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TECHNICAL

CHEMICAL ENGINEERING THERMODYNAMICS

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$$

$$\left(\frac{\partial v}{\partial s}\right)_P = \left(\frac{\partial T}{\partial P}\right)_s$$

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Contents

Preface

Thermodynamics is the science dealing with equilibrium, energy, the transformation of energy from one form to another, and the laws governing such transformation. These laws are of wide applicability and are used in several branches of engineering and science. It is essential that every chemical engineer should have a thorough knowledge of thermodynamics. The purpose of this text is to present an introductory treatment of chemical engineering thermodynamics.

This text differs from most of the existing texts of the same level in several aspects. Emphasis is placed on precise and logical presentation of the basic principles which are essential for the understanding of thermodynamics. Most of the existing books introduce thermodynamic potentials as convenience functions and do not deal with the Jacobian method of deriving thermodynamic relations, the use of the Bridgman Table, and stability and phase transition in thermodynamic systems. This text shows that thermodynamic potentials arise as partial Legendre transforms of internal energy and presents a detailed discussion on the above topics. The estimation of thermodynamic properties of real gases and real gas mixtures is an important application of chemical engineering thermodynamics. With the availability of computers it is possible to predict the properties of real gases and real gas mixtures using the equation of state (EOS) approach. The methods of predicting thermodynamic properties, fugacity, fugacity coefficient and vapor–liquid equilibria (VLE) data using cubic equations of state, and the UNIFAC method of predicting VLE data are presented in this text.

The first two chapters of the book are devoted to reviewing the basic concepts. The P–v–T behavior of real gases, the estimation of vapor and liquid compressibilities from cubic equations of state (using Cardan's method), and generalized equations of state are discussed in Chapter 3. Chapters 4 and 5 are devoted to the recapitulation of the first and second laws of thermodynamics and their applications. An elementary treatment of the postulational approach is presented in Chapter 6. In this chapter the criteria of equilibrium are formally deduced in addition to introducing thermodynamic potentials as partial Legendre transforms of internal energy. The thermodynamic property relations, Jacobian method in thermodynamics, and the use of the Bridgman Table are presented in Chapter 7. Chapter 8 deals with departure functions (and their estimation through equations of state), compressibility and virial coefficient correlations which will enable readers to generate their own thermodynamic property tables and charts. The thermodynamics of multicomponent mixtures is presented in Chapter 9. This chapter deals with the estimation of fugacity and fugacity coefficients for real gases and their mixtures. Chapter 10 presents the stability criteria, phase transition in thermodynamic systems, Gibbs phase rule and the estimation of vapor pressure from an equation of state. The thermodynamic properties of liquid solutions, phase equilibrium, excess Gibbs free energy models and the UNIFAC method of predicting activity coefficients are discussed in Chapter 11. Chapter 12 deals with vapor–liquid equilibria and retrograde condensation, while Chapter 13 presents the laws of dilute solutions. Finally, Chapter 14 presents chemical reaction equilibria.

Thermodynamics is recognized as an important area of study in chemical engineering curriculum and a two-semester thermodynamics course is offered to chemical engineering undergraduate students in all institutes. In some engineering institutes all the students, irrespective of their field of study, are expected to take a one-semester core course in thermodynamics, which deals with basic principles and elementary applications. Chemical engineering students are further expected to take a one-semester course in chemical engineering thermodynamics. This text covers the course on chemical engineering thermodynamics and precisely caters to the needs of undergraduate students of all institutes. Its entire contents can be covered in one semester at the rate of 3 hours per week. In order to keep the book to a reasonable size, the basic concepts, the laws of thermodynamics and their applications are briefly reviewed in Chapters 1, 2, 4 and 5; power and refrigeration cycles are not presented in the text. This is no limitation, since the reader has already been exposed to these topics in the first course. This text can be easily adopted for a two-semester thermodynamics course. Chapters 1–7 of the text supplemented with Chapters 2–4, 6, 7, 12 and 13 from the author's earlier book *An Introduction to Thermodynamics*, Wiley Eastern Ltd. (now New Age International), New Delhi (1993), can be covered in the first semester, while Chapters 8–14 of the text are recommended for the second semester. Readers who do not wish to pursue the subject rigorously may omit Chapter 6 (except Sections 6.7–6.10) and Sections 10.1 and 10.2 without any loss of continuity or content. The entire text, except Chapter 6 and Sections 10.1 and 10.2 have been class-tested by the author and his colleagues at IIT Kanpur.

It is an established fact that thermodynamics is a quantitative subject and can be best imparted by demonstrating the applications of the principles to a few representative problems. Moreover, the readers' confidence and ability to apply the principles of thermodynamics to solve real life problems will be greatly improved if they work out a considerable number of problems. Keeping this objective in mind, numerous solved examples and problems with answers are included in the text.

Though this book is intended for undergraduate students, its logical and comprehensive treatment is such that it can be used as a reference book by graduate students, practising chemical engineers and researchers in R&D organizations. I hope that teachers and students will find the material presented in this text both useful and stimulating. It is also hoped that this text would contribute to effective teaching of chemical engineering thermodynamics to undergraduate students, and that students and professional chemical engineers would derive the maximum benefit from it. Some errors might have inadvertently crept into this book and I would greatly appreciate if readers would bring them to my attention.

The financial support provided by the Curriculum Development Cell, Quality Improvement Programme (at IIT Kanpur) of the Ministry of Human Resource Development for the preparation of the manuscript is gratefully acknowledged. Finally, I wish to sincerely thank the Publishers, Universities Press (India) Ltd., for bringing out the book in its present form.

Kanpur
November 1996

Y.V.C. Rao

Nomenclature

A	Cross-sectional area
A	Ampere
A	Helmholtz free energy
A	Constant in Antoine equation
A	Two suffix Margules parameter
A	Adjustable parameter in Redlich–Kister equation
A	van Laar constant
A_i	Notation for chemical species i
A_{ij}	Three suffix Margules parameter
A_0	Constant in Beattie–Bridgman and BWR equations of state
A_{0m}	Mixture constant in Beattie–Bridgman and BWR equations of state
a	Acceleration
a	Constant in van der Waals, Beattie–Bridgman and BWR equations of state
a	Constant in heat capacity equation
a	Molar (specific) Helmholtz free energy
a_i	Pure component constant in equation of state
a_i	Activity of component i
a_{ji}	UNIQUAC adjustable parameter
a_m	Mixture constant in equation of state
a_{mn}	UNIFAC group interaction parameter
a^E	Excess molar Helmholtz free energy
$(a - a^0)$	Molar Helmholtz free energy departure
B	Second virial coefficient
B	Constant in Antoine equation
B	van Laar constant
B	Adjustable parameter of Redlich–Kister equation
B_{ij}	Interaction virial coefficient
B_m	Mixture second virial coefficient
B_0	Constant in Beattie–Bridgman and BWR equations of state
B_{0m}	Mixture constant in Beattie–Bridgman and BWR equations of state
B'	Second virial coefficient in Berlin form
b	Constant in Beattie–Bridgman and BWR equations of state
b	Constant in heat capacity equation
b_i	Pure component constant in equation of state
b_j	Number of J atoms in a reaction mixture
b_m	Mixture constant in equation of state
C	Third virial coefficient

C	Constant in the Beattie–Bridgman and BWR equations of state
C	Constant in Antoine equation
C	Adjustable parameter of Redlich–Kister equation
C_0	Constant in Beattie–Bridgman and BWR equations of state
C_{0m}	Mixture constant in Beattie–Bridgman and BWR equations of state
C'	Third virial coefficient in Berlin form
Cd	Candela
$(COP)_{\mathrm{HP}}$	Coefficient of performance of a heat pump
$(COP)_{\mathrm{R}}$	Coefficient of performance of a refrigerator
C_p	Isobaric molar (specific) heat capacity
C_p^0	Isobaric molar heat capacity in the ideal gas state
C_{p_m}	Isobaric mean heat capacity
C_p^ℓ	Heat capacity of liquid
C_p^s	Heat capacity of solid
C_p^v	Heat capacity of vapor
C_v	Molar (specific) heat capacity at constant volume
c	Number of components
c	Molar concentration
c	Constant in heat capacity equation
D	Fourth virial coefficient
D_e	Depth of potential well or bond energy
D_0	Dissociation energy of a diatomic molecule
D'	Fourth virial coefficient in Berlin form
d	Constant in heat capacity equation
E	Energy
E	emf of a reversible cell
e	Molar (specific) energy
e	Constant in heat capacity equation
F	Degrees of freedom
F	Force
F	Mole number of feed stream
f	Fugacity
f_i^0	Standard state fugacity of component i
f_i^*	Fugacity of pure component i at the solution T and P
f^ℓ	Fugacity of liquid
f^s	Fugacity of solid
$\hat{f}_i$	Fugacity of component i in a solution
$\hat{f}_i^l$	Fugacity of component i in liquid phase
$\hat{f}_i^v$	Fugacity of component i in vapor phase
G	Gibbs free energy

G_{ij}	NRTL parameter
ΔG^0	Standard Gibbs free energy change of reaction
ΔG_f^0	Standard Gibbs free energy of formation
ΔG_T^0	Standard Gibbs free energy change of reaction at T
g	Molar (specific) Gibbs free energy
g	Acceleration due to gravity
g^0	Standard state molar Gibbs free energy
$(g - g^0)$	Gibbs free energy departure
$\bar{g}_i$	Partial molar Gibbs free energy of component i
g_{ij}	energy of interaction parameter
Δg_m	Gibbs free energy change due to mixing
g^E	Excess Gibbs free energy
$\bar{g}_i^E$	Partial molar excess Gibbs free energy
g^I	Ideal solution Gibbs free energy
H	Enthalpy
ΔH_0	Constant in the relation to express the temperature dependence of standard enthalpy change of a reaction
ΔH_c^0	Standard enthalpy change (heat) of combustion
ΔH_f^0	Standard enthalpy change (heat) of formation
ΔH_T^0	Standard enthalpy change of a reaction at temperature T
h	Molar (specific) enthalpy
h	Planck's constant
h	Distance
h_f	Molar (specific) enthalpy of a liquid
h_g	Molar (specific) enthalpy of a vapor
$\bar{h}_i$	Partial molar enthalpy of component i
h_i^*	Pure component molar enthalpy at solution temperature and pressure
h^E	Excess enthalpy
h^I	Ideal solution enthalpy
Δh_f	Enthalpy of fusion at the normal freezing point
Δh_m	Enthalpy change due to mixing
Δh_v	Enthalpy of vaporization at boiling point
Δh_{vn}	Enthalpy of vaporization at normal boiling point
$(h - h^0)$	Enthalpy departure or residual enthalpy
$(h - h^0)^0$	Simple fluid term or first order enthalpy departure
$(h - h^0)^1$	Correction term or second order enthalpy departure
I	Moment of inertia
I	Constant in the relation to express the temperature dependence of standard Gibbs free energy change of a reaction
i	Electric current

J	Joule
K	Kelvin
K	Distribution (partition) coefficient
K_a	Equilibrium constant of a reaction in terms of activities
K_c	Equilibrium constant of a reaction in terms of molar concentration
K_i	K factor (equilibrium ratio) for component i
K_N	Equilibrium constant of a reaction in terms of mole numbers
K_p	Equilibrium constant of a reaction in terms of partial pressures
K_x	Equilibrium constant of a liquid phase reaction in terms of mole fractions
K_y	Equilibrium constant of a gas phase reaction in terms of mole fractions
K_ϕ	Equilibrium constant of a reaction in terms of fugacity coefficient
k_i	Henry's law constant for component i
k_{ij}	Binary interaction parameter
k'_{ij}	Binary interaction parameter in Lee–Kesler method
L	Mole number of liquid stream
ℓ	Length
M	Magnetization
M	Number of atomic species constituting the reaction mixture
$\mathcal{M}$	General extensive thermodynamic property
M_P	Circondenbar or maxcondenbar point
M_T	Cricondentherm or maxcondentherm point
m	mass
m	metre
m	Molality
$\dot{m}$	Mass flow rate
mol	Mole
N	Newton
N	Mole number
N_f	Mole number of saturated liquid
N_g	Mole number of saturated vapor
P	Pressure
P	Number of phases
Pa	Pascal
P_c	Critical pressure
P_{cm}	Pseudocritical pressure
P_i	Pure component pressure of component i
P_r	Reduced pressure
P_{rm}	Pseudoreduced pressure
P^s	Saturation pressure
P^*	Three phase equilibrium pressure

p_i	Partial pressure of component i
Q	Heat interaction
$\dot{Q}$	Rate of heat interaction
Q_e	Electrical charge
Q_k	Group area parameter
q	Heat interaction per mole or per unit mass
q_i	Surface area parameter of component i
q_i	Measure of volume of component i in Wohl's equation
R	Universal gas constant
R_k	Group volume parameter
r_e	Equilibrium interatomic distance
r_i	Volume parameter of component i
S	Entropy
S	Parameter in SRK and PR equations of state
S_G	Entropy generation
ΔS^0	Standard entropy change of a reaction
s	second
s	Molar (specific) entropy
s^E	Excess molar entropy
s_f	Molar (specific) entropy of liquid
s_{fg}	Molar (specific) entropy change due to vaporization
s_g	Molar (specific) entropy of vapor
$(s - s^0)$	Entropy departure or residual entropy
$(s - s^0)^0$	Simple fluid term or first order entropy departure
$(s - s^0)^1$	Correction term or second order entropy departure
Δs_m	Entropy change due to mixing
T	Absolute temperature
T_B	Boiling point of solvent
T_{br}	Reduced normal boiling point
T_c	Critical temperature
T_{cm}	Pseudocritical temperature
T_f	Normal freezing point of solvent
T_r	Reduced temperature
T_{rm}	Pseudoreduced temperature
T_t	Triple point temperature
t	Time
t	Temperature in °C
t^*	Three phase equilibrium temperature
U	Internal energy
$U[-P]$	Partial Legendre transform of U where V is replaced by P

$U[T]$	Partial Legendre transform of U where S is replaced by T
$U[T,-P]$	Partial Legendre transform of U where S and V are simultaneously replaced by T and P, respectively
u	Molar (specific) internal energy
$(u - u^0)$	Internal energy departure
u^E	Excess molar internal energy
u_f	Molar (specific) internal energy of saturated liquid
u_{fg}	Change in molar (specific) internal energy due to vaporization
u_g	Molar (specific) internal energy of saturated vapor
$\bar{u}_i$	Partial molar internal energy of component i
u_i^*	Pure component molar internal energy at solution temperature and pressure
u^I	Ideal solution molar internal energy
u_{ij}	Average interaction energy between molecules of components i and j
u_{mn}	Measure of interaction energy between groups m and n
$\mathbf{V}$	Velocity
V	Volume
V	Mole number of vapor stream
v	Molar (specific) volume
v_c	Critical volume
v^E	Excess volume
v_f	Molar (specific) volume of saturated liquid
v_{fg}	Change in molar (specific) volume due to vaporization
v_g	Molar (specific) volume of saturated vapor
v^I	Ideal solution volume
$\bar{v}_i$	Partial molar volume of component i
v_i^*	Pure component molar volume at solution temperature and pressure
v^ℓ	Liquid molar volume
Δv_m	Volume change due to mixing
v_r	Reduced volume
v^s	Solid molar volume
v^∞	Ideal gas volume
W	Watt
W	Work
$\dot{W}$	Rate of work done
W_s	Shaft work
$\dot{W}_s$	Rate of shaft work done
$\dot{W}_T$	Rate of work done by turbine
$\dot{W}_P$	Rate of work done by the pump
X	Quality of a mixture
x_f	Mole fraction of liquid

x_g	Mole fraction of vapor
x_i	Mole fraction of component i in liquid phase
y_i	Mole fraction of component i in the vapor phase
Z	Elevation
Z	Compressibility factor
Z^0	Compressibility factor for simple fluid term
Z^I	Compressibility factor for correction term
Z'	Compressibility factor for use with Dalton's law
Z^ℓ	Liquid compressibility factor
Z_m	Mixture compressibility factor
Z^R	Reference fluid compressibility factor
Z^v	Vapor compressibility factor
z	Coordination number
z_F	Composition of feed stream
z_i	Effective volume fraction of component i

Greek Letters

α	Constant in the general cubic equation of state
α	Constant in BWR equation of state
α	Parameter in SRK and PR equations of state
α_{ji}	Number of J atoms per molecule of component i
α_m	Mixture constant in BWR equation of state
α_{12}	Non-randomness parameter in NRTL equation
β	Coefficient of volume expansion
β	Constant in the general cubic equation of state
Γ_k	Group residual activity coefficient
Γ_k^i	Residual activity coefficient of group k in a reference solution containing only molecules of type i
γ	Ratio of heat capacities
γ	Constant in the general cubic equation of state
γ	Constant in BWR equation of state
γ	Activity coefficient
γ^*	Henry's law activity coefficient
γ^∞	Activity coefficient at infinite dilution
γ_i	Activity coefficient of component i
γ_i^c	Combinatorial part of activity coefficient γ_i
γ_i^R	Residual part of activity coefficient γ_i
γ_m	Mixture constant in BWR equation of state
ϵ	Extent of reaction
ϵ	Strain

ϵ_n	Vibrational energy
η	Energy conversion (thermal) efficiency of a heat engine
η_c	Isentropic efficiency of a compressor
η_N	Isentropic efficiency of a nozzle
η_P	Isentropic efficiency of a turbine
τ	Stress
τ	Strain
τ	Surface tension
τ_{ij}	UNIQUAC parameter
τ_{ij}	NRTL parameter
θ_i	Area fraction of component i
θ_m	Surface area fraction of group m
Λ_{ij}	Wilson's parameter
λ_{ij}	Energy interaction parameter between molecules of components i and j
μ	Chemical potential
μ_i	Chemical potential of component i
μ_{JT}	Joule–Thomson (Kelvin) coefficient
ν	Stoichiometric coefficient
ν	Vibrational frequency
ν_k^i	Number of groups of type k in a molecule of component i
π	Osmotic pressure
π_J	Lagrange multiplier
κ	Isothermal compressibility
κ_s	Isentropic compressibility
ρ	Density
ϕ	Fugacity coefficient for fugacity–pressure ratio
ϕ^0	Fugacity coefficient for simple fluid term
ϕ^1	Fugacity coefficient for correction term
ϕ^k	Reference fluid fugacity coefficient
ϕ^s	Fugacity coefficient at saturation pressure
ϕ_i	Volume fraction of component i
$\widehat{\phi}_i$	Fugacity coefficient of component i in a mixture
ϕ^ℓ	Liquid fugacity coefficient
$\widehat{\phi}_i^v$	Fugacity coefficient of component i in vapor phase
ξ	Euken coefficient
ψ_{mn}	UNIFAC parameter
ω	Angular velocity
ω	Acentric factor
ω_m	Mixture acentric factor
ω^R	Reference fluid acentric factor

1 Introduction

Learning Objectives

This chapter will enable readers to

- get acquainted with the basic questions an engineer faces in his professional career;
- understand in principle what thermodynamics is and the essence of the four laws of thermodynamics;
- know the two different approaches, namely macroscopic and microscopic, adopted in the study of thermodynamics; and
- use the International System of Units (SI) in his professional career.

Now a days we are living in a world of chemical products and in our every day activities we use a variety of them. These include tooth pastes, shaving creams, after-shave lotions, cosmetics, toilet soaps and detergents,to name a few. The gasoline and diesel oil used in our automobiles; the tyres of the automobiles made of rubber and nylon fibres, the clothes containing nylon, terylene and polyester fibres are also chemical products. Perhaps we do not spend even a single day without using a variety of products made of plastic material. Similarly we find the extensive use of dyes, paints, varnishes, insecticides, pesticides, chemical fertilizers and life-saving drugs. Finally the paper on which this matter is printed and the ink used for printing are also chemical products. To put it in short, the availability of a variety of chemical products and the chemical engineer's ability to produce them are largely responsible for our comfortable living and for the advancement of civilization.

The main activities of a chemical engineer are concerned with the design and development of new processes or the improvement of the existing processes for converting the raw materials into useful products of greater value in an optimal way. The resources available to an engineer are *material*, *energy*, *space* and *time*. An engineer should make every effort to consume the minimum possible amounts of resources for producing the required products. That is, the processes are to be designed such that they require minimum energy, space and material and the rate of production should be as high as possible. Before an engineer takes up the task of designing a commercial plant or a detailed study on a pilot plant, he should know whether the process is feasible or not. If feasible, how much energy is needed ? What fraction of the raw materials can be converted into products ? How much time is required to produce a specified quantity of product ? Are there alternative processes ? If so which process is preferable ?

The processes normally encountered by a chemical engineer can be classified as unit operations like distillation, absorption, extraction, fluid flow, energy transfer as heat, etc. which are mainly physical in character and unit processes like nitration, halogenation, esterification, hydrogenation, etc. A chemical engineer studies these processes from the following points of view: *(i) limiting conditions of operation and energy requirements*, and *(ii) rates of mass and energy transfer*. Consider the unit operation distillation as an example. It is essential to know the degree of separation that can be achieved under the given conditions of temperature and pressure (irrespective of the mechanism and the type of equipment used), equilibrium relationships and the energy requirement. As a further example, consider the task of producing alcohol according to the reaction

$$C_2H_4 + H_2O \longrightarrow C_2H_5OH$$

A chemical engineer entrusted with the task of producing alcohol should know the answers to the following questions:

- Is the reaction feasible at specified pressure and temperature ?
- Does the reaction go to completion or does it proceed to a certain extent only, beyond which it cannot proceed ?
- How much energy is required for the reaction to take place ?
- Is it possible to increase the conversion by changing the operating conditions ?
- How much energy is required to separate the desired product from the byproducts and reactants ?

The answers to all the above important questions can be obtained by the application of thermodynamic principles to the various stages or processes of manufacture. Hence the study of thermodynamics is essential for the design and development of processes.

1.1 What is thermodynamics ?

Thermodynamics is a science dealing with energy and its transformation and equilibrium. Energy is available in several forms and it transforms from one form to the other when the material under consideration interacts with the surroundings. During this interaction, the state of the matter and its properties change and the matter exchanges energy either as heat or work or both with the surroundings. Thermodynamics relates the change in the state of the matter to the energy exchanged as heat and work with the surroundings. The exchange of energy cannot take place beyond a certain extent and the matter reaches a dead state or equilibrium state. Thermodynamics predicts the state of equilibrium and dictates the limits beyond which a given process at specified conditions cannot proceed. In other words, thermodynamics provides a yardstick to compare the processes. Suppose an engineer is devising a heat engine to continuously convert the energy possessed by the matter into work. Thermodynamics dictates the maximum efficiency of the engine. Thermodynamics also tells whether a given process — physical or chemical — can spontaneously proceed or not in the specified direction, at the given conditions. That is, it predicts whether a particular process is feasible or not at the specified conditions. Thus, thermodynamics is a subject of great generality and finds wide applications in chemical, mechanical, metallurgical and aerospace engineering in addition to the fields of chemistry and physics. Thermodynamics originated as a result of man's constant and continuous effort to devise means of converting the energy possessed by matter into work. Thermodynamics was formalized in the nineteenth century by Joule, Clausius, Kelvin and Carnot. Later Gibbs developed it into a science of such a broad scope that nowadays it is used in all branches of engineering and science.

The principles of thermodynamics can be summarized in the form of four laws, known as the zeroth, first, second and third laws of thermodynamics. The zeroth law of thermodynamics is about thermal equilibrium between a set of bodies. This law forms the basis for the measurement of temperature. The first law of thermodynamics relates the changes in the energy of matter under consideration with the energy exchanged as heat and work with its surroundings. This law is also known as the principle of conservation of energy. The first law of thermodynamics is of much wider applicability than the principle of conservation of energy proposed by Leibnitz, which is applicable to mechanical systems only. The first law of thermodynamics leads to the concept of internal energy. The second law of thermodynamics dictates the limit to which the energy possessed by matter can be converted into work and thus provides a means of comparing the performance of several devices and processes. This law rules out the possibility of a spontaneous process reversing on its own. That is, the second law of thermodynamics tells about the direction in which a process proceeds and provides information regarding the feasibility of a process. The second law of thermodynamics also introduces the concept of entropy and tells that the entropy of the universe can never decrease. This law is also known as the principle of entropy increase. Finally, the third law of thermodynamics defines the absolute zero of entropy, thus providing a means of estimating it in absolute quantities.

These laws of thermodynamics are based on a large number of experimental observations and were deduced through logical reasoning. The laws of thermodynamics cannot be proved the way we prove mathematical theorems. The validity of these laws rests upon the agreement between the experimental results and the predictions made on the basis of these laws. So far no experimental evidence is available to doubt the validity of these laws.

1.2 Macroscopic and microscopic approaches

Thermodynamics can be studied by adopting two different approaches — macroscopic and microscopic. Suppose at a certain instant of time a reactor contains a gas mixture of C_2H_4, H_2O and C_2H_5OH. The quantity and the state of the contents in the reactor can be specified in terms of pressure, volume, temperature and composition of the mixture. The pressure of the gas mixture in the reactor can be easily measured with a pressure gauge, the volume can be estimated from a knowledge of the dimensions of the reactor, the temperature can be measured with a thermometer and the composition of the mixture can be measured with a gas chromatograph. Thus, the state of the matter under consideration is described in terms of macroscopically measurable quantities. The macroscopic approach is adopted in classical thermodynamics. The relations obtained in classical thermodynamics are independent of the structure of matter. In the macroscopic approach:

- Only a small number of variables are used to describe the state of matter.
- These variables can be measured or estimated.
- The structure of the matter under consideration is not taken into account.

We know that all matter consists of a large number of microscopic particles called atoms and molecules. The number of molecules in one mole is equal to *Avogadro's number*, $6.022\,045\times10^{23}$ molecules/mol. The gas mixture in the reactor can be considered as an assembly of a large number of molecules and these molecules move at random with independent velocities. Then the state of a molecule can be specified in terms of its position coordinates (x, y, z) and the velocity components (V_x, V_y, V_z) in the x-, y- and z- directions of motion. Then to describe the state of a collection of a large number of molecules we have to specify a large number of variables. These variables cannot be measured. Moreover, it is known that Newtonian mechanics is inadequate to describe the motion of microscopic particles — atoms and molecules. Heisenberg's uncertainty principle tells us that it is impossible to have a precise knowledge of the position as well as the velocity of a particle at the same instant of time. The behavior of microscopic particles can be predicted by applying quantum mechanics. Application of quantum mechanics to the motion of atoms/molecules gives us the probability of finding the atom/molecule in a given location at the specified time. Macroscopic properties like pressure are the manifestations of the random motion of the molecules. The pressure exerted by a gas is the force per unit area due to molecular impacts on the container wall. At normal conditions of pressure and temperature, the number of molecular impacts experienced by the container wall is of the order of 10^{27} per m^2 per second. An instrument like a pressure gauge which is used to measure pressure takes a definite time, and during this time interval, the container wall experiences an extremely large number of collisions. Therefore, the pressure recorded by the instrument is the *time average value of pressure*. The time average value of pressure can be estimated from a knowledge of the behavior of the independent molecules. For this purpose statistical methods are employed. Thus, in the microscopic approach:

- A large number of variables are needed to specify the state of matter.
- These variables cannot be measured.
- A knowledge of the structure of matter is essential to analyze the behavior of constituent atoms/molecules.

The microscopic approach is adopted in statistical thermodynamics. The purpose of this book is to deal with classical thermodynamics and its applications to analyze problems concerning a chemical engineer. Hence, statistical thermodynamics is not presented. Interested readers are advised to refer to the author's earlier book [1].

1.3 International system of units

In the study of thermodynamics we deal with variables such as pressure, volume, temperature, energy, entropy, heat capacity, work, etc. A thorough knowledge of the units of measurement of the commonly encountered physical quantities is essential for the understanding of thermodynamics. The system of units employed in thermodynamics is not different from that employed in the study of other sciences like physics and chemistry. Over the years many systems of units like FPS (Foot Pound Second), commonly known as the English system of units, CGS (Centimetre Gram Second) and MKS (Metre Kilogram Second) have been used. The CGS and MKS systems of units are also known as the *metric system of units*. In an attempt to standardize the system of units, the General Conference on Weights and Measures (11th Conférence Générale des Poids et Mesures, abbreviated as CGPM) held in 1960 recommended that the International System of Units (Systéme International d'Unites) abbreviated as SI units should replace all other existing systems of units. Many countries have adopted SI units as the legal system of units. In this book the International System of Units only are adopted. For more details on SI units, the reader is advised to consult the references [2]–[6].

A birdseye view of the International System of Units is presented here and the reader who is already quite familiar with the use of SI units may skip the rest of this chapter without any loss of continuity or content. All physical quantities are divided into two groups as primary and secondary quantities. Primary quantities are measured in terms of the base units and the secondary quantities are measured in terms of the derived units. The principal features of the SI units are:

(i) Minimum number of base units (only seven) are used to cover the fields of science and engineering.
(ii) Based on definitions or physical laws the derived units are obtained in terms of the base units. The derived units do not contain any arbitrary constants.
(iii) The familiar derived units have been given internationally accepted names.
(iv) Multiples and submultiples of units have been recommended to facilitate the use of SI units to cover a wide range of values.

1.3.1 Base units

The seven base units adopted in the International System of Units are presented below:

(i) Kilogram The basic SI unit for mass is *kilogram* (abbreviated as kg). The mass of the block of a standard alloy of platinum and iridium maintained at the International Bureau of Weights and Measures at Sevres, Paris, is taken as the base unit of mass.

(ii) Metre The basic SI unit for length is *metre* (abbreviated as m). For several years, the distance between two marks when measured at 0°C, on a bar of platinum–iridium alloy maintained at the International Bureau of Weights and Measures, Sevres, Paris, was taken as one metre. In 1960, the General Conference on Weights and Measures (CGPM 1960) held in Paris redefined the *metre as the length equal to 1 650 763.73 wavelengths, in vacuum, of the radiative transition between* $2p_{10}$ *and* $5d_5$ *in krypton-86.*

(iii) Second In SI units, the base unit for time is *second* (abbreviated as s). For several years, the second was defined as equal to 1/86, 400 of a mean solar day. Later it was recognized that the duration of a mean solar day can vary. The advent of the atomic clock has made it possible to measure frequency with an accuracy of 2 parts in 10^{11}. In view of this, the CGPM 1967 redefined the *second as the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of cesium-133 atom.*

(iv) Kelvin The basic SI unit for temperature is *kelvin* (abbreviated as K). The CGPM 1967 defined *kelvin as equal to 1/273.16 of the thermodynamic temperature of the triple point of water* (the thermodynamic temperature is discussed in Section 5.6). The base unit for temperature is named as kelvin in honour of the scientist Kelvin. It is a common practice to express the temperature of a body in terms of the degree Celsius (symbol °C). The Celsius temperature is given by

$$^\circ\mathrm{C} = \mathrm{K} - 273.15$$

(v) Mole It is known that all matter consists of atoms, molecules, etc. Therefore, the quantity of a substance can be expressed in terms of the number of atoms or molecules constituting the substance. In 1971, the General Conference on Weights and Measures (CGPM 1971) defined the mole (abbreviated as mol) as the *amount of substance which contains as many elementary entities as there are atoms in 0.012 kg of carbon-12.* When the unit mole is used, it is necessary to specify the elementary entities as atoms, molecules, ions, electrons, etc. The number of elementary entities in one mole is equal to Avogadro's number $6.022\,045 \times 10^{23}$.

(vi) Ampere The basic SI unit for electric current is *ampere* (abbreviated as A). In 1948, the General Conference on Weights and Measures (CGPM 1948) defined the ampere as the *constant electric current which, if maintained in two straight parallel conductors of infinite length and negligible cross section placed one metre apart in vacuum would produce a force* 2×10^{-7} *newton per metre length, between the conductors.*

(vii) Candela The *candela* (abbreviated as cd) is the base unit for luminous intensity. The CGPM 1979 defined candela as the *luminous intensity in a given direction of a source which emits monochromatic radiation of frequency* 540×10^{12} *hertz and of which the radiant intensity in that direction is 1/683 watts per steradian.*

1.3.2 Derived units

(i) Force The secondary quantities are expressed in terms of the derived units. The derived units are formed from the base units based on certain physical laws or definitions. For example, velocity (V) is defined as $V = d\ell/dt$ where ℓ is length and t is time. Therefore, the unit of velocity is m/s or m s^{-1}. Similarly, the acceleration (a) is given by $a = dV/dt$ and the unit of acceleration is m/s^2 or m s^{-2}. The SI unit of force is newton (N). The unit newton is derived from Newton's second law of motion which gives force (F) as the product of mass (m) and acceleration (a). That is

$$F = m \times a$$

The unit of force, newton (abbreviated as N) has been named after Newton. Newton is the force required to produce an acceleration of 1 m/s^2 in a body of mass 1 kg. The SI unit of newton is kg m/s^2. It may be noted that in the relation $F = m \times a$, no arbitrary constant is introduced in deriving the units of newton. The gravitational force acting on a mass (m) is given by $F = m \times g$, where g (= 9.81 m/s^2) is the acceleration due to gravity. The force of gravity on a body is usually called the weight of the body and hence the unit of weight is newton. Quite often the mass of a body is usually called its weight in a casual way and one should carefully distinguish between weight and mass.

Example 1.1 A payload weighing 981 N is kept in a spacecraft. If the spacecraft lands on the moon where g = 1.62 m/s^2, calculate the weight of the payload on the moon.

Solution The force of gravity on the payload on the earth's surface is given by

$$F = m \times g \quad \text{or} \quad 981 = m \times 9.81 \quad \text{or} \quad m = 100 \text{ kg}$$

The mass of the payload remains constant whether it is on the earth's surface or on the moon. However, the weight or the force of gravity on the payload depends upon the location, since the acceleration due to gravity differs. The force acting on the payload on the moon's surface $F_{(\text{moon})}$ is given by

$$F_{(\text{moon})} = m \times g \quad \text{or} \quad F_{(\text{moon})} = 100 \times 1.62 = 162 \text{ N}$$

(ii) Pressure The SI unit of pressure is derived from the definition of pressure. Pressure (P) is defined as the force per unit area. Thus, the unit of pressure is N/m^2 or N m^{-2}. The unit of pressure has been named as pascal (abbreviated as Pa) in honour of the scientist Pascal. The air of the atmosphere exerts pressure on all bodies which are exposed to air. At sea level, the pressure exerted by the air is 101 325 Pa. This pressure is usually known as the standard atmospheric pressure. If a long glass tube closed at one end is completely evacuated and the open end is immersed in a pool of mercury, keeping the glass tube upright, the mercury rises to a height of 760 mm. That is, one standard atmosphere balances a column of 760 mm of mercury at 0°C where the density of mercury is $1.359\ 51 \times 10^4$ kg/m^3 and at a location where the acceleration due to gravity is equal to the standard value 9.806 65 m/s^2. The pressure exerted by 1 millimetre column of mercury under these conditions is named as Torr, in honour of the scientist Torricelli. Usually, subatmospheric pressure, or pressure below atmospheric pressure, which are normally encountered in systems under vacuum, are expressed in Torr. Since the SI unit of pressure Pa is quite small in magnitude, for convenience the pressure is usually expressed in kilopascal (kPa). A unit which is equal to 10^5 Pa (which is approximately equal to one atmospheric pressure) has been given the name *bar* and this unit is recognized by the Comite International des poids et Mesures (CIPM) because of its practical importance. Thus, one standard atmospheric pressure (atm) is

$$1 \text{ atm} = 760 \text{ Torr} = 101\ 325 \text{ Pa} = 1.013\ 25 \text{ bar}; \quad 1 \text{ Torr} = 133.322 \text{ Pa}$$

Example 1.2 Calculate the force due to the atmospheric air on a child's head which measures 15 cm × 12 cm.

Solution We know that area, $A = 0.15 \times 0.12 = 0.018\ \text{m}^2$.

$$\text{Pressure} = \text{Force/Area} = F/A \quad \text{or} \quad F = PA = 101\ 325 \times 0.018 = 1\ 823.85\ \text{N}.$$

Example 1.3 In a fluid flow experiment it is required to measure the pressure drop across a definite length of a pipeline. For this purpose an inclined manometer is connected across the two selected stations as shown in Fig.1.1. Suppose liquid water of density $10^3\ \text{kg/m}^3$ is flowing through the pipeline and carbon tetrachloride of density $1.595 \times 10^3\ \text{kg/m}^3$ is used as the manometric fluid. Calculate the pressure drop between the two selected stations when $\ell = 40$ cm.

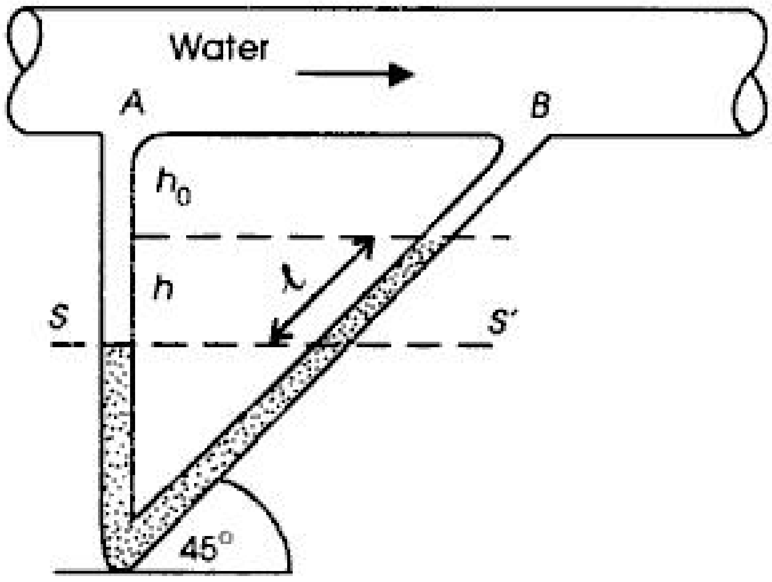


Fig.1.1 *Inclined manometer for measuring pressure drop.*

Solution Let us assume the following:

P_A = pressure at station A; P_B = pressure at station B

ρ_W = density of water; ρ_c = density of carbon tetrachloride

pressure at S = pressure at S′

$$\text{or} \quad \rho_W\, g\, (h_o + h) + P_A = \rho_W\, g\, h_o + \rho_c\, h\, g + P_B$$

$$\text{or} \quad P_A - P_B = hg(\rho_c - \rho_W) = \ell \sin\theta g(\rho_c - \rho_W) = 0.4 \times 0.7071 \times 9.81(1.595 - 1) \times 10^3 = 1650.9\ \text{Pa}$$

(iii) Work and Power *Work done by a body is defined as the product of the force and the distance moved in the direction of the applied force.* Suppose a force F acting on a body moves it through a distance ℓ in the direction of the applied force, then the work done on the body is given by

$$W = F \times \ell = \text{newton} \times \text{metre} = \text{N m} = \text{joule}$$

The unit of work has been given a special name joule, abbreviated as J. The unit of work and energy is joule. *Power is the rate at which work is done or work done per unit time*, i.e.,

$$\text{Power} = \frac{\text{work}}{\text{time}} = \frac{\text{joule}}{\text{second}} = \text{watt}$$

The SI unit of power has been given a special name *watt* and is abbreviated as W. It was internationally agreed to abbreviate the SI units named after scientists by capital letters and all other units in lower case letters. The base units in the International System of Units are presented in Table 1.1, while the derived units with special names are presented in Table 1.2.

Table 1.1 *The base units of the International System of Units*

Quantity	Base unit	Symbol
Mass	kilogram	kg
Length	metre	m
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric current	ampere	A
Luminous intensity	candela	cd

Table 1.2 *Derived units with special names and symbols*

Quantity	Special name	Symbol	Relation with base units or derived units
Force	newton	N	$1\ \text{N} = 1\ \text{kg m s}^{-2}$
Pressure, Stress	pascal	Pa	$1\ \text{Pa} = 1\ \text{N m}^{-2}$
Energy	joule	J	$1\ \text{J} = 1\ \text{N m}$
Power	watt	W	$1\ \text{W} = 1\ \text{J s}^{-1}$
Electric charge	coulomb	C	$1\ \text{C} = 1\ \text{A s}$
Electric potential	volt	V	$1\ \text{V} = 1\ \text{J C}^{-1}$
Electric resistance	ohm	Ω	$1\ \Omega = 1\ \text{V A}^{-1}$
Electric capacitance	farad	F	$1\ \text{F} = 1\ \text{C V}^{-1}$
Frequency	hertz	Hz	$1\ \text{Hz} = 1\ \text{s}^{-1}$

1.3.3 Multiples and submultiples of SI units

The SI unit of pressure is pascal which is very small in magnitude and the standard atmospheric pressure is equal to 101 325 Pa. For convenience, the pressure can be expressed in terms of kilopascal or megapascal. Thus, the standard atmospheric pressure can be expressed as 101.325 kPa or 0.101 325 MPa. Similarly, other units can be expressed in terms of the appropriate multiples of SI units. It is internationally accepted to use the SI prefixes presented in Table 1.3 to form names and symbols of decimal multiples and submultiples of SI units.

Table 1.3 *SI prefixes*

Factor	Prefix	Symbol	Factor	Prefix	Symbol
10	deca	da	10^{-1}	deci	d
10^2	hecto	h	10^{-2}	centi	c
10^3	kilo	k	10^{-3}	milli	m
10^6	mega	M	10^{-6}	micro	μ
10^9	giga	G	10^{-9}	nano	n
10^{12}	tera	T	10^{-12}	pico	p
10^{15}	peta	P	10^{-15}	femto	f
10^{18}	exa	E	10^{-18}	atto	a

The symbol of a prefix is to be combined with the single unit symbol forming a new symbol. For example the symbol of the prefix kilo (k) is combined with the symbol of a single unit pascal (Pa) to form the new symbol kPa. For mass, the SI base unit is kg which already carries the SI prefix symbol k for kilo. Hence the names of the decimal multiple and submultiple of the unit for mass are formed by combining the SI prefix to gram. For example, 10^{-6} kg can be written as mg and not as μkg

1.3.4 Convention for writing quantities and units

- Compound prefixes should not be used for writing the prefixes. For example, 10^{-9} m should be written as 1 nm and not as 1 mμm. 10^{-6} kg should be written as 1 mg and not as 1 μkg.
- The choice of the SI prefix to express the multiples and submultiples of units is governed by convenience. It is recommended that the SI prefixes should be selected such that the numerical values lie between 0.1 and 1000. **Examples**: 101 325 Pa can be written as 101.325 kPa or 0.101 325 MPa; 4.64×10^{-8} s can be written as 46.4 ns; 2.5×10^{-10} m can be written as 0.25 nm or 250 pm.

  However, when the values are presented in a tabular form for the same quantity, it is advisable to use the same SI prefix throughout even if some of the numerical values lie outside the range 0.1 to 1000. For example, the specific volume is reported in the units m³/kg both for saturated liquid and saturated vapor in steam tables as shown below.

T(°C)	Specific volume of saturated liquid	Specific volume of saturated vapor
100	0.001 043 7	1.673

  For certain quantities, the same SI prefix is customarily used. For example, the steam tables give the specific enthalpies of the saturated liquid and saturated vapor at 100°C as 419.06 kJ/kg and 2676 kJ/kg, respectively. Similarly, in engineering drawings the dimensions are shown in mm.
- The unit symbols should not be written in the plural form and no period (full stop) should be placed at the end, unless it is at the end of a sentence. The unit symbol should be placed after the numerical value, leaving a space in between the numerical value and the unit symbol. **Examples**: 101.325 kPa; 120 m.
- The unit symbol should be written in lower case letters unless the unit is named after a scientist. In that case the first letter is written in upper case. **Examples**: metre = m; second = s; newton = N; pascal = Pa.
- When a unit is obtained by multiplication or division of two or more units, they can be indicated as:

  newton × metre can be written as N m

  metre ÷ (second)² can be written as m/s² or m s^{-2}

  Note the gap between newton (N) and metre (m) and metre (m) and second (s). Care should be taken to avoid confusion between the SI prefix milli (m) and the base unit, metre (m). mN is used for millinewton and m N indicates meter × newton. Similarly ms stands for millisecond and not for metre × second. Not more than one solidus (/) can be used on the same line, unless parenthesis are used while combining the units.

