Subject: Thermodynamics & Chemical Kinetics
Course No. ChBC-34
LTP 3:1:0 (Credit: 4)

Syllabus:

Introduction: Thermodynamic system, surroundings, state, process, properties, equilibrium, heat and work.

Properties of Pure Simple Compressible Substance: P-V-T surface, P-V, T-V and T-P diagrams. Equations of state for ideal and real gases. Virial equation of state, van der Waals and Redlich-Kwong equations of state; Use of Thermodynamic tables.

First Law of Thermodynamics: Energy balance for closed systems. Various forms of energy balance. Specific heat, internal energy, enthalpy, and specific heat of ideal gases. Application of first law to non-flow isochoric, isobaric, isothermal, and adiabatic and polytropic processes. Conservation of mass for a control volume, mass and volume flow rates, mass balance for steady flow processes, flow work, steady flow energy equation. Application to various practical systems viz. nozzles, diffusers, etc. Transient Analysis.

Second Law of Thermodynamics: Second law, reversible and irreversible processes, Clausius and Kelvin Planck statements. Carnot cycle, Clausius inequality, entropy as a property, principle of increase of entropy. Calculation of entropy change.

Thermodynamic Cycles: Otto, Diesel, Rankine cycles and their applications.

Rate Expression and Reaction Mechanism: Use of pseudo steady state approximation to get rate expression from mechanism, temperature-dependence of reaction rate-collision theory, transition state theory, thermodynamics and Arrhenius law.

Interpretation of Kinetic Data of Batch Reactors: Constant volume and variable volume batch reactions, Integral and differential methods of analysis of data of uni, bi and tri-molecular irreversible reactions. Reversible reactions, homogeneously catalysed, auto-catalysed, series and parallel reactions. Estimation of rate constants and its temperature-dependence.

Solid-Catalysed Fluid Reactions: Characterization of catalyst, Physical and chemical adsorption, various reaction steps, Langmuir-Hinshelwood kinetics.

Kinetics of Biochemical Reactions: Microbial and enzymatic reactions. Substrate and product inhibition.

Books Suggested:

1. Smith, J.M., Van Ness H.C., Abbott, M.M., “Introduction to Chemical Engineering Thermodynamics”, McGraw-Hill (2005).
2. Çengel, Y.A. , Boles, M.A., “Thermodynamics: An Engineering Approach”, 6th Edn., McGraw-Hill (2008).

3. Borgnakke, C. , Sonntag R.E., “Fundamentals of Thermodynamics”, John Wiley & Sons (2009).
4. Levenspiel, O., “Chemical Reaction Engineering”, John Wiley & Sons (1998).
5. Fogler, H.S., “Elements of Chemical Reaction Eng.”, Prentice Hall of India (2005).

CHAPTER 1: THERMODYNAMIC SYSTEMS: BASIC CONCEPTS

1.1 Introduction

The word "Thermodynamics" originates from its Greek roots (*therme*, heat; *dynamis*, force). As a subject it is concerned with quantification of *inter-relation* between energy and the *change of state* of any real world system. The extent of such change of state due to transfer of energy *to* or *from* the system is captured through the basic equations of thermodynamics which are derived starting from a set of fundamental observations known as "Laws of Thermodynamics". The laws are essentially 'postulates' that govern the nature of interaction of real systems and energy. They are products of human experiential observations to which no exceptions have been found so far, and so are considered to be "laws". The scope of application of the laws of thermodynamics ranges from the microscopic to the macroscopic order, and indeed to cosmological processes. Thus, all processes taking place in the universe, whether in non-living or living systems, are subject to the laws of thermodynamics.

Historically speaking, thermodynamics, is an extension of Newtonian mechanics which considered mechanical forces (or energy) as the agent of change of state of a body (anything possessing mass), the state being defined by its position and momentum with respect to a frame of reference. With the discovery steam power which propelled the so-called 'Industrial Revolution' of the 18th century, it became evident that not only the direct application of mechanical energy can change the state of a system, but that fluids themselves can act as reservoir of energy, which can be harnessed to effect changes in the real world to human advantage. It was this observation that laid the foundations of thermodynamics, which now constitutes a generalized way of understanding and quantifying *all* changes that occur during processes taking place in the universe as a result of application of energy in any form.

1.2 Thermodynamic System: Select Definitions

It may be evident from the foregoing introduction, that for the purpose of any thermodynamic analysis it is necessary to define a 'system'. A ***system***, in general, is any part of the universe which may be defined by a boundary which distinguishes it from the rest of the universe. Such a thermodynamic system is usually referred to as ***control volume*** as it would possess a volume and would also contain a definite quantity of matter. The system boundary may be real or imaginary, and may change in shape as well as in size over time, i.e., increase or decrease.

A system can either be ***closed*** or ***open***. A closed system does not allow any transfer of mass (material) across its boundary, while an open system is one which does. In either case energy transfer can occur across the system boundary in any of its various forms; for example, heat, work, electrical / magnetic energy, etc. However, for most real world systems of interest to chemical engineers the primary forms of energy that may transfer across boundaries are heat and work. In contrast to closed or open systems, a system which is enclosed by a boundary that allows neither mass nor energy transfer is an ***isolated*** system.

All matter *external* to the system constitutes the ***surroundings***. The combination of the system and surroundings is called the ***universe***. For all practical purposes, in any thermodynamic analysis of a system it is necessary to include only the immediate surroundings in which the effects are felt.

A very common and simple example of a thermodynamic system is a gas contained in a piston-and-cylinder arrangement derived from the idea of steam engines, which may typically exchange heat or work with its surroundings. The dotted rectangle represents the 'control volume', which essentially encloses the mass of gas in the system, and walls (including that of the piston) form the boundary of the system. If the internal gas pressure and the external pressure (acting on the moveable piston) is the same, no net force operates on the system. If, however, there is a force imbalance, the piston would move until the internal and external pressures

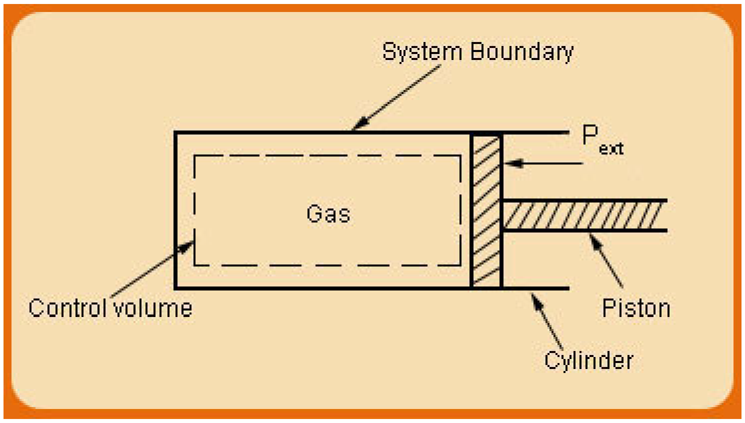


Fig. 1.1 Example of simple thermodynamic system

equalize. In the process, some net work would be either delivered *to* or *by* the system, depending on whether the initial pressure of the gas is lower or higher than the externally applied pressure. In addition, if there is a temperature differential between the system and the surroundings the former may gain or lose energy through heat transfer across its boundary.

This brings us to a pertinent question: how does one characterize the changes that occur in the system during any thermodynamic process? Intuitively speaking, this may be most readily done if one could measure the change in terms of some properties of the system. A thermodynamic system is, thus, characterized by its ***properties***, which essentially are *descriptors* of the *state* of the system. Change of state of a system is synonymous with change in the magnitude of its characteristic properties. The aim of the laws of thermodynamics is to establish a *quantitative* relationship between the energy applied during a process and the resulting *change* in the properties, and hence in the state of the system.

Thermodynamic properties are typically classified as ***extensive*** and ***intensive***. A property which depends on the size (i.e., mass) of a system is an extensive property. The total volume of a system is an example of an extensive property. On the other hand, the properties which are independent of the size of a system are called intensive properties. Examples of intensive properties are *pressure* and *temperature*. The ratio of an extensive property to the mass or the property per unit mass (or mole) is called *specific* property. The ratio of an extensive property to the number of moles of the substance in the system, or the property per mole of the substance, is called the molar property.

Specific volume (volume per mass or mole) $V = V^t / M$ ..(1.1)

Molar Volume (volume per mole) $V = V^t / N$

where,

$V^t =$ total system volume (m^3)
$M =$ total system mass (kg)
$N =$ total moles in system (kg moles)

1.3 Types of Energies associated with Thermodynamic Processes:

We know from the fundamentals of *Mechanics*, that the energy possessed by a body by virtue of its position or configuration is termed potential energy (PE). The potential energy of a body of mass m which is at an elevation z from the earth's surface (or any particular datum) is given by:

$$PE = mgz \qquad ..(1.2)$$

Where, g is the acceleration due to gravity (= 9.81 m/s^2).

The energy possessed by a body by virtue of its motion is called the kinetic energy (KE). For a body of mass m moving with a velocity u, the kinetic energy of the body is given by:

$$KE = \frac{1}{2}mu^2 \qquad ..(1.3)$$

It follows that, like any mechanical body, a thermodynamic system containing a fluid, in principle may possess both *PE* and *KE*. It may be noted that both PE and KE are expressed in terms of macroscopic, directly measurable quantities; they, therefore, constitute macroscopic, mechanical forms of energy that a thermodynamic system may possess. As one may recall from the basic tenets of mechanics, PE and KE are inter-convertible in form.

It may also be noted that PE and KE are forms of energy possessed by a body as a whole by virtue of its *macroscopic* mass. However, matter is composed of atoms /molecules which have the capacity to translate, rotate and vibrate. Accordingly, one ascribes three forms intra-molecular energies: *translational, rotational* and *vibrational.* Further, energy is also associated with the motion of the electrons, spin of the electrons, intra-atomic (nucleus-electron, nucleus-nucleus) interactions, etc. Lastly, molecules are also subject to inter-molecular interactions which are electromagnetic in nature, especially at short intermolecular separation distances. All these forms of energy are *microscopic* in form and they cannot be readily estimated in terms of macroscopically measurable properties of matter. It needs to be emphasized that the microscopic form of energy is distinct from PE and KE of a body or a system, and are generally *independent* of the position or velocity of the body. Thus the energy possessed by matter due to the microscopic modes of motion is referred to as the *internal energy* of the matter. The microscopic variety of energy forms the principal consideration in case of transformations that occur in a thermodynamic system. Indeed, as mentioned earlier, it is the realization that matter or fluids possessed useful form of microscopic energy (independent of macroscopic KE or PE) that formed the basis of the 18th century Industrial Revolution.

As we will see later, the majority of practical thermodynamic systems of interest are the ones that do not undergo change of state that entails significant change in its macroscopic potential and kinetic energies. Thus, it may be intuitively obvious that in a very general sense, when a thermodynamic system undergoes change of state, the attendant change in the internal energy is responsible for the energy leaving or entering the system. Such exchange of energy between a thermodynamic system and its surroundings may occur across the system boundary as either ***heat*** or ***work*** or both.

Thermodynamic Work:

Work can be of various forms: electrical, magnetic, gravitational, mechanical, etc. In general work refers to a form of energy transfer which results due to changes in the external *macroscopic* physical constraints on a thermodynamic system. For example, electrical work results when a charge moves against an externally applied electrical field. As we will see later, it is mechanical work that is most commonly encountered form in real thermodynamic systems, for example a typical chemical plant. In its simplest form, such work results from the energy applied to expand the volume of a system against an external pressure, or by driving a piston-head out of a cylinder against an external force. In both the last examples, work transfer takes place due to the application of a differential (or finite) force applied on the system boundary; the boundary either contracts or expands due to the application of such a force. In effect this results in the applied force acting over a distance, which results in mechanical energy transfer.

Consider the system in fig.1.2, where a force F acts on the piston and is given by pressure x piston area. Work *W* is performed whenever this force translates through a distance.

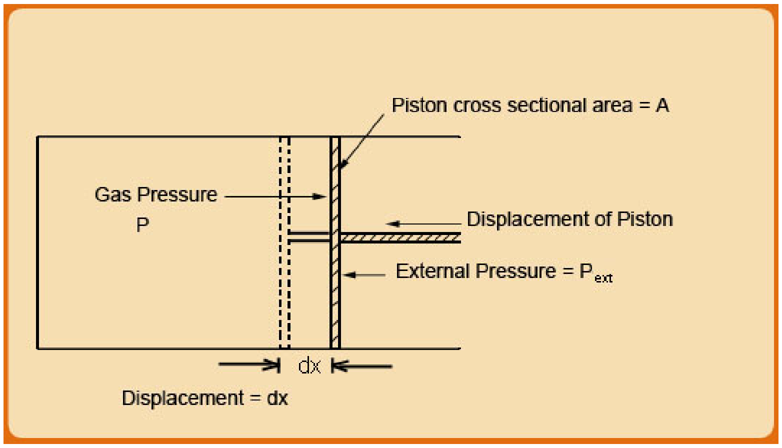


Fig. 1.2 Illustration of Thermodynamic Work

Thus for a differential displacement '*dx*' of the piston the quantity of work is given by the equation:

$$dW = Fdx \qquad ..(1.4)$$

Here *F* is the force acting along the line of the displacement *x*. If the movement takes place over a finite distance, the resulting work is obtained by integrating the above equation. By convention, work is regarded as *positive* when the displacement is in the same direction as the applied force and negative when they are in opposite directions. Thus, for the above example, the equation 1.4 may be rewritten as:

$$dW = -PAd(V^t / A) \qquad ..(1.5)$$

If the piston area 'A' is constant, then:

$$dW = -PdV^t \qquad ..(1.6)$$

As may be evident from eqn. 1.6, when work is done on a system (say through compression) the volume decreases and hence the work term is positive. The reverse is true when the system performs work on the surroundings (through expansion of its boundary).

Heat

We invoke here the common observation that when a hot and a cold object are contacted, the hot one becomes cooler while the cold one becomes warmer. It is logical to argue that this need be due to transfer of ‘something’ between the two objects. The transferred entity is called *heat*. Thus, heat is that form of energy that is exchanged between system and its surrounding owing to a temperature differential between the two. More generally, heat is a form of energy that is transferred due to temperature *gradient* across space. Thus heat always flows down the gradient of temperature; i.e., from a higher to a lower temperature regions in space. In absence of such temperature differential there is no flow of heat energy between two points. Heat flow is regarded to be *positive* for a thermodynamic system, if it enters the latter and *negative* if it leaves.

Like work, heat is a form of energy that exists only in transit between a system and its surrounding. Neither work nor heat may be regarded as being possessed by a thermodynamic system. In a fundamental sense, the ultimate repositories of energy in matter are the atoms and molecules that comprise it. So after transit both work and heat can only transform into the kinetic and potential energy of the constituent atoms and molecules.

1.4 Thermodynamic Equilibrium

In general change of state of a thermodynamic system results from existence of gradients of various types *within* or *across* its boundary. Thus a gradient of pressure results in momentum or convective transport of mass. Temperature gradients result in heat transfer, while a gradient of concentration (more exactly, of *chemical potential*, as we shall see later) promotes diffusive mass transfer. Thus, as long as *internal* or *cross-boundary* gradients of any form as above exist with respect to a thermodynamic system it will undergo change of state in time. The result of all such changes is to annul the gradient that in the first place causes the changes. This process will continue till all types of gradients are nullified. In the ultimate limit one may then conceive of a state where all gradients (external or internal) are non-existent and the system exhibits no further changes. Under such a limiting condition, the system is said to be in a state of thermodynamic *equilibrium*. For a system to be thermodynamic equilibrium, it thus needs to also satisfy the criteria for mechanical, thermal and chemical equilibrium.

Types of Thermodynamic Equilibrium

A thermodynamic system may exist in various forms of equilibrium: *stable, unstable* and *metastable*. These diverse types of equilibrium states may be understood through analogy with a simple mechanical system as depicted in fig. 1.3 – a spherical body in a variety of gradients on a surface.

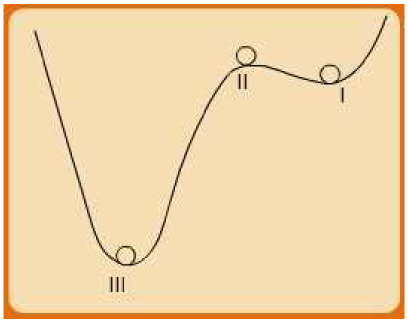


Fig. 1.3 Types of Mechanical Equilibrium

Consider the body to be initially in state ‘I’. If disturbed by a mechanical force of a very small magnitude the body will return to its initial state. However, if the disturbance is of a large magnitude, the body is unlikely to return to its initial state. In this type of situation the body is said to be in *unstable* equilibrium. Consider next the state ‘II’; even a very small disturbance will move the body to either positions ‘I’ or ‘III’. This type of original equilibrium state is termed *metastable*. Lastly, if the body is initially in state ‘III’, it will tend to return to this state even under the influence of relatively larger disturbances. The body is then said to be in a *stable* equilibrium state. If ‘E’ is the potential energy of the body and ‘x’ is the effective displacement provided to the body in the vertical direction, the three equilibrium states may be described by the following equations:

Stable Equilibrium: $\frac{\partial E}{\partial x} = 0; \quad \frac{\partial^2 E}{\partial x^2} > 0$ ..(1.7)

Unstable Equilibrium: $\frac{\partial E}{\partial x} = 0; \quad \frac{\partial^2 E}{\partial x^2} < 0$ ..(1.8)

Metastable Equilibrium: $\frac{\partial E}{\partial x} = 0; \quad \frac{\partial^2 E}{\partial x^2} = 0$ ..(1.9)

The above arguments may well be extended to understand equilibrium states of thermodynamic systems, which are relatively more complex in configuration. The disturbances in such cases could be mechanical, thermal or chemical in nature. As we shall see later (section 6.3), for thermodynamic systems, the *equivalent* of (mechanical) potential energy is *Gibbs free energy*. The considerations of change of Gibbs free energy are required to understand various complex behaviour that a thermodynamic system containing multiple phases and components (either reactive or non-reactive) may display under the influence of changes brought about by exchange of energy across its boundary.

1.5 The Phase Rule

Originally formulated by the American scientist Josiah Willard Gibbs in the 1870's, the phase rule determines the number of independent variables that must be specified to establish the *intensive* state of *any* system at equilibrium. The derivation of the general phase rule is shown in chapter 6, but here we state it without proof:

$F = 2 + N - \pi - r$ ..(1.10)

Here, F = degrees of freedom of the thermodynamic system in question; N = Number of components; π = number of co-existing phases, and r = number of independent reactions that may occur between the system components. For a non-reactive system, the phase rule simplifies to:

$F = 2 + N - \pi$ ..(1.11)

In the most general sense a thermodynamic system may be multiphase and multi-component in nature. A phase is a form of matter that is homogeneous in chemical composition and physical state. Typical phases are solids, liquids and gases. For a multiphase system, interfaces typically demarcate the various phases, properties changing abruptly across such interfaces. Various phases can coexist, but they *must be in equilibrium* for the phase rule to apply. An example of a three-phase system at equilibrium is water at its triple point (~ 0^0C, and 0.0061 bar), with ice, water and steam co-existing. A system involving one pure substance is an example of a single-component system. On the other hand mixtures of water and acetone have two chemically independent components.

The intensive state of a system at equilibrium is established when its temperature, pressure, and the compositions of all phases are fixed. These are therefore, regarded as phase-rule variables; but they are not all independent. The degrees of freedom derivable from the phase rule gives the number of variables which must be specified to fix all other remaining phase-rule variables. Thus, *F* means the number of intensive properties (such as temperature or pressure), which are independent of other intensive variables. For example, for a pure component gaseous system, phase rule yields *two* degrees of freedom. This implies that if one specifies temperature and pressure, all other intensive properties are then uniquely determined these two variables. Similarly for a biphasic system of a pure component – say water and steam – there is only one degree of freedom, i.e., either temperature or pressure may be specified to fix all other intensive properties of the system. At the triple point the degrees of freedom is zero, i.e., any change from such a state causes at least one of the phases to disappear.

1.6 Zeroth Law of Thermodynamics and Absolute Temperature

Thermometers with liquid working fluids are usually used for measurement of temperature. When such a device is brought in contact with a body whose temperature is to be measured, the liquid column inside the thermometer expands due to heat conducted from the body. The expanded length can be said to represent the degree of hotness in a somewhat *quantitative* manner.

The *Zeroth Law of Thermodynamics states* that if two bodies are in thermal equilibrium with a third body, then the two given bodies will be in thermal equilibrium with each other. The zeroth law of thermodynamics is used for measurement of temperature. In the Celsius temperature scale, two fixed points – ice point and steam point – are used to devise the scale. Thus, the freezing point of water (at standard atmospheric pressure) is assigned a value of zero, while the boiling point of pure water (at standard atmospheric pressure) denoted as 100. However for introducing detail, the distance between the two end points of the liquid column marks is arbitrarily divided into 100 equal spaces called *degrees.* This exercise can be extended both below zero and above 100 to expand the range of the thermometer.

The entire exercise can be carried out with any other substance as the thermometric fluid. However, for any specific measured temperature the extent of expansion of the liquid column will vary with the thermometric fluid as each fluid would expand to different extent under the influence of temperature. To overcome this problem, the *ideal gas* (see next section) has been arbitrarily chosen as the thermometric fluid. Accordingly, the temperature scale of the SI system is then described by the Kelvin unit (T^0K). Its relation to the Celsius (t^0C) scale is given by:

$$T(^0K) = 273.15 + t(^0C)$$

Thus the lower limit of temperature, called absolute zero on the Kelvin scale, occurs at –273.15^{0}C.

1.7 The Ideal Gas

In the foregoing discussions we have pointed out that a thermodynamic system typically encloses a fluid (pure gas, liquid or solid or a mixture) within its boundary. The simplest of the intensive variables that can be used to define its state are temperature, pressure and molar volume (or density), and composition (in case of mixtures). Let us consider for example a pure gas in a vessel. As mentioned above, by phase rule the system has two degrees of freedom. It is an experimentally observed phenomenon that in an equilibrium state the intensive variables such as pressure, temperature and volume obey a definitive inter-relationship, which in its simplest form is expressed mathematically by the Boyle's and Charles's laws. These laws are compositely expressed in the form of the following equation that is said to represent a behaviour termed as *Ideal Gas Law*:

$$PV = RT \qquad ..(1.12)$$

Where, P = system pressure (say, Pa = N/m^2), T = system temperature (in ^{0}K), V = gas molar volume (mol/m^3) and, R = universal gas constant $(= 8.314 J/mol\,^0K)$. The above relation is said to represent an equation of state, and may alternately be written as:

$$PV^t = nRT \qquad ..(1.13)$$

Where, V^t = total system volume; n = total moles of gas in the system. Units of typical thermodynamic variables and that of the gas constant are provided in Appendix I.

The equations (1.10) and (1.11) are also termed *Equations of State* (EOS) as they relate the variables that represent the thermodynamic state of a system in the simplest possible manner. It is obvious that the EOS indicates that if one fixes temperature and pressure the molar volume is automatically fixed as well, i.e., the latter is not an independent property in such a case.

The ideal gas law is a limiting law in the sense that it is valid primarily for gaseous systems at low pressure, strictly speaking at pressure far below the atmospheric. However, for practical purposes it is observed to remain valid at atmospheric pressures as well. As we shall see later, the ideal gas law serves as a very useful approximation as well as a datum for estimation of both the volumetric (chapter 2) as well as all other real fluid thermodynamic properties of practical interest (chapter 5, for example).

1.8 State and Path Dependent Thermodynamic Variables

Consider a gas at a certain temperature and a pressure within a piston-cylinder assembly (for example, fig. 1.2), which for arguments' sake we may assume to be isolated. If the piston position is held fixed at this point the gas state is said to be characterized by the temperature and the pressure and its corresponding volume. In its simplest form the relationship between these intensive variables may be described by (say) eqn. 1.12. Consider next that the gas is compressed by application of an extra force on the piston so that it moves inwards into the cylinder. This motion will continue till it reaches a point when the internal gas pressure equals the externally applied pressure on the piston. If there is no further increase in the force applied to the piston, the gas will also attain a new equilibrium state wherein the pressure and temperature would attain a new set of values. If, on the other hand the extra applied pressure is removed and the gas reverts to the earlier state the original temperature and pressure (and, of course volume) is restored. Extending this argument, in general, if the gas is heated or cooled, compressed or expanded, and then returned to its initial temperature and pressure, its intensive properties are restored to their initial values. It is evident, therefore, that such properties do not depend on the past history of the fluid or on the path by which it reaches a given state. They depend only on present state, irrespective of how they are attained. Such quantities are thus defined as *state variables.* Mathematically, this idea may be expressed as follows:

$$\int_{T_1}^{T_2} dT = T_2 - T_1 = \Delta T; \int_{P_1}^{P_2} dP = P_2 - P_1 = \Delta P; \int_{V_1}^{V_2} dV = V_2 - V_1 = \Delta V \qquad ..(1.14)$$

The changes in the above intensive properties depend only on the initial and final states of the system. They constitute point functions and their differentials are exact.

Let us next consider the case of thermodynamic work as defined by eqn. 1.6. It may be readily evident that if one can depict the exact variation of pressure and volume during a change of state of a system on a two-dimensional P-V graph, the area under the curve between the initial and final volumes equal the work associated with process. This is illustrated in fig. 1.4.

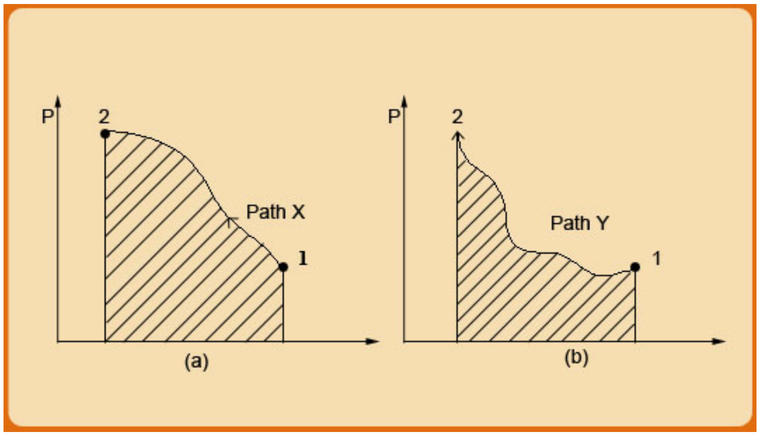


Fig. 1.4: Depiction of thermodynamic work on P-V plot

As shown in the above figure the work associated with a thermodynamic process clearly in dependent on the path followed in terms of P and V. It follows that if one were to go from state ‘1’ to ‘2’ by path X and then return to ‘1’ by path Y the work in the two processes would differ and so one would not be giving and taking work out of the system in equal measure. An entity such as P-V work is, therefore, described as a *path variable*, and therefore is not directly dependent on the state of the system. This is obviously distinctive from the case of state variables such as P and V (and T). Thus, for quantifying work, one cannot write an equation of the same type as (1.12). The more appropriate relation for such variables may be written as:

$$\int_1^2 \delta W = W_{12} \qquad ..(1.15)$$

It may be pointed out that the notation δ is used to depict differential quantum of work in order to distinguish it from the differential quantity of a state variable as in eqn. 1.14. We demonstrate in chapter 3 that, like P-V work, heat transferred between a system and the surrounding is also a path variable and so one may also write:

$$\int_1^2 \delta Q = Q_{12} \qquad ..(1.16)$$

Heat and work are therefore quantities, and not properties; they account for the energy changes that occur in the system and surroundings and appear only when changes occur in a system. Although time is not a thermodynamic coordinate, the passage of time is inevitable whenever heat is transferred or work is accomplished.

1.9 Reversible and Irreversible Thermodynamic Processes

We have seen above that in absence of any gradients (or motive forces) a thermodynamic system continues to remain in a state of equilibrium. Obviously, if a disturbance (i.e., mechanical, thermal or chemical potential gradient) is impressed upon such a system it will transit from its initial state of equilibrium. However, as it moves away from its initial state the originally applied gradients will diminish progressively in time, and ultimately when they are reduced to infinitesimal levels the system will attain a new equilibrium state. A question arises here as to the nature of the process of change: if the initially impressed disturbances are reversed in direction (not magnitude) can the system return to its first equilibrium state back through the same intermediate states as it went through during the first phase of change? If that happens we depict the process as *reversible*, if not, then the process is termed *irreversible*.

It is necessary to understand the concept of *reversibility* of thermodynamic process more deeply as it is an *idealized* form of process of change and without that consideration it is not possible to represent or understand real thermodynamic processes, which are generally irreversible in nature.

What makes a thermodynamic process reversible? To answer the question let us again take the example of the simple gas-in-piston-and-cylinder system as shown in figure 1.5.

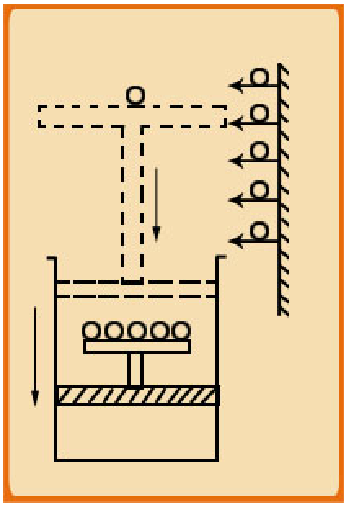


Fig. 1.5 Illustration of Reversibility of Thermodynamic Process

The system initially contains a pure gas whose pressure equals that exerted externally (due to piston weight), and its temperature is the same as that of the environment. Thus it is at equilibrium (say state ‘A’) as there are no mechanical, thermal or chemical concentration gradients in the system. Now a ball of a known weight is transferred on to the piston, whereupon the external pressure exceeds the gas pressure and the piston moves down to attain a new lower position at which point the gas has been compressed and its pressure once again equals that applied externally. At the same time if any differentials in temperature (within or across the system boundary) and internal concentration distribution of the gas molecules result due to the applied mechanical imbalance, heat and mass transfer will take place simultaneously until these gradients are also annulled and the system eventually comes to rest at a new equilibrium point (say, ‘B’). We say that the system has undergone a process due to which its state has changed from A to B. Note that this process can be continued as long as desires by sequentially transferring more and more balls individually onto the piston and impelling the system to change in steps till say the end point state ‘X’. The question that one may pose: is the process A-X reversible? That is, if one reversed all the initial steps of sequentially moving each ball off the piston so as to reach from state ‘X’ back to ‘A’ would all the interim states of the system as defined by temperature, pressure and volume at any point be identical to those obtained during the process of going from A to X?

To answer this question we need to understand the process occurring in the system a little more deeply. Consider first that a mass m_o is suddenly moved onto the piston from a shelf (at the same level). The piston assembly accelerates downwards, reaching its maximum velocity at the point where the downward force on the piston just balanced by the pressure exerted by the gas in the cylinder. However, the initial momentum of the plunging piston would carry it to a somewhat lower level, at which point it reverses direction. If the piston were held in this position of maximum depression brought about by transfer of the mass m_0, the decrease in its potential-energy would very nearly equal the work done on the gas during the downward movement. However, if unrestrained, the piston assembly would oscillate, with progressively decreasing amplitude, and would eventually come to rest at a new equilibrium position at a level below its initial position.

The oscillation of the piston assembly cease because it is opposed by the viscosity of the gas, leading to a gradual conversion of the work initially done by the piston into heat, which in turn is converted to internal energy of the gas.

All processes carried out in finite time with real substances are accompanied in some degree by dissipative effects of one kind or another. However, one may conceive of processes that are free of dissipative effects. For the compression process depicted in Fig. 1.4, such effects issue from sudden addition of a finite mass to the piston. The resulting imbalance of forces acting on the piston causes its acceleration, and leads to its subsequent oscillation. The sudden addition of smaller mass increments may reduce but does not eliminate this dissipative effect. Even the addition of an infinitesimal mass leads to piston oscillations of infinitesimal amplitude and a consequent dissipative effect. However, one may *conceive* of an ideal process in which small mass increments are added one after another at a rate such that the piston movement downwards is continuous, with minute oscillation only at the end of the entire process.

This *idealized* case derives if one imagines of the masses added to the piston as being infinitesimally small. In such a situation the piston moves down at a uniform but infinitesimally slow rate. Since the disturbance each time is infinitesimal, the system is always infinitesimally displaced from the equilibrium state both internally as well with respect to external surroundings. Such a process which occurs very slowly and with infinitesimal driving forces is called a *quasi-static* process. To freeze ideas let us assume that the gas in the system follows the ideal gas law. Thus the pressure, temperature and volume at any point during the process are related by eqn. 1.12 (or 1.13). Now imagine that the process of gradual compression is reversed by removing each infinitesimal mass from the piston just as they were added during the forward process. Since during the expansion process also the system will always be differentially removed from equilibrium state at each point, the pressure, temperature and volume will also be governed by the relation 1.12. Since the latter is an equilibrium relationship and hence a unique one, each interim state of the system would exactly converge during both forward and backward progress of system states. Under such a condition the process of compression is said to be thermodynamically reversible. Both the system and its surroundings are ultimately restored to their initial conditions. In summary, therefore, 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 fulfill this criterion it is called an *irreversible* process.

It need be emphasized that a reversible process need be a quasi-static process, and that the origin of irreversibility lie in the existence of dissipative forces in real systems, such as viscosity, mechanical friction. These forces degrade *useful* work irreversibly into heat which is not re-convertible by simply reversing the direction of the process, since during a reverse process a fraction of useful work will again be lost in the form heat in overcoming the dissipative forces. Thus, in the above example system if there were no viscous or frictional forces opposing the motion of the piston the processes of compression and expansion would be reversible, provided of course all changes occur under infinitesimal gradients of force. The argument in the last sentence may be extended to state that if changes are brought about by finite gradients (in this case finite difference in force across the piston, associated with addition of finite mass to the piston), the process would necessarily be irreversible. This is because finite gradients will force the system to traverse through non-equlibrium interim states, during which the pressure, temperature and volume will not be constrained by a unique relationship such as eqn. 1.12, which holds for equilibrium states. Indeed, it would not be possible to define the non-equilibrium states in terms of a single temperature or pressure, as there would be internal gradients of these variables during processes induced by finite force imbalances across the system boundary. These very same considerations would apply for the reverse process of expansion as well, if it occurs under finite mechanical gradients. So in general during such processes it would not be possible to ascribe unique intensive properties to interim states during a change, and hence the forward and reverse “paths” would not coincide as they would if the process occurs under quasi-static conditions.

An additional point that obtains from the above considerations is that only under reversible conditions can one calculate the thermodynamic work by integrating eqn. 1.6, since at all points during the process the variables P, V and T are always uniquely related by the eqn. 1.12. Clearly if the process were occurring under irreversible conditions no such relation would hold and hence the calculation of the thermodynamic work would not be possible through a simple integration of eqn. 1.6.

The foregoing discussion has used the example of a single-phase closed-system, where compression and expansion processes are induced by gradients of mechanical force across the system boundary. There are, however, many processes which are occur due to potential gradients other than mechanical forces. For example, heat flow is induced by temperature differences, electromotive force gradients lead to flow of electricity, and chemical reactions take place as there is a difference between the chemical potential of reactants and products. In general, it may be shown that all such processes brought about by potential gradients of various kinds would tend to reversibility if the gradients are themselves infinitesimal. For example, heat transfer across the boundary of a thermodynamic system would be reversible if the difference across it is of a differential amount ‘*dT*’, and so on.

1.10 Significance of Chemical Engineering Thermodynamics: Process Plant Schema

Before we conclude the present chapter it would be appropriate to obtain a brief preview of the scope and utility of the principles of thermodynamics insofar as application to real world processes is concerned. Although based on relatively *abstract* principles, the laws of thermodynamics provide the fundamental *constraints* under which all *real* world process take place. The ultimate application of the knowledge of the core principles of chemical engineering is in the design of a chemical process plant. Engineering thermodynamics constitutes one of the principal elements of such knowledge. Typically such a plant converts a set of raw materials to a desired product through a variety of steps that are schematically represented by Fig. 1.6.

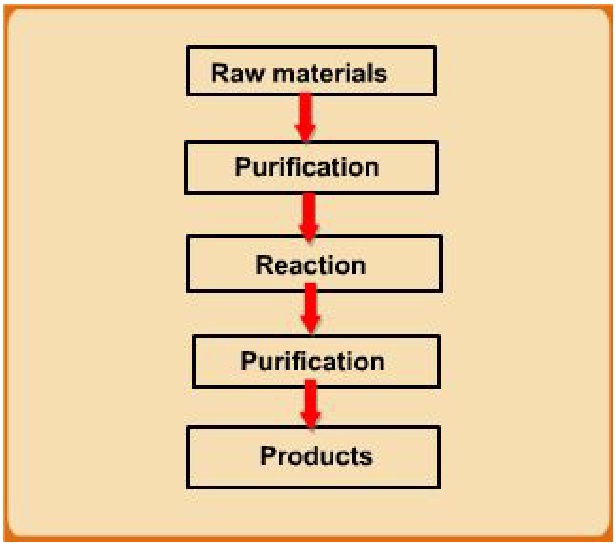


Fig. 1.6 Chemical Process Plant Schema

The raw materials most often are mixtures which need to be purified to obtain the right composition required for conversion to products A wide variety of separation processes are available for carrying out such purification; examples include distillation, liquid-liquid extraction, precipitation from solutions, crystallization, etc. Practically all such separation processes involve generation of two or more phases, in one of which the desired raw material components are *preferentially* concentrated, which is then used recover the substances in a relatively purer form. For a typical large scale chemical plant the separation process equipments may constitute more than half of the total capital investment.

The chemical reactor forms the “heart” of a chemical plant. It is here that once the feed materials are available in the right proportions (and compositions) they are reacted to yield the product. Obtaining the desired product requires an optimal choice of conditions under which the reactor may be operated. However, the product formed is very rarely obtained in a pure form. This is because typically the feed is never fully converted to product molecules and therefore the stream exiting the reactor is not a pure substance. In addition it is usually a common phenomenon that the intended chemical reaction is accompanied by often more than a single side reaction. The latter leads to the formation of side products, which results in “contamination” of the final product. Therefore, it is usually required to subject the reactor exit stream to another round of purification to obtain a product with the desired specifications of the product

With regards to all such processes of purification and reaction, the laws of thermodynamics play a very fundamental role: they allow the calculation of the *principal* entities that form the basis of design and operation of process plants:

1. The *maximum degree of purification* that is possible under a given set of processing conditions
2. The *maximum degree of conversion* possible under the reaction conditions
3. The *optimal operating conditions* for separation and reaction processes
4. The *total energy required* to achieve the intended degree of separation and reaction, and therefore the plant energy load

The calculation of the above parameters tends to constitute 50-70% of the computational load encountered during the stage of basic process plant design. Thus, the principles of chemical engineering thermodynamics is one of the mainstays of knowledge needed to realize the goal of plant design and operation.

Chapter 2: Volumetric Properties of Real Fluids

In the previous chapter we have introduced the concept of ideal gas and the corresponding equation of state (EOS). However, such a state obtains for a gas only at pressures around and below atmospheric (and at high temperatures), and, therefore, constitutes a limiting case. As we know, substances exist also in other forms: solids, liquids, etc. Also more often than not, in practice (as in process plants) gases (as well as other phases) may exist at substantially higher pressures (up to several thousands of atmospheres). This necessitates the development of other EOSs not only for gases, but also for relating *P-V-T* behavior of liquids and solids. Such mathematical relations, if expressed in suitably generalized forms, provide the added advantage of being able to quantify *P-V-T* behaviour for a large number of individual substances.

Such volumetric properties form a group of macroscopic thermodynamic state variables which are most easily measured. As we will see in later chapters, all other intensive thermodynamic properties can be represented in terms of mathematical expressions which denote functions of volumetric and a number of other directly measurable state variables. In the last chapter we have already introduced the ideas of thermodynamic work which clearly can be calculated if the relation between P and V is known. In chapters 3-5 we will demonstrate that heat transfer occurring under reversible conditions, as well as a host of other intensive, state variables (internal energy, enthalpy, entropy, Gibbs free energy, etc) can also be calculated using volumetric properties of a substance in question. Since work and heat are two principal modes of energy transfer in most thermodynamic systems of practical interest, it follows that the knowledge of volumetric properties is fundamental to all such calculations. Finally, as part of process plant design one needs volumetric properties for the purpose of sizing of process pipelines and all major process equipments such as reactors, heat exchangers, distillation columns, and so on. These considerations underscore the precise significance of *P-V-T* behavior of substances in all plant design activity.

