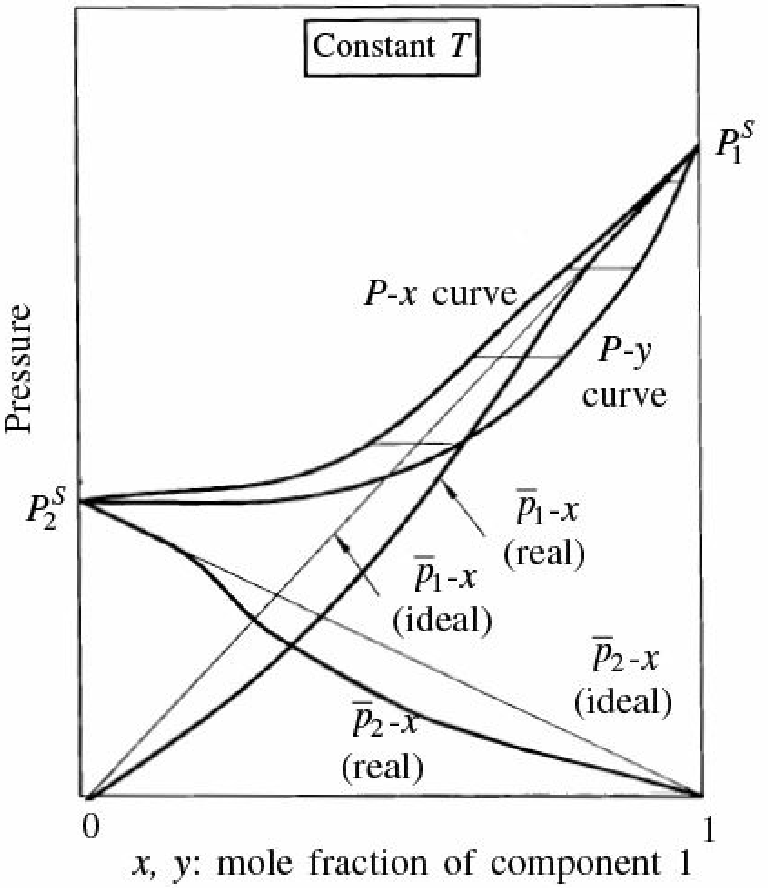
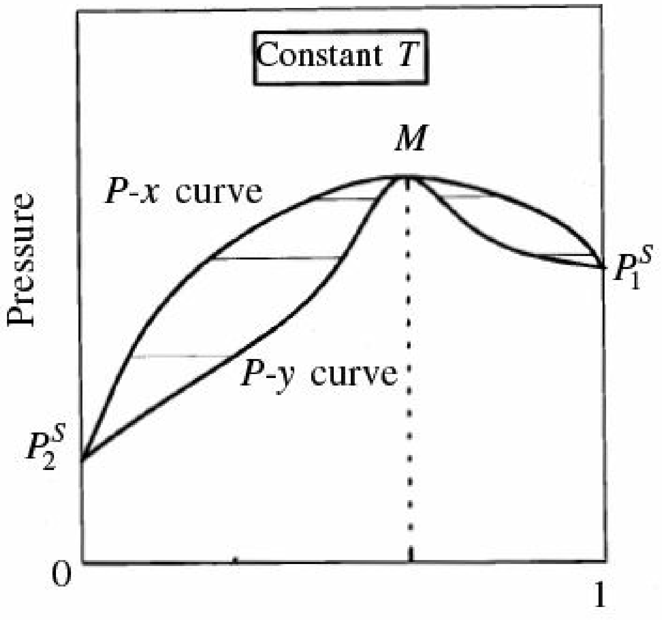


Fig. 8.12(b) Negative deviation from ideality.

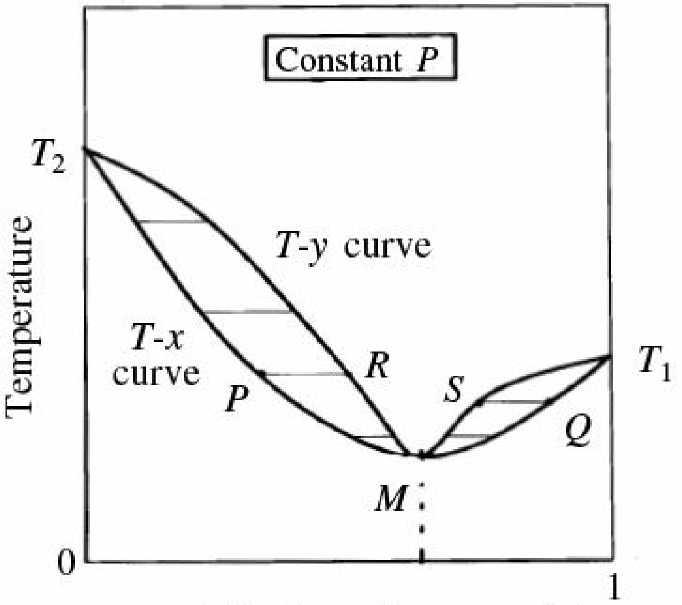
8.10.1 Azeotropes

Azeotropes are constant boiling mixtures. The word ‘azeotrope’ is derived from Greek word meaning ‘boiling without changing’. When an azeotrope is boiled, the resulting vapour will have the same composition as the liquid from which it is produced. Whereas, the equilibrium temperature of an ordinary solution varies from the bubble point to the dew point, the boiling point of an azeotrope remains constant till the entire liquid is vaporised. The azeotropes are formed by solution showing large positive or negative deviation from ideality. If the vapour pressures of the constituents of a solution are very close, then any appreciable positive deviation from ideality will lead to a maximum in the vapour pressure curve and negative deviations from ideality under the same conditions leads to a minimum in the vapour pressure curve. Even if an appreciable difference exists in the vapour pressures of the pure components, the chances for the occurrence of maximum or minimum in the vapour pressures should not be overruled if the deviation from ideal behaviour is quite high. At the composition at which there exists a maximum or minimum in the vapour pressure curve, a minimum or maximum, as the case may be, exists in the boiling point diagrams. The mixture is said to form an azeotrope at this composition under the given temperature and pressure and it will distil without change in composition, because the vapour produced has the same composition as the liquid.

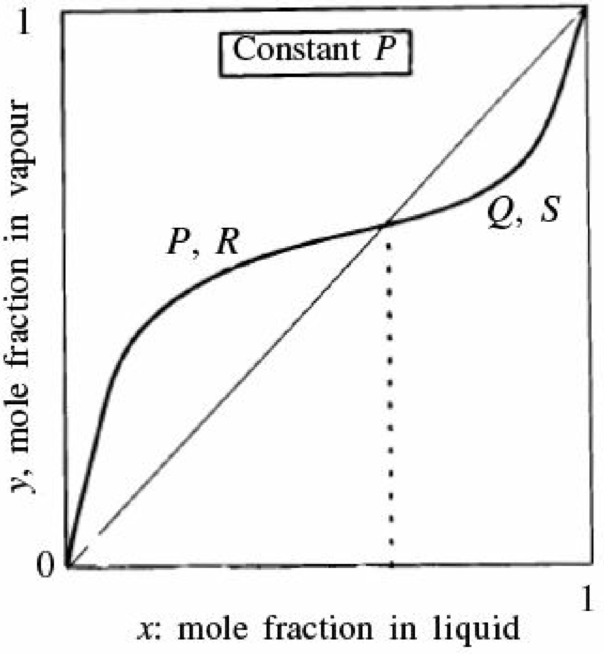
Minimum-boiling azeotropes. Solutions showing positive deviation from ideality in certain cases may lead to the formation of azeotropes of the minimum-boiling type. The P-x-y, T-x-y and x-y curves for the minimum-boiling azeotropes are shown in Fig. 8.13.



(a) *P-x-y* diagram.



(b) *T-x-y* diagram.



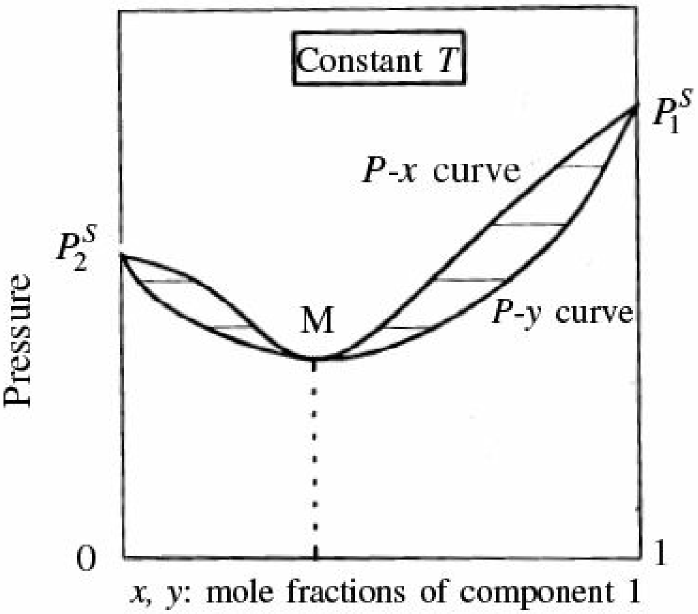
(c) Equilibrium diagram.

Fig. 8.13 Vapour–liquid equilibrium for solution forming minimum-boiling azeotrope.

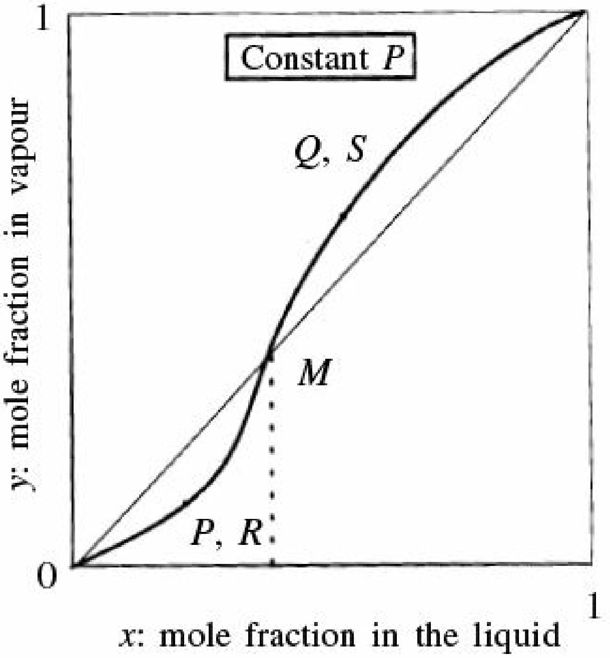
In the boiling point diagram, the liquid and vapour curves are tangent at point *M*, the point of azeotropism at this pressure. The temperature at *M* is the minimum temperature of boiling for the system. For all mixtures of composition less than *M*, the equilibrium vapour is richer than the liquid in the more volatile component. For all mixtures richer than *M*, the vapour is less rich than the liquid in the more volatile component. A mixture of composition *M* boils producing a vapour of identical compositions and consequently at a constant temperature and without change in composition. If solutions either at *P* or *Q* are boiled in an open vessel with continuous escape of vapours, the temperature and composition move along the lower curve away from *M* and towards the pure substances. Solutions like these cannot be distilled by usual distillation methods. One of the most important azeotropes in this category is ethanol–water which forms azeotrope at 89.4% (mol) ethanol at 351.4 K and 101.3 kPa. Other examples are benzene–ethanol (341.2 K, 55%

benzene), carbon disulphide–acetone (312.5 K, 61% carbon disulphide), isopropyl ether–isopropyl alcohol (345.1 K, 39.3% alcohol), all at 101.3 kPa.

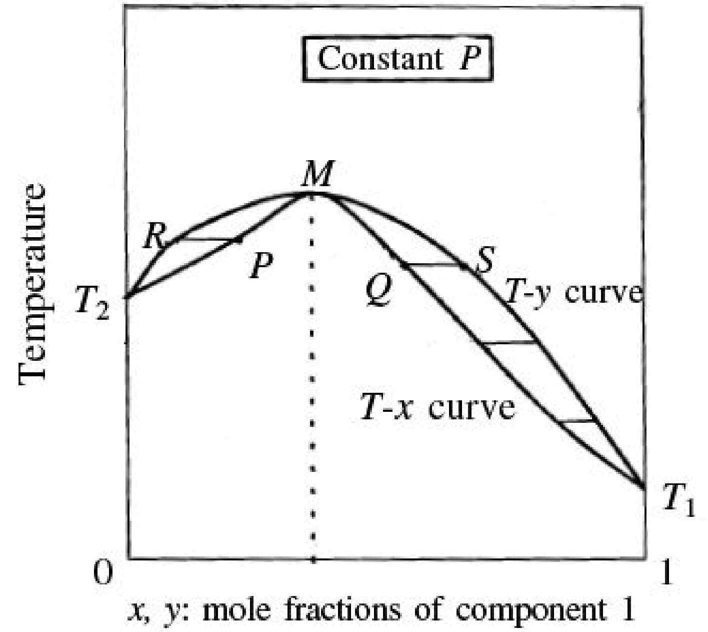
Maximum-boiling azeotropes. When the total pressure of the system at equilibrium is less than the ideal value, the system is said to exhibit negative deviation from ideality. When the difference in vapour pressures of the components is not too great, and in addition, the negative deviations are large, the curve for total pressure against composition passes through a minimum. This condition results in a maximum in the boiling temperature and a condition of azeotropism as at point *M* in Fig. 8.14.



(a) *P*-*x*-*y* diagram.



(c) Equilibrium diagram.



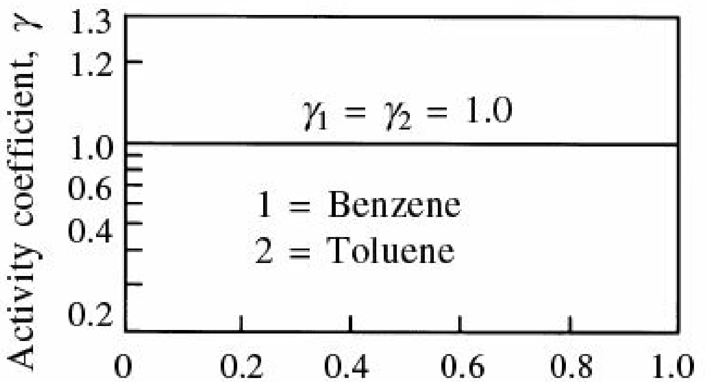
(b) *T*-*x*-*y* diagram.

Fig. 8.14 Vapour-liquid equilibrium for solution forming maximum-boiling azeotrope.

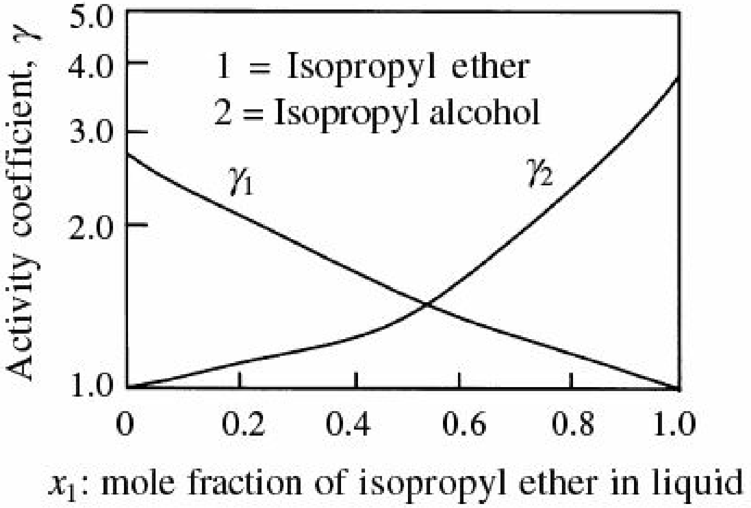
The vapour is leaner in the more volatile component for liquids whose concentration is less than the azeotropic concentration. Solution on either side of the azeotrope, if boiled in an open vessel with escape of vapours will ultimately leave a residual liquid of the azeotropic composition in the vessel. Maximum-boiling azeotropes are less common than the minimum-boiling type. Hydrochloric acid–

water system forms an azeotrope at 11.1% (mol) HCl at 383 K and 101.3 kPa. Other examples are chloroform–acetone (337.7 K and 65.5% acetone), phenol–cyclohexanol (455.65 K, 90% phenol), all at 101.3 kPa.

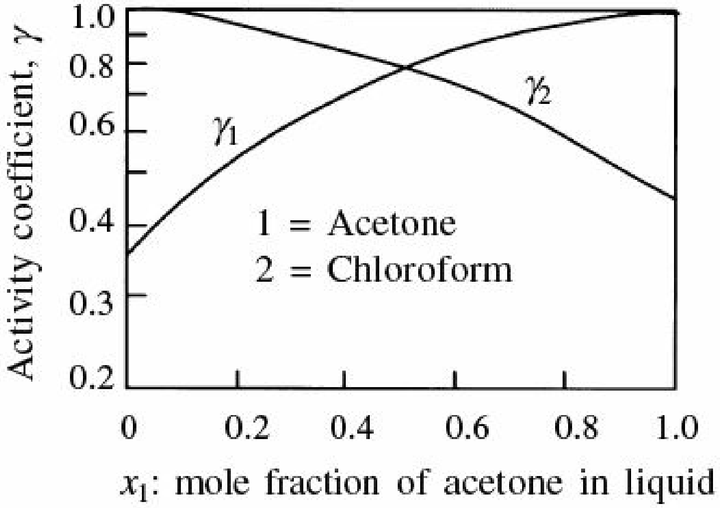
The plot of activity coefficients versus mole fraction in the liquid phase for ideal solutions, minimum-boiling azeotrope and maximum-boiling azeotrope are given in Fig. 8.15.



(a) Ideal solution (benzene–toluene system).



(b) Minimum-boiling azeotrope (isopropyl ether–isopropyl alcohol).



(c) Maximum-boiling azeotrope (acetone–chloroform).

Fig. 8.15 Activity coefficient versus concentration.

Effect of pressure on azeotropes. The azeotropic composition shifts continuously with change in pressure or temperature. In some cases, changing the pressure may eliminate azeotropism from the system. Azeotropism disappears in ethanol–water system at pressures below 9.33 kPa. The table below illustrates the effect of pressure on this system. The last row gives the mole per cent of alcohol in the azeotrope.

P, kPa	13.3	20.0	26.6	53.2	101.3	146.6	193.3
T, K	307.4	315.2	321	336	351.3	361	368.5

%(mol)	99.6	96.2	93.8	91.4	89.43	89.3	89.0

***EXAMPLE* 8.11** Prove that at the azeotropic composition, the vapour and liquid have the same composition.

Solution Refer the Duhem–Margules equation, Eq. (8.57).

$$\frac{d(\ln \bar{f}_1)}{d(\ln x_1)} = \frac{d(\ln \bar{f}_2)}{d(\ln x_2)}$$

Assuming the vapour to behave ideally, it can be written as

$$\frac{d(\ln \bar{p}_1)}{d(\ln x_1)} = \frac{d(\ln \bar{p}_2)}{d(\ln x_2)} \tag{8.60}$$

Noting that $d \ln z = dz/z$, the above result can be rewritten as

$$\frac{x_1}{\bar{p}_1}\frac{d\bar{p}_1}{dx_1} = \frac{x_2}{\bar{p}_2}\frac{d\bar{p}_2}{dx_2} \tag{8.61}$$

In binary mixtures, $dx_1 = -\,dx_2$, so that Eq. (8.61) can be written as

$$\frac{d\bar{p}_1}{dx_1} = -\frac{\bar{p}_1}{x_1}\frac{x_2}{\bar{p}_2}\frac{d\bar{p}_2}{dx_1} \tag{8.62}$$

The total pressure, $P = \bar{p}_1 + \bar{p}_2$. Differentiating this with respect to x_1, we get

$$\frac{dP}{dx_1} = \frac{d\bar{p}_1}{dx_1} + \frac{d\bar{p}_2}{dx_1} \tag{8.63}$$

Eliminating $(d\bar{p}_1/dx_1)$ in Eq. (8.63) using Eq. (8.62) and rearranging we get

$$\frac{dP}{dx_1} = \frac{d\bar{p}_2}{dx_1}\left(1 - \frac{x_2}{x_1}\frac{\bar{p}_1}{\bar{p}_2}\right) \tag{8.64}$$

For a maximum or minimum on the total pressure curve, (dP/dx_1) is zero. Then Eq. (8.64) necessitates that either the terms in the parenthesis should be zero or $(d\bar{p}_2/dx_1)$ is zero. If the latter term is zero the partial pressure would be unaffected by concentration changes, which is not true. Hence, at the point of azeotropism, we have, the following relation:

$$1 - \frac{x_2}{x_1}\frac{\bar{p}_1}{\bar{p}_2} = 0 \quad \text{or} \quad \frac{x_1}{x_2} = \frac{\bar{p}_1}{\bar{p}_2} = \frac{y_1}{y_2}$$

Since $x_2 = 1 - x_1$ and $y_2 = 1 - y_1$, the above result means that at azeotropic condition, $x_1 = y_1$ or the vapour composition and liquid composition are the same.

8.11 VAPOUR–LIQUID EQUILIBRIA (VLE) AT LOW PRESSURES

It has been pointed out that if the pressure is not very high, the fundamental equation relating the compositions of the vapour and liquid under equilibrium is given by Eq. (8.47) as

$y_iP = \mathrm{g}_i x_i P_i^S$

The activity coefficients g_i vary with composition and temperature at a given pressure. In order to calculate the relationship between pressure, temperature and composition of the equilibrium phases for non-ideal solutions at low pressures where the vapour phase is assumed to behave as an ideal gas, we can utilise Eq. (8.47), provided that the equations relating the activity coefficients to compositions and temperature are available. Experimental vapour–liquid equilibrium data can be correlated using such equations and the empirical parameters in them are evaluated. Once an activity coefficient equation suitable for the given system is identified and the parameters evaluated, it can be used for vapour–liquid equilibrium calculations through Eq. (8.47). We have seen that the activity coefficients in a binary solution are not independent, and they are interrelated through the Gibbs–Duhem equations as

$$x_1 \frac{d \ln \gamma_1}{dx_1} = x_2 \frac{d \ln \gamma_2}{dx_2}$$

The minimum requirement to be met by an equation for activity coefficient is that it should conform to the restriction imposed by the above relationship. Among a number of equations between g and x that are available, as far as phase equilibrium problems are concerned, some equations have got wide acceptance. They are discussed in the following sections.

8.11.1 Activity Coefficient Equations

Wohl's three-suffix equations. The relationship between excess free energy and activity coefficient was discussed in Chapter 7. Most of the equations relating activity coefficient and concentration of the solution were derived from these excess free energy relationships. Wohl proposed, statistically, a general method for expressing excess free energy and provided some rough physical significance to the various parameters appearing in the equations. Wohl's equation for excess free energy contained terms for compositions, effective molal volumes and effective volumetric fraction of the separate constituents of the solution. From these equations, the following empirical relations for activity coefficient could be written.

$$\ln \gamma_1 = z_2^2 \left[A + 2\left(B\frac{q_1}{q_2} - A \right) z_1 \right]; \quad \ln \gamma_2 = z_1^2 \left[B + 2\left(A\frac{q_2}{q_1} - B \right) z_2 \right] \tag{8.65}$$

z_1 and z_2 are the effective volume fraction of the separate components in the solution and q_1 and q_2 are the effective molal volumes. z and q are related as

$$z_1 = \frac{x_1}{x_1 + x_2(q_2/q_1)}; \quad z_2 = \frac{x_2}{x_2 + x_1(q_1/q_2)}$$

Equation (8.65) is known as *Wohl's three-suffix equation*. It involves three parameters, A, B and (q_1/q_2) which are characteristics of the binary system.

Margules equation. When the term (q_1/q_2) is unity in Eq. (8.65), we get the following expression, which is known as the *Margules three-suffix equation*.

$$\begin{aligned}\ln \gamma_1 &= x_2^2\,[A + 2(B - A)x_1] = (2B - A)x_2^2 + 2(A - B)\,x_2^3 \\ \ln \gamma_2 &= x_1^2\,[B + 2(A - B)x_2] = (2A - B)x_1^2 + 2(B - A)\,x_1^3\end{aligned} \tag{8.66}$$

The constant A in the above equation is the terminal value of $\ln \gamma_1$ at $x_1 = 0$ and the constant B is the terminal value of $\ln \gamma_2$ at $x_2 = 0$. The three-suffix Margules equation adequately represents the VLE data of systems like acetone–methanol, acetone–chloroform, chloroform–methanol, etc.

When $A = B$ in Eq. (8.66), the Margules equation takes the following simple form:

$$\ln \gamma_1 = Ax_2^2; \quad \ln \gamma_2 = Ax_1^2 \tag{8.67}$$

Equation (8.67) is called the *Margules two-suffix equation*. It represents sufficiently and accurately the activity coefficients of simple liquid mixtures, i.e. mixtures of molecules, which are similar in size, shape and chemical nature. The constant A may be positive or negative. While in general, the constant depends on temperature, for many systems it is a weak function of temperature. Vapour–liquid equilibrium data of argon–oxygen, benzene–cyclohexane, etc., are well represented by the Margules equation [Eq. (8.67)].

van Laar equation. Let $(q_1/q_2) = (A/B)$ in Eq. (8.65). The resulting two-parameter equation is known as the *van Laar equation*. The van Laar equations can be written as

$$\ln \gamma_1 = Az_2^2 = \frac{Ax_2^2}{[(A/B)x_1 + x_2]^2}; \quad \ln \gamma_2 = Bz_1^2 = \frac{Bx_1^2}{[x_1 + (B/A)x_2]^2} \tag{8.68}$$

The constant A is the terminal value of $\ln \gamma_1$ at $x_1 = 0$ and B is the terminal value of $\ln \gamma_2$ at $x_2 = 0$. When A and B are equal, the van Laar equations simplify to the Margules equation, Eq. (8.67). The van Laar equation (8.68) may be rearranged to the following forms, which are very convenient for the evaluation of constants A and B.

$$A = \ln \gamma_1\left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2; \quad B = \ln \gamma_2\left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 \tag{8.69}$$

Strictly speaking, van Laar equations are applicable only for solutions of relatively simple, preferably non-polar liquids. But empirically, it has been found that these are applicable for more complex mixtures. The van Laar equations are widely used for vapour–liquid equilibrium calculations because of their flexibility and mathematical simplicity. Activity coefficients in benzene–isooctane system, *n*-propanol–water system, etc., are accurately represented by the van Laar equations.

The selection of a proper equation for VLE data correlation depends on the molecular complexity of the system and the precision of the experimental data. When an equation is selected that fits the experimental data well, the constants for the constant pressure conditions will be different from those applicable for constant temperature conditions. The effect of pressure on the constants is usually negligibly small, whereas the effect of temperature is appreciable and cannot be neglected. The van Laar constants vary with temperatures unless the temperature range involved is small. However, in vapour–liquid equilibrium calculations, the effect of temperature on the activity coefficient is usually ignored (Prausnitz, 1985).

The Margules three-suffix equation is suited for symmetrical systems, i.e. where the constants *A* and *B* are nearly the same. The van Laar equations can be used for unsymmetrical solutions, where the ratio *A*/*B* does not exceed 2. Though many systems follow van Laar equations, they cannot represent maxima or minima in the ln g curve. Margules three-suffix equation should be used in such cases. For choice of an appropriate equation, a rule of thumb usually employed is this: When the ratio of molar volumes is close to unity, the Margules equation is preferred. When the ratio is quite different from unity, as is the case when water is one of the constituents, the van Laar equations are found to be satisfactory. For example, the chloroform–ethyl alcohol system, which shows a maximum and a minimum on the ln g curves and whose ratio between pure component molar volumes is 1.38, is accurately represented by the Margules equation. For *n*-propanol–water system this ratio is 4.16 and the van Laar equations are found to represent the behaviour accurately.

It is to be remembered that in equations having only two constants, determination of g_1 and g_2 at a single known composition permits the evaluation of the constants and the complete g curve. Equation (8.47) permits the evaluation of g_1 and g_2 when it is rearranged to the following form.

$$\gamma_i = \frac{y_i P}{x_i P_i^S} \tag{8.70}$$

The data required are a single set of equilibrium vapour–liquid composition values and the vapour pressures of the pure components. When an azeotrope is formed, only the azeotropic composition need be known, because it represents the composition of both the liquid and the vapour phases. The activity coefficients can be evaluated by putting $x = y$ in Eq. (8.70).

$$\gamma_i = \frac{P}{P_i^S} \tag{8.71}$$

Wilson equation. All the activity coefficient equations discussed so far can be deduced from the original Wohl's equation under proper simplifying assumptions. However, there are many equations that cannot be derived from the Wohl's general equation. Among such equations, the Wilson equation, the NRTL equation and the UNIQUAC equation are important from practical point of view. All these are based on the concept of local compositions, which are different from the overall mixture compositions. Based on molecular considerations, Wilson (1964) proposed the following equations for activity coefficients in a binary mixture.

$$\begin{aligned} \ln \gamma_1 &= -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \\ \ln \gamma_2 &= -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \end{aligned} \tag{8.72}$$

Wilson equations have two adjustable positive parameters L_{12} and L_{21}. These are related to the pure component molar volumes and to the characteristic energy differences by

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left[-\frac{\lambda_{12}-\lambda_{11}}{RT}\right] = \frac{V_2}{V_1}\exp\left[-\frac{a_{12}}{RT}\right]$$
$$\Lambda_{21} = \frac{V_1}{V_2}\exp\left[-\frac{\lambda_{12}-\lambda_{22}}{RT}\right] = \frac{V_1}{V_2}\exp\left[-\frac{a_{21}}{RT}\right] \tag{8.73}$$

where V_1 and V_2 are the molar volumes of pure liquids and λ's are the energies of interaction between the molecules designated in the subscripts. The differences in the characteristic energies (a_{ij}) are assumed to be temperature independent and this introduces no serious error in practical calculations. Wilson equation provides a good representation of VLE of a variety of miscible mixtures. It is particularly suitable for solutions of polar or associating components like alcohols in non-polar solvents for which the Margules and van Laar equations are generally inadequate.

Wilson equation suffers from two disadvantages, though not serious for many applications. Firstly, it is not suitable for systems showing maxima or minima on the ln γ versus x curves. Secondly, it is not useful for systems exhibiting limited miscibility. The use of Wilson equation is therefore recommended only for liquid systems that are completely miscible, or for partially miscible systems in the region where only one liquid phase exists.

Non-random two-liquid (NRTL) equation. The NRTL model, proposed by Renon and Prausnitz (1968), also is based on the local composition concept. The activity coefficients are

$$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1+x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2+x_1G_{12})^2}\right]$$
$$\ln\gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2+x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1+x_2G_{21})^2}\right] \tag{8.74}$$

In Eq. (8.74), the adjustable parameters are evaluated as

$$G_{12} = \exp(-\alpha_{12}\tau_{12}); \qquad G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{8.75}$$

and

$$\tau_{12} = \frac{b_{12}}{RT}; \qquad \tau_{21} = \frac{b_{21}}{RT} \tag{8.76}$$

The constants b_{12} and b_{21} are similar to the constants representing characteristic energy differences appearing in the Wilson equation. These, as well as the constant α_{12} are independent of composition and temperature. The parameter α_{12} is related to the non-randomness in the mixture. If α_{12} is zero, the mixture is completely random and the NRTL equation reduces to the Margules equation. It is found from fitting of experimental data that α_{12} varies from about 0.20 to 0.47. In the absence of the experimental data, the value of α_{12} is arbitrarily set, a typical choice being a_{12} = 0.3. When a_{12} is arbitrarily fixed, NRTL equation becomes a two-parameter model.

NRTL equation is applicable to partially miscible as well as totally miscible systems. For moderately non-ideal systems, it offers no advantage over the van Laar and Margules equations. But, for strongly non-ideal solutions and especially partially miscible systems, the NRTL equations provide a good representation.

Universal quasi-chemical (UNIQUAC) equation Abrams and Prausnitz (1975) extended the quasi-chemical theory of liquid mixtures to solutions containing molecules of different sizes. This extension is called the UNIQUAC theory. The UNIQUAC model consists of two parts—th combinatorial part, which describes the prominent entropic contribution and a residual part, which is due primarily to the intermolecular forces that are responsible for the enthalpy of mixing. The combinatorial part is determined by the sizes and shape of the molecules and requires only pure-component data. The residual part depends on the intermolecular forces and involves two adjustable binary parameters.

The UNIQUAC equations for activity coefficients are

$$\begin{aligned}\ln \gamma_1 = \ln \frac{\phi_1^*}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\phi_1^*} + \phi_2^* \left(l_1 - \frac{r_1}{r_2} l_2 \right) - q_1' \ln (\theta_1' + \theta_2' \tau_{21}) \\ + \theta_2' q_1' \left(\frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} - \frac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} \right)\end{aligned} \tag{8.77}$$

$$\begin{aligned}\ln \gamma_2 = \ln \frac{\phi_2^*}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\phi_2^*} + \phi_1^* \left(l_2 - \frac{r_2}{r_1} l_1 \right) - q_2' \ln (\theta_2' + \theta_1' \tau_{12}) \\ + \theta_1' q_2' \left(\frac{\tau_{12}}{\theta_2' + \theta_1' \tau_{12}} - \frac{\tau_{21}}{\theta_1' + \theta_2' \tau_{21}} \right)\end{aligned}$$

where

$$l_1 = \frac{z}{2} (r_1 - q_1) - (r_1 - 1), \qquad l_2 = \frac{z}{2} (r_2 - q_2) - (r_2 - 1) \tag{8.78}$$

z is the coordination number, r, q and q□ are pure-component molecular structure constants. The molecular size and surface area are given by r and q respectively. For fluids other than water or lower alcohols, q = q□. For alcohols, the surface of interaction q□ is smaller than the geometric surface q. The adjustable binary parameters t_{12} and t_{21} are related to the characteristic energies Du as follows.

$$\tau_{12} = \exp\left(-\frac{\Delta u_{12}}{RT}\right) = \exp\left(-\frac{a_{12}}{T}\right)$$

$$\tau_{21} = \exp\left(-\frac{\Delta u_{21}}{RT}\right) = \exp\left(-\frac{a_{21}}{T}\right) \tag{8.79}$$

The segment fraction (φ^*) and the area fractions (θ and θ') are obtained as

$$\varphi_1^* = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2}, \qquad \varphi_2^* = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2}$$

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2}, \qquad \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}$$

$$\theta_1' = \frac{x_1 q_1'}{x_1 q_1' + x_2 q_2'}, \qquad \theta_2' = \frac{x_2 q_2'}{x_1 q_1' + x_2 q_2'}$$

The UNIQUAC equation satisfies a large number of non-electrolyte mixtures containing non-pola fluids such as hydrocarbons, alcohols, nitriles, ketones, aldehydes, organic acids, etc., and water, including partially miscible mixtures. The main advantages of this equation are its wide applicability and simplicity arising primarily from the fact that there are only two adjustable parameters.

Universal functional activity coefficient (UNIFAC) method. In the UNIFAC method, the activity coefficients are estimated through group contributions. The liquid is treated as a solution of different structural groups from which the molecules are formed, rather than a solution of molecules themselves. This method is based on the UNIQUAC model where the activity coefficient is divide into two parts—the molecular size contribution (the combinatorial part) and the interaction contributions (the residual part).

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

The combinatorial contribution can be estimated from pure-component properties and the size and shape of the molecules, whereas for the estimation of the second part, group areas and group contributions are needed. A large number of group interaction parameters are already reported. UNIFAC has been successfully used for the design of distillation columns, involving even azeotropic and extractive distillation (Prausnitz et al., 1986).

***EXAMPLE* 8.12** Liquids *A* and *B* form an azeotrope containing 46.1 mole per cent *A* at 101.3 kPa and 345 K. At 345 K, the vapour pressure of *A* is 84.8 kPa and that of *B* is 78.2 kPa. Calculate the van Laar constants.

Solution Let the material *A* be component 1 and *B* be component 2. The activity coefficients at the azeotropic concentration can be evaluated by Eq. (8.71)

$$\gamma_i = \frac{P}{P_i^S}$$

Therefore,

$$\gamma_1 = \frac{P}{P_1^S} = \frac{101.3}{84.8} = 1.195, \qquad \gamma_2 = \frac{P}{P_2^S} = \frac{101.3}{78.2} = 1.295$$

$x_1 = 0.461$ and $x_2 = 0.539$. Substituting these values in Eq. (8.69), the constants A and B in the van Laar equation can be evaluated.

$$A = \ln\gamma_1\left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 = \ln 1.195\left(1 + \frac{0.539 \times \ln 1.295}{0.461 \times \ln 1.195}\right)^2 = 1.2955$$

$$B = \ln\gamma_2\left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 = \ln 1.295\left(1 + \frac{0.461 \times \ln 1.195}{0.539 \times \ln 1.295}\right)^2 = 0.6530$$

***EXAMPLE* 8.13** The azeotrope of the ethanol–benzene system has a composition of 44.8% (mol) ethanol with a boiling point of 341.4 K at 101.3 kPa. At this temperature the vapour pressure of benzene is 68.9 kPa and the vapour pressure of ethanol is 67.4 kPa. What are the activity coefficients in a solution containing 10% alcohol?

Solution Let benzene be component 1 and alcohol component 2. For the azeotrope

$$\gamma_1 = \frac{P}{P_1^S} = \frac{101.3}{68.9} = 1.4702, \qquad \gamma_2 = \frac{P}{P_2^S} = \frac{101.3}{67.4} = 1.5030$$

$x_1 = 0.552$ and $x_2 = 0.448$. Substituting these values in Eq. (8.69) the constants A and B in the van Laar equation can be evaluated.

$$A = \ln \gamma_1 \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 = \ln 1.4702 \left(1 + \frac{0.448 \times \ln 1.5030}{0.552 \times \ln 1.4702}\right)^2 = 1.3305$$

$$B = \ln \gamma_2 \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 = \ln 1.5030 \left(1 + \frac{0.552 \times \ln 1.4702}{0.448 \times \ln 1.5030}\right)^2 = 1.9106$$

For a solution containing 10% alcohol $x_1 = 0.90$ and $x_2 = 0.1$. For calculating the activity coefficient at this concentration, van Laar equations, Eq. (8.69), are used.

$$\ln \gamma_1 = \frac{A x_2^2}{[(A/B) x_1 + x_2]^2} = \frac{1.3305 \times 0.1^2}{[(1.3305/1.9106)\, 0.9 + 0.1]^2} = 0.02519$$

$$\ln \gamma_2 = \frac{B x_1^2}{[x_1 + (B/A)\, x_2]^2} = \frac{1.9106 \times 0.9^2}{[0.9 + (1.9106/1.3305)\, 0.1]^2} = 1.4210$$

Therefore, $\gamma_1 = 1.0255$ and $\gamma_2 = 4.1412$.

***EXAMPLE* 8.14** Water (1)–hydrazine (2) system forms an azeotrope containing 58.5% (mol) hydrazine at 393 K and 101.3 kPa. Calculate the equilibrium vapour composition for a solution containing 20% (mol) hydrazine. The relative volatility of water with reference to hydrazine is 1.6 and may be assumed to remain constant in the temperature range involved. The vapour pressure of hydrazine at 393 K is 124.76 kPa.

Solution The vapour pressure of water at 393 K = 1.6 □ vapour pressure of hydrazine at 393 K = 1.6 □ 124.76 = 199.62 kPa.

$$P_1^S = 199.62 \text{ kPa}; \qquad P_2^S = 124.76 \text{ kPa}$$

For the azeotrope, $x_1 = 0.415$ and $x_2 = 0.585$.

$$\gamma_1 = \frac{P}{P_1^S} = \frac{101.3}{199.62} = 0.5075; \qquad \gamma_2 = \frac{P}{P_2^S} = \frac{101.3}{124.76} = 0.8120$$

Using these in Eq. (8.69), we obtain

$$A = \ln \gamma_1 \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 = -0.6783 \left(1 + \frac{0.585 \times (-\ 0.2083)}{0.415 \times (-\ 0.6783)}\right)^2 = -1.3927$$

$$B = \ln \gamma_2 \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 = -0.2083\left(1 + \frac{0.415 \times (-\ 0.6783}{0.585 \times (-\ 0.2083}\right)^2 = -2.2822$$

For the solution containing 20% (mol) hydrazine, $x_1 = 0.8$ and $x_2 = 0.2$. The activity coefficients are evaluated using Eq. (8.68).

$$\ln \gamma_1 = \frac{Ax_2^2}{[(A/B)x_1 + x_2]^2} = \frac{-1.3927 \times 0.2^2}{[0.8(-1.3927)/(-2.2822) + 0.2]^2} = -0.1176$$

$$\ln \gamma_2 = \frac{Bx_1^2}{[x_1 + (B/A)\,x_2]^2} = \frac{-2.2822 \times 0.8^2}{[0.8 + 0.2(-2.2822)/(-1.3927)]^2} = -1.1485$$

$$\gamma_1 = 0.8891; \qquad \gamma_2 = 0.3171$$

From Eq. (8.47), we see that $y_i P = \gamma_i x_i P_i^S$. That is,

$$y_1 = \gamma_1 x_1 \frac{P_1^S}{P}, \qquad y_2 = \gamma_2 x_2 \frac{P_2^S}{P}$$

To evaluate the vapour compositions using these equations, we should know the vapour pressure values at the new equilibrium temperature. Taking the ratio of the last two equations, we get

$$\frac{y_2}{y_1} = \frac{1 - y_1}{y_1} = \frac{\gamma_2 x_2 P_2^S}{\gamma_1 x_1 P_1^S} = \frac{\gamma_2 x_2}{\gamma_1 x_1}\frac{1}{\alpha_{12}}$$

This can be rearranged to give

$$y_1 = \frac{1}{1 + \dfrac{\gamma_2 x_2 P_2^S}{\gamma_1 x_1 P_1^S}} = \frac{1}{1 + \dfrac{0.3171}{0.8891} \times \dfrac{0.2}{0.8} \times \dfrac{1}{1.6}} = 0.9472$$

$$y_2 = 1 - 0.9472 = 0.0528$$

The composition of the vapour in equilibrium with the liquid containing 20% hydrazine is 5.28% hydrazine and 94.72% water.

***EXAMPLE* 8.15** At 318 K and 24.4 kPa, the composition of the system ethanol (1) and toluene (2) at equilibrium is $x_1 = 0.3$ and $y_1 = 0.634$. The saturation pressure at the given temperature for the pure components are $P_1^S = 23.06$ kPa and $P_2^S = 10.05$ kPa, respectively. Calculate:

(a) The liquid-phase activity coefficients

(b) The value of G^E/RT for the liquid phase

Solution (a) At vapour–liquid equilibrium, the composition of the vapour and liquid phases are related by Eq. (8.48)

$$y_i P = \gamma_i x_i P_i^S$$

Equation (8.48) may be used to evaluate the activity coefficients.

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^S} = \frac{0.634 \times 24.4}{0.3 \times 23.06} = 2.2361$$

$$\gamma_2 = \frac{y_2 P}{x_2 P_2^S} = \frac{0.366 \times 24.4}{0.7 \times 10.05} = 1.2694$$

(b) The excess free energy is related to the activity coefficient and the composition by Eq. (7.145)

$$\frac{G^E}{RT} = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$$

$$= 0.3 \ln 2.2361 + 0.7 \ln 1.2694 = 0.4084$$

***EXAMPLE* 8.16** The activity coefficients in a mixture of components *A* and *B* at 313 K are given by

$$RT \ln \gamma_A = bx_B^2 \quad \text{and} \quad RT \ln \gamma_B = bx_A^2$$

At 313 K, *A* and *B* form an azeotrope containing 49.4 mol percent *A* at a total pressure of 27 kPa. I the vapour pressures of pure *A* and pure *B* are 25.0 and 24.3 kPa, respectively, calculate the total pressure of the vapour at temperature 313 K in equilibrium with a liquid mixture containing 12.5 mol percent *A*.

Solution At the azeotropic composition, Eq. (8.71) is applicable, so that the activity coefficients are:

$$\gamma_A = \frac{P}{P_A^S} = \frac{27}{25} = 1.08$$

$$\gamma_B = \frac{P}{P_B^S} = \frac{27}{24.3} = 1.11$$

The excess Gibbs free energy of mixing is given by Eq. (7.145) as

$$G^E = RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

Noting that $x_A = 0.494$, G^E is evaluated:

$$G^E = RT[0.494 \times \ln(1.08) + 0.506 \times \ln(1.11)] = 0.0908RT \tag{i}$$

Since activity coefficients are given as

$$RT \ln \gamma_A = bx_B^2 \quad \text{and} \quad RT \ln \gamma_B = bx_A^2$$

The excess free energy of the solution is

$$G^E = RT(x_A \ln \gamma_A + x_B \ln \gamma_B) = bx_A x_B^2 + bx_B x_A^2 = bx_A x_B$$

Substituting $x_A = 0.494$ and $x_B = 0.506$ into the above equation,

$$G^E = bx_A x_B = 0.494 \times 0.506b = 0.25b \tag{ii}$$

Comparing Eqs. (i) and (ii), we obtain

$$0.25b = 0.0908RT$$

or

$$b = \frac{0.0908}{0.25} RT = 0.3632RT$$

Now the activity coefficients can be written as

$$RT \ln \gamma_A = bx_B^2 \quad \text{or} \quad \ln \gamma_A = 0.3632\, x_B^2$$

$$RT \ln \gamma_B = bx_A^2 \quad \text{or} \quad \ln \gamma_B = 0.3632\, x_A^2$$

The activity coefficients for a liquid mixture containing 12.5% A are:

$$\ln \gamma_A = 0.3632\, x_B^2 = 0.3632(1 - 0.125)^2 = 0.2781 \text{ which gives } \gamma_A = 1.3206$$

$$\ln \gamma_B = 0.3632\, x_A^2 = 0.3632(0.125)^2 = 0.005675 \text{ which gives } \gamma_B = 1.0057$$

The total pressure of the vapour in equilibrium with the liquid mixture containing 12.5 mol percent A:

$$P = x_A \gamma_A P_A^S + x_B \gamma_B P_B^S = 0.125 \times 1.3206 \times 25 + 0.875 \times 1.0057 \times 24.3 = 25.51 \text{ kPa}$$

***EXAMPLE* 8.17** Using van Laar constants and the vapour pressures of the pure substances how would you prove whether a given binary system forms an azeotrope or not?

Solution If the mixture does not exhibit azeotropic behaviour, the ratio (y_1/x_1) will be greater than (y_2/x_2) for the entire concentration range 0 to 1. Denoting the ratio of (y_1/x_1) to (y_2/x_2) by a, then $a > 1$ for $0 < x < 1$. However, if the mixture forms an azeotrope, then the value of a will be greater than 1 over some concentration range and will be less than 1 over the remaining portion. Since a varies continuously with x, a should have a value equal to 1 at some x which is the azeotropic composition. Writing Eq. (8.47) for both components and rearranging the result, we get

$$\alpha = \frac{(y_1/x_1)}{(y_2/x_2)} = \frac{\gamma_1 P_1^S}{\gamma_2 P_2^S} \tag{8.80}$$

From Eq. (8.68), we see that as $x_1 \to 0$, $\ln \gamma_1 = A$ or $\gamma_1 = \exp A$. Also, $\ln \gamma_2 = 0$ or $\gamma_2 = 1$. Similarly as $x_2 \to 0$ (i.e. as $x_1 \to 1$) $\gamma_2 = \exp B$ and $\gamma_1 = 1$. Using these in Eq. (8.80), we get

$$\alpha_{x_1\to 0} = \frac{(\exp A)\, P_1^S}{P_2^S}, \qquad \alpha_{x_1\to 1} = \frac{P_1^S}{(\exp B)\, P_2^S} \tag{8.81}$$

A and B are the van Laar constants. If the mixture forms an azeotrope, one of the above values will be greater than 1 and the other less than 1.

***EXAMPLE* 8.18** For the binary system methanol (1) and benzene (2), the recommended values of the Wilson parameters at 341 K are $L_{12} = 0.1751$ and $L_{21} = 0.3456$. The vapour pressures of pure species are $P_1^S = 68.75$ kPa and $P_2^S = 115.89$ kPa. Show that the given system can form an azeotrope at 341 K. Assume that the vapour behaves like an ideal gas.

Solution Wilson equations [Eq. (8.72)] provide the activity coefficients in a binary mixture as:

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right]$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right]$$

The activity coefficients at infinite dilution are obtained by putting $x_1 = 0$ in the first equation and $x_2 = 0$ in the second. Thus, we see that as $x_1 \to 0$ (i.e., as $x_2 \to 1$),

$$\ln \gamma_1^\infty = -\ln \Lambda_{12} + 1 - \Lambda_{21} \tag{i}$$

and as $x_2 \to 0$ (i.e., as $x_1 \to 1$),

$$\ln \gamma_2^\infty = -\ln \Lambda_{21} + 1 - \Lambda_{12} \tag{ii}$$

Substituting the values $\Lambda_{12} = 0.1751$ and $\Lambda_{21} = 0.3456$ in Eqs. (i) and (ii), we get

$$\gamma_1^\infty = 10.9879, \quad \gamma_2^\infty = 6.6020$$

Equation (8.48) gives the relationship between activity coefficient and equilibrium phase compositions as

$$y_i P = \gamma_i x_i P_i^S$$

Rearranging this equation, we see that

$$y_1 = \frac{\gamma_1 x_1 P_1^S}{P}, \quad y_2 = \frac{\gamma_2 x_2 P_2^S}{P} \tag{iii}$$

Substituting these values in the definition of relative volatility α, we obtain

$$\alpha = \frac{(y_1/x_1)}{(y_2/x_2)} = \frac{\gamma_1 P_1^S}{\gamma_2 P_2^S} \tag{vi}$$

If the mixture forms an azeotrope, then the value of a will be greater than 1 over some concentration range and will be less than 1 over the remaining portion. Relative volatilities are calculated at $x_1 = 0$ and $x_1 = 1$. If the system forms an azeotrope, one of these values will be greater than unity and the other less than unity.

At $x_1 = 0$,

$$x_2 = 1,\ \gamma_1 = \gamma_1^\infty = 10.9879 \quad \text{and} \quad \gamma_2 = 1$$

and Eq. (iv) gives

$$\alpha_{x_1 \to 0} = 6.5184$$

At $x_2 = 0$,

At $x_2 = 0$,

$$x_1 = 1, \gamma_2 = \gamma_2^{\infty} = 6.6020 \quad \text{and} \quad \gamma_1 = 1$$

and Eq. (iv) gives

$$\alpha_{x_1 \to 1} = 0.0899$$

Since the relative volatility at $x_1 = 0$ is greater than unity, and that at $x_2 = 0$ is less than unity, it is clear that the system forms an azeotrope.

***EXAMPLE* 8.19** A stream of isopropanol–water mixture is flashed into a separation chamber at 353 K and 91.2 kPa. A particular analysis of the liquid product showed an isopropanol content of 4.7% (mol), a value that deviated from the norm. It is suspected that an air leak into the separator might have caused this. Do you agree? The vapour pressures of the pure propanol and water are 91.11 kPa and 47.36 kPa respectively, and the van Laar constants are $A = 2.470$ and $B = 1.094$.

Solution For $x_1 = 0.047$, $x_2 = 0.953$, $A = 2.47$ and $B = 1.094$, Eq. (8.68) gives

$\gamma_1 = 7.388$ and $\gamma_2 = 1.011$

The total pressure corresponding to this equilibrium composition is

$$P = \gamma_1 x_1 P_1^S + \gamma_2 x_2 P_2^S = 0.047 \times 7.388 \times 91.11 + 0.953 \times 1.011 \times 47.36 = 77.27 \text{ kPa}$$

This is less than the total pressure. This error must have been caused by an air-leak.

***EXAMPLE* 8.20** Construct the *P-x-y* diagram for the cyclohexane (1)–benzene (2) system at 313 K given that at 313 K the vapour pressures are $P_1^S = 24.62$ kPa and $P_2^S = 24.41$ kPa. The liquid-phase activity coefficients are given by

$$\ln \gamma_1 = 0.458\, x_2^2, \qquad \ln \gamma_2 = 0.458\, x_1^2$$

Solution Assume $x_1 = 0.4$, then $x_2 = 0.6$. Therefore

$\ln \gamma_1 = 0.458 \times 0.6^2 = 0.16488$; $\gamma_1 = 1.1793$.

Similarly,

$\ln \gamma_2 = 0.458 \times 0.4^2 = 0.0733$; $\gamma_2 = 1.0760$

The total pressure is determined as:

$$P = \gamma_1 x_1 P_1^S + \gamma_2 x_2 P_2^S = 1.1793 \times 0.4 \times 24.62 + 1.0760 \times 0.6 \times 24.41 = 27.37 \text{ kPa}$$

The vapour composition y_1 is found out from

$$y_1 = \frac{\gamma_1 x_1 P_1^S}{P}$$

$$= \frac{1.1793 \times 0.4 \times 24.62}{27.37} = 0.4243$$

The above calculation is repeated for various x_1 values. The results are tabulated below:

x_1	0	0.2	0.4	0.6	0.8	1.0
g_1	1.5809	1.3406	1.1793	1.0760	1.0185	1.000
g_2	1.000	1.0185	1.0760	1.1793	1.3406	1.5809
P	24.41	26.49	27.37	27.41	26.61	24.62
y_1	0	0.2492	0.4243	0.5799	0.7540	1.0

The results are plotted taking P on the y-axis and x_1 and y_1 on the x-axis.

***EXAMPLE* 8.21** From vapour–liquid equilibrium measurements for ethanol–benzene system at 318 K and 40.25 kPa it is found that the vapour in equilibrium with a liquid containing 38.4% (mol) benzene contained 56.6% (mol) benzene. The system forms an azeotrope at 318 K. At this temperature, the vapour pressures of ethanol and benzene are 22.9 and 29.6 kPa respectively. Determine the composition and total pressure of the azeotrope. Assume that van Laar equation is applicable for the system.

Solution Let benzene be component 1 and ethanol component 2. Using Eq. (8.47) the activity coefficients are determined.

$$\gamma_1 = \frac{0.566 \times 40.25}{0.384 \times 29.6} = 2.0043, \qquad \gamma_2 = \frac{0.434 \times 40.25}{0.616 \times 22.9} = 1.2383$$

Using these values in Eq. (8.69) the van Laar constants are evaluated.

$$A = \ln \gamma_1 \left(1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1}\right)^2 = 0.6953\left(1 + \frac{0.616 \times 0.2137}{0.384 \times 0.6953}\right)^2 = 1.5499$$

$$B = \ln \gamma_2 \left(1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2}\right)^2 = 0.2137\left(1 + \frac{0.384 \times 0.6953}{0.616 \times 0.2137}\right)^2 = 1.9597$$

The van Laar equations, Eq. (8.68) can now be written as

$$\ln \gamma_1 = \frac{1.5499\, x_2^2}{\left(\dfrac{1.5499}{1.9597} x_1 + x_2\right)^2}, \qquad \ln \gamma_2 = \frac{1.9597\, x_1^2}{\left(x_1 + \dfrac{1.9597}{1.5499} x_2\right)^2}$$

For any liquid composition, the activity coefficients are calculated using these equations. If the mixture forms an azeotrope at any composition, then as per Eq. (8.71), the following relations also give the activity coefficients.

$$\gamma_1 = \frac{P}{P_1^S}, \qquad \gamma_2 = \frac{P}{P_2^S}$$

Thus, activity coefficients calculated using the van Laar equations should also satisfy the relation $P = \gamma_1 P_1^S = \gamma_2 P_2^S$ at the azeotropic composition. The azeotropic composition is obtained by trial assuming values of x. For $x_1 = 0.6$, $\gamma_1 = 1.3830$ and $\gamma_2 = 1.7806$.

$$P = \gamma_1 P_1^S = 1.3830 \times 29.6 = 40.937 \text{ kPa}$$

$$P = \gamma_2 P_2^S = 1.7806 \times 22.9 = 40.775 \text{ kPa}$$

These values are so close that it can be assumed that the composition corresponds to an azeotrope. Thus, the liquid mixture forms an azeotrope containing 60% benzene which boils at 318 K and approximately 40.86 kPa, (mean of 40.937 and 40.775 kPa).

***EXAMPLE* 8.22** The activity coefficients in a binary system are given by $\ln \gamma_1 = Ax_2^2$, $\ln \gamma_2 = Ax_1^2$.

Show that if the system forms an azeotrope, then $|A| \geq |\ln (P_1^S/P_2^S)|$ and the azeotropic composition is given by

$$x_1 = \frac{1}{2}\left(1 + \frac{1}{A}\ln\frac{P_1^S}{P_2^S}\right)$$

Solution The activity coefficients are:

$$\gamma_1 = \exp(Ax_2^2), \qquad \gamma_2 = \exp(Ax_1^2)$$

The total pressure over the system is given by

$$P = \gamma_1 x_1 P_1^S + \gamma_2 x_2 P_2^S = [\exp(Ax_2^2)](x_1 P_1^S) + [\exp(Ax_1^2)](x_2 P_2^S)$$

Differentiating this with respect to x_1, we get

$$\frac{dP}{dx_1} = P_1^S \exp(Ax_2^2)(1 - 2Ax_1x_2) - P_2^S \exp(Ax_1^2)(1 - 2Ax_1x_2)$$

At the azeotropic composition, the *P*-*x* curve has a maximum or minimum. Therefore, the above result is equated to zero and after rearrangement, we get

$$(1 - 2Ax_1x_2)\left(\frac{P_1^S}{P_2^S} - \exp[A(x_1^2 - x_2^2)]\right) = 0$$

The roots of this equation are given by

$$A(x_1^2 - x_2^2) = \ln\frac{P_1^S}{P_2^S}$$

and

$$2Ax_1x_2 = 1$$

The first root can be rearranged as

$$x_1 = \frac{1}{2}\left(1 + \frac{1}{A}\ln\frac{P_1^S}{P_2^S}\right)$$

Since the value of x_1 lies between 0 and 1 it is essential that $|A| \ge |\ln(P_1^S/P_2^S)|$. Noting that x_1x_2 for a binary mixture is less than or equal to 0.25, the second root leads to $A \ge 2$. This condition usually results in partial miscibility. Thus, condition for homogeneous azeotropy is $|A| \ge |\ln(P_1^S/P_2^S)|$ and $A < 2$.

***EXAMPLE* 8.23** The following values refer to the Wilson parameters for the system acetone(1)–water(2):

a_{12} = 1225.31 J/mol, a_{21} = 6051.01 J/mol, V_1 = 74.05 □ 10^{-6} m^3/mol, V_2 = 18.07 □ 10^{-6} m^3/mol.

The vapour pressures are given by

$$\ln P_1^S = 14.39155 - \frac{2795.817}{T - 43.198}, \qquad \ln P_2^S = 16.26205 - \frac{3799.887}{T - 46.854}$$

where P is in kPa and T is in K. Calculate the equilibrium pressure and composition of

(a) Vapour in equilibrium with a liquid of composition $x_1 = 0.43$ at 349 K.

(b) The liquid in equilibrium with a vapour of concentration $y_1 = 0.8$ at 349 K.

Solution Using the Antoine equations, at 349 K, the vapour pressures are calculated as

$$P_1^S = 190.37 \text{ kPa}, \qquad P_2^S = 39.87 \text{ kPa}$$

The parameters in the Wilson equation [Eq. (8.72)] Λ_{12} and Λ_{21} are calculated using Eq. (8.73). Thus,

$$\Lambda_{12} = \frac{V_2}{V_1} \exp\left[-\frac{a_{12}}{RT}\right] = \frac{18.07}{74.05} \exp\left(-\frac{1225.31}{8.314 \times 349}\right) = 0.1600$$

$$\Lambda_{21} = \frac{V_1}{V_2} \exp\left[-\frac{a_{21}}{RT}\right] = \frac{74.05}{18.07} \exp\left(-\frac{6051.01}{8.314 \times 349}\right) = 0.5092$$

(a) Now from Eq. (8.72), we obtain

$$\ln \gamma_1 = -\ln(0.43 + 0.16 \times 0.57) + 0.57 \left[\frac{0.16}{0.43 + 0.16 \times 0.57} - \frac{0.5092}{0.5092 \times 0.43 + 0.57}\right]$$

$$= -\ln(0.5212) + 0.57(-0.33843) = 0.4587$$

$$\ln \gamma_2 = -\ln(0.5092 \times 0.43 + 0.57) - 0.43 \left[\frac{0.16}{0.43 + 0.16 \times 0.57} - \frac{0.5092}{0.5092 \times 0.43 + 0.57}\right]$$

$$= -\ln(0.7890) - 0.43(-0.33843) = 0.3826$$

Thus $\gamma_1 = 1.5820$ and $\gamma_2 = 1.4661$.

The pressure is calculated as

$$P = \gamma_1 x_1 P_1^S + \gamma_2 x_2 P_2^S = 1.5820 \times 0.43 \times 190.37 + 1.4661 \times 0.57 \times 39.87 = 162.82 \text{ kPa}$$

The vapour composition is found out from the relation $y_1 P = g_1 x_1 P_1^S$

$$y_1 = \frac{\gamma_1 x_1 P_1^S}{P} = \frac{1.5820 \times 0.43 \times 190.37}{162.82} = 0.7954$$

(b) Since the liquid composition is not known, the activity coefficients cannot be calculated. Assume $g_1 = g_2 = 1$. The relation $P y_i = x_i P_i^S$ can be written for component 1 and component 2, which on rearrangement gives

$$x_1 = (Py_1/P_1^S) \text{ and } x_2 = (Py_2/P_2^S)$$

Since $x_1 + x_2 = 1$,

$$\frac{Py_1}{P_1^S} + \frac{Py_2}{P_2^S} = 1$$

Therefore,

$$P = \frac{1}{(y_1/P_1^S) + (y_2/P_2^S)}$$

Using this, the pressure is found out.

$$P = \left(\frac{0.80}{190.37} + \frac{0.20}{39.87}\right)^{-1} = 108.48 \text{ kPa}$$

Use this pressure to calculate x_1.

$$x_1 = \frac{y_1 P}{P_1^S} = \frac{0.80 \times 108.48}{190.37} = 0.4559, \qquad x_2 = 0.5441$$

Activity coefficients can now be determined for this composition using Wilson equations.

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right]$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right]$$

$$\ln \gamma_1 = -\ln(0.4559 + 0.16 \times 0.5441) + 0.5441\left[\frac{0.16}{0.4559 + 0.16 \times 0.5441} - \frac{0.5092}{0.5092 \times 0.4559 + 0.5441}\right]$$

$$= -\ln(0.5430) + 0.5441(-0.3613) = 0.4141$$

$$\ln \gamma_2 = -\ln(0.5092 \times 0.4559 + 0.5441) - 0.4559\left[\frac{0.16}{0.4559 + 0.16 \times 0.5441} - \frac{0.5092}{0.5092 \times 0.4559 + 0.5441}\right]$$

$$= -\ln(0.7762) - 0.4559(-0.3613) = 0.4181$$

Therefore, $\gamma_1 = 1.513$ and $\gamma_2 = 1.5191$.