- There are certain units which are outside the SI and are recognized by the Comité International des poids et Mesures (CIPM) because of their practical importance. These units also can be used alongwith the SI units. The non-SI units recognized by CIPM are presented in Table 1.4.

Table 1.4 *Non-SI units recognized by CIPM*

Quantity	Name of the unit	Symbol	Relation with SI unit
Time	minute	min	1 min = 60 s
	hour	h	1 h = 3.6×10^3 s
	day	d	1 d = 8.64×10^4 s
Volume	litre	l	1 l = 1×10^3 cm^3
Mass	tonne	t	1 t = 10^3 kg
Energy	electronvolt	eV	1 eV = $1.602\ 19\times10^{-19}$ J
Mass of an atom	atomic mass unit	u	1 u = $1.660\ 57\times10^{-27}$ kg
Pressure	bar	bar	1 bar = 10^5 Pa

- While writing a number with several digits, to facilitate reading, they may be separated into groups of three, counting from the decimal point towards right and left. These groups should be separated by a small gap and should not include a comma.

1.4 Summary

The main activities of a chemical engineer are concerned with the design and development of new processes or improving existing processes for converting raw materials into useful products. An engineer has to make every effort to optimally use the available resources — energy, space, material and time — in the development of processes.

Before undertaking the task of designing a commercial plant, or attempting to improve an existing process, an engineer should know the following:

- Is the proposed process feasible or not ?
- Does the process proceed to its completion or to a certain extent only ?
- What is the effect of the variation of the physical factors on the extent to which the process will proceed ?
- How much energy is required to carry out the proposed process ?

The answers to all such questions can be obtained by the application of thermodynamic principles to the process under investigation.

Thermodynamics deals with energy and its transformation, feasibility of a process and the extent to which a process can proceed. Thermodynamics is a subject of wide applicability and is used in all branches of engineering, physical and chemical sciences. The principles of thermodynamics are embodied in four laws, known as the zeroth, first, second and third laws of thermodynamics.

One can adopt two different approaches — macroscopic and microscopic — in the study of thermodynamics. In the macroscopic approach, the structure of matter under investigation is irrelevant and only a few measurable variables are needed to describe the state of matter. This approach is adopted in classical thermodynamics. In the microscopic approach, a knowledge of the structure of matter is essential and a large number of variables which cannot be directly measured is required to specify the state of matter under consideration. This approach is adopted in statistical thermodynamics.

In the study of thermodynamics one deals with a large number of physical quantities. A complete knowledge of the units of the physical quantities is essential in the understanding of thermodynamics. Several systems of units were in use in the earlier days. In 1960 the General Conference on Weights and Measures (CGPM 1960) recommended the use of SI units (International System of Units). Many countries have adopted SI units as the legal system of units.

The base units in the SI system are *kilogram* (kg) for mass, *metre* (m) for length, *second* (s) for time, *kelvin* (K) for temperature, *ampere* (A) for electric current and *candela* (cd) for luminous intensity. The units of several physical quantities can be derived in terms of the base units, based on certain laws or definitions. Such units are called derived units. Some derived units are named after a few scientists and only those units are represented by upper case letters while all other units are denoted by lower case letters. The decimal multiples of the SI units can be expressed by adding SI prefixes like m for milli ($\times 10^{-3}$), k for kilo ($\times 10^{-3}$), etc. to a single unit symbol. The use of more than one SI prefix to express the multiples of the units is not permitted.

Review questions

1. Consider the synthesis of ammonia according to the reaction

   $$N_2 + 3H_2 \longrightarrow 2NH_3$$

   at 500°C and 20 MPa. A chemical engineer is entrusted with the task of designing a suitable reactor for producing 500 kg of NH_3 per hour. In this connection, he would like to know whether he could find answers to the following questions from a thermodynamic analysis of the process. Identify the questions that can be answered.
   (a) What is the maximum conversion of reactants into products at the given conditions ?
   (b) How much time is required to achieve the maximum conversion ?
   (c) What is the rate of the reaction ?
   (d) Is it possible to increase the rate of reaction by adding a catalyst ?
   (e) What is the effect of temperature on the degree of conversion at equilibrium and on the rate of reaction ?
   (f) What is the energy requirement for producing one mole of NH_3 ?
   (g) What size reactor is required ?
2. In the macroscopic study of thermodynamics, the structure of matter is not taken into account. Are the results predicted from this approach applicable to all types of matter ? Give an example.
3. What are the base units in the SI system ?
4. Define the unit mole.
5. A handbook of chemistry gives the atomic weight of carbon as 12. What is atomic weight ? Calculate the mass of one carbon atom and express it in kg and in atomic mass units.
6. An engineer reports the following data based on certain measurements and calculations. Some of them are not in agreement with the SI convention. Identify them and rewrite them after making the necessary corrections.
   (a) 150 gms
   (b) 2.5 Newtons
   (c) 3650 pa
   (d) 22.5 sec
   (e) 12.5 mPa
   (f) 310 Kg
   (g) Water velocity = 3 ms^{-2}
   (h) 46.5 cms
   (i) 268459 J
   (j) 450° K
   (k) 405 j
   (l) 5.5 Kw

Problems

1.1 According to Newton's universal law of gravitation, the gravitational force (F) between two bodies of masses m_1 and m_2 , which are separated by a distance r, is given by

$$F = \frac{Gm_1m_2}{r^2}$$

where $G = 6.672\times10^{-11}$ is the universal gravitational constant. Determine the SI units of G.

1.2 Given that the mass and the radius of earth are 5.9659×10^{24} kg and 6371 km respectively, calculate the gravitational force on a body of mass 1 kg on the earth's surface and the acceleration due to gravity.

1.3 Given that the mass and the diameter of moon are 7.35×10^{22} kg and 1738 km respectively, calculate the acceleration due to gravity on moon. Estimate the weight of an astronaut on moon, if he weighs 800 N on earth.

1.4 The mean diameter of Jupiter is 10.97 earth diameters and its mass is 318.3 earth masses. Estimate $g_{(\text{Jupiter})}/g_{(\text{Earth})}$.

1.5 The van der Waals equation of state is given by

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

where v is in m^3/mol. Determine the SI units of the constants a and b.

1.6 The Redlich–Kwong (RK) equation of state given below is widely used to represent the P–v–T behavior of several gases:

$$P = \frac{RT}{v - b} - \frac{a}{v(v - b)T^{1/2}}$$

where v is in m^3/mol. Determine the units of the constants a and b of the RK equation of state.

1.7 A U-tube manometer with mercury (ρ = 1.3595×10^4 kg/m^3) is used to measure the pressure drop of water (ρ = 1×10^3 kg/m^3) flowing in a pipeline. At a particular flow rate, the difference in the levels of mercury in the two limbs is 30 cm. Determine the pressure drop.

1.8 It is required to maintain a bell jar at subatmospheric pressure. For this purpose it is connected to a vacuum pump and the air inside the bell jar is pumped out. During pumping, the pressure inside the bell jar is monitored with a silicone oil (ρ = 0.8×10^3 kg/m^3) manometer. One limb of the manometer is completely evacuated ($P \simeq 0$ Pa) and sealed and the other limb is connected to the bell jar. At a particular instant, the difference in the levels of the silicone oil is found to be 12 cm. Determine the air pressure in the bell jar.

1.9 The diameters of the cylinders A and B of a hydraulic press are 10 cm and 1 m, respectively. The two cylinders are connected to a common oil reservoir. It is desired to exert a force of 50 kN on the piston attached to cylinder B to compress a cotton packing. Determine the quantity of mass to be loaded on the piston attached to cylinder A.

1.10 Domestic pressure cookers are designed to maintain a maximum pressure of 200 kPa inside the cooker. If the vent port has a diameter of 2 mm, calculate the mass to be placed on the vent port.

1.11 The atmospheric pressure is due to the air surrounding the earth. Suppose the atmospheric air has a uniform temperature of 298 K and the density of air is related to the pressure as $\rho = P/RT$ where ρ is molar density (mol/m^3) and R = 8.314 J/mol K. Estimate the height above the earth's surface where the air pressure is 0.325 kPa. Molar mass of air is 28.97×10^{-3} kg/mol.

1.12 It is known that the temperature and density of atmospheric air change with altitude. Assume that the density of the air is given by $P\rho^{-\gamma} = P_a\rho_a^{-\gamma}$ where the subscript a denotes the conditions at the earth's surface and $\gamma = 1.4$. The pressure and temperature of air at the earth's surface are 101.325 kPa and 298 K respectively, and air obeys the relation $P = \rho RT$ where ρ is the molar density (mol/m^3) and R = 8.314 J/mol K. The molar mass of air is 28.97×10^{-3} kg/mol. Estimate the height above the earth's surface where P = 0.325 kPa.

1.13 A piston cylinder assembly shown in Fig.1.2 contains a gas at a pressure of 0.1 MPa. At this stage the spring is at its natural length. Now, the gas is heated till the piston moves a distance of 30 cm. Given the spring constant as 100 kN/m and the piston diameter as 10 cm, calculate the final pressure of the gas.

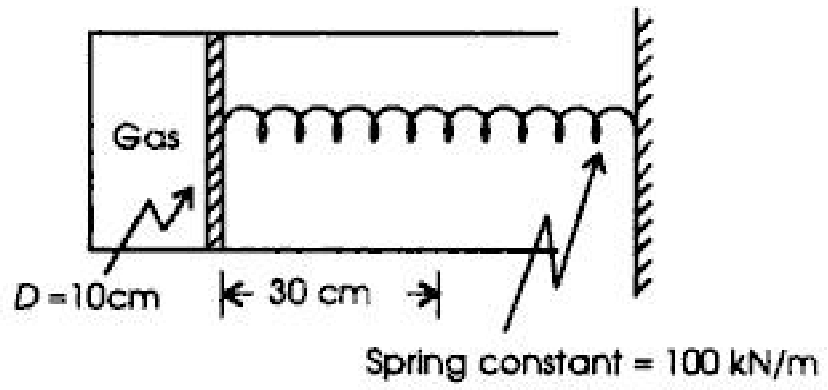


Fig.1.2 *Sketch for Problem 1.13.*

1.14 A tank is filled with 20 kg of CO_2, 16 kg of N_2, 44 kg of O_2 and 20 kg of CH_4. Determine the total mole number of the gas mixture in the tank and the average molar mass of the mixture.

2 Review of basic concepts

Learning Objectives

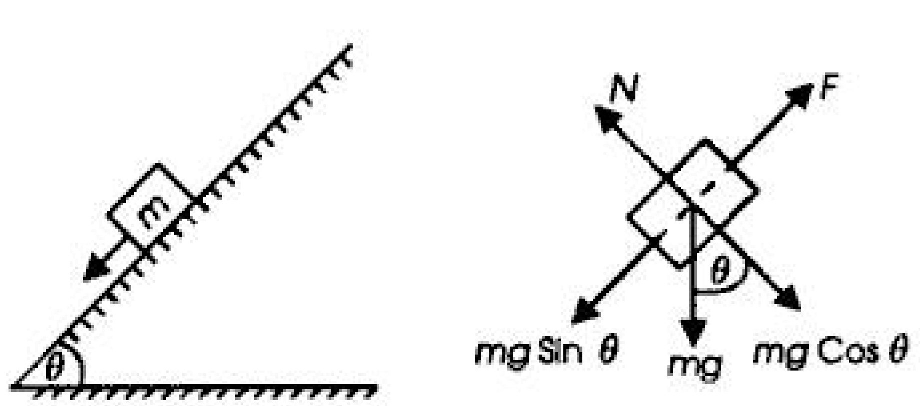
This chapter will enable readers to

- define a system and surroundings in the thermodynamic analysis of processes;
- understand the characteristics of a thermodynamic property and to choose the quantities which can be used as properties;
- distinguish between extensive and intensive properties;
- understand macroscopic and microscopic modes of energy and the concept of internal energy;
- understand the concept of equilibrium and to judge whether a system is in a state of equilibrium or not;
- know the criteria of mechanical, thermal and chemical equilibrium;
- classify the equilibrium states;
- understand the criterion for reversibility of a process;
- distinguish between reversible and irreversible processes;
- understand the thermodynamic definition of work and its importance;
- calculate work done by a thermodynamic system;
- understand various work modes;
- understand the meaning of heat interaction;
- distinguish between work and heat interactions and the importance of the choice of a system;
- understand the state postulate and its importance in the description of the state of a system;
- understand the zeroth law of thermodynamics and its use in the measurement of temperature;
- know the establishment of temperature scales and the drawbacks;
- understand the necessity of ideal gas temperature scale and the measurement of temperature with a constant volume gas thermometer; and
- know about International Practical Temperature Scale and its primary fixed points.

In the study of any physical or chemical science it is essential to be familiar with the terminology and the underlying basic concepts. As this book is devoted to introducing chemical engineering thermodynamics to the reader who has been already exposed to a core course on thermodynamics and adopted any one of the books [7]–[31] as a textbook, the basic concepts and definitions are not presented in great detail but are briefly reviewed in the following. For more details the reader is advised to consult the author's book [7]. The terms like system, work, property, etc. which are frequently used in thermodynamics are briefly reviewed in this chapter, since a sound knowledge of these terms helps in a better understanding of the subject.

2.1 System

In any scientific or engineering analysis it is essential to clearly specify the material on which attention is focused. Suppose a block of mass m is sliding over a rough inclined surface as shown in Fig.2.1(a) and we are interested in analyzing the motion of the block. The motion of the block can be analyzed by applying Newton's laws of motion. For this purpose we focus our attention on the block and represent the various forces acting on the block as shown in Fig.2.1(b) which is called the *free body diagram* (F.B. diagram). Then we make a force balance to determine the velocity and position of the block.



(a) (b)

Fig.2.1 (a) *Schematic representation of a block of mass m sliding over an inclined plane.* **(b)** *Free body diagram. $mg\sin\theta$ and $mg\cos\theta$ are the components of the gravitational force mg acting on the block along the plane and normal to the inclined surface, respectively. F is the frictional force and N is the normal reaction.*

In such an analysis we have isolated the body from its surroundings by an imaginary boundary. This imaginary boundary may coincide with the geometric surface of the body or may pass through the body. Similarly, in thermodynamic analysis, we identify the subject of analysis by enclosing it in a boundary which separates the matter under study from the rest of the universe or surroundings. For simplicity, we use the term *thermodynamic system* or *system* to refer to the subject matter of analysis. That is *a thermodynamic system refers to a definite quantity of matter, enclosed by a boundary on which we focus our attention for thermodynamic analysis.*

If we are interested in a thermodynamic analysis of the process followed by a gas, we choose the gas contained in the piston–cylinder assembly as our system and enclose it by an imaginary boundary as shown by a dotted line in Fig.2.2(a). If the piston–cylinder assembly is brought in contact with a hot body, the temperature as well as the volume of the gas increases and the piston moves up as shown in Fig.2.2(b). In this case we find that the boundary changes in size; energy is transferred as heat to the gas and the gas does some work in lifting the mass through a distance h. However, the amount of gas (N mol) remains constant. That is, a system boundary may change in size and allow the energy to exchange with the surroundings either in the form of heat or work or both. Suppose the same amount of gas is enclosed in an elastic balloon which is spherical as shown in Fig.2.2(c). By doing work on the gas the balloon can be deformed into a cylindrical shape or into a circular disc as shown in Fig.2.2(d) but the quantity of gas inside the balloon remains constant. The system boundary in Figs.2.2(a)–(d) is shown by a dotted line.

Therefore, the system boundary may change in shape as well as in size during a given process. That is, a system boundary may undergo a change in configuration. Similarly, a system boundary may be real or imaginary. A system can be as simple as a certain amount of gas confined in a piston–cylinder assembly or it can be very complex such as a complete petrochemical plant. It should be noted that a thermodynamic system contains a definite quantity of matter. To emphasize this fact sometimes a system is referred to as a *control mass*. A system enclosed by a boundary which does not allow the exchange of energy in the form of heat as well as work is called an *isolated system*.

All matter external to the system constitutes the *surroundings*. The combination of system and surroundings is called the *universe*. In thermodynamic analysis our interest lies in determining the change in the energy and the properties (or the state) of the system when it exchanges energy with its surroundings. Whenever a system undergoes a change, its effects are seen in the immediate surroundings only. At a distance far removed from the system, the effects are not felt and hence for all practical purposes it is necessary to include only the immediate surroundings in thermodynamic analysis.

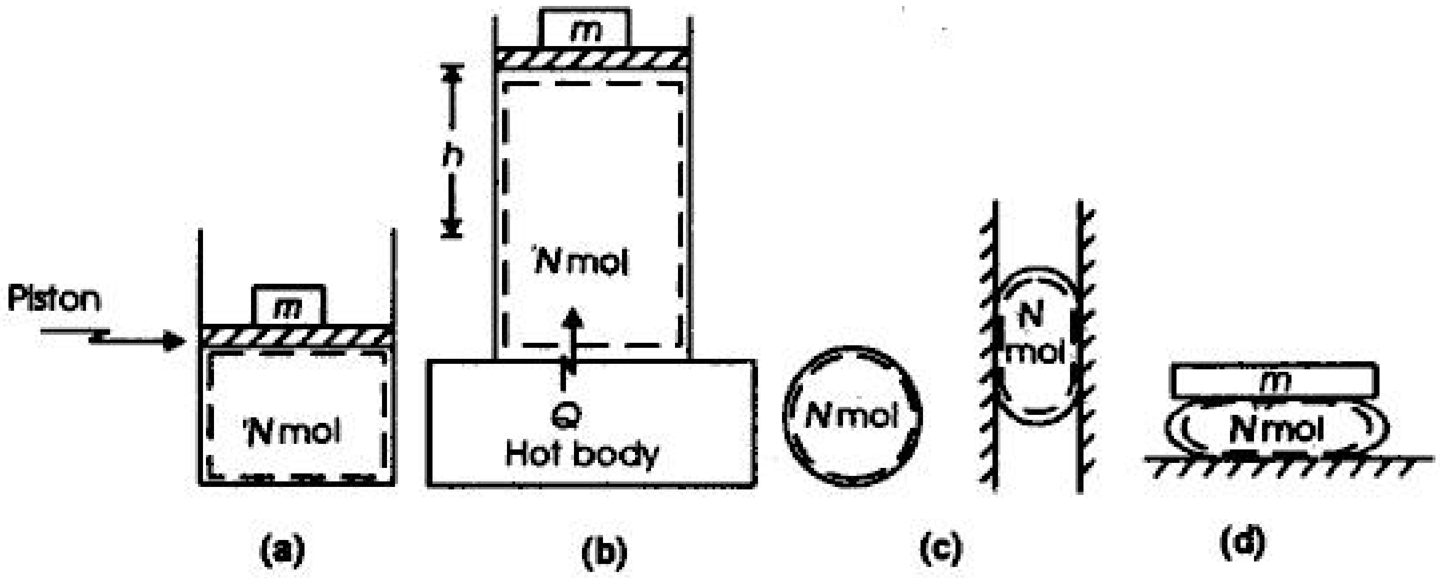


Fig.2.2 **(a)** *System-gas contained in a piston–cylinder assembly.* **(b)** *System-gas contained in a piston–cylinder assembly. The work done by the gas is mgh and Q is the energy transferred as heat to the gas. Energy transfer as heat and work occurs across the system boundary. System boundary changes in size.* **(c)** *System-gas contained in a spherical balloon.* **(d)** *System-gas contained in the balloon which is deformed into a cylindrical shape or circular disc shape, by performing work on it. System boundary changes in shape as well as in size.*

2.2 Property

Suppose the reaction

$$C_2H_4 + H_2O \rightarrow C_2H_5OH$$

is carried out in a reactor which is maintained at constant temperature and pressure. As time progresses, the reaction proceeds and the composition of the mixture changes. To specify the state of the system without any ambiguity, we can select a few characteristics of the system and use them to describe the state of the system. Then the question that naturally arises is — which characteristics can be used to describe a thermodynamic system? The characteristics used to describe the state of matter are called properties. Since our interest in thermodynamic analysis lies in determining the energy changes associated with the interaction of the system and the surroundings, any characteristic or property which is related to or involved with energy changes is a relevant thermodynamic property. Thus *a thermodynamic property is a characteristic of a system which is associated with energy and its transformation and which can be quantitatively evaluated.* Then the state of a system can be described by specifying its properties. A thermodynamic property should have a definite value when the system is in a specified state and the change in the property must be independent of the path followed by the system in reaching that state. That is, the change in the property depends only on the initial and final states of the system. Suppose $z = z\,(x, y)$. Then

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy = Mdx + Ndy \quad \text{where} \quad M = \left(\frac{\partial z}{\partial x}\right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y}\right)_x$$

$$\text{Then}\quad \left(\frac{\partial M}{\partial y}\right)_x = \left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y} = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y = \left(\frac{\partial N}{\partial x}\right)_y$$

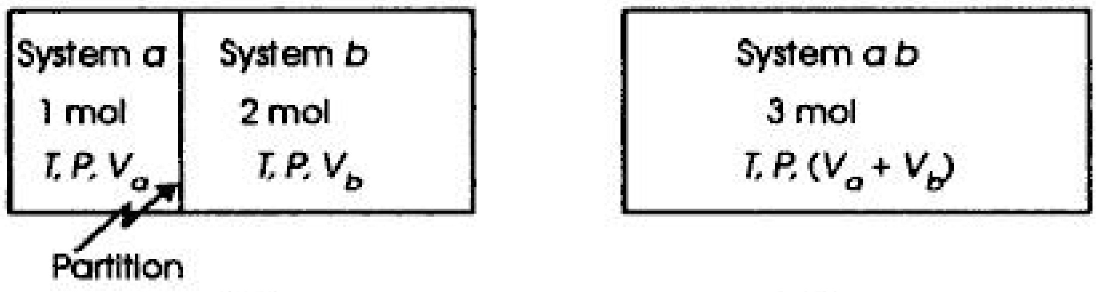
$$\text{or}\quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{2.1}$$

If the condition given by Eqn.2.1 is satisfied, then dz is said to be an exact differential and z is called a point function. The change in the value of z in reaching the state (x_2, y_2) from the state (x_1, y_1) is given by

$$\Delta z = \int_{x_1,y_1}^{x_2,y_2} dz = z(x_2, y_2) - z(x_1, y_1) = z_2 - z_1 \tag{2.2}$$

Then $z = z(x, y)$ can be used as a thermodynamic property. Therefore, it can be said that a thermodynamic property is a point function and not a path function and its differential is exact. Pressure, temperature, volume and energy are some of the physical quantities which satisfy the above requirements, and they are used as properties to describe the thermodynamic state of a system.

Consider two systems a and b such that system a has one mole of gas at temperature T, and pressure P and occupies volume V_a and system b has 2 mol gas at the same T and P and occupies volume V_b as shown in Fig.2.3(a). Initially the two systems are separated from each other by a partition. Suppose the partition is removed and the gases are allowed to mix as shown in Fig.2.3(b). Now consider the combination of the two systems a and b as a new system ab. Measurement of temperature, pressure and volume of the system ab, shows that T and P of system ab are identical to T and P of systems a and b and the volume V_{ab} of system ab is equal to $(V_a + V_b)$. From this observation we notice that there are certain properties like pressure (P) and temperature (T) which do not depend on the size of the system under consideration and there are certain properties like volume (V) which depend on the size of the system under consideration. That is, P and T do not depend on the mass (or mole number) of the system and V depends on the mass (or mole number) of the system. The properties which depend on the mass (or mole number) of a system are called *extensive properties*, whereas the properties which are independent of the mass (or mole number) of a system are called *intensive properties*.



(a) (b)

Fig.2.3 (a) *Systems a and b, separated from each other by a partition.* **(b)** *System ab, in which gases in systems a and b are allowed to mix.*

The ratio of an extensive property to the mass (or the property per unit mass) is called the *specific property* and the ratio of an extensive property to the mole number (or the property per mole) is called the *molar property*. Thus

$$\text{Specific volume} = v = V/m \tag{2.3}$$

$$\text{Molar volume} = v = V/N \tag{2.4}$$

where V = total volume of the system, m = mass of the system and N = mole number of the substance in the system.

For simplicity of notation we use v to denote both the specific volume and molar volume. The units m^3/kg or m^3/mol indicate whether it is specific volume or molar volume.

2.3 Energy

The concept of energy is essential in the understanding of thermodynamics, because thermodynamics deals with energy and its transformation. The concept of energy developed slowly over a period of several years and led to the establishment of the principle of conservation of mechanical energy by Leibnitz in 1693. Prior to the development of the first law of thermodynamics by Joule in 1851, the only known forms of energy were potential energy (PE) and kinetic energy (KE). The potential energy and kinetic energy possessed by a body can be estimated in terms of macroscopically measurable quantities and hence they are called *macroscopic modes of energy*. In addition to PE and KE, matter possesses energy due to random motion of the constituent atoms/molecules and this energy cannot be estimated in terms of macroscopically measurable quantities. These forms of energy are called *microscopic modes of energy*. The sum of the energies associated with all the microscopic modes is called the internal energy (U).

Potential energy Suppose a body of mass m is initially at elevation Z_1 and it is desired to raise the mass to elevation Z_2. Then the work to be done on the body in raising its elevation from Z_1 to Z_2 is given by

$$\begin{aligned} W &= F(Z_2 - Z_1) \\ &= mg(Z_2 - Z_1) \\ &= mgZ_2 - mgZ_1 \\ &= \Delta(mgZ) \end{aligned}$$

If the body is allowed to fall from Z_2 to Z_1, it can do work on some other body, and the amount of work it can perform is equal to $(mgZ_2 - mgZ_1)$. That is, the body at elevation Z_2 is capable of doing work and the capacity to do work is called energy. Thus we observe that the work done on the body in raising its elevation is stored in the body as energy and this energy can be recovered from the body by reducing its elevation. This form of energy which is given by mgZ is named as potential energy (PE) by Lord Rankine. That is

$$\text{PE} = mgZ \tag{2.5}$$

The work done on the body in raising its elevation is equal to the increase in the potential energy of the body. This form of energy can be easily estimated from a measurement of the macroscopic quantities m and Z, and hence it is called a macroscopic mode of energy. Similarly a compressed spring or a stretched rubber band also possesses potential energy. The energy possessed by a body due to its location or configuration is called potential energy.

Kinetic energy Consider a stone of mass m at rest on the top of a mountain cliff which is at an elevation of Z from the earth's surface. The potential energy possessed by the stone is mgZ. If the stone rolls down the cliff, the velocity of the stone increases as it falls down and its acceleration a is equal to g. The velocity ($\mathbf{V}$) of the stone with which it touches the ground can be estimated from the following well-known relation in mechanics (for a freely falling object) which is given by

$$2gZ = \mathbf{V}^2 \tag{2.6}$$

Then the energy possessed by the stone is given by

$$\begin{aligned} mgZ &= mg\left(\frac{\mathbf{V}^2}{2g}\right) \\ &= \frac{1}{2}m\mathbf{V}^2 \end{aligned}$$

The energy of the body can be estimated from a measurement of the macroscopic quantity $\mathbf{V}$. Suppose a body of mass m is accelerated from an initial velocity $\mathbf{V}_1$ to a final velocity $\mathbf{V}_2$, the work to be done on the body is given by

$$W \text{ (on body)} = \frac{1}{2}m\mathbf{V}_2^2 - \frac{1}{2}m\mathbf{V}_1^2$$

On the other hand, if the body is decelerated from $\mathbf{V}_1$ to $\mathbf{V}_2$ by an opposing force, the work done by the body is given by

$$W \text{ (by body)} = \frac{1}{2}m\mathbf{V}_1^2 - \frac{1}{2}m\mathbf{V}_2^2$$

Thus we observe that the work done on the body in accelerating it is stored in the body as energy and this energy can be recovered from the body by decelerating it. The change in the energy of the body when its velocity is changed from $\mathbf{V}_1$ to $\mathbf{V}_2$ is given by

$$\frac{1}{2}m\mathbf{V}_2^2 - \frac{1}{2}m\mathbf{V}_1^2 = \Delta\left(\frac{1}{2}m\mathbf{V}^2\right)$$

The body has the ability to do work and the ability to do work is energy. The energy possessed by the body by virtue of its motion is $m\mathbf{V}^2/2$ and the term $m\mathbf{V}^2/2$ has been named as kinetic energy by Lord Rankine. That is

$$\text{KE} = \frac{1}{2}m\mathbf{V}^2 \tag{2.7}$$

The kinetic energy can be estimated from a measurement of the macroscopically observable quantity ($\mathbf{V}$) and hence it is also a macroscopic mode of energy.

The sum of the kinetic energy and potential energy of a body is called the *mechanical energy* of the body. The principle of conservation of energy proposed by Leibnitz states that for mechanical systems, the sum of the kinetic energy and potential energy remains constant.

Internal energy From a microscopic point of view, matter consists of a large number of atoms/molecules and these molecules move with independent velocities at random. Matter possesses energy due to the random motion of the molecules. Consider CO_2, a linear triatomic molecule, as an example. The centre of mass of this molecule is at the location of the carbon atom. The molecule as a whole moves in space with a velocity $\mathbf{V}$, the components of which in the x-, y- and z- directions are $\mathbf{V}_x$, $\mathbf{V}_y$ and $\mathbf{V}_z$, respectively. Such a motion is termed as the translational motion of the molecule. The translational motion of the molecule is shown in Fig.2.4(a). The kinetic energy associated with the translational motion or the translational energy of the molecule is given by $m\mathbf{V}^2/2$ and its components in the x-, y- and z- directions are $m\mathbf{V}_x^2/2$, $m\mathbf{V}_y^2/2$ and $m\mathbf{V}_z^2/2$, respectively where m is the mass of the molecule. In addition to the translational motion, the molecule can rotate about an axis passing through its centre of mass. Suppose the molecule is placed along the x- axis. Then the molecule can rotate about the y- axis and about the z- axis around its centre of mass as shown in Fig.2.4(b). Such a motion is called the rotational motion of the molecule. The energy associated with each of the rotational motions is given by $I\omega^2/2$, where I is the moment of inertia of the molecule about the centre of mass, along the axis of rotation and ω is the angular velocity.

The atoms of the molecule vibrate about their equilibrium position. In a CO_2 molecule, while the atom C is at rest, both the oxygen atoms move in the same direction — either to the left or to the right and back. Such a vibration is termed as *asymmetric stretch vibration*. If both the oxygen atoms move either towards the carbon atom or away from the carbon atom, such a mode of vibration is termed as *symmetric stretch mode of vibration*. In addition to these, other modes of vibration also are possible. While the carbon atom moves up (down), the oxygen atoms move down (up), causing a bend in the linear structure of CO_2. Such vibration is called a bending mode of vibration. In a second bending mode of vibration, the carbon and oxygen atoms move normal to the plane of the paper. The motion of the carbon atom towards the reader is indicated by a (+) in Fig.2.4(c), while the motion of oxygen atoms away from the reader is indicated by a dot (•). The energy associated with the vibrational motion of the molecule is called the vibrational energy. In an atom, the electrons move in orbits around the nucleus and some energy is associated with the motion of electrons. The energy of the electron depends upon the orbit in which it is in motion. The electrons in the lower orbit have smaller energy than the electrons in the outer orbit. In addition to this, the electrons spin around their axes also and possess additional energy. The nucleus and electrons in an atom are bound together due to coulombic interactions and some energy is associated with these interactions. The electron motion, electron spin and coulombic interactions are shown in Fig.2.4(d). In a molecule, the atoms are bound due to nucleus–nucleus interactions as shown in Fig.2.4(e) and some energy is associated with these interactions also. In a macroscopic system containing a large number of molecules, the molecules are held due to weak intermolecular forces and hence the system possesses additional energy. All these forms of energy cannot be estimated in terms of macroscopically measurable quantities and hence they are called *microscopic modes of energy*. The sum of the microscopic modes of energy is called the *internal energy* (U) of the system. Thus, we observe that the internal energy arises due to the random motion and internal structure of the molecules.

A macroscopic system possesses potential energy by virtue of its location and configuration, kinetic energy by virtue of the motion and internal energy due to the random motion and internal structure of the constituting atoms/molecules. Thus, the energy (E) of a system is given by

$$E = \mathrm{PE} + \mathrm{KE} + U \tag{2.8}$$

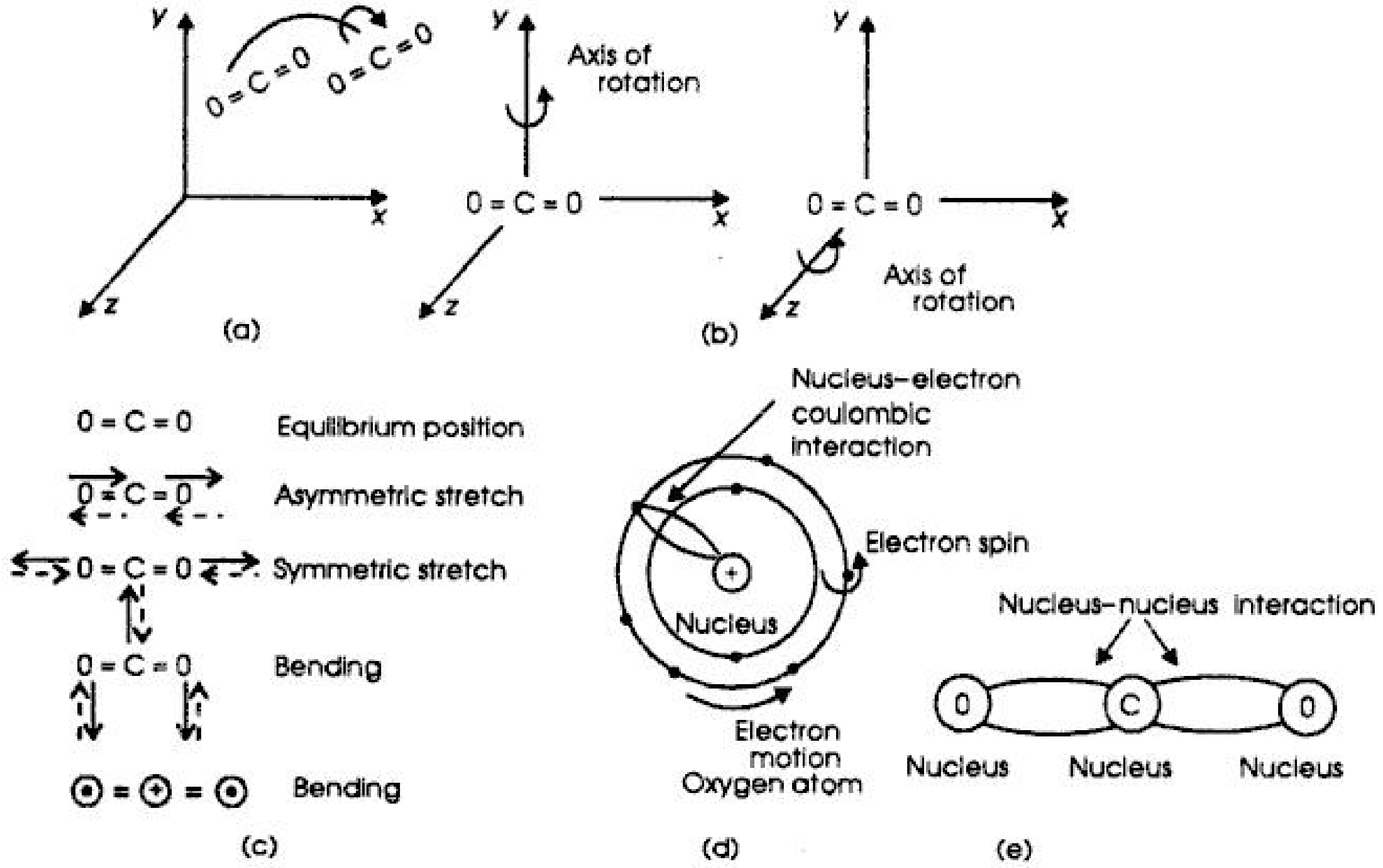


Fig.2.4 *Microscopic modes of energy:* **(a)** *translational energy;* **(b)** *rotational energy;* **(c)** *vibrational energy (+, • in the bending mode shows that the motion of the atoms are from top to bottom, or from bottom to top in the direction perpendicular to the plane of paper);* **(d)** *energy due to electron motion, electron spin and nucleus–electron coulombic interaction; and* **(e)** *nucleus–nucleus interaction energy.*

2.4 Equilibrium

In thermodynamics our interest lies in determining the extent to which a particular change, physical or chemical, takes place under specified conditions. If there is no further change in the state of the system, it reaches a dead state. In that dead state, the system has no tendency to undergo any further change and is said to be in a state of equilibrium. In a state of equilibrium, the system cannot exchange energy in the form of heat as well as work with the surroundings (physical change) and does not undergo any chemical change. In other words, equilibrium is a concept associated with the absence of any tendency for further change at a macroscopic level. The tendency to change occurs due to the presence of driving forces. Thus, equilibrium implies the absence of driving forces between the interacting bodies.

If there is no imbalance of forces in a system when it is isolated, it is said to be in a state of *mechanical equilibrium*. In a state of mechanical equilibrium, the system has a uniform pressure and there is no pressure difference between the two interacting systems. If there is no further change in the thermal condition of a system when it is isolated, it is said to be in a state of *thermal equilibrium*. In a state of thermal equilibrium, there is no temperature gradient within the system and there is no difference in temperature (driving force) between the two interacting systems. Since a system in thermal equilibrium has uniform temperature, a unique value can be specified for the temperature of the system. If the composition of a system does not change due to diffusion/mass transfer or chemical reaction, and there is no tendency for the chemical reaction to occur when the system is isolated, then the system is in a state of *chemical equilibrium.*

Specifically, when two systems a and b are in a state of chemical equilibrium, then

$$\mu_i^a = \mu_i^b \qquad \text{(for all } i\text{)} \tag{2.9}$$

where μ_i^a and μ_i^b represent the chemical potential of component i in systems a and b, respectively.

Thus the criteria of thermal equilibrium, mechanical equilibrium and chemical equilibrium are given by

Equality of temperature - Thermal equilibrium
Equality of pressure - Mechanical equilibrium
Equality of chemical potential - Chemical equilibrium

A system which is simultaneously in a state of thermal equilibrium, mechanical equilibrium and chemical equilibrium is said to be in a state of *thermodynamic equilibrium.*

In presenting the criteria of equilibrium, intuitive knowledge of temperature and pressure has been used and no attempt has been made so far to formally define the temperature and pressure. The thermodynamic definitions of temperature, pressure and chemical potential are presented in Chapter 6. Similarly, the criteria of equilibrium are introduced through qualitative arguments only and a formal deduction of the criteria of equilibrium is presented in Chapter 6. We know that temperature and pressure are intensive properties. It is shown later that chemical potential is also an intensive property. It can be observed that the criteria of equilibrium are expressed in terms of the equality of intensive properties.

Consider a mixture of liquid water and water vapor, contained in a closed vessel, at 100°C and standard atmospheric pressure. The mixture is in a state of equilibrium because it satisfies the criteria of thermal, mechanical and chemical equilibrium. At a macroscopic level, the system (contents of the vessel) does not undergo any change, and appears to be static. However, at a microscopic level some liquid water evaporates and some water vapor condenses. That is, molecules move from liquid to vapor state and *vice versa,* but at such a rate that the rate of vaporization is equal to the rate of condensation. Similarly in chemically reacting systems, the forward and backward reactions take place but at a macroscopic level the composition of the mixture remains unaltered in a state of equilibrium. That is, the microscopic activity (random motion of the molecules, diffusion, etc.) does not cease even in a state of equilibrium.

The equilibrium states of a system can be classified as: stable equilibrium, unstable equilibrium and metastable equilibrium. Considering a mechanical analogy as an example, the equilibrium states are shown in Fig.2.5.

The equilibrium condition shown in Fig.2.5(a) is called metastable equilibrium, because the sphere returns to its original state if it is subjected to small disturbances, but when the disturbance exceeds a certain magnitude, it settles into a new equilibrium state. The magnitude of the disturbance depends on the type of system. Some systems may remain for a sufficiently long time in the metastable state and some systems eventually settle into a new equilibrium state. The equilibrium condition shown in Fig.2.5(b) is called unstable equilibrium, because the sphere settles into a new equilibrium state if it is subjected to a disturbance (even though the disturbance is of small magnitude) and does not return to its original state. The equilibrium condition shown in Fig.2.5(c) is called stable equilibrium, because the sphere returns to its original equilibrium state after it is disturbed, however large the disturbance may be. In thermodynamics we are usually interested in stable equilibrium states.

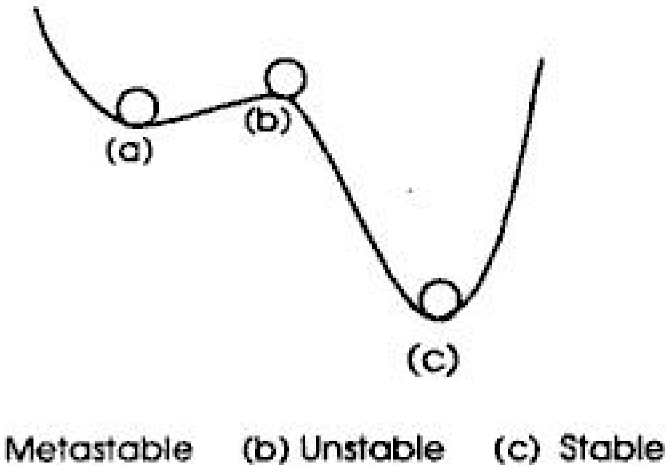


Fig.2.5 *Illustration of equilibrium states.*

In mechanics we learned that the potential energy of a body is an extremum in a state of equilibrium. If the extremum is a maxima, the equilibrium state is called unstable and if the extremum is a minima the equilibrium state is called stable. In thermodynamics also, we classify the stability of a thermodynamic system in terms of extremum of some thermodynamic property (maximum entropy or minimum energy). The criteria of stability of a thermodynamic system is discussed in a later chapter. For a detailed discussion on stability criteria, the reader is advised to consult *Postulational and Statistical Thermodynamics* [1].

2.5 Reversible process

When a system undergoes a change of state or process, it changes from one stable equilibrium state to another stable equilibrium state. In other words, a process is a path followed by a system in reaching the given final state from the given initial state. Consider a certain amount of gas enclosed in an insulated piston–cylinder assembly. Suppose the gas expands from the initial pressure P_1 to the final pressure P_2, then the gas is said to have undergone an adiabatic expansion process. The processes we normally encounter can be classified as reversible and irreversible.

Suppose a certain amount of gas is contained in a cylinder piston assembly shown in Fig.2.6(a) at a pressure P which is greater than the atmospheric pressure P_a. The massless and frictionless piston is loaded with a block of mass m. The atmospheric pressure balances the gas pressure and the system (gas) is in equilibrium. Suppose the mass m is shifted on to a platform which is at the same elevation as the mass, the piston moves up and the gas does some work in pushing the atmospheric air. If the system is to be restored to the original pressure, work has to be done on the system to bring the piston to the position of the block and then the block can be moved on to the piston. Suppose the block is subdivided into 3 blocks each of mass $m/3$. The first block can be moved on to a platform allowing the gas to expand and the piston moves a distance h_1. Then the second block can be moved on to the adjacent platform. The gas expands and the piston moves to a height of h_2 and then the third block can be moved on to the adjacent platform as shown in Fig.2.6(b). Then the piston moves up to the same height as in Fig.2.6(a).