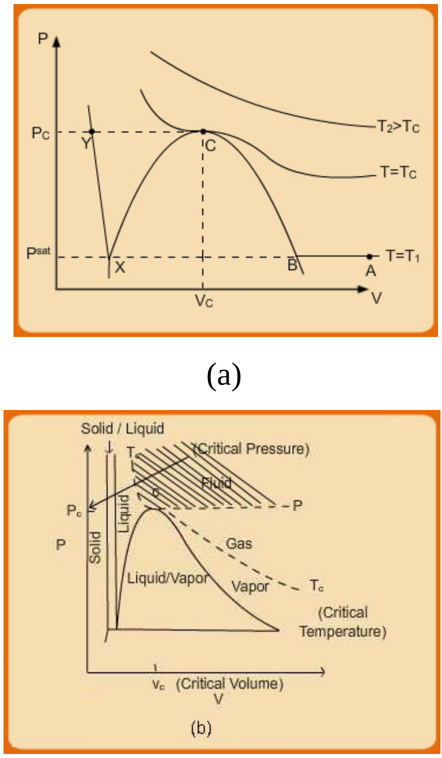
In the following sections we first describe the general nature of the *P-V-T* behavior of pure substances: in gaseous, liquid and solid forms. The various EOSs available to quantify such real fluid behaviour are then considered. Lastly, generalized correlations to relate gas and liquid behaviour are presented. Such analytical EOSs and generalized correlations allow prediction of

P-V-T values of real fluids and are, therefore, of great value as they can obviate the need for detailed experimental data.

2.1 General P-V-T Behaviour of Real Fluids

P-V Diagrams

Fig. 2.1 represents the general pure component, real fluid phase behavior that typically obtains from experimental measurements. Consider first the fig. 2.1a. Let us take a substance at some temperature T_1 and certain pressure P_1 such that it is in a gaseous state A_1. Keeping the temperature fixed at T_1 if one pressurizes the gas (say in a piston-cylinder assembly as in fig. 1.2) its molar volume will decrease along the curve *A-B*. At point *B*, any further pressurization leads to commencement of condensation of the gas into a liquid from. Point '*B*' is thus said to correspond to a state where the substance is in a *saturated vapour state*. Once condensation begins any attempt at reducing the volume by further



(a)

(b)

Fig. 2.1 General P-V plots for real fluids pressurization more of the saturated vapour present at *B* progressively liquefies until a point *X* is reached where all the original gas (or saturated vapour) is fully converted to liquid state. Point *X* is described as a *saturated liquid state*. It follows that at all point between *B* and *X* the substance exists partitioned into two phases, i.e., part vapour and part liquid. As one transits from *B* to *X*, pressure and temperature both remain constant; the only change that occurs is that the fraction of the original gas at point *A* (or *B*) that is liquefied increases, until it is 1.0 at point *X*. The line *B*-*X* connecting the saturated vapour and liquid phases is called the *tie-line*. For a given *T* and *P*, the relative amounts of the phases determine the effective molar (or specific) volume at any point within the two-phase region. Any further attempt to pressurize the saturated liquid results in relatively very little compression, and this is captured by the steep slope of the curve *X*-*Y*, which signifies that the liquid state is far less compressible, compared to the gas state (i.e., points over *A*-*B*). Essentially points between *X*-*Y* (including *Y* itself) represent *compressed liquid* states.

An important point to re-emphasize is that on the two-phase line *B*-*X*, the pressure of the system remains constant at a fixed value. This pressure is termed the *saturation pressure* (P^{sat}) corresponding to the temperature T_1. We recall your attention to the phase rule described in section 1.5, and eqn. 1.11. By this eqn. the degrees of freedom is *one*, which is borne by the fact that if one fixes temperature the system pressure also becomes fixed. However, in both regions *A*-*B* and *X*-*Y* the degrees of freedom is *two*, as pressure becomes fixed only if one defines both temperature and volume.

In general, the same behviour as detailed above may repeat at another temperature *T* (>T_1). One can on the one hand connect all the saturated vapour phase points at different temperatures and on the other connect all the points representing saturated liquid phase, the locus of such points give rise to the dome-shaped portion *X*-*C*-*B* of the *P*-*V* diagram which essentially signifies that at any pressure and volume combination within this dome, the state of the system is biphasic (part gas and part liquid). The region right of the dome *B*-*C* represents saturated gas phase while to the left (*X*-*C*) the state is saturated liquid. If one continues to conduct the pressurization at increasingly higher temperatures, one eventually arrives at a temperature for which the tie-line is reduced to a point and the *P*-*V* curve turns into an inflexion point to the two-phase dome. The temperature which such a behavior obtains is called the *critical temperature* (T_C), while the pressure at corresponding point of inflexion is termed the *critical pressure* (P_C).

The molar volume at the point is termed the *critical volume*, and the state itself the *critical point*. A fluid which is at a temperature and pressure above the critical point values is said to be in a supercritical state; this is indicated by the hatched region in fig. 2b. As has been shown for the *P-V* curves for a $T > T_C$, there exists no liquid phase as the curve passes beyond the two-phase dome region. Thus, the critical temperature is a temperature above which a gas cannot be liquefied by compressing, as can be below it. Compilation of values of critical properties and ω for a large number of substances are available readily from several sources **(see: http://srdata.nist.gov/gateway/gateway).** Values of these parameters for some select substances are provided in *Appendix II*.

In fig. 2.1b the phase behavior depicted in fig. 2.1a is extended and more generalized to include solid phase as well. Accordingly, not only vapour-liquid region, other two phase regions, i.e., solid-vapour and solid-liquid regions are also displayed. The same arguments as made above for explaining the nature of co-existence of vapour and liquid phases apply to the other two biphasic regions.

P-T Diagrams

The phase behaviour described by fig. 2.1 can also be expressed in a more condensed manner by means of a pressure-temperature (*P-T*) diagram shown in fig 2.2. Just as P-V curves were depicted at constant temperature, the P-T diagram is obtained at a constant molar volume. The two phase regions which were areas in the P-V diagram are reduced to lines (or curves) in fig. 2.2. The P-T curves shown by lines *X-Y, Y-Z, and Y-C* result from measurements of the vapour

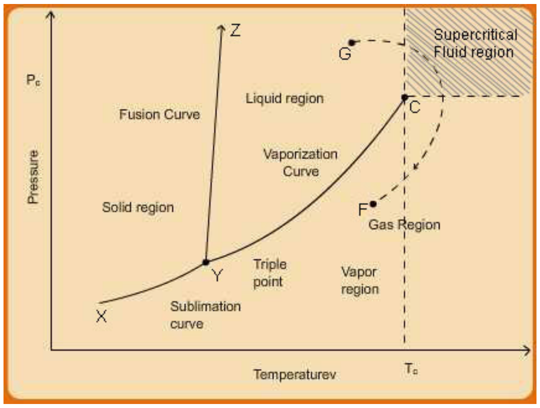


Fig. 2.2 Pressure-Temperature Diagram of a Pure Substance

pressure of a pure substance, both as a solid and as a liquid. *X-Y* corresponds to the solid-vapour (sublimation) line; *X-Y* represents the co-existence of solid and liquid phases or the fusion line, while the curve *Y-C* displays the vapour-liquid equilibrium region. The pressure at each temperature on the *Y-C* curve corresponds to the equilibrium vapour pressure. (Similar considerations apply for *P-T* relation on the sublimation curve, *X-Y*). The terminal point C represents the critical point, while the hatched region corresponds to the supercritical region. It is of interest to note that the above three curves meet at the triple-point where all three phases, solid, liquid and vapour co-exist in equilibrium. By the phase rule (eqn. 1.11) the degrees of freedom at this state is zero. It may be noted that the triple point converts to a line in fig. 2.1b. As already noted, the two phases become indistinguishable at the critical point. Paths such as *F to G* lead from the liquid region to the gas region without crossing a phase boundary. In contrast, paths which cross phase boundary *Z-Y* include a vaporization step, where a sudden change from liquid to gas occurs.

A substance in the compressed liquid state is also often termed as *sub-cooled*, while gas at a pressure lower than its saturation vapour pressure for a given temperature is said to be "superheated". These descriptions may be understood with reference to fig. 2.2. Let us consider a compressed liquid at some temperature (T) and pressure (P). The saturation temperature for the pressure P would be expected to be *above* the given T. Hence the liquid is said to be sub-cooled with respect to its saturation temperature. Consider next a pure vapour at some temperature (T) and pressure (P). Clearly for the given pressure P the saturation temperature for the pressure P would be expected to be *below* the given T. Hence with respect to the saturation temperature the vapour is *superheated*.

The considerations for *P-V* and *P-T* diagrams may be extended to describe the complete P-V-T phase behaviour in the form of three dimensional diagrams as shown in fig. 2.3. Instead of two-dimensional plots in figs. 2.1 and 2.2 we obtain a *P-V-T surface*. The *P-V* plots are recovered

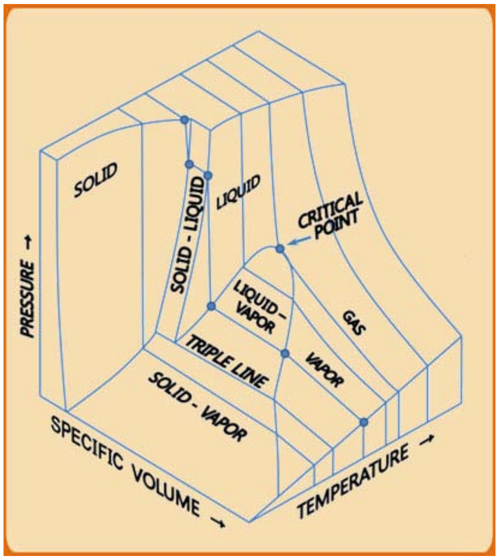


Fig. 2.3 Generalized Three-dimensional P-V-T Surface for a Pure Substance

if one takes a slice of the three dimensional surface for a given temperature, while the *P*-*T* curve obtains if one takes a cross-section at a fixed volume. As may be evident, depending on the volume at which the surface is cut the *P*-*T* diagram changes shape.

Fig. 2.4 illustrates the phase diagram for the specific case of water. The data that is pictorially depicted so, is also available in the form of tables popularly known as the “steam table”. The steam table (see http://www.steamtablesonline.com/) provides values of the following thermodynamic properties of water and

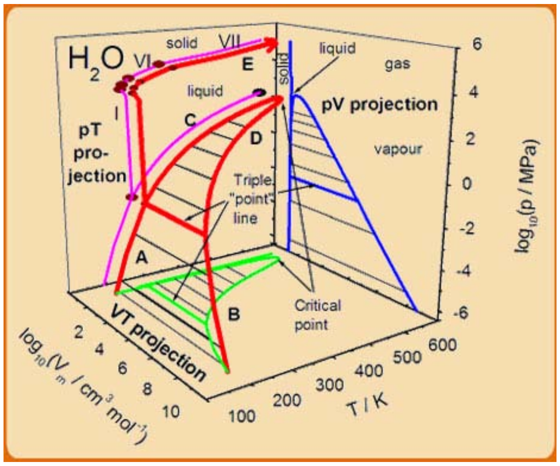


Fig. 2.4 Three-dimensional P-V-T Plot for Water

vapour as a function of temperature and pressure starting from its normal freezing point to the critical point: molar volume, internal energy, enthalpy and entropy (the last three properties are introduced and discussed in detail in chapters 3 and 4).

The steam tables are available for saturated (two-phase), the compressed liquid and superheated vapour state properties. The first table presents the properties of saturated gas and liquid as a function of temperature (and in addition provides the saturation pressure). For the other two states the property values are tabulated in individual tables in terms of temperature and pressure, as the degree of freedom is two for a pure component, single state. For fixing the values of internal energy, enthalpy and entropy at any temperature and pressure those for the saturated liquid state at the triple point are arbitrarily assigned zero value. The steam tables comprise the most comprehensive collection of properties for a pure substance.

2.2 Origins of Deviation from Ideal Gas Behaviour

The ideal gas EOS is given by eqn. 1.12. While this is a relationship between the macroscopic intensive properties there are two assumptions about the microscopic behaviour of molecules in an ideal gas state:

i. The molecules have no extension in space (i.e., they posses zero volume)
ii. The molecules do not interact with each other

In particular, the second assumption is relatively more fundamental to explaining deviations from ideal gas behavior; and indeed for understanding thermodynamic behavior of real fluids (pure or mixtures) in general. For this, one needs to understand the interaction forces that exist between molecules of any substance, typically at very short intermolecular separation distances (~ 5 – 20 $\overset{0}{A}$ (where 1 $\overset{0}{A}$ = 10^{-8}m).

Uncharged molecules may either be polar or non-polar depending on both on their *geometry* as well as the *electro-negativity* of the constituent atoms. If the *centre* of total positive and negative charges in a molecule *do not* coincide (for example, for water), it results in a *permanent* dipole, which imparts a polarity to the molecule. Conversely, molecules for which the centres of positive and negative charge coincide (for example, methane) do not possess a permanent dipole and are termed non-polar. However, even a so-called non-polar molecule, may possess an *instantaneous* dipole for the following reason. At the atomic level as electrons oscillate about the positively charged central nucleus, at any point of time a dipole is set up. However, averaged over time, the net dipole moment is zero.

When two polar molecules approach each other closely the electric fields of the dipoles overlap, resulting in their re-orientation in space such that there is a net *attractive* force between them. If on the other hand a polar molecule approaches a non-polar molecule, the former *induces* a dipole in the latter (due to displacement of the electrons from their normal position) resulting once again in a net attractive interaction between them. Lastly when two non-polar molecules are close enough their instantaneous dipoles interact resulting in an attractive force. Due to these three types of interactions (dipole-dipole, dipole-induced dipole, and induced dipole-induced dipole) molecules of any substance or a mixture are subjected to an attractive force as they approach each other to very short separation distances.

However, intermolecular interactions are not only *attractive*. When molecules approach to distances even less than $\sim 5\,\overset{0}{A}$ or so, a *repulsive* interaction force comes into play due to overlap of the electron clouds of each molecule, which results in a repulsive force field between them. Thus if one combines both the attractive and repulsive intermolecular interactions the overall interaction potential U resembles the schematic shown in fig. 2.5.

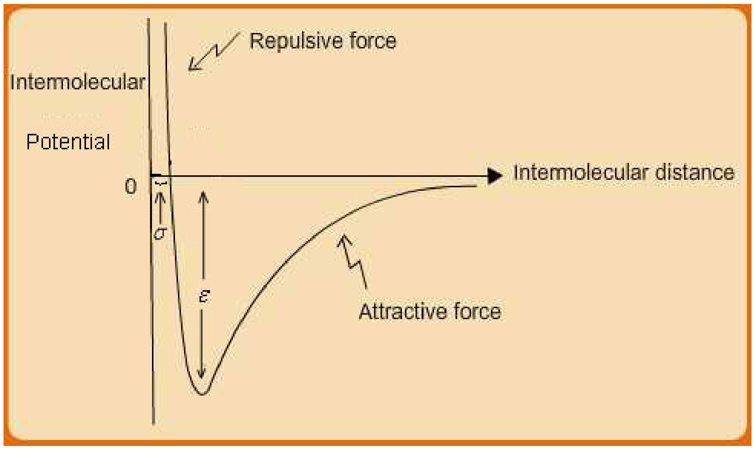


Fig. 2.5 Schematic of Intermolecular potential energy U for a pair of uncharged molecules

Many expressions have been proposed for the overall interaction potential U [see, J.M. Prausnitz, R.N Lichtenthaler and E.G. Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, (3rd ed.), 1999, Prentice Hall, NJ (USA)]. These are essentially empirical, although their functional forms often are based on fundamental molecular theory of matter. The most widely used equation in this genre is the *Lennard-Jones* (LJ) *12/6 pair-potential function* which is given by eqn. 2.1:

$$U(LJ) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad ..(2.1)$$

Where, r = intermolecular separation distance; ε, σ = characteristic L-J parameters for a substance.

The r^{-12} term represents the repulsive interaction, whereas the r^{-6} term corresponds to the attractive interaction potential. As already indicated, the domain of intermolecular interactions is limited to relatively low range of separation distances. In principle they are expected to be operative over $r = 0 - \infty$; but for practical purposes they reduce to insignificant magnitudes for separations exceeding about 10 times the molecular diameter.

The L-J parameters ε, σ are representative of the molecular interaction and size respectively. Typical values of the L-J equation parameters for various substances may be found elsewhere (G. Maitland, M. Rigby and W. Wakeham, 1981, *Intermolecular Forces: Their Origin and Determination*, Oxford, Oxford University Press.)

Since gases behave ideally at low pressures, intermolecular separation distances therein are typically much higher than the range over which intermolecular interactions are significant. This is the reason why such interactions are negligible in case of ideal gas, which essentially is one of the assumptions behind the definition of ideal gas state. Indeed while the ideal gas EOS is expressed in macroscopic terms in eqn. 1.12, the same equation may be derived from microscopic (thermodynamic) theory of matter.

The root of non-ideal gas behavior, which typically obtains at higher pressure, thus is due to the fact that at elevated pressures, the intermolecular separations tend to lie within the interactive range and hence the ideal gas assumption is no longer valid. Thus, the ideal gas EOS is insufficient to describe the phase behavior of gases under such conditions.

Intermolecular interactions also help explain the behavior of fluids in other states. Gases can condense when compressed, as molecules are then brought within the separations where the attractive forces constrain the molecules to remain within distances typical of liquid phase. It follows that a pure component liquid phase cannot be *ideal* in the same sense as a gas phase can be. Further, the fact that liquids are far less compressible also is due to the repulsive forces that operate at close intermolecular distances. Obviously these phenomena would not be observed unless there were interactions between molecules. Thus, it follows that while properties of the ideal gas depend only on those of isolated, non-interacting moleclues, those of real fluids depends additionally on the intermolecular potential. Properties which are determined by the intermolecular interaction are known as *configurational properties,* an example of which is the energy required for vapourization; this is because during the process of vapourization energy has to be provided so as to overcome the intermolecular attractive force between molecules in the liquid phase and achieve the gas state where the seprations are relatively larger.

2.3 Equations of State for Real Fluids

The generic form of an equation of state (EOS) is: $f(P,V,T)=0$

However, as we have already seen by the phase rule, for a single phase pure component the degrees of freedom are two. This may be expressed in the form of an EOS equation as follows:
$V=V(T,P)$

It follows that:

$$dV=\left(\frac{\partial V}{\partial T}\right)_P dT+\left(\frac{\partial V}{\partial P}\right)_T dP \qquad ..(2.2)$$

$$\text{Defining Volume Expansivity as } \beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad ..(2.3)$$

$$\text{Isothermal compressibility as } \kappa \equiv \frac{1}{\mathrm{V}}\left(\frac{\partial V}{\partial P}\right)_T \qquad ..(2.4)$$

The generic EOS (2.2) may be written as:

$$\frac{dV}{V}=\beta dT-kdP \qquad ..(2.5)$$

2.3.1 EOS for Liquids

For **liquids,** which are relatively incompressible, the factors β and κ are generally show an weak dependence on T and P and hence **averaged** values of these parameters may be used for estimating the liquid volume at any temperature using the following integrated form of the equation (2.5):

$$\ln\frac{V_2}{V_1} = \beta(T_2 - T_1) - k(P_2 - P_1) \qquad ..(2.6)$$

For liquids the usual datum volume (i.e., V_1 in eqn.2.6) can be the saturated volume at a given temperature, which may be obtained from the Rackett equation (H. G. Rackett, J. *Chem. Eng. Data*, *1970*, vol. 15, pp. 514-517); i.e.,:

$$V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}\ ;\ where\ T_r = T / T_C = reduced\ temperture. \qquad ..(2.7)$$

Where Z_C is the critical compressibility factor (see below).

Example 2.1

For a liquid 'A' at 350K and 1 bar, κ = 50x10^{-6} bar^{-1}. (i) To what pressure must water be compressed at 350 K to change its density by 0.5%? Assume that κ is independent of P.

(Click for solution)

2.3.2 EOS for Gases

In contrast to liquids, **gases** are relatively far more compressible, and so volume is strongly dependant on temperature and pressure. Consequently eqn. 2.6 cannot be used easily to estimate volume at a given T & P, as both β and κ are strong functions of T and P. Thus, various EOSs have been proposed to describe gas phase volumetric properties. The next section presents select EOSs that are typically used for the gas phase, ranging from those applicable to moderate pressure to others which are more accurate at high pressures.

Virial EOS:

Generally applicable to moderate deviations from ideal gas behavior, the virial EOS is given by two alternate forms:

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \ldots \qquad ..(2.8)$$

Where B, C = second and third virial coefficients

Or: $\frac{PV}{RT} = 1 + B'P + C'P^2 + ...$ ..(2..9)

It may be shown that the following relations hold further:

$$B = \frac{B'}{RT}; \text{ and } C' = \frac{C - B^2}{(RT)^2} \quad ..(2.10)$$

As may be evident, the second and third terms on the right side of eqns. 2.8 and 2.9 constitute corrections for the non-ideal behavior of a gas. The virial coefficients are essentially dependent of temperature. The more the number of virial coefficients used in the equation the better is the prediction of gas molar volume. While the estimation of the second virial coefficient is relatively straightforward, that of the third virial coefficient is generally far more complex, and there is scant data in the literature on its value for different substances. Because of this the virial EOS is most commonly used in the truncated form, and applies to moderate deviations from ideal gas behavior:

$$\frac{PV}{RT} = 1 + \frac{B}{V} \quad ..(2.11)$$

Alternately, $Z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_c}{RT_c}\right)\frac{P_r}{T_r}$ ..(2.12)

Where, P_r and T_r are *reduced* pressure and temperature respectively, given by:

$P_r = P / P_C; T_r = T / T_C$

A set of generalized correlations have been proposed by Pitzer and co-workers (K. S. Pitzer, *Thermodynamics,* 3d ed., App. 3, McGraw-Hill, New York, 1995) for computing the second virial coefficients whereby:

$$\left(\frac{BP_c}{RT_c}\right) = B^0 + \omega B^1 \quad ..(2.13)$$

The terms B^0 and B^1 are given by:

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad ..(2.14)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \qquad ..(2.15)$$

The parameter ω, discussed in a later section, is the *acentric factor*, which is a fundamental thermodynamic property of a substance, and is a measure of *asphericity* of molecular shape (see Appendix II for values of acentric factor for select substances). The value of acentric factor may be obtained from the following expression from experimental vapour pressure data of a pure substance (K. S. Pitzer, *Thermodynamics*, 3d ed., App. 3, McGraw-Hill, New York, 1995):

$$\omega \equiv -1.0 - \log_{10}(P_r^{sat})_{T_r=0.7} \qquad ..(2.16)$$

$(P_r^{sat})_{T_r=0.7}$ = reduced saturation vapour pressure at a reduced temperature equalling 0.7.

Since the virial EOS applies to only moderate deviations from ideal behaviour several complex extensions of it have been proposed for increasing accuracy of prediction at higher pressures; an example of such an EOS is the so-called Benedict-Webb-Rubin (BWR) EOS (G.B.Benedict, G. B. Webb, and L. C. Rubin, *J. Chem.* ***.*** *Phys.*, vol. 8, pp. 334-345, 1940) used in the petroleum and natural-gas industries:

$$P = \frac{RT}{V} + \frac{B_0 - RT - A_0 - C_0/T^2}{V^2} + \frac{bRT - a}{V^3} + \frac{a\alpha}{V^6} + \frac{c}{V^3T^2}\left(1 + \frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right) \qquad ..(2.17)$$

where A_0, B_0, C_o, a, b, c, and γ are all constant for a given fluid.

Example 2.2

Calculate the molar volume for butane at 2.5bar and 298 K using the truncated virial EOS using the following data: $T_C = 425.1K$; $P_C = 37.96bar$; $\omega = 0.2$.

(Click for Solution)

2.3.3 Cubic EOS for Gases

While the truncated virial EOS applies to moderate pressures, it is often necessary to obtain volumetric properties of gases at relatively much higher pressures. It has generally proved to be computationally unwieldy to use extensions of the virial EOS at higher pressure. To obviate this problem an entire range of alternate EOSs, termed *cubic* EOS, have been proposed by various workers. The term “cubic equation of state” implies an equation which, if expanded, would contain the volume terms raised to the first, second, or third power. Such an EOS provides two distinct advantages over many other more complex EOS found in the literature; they allow:

- Prediction of both gas and liquid (saturated) phase molar volumes
- Provide a trade-off between complexity and accuracy of prediction

The first of such cubic EOS was proposed by the Dutch physicist Johannes Diderik van der Waals in 1873, and has the following form:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad ..(2.18)$$

Where, *a* and *b* are characteristic constants for a pure substance. For example, for nitrogen the values of *a* and *b* are $0.1368 Pa.m^6/mol^2$ and $3.864\text{x}10^{-5} m^3/mol$ respectively. Values of these parameters for other substances may be found in the literature (see, for example: S.I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, 4th edition, Wiley India, 2006).

Once can take advantage of the phase P-V behaviour at the critical point (see fig. 2.1) to determine the expressions for *a* and *b*. Since the P-V curve offers a point of inflection at the critical point one may write:

$$(\partial P/\partial V)_{T_C} = 0 \qquad ..(2.19)$$

$$(\partial^2 P/\partial V^2)_{T_C} = 0 \qquad ..(2.20)$$

On applying eqns. (2.19) and (2.20) on 2.18 two independent equations obtain, which may solved simultaneously to show that for the vdW EOS:

$$a = (27/64)R^2T_C^2/P_C$$

$$b = (1/8)RT_C/P_C$$

$$V_C = (3/8)RT_C/P$$

It follows that the critical compressibility factor is then given by:

$$Z_C = P_CV_C/RT_C = 3/8 = 0.375$$

The vdW EOS suggests that for all pure substances the critical compressibility factor is a constant (= 0.375). This, however, is contrary to experience. Indeed, although similar in magnitude, the value of Z_C is specific to a pure substance. For example, for methane it is 0.286, while for helium 0.302. This indicates that although an improvement over ideal gas EOS, the vdW EOS does not reflect the specificity needed to predict the behaviour of all substances at high pressures.

To bridge this gap several other cubic EOS of higher accuracy have been advanced, the three most widely used of which are:

- Redlich-Kwong (RK) EOS (Otto Redlich and J. N. S. Kwong, *Chem. Rev.*,vol. 44, pp. 233-244, 1949)
- Soave-Redlich-Kwong (SRK) EOS (*G.* Soave, *Chem. Eng.* ***Sci.,*** vol. 27, pp. 1197-1203, 1972.)
- Peng-Robinson (PR) EOS (D. **Y.** Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.*, vol. 15, pp. 59-64, 1976.)

All the above EOSs including that due to van der Waals may be expressed by a single equation of the following form:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2} \qquad ..(2.21)$$

As part of a generalized approach to representing non-ideal gas behavior parameter *Z,* termed the *compressibility factor,* may be defined. This is discussed further in the following section. However, here we provide the expression for it:

$$Z = PV/RT \qquad ..(2.22)$$

Using eqn. 2.20, eqn. 2.19 may be rewritten as:

$$Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \qquad ..(2.23)$$

Where:

$$A = aP/(RT)^2$$

$$B = bP/RT$$

$$\alpha = -1 - B + uB$$

$$\beta = A + wB^2 - uB - uB^2$$

$$\gamma = -AB - wB^2 - wB^3$$

Expressions for all the above parameters for each EOS are provided in Table 2.1 below.

Table 2.1 Values of $u, w, \alpha, \beta, \gamma$ for various cubic EOSs

EOS	u	w	α	β	γ	a	b
vdW	0	0	$-1-B$	A	$-AB$	$\frac{27}{64}\frac{R^2T_C^2}{P_C}$	$\frac{RT_C}{8P_C}$
RK	1	0	-1	$A-B-B^2$	$-AB$	$\frac{0.42748R^2T_C^2\alpha_{RK}}{P_C}$	$\frac{0.08664RT_C}{P_C}$
SRK	1	0	-1	$A-B-B^2$	$-AB$	$\frac{0.42748R^2T_C^2\alpha_{SRK}}{P_C}$	$\frac{0.08664RT_C}{P_C}$
PR	2	-1	$-1+B$	$A-2B-3B^2$	$-AB+B^2+B^3$	$\frac{0.45724R^2T_C^2\alpha_{PR}}{P_C}$	$\frac{0.07779RT_C}{P_C}$

The parameters $\alpha_{RK}, \alpha_{SRK}$ and α_{PR} given by:

$$\alpha_{RK} = T_r^{-1/2}$$

$$\alpha_{SRK} = [1+(0.48+1.574\omega-0.176\omega^2)(1-T_r^{1/2})]^2$$

$$\alpha_{PR} = [1+(0.37464+1.5422\omega-0.62992\omega^2)(1-T_r^{1/2})]^2$$

As may be evident from table 2.1 all the parameters are determinable from the critical properties, ω and the temperature at which the molar volume or pressure needs to be calculated. Once these are computed the eqn. 2.21 may be solved to yield the value of Z, which in turn may be used to obtain the molar volume. Eqn. 2.21 may be solved using a suitable *iterative* algorithm or more readily by the general analytical solution for cubic algebraic equations, which is outlined below.

For solving eqn. 2.21, substitute, $Z = X - (\alpha / 3)$ which gives:

$$X^3 + pX + q = 0$$

where:

$$p = \beta - (\alpha^2 / 3)$$

$$q = (2\alpha^2 / 27) - (\alpha\beta / 3) + \gamma$$

Now, let $D = (q^2 / 4) + (p^3 / 27)$

Then the roots of eqn. (2.21) are as follows:

Case 1:

If $D > 0$, then only one real root exists:

$$Z = \left\{-\frac{q}{2} + \sqrt{D}\right\}^{1/3} + \left\{-\frac{q}{2} - \sqrt{D}\right\}^{1/3} - \frac{\alpha}{3}$$

Case 2:

If $D = 0$, then there are three real roots, of which two are equal:

$$Z_1 = -2\left(\frac{q}{2}\right)^{1/3} - \frac{\alpha}{3}; \quad Z_2 = Z_3 = \left(\frac{q}{2}\right)^{1/3} - \frac{\alpha}{3}$$

Case 3:

If $D < 0$, then there are three unequal real roots:

$$Z_1 = 2r^{1/3}\cos(\theta / 3) - \frac{\alpha}{3}$$

$$Z_2 = 2r^{1/3}\cos\left(\frac{2\pi + \theta}{3}\right) - \frac{\alpha}{3}$$

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

where: $\cos\theta = -\dfrac{q}{2}\left(-\dfrac{27}{p^3}\right)^{1/2}$

$$r = \sqrt{\frac{-p^3}{27}}$$

The true advantage of use of cubic EOS derives from the fact that not only can it provide gas phase molar volumes, but also that of saturated liquid at a given temperature (note that this is not feasible by use of virial EOS). To understand this point we refer to fig. 2.6, which is a simplified

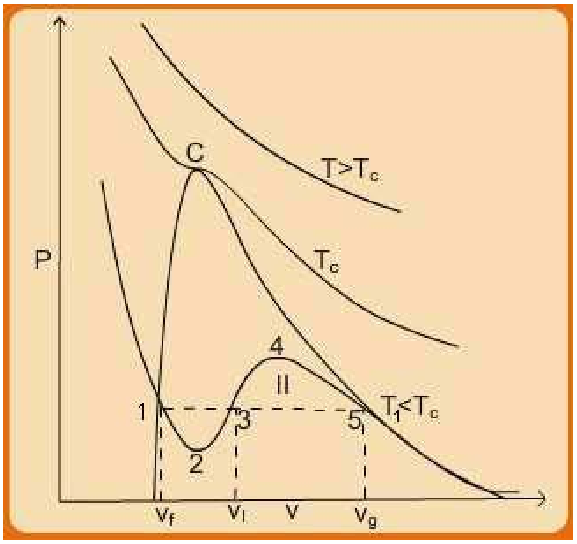


Figure 2.6 P-V plots at constant temperatures (as obtained from a cubic equation of state)

version of fig. 2.1.

For given values of *V* and *T* one can calculate *P* (using any cubic EOS) as a function of *V* for various values of *T*. Figure 2.4 is a schematic *P*-*V* curves for three different temperatures. The variations shown by $T = T_C$ and $T > T_C$ have already been discussed in section 2.1. We draw your attention here to the plot at $T < T_C$. In this case the pressure decreases rapidly in the subcooled liquid region with increasing V; after crossing the saturated-liquid line, it goes through a *minimum* (1-2-3), rises to a *maximum* (3-4-5), and then decreases, crossing the saturated-vapor line and continuing downward into the superheated-vapor region. However, experimentally obtained plots of this kind (at $T < T_C$) do not show this manner of transition from saturated liquid to saturated vapor. As already discussed in section 2.1, in the two phase region within the dome, the curve connecting the saturated vapor and liquid states constitutes a tie-line. Along this horizontal segment the two phases coexist in varying proportions at the saturation vapor pressure. Clearly then the true behavior of the substance cannot be exactly reproduced by an analytical cubic EOS in the two phase region.

Nevertheless, the *P*-*V* behavior that obtains in the two-phase region using the cubic EOS is not entirely unrealistic. Indeed the two *points of intersection* of the analytical *P*-*V* curve (at a given temperature) with the boundary of the dome occurs (approximately) at the points where the experimental saturated vapour and liquid state volumes obtain (i.e., points 1 and 5). Cubic equations of state have three volume roots, of which two may often be complex conjugates.

Physically relevant values of V are always real, positive, and greater than constant b *which* appears in the cubic EOSs. For $T > T_C$, at any pressure the solution for eqn. 2.21 yields one real root. This is also true at any pressure on the $T = T_C$ curve, except for $P = P_C$; at the latter condition three real roots obtain all equal to V_C. For $T < T_C$, in general there could be one or three real roots. If the pressure is different from the saturation vapour pressure (P^{sat}, at the given temperature) the roots are not realistic. If, however, the pressure is taken to be P^{sat}, three real roots are found. The highest amongst these correspond to the saturated vapour phase volume, while the lowest one approximates the saturated liquid phase volume; the third root, however, is not physically meaningful.

Example 2.3

For methane at 298K and 2 MPa compute the molar volume using SRK equation. For methane, $T_c = 190.7$ K, $P_c = 46.41$ bar, $\omega = 0.011$.

(Click for solution)

2.3.4 Principle of Corresponding States

The compressibility factor Z has already been defined in eqn. 2.20. A typical plot of Z as a function of T & P for methane is shown in fig.2.7. Experimentally measured values of Z for different fluids display similar dependence on reduced temperature and pressures, i.e., P_r and T_r.

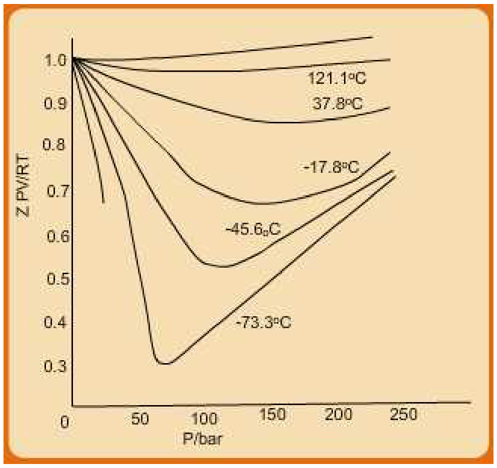


Fig. 2.7 Variation of Compressibility-factor with pressure and temperature (Source: J.M. Smith, H.C. Van Ness and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, 2001)

This observation has been generalized to formulate the *two-parameter theorem of corresponding states* which is stated as follows: *"All fluids at the same reduced temperature and reduced pressure have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree."* Fig. 2.8 presents select experimental data which support this observation.

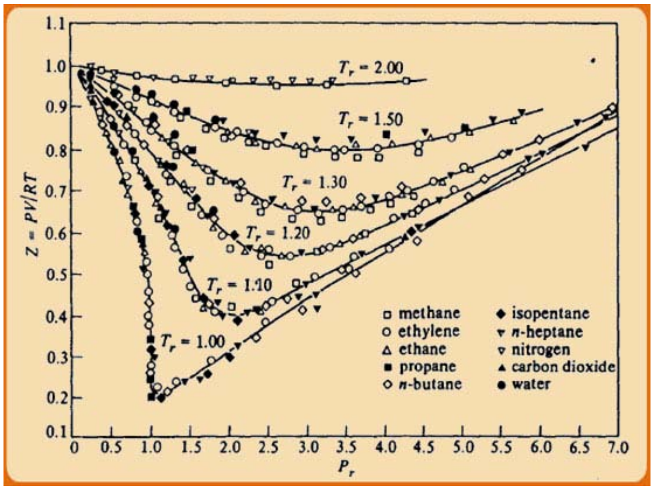


Fig. 2.8 Experimental compressibility factors for different fluids as a function of the reduced temperature and pressure. [Source: H. C.Van Ness and M.M Abbott (1982) based on data from G.-J. Su (1946). *Ind. Engr. Chem.* 38, p 803.]

While this theorem applies fairly reliably to the *simple fluids* (argon, krypton, and xenon), for more complex fluids the deviations are significant. To address this gap Pitzer and coworkers introduced a third corresponding-states parameter, characteristic of molecular structure, more particularly the "degree of sphericity" of the molecule; the most widely used one is *acentric factor* 'ω' (already utilized in eqn. 2.13 and for computation for cubic EOS parameters in table 2.1) (K. S. Pitzer, *Thermodynamics,* 3d ed., App. 3, McGraw-Hill, New York, 1995). The expression for ***ω*** was provided in eqn. 2.16. As is evident, it can be computed for any substance using critical properties and a single vapor-pressure measurement made at $T_r = 0.7$.

By definition ω (see J.M. Smith, H.C. Van Ness and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, 2001) is zero for the *simple* fluids argon, krypton, and xenon, which are generally regarded as spherical molecules. For other substances, the greater the deviation molecular sphericity, the larger is the departure of its corresponding ω from zero. For example for methane it is 0.012, while for butane it is 0.2, and so on. Experimentally determined values of Z for the three simply fluids coincide if measured at identical reduced temperature and pressures. This observation forms the basis for extending the two-parameter theorem (stated above) to the *three-parameter theorem* of corresponding states: *"The compressibility factor for all fluids with the same value of ω, when compared at the same reduced temperature and pressure are approximately the same, and hence the deviation from ideal-gas behavior is nearly the same."*

This theorem leads to vary convenient approach involving generalized correlations for computing not only the volumetric properties but for estimating a wide variety of other thermodynamic properties.

Generalized Compressibility factor Approach to EOS: Pitzer Correlations

For prediction of volumetric properties (using the compressibility factor *Z* or the second virial coefficient) the most commonly used correlations are those due to Pitzer and coworkers (op. cit.). According to this approach, compressibility factor is decomposed as follows:

$$Z = Z^0 + \omega Z^1 \qquad ..(2.24)$$

Where $Z^0$and $Z^1$are both functions of T_r and P_r only. When $\omega = 0$, as for the simple fluids, the second term disappears. Thus the second term generally accounts for relatively small contribution to the overall *Z* due to the *asphericity* of a molecule. As noted earlier, the value of ω may be computed using the following equation:

$$\omega = -1.0 - \log(P_r^{sat})_{T_r=0.7} \qquad ..(2.16)$$

Fig. 2.9 shows a plot of reduced vapor pressures for select substances as a function of reduced temperature. At a value of about ~ 0.7 for the reduced temperature (T_r) of the typical simple fluids (argon, krypton, xenon) the logarithm of reduced pressure is – 1. For other molecules the greater the departure from sphericity of the structure the lesser is the value of reduced pressure at $T_r = 0.7$. This is indicative of lower volatility of the substance, which suggests relatively stronger intermolecular interactions in the condensed phase. Stronger interactions result from higher polarity of molecules, which is in turn originates from the asymmetry of the molecular structure. Equation 2.16 indicates that the difference between the reduced pressures at the common reduced temperature $(T_r = 0.7)$ is the measure for the acentric factor.