Now the pressure is recalculated incorporating the activity coefficient values. The equation

$$P = \frac{1}{(y_1/P_1^S) + (y_2/P_2^S)}$$

becomes

$$P = \frac{1}{[y_1/(\gamma_1 P_1^S)] + [y_2/(\gamma_2 P_2^S)]}$$

Substituting the values, we get P = 164.48 kPa. Liquid compositions are now recalculated.

$$x_1 = \frac{y_1 P}{\gamma_1 P_1^S} = \frac{0.80 \times 164.48}{1.513 \times 190.37} = 0.4568$$

so that x_2 = 0.5432. Activity coefficients under this condition are

$$\ln \gamma_1 = -\ln(0.4568 + 0.16 \times 0.5432) + 0.5432 \left[\frac{0.16}{0.4568 + 0.16 \times 0.5432} - \frac{0.5092}{0.5092 \times 0.4568 + 0.5432}\right]$$

$$= -\ln(0.5437) + 0.5432\ (-0.3621) = 0.4127$$

$$\ln \gamma_2 = -\ln(0.5092 \times 0.4568 + 0.5432) - 0.4568 \left[\frac{0.16}{0.4568 + 0.16 \times 0.5432} - \frac{0.5092}{0.5092 \times 0.4568 + 0.5432}\right]$$

$$= -\ln(0.7758) - 0.4568\ (-0.3621) = 0.4193$$

These give γ_1 =1.5109 and γ_2 = 1.5208.

$$P = \frac{1}{[y_1/(\gamma_1 P_1^S)] + [y_2/(\gamma_2 P_2^S)]} = 164.48$$

This is same as the previous value calculated for P. Therefore, P = 164.48 kPa and x_1 = 0.4568.

***EXAMPLE* 8.24** The system methanol–methyl ethyl ketone forms an azeotrope containing 84.2% (mol) methanol at 337.5 K and 101.3 kPa. The vapour pressures of the pure species are given by the Antoine equation

$$\ln P = A - \frac{B}{T - C}$$

where P is in kPa and T in K. The constants of the Antoine equation are given below:

	A	B	C
Methanol	16.12609	3394.286	43.2
Methyl ethyl ketone	14.04357	2785.225	57.2

Determine the parameters in the Wilson equation.

Solution The vapour pressures at 337.5 K are calculated using Antoine equations.

$$P_1^S = 98.76 \text{ kPa}, \qquad P_2^S = 60.76 \text{ kPa}$$

At the azeotropic composition ($x_1 = 0.842$, $x_2 = 0.158$) the activity coefficients are:

$$\gamma_1 = \frac{P}{P_1^S} = \frac{101.3}{98.76} = 1.026, \qquad \gamma_2 = \frac{P}{P_2^S} = \frac{101.3}{60.76} = 1.667$$

Equation (8.72) can be rearranged as

$$\left[\frac{\gamma_2 x_2}{1 - [\Lambda_{12} x_1/(x_1 + \Lambda_{12} x_2)] + (x_1/x_2)\ln[\gamma_1(x_1 + \Lambda_{12} x_2)]}\right]^{x_2/x_1} \gamma_1(x_1 + \Lambda_{12} x_2) = 1$$

L$_{12}$ is calculated by substituting the known values in the above equation.

$$\left[\frac{1.667 \times 0.158}{1 - [0.842\,\Lambda_{12}/(0.842 + 0.158\,\Lambda_{12})] + (0.842/0.158)\ln[1.026(0.842 + 0.158\,\Lambda_{12})]}\right]^{0.158/0.842}$$
$$\times\, 1.026\,(0.842 + 0.158\,\Lambda_{12}) = 1$$

$$\left[\frac{0.2634}{1 - [0.842\,\Lambda_{12}/(0.842 + 0.158\,\Lambda_{12})] + 5.329\ln(0.8639 + 0.1621\,\Lambda_{12})}\right]^{0.1876}$$
$$\times\,(0.8639 + 0.1621\,\Lambda_{12}) = 1$$

$\Lambda_{12} = 0.935$. Substitute this value in Eq. (8.72) and calculate Λ_{21}. So, $\Lambda_{21} = 0.467$

8.12 VAPOUR-LIQUID EQUILIBRIA INVOLVING HIGH PRESSURES AND MULTICOMPONENT SYSTEMS

8.12.1 Equations of State Approach

The equations of state approach is most useful for vapour–liquid equilibria at high pressures. In this method, the vapour and liquid compositions are related by Eq. (8.45):

$$y_i \bar{\phi}_i^V = x_i \bar{\phi}_i^L$$

The equations of state provide thermodynamic models for evaluating $\bar{\phi}_i^V$ and $\bar{\phi}_i^L$ in Eq. (8.45) from volumetric properties. The fugacity coefficients for the vapour and liquid phases are to be obtained from appropriate equations of state. Equations of state widely used in engineering calculations were discussed in Chapter 3. The most generally used equations of state for VLE calculations are given in Table 8.1.

Table 8.1 Equations of state used for VLE calculations

Name	*Equation*	*Constants and functions*
Ideal gas law	$P = \frac{RT}{V}$	
Generalized equation of state	$P = \frac{ZRT}{V}$	$Z = f(P_r, T_r, Z_c \text{ or } \omega)$ $\omega = \left[-\log\left(\frac{P^S}{P_C}\right)_{Tr=0.7}\right] - 1.00$
Redlich-Kwong (R-K)	$P = \frac{RT}{V-b} - \frac{a}{T^{0.5}V(V+b)}$	$a = 0.42748 R^2T_c^{2.5}/P_c$ $b = 0.08664 RT_c/P_c$
Redlich-Kwong-Soave (R-K-S)	$P = \frac{RT}{V-b} - \frac{a}{V^2+bV}$	$a = 0.42748 R^2T_c^2[1+f_w(1-T_r^{0.5})]^2/P_c$ $b = 0.08664 RT_c/P_c$ $f_w = 0.48 + 1.574\omega - 0.176\omega^2$
Peng-Robinson (P-R)	$P = \frac{RT}{V-b} - \frac{a}{V^2+2bV-b^2}$	$a = 0.45724R^2T_c^2[1+f_w(1-T_r^{0.5})]^2/P_c$ $b = 0.07780RT_c/P_c$ $f_w = 0.37464 + 1.54226\omega - 0.26992\omega^2$

The fugacity coefficients in Eq. (8.45) can be calculated using a suitable equation of state. The relationship between fugacity coefficient and the volumetric properties can be written as

$$\ln \phi_i = \frac{1}{RT}\int_V^\infty \left[\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_j} - \frac{RT}{V}\right] dV - RT\ln Z$$

where Z is the compressibility factor.

The equations of state approach has the advantage that the standard state fugacity f_i^0 need not be specified. Another advantage is that the continuity at the critical point is ensured as the properties in the gas and liquid phases are evaluated using the same model. The equations of state approach is more suitable to mixtures of nonpolar components. Also, the equations of state are widely used to predict VLE of light hydrocarbon mixtures.

8.12.2 Vaporisation Equilibrium Constants

For high-pressure vapour–liquid equilibrium calculations, it is convenient to express the phase equilibrium relations in terms of vaporisation equilibrium constants or K factors. It is defined as the ratio of mole fraction in the vapour phase y to that in the liquid x or $K = (y/x)$. The equation of state form of the K-value is obtained from Eq. (8.45) as follows:

$$K_i = \frac{y_i}{x_i} = \frac{\bar{\phi}_i^L}{\bar{\phi}_i^V}$$

The activity coefficient form of the vaporisation equilibrium constant is obtained from Eq. (8.46).

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^L f_i^0}{\bar{\phi}_i^V P} \tag{8.82}$$

Equation (8.82), can be simplified using the Poynting correction for evaluating the standard state fugacity.

$$K_i = \frac{\phi_i^S \gamma_i^L P_i^S}{\bar{\phi}_i^V P} \exp \frac{V_i (P - P_i^S)}{RT} \tag{8.83a}$$

In Eq. (8.83a), ϕ_i^S is the fugacity coefficient in the saturation state, V_i is the molar volume of pure i as saturated liquid. ϕ_i^S and $\bar{\phi}_i^V$ are evaluated using an equation of state. Assuming the Poynting factor to be unity, Eq. (8.83a) can be rearranged as

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^S}{\bar{\phi}_i^V} \frac{\gamma_i^L P_i^S}{P} \tag{8.83b}$$

The K factors contain all the thermodynamic information needed for VLE calculations and are complex functions of temperature, pressure and the vapour phase and liquid phase compositions.

If the vapour phase is assumed to behave as an ideal gas $(\phi_i^S / \bar{\phi}_i^V) = 1$, Eq. (8.83b) simplifies to

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i^L P_i^S}{P} \tag{8.83c}$$

For ideal solutions, the activity coefficient γ_i is unity and therefore Eq. (8.83b) further simplifies to

$$K_i = \frac{y_i}{x_i} = \frac{P_i^s}{P} \tag{8.83d}$$

which is nothing but Raoult's law which is applicable for ideal solution where the vapour behaves as ideal gas. We see that for ideal solution, the vaporisation equilibrium constant is the ratio of vapour pressure to total pressure. The K-factors for ideal solutions depend only on the temperature and pressure and are readily correlated as a function of these two variables.

For mixtures of light hydrocarbons, Eq. (8.83a) can be simplified using two assumptions:

1. Intermolecular forces are weak, so that vapour phase behaves as an ideal solution, so that $\bar{\phi}_i = \phi_i$, where f_i is the fugacity coefficient of the pure components.

2. Liquid phase behaves as an ideal solution so that γ_i^L =1.0.

The resulting equation is very convenient as it involves properties of pure component only.

$$K_i = \frac{\phi_i^S P_i^S}{\phi_i^V P} \exp \frac{V_i (P - P_i^S)}{RT} \tag{8.83e}$$

Equation (8.83e) reveals that for mixtures of light hydrocarbons, the vaporisation equilibrium constants are independent of the composition of the liquid and vapour phases in equilibrium

and can be evaluated as pure component properties. Since ϕ_i^S and ϕ_i^V can be determined from equations of state or generalised correlations, it is possible to provide correlations for *K*-values of substances as functions of temperature and pressure. DePriester nomographs [C.L. DePriester, Chem Eng. Progr., Symposium Ser. 7, 49 (1953)] provide such correlations for many hydrocarbons. These nomographs are available in standard references such as *Chemical Engineers Handbook*. Figure 8.16 gives the *K*-factor for light hydrocarbons in the high temperature range.

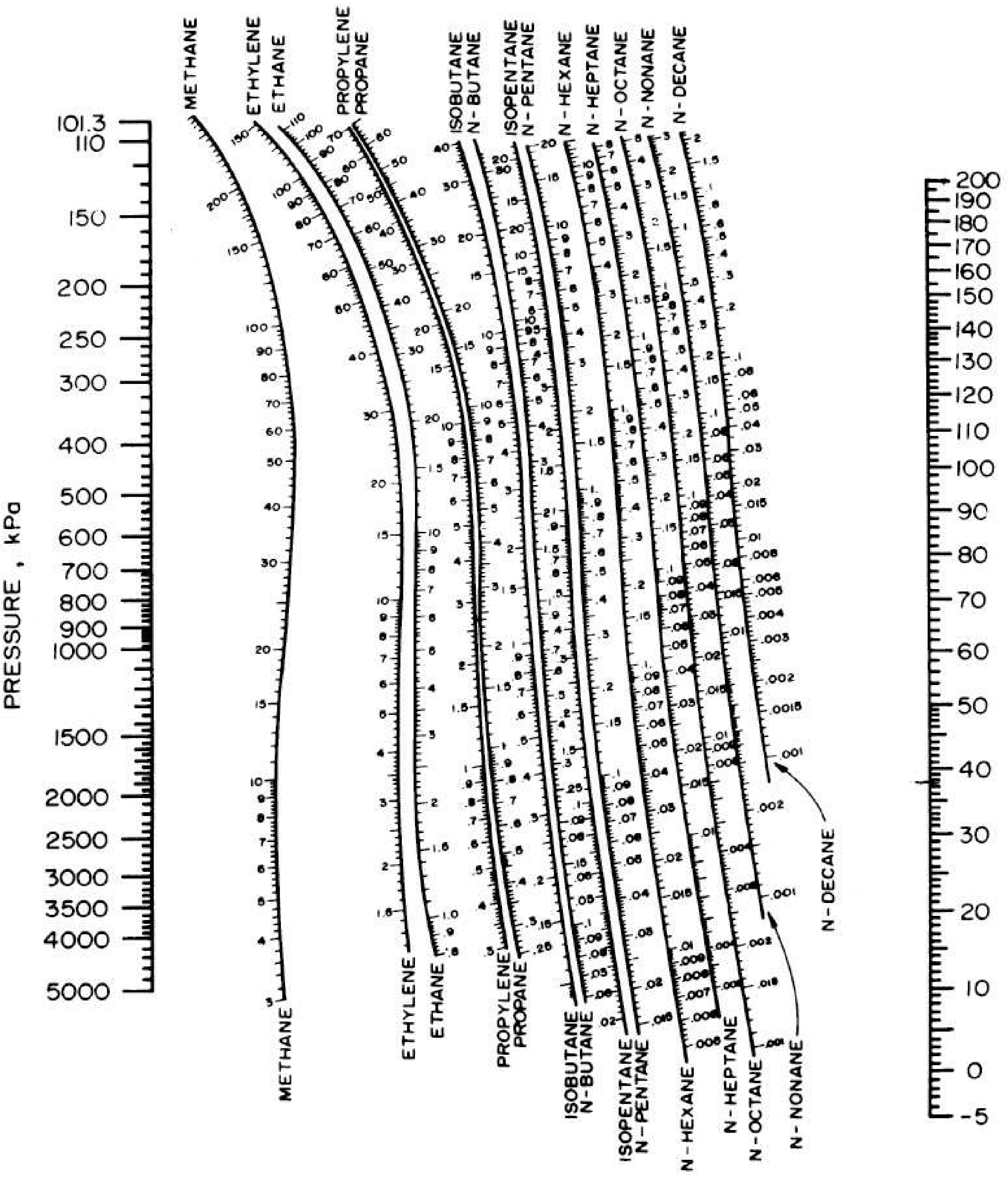


Fig. 8.16 *K*-factor for light hydrocarbons in the high temperature range.

8.12.3 Bubble-point Equilibria

The *bubble-point temperature* is the one at which the first bubble of vapour is produced from the liquid on heating at constant pressure. At the bubble point the liquid has the same composition as the original mixture. Therefore, in problems where bubble-point temperature is to be determined, the x_i

are known. Assume a temperature and get the K_i values at this temperature. Calculate y_i using $y_i = K_i x_i$. If the assumed temperature is correct then

$$\Sigma y_i = \Sigma K_i x_i = 1 \qquad (8.84)$$

Otherwise, repeat the calculations with another temperature. To find the *bubble-point pressure*, a similar procedure as above is adopted by assuming various values of pressure until $\Sigma K_i x_i = 1$.

8.12.4 Dew-point Equilibria

The *dew-point temperature* is the one at which the first drop of condensate is formed on cooling a vapour at constant pressure. The vapour in equilibrium with the liquid at the dew point has the same composition as the original mixture. In order to find the dew-point temperature, a temperature is assumed arbitrarily and K_i is determined. Then,

$$x_i = \frac{y_i}{K_i}$$

At the dew point,

$$\Sigma x_i = \Sigma \frac{y_i}{K_i} = 1.00 \qquad (8.85)$$

Otherwise, repeat the calculation by assuming another temperature till this equation is satisfied. Determination of the *dew-point pressure* involves a similar procedure assuming pressure instead of temperature.

8.12.5 Flash Vaporisation

The general *flash vaporisation* problem can be stated as: Given a mixture of known overall composition z_i at temperature T and pressure P, what is the fraction that is vapour (V) and what are the composition of the liquid and vapour phases in equilibrium? The overall material balance for the system is

$$F = V + L \qquad (8.86)$$

where F is the total number of moles of the initial mixture. The component-*i* balance for the system is

$$F z_i = V y_i + L x_i \qquad (8.87)$$

Since $y_i = K_i x_i$, it can be eliminated from Eq. (8.87) to get the following:

$$x_i = \frac{F z_i}{K_i V + L} = \frac{F}{V} \frac{z_i}{K_i + (L/V)} \tag{8.88}$$

Since $\Sigma\, x_i = 1$, we have

$$\Sigma \frac{z_i}{K_i + (L/V)} = \frac{V}{F} \tag{8.89}$$

The above equation can be used for the calculation of T, P or fractional vaporisation in an iterative procedure. Alternatively, x_i can be eliminated from Eq. (8.87) which leads to

$$y_i = \frac{F z_i}{V + (L/K_i)} = \frac{F}{V} \frac{z_i}{1 + [L/(VK_i)]} \tag{8.90}$$

As $\Sigma\, y_i = 1$, we have

$$\Sigma \frac{z_i}{1 + L/(VK_i)} = \frac{V}{F} \tag{8.91}$$

Equation (8.91) can also be utilised in an iterative procedure to estimate T, P or the fraction of the initial mixture that is vaporised.

***EXAMPLE* 8.25** A mixture contains 45% (mol) methanol (A), 30% (mol) ethanol (B) and the rest n-propanol (C). Liquid solution may be assumed to be ideal and perfect gas law is valid for the vapour phase. Calculate at a total pressure of 101.3 kPa.

(a) The bubble point and the vapour composition

(b) The dew point and the liquid composition.

The vapour pressures of the pure liquids are given below:

Temperature, K	333	343	353	363
P^S_A, kPa	81.97	133.29	186.61	266.58
P^S_B, kPa	49.32	73.31	106.63	166.61
P^S_C, kPa	39.32	62.65	93.30	133.29

Solution The vapour pressures of the components are plotted against temperature so that interpolation of vapour pressure can be done easily.

(a) If the vapour phase can be treated as an ideal gas and liquid phase, an ideal solution, the K-values can be written as $K_i = y_i/x_i = P_i^S/P$. Equation (8.84) can be written as

$$\Sigma\, y_i = \Sigma\, K_i x_i = \Sigma \frac{x_i P_i^S}{P} = 1$$

Now temperatures are assumed till the above equality is satisfied. It is seen that at 344 K,

$$\frac{\sum x_i P_i^S}{P} = 0.98$$

and at 345 K,

$$\sum \frac{x_i P_i^S}{P} = 1.015$$

The bubble-point lies between 344 and 345 K. By interpolation, the bubble-point is obtained as 344.6 K. At this temperature the vapour pressures are obtained from the *P* vs *T* plots. P_A^S = 137.3 kPa, P_B^S = 76.20 kPa and P_C^S = 65.40 kPa.

Component	x_i		$K_i = /P$	$y_i = K_i x_i$
Methanol	0.45	137.30	1.355	0.610
Ethanol	0.30	76.20	0.752	0.226
Propanol	0.25	65.40	0.646	0.162
S $K_i x_i$				0.998

The equilibrium vapour contains 61% methanol, 22.6% ethanol and 16.2% propanol.
(b) Equation (8.85) for the present case becomes

$$\sum x_i = \sum \frac{y_i}{K_i} = \frac{y_i P}{P_i^S} = 1.00$$

The dew-point temperature is to be determined by trial such that the above relation is satisfied. By trial, it can be seen that at 347.5 K, P_A^S = 153.28 kPa, P_B^S = 85.25 kPa and P_C^S = 73.31 kPa.

Component	y_i		$K_i = /P$	$x_i = y_i/K_i$
Methanol	0.45	153.28	1.5131	0.2974
Ethanol	0.30	85.25	0.8416	0.3565
Propanol	0.25	73.31	0.7237	0.3454
Sy_i/K_i				0.9993

The values in the last column are the liquid composition at the dew point. Thus, liquid contains 29.7% methanol, 35.7% ethanol, and 34.5% propanol.

***EXAMPLE* 8.26** A hydrocarbon mixture contains 25% (mol) propane, 40% (mol) *n*-butane and 35% (mol) *n*-pentane at 1447.14 kPa. Assume ideal solution behaviour and calculate

(a) The bubble-point temperature and composition of the vapour
(b) The dew-point temperature and the composition of the liquid
(c) The temperature and the composition of the liquid and vapour in equilibrium when 45% (mol) of the initial mixture is vaporised. (The values of K_i can be obtained from Fig. 13.6 of *Chemical Engineer's Handbook*, 5th ed.)

Solution (a) Assume temperature, say 355.4 K, and the K_i values are found out from the nomograph [Fig. 13.6(b) in *Chemical Engineer's Handbook*]. The products of K_i and x_i are calculated and their sum $\Sigma\ x_iK_i$ is found out. The results for two temperatures 355.4 K and 366.5 K are shown below.

		T = 355.4 K		T = 366.5 K	
Component	x_i	K_i	K_ix_i	K_i	K_ix_i
Propane	0.25	2.000	0.500	2.30	0.575
n-Butane	0.40	0.780	0.312	0.90	0.360
n-Pentane	0.35	0.330	0.116	0.40	0.140
$\Sigma\ K_ix_i$			0.928		1.075

The bubble-point temperature lies between 355.4 K and 366.5 K. By interpolation, the temperature is found out to be 361 K. The calculations are carried out at this temperature and the results are as follows:

Component	x_i	K_i	K_ix_i
Propane	0.25	2.12	0.530
n-Butane	0.40	0.85	0.340
n-Pentane	0.35	0.37	0.130
$\Sigma\ K_ix_i$			1.000

Since $\Sigma\ x_iK_i$ is approximately 1.00, the bubble-point temperature is 361 K. The values in the last column are the mole fraction of various components in the vapour. At the bubble-point, the vapour contains 53% propane, 34% butane and 13% pentane.

(b) At the dew-point temperature, $\Sigma\ y_i/K_i = 1$. At 377.6 K, this value is 1.1598 and at 388.8 K it is 0.9677.

		T = 377.6 K		T = 388.8 K	
Component	y_i	K_i	y_i/K_i	K_i	y_i/K_i
Propane	0.25	2.6	0.0962	2.9	0.0862
n-Butane	0.40	1.1	0.3636	1.3	0.3077
n-Pentane	0.35	0.5	0.7000	0.61	0.5738
$\Sigma y_i/K_i$			1.1598		0.9677

By interpolation, the dew-point temperature is found to be 387 K. The calculations for this temperature is given below.

Component	y_i	K_i	y_i/K_i
Propane	0.25	2.85	0.0877
n-Butane	0.40	1.25	0.3200
n-Pentane	0.35	0.59	0.5932
S y_i/K_i			1.0009

The last column in the above table is the liquid compositions. The equilibrium liquid at the dew point contains 8.77% propane, 32.0% butane and 59.32% pentane.

(c) In the following calculations, temperature is assumed so as to satisfy Eq. (8.91). For a basis of 100 mol of the initial mixture, $F = 100$ mol, $V = 45$ mol and $L = 55$ mol. Equation (8.91) becomes

$$\Sigma \frac{z_i}{1 + L/(VK_i)} = 0.45$$

		$T = 366.5$ K		$T = 377.6$ K	
Component	z_i	K_i	$z_i/[1 + L/(VK_i)]$	K_i	$z_i/[1 + L/(VK_i)]$
Propane	0.25	2.30	0.1632	2.6	0.1701
n-Butane	0.40	0.90	0.1696	1.1	0.1895
n-Pentane	0.35	0.40	0.0863	0.5	0.1016
S $z_i/[1 + L/(VK_i)]$			0.4191		0.4612

From the calculations given above, we see that the equilibrium temperature is between 366.5 K and 377.6 K. By interpolation, $T = 374.6$ K.

		$T = 374.6$ K	
Component	z_i	K_i	$z_i/[1 + L/(VK_i)]$
Propane	0.25	2.50	0.1679
n-Butane	0.40	1.08	0.1876
n-Pentane	0.35	0.48	0.0987
S $z_i/[1 + L/(VK_i)]$			0.4542

Comparing Eqs. (8.90) and (8.91), we can see that

$$y_i = \frac{z_i/[1 + L/(VK_i)]}{\Sigma z_i/[1 + L/(VK_i)]}$$

These are calculated using the values in the last column. Corresponding x_i values are found out using the material balance [Eq. (8.87)].

$$Fz_i = Vy_i + Lx_i$$

The results of the calculation are given below:

Component	y_i	x_i
Propane	0.3697	0.1521
n-Butane	0.4130	0.3894
n-Pentane	0.2173	0.4586

8.13 CONSISTENCY TESTS FOR VLE DATA

Many practical cases like distillation calculations are dependent on vapour–liquid equilibrium data and such data should be reasonably accurate if the results are to be reliable. As the VLE measurements are prone to inaccuracies, it is essential that we have some means for checking the consistency of the measured results. Thermodynamics provides tests for consistency of experimental VLE data. Almost all these tests are based on the Gibbs–Duhem equations written in terms of activity coefficients [Eq. (7.101)].

8.13.1 Using Slope of ln g Curves

The Gibbs–Duhem equation in terms of activity coefficient [Eq. (7.101)] provides a very simple test for thermodynamic consistency.

$$x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} = x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{T,P}$$

This can be put into the following form.

$$x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} = -(1-x_1)\left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_{T,P} \tag{8.92}$$

Plot the logarithm of the activity coefficients against mole fraction x_1 of component 1 in a binary solution as shown in Fig 8.17(a) and measure the slopes of the tangents drawn to the resulting curves at any selected composition x_1.

Equation (8.92) tells us that if the Gibbs–Duhem equation is to be satisfied, both slopes must have opposite sign. Otherwise, the data are inconsistent. If the slopes are of opposite sign, substitute the values in Eq. (8.92) and if it is satisfied reasonably well, then the data is consistent at the selected composition. For a complete test, the slopes determined at other compositions are substituted into Eq. (8.92) to see whether the equality is satisfied or not.

In addition to the above observations, we can make the following generalisations with the help of Eq. (7.101).

1. If one of the ln g curves has a maximum (or minimum) at certain concentration, the other curve should have a minimum (or maximum) at the same composition.
2. If there is no maximum or minimum point, then both curves must be positive or both must be negative over the entire range. Or in other words, if one component has g values always greater than unity and has no maximum, the g values of the other component must likewise be greater than unity. This is a consequence of the fact that Raoult’s law is to be obeyed by the component

as its mole fraction tends to unity.

From the above discussion, it is clear that Fig. 8.17(b) represents plots of consistent data whereas Figs. 8.17(c) and (d) are plots of thermodynamically inconsistent data. In Fig. 8.17(c), though there is maximum on one curve and minimum on the other, these are shown at different compositions. In Fig. 8.17(d), the slopes have the same sign and the data are thermodynamically inaccurate.

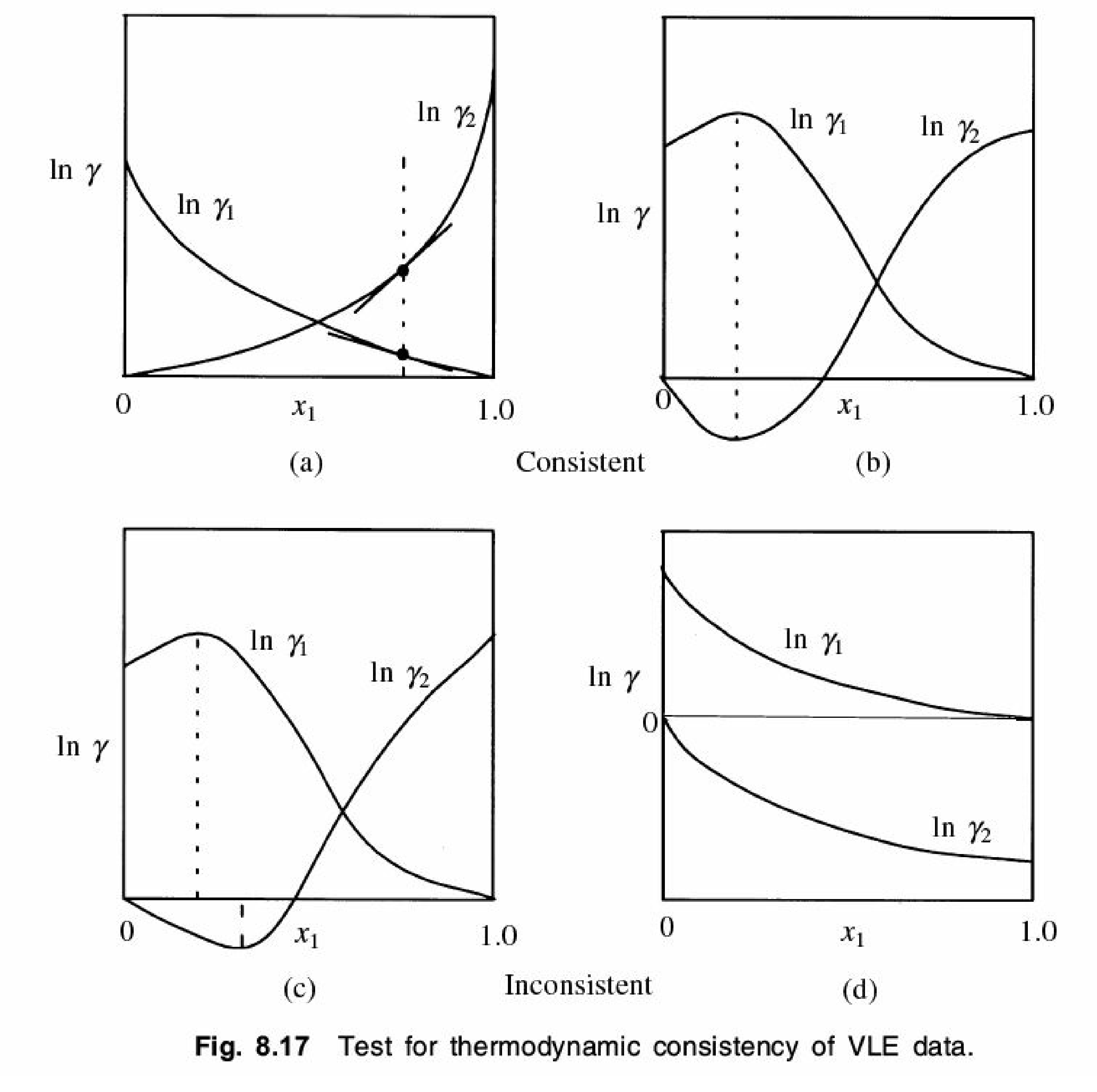


Fig. 8.17 Test for thermodynamic consistency of VLE data.

8.13.2 Using Data at the Mid-point

For testing the thermodynamic consistency of VLE data, the integrated forms of the Gibbs–Duhem equation like the van Laar or the Margules equation are sometimes found very convenient. Consider the van Laar equation Eq. (8.68). Put $x_1 = x_2 = 0.5$ and we see that

$$\frac{\ln \gamma_1}{B} = \frac{\ln \gamma_2}{A} = \frac{AB}{(A+B)^2} \tag{8.93}$$

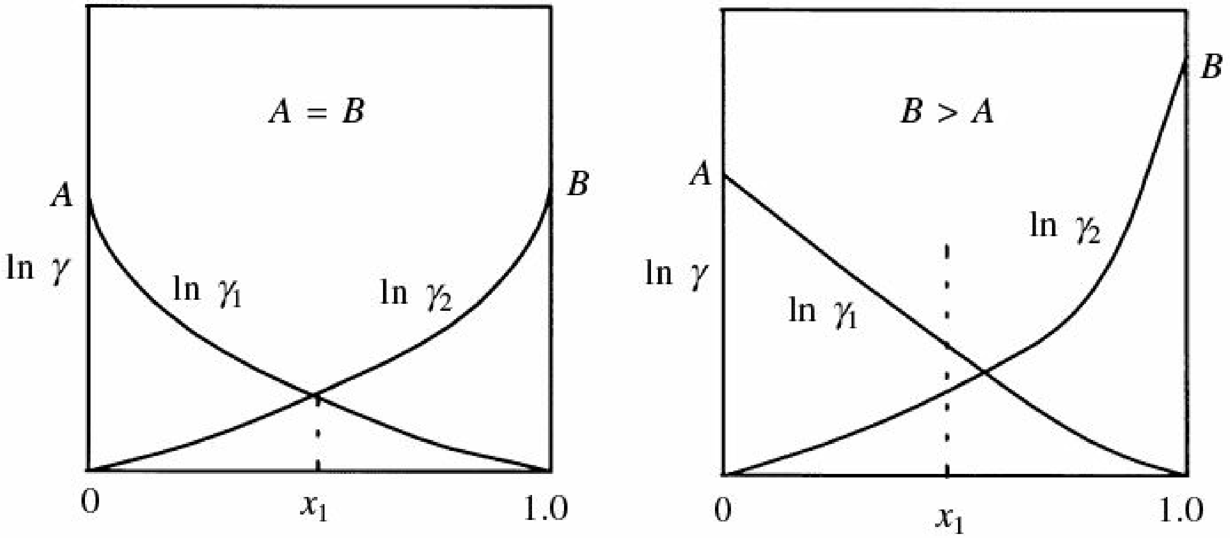
Case 1. Assume that $A = B$. Then $\ln g_1 = B/4$ and $\ln g_2 = A/4$

Case 2. Assume that $A = 2B$. Then $\ln g_1 = (2/9)B$ and $\ln g_2 = (2/9)A$

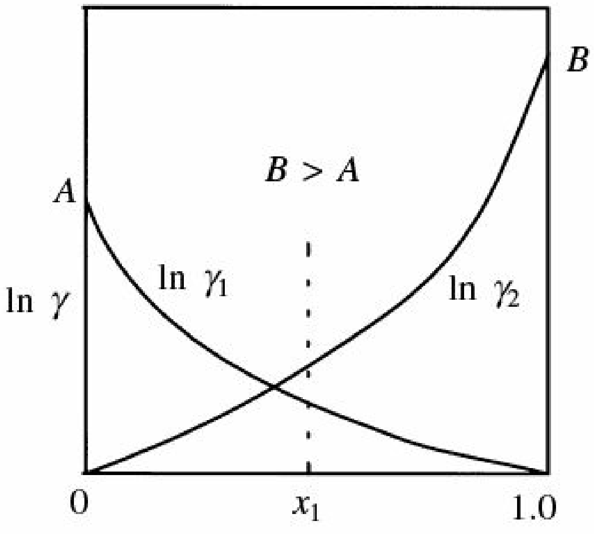
Case 3. Assume that $A = 3B$. Then $\ln g_1 = (3/16)B$ and $\ln g_2 = (3/16)A$

In all cases cited above, the $\ln g_1$ at the mid-point (i.e. at $x_1 = x_2 = 0.5$) is approximately one-fourth the van Laar constant B and $\ln g_2$ approximately one-fourth the constant A. We have already seen that the van Laar constant A is $\ln g_1$ as x_1 tends to zero and B is $\ln g_2$ as x_1 tends to one. Now we have a rough check on the consistency of VLE data for the mid-point. The $\ln g$ value at this point will be approximately one-fourth the terminal value of the other $\ln g$ curve. That is the curve, which is highest at the end-point will be lowest at the mid-point and vice versa, as shown in Figs. 8.18(a) and (b).

The mid-point values are approximately one-fourth the terminal values of the other curves in both the figures. However, Fig. 8.18(c) reveals an inconsistent data, as the curve which is highest at the end-point is also the highest at the mid-point.



(a) Consistent (b) Consistent



(c) Inconsistent

Fig. 8.18 Test for thermodynamic consistency using activity coefficient data at the mid-point.

8.13.3 Redlich–Kister Method

This method, also known as the *zero area method* can be applied to test the consistency of experimental data when the activity coefficient values over the entire concentration range is available. It is based on the excess free energy of mixing which is the difference between the free energy of mixing of a real solution and that of an ideal solution. Referring to Eqs. (7.134) and (7.145) the excess free energy of mixing can be written as

$$\Delta G^E = RT \Sigma x_i \ln \gamma_i \qquad (8.94)$$

For a binary solution, it can be written as

$$\Delta G^E = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)$$

Differentiating this with respect to x_1, we get

$$\frac{d(\Delta G^E)}{dx_1} = RT \left[\ln \frac{\gamma_1}{\gamma_2} + x_1 \frac{d(\ln \gamma_1)}{dx_1} + (1 - x_1) \frac{d(\ln \gamma_2)}{dx_1} \right] \qquad (8.95)$$

Substitution of the Gibbs–Duhem equation [Eq. (8.92)] into Eq. (8.95) leads to

$$\frac{d(\Delta G^E)}{dx_1} = RT \ln \frac{\gamma_1}{\gamma_2} \qquad (8.96)$$

This can be integrated between the limits $x_1 = 0$ and $x_1 = 1$. Since only pure components are involved at these two end states and no mixing effects occur, $\Delta G^E = 0$ at these points. Therefore,

$$0 - 0 = RT \int_0^1 \ln \frac{\gamma_1}{\gamma_2} \, dx_1$$

or

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} \, dx_1 = 0 \qquad (8.97)$$

From the experimental values of activity coefficients, ln (γ_1/γ_2) values are calculated and plotted against x_1 taken on the *x*-axis. The net area of the diagram should equal zero if the data are thermodynamically consistent. That is, the area above the *x*-axis will be equal to the area below it as shown in Fig. 8.19.

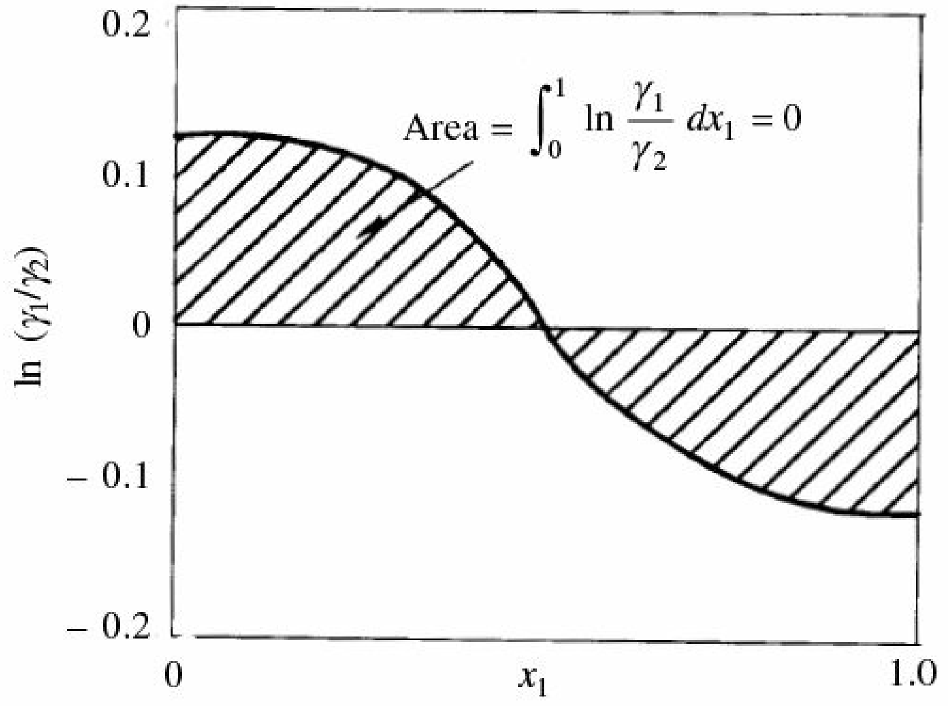


Fig. 8.19 Test for thermodynamic consistency by Redlich–Kister method.

8.13.4 Using the Coexistence Equation

The coexistence equation can be used for testing the consistency of vapour–liquid equilibrium data. If the vapour in equilibrium with a binary liquid mixture behaves as an ideal gas, Eq. (8.47) can be used to describe the equilibrium. Rearranging Eq. (8.47), the activity coefficients can be written as

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^S}, \qquad \gamma_2 = \frac{y_2 P}{x_2 P_2^S}$$

Substitute this in the Gibbs–Duhem Equations [Eq. (8.92)] written in the following form

$$x_1\, d\ln \gamma_1 = -(1 - x_1)\, d\ln \gamma_2 \tag{8.98}$$

$$x_1\, d\ln \frac{y_1 P}{x_1 P_1^S} = -(1 - x_1)\, d\ln \frac{y_2 P}{x_2 P_2^S}$$

Since P_1^S and P_2^S are constants at constant temperature, the above equation can be simplified as

$$d\ln P = \frac{y_1 - x_1}{y_1 (1 - y_1)}\, dy_1$$

which, on rearrangement gives

$$\frac{dP}{dy_1} = \frac{P(y_1 - x_1)}{y_1 (1 - y_1)} \tag{8.99}$$

Equation (8.99) is known as the *coexistence equation*. It can be used to calculate any one of the three variables P, x or y if experimentally measured values of the other two variables are available. If all the three variables are experimentally determined, then Eq. (8.99) can be used to test the consistency of the measured data.

8.13.5 Using the Partial Pressure Data

At low pressures, the fugacity of a gas equals the pressure and therefore, the Gibbs–Duhem equation in terms of fugacity [Eq. (7.99)] can be rewritten as,

$$x_1 \frac{d \ln \bar{p}_1}{dx_1} = -\, x_2 \frac{d \ln \bar{p}_2}{dx_1}$$

or

$$\frac{x_1}{\bar{p}_1} \frac{d\bar{p}_1}{dx_1} = -\, \frac{x_2}{\bar{p}_2} \frac{d\bar{p}_2}{dx_1} \tag{8.100}$$

The partial pressures of both components are plotted against mole fraction x_1 as in Fig. 8.20. The slopes, $(d\bar{p}_1/dx_1)$ and $(d\bar{p}_2/dx_1)$ are determined at any selected composition. $(x_1/\bar{p}_1)\,(d\bar{p}_1/dx_1)$ and $(x_2/\bar{p}_2)\,(d\bar{p}_2/dx_1)$ are calculated. Then, according to Eq. (8.100), the absolute values of these quantities should be the same if the data are thermodynamically consistent.

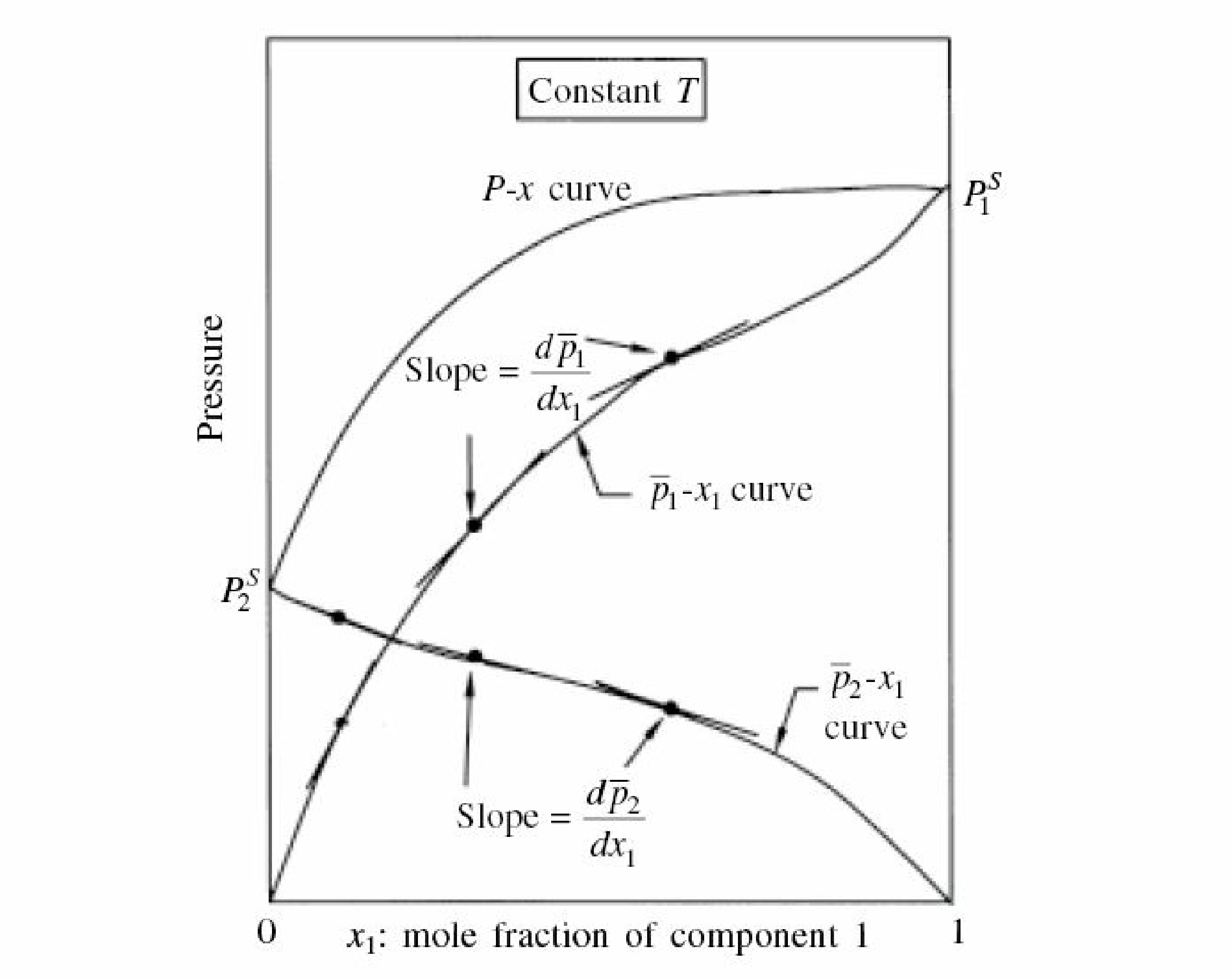


Fig. 8.20 Test for thermodynamic consistency with partial pressure data.

***EXAMPLE* 8.27** The following results were obtained by experimental VLE measurements on the system, ethanol (1)–benzene (2) at 101.3 kPa. Test whether the data are thermodynamically consistent or not.

x_1	0.003	0.449	0.700	0.900
y_1	0.432	0.449	0.520	0.719
, kPa	65.31	63.98	66.64	81.31
, kPa	68.64	68.64	69.31	72.24

Solution Assuming that the gas phase behaves ideally, the activity coefficients are calculated as

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^S}, \qquad \gamma_2 = \frac{y_2 P}{x_2 P_2^S}$$

The values so calculated are listed below:

x_1	0.003	0.449	0.700	0.900
g_1	223.3	1.58	1.13	0.99
g_2	0.841	1.475	2.34	2.92
$\ln(g_1/g_2)$	5.58	0.068	– 0.734	– 1.082

ln (g_1/g_2) values are plotted against x_1. The net area is found out. Since this is not equal to zero, the given experimental measurements do not satisfy the Redlich–Kister criterion [Eq. (8.97)] for consistency.

8.14 CALCULATION OF ACTIVITY COEFFICIENTS USING GIBBS–DUHEM EQUATION

The activity coefficients in a binary solution are related to each other according to the Gibbs–Duhem equations as given below. See Eq. (7.101).

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} = x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{T,P}$$

The above equation can be used to estimate the activity coefficient of one of the components in a binary mixture if the other is known as function of composition. Rewrite Eq. (7.101) as

$$d \ln \gamma_1 = -\frac{x_2}{x_1} d \ln \gamma_2 \tag{8.101}$$

Integrate Eq. (8.101) between limits $x_2 = 0$ where x_1 and γ_1 are both unity and the desired composition x_2 where the activity coefficient γ_1 is to be determined. This results in

$$\ln \gamma_1 = -\int_{\ln \gamma_2 \text{ at } x_2 = 0}^{\ln \gamma_2} \frac{x_2}{x_1} d(\ln \gamma_2) \tag{8.102}$$

The integral can be evaluated analytically if g_2 is expressed as a mathematical function of composition. To find the integral graphically, plot a graph with (x_2/x_1) on the y-axis and ln g_2 on the x-axis. The area under the curve from ln g_2 at $x_2 = 0$ to ln g_2 at any desired composition x_2 gives the value
– ln g_1 for the component 1.

***EXAMPLE* 8.28** The activity coefficients for component 1 in a binary solution can be represented by $\ln \gamma_1 = ax_2^2 + bx_2^3 + cx_2^4$, where a, b and c are concentration independent parameters. Derive an expression for ln g_2.

Solution Equation (8.101) may be written as

$$\ln \gamma_2 = -\int_0^{x_1} \frac{x_1}{x_2}\, d\,(\ln \gamma_1)$$

For the present case,

$$d \ln \gamma_1 = (2\,ax_2 + 3\,bx_2^2 + 4\,cx_2^3)\, dx_2$$

Substituting this in the above equation we get

$$\ln \gamma_2 = -\int_0^{x_1} (2\,ax_1 + 3\,bx_1x_2 + 4\,c\,x_1x_2^2)\, dx_2$$

$$= \int_0^{x_1} [2\,ax_1 + 3\,bx_1\,(1 - x_1) + 4\,c\,x_1\,(1 - x_1)^2]\, dx_1$$

$$= \left(a + \frac{3}{2}\,b + 2c\right) x_1^2 - \left(b + \frac{8}{3}\,c\right) x_1^3 + c\,x_1^4$$

***EXAMPLE* 8.29** The following data gives the composition versus total pressure for the system chloroform (1)–ethyl alcohol (2) at 328 K are:

x_1	0.0331	0.9652
P, kPa	40.84	84.88

Vapour pressures of chloroform and acetone at 328 K are 82.35 and 37.30 kPa respectively. Estimate the constants in the Margules equation [Eq. (8.66)].

Solution The Margules equations are:

$$\ln \gamma_1 = x_2^2[A + 2(B - A)x_1]$$

$$\ln \gamma_2 = x_1^2[B + 2(A - B)x_2]$$

$A = \ln \gamma_1^\infty$ and $B = \ln \gamma_2^\infty$, where γ_1^∞ and γ_2^∞ are the activity coefficient values when the respective mole fractions tend to zero. Assuming that the vapour behaves as ideal gas, $\bar{p}_1 = P - \bar{p}_2$. That is,

$$\gamma_1 x_1 P_1^S = P - \gamma_2 x_2 P_2^S$$

or

$$\gamma_1 = \frac{P - \gamma_2 x_2 P_2^S}{x_1 P_1^S}$$

As x_2 approaches 1, γ_2 becomes unity and the above equation becomes

$$\gamma_1^\infty = \frac{P - x_2 P_2^S}{x_1 P_1^S} \tag{8.103}$$

Similarly

$$\gamma_2^\infty = \frac{P - x_1 P_1^S}{x_2 P_2^S} \tag{8.104}$$

(*Note:* Equations (8.103) and (8.104) are known as Carlson and Colburn relations for activity coefficient.)

Substitute the given data into Eq. (8.103) and Eq. (8.104), we get

$$\gamma_1^\infty = \frac{40.84 - (1 - 0.0331)\,37.30}{0.0331 \times 82.35} = 1.752$$

$$\gamma_2^\infty = \frac{84.88 - 0.9652 \times 82.35}{(1 - 0.9652)\,37.30} = 4.157$$

Therefore, $A = \ln 1.752 = 0.561$ and $B = \ln 4.157 = 1.424$.

***EXAMPLE* 8.30** The following table gives the partial pressure of acetone versus liquid composition for acetone (1)–water (2) system at 333 K.

x_1	0	0.033	0.117	0.318	0.554	0.736	1.000
$_1$, kPa	0	25.33	59.05	78.37	89.58	94.77	114.63

The vapour pressure of water at 333 K is 19.91 kPa. Calculate the partial pressure of water in the vapour phase.

Solution Equation (8.100) is the Gibbs–Duhem equation in terms of partial pressures.

$$\frac{x_1}{\bar{p}_1}\frac{d\bar{p}_1}{dx_1} = -\frac{x_2}{\bar{p}_2}\frac{d\bar{p}_2}{dx_1}$$

It can be put in the following form:

$$\frac{d\bar{p}_2}{\bar{p}_2} = -\frac{x_1}{(1 - x_1)}\frac{d\bar{p}_1}{\bar{p}_1} \tag{8.105}$$

For pure water, $x_1 = 0$, $\bar{p}_1 = 0$ and $\bar{p}_2 = P_2^S$. For getting the partial pressure of water at any composition, integrate the above equation between $\bar{p}_1$ and 0.

$$\ln\frac{\bar{p}_2}{P_2^S} = -\int_0^{\bar{p}_1}\frac{x_1}{(1 - x_1)}\frac{d\bar{p}_1}{\bar{p}_1} \tag{8.106}$$

Using the given data calculate $x_1/[(1 - x_1)\bar{p}_1]$ and this is plotted against $\bar{p}_1$. The area under the curve between the limits 0 and $\bar{p}_1$ gives the integral in Eq. (8.106) from which the partial pressure $\bar{p}_2$ can be calculated. The results are given below:

x_1	0	0.033	0.117	0.318	0.554	0.736	1.000
, kPa	19.91	19.31	18.27	16.99	15.42	13.90	0

8.15 VLE FOR SYSTEMS OF LIMITED MISCIBILITY

8.15.1 Partially Miscible Systems

Figure 8.21 shows the temperature-composition diagram for a partially miscible system at constant total pressure. Points *A* and *B* indicate the boiling points of pure liquids *A* and *B* at this pressure. A binary system consisting of two liquid phases and a vapour phase is univariant according to the phase rule. By fixing the pressure, the system is completely defined. The states of the three phases in equilibrium lie on the horizontal line at T^*, the three-phase equilibrium temperature. Points *C* and *D* represent the saturated liquid phases and point *E* the vapour in equilibrium with these liquids.

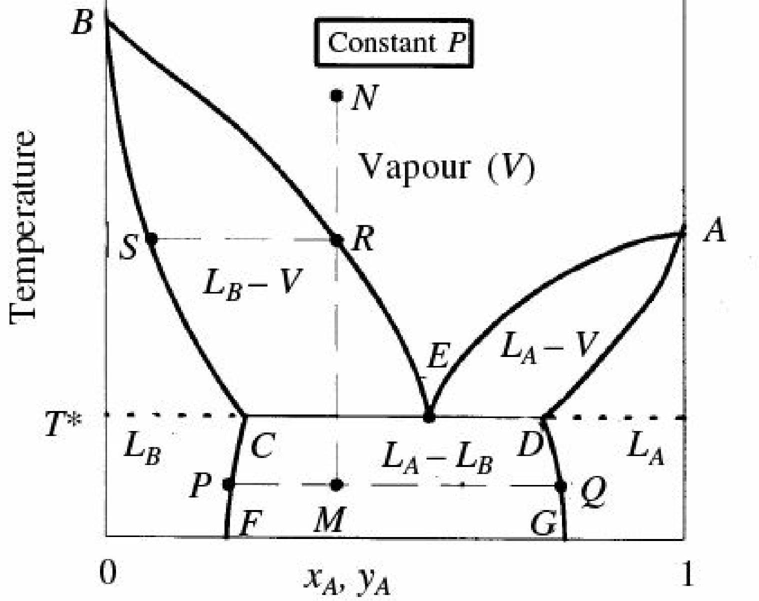


Fig. 8.21(a) Temperature-composition diagram for a partially miscible binary mixture.

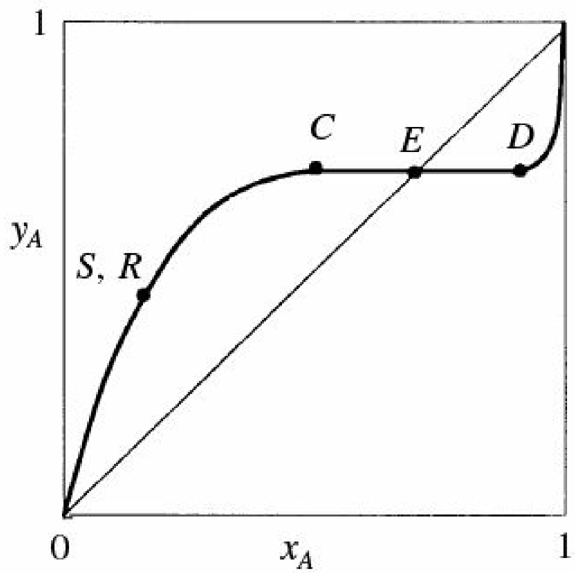


Fig. 8.21(b) Equilibrium diagram of a partially miscible binary mixture.

Below T^* the system is entirely liquid. It may exist as a homogeneous system, or, as a heterogeneous system consisting of two saturated liquid phases, depending upon its overall composition. If the overall composition of the mixture lies within the region bounded by the curves *FC* and *GD* below temperature T^*, the mixture cannot exist as a single phase. It separates into two saturated liquid phases, a *A*-rich phase (L_A) represented by the curve *GD* and a *B*-rich phase (L_B) represented by the curve *FC*. The compositions of these phases are determined by the intersection of a horizontal line corresponding to the temperature of the system and the curves *GD* and *FC*. Consider, for example, a liquid whose combined concentration and temperature are such that it is represented by the point *M* in Fig. 8.21(a). Since *M* lies in the two-liquid region (L_B –L_A), the mixture separates into a *B*-rich phase represented by point *P*, and a *A*-rich phase represented by point *Q*.

The mutual solubility of *A* and *B* increases with increase in temperature as shown by the curves *FC* and *GD* in Fig. 8.21(a). The change in the solubility of liquid *A* in liquid *B* with temperature is along *FC* and that of *B* in *A* is along *GD*. To the right of the curve *GD* and to the left of the curve *CF* the mixture exists as homogeneous liquid, if the temperature is below the three-phase temperature. The higher the three-phase temperature the more the mutual solubility of liquids *A* and *B*. Suppose that the mixture at *M* in Fig. 8.21(a) is heated at constant pressure. Its temperature increases till T^* is reached. At T^*, the vapour of the composition corresponding to point *E* is formed. If additional quantities of liquid *A* or *B* are introduced into the system at this point, the relative amounts of the three phases in equilibrium will change, but the composition of these phases represented by points *C*, *D* and *E* must remain the same. The temperature T^* remains constant until one of the liquid phases disappears. At temperatures above T^*, the system can exist either as two phases (liquid and vapour) or as a single phase depending on the overall composition. The liquid phase that disappears depends on whether the combined mixture composition is to the left or right of point *E*. For the mixture at *M*, the *A*-rich phase disappears. The system now consists of a saturated liquid (L_B) in equilibrium with saturated vapour (*V*). When the temperature is increased the overall composition must lie on the vertical line *MN*, the relative amounts and composition of the liquid and the vapour phases change accordingly. Above the temperature corresponding to point *R*, the mixture is entirely vapour. If the initial mixture were to the right of point *E*, the liquid in equilibrium with the vapour would have been L_A instead of L_B.

The three-phase equilibrium temperature increases with pressure as shown in Fig. 8.22 where temperature-composition diagrams are plotted at various pressures. The curves *FC* and *GD* eventually merge to a single point and the two liquid phases become identical. The temperature at which this occurs is known as the *upper critical solution temperature* (UCST). For pressures above this critical condition, the three-phase equilibrium conditions do not exist.

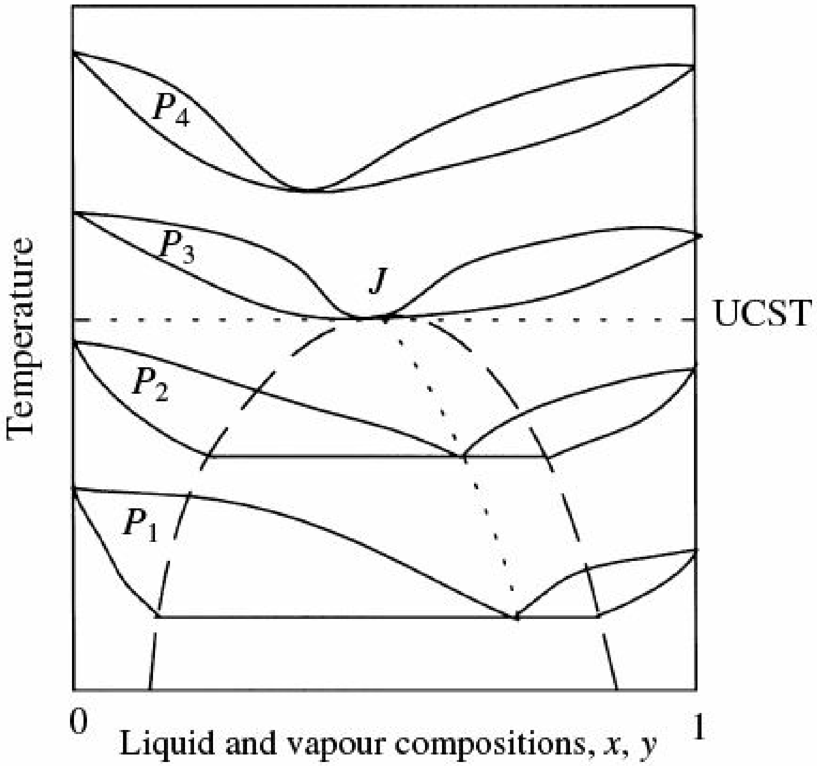


Fig. 8.22 Effect of pressure on the vapour–liquid equilibrium of partially miscible systems.

8.15.2 Immiscible Systems

The phase diagram for a completely immiscible system is shown in Fig. 8.23. This diagram is a special case of Fig. 8.21 occurring when the two liquid phases L_A and L_B are the pure liquids *A* and *B* respectively. Consider a binary mixture of two immiscible liquids having an overall composition represented by point *M*. When this mixture is heated its temperature increases along the line *MN*. For all temperatures up to point *N*, each component exerts its full vapour pressure as its partial pressure in the vapour phase. When the temperature T^* corresponding to point *N* is reached, the sum of the vapour pressures becomes equal to the surrounding pressure and the system cannot exist entirely in the liquid state and vapour is produced. T^* is therefore known as the three-phase temperature.

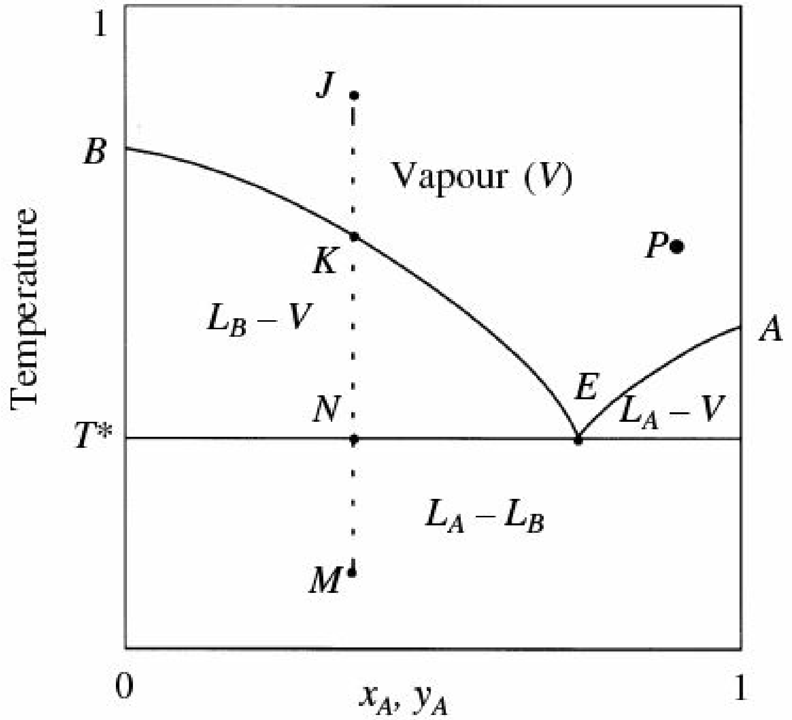


Fig. 8.23 Temperature composition diagram for an immiscible system.