The work done by the gas in this case is $((m/3)\ gh_1 + (m/3)\ gh_2)$ more than the work done in case (a). To restore the system to the original state, work has to be done on it to bring the piston to the height h_2 only. Then the block at height h_2 can be moved on to the

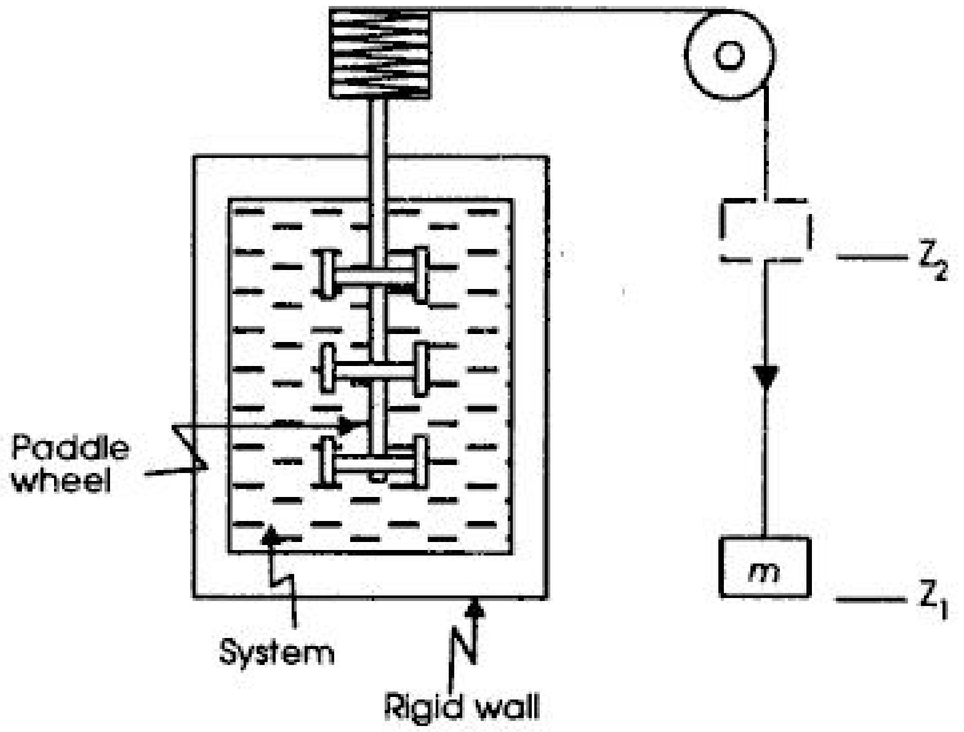
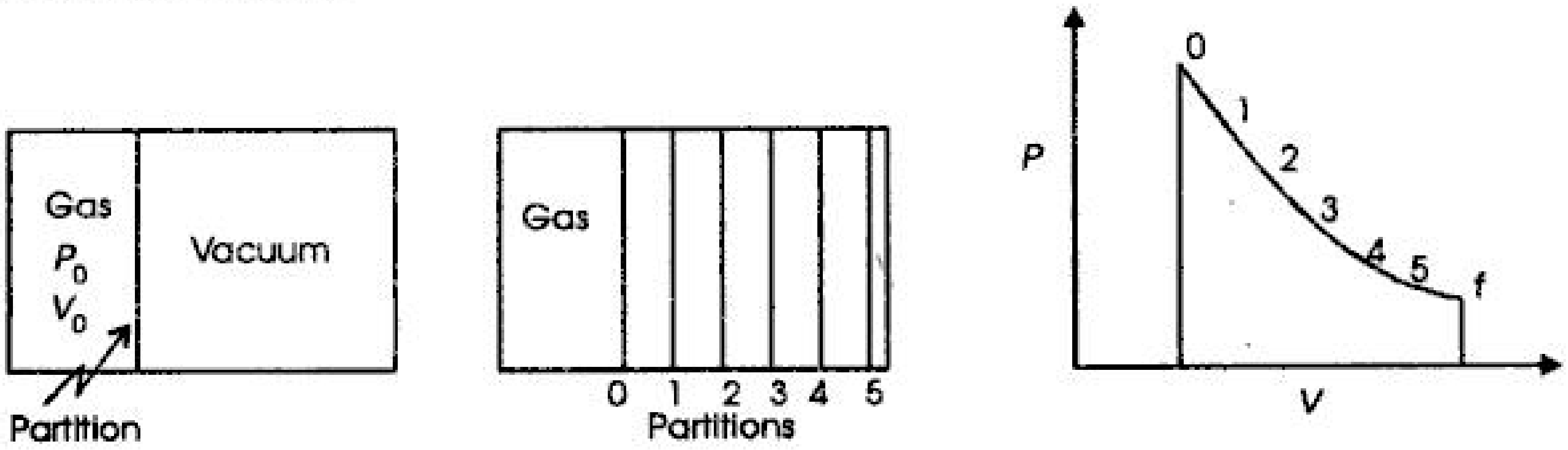


Fig.2.10 *Paddle wheel work $W \neq 0$ even though $dV = 0$.*

There are also situations in which $W = 0$, even though $dV \neq 0$. For example, consider the process of free expansion, that is expansion which is not restrained by an opposing force. Suppose a tank is divided into two compartments and one compartment contains a gas at a given pressure while the second compartment is completely evacuated. If the partition between the compartments is removed, the gas expands and occupies the whole tank. In this case is it possible to evaluate the work done by the gas by making use of Eqn.2.11 ? Since the value of $\int PdV$ depends on the relation between P and V, one question naturally arises — Is it possible to obtain the information regarding P and V at some intermediate stages? To obtain the values of P and V at some intermediate stages, we may subdivide the second compartment by placing several partitions in it as shown in Fig.2.11(a). Then one can remove the partitions one by one and measure P and V. If the values of P and V are plotted, it is possible to obtain the P–V diagram shown in Fig.2.11(b). It is possible to draw a smooth curve through the points 0, 1, 2, 3, 4, 5, f and evaluate the area under the curve. Does the area under the curve represent the work done by the gas? The answer is no, because the expansion of the gas is not restrained. In other words, no force has moved through any distance and hence the work done during free expansion is zero.



(a) (b)

Fig.2.11 (a) *Free expansion of a gas when carried out in successive steps. P_0, V_0 represent the initial conditions, P_1, V_1 represent the conditions when partition 0 is removed and the gas occupies the tank upto partition 1, etc.* **(b)** *P–V diagram for free expansion of a gas when it is carried out in successive steps. P_0 and V_0 represent the initial pressure and volume of the gas, respectively when the gas is confined to one compartment. P_f and V_f represent the final pressure and volume, respectively when the gas occupies the whole tank.*

Example 2.1 One mole of a gas which obeys the relation $Pv = RT$, where $R = 8.314$ J/mol K is initially at 300 K and 0.1 MPa. The gas is heated at constant volume till the pressure rises to 0.5 MPa and then allowed to expand at constant temperature till the pressure reduces to 0.1 MPa. Finally the gas is returned to its original state by compressing at constant pressure. Calculate the work done by the gas in each of the processes and also estimate the net work done by the gas.

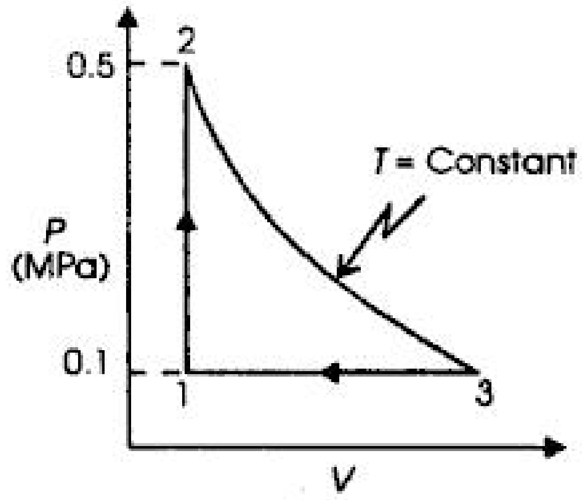


Fig.2.12 *P–V diagram for Example 2.1.*

Solution The process followed by the gas is shown in Fig.2.12. Work done by the gas during process 1–2 is given by

$$W_{1-2} = \int_1^2 P dv = 0 \qquad \text{(since } dv = 0\text{)}$$

We know $P_1 v_1 = RT_1$ and $P_2 v_2 = RT_2$. Therefore

$$\frac{T_2}{T_1} = \frac{P_2 v_2}{P_1 v_1} = \frac{P_2}{P_1} = \frac{0.5 \times 10^6}{0.1 \times 10^6} = 5 \qquad \text{(since } v_2 = v_1\text{)}$$

or $\quad T_2 = 5T_1 = 5 \times 300 = 1500$ K

Work done by the gas during process 2–3 is given by

$$W_{2-3} = \int_2^3 P dv = \int_2^3 \frac{RT}{v} dv = RT_2 \ln \frac{v_3}{v_2}$$

We know $P_2 v_2 = P_3 v_3$ (since $T_2 = T_3$). Therefore

$$\frac{v_3}{v_2} = \frac{P_2}{P_3} = \frac{0.5 \times 10^6}{0.1 \times 10^6} = 5$$

Hence $W_{2-3} = RT_2 \ln 5 = 8.314 \times 1500 \times \ln 5 = 20.071$ kJ. Work done during process 3–1 is given by

$$W_{3-1} = \int_3^1 P dv = P_1(v_1 - v_3) = P_1 v_1 \left(1 - \frac{v_3}{v_1}\right) = RT_1 \left(1 - \frac{v_3}{v_1}\right)$$

We know $P_1 v_1 = RT_1$ and $P_3 v_3 = RT_3$

or $\quad \dfrac{v_3}{v_1} = \dfrac{RT_3}{P_3} \cdot \dfrac{P_1}{RT_1} = \dfrac{T_3}{T_1} \quad$ (since $P_1 = P_3$). Therefore

$$W_{3-1} = RT_1\left(1-\frac{v_3}{v_1}\right) = RT_1\left(1-\frac{T_3}{T_1}\right) = 8.314\times 300\left(1-\frac{1500}{300}\right) = -9.977 \text{ kJ}$$

Net work done by the gas, $W = W_{1-2} + W_{2-3} + W_{2-3} = 0 + 20.071 - 9.977 = 10.094$ kJ.

Example 2.2 A piston–cylinder assembly shown in Fig.2.13 initially contains 0.1 m^3 air at 0.1 MPa. The atmospheric pressure of 0.1 MPa acts on the other side of the piston. At this stage the spring just touches the piston and does not exert any force. Now the gas is heated till the volume is 0.3 m^3 and at this stage the pressure of the gas is 0.6 MPa. When the spring is compressed it exerts a force which is proportional to the decrease in its length. Calculate the work done by the gas.

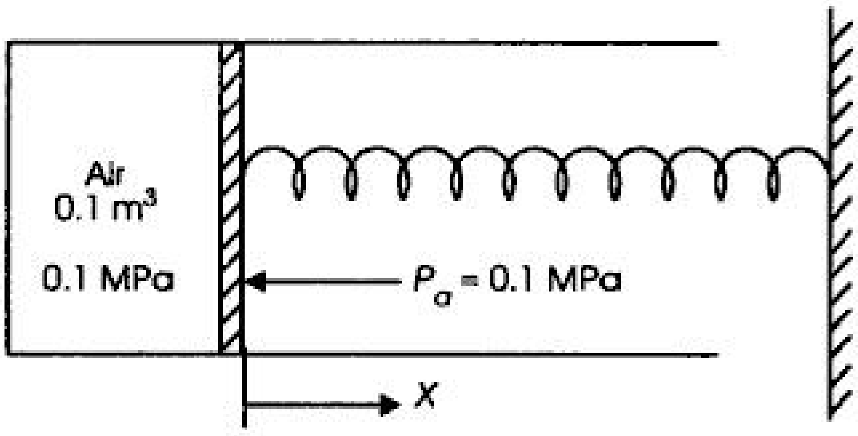


Fig.2.13 *Sketch for Example 2.2.*

Solution Work done by the gas is given by

$$W = \int_1^2 PdV \tag{A}$$

Force balance on the piston gives

$$PA = P_aA + KX \tag{B}$$

where A = cross-sectional area of the piston, P_a = atmospheric pressure (0.1 MPa; given), X = decrease in spring length and K = spring constant.

Equation B can be rewritten as

$$P = P_a + \frac{KX}{A} = P_a + \frac{K}{A^2}(V - V_0) \tag{C}$$

where V = volume of air in the cylinder at any instant and V_0 = volume of air in the cylinder when the spring is at its natural length.

Substituting Eqn.(C) in Eqn.(A), we get

$$\begin{aligned} W &= \int_1^2 \left[P_a + \frac{K}{A^2}(V - V_0)\right] dV = P_a(V_2 - V_1) + \frac{K}{2A^2}\{(V_2 - V_0)^2 - (V_1 - V_0)^2\} \\ &= P_a(V_2 - V_1) + \frac{K}{2A^2}\{(V_2 - V_0 + V_1 - V_0)(V_2 - V_0 - V_1 + V_0)\} \\ &= P_a(V_2 - V_1) + \frac{K}{2A^2}(V_2 - V_1)(V_2 + V_1 - 2V_0) \end{aligned}$$

Table 2.1 *Generalized displacements and forces of a few work modes*

Work mode	Extensive parameter	Intensive parameter	Work done
Compression/expansion	Volume (V)	Pressure (P)	PdV
Extension of elastic rod	Strain (ϵ)	Stress (τ)	$-\tau d\epsilon$
Stretching of an elastic wire	Extension (L)	Tension (τ)	$-\tau dL$
Stretching of a surface film	Surface area (A)	Surface tension (τ)	$-\tau dA$
Discharging of a reversible cell	Electric charge (Q_e)	emf (E)	$-EdQ_e$

2.7 Heat

Depending on the nature of the system, the energy of the system can be changed by one or more work modes. The work done by a system can be estimated in terms of macroscopically measurable parameters like pressure and volume. Work is not the only interaction between a system and its surroundings and the energy of a system can also change by a process which cannot be identified as work at a macroscopic level. Consider the gas contained in a piston–cylinder assembly as the system. If the piston–cylinder assembly is placed in thermal contact with a hot body, the temperature and the energy of the system increases. As the temperature of the cylinder walls increases, the atoms in the cylinder walls vibrate vigorously. The gas molecules during collisions with the walls receive energy from the cylinder walls and the kinetic energy of the gas molecules increases. Subsequently, the energy is transferred to the remaining gas molecules during intermolecular collisions and the gas attains a state of thermal equilibrium. During a collision one molecule does work on another molecule in increasing its velocity and kinetic energy. In fact, at a microscopic level, the energy is transferred through work interaction only. However, this work interaction cannot be detected at a macroscopic level. What we observe at a macroscopic level is the temperature difference between the system and its surroundings. Such a mode of energy transfer which cannot be accounted as work from a macroscopic point of view is termed as heat. Therefore, *energy transfer which occurs by virtue of temperature difference between the two interacting systems is called heat interaction.*

The work and heat interactions can be identified only when the process is in progress. Once the process is completed, we will not be able to specify whether the energy of the system has changed due to work interaction or heat interaction. Consider the liquid contained in the jar of a mixie shown in Fig.2.16 as our system. In Fig.2.16 (a), the jar containing the liquid is placed on a hot plate and energy is transferred to the system by virtue of the temperature difference between the system and the hot plate. In this case the interaction between the system and its surroundings is heat. In Fig.2.16(b), the jar is mounted on the motor of a mixie and the liquid is vigorously stirred. In this case work is done on the system by the surroundings. Given the initial and final energies of the system, it will not be possible to specify whether the energy transfer occurred through heat or work unless the process is observed. Therefore, both work and heat are energy in transit and can be identified during the course of interaction only.

The two modes of energy transfer — work and heat — depend on the choice of the system. Suppose a geyser is initially filled with water at room temperature and then switched on. After some time we find that the geyser contains hot water. Obviously, there is an interaction between the surroundings and the contents of the geyser, since the energy of the contents of the geyser has increased. Can this interaction be called as heat or work? If we consider only the water contained in the geyser as our system, the energy of the system has increased due to the temperature difference between water and the heating element and hence the interaction is heat. On the other hand, if we consider the combination of water and the heating element as our system, the interaction is work because the energy transfer (similar to the interaction of a battery with a resistor) is due to the interaction of the source of electrical energy with the heating element. Therefore, it is essential to specify the choice of the system whenever heat and work interactions are specified.

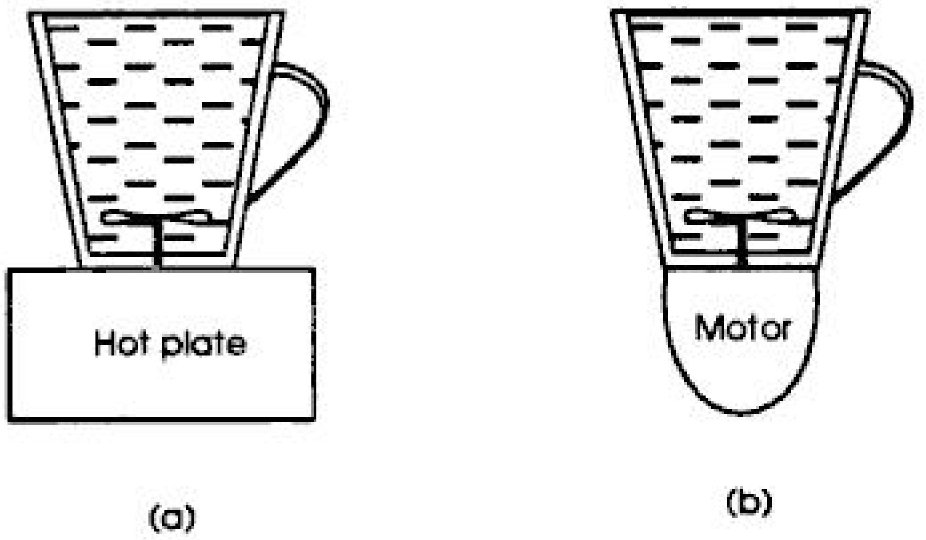


Fig.2.16 (a) *Energy transfer as heat from surroundings to system.* **(b)** *Energy transfer as work from surroundings to system.*

2.8 State postulate

Consider one mole of a gas contained in a cylinder–piston assembly as the system. The gas exerts a certain pressure (P), occupies a certain volume (v), possesses a certain energy (u) and is at a certain temperature (T). Therefore, the state of the system can be described by specifying P, v, T, u, etc. Now the question that naturally arises is how many variables or properties are needed to specify the state of a system. If we consider the properties P, v and T, there exist a relation of the type $f(P, v, T) = 0$ among them. That is, only two of the properties P, v and T are independent. The value of the third property can be expressed in terms of the other two properties. Therefore, we would like to know how many properties of a system can be independently varied. The number of independently variable thermodynamic properties of a system is specified by the state postulate.

The *state postulate* states that the number of independently variable thermodynamic properties of a system is equal to one more than the number of reversible work modes associated with the system. For a simple compressible substance, the independent variables can be chosen as u and v. If the values of u and v are specified the thermodynamic state of the system is completely specified. That is every other thermodynamic property of the system has a definite value in that state, and the property can be estimated from a knowledge of u and v. Specifically the molar entropy s can be expressed as a function of u and v for a single component simple system. Stated mathematically,

$$s = s\ (u, v) \tag{2.18}$$

For a complete description of the system (including the quantity of matter) the mole number N also is to be specified. Then for a single component simple system we can write

$$S = S\ (U, V, N) \tag{2.19}$$

where S is the total entropy of the system. If the system under consideration contains c components, then one can write

$$S = S\,(U,\ V,\ N_1,\ N_2,\ \ldots,\ N_c) \tag{2.20}$$

where N_i represents the mole number of component i. Equations 2.18–2.20 are known as *fundamental relations*, because every thermodynamic property of the system can be obtained from them. That is one can evaluate pressure, temperature, chemical potential and other thermodynamic properties of a system from a knowledge of its fundamental relation. Therefore, a knowledge of the fundamental relation is equivalent to a knowledge of the equations of state, and the property data presented in the form of tables, charts, diagrams, etc. A brief discussion of the fundamental relation is presented in Chapter 6. For complete details the reader is advised to consult the book [1] under References.

2.9 Temperature scale

In thermodynamic analysis of systems the temperature plays an important role. The basis for the measurement of temperature is the zeroth law of thermodynamics which states that if each of the two given systems are in thermal equilibrium with a third system, then the two given systems are in thermal equilibrium with each other. The zeroth law of thermodynamics was formulated by Fowler in 1931 whereas the first law of thermodynamics was formulated in 1851 followed by the second law of thermodynamics within a short span of time. Logic demands the discussion of the zeroth law before discussing the first and second laws of thermodynamics and hence it was named as zeroth law of thermodynamics.

The zeroth law of thermodynamics can be used to compare the temperatures of several bodies. Suppose a particular body called thermometer is placed in diathermal contact with a body, the temperature of which is to be measured, it attains thermal equilibrium with the body. Then the thermometer can be allowed to reach a state of thermal equilibrium with another body, the temperature of which is assigned a standard value. Based on the variation of a measurable property of the thermometer one can estimate the temperature of the body. To quantify the measurements it is necessary that the thermometer should have a property which can be easily measured and such a property is usually called thermometric property. The commonly used thermometric properties are the length of a liquid column in a capillary tube (variation of volume with temperature), the electrical resistance of a wire, the pressure of a gas in a closed vessel, the emf generated at the junction of two dissimilar metal wires, etc. To establish the temperature scale, it is necessary to know the reference state or base value. The establishment of a base value or the choice of zero for the measurement of an extensive quantity like length or mass is easy because the zero value corresponds to the absence of length or mass. However, temperature being an intensive quantity, it is difficult to choose the zero. The temperature scale is established based on two fixed points — ice point and steam point. In the Celsius temperature scale, the ice point (the melting point of pure ice at standard atmospheric pressure) has been assigned a value of 0°C and the steam point (the boiling point of pure water at standard atmospheric pressure) has been assigned a value of 100°C. The difference between these two values is equally divided into 100 units.

Suppose different thermometers with different thermometric properties are used to measure the temperature of a body which lies between 0°C and 100°C, they read different values. The values differ because the variation of the thermometric property with temperature for all these

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reaction, and if there is no tendency for the composition to change then the system is in a state of chemical equilibrium. The criteria of equilibrium are:

Equality of pressure:	mechanical equilibrium
Equality of temperature:	thermal equilibrium
Equality of chemical potential:	chemical equilibrium

A system which simultaneously satisfies the criteria for mechanical, thermal and chemical equilibrium is said to be in a state of thermodynamic equilibrium.

The equilibrium states of a system are classified as stable, unstable and metastable. In a state of stable equilibrium, the system returns to its original equilibrium state after it is disturbed, however large the disturbance may be. In thermodynamics we are mainly interested in stable equilibrium states of a system. In a state of unstable equilibrium, the system settles into a new equilibrium state if it is subjected to a disturbance, even though the magnitude of the disturbance is small. In a state of metastable equilibrium the system returns to its original equilibrium state if subjected to small disturbances, but when the disturbance exceeds a certain magnitude, it settles into a new equilibrium state.

Whenever a system undergoes a change of state it is said to undergo a process. A process is the means by which a system changes from one state to another. The processes are classified as reversible and irreversible. A process which occurs very slowly and with infinitesimal driving forces is called a quasi-static process. If both the system and its surroundings can be restored to their respective initial states by reversing the direction of the process, then the process is said to be reversible. If a process does not fulfil this criterion it is called an irreversible process. A reversible process is a quasi-static process, but the converse need not be true. Motion without friction, expansion/compression with no pressure difference between the interacting systems, energy transfer as heat with no temperature difference across the boundary are examples of reversible processes.

In mechanics, work done by a force is defined as the product of the force and the distance moved in the direction of the applied force. This definition of work is inadequate in thermodynamics as it does not explain all forms of work. In thermodynamics work is said to be done by a system on its surroundings, if the sole effect external to the system could be reduced to the raising of a mass through a distance. The compression/expansion work done by a system, during a reversible process, is given by

$$W = \int P dV \tag{2.11}$$

Work done by a system or work interaction is not a property of the system. It is a path function and its differential is not exact.

Energy transfer which occurs by virtue of temperature difference between the two interacting systems is called heat interaction. The work and heat interactions can be identified only when the process is in progress. Once the process is completed it is not possible to specify whether energy is transferred in the form of work or heat. Work and heat interactions depend on the choice of the system and hence it is essential to specify the choice of the system while specifying the work and heat interactions.

The state postulate states that the number of independently variable thermodynamic properties of a system is equal to one more than the number of reversible work modes associated with the system. For a simple compressible substance, two thermodynamic properties can be independently varied. Hence, the state of such a system can be described by specifying two independently variable properties.

2.13 A piston–cylinder assembly shown in Fig.2.20 contains one mole of a gas at 0.1 MPa and 300 K. The gas obeys the relation $Pv = RT$. The piston is massless and frictionless and atmospheric pressure of 0.1 MPa acts on the other side of the piston. The gas is heated allowing the piston to move. Once the gas volume is doubled, the piston touches a spring which is fixed at a distance above the cylinder. If the heating of the gas is continued till the volume of the gas is three times its original volume the gas pressure rises to 0.3 MPa. Assuming that the spring exerts a force which is proportional to the deformation (the decrease in the length of a spring) calculate the work done by the gas and the change in the potential energy of the spring. Represent the process on a P–V diagram.

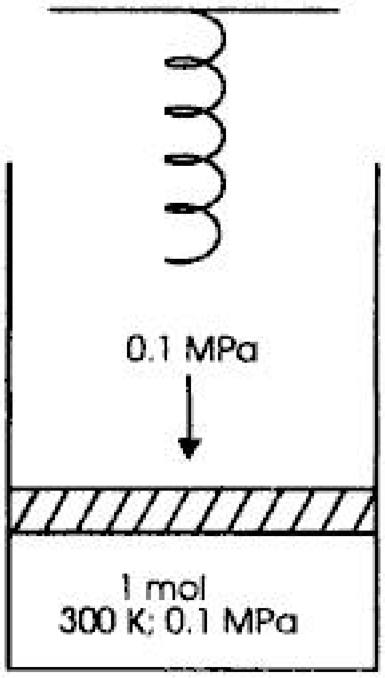

Fig.2.20 *Sketch for Problem 2.13.*

2.14 Suppose 1 kg ice at 0°C and 101.325 kPa is completely converted into steam at 100°C and at the same pressure. Calculate the work done during melting and during vaporization. It is given that the density of ice at 0°C is 916.23 kg/m^3 and the specific volume of steam at 100°C and 101.325 kPa is 1.673 m^3/kg. The specific volume of liquid water at 0°C = 1×10^{-3} m^3/kg.

2.15 Usually the weather data is collected by releasing helium or hydrogen filled balloons carrying the required measuring instruments into the atmosphere. In one such experiment a balloon which is initially flat is slowly filled with hydrogen from a cylinder forming a sphere of 1 m radius. The atmospheric pressure is 101.325 kPa. Calculate the work done by the cylinder–balloon system.

2.16 It is desired to establish a particular temperature scale according to the relation

$$t = ae^r + b$$

where a and b are constants, r is the reading of the thermometric property as read by the thermometer and t is in °C. The values of r at ice point and steam point are 5.6 and 8.19. Determine the temperature of a body which gives r = 7.25 and the value of r at 55°C.

vapor regions are marked as L and V and the two-phase region, where both liquid and vapor phases co-exist, is marked as $(L + V)$. AC is called the saturated liquid curve and BC is called the saturated vapor curve. The constant temperature lines (or isotherms) are shown by T_1, T_2, T_c, T_3, where $T_3 > T_c > T_2 > T_1$. It can be observed that the isotherms T_1 and T_2 split into three segments. The horizontal line segment fg connects the saturated liquid and saturated vapor states. The length of the horizontal line segment decreases as the temperature of the system increases and at T_c the horizontal line segment reduces to a point. At point C, the specific (molar) volumes of the saturated liquid and saturated vapor become identical and the two phases cannot be distinguished from each other. The point C is called the critical point. The *critical point* represents the highest temperature and pressure at which both liquid and vapor phases can co-exist in equilibrium. The temperature and pressure corresponding to the critical point are known as *critical temperature* (T_c) and *critical pressure* (P_c), respectively. The isotherm passing through the critical point is called the *critical isotherm*. The critical constants of several substances are presented in the Appendix (Table A.1).

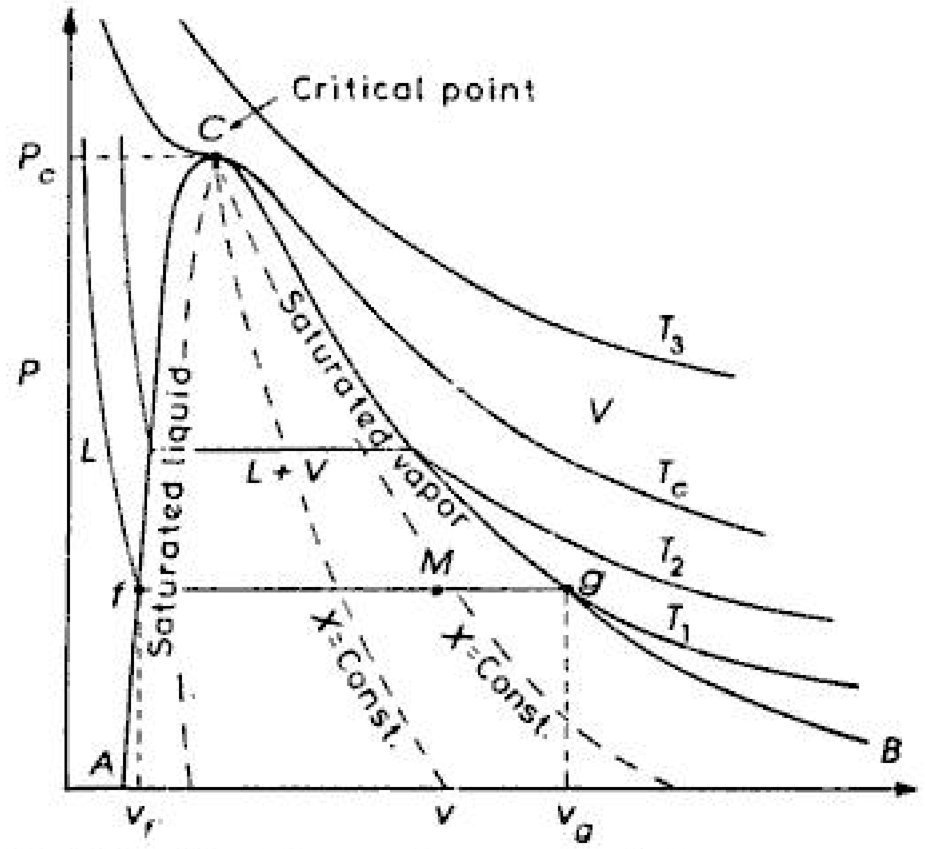

Fig.3.2 *P–v diagram for a pure substance.*

The isothermal compressibility (κ) of a substance is defined as

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{3.1}$$

It can be observed from Fig.3.2 that $[\partial P/\partial v]_T$ or the slope of the isotherm in the liquid region is very high. In other words, the isothermal compressibility of the liquid is very low and hence the liquids are often treated as incompressible. In the vapor region, the isothermal compressibility is quite large and the vapor is highly compressible.

The substance existing at state M (see Fig.3.2) is a mixture of saturated liquid (state f) and saturated vapor (stage g). Since volume is an extensive property which is additive, the molar volume v of the mixture is equal to the sum of the volumes occupied by the saturated liquid and saturated vapor. Hence, one can write

$$(N_f + N_g)v = N_g v_g + N_f v_f \quad \text{or} \quad v = \frac{N_g v_g}{(N_f + N_g)} + \frac{N_f v_f}{(N_f + N_g)} \tag{3.2}$$

The van der Waals equation of state is cubic in volume and, in general, gives three values of volume for a given pressure and temperature. However, in some range of values of P and T it gives only one real value for volume and in some other range of P and T, it gives three real values for volume.

Where $T > T_c$, only one real value of volume exists; and where $T < T_c$, three real values of volume exist.

The P–v–T behavior of a gas which satisfies the van der Waals equation of state is shown in Fig.3.7. The isotherm at $T < T_c$ gives three values v_f, v_i and v_g for volume. Moreover the segment 12345 is not in agreement with the experimental observation. The practically realizable variation of volume is shown by the dotted line 1–5. In the segment 2–3–4, the van der Waals equation predicts an increase in volume with increasing pressure at constant temperature which is not realistic. Based on the stability criterion (which is discussed in Chapter 10) it can be shown that the system is unstable in the region 12345 and the system should move along the straight line path (dotted line) 1–5 in this region. Therefore, the volume v_i is inadmissible. The smallest value v_f corresponds to the liquid volume and the largest value v_g corresponds to the vapor volume. It can also be shown that the straight line path 1–5 should be such that the area of the region I (segment 123) is equal to the area of the region II (segment 345).

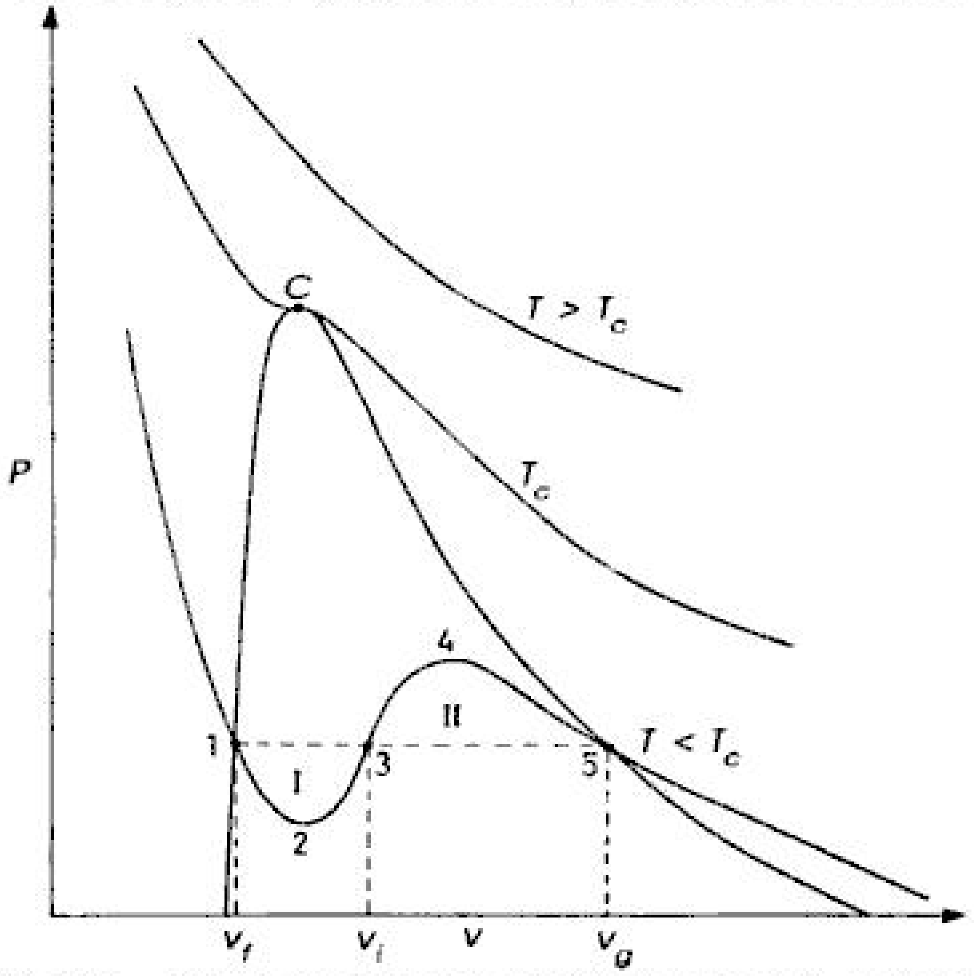

Fig.3.7 *Isotherms of a van der Waals gas on P–v diagram.*

Example 3.6 Calculate the volume occupied by one mole of n-octane vapor at 427.85 K where the saturation pressure is 0.215 MPa. Assume that n-octane follows the van der Waal's equation of state. The van der Waals constants a and b are 3.789 Pa(m^3/mol)^2 and 2.37×10^{-4} m^3/mol, respectively.

Solution The van der Waals equation is cubic in volume. Given the volume, calculation of P or T is straight forward. However, calculation of volume, given P and T requires a trial and error method. The equation can be rearranged as given below for an iterative calculation.

$$v_{i+1} = \frac{RT}{(P + a/v_i^2)} + b \qquad \textbf{(A)}$$

$$D = \frac{q^2}{4} + \frac{p^3}{27} = \frac{(0.0564)^2}{4} - \frac{(0.2786)^3}{27} = -5.6624 \times 10^{-6}$$

Since $D < 0$, there are three unequal real roots

$$r = \left(\frac{-p^3}{27}\right)^{1/2} = \sqrt{\frac{(0.2786)^3}{27}} = 0.0283$$

$$\cos\theta = -\frac{q}{2}\left(\frac{-27}{p^3}\right)^{1/2} = \frac{0.0564}{2} \times \frac{1}{0.0283} = 0.9965 \quad \text{or} \quad \theta = 4.8^\circ$$

$$Z_1 = 2r^{1/3}\cos\left(\frac{\theta}{3}\right) - \frac{\alpha}{3} = 2 \times (0.0283)^{1/3}\cos(1.6^\circ) + \frac{1.0143}{3} = 0.9474$$

$$Z_2 = 2r^{1/3}\cos\left(\frac{2\pi + \theta}{3}\right) - \frac{\alpha}{3} = 2 \times (0.0283)^{1/3}\cos(121.6^\circ) + \frac{1.0143}{3} = 0.0187$$

$$Z_3 = 2r^{1/3}\cos\left(\frac{4\pi + \theta}{3}\right) - \frac{\alpha}{3} = 2 \times (0.0283)^{1/3}\cos(241.6^\circ) + \frac{1.0143}{3} = 0.0482$$

Since $Z = Pv/RT$, the smallest value of $Z = 0.0187$ corresponds to saturated liquid and the largest value of $Z = 0.9474$ corresponds to saturated vapor. The middle value of $Z = 0.0482$ has no physical significance. Therefore

$$v_f = \frac{ZRT}{P} = \frac{0.0187 \times 8.314 \times 427.85}{0.215 \times 10^6} = 3.094 \times 10^{-4} \text{ m}^3/\text{mol}$$

$$v_g = \frac{0.9474 \times 8.314 \times 427.85}{0.215 \times 10^6} = 15.675 \times 10^{-3} \text{ m}^3/\text{mol}$$

The values of the van der Waals constants a and b can be obtained by fitting the experimental P–v–T data to the equation of state. For approximate calculations, the constants can be determined by making use of the fact that the critical isotherm must show a point of inflexion at the critical point, as indicated below. At the point of inflexion

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = 0 \tag{3.39}$$

Applying the criteria given by Eqns.3.39 to the van der Waals equation, we get

$$\left(\frac{\partial P}{\partial v}\right)_{T_c} = -\frac{RT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0 \tag{3.40}$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T_c} = \frac{2RT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0 \tag{3.41}$$

At the critical point, the van der Waals equation is given by

$$\left(P_c + \frac{a}{v_c^2}\right)(v_c - b) = RT_c \tag{3.42}$$

where B, C and D are known as the second, third and fourth virial coefficients, respectively. The virial coefficients express the deviation from ideal gas behavior and they depend on temperature and type of species only. The advantage of the virial equation of state is that it can be made to represent the experimental P–v–T data more accurately by increasing the number of terms. The second virial coefficient takes into account the binary interactions between molecules while the third virial coefficient takes into account the three body interactions. The equation of state can be derived by the application of statistical mechanics and hence has a strong theoretical basis, like the ideal gas law, whereas all other equations of state are either empirical or semiempirical. Equation 3.50 is often called the *Leiden form* or *pressure explicit form* of the virial equation. The values of the second virial coefficients have been determined for a large number of gases and the data can be found in Dymond and Smith [38]. Whenever the data is not available, it is possible to estimate the virial coefficients from intermolecular potential functions [39]. The virial equation can also be written as a power series in pressure as

$$Pv/RT = 1 + B'P + C'P^2 + D'P^3 + \dots \tag{3.51}$$

Equation 3.51 is usually called the *Berlin form* or *the volume explicit virial equation*. The virial coefficients B', C', D' are functions of temperature and the nature of the gas only. The coefficients B', C' and D' are related to B, C and D as given below

$$B' = \frac{B}{RT} \tag{3.52}$$

$$C' = \frac{C - B^2}{(RT)^2} \tag{3.53}$$

$$D' = \frac{D - 3BC + 2B^3}{(RT)^3} \tag{3.54}$$

It is found that if Eqns.3.50 and 3.51 are truncated after the third term, Eqn.3.50 represents the P–v–T data more accurately than Eqn.3.51.

3.3.7 Law of corresponding states

The van der Waals equation of state is a simple cubic equation of state and predicts the P–v–T behavior of several gases with reasonable accuracy. To improve the predictive nature of the cubic equations of state several attempts have been made resulting in the development of the Redlich–Kwong (RK), Soave–Redlich–Kwong (SRK), Peng–Robinson (PR) equations of state etc. Substituting the constants a and b given by Eqn.3.44 in the van der Waals equation of state [Eqn.3.17] we get

$$\left(P_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r \tag{3.55}$$

where $P_r = P/P_c$ = reduced pressure (3.56)

$T_r = T/T_c$ = reduced temperature (3.57)

$v_r = v/v_c$ = reduced volume (3.58)

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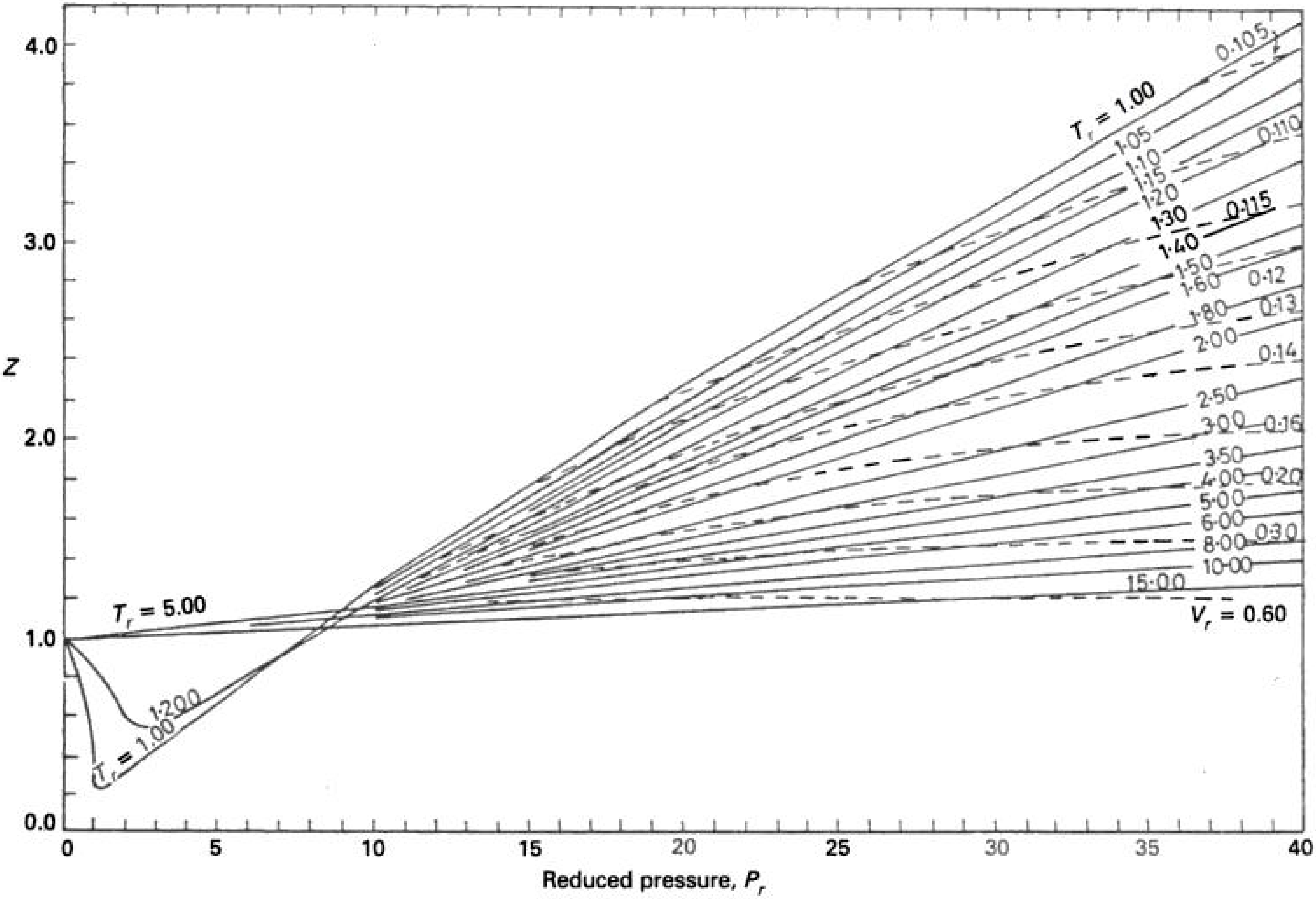


Fig.3.9 (b) *Generalized Compressibility Chart for $P_r \geq 10.0$. Adapted with permission from Nelson, L.C. and Obert, E.F., "Generalized Compressibility Charts", Chemical Engineering, Vol. 61, No. 17, 203–208, McGraw-Hill Inc. (1954).*

Pitzer [43] showed that a group of fluids having identical intermolecular potentials conform to the law of corresponding states. The heavier rare gases, A, Kr and Xe have similar intermolecular potentials and these gases obey the law of corresponding states. These gases are termed as *simple fluids*. Pitzer defined the *acentric factor* ω in terms of the reduced vapor pressure at $T_r = 0.7$ and ω is given by

$$\omega = -\log_{10} P_r^S|_{T_r=0.7} - 1.0 \tag{3.62}$$

where $P_r^S = P^S/P_c$ = reduced vapor pressure at $T_r = 0.7$.