Based on the Pitzer-type correlations, Lee-Kesler (B.I. Lee and M. G. Kesler, *AIChE J.*, vol. 21, pp. 510-527,1975) has developed generalized correlations using a variant of the BWR-EOS (eqn. 2.17) for computing Z^0 and Z^1 as function of T_r and P_r. The values of Z^0 and Z^1 are

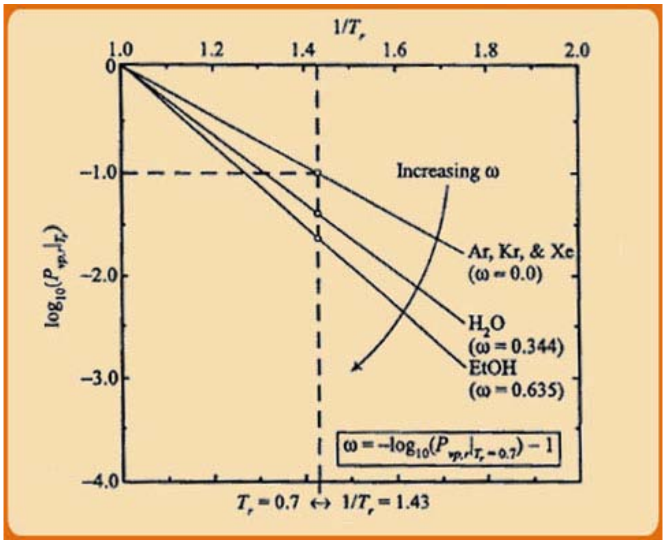
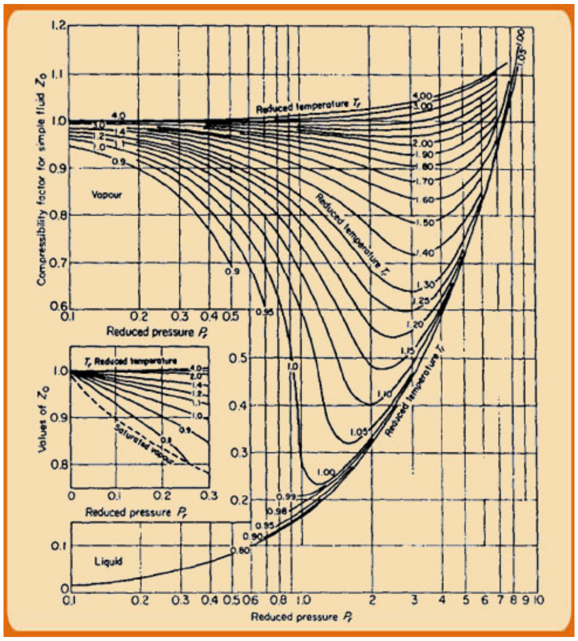
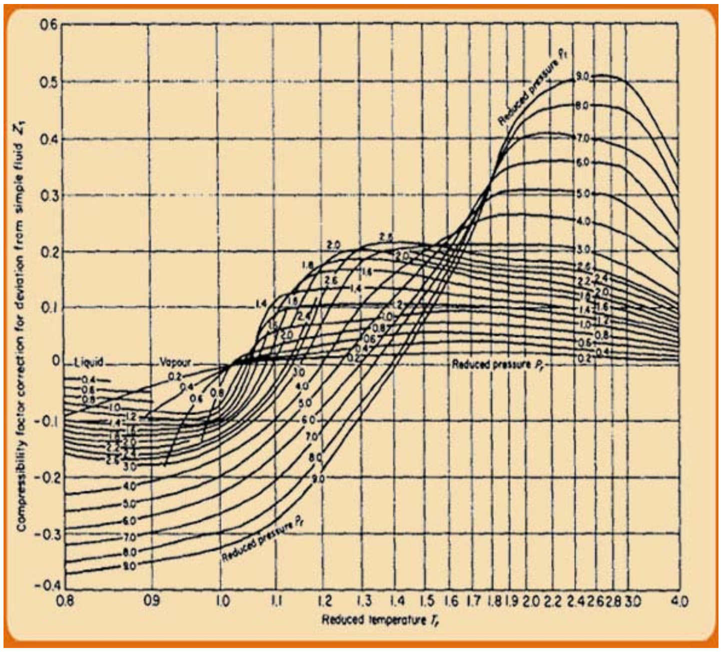


Fig. 2.9 Plot of P_r vs. T_r for select substances of varying polarity (Source: J.W. Tester and M. Modell, *Thermodynamics and its Applications*, 3rd ed., Prentice Hall, 1999).

available in the form of tables from where their values may be read off after due interpolation wherever necessary, or in the form of figures (see figs 2.10a and 2.10b). The method is presented in the detail in Appendix1.1 of this chapter.



(a)



(b)

Fig. 2.10a & 2.10b Z^0 and Z^1 contributions to generalized corresponding states correlation developed by Pitzer and coworkers (1955) [Source: *Petroleum Refiner,* April 1958, Gulf Publishing Co].

Example 2.4

A rigid 0.5-m^3 vessel at 25^oC and 2500kPa holds ethane; compute the number of moles of ethane in the vessel. For ethane: T_c = 305 K; P_c = 48.72 bar, ω = 0.1

(Click for solution)

Example 2.5

Compute the saturate liquid phase molar volume for methane at 150K. For methane T_c= 190.7 K, P_c= 46.41 bar, V_C = 98.6cm^3/mol, Z_C = 0.286, ω = 0.011.

(Click for solution)

2.4 Volumetric Properties of Mixtures

The EOSs discussed in the preceding sections may be applied to mixtures as well, through use of what are called "mixing rules". Such rules help re-define the fundamental parameters of each type of EOS in terms of those corresponding to pure species and overall composition. The principle behind these rules is that the mixture parameters are equivalent to those of a "hypothetical" pure species, which would display the same behaviour as the mixture. They are essentially semi-empirical in nature, in that they contain parameters which although grounded in molecular theory are difficult to predict fully. Nevertheless, such rules have proved reasonably reliable for prediction of mixture properties for most practical, engineering applications.

Virial EOS

For a gas mixture the virial EOS is exactly the same as for a pure species (eqn. 2.12):

$$Z = 1 + \frac{BP}{RT}$$

However, for the mixture the second virial coefficient 'B' is dependent not only on temperature but also on the mixture composition. Its exact composition dependence is derivable from the relations provided by statistical mechanics, and takes the following form:

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \qquad ..(2.26)$$

Where, y_i = mole fractions in a gas mixture. The indices i and j identify species, and both run over all species present in the mixture. The virial coefficient B_{ij} characterizes a bimolecular interaction between molecule i and molecule j, and therefore $B_{ij} = B_{ji}$. The summation in eqn. 2.26 accounts for all possible bimolecular interactions. For a binary mixture i = 2 and j = 2; the expansion of eqn.2.23 yields:

$$B = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \qquad ..(2.27)$$

Since they correspond to pure species, the calculation of the parameters B_{11} and B_{22} can be made directly employing eqns. 2.13 – 2.15. For any cross-coefficient B_{ij} (where i and j are not same) pseudo-critical" parameters need to be employed in general as shown below:

$$\omega_{ij} = (\omega_i + \omega_j)/2$$

$$T_{cij} = (T_{ci}T_{cj})^{1/2}(1-k_{ij})$$

$$k_{ij} = 1 - 8(V_{ci}V_{cj})^{1/2} / (V_{ci}^{1/3} + V_{cj}^{1/3})^3$$

Often k_{ij} is set to zero for simplicity

$$P_{cij} = Z_{cij}RT_{cij} / V_{cij}$$

$$Z_{cij} = (Z_{ci} + Z_{cj})/2$$

$$V_{cij} = [(V_{ci}^{1/3} + V_{cj}^{1/3})/2]^3$$

$$Now,\ T_{rij} = T / T_{cij}$$

$$B_{ij}^0 = 0.083 - (0.422 / T_{rij}^{1.6}); \quad B_{ij}^1 = 0.139 - (0.172 / T_{rij}^{4.2})$$

Finally: $B_{ij} = [(RT_{cij})/P_{cij}][B_{ij}^0 + \omega_{ij}B_{ij}^1]$ ..(2.28)

Next B_m is computed by eqn. 2.26, which is used in eqn. 2.12 for computing the mixture molar volume.

Example 2.6

Estimate the second virial coefficient for an equimolar mixture of propane and n-pentane at 500K and 10 bar.

	T_c (K)	**P_c (bar)**	**V_c x 10^3 (m^3/mol)**	**Z_c**	**ω**	**y_i**
Propane (1)	369.9	42.57	0.2	0.271	0.153	0.5

Pentane (2)	469.8	33.75	0.311	0.269	0.269	0.5

(Click for solution)

Cubic EOS:

The parameters in all cubic EOSs are principally*: a, b and ω.* It follows that for computing the molar volume of a mixture these parameters need to be re-defined using mixing rules. For a binary mixture they are:

For a binary mixture (*m*):

$$a_m = y_1^2 a_1 + 2y_1 y_2 (a_1 a_2)^{1/2} + y_2^2 a_2 \qquad ..(2.29)$$

$$b_m = y_1 b_1 + y_2 b_2 \qquad ..(2.30)$$

$$\omega_m = y_1 \omega_1 + y_2 \omega_2 \qquad ..(2.31)$$

The values of each parameters can be computed after those of the individual species are calculated using the expressions that apply to each type of cubic EOS (see table 2.1).

Generalized Correlations

Generalized correlations presented above for pure species may also be conveniently extended to prediction of volumetric properties of gas phase mixtures as well. For the mixture, the apparent critical properties are computed using the following set of linear relations:

$$T_{C,m} = \sum_i y_i T_{C,i}\ ; \qquad P_{C,m} = \sum_i y_i P_{C,i} \qquad \omega_m = \sum_i y_i \omega_i \qquad ..(2.32)$$

The subscript '*i*' runs over all the species present in the mixture '*m*'. The above properties are designated as "pseudo-critical" as they do not represent the true critical properties of a mixture; indeed the latter are most often difficult to obtain.

The *pseudo-reduced* temperature and pressure, are then determined by: $T_{r,m} = T / T_{C,m}$; $P_{r,m} = P / P_{C,m}$. As for pure components, the compressibility factor for the mixture is next obtained using standard functions of $Z^0(T_r, P_r)\ and\ Z^1(T_r, P_r),$ which are then used in the following equation: $Z_m = Z_m^0 + \omega Z_m^1$ ..(2.33)

Example 2.7

Calculate the molar volume of an ethylene and propylene mixture comprising 70 mole percent ethylene and 30 mole percent propylene at 600 K and 60 bar. Assume that the mixture follows the Redlich-Kwong equation of state.

	T_c (K)	P_c (bar)
Ethylene (1)	283.1	51.17
Propylene (2)	365.1	46.0

(Click for solution)

2.5 Property Representation of 2-phase systems:

Consider a system consisting of liquid and vapor phases of a pure component coexisting in equilibrium. The total value of any extensive property of the two-phase system is the sum of the total properties of the phases. Let the total volume of the system be V^t; n^L = mass (or moles) of liq, n^V = mass (or moles of vapour.

Then:

$$V^t = nV = n^L V^L + n^V V^V$$

$$n = n^L + n^V$$

$$x^L = n^L / n$$

$$x^V = n^V / n$$

$$x^L + x^V = 1$$

$$V = x^L V^L + x^V V^V = (1 - x^V) V^L + x^V V^V = V^L + x^V V^{LV}$$

$$V^{LV} = V^V - V^L$$

Let M = Any Molar Thermodynamic Property

Thus, one may write: $M = M^L + x^V M^{LV}$ ..(2.34)

Where, $M^{LV} = M^V - M^L$ ..(2.35)

It may be noted that M is not a state variable, but an effective molar property of the system. The actual phase rule state variables are M^V and M^L. The parameter x^V – the mass fraction of vapour phase – in the system if called the *'quality'*.

<u>Example 2.8</u>

Find the molar volume and internal energy of a system containing water and steam at 50% quality at 200^{0}C.

(Click for solution)

2.6 Heat Effects of Phase Change

A change of phase is generally accompanied by heat release or absorption. The heat effect during the change of phase from liquid to gas, for example, is called the latent heat (or enthalpy of vapourization), while for a transition from soild to liquid the effect is termed heat of fusion. Such enthalpy changes typically quantify the amount of heat need to change the phase of one mole of a substance and are usually obtained experimentally. However, correlations have been developed for their prediction as well. The Reidel equation (L. Riedel, *Chem. Ing. Tech*., vol. 26, pp. 679-683, 1954) provides a suitable expression for the enthalpy of vapourization at the normal boling point (ΔH_n^{vap}) of a pure substance:

$$\frac{\Delta H_n^{vap}}{T_n} = \frac{1.092(\ln P_C - 1.013)}{(0.093 - T_{rn})} \qquad ..(2.36)$$

Where, n = normal boiling point, P_C (bar).

The Watson equation may be used (K. M. Watson, *Ind. Eng. Chem.*, vol. *35*, pp. 398-406, 1943) for computing the enthalpy of vaporization of a pure liquid at any temperature using its value at a chosen datum temperature:

$$\frac{\Delta H_2^{vap}}{\Delta H_1^{vap}} = \left(\frac{1 - T_{r2}}{1 - T_{r1}}\right)^{0.38}; \Delta H_i^{vap} = Heat\ of\ \ vapourization\ at\ T_i \qquad ..(2.37)$$

<u>Example 9</u>

Using Riedel's correlation, estimate the enthalpy of vaporization of water at its normal boiling point and compare the result with that given in steam tables.

(Click for solution)

Example 2.10

The enthalpy of vaporization of water at 100^oC is 2256.94 kJ/kg. Determine the value at 150^oC, and compare the value with that listed in the steam tables.

(Click for solution)

Appendix: Lee-Kesler and Pitzer Methods

Lee Kesler Method:

The method used a modified Bendict-Webb-Rubin equation using Pitzer's acentric factor (ω). The compressibility factor of a real fluid is related to the properties of a simple fluid (ω= 0) and those of a *reference* fluid; for the latter *n-Octane* is used... The compressibility factor Z for the fluid is given by:

$$Z = Z^0 + \frac{\omega}{\omega^R}\left(Z^R - Z^0\right) \qquad \text{(A.2.1)}$$

Where Z = compressibility factor for the fluid

Z^0 = compressibility factor for the simple fluid

Z^R= compressibility factor for the reference fluid

ω = acentric factor for the fluid

ω^R = acentric factor for the reference fluid (n-octane) = 0.3978.

According to the theory of corresponding states $\omega = 0$, for "simple fluids": i.e. whose molecules are considered spherical; examples include noble gases, such as argon, krypton and xenon. Sphericity of a molecule tends to reduce its polarity, as the centre of negative and positive charges approach each other, leading to low dipole moments. This is also true for relatively linear but symmetric molecule. For example, carbon dioxide has virtually no dipole moment; however, it possesses a *quadrupole* moment. The acentric factor, therefore, is an indirect measure of the dipole moment of a molecule, and hence of the deviation of the intermolecular potential of real fluids from that of simple fluids.

The compressibility factors for the simple fluid (Z^0) and the reference fluid (Z^R) are generated from the following equation which is a variant for the BWR EOS (eqn. 2.17):

$$Z^0 = \frac{P_r V_r^0}{T_r} = 1 + \frac{B}{V_r^0} + \frac{C}{\left(V_r^0\right)^2} + \frac{D}{\left(V_r^0\right)^5} + \frac{C_4}{T_r^3\left(V_r^0\right)^2}\left(\beta + \frac{\gamma}{\left(V_r^0\right)^2}\right)\exp\left(-\frac{\gamma}{\left(V_r^0\right)^2}\right) \qquad ..(A.2.2)$$

$$Z^R = \frac{P_r V_r^R}{T_r} = 1 + \frac{B}{V_r^R} + \frac{C}{\left(V_r^R\right)^2} + \frac{D}{\left(V_r^R\right)^5} + \frac{C_4}{T_r^3\left(V_r^R\right)^2}\left(\beta + \frac{\gamma}{\left(V_r^R\right)^2}\right)\exp\left(-\frac{\gamma}{\left(V_r^R\right)^2}\right) \qquad ..(A.2.3)$$

Where $B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}$ ..(A.2.4)

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \qquad ..(A.2.5)$$

$$D = d_1 + \frac{d_2}{T_r} \qquad ..(A.2.6)$$

Where P_r *and* T_r *are the* reduced pressure and temperature, respectively, at which the volume of the real fluid is required.

Further, $V_r^0 = P_c V^0 / RT_c$ ..(A.2.7)

Where, V^0 = molar volume of the simple fluid (at the given T & P). The Lee-Kesler constants for the simple fluid and the reference fluid to be used with Eqns. 2-6 are enumerated in Table A.1.1 below.

Table A.1.1 Lee-Kesler Constants for use with Eqns.A.2.2-A.2.6

Constant	Simple fluid	Reference fluid	Constant	Simple fluid	Reference fluid
b_1	0.1181193	0.2026579	c_3	0.0	0.016901
b_2	0.265728	0.331511	C	0.042724	0.041577

b_3	0.154790	0.027655	$d_1 \times 10^4$	0.155488	048736
b_4	0.030323	0.203488	$d_2 \times 10^4$	0.623689	0.0740336
c_1	0.0236744	0.0313385	β	0.65392	1.226
c_2	0.0186984	0.0503618	γ	0.060167	0.03754

The method of calculating the volume at a given T_r and P_r is as follows:

- Step 1: using the critical properties of the real fluid find V_r^0 by eqn. A.2.7
- Step 2: using V_r^0, calculate Z^0 by eqn. A.2.1
- Step 3: using the given values of T_r and P_r, Eqn.A.2.2 is solved again, but *with reference fluid constants* from above table. The solution obtained for V_r^0 is now called V_r^R
- Step 4: Z^R, the compressibility for the reference fluid, is next computed with: given by

  $$Z^R = P_r V_r^R / T_r \qquad \text{(A.2.8)}$$

- Step 5: With the above values of Z^0 and Z^R, the compressibility factor Z for the fluid in question can be calculated from Eqn.A.2.1.

The *Generalized* Lee-Kesler Charts essentially present the values of Z^0 and Z^1 obtained by the above procedure as function of T_r and P_r (as). A variety of other thermodynamic variables can also be computed in an identical manner. Examples include *residual* enthalpy and entropy, and gas fugacity. These properties are presented either in the form of figures or charts (see, for example, Appendix E of J.M. Smith, H.C. Van Ness and M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, 6th ed., McGraw-Hill, 2001).

Pitzer Method:

The Pitzer method is nearly identical to that of Lee-Kesler; it assumes that the compressibility factor is linearly dependent on the acentric factor. Thus, eqn. A.2.1 is reformulated using the compressibility factors of *both* the simple (1) and reference fluid (2), whence:

$$Z = Z^{R1} + \frac{\omega - \omega^{R1}}{\omega^{R2} - \omega^{R1}}\left(Z^{R2} - Z^{R1}\right) \qquad \text{..(A.2.9)}$$

Any two fluids may be used as the reference fluids. The method of computing the values of Z^{R2} and Z^{R1} and hence, Z for the fluid of interest follows the same procedure described above for Lee-Kesler.

Assignment-Chapter 2

CHAPTER 3: First Law of Thermodynamics

3.1 Concept of Internal Energy

We have noted in chapter 1 that the two most common modes of energy exchanged by a thermodynamic system and its surroundings are work and heat. The interconvertibility between these two forms of energy was first demonstrated by the British scientist James P. Joule during 1840s by a series of carefully executed experiments. The experimental setup he used is shown as a schematic in fig. 3.1. Known quantities of a set of fluids (water, oil, and mercury) were placed in an insulated, rigid vessel and stirred by means of rotating shaft provided with vanes. The amounts of work done on the fluid by the stirrer were measured in terms that needed to lower or raise a weight, and the resultant change in the temperature of the fluid was recorded. The key observation made by Joule was that for each fluid a *fixed* amount of work was required per unit mass for every degree of temperature rise caused by the rotating paddle wheel. Further, the experiments showed that the temperature of the fluid could be restored to its initial value by the transfer of heat by bringing it in contact with a cooler object. These experimental findings demonstrated for the first time that inter-convertibility exists between work and heat, and therefore the latter was also a form of energy.

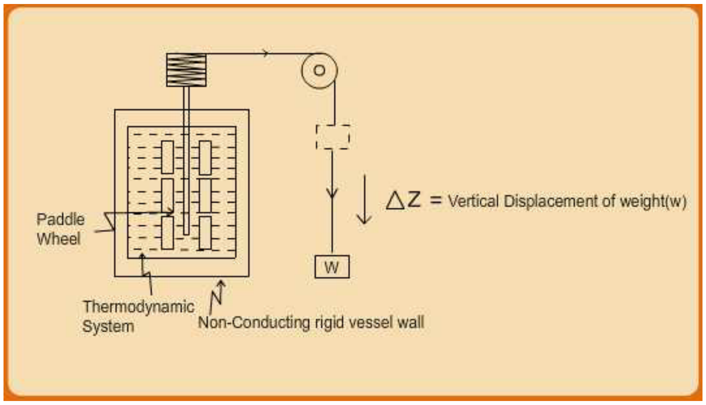


Fig. 3.1 Schematic of Joule's Experimental System

Joule's observation also provided the basis for postulation of the concept of *internal energy* (introduced briefly in section 1.3). Since work are heat are distinctly different forms of energy how is it possible to convert one into another? The question can be answered if one assumes that although these two types of energies are distinct in *transit* across a thermodynamic system boundary, they must eventually be stored within a thermodynamic system in a common form. That common form is the so-called internal energy. As we have already discussed in section 1.3, such a form of energy can only repose at the microscopic level of atoms and molecules, essentially in the form of translational, vibrational and rotational energies. To this may be added the potential energy of intermolecular interactions (as introduced in section 2.2). On a sub-molecular scale energy is associated with the electrons and nuclei of atoms, and with bond energy resulting from the forces holding atoms together as molecules. With these considerations one is in a position to rationalize the observation that while a system may receive energy in the form of work done on it, it may part with it also in the form of heat to another body or surroundings and be restored to its state prior to receipt of work. This is possible as in the interim between these two processes all energy may be stored in the form of internal energy.

As may be evident from the foregoing discussion, the addition of heat or work from an external source can lead to enhancement of the microscopic form of systemic (internal) energy. As also noted in chapter 1 the terminology “internal” is applied mainly to distinguish it from the mechanical potential and kinetic energies that a thermodynamic system may also possess by virtue of its position and velocity with respect to a datum. The latter two may then be thought of as “external” forms of energy.

It is important to note that like other intensive, macroscopic variables such as pressure, temperature, mass or volume, internal energy is a *state variable* as it is wholly dependent on the energy states that its atoms / molecules. Thus any change in the (say, specific) internal energy due to a process would only depend on the initial and final states, and not on the path followed during the change. Thus as for changes in P, V or T, one may write:

$$\int_{U_1}^{U_2} dU = \Delta U = U_2 - U_1$$

However, unlike P, V, T or mass, U is not a directly measurable property. Besides, in common with potential and kinetic energies, no absolute values of internal energy are possible. However, this is not of particular significance as in thermodynamic processes one is always interested in *changes* in energies rather than their absolute values

3.2 The First Law of Thermodynamics

The empirical conclusion that heat and internal energy belong to the general category of energies, help extending the law of conservation of mechanical energy, which states that potential and kinetic energies are fully inter-convertible. As already discussed in chapter 1, a thermodynamic system may possess any other forms of energy such as surface energy, electrical energy, and magnetic energy, etc. Thus one may arrive at an extended postulate that all forms are energies are inter-convertible. This constitutes the basis of the *First Law of Thermodynamics,* which may be stated as follows:

Energy can neither be destroyed nor created, when it disappears in one form it must re-appear at the same time in other forms.

It must be said that there is no *formal* proof of the first law (or indeed of other laws of thermodynamics) is possible, but that no evidence have been found to date that violates the principle enunciated by it.

For any thermodynamic process, in general one needs to account for changes occurring both within a system as well as its surroundings. Since the two together forms the "universe" in thermodynamic terms, the application of the first law to a process leads to the following mathematical form:

$$\Delta(Total\ energy\ of\ the\ universe) = 0$$

$$\Delta(Total\ energy\ of\ the\ system) + \Delta(Total\ energy\ of\ the\ surroundings) = 0$$

Where $\Delta \equiv finite\ change\ occurring\ during\ the\ thermodynamic\ process$

3.2 Application of the First Law to Closed Systems

In general, a thermodynamic system in its most complex form may be multi-component as well as multiphase in nature, and may contain species which react chemically with each other. Thermodynamic analysis tends to focus dominantly on the energy changes occurring within such a thermodynamic system due to change of state (or vice versa), and therefore it is often convenient to formulate the first law specifically for the system in question. Here we focus on closed systems, i.e., one that does not allow transfer of mass across its boundary. As already pointed out work and heat may enter or leave such a system across its boundary (to and fro with respect to the surrounding) and also be stored in the common form of internal energy. Since in a system may also possess potential and kinetic energies, one may reframe the first law as follows. Using the notations U, E_K, E_P for specific internal, kinetic and potential energies, respectively:

$$\Delta[U^{total} + E^{total}_{kinetic} + E^{total}_{potential}]_{system} = \text{Total energy input to system in all forms}$$

If the energy transfer across the system boundary takes place only the form of work and heat:

$$\Delta[U^{total} + E^{total}_{kinetic} + E^{total}_{potential}]_{system} = Q^{total}(heat\ input) + W^{total}(work\ input)$$

The above relation may be written per unit mass / mole of closed system, i.e.,:

$$\Delta U + \Delta E_K + \Delta E_P = Q + W$$

The above equation may also be written in a differential form:

$$dU + dE_K + dE_P = \delta Q + \delta W \qquad ..(3.1)$$

If there is no change in potential and kinetic energies for the system or it is negligible – as is usually true for most thermodynamic systems of practical interest – the above equation reduces to:

$$dU = \delta Q + \delta W \qquad ..(3.2)$$

One of the great strengths of the mathematical statement of the first law as codified by eqn. 3.2 is that it equates a state variable (U) with two path variables (Q, W). As a differentiator we use the symbol δ to indicate infinitesimal work and heat transfer (as opposed to d used state variables). The last equation potentially allows the calculation of work and heat energies required for a process, by simply computing the change in internal energy. As we shall see later (chapters. 4 & 5) changes in internal energy can be conveniently expressed as functions of changes in state properties such as T, P and V.

In the above equation the term δW represents any form of work transfer to or from the system. In many situations of practical interest the thermodynamic work for closed systems is typically the PdV work (eqn. 1.6). Hence in such cases one may reframe eqn. 3.2 as follows:

$$dU = \delta Q + \delta W = \delta Q - \int_{V_1}^{V_2} PdV \qquad ..(3.3)$$

In keeping with the definition of work above, we adopt the following convention:

$W > 0$, if work is done on system
$W < 0$, if work is done by system
$Q > 0$, for heat addition to system
$Q < 0$, for heat removal from system

The process of change in a thermodynamic system may occur under various types of constraints, which are enlisted below:

- Constant pressure (*isobaric*)
- Constant volume (*isochoric*)
- Constant temperature (*isothermal*)
- Without heat transfer (*adiabatic*)

The mathematical treatment of each of these processes is presented below.

For a constant pressure process (fig. 3.2), we may write:

$$\delta Q = dU + PdV$$
$$\delta Q = dU + d(PV)$$
$$\delta Q = d(U + PV)$$
$$or\ \delta Q = dH$$

where, $H = U + PV$

The term H is termed *enthalpy*. It follows that like U, H is also a state variable. On integrating the differential form of the equation above one obtains for the process:

$$\int_1^2 \delta Q = \int_1^2 dH$$

Or: $Q = \Delta H$ ..(3.4)

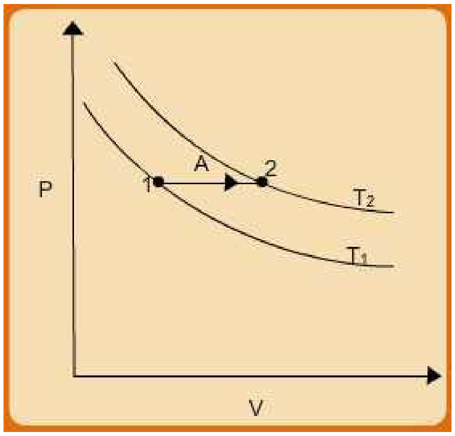


Fig. 3.2 Schematic of an Isobaric Path

On the other hand if the process occurs under isochoric (const. V) conditions (shown in fig. 3.3) the first law leads to:

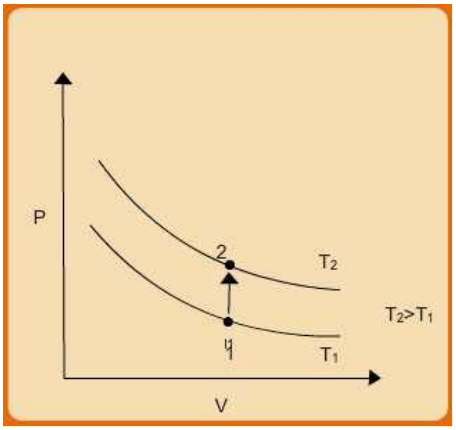


Fig. 3.3 Schematic of an Isochoric Path

$$\delta Q = dU$$

$$\int_1^2 \delta Q = \int_1^2 dH$$

$$Q = \Delta U \qquad ..(3.5)$$

We have already seen that a body can retain heat in the form of internal energy. This gives rise to the concept of heat capacity C and is mathematically defined as:

$$C \equiv \frac{\delta Q}{dT}$$

It follows that using eqns. 3.4 and 3.5 two types of heat capacity may be defined:

- Constant pressure heat capacity C_P such that:

$$C_P = \frac{\delta Q}{dT} = \left(\frac{\partial H}{\partial T}\right)_P \qquad ..(3.6)$$

- Constant volume heat capacity C_V such that:

$$C_V = \frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T}\right)_V \qquad ..(3.7)$$

Thus, using eqns. (3.6) and (3.7) one may rewrite eqns. (3.4) and (3.5) as follows:

$$Q = \Delta H = \int_{T_1}^{T_2} C_P dT \quad \text{(At const P.)} \qquad ..(3.8)$$

$$Q = \Delta U = \int_{T_1}^{T_2} C_V dT \quad \text{(At const V.)} \qquad ..(3.9)$$

With the addition of heat to a system, the translation, vibrational and rotational (as well as subatomic) energies of the molecules are enhanced and so it may be expected that the specific heats would be dependent on temperature. On the other hand when substances are compressed intermolecular interactions begin to contribute to internal energy (as hence to enthalpy) and therefore specific heats are rendered pressure dependent. For the case of ideal gases, however, the specific heats are independent of pressure as there are no intermolecular interactions; they are only temperature dependent. Values of specific heats of ideal gases (*ig*), say at constant pressure, are available from experimental measurements and are typically expressed in the form of polynomials such as:

$$\frac{C_P^{ig}}{R} = A + BT + CT^2 + \frac{D}{T^2} \qquad ..(3.10)$$

Where, A, B, C and D are characteristic constants for a substance, and R is the universal gas constant. Values of the constants in eqn. (3.10) are readily available for a large number of pure substances (see Appendix III for values of select gases). Fig. 3.4 shows typical dependence of const, pressure specific heat for select substances with temperature.

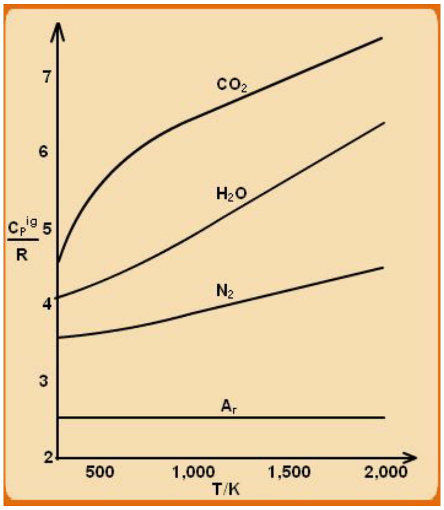


Fig. 3.4 Variation of C_P^{ig}/R vs. Temperature (Source: J. M Smith, H.C. Van Ness, M.M. Abbott, Introduction to Chemical Engineering Thermodynamics, 6th ed., McGraw-Hill, 2001)

Values of the coefficients of similar specific heat capacity polynomials for liquids and solids are available elsewhere (see for example, J.M. Smith, H.C. Van Ness and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics,* 6th ed., McGraw-Hill, 2001).

Applications to Ideal Gases

The other two types of thermodynamic processes – *isothermal and adiabatic* – in closed systems are conveniently understood by applying the first law to a system comprised of an ideal gas. For such a case the relationship between U and H may be rewritten using the EOS:

$$H = U + PV = U + RT$$

Or: $H - U = RT$

Since both H and U are only temperature dependent for ideal gases we write:

$$\frac{dH}{dT} - \frac{dU}{dT} = R$$

Now using eqns. 3.6 and 3.7 it follows that:

$$C_P - C_V = R \qquad ..(3.11)$$

(It may be noted that since the molar volume V is relatively small for both liquids and solids, one may write: $H \approx U$; hence: $C_P \simeq C_V$).

Let us now consider the relationships that obtain for an isothermal process for an ideal gas. Using eqn. 3.2, since $dU = 0$:

$$\delta Q = -\delta W$$

Or, $Q = -W$

If we consider only P-V work, the work term is calculable if the process is carried out reversibly, as the ideal gas EOS relate the P and V at all points of change, hence:

$$W = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \left(\frac{RT}{V}\right) dV = RT\ln\frac{V_1}{V_2} = RT\ln\frac{P_2}{P_1} \qquad ..(3.12)$$

Thus:

$$Q = RT\ln\frac{V_2}{V_1} = RT\ln\frac{P_1}{P_2} \qquad ..(3.13)$$

Example 3.1

A gas initially at 1 MPa, 500°C is contained in a piston-cylinder arrangement of initial volume of 0.1 m^3. The gas expanded isothermally to a final pressure of 100 kPa. Determine the work.

(Click for solution)

For isobaric process: $Q = \Delta H = \int C_P dT; W = -\int_{V_1}^{V_2} PdV = -P(V_2 - V_1) = -R(T_2 - T_1)$ ..(3.14)

For *adiabatic* process $dQ = 0$

Hence : $dU = \delta W$

Or : $C_V dT = -PdV = -\frac{RT}{V} dV$

$$\frac{dT}{T} = -\frac{R}{C_v}\frac{dV}{V}$$ ..(3.15)

The ratio of heat capacities is defined as:

$\gamma = C_P / C_V$

Or:

$$\gamma = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$$ ..(3.16)

On integrating eqn. 3.15 and using the relationship provided by eqn. 3.16, the following set of results may be derived easily:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$ ..(3.17)

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{(\gamma - 1)/\gamma}$$ ..(3.18)

and $P_1 V_1^{\gamma} = P_2 V_2^{\gamma} = PV^{\gamma} = const.$ ..(3.19)

Further: $dW = dU = C_V dT$

Or $W = dU = C_V dT$

Since, $W = -\int PdV$

Using eqn. 3.19 in the expression for work in the last equation:

$$W = \frac{P_2V_2 - P_1V_1}{\gamma - 1} \qquad ..(3.20)$$

Or:

$$W = \frac{P_1V_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] = \frac{RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] \qquad ..(3.21)$$

All the above processes discussed can be captured in the form of a single *P-V* relation, which is termed a *polytropic* equation as it can be reduced to yield all forms of processes. The polytropic relations are written by generalizing eqns. 3.17 – 3.19, as follows:

$$PV^{\delta} = \text{constant} \qquad ..(3.22)$$

$$TV^{\delta-1} = \text{constant} \qquad ..(3.23)$$

$$TP^{(1-\delta)/\delta} = \text{constant} \qquad ..(3.24)$$

The schematic of polytropic process is shown in fig. 3.5.

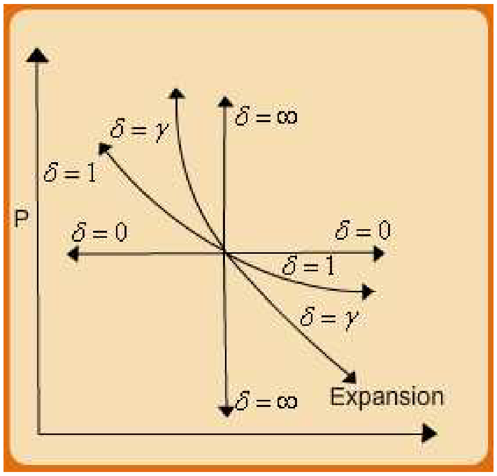


Fig. 3.5 Schematic of Polytropic Processes

As may be seen the various values of δ reproduce the isothermal, isochoric, isobaric and adiabatic processes. In line with eqn. 3.21, for such the generalized expressions for work and heat transfer may be shown to be:

$$W = \frac{RT_1}{\delta - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$ ..(3.25)

Further:

$$Q = \frac{(\delta - \gamma)RT_1}{(\delta - 1)(\gamma - 1)}\left[\left(\frac{P_2}{P_1}\right)^{(\delta-1)/\delta} - 1\right]$$ ..(3.26)

Example 3.2

Helium gas expands from 125 kPa, 350 K and 0.25 m^3 to 100 kPa in a polytropic process with δ = 1.667. How much work does it give out?

(Click for solution)

3.3 Application of the First Law to Open Systems

While the last section addressed processes occurring in closed systems, the wider application of the first law involves formulating the energy balance differently in order to accommodate the fact that most thermodynamic systems, i.e., equipments, in continuous process plants are essentially open systems: they allow mass transfer across their boundaries (i.e., through inlet and outlet). Examples include pumps, compressors, reactors, distillation columns, heat exchangers etc. Since such open systems admit both material and energy transfer across their boundaries the thermodynamic analysis necessarily involves both mass and energy balances to be carried out together. Also such systems may in general operate under both steady (during normal plant operation) and unsteady states (say during startup and shutdown). As we will see the former state is a limiting case of the more general situation of unsteady state behavior.

Mass Balance for Open Systems:

For generality consider an open system with which has multiple inlets (1, 2) and outlets (3, 4). The volume enclosed by the physical boundary is the *control volume* (CV). The general mass balance equation for such a system may be written as:

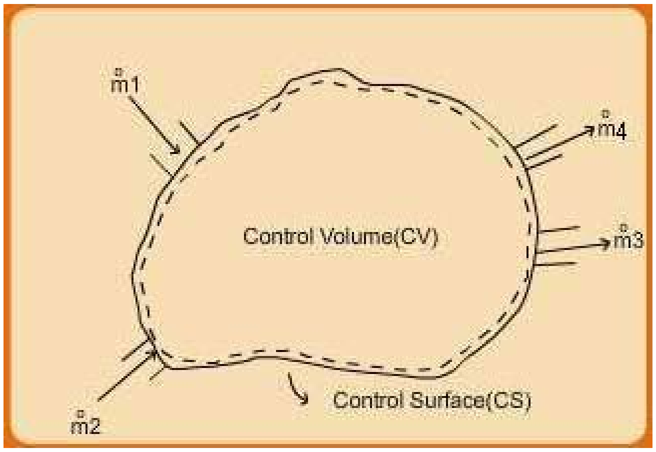


Fig. 3.6 Schematic of an open system

$$\frac{dm_{cv}}{dt} = \sum_{inlet} \dot{m} - \sum_{outlet} \dot{m} \qquad ..(3.27)$$

The mass flow rate $\dot{m}$ is given by:

$$\dot{m} = \rho u A \qquad ..(3.28)$$

Where, $\rho =$ fluid density; $u =$ fluid velocity; and $A =$ aperture cross-sectional area

The first term on the left side of the eqn. (3.27) denotes sum of all flow rates over all inlets, while the second term corresponds to the summation over all outlet flow rates. For the system shown in fig. 3.5 the eqn. 3.27 may be written as:

$$\frac{dm_{cv}}{dt} = \dot{m}_1 + \dot{m}_2 - \dot{m}_3 - \dot{m}_4 \qquad ..(3.28)$$

The last equation may be reframed in a general way as follows:

$$\frac{dm_{cv}}{dt} + \Delta(\dot{m})_{fs} = 0 \qquad ..(3.29)$$

Where the symbol $\Delta \equiv$ oulet-inlet; and the subscript *fs* stands for "flow streams".