The composition of the vapour in equilibrium with the pure liquids at the three-phase temperature is given by point *E*. Since there are three phases and two components present, according to the phase rule, the number of degrees of freedom is one as in the case of partially miscible systems. It means that, when pressure is fixed the system is completely defined. The three-phase temperature and the equilibrium vapour composition get automatically fixed by specifying the pressure in such a way that the sum of the vapour pressures equals the surrounding pressure.

$$P = P_A^S + P_B^S \tag{8.107}$$

On further addition of heat, the temperature remains constant at T^* and more vapour of the same composition as given by point *E* is formed. This continues till one of the components disappears from the liquid and the system becomes a two-phase mixture either $L_A - V$ or $L_B - V$ depending upon the initial composition.

Now let us consider the cooling of a vapour of initial composition and temperature indicated by point *J*. When the temperature is lowered to that corresponding to point *K* the vapour pressure of pure liquid *B* will be equal to the partial pressure of *B* in the vapour. Pure liquid *B* gets condensed and the vapour composition changes along the line *KE*. When the temperature T^* is reached, the partial pressure of *A* in the vapour will be equal to the vapour pressure of *A* and at this condition, pure liquids *A* and *B* and the vapour are present in equilibrium. Further cooling results in the elimination of the vapour phase and the system now consists of two immiscible liquids. If the initial vapour were at point *P*, pure liquid *A* would have condensed out first, instead of *B*.

***EXAMPLE* 8.31** A high boiling organic liquid is purified from non-volatile impurities by allowing it to mix with steam directly at a total pressure of 93.30 kPa. The vapour pressure data are given as follows:

Temperature, K	353	373
Vapour pressure of water, kPa	47.98	101.3
Vapour pressure of liquid, kPa	2.67	5.33

Assume that water and the organic liquid are immiscible and the impurities do not affect the vaporisation characteristics. The vapour pressures vary linearly with temperature. Calculate under three-phase equilibrium

(a) The equilibrium temperature and

(b) The composition of the resulting vapour.

Solution (a) At 353 K, sum of the vapour pressures is 50.65 kPa and at 373 K it is 106.63 kPa. Since the vapour pressures vary linearly, the temperature at which the sum of vapour pressures is 93.3 kPa is obtained by interpolation.

$$T^* = 353 + \frac{373 - 353}{106.63 - 50.65}(93.3 - 50.65) = 368.2 \text{ K}$$

(b) At 368.2 K, the vapour pressure of water is 88.50 kPa and that of the liquid is 4.80 kPa. Since a three-phase equilibrium, the partial pressure is equal to the vapour pressure, the ratio of mole fractions of the components will be same as the ratio of vapour pressures. Let y be the mole fraction of water in the vapour. Then

$$y = \frac{88.5}{9330} = 0.9486$$

The vapour contains 94.86% (mol) water vapour.

EXAMPLE **8.32** Assuming that benzene is immiscible with water, prepare a temperature-composition diagram for benzene (1)–water (2) system at 101.3 kPa using the following vapour pressure data:

T, K	323	333	343	348	353	363	373
, kPa	12.40	19.86	31.06	37.99	47.32	70.11	101.3
, kPa	35.85	51.85	72.91	85.31	100.50	135.42	179.14

The boiling point of pure benzene at 101.3 kPa is 353.1 K.

Solution The three-phase temperature is first found out. At T^*, $P = P_1^S + P_2^S . P_1^S + P_2^S$ is calculated for each given temperature, and this is plotted against temperature. T^* is the temperature at which P is equal to 101.3 kPa. This is found out to be 342 K. The horizontal line CD in Fig. 8.24 is drawn at this temperature. The vapour pressures at this temperature are P_1^S = 71.18 kPa and P_2^S = 30.12 kPa. The mole fraction of benzene in the vapour represented by point E in Fig. 8.24 is 71.18/101.3 = 0.70.

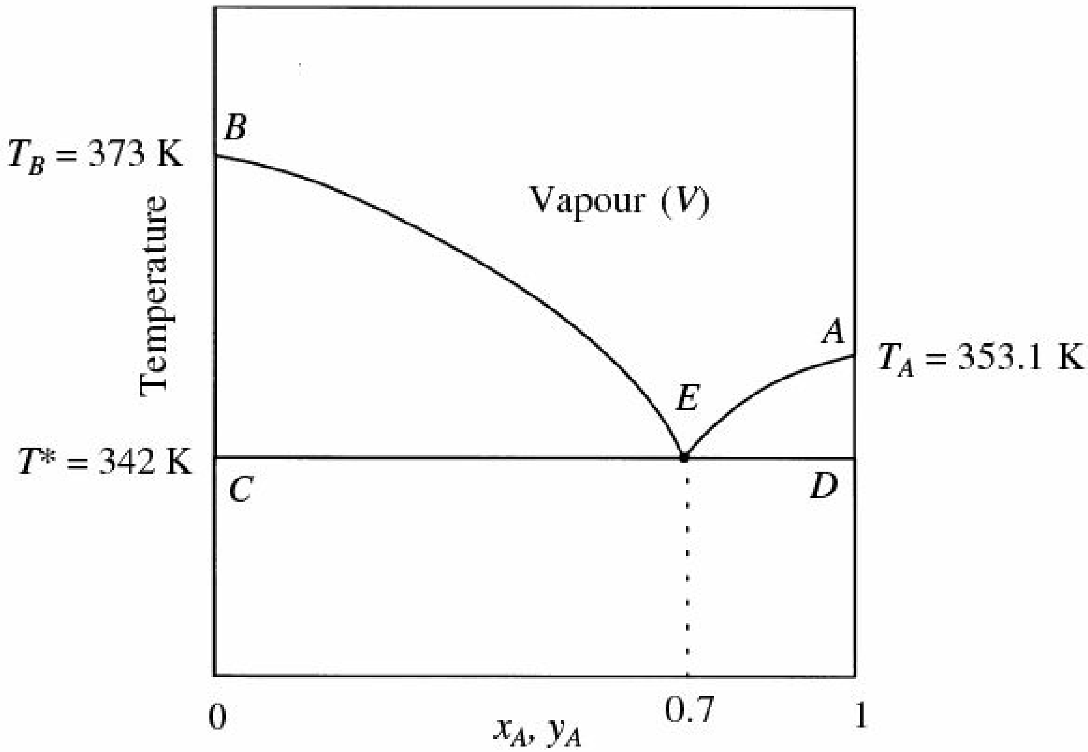


Fig. 8.24 Temperature composition diagram for Example 8.28.

The dew-point curve *BE* is plotted by choosing a temperature lying between 373 K (boiling point of water) and 342 K (the three-phase temperature). For example, take $T = 353$ K. The partial pressure of water at the dew point is equal to the vapour pressure. For the dew-point temperature of 353 K, the partial pressure of water is

$$47.32 = (1 - y) \square P$$

where y is the mole fraction of benzene in the vapour. We get, $y = 0.5329$.

This calculation is repeated for various temperature and the entire curve *BE* is drawn. For getting the curve *AE* the procedure is the same. Here temperatures are assumed between 342 K and 353.1 K, the latter being the boiling point of pure benzene. On the curve *AE*, the partial pressure of benzene in the vapour equals its vapour pressure. For example, for a dew-point temperature of 348 K,

$$85.31 = P \square y, \text{ or } y = 0.8422$$

The following table gives the results of a few such calculations:

T, K	342	348	353	353.1	363	373
y (curve *AE*)	0.70	0.84	0.99	1.00	–	–
y (curve *BE*)	0.70	–	0.53	–	0.31	0

8.16 LIQUID–LIQUID EQUILIBRIUM DIAGRAMS

8.16.1 Binary Liquid–Liquid Equilibria

When two liquids are only partially miscible, the equilibrium can be represented on rectangular coordinates as shown in Fig. 8.25. A dome-shaped region is formed by the mutual solubility curves and within the dome the mixture exists as two phases. The compositions of the equilibrium phases lie at the ends of the horizontal line at a given temperature. For example, the mixture M in Fig. 8.25 will separate into two equilibrium phases A and B. The relative amounts of the phases are given by the inverse lever rule.

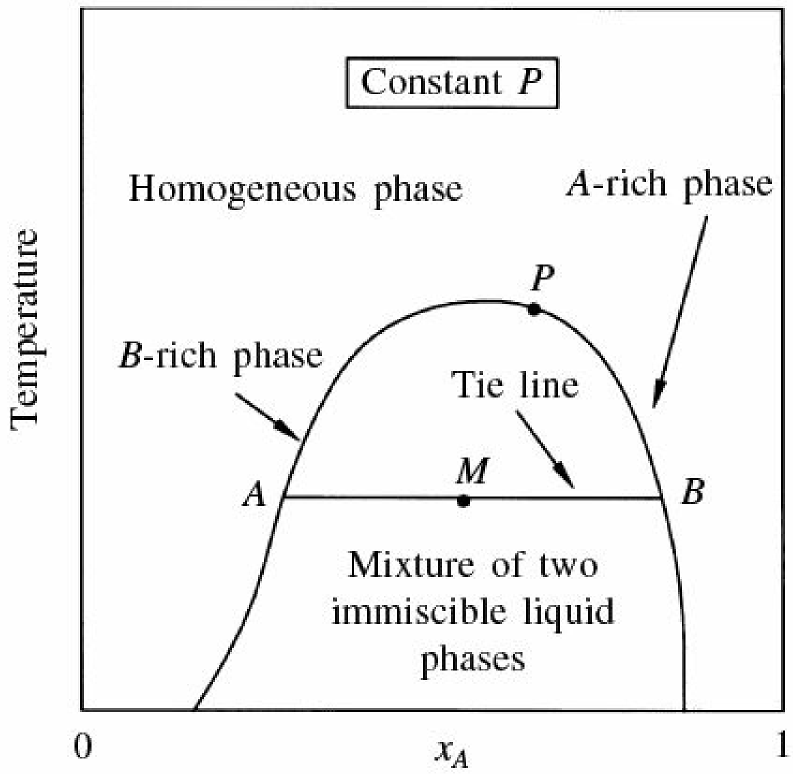


Fig. 8.25 Binary liquid–liquid equilibrium.

$$\frac{\text{Amount of phase } A}{\text{Amount of phase } B} = \frac{\text{Line } MB}{\text{Line } AM}$$

The point P gives the *critical solution temperature*. Outside the dome the mixture is homogeneous.

8.16.2 Ternary Equilibrium Diagrams

Liquid–liquid equilibria involving three components are important in the analysis of extraction operations. The extraction process involves bringing a binary mixture of components A and C into intimate contact with a solvent B. The solvent B is either partially soluble in liquid A or is immiscible with it. The component C gets distributed in different proportions between the two insoluble phases known as the 'raffinate' and the 'extract'. The A-rich phase is known as the *raffinate* and the B-rich phase is known as the *extract*. When the solvent added is only partially miscible with A, the extract and raffinate phases contain three components. The ternary liquid–liquid equilibrium diagrams are usually represented on equilateral triangular coordinates. On the equilateral triangle the length of the altitude is allowed to represent 100% composition and the length of the perpendiculars from any point to the bases represent the percentages of the three components. The apexes of the triangle represent the pure componen ts A, B, and C and points on the sides represent binary mixtures.

Figure 8.26(a) shows the equilibrium diagram of type-I systems in which one pair is partially soluble. The pairs A-C and B-C are miscible in all proportions and the pair A-B is miscible only partially. Examples are water (A)–chloroform (B)–acetone (C), water (A)–benzene (B)–acetic acid (C), water (A)–methyl isobutyl ketone (B)–acetone (C), etc. Liquid C dissolves completely in A and B whereas A

and B dissolve only to a limited extent in each other. In the region below the mutual solubility curves the two liquid phases exist under equilibrium. The compositions of the equilibrium phases are obtained at the ends of the tie line passing through the point representing the overall composition of the mixture. For example, the mixture, whose combined composition is represented by point M separates into a raffinate R and an extract E at equilibrium. Thus, RE is a tie line for the system. The weight fraction of C in the raffinate is denoted by x_R, and that in the extract is denoted by y_E. Several tie lines can be drawn and each gives rise to a set of equilibrium x_R and y_E values, which can be used to plot the equilibrium diagram shown in Fig. 8.26(b).

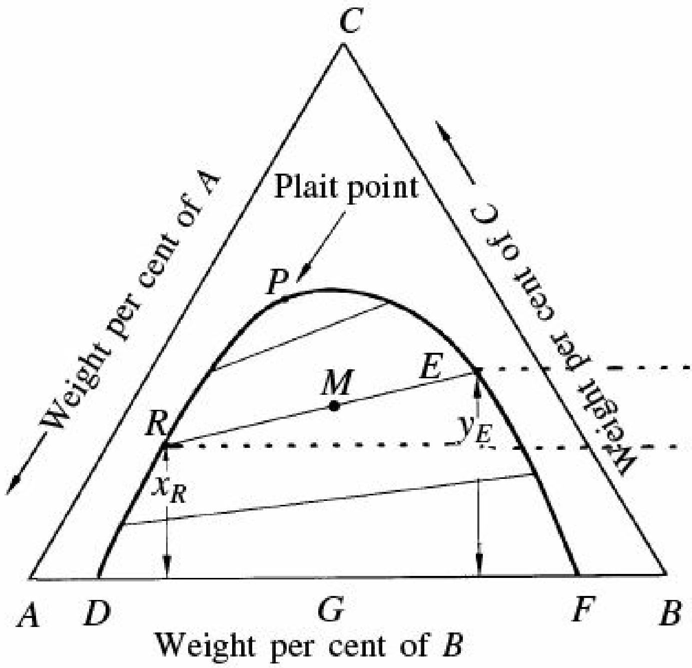


Fig. 8.26(a) Liquid–liquid equilibrium diagram on triangular coordinates for type-I systems.

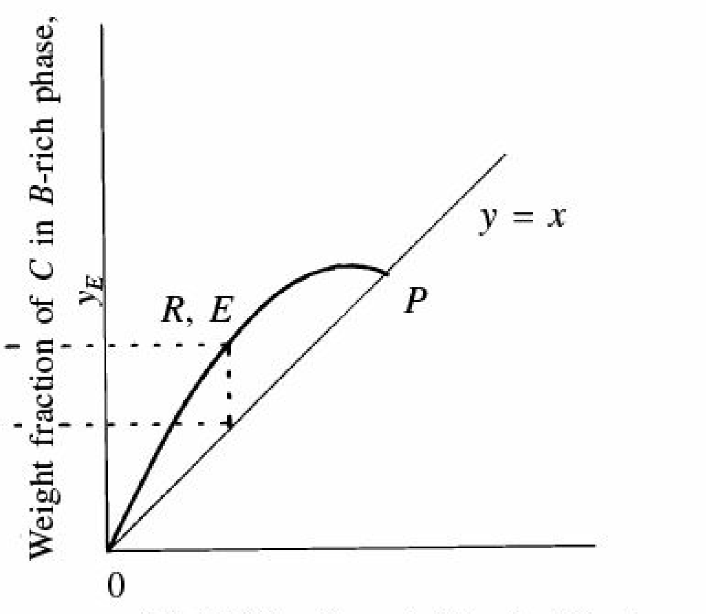


Fig. 8.26(b) Distribution diagram for type-I systems.

The curve $DRPF$ is the binodal solubility curve, which shows the change in the solubility of A-rich and B-rich phases upon addition of C at a fixed temperature. Any mixture outside this curve will be a homogeneous solution of a single liquid phase. There is one point on the binodal curve P, which will represent the last of the tie lines where the A-rich and B-rich phases become identical. It is known as the *plait point*. With increase in temperature the mutual solubilities of A and B increase and as a result the heterogeneous area shrinks. Above the critical solution temperature of the binary A-B they dissolve completely and the heterogeneous area vanishes completely. Extraction is not possible under this condition.

The ternary equilibrium diagram for type II systems is shown in Fig. 8.27. In this type of systems, two pairs are partially soluble. Examples of type II systems are chlorobenzene (A)–water (B)–Methylethyl ketone (C), n-heptane (A)–aniline (B)–methylcyclohexane(C), etc. Here A and C are completely miscible while A-B and B-C pairs show only limited solubility. Points D and F represent the mutual solubility of A and B and points H and G those of B and C at the prevailing temperature. Curves DRH and FEG are the ternary solubility curves. Mixtures such as at M inside the heterogeneous area form two liquid phases in equilibrium at E and R. As temperature is increased the mutual solubilities increase and above the critical solution temperature of the binary pair B-C, the system becomes identical to type I system.

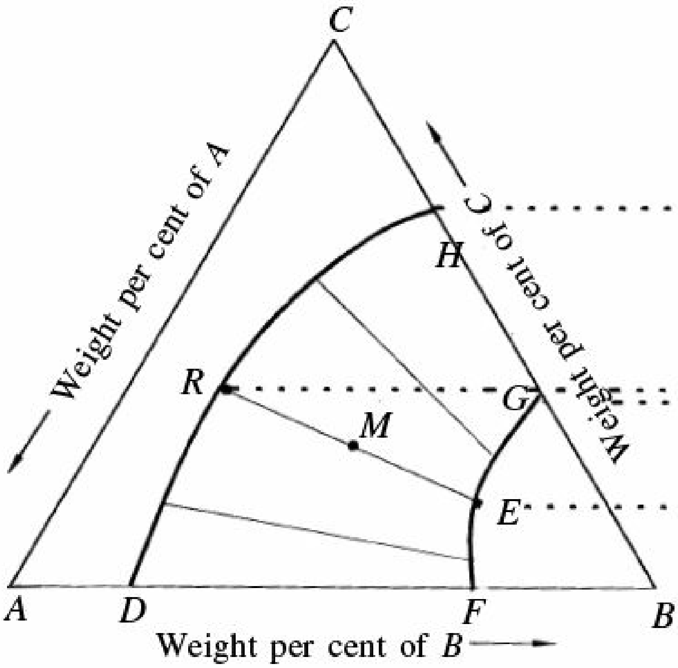


Fig. 8.27(a) Liquid–liquid equilibrium diagram on triangular coordinates for type-II systems.

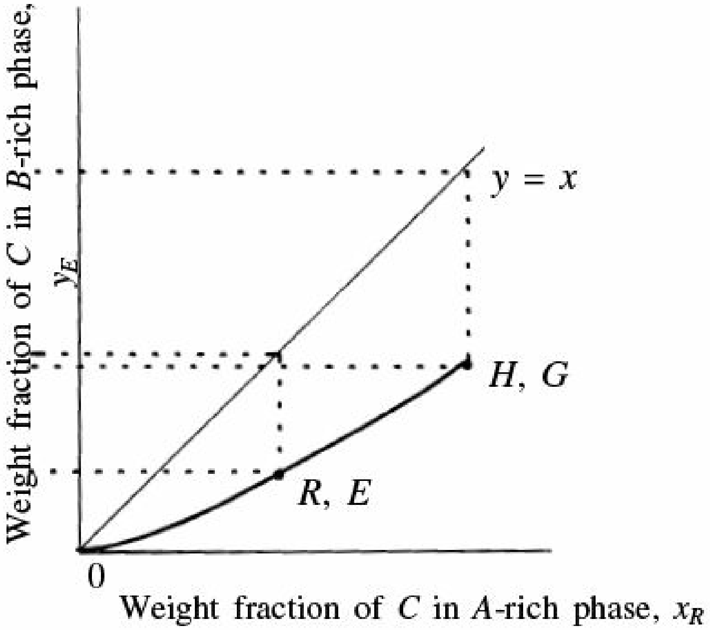


Fig. 8.27(b) Distribution diagram for type-II systems.

SUMMARY

The phase equilibrium thermodynamics is of fundamental importance in chemical engineering, because, majority of chemical process industries employ transfer of mass between phases either during the preparation of the raw materials or during the purification of the finished products. The major thrust of the present chapter was the development of the relationship between the various properties of the system such as pressure, temperature and composition when a state of equilibrium was attained between the different phases constituting the system. For a system to be in mechanical equilibrium, the pressure and temperature should be uniform throughout the system. Since, the uniformity of temperature and pressure do not eliminate the possibility of transfer of mass between the phases, to describe the state of thermodynamic equilibrium, additional criteria are developed (Section 8.1). They are:

$$dS_{U,\,V} \geq 0,\ dA_{T,\,V} \square\ 0,\ dG_{T,\,P} \square\ 0$$

Since, most chemical reactions and physical changes are carried out at constant T and P, the last criterion formed the basis for phase equilibrium calculations. This criterion of equilibrium also led to the criterion of stability as given by Eq. (8.12). The criterion of stability requires that at constant temperature and pressure the free energy change on mixing DG, its first and second derivatives are all continuous functions of the concentration x, and the second derivative should be positive.

For single-component systems in thermodynamic equilibrium under a given temperature and pressure, the molar free energy should be the same in each phase (Section 8.3). Its logical extension to multicomponent multi-phase systems reveals that if a system consisting of several components distributed between various phases is in thermodynamic equilibrium at a definite temperature and pressure, the chemical potential of each component will be the same in all the phases. Since absolute values of fugacities are known, it was found convenient to use fugacities in phase equilibrium calculations, rather than the chemical potentials. Accordingly, the general criterion of phase equilibrium was expressed as the equality of fugacities [Eq. 8.36]. The Gibbs Phase rule follows from the criterion of equilibrium (Section 8.5). The phase rule allows us to determine the number of independent variables that must be arbitrarily fixed so as to establish uniquely the intensive state of the system. The Duhem's theorem helps in establishing the extensive state of the system (Section 8.6).

Vapour–liquid equilibrium problems essentially involve the calculation of the composition of the liquid and vapour phases such that the fugacities of the components are the same in both phases. To evaluate quantitatively the equilibrium compositions, the fugacity need be expressed in terms of the mole fractions in the mixture. The fundamental relationship for a general VLE problem was derived [Eq. (8.45)] and the various possible simplifications were described (Sections 8.7–8.12). For evaluating the liquid phase fugacity, the activity coefficients should be known as a function of the composition. Several equations were used for estimating the activity coefficients as function of composition of the liquid. The Wohl's equations, the Margules equations and the van Laar equations, the local composition models for activity coefficients such as the Wilson equations, the NRTL equations and the UNIQUAC equations, and the UNIFAC group contribution model are some of th widely used activity coefficient equations.

Thermodynamics provides tests for consistency of experimental VLE data (Section 8.13). Almost al these tests are based on the Gibbs–Duhem equations, the Redlich–Kister method [Eq. (8.97)] being the most reliable among them. The discussion on the vapour–liquid equilibrium for systems of limited miscibility (Section 8.15) and the liquid–liquid equilibrium (Section 8.16) would be helpful for the analysis of many important separation processes in chemical engineering.

REVIEW QUESTIONS

1. How would you state the criterion of equilibrium in terms of the entropy, the work function and the Gibbs free energy?

2. What do you know about the free energy change of mixing and its partial derivatives, for stable liquid phases?

3. Show that for equilibrium between phases of a pure substance, the fugacities in both phases should be equal.

4. How do you obtain the Clapeyron equation from the criterion of phase equilibrium? Wha simplifications are used in the derivation of the Clausius–Clapeyron equation?

5. For a heterogeneous multicomponent system, what is the general criterion of phase equilibrium?

6. What do you understand by the number of degrees of freedom? How is it determined using the phase rule for a non-reacting system?

7. State the Duhem's theorem. What is its significance in establishing the state of the system?

8. What are the available degrees of freedom in the following non-reactive equilibrium systems?

(a) Two partially miscible liquid phases, each containing the same three liquid phases.

(b) A vapour phase containing ammonia in air and a liquid phase containing ammonia in water at a specified temperature.

(c) A mixture of benzene and toluene undergoing a simple distillation operation.

9. Write down the equation for solving a general VLE problem. How does this equation ge simplified for (a) ideal gas phase, ideal liquid phase and (b) low-pressure equilibrium?

10. What is Poynting correction?

11. Distinguish between the bubble-point and dew-point temperatures.

12. What is meant by a 'tie line'? How does the tie line help in determining the amount of liquid and vapour in equilibrium?

13. Why does the boiling point diagram at a higher pressure lie above that at a lower pressure?

14. What are the salient features of an ideal liquid solution? How does the total pressure over an ideal solution vary with composition?

15. How would you calculate the constant pressure y-x data of a binary mixture using an average value of the relative volatility?

16. Component 1 in a binary non-ideal solution is found to obey the Raoult's law over a certain concentration range. What do you know about the behaviour of component 2 over the same range?

17. What do you mean by positive and negative deviation from ideality? "A solution exhibiting positive deviation from ideality is formed accompanied by an absorption of heat and a solution exhibiting negative deviation from ideal behaviour is formed accompanied by an evolution of heat". Explain.

18. What are azeotropes? With proper phase diagrams, distinguish between minimum and maximum boiling azeotropes. What is the effect of pressure on the azeotropic composition?

19. Discuss the suitability of different activity coefficient equations for VLE data correlation.

20. What is vaporisation equilibrium constant? How do you estimate the bubble-point temperature and the bubble-point pressure of a multicomponent system?

21. A multicomponent liquid mixture of known composition is flash vaporised at a given pressure and temperature. How would you estimate the fraction of the liquid vaporised?

22. How are the Gibbs–Duhem equations helpful in testing the consistency of the VLE data?

23. What is the zero area method for testing the consistency of VLE data?

24. What is coexistence equation? What are its major applications?

25. The activity coefficients of one of the components in a binary solution are known as function of concentration. How would you evaluate the activity coefficients of the other component as a function of composition?

26. What are the critical solution temperature and the three-phase temperature with reference to partially miscible liquid systems?

27. Why does immiscibility occur in liquid solutions?

28. How would you estimate the composition of the vapour phase in equilibrium with two immiscible liquid phases?

EXERCISES

8.1 Show that the following equations provide the criteria of equilibrium under certain constraints.
(a) $dU_{S,V} = 0$ (b) $dS_{H,P} = 0$ (c) $dH_{S,P} = 0$

8.2 For each of the following non-reactive equilibrium systems, determine the number of available degrees of freedom.

(a) Two miscible materials in vapour–liquid equilibrium with vapour composition specified at a given temperature and pressure.

(b) A mixture of methane and air in contact with a solid adsorbent at atmospheric pressure and a specified temperature.

(c) Liquid water in equilibrium with a mixture of water vapour and nitrogen.

(d) Two partially miscible liquid phases and a vapour phase in equilibrium with them at a constant pressure.

(e) A liquid mixture of benzene and toluene in equilibrium with its vapour at 1 bar.

(f) A vapour phase consisting of ammonia and air and a liquid phase consisting of ammonia and water at a given temperature.

(g) A liquid mixture of components *A* and *C* in equilibrium with a liquid solvent *B* in which only *C* is soluble at a given temperature and pressure.

8.3 Determine the mole fraction of methane, x_i, dissolved in a light oil at 200 K and 20 bar. Henry's law is valid for the liquid phase, and the gas phase may be assumed to be an ideal solution. At these conditions, Henry's law constant for methane in oil = 200 bar, fugacity coefficient of pure methane gas = 0.90 and mole fraction of methane in the gas phase, $y_1 = 0.95$.

8.4 The vapour pressures of benzene and toluene are given below.

T, K	353.1	358	363	368	373	378	383	383.6
P_A^S, kPa	101.3	116.9	135.4	155.7	179.1	204.2	233.0	240.0
P_B^S, kPa	39.6	46.0	54.0	63.3	74.2	86.0	99.0	101.3

Calculate the equilibrium data for the system at 101.3 kPa and formulate an equation for the equilibrium diagram in terms of average relative volatility.

8.5 At 303 K, the vapour pressures of benzene (*A*) and toluene (*B*) are 15.75 kPa and 4.89 kPa respectively. Determine the partial pressures and weight composition of the vapour in equilibrium with a liquid mixture consisting of equal weights of the two components.

8.6 An equimolar mixture of benzene and toluene is contained in a piston/cylinder arrangement at a temperature *T*. What is the maximum pressure below which the mixture exists as a vapour phase alone? At the given *T*, the vapour pressures of benzene and toluene are 203.9 kPa and 85.3 kPa, respectively. Assume that Raoult's law is valid.

8.7 Two substances *A* and *B* are known to form ideal liquid solutions. A vapour mixture containing 50% (mol) *A* and 50% (mol) *B* is at 311 K and 101.3 kPa. This mixture is compressed isothermally until condensation occurs. At what pressure does condensation occur and what is the composition of the liquid that forms? The vapour pressures of *A* and *B* are 142 kPa and 122 kPa respectively.

8.8 Air is cooled to 80 K at 101.3 kPa. Calculate the composition of the liquid and vapour phases at this condition assuming that the mixture behaves ideally. The vapour pressure of nitrogen and oxygen at 80 K are 135.74 kPa and 30.04 kPa respectively.

8.9 The binary system, acetone (1)–acetonitrile (2) conforms closely to Raoult's law. Using the vapour pressure data given below plot the following

(a) P-x_1 and P-y_1 curves at 323 K

(b) T-x_1 and T-y_1 curves at 53.32 kPa

T, K	311.45	315	319	323	327	331	335.33
P_1^S, kPa	53.32	61.09	70.91	81.97	94.36	108.2	124.95
P_2^S, kPa	21.25	24.61	28.90	33.79	39.35	45.62	53.32

8.10 Assuming Raoult's law to be valid for the system benzene (1)–ethyl benzene (2) and the vapour pressures are given by the Antoine equations

$$\ln P_1^S = 13.8858 - \frac{2788.51}{T - 52.41}$$

$$\ln P_2^S = 14.0045 - \frac{3279.47}{T - 60.00}$$

where P is in kPa and T is in K. Construct the following:

(a) The P-x-y diagram at 373 K

(b) The T-x-y diagram at 101.3 kPa.

8.11 A liquid mixture containing 65% (mol) benzene and 35% (mol) toluene is subjected to flash vaporisation at 363 K and 101.3 kPa. The vapour pressure of benzene at this temperature is 136.09 kPa and the vapour pressure of toluene is 54.21 kPa. Flash vaporisation is essentially an equilibrium stage operation. Calculate

(a) The exit vapour composition

(b) The exit liquid composition

(c) The mole per cent of the feed that is vaporised.

8.12 For the system n-pentane (1)–n-heptane (2), the vapour pressures are given by the Antoine equation

$$\ln P = A - \frac{B}{T - C}$$

where P is in kPa and T is in K. The constants are as follows.

System	A	B	C
n-Pentane	13.8183	2477.07	40.00
n-Heptane	13.8587	2911.32	56.56

Assuming that the solution formed is ideal, calculate:

(a) The composition of the liquid and vapour in equilibrium at 95 kPa and 336.2 K.

(b) The composition of the vapour in equilibrium with a liquid containing 34% (mol) pentane and the equilibrium temperature at P = 95 kPa.

(c) The total pressure and the vapour composition in equilibrium with a liquid of composition $x_1 = 0.44$ at $T = 333.2$ K.

8.13 Using Gibbs–Duhem equations prove that if one constituent of a mixture exhibits positive deviation from ideal behaviour the other constituent also shows positive deviation.

8.14 Prove that a solution exhibiting negative deviation from ideal behaviour is formed with an evolution of heat.

8.15 Using van Laar method calculate the vapour–liquid equilibrium compositions for acetone (1)–chloroform (2) system at a pressure of 101.3 kPa. At this pressure, the system forms an azeotrope of composition 66.6% (mol) chloroform which boils at 337.7 K. The vapour pressures of the pure components are given below.

T, K	318	323	333	343	353
P_1^S, kPa	68.04	81.65	114.71	158.61	214.73
P_2^S, kPa	58.51	70.11	98.58	135.82	187.01

The normal boiling points of acetone and chloroform are respectively 329.5 K and 334.1 K. (*Hint:* The ratio of vapour pressures remains almost constant. Use the method employed in Example 8.13 for calculating y for arbitrarily chosen x values.)

8.16 Show that the van Laar equation and Margules equation are consistent with the Gibbs–Duhem equations.

8.17 The toluene–acetic acid mixture forms an azeotrope containing 62.7% (mol) toluene and having a minimum boiling point of 378.6 K at 101.3 kPa. The vapour pressure data are:

T, K	343	353	363	373	383	393
Toluene, kPa	26.98	38.61	53.93	74.27	–	–
Acetic acid, kPa	18.13	26.96	39.05	55.60	77.41	105.83

The normal boiling point of toluene and acetic acid are respectively 383.9 K and 391.7 K.

(a) Calculate the van Laar constants A and B

(b) Plot $\ln g_1$ and $\ln g_2$ as ordinate against mole fraction of toluene.

8.18 Under atmospheric pressure, the acetone–chloroform azeotrope boils at 337.8 K and contains 33.5% (mol) acetone. The vapour pressures of acetone and chloroform at 337.8 K are respectively 132.62 kPa and 113.96 kPa.

(a) Calculate the composition of the vapour in equilibrium with a liquid analysing 11.1% (mol) acetone. How does it compare with the experimental value of 6.5% acetone in the vapour?

(b) What is the total pressure at this condition?

8.19 Ethyl alcohol and hexane form an azeotrope at 33.2% (mol) ethanol. It boils at 331.9 K at 101.3 kPa. At 331.9 K, the vapour pressures are 44.25 kPa for ethanol and 72.24 kPa for hexane. Determine:

(a) The van Laar constants

(b) The vapour composition for a solution containing 50% (mol) hexane boiling at 331.9 K

(c) The total pressure for the conditions in part (b).

8.20 At atmospheric pressure, ethyl acetate and ethyl alcohol form an azeotrope containing 53.9% (mol) acetate boiling at 345 K. Determine:

(a) The van Laar constants

(b) The azeotropic composition and the total pressure if the mixture forms an azeotrope boiling at 329.5 K

(c) The composition of the vapour in equilibrium with a liquid of composition 60% (mol) alcohol and boiling at 329.5 K

Vapour pressure, kPa	at 345 K	at 329.5 K
Ethyl alcohol	78.24	39.72
Ethyl acetate	84.77	47.98

8.21 An organic liquid solution containing A (molecular weight 46) and B (molecular weight 78) form an azeotrope containing 52% by weight A at 333 K and 101.3 kPa. Vapour pressures of A and B are 69.31 kPa and 68 kPa respectively. Determine the van Laar constants.

8.22 For the acetone (1)–diethylamine (2) system the activity coefficients values as function of concentration are given below:

x_1	0.1	0.2	0.3	0.7	0.8	0.9
γ_1	1.1128	1.0840	1.0617	1.0095	1.0041	1.0009
γ_2	1.0015	1.0061	1.0133	1.0639	1.0812	1.1000

Using the above data estimate the van Laar constants for the system.

(*Hint:* $A = \ln g_1$ as x_1 □ 0 and $B = \ln g_2$ as x_2 □ 0)

8.23 Find the van Laar constants for the binary system benzene (1)–ethanol (2) using the following data

x_1	0.1	0.3	0.45	0.7	0.9
P_1^S, kPa	73.31	68.64	63.98	67.98	81.31
P_2^S, kPa	75.98	69.64	67.98	69.31	79.98

8.24 The T-x-y data for the system metaxylene (1)–propionic acid (2) at 101.3 kPa is given below:

T, K	412.6	411.1	408.4	407.1	408.8	411.7
x_1	0.035	0.090	0.258	0.652	0.877	0.989
y_1	0.064	0.133	0.314	0.621	0.821	0.975

Does the system form an azeotrope? Give reasons.

8.25 For the conditions in Example 8.19, calculate (a) the equilibrium temperature and vapour composition for $x_1 = 0.32$ and $P = 101.3$ kPa and (b) the equilibrium temperature and liquid composition for $y_1 = 0.57$ and $P = 101.3$ kPa .

8.26 For isobutanol–water system, it is found from VLE measurements that the composition of the vapour and liquid in equilibrium at 101.3 kPa and 364.7 K are 28.6% (mol) and 1.4% (mol) *i*-butanol respectively. Vapour pressure of *i*-butanol at this temperature is 53.32 kPa. The activity coefficient of water may be taken as 1.0012. Compute the van Laa constants.

8.27 Ethanol–water mixture forms an azeotrope boiling at 351.4 K under a pressure of 101.3 kPa and its composition is 89.4% (mol) ethanol. The vapour pressures of ethanol and water at 351.4 K are 100 kPa and 44 kPa respectively. Using van Laar method and assuming tha the ratio of vapour pressures remains constant calculate the composition of the vapour in equilibrium with a liquid containing 80% ethanol.

8.28 Two liquids *P* and *Q* form an azeotrope containing 58% (mol) *P* at 101.3 kPa pressure. At the azeotropic temperature the vapour pressures of *P* and *Q* are 200 kPa, 125.3 kPa respectively. Construct the equilibrium (*y*–*x*) diagram. List all the assumptions made.

8.29 For the binary system *n*-pentanol (1)–*n*-hexane (2), determine the activity coefficients at 313 K in an equimolal mixture. The Wilson parameters are given as follows:

$a_{12} = 7194.18$ J/mol, $a_{21} = 697.52$ J/mol

$V_1 = 109.2 \times 10^{-6}$ m^3/mol, $V_2 = 132.5 \times 10^{-6}$ m^3/mol

8.30 The Wilson parameters for acetone (1)–methanol (2) are obtained from the following values:

$a_{12} = -712.51$ J/mol, $a_{21} = 2487.71$ J/mol

$V_1 = 74.05 \times 10^{-6}$ m^3/mol, $V_2 = 40.73 \times 10^{-6}$ m^3/mol

The vapour pressures are given by the Antoine equations:

$$\ln P_1^S = 14.39155 - \frac{2795.817}{T - 43.2}$$

$$\ln P_2^S = 16.59381 - \frac{3644.297}{T - 33.435}$$

Calculate the total pressure and vapour composition in equilibrium with a liquid containing 31% (mol) acetone at 333 K.

8.31 For the 2-propanol (1)–water (2) system, the following Wilson parameters are reported.

$a_{12} = 1833.74$ J/mol, $a_{21} = 5183.26$ J/mol

$V_1 = 76.92 \times 10^{-6}$ m^3/mol, $V_2 = 18.07 \times 10^{-6}$m^3/mol

The vapour pressures can be calculated by the Antoine equations, which are given below:

$$\ln P_1^S = 16.678 - \frac{3640.20}{T - 53.54}$$

$$\ln P_2^S = 16.2887 - \frac{3816.44}{T - 46.13}$$

where *T* is in K and the vapour pressures are in kPa. Calculate:

(a) Equilibrium pressure and vapour composition at $T = 353.15$ K and $x_1 = 0.25$

(b) Equilibrium pressure and liquid composition for $T = 353.15$ K and $y_1 = 0.60$

(c) Equilibrium temperature and vapour composition for $P = 101.3$ kPa and $x_1 = 0.85$

(d) Equilibrium temperature and liquid composition for $P = 101.3$ kPa and $y_1 = 0.40$.

8.32 A solution of hydrocarbons contains *n*-propane 5.0%, *n*-butane 30.0%, *n*-pentane 40.0% and *n*-hexane 25.0%. Compute the bubble point and the dew point at 350 kPa. The *K*-values can be taken from the DePriester nomographs.

8.33 A solution has the following composition in mol per cent: ethane 0.25%, propane 25.00%, isobutane 18.5%, *n*-butane 56.0% and isopentane 0.25%. For a pressure of 10 bars, calculate

(a) The bubble point

(b) The dew point

(c) The composition of the liquid and vapour when 40% of the mixture is vaporised.

8.34 A stream of gas in a natural gasoline plant has the following composition by volume: ethane 10%, propane 14%, isobutane 19%, *n*-butane 54% and isopentane 3%.

(a) Calculate the pressure necessary to condense this gas completely at 311 K.

(b) For a condenser operating at the pressure in part (a), calculate the temperature at which condensation starts and the temperature at which 50% (mol) of the vapour gets condensed. Also, calculate the composition of the first liquid to condense and the composition of the liquid and vapour phases at 50% condensation.

8.35 Determine the composition of the vapour in equilibrium with the liquid and the pressure of the system at 313 K for a liquid mixture of 5% (mol) methane, 10% (mol) ethane, 30% (mol) propane, 25% (mol) isobutane, and 30% (mol) *n*-butane. Determine the pressure and composition of the liquid in equilibrium with a vapour mixture of the above composition.

8.36 Calculate the pressure at which condensation starts and the pressure at which condensation is complete when a vapour mixture of the following composition is subjected to condensation at a temperature of 300 K: 20% (mol) ethylene, 20% (mol) ethane, 40% (mol) propane and 20% (mol) *n*-butane.

8.37 A vapour mixture containing 15% ethane, 20% propane, 60% isobutane and the rest *n*-butane is subjected to partial condensation so that 75% of the vapour is condensed. If the condenser temperature is 300 K determine the pressure.

8.38 An equimolal mixture of propane (1) and *n*-butane (2) is partially condensed so that 50% (mol) of the mixture is in the liquid state at 311 K. Using the DePriester nomograph determine the following:

(a) The pressure

(b) The vapour and liquid compositions

(c) The pressure at which condensation begins at the constant temperature of 311K.

8.39 Verify whether the following data are consistent.

x_1	0	0.2	0.4	0.6	0.8	1.0
γ_1	0.576	0.655	0.748	0.856	0.950	1.000
γ_2	1.00	0.985	0.930	0.814	0.626	0.379

8.40 Calculate the constants *A* and *B* in the van Laar equation from the following data. Check whether the data are consistent.

x_1	0.28	0.40	0.60	0.675
y_1	0.420	0.516	0.656	0.710
T, K	331.5	330.4	329.3	328.3
P_1^S, kPa	109.16	104.77	101.17	97.70
P_2^S, kPa	77.17	73.44	69.98	67.04

Assume $P = 101.3$ kPa.

8.41 The following data were reported for vapour–liquid equilibrium for ethanol–water system at 298 K. Test whether the data are thermodynamically consistent.

x_1	0.122	0.163	0.226	0.320	0.337	0.437	0.440	0.579	0.830
y_1	0.474	0.531	0.562	0.582	0.589	0.620	0.619	0.685	0.849
P, kPa	5.57	6.02	6.38	6.76	6.80	7.02	7.04	7.30	7.78

The vapour pressures of ethanol and water are, respectively, 7.86 kPa and 3.17 kPa.

8.42 The following vapour-liquid equilibrium data were obtained for water (1)–nitric acid (2) system at 293 K.

wt. %, HNO_3	100	90	80	70	60	50
$\bar{p}_1$, kPa	0	0.061	0.180	0.377	0.657	1.004
$\bar{p}_2$, kPa	6.398	3.469	1.398	0.411	0.119	0.065

Test the above data for thermodynamic consistency.

8.43 From the data activity coefficient versus mole fraction for the system acetone (1)–dichloroethylene (2) given below check their thermodynamic consistency.

x_1	0.023	0.053	0.357	0.516	0.883	0.979
γ_1	0.608	0.711	0.854	0.917	0.987	1.0
γ_2	0.993	0.974	0.934	0.891	0.781	0.694

8.44 The partial pressure of ether at 303 K for the ether (1)–acetone (2) system is given as follows:

x_1	1.00	0.87	0.50	0.30
$\bar{p}_1$, kPa	86.105	76.11	51.98	35.59

The vapour pressure of pure acetone at 303 K is 37.72 kPa.

(a) Calculate the activity coefficient of ether and plot the logarithm of the activity coefficient as function of concentration.

(b) Predict the partial pressure of acetone in the corresponding solution for which the activity coefficients of ether have been determined.

8.45 Vapour–liquid equilibrium data for the system methanol (1)–benzene (2) at 313 K are given below:

x_1	0	0.141	0.227	0.304	0.402	0.468	0.552	0.643	0.702	0.750	0.834	0.878	0.896	0.915	1.00
y_1	0	0.507	0.524	0.531	0.540	0.543	0.548	0.566	0.578	0.578	0.641	0.670	0.723	0.753	1.000
P, kPa	24.46	46.52	47.45	48.32	48.54	48.73	48.78	48.81	47.61	47.65	46.01	44.52	43.35	42.99	35.12

Use the area test to determine the thermodynamic consistency of the data.

8.46 The activity coefficient of thallium in amalgams at 293 K are given below:

x	0	0.0033	0.0168	0.0486	0.0986	0.1680	0.2701	0.4240
γ	1.0	1.042	1.231	1.776	2.811	4.321	6.196	7.707

Determine the activity coefficient of mercury as function of composition.

8.47 The following data refers to the system water (1)–*n*-propyl alcohol (2) at 298 K.

x_2	0	0.01	0.02	0.05	0.10	0.20
γ_2	12.5	12.3	11.6	9.92	6.05	3.12

What is the activity coefficient of water in a 10% (mol) *n*-propyl alcohol solution?

8.48 At 323 K, the vapour pressures of pure ether and pure ethyl alcohol are 170.13 and 29.47 kPa respectively. The total pressures versus liquid composition data are given below:

x_1	0.065	0.14	0.211	0.293	0.383	0.483	0.587	0.713	0.854
P, kPa	53.36	74.39	92.40	107.24	120.43	132.62	142.98	151.42	161.07

Using Gibbs–Duhem equation compute from these data the partial pressures of ether and alcohol over liquid solutions of various compositions at 323 K.

8.49 The data given below refer to the boiling points of ethanol (1)–benzene (2) system at 100 kPa and the vapour pressures of pure ethanol and benzene at these temperatures.

x_1	0	0.04	0.11	0.28	0.43	0.61	0.80	0.89	0.94	1.00
P_1^S, kPa	107.16	89.44	74.64	67.58	66.24	67.58	72.64	79.71	86.64	100
P_2^S, kPa	100	86.37	74.91	69.04	67.84	69.04	73.18	78.91	84.24	94.77

Calculate the van Laar constants from these data assuming g to be independent of temperature. Also, find g_1 and g_2 from the van Laar equations.

8.50 The total pressure versus solution concentration data for the system dioxane (1)–water (2) at 353 K is given below:

x_2	0.1	0.2	0.3	0.4	0.6	0.7	0.8	0.9
P, kPa	63.45	70.18	74.11	76.11	76.71	75.91	73.31	66.84

The vapour pressures of pure water and dioxane at this temperature are 47.33 and 51.05 kPa. Calculate:

(a) The van Laar constants

(b) The constants in the Margules equation

(c) The vapour composition in equilibrium with a liquid containing 60% water by weight and the total pressure over this solution using van Laar method.

8.51 Benzene (1)–cyclohexane (2) form an azeotrope at 0.525 mole fraction benzene at a temperature of 350.8 K and 101.3 kPa. At this temperature, the vapour pressure of benzene is 99.3 kPa and that of cyclohexane is 98 kPa. Using the van Laar model estimate the activity coefficients at x_1 = 0.2 and 0.9. Using this activity coefficient information calculate the equilibrium pressure and the vapour compositions at 350.8 K for the two liquid compositions.

8.52 The azeotrope of the *n*-propanol–water system has a composition 56.83% (mol) water with a boiling point of 360.9 K at a pressure of 101.3 kPa. At this temperature, the vapour pressures of water and propanol are respectively 64.25 kPa and 69.71 kPa. Evaluate the activity coefficients for a solution containing 20% water through the van Laar equations.

8.53 The pressure exerted over the binary system ethanol–methylcyclohexane containing 40.5% (mol) ethanol at 308 K is 20.31 kPa. The vapour phase contained 54.7% (mol) ethanol. The vapour pressures at 308 K are 13.74 kPa for ethanol and 9.81 kPa for methylcyclohexane. Wha are the total pressure and composition of the vapour in equilibrium with a liquid containing 60% (mol) ethanol at 308 K?

8.54 A binary liquid mixture of components *A* and *B* containing 80% (mol) *A* is in equilibrium with a vapour containing 84.3% (mol) *A* at 101.3 kPa and 339 K. Estimate the pressure and composition of the vapour in equilibrium with a liquid containing 50% *A* at 339 K. The vapour pressures of *A* and *B* at this temperature are 106.6 kPa and 79.97 kPa respectively.

8.55 At 333 K, compounds *A* and *B* each has vapour pressures of 106.63 kPa. The mixture of *A* and *B* forms an azeotrope at 333 K and 133.29 kPa and has a composition of 50% *A*.

(a) Calculate the equilibrium pressure and vapour composition over a liquid solution containing 25% *A*.

(b) If *A* and *B* have equal latent heats of vaporisation, how do you expect the azeotropic composition to respond to an increase in temperature?

8.56 At 353 K, compounds *A* and *B* each has vapour pressures of 93.30 kPa. At this temperature mixtures of *A* and *B* form azeotrope containing 50% (mol) *A* and exerts a pressure of 127.96 kPa. Calculate the equilibrium pressure and vapour composition at 353 K over a liquid solution containing 25% (mol) *A*.

8.57 For the binary mixture of *A* and *B* the activity coefficients are given by

$$\ln \gamma_1 = Ax_2^2, \quad \ln \gamma_2 = Ax_1^2$$

The vapour pressures of *A* and *B* at 353 K are 119.96 kPa and 79.97 kPa respectively. Does an azeotrope exist at 353 K? If so, what is the azeotropic pressure and composition for *A* = 0.6?

8.58 It is proposed to purify benzene from small amounts of non-volatile impurities by subjecting it to distillation with saturated steam at 99.3 kPa. Calculate the temperature at which distillation will proceed and the weight of steam accompanying 1 kg benzene. The vapour pressure data is given in Example 8.28.

8.59 At 383 K, saturated solution of aniline in water contains 7.95% aniline by weight and a saturated solution of water in aniline contains 88.05% aniline by weight. The vapour pressures of pure aniline and of water at 383 K are 9.22 kPa and 143.10 kPa respectively. Construct the *P-x-y* diagram for the mixture at 383 K.

8.60 Construct *T-x-y* diagram for the ether (1)–water (2) system at 101.3 kPa from the following data.

T, K	P, kPa	Water phase x_1	Ether phase x_1	P_2^S, kPa	P_1^S, kPa
307	101.3	0.0123	0.9456	5.37	99.58
313	126.63	0.0116	0.9416	7.39	122.78
323	176.67	0.0103	0.9348	12.26	170.08
333	241.20	0.0093	0.9271	19.85	230.05
343	323.65	0.0075	0.9212	31.00	305.72
353	428.40	0.0069	0.9158	47.31	398.62
363	558.57	0.0058	0.9107	70.00	510.55
373	713.15	–	–	101.3	647.31

Assume that Raoult's law is valid for ether in ether phase and for water in the water phase.

8.61 Dimethylaniline is distilled with steam at 90 kPa to free it from non-volatile impurities. Assuming it to be completely immiscible with water determine

(a) The distillation temperature

(b) The composition of the vapour produced.

The vapour pressure data are following:

T, K	343.2	374.8	399
P^S (aniline), kPa	1.333	5.332	13.329
P^S (water), kPa	31.19	106.91	285.86

Plot of ln P^S versus $1/T$ may be assumed linear.

8.62 A stream contains 30% (mol) toluene, 40% (mol) ethyl benzene and 30% (mol) water. Assuming that mixtures of ethylbenzene and toluene obey Raoult's law and they are completely immiscible in water, calculate the following for a total pressure of 101.3 kPa:

(a) The bubble-point temperature and the composition of the vapour

(b) The dew-point temperature and the composition of the liquid.

The vapour pressure data are given below:

T, K	352.6	361.0	366.5	383.2	388.8
P^S, kPa (Water)	46.29	64.33	79.42	–	–
P^S, kPa (Toluene)	38.49	50.65	60.78	99.27	116.50
P^S, kPa (ethyl benzene)	16.41	22.79	27.35	47.61	56.73

8.63 *n*-Heptane (1) and water (2) are essentially immiscible as liquids. A vapour mixture containing 65% (mol) water at 373 K and 101.3 kPa is cooled slowly at constant pressure until condensation is complete. Construct a plot for the process showing temperature versus equilibrium mole fraction of heptane in the residual vapour. For *n*-heptane,

$$\ln P_1^S = 13.87770 - \frac{2918.738}{T - 56.404}$$

where P is in kPa and T in K.

8.64 Toluene (1) and water (2) are essentially immiscible in the liquid state. Determine the dew-point temperature and the composition of the first drops of liquid formed when the vapour mixtures of these species containing

(a) 23% (mol) toluene

(b) 77% (mol) toluene at 101.3 kPa.

What are the bubble-point temperature and the composition of the last drop of vapour in each case? The vapour pressure of toluene is

$$\ln P_1^S = 14.00976 - \frac{3103.010}{T - 53.413}$$

The vapour pressure of water is

$$\ln P_2^S = 16.287 - \frac{3816.44}{T - 46.11}$$

where P is in kPa and T is in K.

8.65 Components 1 and 2 are insoluble in the liquid phase. Estimate the dew-point temperature and the compositions of the first drop of liquid formed when vapour mixtures of components 1 and 2 containing (a) 75% (mol) component 1; (b) 25% (mol) component 1 are cooled at constant pressure of 101.33 kPa. The vapour pressures of the pure components in kPa are given against temperature in Kelvin in the following table.

T	358	363	368	373	378	383	388	393	398.6
P_1^S	23.53	33.56	39.58	46.59	54.62	63.97	74.32	86.34	101.33
P_2^S	57.82	70.13	84.53	101.33	120.79	143.28	169.02	198.51	239.54

8.66 An experimental determination of vapour–liquid equilibrium state of ether (1) and acetone (2) gave the following results:

$$x_1 = 0.3, y_1 = 0.42, T = 313 \text{ K and } P = 10^5 \text{ Pa}$$

The saturation vapour pressures of the pure components at 313 K are: ether = 1.21 ☐ 10^5 Pa and acetone = 0.56 ☐ 10^5 Pa. The vapour phase can be assumed ideal.

(a) Calculate the liquid-phase activity coefficients.

(b) What is the value of excess Gibbs free energy G^E/RT *for the liquid phase?*

9

Chemical Reaction Equilibria

The chemical process industries are concerned with the transformation of raw materials into useful products. Such transformation in most cases is achieved by means of chemical reactions. The design and operation of reaction equipment are therefore quite an important field in the chemical engineering profession. To be successful in this profession, the chemical engineer should be versatile with the thermodynamics and kinetics of chemical reactions. Thermodynamics predicts the equilibrium conversion that would be achieved in a chemical reaction and also the effect of operating conditions on it, whereas the kinetics deals with the rate or speed with which the desired conversion is attained in practice. Thermodynamic analysis can also give information about the feasibility of chemical reactions.

The progress and extent of a chemical reaction are affected by changes in the reaction conditions like temperature, pressure, composition of the reactants, etc. For example, in the synthesis of methanol from carbon monoxide and hydrogen, the equilibrium conversion as well as the rate of reaction are affected by changing the pressure, temperature or the relative amounts of carbon monoxide and hydrogen in the reactant stream. The influence of these controllable variables on the thermodynamics of reaction, or to be specific, on the equilibrium conversion, in some situation may be in conflict with the influence of these variables on the kinetics of the reaction. This can be illustrated by considering the effect of temperature on the oxidation of sulphur dioxide to sulphur trioxide. The rate of this reaction increases with temperature and from the point of view of rate alone it is better to operate the reactor at as high a temperature as permissible. However, the equilibrium conversion to sulphur trioxide falls off sharply with increase in temperature. The conversion is above 90% at temperatures near 800 K, but it is only 50% at 950 K. It is clear that both the kinetics (the rate) and thermodynamics (the equilibrium) of the reaction must be considered in the choice of reaction conditions in the commercial process for any chemical reaction. The purpose of the present chapter is to identify the role of thermodynamics in the design and operation of chemical reaction systems.

Equilibrium conversion of a reaction sets a limit and provides a goal by which we measure improvement in the process. It is impossible at a given set of conditions to attain a conversion that is better than the equilibrium value calculated from thermodynamic principles. Even if this conversion is not attainable in practice within a reasonable time, its knowledge is valuable because it represents the best that can be expected from the reaction. It tells us whether or not an experimental investigation of a proposed new process is worthwhile. There is no point in trying improvement in the process by improving the rate by introducing suitable catalysts, if thermodynamics predicts an equilibrium yield, of say, only 20% whereas a 50% yield is necessary for the process to be economically viable. The choice of an appropriate catalyst may give a better reaction rate, but it will not alter the equilibrium yield of the product. The emphasis in this chapter is on determining the conversion at equilibrium and on predicting the effect of controllable variables like temperature and pressure on the conversion.

9.1 REACTION STOICHIOMETRY

The generalised representation of a chemical reaction is given by

$$0 = \sum_i \nu_i A_i \tag{9.1}$$

where A is the chemical symbol for the various species taking part in the reaction and n is the stoichiometric number. Consider the reaction

2A + 3B □ L + 2M

This is a special case of the general form of Eq. (9.1), with $n_L = 1$, $n_M = 2$, $n_A = -2$, and $n_B = -3$. In the general form, this reaction may be represented as

0 = L + 2M – 2A – 3B

The stoichiometric numbers are positive for products, negative for reactants and zero for inert species. The changes in the number of moles of various species taking part in the reaction are in direct proportion to their stoichiometric numbers. Let Dn_i denote the change in the number of moles of component *i* due to the reaction. For one mole of *A* disappearing in the reaction Dn_A = –1, Dn_B = –1.5, Dn_L = 0.5 and Dn_M = 1. We see that

$$\frac{\Delta n_A}{\nu_A} = \frac{\Delta n_B}{\nu_B} = \frac{\Delta n_L}{\nu_L} = \frac{\Delta n_M}{\nu_M}$$

For differential amounts of the species, the above result can be written as

$$\frac{dn_A}{\nu_A} = \frac{dn_B}{\nu_B} = \frac{dn_L}{\nu_L} = \frac{dn_M}{\nu_M}$$

For the thermodynamic analysis of chemical reactions the concept of 'extent of reaction,' also called 'reaction coordinate' is useful. It is denoted by e. The reaction coordinate measures the progress of a reaction and is defined as the degree to which a reaction has advanced. It has the advantage that the change in the extent of reaction *d*e is the same for each component, whereas the changes in the number of moles are different for different species taking part in the reaction. The extent of reaction and the number of moles taking part in the reaction are related as

$$\frac{dn_i}{\nu_i} = d\varepsilon$$

or

$$dn_i = \nu_i \, d\varepsilon \tag{9.2}$$

For the initial state of the system, that is, before the reaction, the value of e is zero.

***EXAMPLE* 9.1** Derive the relationship between the mole fraction of the components taking part in the reaction and the extent of the reaction.

Solution Let n_{i0} be the number of moles of the species initially present in the system and n_i the number of moles present after the reaction. Then $n_i = n_{i0}$ + Dn_i where Dn_i is the change in the number of moles of *i* due to the reaction. Integration of Eq. (9.2) yields

$$\Delta n_i = \nu_i \int_0^{\varepsilon} d\varepsilon = \nu_i \varepsilon$$

Therefore,

$$n_i = n_{i0} + \nu_i\varepsilon \tag{9.3}$$

The mole fraction of component i in the reaction mixture is y_i.

$$y_i = \frac{n_i}{\Sigma n_i} = \frac{n_{i0} + \nu_i\varepsilon}{\Sigma n_{i0} + \varepsilon \Sigma \nu_i} = \frac{n_{i0} + \nu_i\varepsilon}{n_0 + \varepsilon\nu} \tag{9.4}$$

where $n_0 = \Sigma n_{i0}$, the total number of moles initially present in the system and $\nu = \Sigma \nu_i$, the sum of the stoichiometric numbers.

***EXAMPLE* 9.2** A gas mixture containing 2 moles nitrogen, 7 moles hydrogen and 1 mole ammonia initially, is undergoing the following reaction:

$N_2 + 3H_2$ □ $2NH_3$

(a) Derive expressions for the mole fractions of various components in the reaction mixture in terms of the extent of reaction.

(b) Explain how the conversion of limiting reactant is related to the extent of reaction.

Solution (a) Equations (9.3) and (9.4) relate the mole fraction of various constituents in the system to the extent of reaction.

$$n_0 = \Sigma n_{i0} = 2 + 7 + 1 = 10$$

$$\nu = \Sigma \nu_i = 2 - 1 - 3 = -2$$

$$y_{N_2} = \frac{n_{N_2,0} + \nu_{N_2}\varepsilon}{n_0 + \varepsilon\nu} = \frac{2 - \varepsilon}{10 - 2\varepsilon}$$

$$y_{H_2} = \frac{n_{H_2,0} + \nu_{H_2}\varepsilon}{n_0 + \varepsilon\nu} = \frac{7 - 3\varepsilon}{10 - 2\varepsilon}$$

$$y_{NH_3} = \frac{n_{NH_3,0} + \nu_{NH_3}\varepsilon}{n_0 + \varepsilon\nu} = \frac{1 + 2\varepsilon}{10 - 2\varepsilon}$$

(b) The limiting reactant here is nitrogen. Let the fractional conversion of nitrogen be z. Then

Moles of nitrogen in the reaction mixture is = $n_{N_2,0} - z n_{N_2,0}$

Moles of nitrogen in the mixture in terms of the extent of reaction is = $n_{N_2,0} + \nu_{N_2}\varepsilon$

Comparing the two results, we see that

$$z = -\frac{\nu_{N_2}\,\varepsilon}{n_{N_2,0}}$$

Since the stoichiometric number is negative for a reactant, the conversion given by the above equation will be always positive. The relationship between conversion and the extent of reaction can be written as

$$z = \frac{|\nu_{N_2}|\,\varepsilon}{n_{N_2,0}}$$

In general, conversion can be treated as the fractional extent of reaction and is written as

$$z = \frac{\varepsilon}{n_{i0}/|\nu_i|} \tag{9.5}$$

***EXAMPLE* 9.3** Derive the relationship between mole fraction of species in multiple reactions and the extent of reactions.

Solution When two or more reactions occur simultaneously, the number of moles of each component changes because of several reactions. Equation (9.2) can be modified as

$$dn_i = \sum_j \nu_{i,j}\, d\varepsilon_j \tag{9.6}$$

Here, $\nu_{i,j}$ is the stoichiometric number for species i in the jth reaction and ε_j is the extent of this reaction. Equation (9.3) is modified to account for the multiple reactions, and the number of moles of i after the reaction is

$$n_i = n_{i0} + \sum_j \nu_{i,j}\,\varepsilon_j \tag{9.7}$$

The total number of moles is obtained by summing the number of moles of individual species.

$$n = \sum_i n_{i0} + \sum_i\sum_j \nu_{i,j}\varepsilon_j = n_0 + \sum_j\left(\sum_i \nu_{i,j}\right)\varepsilon_j$$

Let $\sum_i \nu_{i,j} = \nu_j$, the sum of the stoichiometric numbers in the jth reaction. Then the above equation can be written as

$$n = n_0 + \sum_j \nu_j\varepsilon_j \tag{9.8}$$

The mole fraction of component i in the mixture is

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j \nu_{i,j}\varepsilon_j}{n_0 + \sum_j \nu_j\varepsilon_j} \tag{9.9}$$

***EXAMPLE* 9.4** A gas mixture containing 3 mol CO_2, 5 mol H_2 and 1 mol water is undergoing the following reactions:

$$CO_2 + 3H_2 \square CH_3OH + H_2O$$

$$CO_2 + H_2 \square CO + H_2O$$

Develop expressions for the mole fraction of the species in terms of the extent of reaction.