The acentric factor ω is defined such that its value is equal to zero for the simple fluids (spherical molecules). The acentric factor indicates a measure of deviation of the intermolecular potential of a molecule from that of a simple spherical molecule. Any property of the fluid, expressed in reduced dimensionless form, is assumed to be a function of the three parameters — reduced temperature, reduced pressure and acentric factor. This forms the basis for the *three parameter law of corresponding states* which tells that all fluids having the same acentric factor ω, will have the same value of compressibility factor Z, when considered at given values of P_r and T_r. That is

Since $T_r = 1.2$ at the given conditions, the state of CO_2 must lie on the curve $T_r = 1.2$. To determine the state of CO_2, draw a straight line, passing through the origin, with a slope of 0.595 on the Z^0 versus P_r plot and locate the intersection of this straight line with $T_r = 1.2$ curve, as shown in Fig.3.15. Now $Z^0 = 0.725$.

$$\text{Therefore} \quad P = \frac{Z^0RT}{v} = \frac{0.725 \times 8.314 \times (91.8 + 273.15)}{2.444 \times 10^{-4}} = 9 \text{ MPa}$$

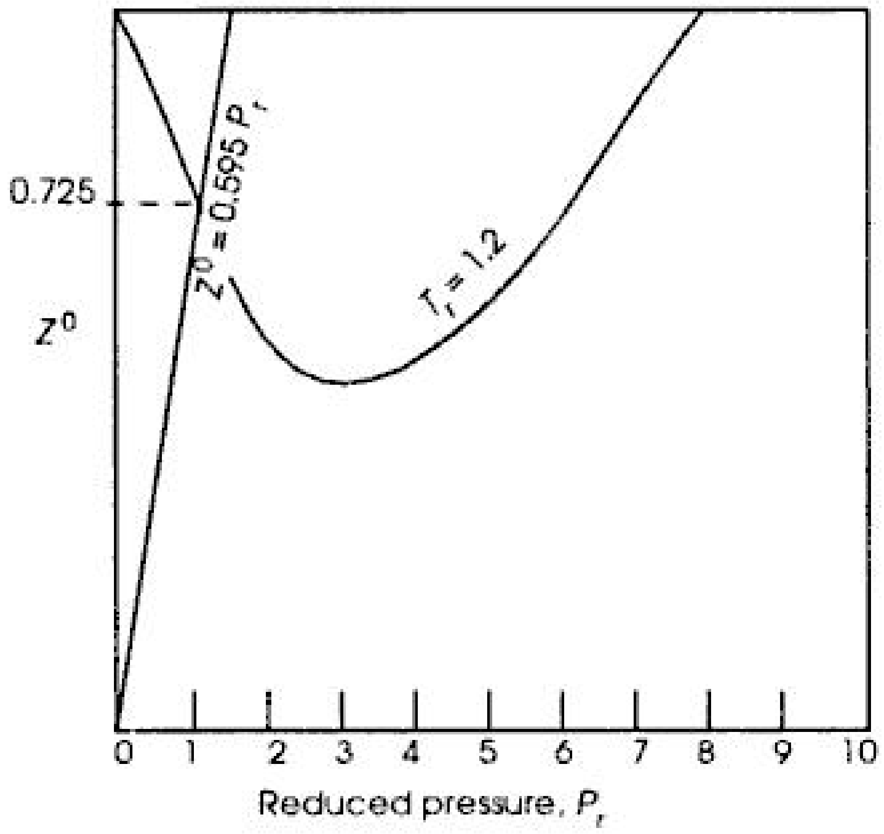


Fig.3.15 *Sketch for Example 3.12.*

Example 3.13 Repeat Example 3.12 by making use of the three parameter compressibility factor correlation. For CO_2, $\omega = 0.239$.

Solution The pressure P is given by

$$P = \frac{ZRT}{v} \quad \text{or} \quad Z = \frac{Pv}{RT} = \frac{vP_cP_r}{RT} \quad \text{or} \quad Z = \frac{2.444 \times 10^{-4} \times 73.87 \times 10^5 \times P_r}{8.314 \times 364.95} = 0.595P_r$$

$$\text{or} \quad P_r = Z/0.595 \tag{A}$$

$$T_r = \frac{364.95}{304.2} = 1.2; \qquad Z = Z^0 + \omega Z^1$$

The term Z^1 is a correction factor. As a first guess one can assume its contribution to be negligible and obtain $Z = Z^0$. The value of Z^0 can be determined as explained in Example 3.12. The result is

$$Z^0 = 0.725 \quad \text{and} \quad P_r = \frac{Z}{0.595} = \frac{0.725}{0.595} = 1.22$$

Now read $Z^1 = 0.1$ at $T_r = 1.2$ and $P_r = 1.22$ from Fig.3.14. Then

$$Z = Z^0 + \omega Z^1 = 0.725 + 0.239 \times 0.1 = 0.749$$

$$\sqrt{\alpha} = 1 + S(1 - \sqrt{T_r}) \tag{3.78}$$

$$S = 0.374\ 64 + 1.542\ 26\omega - 0.269\ 92\omega^2 \tag{3.79}$$

The Peng–Robinson equation can also be expressed in terms of the compressibility factor as

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{3.80}$$

Example 3.15 Calculate the molar volumes of saturated liquid and saturated vapor for n-octane at 427.85 K and 0.215 MPa using the Soave–Redlich–Kwong equation of state. For n-octane, T_c = 569.4 K, P_c = 24.97 bar and ω = 0.398.

Solution Let us use Cardan's method to calculate the molar volumes.

$$T_r = \frac{427.85}{569.4} = 0.7514; \quad P_r = \frac{0.215 \times 10^6}{2.497 \times 10^6} = 0.0861$$

$$S = 0.48 + 1.574\omega - 0.176\omega^2 = 0.48 + 1.574 \times 0.398 - 0.176 \times (0.398)^2 = 1.0786$$

$$\alpha = [1 + S(1 - \sqrt{T_r})]^2 = [1 + 1.0786(1 - \sqrt{0.7514})]^2 = 1.3079$$

$$a = \frac{0.42748 R^2 T_c^2 \alpha}{P_c} = \frac{0.42748 \times (8.314 \times 569.4)^2 \times 1.3079}{24.97 \times 10^5} = 5.0180$$

$$b = \frac{0.08664 R T_c}{P_c} = \frac{0.08664 \times 8.314 \times 569.4}{24.97 \times 10^5} = 1.6426 \times 10^{-4}$$

$$A = \frac{aP}{(RT)^2} = \frac{5.0180 \times 0.215 \times 10^6}{(8.314 \times 427.85)^2} = 0.0853$$

$$B = \frac{bP}{RT} = \frac{1.6426 \times 10^{-4} \times 0.215 \times 10^6}{8.314 \times 427.85} = 9.9282 \times 10^{-3}$$

$$\alpha = -1; \quad \beta = A - B - B^2 = 0.0853 - 9.9282 \times 10^{-3} - (9.9282 \times 10^{-3})^2 = 7.5371 \times 10^{-2}$$

$$\gamma = -AB = -0.0853 \times 9.9282 \times 10^{-3} = -8.4688 \times 10^{-4}$$

$$p = \beta - \frac{\alpha^2}{3} = 7.5371 \times 10^{-2} - \frac{1}{3} = -0.2580$$

$$q = \frac{2\alpha^3}{27} - \frac{\alpha\beta}{3} + \gamma = \frac{-2}{27} + \frac{7.5371 \times 10^{-2}}{3} - 8.4688 \times 10^{-4} = -4.9797 \times 10^{-2}$$

$$D = \frac{q^2}{4} + \frac{p^3}{27} = \frac{(4.9797 \times 10^{-2})^2}{4} - \frac{(0.2580)^3}{27} = -1.6121 \times 10^{-5}$$

$$r = \sqrt{\frac{-p^3}{27}} = \sqrt{\frac{(0.2580)^3}{27}} = 2.5220 \times 10^{-2}$$

linear function of P at constant temperature. Hence at low to moderate pressures, the volume explicit virial equation [Eqn.3.51] when truncated after two terms gives

$$\frac{Pv}{RT} = Z = 1 + B'P \tag{3.89}$$

Substituting for B' from Eqn.3.52, we get

$$Z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_c}{RT_c}\right)\frac{P_r}{T_r} \tag{3.90}$$

For nonpolar molecules, the corresponding states correlation is used to estimate B [47, 48]. The virial coefficient B is expressed as

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1 \tag{3.91}$$

Substituting Eqn.3.91 in Eqn.3.90, we get

$$Z = 1 + \left(\frac{BP_c}{RT_c}\right)\frac{P_r}{T_r} = 1 + B^0\frac{P_r}{T_r} + \omega B^1\frac{P_r}{T_r} \tag{3.92}$$

The Pitzer's correlation for Z gives

$$Z = Z^0 + \omega Z^1 \tag{3.64}$$

Comparing Eqns.3.64 and 3.92, we get

$$Z^0 = 1 + B^0\frac{P_r}{T_r} \tag{3.93}$$

and $$Z^1 = B^1\frac{P_r}{T_r} \tag{3.94}$$

B^0 and B^1 are given by

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \tag{3.95}$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \tag{3.96}$$

The generalized virial coefficient correlation is applicable at low to moderate pressures and for non-polar gases only.

3.6 Summary

In the thermodynamic analysis of processes it is essential to have a knowledge of the properties of the system and the relationships that exist among the various properties. The properties can

where $B, C, D, \ldots, B', C', D'$ are called virial coefficients which depend on temperature and nature of the substance only. The virial coefficients are related as

$$B' = \frac{B}{RT} \tag{3.52}$$

$$C' = \frac{C - B^2}{(RT)^2} \tag{3.53}$$

$$D' = \frac{D - 3BC + 2B^3}{(RT)^3} \tag{3.54}$$

The van der Waals equation can be expressed in terms of reduced parameters as

$$\left(P_r + \frac{3}{v_r^2}\right)(3v_r - 1) = 8T_r \tag{3.55}$$

which is known as the reduced equation of state. The reduced parameters are defined as

Reduced pressure, $P_r = P/P_c$ (3.56)

Reduced temperature, $T_r = T/T_c$ (3.57)

Reduced volume, $v_r = v/v_c$ (3.58)

The reduced equation of state leads to the two parameter law of corresponding states which tells that all fluids when considered at given values of T_r and P_r will have the same value of v_r. The compressibility factor Z is defined as

$$Z = \frac{\text{Actual volume of gas}}{\text{Volume predicted by ideal gas law}} = \frac{v}{RT/P} = \frac{Pv}{RT} \tag{3.59}$$

The reduced equation of state can be rewritten in terms of the compressibility factor as

$$\left(Z + \frac{27P_r}{64ZT_r^2}\right)\left(1 - \frac{P_r}{8ZT_r}\right) = 1 \tag{3.60}$$

This leads to the two-parameter compressibility factor correlation $Z = Z\,(T_r, P_r)$. To improve the accuracy in the predicted volumetric properties of gases, the three parameter compressibility factor correlation was developed. Pitzer's acentric factor ω is defined as

$$\omega = -\log_{10} P_r^s|_{T_r=0.7} - 1.0 \tag{3.62}$$

where $P_r^s = P_s/P_c$ = reduced vapour pressure at $T_r = 0.7$.

The acentric factor ω is defined such that its value is equal to zero for the simple fluids — argon, krypton and xenon (spherical). The acentric factor indicates a measure of deviation of the intermolecular potential of a molecule from that of a simple spherical molecule.

3.9 Rework Problem 3.7 assuming that ethylene obeys the van der Waals equation of state. Use the iterative method to determine the molar volume of ethylene gas. The constants a and b are given in Appendix Table A. 2.

3.10 Assuming that ethylene obeys Van der Waals equation of state with the constants given in Appendix Table A.2, rework Problem 3.7. Use Cardan's method to calculate the molar volume.

3.11 A tank of 1 m^3 volume is filled with 5 kg ammonia at 300 K. Determine the pressure exerted by ammonia (a) using the ideal gas law, and (b) assuming that ammonia obeys the van der Waals equation of state.

3.12 At 321.55 K, liquid and vapor phases of ammonia coexist in a state of equilibrium and exert a pressure of 1.95 MPa. Determine the molar volume of ammonia vapor and ammonia liquid at these conditions, assuming that NH_3 follows the van der Waals equation of state. Use the iterative scheme to determine the molar volumes.

3.13 Rework Problem 3.12 using Cardan's method.

3.14 The Berthelot equation of state is given by

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

where a and b are constants characteristic of the gas. Develop relations to determine the constants a and b in terms of critical temperature and pressure.

3.15 The Dieterici equation of state is given by

$$P(v-b)\exp\left(\frac{a}{RTv}\right)=RT$$

where a and b are constants characteristic of the gas. Determine the relations to evaluate a and b in terms of T_c and P_c.

3.16 Express the Beattie–Bridgeman equation of state in the pressure explicit virial form.

3.17 A tank of 1 m^3 volume is filled with 5 kg ammonia at 300 K. Determine the pressure exerted by ammonia using the Redlich–Kwong equation.

3.18 Rewrite the RK equation of state so that it can be used for iterative calculation of vapor and liquid volumes.

3.19 The saturation pressure of NH_3 at 321.55 K is 1.95 MPa. Determine the molar volumes of saturated vapor and saturated liquid using the RK equation of state. Make use of the iterative scheme developed in Problem 3.18.

3.20 It is desired to store saturated ammonia at 321.55 K and 1.95 MPa in a tank of 10 m^3 volume. Safety considerations dictate that no more than 70 per cent of the volume can be filled with liquid. Determine the maximum mass of ammonia that can be stored in the tank. Use Cardan's method to calculate the molar volumes of saturated vapor and liquid. Assume that NH_3 follows the RK equation of state.

3.21 Show that the virial coefficients B', C', D' of the Berlin form (volume explicit virial equation) are related to B, C, D of the Leiden form (pressure explicit virial equation) by the relations

$$B'=\frac{B}{RT};\quad C'=\frac{C-B^2}{(RT)^2};\quad D'=\frac{D-3BC+2B^3}{(RT)^3}$$

3.22 Express the van der Waals equation of state as a generalized equation of state, that is $Z=Z\ (T_r,\ P_r)$.

With the above sign convention Eqn.4.1 can be rewritten as

$$\oint (dQ - dW) = 0 \tag{4.2}$$

It may be noted that work done by the paddle wheel on the system and the energy transfer as heat from the system to the water bath in Joule's experiment are irreversible processes. Hence Eqn.4.2 is applicable to reversible as well as irreversible processes. Now the first law of thermodynamics can be stated as follows. Whenever a system undergoes a cyclic process, the work done on the system is equal to the energy transferred as heat from the system to the surroundings.

4.2 Consequences of the first law of thermodynamics

The first law of thermodynamics leads to the following interesting consequences. Some of these consequences are used as alternative statements of the first law of thermodynamics.

1. Heat interaction depends on the path followed by a system and it is a path function.
2. There exists a point function, called energy E, such that the change in it is given by

   $$dE = dQ - dW \tag{4.3}$$

   Quite often this consequence is stated as the first law of thermodynamics. It was observed that the energy possessed by a body is given by Eqn.2.8. Hence, Eqn.4.3 can be rewritten as

   $$dE = d(\mathrm{PE}) + d(\mathrm{KE}) + dU = dQ - dW \tag{4.4}$$

   In many processes the PE and KE of the system do not change. Then Eqn.4.4 reduces to

   $$dU = dQ - dW \tag{4.5}$$

   Thus the first law of thermodynamics states that the net change in the energy of a system is equal to the net energy transfer across the boundary of the system.
3. If the system is isolated from the surroundings, it cannot exchange energy as heat as well as work. That is, for an isolated system $dQ = 0$ and $dW = 0$. Hence, Eqns.4.4 and 4.5 reduce to

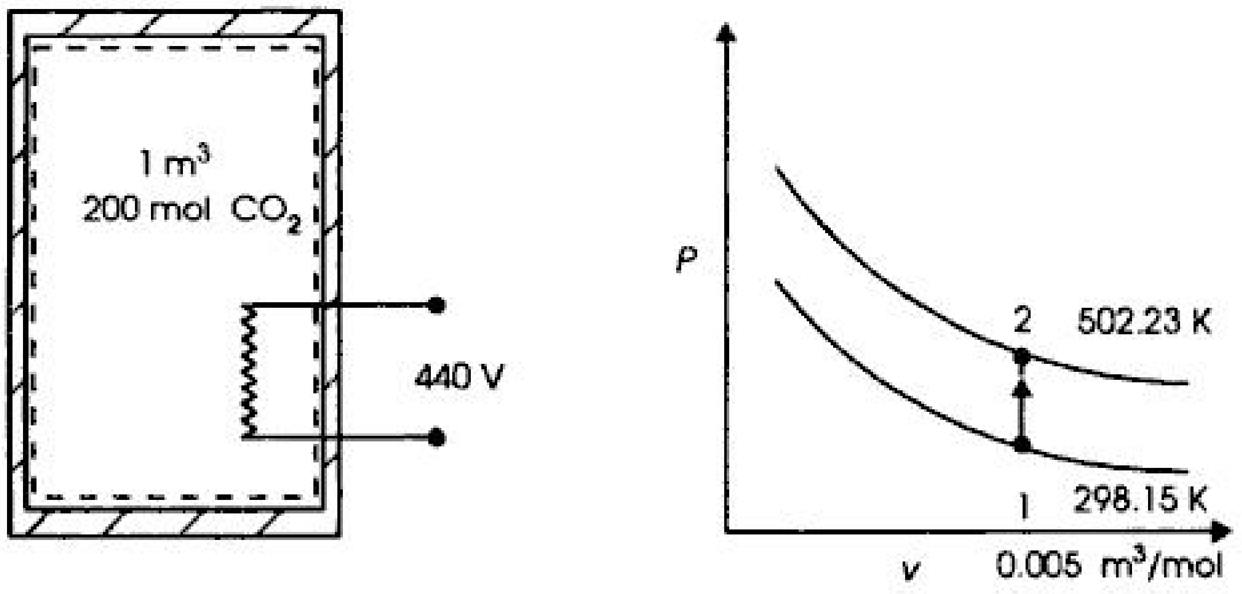
   $$dE = 0 \quad \text{or} \quad E_2 = E_1 \tag{4.6}$$

   $$dU = 0 \quad \text{or} \quad U_2 = U_1 \tag{4.7}$$

   where the subscripts 1 and 2 denote the initial and final conditions of the system, respectively. In other words, the energy of an isolated system is conserved which is known as the *Principle of conservation of energy*. The principle of conservation of energy is another consequence of the first law of thermodynamics. A system undergoing a cyclic change can be represented by Eqn.4.2, or

   $$\oint dQ = \oint dW \tag{4.8}$$

That is, during a cyclic process the net work done by a system is equal to the net energy transferred as heat to the system. In a cyclic process if there is no net energy transfer as heat to



(a) (b)

Fig.4.3 *Sketch for Example 4.3.*

Molar volume of CO_2 in the tank = 1/200 = 0.005 m^3/mol; energy transfer as heat $Q = 0$; work (Pdv) done by system, $W = 0$ (since $dv = 0$) and work (electrical) done on system $= -W_e = Eit$ $= 440 \times 5 \times 10 \times 60 = 1.32$ MJ. The first law of thermodynamics gives

$$U_2 - U_1 = Q - W = Q - (W_{Pdv} + W_e) = 0 - (0 - 1.32) = 1.32 \text{ MJ}$$

For the van der Waals gas

$$du = C_v\, dT + \frac{a}{v^2} dv$$

or $\quad U_2 - U_1 = NC_v\,(T_2 - T_1) \quad$ (since $\int (a/v^2)dv = 0$ at constant volume) (A)

Substituting the values of $U_2 - U_1$, N, C_v and T_1 in Eqn.(A), we get

$$1.32 \times 10^6 = 200 \times 32.34\,(T_2 - 298.15) \quad \text{or} \quad T_2 = 502.23 \text{ K}$$

For a constant volume process $v_2 = v_1 = 0.005$ m^3/mol. Therefore

$$\begin{aligned} P &= \frac{RT}{v-b} - \frac{a}{v^2} \\ &= \frac{8.314 \times 502.23}{(0.005 - 0.043 \times 10^{-3})} - \frac{363.077 \times 10^{-3}}{(0.005)^2} = 827.829 \text{ kPa} \end{aligned}$$

Hence

final pressure = 827.829 kPa; final temperature = 502.23 K

Example 4.4 A rigid tank of volume 0.1 m^3 is filled with saturated steam at 200°C. Due to poor insulation of the tank, the temperature of steam inside the tank reduces to 150°C after some

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For a constant pressure process involving shaft work or electrical work [see Figs.4.5(b) and (c)] there are two work interactions, namely, the Pdv work and shaft work or electrical work. Let us represent the shaft work and electrical work as W_S. Then

$$W = \int Pd V + W_S \tag{4.17}$$

Then the first law of thermodynamics gives

$$dU = dQ - dW = dQ - (Pd V + dW_S) \tag{4.18}$$

If the system is enclosed by an adiabatic wall, $dQ = 0$. Then Eqn.4.18 can be rewritten as

$$dU + Pd V = dU + d(PV) = -dW_S \quad \text{or} \quad dH = -dW_S \tag{4.19}$$

Therefore, when the system is enclosed by an adiabatic wall, the shaft work (or electrical work) done on the system while the pressure is held constant is equal to the increase in the enthalpy of the system.

If a system undergoes a constant pressure process (except when the phase change occurs), there will be a change in the system temperature. We are familiar with the definition of specific heat capacity at constant pressure or isobaric specific heat capacity, as the amount of energy to be transferred as heat to a unit mass to raise its temperature by one degree. That is

$$C_p = \left(\frac{\partial q}{\partial T}\right)_P \tag{4.20}$$

This definition is adopted since the isobaric specific heat capacity is usually determined by measuring the heat interaction and the rise in temperature of the substance. Now, we have noticed that for an isobaric process, the heat interaction is equal to the change in the enthalpy of the system. Hence, we can redefine the isobaric specific heat capacity in terms of the property change of the system as

$$C_p = \left(\frac{\partial h}{\partial T}\right)_P \tag{4.21}$$

where h denotes the specific enthalpy. Similarly we can define the isobaric molar heat capacity C_p as

$$C_p = \left(\frac{\partial h}{\partial T}\right)_P$$

where h now represents the molar enthalpy. At constant pressure, the enthalpy change of a substance is given by

$$\Delta h = h_2 - h_1 = \int_1^2 C_p \, dT \tag{4.22}$$

If C_p is a constant, Eqn.4.22 gives

$$\Delta h = C_p \, (T_2 - T_1) \tag{4.23}$$

From superheated steam tables by interpolation, we obtain at $P = 0.476$ MPa

$$T = 200°\text{C};\quad v = 0.4512\ \text{m}^3/\text{kg};\quad h = 2856.37\ \text{kJ/kg}$$

$$T = 300°\text{C};\quad v = 0.5544\ \text{m}^3/\text{kg};\quad h = 3065.38\ \text{kJ/kg}$$

Again by interpolation, we obtain at $P = 0.476$ MPa; $h = 2982.75$ kJ/kg

$$T_2 = 260.47°\text{C};\quad v_2 = 0.5136\ \text{m}^3/\text{kg}$$

Work done by steam, $W = P(V_2 - V_1) = 476 \times 10^3(0.5136 - 0.314\ 14) = 94.94$ kJ

Final temperature of steam in the cylinder = 260.47°C

Example 4.7 It is desired to raise the temperature of 1 kmol CO_2 at constant pressure from 298 K to 600 K. Determine the amount of energy to be transferred as heat.

Solution For CO_2, $C_p = 45.369 + 8.688 \times 10^{-2}T - 9.619 \times 10^5 T^{-2}$. For a constant pressure process, the first law of thermodynamics gives

$$Q = \Delta H = \int_{T_1}^{T_2} NC_p dT = 1 \times 10^3 \int_{298}^{600} (45.369 + 8.688 \times 10^{-3}T - 9.619 \times 10^5 T^{-2})dT$$

$$= 1 \times 10^3 \left[45.369(600 - 298) + \frac{8.688 \times 10^{-3}}{2}\{(600)^2 - (298)^2\} + 9.619 \times 10^5 \left(\frac{1}{600} - \frac{1}{298}\right)\right]$$

$$= 13.255 \text{ MJ}$$

Example 4.8 Determine the isobaric mean molar heat capacity of CO_2 in the temperature interval 298 K to 600 K.

Solution The isobaric heat capacity of CO_2 is given by

$$C_p = 45.369 + 8.688 \times 10^{-3}\, T - 9.619 \times 10^5\, T^{-2}$$

The isobaric mean heat capacity is given by

$$C_{p_m} = \frac{\int_{T_1}^{T_2} C_p\, dT}{T_2 - T_1} = \frac{\int (a + bT + eT^{-2})dT}{(T_2 - T_1)}$$

$$= \frac{\left[a(T_2 - T_1) + \frac{b}{2}(T_2 - T_1)(T_2 + T_1) - e\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]}{(T_2 - T_1)}$$

$$= \quad a + bT_m + e/T_1T_2 \quad (\text{where } T_m = (T_1 + T_2)/2)$$

$$\therefore \quad C_{p_m} = 45.369 + 8.688 \times 10^{-3}\frac{(298 + 600)}{2} - \frac{9.619 \times 10^5}{298 \times 600} = 43.89 \text{ J/mol K}$$

Example 4.9 Rework Example 4.7 using the isobaric mean molar heat capacity determined in Example 4.8.

Solution We know

$$Q = \Delta H = NC_{p_m}(T_2 - T_1) = 1 \times 10^3 \times 43.89 \times (600 - 298) = 13.255 \text{ MJ}$$

The above examples illustrate the method of estimating the heat interaction from a knowledge of the temperature dependence of isobaric heat capacity or the isobaric mean heat capacity of substances. These calculations are straightforward. Sometimes an engineer is called upon to estimate the temperature of a substance when a given energy is added as heat. The determination of the final temperature involves trial and error or iterative calculations. The method of calculation is illustrated through the following example.

Example 4.10 Determine the final temperature if 1 MJ energy is added as heat at constant pressure to 100 mol of CO_2 at 298 K.

Solution For a constant pressure process: $Q = \Delta H = N\Delta h$. Therefore, $N\Delta h = 100\Delta h = 1 \times 10^6$.

or $\quad \Delta h = 1 \times 10^4$ J; $\quad \Delta h = C_{p_m}(T_2 - T_1)$

or $\quad T_2 = T_1 + \Delta h / C_{p_m}$ (A)

For CO_2: $C_{p_m} = a + bT_m + e/T_1 T_2$ (B)

Guess a value for T_2 and calculate C_{p_m} from Eqn.(B). Then calculate the revised value of T_2 from Eqn.(A) using this value of C_{p_m}. Then substitute the revised value of T_2 in Eqn.(B) to get C_{p_m} and continue the iterative calculations till the calculated T_2 in successive iterations agree with each other.

Guess T_2 = 520 K. Then from Eqn.(B), we get

$$C_{p_m} = 45.369 + 8.688 \times 10^{-3}\left(\frac{298 + 520}{2}\right) - \frac{9.619 \times 10^5}{298 \times 520} = 42.715 \text{ J/mol K}$$

Substituting this value of C_{p_m} in Eqn.(A), we get

$$T_2 = 298 + \frac{1 \times 10^4}{42.715} = 532.1 \text{ K}$$

After three iterations T_2 converges at 531.1 K. Therefore, final temperature = 531.1 K.

4.3.3 Adiabatic process

A process undergone by a system which is enclosed by an insulated boundary is called an *adiabatic* process. Suppose an insulated piston–cylinder assembly contains a gas at high pressure. If the opposing force is gradually reduced allowing the gas to expand in such a way that the forces across the piston are always balanced, then the the system follows a reversible and adiabatic process. A reversible adiabatic process is also known as an *isentropic* process.

4.3.3.1 *Examples of irreversible adiabatic processes*

There are some adiabatic processes which are irreversible. Recall Joule's classic paddle wheel experiment in which a liquid held in an insulated container is vigorously stirred by a paddle wheel. The process undergone by the liquid is irreversible and adiabatic. In the household geyser, electrical work is done on the water in the geyser which is well insulated. This process is also irreversible and adiabatic. Suppose a rigid and insulated vessel is divided into two compartments by a partition and one compartment is evacuated while the other contains a gas. If the partition is punctured, the gas occupies the entire vessel. The process followed by the gas is irreversible and adiabatic. That is free expansion of a gas is an irreversible, adiabatic process. Consider again the rigid and insulated tank which is divided into two compartments by a partition. Suppose one compartment contains a fluid at some temperature and pressure while the other compartment contains a different fluid at a different temperature and pressure. If the partition is ruptured, the fluids mix with each other. The process followed by the contents of the tank is irreversible and adiabatic.

4.3.4 Constant internal energy process

A process in which the internal energy remains constant, or $\Delta U = 0$, is called a constant internal energy process. The first law of thermodynamics gives

$$\Delta U = Q - W$$

Hence $\Delta U = 0$ when $Q = 0$ and $W = 0$ or when $Q = W$.

Consider the free expansion of the gas described in Section 4.3.3.1. Considering the tank and its contents as the system, the heat and work interactions are zero since the tank is insulated and rigid. Hence, the internal energy of the system remains constant. The process is clearly irreversible. Therefore, the system follows an irreversible constant internal energy process. The adiabatic mixing of fluids in a rigid and insulated container is another example of an irreversible constant internal energy process. In this case also the work and heat interactions are zero and the process is irreversible.

Suppose an ideal gas enclosed in a frictionless piston–cylinder assembly undergoes a reversible isothermal process. Since $u = u\,(T)$ only for an ideal gas, the internal energy remains constant and hence it is also a reversible constant internal energy process. Application of the first law of thermodynamics to a constant internal energy process gives $dQ = dW$.

4.3.5 Constant temperature (isothermal) process

A process in which the temperature of a system remains constant is called an isothermal or constant temperature process. For an ideal gas, the work done per mole (or unit mass) in an isothermal process is given by

$$W = \int_1^2 P dv = \int_1^2 RT\frac{dv}{v} = RT\ln\frac{v_2}{v_1} \tag{4.36}$$

Since $u = u\,(T)$ only for an ideal gas, $du = 0$. Application of the first law of thermodynamics gives

$$\Delta u = q - W \quad \text{or} \quad q = W = RT\ln\frac{v_2}{v_1}$$

Note that the lower case letters denote the molar (or specific) properties, whereas capital letters denote the total properties.

4.3.6 Polytropic process

The work done by an ideal gas during a reversible adiabatic expansion is given by

$$W = \frac{P_1 v_1 - P_2 v_2}{\gamma - 1} \tag{4.31}$$

The simplicity of Eqn.4.31 for estimating the work interaction is quite appealing for engineering purposes. For many processes the path can be conveniently represented as

$$Pv^n = \text{constant} \tag{4.37}$$

where n is the *index of expansion*. The process which follows the path represented by Eqn.4.37 is often called the *polytropic* process. The work done during a polytropic process is given by

$$W = \frac{P_1 v_1 - P_2 v_2}{n - 1} \tag{4.38}$$

Application of the first law of thermodynamics to a polytropic process gives

$$u_2 - u_1 = q - W$$

or

$$u_2 - u_1 = q - \frac{P_1 v_1 - P_2 v_2}{n - 1} \tag{4.39}$$

In a polytropic process if n is equal to zero, the process reduces to a constant pressure process, and when n is equal to 1 the process reduces to an isothermal process. Similarly when n is equal to γ the process reduces to an isentropic process. On the other hand, if n is equal to ∞ the process reduces to an isometric process. The polytropic processes are shown in Fig.4.9 on the P–v diagram in which the upper left hand quadrant and the lower right hand quadrant represent the compression and expansion processes, respectively.

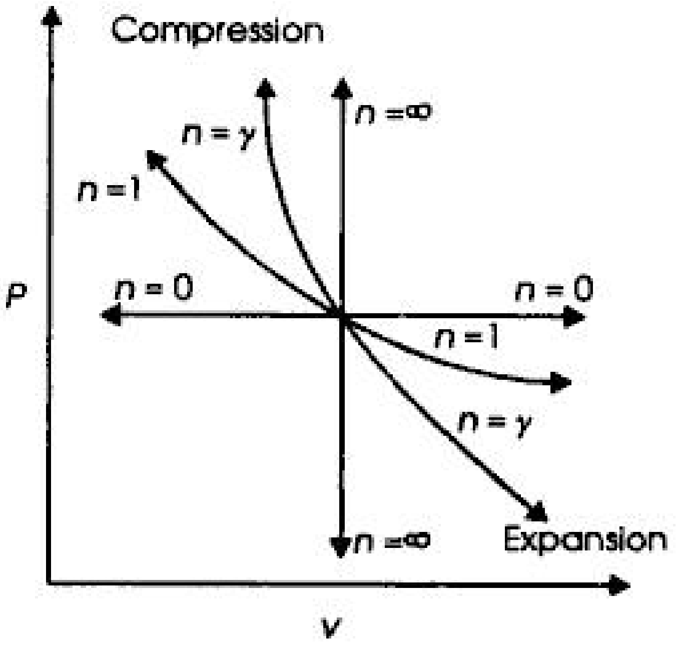

Fig.4.9 *P–v diagram of some polytropic processes.*

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or $N_f u_f - N_0 u_0 = (N_f - N_0)(u + Pv) + Q$

or $N_f u_f - N_0 u_0 = (N_f - N_0)h + Q$ (4.44)

where $h = u + Pv$ = enthalpy of gas in the pipeline.

If the tank is initially empty and insulated, $N_0 = 0$ and $Q = 0$. Then Eqn.4.44 reduces to

$$u_f = h \tag{4.45}$$

Suppose the gas under consideration is an ideal gas. Then $u = C_v T$ and $h = C_p T$. Then, Eqn.4.45 can be rewritten as

$$C_v T_f = C_p T \text{ or } T_f = \gamma T \tag{4.46}$$

Example 4.13 A rigid and insulated tank of volume 1 m^3 contains an ideal gas (γ = 1.4) at 0.1 MPa and 300 K. The tank is connected to a pipeline carrying the same gas at 3 MPa and 500 K. The valve at the top of the tank is opened allowing the gas to enter the tank till the pressure reaches 3 MPa and then closed. Determine the final temperature of the gas inside the tank and the amount of gas that entered the tank.

Solution The first law of thermodynamics for the transient flow [see Eqn.4.44] under consideration gives

$$N_f u_f - N_0 u_0 = (N_f - N_0)h \tag{A}$$

For an ideal gas: $u = C_v T$; $h = C_p T$ and $N = PV/RT$. Therefore, Eqn.(A) can be rewritten as

$$\left(\frac{P_f V}{RT_f}\right)\frac{RT_f}{\gamma - 1} - \left(\frac{P_0 V}{RT_0}\right)\frac{RT_0}{\gamma - 1} = \left(\frac{P_f V}{RT_f} - \frac{P_0 V}{RT_0}\right)\frac{\gamma RT}{\gamma - 1}$$

or $$P_f - P_0 = \gamma T\left(\frac{P_f}{T_f} - \frac{P_0}{T_0}\right) \tag{B}$$

where P_0, P_f = initial and final pressure of the gas in the tank, respectively; T_0, T_f = initial and final temperature of the gas in the tank, respectively; V = volume of the tank; and T = temperature of the gas in the pipeline.

$$C_v = \frac{R}{\gamma - 1}; \quad C_p = \frac{\gamma R}{\gamma - 1}$$

Substituting the values of P_0, P_f, T_0 and T in Eqn.(B), we get

$$3 \times 10^6 - 0.1 \times 10^6 = 1.4 \times 500\left(\frac{3 \times 10^6}{T_f} - \frac{0.1 \times 10^6}{300}\right)$$

or $T_f = 670.2$ K

Amount of gas that entered the tank = $N_f - N_0$

$$= \frac{P_f V}{RT_f} - \frac{P_0 V}{RT_0} = \frac{V}{R}\left(\frac{P_f}{T_f} - \frac{P_0}{T_0}\right) = \frac{1}{8.314}\left(\frac{3 \times 10^6}{670.2} - \frac{0.1 \times 10^6}{300}\right) = 498.31 \text{ mol}$$

Example 4.14 A rigid and insulated tank of 3 m^3 volume contains saturated steam at 100°C. This tank is connected through a valve to a line carrying superheated steam at 3 MPa and 300°C and the steam is allowed to flow into the tank. When the steam pressure inside the tank rises to 3 MPa the tank is disconnected after closing the valve. Determine the final state of steam in the tank and the amount of steam that entered the tank.

Solution Saturated steam at 100°C:

$$P = 101.33 \text{ kPa}; \quad v_g = 1.673 \text{ m}^3/\text{kg}; \quad h_g = 2676.0 \text{ kJ/kg}$$

Superheated steam at 3 MPa and 300°C: $h = 2995.1$ kJ/kg. The first law of thermodynamics for the adiabatic charging of a tank is given by

$$N_f u_f - N_0 u_0 = (N_f - N_0)h \text{ or } \quad m_f u_f - m_0 u_0 = (m_f - m_0)h \tag{A}$$

where m = mass of steam; $u_0 = u_g = 2676.0 \times 10^3 - 101.33 \times 10^3 \times 1.673 = 2506.47$ kJ/kg; $m_0 = V/v_g = 3/1.673 = 1.793$ kg; $h = 2995.1$ kJ/kg.

Substituting these values in Eqn.(A), we get

$$m_f u_f - 1.793 \times 2506.47 = (m_f - 1.793)2995.1$$

$$\text{or} \quad m_f(2995.1 - u_f) = 876.11 \tag{B}$$

Mass of steam inside the tank at the end of the charging operation is given by

$$m_f = \frac{V}{v_f} = \frac{3}{v_f} \tag{C}$$

where v_f = final specific volume of steam in the tank. Equations B and C can be solved along with a knowledge of the properties of steam (from steam tables) by trial and error.

Final pressure = 3 MPa and assume $T_f = 418$°C. From superheated steam tables at P = 3 MPa and T = 418°C

$$v = 0.102\,329 \text{ m}^3/\text{kg}; \quad u = 2965.78 \text{ kJ/kg} \qquad \text{(obtained by interpolation)}$$

From Eqn.(C), we get

$$m_f = \frac{V}{v_f} = \frac{3}{0.102\,329} = 29.317 \text{ kg}$$

Substituting this value of m_f in the LHS of Eqn.(B) gives

$$m_f(2995.1 - u_f) = 29.317(2995.1 - 2965.78) = 859.57$$

This value is approximately equal to 876.11 which is the RHS of Eqn.(B). Say Eqn.(B) is satisfied. Therefore,

Final state of steam (superheated): $P = 3.0$ MPa; $T = 418$°C.

Mass of steam that entered the tank = $m_f - m_0 = 29.317 - 1.793 = 27.524$ kg

4.5 Control-volume analysis

Chemical engineers deal with a variety of devices such as reactors, absorption towers, distillation columns, extraction towers, evaporators, heat exchangers, turbines, compressors, pumps, etc. through which material continuously flows in and out. In the thermodynamic analysis of such equipment it is difficult to focus attention on a specified quantity of matter as it flows to relate the energy changes with heat and work interactions. To analyze such flow processes a control-volume analysis is usually adopted.

Consider the operation of a steam turbine. The turbine delivers some shaft work and energy transfer as heat may occur through the turbine casing. To determine the shaft work or power output of the turbine, we focus our attention on the turbine or the piece of equipment under investigation and enclose it in an imaginary boundary. This imaginary boundary is called *control surface* and the region enclosed by the boundary is called *control-volume*. The control-volume may move in space and may change its configuration also. Matter continuously flows in and out of the control volume and energy transfer as heat and work occurs across the control surface.

We are familiar with the application of the first law of thermodynamics to a system. To analyze the flow process, we choose the system such that it always contains a definite quantity of matter. For simplicity we use the superscript $(\cdot)$ to denote the time derivatives (as $dN/dt = \dot{N}$) in the following.

Let $\dot{N}_i$, $\dot{N}_e$ = molar flow rate through the inlet and outlet of the device, respectively;

v_i, v_e = molar volume at the inlet and outlet of the device, respectively;

Z_i, Z_e = elevation of the inlet and outlet of the device, respectively;

P_i, P_e = pressure at the inlet and outlet of the device, respectively;

e_i, e_e = molar energy at the inlet and outlet of the device, respectively;

$\mathbf{V}_i$, $\mathbf{V}_e$ = velocity with which matter flows at the inlet and outlet of the device, respectively;

$N(t)$ = mole number of matter in the control-volume at time t;

$N(t+dt)$ = mole number of matter in the control-volume at time $(t+dt)$;

$e(t) = (u + (\mathbf{V}^2/2) + gZ)$ = molar energy of matter in control-volume at time t;

$e(t+dt)$ = molar energy of matter in control-volume at time $(t+dt)$;

$\dot{Q}$ = rate of energy transfer as heat into the control-volume from the surroundings; and

$\dot{W}_S$ = power (rate of shaft work) delivered by the control-volume.

A schematic diagram of flow of matter through a device (control-volume) is shown in Fig.4.12. We choose the system at time t such that it contains the matter inside the control-volume and the matter in region A which will enter the control-volume in time dt.

Amount of matter in the system at time $t = N(t) + \dot{N}_i dt$. At time $(t + dt)$, the matter in the control-volume and the matter in the region B, which leaves the control-volume in time dt, constitutes the system.