Equation 3.29 may be recast as:

$$\frac{dm_{cv}}{dt} + \Delta(\rho u A)_{fs} = 0 \qquad ..(3.30)$$

The above equation simplifies under steady flow conditions as the accumulation term for the control volume, i.e., $\frac{dm_{cv}}{dt} = 0$

In such a case for the simplest case of a system with one inlet and outlet (say: 1 and 2 respectively), which typically represents the majority of process plant equipments, the mass balance equation reduces to:

$$\dot{m} = \text{constant}$$
$$\text{Or: } \rho_1 u_1 A_1 = \rho_2 u_2 A_2 \rightarrow u_1 A_1 / V_1 = u_2 A_2 / V_2 \qquad ..(3.31)$$

Where V = specific volume

Energy Balance for Open Systems:

Consider the schematic of an open system as shown in fig. 3.7. For simplicity we assume one inlet and one exit ports to the control volume. The thermodynamic states at the inlet i and exit e are defined by the P, V, T, u (average fluid velocity across the cross section of the port), and Z, the height of the port above a datum plane. A fluid element (consider an unit mole or mass) enters the CV carrying internal energy, kinetic and potential energies at the inlet conditions (P_i, T_i, with molar volume as V_i) and leaves values of these energies at the exit state conditions (P_e, T_e, with molar volume as V_e). Thus the total specific energy of the fluid at the two ports corresponds to the sum of specific internal, potential and kinetic energies, given by: $U + \frac{u^2}{2} + gZ$. In addition, the CV exchanges heat with the surroundings at the rate $\dot{Q}$, and say a total work (in one or more forms) at the rate of $\dot{W}_{total}$

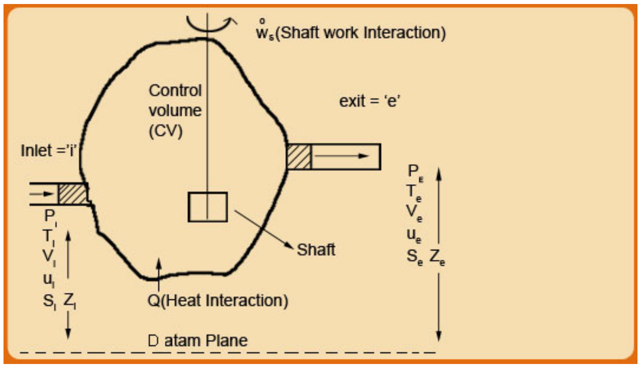


Fig. 3.7 Schematic of an open system showing flow and energy interactions

In the schematic we, however, have shown a specific work form, *shaft work*, that is delivered *to* or *by* the system by means of rotatory motion of a paddle wheel which, as we will see later in the section, is implicated in many typical process plant units. As with material balance one may write a total energy balance equation for the control volume as follows:

$$\frac{d(mU)_{cv}}{dt} = \left[\left(U + \frac{1}{2}(u^2) + zg)\right)\overset{\bullet}{m}\right]_i - \left[\left(U + \frac{1}{2}(u^2) + zg)\right)\overset{\bullet}{m}\right]_e + \overset{\bullet}{Q} + \overset{\bullet}{W}_{total}$$

Or:

$$\frac{d(mU)_{cv}}{dt} + \Delta\left[\left(U + \frac{1}{2}(u^2) + zg)\right)\overset{\bullet}{m}\right]_{fs} = \overset{\bullet}{Q} + \overset{\bullet}{W}_{total} \quad ..(3.32)$$

The general total work term should include all forms of work. We draw the reader's attention to the fact that the total work interaction also should include that needed to push fluid into the CV as well as that implicated in pushing it out of CV. The fluid state at the inlet or exit is characterized by a set of state properties, U, V, H, etc. Consider a unit mass (or mole) of fluid entering the CV. This fluid element obviously needs to be "pushed" by another that follows it so as to make the formed enter the CV. In essence a fluid element of (specific) volume V is pushed into the CV at a pressure P. This is akin to a P-V form of work (as in the case of a piston-in-a-cylinder system) that is done on the CV and so may be quantified as – P_iV_i. The same considerations apply at the exit in which case in pushing out a similar fluid element at exit conditions, i.e., – P_eV_e. Thus, eqn. 3.32 may be rewritten as follows:

$$\frac{d(mU)_{cv}}{dt} + \Delta\left[\left(U + \frac{1}{2}(u^2) + zg)\right)\overset{\bullet}{m}\right]_{fs} = \overset{\bullet}{Q} + \overset{\bullet}{W} - [PV\dot{m}]_i + [PV\dot{m}]_e \quad ..(3.33)$$

Where, $\overset{\bullet}{W}_{total} = \overset{\bullet}{W} - [PV\dot{m}]_i + [PV\dot{m}]_e$

The term $\overset{\bullet}{W}$ represents sum of *all other* forms of work associated with the process occurring within the CV. This residual work term may include the shaft work, P-V work resulting from expansion or contraction of the CV, electrical work, and so on. As the last two work terms on the left side of the eqn. 3.33 are associated with the flow streams we may rewrite the equation as follows:

$$\frac{d(mU)_{cv}}{dt}+\Delta\left[\left(U+\frac{1}{2}(u^2)+zg)\right)\dot{m}\right]_{fs}=\dot{Q}+\dot{W}-\Delta[PV\,\dot{m}]_{fs} \quad ..(3.34)$$

On rearranging:

$$\frac{d(mU)_{cv}}{dt}+\Delta\left[\left\{(U+PV)+\frac{u^2}{2}+zg\right\}\dot{m}\right]_{fs}=\dot{Q}+\dot{W} \quad ..(3.35)$$

Or: $$\frac{d(mU)_{cv}}{dt}+\Delta\left[\left\{H+\frac{u^2}{2}+zg\right\}\dot{m}\right]_{fs}=\dot{Q}+\dot{W} \quad ..(3.36)$$

It may be noted that eqn. 3.34 assumes that the CV is fixed in space and therefore no overall potential of kinetic energy terms depicting these mechanical energies for the control volume is included. This, of course, is valid for all process plant applications. In addition, For many cases of practical importance (though not all) in a chemical plant the kinetic and potential energy changes between the inlet and exit streams may not be significant, whence the last equation may be simplified as: an equipment may be neglected; hence:

$$\frac{d(mU)_{cv}}{dt}+\Delta\left[H\,\dot{m}\right]_{fs}=\dot{Q}+\dot{W} \quad ..(3.37)$$

Further, for the special case where the only shaft work is involved, the above equation may be simplified to:

$$\frac{d(mU)_{cv}}{dt}+\Delta\left[H\,\dot{m}\right]_{fs}=\dot{Q}+\dot{W}_s \quad ..(3.38)$$

For *steady state* applications the eqn. 3.34 reduces to:

$$\Delta\left[\left\{H+\frac{u^2}{2}+zg\right\}\dot{m}\right]_{fs}=\dot{Q}+\dot{W} \quad ..(3.39)$$

Further, if the kinetic and potential energy changes associated with the flow streams are insignificant, it follows that:

$$\Delta\left[H\,\dot{m}\right]_{fs}=\dot{Q}+\dot{W} \quad ..(3.40)$$

Since under steady state $\dot{m}$ is constant we may write:

$\Delta H = Q + W$ ..(3.41)

Where Q and W denote the work and heat interactions per unit mass of mole of fluid flowing through the system flowing through system. Once again if W_s is the only form of work interaction between the system and the surrounding then:

$\Delta H = Q + W_s$ ..(3.42)

Examples of process plant units to which eqn. 3.42 applies are: *pumps*, *compressors*, *turbines*, *fans*, *blowers*, etc. In all cases a rotatory part is used exchange work between the system and surrounding.

Example 3.3

A chiller cools liquid water (Sp. Ht = 4.2 J/gmK) for air-conditioning purposes. Assume 2.5 kg/s water at 20^{o}C and 100 kPa is cooled to 5^{o}C in a chiller. How much heat transfer (kW) is needed?

(Click for solution)

Example 3.4

A piston-cylinder assembly contains 0.1 kg wet steam of quality 0.75 at 100 kPa. If 150 kJ of energy is added as heat while the pressure of the steam is held constant determine the final state of steam.

(Click for solution)

Example 3.5

An adiabatic compressor operating under steady-state conditions receives air (ideal gas) at 0.1 MPa and 300 K and discharges at 1 MPa. If the flow rate of air through the compressor is 2 mol/s, determine the power consumption of the compressor. Constant pressure specific heat for air = 1kJ/kg.

(Click for solution)

Example 3.6

An insulated piston-cylinder system has air at 400kPa & 600K. Through an inlet pipe to the cylinder air at certain temperature T(K) and pressure P (kPa) is supplied reversibly into the cylinder till the volume of the air in the cylinder is 4 times the initial volume. The expansion occurs isobarically at 400kPa. At the end of the process the air temperature inside the cylinder is 450K. Assume ideal gas behaviour compute the temperature of the air supplied through the inlet pipe.

(Click for solution)

3.4 Measurement of Enthalpy and Internal Energy using Flow Calorimeter

The use of the first law for open or closed systems necessitates the experimental determination (or, estimation from thermodynamic relations) of internal energy and enthalpy, both being state properties. The flow calorimeter (fig. 3.8), readily allows measurement of enthalpy, which in turn can be used to compute the internal energy at the same conditions of (say) temperature and pressure. The fluid whose properties are to be measured is pumped through a constant temperature bath so that it attains a desired temperature (say T_1) prior to entry into the vessel provided with an electric heater. The corresponding pressure (P_1) may also be recorded. Heat is next provided to the passing fluid at a pre-determined and fixed rate over a period of time until the temperature and pressure at the exit of the vessel attains steady values (say, T_2, & P_2). At such a condition the calorimeter is under steady state, hence eqn. 3.41 may be applied to the heating vessel. Since there is no work transfer of any kind, the resultant energy balance yields:

$\Delta H = Q$ ..(3.40)

Or: $H_2 - H_1 = Q$

So: $H_2 = H_1 + Q$ ..(3.41)

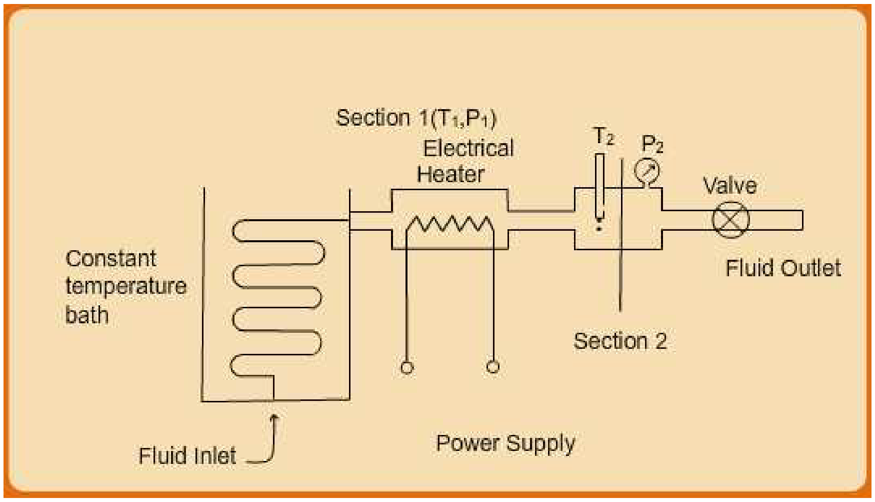


Fig. 3.8 A schematic of a flow calorimeter

Clearly, if we chose the enthalpy H_1 to be a datum state and arbitrarily assign it a zero value, then:

$H_2 = Q$

..(3.42)

The last equation then allows one to uniquely determine the value of H_2 at any condition achieved at state 2 by applying a known quantity of heat through the electric heating system. The internal energy at the same state can next be determined using the relation:

$U = H - PV$ ..(3.42)

Further we can measure the density (in terms of mass or mole) at the same state, and one may rewrite the last equation as: $U = H - P/\rho$ ..(3.43)

Thus using the above relations, U and H may be obtained experimentally at any P, T (and/or V) for any substance. The steam tables discussed at the concluding portion of section 2.1 constitutes such a tabulation of values of standard thermodynamic properties (saturation vapour pressure, internal energy, enthalpy (and entropy) of water obtained empirically over a wide range temperature and pressure.

Assignment-Chapter 3

Chapter 4: Second Law of Thermodynamics

4.1 Heat Engines and Second Law Statements

The First Law provides a constraint on the total energy contained in a system and its surroundings. If it disappears in one form from the system during any thermodynamic process of change, it must reappear in another form either within the system or in the surroundings. However, a pertinent question that one may often need to answer is: Is the process of change aimed at feasible? As may be evident, the first law provides *no constraint* on the possible direction a process may take place. Nevertheless, in the real world such constraints do exist. For example, heat always flows from a high temperature body to one at a lower temperature. Momentum flow is always prompted in the direction of a pressure gradient, and molecules always migrate from a region of higher to lower chemical potential. These observations clearly are indicative of the existence of a constraint on natural processes, which have never been found to be violated.

Further, it is common observation that work is readily transformed into other forms of energy, including heat. But all efforts to develop a device that may work in a continuous manner and convert heat completely into work or any other form of energy have proved impossible. Experimental observations show that typically no more than 40-50% of the total heat available may be converted to work or other energy forms. This finding has led to the conclusion that heat is a lower form of energy in that while it may be feasible to “degrade” work to heat, it is impossible to “upgrade” heat completely into work.

Heat may be seen as a more *primitive* form of energy, as it always has to be made available from matter (say by combustion) and subsequently converted to work for carrying out activities useful to humans. In this sense one never derives work *directly* from the energy locked in matter as enthalpy. This prompts the natural question: what determines the efficiency of such a conversion of heat to work? Evidently one needs a limiting principle that may help answer this question. These considerations provide the basis for formulating the Second Law of Thermodynamics.

2.1 Second Law Statements

It need be mentioned that the second law is a product of experiential observations involving *heat engines* that powered the Industrial Revolution of the 19th century. A heat engine is a machine that produces work from heat through a cyclic process. An example is a steam power plant in which the working fluid (steam) periodically goes through a series of steps in a cyclic manner as follows:

- *Step 1*: Liquid water at ambient temperature is pumped into a boiler operating at high pressure
- *Step 2:* Heat released by burning a fossil fuel is transferred in the boiler to the water, converting it to steam at high-temperature and pressure
- *Step 3:* The energy contained in the steam is then transferred as shaft work to a turbine; during this process steam temperature and pressure are reduced.
- *Step 4:* Steam exiting the turbine is converted to water by cooling it and transferring the heat released to the surroundings. The water is then returned to step 1.

Like the steam power plant all heat engines absorb heat at a higher temperature body (*source*) and release a fraction of it to a low temperature body (sink), the difference between the two quantities constitutes the net work delivered during the cycle. The schematic of a heat engine (for example: steam / gas power plant, automotive engines, etc) is shown in fig. 4.1. As in the case of the steam cycle, a series of heat and work exchanges takes place, in each case a specific hot source and a cold sink are implicated. A schematic of such processes is suggested inside the

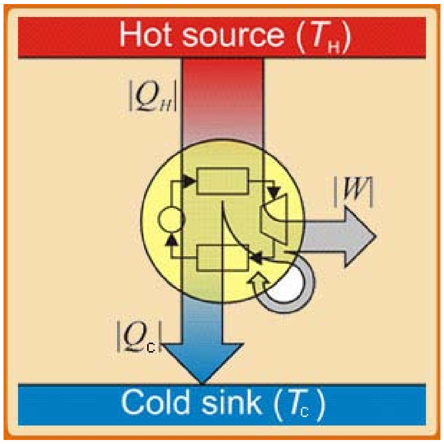


Fig. 4.1 Schematic of Heat Engine

yellow circle between the hot and cold sources. The opposite of a heat engine is called the heat pump (refrigerators being an example of such device) is shown in fig. 4.2. There are indeed a large number other types of practical heat engines and power cycles. Select examples include: Ericsson Cycle, Stirling cycle, Otto cycle (e.g. Gasoline/Petrol engine, high-speed diesel engine), Diesel cycle (e.g. low-speed diesel engine), etc. The Rankine cycle most closely reproduces the functioning of heat engines that use steam as the process fluid function (fig. 4.3); such heat engines are most commonly found in power generation plants. In such plants typically heat is derived from nuclear fission or the combustion of fossil fuels such as coal, natural gas, and oil. Detailed thermodynamic analysis of the various heat engine cycles may be found in a number of textbooks (for example: J.W. Tester and M. Modell, *Thermodynamics and its Applications*, 3rd ed., Prentice Hall, 1999).

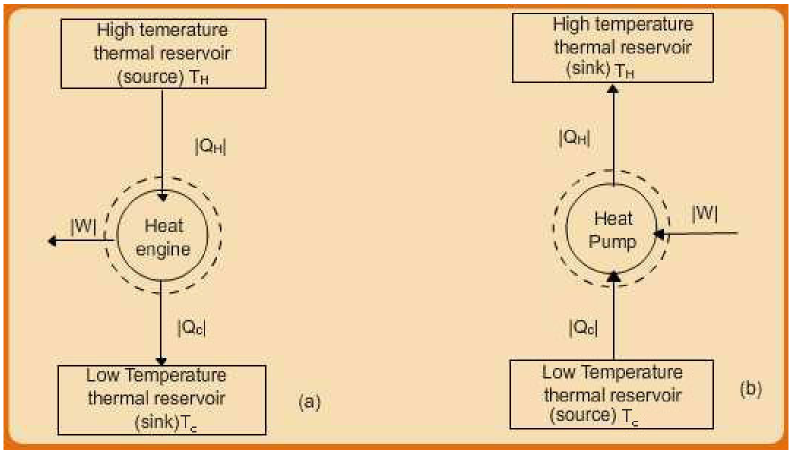


Fig. 4.2 Comparison of Heat Engine and Heat Pump

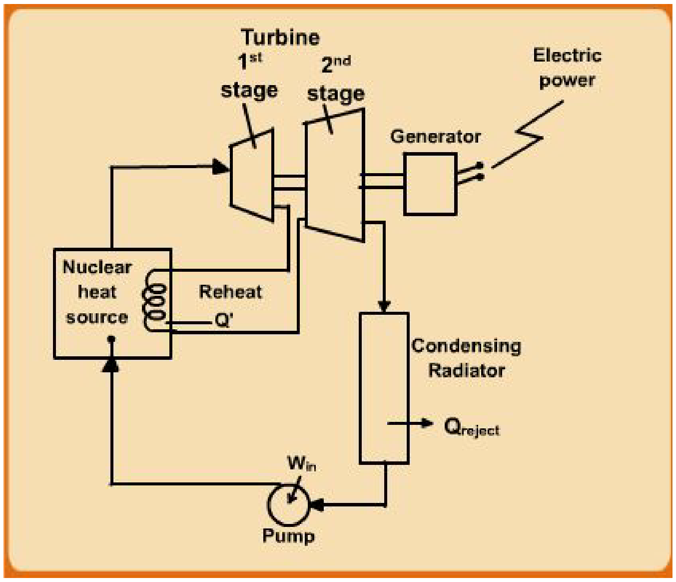


Fig. 4.3 Schematic of a Power Plant (Rankine) Cycle

As evident, the operation of practical heat engines requires two bodies at *constant* differential temperature levels. These bodies are termed *heat reservoirs;* they essentially are bodies with – theoretically speaking – infinite *thermal mass* (i.e., $mC_P \to \infty$) which therefore do not undergo a change of temperature due to either release or absorption of heat. The above considerations may be converted to a set of statements that are *equivalent* descriptors of the second law (R. Balzheiser, M. Samuels, and J. Eliassen, *Chemical Engineering Thermodynamics*, Prentice Hall, 1972):

***Kelvin-Planck Statement*:** It is impossible to devise a cyclically operating device, the sole effect of which is to absorb energy in the form of heat from a single thermal reservoir and to deliver an equivalent amount of work.

***Clausius Statement*:** It is impossible to devise a cyclically operating device, the sole effect of which is to transfer energy in the form of heat from a low temperature body to a high temperature body.

2.2 Carnot Heat Engine Cycle and the 2nd Law

In theory we may say that a heat engine absorbs a quantity of heat $|Q_H|$ from a high temperature reservoir at T_H and rejects $|Q_C|$ amount of heat to a colder reservoir at T_H. It follows that the net work W delivered by the engine is given by:

$$W = |Q_H| - |Q_C| \qquad ..(4.1)$$

Hence the efficiency of the engine is:

$$\eta = \frac{W}{|Q_H|} = \frac{|Q_H| - |Q_C|}{|Q_H|} \qquad ..(4.2)$$

$$\eta = 1 - \frac{|Q_C|}{|Q_H|} \qquad ..(4.3)$$

Of the various forms of heat engines ideated, the *Carnot engine* proposed in 1824 by the French engineer Nicholas Leonard Sadi Carnot (1796-1832), provides a fundamental reference concept in the development of the second law. The so-called Carnot cycle (depicted in fig. 4.4) is a series of *reversible* steps executed as follows:

- **Step 1: A** system at the temperature of a cold reservoir T_C undergoes a *reversible* adiabatic compression which raises it temperature to that of a hot reservoir at T_H.
- **Step 2:** While in contact with the hot reservoir the system absorbs $|Q_H|$ amount of heat through an isothermal process during which its temperature remains at T_H.
- **Step 3:** The system next undergoes a *reversible* adiabatic process in a direction reverse of step 1 during which its temperature drops back to T_C.
- **Step 4:** A *reversible* isothermal process of expansion at T_C transfers $|Q_C|$ amount of heat to the cold reservoir and the system state returns to that at the commencement of step 1.

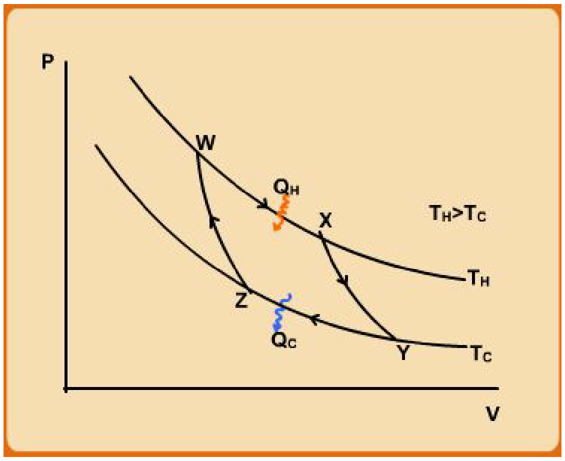


Fig. 4.4 Carnot Cycle Processes

The Carnot engine, therefore, operates between two heat reservoirs in such a way that all heat exchanges with heat reservoirs occur under isothermal conditions for the system and at the temperatures corresponding to those of the reservoirs. This implies that the heat transfer occurs under *infinitesimal* temperature gradients across the system boundary, and hence these processes are reversible (see last paragraph of section 1.9). If in addition the isothermal and adiabatic processes are also carried out under mechanically reversible (quasi-static) conditions the cycle operates in a fully reversible manner. It follows that any other heat engine operating on a different cycle (between two heat reservoirs) must necessarily transfer heat across finite temperature differences and therefore cannot be thermally reversible. As we have argued in section that irreversibility also derives from the existence of dissipative forces in nature, which essentially leads to waste of useful energy in the conversion of work to heat. It follows therefore the Carnot cycle (which also comprises *mechanically reversible* processes) offers the maximum efficiency possible as defined by eqn. 4.3. This conclusion may also be proved more formally (see K. Denbigh, *Principles of Chemical Equilibrium*, 4th ed., Cambridge University Press, 1981).

We next derive an expression of Carnot cycle efficiency in terms of macroscopic state properties. Consider that for the Carnot cycle shown in fig. 4.4 the process fluid in the engine is an ideal gas. Applying the eqn. 3.13 the heat interactions during the isothermal process may be shown to be:

$$\left|Q_H\right| = RT_H \ln\frac{V_x}{V_w} \qquad ..(4.4)$$

And $$\left|Q_C\right| = RT_C \ln\frac{V_y}{V_z} \qquad ..(4.5)$$

Further for the adiabatic paths *xy* and *zw* using eqn. 3.17 one may easily derive the following equality:

$$\ln\frac{V_x}{V_w} = \ln\frac{V_y}{V_z} \qquad ..(4.6)$$

Using eqns. 4.4 – 4.5 we may write:

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H \ln \frac{V_x}{V_w}}{T_C \ln \frac{V_y}{V_z}} \qquad ..(4.7)$$

Finally applying eqn. (4.6) on obtains:

$$\frac{|Q_H|}{|Q_C|} = \frac{T_H}{T_C} \qquad ..(4.8)$$

Hence, using eqn. 4.3: $\eta = 1 - \frac{T_C}{T_H}$ ..(4.9)

Also, $W = |Q_H| - |Q_C|$ ..(4.10)

Eqn. (4.8) may be recast as:

$$\frac{|Q_H|}{T_H} = \frac{|Q_C|}{T_C} \qquad ..(4.10)$$

As heat Q_H enters the system it is *positive,* while Q_C leaves the system, which makes it negative in value. Thus, removing the modulus use, eqn. 4.10 may be written as:

$$\frac{Q_H}{T_H} = -\frac{Q_C}{T_C} \qquad ..(4.11)$$

Or: $\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$ ..(4.12)

Or: $\sum \frac{Q}{T} = 0$ ..(4.13)

Consider now eqn. 4.9. For the Carnot efficiency to approach unity (i.e., 100%) the following conditions are needed: $\mathrm{T}_H \to \infty$; or $\mathrm{T}_C \to 0$. Obviously neither situation are practicable, which suggests that the efficiency must always be less than unity. In practice, the naturally occurring bodies that approximate a cold reservoir are: atmospheres, rivers, oceans, etc, for which a representative temperature T_C is ~ 300^0K. The hot reservoirs, on the other hand are typically furnaces for which T_H ~ 600^0K. Thus the Carnot efficiency is ~ 0.5. However, in practice, due to mechanical irreversibilities associated with real processes heat engine efficiencies never exceed 40%.

Example 4.1

An inventor claims to have devised a cyclic engine which exchanges heat with reservoirs at 27°C and 327°C, and which produces 0.6 kJ of work for each kJ of heat extracted from the hot reservoir. Is the claim believable? If instead he claimed that the delivered work would be 0.25kJ / kJ of extracted heat, would the engine be feasible?

(Click for solution)

It is interesting to note that the final step of thermodynamic analysis of Carnot cycle (i.e., eqn. 4.13) leads to the conclusion that there exists a quantity $\frac{Q}{T}$ which add up to zero for the complete cycle. Let us explore extending the idea to any general *reversible* cycle (as illustrated in fig.4.5) run by any working fluid in the heat engine.

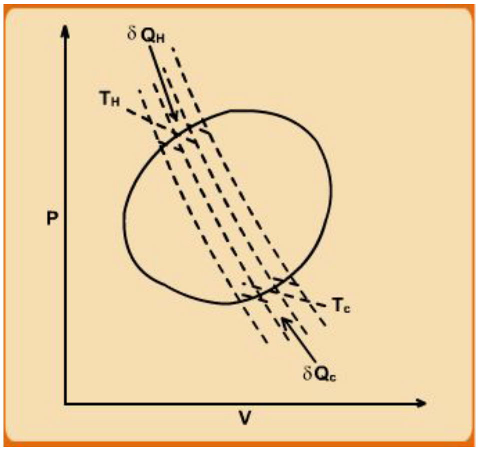


Fig. 4.5 Illustration of an arbitrary cycle decomposed into a series of small Carnot cycles

The complete cycle may, in principle, be divided into a number of Carnot cycles (shown by dotted cycles) in series. Each such Carnot cycle would be situated between two heat reservoirs. In the limit that each cycle becomes infinitesimal in nature and so the number of such cycles infinity, the original, finite cycle is reproduced. Thus for each infinitesimal cycle the heat absorbed and released in a *reversible* manner by the system fluid may be written as $|\delta Q_H|$ and $|\delta Q_C|$ respectively. Thus, now invoking eqn. 4.12 for each cycle:

$$\frac{\delta Q_H}{T_H}+\frac{\delta Q_C}{T_C}=0 \qquad ..(4.14)$$

Hence, applying eqn. 4.13 to sum up the effects of series of all the infinitesimal cycles, we arrive at the following relation for the entire original cycle:

$$\oint \frac{\delta Q_{rev}}{T}=0 \qquad ..(4.15)$$

Clearly, the relation expressed by eqn. 4.15 suggests the existence of a *state* variable of the form $\frac{\delta Q_{rev}}{T}$ as its sum over a cycle is zero. This state variable is termed as "Entropy" (S) such that:

$$dS=\frac{\delta Q_{rev}}{T} \qquad ..(4.16)$$

Thus: $\oint dS=0$

Thus, for a *reversible* process: $dQ_{rev} = TdS$ ..(4.17)

If applied to a perfectly reversible *adiabatic* process eqn. 4.16 leads to the following result: $dS=0.$ Thus, such a process is alternately termed as *isentropic*.

Since entropy is a state property (just as internal energy or enthalpy), even for irreversible process occurring between two states, the change in entropy would be given by eqn. 4.16. However since entropy is calculable directly by this equation one necessarily needs to construct a reversible process by which the system may transit between the same two states. Finite changes of entropy for irreversible processes *cannot* be calculated by a simple integration of eqn. 4.17. However, this difficulty is circumvented by applying the concept that regardless of the nature of the process, the entropy change is identical if the initial and final states are the same for each type of process. This is equally true for any change of state brought about by irreversible heat transfer due to finite temperature gradients across the system and the surroundings. The same consideration holds even for mechanically irreversibly processes.

With the introduction of the definition of entropy the Carnot engine cycle may be redrawn on a temperature-entropy diagram as shown in fig. 4.6.

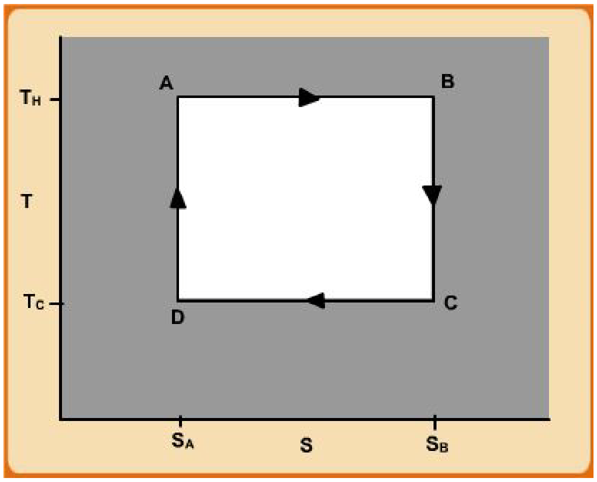


Fig. 4.6 Representation of Carnot cycle on T-S diagram

2.3 Entropy Calculations for Ideal Gases

For a closed system, the first law provides:

$$dU = dQ + dW$$

If the process of change occurs under reversible conditions then the above equation becomes:

$$d(H - PV) = TdS - PdV$$

$$dH - PdV - VdP = TdS - PdV \qquad ..(4.18)$$

However for an ideal gas: $dH = C_P^{ig} dT$ ..(4.19)

Thus combining eqns. 4.18 and 4.19:

$$C_P^{ig} dT = TdS + VdP$$

Or: $$\frac{dS}{R} = \frac{C_P^{ig}}{R}\frac{dT}{T} - d\ln P \qquad ..(4.20)$$

Integrating between an initial (T_0, P_0) and any final (T, P):

$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R}\frac{dT}{T} - \ln\frac{P}{P_0}$$

Or: $$\Delta S\Big|_{P_0}^{P} = \int_{T_0}^{T} C_P^{ig}\frac{dT}{T} - R\ln\frac{P}{P_0} \qquad ..(4.21)$$

The last equation provides a direct expression for computing entropy change between two states for an ideal gas.

For the special case of a reversible adiabatic *dQ* = *0*; hence *dS*= *0*. Thus:

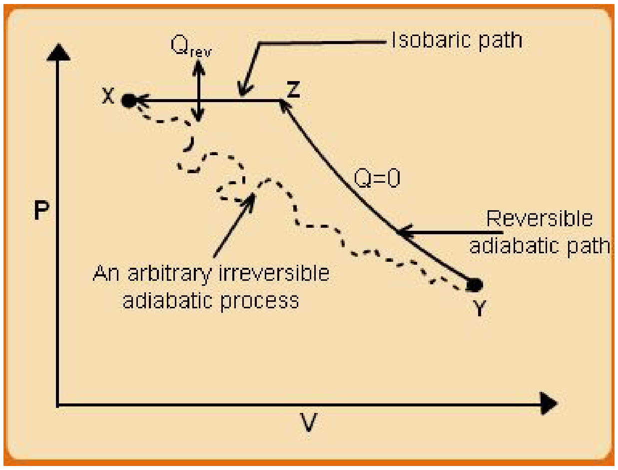
$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R}\frac{dT}{T} - \ln\frac{P}{P_0} = 0$$

For constant C_P^{ig}, it follows that: $T/T_0 = (P/P_0)^{R/C_P^{ig}} = (P/P_0)^{(\gamma-1)/\gamma}$ ..(4.22)

One may note that eqn. 4.22 provides the same relation as obtained by the Fist Law analysis as in eqn. 3.18.

2.4 Mathematical Statement of the 2nd Law:

Consider a mechanically irreversible adiabatic between two equilibrium states X and Y. In fig. 4.7 this path is reproduced as a broken line between points. Next the fluid is returned to the original state by means two sequential processes: (i) a mechanically reversible adiabatic process Y-Z, and then (ii) a reversible isobaric compression Z-X. Assuming that the mechanically irreversible process X-Y leads to an entropy change, heat transfer must occur during process Z-X (since none occurs on Y-Z). This is because for the reversible return path the same entropy change must occur as between X to Y. Since the return path is reversible we must get $dQ_{rev} = TdS$. Thus, integrating this expression for the return path:



4.7 Cycle containing an irreversible adiabatic process A to B

$$\Delta S^t = \int_Y^X dS^t = S_X^t - S_Y^t = \int_Y^X \frac{dQ_{rev}}{T} \qquad ..(4.23)$$

For the entire cycle we must have $\Delta U^t = 0.$ Thus, net total work during the cycle may be written as: $W^t = -Q_{rev}$. However, since (as depicted by the P-V diagram) a net work would need to be done *on* the system over the cycle, it follows that $W^t > 0;$ hence $Q_{rev} < 0.$ Therefore, using eqn. 4.23, it follows that: $S_X^t - S_Y^t = \int_Y^X \frac{dQ_{rev}}{T} < 0,$ that is: $S_X^t < S_Y^t.$ This implies that the entropy change for the original irreversible step A to B, we have: $\Delta S^t = S_Y^t - S_X^t > 0.$ Therefore, we conclude that the original irreversible step is accompanied by a *positive* change of entropy. It may be additionally shown that if the original process occurred through *irreversible heat transfer* process an increase of entropy would result likewise.

It may be pointed out during the return reversible process, since the heat transfer (during the isobaric path) occurs under reversible conditions it must occur under infinitesimal temperature gradient between the system and surrounding. Thus for the system and the surrounding the net entropy change (gives by: Q_{rev} / T) is equal and opposite. Consequently the total entropy change of the universe (system + surrounding) is zero during this step. During the initial irreversible path X to Y, while entropy increases for the system, for the surrounding there is no change. Nevertheless, for the universe as such there is a positive change in entropy.

Since the above conclusion is not premised on any specific internal nature of the system, the above result may be generalized: all irreversible processes are accompanied by a positive change of entropy of the universe. This leads to a mathematical statement of the second law:

$$\Delta S^t \geq 0. \qquad ..(4.24)$$

At this point we can revert to the question that was stated at the beginning of this chapter: what change in a system is thermodynamically feasible? The second law provides answer to this, i.e., a process can only proceed in a direction that results in a positive change in the *total* entropy of the universe, the limiting value of zero being attained only by a fully reversible process. The corollary to this is: *no process is possible for which the total entropy of the universe decreases*.

Example 4.2

A rigid vessel of 0.06 m^3 volume contains an ideal gas, $C_V = (5/2)R$, at 500 K and 1 bar. (a) If 15 kJ of heat is transferred to the gas, determine its entropy change. (b) If the vessel is fitted with a stirrer that is rotated by a shaft so that work in the amount of 15 kJ is done on the gas, what is the entropy change of the gas if the process is adiabatic? What is ΔS^{total}?

(Click for solution)

Example 4.3

An ideal gas, $C_p = (7/2)R$, is heated in a steady-flow heat exchanger from 70°C to 190°C by another stream of the same ideal gas which enters at 320°C. The flow rates of the two streams are the same, and heat losses from the exchanger are negligible. Calculate the molar entropy changes of the two gas streams for both parallel and countercurrent flow in the exchanger. What is ΔS^{total} in each case?

Click for solution

2.5 Entropy Balance for Open Systems

As with energy balance for open systems, once can extend the equation 4.24 to a generalized entropy balance equation that may be written for the system shown in fig. 3.6. There is, however, an important point of departure from the first law. Unlike energy, entropy is *not* a conserved quantity for real world processes in which both mechanical and thermal irreversibilities are inevitable. Hence for such processes are attended by a positive entropy *generation rate,* $\dot{S}_G$. This conclusion may be expressed in mathematical terms as follows:

$$\left\{\begin{matrix} Net \\ rate \\ of \\ entropy \\ change \\ through \\ flow \\ streams \end{matrix}\right\} + \_ \left\{\begin{matrix} Rate \\ of \\ change \\ of \\ entropy \\ change \\ in \\ control \\ volume \end{matrix}\right\} + \left\{\begin{matrix} Rate \\ of \\ entropy \\ change \\ of \\ surrounding \end{matrix}\right\} = \left\{\begin{matrix} Total \\ rate \\ of \\ entropy \\ generation \end{matrix}\right\}$$

$$\Delta(S\dot{m})_{fs} + \frac{d(mS)_{CV}}{dt} + \frac{dS^{t}_{surr}}{dt} = \dot{S}_{G} \geq 0 \qquad ..(4.25)$$

As with eqn. 4.24, for eqn. 4.25 too, the left side reduces to zero if the processes occurring in the open system are *totally* reversible; that is, both with respect to the system as well to the surroundings. Or else there is a net entropy generation.

A process is said to be *internally* reversible if all the processes occurring within the system are mechanically reversible, that is they are not subject to dissipative forces. *External* reversibility, on the other hand, signifies that all heat transfer between the system and surrounding occur under infinitesimal gradients and are therefore thermally reversible. In principle reversible heat transfer is possible if the surroundings have heat reservoirs with temperatures equal to those of the control surface or if reversible Carnot engines operate between the control-surface temperatures and the heat-reservoir temperatures.

We next expand eqn. 4.25 to a further level of detail. Let there be heat transfer at the rate $\dot{Q}_j$ at a particular part of the control surface of the open system where the surrounding temperature is given by $T_{\sigma,j}$.

Thus: $$\frac{dS^{t}_{surr}}{dt} = -\sum_{j} \frac{\dot{Q}_j}{T_{\sigma,j}} \qquad ..(4.26)$$

Here, *j* runs over all the heat reservoirs associated with the system. The negative sign is used for the entropy term for the surroundings as heat transfer terms by convention are associated with the system.

Putting eqn. 4.26 in eqn. 4.25 one obtains:

$$\Delta(S\dot{m})_{fs} + \frac{d(mS)_{CV}}{dt} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0 \qquad ..(4.27)$$

For steady flows through the control volume eqn. 4.27 reduces to:

$$\Delta(S\dot{m})_{fs} - \sum_j \frac{\dot{Q}_j}{T_{\sigma,j}} = \dot{S}_G \geq 0 \qquad ..(4.28)$$

Further, for the simplest case of one inlet and exit, and one surrounding temperature:

$$\dot{m}(\Delta S)_{fs} - \frac{\dot{Q}}{T_\sigma} = \dot{S}_G \geq 0 \qquad ..(4.29)$$

Example 4.4

Ten kmol per hour of air is throttled from upstream conditions of 25°C and 10 bar to a downstream pressure of 1.2 bar. Assume air to be an ideal gas with $C_P = (7/2)R$. (a) What is the downstream temperature? (b) What is the entropy change of the air in J/molK? (c) What is the rate of entropy generation in W/K? (d) If the surroundings are at 20°C, what is the lost work?