Solution The total moles initially present,

$$n_0 = 3 + 5 + 1 = 9$$

For the first reaction,

$$n_1 = -1 - 3 + 1 + 1 = -2$$

For the second reaction,

$$n_2 = -1 - 1 + 1 + 1 = 0$$

The mole fractions are calculated using Eq. (9.9)

$$y_{CO_2} = \frac{3 + (-1) \times \varepsilon_1 + (-1) \times \varepsilon_2}{9 + (-2) \times \varepsilon_1 + (0) \times \varepsilon_2} = \frac{3 - \varepsilon_1 - \varepsilon_2}{9 - 2\varepsilon_1}$$

Similarly,

$$y_{H_2} = \frac{5 - 3\varepsilon_1 - \varepsilon_2}{9 - 2\varepsilon_1}, \qquad y_{CH_3OH} = \frac{\varepsilon_1}{9 - 2\varepsilon_1}$$

$$y_{H_2O} = \frac{1 + \varepsilon_1 + \varepsilon_2}{9 - 2\varepsilon_1}, \qquad y_{CO} = \frac{\varepsilon_2}{9 - 2\varepsilon_1}$$

9.2 CRITERIA OF CHEMICAL REACTION EQUILIBRIUM

We have developed the criteria of phase equilibrium in Chapter 8. At constant temperature and pressure, the transfer of materials from one phase to another under equilibrium is found to occur with no change in the free energy. Stated mathematically,

$$dG^t_{T,P} = 0 \qquad (9.10)$$

Here $G^t_{T,P}$ is the total Gibbs free energy of the system at constant temperature and pressure. This criterion is quite general and is not restricted to physical transformations. When a chemical reaction occurs at equilibrium there is no change in the Gibbs free energy of the system, provided the change is taking place at constant temperature and pressure.

Consider a closed system in which a chemical reaction represented by the following general equation has been allowed to reach a state of equilibrium at a given temperature and pressure.

$$aA + bB \square lL + mM \qquad (9.11)$$

An infinitesimal change is allowed to occur in the system whereby the number of moles of various species change. The increments in the number of moles are dn_A, dn_B, dn_L and dn_M for components

A, B, L and M respectively. The free energy change for the process occurring at constant temperature and pressure is given by [see Eq. (7.36)]

$$dG^t_{T,P} = \Sigma \mu_i \, dn_i \tag{9.12}$$

where m_i is the chemical potential of component *i*. For the reaction under consideration, Eq. (9.12) takes the form

$$dG^t_{T,P} = \mu_L \, dn_L + \mu_M \, dn_M + \mu_A \, dn_A + \mu_B \, dn_B$$

By Eq. (9.2), $dn_i = \nu_i \, d\varepsilon$, so that the above equation becomes

$$dG^t_{T,P} = (\nu_L\mu_L + \nu_M\mu_M + \nu_A\mu_A + \nu_B\mu_B) \, d\varepsilon \tag{9.13}$$

$$= (l\mu_L + m\mu_M - a\mu_A - b\mu_B) \, d\varepsilon$$

where – *a,* – *b, l* and *m* are the stoichiometric numbers which are positive for products and negative for the reactants and e is the extent of reaction. In general, for an infinitesimal change in a reacting system, we can write Eq. (9.13) as

$$dG^t_{T,P} = \Sigma \, \mu_i \nu_i \, d\varepsilon \tag{9.14}$$

Since the process is occurring at equilibrium conditions, Eq. (9.10) should be satisfied so that

$$dG^t_{T,P} = \Sigma \, \mu_i \nu_i \, d\varepsilon = 0$$

or

$$\Sigma \, \mu_i \nu_i = 0 \tag{9.15}$$

This is the criterion of equilibrium for chemical reactions. For the present reaction given by Eq. (9.11), this criterion means

$$(l\mu_L + m\mu_M) - (a\mu_A + b\mu_B) = 0 \tag{9.16}$$

The left-hand side of Eq. (9.16) is the free energy change DG accompanying the complete reaction under equilibrium conditions. Hence, $DG = 0$ under equilibrium.

The physical significance of the criterion of chemical equilibrium can now be examined. Consider a simple chemical reaction equilibrium: A $\leftrightarrows$ B. Let the extent of the reaction be e. The change in the number of moles of A = – de and the change in the number of moles of B = de. The change in free energy at constant temperature and pressure is found out by Eq. (9.14)

$$dG^t = (m_B - m_A) \, de \qquad (9.17)$$

This equation can be written in the following form.

$$\left(\frac{\partial G^t}{\partial \varepsilon}\right)_{T,P} = \mu_B - \mu_A \tag{9.18}$$

Equation (9.18) gives the slope of the curve obtained when the Gibbs free energy is plotted against extent of reaction as in Fig. 9.1.

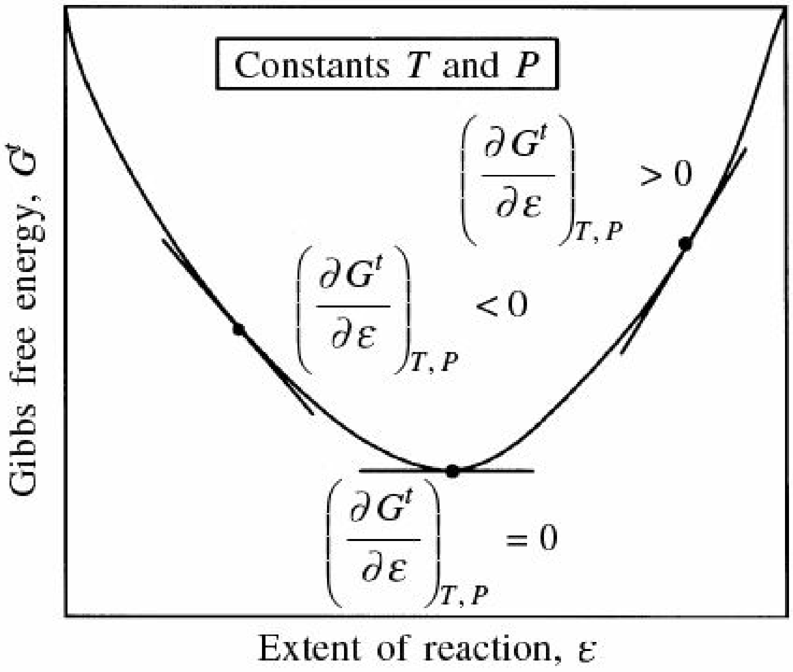


Fig. 9.1 Gibbs free energy of the reaction mixture versus extent of reaction.

The slopes given by Eq. (9.18) are not constant because the chemical potentials are functions of composition, which varies as the extent of reaction changes. Since the reaction proceeds in the direction of decreasing Gibbs free energy *G*, the forward reaction (A □ B) takes place if $m_A > m_B$ and the backward reaction (A □ B) proceeds if $m_A < m_B$. When $m_A = m_B$, the slope of the curve is zero. This occurs at the minimum of the curve and corresponds to the position of chemical equilibrium. The composition of the reaction mixture at the point where the Gibbs free energy is the minimum is the equilibrium composition at the specified temperature and pressure. Thus the criterion of equilibrium, Eq. (9.10), means that differential displacement of chemical reaction can occur at the equilibrium state, but without changing the total Gibbs free energy. If the system is not in chemical equilibrium, the reaction occurring must be irreversible and the total Gibbs free energy must decrease at constant temperature and pressure.

9.3 EQUILIBRIUM CONSTANT

Consider the chemical reaction given by Eq. (9.11)

$a\text{A} + b\text{B} \;\square\; l\text{L} + m\text{M}$

The equilibrium constant K or K_a for this reaction is defined in terms of the activities of the reactants and the products as

$$K = K_a = \frac{a_{\text{L}}^{l}\, a_{\text{M}}^{m}}{a_{\text{A}}^{a}\, a_{\text{B}}^{b}} = \Pi a_i^{\nu_i} \tag{9.19}$$

where a_i is the activity of component *i* in the reaction mixture and n_i is the stoichiometric number of *i*. Activities of the species appearing in Eq. (9.19) are raised to the respective stoichiometric numbers. Since the activity is defined as the ratio of the fugacity of the component in the solution to the fugacity in the standard state,

$$a_i = \frac{\bar{f}_i}{f_i^0}$$

Equation (9.19) can also be written as

$$K = \Pi\left(\frac{\bar{f}_i}{f_i^0}\right)^{\nu_i} \tag{9.20}$$

For gaseous systems, the standard state chosen is the pure component gas at a pressure at which the fugacity is unity. Therefore, $f_i^0 = 1$ and Eq. (9.20) reduces to the following form:

$$K = \Pi(\bar{f}_i)^{\nu_i} = K_f \tag{9.21}$$

where K_f is an equilibrium constant in terms of the fugacity of the components. For liquids and solids, the equilibrium constant K and K_f are not numerically equal as standard state fugacities are not unity.

Another equilibrium constant which is frequently used in the study of gaseous reactions is K_p, the equilibrium constant in terms of partial pressures.

$$K_p = \Pi(\bar{p}_i)^{\nu_i} \tag{9.22}$$

Using the relation that fugacity of a component in a gas mixture is equal to the product of fugacity coefficient and the partial pressure, Eq. (9.21) can be written as

$$K = K_f = \Pi(\bar{\phi}_i\,\bar{p}_i)^{\nu_i} = \Pi(\bar{\phi}_i)^{\nu_i}\,\Pi(\bar{p}_i)^{\nu_i} \tag{9.23}$$

Denoting $\Pi(\bar{\phi}_i)^{\nu_i}$ by $K\mathsf{f}$, we can write Eq. (9.23) as

$$K = K_f = K\mathsf{f}K_p \qquad (9.24)$$

This relationship is applicable for gaseous systems. If the gas mixture behaves as an ideal gas, then $K\mathsf{f} = 1$ and Eq. (9.24) leads to

$$K = K_f = K_p \qquad (9.25)$$

The numerical value of the equilibrium constant depends upon the form of the stoichiometric equation. Consider the decomposition of water vapour into hydrogen and oxygen as represented by the following equation:

$$2H_2O \;\square\; 2H_2 + O_2$$

The equilibrium constant $K\square$ for this reaction is calculated as

$$K' = \frac{a_{H_2}^2 \, a_{O_2}}{a_{H_2O}^2}$$

The same reaction may be represented by the following equation:

$$H_2O \rightarrow H_2 + \frac{1}{2} O_2$$

The equilibrium constant K'' for this reaction is

$$K'' = \frac{a_{H_2} a_{O_2}^{1/2}}{a_{H_2O}}$$

Thus, it is seen that K≤ = (K□)$^{1/2}$. The form of the stoichiometric equation should be specified along with the numerical values of the equilibrium constant.

9.4 EQUILIBRIUM CONSTANT AND STANDARD FREE ENERGY CHANGE

The criterion of equilibrium, Eq. (9.15), can be written for the general chemical reaction represented by Eq. (9.11) as

$$(l\mathrm{m}_L + m\mathrm{m}_M) - (a\mathrm{m}_A + b\mathrm{m}_B) = 0 \qquad (9.16)$$

The chemical potential of a component in the equilibrium state of the reaction mixture is related to its fugacity in that state as given below

$$\mu_i = RT \ln \bar{f}_i + C \qquad (9.26)$$

Suppose that at the same temperature, but at another state, which may be called the standard state, the free energy of component i is μ_i^0. Then,

$$\mu_i^0 = RT \ln f_i^0 + C \qquad (9.27)$$

C is a constant that depends only on temperature. Since the temperature in the standard state is the same as that in the equilibrium state, C can be eliminated from Eq. (9.26) using Eq. (9.27) as,

$$\mu_i = \mu_i^0 + RT \ln \frac{\bar{f}_i}{f_i^0} = \mu_i^0 + RT \ln a_i \qquad (9.28)$$

where a_i is the activity of species i in the mixture. Express the chemical potential of all the components as in Eq. (9.28) and substitute in Eq. (9.16). The resulting expression is

$$(l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0) + RT \ln \frac{a_L^l \, a_M^m}{a_A^a \, a_B^b} = 0 \qquad (9.29)$$

Equation (9.29) can be put into the following form:

$$(l\mu_{\mathrm{L}}^0 + m\mu_{\mathrm{M}}^0) - (a\mu_{\mathrm{A}}^0 + b\mu_{\mathrm{B}}^0) = -RT\ln\frac{a_{\mathrm{L}}^l a_{\mathrm{M}}^m}{a_{\mathrm{A}}^a a_{\mathrm{B}}^b} \tag{9.30}$$

That is,

$$\Sigma\,\mu_i^0 \nu_i = -RT\ln\frac{a_{\mathrm{L}}^l a_{\mathrm{M}}^m}{a_{\mathrm{A}}^a a_{\mathrm{B}}^b}$$

The left-hand side gives the standard free energy change ΔG^0, the free energy change accompanying the reaction when each of the reactants and the products is in its standard state. Using the definition of the equilibrium constant [Eq. (9.19)], the above equation is written as

$$\boxed{\Delta G^0 = -RT\ln K} \tag{9.31}$$

Thus the equilibrium constant is determined by the standard free energy change and the temperature. The standard free energy change depends on the temperature, the specification of standard state for each component and the number of moles involved in the stoichiometric equation under consideration. The numerical values of the equilibrium constant will be of no significance unless accompanied by the specifications for these three factors. However, it is independent of pressure at equilibrium. The effect of the reaction stoichiometry on the equilibrium constant has already been discussed. The choice of standard state is being dealt with in the following section.

9.4.1 Choice of Standard State

Though the choice of standard state in Eq. (9.31) is arbitrary and is left to our convenience, certain conventions are followed in this choice. The choice of pure component standard state will be convenient in many situations, as this requires only the specification of temperature and pressure for defining the state completely. The temperature in the standard state is the same as that of the reaction. If the standard state chosen for a substance is a solution, the composition must also be specified.

For gases, as has been pointed out earlier, the standard state chosen is the pure component at the temperature of the reaction and at unit fugacity. Fugacity will be unity at 1 bar (or 1 atm) if the gas behaves as an ideal gas at this condition. For ideal gases, therefore, the standard state pressure approaches 1 bar and ΔG^0 can be easily evaluated at this pressure. By this choice, $K = K_f$ and Eq. (9.31) becomes

$$\Delta G^0 = -RT\ln K_f \tag{9.32}$$

The standard state of unit fugacity may not be convenient for reactions involving solids, liquids or solutions. By convention, the standard state chosen for solids and liquids is the pure solid or liquid as the case may be, at a pressure of 1 bar (or 1 atm), the temperature being the same as the temperature of the reaction.

9.4.2 Feasibility of a Reaction

From the values of standard free energy change, we can formulate an approximate criterion for the feasibility of a chemical reaction, which will be useful in preliminary exploratory work. It would be worthwhile to have some idea about whether or not the equilibrium is favourable, before we search for catalysts and other conditions necessary to cause the reaction. If the reaction is not thermodynamically feasible, there is no point in pursuing a long and expensive experimental investigation on improving the rate of reaction.

Any reaction starting with pure reactants uncontaminated with any of the products will have a tendency to proceed to some extent, though this may be infinitesimally small. It is the value of the equilibrium constant, which, in turn, is related to the standard free energy of the reaction that gives the necessary information on the thermodynamic possibility of the reaction. Even the decomposition of water vapour to hydrogen and oxygen will proceed to some extent under atmospheric temperature and pressure. From the value of the standard free energy change, DG^0, the equilibrium constant for the reaction

$$H_2O\,(g) \rightarrow H_2 + \frac{1}{2}O_2$$

at 298 K is found to be about 1 □ 10^{-40}. This means that the extent of decomposition of water vapour is infinitesimally small at equilibrium and the reaction is not thermodynamically feasible.

If DG^0 for a reaction is zero, then $K = 1$, the reaction proceeds to a considerable extent before equilibrium is reached. If DG^0 is negative, then $K > 1$, the reaction is quite favourable. But the situation becomes less favourable as DG^0 increases in the positive direction. It should be borne in mind that many reactions with positive values of DG^0 are certainly feasible from the standpoint of industrial operation. For example, the methanol synthesis reaction with $DG^0 = 46{,}200$ kJ/kmol at 600 K is found to be feasible. This reaction is carried out at high pressure to overcome the unfavourable free energy change. In short, there is no well-defined demarcation to separate favourable and unfavourable reactions. The following guide may be useful as an approximate criterion for ascertaining the feasibility of chemical reactions:

$DG^0 < 0$, the reaction is promising.

$0 < DG^0 < 40{,}000$ kJ/kmol, the reaction may or may not be possible and needs further study.

$DG^0 > 40{,}000$ kJ/kmol, the reaction is very unfavourable.

***EXAMPLE* 9.5** Device a series of hypothetical steps for carrying out the gas-phase reaction

$$aA + bB \;\square\; lL + mM$$

when the reactants and the products are at their standard state. Show that the free energy changes calculated for these series of steps add up to give the same result as the one provided by Eq. (9.31).

Solution The free energy change accompanying the process in which the reactants at their standard state are converted to products also at their standard state may be calculated via any convenient path. Let us assume the following computational path for carrying out the reaction, which is represented in Fig. 9.2.

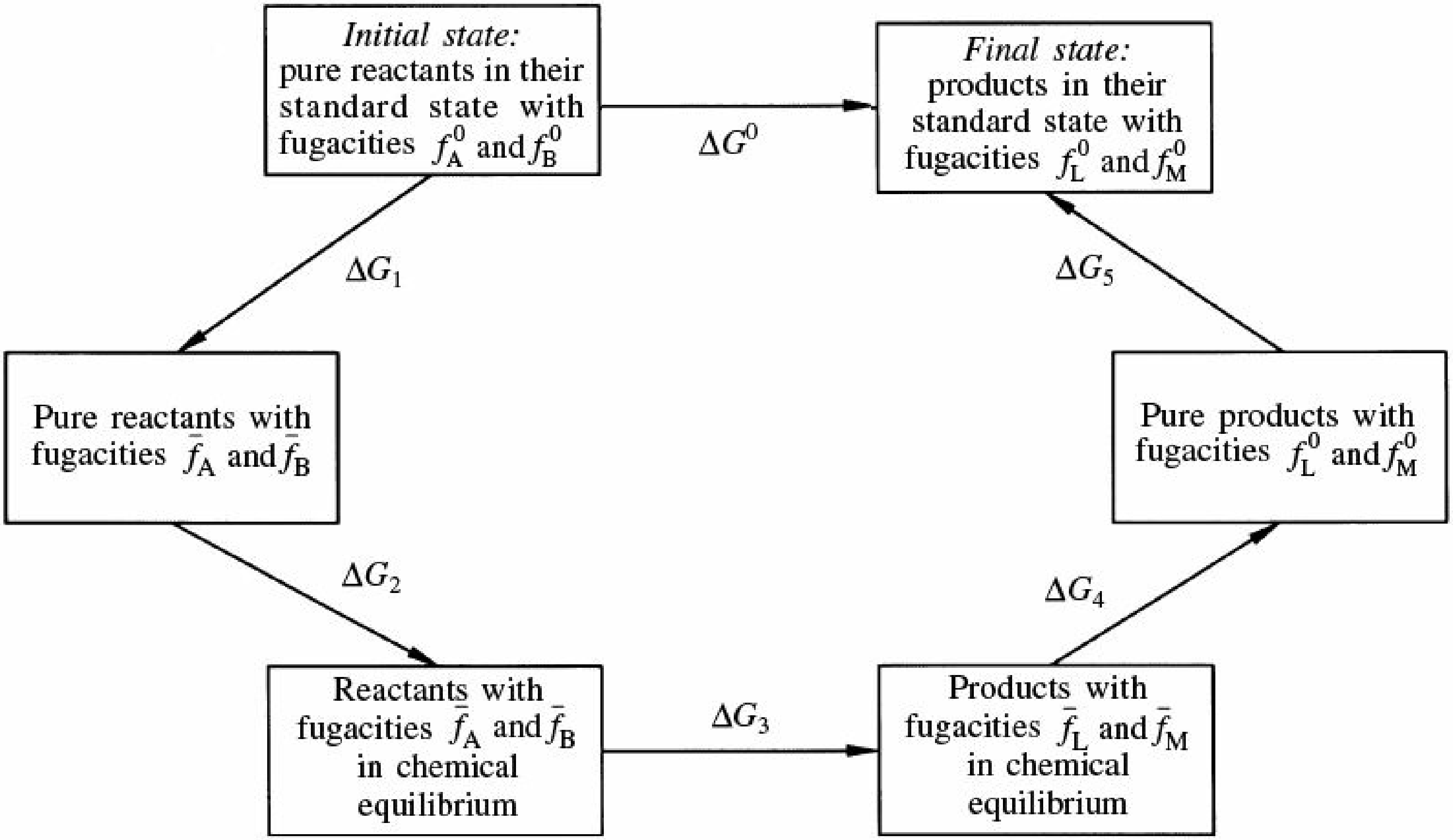


Fig. 9.2 Hypothetical stages through which the reaction in Example 9.5 is carried out.

Step 1: The reactants are initially in their pure form and are at their standard state of unit fugacity and at the temperature of the reaction. Then they are compressed to a fugacity of the reaction mixture at equilibrium. The free energy change for this process is ΔG_1.

$$\Delta G_1 = RT\left(a \ln \frac{\bar{f}_A}{f_A^0} + b \ln \frac{\bar{f}_B}{f_B^0}\right) = RT\ (\ln a_A^a + \ln a_B^b) = RT\ \ln (a_A^a a_B^b)$$

Step 2: The pure reactants are introduced to the reaction system through membranes permeable only to single species. Since the fugacities of the components before and after this step are the same, the free energy change ΔG_2 for this process is zero. $\Delta G_2 = 0$.

Step 3: The introduction of the reactants disturbs the state of equilibrium prevailing in the reaction system. To bring the system back to the equilibrium condition the forward reaction occurs at the given temperature and pressure. According to the criterion of equilibrium, this reaction proceeds without any change in the free energy of the system. Therefore, $\Delta G_3 = 0$.

Step 4: The product gases are separated by means of membranes into pure components at the reaction temperature and pressure. As in step 2, the free energy change in this process is zero. That is, $\Delta G_4 = 0$.

Step 5: The pure components with fugacities equal to $f_i = \bar{f}_i$ are expanded to standard state fugacities f_i^0. The free energy change for this step,

$$\Delta G_5 = RT\left(l \ln \frac{f_L^0}{\bar{f}_L} + m \ln \frac{f_M^0}{\bar{f}_M}\right) = RT\left(l \ln \frac{1}{a_L} + m \ln \frac{1}{a_M}\right) = RT \ln\left(\frac{1}{a_L^l\ a_M^m}\right)$$

As the free energy is a state property, the standard free energy change, ΔG^0, for the reaction should be equal to the sum of the free energy changes in the above five steps.

That is,

$$\Delta G^0 = \Delta G_1 + \Delta G_2 + \Delta G_3 + \Delta G_4 + \Delta G_5 = RT \ln\ (a_A^a\ a_B^b) + RT \ln\left(\frac{1}{a_L^l\ a_M^m}\right)$$

This can be written as

$$\Delta G^0 = -RT \ln \frac{a_L^l\ a_M^m}{a_A^a\ a_B^b} = -RT \ln K$$

which is same as Eq. (9.31).

9.5 EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANT

The effect of the operating variables on equilibrium can be qualitatively explained by means of the *Le Chatelier's principle*, which states that a system at equilibrium when subjected to a disturbance, responds in a way that tends to minimise the effect of that disturbance. An increase in temperature will shift the equilibrium state in the direction of absorption of heat. That is, the equilibrium will shift in the endothermic direction if the temperature is raised, for then, energy is absorbed as heat. In a similar way, the equilibrium can be expected to shift in the exothermic direction if the temperature is lowered, for then the reduction in temperature is opposed. Thus, an endothermic reaction is favoured by an increase in temperature and an exothermic reaction is favoured by a decrease in temperature. Or stated in another way, increased temperature favours the reactants in exothermic reactions and the products in endothermic reactions.

The effect of temperature on equilibrium constant is quantitatively expressed by *van't Hoff equation*, which is developed below. The relationship of equilibrium constant to the standard free energy of reaction is given by Eq. (9.31). The standard state is identified by specifying a definite pressure (or fugacity), but the temperature is always the same as that of the reaction mixture at equilibrium. DG^0 and hence K will vary with this temperature.

For a single species the effect of temperature on its free energy is predicted by Gibbs–Helmholtz equation [Eq. (6.73)].

$$\left(\frac{\partial (G_i/T)}{\partial T}\right)_P = -\frac{H_i}{T^2}$$

For the substance in its standard state, Eq. (6.73) can be written as

$$\left(\frac{d(G_i^0/T)}{dT}\right) = -\frac{H_i^0}{T^2} \tag{9.33}$$

Note that the partial derivative notation is dropped from the above equation, as the standard free energy, by virtue of the definition of the standard state, depends on the equilibrium temperature, but not on the equilibrium pressure. Multiplying the above equation by $\square_i$ and summing over all species present in the system, we get

$$\left(\frac{d\Sigma\, \nu_i G_i^0/T)}{dT}\right) = -\frac{\Sigma\, \nu_i H_i^0}{T^2} \tag{9.34}$$

The standard free energy of the reaction and standard heat of reaction are related to the free energy and enthalpy of individual species respectively as given below.

$$\Delta G^0 = \Sigma\, \nu_i G_i^0, \quad \Delta H^0 = \Sigma\, \nu_i H_i^0$$

Using these in Eq. (9.34) and dividing both sides by R, the following result is obtained.

$$\left(\frac{d(\Delta G^0/RT)}{dT}\right) = -\frac{\Delta H^0}{RT^2} \tag{9.35}$$

Substitute Eq. (9.31) into Eq. (9.35), we get

$$\boxed{\frac{d\ln K}{dT} = \frac{\Delta H^0}{RT^2}} \tag{9.36}$$

Equation (9.36), known as *van't Hoff equation,* predicts the effect of temperature on the equilibrium constant and hence on the equilibrium yield. DH^0 in Eq. (9.36) is the standard heat of reaction. It is apparent that if DH^0 is negative, i.e. if the reaction is exothermic, the equilibrium constant decreases as the reaction temperature increases. Alternatively, for an endothermic reaction, the equilibrium constant will increase with increase in temperature.

If DH^0, the standard heat of reaction, is constant, Eq. (9.36) on integration yields

$$\ln\frac{K}{K_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right) \tag{9.37}$$

K and K_1 are the equilibrium constant values at temperatures T and T_1 respectively. Equation (9.37) may be used to evaluate the equilibrium constant with good results over small temperature ranges.

The equation is exact if $\mathrm{D}H^0$ is independent of temperature. A reasonably accurate method of interpolation or extrapolation of equilibrium constant is provided by plotting $\ln K$ versus reciprocal of temperature, which leads to a straight line according to Eq. (9.37).

The variation of the standard heat of reaction with temperature may be taken into account if the molal heat capacities of the various species taking part in the reaction are known as functions of temperature. Suppose that the specific heats at constant pressure are expressed as a power function in T.

$$C_P = \mathrm{a} + \mathrm{b}T + \mathrm{g}T^2 \qquad (9.38)$$

Then the effect of temperature on the standard heat of reaction may be developed as follows: Since heat of reaction is the enthalpy change between the given initial and final states, it may be evaluated by devising any convenient path between these terminal states for which the enthalpy changes are readily available. Assume that the standard heat at temperature T_1, $\Delta H^0_{T_1}$, is known and it is desired to calculate the standard heat at temperature T.

The actual reaction occurring at temperature T for which the heat of reaction is ΔH^0_T may be treated as occurring along the three paths as depicted in Fig. 9.3.

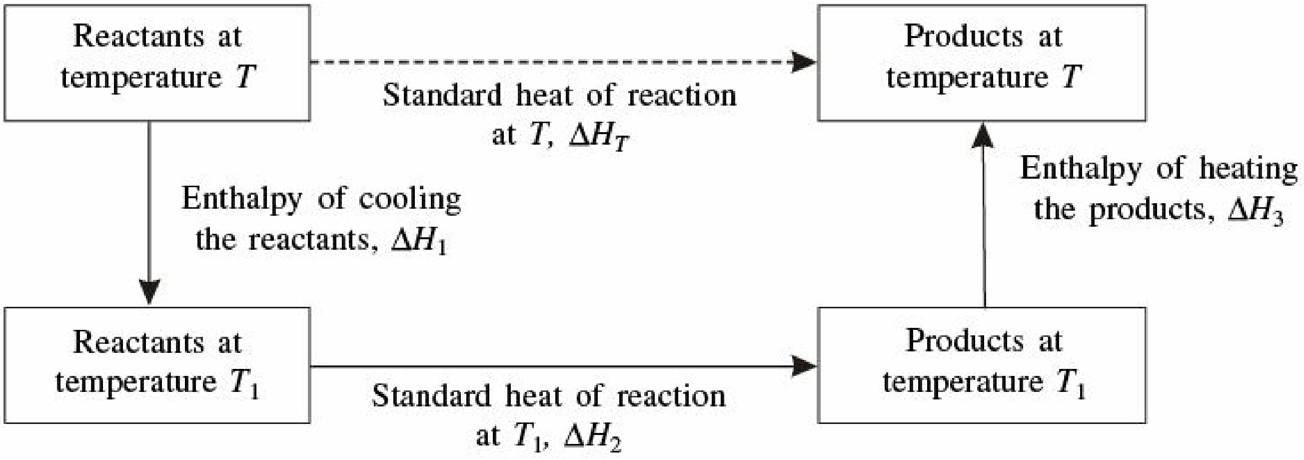


Fig. 9.3 Method of estimating the standard heat of reaction at temperature T given the standard heat of reaction at T_1.

1. The reactants are cooled from temperature T to T_1. The enthalpy change for this step is

$$\Delta H_1 = \sum_{\text{Reactants}} \int_T^{T_1} n_i\, C_{P,i}\, dT = \sum_{\text{Reactants}} \int_{T_1}^{T} \nu_i\, C_{P,i}\, dT \qquad (9.39)$$

2. The reaction is allowed to occur at temperature T_1. The enthalpy change is

$$\Delta H_2 = \Delta H^0_{T_1} \qquad (9.40)$$

3. The temperature of the products is raised from T_1 to T in this step. The enthalpy change is

$$\Delta H_3 = \sum_{\text{Products}} \int_{T_1}^{T} n_i C_{P,i}\, dT = \sum_{\text{Products}} \int_{T_1}^{T} \nu_i C_{P,i}\, dT \qquad (9.41)$$

The standard heat of reaction at temperature *T*, is obtained by adding the preceding three equations.

$$\Delta H_T^0 = \Delta H_1 + \Delta H_2 + \Delta H_3 = \sum_{\text{Reactants}} \int_{T_1}^{T} v_i C_{P,i}\, dT + \Delta H_{T_1}^0 + \sum_{\text{Products}} \int_{T_1}^{T} v_i C_{P,i}\, dT$$

The above result can be written as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^{T} \left(\sum_i v_i C_{P,i} \right) dT \tag{9.42}$$

The summation in the above equation is over all the species taking part in the reaction. Using Eq. (9.38) in Eq. (9.42), we can write it as

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \int_{T_1}^{T} \Delta C_P \, dT \tag{9.43}$$

where

$$\Delta C_P = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \tag{9.44}$$

and

$$\Delta\alpha = \Sigma\, v_i\alpha_i, \quad \Delta\beta = \Sigma\, v_i\beta_i, \quad \Delta\gamma = \Sigma\, v_i\gamma_i \tag{9.45}$$

Equation (9.43) may be expanded to yield the following result.

$$\Delta H_T^0 = \Delta H_{T_1}^0 + \Delta\alpha (T - T_1) + \frac{1}{2}\Delta\beta (T^2 - T_1^2) + \frac{1}{3}\Delta\gamma (T^3 - T_1^3)$$

The constants appearing in the above equation can be grouped together to a single constant $\Delta H'$, so that we have

$$\Delta H_T^0 = \Delta H' + \Delta\alpha T + \frac{\Delta\beta}{2} T^2 + \frac{\Delta\gamma}{3} T^3 \tag{9.46}$$

The constant D*H*□ in the above equation can be evaluated if the heat of reaction at a single temperature is known. Equation (9.46) can then be used for the evaluation of the heat of reaction at any temperature *T*.

Substitute Eq. (9.46) into Eq. (9.36) and integrate the resulting expression. The result is

$$\ln K = -\frac{\Delta H'}{RT} + \frac{\Delta\alpha}{R} \ln T + \frac{\Delta\beta}{2R} T + \frac{\Delta\gamma}{6R} T^2 + A \tag{9.47}$$

A in Eq. (9.47) is a constant of integration, which may be evaluated from the knowledge of the equilibrium constant at one temperature. Equation (9.31) relates the equilibrium constant to the standard free energy change. Using this relationship, we get

$$\Delta G^0 = \Delta H' - \Delta\alpha T \ln T - \frac{\Delta\beta}{2} T^2 - \frac{\Delta\gamma}{6} T^3 - ART \tag{9.48}$$

9.5.1 Evaluation of Equilibrium Constants

Equation (9.47) can be used for the evaluation of the equilibrium constant, provided, we know the dependence of heat capacities on temperature and we also have enough information for the evaluation of the constants DH□ and A. Assuming that the heat capacity data are available, the general methods used for the evaluation of the constants DH□ and A are listed below.

***Method* 1.** K may be calculated from the experimentally measured composition of the equilibrium mixture using Eq. (9.19). If K values are thus known at two different temperatures, they may be substituted into Eq. (9.47). The resulting two equations are solved for the constants DH□ and A.

***Method* 2.** Standard heat of reaction at one temperature and one value for the equilibrium constant that is determined by direct experimental measurements are available. The former is used in Eq. (9.46) for the evaluation of the constant DH□ and the latter in Eq. (9.47) for evaluating the constant A.

***Method* 3.** This method involves no direct experimental measurements for the equilibrium constant and therefore this is the most convenient and most widely used method. The method makes use of thermal data only, usually in the form of standard heat of reaction DH^0, and a standard free energy change of reaction DG^0. Then the constants DH□ and A are evaluated using Eq. (9.46) and
Eq. (9.48) respectively.

DH^0 for a reaction may be evaluated from the standard heat of formation, ΔH_f^0, that are tabulated for most of the compounds. The standard free energy of a reaction can be estimated from the values of standard free energy of formation, ΔG_f^0 of the various species participating in the reaction and their respective stoichiometric numbers as

$$\Delta G^0 = \Sigma\, \nu_i\, \Delta G_{i,f}^0 \tag{9.49}$$

Noting that the stoichiometric numbers are positive for products and negative for the reactants, the above may well be written as

$$\Delta G^0 = \sum_{\text{Products}} |\nu_i|\, \Delta G_{i,f}^0 - \sum_{\text{Reactants}} |\nu_i|\, \Delta G_{i,f}^0 \tag{9.50}$$

That is, the standard free energy of a reaction is the algebraic sum of the free energies of formation of the products minus the algebraic sum of the free energies of formation of the reactants. When an element enters into a reaction, its standard free energy of formation may be taken to be zero.

9.5.2 Giauque Functions

Data for calculation of standard free energy of reactions are sometimes tabulated as *Giauque functions*. These are Gibbs free energy functions that vary very slowly with temperature. Two such functions are in general use—the first is referred to 0 K and the second referred to 298 K. These are written as

$$\phi_0 = \frac{G_T^0 - H_0^0}{T}, \qquad \phi_{298} = \frac{G_T^0 - H_{298}^0}{T} \tag{9.51}$$

where G_T^0, H_T^0, H_{298}^0 are respectively the free energy in the standard state at temperature T, the enthalpy in the standard state at T and the enthalpy in the standard state at 298 K. Because only standard state properties are involved, these functions depend only on temperature. This temperature dependence is found to be very weak which makes these functions suitable for tabular interpolation. Using the definition of free energy, we can show that

$$\begin{aligned} \phi_0 &= \frac{H_T^0 - H_0^0}{T} - S_T^0 \\ \phi_T &= \frac{H_T^0 - H_{298}^0}{T} - S_T^0 \end{aligned} \tag{9.52}$$

From Eq. (9.51) we see that

$$\begin{aligned} \phi_{298} + \frac{H_{298}^0}{T} &= \phi_0 + \frac{H_0^0}{T} \\ \phi_{298} &= \phi_0 - \left(\frac{H_{298}^0 - H_0^0}{T} \right) \end{aligned} \tag{9.53}$$

The difference in enthalpy values, the terms in brackets in Eq. (9.53), needed for applying Eq. (9.53) also are listed in tables along with □$_0$. The standard free energy change of a reaction may be calculated from the Gibbs free energy functions. Equation (9.51) can be rearranged as

$$\frac{G_T^0}{T} = \phi_0 + \frac{H_0^0}{T} \tag{9.54}$$

$$\frac{G_T^0}{T} = \phi_{298} + \frac{H_{298}^0}{T} \tag{9.55}$$

The Gibbs free energy at the standard state for each of the species taking part in the reaction as given by Eq. (9.54) or Eq. (9.55) multiplied by the respective stoichiometric numbers add together to give the standard free energy of the reaction.

$$\frac{\Delta G_T^0}{T} = \frac{\Sigma\, \nu_i G_{T,\,i}^0}{T} = \Sigma\, \nu_i \phi_{0,\,i} + \frac{\Sigma\, \nu_i H_{0,\,i}^0}{T} = \Sigma\, \nu_i \phi_{298,\,i} + \frac{\Sigma\, \nu_i \Delta H_{298,\,i}^0}{T}$$

Noting that the enthalpy of a substance in its standard state, H_i^0, is equal to the standard enthalpy $\Delta H_{f,\,i}^0$, we get the following useful results:

$$\frac{\Delta G_T^0}{T} = \Sigma\, \nu_i \phi_{0,\,i} + \frac{\Sigma\, \nu_i \Delta H_{f,\,0,\,i}^0}{T} \tag{9.56}$$

$$\frac{\Delta G_T^0}{T} = \Sigma\, \nu_i \phi_{298,\,i} + \frac{\Sigma\, \nu_i \Delta H_{f,\,298,\,i}^0}{T} \tag{9.57}$$

Note that the enthalpy of a compound in the standard state, H_i^0, is the same as its standard enthalpy of formation, $\Delta H_{f,\,i}^0$. The standard free energy of a reaction determined using Eqs. (9.56) or (9.57) may be used in Eq. (9.31) to calculate the equilibrium constant.

***EXAMPLE* 9.6** Calculate the equilibrium constant at 298 K of the reaction

N_2O_4 (g) □ $2NO_2$ (g)

given that the standard free energies of formation at 298 K are 97,540 J/mol for N_2O_4 and 51,310 J/mol for NO_2.

Solution Using Eq. (9.50) for the dissociation of N_2O_4,

DG^0 = 2 □ 51,310 – 97,540 = 5080 J/mol

From Eq. (9.31),

DG^0 = – $RT \ln K$

which gives

$$\ln K = -\frac{\Delta G^0}{RT} = -\frac{5080}{8.314 \times 298} = -2.0504$$

Therefore, $K = 0.1287$.

***EXAMPLE* 9.7** The standard heat of formation and standard free energy of formation of ammonia at 298 K are –46,100 J/mol and –16,500 J/mol respectively. Calculate the equilibrium constant for the reaction

N_2 (g) + $3H_2$ (g) □ $2NH_3$ (g)

at 500 K assuming that the standard heat of reaction is constant in the temperature range 298 to 500 K.

Solution The standard free energy of reaction is estimated from Eq. (9.50).

$$\Delta G^0 = \sum_{\text{Products}} |\nu_i| \Delta G^0_{i,f} - \sum_{\text{Reactants}} |\nu_i| \Delta G^0_{i,f}$$

The second summation yields zero as the free energy of formation of the elements are zero.

$$\Delta G^0 = \sum_{\text{Products}} |\nu_i| \Delta G^0_{i,f} = 2 \times -16{,}500 = -33{,}000 \text{ J/mol}$$

Using Eq. (9.31),

$$\ln K = -\frac{\Delta G^0}{RT} = \frac{33{,}000}{8.314 \times 298} = 13.3195$$

Therefore,

$$K \text{ at } 298 \text{ K} = 6.0895 \times 10^5$$

The standard heat of reaction at 298 K = 2 □ – 46,100 = – 92,200 J/mol. This is assumed constant within the temperature range involved. Now use Eq. (9.37) to evaluate the equilibrium constant.

$$\ln \frac{K}{K_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

$$\ln \frac{K}{6.0895 \times 10^5} = \frac{92{,}200}{8.314}\left(\frac{1}{500} - \frac{1}{298}\right) = -15.0344$$

Therefore, the equilibrium constant at 500 K, $K = 0.18$

***EXAMPLE* 9.8** *n*-Butane is isomerised to *i*-butane by the action of catalyst at moderate temperatures. It is found that the equilibrium is attained at the following compositions.

Temperature, K	Mol %, *n*-butane
317	31.00
391	43.00

Assuming that activities are equal to the mole fractions, calculate the standard free energy of the reaction at 317 K and 391 K and average value of heat of reaction over this temperature range.

Solution Since activities are equal to mole fractions, $K = y_{ib}/y_{nb}$, where y_{ib} is the mole fraction of *i*-butane and y_{nb} the mole fraction of *n*-butane in the equilibrium mixture. Therefore,

$$\text{At 317 K,} \qquad K = \frac{0.69}{0.31} = 2.2258$$

$$\text{At 391 K,} \qquad K = \frac{0.57}{0.43} = 1.3255$$

Equation (9.31) gives

$$\Delta G^0 = -RT \ln K$$

$$\Delta G^0_{317} = -8.314 \times 317 \ln 2.2258 = -2108.74 \text{ J/mol}$$

$$\Delta G^0_{391} = -8.314 \times 391 \ln 1.3255 = -916.03 \text{ J/mol}$$

Assuming that the heat of reaction is independent of temperature we can use Eq. (9.37) for calculating it.

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{2.2258}{1.3255} = -\frac{\Delta H^0}{8.314}\left(\frac{1}{317} - \frac{1}{391}\right)$$

Therefore, $\Delta H^0 = -7218.02$ J/mol.

***EXAMPLE* 9.9** Estimate the standard free energy change and equilibrium constant at 700 K for the reaction

N_2 (g) + $3H_2$ (g) □ $2NH_3$ (g)

given that the standard heat of formation and standard free energy of formation of ammonia at 298 K to be – 46,100 J/mol and –16,500 J/mol respectively. The specific heat (J/mol K) data are given below as function of temperature (K):

$C_P = 27.27 + 4.93$ □ $10^{-3}T$ for N_2

$C_P = 27.01 + 3.51$ □ $10^{-3}T$ for H_2

$C_P = 29.75 + 25.11$ □ $10^{-3}T$ for NH_3

Solution The standard heat of reaction and standard free energy of reaction at 298 K were estimated in Example 9.7.

DH^0 = – 92,200 J/mol; DG^0 = – 33,000 J/mol

Also,

Da = 2 □ 29.75 – 27.27 – 3 □ 27.01 = – 48.8

Db = (2 □ 25.11 – 4.93 – 3 □ 3.51) □ 10^{-3} = 34.76 □ 10^{-3}

Equation (9.46) gives

$$-92{,}200 = \Delta H^0 - 48.8T + 17.38 \times 10^{-3}T^2$$

$$= \Delta H^0 - 48.8 \times 298 + 17.38 \times 10^{-3} \times (298)^2$$

$$= \Delta H^0 - 1.3 \times 10^4$$

Therefore, $\Delta H^0 = -7.9201 \times 10^4$. Equation (9.48) gives

$$-33{,}000 = \Delta H^0 - \Delta\alpha T \ln T - \frac{\Delta\beta}{2}T^2 - ART$$

$$= -7.9201 \times 10^4 + 48.8 \times 298 \times \ln 298 - 17.38 \times 10^{-3} \times 298^2 - A \times 8.314 \times 298$$

$$= 2105 - 2477.57\,A$$

Therefore, $A = 14.169$. Substitute ΔH^0 and A into Eq. (9.47) and Eq. (9.48), we get

$$\ln K = \frac{79{,}201}{RT} - \frac{48.8}{R}\ln T + \frac{17.38 \times 10^{-3}}{R}T + 14.169 \tag{9.58}$$

$$\Delta G^0 = -79{,}201 + 48.8\,T\ln T - 17.38 \times 10^{-3}T^2 - 14.169RT \tag{9.59}$$

Put $T = 700$ K in the above equations. Equation (9.58) gives $K = 1 \times 10^{-4}$; Eq. (9.59) gives $\Delta G^0 = 53{,}607$ J/mol.

***EXAMPLE* 9.10** Evaluate the equilibrium constant at 600 K for the reaction

$$\text{CO (g)} + 2\text{H}_2\text{ (g)} \rightleftharpoons \text{CH}_3\text{OH (g)}$$

given that the Gibbs free energy function

$$\phi_{298} = \frac{G_T^0 - H_{298}^0}{T}$$

for CO, H_2 and methanol at 600 K are respectively –203.81, –136.39 and –249.83 J/mol K. The heats of formation at 298 K of CO (g) and CH_3OH (g) at 298 K are –110,500 J/mol and –200,700 J/mol.

Solution The standard free energy of formation at 600 K is evaluated by means of Eq. (9.57).

$$\frac{\Delta G_T^0}{T} = \Sigma \nu_i \phi_{298,\,i} + \frac{\Sigma \nu_i \Delta H^0_{f,\,298,\,i}}{T}$$

$$\frac{\Delta G^0_{600}}{600} = 1(-249.83) - 1(-203.81) - 2(-136.39) + \frac{1}{600}\,[1(-200{,}700) - 1(-110{,}500)]$$

$$= 76.4267$$

From Eq. (9.31),

$$-R \ln K = \frac{\Delta G^0}{T}$$

$$\ln K = -\frac{76.4267}{8.314} = -9.1925$$

$$K = 1.018 \times 10^{-4}$$

***EXAMPLE* 9.11** Calculate the equilibrium constant for the reaction

N_2 (g) + $3H_2$ (g) □ $2NH_3$ (g)

at 500 K, given that the free energy function

$$\phi_0 = \frac{G_T^0 - H_0^0}{T}$$

at 500 K for nitrogen, hydrogen and ammonia are respectively –177.5, –116.9 and –176.9 J/mol K. The function $(H^0_{298} - H^0_0)$ for nitrogen, hydrogen and ammonia are respectively 8669, 8468 and 9920 J/mol. The free energy of formation of ammonia at 298 K is –46,100 J/mol.

Solution Equation (9.53) gives

$$\Sigma \nu_i \phi_{298,\,i} = \Sigma \nu_i\, \phi_{0,\,i} - \Sigma\, \nu_i \left(\frac{H^0_{298,\,i} - H^0_{0,\,i}}{T}\right)$$

$$= 2(-176.9) - 1(-177.5) - 3(-116.9) - (2 \times 9920 - 1 \times 8669 - 3 \times 8468)/500$$

$$= 174.4 + 28.466 = 202.87 \text{ J/mol K}$$

Equation (9.57) can be used to evaluate ΔG^0_{500}.

$$\frac{\Delta G_T^0}{T} = \Sigma \nu_i \phi_{298,\,i} + \frac{\Sigma \nu_i \Delta H_{f,\,298,\,i}^0}{T}$$

$$= 202.87 + 2(-46{,}100)/500 = 18.47 \text{ J/mol K}$$

Therefore, $$\ln K = -\frac{18.47}{R} = -2.2215$$

$$K = 0.1084$$

9.6 EFFECT OF PRESSURE ON EQUILIBRIUM

9.6.1 Effect of Pressure on Equilibrium Constant

We have shown that the equilibrium constant K is related to the standard free energy change by the equation, $\mathrm{D}G^0 = -RT \ln K$, where K is defined by Eq. (9.19) as

$$K = \frac{a_{\mathrm{L}}^l \, a_{\mathrm{M}}^m}{a_{\mathrm{A}}^a \, a_{\mathrm{B}}^b} = \Pi a_i^{\nu_i}$$

The equilibrium constant defined above is independent of the pressure. By Eq. (9.31), the equilibrium constant is known if the standard free energy of the reaction and the reaction temperature are known. The standard free energy of a reaction is determined by the free energies of the substances in their standard states. The standard states are defined by specifying a pressure and are in no way affected by the reaction pressure. That is, the standard free energy of a reaction, and hence, the equilibrium constant are not affected by changes in the equilibrium pressure.

9.6.2 Effect of Pressure on Equilibrium Composition

Though the equilibrium constant is unaffected by pressure, it does affect the equilibrium composition in gas-phase reactions. This effect is explained qualitatively by Le Chatelier's principle. Consider for example, the equilibrium in the gas-phase reaction A ☐ 2B. When pressure is applied to this system, it responds in such a way as to minimise the effect of the increase in pressure. This is achieved by decreasing the number of moles in the system, which in turn is achieved by the reaction A ☐ 2B. Thus, increase in pressure decreases the number of B molecules and increases the number of A molecules. By the same reasoning we can deduce that in the case of the reaction equilibrium for $N_2 + 3H_2$ ☐ $2NH_3$ formation of ammonia will be favoured by an increase in pressure as there is a reduction in the number of moles due to this reaction. It should be remembered that when the composition of the system changes in this manner in response to increase or decrease in pressure, it does so without changing the equilibrium constant.

Except at very high pressures, properties of solids, liquids or solutions are not affected appreciably by pressure. Therefore, the equilibrium concentrations in reactions involving solids, liquids or solutions are not affected significantly by changes in pressure.

To predict the effect of pressure quantitatively, the relationship between equilibrium constant and equilibrium composition must be established. Equation (9.19) defines the equilibrium constant as a function of activities of the species in the reacting system. The activities of the components are affected by changes in pressure, temperature and composition. As K is independent of pressure, and activities are not, it requires that the activities of the components change with pressure in such a way that the complex function of activities, which we have defined as equilibrium constant, remains unaltered. The equilibrium constant written in terms of activities, K, and the equilibrium constant K_f, which is written in terms of the fugacities of the components were shown to be equal for gaseous systems employing ideal-gas standard state through Eq. (9.21).

$$K = \Pi(\bar{f}_i)^{\nu_i} = K_f$$

Fugacities can be written as product of fugacity coefficient and partial pressure of the component in the mixture.

$$\bar{f}_i = \phi_i\,(y_i\,P) \tag{9.60}$$

Rewrite Eq. (9.21) using Eq. (9.60).

$$K = K_f = \Pi\,(\phi_i\,y_i\,P)^{\nu_i}$$

The above equation can be put into the following forms:

$$K = (\Pi\,\phi_i^{\nu_i})\,(\Pi\,y_i^{\nu_i})\,P^{\nu} \tag{9.61}$$

In the above equation, $\nu = \Sigma\,\nu_i = l + m - a - b$, for the general reaction given by Eq. (9.11) and P is the reaction pressure.

Let $K_\phi = \Pi\,\phi_i^{\nu_i}$ and $K_y = \Pi\,y_i^{\nu_i}$. Then Eq. (9.61) gets modified as

$$K = K_\phi K_y P^{\nu} \tag{9.62}$$

K_y in Eq. (9.62) may be treated as an equilibrium constant in terms of composition. Equation (9.62) provides the necessary expression relating the equilibrium constant and the equilibrium composition. If the reaction mixture behaves as an ideal gas, K_ϕ is unity and Eq. (9.62) reduces to

$$K = K_y P^{\nu} \tag{9.63}$$

Since, K is independent of pressure, the variation in the P^{n} term in the above equations must be balanced by a corresponding change in the value for K_y. The change in K_y means the change in the equilibrium compositions. If there is a decrease in the number of moles during the reaction as in the case of ammonia synthesis reaction, n will be negative. An increase in pressure in this case will decrease P^{n} and as a result, K_y and the equilibrium yield would increase. On the other hand, if the reaction results in an increase in the number of moles, n will be positive and the equilibrium yield would decrease with increase in pressure.

The above observations are in agreement with the Le Chatelier's principle. In addition, Eq. (9.62) can be used to explain the effect of pressure on reactions where n is zero, which cannot be explained by Le Chatelier's principle. One would expect pressure to have no effect on reaction such as the water-gas shift reaction

$$CO\ (g) + H_2O\ (g)\ \square\ CO_2\ (g) + H_2\ (g)$$

because there is no change in the number of moles during the reaction. The effect of pressure on the equilibrium composition in this case can be explained by the effect of pressure on K_f. K_f measures the deviation from ideal-gas behaviour, and its value may change with change in pressure. If K_f decreases in any reaction, then K_y and the equilibrium yield would increase even when n is zero. The effect of pressure on K_f can be calculated from fugacity coefficients. It is seen that when the compressibility of the products is greater than the compressibility of the reactants, K_f decreases with pressure, thereby increasing the conversion.

***EXAMPLE* 9.12** Industrial grade methanol can be produced according to the reaction

$$CO(g) + 2H_2(g) \Leftrightarrow CH_3OH(g)$$

For this reaction, $\Delta G^0_{400} = -1.3484$ kJ. If an equimolar mixture of CO and H_2 is fed to a reactor maintained at 400 K and 10 bar, determine the fraction of CO that is converted into CH_3OH at equilibrium. Assume that the reaction mixture behaves like an ideal gas.

Solution Basis: 1 mol CO and 1 mol hydrogen in the reaction mixture.
Let e be the extent of reaction. The mole fractions of the components under equilibrium are:

$$y_{CO}: 0.5,\ y_{H_2}: (1 - 2\varepsilon)/2(1 - \varepsilon),\ y_{CH_3OH}: \varepsilon/2(1 - \varepsilon)$$

$$K_y = \frac{y_{CH_3OH}}{y_{CO}y_{H_2}^2} = \frac{4\varepsilon(1 - \varepsilon)}{(1-2\varepsilon)^2}$$

By Eq. (9.63), $K = K_yP^v$.
Here, $v = -2$. Thus, $K = K_yP^{-2}$. Also,

$$K = \exp\left[-\frac{\Delta G^0}{RT}\right] = \exp\left(\frac{1348.4}{8.314 \times 400}\right) = 1.5$$

so that now we have

$$K_y = \frac{4\varepsilon(1-\varepsilon)}{(1-2\varepsilon)^2} = 1.5 \times P^2 = 1.5 \times 10^2 = 150$$

Solving this, we get $\varepsilon = 0.4593$ and 0.5407. The extent of reaction cannot be greater than 0.5. Therefore, $\varepsilon = 0.4593$. The fraction of CO converted is $z = \dfrac{|v_i|\varepsilon}{n_{i,0}} = 0.4593$.

***EXAMPLE* 9.13** A compound M polymerises in the gas phase at low pressure to M_n, where $n > 1$.

(a) Show that the mole fraction of the polymer at equilibrium increases with increase in pressure at constant temperature

(b) The mole fraction of the polymer in the equilibrium mixture at 300 K is 0.15 at 1 bar and 0.367 at 2 bar. Find the value of n.

Solution (a) The reaction is nM □ M_n. There is a decrease in the number of moles during the forward reaction. The increase in pressure therefore favours the polymerisation reaction and as a result, the mole fraction of the polymer at equilibrium increases with pressure.

(b) From Eq. (9.62), $K_y = (K/K_{\mathsf{f}})P^{-\mathsf{n}}$. Assuming ideal gas behaviour, $K_y = KP^{-\mathsf{n}}$. Here, $\mathsf{n} = 1 - n$ and at 1 bar,

$$K_y = \text{mole fraction of } M_n/(\text{mole fraction of } M)^n = 0.15/0.85^n$$

$$K_y \text{ at 2 bar} = 0.367/0.633^n$$

Therefore,

$$0.15/0.85^n = KP^{n-1} = K$$

$$0.367/0.633^n = KP^{n-1} = K \,\square\, 2^{n-1}$$

Dividing the second equation by the first,

$$2^{n-1} = \frac{0.367}{0.15} \times \left(\frac{0.85}{0.633}\right)^n = 2.4467 \times 1.3428^n$$

On solving, we get $n = 4$.

EXAMPLE **9.14** In the synthesis of ammonia, stoichiometric amounts of nitrogen and hydrogen are sent to a reactor where the following reaction occurs

$$N_2 + 3H_2 \,\square\, 2NH_3$$

The equilibrium constant for the reaction at 675 K may be taken equal to 2 □ 10^{-4}.

(a) Determine the per cent conversion of nitrogen to ammonia at 675 K and 20 bar.

(b) What would be the conversion at 675 K and 200 bar?

Solution Basis: 1 mol nitrogen and 3 mol hydrogen are in the reactant mixture. Let e be the extent of reaction. Then the number of moles of various species at equilibrium are calculated using Eq. (9.3) as $n_i = n_{i0} + \mathsf{n}_i\mathsf{e}$. Thus the moles of nitrogen, hydrogen and ammonia at equilibrium are, respectively, $1 - \mathsf{e}$, $3 - 3\mathsf{e}$ and $2\mathsf{e}$. Total moles at equilibrium is $= 4 - 2\mathsf{e}$. The mole fractions of nitrogen, hydrogen and ammonia are, respectively,

$$\frac{1-\varepsilon}{4-2\varepsilon}, \quad \frac{3(1-\varepsilon)}{4-2\varepsilon}, \quad \frac{2\varepsilon}{4-2\varepsilon}$$

The sum of stoichiometric numbers, $\nu = 2 - 1 - 3 = -2$. Equation (9.62) gives

$$K_y = (K/K_\phi)P^{-\nu} = KP^2$$

In arriving at this result ideal behaviour is assumed, so that $K_\phi = 1$.

Thus we have the necessary relation connecting the equilibrium composition and pressure.

$$\frac{[2\varepsilon/(4-2\varepsilon)]^2}{[(1-\varepsilon)/(4-2\varepsilon)]\,[3(1-\varepsilon)/(4-2\varepsilon)]^3} = 2 \times 10^{-4}\, P^2$$

That is,

$$\frac{4\varepsilon^2(4-2\varepsilon)^2}{27(1-\varepsilon)^4} = 2 \times 10^{-4}\, P^2$$

$$\frac{\varepsilon(4-2\varepsilon)}{(1-\varepsilon)^2} = 3.6742 \times 10^{-2}\, P \tag{9.64}$$

(a) When $P = 20$ bar,

$$\frac{\varepsilon(4-2\varepsilon)}{(1-\varepsilon)^2} = 0.73485$$

$$2.73485\varepsilon^2 - 5.4697\varepsilon + 0.73485 = 0$$

Solving this, $\varepsilon = 0.1448$. Fractional conversion of nitrogen,

$$z = \frac{|\nu_i|\,\varepsilon}{n_{i0}} = \varepsilon = 0.1448$$

That is, conversion of nitrogen = 14.48%.

(b) When $P = 200$ bar,

$$\frac{\varepsilon(4-2\varepsilon)}{(1-\varepsilon)^2} = 7.3485$$

$$9.3485\varepsilon^2 - 18.697\varepsilon + 7.3485 = 0$$

Therefore, e = 0.5375. So, conversion of nitrogen = 53.75%.

We see that the increase in pressure favours the formation of ammonia as this reaction is accompanied by a decrease in the number of moles.

9.7 OTHER FACTORS AFFECTING EQUILIBRIUM CONVERSION

The reaction conditions that influence the extent of reaction under equilibrium are the temperature, pressure, presence of inert materials, presence of excess of reactants and presence of the products of the reaction in the initial mixture. The effects of temperature and pressure on the equilibrium composition have already been discussed in the previous sections. Here, we discuss the effects of other factors.

Rearrange Eq. (9.62) to the following form.

$$K_y = \frac{K}{K_\phi} P^{-\nu} \tag{9.65}$$

K_y in Eq. (9.65) may be written as

$$K_y = \Pi \left(\frac{n_i}{N} \right)^{\nu_i} \tag{9.66}$$

where i is any species taking part in the reaction and n_i is the number of moles of i. N represents the total number of moles in the reaction mixture, and if any inert material is present in the system, N includes n_I moles of inert material also.

$$N = \text{S}\, n_i + n_I$$

Combining Eqs. (9.65) and (9.66) we obtain

$$\Pi \left(\frac{n_i}{N} \right)^{\nu_i} = N^{-\nu}\, \Pi n_i^{\nu_i} = \frac{K}{K_\phi} P^{-\nu}$$

or

$$\Pi n_i^{\nu_i} = \frac{K}{K_\phi} \left(\frac{N}{P} \right)^{\nu} \tag{9.67}$$

Any changes in the reaction conditions that results in an increase in the right-hand side of Eq. (9.67) leads to an improved conversion.

9.7.1 Presence of Inert Materials

Diluting the reaction mixture with an inert material will increase N in Eq. (9.67). This will result in an increased conversion, if n is positive. That is, if the reaction proceeds with an increase in the number of moles, presence of inerts in the system will increase the equilibrium yield. The effect, as we see, is just the opposite to the effect of increased pressure in such reactions. The presence of inerts will decrease conversion if the reaction is accompanied by a decrease in the number of moles; and the inerts present in the system will have no influence on the degree of completion if n is zero, that is, if there is no change in the number of moles during a reaction.

***EXAMPLE* 9.15** A mixture of 1 mol CO, and 1 mol water vapour is undergoing the water-gas shift reaction at a temperature of 1100 K and a pressure of 1 bar.

$$\text{CO (g)} + \text{H}_2\text{O (g)} \;\square\; \text{CO}_2\text{ (g)} + \text{H}_2\text{ (g)}$$

The equilibrium constant for the reaction is $K = 1$. Assume that the gas mixture behaves as ideal gas. Calculate

(a) The fractional dissociation of steam

(b) The fractional dissociation of steam if the reactant stream is diluted with 2 mol nitrogen.

Solution The mole fractions of the species at equilibrium are related to the equilibrium constant which is given by

$$K_y = \frac{K}{K_\phi} P^{-\nu} \tag{9.65}$$

where n is the sum of stoichiometric numbers. Here, n = 1 + 1 – 1 – 1 = 0. As the gas mixture behaves as an ideal gas, $K_f = 1$. Equation (9.65) gives $K_y = K = 1$. K_y is related to the mole fractions of various components as $K_y = \Pi y_i^{\nu_i}$. Equation (9.4) gives the relationship between mole fractions and extent of reaction at equilibrium as

$$y_i = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \varepsilon \nu}$$

(a) The mole fractions of the constituents in the equilibrium mixture are expressed in terms of the extent of reaction as given in the table below:

Component	ν_i	n_{i0}, mol	y_i
CO	–1	1	$(1 - \varepsilon)/2$
H_2O	–1	1	$(1 - \varepsilon)/2$
CO_2	+1	0	$\varepsilon/2$
H_2	+1	0	$\varepsilon/2$
n_0		2	

$$K_y = 1 = \frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = \frac{(\varepsilon/2)\,(\varepsilon/2)}{[(1-\varepsilon)/2]\,[(1-\varepsilon)/2]} = \frac{\varepsilon^2}{(1-\varepsilon)^2}$$

Solving the above, e = 0.5.