Amount of matter in the system at time $(t + dt) = N(t + dt) + \dot{N}_e dt$. Since the system should contain the same quantity of matter at all times it is necessary that

$$N(t) + \dot{N}_i dt = N(t + dt) + \dot{N}_e dt \tag{4.52}$$

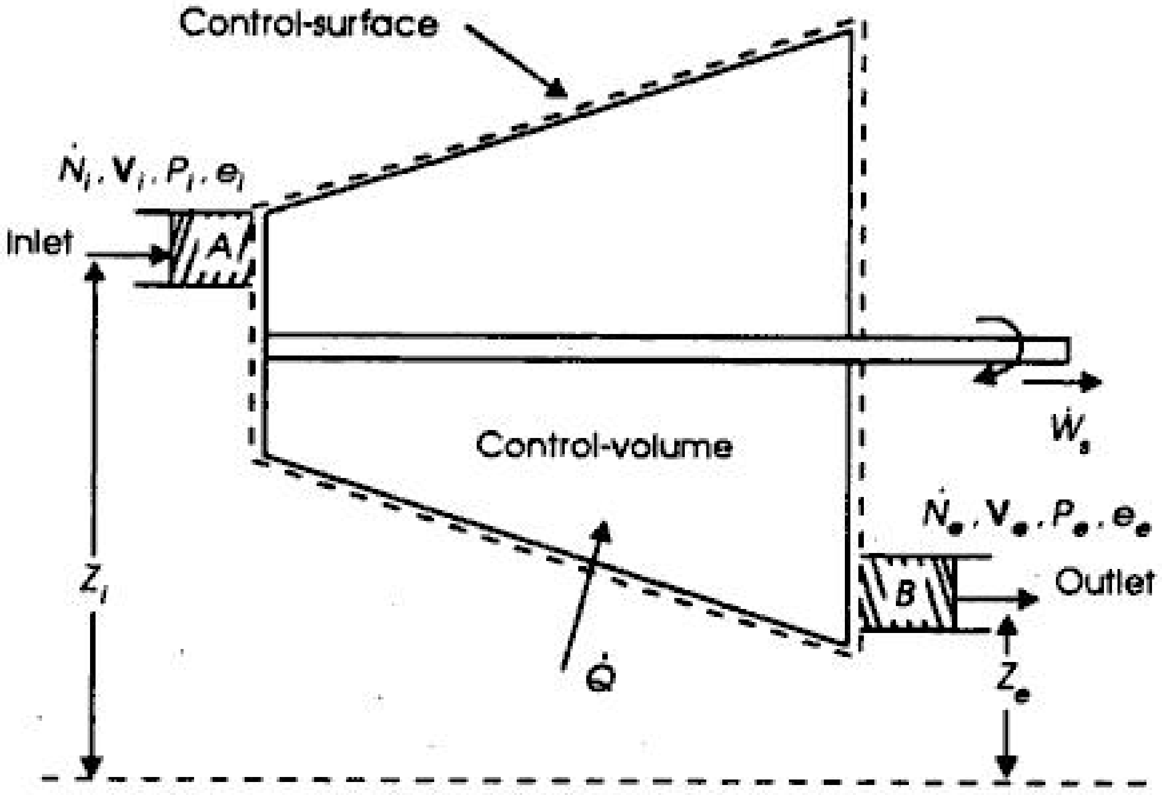

Fig.4.12 *Schematic representation of a control-volume.*

In time dt, the matter in the region A enters the device (control-volume) and some matter comes out of the device and occupies the region B. A continuous flow can be visualized as a succession of such processes.

Energy of system at time t = $E_1 = N(t)e(t) + \dot N_i e_i dt = E(t) + \dot N_i e_i dt$ (4.53)

Energy of system at time $(t+dt) = E_2 = N(t+dt)e(t+dt) + \dot N_e e_e dt = E(t+dt) + \dot N_e e_e dt$ (4.54)

where $E(t)$ = energy of control-volume at time t and $E(t+dt)$ = energy of control-volume at time $(t+dt)$.

$$\left.\begin{array}{l}\text{Energy transferred as heat into the system}\\ \text{during time } dt\end{array}\right\} = Q = \dot Q dt \tag{4.55}$$

$$\left.\begin{array}{l}\text{Work done by the control-volume (device)}\\ \text{during time } dt\end{array}\right\} = W_1 = \dot W_S dt$$

The matter in the inlet pipe at pressure P_i pushes the matter $(\dot N_i dt)$ into the control volume and in this process the change in the volume of the system is $(\dot N_i dt v_i)$. Hence, work is done by the surroundings on the system in pushing the matter. Then

$$\left.\begin{array}{l}\text{Work done (by system) during time } dt\\ \text{for the material to enter control-volume}\end{array}\right\} = -P_i v_i \dot N_i dt$$

Similarly, when the material flows out of the control-volume, work is done by the system on the surroundings. Then

$$\left.\begin{array}{l}\text{Work done (by system) during time } dt \text{ for}\\ \text{the material to flow out of control-volume}\end{array}\right\} = P_e v_e \dot N_e dt$$

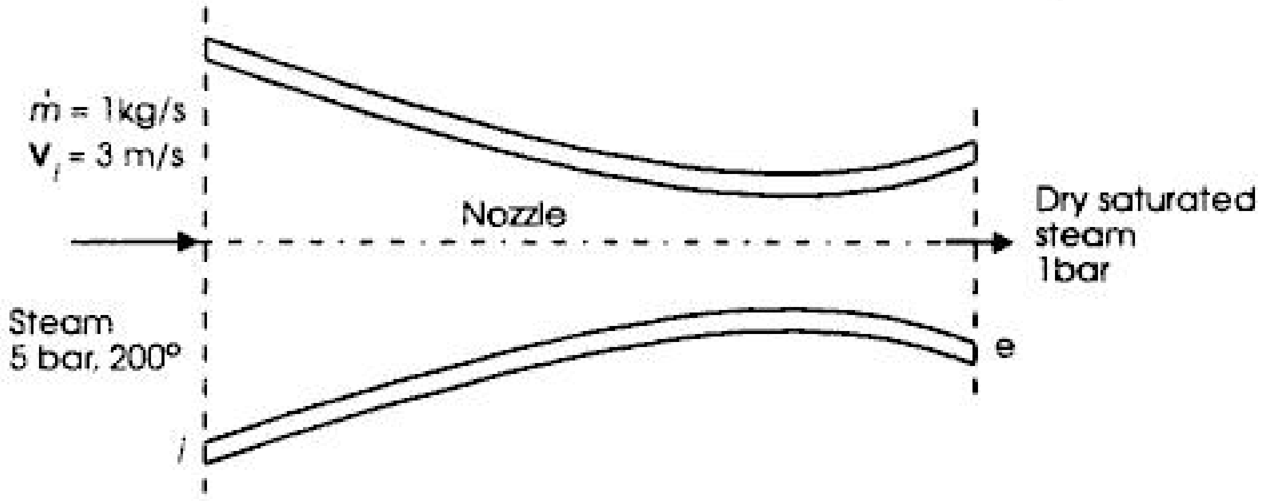

Fig.4.13 *Schematic diagram of a nozzle.*

Assume that the nozzle is horizontal. That is $Z_i = Z_e$. The nozzle is adiabatic. Hence $\dot{Q} = 0$. There is no shaft work delivered in a nozzle. Therefore, $\dot{W}_S = 0$. Flow rate, $\dot{m} = 1$ kg/s. The first law of thermodynamics for a steady-flow process gives

$$\left(h_e + \frac{\mathbf{V}_e^2}{2} + gZ_e\right) - \left(h_i + \frac{\mathbf{V}_i^2}{2} + gZ_i\right) = \frac{\dot{Q} - \dot{W}_S}{\dot{m}}$$

or $$(h_e - h_i) + \frac{\mathbf{V}_e^2 - \mathbf{V}_i^2}{2} + g(Z_e - Z_i) = \frac{\dot{Q} - \dot{W}_S}{\dot{m}} \tag{A}$$

Saturated steam at 5 bar: h_i = 2747.5 kJ/kg. Saturated steam at 2 bar: h_e = 2706.3 kJ/kg; v_e = 0.8854 m^3/kg.

Substituting the values in Eqn.(A), we get

$$(2706.3 \times 10^3 - 2747.5 \times 10^3) + \frac{\mathbf{V}_e^2 - 3^2}{2} + g(0) = 0$$

or $$\frac{\mathbf{V}_e^2 - 9}{2} = 41.2 \times 10^3$$

or $$\mathbf{V}_e = 287.07 \text{ m/s}$$

Mass flow rate = $\dot{m} = A\mathbf{V}/v$ or $A = \dot{m}v/\mathbf{V} = (1 \times 0.8854)/287.07 = 3.084 \times 10^{-3}$ m^2; where A = cross-sectional area of the nozzle at the exit.

It can be shown that if an ideal gas at P_i and T_i enters a reversible adiabatic nozzle with negligible velocity, the exit velocity is given by

$$\mathbf{V}_e = \sqrt{2C_PT_i\left[1 - \left(\frac{P_e}{P_i}\right)^{(\gamma-1)/\gamma}\right]} \tag{4.62}$$

where P_e is the exit pressure.

4.6 Throttling process

In 1853 Joule and Thomson (Lord Kelvin) conducted a porous plug experiment to measure the change in temperature of a gas when it flows steadily through a porous plug. The porous plug apparatus consists of a long horizontal and insulated pipe at the centre of which a porous plug is inserted. On either side of the porous plug, provision is made to measure the temperature and pressure of the flowing fluid as shown in Fig.4.14.

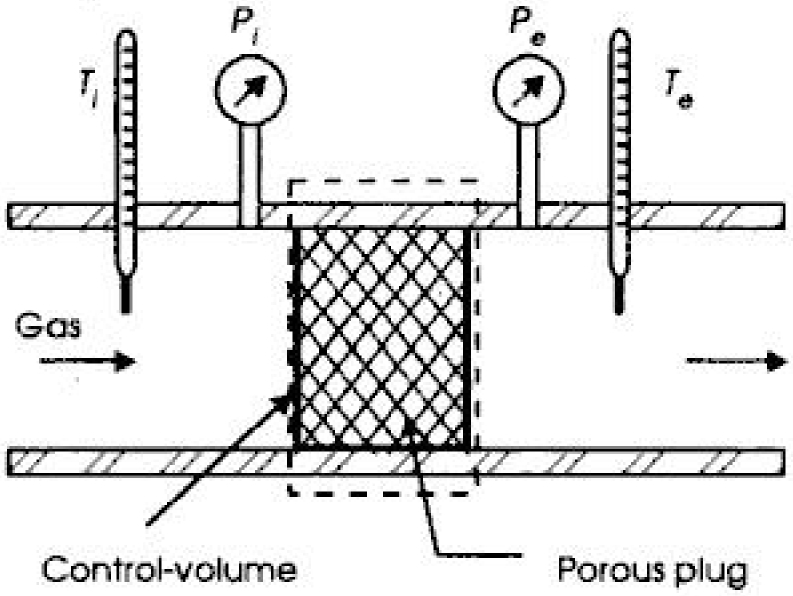

Fig.4.14 *Schematic diagram of porous plug apparatus.*

The pipe is insulated: $\dot{Q} = 0$. There is no shaft work involved: $\dot{W}_S = 0$. Horizontal apparatus: $Z_i = Z_e$. Ignore the change in the velocity due to flow through porous plug: $\mathbf{V}_i - \mathbf{V}_e = 0$.
Substituting these values in Eqn.4.61 we get

$$h_e = h_i$$

That is, whenever a fluid flows steadily from high pressure to low pressure through a porous plug or partially opened valve, inserted in a long horizontal and insulated pipe, the enthalpy of the fluid remains constant. Such a flow is usually called throttling. Therefore, a throttling process is an *isenthalpic process.*

Suppose a series of experiments are conducted with the same inlet pressure P_i, and temperature T_i of the gas, but with different exit pressures P_e, we get different exit temperatures T_e. A plot of T_e versus P_e gives an isenthalpic curve as shown in Fig.4.15. By repeating the experiment with different inlet pressures P_i and temperatures T_i, we can get a series of isenthalpic curves. The slope of the isenthalpic curve is defined as the Joule–Thomson or Joule–Kelvin coefficient μ_{JT}. That is

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h \tag{4.63}$$

The point at which μ_{JT} equals 0, is called the *inversion point*. The locus of the inversion points is called the *inversion curve*. To the left of the inversion curve on P versus T diagram $\mu_{JT} > 0$ and in this region throttling results in cooling of a real gas. To the right of the inversion curve, $\mu_{JT} < 0$ and throttling of a real gas from a high pressure to a low pressure results in heating the gas.

A simple device which uses the principle of throttling to measure the quality of wet steam is called a throttling calorimeter. A schematic diagram of a throttling calorimeter is shown in Fig.4.16.

4.7.2 Discharging of a tank

Let us now consider the problem of discharging a tank and choose the tank as the control volume. During the discharging of a tank, no shaft work is delivered and no material enters the tank. Therefore, $\dot{W}_S = 0$ and $\dot{N}_i = 0$. Ignoring the KE and PE changes, the first law of thermodynamics [Eqn.4.58] reduces to

$$\dot{N}_e h_e = \dot{Q} - \frac{dE}{dt}$$

or $$\int_0^t \dot{N}_e h_e dt = \int_0^t \dot{Q} dt - \int_0^t \frac{dE}{dt} dt \tag{4.66}$$

When the fluid rushes out of the tank, the conditions of the fluid leaving the tank continuously change with time. That is h_e is time dependent. However, at any instant of time, the fluid leaving the tank and the fluid remaining in the tank are in the same state. If the enthalpy of the fluid in the tank at the end of the discharging process is not very much different from that at the beginning of the discharging process, we can assume that the fluid leaves with a constant enthalpy h, which is the mean value of h_0 and h_f. The values h_0 and h_f represent the enthalpy of fluid in the tank at the beginning and at the end of the discharging process, respectively. With this assumption Eqn.4.66 can be integrated to obtain

$$N_f u_f - N_0 u_0 + (N_0 - N_f)h = Q \tag{4.67}$$

Equation 4.67 is identical to Eqn.4.50 which is derived by adopting the control-mass analysis. The first law of thermodynamics given by the relation

$$dE = dQ - dW \tag{4.9}$$

can be restated as

Accumulation of energy = (energy input) − (energy output)

The first law of thermodynamics for a flow process given by Eqn.4.58 can be rearranged as

$$\frac{dE}{dt} = \left\{\dot{N}_i \left(h_i + \frac{V_i^2}{2} + gZ_i\right) + \dot{Q}\right\} - \left\{\dot{N}_e \left(h_e + \frac{V_e^2}{2} + gZ_e\right) + \dot{W}_S\right\} \tag{4.68}$$

or $$\begin{pmatrix}\text{Rate of accumulation} \\ \text{of energy}\end{pmatrix} = \begin{pmatrix}\text{Rate of inflow} \\ \text{of energy}\end{pmatrix} - \begin{pmatrix}\text{Rate of outflow} \\ \text{of energy}\end{pmatrix}$$

Thus the first law of thermodynamics provides a method of book-keeping or accounting for energy. In other words, the first law of thermodynamics is a general law of conservation of energy.

Example 4.19 It is a fact that during discharging of a gas from a tank the conditions (T and P) of the gas leaving the tank as well as the conditions of the gas remaining in the tank change with time. Apply the control-volume analysis and show that for an ideal gas the temperature of the gas remaining in the tank is identical with that estimated from the adiabatic expansion relation.

Solution The first law of thermodynamics for an unsteady flow process is given by

$$\dot{N}_e\left(h_e+\frac{\mathbf{V}_e^2}{2}+gZ_e\right)-\dot{N}_i\left(h_i+\frac{\mathbf{V}_i^2}{2}+gZ_i\right)=\dot{Q}-\dot{W}_S-\frac{dE}{dt} \tag{A}$$

When a gas is discharged from an insulated tank $\dot{Q}=0$ and $\dot{W}_S=0$. Ignore the changes in kinetic energy and potential energy terms as they are insignificant. The rate of inflow of gas $\dot{N}_i$ is equal to zero, since no gas is entering the tank. Then Eqn.(A) reduces to

$$\dot{N}_e h_e=\frac{-dE}{dt}$$

or $$\dot{N}_e C_p T=-\frac{d}{dt}(NC_vT) \tag{B}$$

where, T is the temperature of the gas leaving the tank which is equal to that of the gas remaining in the tank at any instant of time. The mass balance for the control-volume [see Eqn.4.59] gives

$$\frac{dN}{dt}=\dot{N}_i-\dot{N}_e \quad \text{or} \quad \dot{N}_e=-\frac{dN}{dt} \tag{C}$$

Substituting Eqn.(C) in Eqn.(B), we get

$$\gamma T\frac{dN}{dt}=N\frac{dT}{dt}+T\frac{dN}{dt} \quad \text{or} \quad (\gamma-1)T\frac{dN}{dt}=N\frac{dT}{dt} \quad \text{or} \quad \frac{dN}{N}=\frac{1}{(\gamma-1)}\frac{dT}{T}$$

or $$\ln\frac{N_f}{N_0}=\left(\frac{1}{\gamma-1}\right)\ln\frac{T_f}{T_0} \tag{D}$$

$$\frac{N_f}{N_0}=\left(\frac{P_fV}{RT_f}\right)\left(\frac{RT_0}{P_0V}\right)=\left(\frac{P_f}{P_0}\right)\left(\frac{T_0}{T_f}\right) \quad \text{(for an ideal gas)} \tag{E}$$

where, N_0, N_f = initial and final mole number of gas in the tank, respectively; P_0, P_f = initial and final pressure of gas in the tank, respectively; and V = volume of tank.

Substituting Eqn.(E) in Eqn.(D), we get

$$\frac{T_f}{T_0}=\left(\frac{P_f}{P_0}\right)^{(\gamma-1)/\gamma} \tag{F}$$

Equation (F) is identical with the relation for a reversible adiabatic expansion of an ideal gas. Thus, when an ideal gas escapes from a tank, the temperature of the gas remaining in the tank can be estimated by using the reversible adiabatic expansion relation.

4.8 Chemically reacting systems

So far attention was focused on the first law analysis of physical processes. A chemical engineer deals not only with physical processes, but also with chemically reacting systems. A major task of a chemical engineer is to apply the principles of thermodynamics to analyze chemically reacting systems. In this section, the application of the first law of thermodynamics to chemically reactive systems is discussed.

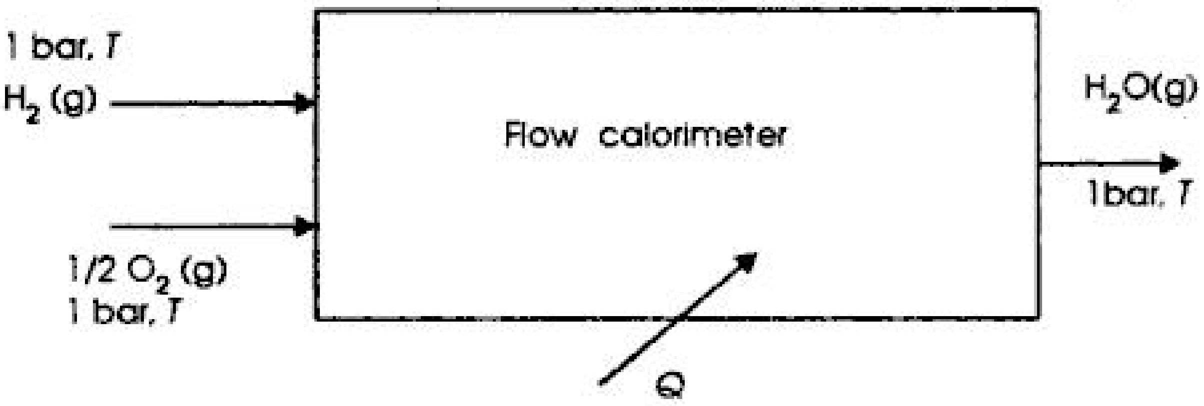

Fig.4.18 *Schematic diagram of a flow calorimeter.*

The chemical reactions can be carried out at different conditions of temperature and pressure and hence it is not possible to tabulate the enthalpy changes for chemical reactions at all possible conditions. Therefore, it is necessary to standardize the chemical reactions. For this purpose, the following standard states are selected. A standard state is a particular state of species at temperature T and at a specified pressure.

- The standard state for a gas is the ideal gas state of pure component at a pressure of 1 bar.
- The standard state for liquid is pure liquid at 1 bar.
- The standard state for solid is pure solid in the most stable form at 1 bar. For example, carbon is found in two different allotropic forms — graphite and diamond. Since graphite is more stable than diamond, graphite is taken as the standard state for carbon.

If a chemical reaction is carried out in which the reactants as well as the products are in their respective standard states and at the same temperature T, the enthalpy change associated with the reaction is called the *standard enthalpy change* or *standard heat of the reaction*. It is denoted by ΔH_T^0 , where the superscript zero denotes that all the reactants and products are in their standard states and the subscript T denotes the temperature at which the reaction is carried out. In the thermodynamic analysis of chemically reacting systems it is essential to specify the state of the species as gas (g), liquid (l) or solid (s). Whenever the standard enthalpy change for a chemical reaction is reported, it is applicable to the stoichiometric coefficients specified in the reaction. If all the stoichiometric coefficients are multiplied by the same constant factor, then ΔH_T^0 also gets multiplied by the same constant.

Example 4.20 The standard enthalpy change for the reaction

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$

at 298.15 K is – 90.135 kJ. Calculate the standard enthalpy change for the following reactions at 298.15 K.

(a) $2CO(g) + 4H_2(g) \rightarrow 2CH_3OH(g)$ (b) $\frac{1}{2}\ CO(g) + H_2(g) \rightarrow \frac{1}{2}\ CH_3OH(g)$

Solution

(a) $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$: $\Delta H_{298}^0 = -\ 90.135$ kJ **(A)**

$$2CO(g) + 4H_2(g) \rightarrow 2CH_3OH(g) \quad \textbf{(B)}$$

The stoichiometric coefficients in Eqn.(A) are multiplied by a factor 2 in rewriting the Eqn.(B). Hence ΔH^0_{298} for reaction (b) is equal to twice that of Eqn.(A). Hence, ΔH^0_{298} for Eqn.(B) = $2 \times (-90.135) = -180.27$ kJ.

(b) ΔH^0_{298} for the reaction

$$\frac{1}{2}\,CO(g) + H_2(g) \rightarrow \frac{1}{2}\,CH_3OH(g)$$

is given by $(1/2) \times (-90.135) = -45.0675$ kJ.

4.8.3 Standard enthalpy of formation

Consider the following chemical reactions

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g) \tag{4.74}$$

$$C(s) + 2H_2(g) + \frac{1}{2}\,O_2(g) \rightarrow CH_3OH(g) \tag{4.75}$$

Equation 4.74 represents the reaction between a compound CO and H_2 whereas Eqns.4.75 represents the reaction between the elements C, H_2 and O_2 to produce methanol. A reaction in which only one mole of a single compound is formed from its constituent elements is called a *formation reaction*. Therefore, Eqn.4.75 represents a formation reaction for methanol. The enthalpy change associated with a formation reaction, when the reactants and products are in the standard states, is called *standard enthalpy (or heat) of formation*. In chemical thermodynamics, by convention the standard enthalpy of formation of an element has been assigned a zero value. For convenience of tabulating the data, the standard enthalpies of formation of compounds are reported at 298.15 K and they are represented as $\Delta H^0_{f\,298}$, where the subscript f denotes the formation reaction. The standard enthalpies of formation of some selected compounds at 298.15 K are presented in Appendix (Table A.4).

The standard enthalpy change of a chemical reaction is the change in the enthalpy for the conversion of reactants into products, and it does not depend on the path followed by the species, but depends only on the initial states of the reactant molecules and the final states of the product molecules. Therefore, to calculate the standard enthalpy change for a reaction, the actual chemical reaction can be replaced by a set of reactions such that the sum of the chosen reactions yields the desired reaction. The following example illustrates the method of combining the reactions.

Example 4.21 Find a set of formation reactions to calculate the standard enthalpy change for the reaction

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

Solution The chemical compounds involved in the given reaction are CO, H_2O and CO_2. The formation reactions for these compounds are given by

$$C(s) + \frac{1}{2}\,O_2(g) \rightarrow CO(g) \tag{A}$$

The standard enthalpy change for the reactions of Examples 4.22 and 4.23 are negative quantitites. Since $\Delta H = Q$, where Q represents the energy transferred as heat into the system, a negative ΔH indicates that energy is transferred from system to surroundings or energy is liberated during the chemical reaction. Since $\Delta H = H_P - H_R$, a negative ΔH implies that the energy of the products is less than the energy of reactants. Reactions with negative ΔH are called *exothermic reactions*. When the energy of the products is greater than that of the reactants, ΔH is positive and energy is absorbed as heat and such reactions are called *endothermic reactions*.

4.8.4 Standard enthalpy change of combustion

The formation reaction for $C_4H_{10}(g)$ is

$$4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g)$$

This reaction is not practically feasible and hence it is not possible to directly measure the standard enthalpy of formation of $C_4H_{10}(g)$. However, the combustion of $C_4H_{10}(g)$ can be carried out in a flow calorimeter to determine the heat interaction. A *combustion reaction* is defined as a reaction between an element or compound and oxygen to form specified products. In case of hydrocarbons containing carbon, hydrogen and oxygen only, the combustion products are CO_2 and H_2O (H_2O may be present either as gas or liquid). The standard enthalpy change associated with a combustion reaction is called *standard enthalpy change* or *standard heat of combustion*, which is usually represented by ΔH_c^0. The standard enthalpies of combustion of some selected compounds at 298.15 K are presented in Appendix (Table A.5).

Quite often the term heating value is used for the negative of the standard enthalpy change of combustion ($-\Delta H_c^0$), because it represents the amount of energy that can be transferred as heat from the reactor or burner to the surroundings. If H_2O in the combustion products is in the gaseous state, $-\Delta H_c^0$ has a lower value and it is usually called as net or lower heating value. If H_2O in the combustion products is in the liquid state $-\Delta H_c^0$ has a higher value and it is called gross or higher heating value. The standard enthalpy of formation of a compound like $C_4H_{10}(g)$ can be estimated from a knowledge of ΔH_c^0 of $C_4H_{10}(g)$ and the standard enthalpies of formation of $CO_2(g)$ and $H_2O(g)$ as illustrated by the following example.

Example 4.24 The gross heating value of *n*-butane gas at 298.15 K is 2880.44 kJ/mol. Calculate the standard enthalpy of formation of $C_4H_{10}(g)$ at 298.15 K.

Solution The combustion reaction is given by

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

$$\Delta H^0_{f\,298}\ CO_2(g) = -393.978 \text{ kJ}; \quad \Delta H^0_{f\,298}\ [H_2O(l)] = -285.958 \text{ kJ}$$

$$\Delta H^0_{c\,298} = \sum \nu_i \Delta H^0_{f\,298i} = 4\Delta H^0_{f\,298}\{CO_2(g)\} + 5\Delta H^0_{f\,298}\{H_2O(l)\} - \Delta H^0_{f\,298}\{C_4H_{10}(g)\}$$

or $$-2880.44 = 4(-393.978) + 5(-285.958) - \Delta H^0_{f\,298}\{C_4H_{10}(g)\}$$

or $$\Delta H^0_{f\,298}\ [C_4H_{10}(g)] = -125.262 \text{ kJ}$$

The standard enthalpy change of a reaction can also be estimated from a knowledge of the standard enthalpies of combustion of the species involved in the reaction. The following example illustrates the method of calculating the standard enthalpy change of a reaction from a knowledge of the standard enthalpies of combustion of the compounds.

Example 4.25 Calculate the standard enthalpy change at 298.15 K for the reaction

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

from the standard enthalpies of combustion of the compounds. The enthalpy of vaporization of H_2O at 298.15 K is 43.966 kJ/mol.

Solution The combustion reactions for $CH_4(g)$; $CO(g)$ and $H_2(g)$ are

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\text{: } \Delta H_c^0 = -890.94 \text{ kJ} \tag{A}$$

$$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)\text{: } \Delta H_c^0 = -283.18 \text{ kJ} \tag{B}$$

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)\text{: } \Delta H_c^0 = -286.03 \text{ kJ} \tag{C}$$

$$H_2O(g) \rightarrow H_2O(l)\text{: } \Delta H^0 = -43.966 \text{ kJ} \tag{D}$$

The desired reaction = (A) – (B) – 3(C) + (D). Therefore,

$$\begin{aligned} \Delta H_{298}^0 &= \Delta H_c^0 \text{ (A) } - \Delta H_c^0 \text{ (B) } - 3\Delta H_c^0 \text{ (C) } + \Delta H^0 \\ &= -890.94 - (-283.18) - 3(-286.03) - 43.966 = 206.364 \text{ kJ} \end{aligned}$$

From the above example, it can be seen that the standard enthalpy change of a reaction $\sum \nu_i A_i = 0$ can be written as

$$\Delta H_{298}^0 = -\sum \nu_i \Delta H_{ci}^0 \tag{4.78}$$

where ΔH_{ci}^0 represents the standard enthalpy change of combustion of species *i*.

4.8.5 Effect of temperature on the standard enthalpy change of a reaction

So far we have discussed the method of estimating the standard enthalpy change of a reaction at 298.15 K. Rarely the chemical reactions are conducted at 298.15 K. Most of the chemical reactions are carried out at higher temperatures because the rate of a reaction increases with increasing temperature resulting in increased production rate of the products. The standard enthalpy change of a reaction depends on temperature and hence, a chemical engineer is naturally interested in estimating the standard enthalpy change of a reaction at a temperature other than 298.15 K. In this subsection the effect of temperature on the standard enthalpy change of a reaction is discussed.

see Example 4.26 for the values of Δa, Δb, Δc, Δd, Δe and ΔH_0. They are given by $\Delta a = -12.355$; $\Delta b = 38.726 \times 10^{-3}$; $\Delta c = -18.717 \times 10^{-6}$; $\Delta d = 2.012 \times 10^{-9}$; $\Delta e = -1.006 \times 10^5$ and $\Delta H_0 = -42747$ J.

$$\therefore \quad \Delta H_T^0 = -42747 - 12.355T + \frac{38.726 \times 10^{-3}}{2}T^2 - \frac{18.717 \times 10^{-6}}{3}T^3$$

$$+\frac{2.012 \times 10^{-9}}{4}T^4 + \frac{1.006 \times 10^5}{T} \quad \text{(where } \Delta H_T^0 \text{ is in J)}$$

4.8.6 Adiabatic flame temperature

In any process plant the fuels burn with air to produce high temperature gases which are in turn used to generate steam or for heating other materials. The fuel and air usually enter the burner at the ambient temperature and high temperature combustion products leave the burner. The material used for construction of the combustion chamber dictates the maximum temperature at which the combustion chamber can be operated. Therefore, it is necessary to know the maximum attainable temperature by burning a fuel. The maximum temperature is attained when pure oxygen is used in stoichiometric requirement for the combustion process. The use of air or excess oxygen reduces the maximum temperature. Moreover, complete combustion may not occur and the CO_2 may dissociate into CO and O_2 at high temperatures resulting in an equilibrium mixture of CO_2, CO and O_2. Incomplete combustion, energy losses as heat from the combustion chamber and dissociation of products also reduce the maximum attainable temperature. The calculated temperature of the combustion products, with the assumption that the burner is adiabatic and no dissociation occurs is called the theoretical flame temperature or adiabatic flame temperature. The calculation of adiabatic flame temperature is illustrated through the following example.

Example 4.28 Calculate the flame temperature when methane is burned with 50% excess air in an adiabatic burner. Assume that methane and air enter the burner at 298.15 K and complete combustion occurs in the burner.

Solution The stoichiometric requirement of oxygen is given by the combustion reaction

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

$$\Delta H_{298}^0 = -393.978 + 2(-241.997) - (-74.943) = -803.029 \text{ kJ}$$

Air contains 79 mol% N_2 and 21 mol% O_2. Therefore, every mole of O_2 is accompanied by (79/21) mol of N_2 in air. The actual combustion reaction can be written as

$$CH_4(g) + 1.5 \times 2O_2(g) + 1.5 \times 2 \times \frac{79}{21}N_2(g) \rightarrow CO_2(g) + 2H_2O(g) + O_2(g) + 11.286\ N_2(g)$$

or $CH_4(g) + 3O_2(g) + 11.286\ N_2(g) \rightarrow CO_2(g) + 2H_2O(g) + O_2(g) + 11.286\ N_2(g)$

To calculate the temperature of the combustion products, the combustion process can be considered to consist of the imaginary steps shown in Fig.4.20.

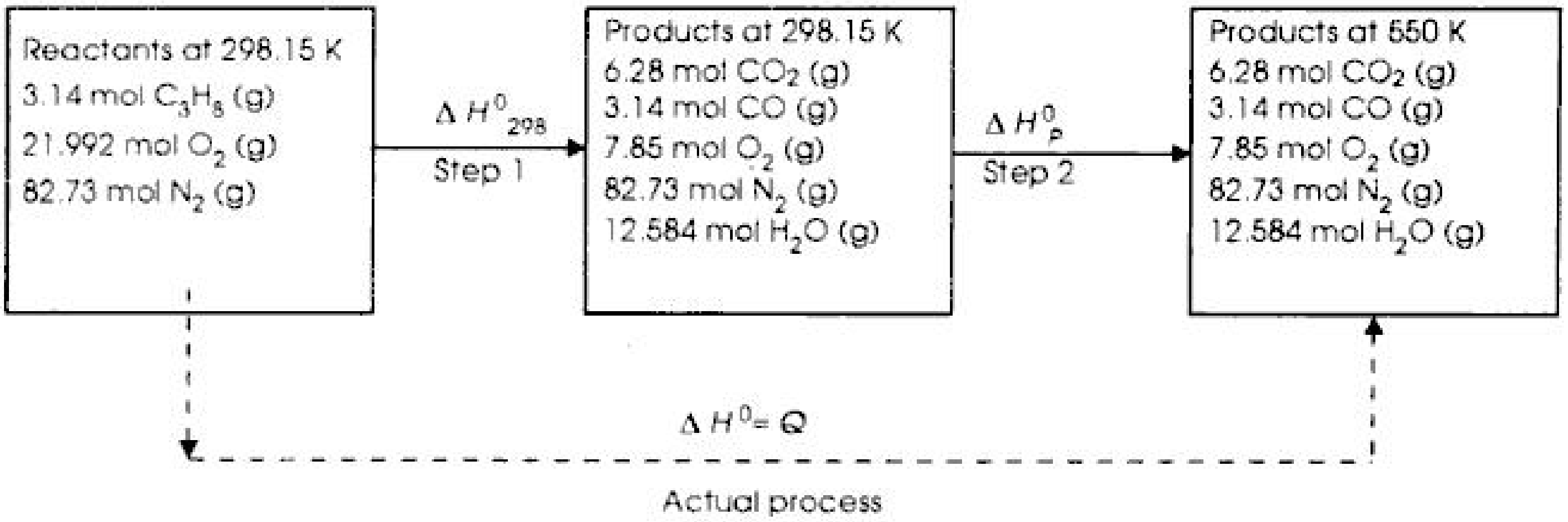

Fig.4.21 *Two-step process for the calculation of* ΔH^0.

$$\begin{aligned}
\Delta H^0 &= \Delta H^0_{298} + \Delta H^0_P \\
&= \Delta H^0_{298} + \int_{298.15}^{550} \left(\sum_P |\nu_i|\, C^0_{p_i} \right) dT \quad \text{(where the summation is over all the products)} \\
&= \Delta H^0_{298} + \Delta a(550 - 298.15) + \frac{\Delta b}{2}\{(550)^2 - (298.15)^2\} \\
&\quad + \frac{\Delta c}{3}\{(550)^3 - (298.15)^3\} + \frac{\Delta d}{4}\{(550)^4 - (298.15)^4\} - \Delta e \left(\frac{1}{550} - \frac{1}{298.15} \right) \\
&= \Delta H^0_{298} + \Delta a \times 251.85 + \frac{\Delta b}{2} \times 213.606 \times 10^3 + \frac{\Delta c}{3} \times 1.3987 \times 10^8 \\
&\quad + \frac{\Delta d}{4} \times 8.3604 \times 10^{10} + \Delta e \times 1.5358 \times 10^{-3}
\end{aligned}$$

$$\begin{aligned}
\Delta a &= 6.28 \times 45.369 + 3.14 \times 28.068 + 7.85 \times 30.255 + 82.73 \times 27.270 + 12.584 \times 28.850 \\
&= 3229.648 \\
\Delta b &= (6.28 \times 8.688 + 3.14 \times 4.631 + 7.85 \times 4.207 + 82.73 \times 4.930 + 12.584 \times 12.055) \times 10^{-3} \\
&= 661.686 \times 10^{-3} \\
\Delta c &= 0; \quad \Delta d = 0 \\
\Delta e &= (-6.28 \times 9.619 - 3.14 \times 0.258 - 7.85 \times 1.887 + 82.73 \times 0.333 + 12.584 \times 1.006) \times 10^5 \\
&= -35.822 \times 10^5
\end{aligned}$$

$$\begin{aligned}
\Delta H^0 &= -5540507 + 3229.648 \times 251.85 + \frac{661.686 \times 10^{-3}}{2} \times 213.606 \times 10^3 \\
&\quad -35.822 \times 10^5 \times 1.5358 \times 10^{-3} = -4661.952 \text{ kJ}
\end{aligned}$$

Molar mass of propane = 44×10^{-3} kg/mol

3.14 mol C_3H_8 = 0.1382 kg

Therefore, energy transferred as heat per kg propane

$$= \frac{4661.952 \times 10^3}{0.1382} = 33.733 \text{ MJ}$$

4.9 Summary

A series of experiments conducted by J.P. Joule between 1843 and 1848 form the basis for the first law of thermodynamics. A process or a combination of processes as a result of which a system is restored to its initial state is called a cycle. The first law of thermodynamics states that whenever a system undergoes a cyclic process the work done on the system is equal to the energy transferred from the system to the surroundings.

The sign convention adopted for work and heat is that the work done by a system and the energy transferred to a system from surroundings are treated as positive quantities. The work done on a system and the energy transferred as heat from the system to its surroundings is assigned a negative sign.

The first law of thermodynamics gives

$$\oint (dQ - dW) = 0 \tag{4.2}$$

where $\oint$ denotes the integral over the entire cycle. The first law of thermodynamics leads to several consequences. They are:

- Heat interaction is a path function.
- There exists a point function E, called energy, such that its differential is given by

$$dE = dQ - dW \tag{4.4}$$

If the potential energy and kinetic energy of the system do not undergo any change, then the above expression reduces to

$$dU = dQ - dW \tag{4.5}$$

- The energy of an isolated system is conserved which is known as the principle of conservation of energy.
- It is impossible to devise a perpetual motion machine of the first kind (PMMFK). A cyclically working device which continuously delivers net work without receiving any energy in the form of heat from the surroundings is called a perpetual motion machine of the first kind.

There are two types of energy analysis. They are control-mass analysis and control-volume analysis. The control-mass analysis is usually used to analyze non-flow processes. In the control-mass analysis attention is focused on a definite quantity of matter and the change in the energy of the system (control-mass) is related to heat and work interactions.

In a constant-volume (isometric) process, the work done $W = 0$ and the first law of thermodynamics reduces to

$$u_2 - u_1 = \Delta u = q \tag{4.9}$$

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

$$\dot{N}_e\left\{h_e+\frac{\mathbf{V}_e^2}{2}+gZ_e\right\}-\dot{N}_i\left\{h_i+\frac{\mathbf{V}_i^2}{2}+gZ_i\right\}=\dot{Q}-\dot{W}_S-\frac{dE}{dt} \tag{4.58}$$

where $\mathbf{V}$ = velocity of the fluid, Z= elevation, $\dot{Q}$ = rate at which energy is transferred as heat into the control-volume, $\dot{W}_S$ = rate at which shaft work is delivered by the control-volume, (dE/dt) = accumulation of energy in the control-volume. Subscripts i and e represent the inlet and exit conditions, respectively.

For steady-state steady flow conditions

$$\dot{N}_i=\dot{N}_e;\ \dot{Q}=\text{constant};\ \dot{W}_S=\text{constant and }\frac{dE}{dt}=0.$$

In analyzing the performance of a turbine it is legitimate to ignore the changes in PE and KE as they are insignificant compared to the change in the enthalpy of the fluid. For analyzing the flow through a nozzle, one cannot ignore the change in KE. If an ideal gas at P_i and T_i enters a nozzle with negligible velocity, the exit velocity of the gas is given by

$$\mathbf{V}_e=\sqrt{2C_pT_i\left[1-\left(\frac{P_e}{P_i}\right)^{(\gamma-1)/\gamma}\right]} \tag{4.62}$$

When a fluid flows from high pressure to low pressure through a partially opened valve or some obstruction, it is said to undergo a throttling process. A throttling process is an isenthalpic process. The Joule–Thomson (Kelvin) coefficient μ_{JT} is defined by

$$\mu_{JT}=\left(\frac{\partial T}{\partial P}\right)_h \tag{4.63}$$

The point where $\mu_{JT}=0$ is called the inversion point. The locus of the inversion points is called an inversion curve. In the region $\mu_{JT}>0$, throttling of a gas reduces its temperature and in the region $\mu_{JT}<0$, throttling of a gas increases its temperature. A throttling calorimeter, a device which uses the principle of throttling, is used to measure the quality of wet steam.

The control-volume analysis of transient flow processes yields results which are identical to those obtained through control-mass analysis.

A chemical reaction can be conveniently represented as $\sum \nu_i A_i = 0$ where ν_i is the stoichiometric coefficient associated with species A_i. The stoichiometric coefficients associated with products are assigned a positive sign, and those associated with reactants are assigned negative sign.

Usually chemical reactions are accompanied by energy absorption or rejection as heat, because the energy associated with the products is different from that associated with the reactants. Such a difference in energy arises because of the difference in the structure of molecules.

In chemical thermodynamics the following standard states are used:

Gases: pure gas in the ideal gas state at 1 bar
Liquids: pure liquid at 1 bar
Solids: pure solid in the most stable form, if there are more than one allotropic forms, at 1 bar

The enthalpy change associated with a chemical reaction can be measured with the help of a flow calorimeter. If the reactants and products are in the standard states and at the same temperature, the enthalpy change associated with a chemical reaction is called standard enthalpy change (or standard heat) of reaction.

A reaction in which only one mole of a single compound is formed from its constituent elements is called a formation reaction. The enthalpy change associated with a formation reaction is called the standard enthalpy of formation of the compound, if the elements and the compound are in the standard states. The standard enthalpy change of a chemical reaction can be estimated from a knowledge of the standard enthalpies of formation of the participating compounds. The standard enthalpy of formation at 298.15 K is represented as ΔH^0_{f298}. The standard enthalpy change (ΔH^0_{298}) of a reaction at 298.15 K can be calculated by making use of the relation

$$\Delta H^0_{298} = \sum \nu_i \Delta H^0_{f\,298i} \tag{4.77}$$

A combustion reaction is defined as a reaction between an element or compound and oxygen to form specified products. In case of hydrocarbons containing hydrogen, carbon and oxygen only, the combustion products are CO_2 and H_2O. H_2O may be present either as gas or liquid. The standard enthalpy change associated with a combustion reaction is called standard enthalpy change (or standard heat) of combustion. Quite often the term heating value is used for the negative of the standard enthalpy change of combustion ($-\Delta H^0_c$), because it represents the amount of energy that can be transferred as heat from the burner to the surroundings. If H_2O is in the liquid state in the combustion products, then ($-\Delta H^0_c$) is called the higher (gross) heating value and if H_2O is in the gaseous state in the combustion products ($-\Delta H^0_c$) is called lower (net) heating value. The standard enthalpy change of a reaction can also be estimated from a knowledge of the standard enthalpy change of combustion of the chemical species involved in the reaction. Then, the standard enthalpy change of a reaction is given by

$$\Delta H^0_{298} = -\sum \nu_i \Delta H^0_{ci} \tag{4.78}$$

The standard enthalpy change of reaction depends on temperature. To estimate ΔH^0_T, the value of ΔH^0 at any temperature other than 298.15 K, one can devise a convenient path connecting the initial state of reactants with the final state of products and estimate ΔH^0 for the devised path. This is possible because enthalpy is a point function. If the isobaric molar heat capacities are given by

$$C^0_p = a + bT + cT^2 + dT^3 + eT^{-2}$$

the standard enthalpy change (ΔH^0_T) of a reaction at temperature T is given by

$$\Delta H^0 = \Delta H_0 + \Delta a T + \frac{\Delta b}{2}T^2 + \frac{\Delta c}{3}T^3 + \frac{\Delta d}{4}T^4 - \frac{\Delta e}{T} \tag{4.82}$$

where $\Delta a = \sum \nu_i a_i;\ \Delta b = \sum \nu_i b_i;\ \Delta c = \sum \nu_i c_i;\ \Delta d = \sum \nu_i d_i;\ \Delta e = \sum \nu_i e_i$ (4.83)

and ΔH_0 is a constant, the value of which can be determined from a knowledge of ΔH^0_T at one temperature.