Click for solution

2.6 Ideal and Lost Work for Flow Systems

We next derive the expressions for work exchange between system and surroundings for an open system operating under steady state by incorporating the idea of irreversibility. As we have discussed earlier, mechanical irreversibilities lead to *loss of work* due to dissipative conversion to heat. Thus, if work is to be delivered *by* an open system the *maximum* work obtains when the processes are mechanically reversible, we call that *ideal work*. Conversely, when work is done *on* the system the ideal work provides the *minimum* work needed to change the fluid state between the inlet and the exit. This is because an extra work would need to be provided beyond the ideal work against mechanical dissipative forces. From the considerations in the last section it may be evident that ideal work obtains when the processes associated with the open system are both internally and externally reversible. For such a case one may write eqn. 4.29 as follows:

$$\dot{m}(\Delta S)_{fs} - \frac{\dot{Q}}{T_\sigma} = \dot{S}_G = 0 \qquad ..(4.30)$$

Thus: $\dot{Q} = T_\sigma \, \dot{m}(\Delta S)_{fs}$ ..(4.31)

From the 1st Law applied to the ideal case:

$$:\Delta\left[\left(H + \frac{1}{2}(u^2/g_c) + z(g/g_c)\right)\dot{m}\right]_{fs} = \dot{Q} + \dot{W}_{ideal} \qquad ..(4.32)$$

Putting eqn. 4.31 into 4.32 and simplifying (assuming negligible kinetic and potential energy changes): $\dot{W}_{ideal} = \Delta\left[H\,\dot{m}\right]_{fs} - T_\sigma \Delta(S\,\dot{m})_{fs}$ ..(4.33)

Or: $\dot{W}_{ideal} = \dot{m}[\Delta H - T_\sigma \Delta S_{fs}]$

..(4.34)

In real processes however, actual work involved will depend on the extent of associated irreversibilities; hence we define *lost work* as follows:

$$\dot{W}_{lost} = \dot{W}_{actual} - \dot{W}_{ideal} \qquad ..(4.35)$$

Now from eqn. 4.32 for the simplest case where kinetic and potential energy changes are negligible:

$$\Delta\left[H\,\dot{m}\right]_{fs} = \dot{Q}_{actual} + \dot{W}_{actual} \qquad ..(4.36)$$

Using eqns. 4.34 and 4.35:

$$\dot{W}_{lost} = T_\sigma \Delta(S\,\dot{m})_{fs} - Q_{actual} \qquad ..(4.37)$$

Applying eqn. 4.30, to a real process: $\dot{m}(\Delta S)_{fs} - \frac{\dot{Q}_{actual}}{T_\sigma} = \dot{S}_G$

..(4.38)

Or: $\dot{Q}_{actual} = T_\sigma \, \dot{m}(\Delta S)_{fs} - T_\sigma \, \dot{S}_G$ ..(4.39)

Thus from eqns. 4.37 and 4.39 it follows that:

$$\dot{W}_{lost} = T_\sigma \dot{S}_G \quad ..(4.40)$$

Eqn. 4.40 suggests that greater the entropy generation rate $\dot{S}_G$ due to process irreversibility, greater is the lost work. Since irreversibilities implicit in a process cannot be calculated theoretically, it is indirectly expressed by a process efficiency factor, η. The expression for such efficiency is as follows.

For work done by system, $\eta = \dot{W}_{actual} / \dot{W}_{ideal}$ . .(4.41)

For work done on a system, $\eta = \dot{W}_{ideal} / \dot{W}_{actual}$ ..(4.42)

Example 4.5

A steady-flow adiabatic turbine (expander) accepts gas at conditions T_1 = 500 K, P_1 = 6 bar, and discharges at conditions T_2 = 371 K, P_2 = 1.2 bar. Assuming ideal gases, determine (per mole of gas) W_{actual}, W_{ideal}, W_{lost}, and entropy generation rate. T_{surr} = 300 K, C_P/R = 7/2.

Click for solution

Example 4.6

A steam turbine operates adiabatically at a power level of 3500 kW. Steam enters the turbine at 2400 kPa and 500°C and exhausts from the turbine at 20 kPa. What is the steam rate through the turbine, and what is the turbine efficiency?

Click for solution

Appendix: 4.1

Entropy: A Statistical Thermodynamic Interpretation

As with internal energy the concept of entropy may be provided a microscopic, molecular interpretation. However, it may be noted that unlike internal energy, molecules *do not* possess entropy. Entropy is purely a measure thermodynamic probability associated with the distribution of various positional and energy states that molecules of a substance may exist under given conditions of temperature and pressure. To understand this, consider a simple system comprised of a rigid, insulated vessel divided into two compartments of equal volume by a partition (of negligible volume, fig. A.4.1). Initially, the left compartment contains gas at a temperature T_1 and pressure P_1, and the volume of each compartment is V_1^t; the right compartment is fully evacuated. The system is at equilibrium under the above conditions, and is described by the ideal

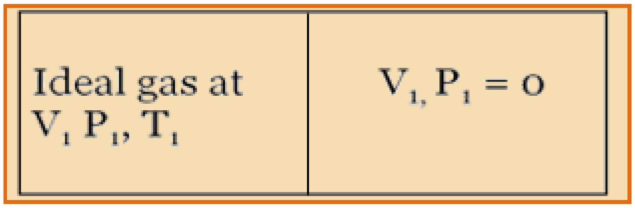


Fig. A.4.1 Ideal Gas Expansion into an evacuated chamber

gas EOS. At a certain point of time the partition is ruptured and the gas contained in the left compartment allowed to fill the entire system volume. Eventually the gas would reach a new equilibrium state (2) that is characterized by a pressure $P_1/2$ throughout. For the above process, applying the first law:

$$\Delta U = Q + W$$

$$\text{But}: Q = W = 0$$

$$\text{Hence, } \Delta U = 0 \qquad \text{..(A.4.1.1)}$$

This implies that for the gas initially on the left side: $\Delta T = 0$; or $T_2 = T_1$

The entropy change per mole of the gas then is given by eqn. 4.21:

$$\text{Thus, } \Delta S = C_P \frac{dT}{T} - R\frac{dP}{P} = -R\frac{dP}{P}$$

$$\Delta S = -R\ln\frac{P_2}{P_1} = R\ln\frac{V_2}{V_1} = R\ln 2 \qquad \text{..(A.4.1.2)}$$

From a microscopic point of view the molecular state variables are: position and energy. Since there is no change of temperature during the expansion process, the internal energy of each molecule does not change. There, is, however, a possible change in the position occupied a molecule. After the expansion a molecule may be located either on the left half or in the right half of the compartment at any point of time. We may say, in a simplified sense, there are two possible positions that it may have. Considering one mole of gas as basis, if there are, in general, *j* such states (either of position or energy) that a molecule may exist in, the total number of ways that an Avogadro number of molecules $(N_A = 6.023x10^{23})$ may be distributed over all the available states is given by (with n_j molecules in the j^{th} state):

$$\Omega = \frac{N_A!}{(n_1!)(n_2!)...(n_j!)}; N_A = n_1 + n_2 + ... + n_j \qquad ..(A.4.1.3)$$

The notation used for the right side of the above equation, Ω is called the *thermodynamic probability*. Thus for the system in question, in the initial state *all* the molecules are located in the left half of the compartment, so there is only 'one' positional state; thus:

$$\Omega_1 = \frac{N_A!}{(N_A!)(0!)} = 1 \qquad ..(A.4.1.4)$$

However, in the final state as there are two possible positional states, the corresponding *maximum* thermodynamic probability is:

$$\Omega_2 = \frac{N_A!}{[(N_A/2)!][(N_A/2)!]} \qquad ..(A.4.1.5)$$

The description 'maximum' is important, as the exact number of molecules that may be distributed between the two compartments at any point of time need not be as the same, as assumed in eqn. A.4.1.5. In general there could be many possible bifurcations of the total number molecules into the two compartments, each characterized by a corresponding thermodynamic probability. However, simple calculations suggest that Ω_2 has the *highest* possible value if each compartment contains equal number of molecules, i.e., $N_A/2$. Indeed, intuitively speaking, one would expect that to be the most *likely* distribution in the second equilibrium state. This implies that the system would tend to move to an equilibrium state that has the highest of all the possible values of the thermodynamic probability that one may attribute to the system. It was Ludwig Eduard Boltzmann (1844–1906) the Austrian physicist, who is credited with the development of the statistical concept of nature (now known as *statistical mechanics*), first proposed the relation between entropy and thermodynamic probability:

$$S = k \ln \Omega \qquad ..(A.4.1.6)$$

$$k = Boltzmann\ constant = R / N_A$$

If one applies the equation to the expansion process, one obtains the following relation:

$$\Delta S = S_2 - S_1 = k \ln \Omega_2 - k \ln \Omega_1 = k \ln \frac{\Omega_2}{\Omega_1} \qquad ..(A.4.1.7)$$

Thus: $\Delta S = k \ln \left[\frac{N_A!}{[(N_A/2)!][(N_A/2)!]} \right]$

Or: $\Delta S = k\left[\ln N_A! - 2\ln(N_A/2)!\right]$ ..(A.4.1.8)

By the well-known Stirling's formula, or large values of an integer N, one has:

$\ln N! = N \ln N - N$ ..(A.4.1.9)

On applying eqn. A.4.1.9 in A.4.1.8 and simplifying the following result obtains:

$$\Delta S = kN_A \left[\ln \frac{N_A}{N_A/2} \right] = kN_A \ln 2 = R \ln 2 \qquad ..(A.4.1.10)$$

Thus we see that the results of both eqns. A.4.1.2 and A.4.1.10 are identical. There is thus a convergence between the macroscopic and microscopic description of the concept of entropy.

It is particularly significant that the above result obtains if one assumes the highest value of Ω_2 as its most likely value. It may be argued that the highest value of Ω_2 corresponds to the most *disordered* state at the molecular level. Indeed extending the argument, since $\Omega_1 = 1$ the initial state is more ordered than state 2, as in the former all molecules are characterized by a single position coordinate, and therefore the probability of finding a molecule in that position is unity; in other words one has complete (or 'certain') information about position of any molecule. In contrast in the second state the probability of finding a molecule at any one position is half. This obtains if each compartment contains exactly half the total number of molecules. Any other distribution would be *less* disordered than this state, and also less probable! This is the reasoning which lies at the root of the popular description of entropy as a *measure* of disorder at the molecular level. It follows that a system at non-equilibrium state (say, at the point of rupture of the partition) always *tends* to the most disordered molecular state when it attains a new equilibrium. Since one has *less* microscopic *information* about a system with a greater degree of disorder, 'information' is also described as *negentropy*.

Assignment- Chapter 4

Chapter 5 Thermodynamic Properties of Real Fluids

It has already been demonstrated through the first and second laws, that the work and heat interactions between a system and its surroundings may be related to the state variables such as internal energy, enthalpy and entropy. So far we have illustrated the calculations of energy and entropy primarily for pure (component) ideal gas systems. However, in practice this is an *exception* rather than a rule as one has to deal with not only gases removed from ideal gas state, but also with liquids and solids. In addition, mixtures rather than pure components are far more common in chemical process plants. Therefore, computation of work and heat interactions for system comprised of *real* fluids requires more complex thermodynamic formulations. This chapter is devoted to development of such relations that can help calculate energy requirements for given changes of state for real systems. As in the case of ideal gases the goal is to correlate the energy and entropy changes for real fluids in terms of their volumetric and other easily measurable macroscopic properties.

5.1 Thermodynamic Property Relations for Single Phase Systems

Apart from internal energy and enthalpy, two other ones that are particularly useful in depiction of thermodynamic equilibrium are Helmholtz free energy (A) and Gibbs free energy (G). We defer expanding upon the concept of these two types of energies to chapter 6; however, we state their definition at this point as they are instrumental in the development of property correlations for real fluids.

- Specific Helmholtz free energy: $A = U - TS$ ..(5.1)
- Specific Gibbs free energy: $G = H - TS$ ..(5.2)

For a reversible process in a closed system the first law gives:

$$dU = dQ + dW$$

Or:

$$dU = TdS - PdV \qquad ..(5.3)$$

Using $H = U + PV$ and taking a total differential of both sides:

$$dH = dU + PdV + VdP \qquad ..(5.4)$$

Putting eqn. 5.3 in 5.4 we get:

$$dH = TdS + VdP \qquad ..(5.5)$$

In the same manner as above one may easily show that the following two relations obtain:

$$dA = -SdT - PdV \qquad ..(5.6)$$

$$dG = VdP - SdT \qquad ..(5.7)$$

Equations 5.3 to 5.7 comprise the fundamental energy relations for thermodynamic systems where there is a single phase with constant composition. In principle, they may be integrated to compute the energy changes for a system transiting from one equilibrium state to another.

5.2 Maxwell Relations

All the four types of energy relations above satisfy the mathematical condition of being continuous variables, as they are themselves functions of state variables. One can thus apply of the criterion of exact differential for these functions.

For a function of the form $P = P(X,Y)$ one can write the following total differential:

$$dP = \left(\frac{\partial P}{\partial X}\right)_Y dX + \left(\frac{\partial P}{\partial Y}\right)_X dY = MdX + NdY \qquad ..(5.8)$$

Where: $M = \left(\frac{\partial P}{\partial X}\right)_Y \quad and \quad N = \left(\frac{\partial P}{\partial Y}\right)_X \qquad ..(5.9)$

Further, $\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial^2 P}{\partial Y \partial X}\right) \quad and \quad \left(\frac{\partial N}{\partial X}\right)_Y = \left(\frac{\partial^2 P}{\partial X \partial Y}\right) \qquad ..(5.10)$

It follows: $\left(\frac{\partial M}{\partial Y}\right)_X = \left(\frac{\partial N}{\partial X}\right)_Y \qquad ..(5.11)$

Applying eqn. 5.11 to 5.3, 5.5, 5.6 and 5.7 one may derive the following relationships termed Maxwell relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad ..(5.12)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad ..(5.13)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad ..(5.14)$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \qquad ..(5.15)$$

5.4 Relations for Enthalpy, Entropy and Internal Energy

One may conveniently employ the general energy relations and Maxwell equations to obtain expressions for change in enthalpy and entropy and internal energy for any process, which in turn may be used for computing the associated heat and work interactions.

Let $H = H(T,P)$

Then: $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

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

Thus: $dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$ ..(5.16)

Using $dH = TdS + VdP \Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$ ..(5.17)

From Maxwell relations as in eqn. 5.15: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ ..(5.18)

Thus using eqns. 5.17 and 5.18 in 5.16 we get:

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP \qquad ..(5.20)$$

In the same manner starting from the general function: $U = U(T,V)$ and $S = S(T,P)$ and applying appropriate Maxwell relations one may derive the following general expressions for differential changes in internal energy and entropy.

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \qquad ..(5.21)$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad ..(5.22)$$

Or, alternately: $dS = C_V \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV$ ..(5.23)

Thus, eqns. 5.20 to 5.23 provide convenient general relations for computing enthalpy, internal energy and entropy changes as function of volumetric properties and specific heats. If a fluid is described by a suitable EOS, these equations may be conveniently integrated to obtain analytical expressions for energy and entropy changes.

Example 5.1

Derive an expression for enthalpy change of a gas during an isothermal process assuming using the following EOS: $P(V-b) = RT$

(Click here for solution)

5.5 Residual Property Relations

An alternate method of computing energy and entropy changes for real gases involves the definition of *residual property*. The specific residual property M^R is defined as follows:

$$M^R = M(T,P) - M^{ig}(T,P) \qquad ..(5.24)$$

Where, $M(T,P)$ is the specific property of a real gas at a given T & P, and $M^{ig}(T,P)$ is the value of the same property if the gas were to behave ideally at the same T & P. Thus for example:

$V^R = V - V^{ig}$

Using the generalized compressibility factor 'Z':

$V^R = (ZRT/P) - (RT/P)$

$$V^R = (Z-1)RT/P \qquad ..(5.25)$$

The residual properties are usually used for gases *only*. Using such a property for a liquid (or solid) is inconvenient as then it would also include the *property change* of vapourization (and solidification) which generally are large in magnitude. This detracts from the advantage of working with the residual property as a measure of small corrections to ideal gas behaviour. Thus the use of residual functions is restricted to prediction of real gas behaviour only. To exploit the concept of residual properties we take advantage of the Gibbs free energy as it can be used as a generating function for other thermodynamic properties.

Derivation of Residual functions:

We start from the generic equation: $G = H - TS$ ..(5.2)

And $dG = VdP - SdT$ ..(5.7)

Taking the total differential for the function G / RT :

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}dG - \frac{G}{RT^2}dT \qquad ..(5.26)$$

Substituting eqn. 5.2 and 5.7 in 5.26 we get:

$$d\left(\frac{G}{RT}\right) = \frac{V}{RT}dP - \frac{H}{RT^2}dT \qquad ..(5.27)$$

One may write the same equation specifically for an ideal gas, whence:

$$d\left(\frac{G^{ig}}{RT}\right) = \frac{V^{ig}}{RT}dP - \frac{H^{ig}}{RT^2}dT \qquad ..(5.28)$$

Subtracting eqn. 5.28 from 5.27:

$$d\left(\frac{G^{R}}{RT}\right) = \frac{V^{R}}{RT}dP - \frac{H^{R}}{RT^2}dT \qquad ..(5.29)$$

Thus we may write the following further *generative* relations:

$$\frac{V^R}{RT} = \left[\frac{\partial(G^R / RT)}{\partial P}\right]_T \qquad ..(5.30)$$

$$\frac{H^R}{RT} = -T\left[\frac{\partial(G^R / RT)}{\partial T}\right]_P \qquad ..(5.31)$$

And further: $\frac{S^R}{RT} = \frac{H^R}{RT} - \frac{G^R}{RT}$ ..(5.32)

From eqn. 5.29: $\int_0^P d\left(\frac{G^R}{RT}\right) = \left.\frac{G^R}{RT}\right|_P - \left.\frac{G^R}{RT}\right|_{P=0}$; but $\left.\frac{G^R}{RT}\right|_{P=0} = 0$

Thus: $$\frac{G^R}{RT} = \int_0^P \frac{V^R}{RT} dP \qquad ..(5.33)$$

Putting eqn. 5.25 in 5.33: $$\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P} \qquad ..(5.34)$$

Differentiating eqn. 5.34 w.r.t T in accordance with 5.31 gives:

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad ..(5.35)$$

Finally using eqns 5.32, 5.34, and 5.35:

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} \qquad ..(5.36)$$

The last two equations may be expressed in alternative forms in terms of reduced temperature and pressure:

$$\frac{H^R}{RT_C} = -T_r^2\int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \qquad ..(5.37)$$

$$\frac{S^R}{R} = -T_r\int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z-1)\frac{dP_r}{P_r} \qquad ..(5.38)$$

Example 5.2

Derive an expression for enthalpy change of a gas during an isothermal process assuming using the following EOS: $Z = 1 + AP_r / T_r$

(Click here for solution)

5.6 Residual Property Calculation from EOS

From Virial EOS:

Using 5.35 and 2.12 one obtains:

$$\frac{H^R}{RT} = \frac{P}{R}\left(\frac{B}{T} - \frac{dB}{dT}\right) \qquad ..(5.39)$$

Next, on substituting eqns. 2.13 – 2.15 in 5.37 the following relations result:

$$\frac{H^R}{RT_C} = P_r \left[\left(0.083 - \frac{1.097}{T_r^{1.6}} \right) + \omega \left(0.139 - \frac{0.894}{T_r^{4.2}} \right) \right] \qquad ..(5.40)$$

Similarly using 5.36 and 2.12 we get:

$$\frac{S^R}{R} = -\frac{P}{R} \left(\frac{dB}{dT} \right) \qquad ..(5.40)$$

Finally employing eqns. 2.13 – 2.15 in 5.38:

$$\frac{S^R}{R} = -P_r \left[\left(\frac{0.675}{T_r^{1.6}} \right) + \omega \left(\frac{0.722}{T_r^{4.2}} \right) \right] \qquad ..(5.41)$$

From Cubic EOS:

One may use the following form of the cubic EOS presented in chapter 2:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2} \qquad ..(2.21)$$

Or equivalently: $Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$ ..(2.23)

While the eqns. 5.35 and 5.36 are useful for volume explicit EOS, they are unsuitable for cubic EOS which are pressure explicit. For the latter type of EOS one may show that the appropriate equations for residual enthalpy and entropy are (see S.I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics,* ch. 6, 4th Edition, Wiley India, 2006):

$$\frac{H^R}{RT} = Z - 1 + \frac{1}{RT} \int_{V=\infty}^{V} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV \qquad ..(5.42)$$

$$\frac{S^R}{R} = \ln Z + \frac{1}{R} \int_{V=\infty}^{V} \left[\left(\frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV \qquad ..(5.43)$$

The above relations may be applied to the various cubic EOSs to obtain the necessary residual property relations. The final results are shown below.

From RK-EOS:

$$\frac{H^R}{RT} = (Z-1) - \frac{3a}{2bRT}\ln\left(\frac{Z+B}{Z}\right)$$ ..(5.44)

$$\frac{S^R}{R} = \ln(Z-B) - \frac{a}{2bRT}\ln\left(\frac{Z+B}{Z}\right)$$ ..(5.47)

$$where,\ a = \frac{0.42748R^2T_C^2\alpha_{RK}(T_r)}{P_C};\ b = \frac{0.08664RT_C}{P_C}$$
$$\alpha_{RK}(T_r) = T_r^{-1/2}$$

For SRK-EOS:

$$\frac{H^R}{RT} = (Z-1) + \frac{1}{RT} - \frac{T\left(\frac{\partial a}{\partial T}\right) - a}{bRT}\ln\left(\frac{Z+B}{Z}\right)$$ (5.48)

$$\frac{S^R}{R} = \ln(Z-B) - \frac{1}{bRT}\frac{\partial a}{\partial T}\ln\left(\frac{Z+B}{Z}\right)$$ ..(5.49)

$$\frac{\partial a}{\partial T} = -\frac{a}{\sqrt{\alpha_{SRK}(T_r)TT_C}}\left[(0.48 + 1.574\omega - 0.176\omega^2)\right]$$ ..(5.51)

$$where,\ a = \frac{0.42748R^2T_C^2\alpha_{SRK}(T_r)}{P_C};\ b = \frac{0.08664RT_C}{P_C}$$
$$and,\ \alpha_{SRK}(T_r) = [1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - T_r^{1/2})]^2$$

For PR-EOS:

$$\frac{H^R}{RT} = (Z-1) + \frac{\left\{T\left(\frac{\partial a}{\partial T}\right) - a\right\}}{2\sqrt{2}bRT}\ln\left[\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})}\right]$$ ..(5.52)

$$\frac{S^R}{R} = \ln(Z-B) - \frac{1}{2\sqrt{2}bRT}\frac{\partial a}{\partial T}\ln\left[\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})}\right]$$ ..(5.53)

$$\frac{\partial a}{\partial T} = -\frac{a}{\sqrt{\alpha_{PR}(T_r)TT_C}}\left[(0.37464 + 1.5422\omega - 0.62992\omega^2)\right]$$ ..(5.54)

$$where,\ a = \frac{0.45724R^2T_C^2\alpha_{PR}(T_r)}{P_C};\ b = \frac{0.07779RT_C}{P_C}$$
$$and,\ \alpha_{PR}(T_r) = [1 + (0.37464 + 1.5422\omega - 0.62992\omega^2)(1 - T_r^{1/2})]^2$$

As part of computing the residual enthalpy or entropy (and internal energy) at any set of temperature and pressure, the molar volume or correspondingly Z^{vap} needs to be *first* computed employing the usual algorithm for solving cubic EOS described in section 2.3.3.

Example 5.3

Derive expressions for H^R, S^R from RK-EOS.

(Click here for solution)

5.7 Generalized Correlations for computing *dH and dS* for a real gas:

The approach based on the use of the compressibility factors can be applied to the present instance to evolve generalized correlations for computing enthalpy and entropy changes for gases. We start with the Pitzer-type expression for the compressibility factor:

$$Z = Z^0 + \omega Z^1 \qquad ..(2.25)$$

Differentiating with respect to the reduced temperature we get:

$$\left(\frac{\partial Z}{\partial T_r}\right)_{P_r} = \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} + \omega\left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \qquad ..(5.55)$$

Thus using eqn. 5.54 we may recast eqns. 5.37 and 5.38 as follows:

$$\frac{H^R}{RT_c} = -T_r^2\int_0^{P_r}\left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} - \omega T_r^2\int_0^{P_r}\left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r}\frac{dP_r}{P_r} \qquad ..(5.56)$$

And: $$\frac{S^R}{R} = -\int_0^{P_r}\left[T_r\left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} + Z^0 - 1\right]\frac{dP_r}{P_r} - \omega\int_0^{P_r}\left[\left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} + Z^1\right]\frac{dP_r}{P_r} \qquad ..(5.57)$$

Both the above equations may be rewritten individually as follows:

$$\frac{H^R}{RT_c} = \frac{\left(H^R\right)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \qquad ..(5.58)$$

Where, $$\frac{\left(H^R\right)^0}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} \qquad ..(5.59a)$$

And:

$$\frac{(H^R)^1}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r} \qquad ..(5.59b)$$

Similarly:

$$\frac{S^R}{R} = \frac{\left(S^R\right)^0}{R} + \omega \frac{(S^R)^1}{R} \qquad ..(5.60)$$

$$\frac{\left(S^R\right)^0}{R} = -\int_0^{P_r} \left[T_r \left(\frac{\partial Z^0}{\partial T_r}\right)_{P_r} + Z^0 - 1\right] \frac{dP_r}{P_r} \qquad ..(5.61a)$$

$$\frac{\left(S^R\right)^1}{R} = -\int_0^{P_r} \left[\left(\frac{\partial Z^1}{\partial T_r}\right)_{P_r} + Z^1\right] \frac{dP_r}{P_r} \qquad ..(5.61b)$$

The term $\frac{\left(H^R\right)^0}{RT_c}$ in eqn. 5.59a constitutes the *first order* enthalpy departure, and $\frac{(H^R)^1}{RT_c}$ (in eqn. 5.59b) the *second order* (with respect to simple fluids) enthalpy departure at specified T_r and P_r. The same is true for the corresponding entropic terms provided by eqns. 5.61a and 5.61b.

The evaluation of the integrals in eqns. 5.59 to 5.62 may be carried out assuming an EOS. The most widely used approach is that of Lee and Kesler who employed a modified form of the BWR EOS (eqn. 2.17) to extend their generalized correlation to residual property estimation. Figs. 5.1 and 5.2 respectively provide values of $(H^R)^0/RT_C$, and $(H^R)^1/RT_C$ respectively. Similar plots for the entropy terms $(S^R)^0/R$, and $(S^R)^1/R$ are also available; however, here the plot of the entire entropy term $(-S^R)$ as function of T_r and P_r is shown in fig. 5.3. Table of values of all the above (eqns. 5.59 to 5.62) are also available as functions of T_r and P_r at discrete intervals (see for example: J.M. Smith, H.C. Van Ness and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, 2001.

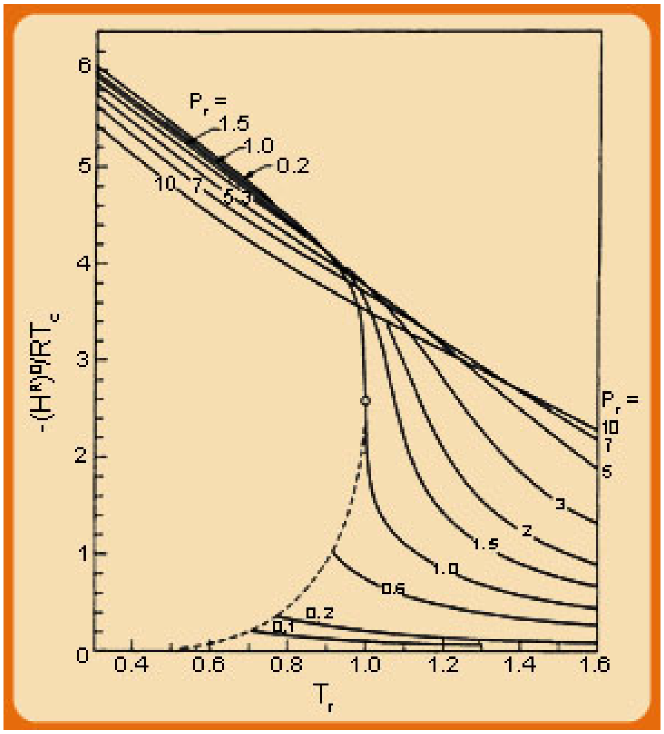


Fig. 5.1 Correlation of $-H_R^0/RT_C$ drawn from tables of Lee-Kesler (Source: *AIChE J.*, pp. 510-527, 1975)

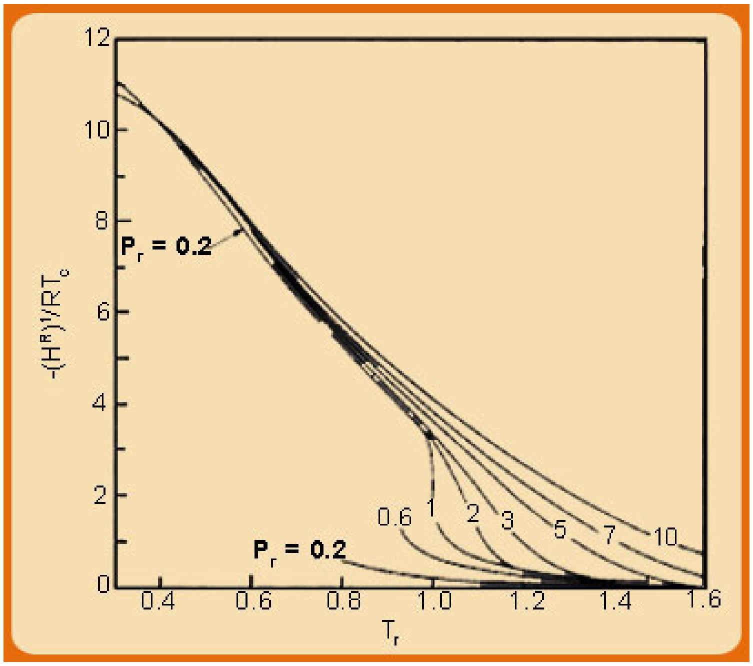


Fig. 5.2 Correlation of $-H_R^1/RT_C$ drawn from tables of Lee-Kesler (Source: *AIChE J.*, pp. 510-527, 1975)

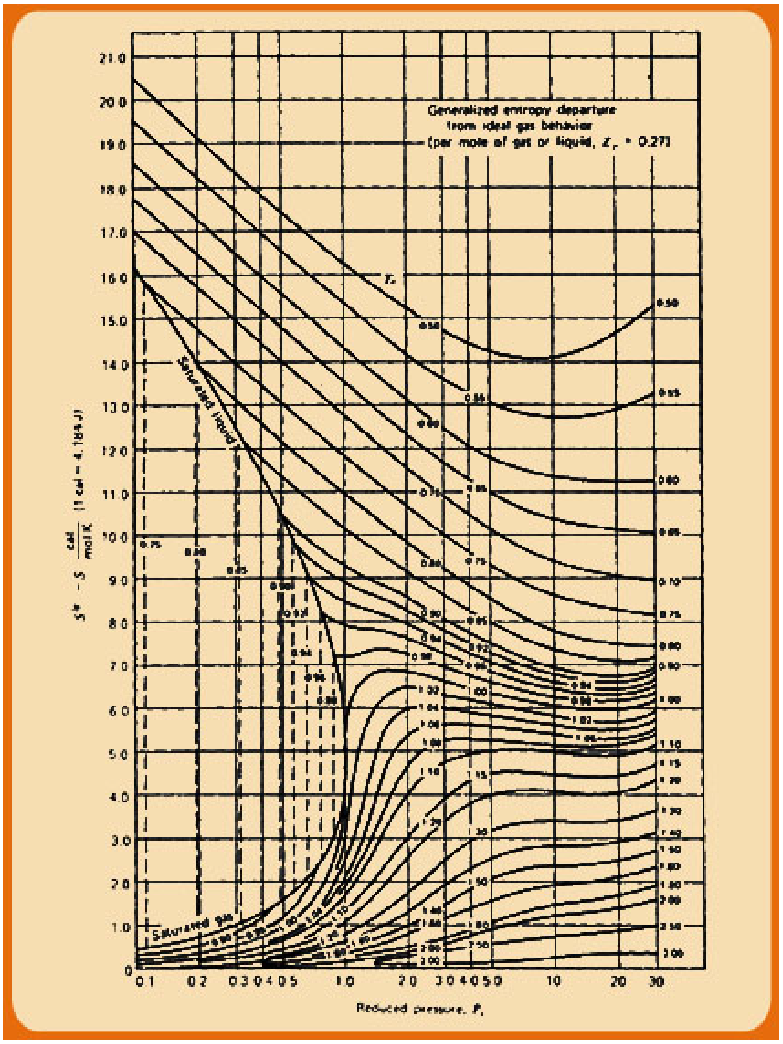


Figure 5.3 Generalized entropy departure functions using corresponding states. [Source: O.A. Hougen, K.M. Watson, and R.A. Ragatz, *Chemical Process Principles Charts,* 2nd ed., John Wiley & Sons, New York, 1960]

5.8 Computation of Δ*H* and Δ*S* for a Gas using Generalized Departure Functions

The residual function equations presented in the last section are particularly useful for estimating finite changes in enthalpy and entropy for real gases undergoing change in either closed or open system processes. We consider that a pure fluid changes state from (T_1, P_1) to (T_2, P_2); shown schematically in fig. 5.4.

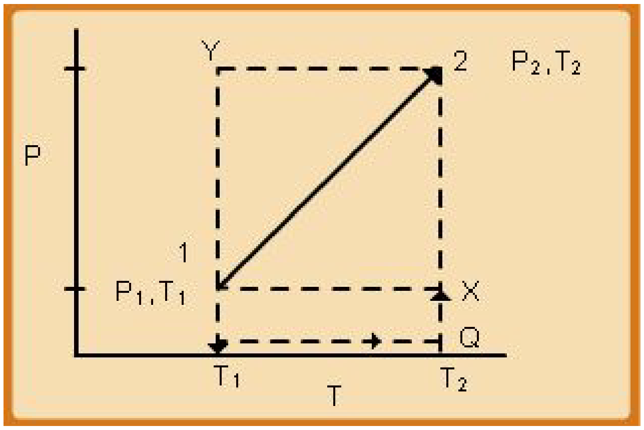


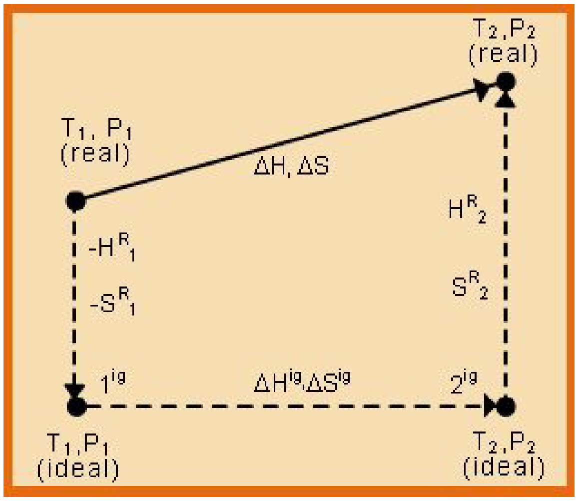
Fig. 5.4 Schematic of a General Thermodynamic Process on P – T co-ordinates

Since the departure functions H^R and S^R capture deviations from ideal gas behaviour at the same temperature as the real gas, one can conceive of the pathway between states '1' and '2' to be decomposed into following steps (see fig 5.5):

a) Real gas state at (T_1, P_1) to ideal gas state (ig) at (T_1, P_1)

b) Ideal gas state at (T_1, P_1) to ideal gas state at (T_2, P_2)

c) Ideal gas state at (T_2, P_2) to real gas state at (T_2, P_2)



5.5 Pathway for calculating ΔH and ΔS for Real Gases

- For step 'a' the change of enthalpy is given by: $H_1^{ig} - H_1 = -H_1^R$
- For step 'b' the change of enthalpy is given by: $H_2^{ig} - H_1^{ig} = \Delta H^{ig}$
- For step 'c' the change of enthalpy is given by: $H_2 - H_2^{ig} = H_2^R$

Therefore, the overall change of enthalpy is given by:

$$\Delta H = H_2 - H_1 = H_2^R - H_1^R + \Delta H^{ig} \int_{T_1}^{T_2} C_p^{ig} dT$$

Using eqn. 3.8: $H_2 - H_1 = H_2^R - H_1^R + \int_{T_1}^{T_2} C_p^{ig} dT$ ..(5.63)

The same considerations apply for computing the change of entropy between the two states:

$$\Delta S = S_2 - S_1 = S_2^R - S_1^R + \Delta S^{ig}$$

Using eqn. 4.21: $S_2 - S_1 = S_2^R - S_1^R + \int_{T_1}^{T_2} C_p^{ig} dT / T - R \ln(P_2 / P_1)$ ..(5.64)

Generalized residual property relations may be used for calculation of change in internal energy i.e. $U_2 - U_1$ for a process in the following manner:

$$U_2 - U_1 = (H_2 - P_2V_2) - (H_1 - P_1V_1)$$

Or: $U_2 - U_1 = (H_2 - H_1) - (P_2V_2 - P_1V_1)$ ..(5.65)

The term $(H_2 - H_1)$ can be calculated using eqn. 5.63, while the term $(P_2V_2 - P_1V_1)$ may be computed after obtaining V_1 and V_2 applying the generalized compressibility factor approach.

One may, however, also use the generalized residual property charts for internal energy for the same purpose (fig. 5.6).

Example 5.5

Estimate the final temperature and the work required when 1 mol of n-butane is compressed isentropically in a steady-flow process from 1 bar and 50^{o}C to 7.8 bar.

(Click here for solution)

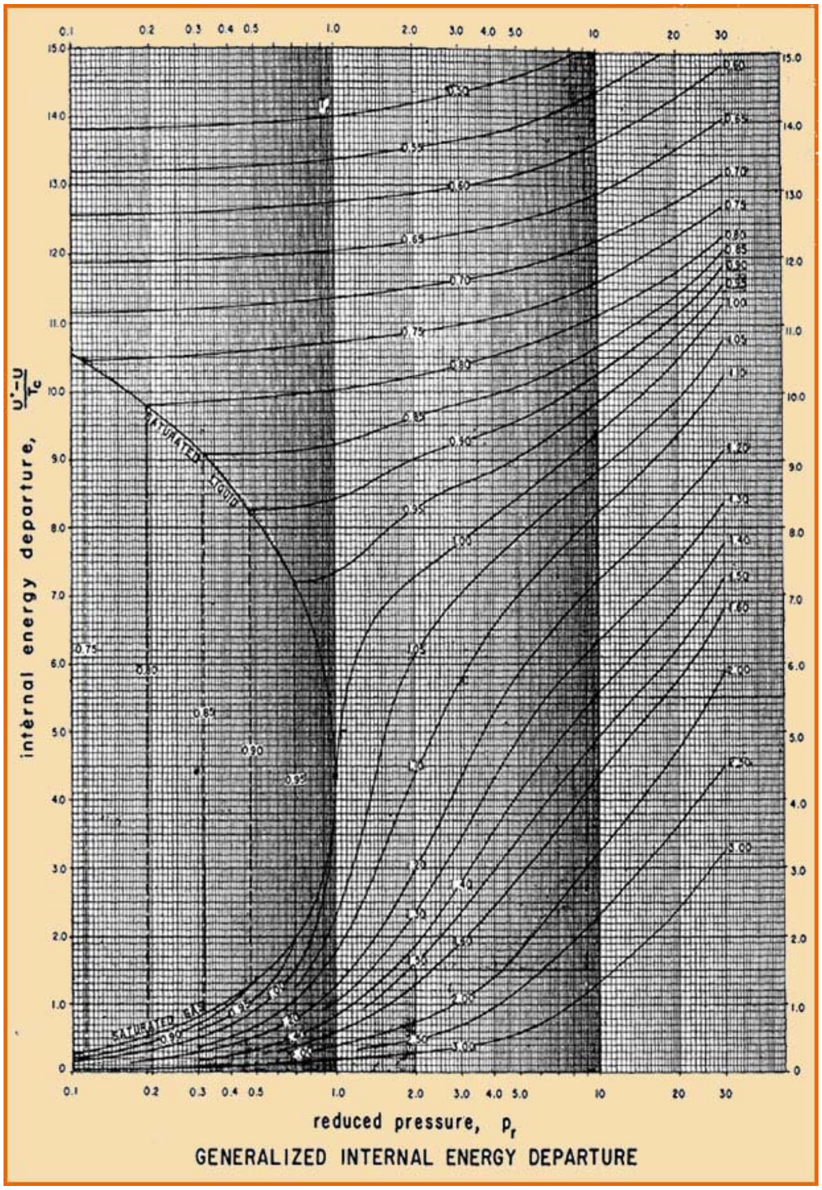


Figure 5.6 Generalized internal energy departure functions using corresponding states [Source: O.A. Hougen, K.M. Watson, and R.A. Ragatz (1960), *Chemical Process Principles Charts,* 2nd ed., John Wiley & Sons, New York]

5.9 Extension to Gas Mixtures

The generalized equations developed for ΔH and ΔS in the last section may be extended to compute corresponding changes for a real gaseous mixture. The method used is the same as that developed in section 2.4 through the definition of pseudo-critical mixture properties using linear mixing rules:

$$T_{C,m} = \sum_i y_i T_{C,i} \qquad P_{C,m} = \sum_i y_i P_{C,i} \qquad \omega_m = \sum_i y_i \omega_i \qquad ..(2.32)$$

Using the above equations pseudo-reduced properties are computed:

$T_{r,m} = T / T_{C,m}$ and $P_{r,m} = P / P_{C,m}$

Further calculations of changes in internal energy, enthalpy, and entropy follow the same principles developed in the last section.