Conversion of steam *z* is obtained from Eq. (9.5)

$$z = \frac{|\nu_i|\,\varepsilon}{n_{i0}} = 0.5$$

This means that 50% of steam is converted in the reaction.

(b)

Component	ν_i	n_{i0}, mol	y_i
CO	–1	1	$(1 - \varepsilon)/4$
H_2O	–1	1	$(1 - \varepsilon)/4$
CO_2	+1	0	$\varepsilon/4$
H_2	+1	0	$\varepsilon/4$
N_2		2	
n_0		4	

$$K_y = 1 = \frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = \frac{(\varepsilon/4)\,(\varepsilon/4)}{[(1-\varepsilon)/4]\,[(1-\varepsilon)/4]} = \frac{\varepsilon^2}{(1-\varepsilon)^2}$$

e = 0.5. The conversion of water vapour is 50%.

The conversion remains the same as that resulted when the reactant stream contained only the stoichiometric quantities of CO and H_2O vapour. This is because n = 0 or the reaction produces no change in the number of moles.

***EXAMPLE* 9.16** Ammonia synthesis reaction is represented by

$N_2 + 3H_2$ □ $2NH_3$

The reactant stream consists of 1 mol N_2, 3 mol H_2 and 2 mol argon. The temperature and pressure of the reaction are 675 K and 20 bar. The equilibrium constant for the reaction is 2 □ 10^{-4}. Determine how the conversion of nitrogen is affected by the presence of argon.

Solution The total number of moles of the initial mixture, $n_0 = 1 + 3 + 2 = 6$.

$$\nu = \Sigma\, \nu_i = -1 - 3 + 2 = -2$$

$$y_i = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \varepsilon \nu} = \frac{n_{i0} + \nu_i \varepsilon}{6 - 2\varepsilon}$$

Component	ν_i	n_{i0}, mol	y_i
N_2	–1	1	$(1 - \varepsilon)/(6 - 2\varepsilon)$
H_2	–3	3	$3(1 - \varepsilon)/(6 - 2\varepsilon)$
NH_3	+2	0	$2\varepsilon/(6 - 2\varepsilon)$
A		2	
n_0		6	

$$K_y = \frac{K}{K_\phi} P^{-\nu} = KP^2$$

$$\frac{[2\varepsilon/(6-2\varepsilon)]^2}{[(1-\varepsilon)/(6-2\varepsilon)]\,[3(1-\varepsilon)/(6-2\varepsilon)]^3} = 2\times 10^{-4}\times 20^2$$

$$\frac{[\varepsilon/(3-\varepsilon)]^2}{[(1-\varepsilon)/(3-\varepsilon)]\,[(1-\varepsilon)/(3-\varepsilon)]^3} = 2\times 10^{-4}\times 20^2\times\frac{1}{2}\times\left(\frac{3}{2}\right)^3 = 0.1350$$

$$\frac{\varepsilon(3-\varepsilon)}{(1-\varepsilon)^2} = 0.3674$$

Solving we get, e = 0.1022. Thus, it is seen that the conversion of nitrogen decreases to 10.22% in the presence of argon, from a value of 14.48% (Example 9.14) achieved in the absence of argon.

***EXAMPLE*9.17** The reaction $N_2 + O_2 \Leftrightarrow 2NO$ takes place in the gas phase at 2975 K and 2025 kPa. The reaction mixture initially comprises 15 mol percent oxygen, 77 mol percent nitrogen and the rest inerts. The standard Gibbs free energy change for the reaction is 113.83 kJ/mol at this temperature. Assuming ideal gas behaviour, calculate the partial pressures of all species at equilibrium. How is the conversion of oxygen affected when the initial mixture were free of inerts?

Solution Basis: 15 mol oxygen, 77 mol nitrogen and 8 mol inert in the reaction mixture. Let e be the extent of reaction. The mole fractions of the components under equilibrium are:

Oxygen: (15 – e)/100, Nitrogen: (77 – e)/100, NO: 2e/100

$$K_y = \frac{(2\varepsilon)^2}{(15-\varepsilon)\,(77-\varepsilon)}$$

$K = K_y P^\nu$. Here, $\nu = 0$. Thus, $K = K_y$. Also,

$$K = \exp\left[-\frac{\Delta G^0}{RT}\right] = \exp\left(-\frac{113.83 \times 1000}{8.314 \times 2975}\right) = 0.01$$

so that now we have

$$K_y = 0.01 = \frac{(2\varepsilon)^2}{(15 - \varepsilon)(77 - \varepsilon)}$$

or $\varepsilon = 1.59$

Mole fractions are:

$$\text{Oxygen:} \quad \frac{15 - 1.59}{100} = 0.1341$$

$$\text{Nitrogen:} \quad \frac{77 - 1.59}{100} = 0.7541$$

$$\text{NO:} \quad \frac{2 \times 1.59}{100} = 0.0318$$

$$\text{Inerts:} \quad \frac{8}{100} = 0.08$$

Partial pressures are obtained by multiplying the mole fractions by the total pressure. The values are given below:

O_2: 271.6 kPa, N_2: 1527.1 kPa, NO: 64.4 kPa, Inerts: 162 kPa

If the initial mixture were free of inerts, the mole fractions of the components under equilibrium will be Oxygen: (15 – e)/92, Nitrogen: (77 – e)/92, NO: 2e/92 and the equilibrium constant will be given by the same expression as before:

$$K_y = \frac{(2\varepsilon)^2}{(15 - \varepsilon)(77 - \varepsilon)}$$

which means that $\varepsilon = 1.59$ or the conversion of oxygen is $z = \frac{|\nu_i|\varepsilon}{n_{i0}} = \frac{1.59}{15} \times 100 = 10.6\%$,

which is the same as the conversion obtained in the presence of inerts. Inerts will not influence the conversion in those reactions in which $\nu = 0$.

9.7.2 Presence of Excess of Reactants

When the reactants are not present in stoichiometric proportions, increasing the number of moles of the excess reactant will result in increase in the number of moles of the products and improved conversion of the limiting reactant at equilibrium. This is evident from the left-hand side of Eq. (9.67), the value of which increases when the number of moles of the excess reactant is increased. Therefore, it is desirable to supply all the reactants except the limiting reactant in excess of the stoichiometric requirement, in order to increase the conversion with respect to the limiting reactant.

***EXAMPLE* 9.18** One mole steam undergoes the water-gas shift reaction at a temperature of 1100 K and a pressure of 1 bar.

$$CO\ (g) + H_2O\ (g) \square\ CO_2\ (g) + H_2\ (g)$$

The equilibrium constant for the reaction is $K = 1$. Assuming ideal gas behaviour, calculate the fractional dissociation of steam in the following cases and discuss the effect of the presence of excess reactant on the extent of reaction.

(a) CO supplied is 100% in excess of the stoichiometric requirement.
(b) CO supplied is only 50% of the theoretical requirement.

Solution Basis: 1 mol water vapour present in the reactant stream.

(a)

Component	ν_i	n_{i0}, mol	y_i
CO	–1	2	$(2-\varepsilon)/3$
H_2O	–1	1	$(1-\varepsilon)/3$
CO_2	+1	0	$\varepsilon/3$
H_2	+1	0	$\varepsilon/3$
n_0		3	

Therefore,

$$\frac{\varepsilon^2}{(1-\varepsilon)\,(2-\varepsilon)} = 1$$

Therefore, $\varepsilon = 0.667$ and $z = 0.667/1 = 0.667$. That is, conversion of steam is 66.7%.

(b)

Component	v_i	n_{i0}, mol	y_i
CO	–1	0.5	$(0.5 - \varepsilon)/1.5$
H_2O	–1	1	$(1 - \varepsilon)/1.5$
CO_2	+1	0	$\varepsilon/1.5$
H_2	+1	0	$\varepsilon/1.5$
n_0		1.5	

Therefore,

$$\frac{\varepsilon^2}{(0.5 - \varepsilon)(1 - \varepsilon)} = 1$$

Therefore, $\varepsilon = 0.333$; $z = 0.333$. So only 33.3% of steam get converted.

We see that the equilibrium conversion of water vapour was 50% when the reactants were in stoichiometric proportions, it increases to 66.7% when CO was present 100% in excess and falls to 33.3% when CO becomes the limiting reactant.

EXAMPLE9.19 Ethanol is produced by the vapour phase hydration of ethylene according to the reaction:

$$C_2H_4(g)+H_2O(g) \Leftrightarrow C_2H_5OH(g)$$

The reactor operates at 400 K and 2 bar and the feed is a gas mixture of ethylene and steam in the ratio 1:3. The equilibrium constant is 0.25. Estimate the composition (mol %) of the equilibrium mixture. Assume ideal gas behaviour. How is the conversion of ethylene affected when the initial reactant stream contains stoichiometric quantities of the reactants?

Solution Basis: 1 mole of ethylene and 3 moles of N_2 in the reactant stream.

$K = K_y P^v$. Here, n = –1. Therefore, $0.25 = K_y 2^{-1}$.

Hence, $K_y = 2K = 0.5$

Let e be the extent of reaction. Then the mole fraction in the equilibrium mixture are:

Ethylene: (1 – e)/(4 – e), Steam: (3 – e)/(4 – e), Ethanol: e/(4 – e)

Using these values, we get

$$K_y = 0.5 = \frac{\varepsilon(4 - \varepsilon)}{(1 - \varepsilon)(3 - \varepsilon)}$$

This gives $\varepsilon = 0.268$. The mol fractions in the equilibrium mixture are:

$$\text{Ethylene: } \frac{1-\varepsilon}{4-\varepsilon} = \frac{0.732}{3.732} = 0.196$$

$$\text{Steam: } \frac{3-\varepsilon}{4-\varepsilon} = \frac{2.732}{3.732} = 0.732$$

$$\text{Ethanol: } \frac{\varepsilon}{4-\varepsilon} = \frac{0.268}{3.732} = 0.072$$

Equilibrium mixture contains 19.6% ethylene, 73.2% steam and 7.2% ethanol.

Let the initial mixture contain 1 mol ethylene and 1 mol steam and let e be the extent of reaction. Then the mole fraction in the equilibrium mixture are:

Ethylene: $(1 – e)/(2 – e)$, Steam: $(1 – e)/(2 – e)$, Ethanol: $e/(2 – e)$

Using these values, we get

$$K_y = 0.5 = \frac{\varepsilon(2-\varepsilon)}{(1-\varepsilon)^2}$$

Solving this, we get $e = 0.183$. That is, conversion of ethylene is 18.3%. The conversion was 26.8% in the first case when excess of water vapour was present in the reactant stream.

9.7.3 Presence of Products

If the initial reaction mixture contained any of the products of the reaction, then the number of moles of that product formed by the reaction so as to establish equilibrium will decrease as indicated by Eq. (9.67). Therefore, the addition of the products to the original reactant stream decreases the equilibrium conversion.

***EXAMPLE* 9.20** A gas mixture which contained 1 mol CO, 1 mol water vapour and 1 mol CO_2 is undergoing the following reaction at a temperature of 1100 K and a pressure of 1 bar.

$CO (g) + H_2O (g)$ □ $CO_2 (g) + H_2 (g)$

The equilibrium constant for the reaction is $K = 1$. Assume that the gas mixture behaves as ideal gas. Calculate the fractional dissociation of steam and discuss the effect of the presence of the products on the equilibrium conversion.

Solution The mole fractions of the different species in the equilibrium mixture is expressed in terms of the extent of reaction as below:

Component	ν_i	$n_{i\,0}$, mol	y_i
CO	–1	1	$(1 - \varepsilon)/3$
H_2O	–1	1	$(1 - \varepsilon)/3$
CO_2	+1	1	$(1 + \varepsilon)/3$
H_2	+1	0	$\varepsilon/3$
n_0		3	

$$K_y = 1 = \frac{y_{CO_2}\, y_{H_2}}{y_{CO}\, y_{H_2O}} = \frac{[(1+\varepsilon)/3]\,\varepsilon/3}{[(1-\varepsilon)/3]\,[(1-\varepsilon)/3]} = \frac{\varepsilon(1+\varepsilon)}{(1-\varepsilon)^2}$$

Solving the above equation, we get e = 0.333, which means that the conversion of water vapour gets reduced to 33.3% due to the presence of CO_2, the product of the reaction in the reactant stream.

EXAMPLE **9.21** A gas mixture containing 25% CO, 55% H_2 and 20% inert gas is to be used for methanol synthesis. The gases issue from the catalyst chamber in chemical equilibrium with respect to the reaction

$CO\ (g) + 2H_2\ (g)$ □ $CH_3OH\ (g)$

at a pressure of 300 bar and temperature of 625 K. Assume that the equilibrium mixture forms an ideal solution and K_f and Kf are 4.9 □ 10^{-5} and 0.35 respectively. What is the per cent conversion of CO?

Solution Basis: 100 moles of initial gas mixture.

Let e be the extent of reaction at equilibrium. $n_0 = 100$.

n = – 1 – 2 + 1 = – 2

The mole fractions in the equilibrium mixture are calculated using Eq. (9.4)

$$y_i = \frac{n_{i0} + \nu_i \varepsilon}{n_0 + \varepsilon \nu} = \frac{n_{i0} + \nu_i \varepsilon}{100 - 2\varepsilon}$$

Component	ν_i	n_{i0}, mol	y_i
CO	–1	25	$(25 - \varepsilon)/(100 - 2\varepsilon)$
H_2	–2	55	$(55 - 2\varepsilon)/(100 - 2\varepsilon)$
Inert gas	–	20	–
CH_3OH	+1	0	$\varepsilon/(100 - 2\varepsilon)$
n_0		100	

For gases, $K = K_f$. Therefore,

$$K_y = \frac{K_f}{K_\phi} P^{-\nu}$$

$$\frac{\varepsilon/(100 - 2\varepsilon)}{[(25 - \varepsilon)/(100 - 2\varepsilon)]\,[(55 - 2\varepsilon)/(100 - 2\varepsilon)]^2} = \frac{4.9 \times 10^{-5}}{0.35} \times 300^2$$

$$\frac{\varepsilon(100 - 2\varepsilon)^2}{(25 - \varepsilon)\,(55 - 2\varepsilon)^2} = 12.6$$

Solving this we get $\varepsilon = 15.25$; fractional conversion of CO,

$$z = \frac{|\nu_i|\,\varepsilon}{n_{i0}} = 15.25/25 = 0.61$$

Therefore, 61% of CO gets converted.

***EXAMPLE* 9.22** A gas mixture consisting of 60% H_2, 20% N_2 and the rest inert gas is passed over a suitable catalyst for the production of ammonia.

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightarrow NH_3$$

The equilibrium constant $K_p = 1.25$ □ 10^{-2}. The pressure is maintained at 50 bar. Assume ideal gas behaviour for the gas mixture. Determine the composition of the gases leaving the reactor.

Solution Basis: 100 moles of the reactant gases.

$$\nu = -\frac{1}{2} - \frac{3}{2} + 1 = -1$$

Component	ν_i	n_{i0}, mol	y_i
N_2	–1/2	20	$[20 - (\varepsilon/2)]/(100 - \varepsilon)$
H_2	–3/2	60	$[60 - (3\varepsilon/2)]/(100 - \varepsilon)$
NH_3	+1	0	$\varepsilon/(100 - \varepsilon)$
Inert gas	–	20	–
n_0		100	

Since,

$$K_y = K_P P^{-\nu}$$

Then,

$$\frac{\varepsilon/(100 - \varepsilon)}{[\{20 - (\varepsilon/2)\}/(100 - \varepsilon)]^{1/2}\,[\{60 - (3\varepsilon/2)\}/(100 - \varepsilon)]^{3/2}} = (1.25 \times 10^{-2})\,50 = 0.625$$

$$\frac{\varepsilon(100-\varepsilon)}{[20-(\varepsilon/2)]^{1/2}\,[60-(3\varepsilon/2)]^{3/2}} = 0.625$$

Solving this, we get e = 8.71. Mole fraction of nitrogen is obtained as

$[20 - (e/2)]/(100 - e) = 0.1714$

and mole fraction of hydrogen is

$[60 - (3e/2)]/(100 - e) = 0.5141$

Mole fraction of ammonia:

$e/(100 - e) = 0.0954$

Mole fraction of inert gas:

$1 - 0.1714 - 0.5141 - 0.0954 = 0.2191$

Analysis of exit gases from the reactor:

N_2 = 17.14%, H_2 = 51.41%, NH_3 = 9.54% and inert gas = 21.91%

9.8 LIQUID-PHASE REACTIONS

The equilibrium constant as defined by Eq. (9.19) is applicable for all chemical reactions.

$K = \Pi a_i^{\nu_i}$

For liquid-phase reactions, the evaluation of equilibrium constant using this equation requires a relationship between activity and composition. Since, activity is the ratio of the fugacity to the fugacity in the standard state, such a relationship can be established once the standard state is specified. The standard state for liquid-phase reactions may be the pure liquid at 1 bar and the reaction temperature. The fugacity in this state is not much different from the fugacity of pure liquid at the pressure and temperature of the reaction f_i. This is because, pressure has very negligible effect on the properties of liquids. With this choice, the equilibrium constant becomes

$$K = \Pi\left(\frac{\bar{f}_i}{f_i^0}\right)^{\nu_i} = \Pi\left(\frac{\bar{f}_i}{f_i}\right)^{\nu_i} \tag{9.68}$$

The fugacity of a component in the solution is related to the fugacity in the pure state by $\bar{f}_i = g_i x_i f_i$, where $□_i$ is the activity coefficient in the solution. Using this in Eq. (9.68), we get

$$K = \Pi\gamma_i^{\nu_i} x_i^{\nu_i} = K_\gamma K_x \tag{9.69}$$

$K_□$ is an equilibrium constant in terms of activity coefficients. Accurate values of activity coefficients are rarely available and in practical calculations we set $K_□ = 1$. This is equivalent to assuming that the solution is ideal and $a_i = x_i$. The components present in large proportions obey Lewis–Randall rule and for them the activity and the mole fraction in the solution are the same. Even if Lewis–Randall rule is not applicable, the assumption that $K_□ = 1$ is not a very serious limitation as the function denoted by $K_□$ may become nearly unity even if the individual activity coefficients are not. Thus

$$K = K_x = \Pi x_i^{\nu_i} \tag{9.70}$$

For components present in low concentration, the standard state of the solute is usually the fictitious or hypothetical state which would exist if the solute obeyed Henry's law over a concentration range extending up to a molality of unity. This hypothetical state is illustrated in Fig. 9.4.

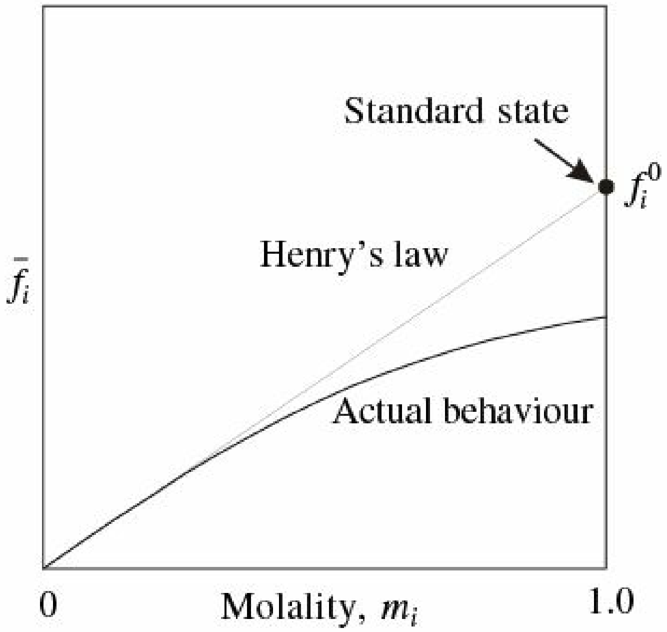


Fig. 9.4 Standard state based on Henry's law.

The fugacity and molality (mol/kg solvent) are related as

$$\bar{f}_i = K_i m_i \tag{9.71}$$

where K_i is the Henry's law constant and m_i is the molality. Using the hypothetical standard state, it can be shown that the standard state fugacity is equal to the Henry's law constant and the activity and the molality are equal. That is

$$a_i = m_i \tag{9.72}$$

With this choice for the standard state, a very simple relationship exists between the activity and the concentration for cases where Henry's law is applicable.

9.9 HETEROGENEOUS REACTION EQUILIBRIA

In the study of heterogeneous reaction equilibria presented in this section, we are concerned with a gas phase that is in equilibrium with a liquid or a solid phase. When the heterogeneous system is in equilibrium we would have to consider the equilibrium with respect to chemical reactions in the gas phase as well as the phase equilibria between the components in the gas phase and the liquid or the solid phase as the case may be.

9.9.1 Reactions in Solutions

Consider the reaction between a gas A and liquid B to produce a solution C.

A (g) + B (l) ☐ C (aq)

The equilibrium in this reaction can be studied in different ways:

1. The reaction may be assumed to take place entirely within the gas phase and the equilibrium constant for the reaction is evaluated using the standard state for gases, i.e. the ideal gas standard state at a pressure of 1 bar and the reaction temperature. The resulting equations are coupled with equations for material transfer between phases to maintain equilibrium.
2. The reaction is assumed to occur in the liquid phase with simultaneous transfer of material between phases to maintain equilibrium. The calculations of reaction equilibria are based on the liquid standard state.
3. The third method involves the use of mixed standard states. Thus, the standard state for A is the pure ideal gas at 1 bar, that for B is pure liquid at 1 bar, and for C it is the solute in an ideal 1-molal aqueous solution. The equilibrium constant in this case may be evaluated as

$$K = \frac{a_{\mathrm{C}}}{a_{\mathrm{A}}\,a_{\mathrm{B}}} = \frac{m_{\mathrm{C}}}{(\bar{f}_{\mathrm{A}})\,(\gamma_{\mathrm{B}}x_{\mathrm{B}})} \tag{9.73}$$

All the above methods give the same results for equilibrium compositions, but the values for equilibrium constant depend on the choice of the standard state.

9.9.2 Equilibria involving Pure Solids and Liquids

When a pure liquid or a pure solid is involved in a heterogeneous reaction with gases, its activity may be taken as unity provided the pressure of the system is not much different from the standard state. Activity as we know, is defined as the ratio of the fugacity to the fugacity in the standard state. The fugacity in the standard state is almost equal to that in the equilibrium state, as these two states differ only in their pressures and not in their temperatures. Pressure, unless extremely high, has only a negligible effect on the properties of liquids and solids. Where the standard state for solids and liquids is taken at 1 bar or at low equilibrium vapour pressures, the activities of pure solids and pure liquids may be taken as unity at moderate pressures. Therefore, the composition of the gaseous phase at equilibrium is not affected by the presence of the solid or liquid.

9.9.3 Pressures of Decomposition

Many solid compounds decompose to give another solid and a gas, as in the calcination of calcium carbonate to CO_2 and lime.

$CaCO_3$ (s) ☐ CaO (s) + CO_2 (g)

The equilibrium constant for this reaction is

$$K = \frac{a_{\mathrm{CO_2}}\,a_{\mathrm{CaO}}}{a_{\mathrm{CaCO_3}}} \tag{9.74}$$

The activities of the solid components present at equilibrium are close to unity provided the pressure is moderate and both solids are present at equilibrium. Since the standard state for gases is the ideal-gas state at 1 bar, the standard state fugacity is equal to unity and therefore, the activity of CO_2 in the equilibrium mixture is equal to its fugacity, $\bar{f}_{\mathrm{CO_2}}$. But fugacity of a component is equal to its partial pressure at low pressures and, therefore, Eq. (9.74) reduces to

$$K = \bar{p}_{\mathrm{CO_2}} \tag{9.75}$$

This is the equilibrium partial pressure exerted by CO_2 and its value depends only on temperature. If the partial pressure is lowered below this equilibrium value, $CaCO_3$ will decompose and will eventually disappear. On the other hand, if the pressure on the system is kept above the equilibrium partial pressure, CaO will combine with CO_2 resulting in the formation of $CaCO_3$.

For a general solid decomposition reaction represented by

aA (s) □ lL (s) + mM (g)

the above treatment can be generalised as

$$K = a_{\mathrm{M}}^{m} = \bar{p}_{\mathrm{M}}^{m} = \exp\left(\frac{-\Delta G^0}{RT}\right) \tag{9.76}$$

or

$$\ln \bar{p}_{\mathrm{M}} = \frac{-\Delta G^0}{mRT} = -\frac{1}{mRT}(\Delta H^0 - T\Delta S^0) \tag{9.77}$$

In the above equation, m is the stoichiometric coefficient; DH^0 and DS^0 are the standard heat of reaction and standard entropy of reaction respectively.

***EXAMPLE* 9.23** Ethylene gas reacts with water forming aqueous solution of ethanol.

C_2H_4 (g) + H_2O (l) □ C_2H_5OH (aq)

Equilibrium measurements at 530 K and 85 bar showed that the aqueous phase contained 1.5% (mole) ethanol and 95.0% (mole) water. The vapour phase analysed 48% ethylene. The fugacity coefficient for ethylene is estimated to be 0.9. Evaluate the equilibrium constant.

Solution Equation (9.73) may be used for evaluating K.

$$K = \frac{a_{\mathrm{C}}}{a_{\mathrm{A}}\, a_{\mathrm{B}}} = \frac{m_{\mathrm{C_2H_5OH}}}{(\bar{f}_{\mathrm{C_2H_4}})(\gamma_{\mathrm{H_2O}}\, x_{\mathrm{H_2O}})}$$

The standard state for aqueous solution is 1 molal solution; for water, it is pure liquid water at 1 bar; and for gaseous ethylene, it is the pure ethylene at 1 bar.

The molality of aqueous solution = moles ethanol/kg water

= 1.5/(95.0 □ 18 □ 10^{-3}) = 0.8772 mol/kg water

Fugacity of ethylene is denoted by $\bar{f}_{C_2H_4}$, and it is estimated as

$$\bar{f}_{C_2H_4} = \phi_{C_2H_4}\,\bar{p}_{C_2H_4} = \phi_{C_2H_4}\,y_{C_2H_4}\,P = 0.9 \times 0.48 \times 85 = 36.72 \text{ bar}$$

The mole fraction of water is close to 1 so that Raoult's law is applicable. Therefore, the activity coefficient of water may be taken to be unity.

$$K = \frac{0.8772}{36.72 \times 0.95} = 2.5146 \times 10^{-2} \text{ (mol } C_2H_4\text{)/(kg water bar)}$$

***EXAMPLE* 9.24** Calculate the decomposition pressure of limestone at 1000 K.

$CaCO_3$ (s) □ CaO (s) + CO_2 (g)

The standard free energy of this reaction as function of temperature is

D$G^0 = 1.8856$ □ $10^5 - 243.42T + 11.8478T \ln T - 3.1045$ □ $10^{-3}T^2 + 1.7271$ □ $10^{-6}\,T^3$
$- 4.1784$ □ $10^5/T$

Also calculate the decomposition temperature at 1 bar.

Solution From Eq. (9.75), the decomposition pressure is $\bar{p}_{CO_2} = K$, where K can be calculated by

$$K = \exp\left(-\frac{\Delta G^0}{RT}\right)$$

At 1000 K,

$$\Delta G^0 = 1.8856 \times 10^5 - 243420 + 81842 - 3105 + 1727 - 418 = 25186 \text{ J}$$

Therefore,

$$K = \exp\left(-\frac{25186}{8.314 \times 1000}\right) = 0.048 = \bar{p}$$

Decomposition pressure at 1000 K = 0.048 bar.

The decomposition temperature at 1 bar can now be determined. $\bar{p}_{CO_2} = K = 1$, so that

$$\Delta G^0 = 0 = 1.8856 \times 10^5 - 243.42T + 11.8478T \ln T - 3.1045 \times 10^{-3}T^2 + 1.7271 \times 10^{-6}T^3 - 4.1784 \times 10^5/T$$

The above equation is solved for T, the temperature at decomposition, 1180 K.

***EXAMPLE* 9.25** Solid calcium oxalate dissociates at high temperatures into solid calcium carbonate and carbon monoxide:

$$CaC_2O_4(s) \Leftrightarrow CaCO_3(s) + CO(g)$$

The equilibrium pressure of CO between 670 and 700 K is given by

$$\ln P = 14.4 - \frac{9600}{T}$$

where P is in bar and T is in K. Assuming ideal behaviour, calculate ΔG^0, ΔH^0 and ΔS^0 at 675 K.

Solution By Eq. (9.75), $K = \bar{p}_{CO}$
Therefore,

$$\ln K = 14.4 - \frac{9600}{675} = 0.1777 \quad \text{or} \quad K = 1.1946$$

By Eq. (9.31),

$$\Delta G^0 = -RT \ln K = -8.314 \times 675 \times \ln 1.1946 = -997.68 \text{ kJ}$$

By Eq. (9.36),

$$\frac{\Delta H^0}{RT^2} = \frac{d \ln K}{dT} = \frac{d \ln P}{dT} = \frac{9600}{T^2}$$

Therefore, $\Delta H^0 = 9600 R = 79814.4$ kJ

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

Thus,

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = 119.72 \text{ kJ/K}$$

***EXAMPLE* 9.26** Iron oxide is reduced to iron by passing over it a mixture of 20% CO and 80% N_2 at 1200 K and 1 bar.

$$FeO (s) + CO (g) \square Fe (s) + CO_2 (g)$$

The equilibrium constant for this reaction is 0.403. Assuming that equilibrium is attained, calculate the weight of metallic iron produced per 100 m^3 of gas admitted at 1200 K and 1 atm. Gas mixture may be assumed to behave as ideal gas.

Solution Basis: 100 mol of gas entering.
The activities of solid components can be taken to be unity.

$$K = \frac{a_{Fe}\, a_{CO_2}}{a_{FeO}\, a_{CO}} = \frac{a_{CO_2}}{a_{CO}}$$

If the gases are assumed to be ideal, then

$$a_i = \bar{p}_i = y_i P$$

and the given equation for equilibrium constant gives

$$y_{CO_2}/y_{CO} = 0.403$$

Let ε be the extent of reaction. Since the initial mixture consists of 20 mol CO and 80 mol N_2, the mole fractions of CO and CO_2 at equilibrium are $(20 - \varepsilon)/100$ and $\varepsilon/100$, respectively. Therefore,

$$\frac{\varepsilon}{20 - \varepsilon} = 0.403$$

Solving this, $\varepsilon = 5.745$. The equilibrium mixture contains 5.745 mol CO_2. Moles of iron produced = 5.745 per 100 mol of initial gas mixture. Also, 100 mol gas mixture at 1200 K and 1 bar is equivalent to

$$100 \times 22.4 \times 10^{-3} \times (1200/273) = 9.846 \text{ m}^3$$

Iron produced per 100 m^3 of gas = $(5.745 \times 55.8 \times 100)/9.846 = 3256$ g = 3.256 kg

9.10 SIMULTANEOUS REACTIONS

With a given set of reactants many reactions may be possible. When we consider the equilibrium yield of methanol in the reaction

$$CO + 2H_2 \; \square \; CH_3OH \qquad (9.78)$$

by the methods already discussed, we are in fact ignoring the presence of intermediate product, formaldehyde in the reaction mixture. The above reaction proceeds in two steps in series as:

$$CO + H_2 \; \square \; HCHO \qquad (9.79)$$

$$HCHO + H_2 \; \square \; CH_3OH \qquad (9.80)$$

For the thermodynamic analysis of a reaction that proceeds in two or more steps, the presence of intermediate products can sometimes be ignored on the assumption that they are very unstable and their concentrations at equilibrium are negligible in comparison with that of the main product. The above assumption is implicit in treating the equilibrium mixture in the methanol synthesis as consisting of only CO, H_2 and CH_3OH. In this case, this assumption is a valid one as formaldehyde is very unstable, but in many other situations, the presence of intermediate products in the reaction mixture at equilibrium also should be taken into account as explained below:

The free energy change for a reaction is equal to the sum of the free energy changes in the individual step reactions. Thus,

$$\Delta G^0 = \Delta G_1^0 + \Delta G_2^0$$

where ΔG_1^0 and ΔG_2^0 are the free energy changes in the two step reactions that occur and DG^0 is the standard free energy change in the overall reaction. Since $DG^0 = -RT \ln K$, the above equation gives

$$K = K_1 K_2$$

K_1 and K_2 are the equilibrium constants for the individual steps and K is the equilibrium constant for the combined reaction. For a given value of K, an infinite number of combinations of K_1 and K_2 are possible such that $K = K_1 K_2$. For example, let us take $K = 10^{-4}$ and consider the cases where (a) $10^{-4} = 10^{-10}$ □ 10^{6}, (b) $10^{-4} = 10^{-2}$ □ 10^{-2}, and (c) $10^{-4} = 10^{6}$ □ 10^{-10}. For case (a), the concentration of intermediate products at equilibrium would be negligible and correct result would be obtained by considering only the overall reaction. For case (b), there would be considerable amounts of intermediates at equilibrium and their presence cannot be ignored. For case (c), the equilibrium mixture would be mostly intermediates. The use of an overall equilibrium constant for the calculation of equilibrium compositions is limited to cases where the intermediate products are not present in significant quantities.

In addition to the formation of intermediate products, which subsequently reacts to form the final desired products, many side reactions may also occur within the system. For example, starting with the pairs CO and H_2 some of the possible reactions are:

$CO + H_2$ □ $HCHO$

$CO + 2H_2$ □ CH_3OH

$CO + 3H_2$ □ $CH_4 + H_2O$

$2CO + 5H_2$ □ $C_2H_6 + 2H_2O$

$3CO + 6H_2$ □ $C_3H_7OH + 2H_2O$

In dealing with methanol synthesis, it was assumed that the side reactions proceeded at a negligible rate in comparison with the steps involved in the synthesis reaction. Theoretically, when the equilibrium yield of a particular component is to be determined, we should consider simultaneous equilibria in all possible reactions between the substances involved. However, for practical calculations, it is possible to reduce the number of reactions that are to be considered.

In the general case when all intermediates and final products must be considered, it is necessary that the equilibrium equations of all reactions must be satisfied by the compositions of the system at equilibrium. Determination of the equilibrium compositions involves simultaneous solution of r equilibrium equations where r is the number of independent reactions that can be written. After determining the number of independent reactions as explained later, the equilibrium constant is evaluated for each reaction by

$$K_j = \Pi a_i^{\nu_{i,j}} \tag{9.81}$$

The mole fractions can be related to the extent of reaction for each reaction and the resulting equations are solved simultaneously.

$$K_j = P^{\nu_j} \Pi y_i^{\nu_{i,j}} \tag{9.82}$$

Here the suffix j is used to represent the jth reaction under consideration. The above equation is written for all r independent reactions. Assuming the equilibrium mixture to behave as ideal gases, these lead to r equations relating the composition to the pressure and the equilibrium constant.

$$K_{y,j} = K_j P^{-\nu_j} \tag{9.83}$$

The method can be illustrated by considering the following simultaneous reactions:

$$a\mathrm{A} + b_1\mathrm{B} \rightarrow l\mathrm{L} + m_1\mathrm{M} \tag{9.84}$$

$$l\mathrm{L} + b_2\mathrm{B} \rightarrow m_2\mathrm{M} + n\mathrm{N} \tag{9.85}$$

Let the equilibrium constants be K_1 and K_2 for the reactions indicated by Eqs. (9.84) and (9.85) respectively and let the corresponding extent of reaction be e_1 for reaction (9.84) and e_2 for reaction (9.85). The initial reactant mixture is assumed to consist of 1 mol A and x mol B. The mole fractions in simultaneous reactions can be calculated using Eq. (9.9).

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j \nu_{i,j}\varepsilon_j}{n_0 + \sum_j \nu_j \varepsilon_j}$$

The mole fractions of various components are

$$y_\mathrm{A} = (1 - ae_1)/[1 + x + (l + m_1 - a - b_1)e_1 + (m_2 + n - l - b_2)e_2]$$

$$y_\mathrm{B} = (x - b_1e_1 - b_2e_2)/[1 + x + (l + m_1 - a - b_1)e_1 + (m_2 + n - l - b_2)e_2]$$

$$y_\mathrm{L} = l(e_1 - e_2)/[1 + x + (l + m_1 - a - b_1)e_1 + (m_2 + n - l - b_2)e_2]$$

$$y_\mathrm{M} = (m_1e_1 + m_2e_2)/[1 + x + (l + m_1 - a - b_1)e_1 + (m_2 + n - l - b_2)e_2]$$

$$y_\mathrm{N} = ne_2/[1 + x + (l + m_1 - a - b_1)e_1 + (m_2 + n - l - b_2)e_2]$$

These are substituted into the following equilibrium relations.

$$\frac{y_\mathrm{L}^l\, y_\mathrm{M}^{m_1}}{y_\mathrm{A}^a\, y_\mathrm{B}^{b_1}} = K_1 P^{-(l + m_1 - a - b_1)} \tag{9.86}$$

$$\frac{y_\mathrm{M}^{m_2}\, y_\mathrm{N}^{n}}{y_\mathrm{L}^l\, y_\mathrm{B}^{b_2}} = K_2 P^{-(m_2 + n - l - b_2)} \tag{9.87}$$

These two equations are solved simultaneously to obtain the variables e_1 and e_2. Equation (9.9) can now be utilised to evaluate the equilibrium compositions.

***EXAMPLE* 9.27** Five moles of steam reacts with one mole methane according to the following reaction at 850 K and 1 bar.

$CH_4 + H_2O$ □ $CO + 3H_2$; $K_1 = 0.574$ (9.88)

$CO + H_2O$ □ $CO_2 + H_2$; $K_2 = 2.21$ (9.89)

Calculate the composition at equilibrium assuming ideal gas behaviour.

Solution Number of moles of a component at equilibrium = $n_i = n_{i0} + \sum_j \nu_{i,j}\,\varepsilon_j$

Let e_1 and e_2 be the extent of reactions for reaction (9.88) and (9.89) respectively. Thus at equilibrium the number of moles are,

CH_4: $1 - e_1$, H_2O: $5 - e_1 - e_2$, CO: $e_1 - e_2$, H_2: $3e_1 + e_2$, CO_2: e_2

Total number of moles at equilibrium = $6 + 2e_1$. The mole fractions of various components in the equilibrium mixture are:

CH_4: $(1 - \varepsilon_1)/(6 + 2\varepsilon_1)$, H_2O: $(5 - \varepsilon_1 - \varepsilon_2)/(6 + 2\varepsilon_1)$

CO: $(\varepsilon_1 - \varepsilon_2)/(6 + 2\varepsilon_1)$, H_2: $(3\varepsilon_1 + \varepsilon_2)/(6 + 2\varepsilon_1)$, CO_2: $\varepsilon_2/(6 + 2\varepsilon_1)$

$$K_{y,1} = \frac{y_{CO}\,y_{H_2}^3}{y_{CH_4}\,y_{H_2O}} = \frac{(\varepsilon_1 - \varepsilon_2)(3\varepsilon_1 + \varepsilon_2)^3}{(1 - \varepsilon_1)(5 - \varepsilon_1 - \varepsilon_2)(6 + 2\varepsilon_1)^2}$$

$$K_{y,2} = \frac{y_{CO_2}\,y_{H_2}}{y_{CO}\,y_{H_2O}} = \frac{\varepsilon_2(3\varepsilon_1 + \varepsilon_2)}{(\varepsilon_1 - \varepsilon_2)(5 - \varepsilon_1 - \varepsilon_2)}$$

$$\nu_1 = 1 + 3 - 1 - 1 = 2; \qquad \nu_2 = 1 + 1 - 1 - 1 = 0$$

Substitute these into the following relationships.

$$K_{y,1} = K_1 P^{-\nu_1}, \qquad K_{y,2} = K_2 P^{-\nu_2}$$

Note that $K_1 = 0.574$, $K_2 = 2.21$ and $P = 1$ bar. The resulting equations are solved for e_1 and e_2. Assume a value for e_1 and calculate e_2 by each equation. These two e_2 values are plotted against e_1. This is repeated for various assumed e_1 values. The intersection of the two curves gives the solution. $e_1 = 0.9124$; and $e_2 = 0.623$. The mole fractions are evaluated by supplying the values of e_1 and e_2. The results are:

CH_4: 0.0112, H_2O: 0.4415, CO: 0.0357, H_2: 0.4307 and CO_2: 0.0804

9.11 PHASE RULE FOR REACTING SYSTEMS

We have used the criteria of phase equilibrium to develop the phase rule for non-reacting systems in

Chapter 8.

$$F = C - p + 2$$

The criterion of phase equilibrium is valid even when chemical reactions occur within the system. However, the phase rule needs modification for it to be applicable for reacting systems. This is because for each independent reaction occurring, an additional constraint is imposed on the system through Eq. (9.15) or (9.31). Thus, the number of degrees of freedom will be reduced by one for each independent chemical reaction. If r independent reactions occur in the system, then the phase rule becomes

$$F = C - p - r + 2 \qquad (9.90)$$

For example, consider a system containing five components distributed between two phases. If the number of independent chemical reactions occurring is one, then the number of degrees of freedom will be 5 – 2 – 1 + 2 = 4. Assuming that the reaction occurring is a gas-phase isomerisation reaction involving two of the components (say, A and B), we can write the equilibrium relationship as

$$K = \frac{y_A}{y_B}$$

This in fact is a relationship between T, y_A and y_B. Only two of these three variables are therefore independent. As the degree of freedom is 4 it means that in addition to these three variables, two more variables are to be specified to define the intensive state of the system uniquely.

O.A. Hougen, et al., define the number of independent reactions that must be considered as the *least number that includes every reactant and product present to an appreciable extent in all phases of the equilibrium system, and accounts for the formation of each product from the original reactants.* It can be determined as follows:

1. For each chemical compound present in the system, equation for its formation reaction from its elements is written.
2. The elements that are not present in the system are eliminated by properly combining the equations written in step 1.

The number of equations, r, that results from the above procedure is equal to the number of independent chemical reactions occurring.

***EXAMPLE* 9.28** Determine the number of degrees of freedom in a gaseous system consisting of CO, CO_2, H_2, H_2O and CH_4 in chemical equilibrium.

Solution The number of independent chemical reactions occurring in the system is first determined. The formation reactions for each of the compounds are written:

$$C + \frac{1}{2}O_2 \rightarrow CO \qquad (9.91)$$

$$C + O_2 \rightarrow CO_2 \qquad (9.92)$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad (9.93)$$

$$C + 2H_2 \rightarrow CH_4 \qquad (9.94)$$

The elements C and O_2 are not present in the system. C is eliminated first, from Eqs. (9.91), (9.92) and (9.94). Combining Eq. (9.91) with Eq. (9.92) we get

$$CO_2 \rightarrow CO + \frac{1}{2}O_2 \tag{9.95}$$

Combining Eq. (9.91) with Eq. (9.94) gives

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \tag{9.96}$$

Equations (9.95), (9.96) and (9.93) form the new set from which O_2 is to be eliminated. Combining Eq. (9.93) with Eq. (9.95) gives

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{9.97}$$

Equation (9.93) is combined with Eq. (9.96) to give

$$3H_2 + CO \rightarrow CH_4 + H_2O \tag{9.98}$$

The equations that remain after this elimination process are Eqs. (9.97) and (9.98) which represent the independent chemical reactions occurring in the system. Therefore, $r = 2$. Equation (9.90) gives the degrees of freedom as $F = C - \pi - r + 2$. Here $C = 5$; $\pi = 1$ and therefore, $F = 4$.

SUMMARY

Thermodynamics of chemical reactions is mainly concerned with the prediction of the equilibrium conversion attainable in a chemical reaction and the effect of operating conditions on the degree of completion of the reaction. The criterion of chemical equilibrium requires that for a chemical reaction occurring at equilibrium, there should be no change in the Gibbs free energy of the system at constant temperature and pressure. If the system is not in chemical equilibrium, the reaction occurring must be irreversible and the total Gibbs free energy must decrease at constant temperature and pressure (Section 9.2).

The equilibrium constant K for a reaction was defined in terms of the activities of the reactants and the products as

$$K = \Pi a_i^{\nu_i}$$

where a_i is the activity of component i in the reaction mixture and ν_i is the stoichiometric number of i (Section 9.3). The equilibrium constant was related to the standard free energy change by Eq. (9.31). Thus the numerical value of the equilibrium constant depends upon the temperature, the form of the stoichiometric equation and the definition of the standard state for each component. However, it is independent of the pressure at equilibrium (Section 9.4). Equation (9.31) also provided an approximate criterion for feasibility of reactions. If ΔG^0 for a reaction is zero, then $K = 1$, the reaction proceeds to a considerable extent before equilibrium is reached. If ΔG^0 is negative, then $K > 1$, the reaction is quite favourable.

The effect of temperature on the equilibrium constant was quantitatively expressed by van’t Hoff equation [Eq. (9.36)]. For an exothermic reaction, the equilibrium constant decreases as the reaction temperature increases and for an endothermic reaction, the equilibrium constant will increase with increase in temperature (Section 9.5). Three methods for the evaluation of equilibrium constant were discussed; the one which made use of thermal data in the form of standard heat of reaction ΔH^0, and a standard free energy change of reaction ΔG^0 at a given temperature was found to be the most convenient and widely used. The usefulness of the Giauque functions for tabulation of standard free energy of reactions and calculation of the equilibrium constant was also established.

The equilibrium constant is independent of pressure whereas the composition at equilibrium varies with pressure as evident from Eq. (9.62). If there is a decrease in the number of moles during the reaction, the equilibrium yield would increase with increase in the pressure, whereas if the reaction results in an increase in the number of moles, the equilibrium yield would decrease with increase in pressure. It was also shown that the effect of the presence of inert gas in the reactant stream on the equilibrium conversion was just the opposite of the effect of pressure (Section 9.7).

For liquid-phase reactions, the equilibrium constant may be written as $K = K_\gamma K_x$. K_γ is an equilibrium constant in terms of activity coefficients, which may be assumed, equal to unity. For components present in low concentration, the activity and the molality are equal (Section 9.8). Under heterogeneous equilibrium (Section 9.9), a brief discussion on the reaction between a gas and liquid resulting in the formation of a solution and reaction equilibria in which a solid or liquid reacted with a gas, were provided. Also, it was seen that for reactions in which solid compounds decomposed to give another solid and a gas, the equilibrium constant was equal to the partial pressure of the gas. If the partial pressure was lowered below this equilibrium value the solid would decompose and if the pressure on the system was maintained above this value, the formation of solid was favoured. For simultaneous reactions in which all intermediate and final products in the equilibrium mixture were to be considered for determining the composition, equilibrium equations were written for all the independent reactions and these were solved simultaneously (Section 9.10).

REVIEW QUESTIONS

1. What do you mean by the ‘extent of reaction’? How is it related to the mole fraction of the species in the reaction mixture?
2. What is the criterion of chemical reaction equilibria?
3. Define equilibrium constant K of a chemical reaction. How is it related to K_f and K_P?
4. Does the numerical value of the equilibrium constant depend on the form of the stoichiometric equation?
5. How is the equilibrium constant K related to the standard free energy change? Does K vary with pressure?
6. What is the effect of temperature on the equilibrium constant? Using van’t Hoff equation predict the effect of increasing the temperature on endothermic and exothermic reactions.
7. How would you predict the feasibility of a reaction from the value of the standard free energy change?
8. How would the equilibrium yield in a gaseous chemical reaction be affected by increasing the pressure, if there is a decrease in the number of moles during the reaction? How would you

explain the effect of pressure on reactions such as the water–gas shift reaction, where there is no change in the number of moles?

9. How would the equilibrium yield of ammonia be affected if argon is present in the synthesis gas fed to the ammonia converter?

10. Explain how the equilibrium constant for liquid-phase reactions is evaluated.

11. Show that the equilibrium constant in the decomposition of calcium carbonate into CO_2 and lime is equal to the partial pressure of carbon dioxide. Explain how would you estimate the decomposition pressure? What would happen if the CO_2 pressure is reduced below this value?

12. A reaction proceeds in two steps. The equilibrium constants for the individual steps are K_1 and K_2. What would be the equilibrium constant for the overall reaction?

13. What do you mean by the number of independent reactions in a chemically reacting system? How would you determine it?

14. What is phase rule as applicable to a reacting system?

EXERCISES

9.1 Water vapour decomposes according to the following reaction:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$

Derive expressions for the mole fraction of each species in terms of the extent of reaction assuming that the system contained n_0 moles of water vapour initially.

9.2 The following reaction occurs in a mixture consisting of 2 mol methane, 1 mol water, 1 mol carbon monoxide and 4 mol hydrogen initially.

$$CH_4 + H_2O \ \square\ CO + 3H_2$$

Deduce expression relating the mole fractions of various species to the extent of reaction.

9.3 A system consisting of 2 mol methane and 3 mol water is undergoing the following reaction

$$CH_4 + H_2O \ \square\ CO + 3H_2$$

$$CH_4 + 2H_2O \ \square\ CO_2 + 4H_2$$

Derive expressions for mole fractions in terms of the extent of reactions.

9.4 The following gas-phase reactions occur in a mixture initially containing 3 mol ethylene and 2 mol oxygen.

$$C_2H_4 + \frac{1}{2}O_2 \rightarrow (CH_2)_2O$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

Derive expressions for mole fractions in terms of extent of reactions.

9.5 Calculate the equilibrium constant at 298 K of the reaction $N_2 + 3H_2 \ \square\ 2NH_3$, given that the free energy of formation of ammonia at 298 K is –16,500 J/mol.

9.6 Calculate the standard free energy change at 298 K in the gas-phase alkylation of isobutane with ethylene to form neohexane.

C_4H_{10} (g) + C_2H_4 (g) □ C_6H_{14} (g)

The free energies of formation at 298 K are –21,000 J/mol, 68,460 J/mol and –9,950 J/mol for isobutane, ethylene and neohexane respectively.

9.7 Calculate the equilibrium constant at 673 K and 1 bar for the reaction

N_2 (g) + $3H_2$ (g) □ $2NH_3$ (g)

assuming that the heat of reaction remains constant in the temperature range involved. Take the standard heat of formation and standard free energy of formation of ammonia at 298 K to be –46,110 J/mol and –16,450 J/mol respectively.

9.8 Is the following reaction promising at 600 K?

NaOH (s) + CO (g) □ HCOONa (s)

The free energy of formation, the heat of formation and the specific heat of the components are given below:

	$\Delta G^0_{f,298}$, J/mol	$\Delta H^0_{f,298}$, J/mol	C_P, J/mol K
CO (g)	-1.37×10^5	-1.11×10^5	$26.64 + 7.7125 \times 10^{-3}T$
HCOONa (s)	-6.17×10^5	-6.51×10^5	76.86
NaOH (s)	-3.79×10^5	-4.27×10^5	52.50

9.9 Methanol is produced by the following reaction:

CO (g) + $2H_2$ (g) □ CH_3OH (g)

The standard heat of formation of CO (g) and CH_3OH (g) at 298 K are –110,500 J/mol and –200,700 J/mol respectively. The standard free energies of formation are –137,200 J/mol and –162,000 J/mol respectively.

(a) Calculate the standard free energy change and determine whether the reaction is feasible at 298 K.

(b) Determine the equilibrium constant at 400 K assuming that the heat of reaction is constant.

(c) Derive an expression for the standard free energy of reaction as function of temperature if the specific heats of the components are:

$C_P = 3.376R + 0.557$ □ $10^{-3}RT - 0.031$ □ 10^5RT^{-2} for CO

$C_P = 3.249R + 0.422$ □ $10^{-3}RT + 0.083$ □ 10^5RT^{-2} for H_2

$C_P = 2.211R + 12.216$ □ $10^{-3}RT - 3.450$ □ $10^{-6}RT^2$ for CH_3OH

(d) Use the equation obtained in part (c) to calculate the equilibrium constant at 400 K and compare with the result in part (b).

9.10 Calculate the equilibrium constant at 298 K for the reaction

$$C_2H_4\,(g) + H_2O\,(g) \rightarrow C_2H_5OH\,(g)$$

given the following data:

	S^0_{298}, J/mol K	H^0_{298}, J/mol
C_2H_4 (g)	220.85	48,986
H_2O (g)	189.12	– 241,997
C_2H_5OH (g)	278.00	– 238,941

9.11 The standard free energy change for the reaction

C_4H_8 (g) □ C_4H_6 (g) + H_2 (g)

is given by the relation

$$\Delta G^0_T = 1.03665 \times 10^5 - 20.9759\,T \ln T + 12.9372\,T$$

where ΔG^0_T is in J/mol and T is in K.

(a) Over what range of temperature is the reaction promising from a thermodynamic viewpoint?

(b) For reaction of pure butene at 800 K, calculate the equilibrium conversion for operation at 1 bar and 5 bar.

(c) Repeat part (b) if the feed consists of 50% (mol) butene and the rest inerts.

9.12 Calculate the equilibrium constant for the vapour-phase hydration of ethylene to ethanol at 600 K

$C_2H_4 + H_2O$ □ C_2H_5OH

The following data are available:

	$\Delta H^0_{f,\,298} \times 10^{-3}$ J/mol	$\Delta G^0_{f,\,298} \times 10^{-3}$ J/mol	C_P, J/mol K
Ethylene	52.51	68.46	$11.886 + 120.12 \times 10^{-3}T - 36.649 \times 10^{-6}T^2$
Water	– 241.818	– 228.57	$30.475 + 9.652 \times 10^{-3}T + 1.189 \times 10^{-6}T^2$
Ethanol	– 235.1	– 168.49	$29.358 + 166.9 \times 10^{-3}T - 50.09 \times 10^{-6}T^2$

9.13 The equilibrium constant at 420 K for the vapour-phase hydration of ethylene to ethanol according to the reaction

$C_2H_4 + H_2O$ □ C_2H_5OH

is 6.8 □ 10^{-2} and standard heat of reaction at 298 K is –45.95 □ 10^3 J. The specific heat data are as follows:

	C_P, J/mol K
Ethylene	$11.886 + 120.12 \times 10^{-3}T - 36.649 \times 10^{-6}T^2$
Water	$30.475 + 9.652 \times 10^{-3}T + 1.189 \times 10^{-6}T^2$
Ethanol	$29.358 + 166.9 \times 10^{-3}T - 50.09 \times 10^{-6}T^2$

Formulate general relationships for estimating the equilibrium constant and standard free energy change as functions of temperature.

9.14 For the vapour-phase hydration of ethylene to ethanol according to

$C_2H_4 + H_2O$ □ C_2H_5OH

the equilibrium constants were measured at temperature 420 K and 600 K. They are 6.8 □ 10^{-2} and 1.9 □ 10^{-3} respectively. The specific heat (J/mol K) data are:

	C_P, J/mol K
Ethylene	$11.886 + 120.12 \times 10^{-3}T - 36.649 \times 10^{-6}T^2$
Water	$30.475 + 9.652 \times 10^{-3}T + 1.189 \times 10^{-6}T^2$
Ethanol	$29.358 + 166.9 \times 10^{-3}T - 50.09 \times 10^{-6}T^2$

Develop general expressions for the equilibrium constant and standard free energy change as functions of temperature.

9.15 The water–gas shift reaction

CO (g) + H_2O (g) □ CO_2 (g) + H_2 (g)

takes place at 373 K. The equilibrium constant K_P for this reaction at 537 K = 9.8 □ 10^{-4}. The heats of formation at 298 K are: CO = –110,525 J/mol, CO_2 = –393,509 J/mol, H_2O = –241,818 J/mol. Calculate the equilibrium constant at 1000 K.

9.16 Calculate the fraction of pure ethane that would dehydrogenate at 750 K and 5 atm, if the following reaction goes to equilibrium.

$C_2H_6(g) \Leftrightarrow C_2H_4(g) + H_2(g)$

DG^0 for the reaction at 750 K is 42.576 kJ. Assume ideal behaviour.

9.17 Ethanol can be prepared by the following vapour-phase reaction from ethylene:

$$C_2H_4(g) + H_2O \Leftrightarrow C_2H_5OH(g)$$

The value of DG^0 for the above reaction at 1 bar and 398 K is 5040 J. Calculate the conversion obtained if an isothermal reactor operating at 398 K and 2 bar is fed with a mixture containing 50 mol percent ethylene and 50 mol percent steam. Assume that equilibrium is reached at the exit of the reactor and the gases behave ideally.

9.18 A gaseous mixture containing 30% CO, 50% H_2 and the rest inert gas is sent to a reaction chamber for methanol synthesis. The following reaction occurs at 635 K and 310 bar.

$CO\ (g) + 2H_2\ (g) \square\ CH_3OH\ (g)$

Assuming that the gas mixture behaves as an ideal solution calculate the per cent conversion of CO given that $K_f = 5 \square 10^{-5}$ and $K_f = 0.35$.

9.19 Estimate the maximum conversion of ethylene to alcohol by vapour phase hydration at 523 K and 34 bar.

$C_2H_4\ (g) + H_2O\ (g) \square\ C_2H_5OH\ (g)$

The equilibrium constant varies with temperature as

$\ln K = 4760/T - 1.558 \ln T + 2.22 \square 10^{-3}T - 0.29 \square 10^{-6}T^2 - 5.56$

The steam–ethylene ratio in the initial mixture is 5.0. The fugacity coefficients for ethylene, ethanol and water vapour are 0.98, 0.84 and 0.91.

9.20 Ethanol is manufactured by the vapour-phase hydration of ethylene to ethanol according to the reaction,

$C_2H_4\ (g) + H_2O\ (g) \square\ C_2H_5OH\ (g)$

Starting with a gas mixture containing 25% ethylene and 75% steam, determine the composition of the products if the reaction were carried out at 400 K and 1 bar. The standard free energy of reaction at 400 K is 4548.3 J.

9.21 What would be the equilibrium yield of ethanol at 1 bar and 373 K in the following reaction?

$C_2H_4\ (g) + H_2O\ (g) \square\ C_2H_5OH\ (g)$

The reactant stream consists of an equimolar mixture of steam and ethylene. The standard free energy change may be taken as $\Delta G^0_{373} = 1264$ J/mol.

9.22 Calculate the equilibrium percentage conversion of nitrogen to ammonia at 700 K and 300 bar, if the gas enters the converter with a composition of 75% (mol) hydrogen and 25% (mol) nitrogen. For the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$$

equilibrium constant may be taken as $K = 9.1 \square 10^{-3}$. Assume that $K_f = 0.72$.

9.23 The gases from the pyrites burner of a contact sulphuric acid plant have the following composition: SO_2 = 7.80%, O_2 = 10.80% and N_2 = 81.40%. This is then passed into a converter where the SO_2 is converted to SO_3. The temperature and pressure in the converter are 775 K and 1 bar. The equilibrium constant for the reaction

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

may be taken as $K = 85$. Calculate the composition of gases leaving the converter.

9.24 One mol carbon at 298 K reacts with 2 mol oxygen at 298 K to form an equilibrium mixture of CO_2, CO and O_2 at 3000 K and 1 bar. If the equilibrium constant K = 0.328, determine the equilibrium composition.

9.25 One mol carbon at 298 K and 1 bar reacts with 1 mol oxygen at 298 K and 1 bar to form ar equilibrium mixture of CO_2, CO and O_2 at 3000 K and 1 bar in a steady flow process. Determine the equilibrium composition and heat transfer for this process if the equilibrium constant $K = 0.328$. Standard heat of formation are 393.509 kJ/mol for CO_2, 110.525 kJ/mol for CO. The mean heat capacity of products = 45 J/mol K.

9.26 Pure N_2O_4 at a low temperature is diluted with air and heated to 298 K and 1 bar. The following reaction occurs

N_2O_4 (g) □ $2NO_2$ (g)

If the mole fraction of N_2O_4 in the N_2O_4–air mixture before dissociation begins is 0.2, calculate the extent of decomposition and mole fraction of NO_2 and N_2O_4 present at equilibrium. The standard free energy change for the reaction at 298 K = 4644.7 J/mol.

9.27 Methanol is manufactured according to the reaction

CO (g) + $2H_2$ (g) □ CH_3OH (g)

The reaction is carried out at 400 K and 1 bar. The standard heat of reaction at this condition is – 9.4538 □ 10^4 J and the equilibrium constant is 1.52. Analysis of the equilibrium vapour product from the reactor shows 40% hydrogen. Equilibrium gas mixture can be treated as an ideal gas.

(a) Determine the concentrations of CO and CH_3OH in the product.

(b) If the reaction occurred at 500 K and 1 bar starting with the same feed as in part (a) would you expect the concentration of hydrogen in the equilibrium mixture to be greater or less than 40% mole? Why?

9.28 Determine the maximum percentage of ethane that may get dehydrogenated to ethylene at 750 K and 5 bar according to the reaction

C_2H_6 (g) □ C_2H_4 (g) + H_2 (g)

The standard free energy of reaction at 750 K is 4.2593 □ 10^4 J.

9.29 Hydrogen cyanide can be produced by the gas-phase nitrogenation of acetylene according to the reaction

N_2 (g) + C_2H_2 (g) □ 2HCN (g)

The feed to the reactor consists of an equimolar mixture of acetylene and nitrogen. The temperature of the reaction is 575 K. At this temperature, the standard free energy of reaction is 3.0181 □ 10^4 J. Determine the percentage of cyanide in the reaction mixture if

(a) The pressure is 1 bar

(b) The pressure is 200 bar. The fugacity coefficients for HCN, C_2H_2 and N_2 may be taken as 0.607, 0.942 and 1.07 respectively.

9.30 For the synthesis of ammonia according to the reaction

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$$

a mixture consisting of 0.5 mol N_2, and 1.5 mol H_2 is send to the reactor. The equilibrium mixture behaves as ideal gas. Show that the extent of reaction e is given by

$e = 1 – (1 + 1.299\ KP)^{–1/2}$

9.31 For the reaction

$$SO_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow SO_3\,(g)$$

in equilibrium at 775 K what pressure is required for a 90 per cent conversion of SO_2 if the initial mixture is equimolar in the reactants. Assume ideal gases. Take the free energy of the reaction at 775 K to be –2.8626 □ 10^4 J.

9.32 1-butene is dehydrogenated to 1,3-butadiene according to the reaction

C_4H_8 (g) □ C_4H_6 (g) + H_2 (g)

Determine the extent of reaction at equilibrium at 900 K and 1 bar with

(a) 1 mol butene as the reactant

(b) a reactant mixture consisting of 1 mol butene and 10 mol steam.

The following free energy functions and heat of formation data are available:

	$(G^0_{900} - H^0_{298})/T$, J/K	$H^0_{f,\,298}$, J
C_4H_6	– 336.41	1.1024×10^5
C_4H_8	– 368.56	$– 1.256 \times 10^2$
H_2	– 145.54	–

9.33 An experimental investigation on the effect of temperature on the reaction

A (g) + B (g) □ C (g)

gave the following equilibrium compositions at 373 K and 473 K. The pressure was maintained at 1 bar. At 373 K, $y_A = 0.414$, $y_B = 0.414$ and $y_C = 0.172$; At 473 K, $y_A = 0.179$, $y_B = 0.179$ and $y_C = 0.642$. What will be the equilibrium composition at 423 K and 10 bar if equimolar quantities of the reactants are used?