4.9 The isobaric molar heat capacity of ethane is given by

$$C_p = 4.493 + 182.229 \times 10^{-3}T - 74.843 \times 10^{-6}T^2 + 10.797 \times 10^{-9}T^3$$

where C_p is in J/mol K and T in K. Calculate the energy required to raise the temperature of 100 mol ethane from 298 K to 370 K at constant pressure.

4.10 A heat exchanger is to be designed to raise the temperature of 10 kmol per hour of ammonia from 300 K to 400 K. The inlet and exit pressure of ammonia in the heat exchanger are almost identical. Determine the amount of energy to be transferred to ammonia in the heat exchanger if the isobaric molar heat capacity of ammonia is given by

$$C_p = 29.747 + 25.108 \times 10^{-3}T - 1.546 \times 10^{5}T^{-2}$$

where C_p is in J/mol K and T in K.

4.11 If the isobaric molar heat capacity is given by

$$C_p = a + bT + cT^2 + dT^3$$

develop a relation to calculate the isobaric mean molar heat capacity. Calculate the isobaric mean heat capacity of methane in the temperature interval 298 K to 400 K.

4.12 Calculate the isobaric mean heat capacity of ammonia in the temperature range 300 K to 500 K.

4.13 In a particular fertilizer plant ammonia vapor leaves a reactor at 500°C. It is required to cool the vapors to 40°C in a heat exchanger using water as the coolant. The water is available at 25°C and it has to leave the heat exchanger at 35°C to maintain enough temperature gradient for energy transfer in the heat exchanger. Determine the amount of water required to cool 1 kmol/s of ammonia. Use the isobaric mean heat capacity of ammonia.

4.14 Nitrogen at 25°C and ammonia gas at 500°C in the mole ratio 1 : 1 enter at the opposite ends of a heat exchanger. The nitrogen leaves the heat exchanger at 450°C. The pressure drop for both the streams in the heat exchanger is negligible. Set up the necessary equations to facilitate iterative calculations and determine the exit temperature of ammonia gas.

4.15 Rework Problem 4.14 using the isobaric mean heat capacity for ammonia gas.

4.16 One mole of an ideal gas at P_1 and T_1 is compressed reversibly and adiabatically to a pressure of P_2 and then it is cooled at constant volume till the pressure reduces to P_1. Finally energy is transferred as heat at constant pressure till the gas is restored to T_1. Show that the net work done is given by

$$RT_1\left[\frac{1-(P_2/P_1)^{(\gamma-1/\gamma)}}{\gamma-1} + 1 - \left(\frac{P_2}{P_1}\right)^{-1/\gamma}\right]$$

4.17 A rigid and insulated tank of 2 m^3 capacity is divided into two equal compartments by a partition. One compartment contains an ideal gas at 600 K and 1 MPa while the second compartment contains the same gas at 300 K and 0.1 MPa. Determine the final temperature and pressure of the gas in the tank if the partition gets punctured. Assume γ = 1.4 for the gas.

4.18 One mole of an ideal gas is taken through a series of processes as shown in Fig.4.23 and restored to the initial state, thus completing a cycle. The efficiency of the cycle is defined as the ratio of the net work done to the energy absorbed as heat by the gas. Determine the efficiency of the cycle.

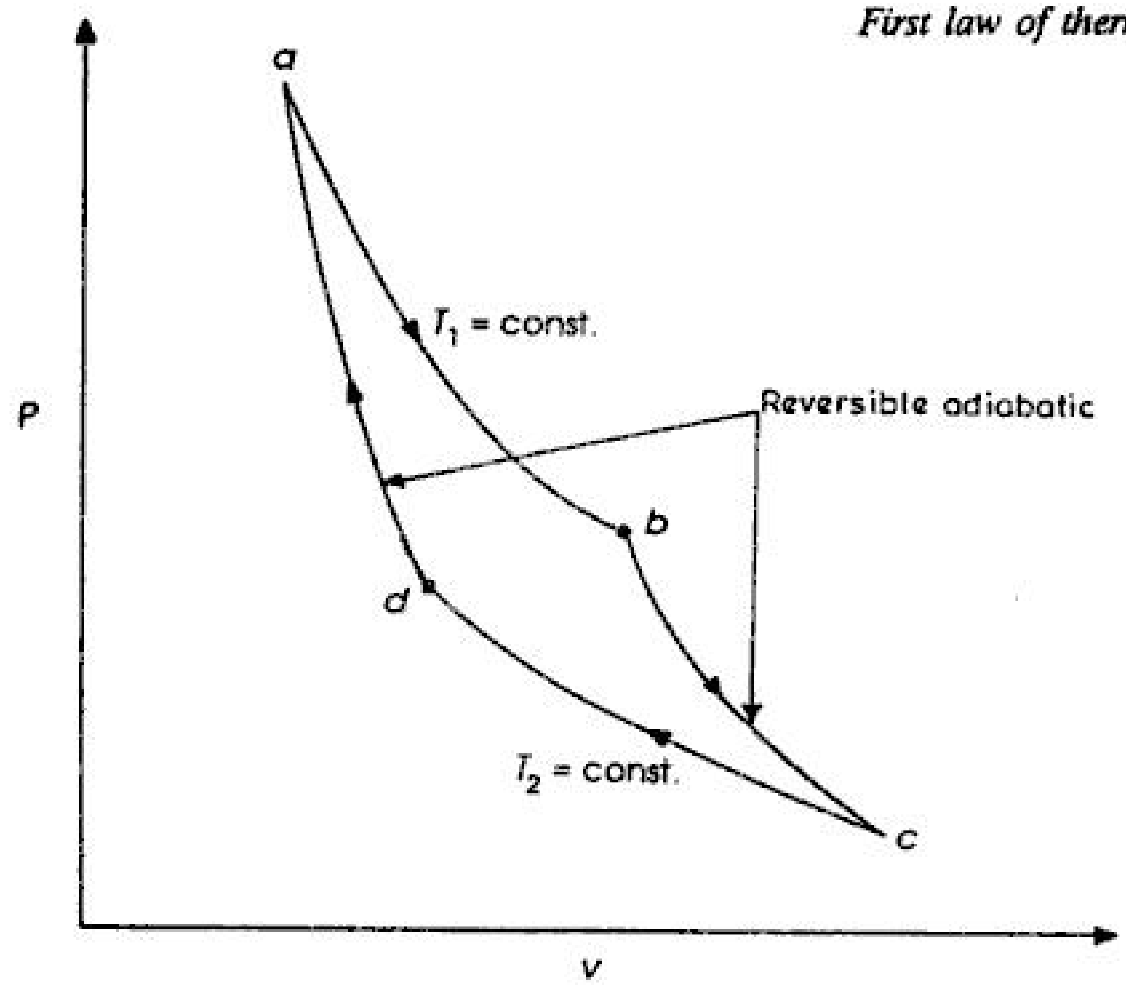

Fig.4.23 *Sketch for Problem 4.18.*

4.19 In a particular engine cylinder one mole of an ideal gas ($\gamma = 1.4$) is compressed from 25°C and 0.1 MPa till its volume is reduced to 1/12 of the original value. The process of compression can be approximated to follow the relation $Pv^{1.25}$ = constant. Determine the work and heat interactions. Also calculate the final temperature and pressure of the gas.

4.20 An empty hydrogen gas cylinder is sent for refilling. The cylinder after filling has been returned with a guarantee certificate that the cylinder contains hydrogen at a pressure of 15 MPa. The customer lodges a complaint that the cylinder as received by him did not show the guaranteed pressure and it contained much less gas. The engineer incharge of the filling station verified that the cylinder was not leaking and the line pressure from which the gas is usually filled is always maintained at 15 MPa and 25°C. As an engineer you may resolve the dispute by performing a thermodynamic analysis of the filling process. Assume that the ambient temperature is 25°C.

4.21 An insulated tank A of volume 1 m^3 initially contains air (ideal gas, $\gamma = 1.4$) at 10 MPa and 300 K. This tank is connected through a valve to another insulated tank of volume 9 m^3 which is evacuated. The valve in between the two tanks is opened till the pressure in both the tanks equalizes and then closed. Determine the pressure and temperature of the air in each tank immediately after the valve is closed. Assume that the air left in tank A has undergone adiabatic expansion.

4.22 An insulated tank of volume 100 m^3 is half filled with water at 300 K and the remaining space contains air at 0.1 MPa. It is required to pressurize the tank to 5 MPa to drain the water at a faster rate in case of emergency. For this purpose the tank is connected to a large compressed air reservoir which contains air at 10 MPa and 300 K. The valve between the tanks is opened till the water tank pressure rises to 5 MPa. Assume that the filling process is very fast and there is no energy transfer between the air and water. Determine the final temperature of air in the water tank and the mole number of air that enters the tank. Solve the problem by adopting control-mass analysis.

4.23 An adiabatic steam turbine operating under steady-state conditions receives superheated steam at 4 MPa and 400°C. The steam enters the turbine with a velocity of 5 m/s at an elevation of 10 m and leaves as wet steam of quality 0.9 at 35°C, at an elevation of 3 m and with a velocity of 20 m/s. Estimate the steam consumption rate if the power output of the turbine is 200 MW. Estimate the percent error, if changes in KE and PE are ignored.

liquid ammonia is withdrawn from the bottom of the tank by opening a valve, determine the final pressure, temperature and masses of liquid and vapor ammonia left in the tank.

4.35 An insulated storage tank of volume 10 m^3 is filled with saturated ammonia at 40°C. It contains 5 m^3 of liquid and 5 m^3 of vapor. Ammonia vapor is continuously withdrawn from the top of the tank during a particular experiment. If 50 kg ammonia is withdrawn as vapor, determine the final temperature, pressure and masses of liquid and vapor ammonia left in the tank.

4.36 A large storage tank B for ammonia is kept underground. The operator who was familiar with the specifications of the tank is away and no one else is aware of the size of the tank. An engineer needs this information and it is not possible to directly measure the volume of the tank. He plans to evacuate the tank first and then fill it with nitrogen from another tank A till the pressures in both the tanks are equalized. By knowing the initial P_0 and T_0 of nitrogen in tank A as well as its volume and by measuring the final pressure P of gas, the volume of tank B can be estimated. **(a)** Develop the necessary equations for the estimation of volume of the tank B. **(b)** Calculate the volume of tank B if $V_A = 100$ m^3; $P_0 = 5$ MPa; $T_0 = 300$ K and final pressure $P = 0.5$ MPa. Assume that nitrogen behaves as an ideal gas.

4.37 Express the following chemical reactions in the form $\sum \nu_i A_i = 0$ and specify the values of the stoichiometric coefficients.

(a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

(b) $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

4.38 The standard enthalpy change for the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

at 298.15 K is −92.11 kJ. Calculate the standard enthalpy change for the following reactions at 298.15 K.

(a) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g)$ **(b)** $NH_3(g) \rightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$

(c) $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

4.39 Which of the following reactions can be called formation reactions?

(a) $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$ **(b)** $C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(g)$

(c) $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ **(d)** $H_2(g) + O(g) \rightarrow H_2O(g)$

4.40 It is required to determine the standard enthalpy change of the reaction

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

Write down the set of formation reactions involved in the estimation of ΔH^0.

4.41 Calculate the standard enthalpy change for the following reactions at 298.15 K from the standard enthalpy of formation data.

(a) $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

(b) $2H_2S(g) + 3O_2(g) \rightarrow 2H_2O(g) + 2SO_2(g)$

(c) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

(d) $C_6H_6(g) + 9O_2(g) \rightarrow 6CO_2(g) + 3H_2O(g)$

The enthalpy of vaporization of C_6H_6 at 298.15 K is 33.61 kJ/mol.

4.42 Rework Problem 4.41 if H_2O in the products is in the liquid state. The enthalpy of vaporization of water at 298.15 K is 43.966 kJ/mol. Use ΔH^0_{f298} for $H_2O(g)$ in solving this problem.

4.43 The standard enthalpy change of combustion of acetylene is −1300.48 kJ at 298.15 K with H_2O in the liquid state. Calculate the standard enthalpy of formation of acetylene.

4.44 The higher heating value of *n*-propane at 298.15 K is 2221.54 kJ/mol. Estimate the standard enthalpy of formation of *n*-propane gas.

4.45 Calculate the standard enthalpy change of combustion at 298.15 K for $C_2H_5OH(l)$ if H_2O in the products is in the gas state.

4.46 The industrially important *water-gas shift reaction* is given by

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

Determine the standard enthalpy change of this reaction at 298.15 K from the standard enthalpy change of combustion data.

4.47 It is desired to carry out the following reaction at 800°C. Estimate the standard enthalpy change of the reaction at 800°C.

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

4.48 Estimate the standard enthalpy change of the following reaction at 600°C.

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

4.49 Quite often it is necessary to calculate the standard enthalpy change for the reaction of Problem 4.47 at several temperatures. To facilitate the calculations, develop a general expression for ΔH^0_T as a function of temperature.

4.50 Develop a general expression to calculate ΔH^0_T as a function of temperature for the reaction of Problem 4.48.

4.51 In a domestic gas stove, liquefied petroleum gas, which may be considered as pure *n*-butane, is supplied with 100% excess air to ensure complete combustion of the fuel. Both the fuel and air enter the burner at 25°C. Assume that complete combustion occurs in the burner and there are no energy losses. Develop the necessary expression to calculate the flame temperature by iterative calculations and determine the value.

4.52 Develop the necessary expression to solve Problem 4.51, with isobaric mean heat capacities of the compounds, for iterative calculations to estimate the flame temperature and determine the value.

4.53 In a laboratory, a steam boiler is fired using liquefied petroleum gas (treat as pure *n*-butane). The fuel and air enter the combustion chamber at 298.15 K and the flue gas leaves the boiler at 250°C. If 100% excess air is used in burning the fuel, determine the amount of energy transferred in the boiler for 15 kg fuel. Assume that the boiler is insulated and complete combustion occurs in the combustion chamber.

4.54 A particular petrol engine working under steady-state conditions receives gasoline (which may be treated as pure octane) and air at 25°C; the combustion products leave at 200°C. The volumetric composition of the combustion products on dry basis is as follows: 10% CO_2; 1.4% CO; 2.9% O_2 and 72.8% N_2. The energy loss as heat from the engine cylinder is estimated at 10 kJ/s. Determine the energy supplied as heat to the engine, if the fuel consumption rate is 0.1 kg/min.

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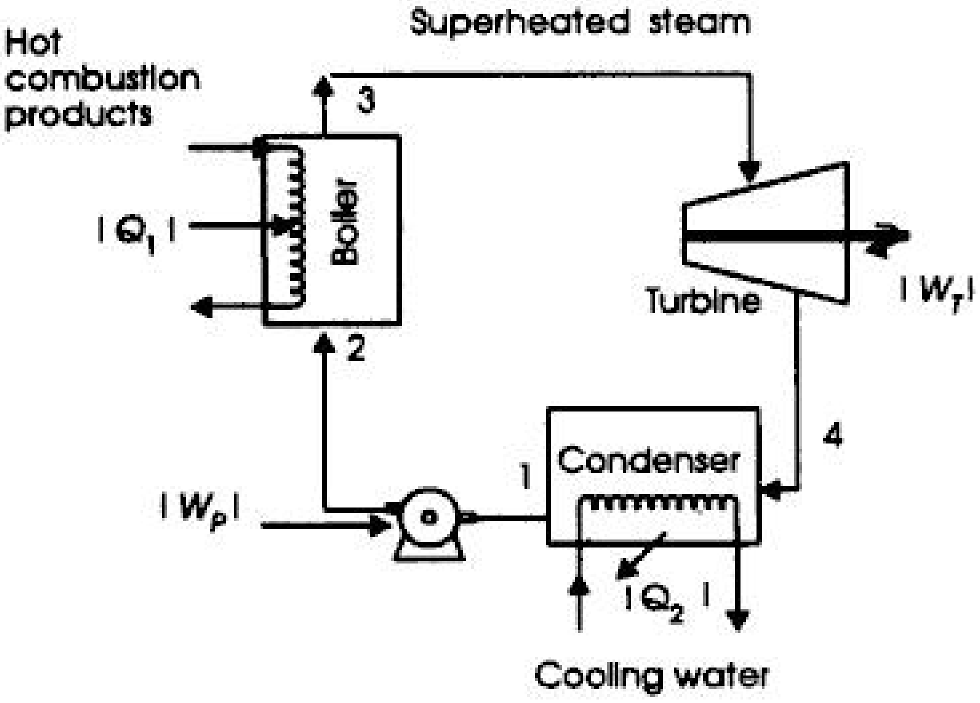

Fig.5.1 *Schematic diagram of a steam power plant.*

Quite often we use energy (in the form of work) consuming devices like refrigerators also. A device which absorbs energy in the form of heat from a body at low temperature and rejects energy as heat to a body at high temperature when work is done on it is called a heat pump or refrigerator. If the objective of the device is to maintain a body at low temperature by absorbing energy in the form of heat from the body it is called a *refrigerator*. Usually, the refrigerator rejects energy in the form of heat to the ambient atmosphere. If the objective of the device is to maintain a body at high temperature by rejecting energy in the form of heat to the body it is called a *heat pump*. In a heat pump usually the ambient atmosphere is used as a low temperature body from which energy is absorbed as heat. For thermodynamic analysis, a heat engine and a heat pump/refrigerator can be schematically represented as shown in Fig.5.2.

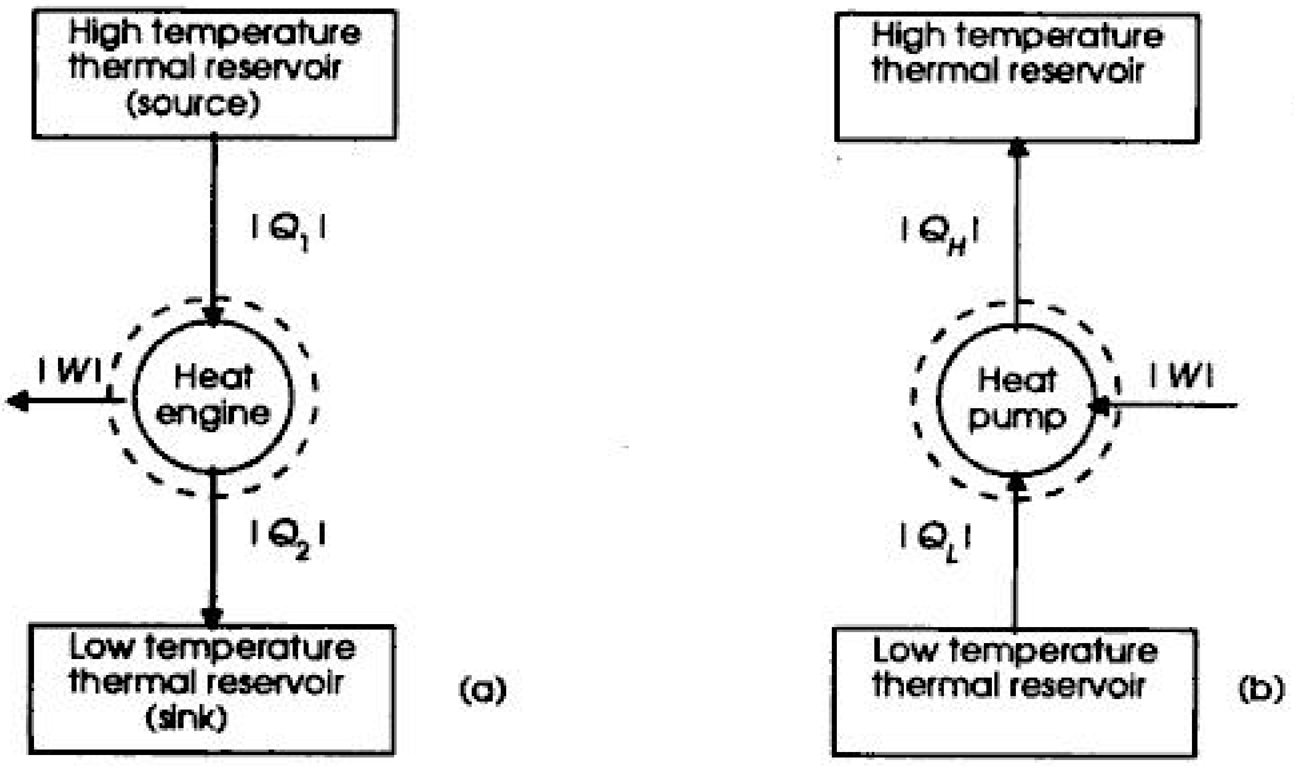

Fig.5.2 *Schematic representation of* **(a)** *a heat engine, and* **(b)** *a heat pump/refrigerator.*

In Fig.5.2 $|Q_1|$ and $|Q_2|$ represent the magnitude of energy absorbed and rejected in the form of heat by the working medium of the heat engine, respectively; $|Q_H|$ and $|Q_L|$ represent the magnitude of energy rejected and absorbed as heat by the working medium of the heat pump/refrigerator, respectively; and $|W|$ denotes the net work delivered by the engine or consumed by the heat pump/refrigerator.

Since a heat engine is an energy conversion device its performance is expressed in terms of the energy conversion efficiency or simply efficiency (η) which is defined as the ratio of the net work delivered to the energy absorbed as heat from the high temperature body. That is

$$\eta = \frac{\text{Net work delivered}}{\text{Energy absorbed as heat from the high temperature body}}$$

$$= \frac{|W|}{|Q_1|} = \frac{|Q_1| - |Q_2|}{|Q_1|} \tag{5.1}$$

If the system is selected as shown by the dotted circle in Fig.5.2(a), application of the first law of thermodynamics gives

$$|W| = |Q_1| - |Q_2| \tag{5.2}$$

Quite often, the energy conversion efficiency is also called *thermal efficiency.*

A heat pump or refrigerator is not an energy conversion device and hence its performance cannot be expressed in terms of energy conversion efficiency. On the other hand, the performance is expressed in terms of *coefficient of performance* (COP) which is defined as the ratio of the energy effect sought to the energy consumed to accomplish the task. That is

$$\text{COP} = \frac{\text{Energy effect sought}}{\text{Energy consumed to accomplish the task}} \tag{5.3}$$

For a refrigerator, the coefficient of performance $(\text{COP})_\text{R}$ is given by

$$(\text{COP})_\text{R} = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_H| - |Q_L|} \tag{5.4}$$

The coefficient of performance of a heat pump $(\text{COP})_\text{HP}$ is given by

$$(\text{COP})_\text{HP} = \frac{|Q_H|}{|W|} = \frac{|Q_H|}{|Q_H| - |Q_L|} \tag{5.5}$$

Considering the system as the cyclically operating device, [shown by dotted circle in Fig.5.2(b)], the first law of thermodynamics gives

$$|W| = |Q_H| - |Q_L| \tag{5.6}$$

5.3 Second law of thermodynamics

While discussing the applications of the first law of thermodynamics, it was stated that for a constant internal energy process

$$dU = 0 = dQ - dW \quad \text{or} \quad dQ = dW$$

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Consider $m = m\ (U, X)$. Then

$$dm = \left(\frac{\partial m}{\partial U}\right)_X dU + \left(\frac{\partial m}{\partial X}\right)_U dX$$

or $$\left(\frac{\partial m}{\partial X}\right)_S = \left(\frac{\partial m}{\partial U}\right)_X \left(\frac{\partial U}{\partial X}\right)_S + \left(\frac{\partial m}{\partial X}\right)_U = \left(\frac{\partial m}{\partial X}\right)_U \tag{6.109}$$

since $(\partial U/\partial X)_S = 0$; see Eqn.6.106. Therefore, from Eqns.6.107 and 6.109, we get

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \left(\frac{\partial m}{\partial X}\right)_U \tag{6.110}$$

Substituting for m from Eqn.6.108 in Eqn.6.110, we get

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \left[\frac{\partial}{\partial X}\left(\frac{\partial U}{\partial X}\right)_S\right]_U \tag{6.111}$$

Substituting for $\left(\frac{\partial U}{\partial X}\right)_S$ from Eqn.6.106 in Eqn.6.111, we get

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = \left[\frac{\partial}{\partial X}\left\{-T\left(\frac{\partial S}{\partial X}\right)_U\right\}\right]_U$$

or $$\left(\frac{\partial^2 U}{\partial X^2}\right)_S = -T\left(\frac{\partial^2 S}{\partial X^2}\right)_U - \left(\frac{\partial S}{\partial X}\right)_U \left(\frac{\partial T}{\partial X}\right)_U = -T\left(\frac{\partial^2 S}{\partial X^2}\right)_U \tag{6.112}$$

since $(\partial S/\partial X)_U = 0$; see Eqn.6.101. Substituting Eqn.6.102 in Eqn.6.112, we get

$$\left(\frac{\partial^2 U}{\partial X^2}\right)_S > 0 \tag{6.104}$$

Thus we find that the entropy maximum and energy minimum principles are equivalent.

Now it is possible to recast the energy minimum principle in terms of the other thermodynamic potentials also. Consider a system in diathermal contact with a constant temperature bath. If the system undergoes a process while in interaction with the constant temperature bath, the system eventually settles into a state of equilibrium and the system temperature will be identical to that of the constant temperature bath. Consider the combination of the system and the constant temperature bath as the supersystem and apply the energy minimum principle. Then

$U + U^B$ = minimum (subject to $S + S^B$ = constant)

or $$dU + dU^B = 0 \tag{6.113}$$

and $$d^2U + d^2U^B > 0 \tag{6.114}$$

subject to $$dS + dS^B = 0 \tag{6.115}$$

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Solution Consider $s = s\ (T,\ P)$. Then

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP \tag{A}$$

Substitute $C_p = T\ (\partial s/\partial T\ )_P$ [see Eqn.7.42] and the Maxwell relation given by Eqn.7.46 in Eqn.(A), to get

$$ds = C_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP \tag{B}$$

We know that $\beta = (1/v)[\partial v/\partial T]_P$ [see Eqn.7.51]. Therefore, Eqn.(B) can be rewritten as

$$ds = C_p \frac{dT}{T} - \beta v dP \quad \text{or} \quad Tds = C_p\, dT - Tv\,\beta dP$$

Example 7.4 Use the Jacobian method to show that

$$Tds = C_p\, dT - \beta v T dP$$

Solution Consider $s = s\ (T,\ P)$. Then

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP \quad \text{or} \quad ds = \frac{[s, P]}{[T, P]}\, dT + \frac{[s, T]}{[P, T]} dP$$

$$= \quad C_p \frac{dT}{T} + \frac{[v, P]}{[P, T]} dP \qquad \text{[see Eqns.7.42 and 7.49]}$$

$$= \quad C_p \frac{dT}{T} - \beta v dP \qquad \text{[see Eqn.7.51]}$$

or $Tds = C_p\, dT - Tv\beta dP$

It was shown [see Eqn.7.68 and Example 7.3] that the change in entropy of a substance is given by

$$Tds = C_v\, dT + \frac{T\beta}{\kappa} dv \tag{7.68}$$

and $Tds = C_p\, dT - Tv\,\beta dP$ (7.71)

Equations 7.68 and 7.71 are quite often called *Tds* equations.

7.6 Difference between heat capacities

Let us find the difference between the two heat capacities of a substance. For this purpose consider

$$s = s\ (T,\ v)$$

8 Thermodynamic properties of real gases

Learning Objectives

This chapter will enable readers to

- estimate the thermodynamic properties of an ideal gas in terms of P, v, T and C_p^0;
- define enthalpy, entropy and other departure functions;
- calculate the departure functions from a knowledge of the equation of state of a fluid;
- calculate the departure functions from generalized RK, SRK and PR equations of state;
- calculate the departure functions using Edmister charts;
- extend the Lee–Kesler method for the prediction of departure functions;
- calculate the departure functions using Lee–Kesler data;
- calculate the departure functions from generalized virial coefficient correlation;
- calculate the required thermodynamic properties of a real gas from the ideal gas heat capacity and P–v–T data only; and
- construct thermodynamic property tables and diagrams;

The relationships between the nonmeasurable and measurable properties discussed in Chapter 7 are valid for any substance and the required properties can be estimated in terms of the measurable quantities P, v, T, C_p, C_v, β and κ. In this chapter, the estimation of enthalpy and entropy of a real gas is discussed. Before we discuss the estimation of the properties of a real gas, let us study the properties of an ideal gas.

8.1 Thermodynamic properties of an ideal gas

The change in the internal energy, enthalpy and entropy of a system can be estimated from the relations

$$du = C_v dT + \left(\frac{T\beta}{\kappa} - P\right) dv \qquad (7.58)$$

$$dh = C_p dT + v(1 - \beta T)dP \qquad (7.64)$$

$$ds = C_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_v dv \qquad (7.67)$$

or $$ds = C_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP \qquad \text{[See Example 7.3]}$$

For an ideal gas:

$$\beta = \frac{1}{T}; \quad \kappa = \frac{1}{P}; \quad \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v} \quad \text{and} \quad \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

$$\therefore \quad \left(\frac{\partial u}{\partial v}\right)_T = \frac{T\beta}{\kappa} - 1 = 0 \quad \text{and} \quad \left(\frac{\partial u}{\partial P}\right)_T = \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T = 0$$

The thermodynamic properties of a real gas can be estimated from a knowledge of the departure functions. For example, the change in the enthalpy $(h_2 - h_1)$ and entropy $(s_2 - s_1)$ of a real gas can be expressed as

$$(h_2 - h_1) = (h_2 - h_1) + (h_2^0 - h_1^0) - (h_2^0 - h_1^0) = (h_2 - h_2^0) - (h_1 - h_1^0) + (h_2^0 - h_1^0)$$

or $$(h_2 - h_1) = (h_2 - h_2^0) - (h_1 - h_1^0) + \textstyle\int_{T_1}^{T_2} C_p^0 dT \qquad (8.18)$$

$$(s_2 - s_1) = (s_2 - s_1) + (s_2^0 - s_1^0) - (s_2^0 - s_1^0) = (s_2 - s_2^0) - (s_1 - s_1^0) + (s_2^0 - s_1^0)$$

or $$(s_2 - s_1) = (s_2 - s_2^0) - (s_1 - s_1^0) + \int_{T_1}^{T_2} C_p^0 \frac{dT}{T} - R \ln \frac{P_2}{P_1} \qquad (8.19)$$

8.3 Departure functions from equations of state

The P–v–T behavior of a fluid is conveniently expressed in the form of an equation of state. The equations of state in common use are discussed in Section 3.3. It can be observed that the equations of state in common use are pressure explicit, i.e., volume and temperature appear as independent variables. The evaluation of the enthalpy and entropy departures requires a knowledge of the partial derivative $(\partial v/\partial T)_P$, which cannot be directly obtained from pressure explicit equations of state. In such cases it is useful to develop alternative expressions for the departure functions as shown below.

We know that $d(Pv) = Pdv + vdP$

or $$vdP = d(Pv) - Pdv \qquad (8.20)$$

and the cyclic relation among the three variables P, v and T is given by

$$\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v = -1 \quad \text{or} \quad \left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial P}\right)_T$$

or $$\left[\left(\frac{\partial v}{\partial T}\right)_P dP\right]_T = -\left[\left(\frac{\partial P}{\partial T}\right)_v dv\right]_T \qquad (8.21)$$

Substituting Eqns.8.20 and 8.21 in Eqns.8.9 and 8.14, we get

$$\begin{aligned}
(h - h^0)_{T,P} &= \int_{P=0}^{P} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]_T dP \\
&= \int_{P=0}^{P} d(Pv) + \int_{v=\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]_T dv \quad (\text{since } v = \infty \text{ as } P = 0) \\
&= Pv - (Pv)_{P=0} + \int_{v=\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]_T dv \\
&= Pv - RT + \int_{v=\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]_T dv
\end{aligned}$$

$$(s - s^0) = R\ln(Z + B) + \frac{1}{2\sqrt{2}b}\left(\frac{\partial a}{\partial T}\right)\ln\left\{\frac{Z + B(1+\sqrt{2})}{Z + B(1-\sqrt{2})}\right\}$$

$$= 8.314\ln(0.9991 - 5.6993 \times 10^{-5}) - \frac{1.27 \times 10^{-2} \times 1.6134 \times 10^{-4}}{2\sqrt{2} \times 1.4750 \times 10^{-4}}$$

$$= -\ 0.013 \text{ J/mol K}$$

$$\therefore \quad \Delta h_b = (h^0 - h) = 6.03 \text{ J/mol}$$

$$\Delta s_b = (s^0 - s) = 0.013 \text{ J/mol K}$$

Step c: Change n-octane in the ideal gas state at 273.15 K and 0.7396 kPa to n-octane in the ideal gas state at 427.85 K and 0.215 MPa.

$$\Delta h_c = \int_{T_1}^{T_2} C_p^0 dT$$

$$= \int_{273.15}^{427.85} (6.907 + 741.770 \times 10^{-3}T - 397.204 \times 10^{-6}T^2 + 82.629 \times 10^{-9}T^3)dT$$

$$= 6.907(427.85 - 273.15) + \frac{741.770 \times 10^{-3}}{2}\{(427.85)^2 - (273.15)^2\}$$

$$-\frac{397.204 \times 10^{-6}}{3}\{(427.85)^3 - (273.15)^3\} + \frac{82.629 \times 10^{-9}}{4}\{(427.85)^4 - (273.15)^4\}$$

$$= 34.195 \text{ kJ/mol}$$

$$\Delta s_c = \int_{T_1}^{T_2} C_p^0 \frac{dT}{T} - R\ln\frac{P_2}{P_1} = \int_{T_1}^{T_2}\left(\frac{a + bT + cT^2 + dT^3}{T}\right)dT - R\ln\frac{P_2}{P_1}$$

$$= a\ln\frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2) + \frac{d}{3}(T_2^3 - T_1^3) - R\ln\frac{P_2}{P_1}$$

$$= 6.907\ln\frac{427.85}{273.15} + 741.770 \times 10^{-3}(427.85 - 273.15)$$

$$-\frac{397.204 \times 10^{-6}}{2}\{(427.85)^2 - (273.15)^2\}$$

$$+\frac{82.629 \times 10^{-9}}{3}\{(427.85)^3 - (273.15)^3\} - 8.314\ln\frac{0.215 \times 10^6}{0.7396 \times 10^3}$$

$$= 50.75 \text{ J/mol K}$$

$$(s - s^0) = R \ln (Z - B) + \frac{1}{b}\left(\frac{\partial a}{\partial T}\right) \ln \left(\frac{Z+B}{Z}\right) \tag{8.39–43}$$

Peng–Robinson (PR) equation of state:

$$h - h^0 = RT(Z-1) + \frac{T\left(\frac{\partial a}{\partial T}\right) - a}{2\sqrt{2}b} \ln \left\{\frac{Z + B(1+\sqrt{2})}{Z + B(1-\sqrt{2})}\right\} \tag{8.45}$$

$$s - s^0 = R \ln (Z - B) + \frac{1}{2\sqrt{2}b}\left(\frac{\partial a}{\partial T}\right) \ln \left\{\frac{Z + B(1+\sqrt{2})}{Z + B(1-\sqrt{2})}\right\} \tag{8.46}$$

The departure functions can also be estimated from the generalized compressibility factor correlation. The three parameter law of corresponding states, with Pitzer's acentric factor, is used to determine the departure functions. The Edmister charts based on Pitzer's results can be used to read $[(h - h^0)/RT_c]^0$ — the first order enthalpy departure, and $[(h^0 - h)/RT_c]^1$ — the second order enthalpy departure at specified T_r and P_r. Then

$$\left(\frac{h^0 - h}{RT_c}\right) = \left(\frac{h^0 - h}{RT_c}\right)^0 + \omega \left(\frac{h^0 - h}{RT_c}\right)^1 \tag{8.52}$$

Similar charts are also available for calculating entropy departure from the relation

$$\left(\frac{s^0 - s}{R}\right) = \left(\frac{s^0 - s}{R}\right)^0 + \omega \left(\frac{s^0 - s}{R}\right)^1 \tag{8.56}$$

The Lee–Kesler method based on a reference fluid, can be extended to predict the departure functions. The values predicted by the Lee–Kesler method are found to be in good agreement with the experimental values as compared to the values read from Edmister charts.

At low to moderate pressures, the virial coefficient correlation can be used to predict the departure functions. They are given by

$$\left(\frac{h - h^0}{RT_c}\right) = P_r \left[\left(0.083 - \frac{1.097}{T_r^{1.6}}\right) + \omega \left(0.139 - \frac{0.894}{T_r^{4.2}}\right)\right] \tag{8.75}$$

$$\left(\frac{s - s^0}{R}\right) = -P_r \left[\frac{0.675}{T_r^{2.6}} + \omega \frac{0.722}{T_r^{5.2}}\right] \tag{8.76}$$

Review questions

1. Is it true that $u_2^0 - u_1^0 = C_v^0\,(T_2 - T_1)$? Is this implied by the statement that $u = u\,(T)$ only?
2. Is it true that the entropy change of an ideal gas is given by

$$(s_2^0 - s_1^0) = C_p^0 \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}\ ?$$

3. What is a departure function ?
4. Why are the departure functions important in the estimation of thermodynamic properties of a real gas?

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Since v^∞ is large, $(a/v^\infty) \simeq 0$ and $v^\infty - b = v^\infty = (RT/P)$. Therefore

$$\int P dv = RT \ln \frac{P(v-b)}{RT} + \frac{a}{v}$$

$$\ln \phi = \ln\left(\frac{f}{P}\right) = Z - 1 - \frac{1}{RT}\int P dv = Z - 1 - \ln \frac{P(v-b)}{RT} - \frac{a}{RTv}$$

$$v = 15.675 \times 10^{-3} \text{ m}^3/\text{mol} \qquad \text{(see Example 3.8)}$$

$$\therefore \quad Z = \frac{Pv}{RT} = \frac{0.215 \times 10^6 \times 15.675 \times 10^{-3}}{8.314 \times 427.85} = 0.9474$$

$$\ln \phi = 0.9474 - 1 - \ln\left\{\frac{0.215 \times 10^6 (15.675 \times 10^{-3} - 2.37 \times 10^{-4})}{8.314 \times 427.85}\right\} - \frac{3.789}{8.314 \times 427.85 \times 15.675 \times 10^{-3}}$$

or $\quad \phi = 0.95$

or $\quad f = P\phi = 0.215 \times 10^6 \times 0.95 = 0.2043$ MPa

It can be observed from Eqn.9.38 that the fugacity coefficient is related to the Gibbs free energy departure function as

$$\ln \phi = \frac{g - g^0}{RT} = \frac{h - h^0}{RT} - \frac{T(s - s^0)}{RT} \tag{9.43}$$

Therefore, there exists a relation among the enthalpy departure, entropy departure and fugacity coefficient. Hence ϕ can be estimated from a knowledge of the departure functions also.

Example 9.4 Show that the expression for fugacity coefficient for a van der Waals gas obtained by the relation

$$\ln \phi = \frac{1}{RT}\int_0^P \left(v - \frac{RT}{P}\right) dP$$

is identical with that obtained by the relation

$$\ln \phi = \frac{h - h^0}{RT} - \frac{T(s - s^0)}{RT}$$

Solution In Example 9.3, the fugacity coefficient ϕ for a van der Waals gas is obtained by using the relation

$$\ln \phi = \frac{1}{RT}\int_0^P \left(v - \frac{RT}{P}\right) dP$$

The fugacity coefficient is given by

$$\ln \phi = Z - 1 - \ln \frac{P(v-b)}{RT} - \frac{a}{RTv} \tag{A}$$

At $T_r = 0.751$ and $P_r = 0.086$, read $\log_{10}\phi^0 = -0.032$ from Fig.9.2 and $\log_{10}\phi^1 = -0.025$ from Fig.9.4. Then

$$\log_{10}\phi = \log_{10}\phi^0 + \omega\log_{10}\phi^1 = -0.032 + 0.398(-0.025) = -0.042$$

or $\phi = 1.1014$; $f = \phi P = 1.1014 \times 0.215 \times 10^6 = 0.2368$ MPa

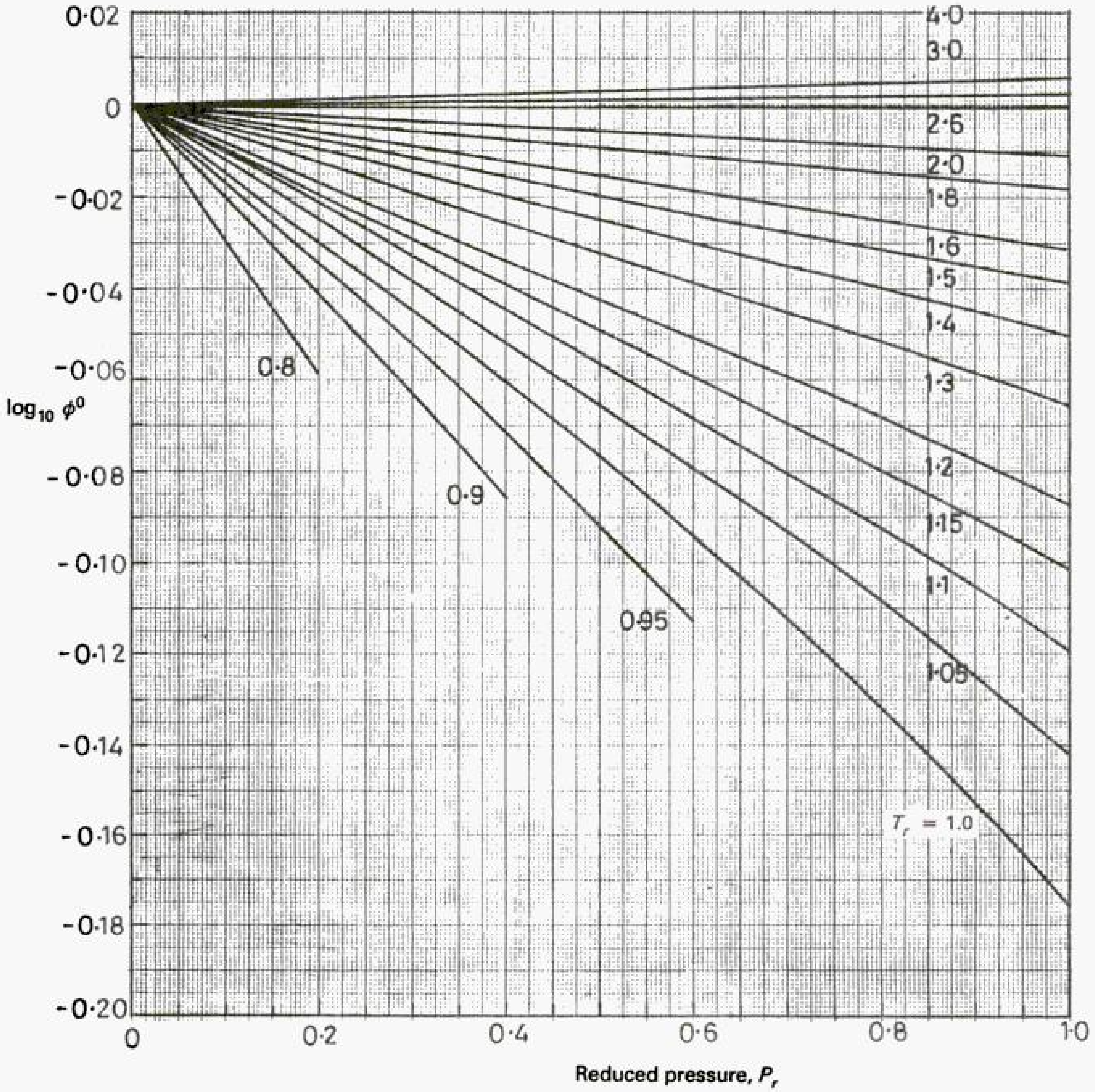

Fig.9.2 *Fugacity coefficient: Simple fluid term ($\log_{10}\phi^0$) for pressures $P_r \leq 1.0$. Chart prepared based on the data of Lee, B.I., and Kesler, M.G., AIChEJ, 21, 510 (1975).*

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gas which obeys the relation $Pv = RT$. In reality, no gas obeys the relation $Pv = RT$ and it is only an idealization to express the P–v–T behavior of gases. Similar idealization can be made to express the behavior of solutions also.