<u>Example 5.6</u>

Calculate the changes in enthalpy and entropy per mole when a mixture of 70 mole % ethylene (1) and 30 mole% propylene (2) at 323K and 10 bar is taken to 60 bar and 600 K using the generalized compressibility factor approach.

$$C_{p1}^{ig} = 4.196 + 154.565x10^{-3}T - 81.076x10^{-6}T^2 + 16.813x10^{-9}T^3;$$

$$C_{p2}^{ig} = 3.305 + 235.821x10^{-3}T - 117.58x10^{-6}T^2 + 22.673x10^{-9}T^3$$

(Click here for solution)

5.10 Relations for Δ*H* and Δ*S* for Liquids

One starts with the generic equations for *dH* and *dS* developed in section 5.4.

$$dH = C_P dT + \left[V - T\left(\frac{\partial V}{\partial P}\right)_T \right] dP \qquad ..(5.20)$$

$$dS = C_P \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP \qquad ..(5.22)$$

As discussed in section 2.3, for liquids it is often simpler to use *volume expansivity* and *isothermal compressibility* parameters for computing thermodynamic properties of interest. Thus from eqn. 2.3:

$$Volume\ Expansivity, \beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

Using eqn. 2.3 in 5.20 and 5.22 the following relations obtain:

$$dH = C_P dT + \left[1 - \beta T\right] dP \qquad ..(5.66)$$

$$dS = C_P \frac{dT}{T} - \beta V dP \qquad ..(5.67)$$

The above equations may also be used to compute the properties of a compressed liquid state. Since the volumetric properties of liquids are very weakly dependent of pressure one can often use the saturated liquid phase properties as reference points and integrate the eqns. 5.66 to 5.67 (at constant temperature) to obtain enthalpy and entropy respectively. The relevant equations are:

$$H_i = H_i^{sat} + \int_{P_i^{sat}}^{P} V_i (1 - \beta_i T) dP \qquad ..(5.68)$$

$$S_i = S_i^{sat} - \int_{P_i^{sat}}^{P} \beta_i V_i dP \qquad ..(5.69)$$

In the last two equations, the molar volume V_i may be set equal to $V_i^{sat}(liq.)$, and the volume expansivity approximated to that at the saturated liquid point at the given temperature.

5.11 Applications to real fluid processes in process plant equipments

In a typical process plant one encounters a variety of flow devices such pumps, compressors, turbines, nozzles, diffusers, etc. Such devices are not subject to heat transfer *by design* as are heat exchangers, condensers, evaporators, reactors, etc. However, the flow devices typically are subject to mechanical irreversibility owing to existence of dissipative forces such as fluid viscosity and mechanical friction, which results in reduction of their efficiency. In addition such devices may be subject to thermal irreversibility as their operation may not be truly adiabatic. Therefore, it is necessary to compute the efficiency of such devices in relation to a perfectly reversible (isentropic) process between their inlet and outlet.

The performance of a flow device is expressed in terms of *isentropic efficiency* in which the actual performance of the device is compared with that of an isentropic device for the same inlet conditions and exit pressure. For example, the isentropic efficiency η_T of a **turbine** (which essentially converts fluid enthalpy to shaft work, fig. 5.7) is defined as:

$$\eta_T = \frac{Power\ output\ of\ the\ actual\ turbine}{Power\ out\ put\ of\ the\ turbine, if\ it\ were\ isentropic} = \frac{H_i - H_e}{H_i - H_e^s} \qquad ..(5.69)$$

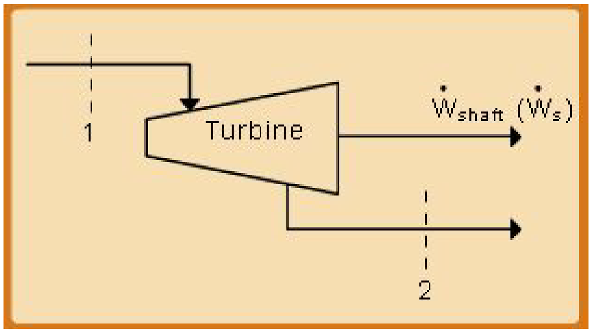


Fig.5.7 Schematic of a Turbine

Where, H_i = enthalpy of the fluid at the inlet of the turbine, H_e = enthalpy of the fluid at the exit of the actual turbine, H_e^s = enthalpy of the fluid at the exit of the turbine, if it were isentropic.

Similarly, the isentropic efficiency η_c of a **compressor** (fig. 5.8) or a pump η_p (which convert applied shaft work to fluid enthalpy) is given by:

$$\eta_c(or\ \eta_P) = \frac{(W_s)^s}{(W_s)} = \frac{H_e^s - H_i}{H_e - H_i} \quad ..(5.70)$$

Where, H_i = enthalpy of the fluid at the inlet to the compressor (or pump), H_e = enthalpy of the fluid at the exit of the *actual* compressor (pump), and H_e^s = enthalpy of the fluid at the exit of an isentropic compressor (or pump), and W_s represents the shaft work per mole (or mass) of fluid in the two situations.

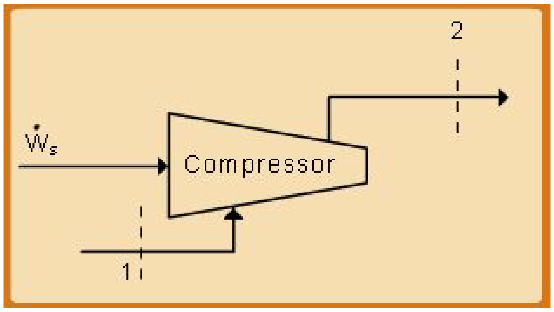


Fig.5.8 Schematic of a Turbine

The isentropic efficiency η_N of a **nozzle**, which is used to achieve high fluid velocity at exit (by conversion of enthalpy to kinetic energy) is given by:

$$\eta_N = \frac{(V_2^2)/2}{(V_2^2)^s/2} = \frac{\text{Kinetic energy of gas leaving the actual nozzle}}{\text{Kinetic energy of gas leaving the nozzle, if it were isentropic}} \qquad ..(5.71)$$

Example 5.7

A certain gas is compressed adiabatically from 293 K and 135 KPa to 550 KPa. What is the work needed? What is the final T_2? Assume ideal gas behavior. Compressor $\eta = 0.8$.

For the gas: $C_p^{ig} = 1.65 + 8.9 \times 10^{-3}T - 2.2 \times 10^{-6} T^2$

Assignment - Chapter 5

Chapter 6: Solution Thermodynamics and Principles of Phase Equilibria

In all the preceding chapters we have focused primarily on thermodynamic systems comprising pure substances. However, in all of nature, mixtures are ubiquitous. In chemical process plants – the ultimate domain of application of the principles of chemical engineering thermodynamics – matter is dominantly processed in the form of mixtures. Process streams are typically comprised of multiple components, very often distributed over multiple phases. Separation or mixing processes necessitate the use of multiple phases in order to *preferentially* concentrate the desired materials in one of the phases. Reactors very often bring together various reactants that exist in different phases. It follows that during mixing, separation, inter-phase transfer, and reaction processes occurring in chemical plants multi-component gases or liquids undergo composition changes. Thus, in the thermodynamic description of such systems, in addition to pressure and temperature, *composition* plays a key role.

Further, whenever multiple phases are present in a system, material and energy transfer occurs between till the phases are in *equilibrium* with each other, i.e., the system tends to a state wherein the all thermal, mechanical and *chemical potential* (introduced earlier in section 1.4) gradients *within* and *across* all phases cease to exist.

The present chapter constitutes a systematic development of the concept of a new class of properties essential to description of real mixtures, as well of the idea of the chemical potential necessary for deriving the *criterion* of phase and chemical reaction equilibrium. Such properties facilitate the application of the first and second law principles to quantitatively describe changes of internal, energy, enthalpy and entropy of multi-component and multiphase systems.

Of the separate class of properties relevant to multi-component and multi-phase systems, the *partial molar property* and the *chemical potential* are particularly important. The former is used for describing behaviour of homogeneous multi-component systems, while the latter forms the fundament to description equilibrium in multi-phase, as well as reactive systems.

As in the case of pure gases, the ideal gas mixture acts as a datum for estimating the properties of real gas mixtures. The comparison of the properties of the real and ideal gas mixtures leads to the introduction of the concept of *fugacity*, a property that is further related to the chemical potential. Fugacity may also be expressed as a function of volumetric properties of fluids. As we will see, the *functional* equivalence of fugacity and the chemical potential provides a convenient pathway for relating the temperature, pressure and phase composition of a system under equilibrium.

In the last chapter it was demonstrated that residual properties provide very suitable means of estimating real gas properties. But as pointed out its usage for description of liquid states is not convenient. This difficulty is overcome by the formulation of a concept of *ideal solution* behaviour, which serves as a datum for estimating properties of *real liquid solutions*. The departure of the property of a real solution from that of an ideal one is termed as *excess property*. In other words, the excess property plays a role similar to that of residual property. In the description of solution behaviour at low to moderate pressures, we employ yet another property, the *activity coefficient;* which originates from the concept of fugacity. The activity coefficient may also be related to the excess Gibbs energy. It is useful not only as a measure of the extent of non-ideality of a real solution but also, more significantly in describing phase equilibria at low to moderate pressures.

6.1 Partial Molar Property

We consider first the case of a homogenous (single-phase), open system that can interchange matter with its surroundings and hence undergo a change of composition. Therefore, the total value of any extensive property $M^t \ (M \equiv V, U, H, S, A, G)$ is not only a function of T and P, but also of the actual number of moles of each species present in the system. Thus, we may write the following general property relation:

$$M^t = nM = M\left(T, P,\ n_1, n_2 \ldots..n_i \ldots.n_N\right) \qquad ..(6.1)$$

Where $N \equiv \text{total number of chemical species in the system}$

$$n = \text{total number of moles in the system} = \sum_i^N n_i \qquad ..(6.2)$$

Taking the total derivative for both sides of eqn. 6.1:

$$d\left(nM\right) = \left[\frac{\partial(nM)}{\partial P}\right]_{T,n} dP + \left[\frac{\partial(nM)}{\partial T}\right]_{P,n} dT + \left[\frac{\partial(nM)}{\partial n_i}\right]_{T,P,n_{j\neq i}} dn_i \qquad ..(6.2)$$

Where, subscript *n* indicates that all mole numbers are held constant and subscript $n_{j\neq i}$ that all mole numbers except n_i are held constant. This equation has the simpler form:

$$d\left(nM\right) = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial M}{\partial T}\right)_{T,x} dT + \sum_i \bar{M}_i dn_i \qquad ..(6.3)$$

(the subscript *x* denotes differential at constant composition)

Where: $\bar{M}_i = \left[\dfrac{\partial(nM)}{\partial n_i}\right]_{P,T,n_{j\neq i}}$ ..(6.4)

Eqn. 6.4 defines the *partial molar property* $\bar{M}_i$ of species *i* in solution. It represents the change of total property '*nM*' of a mixture resulting from addition at constant T and P of a differential amount of species '*i*' to a finite amount of solution. In other words it also signifies the value of the property per mole of the specific species when it exists in solution. In general, the partial molar property of a substance differs from the molar property of the same substance in a pure state at the same temperature and pressure as the mixture or solution. This owing to the fact that while in a pure state the molecules interact with its own species, in a solution it may be subjected to different interaction potential with dissimilar molecules. This may render the value of a molar property different in mixed and pure states.

Now, $n_i = x_i n;\ dn_i = x_i dn + n\, dx_i$

Or: $dn_i = x_i dn + n\, dx_i$ ..(6.5)

Also: $d(nM) = ndM + Mdn$ ..(6.6)

Substituting eqns. 6.5 and 6.6 in eqn. 6.3 leads to:

$$ndM + Mdn = n\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial M}{\partial T}\right)_{T,x} dT + \sum_i \bar{M}_i (x_i dn + n\, dx_i) \quad ..(6.7)$$

On re-arranging:

$$\left[dM - \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{T,x} dT + \sum_i \bar{M}_i dx_i\right] n + \left[M - \sum_i \bar{M}_i x_i\right] dn = 0 \quad ..(6.8)$$

While deriving eqn. 6.8 no specific constraints on the values of either *n* or *dn* have been applied. This suggests that the equation is valid for any arbitrary values of these two variables. Thus *n* and *dn* are independent of each other. Therefore, eqn. 6.8 can only be valid if the coefficients of these two variables are identically zero. On putting the coefficients to zero the following equations obtain:

$$dM = \left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{T,x} dT + \sum_i \bar{M}_i dx_i \quad ..(6.9)$$

$$M = \sum_i \bar{M}_i x_i \quad (at\ constant\ T\ \&\ P) \quad ..(6.10)$$

From eqn. 6.10, it follows, that $nM = n\sum_i x_i\bar{M}_i$ …(6.11)

And also: $dM = \sum_i x_i d\bar{M}_i + \sum_i \bar{M}_i dx_i$ …(6.12)

Equating (6.19) and (6.21) yields the well-known *Gibbs-Duhem* equation (*GDE*):

$$\left(\frac{\partial M}{\partial P}\right)_{T,x} dP - \left(\frac{\partial M}{\partial T}\right)_{T,x} dT - \sum_i x_i d\bar{M}_i = 0$$

..(6.13)

The GDE must be satisfied for all changes in P, T, and in $\bar{M}_i$ caused by changes of state in a homogeneous phase. For the important special case of changes at constant T and P, it simplifies to:

$$\sum_i x_i d\bar{M}_i = 0$$ ..(6.14)

Or, taking any arbitrary species '*j*': $\sum_i x_i \frac{d\bar{M}_i}{dx_j} = 0$ (*at const T, P*) ..(6.15)

Equations (6.14 and 6.15) implies that the partial molar properties of the various species ($\bar{M}_i$'s are not independent. Some key properties of partial molar properties are defined as follows:

$$\lim_{x_i \to o} \bar{M}_i = \bar{M}_i^{\infty}$$

$$\lim_{x_i \to 1} \bar{M}_i = M_i$$

$$\lim_{x_i \to 1} M = M_i$$

Select additional relations among partial properties are demonstrated in the Appendix 6.1.

Based on the foregoing considerations one may define an *isothermal molar property change of mixing* ΔM_{mix} as follows:

$$\Delta M_{mix}(T,P) = M(T,P) - \Sigma x_i M_i(T,P)$$ ..(6.16)

Or: $\Delta M_{mix} = M - \Sigma x_i M_i = \Sigma x_i \bar{M}_i - \Sigma x_i M_i = \Sigma x_i(\bar{M}_i - M_i)$ ..(6.17)

(*M can be = V, U, H, S, A, G*)

Typical examples of molar volume change of mixing for a number of binary solutions are shown in figs. 6.1 and 6.2. Clearly then there can be substantial variation of this property depending upon the nature of the constituent molecules.

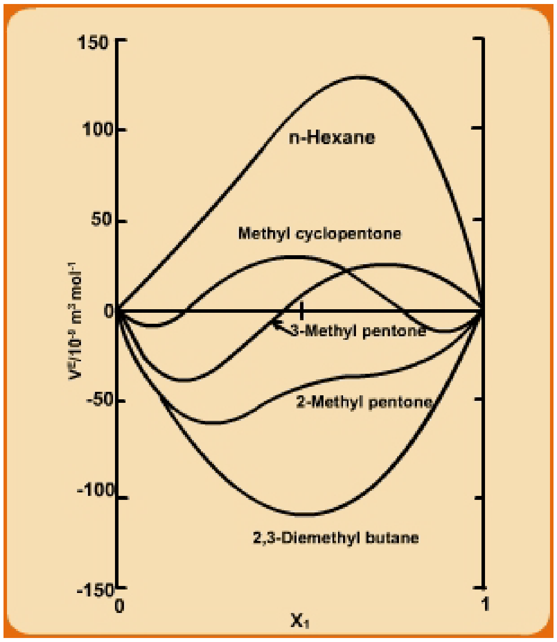


Fig. 6.1 Molar volume change of mixing for solutions of cyclohexane (1) with some other C_6 hydrocarbons (Source: H.C Van Ness and M. M. Abbott, *Perry's Chemical Engineer's Handbook* (7th ed.), McGraw Hill, 1997.

Example 6.1

Consider a solution of two species S1/S2 at 25°C such that $x_1 = 0.4$. If $\overline{V}_1 = 40 \times 10^{-6}$ m^3/mol, find $\overline{V}_2$. The solution specific gravity is = 0.90, and the molecular weights of the species are 32 and 18 respectively.

(Click for solution)

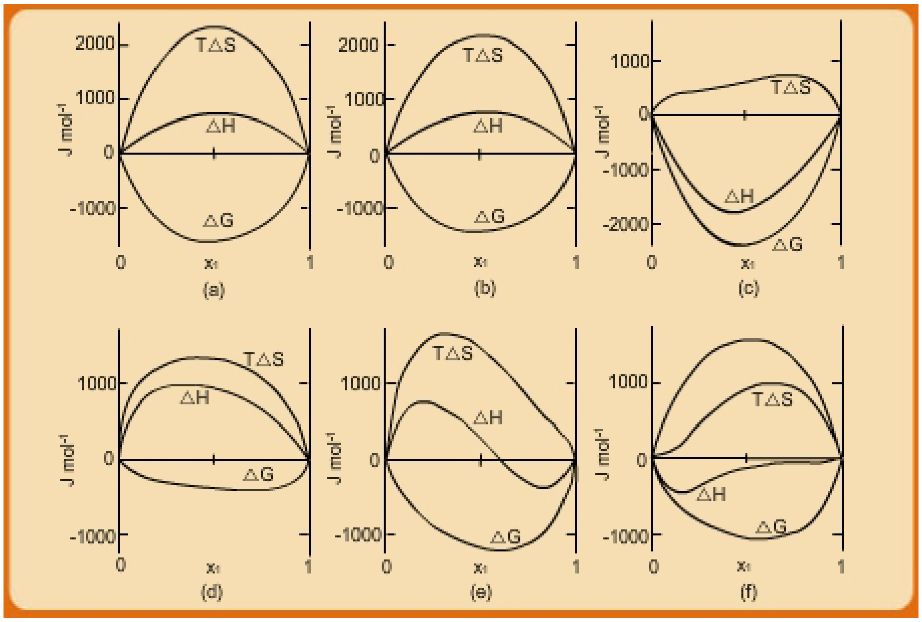


Fig. 6.2 Property changes of mixing at 50°C for 6 binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2). (Source: H.C Van Ness and M. M. Abbott, *Perry's Chemical Engineer's Handbook* (7th ed.), McGraw Hill, 1997.

6.2 Partial Properties for Binary Solutions

The partial property is generally not amenable to *ab initio* computation from theory, but may be conveniently determined by suitably designed experiments that help obtain isothermal molar property of mixing (eqn. 6.17). Here we illustrate a set of results that derive for a binary mixture, and which may be applied to compute the relevant partial molar properties at any composition. Applying eqn. 6.10:

$$M = \bar{M}_1 x_1 + \bar{M}_2 x_2 \quad (at\ constant\ T\ \ \&\ P) \qquad ..(6.18)$$

Or: $dM = (x_1 d\bar{M}_1 + \bar{M}_1 dx_1) + (x_2 d\bar{M}_2 + \bar{M}_2 dx_2)$ ..(6.19)

Applying the Gibbs-Duhem equation (6.14) gives:

$$x_1 d\bar{M}_1 + x_2 d\bar{M}_2 = 0 \qquad ..(6.20)$$

Now, since $x_1 + x_2 = 1,\ dx_1 = -dx_2$ ..(6.21)

Using Eqns. 6.19 – 6.21:

$$dM = \bar{M}_1 dx_1 - \bar{M}_2 dx_1 \qquad ..(6.22)$$

Or: $\dfrac{dM}{dx_1} = \bar{M}_1 - \bar{M}_2$ ..(6.23)

On solving eqns. 6.22 and 6.23 simultaneously:

$$\bar{M}_1 = M + x_2 \frac{dM}{dx_1} \qquad ..(6.24)$$

$$\bar{M}_2 = M - x_1 \frac{dM}{dx_1} \qquad ..(6.25)$$

If the molar property of the mixture M is available either from experiments or in analytical form, the partial molar properties may be estimated by applying the last two equations. Alternately, the experimental values of the mixture molar property (at a given T & P) may be plotted as a function of x_1 as shown in fig.6.3.

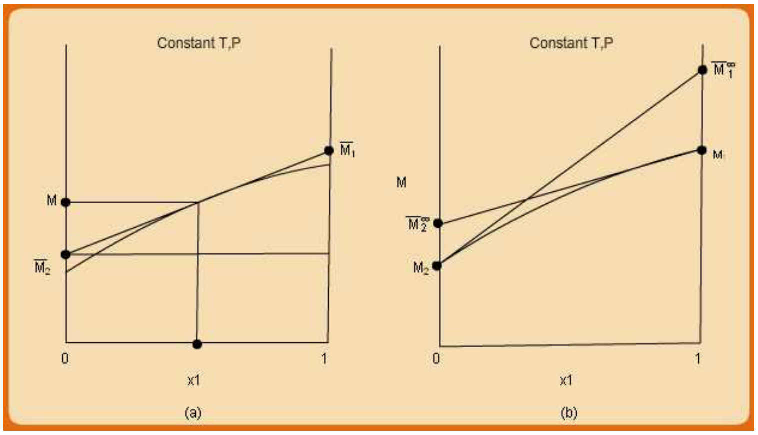


Fig. 6.3. Graphical method of determination of partial molar properties for a binary solution

For determining the partial molar properties at a given concentration one may draw a tangent to the M *vs.* x_1 curve, and $\bar{M}_1$ and $\bar{M}_2$ obtain as the right and left intercepts on the *y*-axis. This may be evident on comparing with the equations 6.24 and 6.25.

Using eqn. 6.17, the molar property M of a mixture is also written as:

$$M = \sum x_i M_i + \Delta M_{mix} \qquad ..(6.26)$$

In general the most common form of analytical relation (obtained by fitting a polynomial to the experimentally determined values of isothermal ΔM_{mix} as a function of composition) is the well-known Redlich-Kister equation, which for a binary solution is given by:

$$\Delta M_{mix} = x_1 x_2 [A + B(x_2 - x_1) + C(x_2 - x_1)^2 + ...] \qquad ..(6.27)$$

Where, *A*, *B*, *C* are temperature dependent and are determined from experimental measurements of ΔM_{mix}. For many practical applications the above equation is usually truncated to include only the terms corresponding to the parameters A and B. Fig. 6.4 shows the relation between the mixture enthalpy, the enthalpy change of mixing, the pure component and the partial molar enthalpies for a representative binary system.

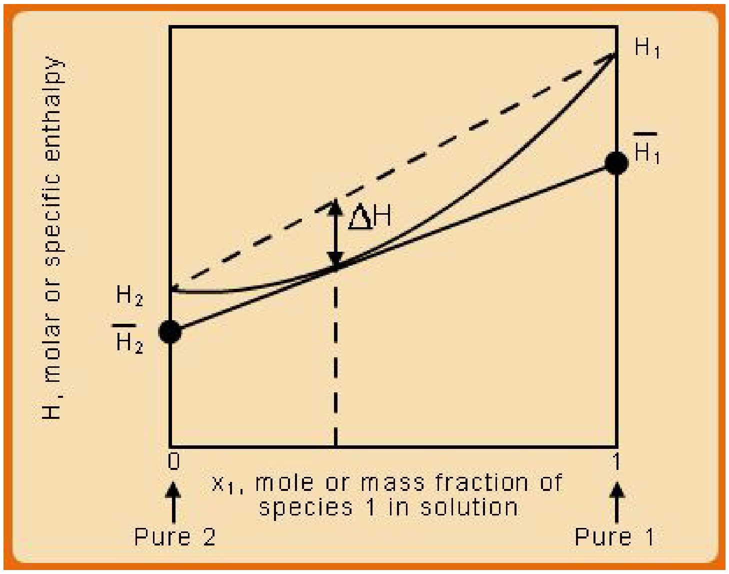


Fig. 6.4. Schematic showing pure component and partial molar enthalpies for a binary solution

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Example 6.2

The molar enthalpy of a binary solution is given by:

V = 500 x_1 + 1000 x_2 + x_1x_2 (50 x_1+40x_2) cm^3/mol. Find the expressions for: $\bar{V}_1$, and $\bar{V}_1^{\infty}$.

(Click for solution)

6.3 Criteria of Thermodynamic Equilibrium

The nature of thermodynamic equilibrium has been introduced in section 1.4. As we know, it involves simultaneous thermal and mechanical equilibrium within a system. Apart from these constraints, the system must also be in a state of *chemical equilibrium*. In the most general sense, chemical equilibrium subsumes the following restrictions: (i) the various phases that may exist within the system are in equilibrium with each other in that there is no mass transfer of any chemical species between the phases; (ii) all reactions occurring in the system are also equilibrated, i.e., there is no further progress of the reaction in terms of conversion of the reactants to products. The last two criteria are better understood in terms of the property called *chemical potential,* which we shall introduce in the following section. Here we focus on the overall, general criterion that must be in obeyed for any chemical system in equilibrium regardless of whatever species, phases or reactions that defines it.

Consider a closed system, which can be either homogeneous or heterogeneous, and which exists in a state of thermal and mechanical equilibrium with its surroundings. However, we assume that it is not under equilibrium with respect to possible inter-phase transfer of the chemical species or reactions between them. If the latter conditions prevail, all inter-phase transfer processes or reactive transformation of species must continue to occur till the point when the system is also at chemical equilibrium. In all real systems such changes are induced by finite gradients and are therefore are irreversible in nature. Applying the first law equation for all such changes for the system:

$$dU^t = dQ + dW \qquad ..(6.28)$$

We next consider that the system is under thermal and mechanical equilibrium with the surroundings (surr). Under such a situation:

$$dW = -PdV^t \qquad ..(6.29)$$

And also: $dS_{surr} = \dfrac{dQ_{surr}}{T_{surr}} = -\dfrac{dQ^t}{T}$ (note that $dQ_{surr} = -dQ^t$ for system) ..(6.30)

But by the second law: $dS_{surr} + dS^t \geq 0$ ..(6.31)

On combining eqns. 6.30 and 6.31 we get:

$$dQ^t \leq TdS^t \qquad ..(6.32)$$

Combining eqns. 6.28, 6.29 and 6.32:

$$dU^t + PdV^t - TdS^t \leq 0 \qquad ..(6.33)$$

It follows that for all incremental changes within the system, which take it closer to the final thermodynamic equilibrium, the property changes must satisfy the constraint imposed by eqn. 6.33. If the changes internal to the system occur under reversible conditions, the *equality* sign is valid; on the other hand, for irreversible processes the inequality condition holds.

Equation 6.33 can be used to generate alternate criteria of thermodynamic equilibrium, namely:

$$(dU^t)_{V^t,S^t} \leq 0 \qquad ..(6.34)$$

$$(dS^t)_{U^t,V^t} \leq 0 \qquad ..(6.35)$$

The other two criteria which are most apt in relation to thermodynamics of phase equilibria involve the use of Helmholtz and Gibbs free energy. If a process takes place under the constraints of constant temperature and volume then:

$$\left[dU^t - d(TS^t)\right]_{T,V^t} \le 0$$

Or:

$$\left[d(U^t - TS^t)\right]_{T,V^t} \le 0$$

$$(dA^t)_{T,V^t} \le 0 \qquad ..(6.36a)$$

And, if the process occurs under constant temperature and pressure one may write:

$$\left[dU^t + d(PV^t) - d(TS^t)\right]_{T,P} \le 0$$

Or: $\left[dG^t\right]_{T,P} \le 0$ ..(6.36b)

Equation 6.36b provides the most practical of the three versions of general criteria of approach to equilibrium, as temperature and pressure are the most easily measurable of all the thermodynamic properties. As we have argued at the early part of this section at total thermodynamic equilibrium not only are thermal and mechanical gradients non-existent, there can be no further change in either the composition of any of the phases, or that of the reactive species. If there are any such incremental, *infinitesimal* changes of composition variables at the state of complete equilibrium the system once again must return to its stable state. This is exactly akin to the concept of equilibrium for mechanical systems presented in section 1.4. Therefore one may write the following equation to characterize thermodynamic equilibrium:

$$\left[dG^t\right]_{T,P} = 0 \qquad ..(6.37)$$

In summary, therefore, eqn. 6.37 constitutes a generalized description of thermodynamic equilibrium, which may be stated as follows:

“*The equilibrium state of a closed system is that state for which the total Gibbs energy is a minimum with respect to all possible changes at the given T and P”.*

This criterion of equilibrium can be employed for determination of equilibrium states of a system in terms of its T, P and compositions. In principle, one first expresses G^t (at a given temperature and pressure) as a function of the numbers of moles of each chemical species present in the various phases. Next one makes a partial differential operation on G^t with respect to moles of each species in the phases, and sets each such differential to zero to obtain the set of values for the mole numbers that *minimizes* G^t, subject to the constraints of conservation of mass. This procedure can be applied to problems of phase, chemical-reaction equilibria; and, of course, the most complex of chemical thermodynamic problems, where the criteria of phase and chemical-reaction equilibrium are valid simultaneously. As we will see, eqn. 6.37 forms the foundation for developing more *specific* criteria that can help describe both phase (section 6.3) and chemical reaction equilibria (section 8.3).

6.3 The Chemical Potential

In this section we focus on the properties of partial molar Gibbs free energy, which as we observed at the beginning of the chapter, is used for the description of phase and chemical reaction equlibria. The application of eqn. 6.3 to the molar Gibbs free energy of a mixture gives:

$$d(nG) = n\left(\frac{\partial G}{\partial P}\right)_{T,x} dP + n\left(\frac{\partial G}{\partial T}\right)_{T,x} dT + \sum_i \bar{G}_i dn_i \quad ..(6.38)$$

By definition the partial molar Gibbs free energy is termed the ***chemical potential*** of species *i* in the mixture, i.e.,:

$$\mu_i = \left.\frac{\partial(nG)}{\partial n_i}\right|_{T,P,n_{j\neq i}} \quad ..(6.39)$$

Or: $\mu_i = \bar{G}_i$ ..(6.40)

Using the result in eqn. 5.7 the first two partial derivatives in eqn. 6.28, may be replaced by (nV) and $-(nS)$. Eqn. 6.38 then becomes:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i dn_i \quad ..(6.41)$$

With $n = 1$, and so $n_i = x_i$, eqn. 6.41 becomes:

$$dG = VdP - SdT + \sum_i \mu_i dx_i \quad ..(6.42)$$

We next consider the use of chemical potential for obtaining a general criterion of thermodynamic equilibrium. Consider a closed system consisting of two phases α and β which are in equilibrium with each other. These phases could be vapour and liquid, solid and liquid, solid and vapour etc. Each phase in the system may be treated as an open system, the interface between the two phases acting as the boundary across which material may be transferred. Thus we can apply 6.41 to both phases *individually*:

$$d(nG)^{\beta} = (nV)^{\beta}\, dP - (nS)^{\beta}\, dT + \sum_i \mu_i^{\beta} dn_i^{\beta} \qquad ..(6.43)$$

$$d(nG)^{\alpha} = (nV)^{\alpha}\, dP - (nS)^{\alpha}\, dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha} \qquad ..(6.44)$$

In general we should denote the temperature and pressure of each phase also with the superscript in order to distinguish them. However, for the present purpose we assume thermal and mechanical equilibrium to prevail, i.e.

$$T^{\alpha} = T^{\beta}$$

$$P^{\alpha} = P^{\beta}$$

The total Gibbs free energy of the system changes with mass transfer between the two phases. The change in the total Gibbs energy of the two-phase system is the sum of the changes in each phase. The total volume and entropy of each phase is expressed by the following equations.

$$nV = (nV)^{\alpha} + (nV)^{\beta} \qquad ..(6.45)$$

And $nS = (nS)^{\alpha} + (nS)^{\beta}$ ..(6.46)

Summing eqns. 6.43 and 6.44 and using eqns. 6.55 and 6.46 we get:

$$d(nG) = (nV)dP - (nS)dT + \sum_i \mu_i^{\alpha} dn_i^{\alpha} + \sum_i \mu_i^{\beta} dn_i^{\beta} = 0 \qquad ..(6.47)$$

Since the mass transfer of each species takes place between the two phases in question, their change of mass in each phase must be equal and opposite: $dn_i^{\alpha} = -dn_i^{\beta}$

In which case eqn. 6.47 becomes:

$$d(nG) = (nV)dP - (nS)dT + \sum_i (\mu_i^{\alpha} - \mu_i^{\beta}) dn_i^{\alpha} = 0 \qquad ..(6.48)$$

If the system is considered to be already under thermal and mechanical equilibrium no changes in temperature and pressure may occur, then the last equation simplifies to:

$$\sum_i (\mu_i^{\alpha} - \mu_i^{\beta}) dn_i^{\alpha} = 0 \qquad ..(6.49)$$

We note that in the above sequence of equations no explicit constraint has been placed on the individual dn_i^α, which then are independent of each other. Thus for eqn. 6.49 to have general validity the coefficient of each dn_i^α has to be identically zero. Thus:

$$\mu_i^\alpha = \mu_i^\beta \qquad (i = 1, 2, \ldots N). \qquad ..(6.50)$$

The above proof has been simplified by assuming identical temperature and pressure for each phase. However, a more rigorous mathematical derivation of the phase equilibrium criterion leads to the result that if a system is under thermodynamic equilibrium, the temperature and pressures of all the phases are the same. If there is third phase ψ in the system we have considered, a second equation of the type (6.50) obtains:

$$\mu_i^\alpha = \mu_i^\psi \qquad ..(6.51)$$

Thus, if there are a total of δ phases in the system, one can generalize the result as follows:
By considering successive pairs of phases, we may readily generalize to more than two phases the equality of chemical potentials; thus for δ phases:

$$\mu_i^\alpha = \mu_i^\psi = \ldots = \mu_i^\delta \qquad (i = 1, 2, ..N) \qquad ..(6.52)$$

The above result allows us to advance a more general statement of the phase equilibrium criterion:

For a system under thermodynamic equilibrium, along with equality of the temperature and pressures of all phases, the chemical potential of each species is identical across all the phases.

6.4 Ideal Gas Mixtures and Liquid Solutions

We next explore the development of a quantitative definition of the chemical potential in terms of the volumetric properties and composition of mixtures. We have observed earlier that just as ideal gas state is a reference for real gas properties, ideal gas mixtures play the same role with respect to real gas mixtures. Therefore, it is instructive to establish the property relations for ideal gas mixture first.

Consider the constitution of an ideal gas mixture (containing N species) at a given temperature (T) and pressure (P). To obtain n moles of the total mixture we need to bring together n_i moles of each species $(n = \sum_i^N n_i)$ at temperature T but at a pressure p_i which corresponds to the *partial pressure* that each species would exert in the final mixture. If V^t is the total volume of the mixture, the following set of relations hold.

$$P = nRT / V^t \Rightarrow p_i = n_i RT / V^t$$
$$Or \Rightarrow p_i / P = n_i / n = y_i$$

$$n = n_i + \sum_j n_j \quad \Rightarrow \quad Hence: \left[\frac{\partial n}{\partial n_i}\right]_{T,P,n_{j\neq i}} = 1$$

$$\bar{V}_i^{ig} = \left[\frac{\partial (nV^{ig})}{\partial n_i}\right]_{T,P,n_{j\neq i}} = \left[\frac{\partial (nRT/P)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = (RT/P)\left[\frac{\partial n}{\partial n_i}\right]_{T,P,n_{j\neq i}} = RT/P \qquad ..(6.53)$$

But the molar volume of the i^{th} species $V^{ig} = RT/P$

Hence it follows:

$$\bar{V}_i^{ig} = V^{ig} \qquad ..(6.54)$$

The last result indicates that the molar volume for a species does not change between its pure state and in an ideal gas mixture at the same T & P. It may then be concluded that for an ideal gas mixture the properties of each species are independent of that of the other ones. This may be easy to appreciate as the concept of an ideal gas is premised on the idea that the intermolecular interaction is non-existent in such a state. This conclusion leads to the well-known *Gibbs theorem***:**

"Except for volume all other partial molar property of a species in an ideal-gas mixture is equal to the corresponding molar property of the species as a pure ideal gas at a temperature same as that of the mixture, but at a pressure equal to its partial pressure in the mixture."

In mathematical terms: $\bar{M}_i^{ig}(T,P) = M_i^{ig}(T,p_i)$ ..(6.55)

As an example let us consider the case of enthalpy of an ideal gas mixture. By Gibbs theorem:

$$\bar{H}_i^{ig}(T,P) = H_i^{ig}(T,p_i) \qquad ..(6.56)$$

But, as the enthalpy of an ideal gas is independent of pressure it follows that:

$$H_i^{ig}(T,p_i) = H_i^{ig}(T,P) \qquad ..(6.57)$$

It follows: $\bar{H}_i^{ig}(T,P) = H_i^{ig}(T,P)$ ..(6.58)

By the standard definition, the enthalpy of the mixture is:

$$H_{mix}^{ig}(T,P) = \sum_i y_i \bar{H}_i^{ig}(T,P) \qquad ..(6.59)$$

Thus, using eqns. 6.56 – 6.59 we get:

$$H_{mix}^{ig}(T,P) = \sum_i y_i H_i^{ig}(T,P) \qquad ..(6.60)$$

It follows: $\Delta H_{mix}^{ig} = H_{mix}^{ig} - \Sigma y_i H_i^{ig} = 0$ ..(6.61)

Employing the same reasoning: $\Delta U_{mix}^{ig} = U_{mix}^{ig} - \Sigma y_i U_i^{ig}$ ..(6.62)

The molar entropy of mixing of ideal gas mixture, however, is not zero. As stated above, the formation of 1 mole of mixture results from bringing together y_i moles each species at T and partial pressure p_i to form a mixture at T and P, Hence for isothermal mixing, y_i moles of each species goes from *(T, p_i)* to *(T, P)*. Therefore:

$$S_i^{ig}(T,P) - S_i^{ig}(T,p_i) = -R\ln(P/p_i) = R\ln y_i \qquad ..(6.63)$$

On transposing: $S_i^{ig}(T,p_i) = S_i^{ig}(T,P) - R\ln y_i$ ..(6.64)

But: $S^{ig}(T,P) = \sum_i y_i \bar{S}_i^{ig}(T,P)$ ..(6.65)

So: $S^{ig}(T,P) = \sum_i y_i S_i^{ig}(T,p_i)$ ..(6.66)

Using eqns. 6.63 - 6.67, one obtains:

$$S^{ig}(T,P) = \sum_i y_i S_i^{ig}(T,P) - R\sum_i y_i \ln y_i \qquad ..(6.67)$$

On applying the partial molar property operation (as given by eqn. 6.4) on 6.58, it may be shown that:

$$\bar{S}_i^{ig}(T,P) = S_i^{ig}(T,P) - R\ln y_i \qquad ..(6.68)$$

It further follows: $\Delta S_{mix}^{ig} = S^{ig}(T,P) - \Sigma y_i S_i^{ig}(T,P) = R\sum_i y_i \ln y_i$ ..(6.69)

For Gibbs free energy relation we start from: $G = H - TS$

For an ideal gas mixture: $G^{ig} = H^{ig} - TS^{ig}$ ..(6.70)

Taking the partial molar property derivative: $\bar{G}_i^{ig} = \bar{H}_i^{ig} - T\bar{S}_i^{ig}$ ..(6.71)

On putting eqns. 6.58 and 6.59 into 6.71 we get the following relation for the chemical potential of each species in an ideal gas mixture:

$$\bar{G}_i^{ig} = \mu_i^{ig} \equiv G_i^{ig} + RT\ln y_i \qquad ..(6.72)$$

Using eqns. 6.51 and 6.58, it may be also shown that:

$$G_{mix}^{ig} = \sum_i y_i G_i^{ig} + RT\sum_i y_i \ln y_i \qquad ..(6.73)$$

Example 6.3

What is the change in entropy when 0.6 m^3 of CO_2 and 0.4 m^3 of N_2, each at 1 bar and 25^oC blend to form a gas mixture at the same conditions? Assume ideal gases.