9.34 Determine the ranges of temperature and pressure for which the equilibrium conversion is at least 10% in the following reaction:

CO (g) + $2H_2$ (g) □ CH_3OH (g)

Assume that stoichiometric quantities of reactants are used. The standard free energy of formation of methanol and CO are respectively –1.626 □ 10^5 J/mol and –1.374 □ 10^5 J/mol at 298 K. The standard heat of formation at 298 K are –2.013 □ 10^5 J/mol and –1.106 □ 10^5 J/mol. Heat of reaction may be assumed to remain constant.

9.35 The equilibrium constant for the oxidation of SO_2 to SO_3 according to the reaction

$$SO_2\,(g) + \frac{1}{2}O_2\,(g) \rightarrow SO_3\,(g)$$

was found to be related to temperature as

$$-R \ln K = \frac{-22{,}630}{T} + 5.281 \ln T - 0.959 \times 10^{-2} T + 0.28 \times 10^{-5} T^2 - 7.68$$

where T is in K and K is in $(\text{bar})^{-1/2}$. A feed mixture containing 12% SO_2, 9% O_2 and 79% N_2 is reacted at 749 K and 1 bar. Calculate the fractional conversion of SO_2.

9.36 Ethanol is produced by vapour-phase hydration of ethylene:

C_2H_4 (g) + H_2O (g) □ C_2H_5OH (g)

(a) Calculate the equilibrium constant at 298 K using the following data:

	S^0_{298} J/mol K	H^0_{298} J/mol
C_2H_4 (g)	220.85	4.9×10^4
H_2O (g)	189.12	-2.42×10^5
C_2H_5OH (g)	278.00	-2.39×10^5

(b) If the standard free energy for the reaction can be expressed as

$$\Delta G^0 = -4.0486 \times 10^4 + 26.92T \ln T - 37.72T - 6.65 \times 10^{-3} T^2$$

where ΔG^0 is in J/mol ethanol. Discuss the feasibility of the reaction for a temperature range of 298 K to 773 K.

(c) Calculate the equilibrium conversion of ethylene at 450 K at a pressure of 1 bar and 5 bar when the feed contains equimolar quantities of ethylene and water.

(d) Repeat part (c) when the feed contains 100% excess water.

(e) Calculate the equilibrium conversion at 450 K and 1 bar, if the feed consists of 1 mol ethylene, 2 mol water and 1 mol inert gas.

9.37 Acetic acid is esterified in the liquid phase with ethanol at 373 K and 1 bar to produce ethyl acetate and water according to the reaction

CH_3COOH (l) + C_2H_5OH (l) □ $CH_3COOC_2H_5$ (l) + H_2O (l)

The feed consists of 1 mol each of acetic acid and ethanol, estimate the mole fraction of ethyl acetate in the reacting mixture at equilibrium. The standard heat of formation and standard free energy of formation at 298 K are given below:

	CH_3COOH (l)	C_2H_5OH (l)	$CH_3COOC_2H_5$ (l)	H_2O (l)
ΔH_f^0, J	– 484,500	– 277,690	– 463,250	– 285,830
ΔG_f^0, J	– 389,900	– 174,780	– 318,218	– 237,130

Assume that the heat of reaction is independent of temperature and the liquid mixture behaves as ideal solution.

9.38 The esterification of ethanol with acetic acid occurs in an aqueous solution as follows:

C_2H_5OH (aq) + CH_3COOH (aq) □ $CH_3COOC_2H_5$ (aq) + H_2O (l)

The free energies of formation of acetic acid, ethanol and ethyl acetate in a hypothetical 1 molal solution at 298 K are –3.9645 □ 10^5 J, –1.8053 □ 10^5 J and –3.3296 □ 10^5 J respectively. The free energy of formation of water at 298 K is –2.3735 □ 10^5 J. What is the equilibrium constant? Starting with a dilute equimolar mixture of ethanol and acetic acid, calculate the extent of reaction and the molalities of ethyl acetate and acetic acid in the equilibrium solution. Assume dilute solution behaviour.

9.39 Carbon dioxide is reduced by graphite according to the equation

C (s) + CO_2 (g) □ 2CO (g)

Assuming that equilibrium is attained at 1000 K and 1 bar, calculate the degree of completion of reduction of CO_2. The following data are available:

	$(G_{1000}^0 - H_0^0)/T$, J/mol K	$\Delta H_{f,0}^0$, J
CO	– 204.57	-1.1389×10^5
CO_2	– 226.54	-3.9343×10^5

9.40 Carbon dioxide is reduced by graphite according to the equation

C (s) + CO_2 (g) □ 2CO (g)

Calculate the effect of pressure on the degree of completion of pure CO_2 at 1000 K assuming total pressures of 1, 2 and 3 bar. Gas mixture may be treated as ideal gas and an equilibrium constant value of $K = 1.778$ may be assumed.

9.41 Calculate the decomposition pressure of limestone at 1000 K given that

$$\Delta H_{1000}^0 = 1.7553 \times 10^5 \text{ J and } \Delta S_{1000}^0 = 150.3 \text{ J/mol K}$$

9.42 Ammonium chloride decomposes upon heating to yield a gas mixture of ammonia and hydrochloric acid. At what temperature does ammonium chloride exert a decomposition pressure of 1 bar? The standard heat of formation and the standard free energy of formation are as follows:

	ΔH_f^0, J	ΔG_f^0, J
NH_4Cl (s)	– 314,430	– 202,870
NH_3 (g)	– 46,110	– 16,450
HCl (g)	– 92,307	– 95,299

9.43 The following decomposition reaction occurs at 373 K in the liquid phase.

A □ B + C

The equilibrium constant based on pure liquid standard state is 2. The vapour pressures are P_A = 5 bar, P_B = 20 bar and P_C = 2 bar. Assume that all vapours are ideal, liquid B is immiscible with A–C liquid mixture and the A–C mixture is ideal. Calculate the equilibrium pressure and the composition of the liquid and vapour phases.

9.44 The equilibrium constant for the following reaction is found to be 2.

A (l) □ B (l) + C (l)

The vapour pressures are P_A = 5 bar, P_B = 20 bar and P_C = 2 bar. A and C form ideal solution and B is immiscible with either A and C or their mixtures. The system consisted of pure A initially. Find the pressure below which only a gas phase exists.

9.45 Mixtures of CO and CO_2 are to be processed at temperatures between 900 K and 1000 K. Determine the conditions under which solid carbon might deposit according to the reaction

CO_2 (g) + C (s) □ 2CO (g)

The equilibrium constants for this reaction are 0.178 at 900 K and 1.58 at 1000 K. (*Hint:* The activity of solid carbon is less than unity if carbon is not present in the system.)

9.46 Acetylene is catalytically hydrogenated to ethylene at 1500 K and 1 bar. Starting with an equimolar mixture of acetylene and hydrogen what will be the mole fractions at equilibrium? Assume ideal gases.

C_2H_2 □ 2C + H_2; $K = 5.2$

2C + 2H_2 □ C_2H_4; $K = 0.1923$

9.47 What would be the equilibrium conversion of ethyl alcohol to butadiene at 700 K and 1 bar given the following reactions?

C_2H_5OH □ C_2H_4 + H_2O; $DG^0 = – 45,427$ J/mol

C_2H_5OH □ CH_3CHO + H_2; $DG^0 = – 15,114$ J/mol

C_2H_4 + CH_3CHO □ C_4H_6 + H_2O; $DG^0 = – 5,778$ J/mol

9.48 The feed to a reactor consists of an equimolar mixture of A and B. Determine the equilibrium composition of the mixture if the following gas-phase reaction occurs at 1000 K and 1 bar.

A + B □ C + D; $K = 0.4$

A + 2B □ C + E; $K = 0.5067$

9.49 The following reactions occur at 1500 K and 10 bar.

A + B □ C + D; $K = 2.67$

A + C □ 2E; $K = 3.20$

The initial mixture consists of 2 mol A and 1 mol B, determine the composition at equilibrium assuming ideal gas behaviour.

9.50 Determine the number of degrees of freedom in a gaseous system consisting of NH_3, NO_2, NO, H_2O, O_2 and N_2.

9.51 Determine the number of degrees of freedom in a gaseous system consisting of H_2O, HCl, O_2 and Cl_2.

APPENDIX A

Table for Thermodynamic Properties of Saturated Steam

		Specific volume		*Internal energy*		*Enthalpy*		*Entropy*	
Pressure kPa	*Temp.* K	*Sat. liquid*	*Sat. vapour*	*Sat. liquid*	*Sat. vapour*	*Sat. liquid*	*Sat. vapour*	*Sat. liquid*	*Sat. vapour*
0.6113	273.16	1.000	206140	0.00	2375.30	0.01	2501.40	0.0000	9.1562
1.00	280.13	1.000	129210	29.30	2385.00	29.30	2514.20	0.1059	8.9756
1.50	286.18	1.001	87980	54.71	2393.30	54.71	2525.30	0.1957	8.8279
2.00	290.65	1.001	67000	73.48	2399.50	73.48	2533.50	0.2607	8.7237
2.50	294.23	1.002	54250	88.48	2404.40	88.49	2540.00	0.3120	8.6432
3.00	297.23	1.003	45670	101.04	2408.50	101.05	2545.50	0.3545	8.5776
4.00	302.11	1.004	34800	121.45	2415.20	121.46	2554.40	0.4226	8.4746
5.00	306.03	1.005	28190	137.81	2420.50	137.82	2561.50	0.4764	8.3951
7.50	313.44	1.008	19240	168.78	2430.50	168.79	2574.80	0.5764	8.2515
10.00	318.96	1.010	14670	191.82	2437.90	191.83	2584.70	0.6493	8.1502
15.00	327.12	1.014	10020	225.92	2448.70	225.94	2599.10	0.7549	8.0085
20.00	333.21	1.017	7649	251.38	2456.70	251.40	2609.70	0.8320	7.9085
25.00	338.12	1.020	6204	271.90	2463.10	271.93	2618.20	0.8931	7.8314
30.00	342.25	1.022	5229	289.20	2468.40	289.23	2625.30	0.9439	7.7686
40.00	349.02	1.027	3993	317.53	2477.00	317.58	2636.80	1.0259	7.6700
50.00	354.48	1.030	3240	340.44	2483.90	340.49	2645.90	1.0910	7.5939
75.00	364.93	1.037	2217	384.31	2496.70	384.39	2663.00	1.2130	7.4564
100.00	372.78	1.043	1694.0	417.36	2506.10	417.46	2675.50	1.3026	7.3594
125.00	379.14	1.048	1374.9	444.19	2513.50	444.32	2685.40	1.3740	7.2844
150.00	384.52	1.053	1159.3	466.94	2519.70	467.11	2693.60	1.4336	7.2233
175.00	389.21	1.057	1003.6	486.80	2524.90	486.99	2700.60	1.4849	7.1717
200.00	393.38	1.061	885.7	504.49	2529.50	504.70	2706.70	1.5301	7.1271
225.00	397.15	1.064	793.3	520.47	2533.60	520.72	2712.10	1.5706	7.0878
250.00	400.59	1.067	718.7	535.10	2537.20	535.37	2716.90	1.6072	7.0527
275.00	403.75	1.070	657.3	548.59	2540.50	548.89	2721.30	1.6408	7.0209
300.00	406.70	1.073	605.8	561.15	2543.60	561.47	2725.30	1.6718	6.9919
325.00	409.45	1.076	562.0	572.90	2546.40	573.25	2729.00	1.7006	6.9652
350.00	412.03	1.079	524.3	583.95	2548.90	584.33	2732.40	1.7275	6.9405
375.00	414.47	1.081	491.4	594.40	2551.30	594.81	2735.60	1.7528	6.9175
400.00	416.78	1.084	462.5	604.31	2553.60	604.74	2738.60	1.7766	6.8959
450.00	421.08	1.088	414.0	622.77	2557.60	623.25	2743.90	1.8207	6.8565
500.00	425.01	1.093	374.9	639.68	2561.20	640.23	2748.70	1.8607	6.8213
550.00	428.63	1.097	342.7	655.32	2564.50	655.93	2753.00	1.8973	6.7893

600.00	432.00	1.101	315.7	669.90	2567.40	670.56	2756.80	1.9312	6.7600
650.00	435.16	1.104	292.7	683.56	2570.10	684.28	2760.30	1.9627	6.7331
700.00	438.12	1.108	272.9	696.44	2572.50	697.22	2763.50	1.9922	6.7080
750.00	440.93	1.112	255.6	708.64	2574.70	709.47	2766.40	2.0200	6.6847
800.00	443.58	1.115	240.4	720.22	2576.80	721.11	2769.10	2.0462	6.6628
850.00	446.11	1.118	227.0	731.27	2578.70	732.22	2771.60	2.0710	6.6421
900.00	448.53	1.121	215.0	741.83	2580.50	742.83	2773.90	2.0940	6.6226
950.00	450.84	1.124	204.2	751.95	2582.10	753.02	2776.10	2.1172	6.6041
1000	453.06	1.127	194.4	761.68	2583.60	762.81	2778.10	2.1387	6.5865
1100	457.24	1.133	177.53	780.09	2586.40	781.34	2781.70	2.1792	6.5536
1200	461.14	1.139	163.33	797.29	2588.80	798.65	2784.80	2.2166	6.5233
1300	464.79	1.144	151.25	813.44	2591.00	814.93	2787.60	2.2515	6.4953
1400	468.22	1.149	140.84	828.70	2592.80	830.30	2790.00	2.2842	6.4693
1500	471.47	1.154	131.77	843.16	2594.50	844.89	2792.20	2.3150	6.4448
1750	478.91	1.166	113.49	876.46	2597.80	878.50	2796.40	2.3851	6.3896
2000	485.57	1.177	99.63	906.44	2600.30	908.79	2799.50	2.4474	6.3409
2250	491.60	1.187	88.75	933.83	2602.00	936.49	2801.70	2.5035	6.2972
2500	497.14	1.197	79.98	959.11	2603.10	962.11	2803.10	2.5547	6.2575
3000	507.05	1.217	66.68	1004.78	2604.10	1008.42	2804.20	2.6457	6.1869
3500	515.75	1.235	57.07	1045.43	2603.70	1049.75	2803.40	2.7253	6.1253
4000	523.55	1.252	49.78	1082.31	2602.30	1087.31	2801.40	2.7964	6.0701
5000	537.14	1.286	39.44	1147.81	2597.10	1154.23	2794.30	2.9202	5.9734
6000	548.79	1.319	32.44	1205.44	2589.70	1213.35	2784.30	3.0267	5.8892
7000	559.03	1.351	27.37	1257.55	2580.50	1267.00	2772.10	3.1211	5.8133
8000	568.21	1.384	23.52	1305.57	2569.80	1316.64	2758.00	3.2068	5.7432
9000	576.55	1.418	20.48	1350.51	2557.80	1363.26	2742.10	3.2858	5.6772
10000	584.21	1.452	18.026	1393.04	2544.40	1407.56	2724.70	3.3596	5.6141
11000	591.30	1.489	15.987	1433.70	2529.80	1450.10	2705.60	3.4295	5.5527
12000	597.90	1.527	14.263	1473.00	2513.70	1491.30	2684.90	3.4962	5.4924
13000	604.08	1.567	12.780	1511.10	2496.10	1531.50	2662.20	3.5606	5.4323
14000	609.90	1.611	11.485	1548.60	2476.80	1571.10	2637.60	3.6232	5.3717
15000	615.39	1.658	10.337	1585.60	2455.50	1610.50	2610.50	3.6848	5.3098
16000	620.59	1.711	9.306	1622.70	2431.70	1650.10	2580.60	3.7461	5.2455
17000	625.52	1.770	8.364	1660.20	2405.00	1690.30	2547.20	3.8079	5.1777
18000	630.21	1.840	7.489	1698.90	2374.30	1732.00	2509.10	3.8715	5.1044
19000	634.69	1.924	6.657	1739.90	2338.10	1776.50	2464.50	3.9388	5.0228
20000	638.96	2.036	5.834	1785.60	2293.00	1826.30	2409.70	4.0139	4.9269
21000	643.04	2.207	4.952	1842.10	2230.60	1888.40	2334.60	4.1075	4.8013
22000	646.95	2.742	3.568	1961.90	2087.10	2022.20	2165.60	4.3110	4.5327
22090	647.29	3.155	3.155	2029.60	2029.60	2099.30	2099.30	4.4298	4.4298

Specific volume, $V \times 10^3$ m^3/kg
Internal energy, kJ/kg
Enthalpy, kJ/kg
Entropy, kJ/kg K

APPENDIX B

Table for Thermodynamic Properties of Superheated Steam

	V	*U*	*H*	*S*	*V*	*U*	*H*	*S*
T, K	*P* = 10 kPa (Sat. Temp = 318.96 K)				*P* = 50 kPa (Sat. Temp = 354.48 K)			
Sat.	14.674	2437.9	2584.7	8.1502	3.240	2483.9	2645.9	7.5939
323.15	14.869	2443.9	2592.6	8.1749				
373.15	17.196	2515.5	2687.5	8.4479	3.418	2511.6	2682.5	7.6947
423.15	19.512	2587.9	2783.0	8.6882	3.889	2585.6	2780.1	7.9401
473.15	21.825	2661.3	2879.5	8.9038	4.356	2659.9	2877.7	8.1580
523.15	24.136	2736.0	2977.3	9.1002	4.820	2735.0	2976.0	8.3556
573.15	26.445	2812.1	3076.5	9.2813	5.284	2811.3	3075.5	8.5373
673.15	31.063	2968.9	3279.6	9.6077	6.209	2968.5	3278.9	8.8642
773.15	35.679	3132.3	3489.1	9.8978	7.134	3132.0	3488.7	9.1546
873.15	40.295	3302.5	3705.4	10.1608	8.057	3302.2	3705.1	9.4178
973.15	44.911	3479.6	3928.7	10.4028	8.981	3479.4	3928.5	9.6599
1073.15	49.526	3663.8	4159.0	10.6281	9.904	3663.6	4158.9	9.8852
1173.15	54.141	3855.0	4396.4	10.8396	10.828	3854.9	4396.3	10.0967
1273.15	58.757	4053.0	4640.6	11.0393	11.751	4052.9	4640.5	10.2964
1373.15	63.372	4257.5	4891.2	11.2287	12.674	4257.4	4891.1	10.4859
1473.15	67.987	4467.9	5147.8	11.4091	13.597	4467.8	5147.7	10.6662
1573.15	72.602	4683.7	5409.7	11.5811	14.521	4683.6	5409.6	10.8382
	P = 100 kPa (Sat. Temp = 372.78 K)				*P* = 200 kPa (Sat. Temp = 393.38 K)			
Sat.	1.6940	2506.1	2675.5	7.3594	0.8857	2529.5	2706.7	7.1272
373.15	1.6958	2506.7	2676.2	7.3614				
423.15	1.9364	2582.8	2776.4	7.6134	0.9596	2576.9	2768.8	7.2795
473.15	2.1720	2658.1	2875.3	7.8343	1.0803	2654.4	2870.5	7.5066
523.15	2.4060	2733.7	2974.3	8.0333	1.1988	2731.2	2971.0	7.7086
573.15	2.6390	2810.4	3074.3	8.2158	1.3162	2808.6	3071.8	7.8926
673.15	3.1030	2967.9	3278.2	8.5435	1.5493	2966.7	3276.6	8.2218
773.15	3.5650	3131.6	3488.1	8.8342	1.7814	3130.8	3487.1	8.5133
873.15	4.0280	3301.9	3704.7	9.0976	2.0130	3301.4	3704.0	8.7770
973.15	4.4900	3479.2	3928.2	9.3398	2.2440	3478.8	3927.6	9.0194

	V	U	H	S	V	U	H	S
T, K	P = 100 kPa (Sat. Temp = 372.78 K)				P = 200 kPa (Sat. Temp = 393.38 K)			
1073.15	4.9520	3663.5	4158.6	9.5652	2.4750	3663.1	4158.2	9.2449
1173.15	5.4140	3854.8	4396.1	9.7767	2.7060	3854.5	4395.8	9.4566
1273.15	5.8750	4052.8	4640.3	9.9764	2.9370	4052.5	4640.0	9.6563
1373.15	6.3370	4257.3	4891.0	10.1659	3.1680	4257.0	4890.7	9.8458
1473.15	6.7990	4467.7	5147.6	10.3463	3.3990	4467.5	5147.3	10.0262
1573.15	7.2600	4683.5	5409.5	10.5183	3.6300	4683.2	5409.3	10.1982
	P = 300 kPa (Sat. Temp = 406.7 K)				P = 400 kPa (Sat. Temp = 416.78 K)			
Sat.	0.6058	2543.6	2725.3	6.9919	0.4625	2553.6	2738.6	6.8959
423.15	0.6339	2570.8	2761.0	7.0778	0.4708	2564.5	2752.8	6.9299
473.15	0.7163	2650.7	2865.6	7.3115	0.5342	2646.8	2860.5	7.1706
523.15	0.7964	2728.7	2967.6	7.5166	0.5951	2726.1	2964.2	7.3789
573.15	0.8753	2806.7	3069.3	7.7022	0.6548	2804.8	3066.8	7.5662
673.15	1.0315	2965.6	3275.0	8.0330	0.7726	2964.4	3273.4	7.8985
773.15	1.1867	3130.0	3486.0	8.3251	0.8893	3129.2	3484.9	8.1913
873.15	1.3414	3300.8	3703.2	8.5892	1.0055	3300.2	3702.4	8.4558
973.15	1.4957	3478.4	3927.1	8.8319	1.1215	3477.9	3926.5	8.6987
1073.15	1.6499	3662.9	4157.8	9.0576	1.2372	3662.4	4157.3	8.9244
1173.15	1.8041	3854.2	4395.4	9.2692	1.3529	3853.9	4395.1	9.1362
1273.15	1.9581	4052.3	4639.7	9.4690	1.4685	4052.0	4639.4	9.3360
1373.15	2.1121	4256.8	4890.4	9.6585	1.5840	4256.5	4890.2	9.5256
1473.15	2.2661	4467.2	5147.1	9.8389	1.6996	4467.0	5146.8	9.7060
1573.15	2.4201	4683.0	5409.0	10.0110	1.8151	4682.8	5408.8	9.8780
	P = 500 kPa (Sat. Temp = 425.01 K)				P = 600 kPa (Sat. Temp = 432 K)			
Sat.	0.3749	2561.2	2748.7	6.8213	0.3157	2567.4	2756.8	6.7600
473.15	0.4249	2642.9	2855.4	7.0592	0.3520	2638.9	2850.1	6.9665
523.15	0.4744	2723.5	2960.7	7.2709	0.3938	2720.9	2957.2	7.1816
573.15	0.5226	2802.9	3064.2	7.4599	0.4344	2801.0	3061.6	7.3724
623.15	0.5701	2882.6	3167.7	7.6329	0.4742	2881.2	3165.7	7.5464
673.15	0.6173	2963.2	3271.9	7.7938	0.5137	2962.1	3270.3	7.7079
773.15	0.7109	3128.4	3483.9	8.0873	0.5920	3127.6	3482.8	8.0021
873.15	0.8041	3299.6	3701.7	7.3522	0.6697	3299.1	3700.9	8.2674
973.15	0.8969	3477.5	3925.9	8.5952	0.7472	3477.0	3925.3	8.5107
1073.15	0.9896	3662.1	4156.9	8.8211	0.8245	3661.8	4156.5	8.7367
1173.15	1.0822	3853.6	4394.7	9.0329	0.9017	3853.4	4394.4	8.9486
1273.15	1.1747	4051.8	4639.1	9.2328	0.9788	4051.5	4638.8	9.1485
1373.15	1.2672	4256.3	4889.9	9.4224	1.0559	4256.1	4889.6	9.3381
1473.15	1.3596	4466.8	5146.6	9.6029	1.1330	4466.5	5146.3	9.5185
1573.15	1.4521	4682.5	5408.6	9.7749	1.2101	4682.3	5408.3	9.6906

	V	U	H	S	V	U	H	S
T, K	P = 800 kPa (Sat. Temp = 443.58 K)				P = 1000 kPa (Sat. Temp = 453.06 K)			
Sat.	0.2404	2576.8	2769.1	6.6628	0.19444	2583.6	2778.1	6.5865
473.15	0.2608	2630.6	2839.3	6.8158	0.2060	2621.9	2827.9	6.6940
523.15	0.2931	2715.5	2950.0	7.0384	0.2327	2709.9	2942.6	6.9247
573.15	0.3241	2797.2	3056.5	7.2328	0.2579	2793.2	3051.2	7.1229
623.15	0.3544	2878.2	3161.7	7.4089	0.2825	2875.2	3157.7	7.3011
673.15	0.3843	2959.7	3267.1	7.5716	0.3066	2957.3	3263.9	7.4651
773.15	0.4433	3126.0	3480.6	7.8673	0.3541	3124.4	3478.5	7.7622
873.15	0.5018	3297.7	3699.4	8.1333	0.4011	3296.8	3697.9	8.0290
973.15	0.5601	3476.2	3924.2	8.3770	0.4478	3475.3	3923.1	8.2731
1073.15	0.6181	3661.1	4155.6	8.6033	0.4943	3660.4	4154.7	8.4996
1173.15	0.6761	3852.8	4393.7	8.8153	0.5407	3852.2	4392.9	8.7118
1273.15	0.7340	4051.0	4638.2	9.0153	0.5871	4050.5	4637.6	8.9119
1373.15	0.7919	4255.6	4889.1	9.2050	0.6335	4255.1	4888.6	9.1017
1473.15	0.8497	4466.1	5145.9	9.3855	0.6798	4465.6	5145.4	9.2822
1573.15	0.9076	4681.8	5407.9	9.5575	0.7261	4681.3	5407.4	9.4543
	P = 1200 kPa (Sat. Temp = 461.14 K)				P = 1400 kPa (Sat. Temp = 468.22 K)			
Sat.	0.16333	2588.8	2784.8	6.5233	0.14084	2592.8	2790.0	6.4693
473.15	0.16930	2612.8	2815.9	6.5898	0.14302	2603.1	2803.3	6.4975
523.15	0.19234	2704.2	2935.0	6.8294	0.16350	2698.3	2927.2	6.7467
573.15	0.2138	2789.2	3045.8	7.0317	0.18228	2785.2	3040.4	6.9534
623.15	0.2345	2872.2	3153.6	7.2121	0.2003	2869.2	3149.5	7.1360
673.15	0.2548	2954.9	3260.7	7.3774	0.2178	2952.5	3257.5	7.3026
773.15	0.2946	3122.8	3476.3	7.6759	0.2521	3121.1	3474.1	7.6027
873.15	0.3339	3295.6	3696.3	7.9435	0.2860	3294.4	3694.8	7.8710
973.15	0.3729	3474.4	3922.0	8.1881	0.3195	3473.6	3920.8	8.1160
1073.15	0.4118	3659.7	4153.8	8.4148	0.3528	3659.0	4153.0	8.3431
1173.15	0.4505	3851.6	4392.2	8.6272	0.3861	3851.1	4391.5	8.5556
1273.15	0.4892	4050.0	4637.0	8.8274	0.4192	4049.5	4636.4	8.7559
1373.15	0.5278	4254.6	4888.0	9.0172	0.4524	4254.1	4887.5	8.9457
1473.15	0.5665	4465.1	5144.9	9.1977	0.4855	4464.7	5144.4	9.1262
1573.15	0.6051	4680.9	5407.0	9.3698	0.5186	4680.4	5406.5	9.2984
	P = 1600 kPa (Sat. Temp = 474.56 K)				P = 1800 kPa (Sat. Temp = 480.3 K)			
Sat.	0.12380	2596.0	2794.0	6.4218	0.11042	2598.4	2797.1	6.3794
498.15	0.13287	2644.7	2857.3	6.5518	0.11673	2636.6	2846.7	6.4808
523.15	0.14184	2692.3	2919.2	6.6732	0.12497	2686.0	2911.0	6.6066
573.15	0.15862	2781.1	3034.8	6.8844	0.14021	2776.9	3029.2	6.8226
623.15	0.17456	2866.1	3145.4	7.0694	0.15457	2863.0	3141.2	7.0100
673.15	0.19005	2950.1	3254.2	7.2374	0.16847	2947.7	3250.9	7.1794

	V	*U*	*H*	*S*	*V*	*U*	*H*	*S*
T, K	*P* = 1600 kPa (Sat. Temp = 474.56 K)				*P* = 1800 kPa (Sat. Temp = 480.3 K)			
773.15	0.2203	3119.5	3472.0	7.5390	0.19550	3117.9	3469.8	7.4825
873.15	0.2500	3293.3	3693.2	7.8080	0.2220	3292.1	3691.7	7.7523
973.15	0.2794	3472.7	3919.7	8.0535	0.2482	3471.8	3918.5	7.9983
1073.15	0.3086	3658.3	4152.1	8.2808	0.2742	3657.6	4151.2	8.2258
1173.15	0.3377	3850.5	4390.8	8.4935	0.3001	3849.9	4390.1	8.4386
1273.15	0.3668	4049.0	4635.8	8.6938	0.3260	4048.5	4635.2	8.6391
1373.15	0.3958	4253.7	4887.0	8.8837	0.3518	4253.2	4886.4	8.8290
1473.15	0.4248	4464.2	5143.9	9.0643	0.3776	4463.7	5143.4	9.0096
1573.15	0.4538	4679.9	5406.0	9.2364	0.4034	4679.5	5405.6	9.1818
	P = 2000 kPa (Sat. Temp = 487.57 K)				*P* = 2500 kPa (Sat. Temp = 497.14 K)			
Sat.	0.09963	2600.3	2799.5	6.3409	0.07998	2603.1	2803.1	6.2575
498.15	0.10377	2628.3	2835.8	6.4147	0.08027	2605.6	2806.3	6.2639
523.15	0.11144	2679.6	2902.5	6.5453	0.08700	2662.6	2880.1	6.4085
573.15	0.12547	2772.6	3023.5	6.7664	0.09890	2761.6	3008.8	6.6438
623.15	0.13857	2859.8	3137.0	6.9563	0.10976	2851.9	3126.3	6.8403
673.15	0.15120	2945.2	3247.6	7.1271	0.12010	2939.1	3239.3	7.0148
723.15	0.16342	3031.0	3357.8	7.2859	0.13014	3025.5	3350.8	7.1746
773.15	0.17568	3116.2	3467.6	7.4317	0.13998	3112.1	3462.1	7.3234
873.15	0.19960	3290.9	3690.1	7.7024	0.15930	3288.0	3686.3	7.5960
973.15	0.22320	3470.9	3917.4	7.9487	0.17832	3468.7	3914.5	7.8435
1073.15	0.24670	3657.0	4150.3	8.1765	0.19716	3655.3	4148.2	8.0720
1173.15	0.27000	3849.3	4389.4	8.3895	0.21590	3847.9	4387.6	8.2853
1273.15	0.29330	4048.0	4634.6	8.5901	0.2346	4046.7	4633.1	8.4861
1373.15	0.31660	4252.7	4885.9	8.7800	0.2532	4251.5	4884.6	8.6762
1473.15	0.33980	4463.3	5142.9	8.9607	0.2718	4462.1	5141.7	8.8569
1573.15	0.36310	4679.0	5405.1	9.1329	0.2905	4677.8	5404.0	9.0291
	P = 3000 kPa (Sat. Temp = 507.05 K)				*P* = 3500 kPa (Sat. Temp = 515.75 K)			
Sat.	0.06668	2604.1	2804.2	6.1869	0.05707	2603.7	2803.4	6.1253
523.15	0.07058	2644.0	2855.8	6.2872	0.05872	2623.7	2829.2	6.1749
573.15	0.08114	2750.1	2993.5	6.5390	0.06842	2738.0	2977.5	6.4461
623.15	0.09053	2843.7	3115.3	6.7428	0.07678	2835.3	3104.0	6.6579
673.15	0.09936	2932.8	3230.9	6.9212	0.08453	2926.4	3222.3	6.8405
723.15	0.10787	3020.4	3344.0	7.0834	0.09196	3015.3	3337.2	7.0052
773.15	0.11619	3108.0	3456.5	7.2338	0.09918	3103.0	3450.9	7.1572
873.15	0.13243	3285.0	3682.3	7.5085	0.11324	3282.1	3678.4	7.4339
973.15	0.14838	3466.5	3911.7	7.7571	0.12699	3464.3	3908.8	7.6837
1073.15	0.16414	3653.5	4145.9	7.9862	0.14056	3651.8	4143.7	7.9134
1173.15	0.17980	3846.5	4385.9	8.1999	0.15402	3845.0	4384.1	8.1276
1273.15	0.19541	4045.4	4631.6	8.4009	0.16743	4044.1	4630.1	8.3288

(Contd.)

	V	U	H	S	V	U	H	S
T, K	P = 3000 kPa (Sat. Temp = 507.05 K)				P = 3500 kPa (Sat. Temp = 515.75 K)			
1373.15	0.21098	4250.3	4883.3	8.5912	0.18080	4249.2	4881.9	8.5192
1473.15	0.22652	4460.9	5140.5	8.7720	0.19415	4459.8	5139.3	8.7000
1573.15	0.24206	4676.6	5402.8	8.9442	0.20749	4675.5	5401.7	8.8723
	P = 4000 kPa (Sat. Temp = 523.55 K)				P = 4500 kPa (Sat. Temp = 530.64 K)			
Sat.	0.04978	2602.3	2801.4	6.0701	0.04406	2600.1	2798.3	6.0198
548.15	0.05457	2667.9	2886.2	6.2285	0.04730	2650.3	2863.2	6.1401
573.15	0.05884	2725.3	2960.7	6.3615	0.05135	2712.0	2943.1	6.2828
623.15	0.06645	2826.7	3092.5	6.5821	0.05840	2817.8	3080.6	6.5131
673.15	0.07341	2919.9	3213.6	6.7690	0.06475	2913.3	3204.7	6.7047
723.15	0.08002	3010.2	3330.3	6.9363	0.07074	3005.0	3323.3	6.8746
773.15	0.08643	3099.5	3445.3	7.0900	0.07651	3095.3	3439.6	7.0301
873.15	0.09885	3279.1	3674.4	7.3688	0.08765	3276.0	3670.5	7.3110
973.15	0.11095	3462.1	3905.9	7.6198	0.09847	3459.9	3903.0	7.5631
1073.15	0.12287	3650.0	4141.5	7.8502	0.10911	3648.3	4139.3	7.7942
1173.15	0.13469	3843.6	4382.3	8.0647	0.11965	3842.2	4380.6	8.0091
1273.15	0.14645	4042.9	4628.7	8.2662	0.13013	4041.6	4627.2	8.2108
1373.15	0.15817	4248.0	4880.6	8.4567	0.14056	4246.8	4879.3	8.4015
1473.15	0.16987	4458.6	5138.1	8.6376	0.15098	4457.5	5136.9	8.5825
1573.15	0.18156	4674.3	5400.5	8.8100	0.16139	4673.1	5399.4	8.7549
	P = 5000 kPa (Sat. Temp = 537.14 K)				P = 6000 kPa (Sat. Temp = 548.79 K)			
Sat.	0.03944	2597.1	2794.3	5.9734	0.03244	2589.7	2784.3	5.8892
548.15	0.04141	2631.3	2838.3	6.0544				
573.15	0.04532	2698.0	2924.5	6.2084	0.03616	2667.2	2884.2	6.0674
623.15	0.05194	2808.7	3068.4	6.4493	0.04223	2789.6	3043.0	6.3335
673.15	0.05781	2906.6	3195.7	6.6459	0.04739	2892.9	3177.2	6.5408
723.15	0.06330	2999.7	3316.2	6.8186	0.05214	2988.9	3301.8	6.7193
773.15	0.06857	3091.0	3433.8	6.9759	0.05665	3082.2	3422.2	6.8803
823.15	0.07360	3181.0	3549.0	7.1215	0.06101	3174.6	3540.6	7.0288
873.15	0.07869	3273.0	3666.5	7.2589	0.06525	3266.9	3658.4	7.1677
973.15	0.08849	3457.6	3900.1	7.5122	0.07352	3453.1	3894.2	7.4234
1073.15	0.09811	3646.6	4137.1	7.7440	0.08160	3643.1	4132.7	7.6566
1173.15	0.10762	3840.7	4378.8	7.9593	0.08958	3837.8	4375.3	7.8727
1273.15	0.11707	4040.4	4625.7	8.1612	0.09749	4037.8	4622.7	8.0751
1373.15	0.12648	4245.6	4878.0	8.3520	0.10536	4243.3	4875.4	8.2661
1473.15	0.13587	4456.3	5135.7	8.5331	0.11321	4454.0	5133.3	8.4474
1573.15	0.14526	4672.0	5398.2	8.7055	0.12106	4669.6	5396.0	8.6199

T, K	V	U	H	S	V	U	H	S
	P = 7000 kPa (Sat. Temp = 559.03 K)				P = 8000 kPa (Sat. Temp = 568.21 K)			
Sat.	0.02737	2580.5	2772.1	5.8133	0.02352	2569.8	2758.0	5.7432
573.15	0.02947	2632.2	2838.4	5.9305	0.02426	2590.9	2785.0	5.7906
623.15	0.03524	2769.4	3016.0	6.2283	0.02995	2747.7	2987.3	6.1301
673.15	0.03993	2878.6	3158.1	6.4478	0.03432	2863.8	3138.3	6.3634
723.15	0.04416	2978.0	3287.1	6.6327	0.03817	2966.7	3272.0	6.5551
773.15	0.04814	3073.4	3410.3	6.7975	0.04175	3064.3	3398.3	6.7240
823.15	0.05195	3167.2	3530.9	6.9486	0.04516	3159.8	3521.0	6.8778
873.15	0.05565	3260.7	3650.3	7.0894	0.04845	3254.4	3642.0	7.0206
973.15	0.06283	3448.5	3888.3	7.3476	0.05481	3443.9	3882.4	7.2812
1073.15	0.06981	3639.5	4128.2	7.5822	0.06097	3636.0	4123.8	7.5173
1173.15	0.07669	3835.0	4371.8	7.7991	0.06702	3832.1	4368.3	7.7351
1273.15	0.08350	4035.3	4619.8	8.0020	0.07301	4032.8	4616.9	7.9384
1373.15	0.09027	4240.9	4872.8	8.1933	0.07896	4238.6	4870.3	8.1300
	P = 10000 kPa (Sat. Temp = 584.11 K)				P = 12000 kPa (Sat. Temp = 597.8 K)			
Sat.	0.01803	2544.4	2724.7	5.6141	0.01428	2517.8	2689.2	5.5002
623.15	0.02242	2699.2	2923.4	5.9443	0.01715	2640.6	2846.4	5.7578
673.15	0.02641	2832.4	3096.5	6.2120	0.02108	2801.8	3054.8	6.0810
723.15	0.02975	2943.4	3240.9	6.4190	0.02411	2921.7	3211.0	6.2944
773.15	0.03279	3045.8	3373.7	6.5966	0.02679	3028.2	3349.6	6.4906
823.15	0.03564	3144.6	3500.9	6.7561	0.02925	3128.5	3479.5	6.6532
873.15	0.03837	3241.7	3625.3	6.9029	0.03160	3226.4	3605.7	6.8022
923.15	0.04101	3338.2	3748.2	7.0398	0.03387	3323.8	3730.2	6.9409
	P = 14000 kPa (Sat. Temp = 609.79 K)				P = 15000 kPa (Sat. Temp = 615.28 K)			
Sat.	0.01150	2481.4	2642.4	5.3803	0.01034	2455.5	2610.5	5.3098
623.15	0.01311	2563.4	2746.9	5.5492	0.01147	2520.4	2692.4	5.4421
673.15	0.01723	2764.4	3005.6	5.9513	0.01565	2740.7	2975.5	5.8811
723.15	0.02007	2896.0	3177.0	6.1969	0.01845	2879.5	3156.2	6.1404
773.15	0.02251	3008.7	3323.8	6.3937	0.02080	2996.6	3308.6	6.3443
823.15	0.02472	3112.7	3458.8	6.5627	0.02293	3104.7	3448.6	6.5199
873.15	0.02680	3213.2	3588.5	6.7159	0.02491	3208.6	3582.3	6.6776
923.15	0.02880	3312.5	3715.6	6.8575	0.02680	3310.3	3712.3	6.8224

Specific volume, m^3/kg
Internal energy, kJ/kg
Enthalpy, kJ/kg
Entropy, kJ/kg K

APPENDIX C

Aptitude Test in Chemical Engineering Thermodynamics

Given below are some questions which will help the students to check their knowledge in the subject of Chemical Engineering Thermodynamics. These questions are prepared for the benefit of student appearing for various competitive examinations. In fact, some of these are taken from the GATE (Graduate Aptitude Test in Engineering) question papers.

C.1 Write the most appropriate answer to the following multiple-choice questions:

1. The major limitation of the first law of thermodynamics is that it does not consider
   A. Heat as a form of energy
   B. Rate of change of a process
   C. Direction of change
   D. Spontaneous processes
2. All spontaneous processes are
   A. Reversible
   B. Irreversible
   C. Reversible adiabatic
   D. Adiabatic
3. Which one of the following may be treated as a statement of the second law of thermodynamics
   A. Heat and work are energy in transit
   B. It is impossible to convert mechanical work to heat with 100% efficiency
   C. Absolute zero of temperature cannot be attained in practice
   D. Energy of an isolated system is conserved
4. $C_P = C_V$ for a fluid
   A. Which is compressible
   B. Whose volume coefficient of expansion is negligible
   C. Which is homogeneous
   D. Under normal temperature and pressure
5. Compared to an ordinary vapour compression refrigerator, the COP of an expansion engine vapour compression cycle is
   A. Greater
   B. Lesser
   C. Equal
   D. No generalisation possible
6. Entropy change of a system is zero in
   A. Reversible process

B. Adiabatic process
C. Reversible adiabatic process
D. Isothermal process

7. The heat capacity at constant pressure of a single component system consisting of liquid and vapour phases in equilibrium is
A. Infinite
B. Zero
C. Positive
D. Negative

8. The ratio of the fugacity to the pressure is known as
A. Activity
B. Activity coefficient
C. Fugacity coefficient
D. Acentric factor

9. Which one of the following is not a property of an ideal gas?
A. Internal energy U is a function of temperature alone
B. Enthalpy H is a function of temperature alone
C. Entropy S is a function of temperature alone
D. Heat capacities C_P and C_V are functions of temperature alone

10. For ideal gases, D$H = \int C_P \, dT$ is valid
A. For constant volume process
B. For constant pressure process
C. Irrespective of the nature of the process
D. The statement is never true

11. The equation of state for a certain gas is given by $P(V - b) = RT$, where b is a positive constant. The Joule–Thomson coefficient of this gas would be
A. Positive
B. Negative
C. Zero
D. Positive within the inversion points

12. A three-stage compressor is used to compress a gas at 1 bar to a final pressure of 125 bar. For minimum work, the pressure ratios in each stage should be
A. 25
B. 5
C. 41.67
D. None of the above

13. The ordinary vapour compression cycle for refrigeration is less efficient than the Carnot cycle, because in the former,
A. Evaporation process is non-isothermal
B. A two-phase mixture is to be compressed

C. Vapour leaving the compressor is superheated

D. Expansion process results in liquefaction

14. The main feature of an absorption refrigeration unit is

A. The absence of compression step

B. The absence of expansion step

C. The absence of condensation step

D. None of the above

15. The shaft work done by the fluid in a reversible flow process in which there are no changes in the kinetic, potential and surface energies, is given by

A. $W_S = \int_1^2 P\,dV$

B. $W_S = \int_2^1 P\,dV$

C. $W_S = \int_1^2 V\,dP$

D. $W_S = \int_2^1 V\,dP$

16. The reversible work of expansion in a flow process under isothermal condition is equal to

A. $-(\mathrm{D}A)_T$

B. $-(\mathrm{D}G)_T$

C. $-(\mathrm{D}U)_T$

D. $-(\mathrm{D}H)_T$

17. The decrease in enthalpy accompanying a reversible expansion measures the shaft work in the case of

A. A non-flow isothermal process

B. An isothermal flow process

C. An isentropic non-flow process

D. An isentropic flow process

18. For a reversible process occurring at constant temperature and pressure, the decrease in Gibbs free energy measures

A. The maximum reversible work

B. The maximum reversible work, other than the electrical work

C. The maximum reversible work, other than the wok of expansion

D. The heat supplied

19. $C_P = C_V$ when

A. $\left(\frac{\partial V}{\partial P}\right)_T = 0$

B. $\left(\frac{\partial V}{\partial T}\right)_P = 0$

C. $\left(\frac{\partial T}{\partial P}\right)_H = 0$

D. $\left(\frac{\partial S}{\partial V}\right)_T = 0$

20. At the triple point of water, the number of degrees of freedom is

A. zero

B. one

C. two

D. three

21. The canonical variables for H are:

A. P and T

B. V and T

C. P and S

D. V and S

22. Which one of the following is incorrect?

A. $dU = T\,dS - P\,dV$

B. $dH = T\,dS - V\,dP$

C. $dA = -S\,dT - P\,dV$

D. $dG = -S\,dT + V\,dP$

23. The volume coefficient of expansion b of an ideal gas equals

A. $1/T$

B. $1/P$

C. T

D. P

24. Fugacity has the same dimensions as that of

A. Gibbs free energy

B. Pressure

C. Temperature

D. Fugacity is dimensionless

25. The change in free energy when a real gas undergoes an isothermal change in state is

A. $\mathrm{D}G = RT \ln (V_2/V_1)$

B. $\mathrm{D}G = RT \ln (P_2/P_1)$

C. $\mathrm{D}G = RT \ln (f_2/f_1)$

D. $\mathrm{D}G = RT \ln (\mathrm{g}_2/\mathrm{g}_1)$

26. The difference between the heat supplied and the work extracted in a steady flow process in which the kinetic and potential energy changes are negligible, is equal to

A. The change in internal energy

B. The change in enthalpy

C. The change in the work function

D. The change in the Gibbs free energy

27. Compressibility factor Z of a gas is

A. The ratio of fugacity in the given state to fugacity in the standard state
B. The ratio of actual volume to the volume of the gas if it were ideal
C. The change in volume with temperature at constant pressure
D. The difference between actual volume and ideal gas volume

28. The temperature at which a transition occurs from a compressibility factor less than 1.00 to that greater than 1.00 is known as

A. The critical temperature
B. The critical solution temperature
C. The inversion point
D. The Boyle point

29. The coefficient of compressibility k is defined as

A. $-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$
B. $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$
C. $\left(\frac{\partial T}{\partial P}\right)_H$
D. $\left(\frac{\partial Q}{\partial T}\right)_V$

30. For any equation of state to be valid, at the critical point the critical isotherm should have

A. A maximum
B. A minimum
C. A point of inflection
D. Negative slope

31. At constant temperature and pressure, the decrease in Gibbs free energy is a measure of

A. The maximum work
B. The maximum net work
C. The unavailable energy
D. The loss in capacity to do work

32. In thermodynamics, a *phase* means

A. A closed system
B. An open system
C. A homogeneous system
D. A heterogeneous system

33. The net change in a state function is zero for

A. A reversible process
B. An Irreversible process

C. A cyclic process
D. A non-cyclic process

34. The third law of thermodynamics deals with
A. Chemical reactions
B. Quantitative equivalence between heat and work
C. Rate of change of a process
D. Absolute entropy of perfect crystalline substances

35. $DG = DA$ for a process occurring at
A. Constant pressure
B. Constant volume
C. Constant pressure and constant temperature
D. Constant pressure and constant volume

36. As pressure approaches zero, fugacity coefficient value tends to
A. Pressure
B. Zero
C. Unity
D. Infinity

37. For a gas obeying the van der Waals equation of state, at the critical temperature,
A. Both $(\partial P/\partial V)_T$ and $(\partial^2 P/\partial V^2)_T$ are zero
B. The first derivative is zero, while the second derivative is non-zero
C. The second derivative is zero while the first derivative is non-zero
D. Both the derivatives are non-zero

(1991)

38. For an ideal gas, the slope of the pressure-volume curve at a given point will be
A. Steeper for an isothermal than for an adiabatic process
B. Steeper for an adiabatic than for an isothermal process
C. Identical for both the processes
D. Of opposite sign

(1991)

39. The shape of *T-S* diagram for Carnot cycle is
A. A rectangle
B. A rhombus
C. A trapezoid
D. A circle

(1991)

40. During Joule–Thomson expansion of gases,
A. Enthalpy remains constant
]B. Entropy remains constant
C. Temperature remains constant
D. None of the above

(1992)

41. For a single-component, two-phase mixture, the number of independent variable properties are
A. Two
B. One
C. Zero
D. Three

(1992)

42. Ideal gas law is applicable at
A. Low T, low P
B. High T, high P
C. Low T, high P
D. High T, low P

(1994)

43. The second law of thermodynamics states that
A. The energy change of a system undergoing any reversible process is zero
B. It is not possible to transfer heat from a lower temperature to a higher temperature
C. The total energy of the system and the surroundings remain constant
D. None of the above

(1994)

44. A solid is transformed into vapour without changing into the liquid phase
A. At the triple point
B. At the boiling point
C. Below the triple point
D. Always

(1995)

45. At the inversion point, the Joule–Thomson coefficient is
A. Positive
B. Negative
C. Zero
D. Cannot be generalised

(1995)

46. The kinetic energy of a gas molecule is zero at
A. 0∞C
B. 273∞C
C. 100∞C
D. –273∞C

(1995)

47. Assuming that CO_2 obeys the perfect gas law, the density of CO_2 in kg/m^3 at 536 K and 202.6 kPa is
A. 1
B. 2

C. 3
D. 4

(1995)

48. A closed system is cooled reversibly from 373 K to 323 K. If no work is done on the system

A. Its internal energy (U) decreases and its entropy (S) increases
B. U and S both decrease
C. U decreases but S is constant
D. U is constant but S decreases

(1995)

49. The equation $dU = T\,dS - P\,dV$ is applicable to infinitesimal changes occurring in

A. An open system of constant composition
B. A closed system of constant composition
C. An open system with changes in composition
D. A closed system with changes in composition

(1996)

50. A system undergoes a change from a given initial state to a given final state either by an irreversible process or by a reversible process. Then

A. $\mathsf{D}S_I$ is always $>$ $\mathsf{D}S_R$
B. $\mathsf{D}S_I$ is sometimes $>$ $\mathsf{D}S_R$
C. $\mathsf{D}S_I$ is always $<$ $\mathsf{D}S_R$
D. $\mathsf{D}S_I$ is always $=$ $\mathsf{D}S_R$

where $\mathsf{D}S_I$ and $\mathsf{D}S_R$ are the entropy changes of the system for the irreversible and reversible processes, respectively.

(1997)

51. The change in Gibbs free energy for vaporisation of a pure substance is

A. Positive
B. Negative
C. Zero
D. May be positive or negative

(1997)

52. A change in state involving a decrease in entropy can be spontaneous only if

A. It is exothermic
B. It is isenthalpic
C. It takes place isothermally
D. It takes place at constant volume

(1998)

53. A Carnot cycle consists of the following steps:

A. Two isothermals and two isentropics
B. Two isobarics and two isothermals
C. Two isochorics and two isobarics

D. Two isothermals and two isochorics

(1998)

54. It is desired to bring about certain change in the state of a system by performing work on the system under adiabatic conditions

A. The amount of work needed is path-dependent

B. Work alone cannot bring about such a change of state

C. The amount of work needed is independent of path

D. More information is needed to conclude anything about the path-dependence or otherwise of the work needed.

(1998)

55. Chemical potential is

A. An extensive property

B. An intensive property

C. A path property

D. A reference property

56. According to the phase rule, the triple point of a pure substance is

A. Invariant

B. Univariant

C. Bivariant

D. None of the above

57. Which one of the following is incorrect with reference to partial molar properties?

A. They are intensive properties

B. They are always positive

C. They represent the contribution of individual components to the total solution property

D. They vary with composition of the solution

58. All but one of the following represent the chemical potential of component *i* in solution. Find the odd man out.

A. $\mu_i = \left(\frac{\partial G^t}{\partial n_i}\right)_{T,P,n_j}$

B. $\mu_i = \left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_j}$

C. $\mu_i = \left(\frac{\partial A^t}{\partial n_i}\right)_{T,P,n_j}$

D. $\mu_i = \left(\frac{\partial H^t}{\partial n_i}\right)_{S,P,n_j}$

59. Which one of the following statements is not valid for an ideal solution?

A. There is no volume change on mixing

B. There is no enthalpy change on mixing

C. There is no entropy change on mixing

D. Fugacity is directly proportional to concentration.

60. For the standard state of pure component at the solution pressure, the activity of a component in an ideal solution is equal to

A. its fugacity in the solution

B. its mole fraction in the solution

C. its partial pressure

D. its chemical potential

61. Which one of the following is the correct form of Gibbs–Duhem equation for a binary solution?

A. $x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right) = x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)$

B. $x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right) = -\,x_2\left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)$

C. $x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right) = x_2\left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)$

D. $x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right) = (1 - x_1)\left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)$

62. Which one of the following is true for the excess property M^E?

A. $M^E = M - \mathsf{S}\, x_i M_i$

B. $M^E = M - \mathsf{S}\, x_i \overline{M_i}$

C. $M^E = M - M^{\mathrm{id}}$

D. $M^E = \mathsf{D}M$

63. One of the following statements is incorrect for a multicomponent system consisting of two phases in thermodynamic equilibrium. Identify it.

A. The temperatures of both phases are the same

B. The pressure is uniform throughout

C. The concentrations of a component in both phases are equal

D. The chemical potentials of a component in both phases are equal

64. When an ideal binary solution is boiled at constant pressure in a closed container,

A. The boiling temperature remains constant at some value between the bubble point and the dew point, till the entire liquid is vaporised

B. The boiling temperature varies between the bubble point and the dew point of the solution

C. The boiling occurs at a constant temperature known as the bubble point

D. The boiling occurs either at the bubble point or at the dew point

65. The value of activity coefficient for an ideal solution is

A. One

B. Zero

C. Equal to Henry’s law constant

D. Equal to the vapour pressure

66. A solution exhibiting positive deviation from ideality

A. Always forms a minimum boiling azeotrope
B. Always forms a maximum boiling azeotrope
C. Has a total vapour pressure that is less than that predicted by Raoult’s law
D. When formed from its constituents there is an absorption of heat

67. Which one of the following statements is true with reference to the minimum boiling azeotropes?

A. There is a minimum on the vapour-pressure curve
B. The solution exhibits positive deviation from ideality
C. The dew point is greater than the bubble point
D. The activity coefficients are less than unity

68. The vaporisation equilibrium constant (*K*-factor) depends upon

A. Temperature only
B. Pressure only
C. Temperature and pressure only
D. Temperature, pressure and concentration

69. The vapour–liquid equilibrium data are thermodynamically inconsistent if

A. The slopes of the $\ln \gamma_1$ vs x_1 and $\ln \gamma_2$ vs x_1 curves have opposite signs
B. When plotted against x_1, $\ln \gamma_2$ and $\ln \gamma_1$ curves pass through a maximum at the same composition
C. Both γ_1 and γ_2 are greater than unity
D. $\ln \gamma_1$ vs x_1 curve has a maximum and $\ln \gamma_2$ vs x_1 curve has a minimum at a particular x_1.

70. A mixture of two immiscible liquids A and B is in equilibrium with its vapour at temperature *T* and pressure *P*. The vapour pressures of pure A and pure B are P_A^S and P_B^S respectively. The relation applicable to the system is

A. $P = P_A^S + P_B^S$
B. $P = x_A P_A^S + x_B P_B^S$
C. $P = \gamma_A x_A P_A^S + \gamma_B x_B P_B^S$
D. $T > T_A + T_B$, where T_A and T_B are boiling points of pure A and pure B respectively

71. The mutual solubility of two partially miscible liquids increases with temperature. At what temperature do the two liquid phases become identical?

A. At the critical point
B. At the three-phase temperature
C. At the upper critical solution temperature
D. At the dew point

72. Benzene and water may be considered immiscible. A mixture of benzene (20 g) and water (80 g) is taken in a vessel and boiled. It boils at 101.3 kPa and 342 K. At this temperature vapour pressure of benzene is 71.18 kPa and that of water is 30.12 kPa. What is the concentration of benzene in the vapour in mass per cent?

A. 70%
B. 91%
C. 20%
D. 80%

73. The necessary and sufficient condition for equilibrium between two phases is
A. Concentration of each component should be same in the two phases
B. The temperature of each phase should be the same
C. The pressure should be same in the two phases
D. The chemical potential of each component should be same in the two phases

(1992)

74. For a system in equilibrium, at a given temperature and pressure,
A. The entropy must be a minimum
B. The enthalpy must be a minimum
C. The internal energy must be a minimum
D. The Gibbs free energy must be a minimum

(1991)

75. To obtain the integrated form of Clausius–Clapeyron equation

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_V}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

from the exact Clapeyron equation, it is assumed that:
A. The volume of the liquid phase is negligible compared to that of the vapour phase
B. The vapour phase behaves as an ideal gas
C. The heat of vaporisation is independent of temperature
D. All the above are applicable

(1991)

76. One mole of a binary mixture of a given composition is flash vaporised at a fixed P and T. If Raoult's law is obeyed, then changing the feed composition would affect
A. The product composition but not the fraction vaporised
B. The product composition as well as the fraction vaporised
C. The fraction vaporised but not the product composition
D. Neither the product composition nor the fraction vaporised

(1997)

77. The molar excess free energy, G^E, for a binary liquid mixture at T and P is given by $G^E/RT = Ax_1x_2$, where A is constant. The corresponding equation for $\ln g_1$, where g_1 is the activity coefficient of component 1, is
A. Ax_2^2
B. Ax_1
C. Ax_2
D. Ax_1^2

(1997)

78. A liquid mixture contains 30% *o*-xylene, 60% *p*-xylene and 10% *m*-xylene (all percentages in w/w). Which of the following statements would be true for this mixture?
   A. The mixture exhibits an azeotrope at 101.3 kPa
   B. The composition of the mixture in per cent by volume is: *o*-xylene 30, *p*-xylene 60 and *m*-xylene 10
   C. The composition of the mixture in mole per cent is: *o*-xylene 30, *p*-xylene 60 and *m*-xylene 10
   D. The mixture contains optical isomers

(1998)

79. The theoretical minimum work required to separate one mole of a liquid mixture at 1 bar, containing 50 mole per cent each of *n*-heptane and *n*-octane into pure compounds each at 1 bar is
   A. $-2RT \ln 0.5$
   B. $-RT \ln 0.5$
   C. $0.5RT$
   D. $2RT$

(1996)

80. If the heat of solution of an ideal gas in a liquid is negative, then its solubility at a given partial pressure varies with temperature as
   A. Solubility increases as temperature increases
   B. Solubility decreases as temperature increases
   C. Solubility is independent of temperature
   D. Solubility increases or decreases with temperature depending on the Gibbs free energy of the solution

(1998)

81. For evaluation of heat effects, all thermochemical equations can be treated as algebraic equations. This is a consequence of
   A. Le Chatlier's principle
   B. Third law of thermodynamics
   C. Hess's law
   D. Principle of corresponding states

82. For a chemical reaction occurring at equilibrium under constant temperature and pressure, the change in Gibbs free energy is
   A. Maximum
   B. Minimum
   C. Zero
   D. None of the above

83. The equilibrium constant for the reaction $N_2 + 3H_2 = 2NH_3$ is 0.1084. Under the same conditions, the equilibrium constant for the reaction $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$ is
   A. 0.1084

B. 0.3292
C. 0.0118
D. 0.0542

84. The equilibrium constant is independent of
A. The pressure at equilibrium
B. The temperature at equilibrium
C. The number of moles involved in the stoichiometric equation for the reaction
D. The temperature and pressure at the equilibrium

85. For a highly favourable chemical reaction, the standard free energy change is
A. Zero
B. Unity
C. Positive
D. Negative

86. For an exothermic reaction, the increase in temperature results in
A. Increase of K
B. Decrease of K
C. No change of K
D. None of the above

87. For the reaction $N_2 + 3H_2$ □ $2NH_3$, the increase in pressure results in
A. Increase of K
B. Increase in the concentration of ammonia at equilibrium
C. Decrease of K
D. Decrease in the concentration of ammonia at equilibrium

88. For the equilibrium yield in a gas-phase reaction, diluting the reaction mixture with an inert gas
A. Has the same effect as that of an increase in pressure
B. Has the same effect as that of a decrease in pressure
C. Has no correlation with a change in pressure
D. Always produces unfavourable results

89. Which one of the following statements is true for ammonia synthesis reaction?
A. Increase in temperature increases K
B. Increase in pressure decreases the conversion
C. Presence of argon in the reactant stream decreases conversion
D. Increase in pressure increases K

90. The number of degrees of freedom for a system prepared by partially decomposing $CaCO_3$ into an evacuated space is
A. 0
B. 1
C. 2
D. 3

91. An exothermic gas-phase reaction proceeds according to the equation

$3A + 2B \square 2R$

The equilibrium conversion for this reaction:

A. Increases with an increase in temperature
B. Decreases on dilution with an inert gas
C. Decreases with an increase in pressure
D. Is affected by the presence of a catalyst

(1990)

92. The reaction A (l) = R (g) + S (g) is allowed to reach equilibrium conditions in an autoclave. At equilibrium there are two phases, one pure liquid phase of A and the other a vapour phase of A, R and S. Initially, A alone is present. The number of degrees of freedom are

A. 1
B. 2
C. 3
D. 0

(1996)

93. Given

$3H_2 + CO \square CH_4 + H_2O, K_p = 10^{1.84}$

and

$4H_2 + CO_2 \square CH_4 + 2H_2O, K_p = 10^{1.17}$

the K_p for the reaction $CO + H_2O \square CO_2 + H_2$ is

A. $10^{3.01}$
B. $10^{-0.67}$
C. $10^{-3.01}$
D. $10^{0.67}$

(1996)

94. Which of the following is true for virial equation of state?

A. Virial coefficients are universal constants
B. Virial coefficient B represents three-body interactions
C. Virial coefficients are functions of temperature only
D. For some gases, virial equations and ideal gas equation are the same

(1999)

95. A gas mixture of three components is brought in contact with a dispersion of an organic phase in water. The degrees of freedom of the system are

A. 4
B. 3
C. 5
D. 6

(1999)

96. Maxwell's equation corresponding to the identity, $dH = T\,dS + V\,dP + \Sigma \mu_i\, dn_i$, is

A. $\left(\frac{\partial T}{\partial V}\right)_{S,\,n_i} = -\left(\frac{\partial P}{\partial S}\right)_{V,\,n_i}$

B. $\left(\frac{\partial V}{\partial T}\right)_{P,\,n_i} = -\left(\frac{\partial S}{\partial P}\right)_{T,\,n_i}$

C. $\left(\frac{\partial P}{\partial T}\right)_{V,\,n_i} = \left(\frac{\partial S}{\partial V}\right)_{T,\,n_i}$

D. $\left(\frac{\partial T}{\partial P}\right)_{S,\,n_i} = \left(\frac{\partial V}{\partial S}\right)_{P,\,n_i}$

(1999)

97. In a binary liquid solution of components A and B, if component A exhibits positive deviation from Raoult's law then component B

A. exhibits positive deviation from Raoult's law

B. exhibits negative deviation from Raoult's law

C. obeys Raoult's law

D. may exhibit either positive or negative deviation from Raoult's law

(2000)

98. Assume that benzene is insoluble in water. The normal boiling points of benzene and water are 353.3 K and 373.2 K, respectively. At a pressure of 1 atm, the boiling point of a mixture of benzene and water is

A. 353.3 K

B. less than 353.3 K

C. 373.2 K

D. greater than 353.3 K but less than 373.2 K

(2000)

99. On a *P*-*V* diagram of an ideal gas, suppose a reversible adiabatic line intersects a reversible isothermal line at point A. Then at point A, the slope of the reversible adiabatic line $(\partial P/\partial V)_S$ and the slope of the reversible isothermal line $(\partial P/\partial V)_T$ are related as

A. $\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial V}\right)_T$

B. $\left(\frac{\partial P}{\partial V}\right)_S = \left(\frac{\partial P}{\partial V}\right)_T^{\gamma}$

C. $\left(\frac{\partial P}{\partial V}\right)_S = \gamma\left(\frac{\partial P}{\partial V}\right)_T$

D. $\left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{\gamma}\left(\frac{\partial P}{\partial V}\right)_T$

where g = C_P/C_V.