An ideal solution is defined as a solution that obeys the *Lewis* and *Randall* rule which states that $\widehat{f}_i$ (the fugacity of a component i in a solution) is equal to the product of the mole fraction x_i and f_i^* (the fugacity of the pure component i in the same phase and at the solution temperature and pressure). In other words, in an ideal solution

$$\widehat{f}_i = x_i f_i^* \tag{11.1}$$

If the composition of the mixture is known, the partial fugacity $\widehat{f}_i$ of the component i in an ideal solution can be estimated from a knowledge of the pure component fugacity f_i^* which can be evaluated by the methods discussed in Chapter 9. Equation 11.1 can be used to estimate the partial fugacities in gaseous and vapor mixtures at low to moderate pressures since they obey the Lewis and Randall rule. From Eqn.11.1, we can obtain

$$\left(\frac{\partial \ln \widehat{f}_i}{\partial P}\right)_{T,x} = \left(\frac{\partial \ln f_i^*}{\partial P}\right)_T$$

$$\text{or} \quad \overline{v}_i = v_i^* \qquad \text{[see Eqns.9.137–9.142]} \tag{11.2}$$

$$\left(\frac{\partial \ln \widehat{f}_i}{\partial T}\right)_{P,x} = \left(\frac{\partial \ln f_i^*}{\partial T}\right)_P$$

$$\text{or} \quad \overline{h}_i = h_i^* \tag{11.3}$$

Since $h = u + Pv$, from Eqns.11.2 and 11.3, we obtain

$$\overline{u}_i = u_i^* \tag{11.4}$$

where the superscript * indicates the properties of the pure component i at the solution temperature and pressure. Thus we find that in an ideal solution, the partial molar volume, enthalpy and internal energy of a component i are identical to the pure component properties at the same temperature and pressure.

The changes in molar volume (Δv_m), enthalpy (Δh_m) and internal energy (Δu_m) upon mixing the components to form an ideal solution are given by

$$\Delta v_m = \sum_{i=1}^{c} x_i \left(\overline{v}_i - v_i^*\right) = 0 \tag{11.5}$$

$$\Delta h_m = \sum_{i=1}^{c} x_i \left(\overline{h}_i - h_i^*\right) = 0 \tag{11.6}$$

$$\Delta u_m = \sum_{i=1}^{c} x_i \left(\overline{u}_i - u_i^*\right) = 0 \tag{11.7}$$

Choose a temperature t such that 80.1°C $< t <$ 110.61°C and at that temperature calculate P_1^s, P_2^s and hence x_1 and y_1. Assume t = 85°C. Then

$$P_1^s = 881.54 \text{ Torr}; \quad P_2^s = 345.22 \text{ Torr}$$

Equation (B) can be rearranged as

$$x_1 = \frac{P - P_2^s}{P_1^s - P_2^s}$$

$$\therefore \quad x_1 = \frac{760 - 345.22}{881.54 - 345.22} = 0.7734$$

Then $y_1 = \dfrac{x_1 P_1^s}{P} = \dfrac{0.7734 \times 881.54}{760} = 0.8971$

Results of similar calculations performed at other temperatures are presented below.

t (°C)	P_1^s (Torr)	P_2^s (Torr)	x_1	y_1
80.1	760.0	-	1.0	1.0
85	881.54	345.22	0.7734	0.8971
90	1020.65	406.87	0.5753	0.7727
95	1176.21	477.03	0.4047	0.6263
100	1349.47	556.50	0.2566	0.4557
105	1541.70	646.14	0.1271	0.2578
110.61	-	760.0	0.0	0.0

The T–x–y diagram for benzene–toluene system at 760 Torr is shown in Fig.11.3.

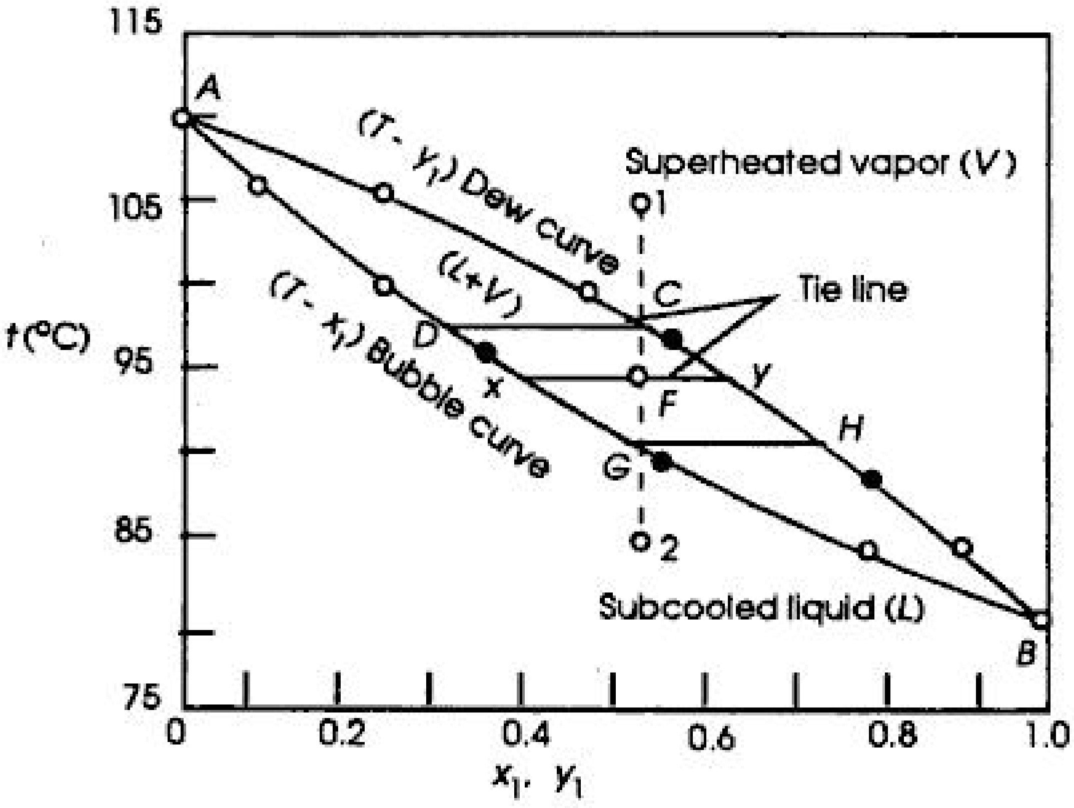

Fig.11.3 *T–x–y diagram for benzene–toluene system at 760 Torr.*

At 90°C, the vapor pressures of the pure components are given by

$$\log_{10} P_1^s = 6.87632 - \frac{1075.780}{90 + 233.205} = 3.5478$$

or $\quad P_1^s = 3530.57$ Torr $= 470.7$ kPa $\quad$ (1 Torr = 133.322 Pa)

Similarly one can calculate $P_2^s = 187.99$ kPa; $P_3^s = 78.61$ kPa. The K factors of the components are

$$K_1 = \frac{P_1^s}{P} = \frac{470.7}{200} = 2.354; \quad K_2 = 0.940 \quad \text{and} \quad K_3 = 0.393$$

Assume $L/F = 0.4$. Then

$$x_1 = \frac{z_{F_1}}{\left(\frac{L}{F}\right) + \left(1 - \frac{L}{F}\right) K_1} = \frac{0.3}{0.4 + 0.6 \times 2.354} = 0.1655$$

$$x_2 = \frac{0.3}{0.4 + 0.6 \times 0.940} = 0.3112; \quad x_3 = \frac{0.4}{0.4 + 0.6 \times 0.393} = 0.6291$$

$$\sum x_i = 0.1655 + 0.3112 + 0.6291 = 1.1058$$

Assume $L/F = 0.752$. Then

$$x_1 = 0.2246; \quad x_2 = 0.3045; \quad x_3 = 0.4709$$

$$\sum x_i = 1.0$$

Hence assumed value of $L/F = 0.752$ is correct.

$$y_1 = K_1 x_1 = 2.354 \times 0.2246 = 0.5287$$

$$y_2 = K_2 x_2 = 0.940 \times 0.3045 = 0.2862; \quad y_3 = K_3 x_3 = 0.393 \times 0.4709 = 0.1851$$

Hence, fraction vaporized, $V/F = 1 - (L/F) = 0.248$. Compositions of liquid and vapor leaving the flash unit are

$x_1 = 0.2246 \qquad y_1 = 0.5287$
$x_2 = 0.3045 \qquad y_2 = 0.2862$
$x_3 = 0.4709 \qquad y_3 = 0.1851$

11.5 Excess properties

It was observed that in an ideal solution there is no change in molar volume, enthalpy and internal energy upon mixing the components. Most of the solutions a chemical engineer deals with do not follow the ideal solution behavior and they are called *non-ideal* or *real solutions*. The

where v_i = molar volume of pure component i and λ_{ij} = energy of interaction between a molecule of component i and a molecule of component j. The activity coefficients can be derived from Eqn.11.86 and are given by

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{11.89}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \tag{11.90}$$

Orye and Prausnitz [71] studied the application of this equation to several miscible binary systems and found it to represent the excess Gibbs free energy quite satisfactorily. The advantage of Wilson's equation is that it predicts the temperature dependence of the activity coefficients. However, Wilson's equation has two disadvantages. The first disadvantage is that it is not applicable to systems in which $\ln \gamma$ exhibits a maxima or minima. The second disadvantage is its inability to predict limited miscibility. Hence the Wilson equation can be used only for completely miscible systems or for partially miscible systems in the regions where only one liquid phase exists.

Example 11.9 Wilson's parameters Λ_{12} and Λ_{21} for the system nitromethane(1)–carbon tetrachloride(2) at 45°C are 0.1156 and 0.2879 respectively. Calculate the activity coefficients for a nitromethane/carbon tetrachloride solution at $x_1 = 0.3$.

Solution We have

$$\ln \gamma_1 = -\ln(0.3 + 0.1156 \times 0.7) + 0.7 \left[\frac{0.1156}{0.3 + 0.1156 \times 0.7} - \frac{0.2879}{0.2879 \times 0.3 + 0.7}\right]$$

$$\ln \gamma_1 = 0.9213 \qquad \text{or} \qquad \gamma_1 = 2.5126$$

$$\ln \gamma_2 = -\ln(0.7 + 0.2879 \times 0.3) - 0.3 \left[\frac{0.1156}{0.3 + 0.1156 \times 0.7} - \frac{0.2879}{0.2879 \times 0.3 + 0.7}\right]$$

$$\ln \gamma_2 = 0.2591 \qquad \text{or} \qquad \gamma_2 = 1.2958$$

11.7.5.2 Non-random two liquid (NRTL) equation The Non-random two liquid (NRTL) equation proposed by Renon [72] is applicable to partially miscible as well as completely miscible systems. The NRTL equation for the excess Gibbs free energy is given by

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right] \tag{11.91}$$

where $$\tau_{12} = \frac{g_{12} - g_{22}}{RT} \tag{11.92}$$

$$\tau_{21} = \frac{g_{21} - g_{11}}{RT} \tag{11.93}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \tag{11.94}$$

$$G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{11.95}$$

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Non-random Two Liquid (NRTL) equation

$$\frac{g^E}{RT} = x_1 x_2 \left[\frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}}\right] \tag{11.91}$$

$$\ln \gamma_1 = x_2^2 \left[\tau_{21} \left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2}\right] \tag{11.96}$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2}\right] \tag{11.97}$$

where $G_{ij} = exp(-\alpha_{12}\tau_{ij})$.

τ_{12} and τ_{21} are related to energy parameters characteristic of interaction between molecules of components 1 and 2. α_{12} takes into account the non-randomness of the solution. α_{12} varies from 0.20 to 0.47. If $\alpha_{12} = 0$, the NRTL equation reduces to the two suffix Margules equation.

The universal quasichemical (UNIQUAC) equation is given by

$$\frac{g^E}{RT} = \frac{g^E}{RT}\text{ (combinatorial) } + \frac{g^E}{RT}\text{ (residual)} \tag{11.98}$$

The combinatorial part takes into account the size and shape of the molecules and the residual part takes into account the intermolecular forces.

The analytical solution of groups (ASOG) model which is a group contribution method considers a solution as a solution of functional groups. The functional groups are structural units such as CH_3, OH and others. The activity coefficients of the components are determined from the properties of the functional groups rather than by those of the components.

The UNIQUAC functional group activity coefficients (UNIFAC) method is another group contribution method for the estimation of γ_i. In this method also $\ln\gamma_i$ consists of two parts — a combinatorial part and a residual part. In this method the UNIQUAC relation for $\ln\gamma_i$ is directly used and the ASOG concept is adopted to evaluate the residual part $\ln\gamma_i^R$.

Solutions formed by mixing pure liquid components, each of which can exist as liquid at solution temperature, are called simple liquid solutions. The behavior of such solutions can be expressed in terms of the Lewis–Randall rule. Solutions of gases or solids in liquids are called non-simple liquid solutions because one of the components cannot exist as liquid at solution temperature. The fugacity of the component which cannot exist as liquid at the solution temperature is expressed in terms of Henry's Law.

Henry's law is given by $\hat{f}_i = x_i k_i$ where k_i is called the Henry's constant. k_i represents the fugacity which the component would exhibit had it existed as a liquid. This is a hypothetical or fictitious state.

Both the Lewis–Randall rule and Henry's law are used to define an ideal solution as

$$\hat{f}_i = x_i f_i^0 \tag{11.121}$$

where f_i^0 is the standard state or reference state fugacitv

$f_i^0 = f_i^*$ [for Lewis–Randall rule]

$f_i^0 = k_i$ [for Henry's law]

The Eqn.9.148 can be rewritten as

$$\gamma_i x_i f_i^* = \hat{\phi}_i^v y_i P \qquad [i = 1, 2, \ldots, c] \tag{12.1}$$

where γ_i = activity coefficient of component i in the solution, x_i = mole fraction of component i in the liquid phase, f_i^* = fugacity of component i in the standard state, $\hat{\phi}_i^v$ = fugacity coefficient of component i in the vapor phase, y_i = mole fraction of component i in the vapor phase and P = pressure at which the system is held.

The fugacity of a liquid at T and P is given by

$$(f^\ell)_{T,P} = P^s \left(\frac{f}{P}\right)_{T,P^s} \exp\left\{\frac{v^\ell(P-P^s)}{RT}\right\} \tag{9.149}$$

$$= P^s \phi^s \exp\left\{\frac{v^\ell(P-P^s)}{RT}\right\} \tag{12.2}$$

where $\phi^s = (f/P)_{T,P^s}$ = fugacity coefficient at saturation pressure P^s (12.3)

The standard state fugacity (f_i^*) is the fugacity of component i at the mixture temperature and at some arbitrarily chosen pressure and composition. The choice of standard state pressure and composition is dictated by convenience only. For most of the liquid solutions it is customary to choose the pure component liquid i at system temperature and pressure as the standard state for the component i. That is, the arbitrarily chosen pressure is the system pressure and the arbitrarily chosen composition is $x_i = 1$. Sometimes this standard state refers to a hypothetical state since the component i may not exist as pure liquid at system temperature and pressure. With this choice of the standard state, f_i^* is given by,

$$f_i^* = P_i^s \phi_i^s \exp\left\{\frac{v_i^\ell(P-P_i^s)}{RT}\right\} \tag{12.4}$$

where P_i^s = saturation pressure of component i at temperature T, v_i^ℓ = molar volume of liquid for component i, ϕ_i^s = fugacity coefficient of component i at saturation pressure, and the superscript s refers to saturation condition.

Substituting Eqn.12.4 in Eqn.12.1, we get

$$\gamma_i x_i P_i^s = \frac{\hat{\phi}_i^v}{\phi_i^s} y_i P \exp\left\{-\frac{v_i^\ell(P-P_i^s)}{RT}\right\} \quad [i = 1,2, \ldots, c] \tag{12.5}$$

Equation 12.5 is thermodynamically rigorous and can be called as the *basic equation for vapor–liquid equilibrium*. This equation provides a systematic means of analyzing vapor–liquid equilibrium data. We know that

$$\gamma_i = \gamma\,(T, P, x_i\text{'s}); \quad P_i^s = P(T)$$

$$\hat{\phi}_i^v = \phi\,(T, P, y_i\text{'s}); \quad \phi_i^s = \phi\,(T, P)$$

Thus Eqn.12.5 provides a relation among the variables T, P, x_i's and y_i's.

Application of the phase rule to an equilibrium vapor–liquid mixture gives that the number of degrees of freedom (F) is equal to the number of components (c) in the system since the number of phases P is equal to two. Usually one measures T or P and either x's or y's ($i = 1, 2, \ldots, c-1$ since $\sum x_i = 1$ and $\sum y_i = 1$). Then the remaining c variables can be estimated by solving Eqn.12.5 [which is a set of c equations]. Usually in the analysis of vapor–liquid equilibrium (VLE) data an engineer encounters one of the following problems.

Problem	Known	To estimate
Bubble pressure calculation	T, x_i's	P, y_i's
Dew pressure calculation	T, y_i's	P, x_i's
Bubble temperature calculation	P, x_i's	T, y_i's
Dew temperature calculation	P, y_i's	T, x_i's

Let us study the reduction of the experimental VLE data before we discuss these problems.

12.2 Reduction of VLE data

At low pressures (upto atleast 1 bar) the vapor phase can be assumed to behave like an ideal gas and hence $\hat{\phi}_i^v = 1$ and $\phi_i^s = 1$. At low pressures the Poynting correction factor $\exp\{v^\ell(P-P^s)/RT\}$ is negligibly small and it is approximately equal to unity. At low to moderate pressures (up to 10 bar) $\hat{\phi}_i^v$ and ϕ_i^s are approximately equal to each other and hence it is reasonable to assume that $(\hat{\phi}_i^v/\phi_i^s) = 1$. Thus at low to moderate pressures Eqn.12.5 reduces to

$$\gamma_i x_i P_i^s = y_i P \qquad (i = 1,2, \ldots, c)$$

$$\text{or} \quad \gamma_i = \frac{y_i P}{x_i P_i^s} \qquad (i = 1,2, \ldots, c) \tag{12.6}$$

Equation 12.6 is adequate to calculate the activity coefficients γ_i from experimental low pressure VLE data. For an ideal solution, $\gamma_i = 1$ and Eqn.12.6 reduces to the Raoult's law which is given by

$$y_i P = x_i P_i^s \qquad (i = 1, 2, \ldots, c) \tag{11.15}$$

Summing Eqn.12.6 over all the components, we get

$$\sum_i^c y_i P = P = \sum_i^c \gamma_i x_i P_i^s \tag{12.7}$$

Suppose isothermal VLE data is available and it is desired to obtain a correlation which fits the experimental data. The following procedure may be adopted for the reduction of the data.

- Determine P_i^s ($i = 1, 2, \ldots, c$) at the specified temperature.
- Calculate γ_i from the experimental values of x_i, y_i and P using Eqn.12.6.
- Calculate the molar excess Gibbs free energy g^E given by

$$\frac{g^E}{RT} = \sum x_i \ln \gamma_i \tag{11.36}$$

where α and β are unknown constants which are to be determined from the experimental P–x_1 data. For a binary system, the Gibbs–Duhem relation is given by

$$x_1\left(\frac{\partial \ln \gamma_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial \ln \gamma_2}{\partial x_1}\right)_{T,P} = 0 \tag{11.60}$$

or $$-(1-x_2)\frac{d\ln \gamma_1}{dx_2} = x_2\frac{d\ln \gamma_2}{dx_2} \tag{12.10}$$

Equation 12.10 can be rewritten as

$$\frac{d\ln(\gamma_1/\gamma_2)}{dx_2} = \frac{1}{x_2}\frac{d\ln \gamma_1}{dx_2} \tag{12.11}$$

Substituting Eqn.12.9 in Eqn.12.11, we get

$$\frac{d\ln(\gamma_1/\gamma_2)}{dx_2} = 2\alpha + 3\beta x_2 \tag{12.12}$$

Integrating Eqn.12.12, we get

$$\ln \gamma_2 = \ln \gamma_1 - 2\alpha x_2 - \frac{3\beta}{2}x_2^2 + K \tag{12.13}$$

where K is a constant. Making use of the fact that $\gamma_2 = 1$ at $x_2 = 1$, we get

$$K = \alpha + \frac{\beta}{2}$$

$$\therefore \quad \ln \gamma_2 = \left(\alpha + \frac{3}{2}\beta\right)x_1^2 - \beta x_1^3 \tag{12.14}$$

In principle one can solve Eqns.12.8, 12.9 and 12.14 and determine the values of α and β using the experimental P–x data. Knowing the values of α and β one can calculate γ_1 and γ_2 from Eqns.12.9 and 12.13 and hence y_1 and y_2 from Eqn.12.6.

In chemical process industries the distillation operation is usually carried at constant pressure and hence the isobaric VLE data is of much practical use. Let us now discuss the method of reducing the isobaric VLE data. Suppose the experimental isobaric VLE data for a system is available (may be fragmentary data only) and it is desired to compute the T–x–y data and to compare with the experimental results. For this purpose the following procedure may be adopted.

- Calculate the saturation pressures P_i^s of the components at the experimentally determined temperatures specified in the data.
- Calculate γ_i from the experimental values of P, T, x_i and y_i using Eqn.12.6.
- For each data point calculate the molar excess Gibbs free energy from the relation

$$\frac{g^E}{RT} = \sum x_i \ln \gamma_i$$

- Choose one of the molar excess Gibbs free energy models and determine the parameters.

Solution The Antoine constants of acetone (1) and cyclohexane (2) are given by

	A	B	C
Acetone (1)	7.11714	1210.595	229.664
Cyclohexane (2)	6.85146	1206.470	223.136

The Margules equations for the activity coefficients are given by

$$\ln\gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1] \tag{A}$$

$$\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2] \tag{B}$$

The saturation pressure is given by the Antoine equation

$$\log_{10} P_i^s = A - \frac{B}{t + C} \tag{C}$$

Choose $x_1 = 0.0115$. Then

$$\ln\gamma_1 = (1 - 0.0115)^2[2.0522 + 2(1.7201 - 2.0522) \times 0.0115] = 1.9978 \quad \text{or} \quad \gamma_1 = 7.3728$$

$$\ln\gamma_2 = (0.0115)^2[1.7201 + 2(2.0522 - 1.7201) \times (1 - 0.0115)] = 3.1431 \times 10^{-4}$$

or $\gamma_2 = 1.0003$

At 25°C: $P_1^s = 230.89$ Torr; $P_2^s = 97.57$ Torr

$$\begin{aligned} P &= \gamma_1 x_1 P_1^s + \gamma_2 x_2 P_2^s = 7.3728 \times 0.0115 \times 230.89 + 1.0003 \times (1 - 0.0115) \times 97.57 \\ &= 116.05 \text{ Torr} \end{aligned}$$

$$y_1 = \frac{\gamma_1 x_1 P_1^s}{P} = \frac{7.3728 \times 0.0115 \times 230.89}{116.05} = 0.1687$$

Similar calculations have been performed at other values of x_1 corresponding to the experimental values and the results are summarized below.

x_1	γ_1	γ_2	P (Torr)	y_1
0.0115	7.3728	1.0003	116.05	0.1687
0.1125	4.7473	1.0297	212.48	0.5804
0.3090	2.4155	1.2313	255.35	0.6749
0.5760	1.3501	1.9428	259.93	0.6908
0.6920	1.1631	2.5135	261.37	0.7110
0.7390	1.1122	2.8125	261.40	0.7260
0.7575	1.0954	2.9430	261.22	0.7334
0.8605	1.0292	3.8277	256.58	0.7969
0.9250	1.0081	4.5466	248.57	0.8662

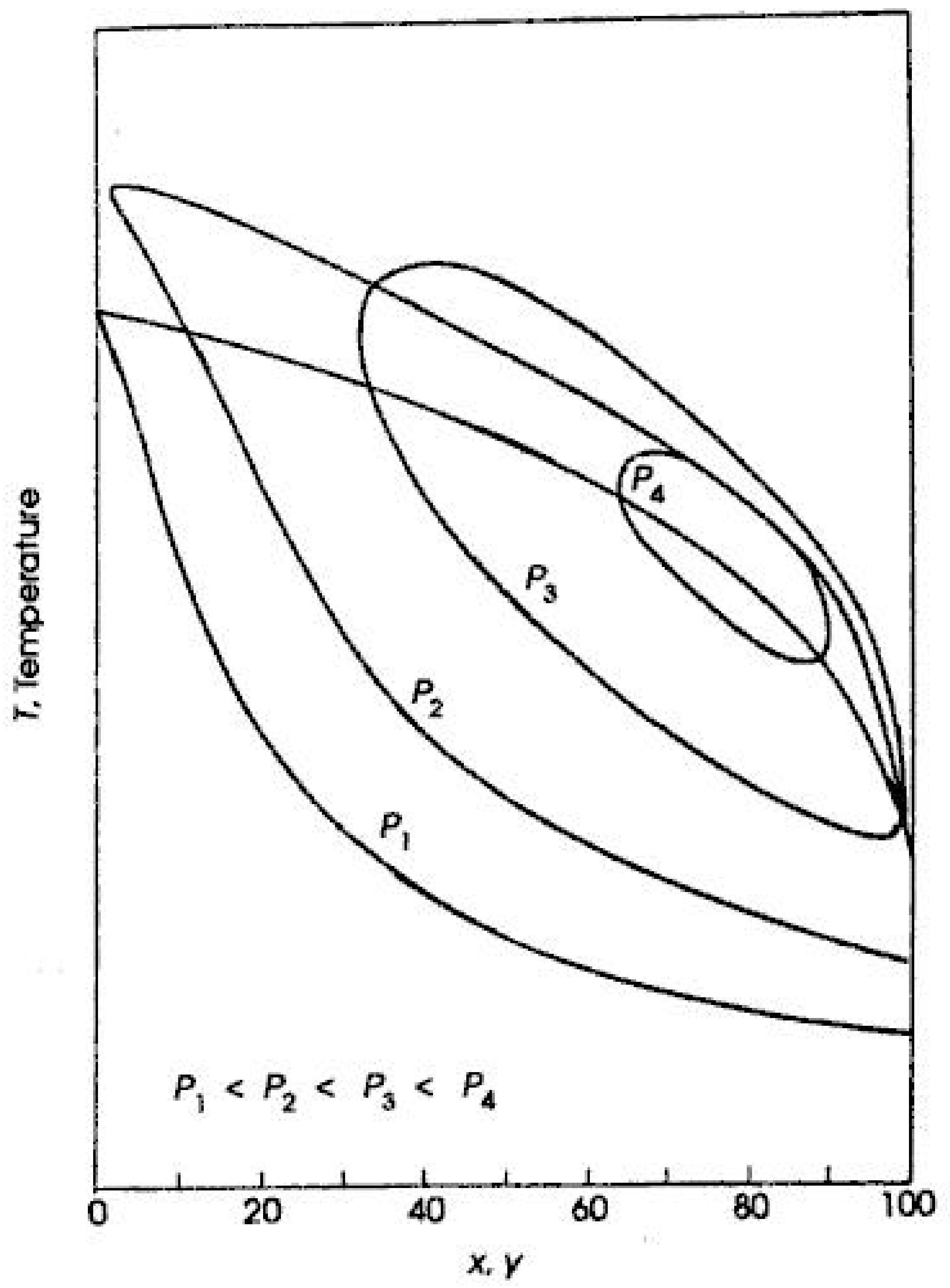

Fig.12.16 *Typical temperature–composition diagram at different pressures.*

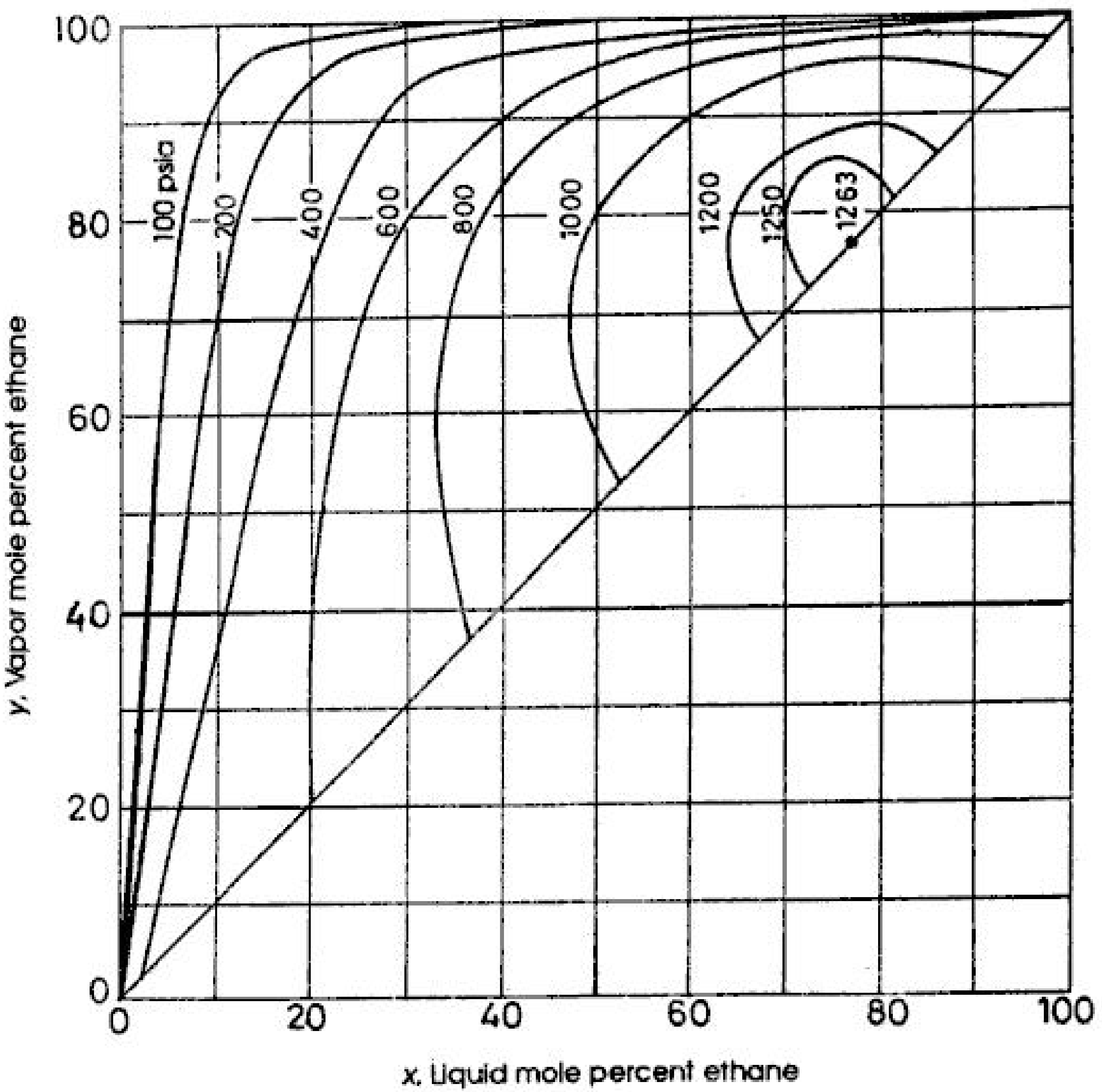

Fig.12.17 *y–x diagram for the ethane/heptane system at different pressures from "Notes on Phase Relations of Binary Mixtures in the Region of the Critical Point", by F.H. Barr-David, AIChE Journal, Vol. 2, No. 3, pp.426–427 (1956). Reproduced by permission of the American Institute of Chemical Engineers.*

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$$\text{or} \quad \sum_{i=1}^{c} \nu_i g_i^0 + RT \sum_{i=1}^{c} \ln (a_i)^{\nu_i} = 0$$

$$\text{or} \quad \Delta G^0 = -RT \ln K_a \quad \text{or} \quad K_a = \exp\left(-\frac{\Delta G^0}{RT}\right) \tag{14.9}$$

$$\text{where } \Delta G^0 = \sum_{i=1}^{c} \nu_i g_i^0 = \text{standard Gibbs free energy change of reaction} \tag{14.10}$$

$$K_a = \prod_i (a_i)^{\nu_i} = \text{equilibrium constant (expressed in activities) of reaction} \tag{14.11}$$

The quantity g_i^0 refers to the molar Gibbs free energy of pure component i in its standard state at a specified pressure and it is a function of temperature only. Therefore ΔG^0 and hence the equilibrium constant K_a is a function of temperature only. The equilibrium constant K_a for a reaction can be estimated through Eqn.14.9 from a knowledge of the standard Gibbs free energy change of the reaction.

Suppose one mole of H_2(g) and (1/2) mol of O_2(g) at a specified temperature T and pressure P enter a steady state flow reactor (say a fuel cell) in which the reaction between H_2(g) and O_2(g) occurs and HO_2(g) leaves the reactor at the same temperature and pressure. Then the useful work (electrical work in this case) that can be obtained per mole of H_2O(g) formed is equal to the decrease in the Gibbs free energy due to the reaction. That is

$$W = -\Delta G = g_{\mathrm{H_2(g)}} + \frac{1}{2} g_{\mathrm{O_2(g)}} - g_{\mathrm{H_2O(g)}}$$

If the reactants H_2(g) and O_2(g) as well as the product H_2O(g) are in their standard states then $W = -\Delta G^0$. Thus, one can measure the standard Gibbs free energy change for a reaction by measuring the useful work when the reaction is carried out in a steady flow reactor. In view of the large number of chemical reactions which can be carried out at different temperatures and pressures it is not possible to measure and tabulate ΔG^0 for all the reactions at all possible conditions. Therefore, it is convenient to tabulate the standard Gibbs free energy of formation (ΔG_f^0) of compounds from which ΔG^0 of a chemical reaction can be estimated. The *standard Gibbs free energy of formation* (ΔG_f^0) of a compound is the change in the Gibbs free energy of a formation reaction when the compound and its constituent elements are in their standard states. In the study of chemical reaction equilibrium, the usual standard states are the same as described in Section 4.8 and the standard state temperature is selected as the reaction temperature. The standard Gibbs free energies of formation (ΔG_{f298}^0) of several compounds at 298.15 K are presented in Appendix Table A.4. By convention ΔG_f^0 for elements has been assigned a value of zero.

Example 14.1 Calculate the standard Gibbs free energy change (ΔG_{298}^0) and the equilibrium constant at 298.15 K for the water-gas shift reaction

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$$

Solution We have

$$\begin{aligned} \Delta G_{298}^0 &= \Delta G_{f298}^0 \,[\mathrm{CO(g)}] + \Delta G_{f298}^0 \,[\mathrm{H_2O(g)}] - \Delta G_{f298}^0 \,[\mathrm{CO_2(g)}] - \Delta G_{f298}^0 \,[\mathrm{H_2(g)}] \\ &= -137.327 + (-228.600) - (-394.815) - 0 = 28.888 \text{ kJ} \end{aligned}$$

or $$K_a = K_\phi K_P = K_\phi K_y P^{\Sigma \nu_i} \tag{14.26}$$

where $$K_\phi = \prod_i \widehat{\phi}_i^{\nu_i} \tag{14.27}$$

$$K_P = \prod_i (y_i P)^{\nu_i} = \prod_i (P_i)^{\nu_i} = \text{equilibrium constant in terms of partial pressures} \tag{14.28}$$

$$K_y = \prod_i y_i^{\nu_i} = \text{equilibrium constant in terms of mole fractions} \tag{14.29}$$

At low to moderate pressures, the gas phase can be assumed to behave like an ideal gas and hence $\widehat{\phi}_i = 1$ for all i and hence $K_\phi = 1$. Thus for an ideal gas phase reaction we get

$$K_a = K_y P^{\Sigma \nu_i} \tag{14.30}$$

Example 14.5 Industrial methanol is produced according to the reaction

$$CO(g)+2H_2(g) \rightarrow CH_3OH\ (g)$$

Assuming that the reaction mixture attains a state of equilibrium, estimate the degree of conversion at 500 K and 5 bar pressure. If the reactor is fed with a stoichiometric mixture of $CO(g)$ and $H_2(g)$, determine the composition of the equilibrium mixture at 500 K and 5 bar pressure. The enthalpy of vaporization of CH_3OH at 298.15 K is 37.988 kJ/mol.

Solution We have

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$$

$$\Delta G_f^0 \text{ for } CH_3OH\ (g) = -161.781 \text{ kJ [see Example 14.2]}$$

$$\Delta G_{298}^0 = -161.781 - (-137.327) = -24.454 \text{ kJ};$$

$$\Delta H_{298}^0 = -200.660 - (-110.532)$$

$$= -90.128 \text{ kJ}$$

$$\Delta a = 18.382 - 28.068 - 2 \times 27.012 = -63.710;$$

$$\Delta b = (101.564 - 4.631 - 2 \times 3.509) \times 10^{-3}$$

$$= 89.915 \times 10^{-3}$$

$$\Delta c = -28.683 \times 10^{-6}; \quad \Delta d = 0; \quad \Delta e = (0.258 - 2 \times 0.690) \times 10^5 = -1.122 \times 10^5$$

$$\Delta H_{f298}^0 [CH_3OH(g)] = \Delta H_{f298}^0 [CH_3OH(l)] + \Delta h_v = -238.648 + 37.988 = -200.660 \text{ kJ}$$

$$\Delta H_T^0 = \Delta H_0 + \Delta a T + \frac{\Delta b}{2} T^2 + \frac{\Delta c}{3} T^3 + \frac{\Delta d}{4} T^4 - \frac{\Delta e}{T}$$

$$-901\ 28 = \Delta H_0 - 63.710 \times 298.15 + \frac{89.915 \times 10^{-3}}{2} \times (298.15)^2 - \frac{28.683 \times 10^{-6}}{3} (298.15)^3 + \frac{1.122 \times 10^5}{298.15}$$

Solution

Component	Mole number in feed	Mole number at exit	Mole fraction at exit
CO	1	$1-\epsilon$	$(1-\epsilon)/(3.02-2\epsilon)$
H_2	2	$2(1-\epsilon)$	$2(1-\epsilon)/(3.02-2\epsilon)$
CH_3OH	0.02	$0.02+\epsilon$	$(0.02+\epsilon)/(3.02-2\epsilon)$
	Total	$(3.02-2\epsilon)$	

$$K_y = \frac{(0.02+\epsilon)/(3.02-2\epsilon)}{\left(\frac{(1-\epsilon)}{(3.02-2\epsilon)}\right)\left(\frac{2(1-\epsilon)}{(3.02-2\epsilon)}\right)^2} \doteq \frac{(0.02+\epsilon)(1.51-\epsilon)^2}{(1-\epsilon)^3}$$

$$K_a = K_\phi K_y P^{\Sigma\nu_i} = K_y(5)^{-2} \qquad \text{[since } K_\phi = 1 \text{ at low pressure]}$$

$$K_a = 4.973\times10^{-3} \qquad \text{[see Example 14.5]}$$

$$\therefore \quad 25\times4.973\times10^{-3} = \frac{(0.02+\epsilon)(1.51-\epsilon)^2}{(1-\epsilon)^3} \quad \text{or} \quad \epsilon = 0.031\,65$$

The degree of conversion reduced from 0.0506 to 0.03165 by the addition of 0.02 mol CH_3OH to the stoichiometric mixture of CO and H_2 [compare with the result of Example 14.5].

14.5 Adiabatic reaction temperature

In industries several reactions are carried out under adiabatic conditions where the reactants enter the reactor at some temperature and the reactor effluent leaves at a different temperature. For example, in a combustion chamber, the gaseous fuel and air or oxygen enter at the ambient temperature and the combustion products leave at a higher temperature. In Section 4.8.6 the calculation of adiabatic flame temperature is discussed where it was assumed that the reaction goes to completion and the dissociation of the products does not occur. In reality the reaction may not go to completion and some products may dissociate also at the reaction temperature. Therefore it is necessary to take into account the equilibrium conversion in the calculation of adiabatic flame temperature. To estimate the equilibrium conversion it is necessary to know the reaction temperature and to estimate the exit temperature, it is necessary to have a knowledge of the equilibrium conversion. Since the equilibrium conversion and exit temperature are interrelated, they should be determined simultaneously. The following example illustrates the method of estimating adiabatic reaction temperature.

Example 14.10 A stoichiometric mixture of $H_2(g)$ and $O_2(g)$ at 298.15 K and 0.1 MPa enters an adiabatic burner. Assuming that the burner is operating at 0.1 MPa pressure determine the adiabatic reaction temperature and the composition of the burned gases.

Solution The reaction in the burner can be considered to follow the two-step imaginary process as shown in Fig.14.1. Energy balance on the steady flow adiabatic reactor gives

$$Q = \Delta H_1 + \Delta H_2 = \int_{298.15}^{T}\left(\sum_R N_i C_{p_i}^0\right) dT + \epsilon\Delta H_T^0 = 0$$

Divide the first row by −1 and introduce zeros in the first column [except the diagonal element (1, 1)] to obtain the following matrix:

$$\begin{pmatrix} 1 & 1 & -1 & -3 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 & 0 \\ 0 & -1 & -1 & 1 & 1 & 0 \\ 0 & 0 & 1 & 0 & -1 & 1/2 \\ 0 & 3 & -1 & -3 & 1 & -2 \\ 0 & 2 & 0 & -2 & 0 & -1 \end{pmatrix}$$

Divide the second row with −1 and introduce zeros in the second column (except the first two elements) to obtain the following matrix:

$$\begin{pmatrix} 1 & 1 & -1 & -3 & 0 & 0 \\ 0 & 1 & 1 & -1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & -1 & 1/2 \\ 0 & 0 & -4 & 0 & 4 & -2 \\ 0 & 0 & -2 & 0 & 2 & -1 \end{pmatrix}$$

Now we have a zero in the third diagonal element. Since all other elements in the third row are zeros it is not possible to get a nonzero element as the third diagonal element. Therefore, we proceed to the fourth row. The element at (4, 4) is zero. Hence we interchange the third and fourth columns to obtain a nonzero diagonal element. Then the matrix appears as

$$\begin{pmatrix} 1 & 1 & -3 & -1 & 0 & 0 \\ 0 & 1 & -1 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 1/2 \\ 0 & 0 & 0 & -4 & 4 & -2 \\ 0 & 0 & 0 & -2 & 2 & -1 \end{pmatrix}$$

Now the fourth diagonal element is 1. Therefore, we introduce zeros for the elements below the diagonal element in the fourth column to obtain the following matrix:

$$\begin{pmatrix} 1 & 1 & -3 & -1 & 0 & 0 \\ 0 & 1 & -1 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 1/2 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

This matrix contains ones and zeros only as diagonal elements and all the elements below the diagonal are zeros. This indicates that the elimination is complete. Only three diagonal elements contain nonzero values and hence only three primary reactions are needed for the complete description of the reaction mixture. The set of primary reactions are given by the rows (1, 2 and 4) which contain nonzero diagonal elements. They are

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

where $N = \sum_{i=1}^{c} N_i$ (since for an ideal gas mixture $\hat{f}_i/f_i^0 = (y_i f_i^0)/f_i^0 = N_i/N$). The mole numbers N_i must satisfy the conservation condition

$$\sum a_{ji} N_i = b_j \qquad [j = 1, 2, \ldots, M] \qquad (14.40)$$

where a_{ji} = number of j atoms per molecule of component i, b_j = number of j atoms in the reaction mixture and M = number of atoms (like C, H, O, N) constituting the reaction mixture. Then the problem reduces to minimizing G/RT given by Eqn.14.39 subject to the mass balance conditions given by Eqns.14.40.