(Click for solution)

The Ideal Solution:

We have already seen that owing to the fact that pure ideal gases and mixtures are not subject to intermolecular interactions the partial molar properties (apart from volume) of each species is the same as that of the pure species at the same temperature and pressure. In other words each species "sees" no difference in their environment in pure or mixed state. One can conceptually extend this idea to posit an ideal solution behaviour which may serve as a model to which real-solution behavior can be compared. Consider a solution of two liquids, say A and B. If the intermolecular interaction in the pure species, (i.e., A-A and B-B) is equal to the *cross-species* interaction A-B, neither A nor B type molecules will "see" any difference in their environment before and after mixing. This is in a sense the same condition as one obtains with idea gas mixtures. Hence an *identical* set of ideal solution property relations may be constructed based on the model of ideal gas mixture. By convention while describing properties of liquid solutions mole fractions y_i are replaced by x_i. The following relations therefore, derive for ideal (liquid) solution properties (denoted by a superscript '*id*'):

$$H^{id} = \sum_i x_i H_i \text{ and, } V^{id} = \sum_i x_i V_i \qquad ..(6.74)$$

$$S^{id} = \sum_i x_i S_i - R\sum_i x_i \ln x_i \qquad ..(6.75)$$

Hence $G^{id} = \sum_i x_i G_i + RT\sum_i x_i \ln x_i$ ..(6.76)

Lastly, $\mu_i^{id} = \bar{G}_i^{id} = G_i + RT\ln x_i$ ..(6.77)

As we will see later the ideal solution model can also serve to describe the behaviour of mixtures of real gases or solids.

6.5 Excess Properties

Unlike for real gases (pure or mixtures) the EOS based approach to calculation of thermodynamic properties of real liquid solutions have not proved very successful. However, as molar *residual property* is defined for real gases, for *real* liquid solutions one may formulate a different departure function called the molar *excess property* that quantify the deviation from ideal solution property. The mathematical formalism of excess properties is, therefore, analogous to that of the residual properties.

If M represents the molar (or unit-mass) value of any extensive thermodynamic property(e.g., *V*,***U*****,** *H, S, G,* etc.), then an excess property M^E is defined as the difference between the actual property value of a solution and the value it would have as an ideal solution at the same temperature, pressure, and composition. Thus:

$$M^E \equiv M - M^{id} \qquad ..(6.78)$$

The excess property bear a relationship to the property change of mixing. One may take the example of excess Gibbs free energy to illustrate the point. Thus:

$$G^E = G - G^{id} \qquad ..(6.79)$$

Or: $$G^E = G - \left(\sum_i x_i G_i + RT \sum_i x_i \ln x_i \right) \qquad ..(6.80)$$

Thus: $$G^E = \Delta G_{mix} - RT \sum_i x_i \ln x_i \qquad ..(6.81)$$

Other relations include:

$$H^E = H - H^{id} = \Delta H_{mix} \qquad ..(6.82)$$

$$S^E = \Delta S_{mix} + R \sum_i y_i \ln y_i \qquad ..(6.83)$$

Also: $G^E = H - TS^E$

The non-ideality of real liquid solutions are depicted well by use of excess properties, especially through the behaviour of G^E, H^E and S^E. The excess Gibbs energy is typically obtained from low pressure vapour-liquid equilibrium data, while H^E is obtained by measuring isothermal enthalpy change of mixing. Lastly S^E is derived using the following relation:

$$S^E = \frac{H_E - G^E}{T} \qquad ..(6.84)$$

Fig. 6.5 shows the variation of each of the excess property as a function of liquid mole fraction for a number of binary solutions.

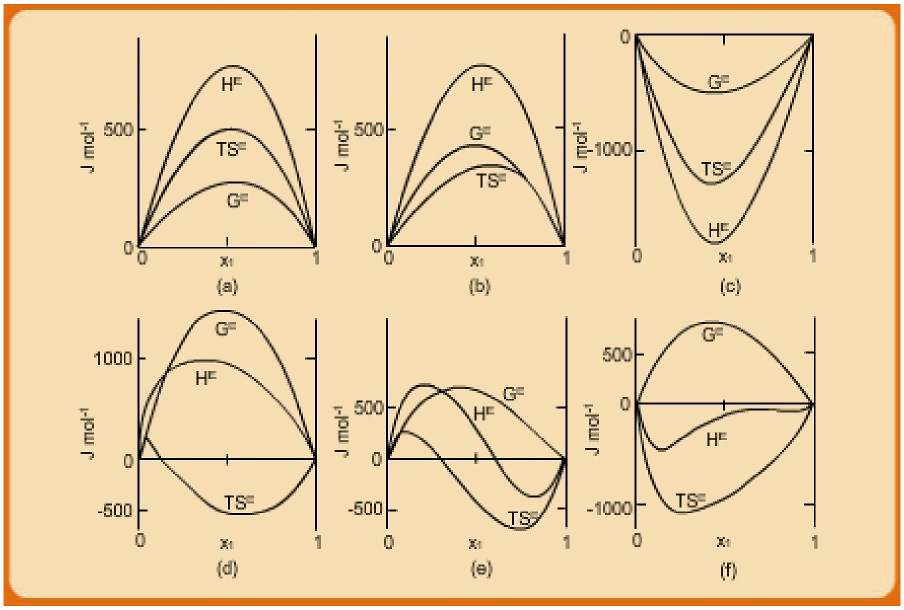


Fig. 6.5 Excess properties at 50°C for 6 binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2);(*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2). (Source: H.C Van Ness and M. M. Abbott, *Perry's Chemical Engineer's Handbook* (7th ed.), McGraw Hill, 1997.

6.6 Fugacity of pure substances

It has been shown in section 6.3 that the chemical potential provides a fundamental description of phase equilibria. As we shall further see in chapter 8, it also proves an effective tool for depicting chemical reaction equilibria. Nevertheless, its direct usage is restricted, as it is not easy to directly relate the chemical potential to thermodynamic properties amenable to easy experimental determination, such as the volumetric properties. The definition of a new function called fugacity, itself related to the chemical potential, helps bridge the gap.

The concept of fugacity is advanced based on the following thermodynamic relation for an ideal gas. For a single component closed system containing an ideal gas we have (from eqn. 5.7):

$$dG = VdP - SdT$$

At constant temperature, for a pure ideal gas 'i' the above equation reduces to:

$$dG_i^{ig} = V_i^{ig}dP = RTdP/P = RTd\ln P \qquad ..(6.85)$$

$G_i^{ig} = \Gamma_i(T) + RTd\ln P$ [Where, $\Gamma_i\left(T\right)$ is the constant of integration]

Utilizing the essential simplicity of eqn. 6.85 we apply it a real fluid but by replacing pressure with fugacity (since it is not valid for a real fluid):

$dG_i = V_i dP$ (At const. T)

Thus, $dG_i = RTd\ln f_i$

Hence, $G_i = \Gamma_i(T) + RTd\ln f_i$ ..(6.86)

Since f_i has the units of pressure, it is often described as a "fictitious pressure". It may be noted that the definition of fugacity as provided by eqn. 6.86 is completely general in nature, and so can be extended to liquids and solids as well. However, the calculation of fugacity for the latter will differ from that for gases. This equation provides a partial definition of f_i, the fugacity of pure species '*i*'. Subtracting eqn. 6.85 form 6.86 gives:

$$G - G^{ig} = G_i^R = RT\ln\frac{f_i}{P} \quad ..(6.87)$$

The dimensionless ratio f_i / P is termed *fugacity coefficient* (ϕ).

Thus: $G_i^R = RT\ln\phi_i$ ..(6.88)

Where, $\phi_i \equiv f_i / P$ ..(6.89)

Clearly for an ideal gas the following relations hold: $G_i^R = 0;\ f_i^{ig} = P;$ accordingly, $\phi_i = 1$.

However, by eqn. 5.38: $\dfrac{G^R}{RT} = \int_0^P (Z-1)\dfrac{dP}{P}$

Thus, using the last relation in eqn. 6.78:

$$\ln\phi_i = \int_0^P (Z_i - 1)\frac{dP}{P} \qquad \text{(At const. T)} \quad ..(6.90)$$

6.7 Fugacity-based phase equilibrium criterion for pure component system

The general criterion of thermodynamic equilibrium has been defined by eqn. 6.38. Applying it to, for example, a vapour (V) and liquid (L) system of a pure component '*i*' we have:

$$\mu_i^V = \mu_i^L \quad ..(6.91)$$

However, for a pure component system: $\lim_{x_i \to 1} \bar{M}_i = M_i$.

Thus: $\mu_i^V \equiv \bar{G}_i^V = G_i^V$ and $\mu_i^L \equiv \bar{G}_i^L = G_i^L$ ..(6.92)

Thus, using eqn. 6.91 and 6.92 we have:

$$G_i^V = G_i^L \quad ..(6.93)$$

The above equation may be generalized for any other types of phases. However, the eqn. 6.93 is rendered more easily applicable if the chemical potential is replaced by fugacity. Thus integrating eqn. 6.86 between vapour and liquid states of a pure component:

$$\int_L^V dG_i = RT\int_L^V d\ln f_i \qquad ..(6.94)$$

$$G_i^V - G_i^L = RT\ln(f_i^V / f_i^L) \qquad ..(6.95)$$

Now applying eqn. 6.93 to 6.95 it follows $RT\ln(f_i^V / f_i^L) = 0$

Or:

$$f_i^V = f_i^L = f_i^{sat} \qquad ..(6.96)$$

In eqn. 6.86 f_i^{sat} indicates the value for either saturated liquid or saturated vapor, this is because the coexisting phases of saturated liquid and saturated vapor are in equilibrium. Since under such condition the pressure is P_i^{sat}, we can write:

$$\varphi_i^V = \frac{f_i^V}{P_i^{sat}}$$

$$\phi_i^L = \frac{f_i^L}{P_i^{sat}}$$

$$\phi_i^{sat} = \frac{f_i^{sat}}{P_i^{sat}}$$

Thus, employing eqn. 6.86 again, it follows:

$$\phi_i^V = \phi_i^L = \phi_i^{sat} \qquad ..(6.97)$$

Both eqns. 6.93, 6.96 and 6.97 represent *equivalent* criterion of vapor/liquid equilibrium for pure species.

6.8 Fugacity expressions for pure gases

Fugacity coefficient (and hence fugacity) of pure gases may be conveniently evaluated by applying eqn. 6.80 to a *volume-explicit* equation of state. The truncated virial EOS is an example of the latter type, for which the compressibility factor of pure species (i) is given by:

$$Z_i = 1 + \frac{B_{ii}P}{RT}$$

Or $Z_i - 1 = \frac{B_{ii}P}{RT}$

Thus, on using eqn. 6.80: $\ln \phi_i = \frac{B_{ii}}{RT}\int_0^P dP$ (at const T)

Hence, $\ln \phi_i = \frac{B_{ii}P}{RT}$ ..(6.98)

Eqn. 6.80 is, however, not amenable to use for obtaining expressions using cubic EOSs. The general equation for such purposes is relatively more involved and we derive it below.

Example 6.4

Estimate the fugacity of ethane at 122.2 K and 5 bar using the truncated virial EOS. For ethane T_c = 305.4K, P_c = 48.84 bar, ω = 0.099

(Click for solution)

==

Derivation of fugacity coefficient expression for cubic EOS:

Starting from eqn. 5.38:

$$\frac{G^R}{RT} = \ln \phi = \ln\left(\frac{f}{P}\right) = \frac{1}{RT}\int_0^P \left(V - \frac{RT}{P}\right) dP \quad ..(6.99)$$

Now: $\int VdP = \int d(PV) - \int PdV$ ..(6.100)

Using Eqn. 6.100 in 6.99:

$$\ln \phi = \frac{1}{RT}(PV - RT) - \int_{V=\infty}^{V} \frac{P}{RT} dV - \int_{PV=RT}^{PV} \frac{d(PV)}{PV} + \int_{V=\infty}^{V} \frac{dV}{V}$$

$$= (Z-1) - \int_{PV=RT}^{PV} d\ln(PV) + \int_{V=\infty}^{V} \frac{dV}{V} - \int_{V=\infty}^{V} \frac{P}{RT} dV$$

On simplifying:

$$\ln \phi = (Z-1) - \ln Z + \ln \frac{V}{V_\infty} - \frac{1}{RT}\int_{V=\infty}^{V} PdV \quad ..(6.101)$$

Here: V_∞ = molar volume at $P \to 0$, or V_∞ = ideal gas volume

Therefore: $V / V_\infty = Z$ ..(6.102)

Using eqn. 6.102 in 6.101 one arrives at:

$$\ln \phi = (Z-1) - \frac{1}{RT}\int_{V=\infty}^{V} PdV \quad ..(6.103)$$

==

Equation 6.103 is a generalized expression for obtaining pure component fugacity from a pressure explicit EOS. We show below the expressions for fugacity coefficients that derive on application of the above equation to various cubic EOSs. (The reader may refer to section 2.3.3 for various forms of cubic EOS).

VdW EOS:

$$\ln\phi = Z - 1 - \ln\frac{P(V-b)}{RT} - \frac{a}{RTV} \qquad ..(6.104)$$

RK-EOS:

$$\ln\phi = Z - 1 - \ln(Z-B) - \frac{a}{bRT}\ln\left(\frac{Z+B}{Z}\right); B = \frac{bP}{RT} \qquad ..(6.105)$$

SRK EOS:

$$\ln\phi = Z - 1 - \ln(Z-B) - \frac{a}{bRT}\ln\left(\frac{Z+B}{Z}\right); B = \frac{bP}{RT} \qquad ..(6.106)$$

PR-EOS:

$$\ln\phi = Z - 1 - \ln(Z-B) - \frac{a}{2\sqrt{2}bRT}\ln\left[\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})}\right]; B = \frac{bP}{RT} \qquad ..(6.107)$$

Example 6.5

Estimate the fugacity of ammonia vapor at 4.0 MPa and 321K assuming that it obeys the RK equation of state.

(Click for solution)

6.9 Generalized Correlations for the Fugacity Coefficient

The generalized correlation approach which has been presented earlier for calculation compressibility factor Z (section 2.3), and the residual enthalpy and entropy of gases (section 5.7), can also be applied for computing fugacity coefficients for pure gases and gaseous mixtures. Equation (6.90) can be rewritten in a generalized form as follows:

$P = P_C P_r$; hence, $dP = P_c dP_r$

Hence, an alternately, $\ln\phi = \int_O^{P_r} (Z-1)\frac{d\,P_r}{P_r}$ (at const. T_r) ..(6.109)

Substitution for $Z = Z_0 + \omega Z_1$, gives:

$$\ln\phi = \int_O^{Pr} (Z^O - 1)\frac{d\,P_r}{P_r} + \omega\int_O^{Pr} Z^1 \frac{d\,P_r}{P_r} \qquad ..(6.110)$$

The last equation may be written in alternative form:

$$\ln\phi = \ln\phi^0 + \omega\ln\phi^1 \qquad ..(6.111)$$

Or: $\phi = (\phi^0)(\phi^1)^\omega$ ..(6.112)

Where, $\ln\phi^0 = \int_O^{P_r} (Z^O - 1)\frac{d\,P_r}{P_r}$ ..(6.113)

$$\ln\phi^1 = \int_O^{P_r} Z^1 \frac{d\,P_r}{P_r} \qquad ..(6.114)$$

For obtaining the values of the integrals in the last two equations, the tabulated data for Z^0 and Z^1 for various values of T_r and P_r may be used for numerical or graphical computations. Yet another approach is due to Lee-Kesler which employsa variant of the BWR-EOS (eqn. 2.17) to evaluate the expressions for $\ln\phi^0$ and $\ln\phi^1$ for a wide range of values of T_r and P_r and are available in the form of extended tables. In either case the fugacity coefficient is finally computed using eqn. 6.112. **(**see figs 6.6 and 6.7).

Example 6.6

Estimate the fugacity of methane at 32C and 9.28 bar. Use the generalized correlation approach.

(Click for solution)

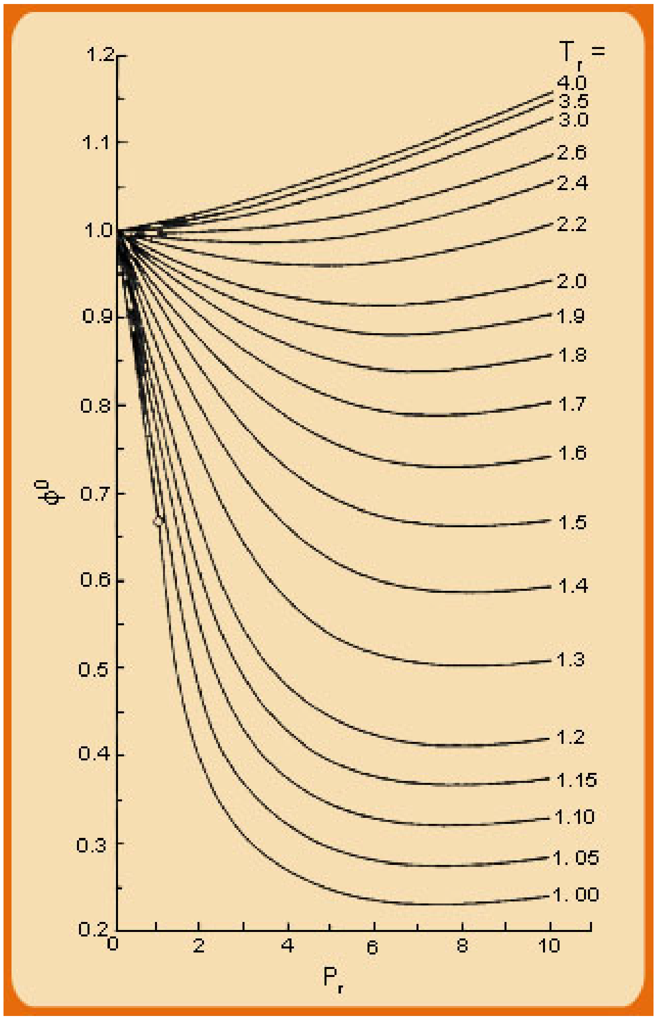


Fig. 6.6 Correlation of ϕ^0 drawn from tables of Lee-Kesler (Source: *AIChE J.*, pp. 510-527, 1975)

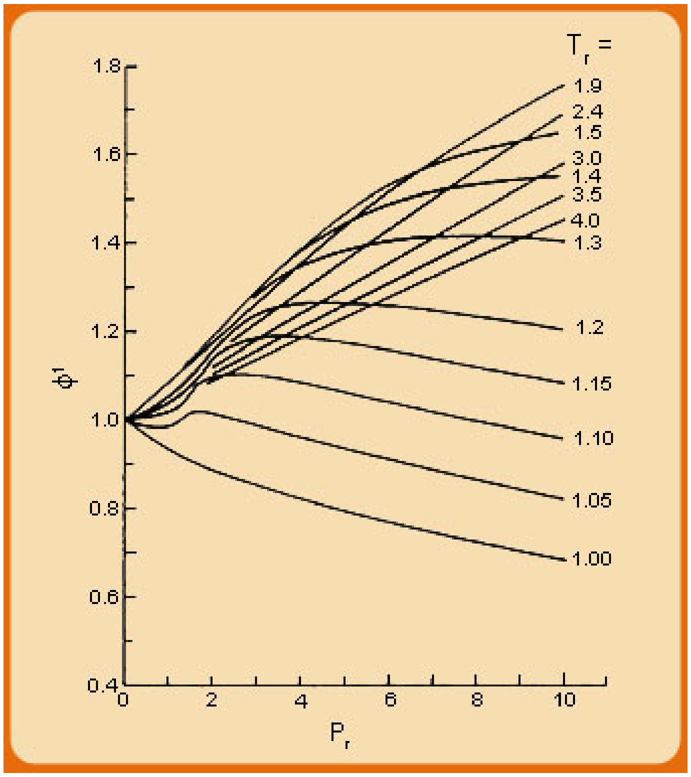


FIG 6.7 Correlation of ϕ^1 drawn from tables of Lee-Kesler (Source: *AIChE J.*, pp. 510-527, 1975)

The above set of equations may well be used for estimating the *overall* fugacity coefficient of a gaseous mixture. As in earlier instance (sections, 2.3 and 5.7) one makes use of pseudo-critical properties that are estimated from the following set of linear relations:

$$T_{C,m} = \sum_i y_i T_{C,i}\ ; \qquad P_{C,m} = \sum_i y_i P_{C,i} \qquad \omega_m = \sum_i y_i \omega_i \qquad ..(2.32)$$

The subscript 'i' runs over all the species present in the mixture 'm'. The above relations allow the mixture to be treated as *single* substance; the methodology outlined above for pure species may then be used to compute the fugacity coefficient of the mixture.

6.10 Expression for Fugacity of a Pure Liquid

Since the representation of liquid state by EOS is generally difficult, the calculation of fugacity of a compressed (or sub-cooled) liquid is based on the *saturated liquid* state as a reference state. One starts with the two generic relations (that apply to any pure real fluid 'i') already introduced in the section 6.7, namely:

$dG_i = V_i dP$ (at const. T)

$$dG_i = RTd\ln f_i$$

The two equations above may be combined to yield:

$$V_i dP = RTd\ln f_i \quad ..(6.115)$$

As shown (eqn. 6.96) at the saturation condition for co-existing vapour and liquid phases:

$$f_i^V = f_i^L = f_i^{sat}$$

Thus for a compressed liquid state at a given pressure one can write for an isothermal change of pressure from P_i^{sat} to the compressed liquid pressure P:

$$G_i - G_i^{sat} = \int_{P_i^{sat}}^{P} V_i dP \quad ..(6.116)$$

Alternately, $G_i - G_i^{sat} = RT\frac{f_i}{f_i^{sat}}$ ..(6.117)

On equating the last two equations:

$$\ln\frac{f_i}{f_i^{sat}} = \frac{1}{RT}\int_{P_i^{sat}}^{P} V_i dP \quad ..(6.118)$$

Since V_i, the liquid–phase molar volume, is a relatively weak function of pressure at temperatures well below the critical temperature, one may approximate $V_i \cong V_i^l$, where, V_i^l is the molar volume of the saturated liquid at the temperature of interest.

Using $f_i^{sat} = \phi_i^{sat} P_i^{sat}$ in the integrated form of eqn. 6.108 gives:

$$f_i(T,P) = \phi_i^{sat} P_i^{sat} \exp[\frac{V_i^l(P - P_i^{sat})}{RT}] \quad ..(6.119)$$

The exponential term on the left side of the last equation is known as a *Poynting factor***.** It may be noted that the calculation of the term ϕ_i^{sat} can be made based on any EOS suitable for gases at the given temperature T and pressure P_i^{sat}.

Example 6.7

Estimate the fugacity of cyclopentane at 110 C and 275 bar. At 110 C the vapor pressure of cyclopentane is 5.267 bar.

(Click for solution)

6.11 Fugacity and Fugacity Coefficient of Species in Mixture

The definition of the fugacity of a species in a mixture is similar to the definition of the pure species fugacity. For an ideal gas mixture the chemical potential is given by eqn. (6.63):

$$\mu_i^{ig} \equiv G_i^{ig} + RT \ln y_i \qquad ..(6.63)$$

Or: $d\mu_i^{ig} = dG_i^{ig} + RTd\ln y_i$ (at const. T) ..(6.120)

But $dG_i^{ig} = V_i dP = RTd\ln P$ (at const. T)

Thus: $d\mu_i^{ig} = RTd\ln P + RTd\ln y_i = RTd\ln(y_i P)$ ..(6.121)

Or: $d\mu_i^{ig} = RTd\ln p_i$ (where $p_i =$ partial pressure of i^{th} species) ..(6.122)

Using the same idea implicit in eqn. 6.86, we extend eqn. 6.122 to define a similar expression for fugacity of species in a *real* mixture:

$$d\mu_i = RTd\ln \hat{f}_i \qquad ..(6.123)$$

Here, $\hat{f}_i$ is the fugacity of species *i* in the mixture, which replaces the partial pressure p_i of eqn. 6.122. As we will demonstrate later, $\hat{f}_i$ is not a partial molar property, and is therefore denoted by a *circumflex* rather than by an *overbar*, as are partial properties. On integrating eqn. 6.123 between the any two multi-component phases α and ψ in equilibrium with each other:

$$\int_{\mu_i^{\psi}}^{\mu_i^{\alpha}} d\mu_i = RT\int_{\hat{f}_i^{\psi}}^{\hat{f}_i^{\alpha}} d\ln \hat{f}_i \qquad ..(6.124)$$

Hence, $\mu_i^{\alpha} - \mu_i^{\beta} = RT\ln\left(\hat{f}_i^{\alpha} / \hat{f}_i^{\beta}\right)$ ..(6.125)

But by eqn. 6.42, for equilibrium: $\mu_i^{\alpha} = \mu_i^{\psi}$

It follows, therefore, $\mu_i^{\alpha} - \mu_i^{\psi} = RT\ln\left(\hat{f}_i^{\alpha} / \hat{f}_i^{\psi}\right) = 0$

Or: $\hat{f}_i^{\alpha} / \hat{f}_i^{\psi} = 1$

That is: $\hat{f}_i^{\alpha} = \hat{f}_i^{\psi}$ ..(6.126)

Therefore, for an arbitrary number of phases in equilibrium with each other:

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\psi} = \ldots = \hat{f}_i^{\delta} \; (i = 1,2,..N) \qquad ..(6.127)$$

Thus, eqn. 6.126 offers a criterion of equilibrium corresponding to that provided by eqn. 6.42. The great advantage this equivalence offers is that, the fugacity coefficients of species in a mixture can be related to the volumetric properties of the mixtures, which facilitates the solution of phase and chemical reaction equilibria problems.

On comparing eqns. 6.122 and 6.123, the following limiting condition obtains:

$$\lim_{P \to 0} \hat{f}_i = y_i P \qquad ..(6.128)$$

It follows that a *fugacity coefficient* $\hat{\phi}_i$ (dimensionless) of a species in a real gas mixture may be defined as:

$$\hat{\phi}_i^V \equiv \frac{\hat{f}_i^V}{y_i P} \qquad ..(6.129)$$

Although the derivation above defines the fugacity coefficient with respect to gaseous mixture the definition may be extended to represent fugacity coefficient of a species in a real liquid solution as well. Accordingly, in that case it is defined in the following manner:

$$\hat{\phi}_i^L \equiv \frac{\hat{f}_i^L}{x_i P} \qquad ..(6.130)$$

6.12 Relation between residual property and species fugacity coefficients in mixtures

As we know, for any molar property (M), the definition of residual property M^R is given by:

$$M^R = M - M^{ig} \quad \Rightarrow \quad nM^R = nM - nM^{ig}$$

It follows that:

$$\left[\frac{\partial (nM^R)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = \left[\frac{\partial (nM)}{\partial n_i}\right]_{T,P,n_{j\neq i}} - \left[\frac{\partial (nM^{ig})}{\partial n_i}\right]_{T,P,n_{j\neq i}} \qquad ..(6.131)$$

Or: $\bar{M}_i^R = \bar{M}_i - \bar{M}_i^{ig}$ ..(6.132)

For the specific case of molar Gibbs free energy:

$$\bar{G}_i^R = \bar{G}_i - \bar{G}_i^{ig} = \mu_i - \mu_i^{ig} \qquad ..(6.133)$$

From eqns. 6.122 and 6.123 $d\mu_i^{ig} = RTd\ln p_i$; and $d\mu_i = RTd\ln \hat{f}_i$

On integrating between the real and ideal states:

$$\mu_i - \mu_i^{ig} = RT\ln\frac{\hat{f}_i}{p_i} = RT\ln\frac{\hat{f}_i}{y_i P} = RT\ln\hat{\phi}_i \qquad ..(6.134)$$

On comparing eqns. 6.131 and 6.122:

$$\bar{G}_i^R = RT\ln\hat{\phi}_i \qquad ..(6.135)$$

But by definition: $G^R = \sum_i y_i \bar{G}_i^R$ ..(6.136)

Thus, on inspecting 6.133 and 6.135:

$$\ln\hat{\phi}_i = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{T,P,n_{j\neq i}} \qquad ..(6.137)$$

It follows that:

$$\frac{G^R}{RT} = \sum_i y_i \ln\hat{\phi}_i \qquad ..(6.138)$$

Since $\ln\hat{\phi}_i$ is a partial molar property, the Gibbs-Duhem relation (eqn. 6.14) applies, that is:

$$\sum_i x_i d\ln\hat{\phi}_i = 0 \quad \text{(at const. T and P)} \qquad ..(6.139)$$

6.13 Expressions for gas phase $\hat{\phi}_i$ using EOS

In this section we derive the expressions for computing the fugacity coefficients for individual species in a real gas mixture. As in the case of pure real gases (section 6.8) we consider the truncated virial EOS and the various cubic EOSs. From eqn. (6.90):

$$\ln\phi = \int_0^P (Z-1)\frac{dP}{P}$$

Further by eqn. (6.137):

$$\ln\hat{\phi}_i = \left[\frac{\partial(nG^R/RT)}{\partial n_i}\right]_{T,P,n_{j\neq i}} \qquad .$$

From these two relations we obtain the following equations:

$$\frac{nG^R}{RT} = \int_0^P (nZ - n)\frac{dP}{P} \qquad ..(6.140)$$

$$\ln\hat{\phi}_i = \int_0^P \left[\frac{\partial(nZ-n)}{\partial n_i}\right]_{T,P,n_{j\neq i}} \frac{dP}{P} \qquad ..(6.141)$$

Now, $\frac{\partial(nZ)}{\partial n_i} = \bar{Z}_i$; and $\frac{\partial n}{\partial n_i} = 1$

Hence: $$\ln\hat{\phi}_i = \int_0^P \left(\bar{Z}_i - 1\right)\frac{dP}{P} \qquad ..(6.142)$$

Species Fugacity Coefficients (in a gas mixture) from the Virial EOS:

The expression for computing the mixture virial coefficient corresponds to eqn. 2.25. One may rewrite the expression for a binary mixture as follows:

$$B = y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12} \qquad ..(6.143)$$

Where, $$\delta_{12} = 2B_{12} - B_{11} - B_{22} \qquad ..(6.144)$$

Using (6.140 / 6.141): $nZ = n + \frac{nBP}{RT}$

Or: $$nZ - n = \frac{nBP}{RT} \qquad ..(6.145)$$

Therefore:

$$\bar{Z}_1 \equiv \left[\frac{\partial(nZ)}{\partial n_1}\right]_{T.P,n_2} = \left[\frac{\partial\left(n + \frac{nBP}{RT}\right)}{\partial n_1}\right]_{T.P,n_2} = 1 + \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} \qquad ..(6.146)$$

Using (6.148) in (6.142):

$$\ln\hat{\phi}_1 = \int_0^P \left(\bar{Z}_1 - 1\right)\frac{dP}{P} = \frac{1}{RT}\int_0^P \left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} dP = \frac{P}{RT}\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} \qquad ..(6.147)$$

Now putting (6.133) it may be shown that:

$$\left[\frac{\partial(nB)}{\partial n_1}\right]_{T,n_2} = B_{11} + y_2^2\delta_{12} \qquad ..(6.148)$$

Therefore putting (6.148) in (6.147), one obtains:

$$\ln \hat{\phi}_1 = \frac{P}{RT}(B_{11} + y_2^2 \delta_{12}) \quad ..(6.149)$$

In a similar manner, one may show that:

$$\ln \hat{\phi}_2 = \frac{P}{RT}(B_{22} + y_1^2 \delta_{12}) \quad ..(6.150)$$

Example 6.8

For the following system compute the species fugacity coefficients for an equimolar mixture at 20 bar and 500K.

	T_c (K)	P_c (bar)	V_c X 10^3 (m^3/mol)	Z_c	ω	y_i
Propane (1)	369.9	42.57	0.2	0.271	0.153	0.4
Pentane (2)	469.8	33.75	0.311	0.269	0.269	0.6

(Click for solution)

Fugacity coefficient expression for species in a mixture by pressure explicit EOS:

The eqn. 6.130 is useful for application to volume explicit EOSs only. For pressure explicit EOS (cubic EOSs) the expression for obtaining the species fugacity coefficient in a mixture is relatively complex. For the present purpose we provide below the generic equation used for pressure explicit EOS, while its proof is provided at the end of the present chapter.

$$RT \ln \hat{\phi}_i = -\int_{V=\infty}^{V} \left\{ \left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} - \right\} dV - RT \ln Z \quad ..(6.153)$$

We enlist below the resultant final expressions that obtain for species fugacity in a gaseous mixture corresponding to various forms of cubic EOSs.

For illustration we take the RK-EOS:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad ..(6.154)$$

Next one writes the parameters ‘a’ and ‘b’ for the mixture using typical mixing rules described by eqns. 2.29 to 2.31:

$$a = \sum_i \sum_j y_i y_j \sqrt{a_i a_j}\,(1 - k_{ij})$$

k_{ij} = binary interaction parameter

where, $k_{ii} = k_{jj} = 0;\ k_{ij(i \neq j)}$ is very often also put to zero, as it is difficult to obtain.

$$b = \sum_i y_i b_i$$

$$\omega = \sum_i y_i \omega_i$$

Thus the RK-EOS may be written as:

$$P = \frac{RT}{V - \sum_i (n_i / n) b_i} - \frac{\sum_i \sum_j (n_i n_j / n^2) \sqrt{a_i a_j}\,(1 - k_{ij})}{V(V + \sum_i (n_i / n) b_i)}$$

Using the last expression one can derive the expression for $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}$ and use it in (6.153) to obtain:

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z - 1) - \ln(Z - B) + \frac{a_m}{b_m RT}\left[(\frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}} \right] \ln(\frac{Z + B}{Z});\ B = \frac{b_m P}{RT} \qquad ..(6.155)$$

Similarly for *SRK EOS:*

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z - 1) - \ln(Z - B) + \frac{a_m}{b_m RT}\left[(\frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}} \right] \ln(\frac{Z + B}{Z});\ B = \frac{b_m P}{RT} \qquad ..(6.156)$$

For PR EOS:

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z - 1) - \ln(Z - B) + \frac{a_m}{2\sqrt{2} b_m RT}\left[\frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}} \right] \ln\left[\frac{Z + B(1 + \sqrt{2})}{Z + B(1 - \sqrt{2})} \right];B = \frac{b_m P}{RT} \qquad ..(6.157)$$

Example 6.9

Calculate the fugacities of ethylene and propylene in a mixture of 70 mole percent ethylene and 30 mole percent propylene at 600 K and 60 bar. Assume that the mixture follows the Redlich-Kwong equation of state.

	T_c (K)	**P_c (bar)**
Ethylene (1)	283.1	51.17
Propylene (2)	365.1	46.0

(Click for solution)

6.14 The Lewis/Randall Rule:

A simple equation for the fugacity of a species in an ideal solution follows from the following equations. In general, for any solution: $\mu_i = \Gamma_i(T) + RT \ln \hat{f}_i$ ..(6.158)

Applying to ideal solution, $\mu_i^{id} = \bar{G}_i^{id} = \Gamma_i(T) + RT \ln \hat{f}_i^{id}$ ..(6.159)

However we know (eqn. 6.77) that: $\mu_i^{id} = \bar{G}_i^{id} = G_i + RT \ln x_i$ ..(6.160)

Also, from eqn. 6.86: $G_i = \Gamma_i(T) + RT \ln f_i$

Thus, $\mu_i^{id} = \bar{G}_i^{id} = \Gamma_i(T) + RT \ln x_i f_i$ ..(6.161)

on comparing eqns. 6.158&6.160: $\hat{f}_i^{id} = x_i f_i$ ..(6.162)

The last relation is known as the *Lewis/Randall rule*, and applies to each species in an ideal solution at all conditions of temperature, pressure, and composition. It shows that the fugacity of each species in an ideal solution is proportional to its mole fraction; the proportionality constant being the fugacity of pure species *i* in the same physical state as the solution and at the same T and P.

6.15 Dependence of G^E on temperature and pressure

The idea of the molar excess property has been introduced in section 6.5 with the following definition:

$M^E = M - M^{id}$ ..(6.163)

Typically the property M can be an intensive property such as: V, U, H, S, G, A, etc. The relations between the molar excess properties of V, H and G is particular significant for description of non-ideal solution thermodynamics. One may start from the generic total derivative of the Gibbs free energy for a real solution and an ideal solution in the same way as eqns. 5.27 and 5.28:

$$d\left(\frac{G}{RT}\right)=\frac{V}{RT}dP-\frac{H}{RT^{2}}dT \qquad ..(6.164)$$

One may write the same equation specifically for an ideal solution, whence:

$$d\left(\frac{G^{id}}{RT}\right)=\frac{V^{id}}{RT}dP-\frac{H^{id}}{RT^{2}}dT \qquad ..(6.165)$$

Thus subtracting eqn. 6.165 from 6.164:

$$d\left(\frac{G^{E}}{RT}\right)=\frac{V^{E}}{RT}dP-\frac{H^{E}}{RT^{2}}dT \qquad ..(6.166)$$

Thus we may write the following further *generative* relations:

$$\frac{V^{E}}{RT}=\left[\frac{\partial(G^{E}/RT)}{\partial P}\right]_{T} \qquad ..(6.167)$$

$$\frac{H^{E}}{RT}=-T\left[\frac{\partial(G^{E}/RT)}{\partial T}\right]_{P} \qquad ..(6.168)$$

And further: $\frac{S^{E}}{RT}=\frac{H^{E}}{RT}-\frac{G^{E}}{RT}$ ..(6.169)

The sensitivity of the excess Gibbs free energy to changes in temperature and pressure may be estimated to show the effect of pressure and temperature on liquid phase properties. For example, for an equimolar mixture of benzene and cyclohexane at 298K and 1 bar are **(**source: J.M. Smith, H.C. Van Ness and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, 2001):

$$V^{E}=0.65cm^{3}/mol$$

$$H^{E}=800cm^{3}/mol$$

Thus it follows:

$$\left[\frac{\partial(G^{E}/RT)}{\partial P}\right]_{T,x}=\frac{V^{E}}{RT}=\frac{0.65}{83.14x298}=2.62x10^{-5}bar^{-1}$$

$$\left[\frac{\partial(G^{E}/RT)}{\partial T}\right]_{P,x}=-\frac{H^{E}}{RT^{2}}=-\frac{800}{83.14x298^{2}}=-1.08x10^{-3}K^{-1}$$

$$\Delta G^{E}(\text{for}\Delta\text{T}=1\ K)\approx\Delta G^{E}(\text{for }\Delta\text{P}=40\ bar)$$

The above calculations suggest that to effect the same change in excess Gibbs free energy brought about a change of 1K, one needs to change the pressure to change by about 40bar. Hence the excess Gibbs free energy exhibits a relatively weak dependence on pressure.

6.16 The Activity Coefficient

While we have defined fugacity coefficients of individual species in a liquid solution by 6.153, we may define yet another parameter called *activity coefficient* in order to describe the non-ideality of a liquid solution, especially at low to moderate system pressure.

We have by eqn. 6.155: $\bar{G}_i = \Gamma_i(T) + RT\ln \hat{f}_i$

And from eqn. 6.158: $\bar{G}_i^{id} = \Gamma_i(T) + RT\ln x_i f_i$

Using the above equations: $\bar{G}_i - \bar{G}_i^{id} = \bar{G}_i^E = RT\ln\dfrac{\hat{f}_i}{x_i f_i}$ ..(6.170)

The left side of this equation is the partial excess Gibbs energy $\bar{G}_i^E$; the dimensionless ratio $\hat{f}_i / x_i f_i$ appearing on the right is the *activity coefficient* of species *i* in solution, represented by the symbol γ_i. Thus, by definition:

$$\gamma_i \equiv \frac{\hat{f}_i}{x_i f_i}$$

$$\hat{f}_i = x_i \gamma_i f_i \quad ..(6.171)$$

Whence, $\bar{G}_i^E / RT = \ln \gamma_i$ ..(6.172)

But $G^E = \sum_i x_i \bar{G}_i^E$ ..(6.173)

On comparing the last two equations we conclude that γ_i is a partial molar property with respect to G^E. Thus, we have:

$$\ln \gamma_i = \left.\frac{\partial(nG^E / RT)}{\partial n_i}\right|_{T,P,n_{j\neq 1}} \quad ..(6.174)$$

It follows from the definition of activity coefficient (eqn. 6.163) that for an ideal solution its value is unity for all species as $G^E = 0$. For a non-ideal solution, however, it may be either greater or less than unity, the larger the departure from unity the greater the non-ideality of the solution. The derivatives of the activity coefficient with respect to pressure and temperature can be correlated to the partial molar excess volume and enthalpy respectively.

Using eqn. 6.167 and 6.168 in conjunction with 6.173/6.174 the following results are obtained:

$$\frac{\bar{V}_i^E}{RT} = \left[\frac{\partial \ln \gamma_i}{\partial P}\right]_{T,x} \quad ..(6.175)$$

$$\frac{\bar{H}_i^E}{RT^2} = \left[\frac{\partial \ln \gamma_i}{\partial T}\right]_{P,x} \quad ..(6.176)$$

As we have seen in the last section that the value of the function $\left[\frac{\partial (G^E / RT)}{\partial T}\right]_{P,x}$ is relatively larger compared to $\left[\frac{\partial (G^E / RT)}{\partial P}\right]_{T,x}$; thus comparing eqns. 6.167 and 6.168 with 6.175 and 6.176 respectively, one may conclude that the activity coefficients are far *more* sensitive to changes in temperature than to changes in pressure. For this reason for phase equilibria computations at low to moderate pressures, the activity coefficients are assumed invariant with respect to pressure.