(2000)

100. The thermal efficiency of a reversible heat engine operating between two given thermal reservoirs is 0.4. The device is used either as a refrigerator or as a heat pump between the same reservoirs. The coefficient of performance as a refrigerator $(COP)_R$ and the coefficient of performance as a heat pump $(COP)_{HP}$ are

A. $(COP)_R = (COP)_{HP} = 0.6$

B. $(COP)_R = 2.5$; $(COP)_{HP} = 1.5$

C. $(COP)_R = 1.5$; $(COP)_{HP} = 2.5$

D. $(COP)_R = (COP)_{HP} = 2.5$

(2000)

101. At a given temperature, K_1, K_2 and K_3 are the equilibrium constants for the following reactions 1, 2, 3 respectively:

$$CH_4\,(g) + H_2O\,(g) \Leftrightarrow CO\,(g) + 3H_2\,(g) \qquad (1)$$

$$CO\,(g) + H_2O\,(g) \Leftrightarrow CO_2\,(g) + H_2\,(g) \qquad (2)$$

$$CH_4\,(g) + 2H_2O\,(g) \Leftrightarrow CO_2\,(g) + 4H_2\,(g) \qquad (3)$$

Then K_1, K_2 and K_3 are related as

A. $K_3 = K_1K_2$

B. $K_3 = (K_1K_2)^{0.5}$

C. $K_3 = (K_1 + K_2)/2$

D. $K_3 = (K_1K_2)^2$

(2000)

102. A reasonably general expression for vapour–liquid equilibrium at low to moderate pressures is

$$\phi_i y_i P = \gamma_i x_i f_i^0$$

where f_i is a vapour fugacity coefficient, g_i is the liquid activity coefficient and f_i^0 is the fugacity of pure component i. The K_i value ($y_i = K_i x_i$) is therefore, in general, a function of

A. temperature only

B. temperature and pressure only

C. temperature, pressure and liquid composition x_i only

D. temperature, pressure, liquid composition x_i, and vapour composition y_i

(2001)

103. High pressure steam is expanded adiabatically and reversibly through a well insulated turbine which produces some shaft work. If the enthalpy change and entropy change across the turbine are represented by DH and DS respectively, for this process:

A. D$H = 0$ and D$S = 0$

B. DH □ 0 and D$S = 0$

C. DH □ 0 and DS □ 0

D. D$H = 0$ and DS □ 0

(2001)

104. For the case of a fuel gas undergoing combustion with air, if the air/fuel ratio is in-creased, the adiabatic flame temperature will

A. increase

B. decrease

C. increase or decrease depending on the fuel type

D. not change (2001)

105. The Maxwell relation derived from the differential equation for the Helmholtz free energy (DA) is

A. $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

B. $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

C. $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$

D. $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(2001)

106. At 373 K, water and methyl cyclohexane both have a vapour pressure of 1.0 atm. The latent heats of vaporization are 40.63 kJ/kmol for water and 31.55 kJ/kmol for cyclohexane. The vapour pressure of water at 423 K is 4.69 atm. The vapour pressure of methyl-cyclohexane at 423 K is expected to be

A. Significantly less than 4.69 atm

B. Nearly equal to 4.69 atm

C. Significantly more than 4.69 atm

D. Indeterminate due to lack of data

(2001)

107. Air enters an adiabatic compressor at 300 K. The exit temperature for a compression ratio of 3, assuming air to be an ideal gas (g $= C_p/C_V = 7/5$) and the process to be reversible, is

A. $300(3^{2/7})$

B. $300(3^{3/5})$

C. $300(3^{3/7})$

D. $300(3^{5/7})$

(2001)

108. The extent of reaction is

A. different for reactants and products

B. dimensionless

C. dependent on the stoichiometric coefficients

D. all of the above

(2002)

109. An exothermic reaction takes place in an adiabatic reactor. The product temperature the reactor feed temperature.

A. is always equal to

B. is always greater than

C. is always less than

D. may be greater or less than

(2002)

110. The number of degrees of freedom for an azeotropic mixture of ethanol and water in vapour-liquid equilibrium is

A. 3

B. 1

C. 2

D. 0

(2002)

111. The partial molar enthalpy of a component in an ideal binary gas mixture of composition *z*, at a temperature *T* and pressure *P*, is a function only of

A. *T*

B. *T* and *P*

C. *T*, *P* and *z*

D. *T* and *z*

(2002)

112. Which of the following identities can most easily be used to verify steam table data for superheated steam?

A. $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

B. $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

C. $\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$

D. $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(2002)

113. Steam undergoes isentropic expansion in a turbine from 5000 kPa and 673 K (entropy = 6.65 kJ/kg K) to 150 kPa (entropy of saturated liquid = 1.4336 kJ/kg K, entropy of saturated vapour =

7.2234 kJ/kg K). The exit condition of steam is

A. superheated vapour
B. partially condensed vapour with quality of 0.9
C. saturated vapour
D. partially condensed vapour with quality of 0.1

(2002)

114. A rigid vessel, containing three moles of nitrogen gas at 303 K is heated to 523 K. Assume the average heat capacities of nitrogen to be C_P = 29.1 J/mol K and C_V = 20.8 J/mol K. The heat required, neglecting the heat capacity of the vessel, is

A. 13728 J
B. 19206 J
C. 4576 J
D. 12712 J

(2002)

115. One cubic metre of an ideal gas at 500 K and 1000 kPa expands reversibly to 5 times its volume in an insulated container. If the specific heat capacity (at constant pressure) of the gas is 21 J/mol K, the final temperature will be

A. 35 K
B. 174 K
C. 274 K
D. 154 K

(2002)

116. Ammonia is produced by the following reaction:

$N_2 + 3H_2$ □ $2NH_3$

In a commercial process for ammonia production, the feed to an adiabatic reactor con-tains 1 kmol/s of nitrogen and stoichiometric amounts of hydrogen at 700 K. Assume the feed and product streams to be ideal gas mixtures. The heat of reaction at 700 K for the above reaction is calculated to be – 94.2 kJ/mol. The mean molar heat capacity in the range of 700–800 K are 0.03, 0.0289 and 0.0492 kJ/mol K for nitrogen, hydrogen and ammonia respectively. What is the maximum allowable conversion in the reactor, if the adiabatic temperature rise across the reactor should not exceed 100 K?

A. 87.9%
B. 12.1%
C. 25.8%
D. 74.2%

(2002)

117. In Joule's experiments, an insulated container contains 20 kg of water initially at 25°C. It is stirred by an agitator, which is made to turn by a slowly falling body weighing 40 kg through a height of 4 m. The process is repeated 500 times. The acceleration due to gravity is 9.8 m/s^2. Neglecting the heat capacity of the agitator, the temperature of water in (°C) is

A. 40.5

B. 34.4
C. 26.8
D. 25

(2003)

118. One mole of nitrogen at 8 bar and 600 K is contained in a piston-cylinder assembly. It is brought to 1 bar isothermally against a resisting pressure of 1 bar. The work done (in joules) by the gas is

A. 30554
B. 10373
C. 4988.4
D. 4364.9

(2003)

119. For water at 573 K, it has a vapour pressure of 8592.7 kPa and fugacity 6738.9 kPa. Under these conditions, one mole of water in liquid phase has a volume of 25.28 cm^3, and that in vapour phase 391.1 cm^3. The fugacity of water (in kPa) at 9000 kPa is

A. 6738.9
B. 6753.5
C. 7058.3
D. 9000

(2003)

120. The heat capacity of air can be approximately expressed as

$$C_P = 26.693 + 7.365 \square 10^{-3}T$$

where C_P is in J/mol K and T is in K. The heat given off by one mole of air when cooled at 1 atmospheric pressure from 500°C to –100°C is

A. 10.73 kJ
B. 16.15 kJ
C. 18.11 kJ
D. 18.33 kJ

(2003)

121. A solid metallic block weighing 5 kg has an initial temperature of 500°C; 40 kg of water initially at 25°C is contained in a perfectly insulated tank. The metallic block is brought into contact with water. Both of them come to equilibrium. The specific heat of the block material is 0.4 kJ/kg K. Ignoring the effect of expansion and contraction, and also the heat capacity of the tank, the total entropy change in kJ/kg K is

A. –1.87
B. 0.0
C. 1.26
D. 3.91

(2003)

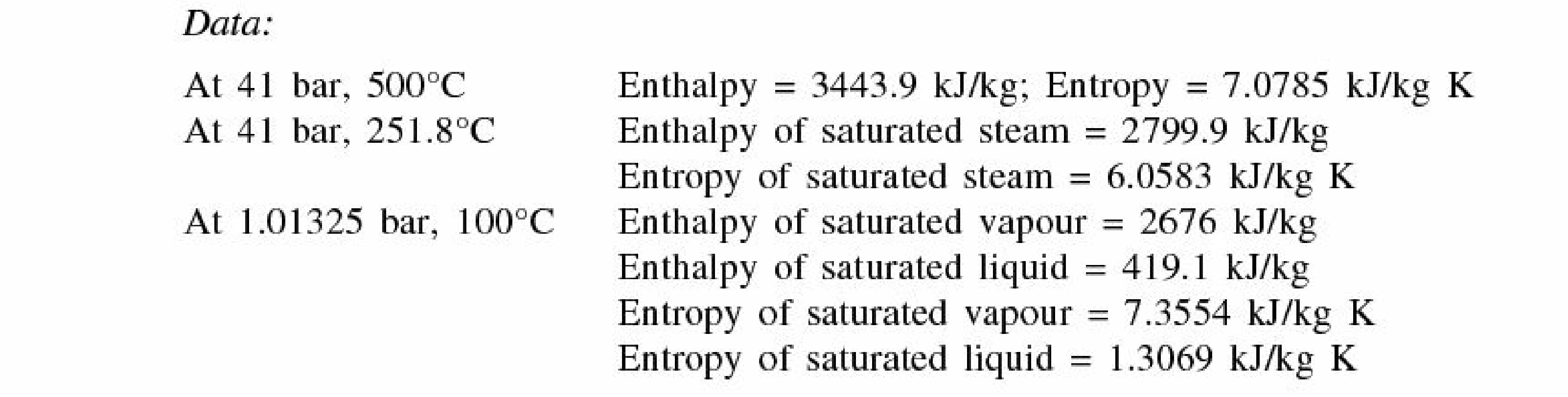
122. The following heat engine produces a power of 100,000 kW. The heat engine operates

between 800 K and 300 K. It has a thermal efficiency equal to 50% of that of the Carnot engine for the same temperatures. The rate at which heat is absorbed from the hot reservoir is

A. 100,000 kW
B. 160,000 kW
C. 200,000 kW
D. 320,000 kW

(2003)

123. A steam turbine operates with a superheated steam flowing at 1 kg/s. The steam is supplied at 41 bar and 500°C, and discharges at 1.01325 bar and 100°C.



Data:

At 41 bar, 500°C	Enthalpy = 3443.9 kJ/kg; Entropy = 7.0785 kJ/kg K
At 41 bar, 251.8°C	Enthalpy of saturated steam = 2799.9 kJ/kg Entropy of saturated steam = 6.0583 kJ/kg K
At 1.01325 bar, 100°C	Enthalpy of saturated vapour = 2676 kJ/kg Enthalpy of saturated liquid = 419.1 kJ/kg Entropy of saturated vapour = 7.3554 kJ/kg K Entropy of saturated liquid = 1.3069 kJ/kg K

The maximum power output (in kW) will be

A. 644.0
B. 767.9
C. 871.3
D. 3024.8

(2003)

124. At 60°C, the vapour pressures of methanol and water are 84.562 kPa and 19.953 kPa respectively. An aqueous solution of methanol at 60°C exerts a pressure of 39.223 kPa; the liquid phase and the vapour phase mole fractions of methanol are 0.1686 and 0.5714 respectively. The activity coefficient of methanol is

A. 1.572
B. 1.9398
C. 3.389
D. 4.238

(2003)

125. One kilogram of saturated steam at 373 K and 1.01325 bar is contained in a rigid walled vessel. It has a volume of 1.673 m^3. It is cooled to 371 K; the saturation pressure is 0.943 bar. One kilogram of water vapour under these conditions has a volume of 1.789 m^3. The amount of water vapour condensed in kilograms is

A. 0.0
B. 0.065
C. 0.1
D. 1.0

(2003)

126. One kilogram of saturated steam at 373 K and 1.01325 bar is contained in a rigid walled vessel. It has a volume of 1.673 m^3. It is cooled to 371 K; the saturation pressure is 0.943 bar. One kilogram of water vapour under these conditions has a volume of 1.789 m^3. The latent heat of condensation in kJ/kg under these conditions is

A. 40732
B. 2676
C. 2263
D. 540

(2003)

127. For an ideal gas mixture undergoing a reversible gaseous phase chemical reaction, the equilibrium constant

A. is independent of pressure
B. increases with pressure
C. decreases with pressure
D. increases/decreases with pressure depending on the stoichiometric coefficients of the reaction

(2004)

128. As pressure approaches zero, the ratio of fugacity to pressure (f/P) for a gas approaches

A. zero
B. unity
C. infinity
D. an indeterminate value.

(2004)

129. A perfectly insulated container of volume V is divided into two equal halves by a partition. One side is under vacuum and the other side contains one mole of an ideal gas (with constant heat capacity) at 298 K. If the partition is broken, the final temperature of the gas in the container

A. will be greater than 298 K
B. will be 298 K
C. will be less than 298 K
D. cannot be determined

(2004)

130. One mole of methane at 298 K undergoes complete combustion in a stoichiometric amount of air also at 298 K. Both the reactants and products are in the gas phase.

$$CH_4 + 2CO_2 \square CO_2 + 2H_2O \; \mathrm{D}H^0{}_{298} = -730 \text{ kJ/mol}$$

If the average specific heat of all the gases/vapours is 40 J/mol K, the maximum temperature rise (in K) of the exhaust gases would be approximately

A. 1225
B. 1335
C. 1525
D. 1735

(2004)

131. A vessel of volume 1000 m^3 contains air which is saturated with water vapour. The total pressure and temperature are 100 kPa and 293 K respectively. Assuming that the vapour pressure of water at 293 K is 2.34 kPa, the amount of water vapour in kilograms in the vessel is approximately

A. 17
B. 20
C. 25
D. 34

(2004)

132. A car tyre of volume 0.057 m^3 is inflated to 300 kPa and 300 K. After the car is driven for 10 hours, the pressure in the tyre increases to 330 kPa. Assume air is an ideal gas and C_V for air is 21 J/mol K. The change in internal energy of air in tyre in J/mol is

A. 380
B. 630
C. 760
D. 880

(2004)

133. A gas obeys $P(V - b) = RT$. The work obtained from reversible isothermal expansion of one mole of this gas from an initial volume V_i to a final volume V_f is

A. $RT \ln \frac{V_f}{V_i}$

B. $RT \ln \frac{V_f - b}{V_i}$

C. $RT \ln \frac{V_f}{V_i - b}$

D. $RT \ln \frac{V_f - b}{V_i - b}$

(2004)

134. A cyclic engine exchanges heat with two reservoirs maintained at 100°C and 300°C, respectively. The maximum work (in J) that can be obtained from 1000 J of heat extracted from the hot reservoir is

A. 349
B. 651
C. 667
D. 1000

(2004)

135. The vapour pressure of water is given by $P^{sat} = A - \frac{5000}{T}$, where A is a constant, P^{sat} is

vapour pressure in atm, and T is temperature in K. The vapour pressure of water (in atm) at 50°C is approximately

A. 0.07
B. 0.09
C. 0.11
D. 0.13

(2004)

136. At standard conditions,

$$N_2 + 2O_2 \rightarrow 2NO_2;\ \Delta G^0 = 100 \text{ kJ/mol}$$

$$NO + \frac{1}{2} O_2 \rightarrow NO_2;\ \Delta G^0 = -35 \text{ kJ/mol}$$

The standard free energy of formation of NO in kJ/mol is

A. 15
B. 30
C. 85
D. 170

(2004)

137. The boiling points for pure water and toluene are 100°C and 110.6°C respectively. Toluene and water are completely immiscible in each other. A well-agitated equimolar mixture of toluene and water is prepared. The temperature at which the above mixture will exert a pressure of one standard atm is

A. less than 100°C
B. 100°C
C. between 100 and 110.6°C
D. 110.6°C

(2004)

138. The boiling points for pure water and toluene are 100°C and 110.6°C respectively. Toluene and water are completely immiscible in each other. A well-agitated equimolar mixture of toluene and water is prepared. At a total pressure of one standard atm exerted by the vapours of water and toluene, the mole fraction of water x_W in the vapour phase satisfies

A. $0 < x_W < 0.5$
B. $x_W = 0.5$
C. $0.5 < x_W < 1.0$
D. $x_W = 1.0$

(2004)

139. In the van der Waal equation of state, what are the criteria applied at the critical point to determine the parameters a and b?

A. $\left(\frac{\partial P}{\partial V}\right)_T = 0 \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$

B. $\left(\frac{\partial V}{\partial P}\right)_T = 0 \quad \left(\frac{\partial^2 V}{\partial P^2}\right)_T = 0$

C. $\left(\frac{\partial P}{\partial T}\right)_V = 0 \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0$

D. $\left(\frac{\partial V}{\partial T}\right)_P = 0 \quad \left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0$

(2005)

140. Which one of the following statements is true?

A. Heat can be fully converted into work.

B. Work cannot be fully converted to heat.

C. The efficiency of a heat engine increases as the temperature of the heat source is increased while keeping the temperature of the heat sink fixed.

D. A cyclic process can be devised whose sole effect is to transfer heat from a lower temperature to a higher temperature.

(2005)

141. A Carnot heat engine cycle is working with an ideal gas. The work performed by the gas during the adiabatic expansion and compression steps, W_1 and W_2 respectively, are related as

A. $|W_1| > |W_2|$

B. $|W_1| < |W_2|$

C. $W_1 = W_2$

D. $W_1 = -W_2$

(2005)

142. The van Laar activity coefficient model for a binary mixture is given in the form

$$\ln \gamma_1 = \frac{A^*}{\left[1 + (A^*/B^*)\dfrac{x_1}{x_2}\right]^2}$$

$$\ln \gamma_2 = \frac{B}{\left[1 + (B^*/A^*)\dfrac{x_2}{x_1}\right]^2}$$

Given $g_1 = 1.40$, $g_2 = 1.25$, $x_1 = 0.25$, $x_2 = 0.75$, determine the constants A^* and B^*.

A. $A^* = 0.5$, $B^* = 0.3$

B. $A^* = 3$, $B^* = 0.5$

C. $A^* = 0.333$, $B^* = 0.2$
D. $A^* = 2$, $B^* = 0.333$

(2005)

143. A liquid mixture of benzene and toluene is in equilibrium with its vapour at 101.3 kPa and 373 K. The vapour pressures of benzene and toluene at 373 K are 156 and 63 kPa respectively. Assuming that the system obeys Raoult's law, the mole fraction of benzene in the liquid phase is
A. 0.65
B. 0.41
C. 0.065
D. 0.04

(2005)

144. A frictionless cylinder piston assembly contains an ideal gas. Initially at pressure (P_1) = 100 kPa, temperature (T_1) = 500 K and volume (V_1) = $700 \square 10^{-6}$ m^3. This system is supplied with 100 J of heat and pressure is maintained constant at 100 kPa. The enthalpy variation is given by h (J/mol) = 30000 + 50T, where T is the temperature in K, and the universal gas constant R = 8.314 J/mol K. The final volume of the gas (V_2) in m^3 is
A. $700 \square 10^{-6}$
B. $866.32 \square 10^{-6}$
C. $934.29 \square 10^{-6}$
D. $1000.23 \square 10^{-6}$

(2005)

145. A frictionless cylinder piston assembly contains an ideal gas. Initially pressure (P_1) = 100 kPa, temperature (T_1) = 500 K and volume (V_1) = $700 \square 10^{-6}$ m^3. This system is supplied with 100 J of heat and pressure is maintained constant at 100 kPa. The enthalpy variation is given by h (J/mol) = 30000 + 50T, where T is the temperature in K, and the universal gas constant R = 8.314 J/mol K. The change in internal energy of the gas is
A. 0
B. 100
C. 23.43
D. 83.37

(2005)

146. Heat and work are
A. intensive properties
B. extensive properties
C. point functions
D. path functions

147. A frictionless piston-cylinder device contains a gas initially at 0.8 MPa and 0.015 m^3. It expands quasi-statically at constant temperature to a final volume of 0.030 m^3. The work output

(in kJ) during the process will be

A. 8.32

B. 12.0

C. 554.67

D. 8320.00

148. The contents of a well-insulated tank are heated by a resistor of 23 W in which 10 A current is flowing. Consider the tank along with its contents as a thermodynamic system. The work done by the system and the heat transfer to the system are positive. The rates of heat Q, work W and change in internal energy DU during the process in kW are

A. $Q = 0$, $W = -2.3$, D$U = +2.3$

B. $Q = +2.3$, $W = 0$, D$U = +2.3$

C. $Q = +2.3$, $W = 0$, D$U = -2.3$

D. $Q = 0$, $W = +2.3$, D$U = -2.3$

149. A compressor undergoes a reversible steady-flow process. The gas at inlet and outlet of the compressor is designated as state 1 and state 2, respectively. Potential and kinetic energy changes are to be ignored. The following notations are used:

V specific volume and P pressure of the gas

The specific work required to be supplied to the compressor for this gas compression process is

A. $\int_1^2 P\,dV$

B. $\int_1^2 V\,dP$

C. $V_1(P_2 - P_1)$

D. $P_2(V_1 - V_2)$

150. A gas contained in a cylinder is compressed, the work required for compression being 5000 kJ. During the process heat interaction of 2000 kJ causes the surroundings to be heated. The change in internal energy of gas during the process is

A. –7000 kJ

B. –3000 kJ

C. 3000 kJ

D. 7000 kJ

151. A mono-atomic ideal gas (g = 1.67, molecular weight = 40) is compressed adiabatically from 0.1 MPa, 300 K to 0.2 MPa. The universal gas constant is 8.314 kJ/kmol K. The work o compression of the gas (in kJ/kg) is

A. 29.7

B. 19.9

C. 13.3

D. 0

152. A gas expands in a frictionless piston-cylinder arrangement. The expansion process is very

slow and is resisted by an ambient pressure of 100 kPa. During the expansion process, the pressure of the system (gas) remains constant at 300 kPa. The change in volume of the gas is 0.01 m^3. The maximum amount of work that could be utilized from the above process is

A. zero
B. 1 kJ
C. 2 kJ
D. 3 kJ

153. One kilogram water at room temperature is brought into contact with a high temperature thermal reservoir. The entropy change of the universe is

A. equal to entropy change of the reservoir
B. equal to entropy change of water
C. equal to zero
D. always positive

154. If a closed system is undergoing an irreversible process, the entropy of the system

A. must increase
B. always remains constant
C. must decrease
D. can increase, decrease or remain constant

155. Two moles of oxygen are mixed adiabatically with another 2 mol of oxygen in a mixing chamber, so that the final total pressure and temperature of the mixture become equal to that of the individual constituents at their initial states. The universal gas constant is given as R. The change in entropy due to mixing per mole of oxygen is given by

A. $-R \ln 2$
B. zero
C. $R \ln 2$
D. $R \ln 4$

156. Availability of a system at any given state is

A. a property of the system
B. the maximum work obtainable as the system goes to dead state
C. the total energy of the system
D. the maximum useful work obtainable as the system goes to dead state

157. Consider the following two processes:

I. A heat source at 1200 K loses 2500 kJ of heat to sink at 800 K
II. A heat source at 800 K loses 2000 kJ of heat to sink at 500 K

which of the following statements is true?

A. Process I is more irreversible than Process II
B. Process II is more irreversible than Process I
C. Irreversibility associated in both the processes is equal
D. Both the processes are reversible

158. An irreversible heat engine extracts heat from a high temperature source at a rate of 100 kW and rejects heat to a sink at a rate of 50 kW. The entire work output of the heat engine is

used to drive a reversible heat pump operating between a set of independent isothermal heat reservoirs at 17°C and 75°C. The rate (in kW) at which the heat pump delivers heat to its high temperature sink is

A. 50

B. 250

C. 300

D. 360

Common data for Questions 159 and 160.

In an experimental set-up, air flows between two stations P and Q adiabatically. The direction of flow depends on the pressure and temperature conditions maintained at P and Q. The conditions at station P are 150 kPa and 350 K. The temperature at station Q is 300 K. The following are the properties and relations pertaining to air:

Specific heat at constant pressure C_P = 1.005 kJ/kg K, Specific heat at constant volume C_V = 0.718 kJ/kg K, Universal gas constant R = 0.287 kJ/kg K, Enthalpy $H = C_pT$, Internal energy $U = C_VT$.

159. If the air has to flow from station P to station Q, the maximum possible value of pressure in kPa at station Q is close to

A. 50

B. 87

C. 128

D. 150

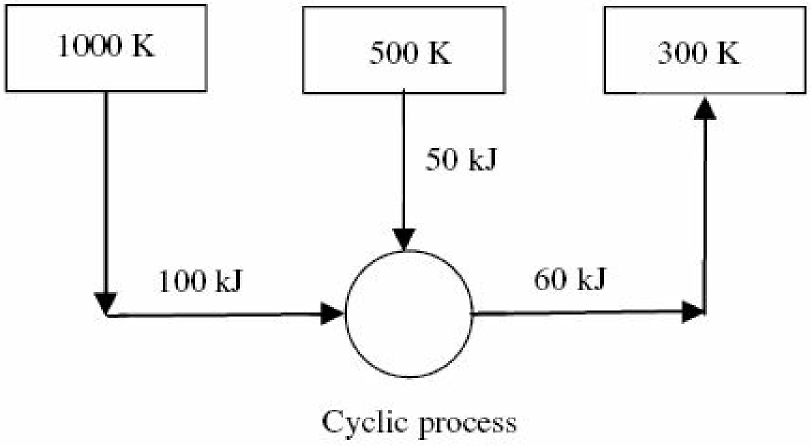
160. If the pressure at station Q is 50 kPa, the change in entropy ($S_Q - S_P$) in kJ/kg K is

A. – 0.155

B. 0 C. 0.160

D. 0.355

161. A cyclic device operates between three thermal reservoirs, as shown in the figure. Heat is transferred to/from the cyclic device. It is assumed that heat transfer between each thermal reservoir and cyclic device takes place across negligible temperature difference. Interactions between the cyclic device and the respective thermal reservoirs that are shown in the figure are all in the form of heat transfer.



The cyclic device can be:

A. A reversible heat engine

B. A reversible heat pump or a reversible refrigerator

C. An irreversible heat engine

D. An irreversible heat pump or an irreversible refrigerator

162. A heat transformer is a device that transfers a part of the heat supplied to it at an intermediate temperature, to a high temperature reservoir while rejecting the remaining part to a low temperature heat sink. In such a heat transformer, 100 kJ of heat is supplied at 350 K. The maximum amount of heat in kJ that can be transferred to
400 K, when the rest is rejected to a heat sink at 300 K, is

A. 12.50

B. 14.29 C. 33.33

D. 57.14

163. An ideal gas of mass m and temperature T_1 undergoes a reversible isothermal process from an initial pressure P_1 to final pressure P_2. The heat loss during the process is Q. The entropy change DS of the gas is

A. $mR \ln \frac{P_2}{P_1}$

B. $mR \ln \frac{P_1}{P_2}$

C. $mR \ln \frac{P_2}{P_1} - \frac{Q}{T_1}$

D. zero

Common data for Questions 164 and 165.

Nitrogen gas (molecular weight 28) is enclosed in a cylinder by a piston, at the initial condition of 2 bar, 298 K and 1 m^3. In a particular process, the gas slowly expands under isothermal condition, until the volume becomes 2 m^3. Heat exchange occurs with the atmosphere at 298 K during this process.

164. The work interaction for the nitrogen gas is

A. 200 kJ

B. 138.6 kJ

C. 2 kJ

D. –200 kJ

165. The entropy change for the universe during the process in kJ/K is

A. 0.4652

B. 0.0067 C. 0

D. – 0.6711

166. A Carnot cycle is having an efficiency of 0.75. If the temperature of the high temperature reservoir is 727°C, what is the temperature of the low temperature reservoir?

A. 23°C

B. –23°C

C. 0°C

D. 250°C

167. A cyclic heat engine does 50 kJ of work per cycle. If the efficiency of the heat engine is 75%, the heat rejected per cycle is

A. $16\frac{2}{3}$ kJ

B. $33\frac{1}{3}$ kJ

C. $37\frac{1}{3}$ kJ

D. $66\frac{2}{3}$ kJ

168. A solar collector receiving solar radiation at the rate of 0.6 kW/m^2 transforms it to the internal energy of a fluid at an overall efficiency of 50%. The fluid heated to 350 K is used to run a heat engine which rejects heat at 313 K. If the heat engine is to deliver 2.5 kW power, the minimum area of the solar collector required would be

A. 8.33 m^2

B. 16.66 m^2

C. 39.68 m^2

D. 79.36 m^2

169. Considering the relationship $TdS = dU + PdV$ between the entropy S, internal energy U, pressure P, temperature T and volume V, which of the following statements is correct?

A. It is applicable only for a reversible process

B. For an irreversible process, $TdS > dU + PdV$

C. It is valid only for an ideal gas

D. It combines first and second laws for a reversible process

170. A balloon containing an ideal gas is initially kept in an evacuated and insulated room. The balloon ruptures and the gas fills up the entire room. Which one of the following statements is true at the end of the above process?

A. The internal energy of the gas decreases from its initial value but the enthalpy remains constant.

B. The internal energy of the gas increases from its initial value but the enthalpy remains constant.

C. Both internal energy and enthalpy of the gas remain constant.

D. The internal energy and enthalpy of the gas increase.

171. In a steady-state flow process taking place in a device with a single inlet and single outlet, the

work done per unit mass flow rate is given by $W = -\int_{\text{inlet}}^{\text{outlet}} V\,dP$, where *V* is the specific volume and *P* is the pressure. The expression for *W* given above is

A. valid only if the process is both reversible and adiabatic

B. valid only if the process is both reversible and isothermal

C. valid for any reversible process

D. incorrect; it must be $W = \int_{\text{inlet}}^{\text{outlet}} P\,dV$

172. The following four figures have been drawn to represent a fictitious thermodynamic cycle on the *P*–*V* and *T*–*S* planes:

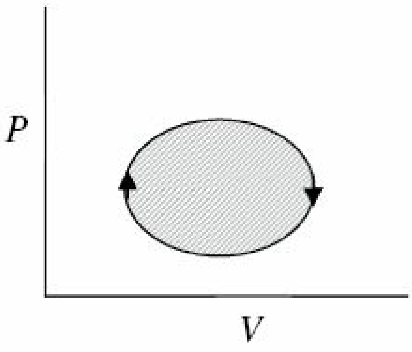


Fig. 1

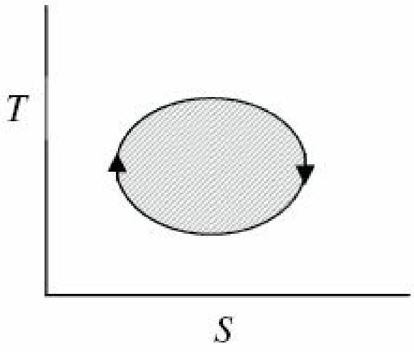


Fig. 2

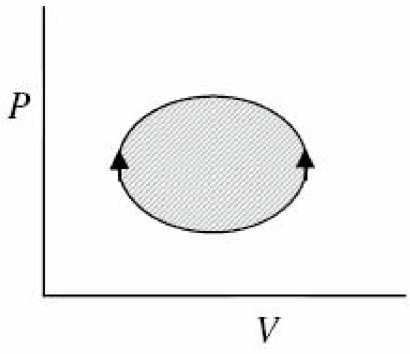


Fig. 3

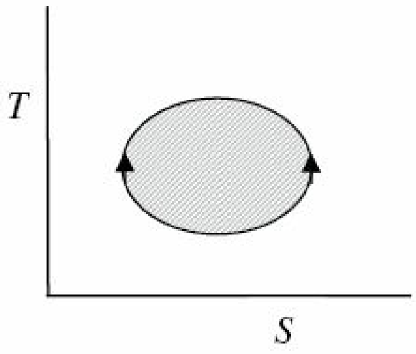


Fig. 4

According to the first law of thermodynamics, equal areas are enclosed by

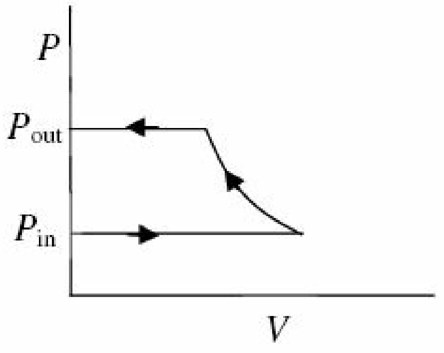
A. Figs. 1 and 2

B. Figs. 1 and 3

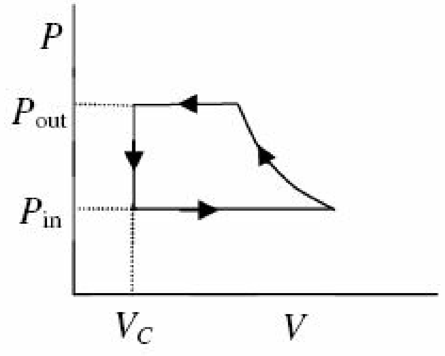
C. Figs. 1 and 4

D. Figs. 2 and 3

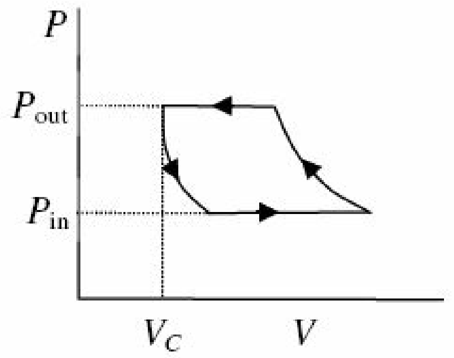
173. A *P*–*V* diagram has been obtained from a test on a reciprocating compressor. Which of the following represents that diagram?



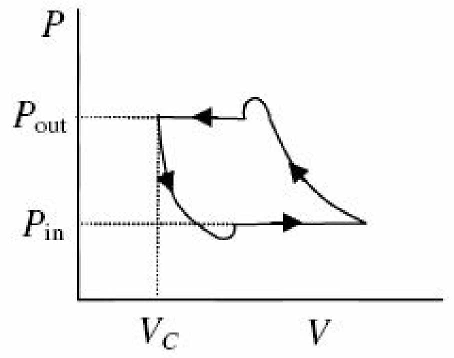
(A)



(B)



(C)



(D)

Common data for Questions 174 and 175

A football was inflated to a gauge pressure of 1 bar when the ambient temperature was 15°C. When the game started next day, the air temperature at the stadium was 5°C. Assume that the volume of the football remains constant at 2.5×10^{-3} m^3. Take ratio of specific heats to be 1.4.

174. The amount of heat lost by the air in the football and the gauge pressure of air in the football at the stadium respectively equal

A. 30.6 J, 1.94 bar
B. 21.8 J, 0.93 bar
C. 61.1 J, 1.94 bar
D. 43.7 J, 0.93 bar

175. Gauge pressure of air to which the ball must have been originally inflated so that it would equal 1-bar gauge at the stadium is

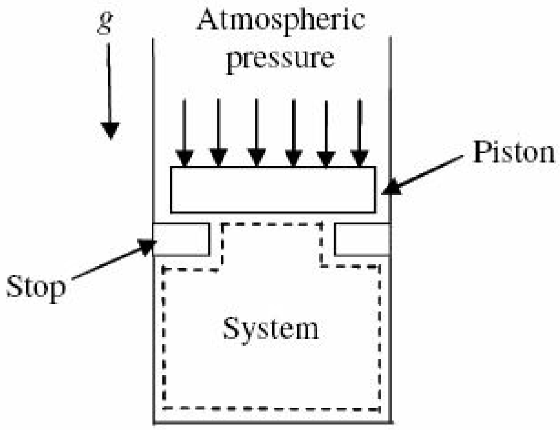
A. 2.23 bar
B. 1.94 bar
C. 1.07 bar
D. 1.00 bar

176. A positive value of Joule Thomson coefficient of a fluid means

A. Temperature drops during throttling
B. Temperature remains constant during throttling
C. Temperature rises during throttling
D. None of the above

Common data for Questions 177, 178 and 179

In the figure shown, the system is a pure substance kept in a piston-cylinder arrangement. The system is initially a two-phase mixture containing 1 kg of liquid and 0.03 kg of vapour at a pressure of 100 kPa. Initially the piston rests on a set of stops as shown in the figure. A pressure of 200 kPa is required to exactly balance the weight of the piston and the outside atmospheric pressure. Heat transfer takes place into the system until its volume increases by 50%. Heat transfer to the system occurs in such a manner that the piston, when allowed to move, does so in a very slow quasi-static/quasi-equilibrium process. The thermal reservoir from which heat is transferred to the system has a temperature of 400°C. Average temperature of the system boundary can be taken as 175°C. The heat transfer to the system is 1 kJ, during which its entropy increases by 10 J/K. Specific volumes of liquid (V_l) and vapour (V_g) phases, as well as values of saturation temperatures, are given in the table below.



Pressure, (kPa)	*Saturation temperature* T^{sat} (°C)	V_l (m^3/kg)	V_g (m^3/kg)
100	100	0.001	0.1
200	200	0.0015	0.002

177. At the end of the process, which one of the following situations will be true?
   A. Superheated vapour will be left in the system
   B. No vapour will be left in the system
   C. A liquid + vapour mixture will be left in the system
   D. The mixture will exist at a dry saturated vapour state

178. The work done by the system during the process is
   A. 0.1 kJ
   B. 0.2 kJ
   C. 0.3 kJ
   D. 0.4 kJ

179. The net entropy generation (considering the system and the thermal reservoir together) during the process is closest to
   A. 7.5 J/K
   B. 7.7 J/K

C. 8.5 J/K

D. 10 J/K

180. A gas having a negative Joule Thomson coefficient ($m < 0$), when throttled will

A. become cooler

B. become warmer

C. remain at the same temperature

D. either be cooler or warmer depending on the type of gas

181. An ideal Brayton cycle operating between the pressure limits of 1 bar and 6 bar has minimum and maximum temperatures of 300 K and 1500 K. The ratio of the specific heats of the working fluid is 1.4. The approximate final temperatures in kelvin at the end of the compression and expansion processes are, respectively

A. 500 and 900

B. 900 and 500

C. 500 and 500

D. 900 and 900

182. The values of enthalpy of steam at the inlet and outlet of a steam turbine in a Rankine cycle are 2800 kJ/kg and 1800 kJ/kg respectively. Neglecting pump work, the specific steam consumption in kg/kWh is

A. 3.6

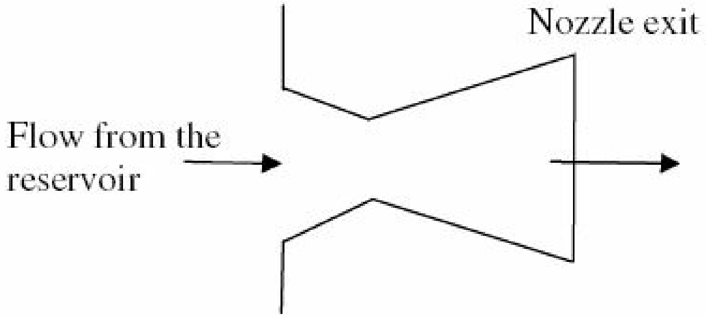
B. 0.36

C. 0.06

D. 0.01

Statements for linked answer Questions 183 and 184.

The temperature and pressure of air in a large reservoir are 400 K and 3 bar, respectively. A converging-diverging nozzle of exit area 0.005 m^2 is fitted to the reservoir as shown in the figure. The static pressure of air at the exit section, for isentropic flow through the nozzle, is 50 kPa. The characteristic gas constant and the ratio of specific heats of air are 0.287 kJ/kg K and 1.4, respectively.



183. The density of air in kg/m^3 at the nozzle exit is

A. 0.560

B. 0.600

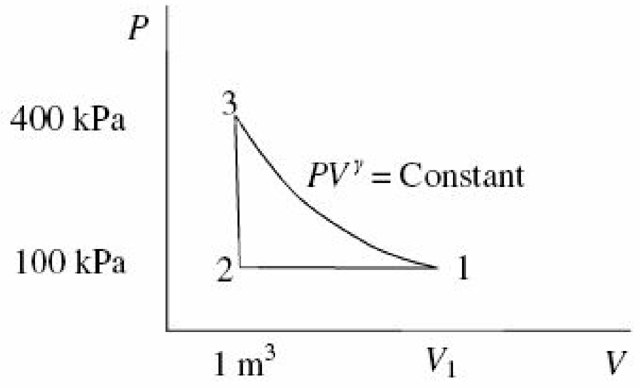
C. 0.727

D. 0.800

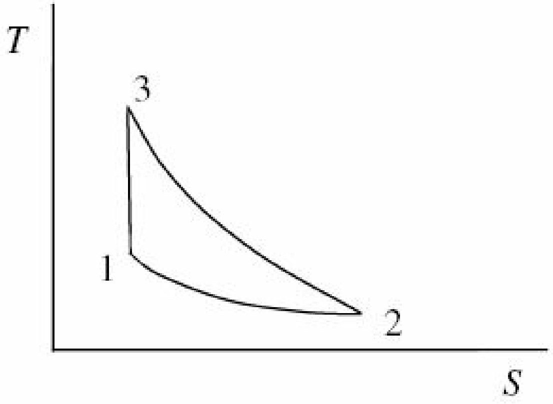
184. The mass flow rate of air through the nozzle in kg/s is

- A. 1.30
- B. 1.77
- C. 1.85
- D. 2.06

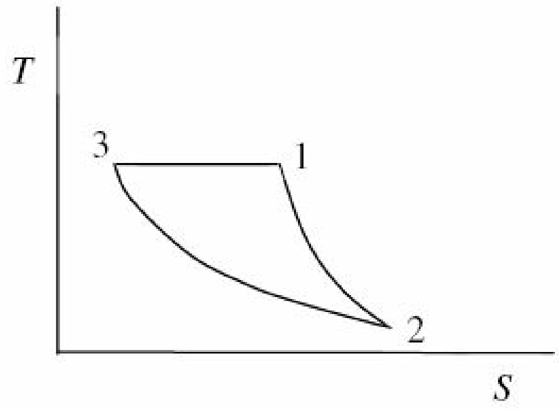
185. A cyclic process is represented on P–V diagram as shown below:



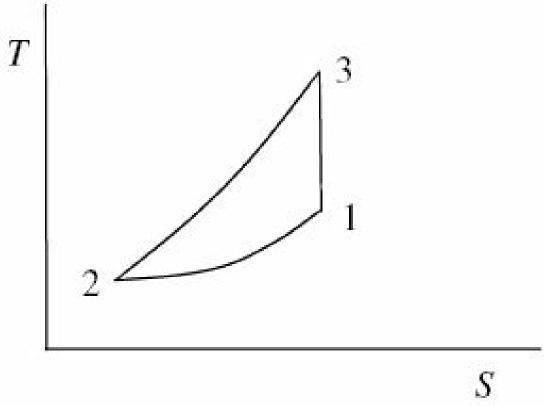
The above cycle can be equivalently represented on a T–S plane by



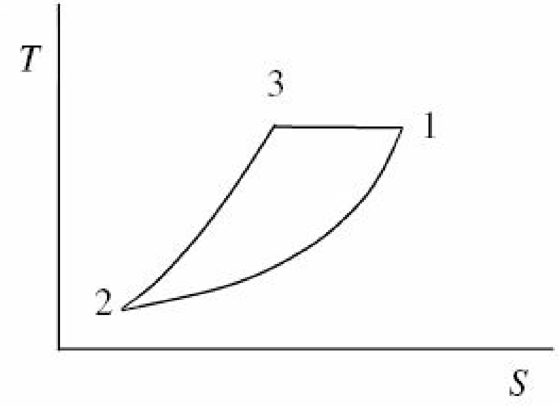
(A)



(B)



(C)



(D)

186. Nitrogen at an initial state of 10 bar, 1 m^3 and 300 K is expanded isothermally to a final

volume of 2 m^3. The *P*-*V*-*T* relation is $\left(P + \frac{a}{V^2}\right)V = RT$, where *a* > 0. The final pressure.

A. will be slightly less than 5 bar

B. will be slightly more than 5 bar

C. will be exactly 5 bar

D. cannot be ascertained in the absence of the value of *a*

Common data for Questions 187 and 188

The following table of properties was printed out for saturated liquid and saturated vapour of ammonia. The titles for only the first two columns are available. All that we know is that the other columns (columns 3 to 8) contain data on specific properties, namely, internal energy (kJ/kg), enthalpy (kJ/kg) and entropy (kJ/kg K).

T °C	*P*, bar						
–20	190.2	88.76	0.3657	89.05	5.6155	1299.5	1418.0
0	429.6	179.69	0.7114	180.36	5.3309	1318.0	1442.2
20	857.5	272.89	1.0408	274.30	5.0860	1332.2	1460.2
40	1554.9	368.74	1.3574	371.43	4.8662	1341.0	1470.2

187. The specific enthalpy data are in columns

A. 3 and 7

B. 3 and 8

C. 5 and 7

D. 5 and 8

188. When the saturated liquid at 40°C is throttled to –20°C, the quality at exit will be

A. 0.189

B. 0.212

C. 0.231

D. 0.788

189. A single acting two-stage compressor with complete intercooling delivers air at 16 bar. Assuming an intake state of 1 bar at 15°C, the pressure ratio per stage is

A. 16

B. 8

C. 4

D. 2

190. A small steam whistle (perfectly insulated and doing no shaft work) causes a drop of 0.8 kJ/kg in the enthalpy of steam from entry to exit. If the kinetic energy of the steam at entry is negligible, the velocity of the steam at exit is

A. 4 m/s

B. 40 m/s

C. 80 m/s

D. 120 m/s

191. When an ideal gas with constant specific heats is throttled adiabatically, with negligible changes in kinetic and potential energies

A. $DH = 0$, $DT = 0$

B. $DH > 0$, $DT = 0$

C. $DH > 0$, $DS > 0$

D. $DH = 0$, $DS > 0$

where H, T and S represent respectively, enthalpy, temperature and entropy.

Common data for Questions 192 and 193.

Air enters an adiabatic nozzle at 300 kPa, 500 K with a velocity of 10 m/s. It leaves the nozzle at 100 kPa with a velocity of 180 m/s. The inlet area is 80 cm^2. The specific heat C_P of air is 1008 J/kg K.

192. The exit temperature of air is

A. 516 K

B. 532 K

C. 484 K

D. 468 K

193. The exit area of the nozzle in cm^2 is

A. 90.1

B. 56.3

C. 4.4

D. 12.9

194. A heat engine operates at 75% of the maximum possible efficiency. The ratio of the heat source temperature (in K) to the heat sink temperature (in K) is 5/3. The fraction of the heat supplied that is converted to work is

A. 0.2

B. 0.3

C. 0.4

D. 0.6

(2006)

195. For the isentropic expansion of an ideal gas from the initial conditions P_1, T_1 to the final conditions P_2, T_2, which one of the following relations is valid? ($g = C_P/C_V$)

A. $(P_1/P_2) = (T_2/T_1)^{g}$

B. $(P_1/P_2) = (T_1/T_2)^{g/(g-1)}$

C. $(P_1/P_2) = (T_1/T_2)$

D. $(P_1/P_2) = (T_1/T_2)^{(g-1)/g}$

(2006)

196. Match the following:

(a) Heat	(i) State function
(b) Internal energy	(ii) Path function
(c) Work	
(d) Entropy	

A. (a)-(ii), (b)-(i), (c)-(i), (d)-(i)
B. (a)-(ii), (b)-(i), (c)-(ii), (d)-(ii)
C. (a)-(ii), (b)-(ii), (c)-(i), (d)-(i)
D. (a)-(ii), (b)-(i), (c)-(ii), (d)-(i)

(2006)

197. For a reversible exothermic gas phase reaction, $A + B$ □ C, the equilibrium conversion will increase with

A. increase in pressure and increase in temperature
B. decrease in pressure and increase in temperature
C. increase in pressure and decrease in temperature
D. decrease in pressure and decrease in temperature

(2006)

198. For a binary mixture of A and B at 400 K and 1 atm, which one of the following equilibrium states deviates significantly from ideality?

$\ln P_A^S = 6.2 - \frac{2758}{T}$, where P_A^S is vapour pressure of A in atm, T = temperature, K, $\bar{p}_A$ is partial pressure of A in atm, x_A is mole fraction of A in liquid and y_A is mole fraction of A in vapour.

A. $x_A = 0.5; y_A = 0.25$
B. $x_A = 0.5;$ $\bar{p}_A = 0.25$
C. $x_A = 0.5;$ $\bar{p}_A = 0.5$
D. $x_A = 0.6; y_A = 0.3$

(2006)

199. Pure A at 473 K is fed to a steady-state adiabatic continuous reactor at the rate of 100 kg/h, where it undergoes an exothermic reaction to give its isomer B. The product stream is at temperature 773 K. The heat of reaction is 21 kJ/mol of A and the specific heat of the reaction mixture is constant at 35 J/mol K. The conversion in the reactor is

A. 25%
B. 50%
C. 75%
D. 100%

(2006)

200. The molar density of water vapour at the normal boiling point of water is 33 mol/m^3. The compressibility factor under these conditions is close to which one of the following? R = 8.314

J/mol K.

A. 0.75

B. 1

C. 1.25

D. 1.5

(2006)

201. If T_A and T_B are the boiling points of pure A and pure B respectively, and T_{AB} is that of a non-homogeneous immiscible mixture of A and B, then

A. $T_{AB} < T_A$ and T_B

B. $T_{AB} > T_A$ and T_B

C. $T_A > T_{AB} > T_B$

D. $T_B > T_{AB} > T_A$

(2007)

202. The state of an ideal gas is changed from (T_1, P_1) to (T_2, P_2) in a constant volume process. To calculate the change in enthalpy, $\mathrm{D}H$, all of the following properties/variables are required.

A. C_V, P_1, P_2

B. C_P, T_1, T_2

C. C_P, T_1, T_2, P_1, P_2

D. C_V, P_1, P_2, T_1, T_2

(2007)

203. The change in entropy of the system $\mathrm{D}S_{\mathrm{sys}}$, undergoing a cyclic irreversible process, is

A. greater than zero

B. equal to zero

C. less than zero

D. equal to the $\mathrm{D}S_{\mathrm{surroundings}}$

(2007)

204. Parameters *a* and *b* in the van der Waals and other cubic equations of state represent

A. *a*-molecular weight, *b*-molecular polarity

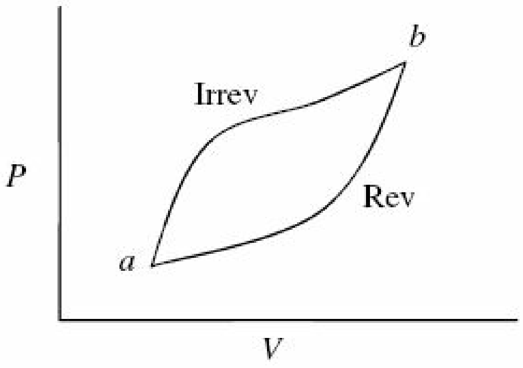
B. *a*-molecular size, *b*-molecular attraction

C. *a*-molecular size, *b*-molecular speed

D. *a*-molecular attraction, *b*-molecular size

(2007)

205. For the two paths as shown in the figure, one reversible and one irreversible, to change the state of the system from *a* to *b*,



A. ΔU, Q, W are the same
B. ΔU are the same
C. Q, W are the same
D. ΔU, Q are different

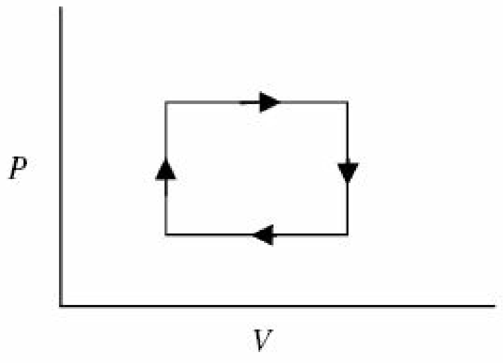
(2007)

206. For a pure substance, the Maxwell's relation obtained from the fundamental property relation $dU = TdS - PdV$ is

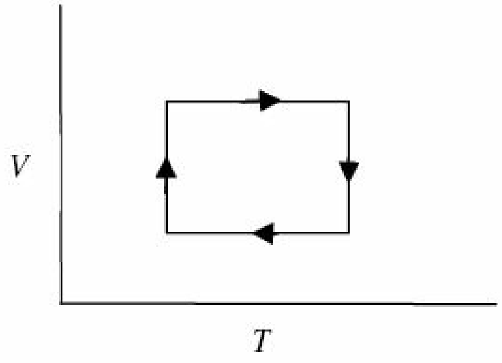
A. $(\partial T/\partial V)_S = -(\partial P/\partial S)_V$
B. $(\partial P/\partial T)_V = (\partial S/\partial V)_T$
C. $(\partial T/\partial P)_S = (\partial V/\partial S)_P$
D. $(\partial V/\partial T)_P = -(\partial S/\partial P)_T$

(2007)

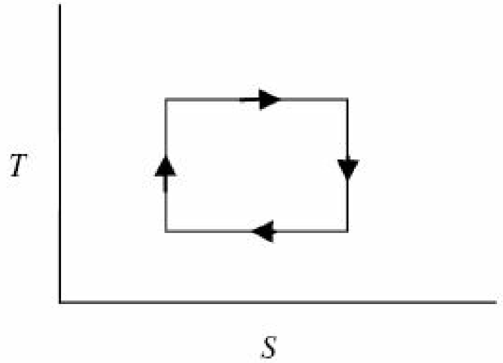
207. Which of the following represents the Carnot cycle (ideal engine)?



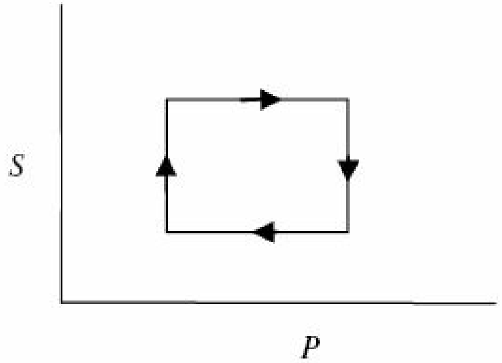
(a)



(b)



(c)



(d)

(2007)

208. Two kilograms of steam in a piston-cylinder device at 400 kPa and 448 K undergoes a mechanically reversible, isothermal compression to a final pressure such that the steam becomes just saturated. What is the work *W*, required for the process?

Data:

$T = 448$ K, $P = 400$ kPa, $V = 0.503$ m^3/kg, $U = 2606$ kJ/kg, $S = 7.055$ kJ/kg K

$T = 448$ K, saturated vapour, $V = 0.216$ m^3/kg, $U = 2579$ kJ/kg, $S = 6.622$ kJ/kg K

A. 0 kJ
B. 230 kJ
C. 334 kJ
D. 388 kJ

(2007)

209. Vapour-phase hydration of C_2H_4 to ethanol by the following reaction

$$C_2H_4(g) + H_2O(g) \Leftrightarrow C_2H_5OH(g)$$

attains equilibrium at 400 K and 3 bar. The standard Gibbs free energy change of reaction at these condition is DG^0 = 4000 J/mol. For two moles of an equimolar feed of ethylene and steam, the equation in terms of the extent of reaction e (in moles) at equilibrium is

A. $\frac{\varepsilon(2-\varepsilon)}{(1-\varepsilon)^2} - 0.3 = 0$

B. $\frac{(1-\varepsilon)^2}{\varepsilon(2-\varepsilon)} - 0.9 = 0$

C. $\frac{\varepsilon}{(1-\varepsilon)^2} - 0.3 = 0$

D. $\frac{\varepsilon(2-\varepsilon)}{(1-\varepsilon)^2} - 0.9 = 0$

(2007)

210. A methanol-water vapour liquid system is at equilibrium at 333 K and 60 kPa. The mole fraction of methanol in liquid is 0.5 and in vapour is 0.8. Vapour pressures of methanol and water at 333 K are 85 kPa and 20 kPa, respectively. Assuming vapour phase to be an ideal gas mixture, what is the activity coefficient of water in the liquid phase?

A. 0.3
B. 1.2
C. 1.6
D. 7.5

(2007)

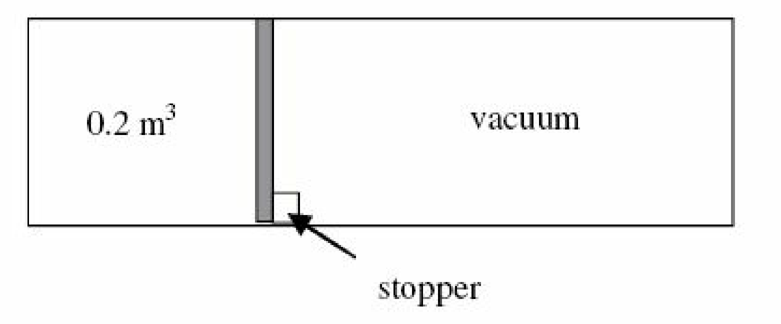
211. For conditions in Question 210, what is the excess Gibbs free energy (G^E, J/mol) of the liquid mixture?

A. 9.7

B. 388
C. 422
D. 3227

(2007)

212. A perfectly insulated cylinder of volume 0.6 m^3 is initially divided into two parts by a thin, frictionless piston, as shown in the figure. The smaller part of volume 0.2 m^3 has ideal gas at 6 bar pressure and 373 K. The other part is evacuated.



At certain instant of time *t*, the stopper is removed and the piston moves out freely to the other end. The final temperature is
A. 124 K
B. 240 K
C. 306 K
D. 373 K

(2007)

213. The cylinder insulation is removed and the piston is pushed back to restore the system to the initial state. If this is to be achieved only by doing work on the system (no heat addition, only heat removal allowed), what is the minimum work required?
A. 3.4 kJ
B. 107 kJ
C. 132 kJ
D. 240 kJ

(2007)

214. For a Carnot refrigerator operating between 40°C and 25°C, the coefficient of performance is
A. 1
B. 1.67
C. 19.88
D. 39.74

(2008)

215. The work done by one mole of a van der Waals fluid undergoing reversible isothermal expansion from initial volume V_i to final volume V_f is

A. $RT \ln\left(\frac{V_f}{V_i}\right)$

B. $RT\ln\left(\frac{V_f-b}{V_i-b}\right)$

C. $RT\ln\left(\frac{V_f-b}{V_i-b}\right)-a\left(\frac{1}{V_f}-\frac{1}{V_i}\right)$

D. $RT\ln\left(\frac{V_f-b}{V_i-b}\right)+a\left(\frac{1}{V_f}-\frac{1}{V_i}\right)$

(2008)

216. The standard Gibbs free energy change and enthalpy change at 298 K for the liquid phase reaction $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ are given as $\Delta G^0 = -4650$ J/mol and $\Delta H^0 = -3640$ J/mol. If the solution is ideal and enthalpy change is assumed to be constant, the equilibrium constant at 368 K is

A. 0.65
B. 4.94
C. 6.54
D. 8.65

(2008)

217. A binary mixture containing species 1 and 2 forms an azeotrope at 378.6 K and 1.013 bar. The liquid phase mole fraction of component 1 (x_1) of this azeotrope is 0.62. At 378.6 K, the pure component vapour pressures for species 1 and 2 are 0.878 bar and 0.665 bar, respectively. Assume that the vapour phase is an ideal gas mixture. The van Laar constants, A and B, are given by the expressions

$$A = \ln\gamma_1\left[1+\frac{x_2\ln\gamma_2}{x_1\ln\gamma_1}\right]^2,\ B = \ln\gamma_2\left[1+\frac{x_1\ln\gamma_1}{x_2\ln\gamma_2}\right]^2$$

The activity coefficients γ_1 and γ_2 under these conditions are

A. 0.88, 0.66
B. 1.15, 1.52
B. 1.52, 1.15
D. 1.52, 0.88

(2008)

218. The van Laar constants A and B for conditions in Question 217 are:

A. 0.92, 0.87
B. 1.00, 1.21
C. 1.12, 1.00
D. 1.52, 1.15

(2008)

219. An ideal gas at temperature T_1 and pressure P_1 is compressed isothermally to pressure P_2 (>

P_1) in a closed system. Which one of the following is true for internal energy (U) and Gibbs free energy G of the gas at the two states?

A. $U_1 = U_2, G_1 > G_2$

B. $U_1 = U_2, G_1 < G_2$

C. $U_1 > U_2, G_1 = G_2$

D. $U_1 < U_2, G_1 = G_2$

(2009)

220. For a binary mixture at constant temperature and pressure, which one of the following relations between activity coefficient g_i and mole fraction x_i is thermodynamically consistent?