Let us now develop an iterative method of solving the set of above equations. Suppose the mole numbers of the species, that satisfy the mass balance constraints, after the kth iteration are denoted by N_i^k. Then Eqn.14.39 gives

$$\frac{G^k}{RT} = \sum_{i=1}^{c} N_i^k \left(\frac{g_i^0}{RT} + \ln \frac{N_i^k}{N^k} \right) \qquad (14.41)$$

Expanding (G/RT) in a Taylor's series around N_i^k and dropping the higher order terms, we get

$$\frac{G^{k+1}}{RT} = \frac{G^k}{RT} + \sum_{i=1}^{c} \left(\frac{g_i^0}{RT} + \ln \frac{N_i^k}{N^k} \right) (N_i^{k+1} - N_i^k) + \frac{1}{2} \sum_{i=1}^{c} N_i^k \left\{ \frac{N_i^{k+1} - N_i^k}{N_i^k} - \frac{N^{k+1} - N^k}{N^k} \right\}^2 \qquad (14.42)$$

Let us now associate the Lagrange multipliers Π_j with the mass balance constraints and define ϕ^{k+1} as

$$\phi^{k+1} = \frac{G^{k+1}}{RT} + \sum_{j=1}^{M} \Pi_j \left(b_j - \sum_{i=1}^{c} a_{ji} N_i^{k+1} \right) \qquad (14.43)$$

The minimum in ϕ^{k+1} occurs when

$$\frac{\partial \phi^{k+1}}{\partial N_i^{k+1}} = \left(\frac{g_i^0}{RT} + \ln \frac{N_i^k}{N^k} \right) + \left(\frac{N_i^{k+1}}{N_i^k} - \frac{N^{k+1}}{N^k} \right) - \sum_{j=1}^{M} \Pi_j a_{ji} = 0 \quad [i = 1, 2, \ldots, c] \qquad (14.44)$$

The unknowns in Eqn.14.44 are N_i^{k+1} (c values), N^{k+1} and M values of Π_j. That is a total of $(c + M + 1)$ unknowns are to be estimated from Eqns.(14.44) which are c in number, and mass balance equations (which are M in number) given by

$$\sum_{i=1}^{c} a_{ji} N_i^{k+1} = b_j \qquad [j = 1, 2, \ldots, M] \qquad (14.45)$$

and the total mole number of the mixture given by

$$N^{k+1} = \sum_{i=1}^{c} N_i^{k+1} \qquad (14.46)$$

The set of Eqns.(14.44)–(14.46) can be simplified and rearranged as shown below. Equation (14.44) can be rearranged to obtain

$$N_i^{k+1} = N^{k+1} \frac{N_i^k}{N^k} + N_i^k \left(\sum_{j=1}^{M} \Pi_j a_{ji} \right) - N_i^k \alpha_i^k \qquad (14.47)$$

14.29 In the steam cracking of methane for the production of hydrogen the following reactions are believed to occur:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

$$CO_2 \rightarrow CO + \frac{1}{2}O_2$$

Determine the number of independent reactions using the Gauss elimination method.

14.30 Rework Problem 14.28 using Denbigh's method.

14.31 Rework Problem 14.29 using Denbigh's method.

14.32 In the steam cracking of methane, H_2O, CO, CO_2 and H_2 only are present to a significant amount in the product gas. Determine a set of primary reactions to describe the state of the reaction mixture.

14.33 The following two independent reactions occur in the steam cracking of methane at 1000 K and 1 bar:

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

Assuming that the reaction mixture is an ideal gas determine the equilibrium composition of the gas leaving the reactor if an equimolar mixture of CH_4 and H_2O is fed to the reactor.

14.34 Carbon black is produced from methane at 1000 K and 1 bar according to the reaction

$$CH_4(g) \rightarrow C(s) + 2H_2(g)$$

Estimate the equilibrium constant at 1000 K and determine the fraction of methane converted into carbon black. Assume that the molar heat capacity of C(s) is constant and is equal to 8.792 J/mol K.

14.35 Ferrous oxide (FeO) is reduced to metallic iron by reacting it with carbon monoxide at 1000°C and 1 bar according to the reaction

$$FeO(s) + CO(g) \rightarrow Fe(s) + CO_2(g)$$

Assuming that equilibrium is attained, determine the mass of metallic iron produced for one kmol of CO admitted into the reactor. At 1000°C, the equilibrium constant K_a is 0.403 with the conventional standard states for gases and solids. The atomic mass of Fe is 55.85 amu.

14.36 Estimate the decomposition pressure of calcium carbonate at 500 K and 1000 K. Also determine the temperature necessary to produce a decomposition pressure of 1 bar.

14.37 Hydrated sodium carbonate decomposes according to the reaction

$$Na_2CO_3.H_2O(s) \rightarrow Na_2CO_3(s) + H_2O(g)$$

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Table A.7 *Contd.*

S.No.	Substance	Antoine constants			Temperature range (°C)
		A	B	C	
38.	Methyl acetate	7.06524	1157.630	219.726	2 − 56
39.	2-Methyl butane	6.80464	1027.110	233.945	−83 − 28
40.	3-Methyl butanol	7.38170	1373.780	174.333	10 − 131
41.	2-Methyl-1-butene	6.86364	1048.876	232.194	1 − 63
42.	2-Methyl-2-butene	6.92322	1099.075	233.317	2 − 70
43.	Methyl cyclohexane	6.83900	1278.570	222.168	−36 − 102
44.	Methyl cyclopentane	6.86640	1188.050	226.276	15 − 73
45.	Methyl formate	7.34684	1216.480	240.370	−74 − 32
46.	Methyl methacrylate	8.38448	2191.430	297.058	−31 − 101
47.	2-Methyl pentane	6.86839	1151.401	228.477	12 − 61
48.	3-Methyl pentane	6.86532	1161.429	228.205	15 − 64
49.	4-Methyl-2-pentanone	6.67272	1168.408	191.944	22 − 116
50.	2-Methyl-1-propanol	8.53516	1950.940	237.147	−9 − 108
51.	Methyl propionate	6.94244	1170.236	208.751	21 − 79
52.	2-Methyl pyridine	7.03237	1415.725	211.625	80 − 168
53.	Nitromethane	7.28166	1446.937	227.600	56 − 136
54.	Pentane	6.87632	1075.780	233.205	−50 − 58
55.	1-Pentanol	7.39824	1435.570	179.798	14 − 138
56.	2-Pentanone	7.02193	1313.847	215.009	57 − 112
57.	3-Pentanone	7.23064	1477.021	237.517	36 − 102
58.	1-Pentene	6.84268	1043.206	233.344	13 − 31
59.	1-Propanol	8.37895	1788.020	227.438	−15 − 98
60.	2-Propanol	8.87829	2010.330	252.636	−26 − 83
61.	Propionic acid	7.99064	1929.300	236.430	25 − 141
62.	Propionic aldehyde	6.39172	830.802	188.670	18 − 48
63.	Propylene oxide	7.01443	1086.369	228.594	−19 − 115
64.	Pyridine	7.01328	1356.930	212.655	−19 − 115
65.	Tert-butanol	7.36168	1180.930	180.476	−20 − 83
66.	Triethyl amine	6.89890	1251.800	222.000	−13 − 127
67.	2,2,4-Trimethyl pentane	6.80304	1252.590	220.119	24 − 100
68.	Tetrachloro ethylene	7.62930	1803.960	258.976	2 − 121
69.	Tetrahydrofuran	6.99515	1202.290	226.254	23 − 100
70.	Tribromo methane	6.82182	1376.748	200.966	30 − 101
71.	Toluene	6.95087	1342.310	219.187	−27 − 111
72.	p-Xylene	6.99053	1453.430	215.310	27 − 166

$$\log_{10} P = A - \frac{B}{t + C}$$

where P is vapor pressure in Torr and t is in °C.

[*] Source: Gmehling, J., Onken, U. and Arit, W., "*Vapor–Liquid Equilibrium Data Collection*", *DECHEMA Chemistry Data Series*, Vol. I (1977).

Table A.10 *Saturated steam: Pressure table**

Pressure	Temperature	Specific volume		Specific enthalpy		Specific entropy	
P (bar)	t (°C)	v_f m^3/kg	v_g m^3/kg	h_f kJ/kg	h_g kJ/kg	s_f kJ/kg K	s_g kJ/kg K
0.01	6.9828	0.001 000 1	129.20	29.34	2514.4	0.1060	8.9767
0.05	32.8980	0.001 005 2	28.19	137.77	2561.6	0.4763	8.3960
0.10	45.8330	0.001 010 2	14.67	191.83	2584.8	0.6493	8.1511
0.15	53.9970	0.001 014 0	10.02	225.97	2599.2	0.7549	8.0093
0.20	60.0860	0.001 017 2	7.650	251.45	2609.9	0.8321	7.9094
0.3	69.1240	0.001 022 3	5.229	289.30	2625.4	0.9441	7.7695
0.4	75.8860	0.001 026 5	3.993	317.65	2636.9	1.0261	7.6709
0.5	81.3450	0.001 030 1	3.240	340.56	2646.0	1.0912	7.5947
0.6	85.9540	0.001 033 3	2.732	359.93	2653.6	1.1454	7.5327
0.7	89.9590	0.001 036 1	2.365	376.77	2660.1	1.1921	7.4804
0.8	93.5120	0.001 038 7	2.087	391.72	2665.8	1.2330	7.4352
0.9	96.7130	0.001 041 2	1.869	405.21	2670.9	1.2696	7.3954
1.0	99.6320	0.001 043 4	1.694	417.54	2675.4	1.3027	7.3598
1.5	111.3700	0.001 053 0	1.159	467.13	2693.4	1.4336	7.2234
2.0	120.2300	0.001 060 8	0.8854	504.70	2706.3	1.5301	7.1268
2.5	127.4300	0.001 067 5	0.7184	535.34	2716.4	1.6071	7.0520
3.0	133.5400	0.001 073 5	0.6056	561.43	2724.7	1.6716	6.9909
3.5	138.8700	0.001 078 9	0.5240	584.27	2731.6	1.7273	6.9392
4.0	143.6200	0.001 083 9	0.4622	604.67	2737.6	1.7764	6.8943
5.0	151.8400	0.001 092 8	0.3747	640.12	2747.5	1.8604	6.8192
6.0	158.8400	0.001 100 9	0.3155	670.42	2755.5	1.9308	6.7575
7.0	164.9600	0.001 108 9	0.2727	697.06	2762.0	1.9918	6.7052
8.0	170.4100	0.001 115 0	0.2403	720.94	2767.5	2.0457	6.6596
9.0	175.3600	0.001 121 3	0.2148	742.64	2772.1	2.0941	6.6192
10.0	179.8800	0.001 127 4	0.1943	762.61	2776.2	2.1382	6.5862
11.0	184.0700	0.001 133 1	0.1774	781.13	2779.7	2.1786	6.5497
12.0	187.9600	0.001 138 6	0.1632	798.43	2782.7	2.2161	6.5194
13.0	191.6100	0.001 143 8	0.1511	814.70	2785.4	2.2510	6.4913
14.0	195.0400	0.001 148 9	0.1407	830.08	2787.8	2.2837	6.4651
15.0	198.2900	0.001 153 9	0.1317	844.67	2789.8	2.3145	6.4406
16.0	201.3700	0.001 158 6	0.1237	858.56	2791.7	2.3436	6.4175
17.0	204.3100	0.001 163 3	0.1166	871.84	2793.4	2.3713	6.3957
18.0	207.1100	0.001 167 8	0.1103	884.58	2794.8	2.3976	6.3751
19.0	209.8000	0.001 172 3	0.1047	896.81	2796.1	2.4228	6.3554
20.0	212.3700	0.001 176 6	0.099 54	908.59	2797.2	2.4469	6.3367

Contd.

Table A.11 *Contd.*

Pressure (bar) (saturation temperature)		Temperature (°C)					
		300	400	500	600	700	800
18	*v*	0.1402	0.1684	0.1954	0.2219	0.2481	0.2742
(207.11°C)	*h*	3030.7	3251.9	3469.5	3690.9	3917.7	4150.3
	s	6.8257	7.1816	7.4830	7.7522	7.9981	8.2256
19	*v*	0.1325	0.1593	0.1849	0.2101	0.2350	0.2597
(209.80°C)	*h*	3027.9	3250.3	3468.4	3690.0	3917.1	4149.9
	s	6.7970	7.1550	7.4570	7.7265	7.9727	8.2003
20	*v*	0.1255	0.1511	0.1756	0.1995	0.2232	0.2467
(212.37°C)	*h*	3025.0	3248.7	3467.3	3689.2	3916.5	4149.4
	s	6.7696	7.1296	7.4323	7.7022	7.9485	8.1763
22	*v*	0.113 43	0.137 00	0.159 34	0.181 19	0.202 76	0.224 15
(217.24°C)	*h*	3019.3	3245.5	3465.1	3687.6	3915.2	4148.4
	s	6.7179	7.0821	7.3862	7.6568	7.9035	8.1316
24	*v*	0.103 36	0.125 22	0.145 82	0.165 92	0.185 75	0.205 39
(221.78°C)	*h*	3013.4	3242.3	3462.9	3685.9	3914.0	4147.5
	s	6.6699	7.0384	7.3439	7.6152	7.8624	8.0908
26	*v*	0.094 83	0.115 26	0.134 38	0.153 01	0.171 35	0.189 52
(226.04°C)	*h*	3007.4	3239.0	3460.6	3684.3	3912.7	4146.6
	s	6.6249	6.9979	7.3048	7.5768	7.8245	8.0531
28	*v*	0.087 51	0.106 71	0.124 58	0.141 94	0.159 02	0.175 91
(230.05°C)	*h*	3001.3	3235.8	3458.4	3682.6	3911.5	4145.6
	s	6.5824	6.9601	7.2685	7.5412	7.7893	8.0183
30	*v*	0.081 16	0.099 31	0.116 08	0.132 34	0.148 32	0.164 12
(233.84°C)	*h*	2995.1	3232.5	3456.2	3681.0	3910.3	4144.7
	s	6.5422	6.9246	7.2345	7.5079	7.7564	7.9857
32	*v*	0.075 59	0.092 83	0.108 65	0.123 95	0.138 97	0.153 81
(237.45°C)	*h*	2988.7	3229.2	3454.0	3679.3	3909.0	4143.8
	s	6.5037	6.8912	7.2026	7.4767	7.7257	7.9552
34	*v*	0.070 68	0.087 11	0.102 09	0.116 57	0.130 71	0.144 70
(240.88°C)	*h*	2982.2	3225.9	3451.7	3677.7	3907.8	4142.8
	s	6.4669	6.8595	7.1724	7.4473	7.6967	7.9266
36	*v*	0.066 30	0.082 02	0.096 26	0.109 96	0.123 37	0.136 61
(244.16°C)	*h*	2975.6	3222.5	3449.5	3676.1	3906.5	4141.9
	s	6.4315	6.8294	7.1439	7.4195	7.6693	7.8995

Contd.

Table A.12 *Contd.*

T (°C)	P^s	v_f	v_{fg}	v_g	h_f	h_{fg}	h_g	s_f	s_{fg}	s_g
	kPa		(m³/kg)			(kJ/kg)			(kJ/kgK)	
−12.0	203.771	0.000 697	0.081 369	0.082 065	25.2589	157.2262	182.4851	0.1019	0.6021	0.7039
−10.0	218.985	0.000 700	0.075 967	0.076 667	27.0978	156.2717	183.3695	0.1089	0.5939	0.7027
−8.0	235.050	0.000 703	0.070 994	0.071 697	28.9417	155.3070	184.2487	0.1158	0.5857	0.7015
−6.0	251.998	0.000 706	0.066 409	0.067 115	30.7908	154.3320	185.1227	0.1227	0.5777	0.7004
−4.0	269.859	0.000 709	0.062 178	0.062 887	32.6450	153.3461	185.9911	0.1296	0.5697	0.6993
−2.0	288.661	0.000 712	0.058 268	0.058 981	34.5045	152.3493	186.8538	0.1364	0.5619	0.6983
0.0	308.440	0.000 716	0.054 650	0.055 366	36.3695	151.3409	187.7104	0.1432	0.5541	0.6973
2.0	329.222	0.000 719	0.051 300	0.052 019	38.2398	150.3209	188.5608	0.1500	0.5463	0.6963
4.0	351.047	0.000 723	0.048 192	0.048 914	40.1161	149.2884	189.4095	0.1567	0.5387	0.6954
6.0	373.944	0.000 726	0.045 307	0.046 033	41.9981	148.2433	190.2414	0.1634	0.5311	0.6945
8.0	397.942	0.000 730	0.042 625	0.043 355	43.8861	147.1851	191.0712	0.1701	0.5235	0.6936
10.0	423.083	0.000 733	0.040 130	0.040 863	45.7805	146.1131	191.8935	0.1768	0.5160	0.6928
12.0	449.392	0.000 737	0.037 806	0.038 542	47.6811	145.0271	192.7082	0.1834	0.5086	0.6920
14.0	476.905	0.000 741	0.035 639	0.036 379	49.5883	143.9266	193.5149	0.1900	0.5012	0.6912
16.0	505.660	0.000 744	0.033 616	0.034 361	51.5024	142.8109	194.3132	0.1965	0.4939	0.6904
18.0	535.684	0.000 748	0.031 727	0.032 476	53.4234	141.6796	195.1030	0.2031	0.4866	0.6897
20.0	567.019	0.000 752	0.029 960	0.030 713	55.3518	140.5318	195.8836	0.2096	0.4794	0.6890
22.0	599.698	0.000 756	0.028 307	0.029 063	57.2878	139.3671	196.6550	0.2161	0.4722	0.6883
24.0	633.756	0.000 761	0.026 757	0.027 518	59.2318	138.1847	197.4165	0.2226	0.4650	0.6876
26.0	669.233	0.000 765	0.025 304	0.026 069	61.1841	136.9837	198.1679	0.2290	0.4579	0.6869
28.0	706.156	0.000 769	0.023 940	0.024 709	63.1449	135.7638	198.9088	0.2355	0.4508	0.6863
30.0	744.567	0.000 774	0.022 659	0.023 432	65.1147	134.5240	199.6387	0.2419	0.4438	0.6856
32.0	784.508	0.000 778	0.021 454	0.022 232	67.0939	133.2632	200.3571	0.2483	0.4367	0.6850
34.0	826.003	0.000 783	0.020 320	0.021 103	69.0827	131.9810	201.0637	0.2547	0.4297	0.6844
36.0	869.108	0.000 788	0.019 252	0.020 040	71.0821	130.6755	201.7577	0.2611	0.4227	0.6838
38.0	913.842	0.000 793	0.018 245	0.019 038	73.0921	129.3468	202.4388	0.2674	0.4157	0.6831
40.0	960.255	0.000 798	0.017 295	0.018 093	75.1134	127.9930	203.1063	0.2738	0.4087	0.6825
42.0	1008.379	0.000 803	0.016 399	0.017 202	77.1464	126.6134	203.7598	0.2801	0.4018	0.6819
44.0	1058.266	0.000 808	0.015 551	0.016 359	79.1921	125.2061	204.3982	0.2865	0.3498	0.6813
46.0	1109.948	0.000 814	0.014 749	0.015 563	81.2510	123.7702	205.0212	0.2928	0.3878	0.6806
48.0	1163.453	0.000 820	0.013 990	0.014 810	83.3234	122.3046	205.6281	0.2992	0.3808	0.6800
50.0	1218.838	0.000 826	0.013 272	0.014 097	85.4106	120.8071	206.2177	0.3055	0.3738	0.6793
52.0	1276.143	0.000 832	0.012 590	0.013 422	87.5132	119.2762	206.7894	0.3118	0.3668	0.6787
54.0	1335.408	0.000 838	0.011 943	0.012 781	89.6322	117.7099	207.3421	0.3182	0.3598	0.6780
56.0	1396.661	0.000 844	0.011 329	0.012 173	91.7681	116.1071	207.8752	0.3245	0.3527	0.6773
58.0	1459.963	0.000 851	0.010 745	0.011 596	93.9224	114.4648	208.3872	0.3309	0.3457	0.6766
60.0	1525.354	0.000 858	0.010 190	0.011 048	96.0960	112.7809	208.8769	0.3373	0.3385	0.6758

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Table A.14 *Contd.*

	1.40 MPa (56.1°C)				1.60 MPa (62.2°C)			
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
60	0.012 505	193.7127	211.2190	0.6873				
70	0.013 376	200.7568	219.4826	0.7117	0.011 142	198.4436	216.2704	0.6952
80	0.014 181	207.6403	227.4935	0.7347	0.011 922	205.6446	224.7200	0.7195
90	0.014 938	214.4275	235.3413	0.7566	0.012 642	212.6681	232.8954	0.7423
100	0.015 659	221.1581	243.0814	0.7776	0.013 318	219.5833	240.8924	0.7640
110	0.016 352	227.8582	250.7506	0.7979	0.013 961	226.4324	248.7697	0.7849
120	0.017 021	234.5454	258.3745	0.8176	0.014 577	233.2430	256.5664	0.8050
130	0.017 671	241.2324	265.9712	0.8367	0.015 172	240.0340	264.3094	0.8244
140	0.018 304	247.9281	273.5542	0.8552	0.015 749	246.8188	272.0179	0.8433
150	0.018 924	254.6391	281.1333	0.8734	0.016 312	253.6069	279.7063	0.8617
160	0.019 533	261.3703	288.7162	0.8911	0.016 862	260.4057	287.3852	0.8796
170	0.020 131	268.1250	296.3084	0.9084	0.017 402	267.2200	295.0625	0.8971
180	0.020 720	274.9058	303.9144	0.9254	0.017 932	274.0540	302.7445	0.9143
190	0.021 302	281.7146	311.5376	0.9420	0.018 453	280.9103	310.4359	0.9311
200	0.021 877	288.5527	319.1803	0.9583	0.018 968	287.7911	318.1403	0.9475

	1.80 MPa (67.8°C)				2.00 MPa (72.9°C)			
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
70	0.009 347	195.8272	212.6519	0.6787				
80	0.010 130	203.4585	221.6927	0.7047	0.008 654	201.0172	218.3260	0.6898
90	0.010 833	210.7793	230.2780	0.7287	0.009 359	208.7290	227.4472	0.7153
100	0.011 481	217.9157	238.5811	0.7512	0.009 994	216.1377	236.1250	0.7389
110	0.012 089	224.9376	246.6985	0.7727	0.010 580	223.3633	244.5238	0.7611
120	0.012 668	231.8877	254.6898	0.7933	0.011 132	230.4731	252.7364	0.7823
130	0.013 222	238.7942	262.5944	0.8131	0.011 656	237.5089	260.8211	0.8026
140	0.013 757	245.6764	270.4398	0.8324	0.012 159	244.4985	268.8165	0.8222
150	0.014 277	252.5482	278.2460	0.8510	0.012 645	251.4609	276.7499	0.8411
160	0.014 782	259.4193	286.0273	0.8692	0.013 115	258.4099	284.6408	0.8596
170	0.015 276	266.2971	293.7947	0.8869	0.013 574	265.3553	292.5038	0.8775
180	0.015 761	273.1871	301.5565	0.9043	0.014 023	272.3047	300.3499	0.8950
190	0.016 237	280.0934	309.3193	0.9212	0.014 462	279.2635	308.1874	0.9121
200	0.016 705	287.0190	317.0879	0.9378	0.014 894	286.2359	316.0230	0.9289

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Table A.17 *Contd.*

	0.350 MPa (−5.60°C)				0.400 MPa (−2.13°C)			
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
0	0.366 716	1331.9115	1460.2622	5.4874	0.319 029	1330.6504	1458.2621	5.4175
10	0.381 557	1347.9911	1481.5361	5.5639	0.332 138	1346.7958	1479.6510	5.4944
20	0.396 321	1364.2170	1502.9296	5.6381	0.345 168	1363.0817	1501.1489	5.5690
30	0.411 019	1380.5946	1524.4512	5.7103	0.358 129	1379.5140	1522.7657	5.6415
40	0.425 656	1397.1278	1546.1075	5.7806	0.371 030	1396.0972	1544.5090	5.7121
50	0.440 241	1413.8203	1567.9048	5.8491	0.383 876	1412.8357	1566.3861	5.7808
60	0.454 779	1430.6749	1589.8477	5.9160	0.396 675	1429.7328	1588.4027	5.8479
70	0.469 275	1447.6946	1611.9408	5.9813	0.409 431	1446.7920	1610.5642	5.9135
80	0.483 732	1464.8820	1634.1884	6.0452	0.422 148	1464.0159	1632.8750	5.9776
90	0.498 156	1482.2386	1656.5930	6.1078	0.434 830	1481.4069	1655.3387	6.0403
100	0.512 548	1499.7666	1679.1583	6.1691	0.447 480	1498.9668	1677.9591	6.1017
110	0.526 911	1517.4680	1701.8870	6.2292	0.460 102	1516.6981	1700.7393	6.1620
120	0.541 249	1535.3442	1724.7815	6.2882	0.472 698	1534.6022	1723.6816	6.2211

	0.500 MPa (3.90°C)				0.600 MPa (9.07°C)			
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
10	0.262 916	1344.3702	1475.8282	5.3767	0.216 727	1341.8949	1471.9315	5.2787
20	0.273 525	1360.7814	1497.5437	5.4521	0.225 729	1358.4395	1493.8770	5.3549
30	0.284 061	1377.3273	1519.3577	5.5253	0.234 655	1375.1057	1515.8984	5.4288
40	0.294 533	1394.0143	1541.2808	5.5964	0.243 513	1391.9017	1538.0096	5.5005
50	0.304 949	1410.8478	1563.3225	5.6657	0.252 313	1408.8347	1560.2225	5.5704
60	0.315 316	1427.8329	1585.4906	5.7332	0.261 061	1425.9110	1582.5477	5.6384
70	0.325 638	1444.9731	1607.7919	5.7992	0.269 763	1443.1353	1604.9932	5.7048
80	0.335 920	1462.2720	1630.2321	5.8637	0.278 424	1460.5120	1627.5665	5.7696
90	0.346 166	1479.7328	1652.8159	5.9267	0.287 049	1478.0448	1650.2739	5.8330
100	0.356 380	1497.3580	1675.5482	5.9885	0.295 640	1495.7369	1673.1208	5.8951
110	0.366 565	1515.1505	1698.4330	6.0490	0.304 201	1513.5922	1696.1125	5.9559
120	0.376 723	1533.1119	1721.4734	6.1084	0.312 734	1531.6121	1719.2528	6.0155
130	0.386 856	1551.2443	1744.6725	6.1666	0.321 243	1549.7991	1742.5452	6.0740
140	0.396 968	1569.5487	1768.0327	6.2239	0.329 730	1568.1555	1765.9934	6.1315
150	0.407 059	1588.0277	1791.5570	6.2801	0.338 195	1586.6829	1789.6000	6.1879
160	0.417 131	1606.6815	1815.2469	6.3355	0.346 642	1605.3827	1813.3677	6.2434

	0.700 MPa (13.61°C)				0.800 MPa (17.67°C)			
T (°C)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)	v (m^3/kg)	u (kJ/kg)	h (kJ/kg)	s (kJ/kg K)
20	0.191 560	1356.0538	1490.1458	5.2713	0.165 905	1353.6221	1486.3459	5.1976
30	0.199 340	1372.8473	1512.3854	5.3459	0.172 832	1370.5504	1508.8159	5.2729
40	0.207 050	1389.7581	1534.6932	5.4183	0.179 685	1387.5819	1531.3301	5.3460
50	0.214 699	1406.7954	1557.0850	5.4887	0.186 474	1404.7285	1553.9080	5.4170
60	0.222 294	1423.9666	1579.5728	5.5572	0.193 207	1421.9989	1576.5648	5.4860
70	0.229 842	1441.2781	1602.1675	5.6241	0.199 891	1439.4010	1599.3138	5.5533
80	0.237 347	1458.7351	1624.8781	5.6893	0.206 531	1456.9410	1622.1658	5.6190
90	0.244 814	1476.3424	1647.7124	5.7530	0.213 132	1474.6251	1645.1305	5.6831
100	0.252 247	1494.1038	1670.6769	5.8154	0.219 698	1492.4573	1668.2155	5.7458
110	0.259 650	1512.0228	1693.7777	5.8765	0.226 232	1510.4424	1691.4280	5.8072
120	0.267 024	1530.1027	1717.0197	5.9364	0.232 738	1528.5836	1714.7740	5.8673
130	0.274 374	1548.3458	1740.4073	5.9951	0.239 218	1546.8842	1738.2588	5.9263
140	0.281 700	1566.7548	1763.9447	6.0528	0.245 675	1565.3469	1761.8867	5.9842
150	0.289 005	1585.3319	1787.6353	6.1095	0.252 110	1583.9742	1785.6622	6.0411
160	0.296 290	1604.0781	1811.4816	6.1652	0.258 526	1602.7681	1809.5886	6.0969
170	0.303 558	1622.9961	1835.4871	6.2200	0.264 923	1621.7307	1833.6693	6.1519
180	0.310 810	1642.0865	1859.6537	6.2739	0.271 304	1640.8634	1857.9069	6.2060
190	0.318 046	1661.3511	1883.9836	6.3270	0.277 670	1660.1681	1882.3040	6.2592
200	0.325 269	1680.7908	1908.4790	6.3793	0.284 021	1679.6455	1906.8627	6.3117

Contd.

Table A.20 *Contd.*

		11	12	13	14	15	16	17	18	19	20
		CCOO	HCOO	CH_2O	CNH_2	CNH	$(C)_3N$	$ACNH_2$	Pyridine	CCN	COOH
1	CH_2	232.1	507.0	251.5	391.5	255.7	206.6	920.7	287.8	597.0	663.5
2	C=C	37.85	333.5	214.5	240.9	163.9	61.11	749.3	280.5	336.9	318.9
3	ACH	5.994	287.1	32.14	161.7	122.8	90.49	648.2	−4.449	212.5	537.4
4	$ACCH_2$	5688.	197.8	213.1	19.02	−49.29	23.50	664.2	52.80	6096.	872.3
5	OH	101.1	267.8	28.06	8.642	42.70	−323.0	−52.39	170.0	6.712	199.0
6	CH_3OH	−10.72	179.7	−128.6	359.3	−20.98	53.90	489.7	580.5	53.28	−202.0
7	H_2O	72.87	n.a.	540.5	48.89	168.0	304.0	243.2	459.0	112.6	−14.09
8	ACOH	−449.4	n.a.	−162.9	n.a.	n.a.	n.a.	119.9	−305.5	n.a.	408.9
9	CH_2CO	−213.7	−190.4	−103.6	n.a.	−174.2	−169.0	6201.	7.341	481.7	669.4
10	CHO	−110.3	766.0	304.1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	497.5
11	CCOO	0.0	−241.8	−235.7	n.a.	−73.50	−196.7	475.5	n.a.	494.6	660.2
12	HCOO	1167.	0.0	−234.0	n.a.	n.a.	n.a.	n.a.	−233.4	−47.25	−268.1
13	CH_2O	461.3	457.3	0.0	−78.36	251.5	5422.	n.a.	213.2	−18.51	664.6
14	CNH_2	n.a.	n.a.	222.1	0.0	−107.2	−41.11	−200.7	n.a.	358.9	n.a.
15	CNH	136.0	n.a.	−56.08	127.4	0.0	−189.2	n.a.	n.a.	147.1	n.a.
16	$(C)_3N$	2889.	n.a.	−194.1	38.89	865.9	0.0	n.a.	n.a.	n.a.	n.a.
17	$ACNH_2$	−294.8	n.a.	n.a.	−15.07	n.a.	n.a.	0.0	89.70	−281.6	−396.0
18	Pyridine	n.a.	554.4	−156.1	n.a.	n.a.	n.a.	117.4	0.0	−169.7	−153.7
19	CCN	−266.6	99.37	38.81	−157.3	−108.5	n.a.	777.4	134.3	0.0	n.a.
20	COOH	−256.3	193.9	−338.5	n.a.	n.a.	n.a.	493.8	−313.5	n.a.	0.0
21	CCl	35.38	n.a.	225.4	131.2	n.a.	n.a.	429.7	n.a.	54.32	519.1
22	CCl_2	−133.0	n.a.	−197.7	n.a.	n.a.	−141.4	140.8	587.3	258.6	543.3
23	CCl_3	176.5	235.6	−20.93	n.a.	n.a.	−293.7	n.a.	18.98	74.04	504.2
24	CCl_4	129.5	351.9	113.9	261.1	91.13	316.9	898.2	368.5	492.0	631.0
25	ACCl	−171.1	383.3	−25.15	108.5	102.2	2951.	334.9	n.a.	363.5	993.4
26	CNO_2	129.3	n.a.	−94.49	n.a.	n.a.	n.a.	n.a.	n.a.	0.2830	n.a.
27	$ACNO_2$	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	134.9	2475.	n.a.	n.a.
28	CS_2	243.8	n.a.	112.4	n.a.	n.a.	n.a.	n.a.	n.a.	335.7	n.a.
29	CH_3SH	n.a.	201.5	63.71	106.7	n.a.	n.a.	n.a.	n.a.	161.0	n.a.
30	Furfural	−146.3	n.a.	−87.31	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	570.6
31	DOH	152.0	n.a.	9.207	n.a.	n.a.	n.a.	192.3	n.a.	169.6	n.a.
32	I	21.92	n.a.	476.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	616.6
33	Br	24.37	n.a.	736.4	n.a.	n.a.	n.a.	n.a.	−42.71	136.9	5256.
34	$C \equiv C$	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	329.1	n.a.
35	DMSO	41.57	n.a.	−93.51	n.a.	n.a.	−257.2	n.a.	n.a.	n.a.	−180.2
36	ACRY	175.5	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−42.31	n.a.
37	ClCC	611.3	134.5	−217.9	n.a.	n.a.	n.a.	n.a.	281.6	335.2	898.2
38	ACF	n.a.	n.a.	167.3	n.a.	−198.8	116.5	n.a.	159.8	n.a.	n.a.
39	DMF	−82.12	−116.7	−158.2	49.70	n.a.	−185.2	343.7	n.a.	150.6	−97.77
40	CF_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
41	COO	−234.9	145.4	−247.8	n.a.	284.5	n.a.	−22.10	n.a.	−61.6	1179.
42	SiH_2	n.a.	n.a.	448.5	961.8	1464.	n.a.	n.a.	n.a.	n.a.	n.a.
43	SiO	n.a.	n.a.	n.a.	−125.2	1604.	n.a.	n.a.	n.a.	n.a.	n.a.
44	NMP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
45	CClF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
46	CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	−70.25
47	OCCOH	−3.444	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	119.2	n.a.
48	CH_2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
49	Morph	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50	Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	221.4	n.a.	n.a.

Contd.

Answers to problems

Chapter 1

1.1 N m^2 kg^{-2} **1.2** 9.8066 N; 9.8066 m/s^2; **1.3** 1.6235 m/s^2; 132.4 N

1.4 2.645 **1.5** Pa (m^3/mol)^2; m^3/mol **1.6** Pa (m^3/mol)^2 K$^{1/2}$; m^3/mol

1.7 37.067 kPa **1.8** 941.76 Pa **1.9** 50.97 kg

1.10 0.071 kg **1.11** 50.06 km **1.12** 24.597 km

1.13 3.9197 MPa **1.14** 3.6509 kmol; 27.391 × 10^{-3} kg/mol

Chapter 2

2.3 $Pv = RT$; R is a constant **2.5** Extensive **2.6** 127.42 m; 50 m/s

2.7 No **2.8** Metastable equilibrium

2.9 $RT \ln\left(\frac{v_2 - b}{v_1 - b}\right) + \left(\frac{a}{v_2} - \frac{a}{v_1}\right)$ **2.10** $\frac{P_2 v_2 - P_1 v_1}{1 - n}$ **2.11** 1 MJ

2.12 0.135 MJ; 0.105 MJ **2.13** 7.4826 kJ; 2.4942 kJ **2.14** −9.264 J; 169.415 kJ

2.15 424.429 kJ **2.16** 34.13°C; 7.6515

Chapter 3

3.1 1.083 m^3; 23.3172 mJ **3.2** 0.448 **3.3** 19.984 kg;19.398 kg; 0.586 kg

3.4 8.5836 **3.5** No **3.7** 9.319 kg

3.8

	n-Butane	Ethylene	Acetylene	Ammonia	CO_2
a[Pa(m^3/mol)^2]	1.3885	0.4567	0.4475	0.4252	0.3653
$b \times 10^4$(m^3/mol)	1.163	0.574	0.515	0.373	0.427

3.9 23.411 kg **3.10** 23.987 kg **3.11** (a) 0.7336 MPa; (b) 0.7051 MPa

3.12 1.2382 × 10^{-3} m^3/mol; 5.6668 × 10^{-5} m^3/mol

3.13 1.2382 × 10^{-3} m^3/mol; 5.7735 × 10^{-5} m^3/mol

6.6 $\mu = -\dfrac{KT^3}{27P}$ **6.7** $d\left(\dfrac{\mu}{T}\right) = -\dfrac{3R}{2}\dfrac{du}{u} - R\dfrac{dv}{v}$

6.8 $S = \dfrac{NS_0}{N_0} + NR\ln\left[\left(\dfrac{U}{U_0}\right)^{3/2}\dfrac{V}{V_0}\left(\dfrac{N}{N_0}\right)^{-5/2}\right]$ where $S_0 = \dfrac{5}{2}N_0R - N_0\left(\dfrac{\mu}{T}\right)_0$

6.9 70.47 kJ **6.10** 455.84 kJ **6.11** $H = 2\sqrt{\dfrac{KS^3P}{N}}$

6.12 $H = H_0\left(\dfrac{P}{P_0}\right)^{2/5}\left(\dfrac{N_0}{N}\right)^{-1}\exp\left(-\dfrac{2S_0}{5N_0R}\right)\exp\left(\dfrac{2S}{5NR}\right)$ where $H_0 = U_0 + P_0V_0$

6.13 203.92 kW **6.14** 29.5 kW **6.15** $A = -\dfrac{2T}{3}\sqrt{\dfrac{TVN}{3K}}$

6.16 $A = NRT\left[\dfrac{A_0}{N_0RT_0} - \ln\left\{\left(\dfrac{T}{T_0}\right)^{3/2}\dfrac{V}{V_0}\left(\dfrac{N}{N_0}\right)^{-1}\right\}\right]$ where $\dfrac{A_0}{N_0RT_0} = \dfrac{3}{2} - \dfrac{S_0}{N_0R}$

6.17 205.2 kJ **6.18** 351.42 kJ **6.19** $G = -\dfrac{T^3N}{27KP}$

6.20 $G = NRT\left[\dfrac{G_0}{N_0RT_0} - \ln\left\{\left(\dfrac{T}{T_0}\right)^{5/2}\dfrac{P_0}{P}\right\}\right]$ where $\dfrac{G_0}{N_0RT_0} = \dfrac{5}{2} - \dfrac{S_0}{N_0R}$

6.21 259.24 kW **6.22** $T^a = T^b$ **6.23** $P^a = P^b$ **6.24** $P^a = P^b$

Chapter 7

7.7 (a) $v(1 - T\beta)$; (b) $C_p/\beta v$; (c) $C_v + v\beta/\kappa$ **7.8** (a) $v(1 - T\beta)$; (b) $C_p/\beta v$; (c) $C_v + v\beta/\kappa$

7.13 $\dfrac{Rv^2(v-b)}{RTv^3 - 2a(v-b)^2}$; $\dfrac{v^2(v-b)^2}{RTv^3 - 2a(v-b)^2}$ **7.14** $\dfrac{v}{C_p}\left\{\dfrac{2a(v-b)^2 - RTv^2b}{RTv^3 - 2a(v-b)^2}\right\}$

7.16 2 MPa **7.17** $\dfrac{1}{C_v}\left(P - \dfrac{T\beta}{\kappa}\right)$; 0 **7.19** $T - \dfrac{P\kappa Ts}{\beta Ts - PC_v\kappa}$; $\dfrac{TC_v}{C_v - s}$ **7.20** 450.94 K

7.21 $V = \sqrt{\gamma v/\kappa}$ **7.22** 223 m **7.23** 187.65 m

7.24 T/C_v; T/C_p **7.25** ∞; $v + C_v\kappa/\beta$; $v(1 - T\beta)$

7.27 (a) $v(1 - T\beta)$; (b) $C_p/\beta v$; (c) $C_v + v\beta/\kappa$

7.29 $\dfrac{1}{C_v}\left(P - \dfrac{T\beta}{\kappa}\right)$; 0 **7.31** $T - \dfrac{P\kappa Ts}{\beta Ts - PC_v\kappa}$

12.12 $A = 1.3974$; $B = 2.4175$

P (Torr)	575.54	719.13	757.64	759.58	724.33
x_1	0.1	0.3	0.5	0.7	0.9
y_1	0.3099	0.5316	0.6007	0.6166	0.6691

12.13 $A = 0.4786$; $B = 0.7878$

P (Torr)	757.62	758.00	738.98	698.24	615.01
x_1	0.1	0.3	0.5	0.7	0.9
y_1	0.1067	0.2840	0.4324	0.5777	0.7860

12.14 $\gamma_i = P/P_i^s$; $A_{12} = \dfrac{2\ln\gamma_2}{x_1} + \dfrac{(x_2 - x_1)\ln\gamma_1}{x_2^2}$

$$A_{21} = \frac{2\ln\gamma_1}{x_2} + \frac{(x_2 - x_1)\ln\gamma_2}{x_1^2}$$

12.15 $A_{12} = 1.2273$; $A_{21} = 2.3001$

P (Torr)	562.16	718.72	758.75	760.23	719.30
x_1	0.1	0.3	0.5	0.7	0.9
y_1	0.2970	0.5422	0.6082	0.6113	0.6706

12.16 $A_{12} = 0.4752$; $A_{21} = 0.6963$

P (Torr)	757.58	757.90	738.04	695.32	609.21
x_1	0.1	0.3	0.5	0.7	0.9
y_1	0.1068	0.2831	0.4281	0.5737	0.7913

12.17 yes; $x_1 = 0.9055$; 904.05 Torr **12.19** 0.338; 0.28

12.20 2.59; 2.5 **12.21** 2.65 MPa; $x_1 = 0.1569$

12.22 2.15 MPa; $x_1 = 0.0247$; $x_2 = 0.1648$ **12.23** −8.5°C; $y_1 = 0.6375$

12.24 19°C; $y_1 = 0.65$; $y_2 = 0.228$ **12.27** No **12.28** No

Chapter 13

13.4 1.83°C **13.5** 5.46°C **13.6** $x_2 = 0.0457$

13.7 −2.07°C **13.8** 0.5478 kg **13.9** $x_2 = 0.0889$

13.10 112.9°C **13.11** (a) 6.1696 kJ/mol; (b) 80.36°C; (c) 94.4 Torr

13.13 485.69 kPa **13.14** 96.92 kPa **13.15** 0.3025 mol/litre

13.16 (a) 3.156 kPa; (b) −0.34°C; (c) 100.09°C

13.17 $x_2 = 0.3519$; 0.4453; 0.5553

13.18 $x_2 = 0.3520$ **13.19** $x_2 = 0.2721 \times 10^{-3}$ **13.20** $x_2 = 0.0212$

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