A. $\ln \gamma_1 = -1 + 2x_1 - x_1^2,\ \ln \gamma_2 = \frac{1}{2} x_1^2$

B. $\ln \gamma_1 = -1 + 2x_1 - x_1^2,\ \ln \gamma_2 = x_1^2$

C. $\ln \gamma_1 = -1 + 2x_1 - x_1^2,\ \ln \gamma_2 = -\frac{1}{2} x_1^2$

D. $\ln \gamma_1 = -1 + 2x_1 - x_1^2,\ \ln \gamma_2 = -x_1^2$

(2009)

221. An ideal gas with molar heat capacity $C_P = 5/2\ R$ (where $R = 8.314$ J/mol K) is compressed adiabatically from 1 bar and 300 K to pressure P_2 in a closed system. The final temperature after compression is 600 K and the mechanical efficiency of compression is 50%. The work required for compression in (kJ/mol) is

A. 3.74

B. 6.24

C. 7.48

D. 12.48

(2009)

222. In the above problem, the pressure P_2 (in bar) is

A. $2^{3/4}$

B. $2^{5/4}$

C. $2^{3/2}$

D. $2^{5/2}$

(2009)

223. A new linear temperature scale, denoted by °S, has been developed, where the freezing point of water is 200°S and the boiling point is 400°S. On this scale, 500°S corresponds, in degree Celsius, to

A. 100°C

B. 125°C

C. 150°C

D. 300°C

(2010)

224. An equimolar mixture of species 1 and 2 is in equilibrium with its vapour at 400 K. At this temperature, the vapour pressures of the species are $P_1^S = 180$ kPa and $P_2^S = 120$ kPa. Assuming Raoult's law is valid, the value of y_1 is

A. 0.30
B. 0.41
C. 0.50
D. 0.60

(2010)

225. A saturated liquid at 1500 kPa and 500 K, with an enthalpy of 750 kJ/kg, is throttled to a liquid-vapour mixture at 150 kPa and 300 K. At the exit conditions, the enthalpy of the saturated liquid is 500 kJ/kg and the enthalpy of the saturated vapour is 2500 kJ/kg. The percentage of the original liquid, which vaporises, is

A. 87.5%
B. 67%
C. 12.5%
D. 10%

(2010)

226. At constant temperature and pressure, the molar density of a binary mixture is given by r = 1 + x_2, where x_2 is the mole fraction of component 2. The partial molar volume at infinite dilution of component 1, $\overline{V}_1^\infty$ is

A. 0.75
B. 1.0
C. 2.0
D. 4.0

(2010)

227. Minimum work (W) required to separate a binary gas mixture at a temperature T_0 and pressure P_0 is

$$W = -RT_0\left[y_1 \ln\left(\frac{\overline{f}_1}{f_{\text{pure},1}}\right) + y_2 \ln\left(\frac{\overline{f}_2}{f_{\text{pure},2}}\right)\right]$$

where, y_1 and y_2 are mole fractions, $f_{\text{pure, 1}}$, and $f_{\text{pure, 2}}$ are fugacities of pure species at T_0 and P_0 and $\overline{f}_1$ and $\overline{f}_2$ are fugacities of species in the mixture at T_0, P_0 and y_1. If the mixture is ideal, then W is

A. 0
B. $W = -RT_0[y_1 \ln y_1 + y_2 \ln y_2]$

C. $W = RT_0[y_1 \ln y_1 + y_2 \ln y_2]$

D. $W = RT_0$

(2011)

228. The partial molar enthalpies of mixing (in J/mol) for benzene (component 1) and cyclohexane (component 2) at 300 K and 1 bar are given by $\Delta\overline{H}_1 = 3600\,x_2^2$ and $\Delta\overline{H}_2 = 3600\,x_1^2$, where x_1 and x_2 are the mole fractions. When 1 mol of benzene is added to 2 mol of cyclohexane, the enthalpy change (in J) is

A. 3600

B. 2400

C. 2000

D. 800

(2011)

229. One mol of methane is contained in a leak-proof piston-cylinder assembly at 8 bar and 1000 K. The gas undergoes isothermal expansion to 4 bar under reversible conditions. Methane can be considered as an ideal gas under these conditions. The value of universal gas constant is 8.314 J/mol K. The heat transferred (in kJ) during the process is

A. 11.52

B. 5.76

C. 4.15

D. 2.38

(2011)

230. Consider a binary mixture of methyl ethyl ketone (component 1) and toluene (component 2). At 323 K, the activity coefficients g_1 and g_2 are given by

$$\ln \gamma_1 = x_2^2(\Psi_1 - \Psi_2 + 4\Psi_2 x_1),\ \ln \gamma_2 = x_1^2(\Psi_1 + \Psi_2 - 4\Psi_2 x_2)$$

where x_1 and x_2 are the mole fractions in the liquid mixture, and Y_1 and Y_2 are parameters independent of composition. At the same temperature, the infinite dilution activity coefficients, γ_1^∞ and γ_2^∞ are given by $\ln \gamma_1^\infty = 0.4$ and $\ln \gamma_2^\infty = 0.2$. The vapour pressures of methyl ethyl ketone and toluene at 323 K are 36.9 and 12.3 kPa, respectively. Assuming that the vapour phase is ideal, the equilibrium pressure (in kPa) of a liquid mixture containing 90 mol % toluene is

A. 19

B. 18

C. 16

D. 15

(2011)

231. In a throttling process, the pressure of an ideal gas reduces by 50%. If C_P and C_V are the heat capacities at constant pressure and constant volume, respectively ($g = C_P/C_V$), the specific volume will change by a factor of

A. 2

B. $2^{1/g}$

C. $2^{g-1/g}$

D. 0.5

(2012)

232. If the temperature of saturated water is increased infinitesimally at constant entropy, the resulting state of water will be

A. liquid

B. liquid-vapour coexistence

C. saturated vapour

D. solid

(2012)

233. In a parallel flow heat exchanger operating under steady state, hot liquid enters at a temperature $T_{h,\ \mathrm{in}}$ and leaves at a temperature $T_{h,\ \mathrm{out}}$. Cold liquid enters at a temperature $T_{c,\ \mathrm{in}}$ and leaves at a temperature $T_{c,\ \mathrm{out}}$. Neglect any heat loss from the heat exchanger to the surrounding. If $T_{h,\ \mathrm{in}} >> T_{c,\ \mathrm{in}}$, then for a given time interval, which one of the following statements is true?

A. Entropy gained by the cold stream is greater than the entropy lost by the hot stream

B. Entropy gained by the cold stream is equal to the entropy lost by the hot stream

C. Entropy gained by the cold stream is less than the entropy lost by the hot stream

D. Entropy gained by the cold stream is zero.

(2012)

234. For an exothermic reversible reaction, which one of the following correctly describes the dependence of the equilibrium constant (K) with temperature (T) and pressure (P)?

A. K is independent of T and P.

B. K increases with an increase in T and P.

C. K increases with T and decreases with P.

D. K decreases with an increase in T and is independent of P.

(2012)

235. An insulated, evacuated container is connected to a supply line of an ideal gas at pressure P_S, temperature T_S and specific volume V_S. The container is filled with the gas until the pressure in the container reaches P_S. There is no heat transfer between the supply line to the container, and kinetic and potential energies are negligible. If C_P and C_V are the heat capacities at constant pressure and constant volume, respectively ($g = C_P/C_V$), then the final temperature of the gas in the container is

A. gT_S

B. T_S

C. $(g - 1)\ T_S$

D. $(g - 1)T_S/g$

(2012)

236. Consider a binary liquid mixture at constant temperature T and pressure P. If the enthalpy change of mixing $\Delta H = 5x_1x_2$, where x_1 and x_2 are mole fraction of species 1 and 2, respectively, and the entropy change of mixing $\Delta S = -R(x_1 \ln x_1 + x_2 \ln x_2)$ with $R = 8.314$ J/mol K, then the minimum value of the Gibbs free energy change of mixing at 300 K occurs when

A. $x_1 = 0$

B. $x_1 = 0.2$

C. $x_1 = 0.4$

D. $x_1 = 0.5$

(2012)

C.2 Fill in the blanks:

1. properties of a system do not depend on the quantity of matter contained in it.
2. An open system exchanges with the surroundings.
3. The maximum efficiency of a heat engine depends only on the between which it operates and is independent of the nature of the cyclic process.
4. Gibbs free energy is defined as .
5. Mollier diagram is a plot of versus .
6. The efficiency of a Carnot engine working between 1000 K and 300 K is .
7. In the statement $(\Delta S)_{total} \geq 0$, the inequality refers to process.
8. P, V, T and S are properties whereas U, H, G, A are properties.
9. The principle of corresponding states may be stated thus: “At same T_R and P_R all gases have the same .”
10. A gaseous phase may be termed a vapour, if it can be condensed by .
11. A refrigerator of capacity 2 tons is working on ammonia at 273 K. The heat of vaporisation of ammonia is 1260 kJ/kg. The circulation rate of ammonia under this condition is approximately kg/h.
12. Gibbs–Helmholtz equation relates the change in with changes in .
13. A system from which finite quantities of heat can be removed without affecting its temperature is called .
14. The maximum velocity attained by a fluid in a pipe of uniform cross-section is equal to the in the fluid.
15. The maximum velocity attainable in a convergent nozzle is equal to and it is attained when the equals the critical value.
16. The ratio of the intake volume to the displacement volume in a single-stage compressor is called the .
17. The ratio of the velocity of flow to the sonic velocity is designated as .
18. The decrease in is a measure of the maximum work obtainable in an isothermal process.

19. As pressure tends to zero, fugacity of a pure gas becomes equal to its .
20. The ratio of the fugacity to the fugacity in the standard state is called .
21. Isothermal mixing of pure gases always produces a decrease in the . Hence work has to be done the system for separating a mixture of gases into its components.

(1990)

22. The maximum work obtainable from a closed system under isothermal expansion is given by ; For one mole of an ideal gas expanding isothermally to twice its volume this is equal to .

(1990)

23. The phase rule is given as .

(1994)

24. Raoult's law states that the of a component over an ideal solution is directly proportional to its mole fraction in the solution.
25. In a dilute solution, the obeys Henry's law and the obeys Raoult's law.
26. When the Henry's law constant is equal to , Henry's law becomes identical to Raoult's law.
27. The activity coefficient (g_i) in a solution is related to the chemical potential as $\mu_i^E =$.
28. The phase rule indicates the number of variables needed to specify the intensive state of the system whereas the indicates those needed to specify the extensive state of the system.
29. A mixture exists as a superheated vapour above its temperature.
30. If the intermolecular forces between unlike molecules are than those between like molecules, the solution will exhibit negative deviation from ideality.
31. The constant boiling mixtures are called .
32. The vaporisation equilibrium constant K_i is defined as $K_i =$.
33. Among three liquids A, B and C, the A-B binary is partially miscible whereas A-C and B-C binaries are totally soluble. On the binodal curve, the A-rich and B-rich phases in equilibrium become identical in properties at the of the system.
34. The number of degrees of freedom for a system consisting of two miscible non-reacting species which exists as an azeotrope in vapour–liquid equilibrium is .
35. The equilibrium state for a closed system is the state for which the total is a minimum at constant temperature and pressure.
36. A binary hydrocarbon liquid mixture of A and B ($K_A = 1.5$) containing 60% (mol) A is flash vaporised. If 40% of the feed is vaporised, the mole fraction of A in the liquid product is .

(1990)

37. A system of unit mass at equilibrium consists of two phases a and b of extent x and $(1 - x)$ respectively. Write down expressions for the pressure and the specific enthalpy of the system as a whole in terms of the properties P^a, P^b, H^a and H^b of the individual phases: (a) $P =$, (b) $H =$.

(1990)

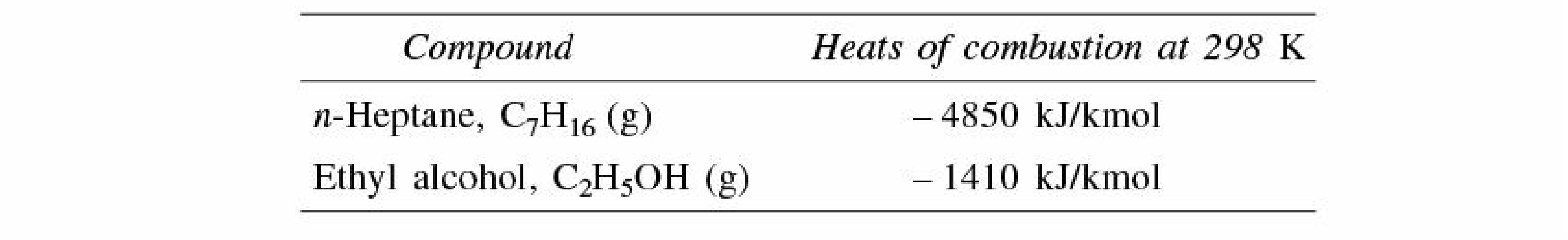
38. The heats of formation of CO (g), H_2O (g), and CO_2 (g) are respectively –110.525 kJ, –393.509 kJ and –241.818 kJ. The heat of reaction for

CO (g) + H_2O (g) □ CO_2 (g) + H_2 (g)

is kJ.

39. reactions are favoured by increase in temperature.

40. The following data on heats of combustion at 298 K are given:



Compound	*Heats of combustion at 298* K
n-Heptane, C_7H_{16} (g)	– 4850 kJ/kmol
Ethyl alcohol, C_2H_5OH (g)	– 1410 kJ/kmol

Heats of formation of CO_2 (g) and H_2O (l) are –390 and –280 kJ/kmol respectively.

(a) The heat of formation of gaseous *n*-heptane at 298 K is .

(b) The heat of formation of gaseous ethyl alcohol at 298 K is .

(1990)

41. The heat absorbed for isothermal reaction

C_4H_{10} (g) □ C_2H_4 (g) + C_2H_6 (g)

at 298 K and 101.3 kPa is . Standard heat of combustion in kJ/kmol are:

C_4H_{10} (g) = – 2873.5, C_2H_4 (g) = – 1411.9 and C_2H_6 (g) = – 1561.0

(1991)

42. The heat of formation of a compound is defined as the heat of reaction leading to the formation of the compound from its .

(1994)

C.3 Say, whether the following statements are TRUE or FALSE. Give correct statements to the fals ones.

1. Internal energy is a state function whereas entropy is a path function.
2. Heat capacity and specific heat are extensive properties whereas volume and temperature are intensive properties.
3. Heat and work are not properties of a system; they are properties of a process.
4. At constant pressure, the change in enthalpy DH = $\int C_p \, dT$.
5. Entropy cannot have absolute values; they are always expressed as a difference.
6. Energy of the universe is conserved whereas entropy is increasing.
7. So long as the process is reversible, the value of $\int P \, dV$ is the same for the change of the gas from any given state to another.
8. Heat involved in any process can be expressed as $dQ = T \, dS$.
9. Enthalpy and entropy of an ideal gas are functions of temperature alone.
10. If DS refers to the entropy change between the same initial and final states of the system for two

different processes, one reversible (R) and the other irreversible (I), then $\Delta S_I = \Delta S_R$.

11. The heat capacities C_P and C_V of an ideal gas are independent of temperature.
12. The second law of thermodynamics states that heat cannot be completely converted to work.
13. For any process, the second law of thermodynamics requires that the entropy change of the system is either zero or positive.
14. The entropy change of a chemical reaction is calculated as the ratio of the heat of reaction to the temperature of the reaction.
15. When water freezes to form ice, the atoms arrange themselves in a highly ordered manner. Since the increasing order is associated with the decreasing entropy, we must conclude that entropy of the universe decreases as a result of this process.
16. Entropy of a rotating flywheel is the same as that of the flywheel at rest.
17. For given operating temperatures all heat engines have the same efficiency regardless of the nature of the working substance.
18. Real gases behave ideally at high pressures and temperatures.
19. A reversible adiabatic process is essentially isenthalpic.
20. The heat capacity at constant pressure and constant volume of all gases are related as $C_P - C_V = R$.
21. For an ideal gas, the activity and fugacity are numerically equal.
22. For an ideal solution, all property changes of mixing are zero.
23. Raoult's law is applicable to all ideal liquid solutions.
24. On the P-T diagram of a pure substance, the vaporisation curve and the fusion curve extend up to infinity.
25. The change in internal energy of an ideal gas is $\Delta U = \int C_V \, dT$ irrespective of the nature of the process.
26. For gases, the Joule–Thomson coefficient is always positive.
27. Work required for isothermal compression is less than that of adiabatic compression.
28. The clearance has no effect on the work of compression in a single-stage compressor.
29. The reversible work of expansion in a non-flow process under isentropic condition is equal to $-(\Delta U)_S$.
30. For an ideal gas, the fugacity and pressure are equal.
31. The excess volume and the volume change on mixing are the same.
32. For a multicomponent system, equilibrium between two phases is established when the concentrations in both the phases are uniform.
33. For a solution at a given pressure, the vapour phase can exist in equilibrium with the liquid phase only at its bubble point.
34. In an ideal binary solution, component A obeys Raoult's law and component B obeys Henry's law.
35. Maximum boiling azeotropes may be formed if the solution exhibits very large positive deviation from ideality.

36. Azeotropic composition can be shifted by changing the pressure.

37. For a chemically reacting system at equilibrium at constant temperature and pressure, the Gibbs free energy is maximum.

38. The numerical value of the equilibrium constant depends upon the stoichiometric equation.

39. If there is decrease in the total number of moles during a gas-phase chemical reaction, the increase in pressure decreases the formation of products.

40. The equilibrium conversion in a gaseous reaction which produces no change in the number of moles (e.g., the water-gas shift reaction) is not affected by the change in pressure.

Answers

C.1

1. C 2. B 3. C 4. B 5. A 6. C 7. A
8. C 9. C 10. C 11. B 12. B 13. C 14. A
15. D 16. B 17. D 18. C 19. B 20. A 21. C
22. B 23. A 24. B 25. C 26. B 27. B 28. D
29. A 30. C 31. B 32. C 33. C 34. D 35. D
36. C 37. A 38. B 39. A 40. A 41. B 42. D
43. B 44. C 45. C 46. D 47. B 48. B 49. B
50. D 51. C 52. A 53. A 54. C 55. B 56. A
57. B 58. C 59. C 60. B 61. A 62. C 63. C
64. B 65. A 66. D 67. B 68. D 69. B 70. A
71. C 72. B 73. D 74. D 75. D 76. C 77. A
78. C 79. B 80. B 81. C 82. C 83. B 84. A
85. D 86. B 87. B 88. B 89. C 90. B 91. B
92. A 93. D 94. D 95. A 96. D 97. A 98. B
99. C 100. C 101. A 102. C 103. B 104. B 105. D
106. A 107. A 108. B 109. B 110. B 111. D 112. B
113. B 114. A 115. B 116. B 117. B 118. B 119. B
120. C 121. C 122. D 123. C 124. A 125. B 126. C
127. A 128. B 129. B 130. D 131. A 132. B 133. D
134. A 135. D 136. C 137. A 138. C 139. A 140. C
141. D 142. B 143. B 144. B 145. D 146. D 147. A
148. A 149. B 150. C 151. A 152. C 153. D 154. D
155. B 156. D 157. B 158. C 159. B 160. C 161. A
162. D 163. B 164. B 165. A 166. B 167. A 168. D
169. D 170. C 171. C 172. A 173. D 174. D 175. C
176. A 177. A 178. D 179. C 180. B 181. A 182. A
183. C 184. D 185. C 186. B 187. B 188. B 189. C
190. B 191. A 192. C 193. D 194. B 195. B 196. D

197. C	198. C	199. B	200. B	201. A	202. B	203. B
204. D	205. B	206. A	207. C	208. C	209. D	210. B
211. C	212. D	213. C	214. C	215. D	216. B	217. B
218. C	219. B	220. D	221. C	222. D	223. C	224. D
225. C	226. A	227. B	228. D	229. B	230. C	231. A
232. A	233. A	234. D	235. A	236. D		

C.2

1. Intensive
2. Mass and energy
3. Temperature
4. $G = H - TS$
5. Enthalpy, entropy
6. 70%
7. Irreversible
8. Reference, energy
9. Z (Compressibility factor)
10. Compression at constant temperature
11. 20 kg/h
12. G/T with T
13. Heat reservoir
14. Sonic velocity
15. Sonic velocity, Pressure ratio
16. Theoretical volumetric efficiency
17. Mach number
18. Helmholtz free energy
19. Pressure
20. Fugacity coefficient
21. Gibbs free energy, on
22. $\int P\,dV$, $RT \ln 2$
23. $F = C - \pi + 2$
24. Partial pressure (fugacity)
25. Solute, solvent
26. Vapour pressure
27. $RT \ln \gamma_i$
28. Duhem’s theorem
29. Dew point
30. Stronger (greater)
31. Azeotropes

32. y_i/x_i
33. Plait point
34. One
35. Gibbs free energy
36. 0.46
37. (a) $P^a = P^b$ (b) $xH^a + (1 - x)H^b$
38. 262.22
39. Endothermic
40. (a) – 120 kJ/kmol (b) – 210 kJ/kmol
41. 99.4 kJ
42. Constituent elements

C.3

1. False. Both are state functions.
2. False. Heat capacity and volume are extensive properties whereas specific heat and temperature are intensive properties.
3. True.
4. True.
5. False. Entropy can have absolute values.
6. True.
7. False. The value of $\int P\,dV$ is dependent on the path followed.
8. False. Heat involved in a reversible process can be expressed as $dQ = T\,dS$.
9. False. Enthalpy of an ideal gas is a function of temperature only. Entropy depends on pressure as well.
10. True.
11. False. The heat capacities C_P and C_V of an ideal gas are dependent on temperature only.
12. False. The second law of thermodynamics states that heat cannot be completely converted into work continuously (or in a cyclic process).
13. False. For any process, the second law of thermodynamics requires that the entropy change of the system and the surroundings together is either zero or positive.
14. False. The entropy change of a chemical reaction is to be computed as the sum of the absolute entropies of the products minus the sum of the absolute entropies of the reactants.
15. False. When water freezes to form ice, greater disorder may result in the surroundings due to transfer of heat with a consequent increase in the total entropy.
16. True.
17. False. For given operating temperatures all reversible heat engines (Carnot engines) have the same efficiency regardless of the nature of the working substance.
18. False. Real gases behave ideally at low pressures and or high temperatures.
19. False. A reversible adiabatic process is essentially isentropic.
20. False. The heat capacity at constant pressure and constant volume of ideal gases are related as

$C_P - C_V = R.$

21. True.
22. False. For an ideal solution, property changes of mixing are not zero for entropy and entropy-related functions such as the free energy.
23. False. Raoult's law is applicable to all ideal liquid solutions provided the vapour phase is an ideal gas.
24. False. On the P-T diagram of a pure substance, the vaporisation curve lies between the triple point and the critical point whereas the fusion curve extends up to infinity.
25. True.
26. False. For gases the Joule–Thomson coefficient may be positive, zero or negative.
27. True.
28. True.
29. True.
30. True.
31. True.
32. False. For a multicomponent system in equilibrium, the chemical potentials in both phases are uniform.
33. False. For a solution at a given pressure, the vapour phase can exist in equilibrium for a range of temperatures lying between the bubble point and the dew point.
34. False. In an ideal binary solution both components obey Raoult's law.
35. False. Minimum boiling azeotropes may be formed if the solution exhibits very large positive deviation from ideality.
36. True.
37. False. The Gibbs free energy is minimum.
38. True.
39. False. If there is decrease in the total number of moles during a gas-phase chemical reaction, the increase in pressure favours the formation of products.
40. False. If the compressibility of the components are affected by the change in pressure, the equilibrium conversion also will be affected.

References

1. Abrams, D. and Prausnitz, J.M., *AIChE J.*, **21**, 116, 1975.
2. Atkins, P.W., *Physical Chemistry*, 4th ed., ELBS-Oxford, Oxford University Press, 1990.
3. Benedict, M., Webb, G. and Rubin, L., *J. Chem. Phys.*, **8**, 334, 1940.
4. Callen, H.B., *Thermodynamics*, John Wiley, New York, 1960.
5. Daubert, T.E., *Chemical Engineering Thermodynamics*, McGraw-Hill, New York, 1985.
6. Denbigh, K., *The Principles of Chemical Equilibrium*, 4th ed., Cambridge, New York, 1981.
7. Dodge, B.F., *Chemical Engineering Thermodynamics*, McGraw-Hill, New York, 1944.
8. Fredenslund, Aa., Jones, R.L. and Prausnitz, J.M., *AIChE J.*, **21**, 1086, 1975.
9. Glasstone, S., *Thermodynamics for Chemists*, Van Nostrand, New York, 1958.
10. Hill, L., *Statistical Mechanics*, McGraw-Hill, New York, 1956.
11. Hougen, O.A., Watson, K.M. and Ragatz, R.A., *Chemical Process Principles, Part II*, 2nd ed., John Wiley, New York, 1960.
12. Karapetyants, M.Kh., *Chemical Thermodynamics*, Mir Publishers, Moscow, 1978.
13. Kirkwood, I.J. and Oppenheim, I.,*Chemical Thermodynamics*, McGraw-Hill, New York, 1961.
14. Kyle, B.G., *Chemical and Process Thermodynamics*, 2nd ed., Prentice-Hall of India, New Delhi, 1994.
15. Lewis, G.N., Randall, M., Pitzer, K.S. and Brewer, L., *Thermodynamics*, McGraw-Hill, New York, 1981.
16. Modell, M. and Reid, R.C.,*Thermodynamics and Its Applications*, Prentice Hall, New Jersey, 1974.
17. Peng, D.Y. and Robinson, D.B., *Ind. Eng. Chem. Fundam.*, **15**, 59, 1976.
18. Perry, J.H. and Chilton, C.H. (Eds.),*Chemical Engineers' Handbook*, 5th ed., McGraw-Hill, Tokyo, 1973.
19. Prausnitz, J.M., Lichtenthaler, R.N. and Azevedo, E.G.,*Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed., Prentice Hall, New Jersey, 1986.
20. Rao, Y.V.C., *An Introduction to Thermodynamics*, Wiley Eastern, New Delhi, 1993.
21. Redlich, O. and. Kwong, J.N.S., *Chem. Rev.*, **44**, 233, 1949.
22. Renon, H. and Prausnitz, J.M., *AIChE J.*, **14**, 135, 1968.
23. Reynolds, W.C. and Perkins, H.C.,*Engineering Thermodynamics*, McGraw-Hill, Tokyo, 1977.
24. Saad, M.A., *Thermodynamics for Engineers*, Prentice-Hall of India, New Delhi, 1969.
25. Sandler, S.I., *Chemical and Engineering Thermodynamics*, John Wiley, New York, 1977.
26. Smith, J.M. and Van Ness, H.C.,*Introduction to Chemical Engineering Thermodynamics*, 4th ed., McGraw-Hill, New York, 1987.
27. Smith, N.O., *Chemical Thermodynamics: A Problems Approach*, Reinhold, New York, 1967.
28. Soave, G., *Chem. Engg. Sci.*, **27**, 1197, 1972.
29. Sonntag, R.E. and Van Wylen, G.J., *Introduction to Thermodynamics*, John Wiley,

New York, 1971.

30. Treybal, R.E., *Mass-Transfer Operations*, 3rd ed., McGraw-Hill, New York, 1981.
31. Wark, K., *Thermodynamics*, 2nd ed., McGraw-Hill, New York, 1971.
32. Weber, H.E. and Meissner, H.C., *Thermodynamics for Chemical Engineers*, 2nd ed., John Wiley, New York, 1957.
33. Wilson, E.D. and Ries, H.C., *Principles of Chemical Engineering Thermodynamics*, McGraw-Hill, New York, 1956.

Answers to Exercises

CHAPTER 1

1.1 89.55 kg; 878.51 N
1.2 102.14 N
1.3 698 mm
1.4 1.6783 bar
1.5 3.02 bar
1.6 1.5453 □ 10^5 N/m^2
1.7 17.845 m, 25 kJ
1.8 1.667 □ 10^2 kJ
1.9 7.355 kJ; 61.29 W
1.10 16.8 W
1.11 20.39 m
1.12 (a) 4.164 □ 10^3 N
  (b) 1.3254 □ 10^5 N/m^2
  (c) 2.082 □ 10^3 J
  (d) 490.5 J
1.13 2.156 □ 10^5 J
1.14 17.15 m/s
1.15 1.146 □ 10^4 kJ
1.16 6.073 □ 10^4 J

CHAPTER 2

2.1 40.75 kJ
2.2 400 K, 500 kPa
2.3 (a) 183.94 kJ
  (b) 1839.4 kJ
  (c) 1655.46 kJ
  (d) 38.36 m/s
  (e) 1839.4 kJ
2.4 (a) 981 J
  (b) 981 J
  (c) 0.234 K
2.5 (a) 14 m/s
  (b) 0.78 K
2.6 18,467 kJ

2.7 4466 kJ
2.8 195,814 kJ
2.9 2423.9 kJ/kg; 2214 kJ/kg
2.10 (a) 3.572 kJ
  (b) 10.97 min
2.11 Q = 914.86 kJ, W = 139.35 kJ
2.12 227 V
2.13 Q = 1.246 □ 10^6 kJ
2.14 Q = 58.4 □ 10^4 J
2.15 435.5 HP
2.16 35 kJ
2.17 70 kJ
2.18 2453 kJ/kg
2.19 389.9 K
2.20 (a) 78.9 m/s
  (b) 72.7 kPa
2.21 870.9 kJ/kg, 5.74 kg/s
2.22 55.5 kW
2.23 3.68 MW
2.24 75%
2.25 141.3 MW
2.26 1.722 K
2.27 100 kJ
2.28 (a) 22,480 kJ
  (b) 8730 kJ
2.29 166.67 kJ
2.30 (a) V = 4.65584 m^3, P = 1 bar, T = 56 K
    DU = 4656 kJ, DH = 6518 kJ,
    W = 0, Q = 4656 kJ
  (b) V = 23.2792 m^3, P = 5 bar, T = 1400 K, DU = 22,380.3 kJ, DH = 32,592.0 kJ, W = 0, Q = 22,380.3 kJ
2.31 DU = 2168.6 kJ, DH = 3000 kJ, W = – 125.32 kJ, Q = 2043.28 kJ

CHAPTER 3

3.1 (a) 38.301 □ 10^3 J
  (b) 0
  (c) 4.31 bar
  (d) – 47.817 □ 10^3 J
3.2 (a) 24.0685 kJ

(b) – 17.695 kJ

(c) 6.374 kJ

3.3 (a) 2282 kJ

(b) 2206 kJ

(c) 0

3.4 (a) 472.5 kJ

(b) – 4863 kJ

(c) 0

(d) 4863 kJ

(e) 5981 kJ

3.5 (a) $\Delta U = 997.68$ kJ/kmol;

$\Delta H = 1662.8$ kJ/kmol;

$W = -997.68$ kJ/kmol; $Q = 0$

(b) $\Delta U = -997.68$ kJ/kmol;

$\Delta H = -1662.8$ kJ/kmol;

$W = -665.12$ kJ/kmol;

$Q = -1662.8$ kJ/kmol

(c) $\Delta U = 0$; $\Delta H = 0$;

$W = 1490$ kJ/kmol;

$Q = 1490$ kJ/kmol

(d) $\Delta U = 0$; $\Delta H = 0$;

$W = -172.8$ kJ/kmol;

$Q = -172.8$ kJ/kmol

3.6 $\Delta U = -2329$ kJ/kmol;

$\Delta H = -3252$ kJ/kmol;

$W = 3395$ kJ/kmol;

$Q = 1066$ kJ/kmol

3.7 (a) 0.373 kg

(b) 0.304 kg

3.8 418.5 K, 7.65 bar

3.9 (a) 4605 kJ

(b) 132.9 K, 2376 kJ

(c) 900 kJ

3.10 3.66×10^{-4} m^3/mol

3.11 (a) 3×10^{-3} m^3/mol

(b) 2.98×10^{-3} m^3/mol

3.12 23.84 bar

3.13 (a) 65.54 bar

(b) 57.23 bar

(c) 57.87 bar

3.14 $1.8 \square 10^{-4}$ m^3/mol

3.15 $7.134 \square 10^{-5}$ m^3/mol (liquid),
$1.712 \square 10^{-3}$ m^3/mol (vapour)

3.16 $3.485 \square 10^{-3}$ m^3/mol, 0.8862

3.17 (a) $4.157 \square 10^{-5}$ m^3/mol
(b) $6.44 \square 10^{-5}$ m^3/mol
(c) $5.3 \square 10^{-5}$ m^3/mol

3.19 – 110.6 kJ/mol

3.20 – 1207.69 kJ/mol

3.21 – 1655.07 kJ/mol

3.22 48.70 kJ/mol

3.23 – 42.62 kJ

3.24 – 395.2 kJ/mol

3.25 – 799.3 kJ/mol

3.26 $\Delta H_T^0 = -3.8235 \square 10^4 - 31.82\,T + 1.776 \square 10^{-2} T^2 - 3.108 \square 10^{-6}\,T^3$

3.27 – 224.673 kJ

3.28 – $207.2 \square 10^3$ kJ

3.29 32,528.5 kJ

3.30 1360 K

3.31 1216 K

3.32 – 311.627 kJ/mol

3.33 – 3283.5 kJ

3.34 $2.7989 \square 10^4$ kJ

3.35 2089.5 K

3.36 – 114.408 kJ/mol

3.38 (a) – 103.2 kJ/mol
(b) $\Delta H_T^0 = -75{,}964 - 62.71T + 4.496 \square 10^{-2} T^2 - 9.561 \square 10^{-6} T^3 + 11.224 \square 10^4 (1/T)$

3.39 2055.8 K

3.40 $3.766 \square 10^6$ kJ

3.41 – 3535.50 kJ

3.42 2141.9 K

CHAPTER 4

4.1 329.84 kJ

4.2 $1.448 \square 10^9$ J/s

4.3 (a) $2.1502 \square 10^6$ kJ/h
(b) 18.1%

4.4 (a) 2.9736 kJ
(b) 3.9736 kJ
4.5 Unacceptable
4.6 Unacceptable
4.7 Unrealistic
4.8 (a) –19.1437 J/mol K
(b) 30.63 J/K
(c) 11.49 J/K
4.9 79.91 J/K
4.10 (a) 6.66 kJ/K, – 4.6204 kJ/K, 2.04 kJ/K
(b) 6.66 kJ/K, – 4.925 kJ/K, 1.735 kJ/K
(c) 6.66 kJ/K, – 4.89 kJ/K, 1.77 kJ/K
(d) 6.66 kJ/K, – 6.66 kJ/K, 0
4.11 18.531 kJ/kmol K, Possible
4.12 4579.6 kJ/kmol
4.13 7.1 □ 10^5 kJ
4.14 0.0508 kJ
4.16 31.28 kJ/kmol K, 111.9 kJ/kmol K
4.17 – 2.46 kJ/kmol K
4.18 (a) – 1.99 kJ/K
(b) 3.44 kJ/K
(c) 1.45 kJ/K
4.19 (a) 0.37
(b) 0.56
4.20 (a) 0
(b) 19.5 kJ
4.21 5966 kJ/kmol
4.22 Yes
4.23 10.65 J/K
4.24 1.07 kJ/K
4.25 (a) 5.46 kJ/kmol K, – 4.48 kJ/kmol K, 0.98 kJ/kmol K
(b) 8.6 kJ/kmol K, – 7.9 kJ/kmol K, 0.70 kJ/kmol K
4.26 348.5 K
4.27 64.6%
4.28 21.995 □ 10^3 kJ/kmol
4.29 13.38 kJ/kmol K
4.30 76.1%
4.31 (a) – 1375.35 kJ/K
(b) 326.45 kJ/K
(c) 1.16887 □ 10^5 kJ
4.32 (a) 397.7 kW

(b) 329.2 kW
4.33 8.62 J/g K

CHAPTER 5

5.1 13.54 m/s
5.2 0.9948 kg/s
5.3 350 K
5.4 722.51 kW
5.5 6.877 □ 10^{5} kJ
5.6 144.1 kJ/h
5.7 567 K
5.8 6558 kg
5.9 759 K
5.10 0.9159 kg
5.11 229 K, 3.82 bar
5.12 420 K
5.13 (a) 865.8 K
(b) 18.4 kg
5.14 (a) 45.61 kg
(b) –104594 kJ
5.15 0.0744, 9018 kJ
5.16 343.3 K
5.17 109.3 HP
5.18 1481.3 W, 2.95 □ 10^{5} N/m^{2}
5.19 4.316 kW, 0.8662 □ 10^{5} N/m^{2},
9.66 □ 10^{5} N/m^{2}
5.20 (a) 402.64 m/s
(b) 5.751 □ 10^{-4} m^{2}
5.21 1.14 kg/s
5.22 2.19
5.23 61.04 K
5.24 813.8 m/s
5.25 11.33
5.26 (a) 0.5457, 542.96 m/s
(b) 28.323 kPa
5.27 429.4 K, 3.65P_{2}
5.29 541 kW, 3060.97 kJ/kg, 7.3544 kJ/kg K
5.30 (a) 114.91 kW
(b) 0.49 m^{3}/s

5.31 31.84 kW, 0.2963 m^3/s, 393 K
5.32 71.8 kJ/kg, 339 K
5.33 14
5.34 1.11 kJ/s, 2.5 kJ/s
5.35 2.525 kg/s, 280 kJ/s, 4
5.36 419.32 kg/h
5.37 (a) 0.5079 kg/min
(b) 0.311 kW
(c) 2.857
5.38 (a) 3.42 HP
(b) 63.3 kg/h
(c) 1731.1 kg/h
(d) 6.9
5.39 11.39 kg/h, 5.03
5.40 (a) 162.2 kg/h
(b) 3.5%
(c) 131.55 kg/h
(d) 4.11, 5.0, 3.76
5.41 4.78 kW, 8.9214 □ 10^3 kg/h
5.42 (a) 3
(b) 4 kJ/s
(c) 231 K
5.43 6976.7 kg/h, 57.67 ton
5.44 9.73 kW
5.45 0.084 (winter), 0.048 (summer)
5.46 (a) 2% liquefied
(b) 23% liquefied
5.47 (a) 0.048, 4.92 kg/h
(b) 0.006, 0.65 kg/h
5.48 (a) 0.054
(b) 230 K
5.49 (a) 13.3 kg/h
(b) 58.87 kW
5.50 40%
5.51 (a) 2.9245 kJ/kg
(b) 578.17 kJ/kg
(c) 55.4 kJ/kg
(d) 2867.4 kJ/kg
(e) 2211.6 kJ/kg
5.52 (a) 38.83%
(b) 37.22%

5.53 38.42%
5.54 54.14%
5.55 (a) 34.95%
(b) 29.68%
(c) 4232 kg/h
5.56 34.25%
5.57 34.81%
5.58 (a) 29.72%
(b) 4000 kg/h
5.59 (a) 39.66%
(b) 29.61%
(c) 3.0505 □ 10^5 kg/h
(d) 2.7016 □ 10^5 kW, 1.9016 □ 10^5 kW
5.60 39.12%
5.61 25.45%, 0.941 (at 700 kPa), 33.34%,
0.8627 (at 3500 kPa), 36.16%,
0.771 (at 7000 kPa), 38.22%,
0.6944 (at 14,000 kPa)
5.62 32.42%, 0.7835 (at 573 K), 32.99%,
0.8128 (at 623 K), 36.69%,
0.920 (at 873 K), 37.64%,
0.9361 (at 923 K)
5.63 (a) 510.34 kJ/kg
(b) 222.15 kJ/kg
(c) 56.47%
5.64 1129.4 kJ/kg
5.65 (a) 7.233
(b) 54.68%
(c) 909.24 kJ/kg
5.66 6.13
5.67 (a) 13.94
(b) 1.578
(c) 17.874 kJ
(d) 61.49%
5.68 (a) 80 kPa, 310 K (step 1),
2009.5 kPa, 778.69 K (step 2),
2368.9 kPa, 917.96 K (step 3),
94.3 kPa, 365.45 K (step 4)
(b) 300.93 kJ
(c) 60.2%
5.69 43.2%

5.70 (a) 9
(b) 2167.4 kPa
(c) 49.68%
(d) 78.618 kW
5.71 (a) 13.94
(b) 1.64
(c) 366.81 kJ/kg
(d) 61.13%
5.72 Compression ratio = 2.69
Expansion ratio = 2.408
5.73 (a) 3101.3 K
(b) 3.3
(c) 2172.5 kJ/kg
(d) 55.74%
5.74 19.16
5.75 (a) 40.62%
(b) 543.27 kJ/kg
(c) 1.22 kJ/kg K
5.76 (a) 1828 kJ/kg
(b) 1040.6 kJ/kg
(c) 56.93%
5.77 (a) 1203.26 kJ/kg
(b) 1976.9 kJ/kg
5.78 (a) 220 kJ/kg
(b) 372.2 kJ
(c) 22.2%
5.79 (a) 100 kPa
(b) 244.6 kJ
(c) 585.2 kJ
(d) 44.79%
5.80 (a) 40.06%
(b) 24.7%
5.81 (a) 1416 kW
(b) 3616 kW
(c) 32.72%
(d) 421 kPa
5.82 (a) 24,714.4 kJ/s
(b) 0.3973
(c) 66.54 kg/s
5.83 (a) 300 K, 100 kPa (point 1), 445.8 K, 400 kPa (point 2), 900 K, 390 kPa(point 3), 618.6 K, 105 kPa (point 4)

(b) 29.85%

CHAPTER 6

6.11 m = – b/C_P, Temperature increases

6.12 $z = (1 + 2\text{a}P)/(1 + \text{a}P)$

6.13 $RT \ln \text{f} = PV - RT - RT \ln \dfrac{P(V-b)}{RT}$

$+ \dfrac{a}{T^{0.5}\,b} \ln \dfrac{V}{V+b}$

6.16 DV = 1.378 □ 10^{-5} m^3/kg

6.17 377.24 K

6.18 33.51 □ 10^3 kJ/kmol, $P^S = a \exp(b/T)$

6.19 393.43 K

6.20 (a) 1832.4 kJ/kg

(b) 2145.4 kJ/kg

6.21 (b) – 0.0982 (kJ/kmol) $(\text{bar})^{-1}$

6.22 0.1451 kJ/kmol K

6.23 DH = 51,666.14 kJ/kmol

DU = 47,731.74 kJ/kmol

DS = 131.72 kJ/kmol K

6.24 DH = 5796 kJ/kmol

DU = 4133.20 kJ/kmol

DS = – 23.50 kJ/kmol K

DG = – 8754 kJ/kmol

6.25 H = 421.48 kJ/kg, S = 1.22 kJ/kg K

6.26 8.434 J/mol K

6.27 59.65 J/mol K

6.28 97.34% vapour

6.29 $\left(\dfrac{\partial U}{\partial P}\right)_T$ = – 2.681 □ 10^{-3} kJ/kmol bar

$\left(\dfrac{\partial H}{\partial P}\right)_T$ = 8.997 kJ/kmol bar

m = – 0. 0652 K $(\text{bar})^{-1}$

6.31 73.1 bar

6.32 (a) 48.9 bar, 406.9 bar

(b) 48.78 bar, 408.8 bar

6.33 50.41 bar

6.34 1156 bar

6.35 0.2%

6.36 9.94 bar, 15.79 bar

6.37 0.9954 bar

6.38 50.71 bar

6.39 (a) $\ln f = A \ln P + BP + CP^2/2 + DP^3/3$

(b) 301.02 bar

6.40 (a) $\ln \mathsf{f} = BP/RT + (C - B^2)\, P^2/(2R^2T^2)$

(b) 0.9991 bar

6.41 $\mathsf{f} = (a - 1) \ln P + BP + CP^2/2$ 93.44 bar

CHAPTER 7

7.4 $\overline{V_1} = V_1 + x_2^2\,[B + C(4x_2 - 3)]$

$\overline{V_2} = V_2 + x_1^2\,[B + C(3 - 4x_1)]$

7.6 $\ln \gamma' = A(x_2^2 - 1)$, $\ln \gamma_2' = A(x_1^2 - 1)$

7.8 (a) 400 J/mol, 600 J/mol

(b) $\overline{H}_1 = 400 + 4x_2^2\,(18x_1 + 1)$

$\overline{H}_2 = 600 + 4x_1^2\,(10 - 18x_2)$

7.9 $\overline{V_1} = 93.0 - 2.5x_1(1 + x_2)$

$\overline{V_2} = 110.0 + 2.5\,x_1^2$

$\Delta V = 2.5x_1x_2$

7.10 $\overline{V_2} = V_2 + \alpha x_1^2$

$V = x_1V_1 + x_2V_2 + \alpha x_1x_2$

7.11 $\overline{H}_1 = (a_1 + b_1x_1) - x_2(b_2x_2 - b_1x_1)$

7.12 $\overline{V}$ □ 10^3 (m^3/kmol) are given in brackets against x : 0.0667 (10.332), 0.16(13.86), 0.30 (19.78), 0.3634 (22.16), 0.84 (36.83)

7.14 0.8866 □ 10^{-3} m^3/kg

7.15 $\overline{V_1}$ = – 1.3873 □ 10^{-6} m^3/mol (salt)

$\overline{V_2}$ = 18.023 □ 10^{-6} m^3/mol (solvent)

7.16 $\overline{V_1}$ = 0.0389 □ 10^{-6} m^3/mol (methanol)

$\overline{V_2}$ = 0.0175 □ 10^{-6} m^3/mol (water)

7.17 – 22 kJ/kmol (HCl),

– 9.1 kJ/kmol (water)

7.18 0.02903 m^3/mol

7.19 5.056 □ 10^{-4} mol/kg (water)

7.20 533 bar

7.21 – 9.74 kJ, – 9.46 kJ

7.22 g$_A$ and γ'_A are shown in brackets against mole fraction *x*.

0 (–, 1.00), 0.2 (0.5361, 1.0652), 0.4 (0.7330, 1.4565), 0.6 (0.8862, 1.7609), 0.8 (0.9710, 1.9273), 1.0 (1.0, 1.987)

7.23 Yes

7.24 $R \ln \gamma_2 = \dfrac{2A + 3B}{2} x_1^2 - Bx_1^3$

7.25 (a) 1.27, 0.652

(b) 0.4174, 0.2145

7.26 1.331

7.27 (a) 0.0834

(b) 0.36 bar

7.28 0.953

7.29 0.8939

7.30 34.2589 J/K

7.31 – 4675.3 kJ/kmol K h

7.32 $\overline{V}_1 \times 10^3 = 90 + x_2^2\,(9x_2 + 3x_1)$

$\overline{V}_2 \times 10^3 = 50 + x_1^2\,(12x_2 + 6x_1)$

7.33 9.661 □ 10^6 kJ

7.34 340.62 K

7.35 – 10.217 kJ/mol

7.36 5100 kJ to be removed

7.37 1.2914 □ 10^9 kJ/h

7.38 – 1.17 kJ/mol

7.39 $\left(\dfrac{G^E}{RT}\right)' = \dfrac{G^E}{RT} + x_1 \ln \dfrac{f_1}{K_1}$

7.40 $\overline{H}_1^E = 20 - 60\,x_1^2 + 40\,x_1^3$; $\overline{H}_2^E = 40x_1^3$

7.41 $\overline{M}_1^E = 3(B + C)\,x_2^2 + (A - 4B - 10C)\,x_2^3$

$+ 8Cx_2^4$

$\overline{M}_2^E = (A - 3B + 5C)\,x_1^2 + (4B - 16C)\,x_1^3$

$+ 12Cx_1^4$

$\overline{M}_1^E, \overline{M}_2^E$ and M^E/x_1x_2 are respectively,

A – *B* + *C*, 0, *A* – *B* + *C* (for x_1 □ 0) and

0, *A* + *B* + *C*, *A* + *B* + *C* (for x_1 □ 1)

7.42 $\ln \gamma_1 = -\,3x_2^2\,(0.3x_1 + 0.5x_2)$

$\ln \gamma_2 = -\,6x_1^2\,(0.3x_2 + 0.2x_1)$

7.43 $G^E/RT = x_1x_2\,[A + B(x_1 - x_2)]$

7.44 $\overline{V}_1 = 0.1275$ m^3/kmol

$\overline{V}_2 = 0.1625$ m^3/kmol

CHAPTER 8

8.2 (a) 2, overdefined (b) 1 (c) 2 (d) 0 (e) 1 (f) 2 (g) 1

8.3 0.0855

8.4 x and y are given in brackets against T

353.1 (1, 1), 358 (0.78, 0.90),
363 (0.581, 0.777), 368 (0.411, 0.632), 373 (0.258, 0.456), 378 (0.130, 0.261), 383 (0.017, 0.039), 383.6 (0, 0)

$y = 2.45\,x/(1 + 1.45\,x)$

8.5 8.5239 kPa, 76.3% benzene

8.6 120.3 kPa

8.7 131.24 kPa, 46.2% A

8.8 N_2: 67.4% (liquid), 90.34% (vapour)

8.9 (a) x_1 and y_1 are given in brackets against P in kPa:

33.79 (0, 0), 43.426 (0.2, 0.3775),
53.062 (0.4, 0.6179), 62.698 (0.6, 0.7844), 72.334 (0.8, 0.9066), 81.79 (1, 1)

(b) x_1 and y_1 are given in brackets against T in K:

311.45 (1, 1), 315 (0.787, 0.902),
319 (0.581, 0.773), 323 (0.405, 0.623), 327 (0.254, 0.449), 331 (0.123, 0.250),
335.33 (0, 0)

8.10 (a) x_1 and y_1 are given in brackets against P in kPa:

34.02(0, 0), 63.03(0.2, 0.568),
92.04(0.4, 0.778), 121.04(0.6, 0.888),
150.05(0.8, 0.995), 179.06(1, 1)

(b) x_1 and y_1 are given in brackets against T in K:

353.3(1, 1), 363.3(0.686, 0.925),
373.3(0.458, 0.816), 383.3(0.287, 0.666), 393.3(0.156, 0.464), 403.3(0.053, 0.198), 409.4(0, 0)

8.11 (a) 77.3% benzene (b) 57.5% benzene

37.9% benzene

8.12 (a) $x_1 = 0.3138$, $y_1 = 0.7730$

(b) 334.4 K, 79.6% pentane

(c) 110.25 kPa, 85.7% pentane

8.15 x_1 and y_1 are given in brackets against T in K:

334.4 (0, 0), 336.5 (0.2, 0.165), 337.7 (0.334, 0.334), 337 (0.4, 0.4277), 335 (0.6, 0.6858), 331.5 (0.8, 0.8750), 329.5 (1, 1)

8.17 (a) $A = 1.0624$, $B = 1.0217$

(b) $\ln g_1$ and $\ln g_2$ are shown in brackets against x_1:

0 (1.0624, 0), 0.2 (0.6299, 0.0435), 0.4 (0.3706, 0.1713), 0.6 (0.1621, 0.3793), 0.8 (0.0399, 0.6640), 1.0 (0, 1.0217)

8.18 (a) 7.19% acetone

(b) 108.35 kPa

8.19 (a) $A = 1.6625$, $B = 2.7475$

(b) 67.81% hexane

(c) 101.56 kPa

8.20 (a) $A = 0.8940$, $B = 0.8426$

(b) 60.3% acetate, 54.72 kPa

(c) 48.64% acetate

8.21 $A = 0.9376$, $B = 3.0119$

8.22 $A = 0.1365$, $B = 0.1122$

8.23 $A = 1.7492$, $B = 1.4446$

8.24 Yes

8.25 (a) 335.53 K, 80.9% acetone

(b) 351.96 K, 4.07% acetone

8.26 $A = 3.8297$, $B = 2.3540$

8.27 83.16% alcohol

8.28 y_1 is shown in brackets against x_1:

0 (0), 0.2 (0.1355), 0.4 (0.3299),
0.6 (0.6123), 0.8 (0.9212), 1.0 (1.0)

8.29 $g_1 = 1.3551$, $g_2 = 1.682$

8.30 108.4 kPa, 43.46% acetone

8.31 (a) 91.50 kPa, 53.77% propanol

(b) 96.75 kPa, 43.91% propanol

(c) 353.84 K, 81.5% propanol

(d) 360.615 K, 6.38% propanol

8.32 329.7 K, 356.9 K

8.33 (a) 330 K

(b) 340.6 K

(c) Mole % in the liquid and vapour are given in brackets: Ethane (0.48, 0.09), Propane (36.3, 17.45), Isobutane (18.18, 18.74), *n*-Butane (44.98, 63.35), Isopentane (0.13, 0.38)

8.34 (a) 930.3 kPa

(b) 337.4 K, Composition of condensate: Ethane (1.8%), Propane (6.2%), Isobutane (17.3%),*n*-Butane (67.1%), Isopentane (7.50%) 330.2 K, Composition of the liquid and vapour: Ethane (3.22%, 16.81%), Propane (9.31%, 18.7%), Isobutane (19.55%, 18.46%), *n*-Butane (63.38%, 44.57%), Isopentane (4.54%, 1.46%)

8.35 2205 kPa, Methane: 41.91, Ethane: 20.25, Propane: 21.96, Isobutane: 8.57, *n*-Butane: 7.31

706 kPa, Methane: 0.2, Ethane: 1.91, Propane: 16.14, Isobutane: 30.88, *n*-Butane: 50.88

8.36 861.4 kPa, 2446 kPa

8.37 758 kPa

8.38 (a) 717 kPa

(b) Propane: 63.93%, *n*-Butane: 36.07%

(c) Propane: 36.07%, *n*-Butane: 63.93%

8.39 Consistent

8.40 $A = 0.685$, $B = 0.785$, consistent

8.41 Inconsistent

8.42 Consistent

8.43 Consistent

8.44 (a) g_1 given in brackets against x_1: 1.0 (1.00), 0.87 (1.016), 0.50 (1.2074), 0.30 (1.3778)

(b) $\bar{p}_2$ (kPa) in brackets against x_1: 1.0 (0), 0.87 (7.45), 0.50 (20.05), 0.30 (31.63), 0 (37.72)

8.45 Inconsistent

8.46 g_2 in brackets against x_1: 0 (1.0), 0.0033 (0.9999), 0.0168 (0.9982), 0.0486 (0.9854), 0.0986 (0.9746), 0.168 (0.9313), 0.2701 (0.8535), 0.424 (0.7688)

8.47 1.0493

8.48 $\bar{p}_1$ (kPa) in brackets against x_1: 0.065 (24.20), 0.14 (47.90), 0.211 (66.67), 0.293 (84.56), 0.383 (100.31), 0.483 (114.08), 0.587 (125.48), 0.713 (137.19), 0.854 (150.67)

8.49 $A = 1.7405$, $B = 1.4012$. g_1 and g_2 are in brackets against x_1: 0 (5.7, 0), 0.04 (4.8231, 1.0034), 0.11 (3.6990, 1.0251), 0.28 (2.2064, 1.1603), 0.43 (1.5902, 1.3880), 0.61(1.2226, 1.8417), 0.80 (1.0561, 2.6406), 0.89 (1.0144, 3.1869), 0.94 (1.004, 3.5522), 1.00 (1.0, 4.06)

8.50 (a) 1.7951, 1.4679

(b) 1.7951, 1.4679

(c) 65.21% water, 65.82 kPa

8.51 $x_1 = 0.20$, $g_1 = 1.0720$, $g_2 = 1.0059$, $P = 100.15$ kPa, $y_1 = 0.2126$

$x_1 = 0.90$, $g_1 = 1.0007$, $g_2 = 1.0815$,

$P = 100.03$ kPa, $y_1 = 0.894$

8.52 $g_1 = 1.0288$, $g_2 = 2.6100$

8.53 20.22 kPa, 53.57% ethanol

8.54 93.3 kPa, 57.1% *A*

8.55 (a) 128.6 kPa, 34.25% *A*

(b) No change

8.56 123.21 kPa, 38.54% *A*

8.57 Azeotrope exists at

$$x_1 = 0.5\left(1 + \frac{1}{A}\ln\frac{P_1^S}{P_2^S}\right)$$

121.8672 kPa, $y_1 = 0.8379$

8.58 342 K, 0.0975 kg

8.59 Mole fractions of water in the liquid and vapour against pressure (kPa):
Aniline-rich phase:
9.22 (0, 0), 42.475 (0.1, 0.805), 75.73 (0.2, 0.903), 108.99 (0.3, 0.941), 142.24 (0.4, 0.961), 146.23 (0.412, 0.963)
Water-rich phase:
146.23 (0.984, 0.963), 145.06 (0.990, 0.977), 144.67 (0.992, 0.981), 144.08 (0.995, 0.988), 143.49 (0.998, 0.995), 143.10 (1.00, 1.00)

8.60 Mole fractions of ether in the liquid and vapour against temperature in K:
Water-rich phase:
307 (0.0123, 0.9295), 313 (0.00914, 0.9277), 323 (0.0056, 0.8796), 333 (0.0034, 0.8047), 343 (0.0018, 0.6945), 353 (0.00098, 0.5334), 363 (0.00037, 0.3092)

8.61 (a) 369.2 K,
(b) 4.78% aniline

8.62 (a) 361.6 K, 21.9% toluene, 13.1% ethylbenzene, 65.0% water
(b) 387.8 K, 26.8% toluene, 73.2% ethyl benzene

8.63 Mole fraction of heptane in the vapour against temperature in K:
361.53 (0.35), 359.45 (0.40), 357.23 (0.45), 354.83 (0.50), 353.82 (0.52), 352.40 (0.548)

8.64 (a) 366 K, pure water
(b) 374.9 K, pure toluene
Last drop of vapour contains 44.36% toluene

8.65 (a) 388.8 K, pure component 1
(b) 365.5 K, pure component 2

8.66 (a) $g_1 = 1.1570$, $g_2 = 1.4796$
(b) 0.318

CHAPTER 9

9.1 $y_W = \dfrac{n_0 - \varepsilon}{n_0 + (1/2)\,\varepsilon}, y_H = \dfrac{\varepsilon}{n_0 + (1/2)\,\varepsilon}$

$y_O = \dfrac{(1/2)\,\varepsilon}{n_0 + (1/2)\,\varepsilon}$

9.2 $y_{CH_4} = \dfrac{2 - \varepsilon}{8 + 2\varepsilon}, y_{H_2O} = \dfrac{1 - \varepsilon}{8 + 2\varepsilon}$

$y_{CO} = \dfrac{1 + \varepsilon}{8 + 2\varepsilon}, y_{H_2} = \dfrac{4 + 3\varepsilon}{8 + 2\varepsilon}$

9.3 $y_{CH_4} = \dfrac{2 - \varepsilon_1 - \varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}, y_{H_2O} = \dfrac{3 - \varepsilon_1 - 2\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2},$

$y_{CO} = \dfrac{\varepsilon_1}{5 + 2\varepsilon_1 + 2\varepsilon_2}, y_{CO_2} = \dfrac{\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2},$

$y_{H_2} = \dfrac{3\varepsilon_1 + 4\varepsilon_2}{5 + 2\varepsilon_1 + 2\varepsilon_2}$

9.4 $y_{C_2H_4} = \dfrac{3 - \varepsilon_1 - \varepsilon_2}{5 - (1/2)\,\varepsilon_1}, y_{O_2} = \dfrac{2 - (1/2)\varepsilon_1 - 3\varepsilon_2}{5 - (1/2)\,\varepsilon_1},$

$y_{(CH_2)_2O} = \dfrac{\varepsilon_1}{5 - (1/2)\varepsilon_1}, y_{CO_2} = \dfrac{2\varepsilon_2}{5 - (1/2)\varepsilon_1},$

$y_{H_2O} = \dfrac{2\varepsilon_2}{5 - (1/2)\,\varepsilon_1}$

9.5 6.09×10^5
9.6 – 57,350 J/mol
9.7 5.7498×10^{-4}
9.8 Yes
9.9 (a) – 24,800 J/mol, feasible
(b) 2.067
(c) $\Delta G^0 = -\,7.53305 \times 10^4 + 6.12 \times 10^4 (T)^{-1} + 63.710 T \ln T - 181.11 T - 44.958 \times 10^{-3} T^2 + 4.7805 \times 10^{-6} T^3$
(d) 1.7297
9.10 14.3692
9.11 (a) Above 812.4 K, quite favourable
Below 550 K, unfavourable
(b) 75.42%, 45.69%

(c) 81.94%, 55%

9.12 1.0506×10^{-3}

9.13 $\Delta G^0 = -4.35946 \times 10^4 + 13.003\, T \ln T$
$-1.8564 \times 10^{-2} T^2 + 2.43835 \times 10^{-6} T^3$
$+54.972 T$

$$\ln K = \frac{5243.52}{T} - 0.2933 \times 10^{-6} T^2$$

$+2.2329 \times 10^{-3} T - 1.5640 \ln T - 6.612$

9.14 $\Delta G^0 = -3.92016 \times 10^4 + 13.003 T \ln T$
$-1.8564 \times 10^{-2} T^2 + 2.43835 \times 10^{-6} T^3$
$+44.51 T$

$$\ln K = \frac{4715.13}{T} - 0.2933 \times 10^{-6} T^2$$

$2.2329 \times 10^{-3} T - 1.5640 \ln T - 5.3538$

9.15 1.37×10^{-5}

9.16 40.7%

9.17 16.6%

9.18 51.35%

9.19 15.05%

9.20 Ethylene: 21.9%, Steam: 74.0%, Ethanol: 4.1%

9.21 22.51%

9.22 58.92%

9.23 7.77% SO_3, 0.34% SO_2, 7.34% O_2, 84.55% N_2

9.24 32.05% CO_2, 14.36% CO, 53.59% O_2

9.25 46.3% CO_2, 35.8% CO, 17.9% O_2
$Q = -121.859$ kJ/mol C burned

9.26 $\varepsilon = 0.07243$, $y_{NO2} = 0.135$
$y_{N2O4} = 0.119$

9.27 (a) CO = 48.26%, CH_3OH = 11.74%
(b) Concentration will increase.

9.28 3.285%

9.29 (a) 2.08%
(b) 3.4%

9.31 11.58 bar

9.32 (a) 0.4976
(b) 0.8251

9.33 11.93% A, 11.93% B, 76.14% C

9.34 Pressure in bar is given in brackets against temperature in K:

298 (0.0032), 400 (0.342), 500 (5.23) 600 (32.22), 700 (118.06)

9.35 0.4192

9.36 (a) 14.781

(b) Below about 345 K, the reaction is highly favourable. But above 420 K, unfavourable (c) 0.85%, 4.04%

(d) 1.13%, 5.38%

(e) 0.847%

9.37 0.1028

9.38 0.003733, $2.074 \square 10^{-4}$ mol/kg, 0.0553 mol/kg

9.39 81.09%

9.40 1 bar (55.47%), 2 bar (42.64%), 3 bar (35.92%)

9.41 0.0481 bar

9.42 617.87 K

9.43 23 bar, $y_A = 0.072$, $y_B = 0.87$, $y_C = 0.058$

9.44 4.1 bar

9.45 T (K) and P (bar) given in brackets against mole fraction of CO resulting in deposition of C: 0.3422 (900, 1), 0.3434 (900, 5), 0.1248 (900, 10), 0.6946 (1000, 1), 0.4259 (1000, 5), 0.3263 (1000, 10)

9.46 Acetylene: 0.4142, Hydrogen: 0.4142, Ethylene: 0.1716

9.47 8%

9.48 A: 31.58%, B: 26.32%, C: 21.05%,
D: 15.79%, E: 5.26%

9.49 A: 23.54%, B: 5.53%, C: 12.47%, D: 27.81%, E: 30.65%

9.50 4

9.51 4

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