Since the activity coefficients are partial molar properties, they are related by the Gibbs Duhem equation (at constant temperature and pressure) as follows:

$$\sum_i x_i d \ln \gamma_i = 0 \quad ..(6.177)$$

The above equation may be used to validate or check the consistency of experimental data on isothermal activity coefficients for a binary system. The following equation may be derived from eqn. 6.177 for this purpose (by assuming negligible effect of pressure on the liquid phase properties):

$$\int_{x_1=0}^{x_1=1} \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 = 0 \quad ..(6.178)$$

Thus, if the function ln (γ_1 / γ_2) is plotted over the entire range of x_1, (fig. 6.8) the two areas above and below the x-axis in the resulting curve must add up to zero, if the activity coefficients are consistent. Representative values and the

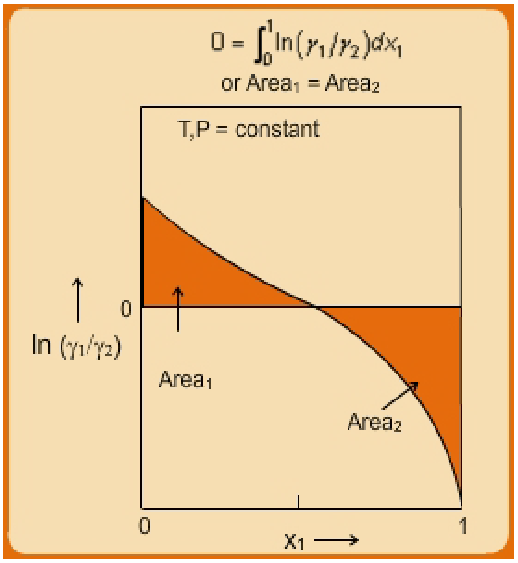


Figure 6.8 Thermodynamic consistency tests for activity coefficients in binary mixtures.

nature of variation in the magnitude of activity coefficients is shown in fig. 6.9; they correspond to the same systems for which excess property variations were depicted in fig. 6.5.

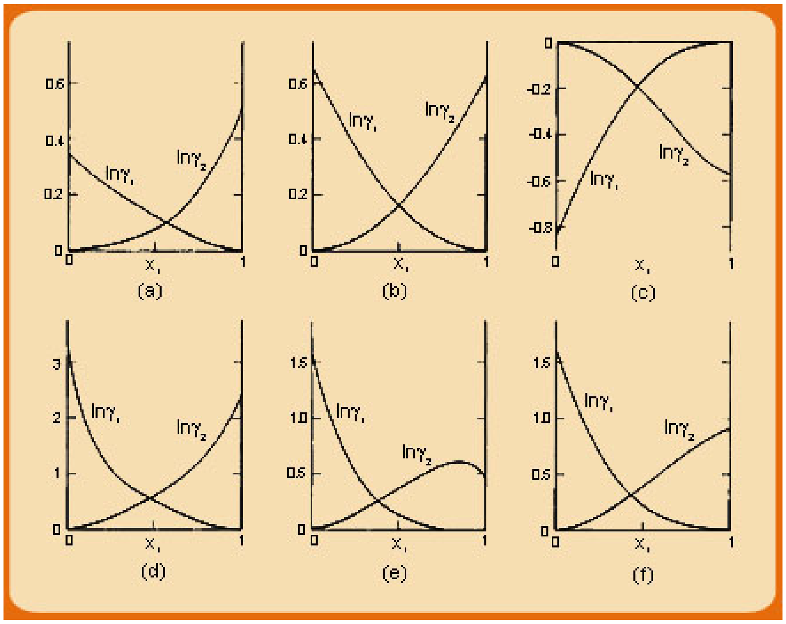


Fig. 6.9 Activity coefficients at 50°C for 6 binary liquid systems: (*a*) chloroform(1)/*n*-heptane(2); (*b*) acetone(1)/methanol(2); (*c*) acetone(1)/chloroform(2); (*d*) ethanol(1)/*n*-heptane(2); (*e*) ethanol(1)/chloroform(2); (*f*) ethanol(1)/water(2). (Source: H.C Van Ness and M. M. Abbott, *Perry's Chemical Engineer's Handbook* (7th ed.), McGraw Hill, 1997.

6.17 Use of VLE data for generation of activity coefficient models

In general during the process design of chemical plants, especially for distillation and liquid-liquid separation systems, it is necessary to predict the values of activity coefficients for carrying out phase equilibrium calculations. However, experimental data on activity coefficients of various types of liquid solutions are often not available at conditions (of temperature and/or composition) of interest. In such cases activity coefficient models - which relate G^E to solution composition (at a given T&P) - are useful. Most of such models are based on semi-empirical considerations. These models are all characterized by a set of parameters that are temperature dependent. Vapour-liquid equilibrium (VLE) data at low pressures are readily used for computing the value of such parameters. The more general form of the VLE relationship is discussed in the next chapter. The VLE equation is essentially a relation that relates the equilibrium vapour and liquid phase compositions at a given temperature and pressure. For the purpose of demonstrating the method of generating the activity coefficient models, we state here without proof, the simple VLE relation that applies to low pressure systems containing an ideal gas phase, but a non-ideal liquid phase. At low pressures it is of the following form:

$$y_i P = x_i \gamma_i P_i^{sat} \quad ..(6.179)$$

Where, i = 1, 2…N; y_i, x_i, P, & P_i^{sat} denote the vapour phase compos

$y_i \equiv$ equilibrium vapour phase mole fraction of ith species

$x_i \equiv$ equilibrium liquid phase mole fraction of ith species

$\gamma_i \equiv$ activity coefficeint of ith species in the liquid phase; i.e., at the given x_i

$P_i^{sat} =$ saturation vapour pressure of ith species at the equilibrium temperature

And $P =$ equilibrium pressure

It follows from eqn. 6.179 that: $\gamma_i = \dfrac{y_i P}{x_i P_i^{sat}}$ ..(6.180)

In a typical *isothermal* VLE data generation experiment, the equilibrium pressure and the corresponding vapour and liquid phase compositions are measured and the activity coefficients of each species estimated at each set of liquid phase composition using eqn. 6.180. For freezing ideas let us consider a binary system. Once the different sets of activity coefficient values for various liquid phase compositions, ideally ranging over $x_i = 0 \text{ to } 1$, the excess molar Gibbs free energy is computed at each composition using the following equation (obtained by combining eqns. 6.172, and 6.173):

$$G^E/RT=\sum_i x_i \ln\gamma_i \text{ (At const. T)} \qquad ..(6.181)$$

The values of $G^E/RT$are in turn used to obtain a set of values of a new function: (G^E/x_1x_2RT) are generated which is then fitted using a polynomial function of the following form:

$$G^E/x_1x_2RT = A + Bx_1 + Cx_1^2 + ... \qquad ..(6.182)$$

The final form of the polynomial is generally dependent on the nature of the constituent species of the liquid phase as well as the temperature. Representative plots for this form of data reduction for generating the (G^E/x_1x_2RT) function are shown in figures 6.10 and 6.11.

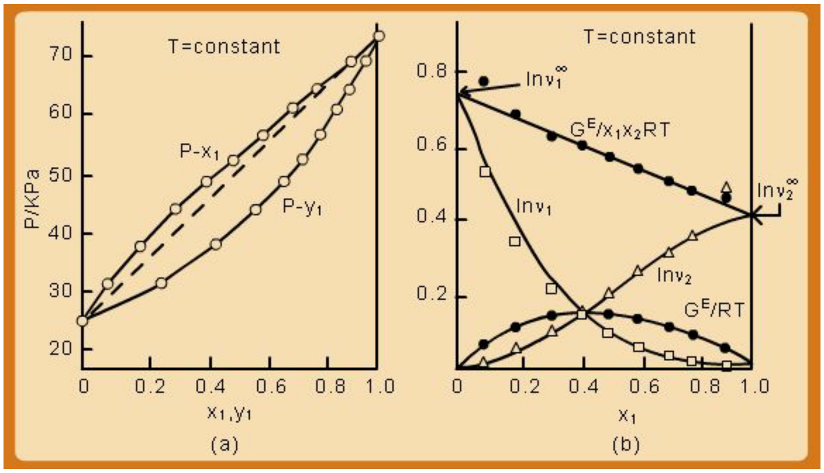


Fig. 6.10 Representative plot of experimental P-x-y, activity coefficient and molar excess Gibbs free energy data for systems exhibiting positive deviation from Raoult's Law

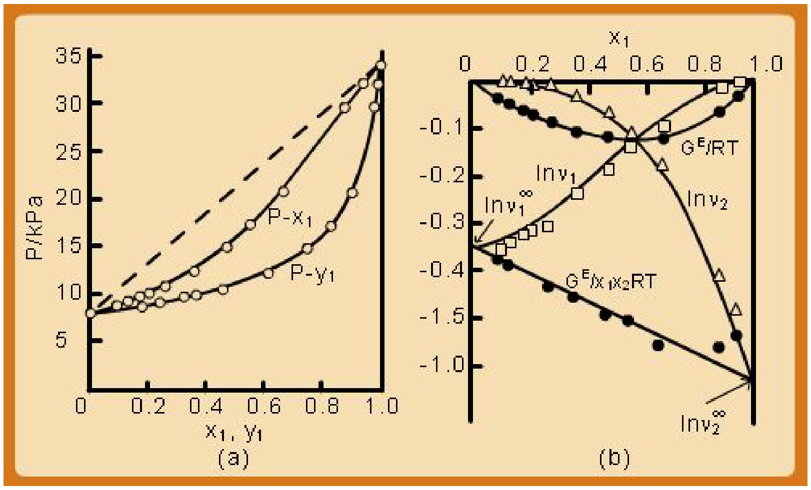


Fig. 6.11 Representative plot of experimental P-x-y, activity coefficient and molar excess Gibbs free energy data for systems exhibiting negative deviation from Raoult's Law

Once the values of the parameters A, B, C etc., have been calculated from an isothermal set of VLE data, the actual function for the activity coefficients may be derived by applying eqn. 6.174.

6.18 Activity Coefficient Models

In this section we present the forms of the various activity coefficient models commonly used for VLE calculations. Such models may be divided into two major groups depending upon their applicability to various types of solutions:

1. Margules/Van Laar/Regular Solution Models
2. Wilson/NRTL (Non-Random Two Liquid)/UNIQUAC (Universal Quasi Chemical) Model.

The models in Group 1 are termed as "Homogeneous Mixture" models, while those in Group 2 are termed "Local Composition" models. The reason for such distinction is as follows. The non-ideal behaviour of liquid solutions derives from two sources: (i) difference in *molecular size/shape* of constituent (ii) and the difference between the *inter-species and intra-species molecular interaction energies*. The Group 1 models generally apply to systems in which the inter-species and intra-species molecular interaction energies differ from each other, but in a relatively moderate measure. On the other hand type 2 models are principally useful for describing systems where the constituent molecular species differ on account of both size/shape as well molecular interaction energies. Thus while group I models useful for moderate deviation from ideal solution behaviour, those in group 2 represent strongly non-ideal solutions.

In case the chemical species in the solution do not differ significantly in terms of size/shape, they tend to distribute uniformly across the entire solution volume. Accordingly Group 1 models are based on the premise that molecules are “homogeneously” distributed over the solution volume in that there is no difference between the overall *macroscopic* composition and *microscopic* (local) composition around a single central molecule. The Group 2 models, however, account for both types of differences: in the size of the molecules of the chemical species as well as in their interaction energies. It is reasonable to expect that owing to such differences molecular packing at the microscopic level to be non-homogeneous. As a result, the local composition around a central molecule is likely to differ from the average macroscopic composition.

All models used for predicting species activity coefficient contain about 2 – 3 parameters. Models which employ a larger number of parameters improve the accuracy of prediction but at the same time are rendered computationally difficult. Additionally a larger number of experimentally determined values of activity coefficients are needed for fixing the values of the model parameters. In general, these parameters are much more sensitive to variations in temperature than pressure. This has already been highlighted while discussing the significance of eqns. 6.175 and 6.176. Thus, if computations of the activity coefficients occur over reasonably low range of pressures (typically about 10-20 bar) the model parameters may be assumed to remain invariant. The dependence of enthalpic quantities on temperature is usually strong. Thus, once again inspecting eqn. 6.176, we may conclude that, in general, the dependence of activity coefficients on temperature variations is relatively more significant. If the temperature variations over which activity coefficients are needed exceed ~ 10^0C, the effect of temperature on model parameters need to be considered. Table 6.1 presents the domain of applicability of the various commonly used activity coefficient models. For simplicity, we provide in the table 6.2 the model expressions for *binary solutions* and that of the corresponding activity coefficient formulas. In table 6.3 expressions of select models for higher order liquid mixtures are presented.

Table 6.1 Applicability of Activity Coefficient Models

System Type	**Models**
Species similar in size and shape	One-constant Margules
Moderately non-ideal mixtures	Two-constant Margules, Van Laar, Regular Solution
Strongly non-ideal mixtures (for example Alcohols+Hydrocarbons)	Wilson, NRTL, UNIQUAC
Solutions with miscibility gap	NRTL, UNIQUAC

Table 6.2: Select Models for the Excess Gibbs Energy and Activity Coefficients for Binary Systems

Model Name	**G^E/RT**	**Binary parameters**	$\ln\gamma_1$ and $\ln\gamma_2$
Two-suffix Margules	$G^E/RT = Ax_1x_2$ (One-constant)	A	$\ln\gamma_1 = Ax_2^2$
			$\ln\gamma_2 = Ax_1^2$
Three-suffix Margules	$G^E/RT = x_1x_2(A_{21}x_1$ (Two-constant)	A_{21}, A_{12}	$\ln\gamma_1 = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1]$
			$\ln\gamma_2 = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$
Van Laar	$G^E/RT = \frac{A_{12}A_{21}x_1x}{A_{12}x_1 + A_{21}}$	A_{21}, A_{12}	$\ln\gamma_1 = A_{12}/(1 + \frac{A_{12}}{A_{21}}\frac{x_1}{x_2})^2$; $\ln\gamma_2 = A_{21}/(1 + \frac{A_{21}}{A_{12}}\frac{x_2}{x_1})^2$
			Conversely: $A_{12} = \ln\gamma_1(1 + \frac{x_2\ln\gamma_2}{x_1\ln\gamma_1})^2; A_{21} = \ln\gamma_2(1$
Wilson	$\frac{G^E}{RT} = -x_1\ln(x_1 + x_2\Lambda_{12}$	$\Lambda_{12}, \Lambda_{21}$	$\ln\gamma_1 = \ln(x_1 + x_2\Lambda_{12}) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}}\right.$
			$\ln\gamma_2 = \ln(x_2 + x_1\Lambda_{21}) + x_1\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}}\right.$
NRTL	$G^E/RT = x_1x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_1}\right.$		$\ln\gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau}{(x_2 +}\right.$

	Where, $G_{12} = \exp(-\alpha_{12}\tau_{12}); G_{21} = \exp(-\alpha_{12}\tau_{21})$ $\tau_{12} = \frac{b_{12}}{RT} \; ; \; \tau_{21} = \frac{b_{21}}{RT}$	$\ln \gamma_2 = x_1^2 \Big[\tau_{12} \left(\frac{G_{12}}{x_2 + x_1 G_{12}} \right)^2 + \frac{\tau}{(x_1 +}$

Except for the NRTL model, all others are characterized by two parameters that are essentially *adjustable* with variations of temperature. For the Wilson equation in the above table the parameters are defined as follows:

$$\Lambda_{12} = \frac{V_2}{V_1}\exp\left(-\frac{a_{12}}{RT}\right); \Lambda_{21} = \frac{V_1}{V_2}\exp\left(-\frac{a_{21}}{RT}\right) \qquad ..(6.183)$$

Here V_1 and V_2 are the pure component molar volumes at the temperature of the system; and a_{12} and a_{21} are constants for a given pair of components. However, as the expressions in 6.183 indicate, the parameters Λ_{12} and Λ_{21} are temperature dependent. The parameters for NRTL are, α, τ_{12}, and τ_{21}, the latter two are temperature dependent.

Table 6.3 Expressions for the Molar Excess Gibbs Energy and Activity Coefficients of Multi-component Systems obeying Wilson & NRTL Models

Name	**Molar excess Gibbs energy**	**Activity coefficient for component *i***
Wilson	$\frac{G^E}{RT} = -\sum_i^N x_i \ln\left(\sum_j^N x_j\Lambda_{ij}\right)$	$\ln\gamma_i = 1 - \ln\left(\sum_j^N x_j\Lambda_{ij}\right) - \sum_k \frac{x_k\Lambda_{ki}}{\sum_j x_j\Lambda_{kj}}$
NRTL	$\frac{G^E}{RT} = \sum_i^N x \frac{\sum_j^N \tau_{ji}G_{ji}x_j}{\sum_k^N G_{ki}x_k}$	$\ln\gamma_i = \frac{\sum_j^N \tau_{ji}G_{ji}x_j}{\sum_k^N G_{ki}x_k} + \sum_k^N \frac{x_jG_{ij}}{\sum_k^N G_{kj}x_k}\left(\tau_{ij} - \frac{\sum_k^N x_k\tau_{kj}G_{kj}}{\sum_k^N G_{kj}x_k}\right)$

A common feature of all the models are that the parameters are basically related to the infinite dilute activity coefficients for each binary. Table 6.4 provides the relevant relations for each model.

Table 6.4 Relation between the model parameters and infinite dilute activity coefficients

Model	**Relation between the model parameters and infinite dilute activity coefficients**
Two-suffix Margules	$\ln\gamma_1^\infty = \ln\gamma_2^\infty = A$
Three-suffix Margules	$\ln\gamma_1^\infty = A_{12}$; $\ln\gamma_2^\infty = A_{21}$
Van Laar	$\ln\gamma_1^\infty = A_{12}$; $\ln\gamma_2^\infty = A_{21}$
Wilson	$\ln\gamma_1^\infty = 1 - \Lambda_{21} - \ln\Lambda_{12}$; $\ln\gamma_2^\infty = 1 - \Lambda_{12} - \ln\Lambda_{21}$
NRTL	$\ln\gamma_1^\infty = \tau_{21} + \tau_{12}\exp(-\alpha\tau_{12})$; $\ln\gamma_2^\infty = \tau_{12} + \tau_{21}\exp(-\alpha\tau_{21})$

Example 6.10

Methanol (1)-acetone (2) system is described by the Van Laar activity coefficient model. At 60^0C, the model parameters are $A_{12} = 0.47; A_{21} = 0.78$. Estimate the activity coefficients for a solution containing 10mole% of methanol.

(Click for solution)

Regular Solution (RS) Model

This activity coefficient model is derived for solutions that show moderate deviations from ideal solution behaviour, and for which V^E and S^E are both zero. The model was proposed by Scatchard and Hildebrand (J. H. Hildebrand & R. L Scott. *The Solubility of Non-electrolytes*, Dover, 1964) and constitutes one of few models that are derived from theory. Known as the *Regular Solution Model*, the molar excess Gibbs free energy function is given by:

$$G^E / RT = (x_1V_1 + x_2V_2)\Phi_1\Phi_2(\delta_1 - \delta_2)^2 \qquad ..(6.184)$$

It follows that:

$$\ln\gamma_1 = V_1\Phi_2^2(\delta_1 - \delta_2)^2 \qquad ..(6.185)$$

$$\ln\gamma_2 = V_2\Phi_1^2(\delta_1 - \delta_2)^2 \qquad ..(6.186)$$

where, Φ_i = volume fraction = $\dfrac{x_iV_i}{V_m}$; V_i = molar volume of pure i$^{\text{th}}$ species, and $V_m = \sum_i x_iV_i$

Further: δ_i = solubility parameter for i^{th} species, which is given by:

$$\delta_i = \sqrt{\frac{(\Delta U_i^{vap})}{V_i}} \cong \sqrt{\frac{(\Delta H_i^{vap} - RT)}{V_i}} \qquad ..(6.187)$$

Where, ΔU_i^{vap}, ΔH_i^{vap} are molar internal energy, and enthalpy of vapourization of i^{th} species at the temperature of interest.

The above relations may be extended to multi-component mixtures for which:

$$\mathrm{R}T\ln\gamma_i = V_i(\delta_1 - \bar{\delta})^2 \qquad ..(6.188)$$

$$\bar{\delta} = \sum_j \Phi_j\delta_j \qquad ..(6.189)$$

$$\Phi_j = \frac{x_j V_j}{\sum_j x_j V_j}$$; (where, j → runs over all the species) ..(6.190)

The solubility parameters for a set of select substances are provided in Appendix IV.

Example 6.11

Use of Regular Solution Model to estimate activity coefficients for an equimolar benzene (1) / cyclohexane (2) solution 350°K. The solubility parameters are: δ_1 = 9.2 $(cal/cm^3)^{1/2}$; δ_2 = 8.2 $(cal/cm^3)^{1/2}$. The molar volumes: V_1^L = 88 cm^3/mol; V_2^L = 107 cm^3/mol

(Click for solution)

UNIQUAC: Group Contribution Method for Evaluation of Activity Coefficients

The acronym UNIQUAC stands for *Universal Quasi Chemical Equation*. The principle that the UNIQUAC method is founded on is that of *group contribution*. The methodology is based on the postulate that any thermo-physical property of a pure substance is a *weighted sum* of the chemical groups that constitute it. Since the number of functional groups (such as $-CH_3, -CH_2, -OH, -COOH,$ etc.) are few (about 50 or so) in comparison to the vast number of chemical species they can form, the approach based on group contribution constitutes an universal, and indeed a versatile method of prediction of a wide variety of properties of a very large number of substances. Properties as diverse as normal boiling point, enthalpy of vapourization, molar volume, thermal conductivity, viscosity, surface tension, etc may be estimated when no direct experimental data are available.

While estimating any property, a molecule is decomposed into the functional groups that make it up. Intermolecular interactions (in a pure fluid or a mixture) are then considered to be approximately equal to the weighted sum of group-group interactions. Characteristic quantitative values representing group interactions have been obtained from regression of experimental data for binary systems. The use of this approach for predicting a wide variety of number of physic-chemical properties has been demonstrated comprehensively by Reid et. al. (J C. Reid, J. M. Prausnitz, and B. E. Polling, *The Properties of Gases and Liquids*, 4th ed. McGraw Hill, 1987). A group contribution method is, however, necessarily approximate as it is based on the simple additivity of contributions from each group; further it assumes the contribution made by each group is independent of the nature of the adjacent group.

In extending the method to prediction of activity coefficients, the molar excess Gibbs free energy is divided into two parts: *combinatorial* and *residual*. The combinatorial part accounts for non-ideality of a mixture arising from *differences in size and shape* of constituent molecular species; whereas the residual part considers the *difference between inter-molecular and intra-molecular interaction energies.*

We provide there the final UNIQUAC activity coefficient relations for a binary. It is may be easily extended to represent ternary and higher order mixtures (J.M. Prausnitz, R.N. Lichtenthaler and E.G. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, 1998). The function $g \equiv G^E / RT$ is comprised of the combinatorial and residual parts as follows:

$$g = g^C + g^R \qquad ..(6.191)$$

The combinatorial part represents pure species parameters, while the residual part contains two binary parameters for each pair of molecules. In general for a system comprised of N molecular species, we have the following relations:

$$g^C = \sum_i^N x_i \ln \frac{\Phi_i}{x_i} + 5 \sum_i^N q_i x_i \ln \frac{\theta_i}{\Phi_i} \qquad ..(6.192)$$

$$g^R = -\sum_i^N q_i x_i \ln \left(\sum_j \theta_i \tau_{ji} \right) \qquad ..(6.193)$$

Where:

$$\Phi_i = \frac{x_i r_i}{\sum_j^N x_j r_j} \qquad ..(6.194)$$

$$\theta_i = \frac{x_i q_i}{\sum_j^N x_j q_j} \qquad ..(6.195)$$

r_i = relative molecular volume; q_i = relative molecular surface area (both are pure species parameters)

The binary interaction parameters τ_{ji} and τ_{ij} which need to be regressed from binary VLE data are temperature dependent. They are the UNIQUAC *model parameters* and are provided by:

$$\tau_{ji} = \exp\left[-\left(\frac{u_{ji} - u_{ii}}{RT}\right)\right]; \text{ and, } \tau_{ij} = \exp\left[-\left(\frac{u_{ij} - u_{jj}}{RT}\right)\right] \quad ..(6.196)$$

The activity coefficient is also divided into two parts:

$$\ln\gamma_i = \ln\gamma_i^C(combinatorial) + \ln\gamma_i^R(residual) \quad ..(6.197)$$

$$\ln\gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln\frac{J_i}{L_i}\right) \quad ..(6.198)$$

$$\ln\gamma_i^R = q_i\left(1 - \ln s_i - \sum_j^N \theta_j \frac{\tau_{ij}}{s_j}\right); \to (j \equiv \text{dummy variable}) \quad ..(6.199)$$

$$J_i = \frac{r_i}{\sum_j^N r_j x_j} \quad ..(6.200)$$

$$L_i = \frac{q_i}{\sum_j^N q_j x_j} \quad ..(6.201)$$

$$s_i = \sum_l^N \theta_l \tau_{li}; (l \to dummy\ index)$$

The computation of the parameters J_i, L_i and s_i is based on the UNIFAC (*Universal Functional Group Activity Coefficients*) method (see eqns. 6.202 and 6.203 below), which is an extension of the UNIQUAC model. The application of the UNIFAC method is premised on the idea that a solution is composed of the sub-groups rather than molecules themselves. The groups are essentially small, self-contained chemical units, each designated as *k*, for which the relative volume and surface areas are denoted as R_k and Q_k respectively. When a molecule may be constructed from more than a single set of subgroups, the one with the least number of different subgroups is assumed as the correct one. The values of R_k and Q_k for various common subgroups are shown in table 1 of *Appendix V*. More exhaustive tables may be found elsewhere (J.M. Prausnitz, R.N. Lichtenthaler and E.G. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed., Prentice Hall, 1998).

Apart from the dependence on pure species properties species R_k and Q_k, the activity coefficients are functions of interaction between the various subgroups. As shown in table 1 of Appendix V, a cluster of sub-groups are classified under a main group, which are primarily descriptive. All subgroups under a main group are identical with respect to group interactions. Accordingly the interaction between group parameters is identified with pairs of main groups under which the former are classified. Parametric values of select pairs of main groups are provided in table 2 of *Appendix V.*

One of the distinct advantages of the UNIFAC model is that it is able to predict activity coefficients more effectively in mixtures where constituent molecules have large size differences, as in polymer solutions.

In the UNIFAC method the expression for the combinatorial part of the activity coefficient is the same as that in eqn. 6.196. However, the residual part takes a somewhat different form.

$$\ln \gamma_i^C = 1 - J_i + \ln J_i - 5q_i\left(1 - \frac{J_i}{L_i} + \ln \frac{J_i}{L_i}\right) \quad ..(6.200)$$

$$\ln \gamma_i^R = q_i\left[1 - \sum_k \left(\theta_k \frac{\beta_{ik}}{s_k} - e_{ki} \ln \frac{\beta_{ik}}{s_k}\right)\right] \rightarrow (k \equiv subgroup) \quad ..(6.201)$$

The terms J_i *and* L_i are given by eqns. 6.198 and 6.199. However, the other parameters are defined as:

$$r_i = \sum_k \nu_k^{(i)} R_k \quad ..(6.202)$$

$$q_i = \sum_k \nu_k^{(i)} Q_k \quad ..(6.203)$$

$$e_{ki} = \frac{\nu_k^{(i)} Q_k}{q_i} \quad ..(6.204)$$

$$\beta_{ik} = \sum_m e_{mi} \tau_{mk} \quad ..(6.205)$$

$\nu_k^{(i)} \equiv$ number of k^{th} subgroup in i^{th} molecular species

$$\theta_k = \frac{\sum_i x_i q_i e_{ki}}{\sum_j x_j q_j} \quad ..(6.206)$$

$$s_k = \sum_m \theta_m \tau_{mk} \quad ..(6.207)$$

$$\tau_{mk} = \exp\left(-\frac{a_{mk}}{T}\right) \quad ..(6.208)$$

Thus, in summary the key UNIFAC parameters are R_K, Q_K and a_{mk}. Tables containing the values of these parameters are recorded more exhaustively elsewhere (H. K. Hansen, P. Rasmusen, Aa.

Fredenslund, M.Schiller, and J. Gmehling, *IEC Research*, Vol 30, pp 2352 – 2355, 1991; and R.C Reid, J, M., Prausnitz, and B.E. Poling, in Properties of Gases and Liquids, 4th ed., McGraw-Hill, 1987). All the parameters in the UNIFAC approach are essentially binary and there are effectively two parameters that need to be determined from experimental VLE data.

Example 6.12

Use UNIFAC model to estimate activity coefficients for an equimolar n-pentane (1) /acetone (2) solution 320^{o}K.

(Click for solution)

Appendix 6.1

Some relations among partial properties

Every equation that provides a *linear* relation among thermodynamic properties of a *constant-composition* (single-phase) solution can be used to derive a corresponding equation relating the partial molar properties. As an example, this is demonstrated below for the property enthalpy.

One may write for a constant composition solution: $H = U + PV$

It follows that for the entire system: $nH = nU + P(nV)$

Applying the definition of partial molar properties:

$$\left[\frac{\partial(nH)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = \left[\frac{\partial(nU)}{\partial n_i}\right]_{T,P,n_{j\neq i}} + P\left[\frac{\partial(nV)}{\partial n_i}\right]_{T,P,n_{j\neq i}} \quad ..(A.6.1.1)$$

Hence: $\overline{H}_i = \overline{U}_i + P\overline{V}_i$

Similar relations may be derived for other thermodynamic properties. Other forms of relationships are also derivable as is illustrated below, as an example, using Gibbs free energy relations.

For an open multi-component system: $d(nG) = (nV)dP - (nS)dT + \sum_i \overline{G}_i dn_i$ ..(A.6.1.2)

By Maxwell Relations: $\left(\frac{\partial V}{\partial T}\right)_{P,n} = -\left(\frac{\partial S}{\partial P}\right)_{T,n}$

Also for both P and n = constant, we have: $d(nG) = -(nS)dT$

Or $\left[\frac{\partial(nG)}{\partial T}\right]_{P,n} = -(nS)$ ..(A.6.1.3)

Thus: $\left[\frac{\partial}{\partial n_i}\left\{\frac{\partial(nG)}{\partial T}\right\}_{P,n}\right]_{T,P,n_{j\neq i}} = -\left[\frac{\partial(nS)}{\partial n_i}\right]_{T,P,n_{j\neq i}}$

Or: $\left[\frac{\partial}{\partial T}\left\{\frac{\partial(nG)}{\partial n_i}\right\}_{T,P,n_{j\neq i}}\right]_{P,n} = -\left[\frac{\partial(nS)}{\partial n_i}\right]_{T,P,n_{j\neq i}}$

Hence $\left[\frac{\partial \overline{G}_i}{\partial T}\right]_{P,n} = -\left[\frac{\partial(nS)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = -\overline{S}_i$ ..(A.6.1.4)

In the same manner, it may be shown that: $\left[\frac{\partial \overline{G}_i}{\partial P}\right]_{T,n} = -\left[\frac{\partial(nV)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = \overline{V}_i$ ..(A.6.1.5)

So if one writes at const n, $\overline{G}_i = \overline{G}_i(T,P)$, it follows:

$$d\overline{G}_i = \left(\frac{\partial \overline{G}_i}{\partial P}\right)_{T,x_i} dP + \left(\frac{\partial \overline{G}_i}{\partial T}\right)_{P,x_i} dT \qquad ..(A.6.1.6)$$

Using (A.6.1.4) and (A.6.1.5) in (A.6.1.6) one obtains:

$$d\overline{G}_i = \overline{V}_i dP - \overline{S}_i dT \qquad ..(A.6.1.7)$$

Equation A.6.1.7 is exploited in the derivation of relations for fugacity of individual species in real mixtures. As with the Gibbs free energy function; those given by eqns. 5.3 – 5.5 can be used as starting points for the corresponding relations of the form given by eqn. A.6.1.7.

Appendix 6.2

Derivation of the expression for species fugacity coefficient for pressure explicit EOS

$dG = VdP - SdT$

It may be shown that: $d\overline{G}_i = \overline{V}_i dP - \overline{S}_i dT$

At constant T: $d\overline{G}_i = \overline{V}_i dP$ ..(A.6.2.1)

Using (A.6.2.1) and (A.6.2.2): $\overline{V}_i dP = RTd\ln \hat{f}_i$ ..(A.6.2.3)

But by defintion: $d\overline{G}_i = RTd\ln \hat{f}_i$ ..(A.6.2.2)

We may also write for the pure compoent: $dG_i^{ig} = V_i^{ig} dP$ ..(A.6.2.4)

$$dG_i^{ig} = RT\ln \hat{f}_i^{ig} \qquad ..(A.6.2.5)$$

Using $(A.6.2.2)$ and $(A.6.2.5)$ and integrating: $\bar{G}_i - G_i^{ig} = RT\ln\left(\dfrac{\hat{f}_i}{\hat{f}_i^{ig}}\right)$

Or: $$\bar{G}_i - G_i^{ig} = RT\ln\left(\frac{\hat{f}_i}{y_i P}\right) \qquad ..(A.6.2.6)$$

Equivalently, using $(A.6.2.3)$ and $(A.6.2.4)$: $\bar{G}_i - G_i^{ig} = \dfrac{1}{RT}\int_0^P (\bar{V}_i - V_i^{ig})dP$

Or: $$\bar{G}_i - G_i^{ig} = \frac{1}{RT}\int_0^P \left(\bar{V}_i - \frac{RT}{P}\right)dP \qquad ..(A.6.2.7)$$

Next we develop the expression for fugacity coefficient using the foregoing relations.

Using $(A.6.2.2)$ and $(A.6.2.3)$:

$$RT\left(\frac{\partial \ln \hat{f}_i}{\partial P}\right)_{T,n_i} = \bar{V}_i = \left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} \qquad ..(A.6.2.8)$$

In the last eqn. $(\;)_{\text{n}_i}$ implies that all $\text{n}_i = \text{constant}$

Now: $$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n_i} = \left(\frac{\partial \mu_i}{\partial V}\right)_{T,n_i}\left(\frac{\partial V}{\partial P}\right)_{T,n_i} \qquad ..(A.6.2.9)$$

Putting $(A.6.2.9)$ in $(A.6.2.8)$ and rearranging:

$$RT\left(\frac{\partial \ln \hat{f}_i}{\partial P}\right)_{T,n_i}\left[\frac{1}{\left(\frac{\partial V}{\partial P}\right)_{T,n_i}}\right] = \left(\frac{\partial \mu_i}{\partial V}\right)_{T,n_i}$$

$$RT\left(\frac{\partial \ln \hat{f}_i}{\partial P}\right)_{T,n_i}\left(\frac{\partial P}{\partial V}\right)_{T,n_i} = \left(\frac{\partial \mu_i}{\partial V}\right)_{T,n_i}$$

$$RT\left(\frac{\partial \ln \hat{f}_i}{\partial V}\right)_{T,n_i} = \left(\frac{\partial \mu_i}{\partial V}\right)_{T,n_i} \qquad ..(A.6.2.10)$$

For a multi-component mixture we may write the following expression for the total Helmholtz free energy:

$A^t = A^t(T, V, n_1, n_2, \ldots n_N)$

One may write: $\left(\dfrac{\partial^2 A^t}{\partial V \partial n_i}\right) = \left(\dfrac{\partial^2 A^t}{\partial n_i \partial V}\right)$

Or: $\left[\dfrac{\partial}{\partial V}\left(\dfrac{\partial A^t}{\partial n_i}\right)_{T,V,n_j}\right]_{T,n_i} = \left[\dfrac{\partial}{\partial n_i}\left(\dfrac{\partial A^t}{\partial V}\right)_{T,n_i}\right]_{T,V,n_j}$ ..(A.6.2.11)

One can also prove that the chemical potential may be expressed in any of the following forms:

$$\mu_i = \left(\frac{\partial U^t}{\partial n_i}\right)_{S,V,n_{j\neq i}} = \left(\frac{\partial H^t}{\partial n_i}\right)_{S,P,n_{j\neq i}} = \left(\frac{\partial A^t}{\partial n_i}\right)_{T,V,n_{j\neq i}} = \left(\frac{\partial G^t}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Also, since $A^t = A^t(T, V^t, n_1, \ldots, n_N);\ t = total$

$$dA^t = \left(\frac{\partial A^t}{\partial V^t}\right)_{T,n_i} dV + \left(\frac{\partial A^t}{\partial T}\right)_{V^t,n_i} dT + \sum_i \left(\frac{\partial A^t}{\partial n_i}\right)_{T,V^t,n_j} dn_i$$

By comparison to the coresponding closed system expression:

$$dA^t = -PdV^t - S^t dT + \sum_i \left(\frac{\partial A^t}{\partial n_i}\right)_{T,V,n_j} dn_i$$

Thus: $\left(\dfrac{\partial A^t}{\partial V^t}\right)_{T,n_i} = \left(\dfrac{\partial A}{\partial V}\right)_{T,n_i} = -P$

Therefore, eqn. (A.6.2.11) may be written as:

$$\left(\frac{\partial \mu_i}{\partial V}\right)_{T,n_i} = -\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} \qquad \text{(A.6.2.12)}$$

Using $(A.6.2.10)$ and $(A.6.2.12)$:

$$RT\left(\frac{\partial \ln \hat{f}_i}{\partial V}\right)_{T,n_i} = -\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} \qquad \text{(A.6.2.13)}$$

In general: $RT\left(\dfrac{\partial \ln PV}{\partial V}\right)_{T,n_i} = RT\left(\dfrac{\partial \ln PV}{\partial V}\right)_{T,n_i} + RT\left(\dfrac{\partial \ln PV}{\partial V}\right)_{T,n_i}$

$$= RT\left(\frac{\partial \ln P}{\partial V}\right)_{T,n_i} + RT\left(\frac{\partial \ln V}{\partial V}\right)_{T,n_i} = RT\left(\frac{\partial \ln P}{\partial V}\right)_{T,n_i} + \frac{RT}{V}$$

Thus: $-RT\left(\dfrac{\partial \ln P}{\partial V}\right)_{T,n_i} = \dfrac{RT}{V} - RT\left(\dfrac{\partial \ln PV}{\partial V}\right)_{T,n_i}$ ..(A.6.2.14)

Adding (13) and (14) one gets:

$$\int_{V=\infty}^{V}\left\{RT\left(\frac{\partial \ln(\hat{f}_i/P)}{\partial V}\right)_{T,n_i}\right\}dV=\int_{V=\infty}^{V}\left\{\frac{RT}{V}-\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}-RT\left(\frac{\partial \ln PV}{\partial V}\right)_{T,n_i}\right\}dV$$

$$RT\ln\left(\frac{\hat{f}_i}{P}\right)-\left[RT\ln\left(\frac{\hat{f}_i}{P}\right)\right]_{V=\infty}=\int_{V=\infty}^{V}\left\{\frac{RT}{V}-\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}\right\}dV-RT\ln PV+RT\ln RT$$

..(A.6.2.15)

But : $\left[RT\ln\left(\frac{\hat{f}_i}{P}\right)\right]_{V=\infty}=\left[RT\ln\left(\frac{y_iP}{P}\right)\right]_{V=\infty}$; since at $V=\infty$, i.e. ideal gas situation, $\hat{f}_i=y_iP$

Thus eqn. $(A.6.2.15)$ becomes:

$$RT\ln\left(\frac{\hat{f}_i}{y_iP}\right)=\int_{V=\infty}^{V}\left\{\frac{RT}{V}-\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}\right\}dV-RT\ln(PV/RT)$$

$$RT\ln\hat{\phi}_i=-\int_{V=\infty}^{V}\left\{\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}-\frac{RT}{V}-\right\}dV-RT\ln Z \qquad ..(A.6.2.16)$$

Equation (A.6.2.16) is useful for deriving the analytical expression for the fugacity coefficient of species in a mixture using typical pressure explicit cubic EOSs. However, for doing that the expression for $\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j}$ has to be obtained. This has been presented earlier in section 6.14.

Assignment- Chapter 6

Chapter 7 Vapour-Liquid Equilibria

7.1 Introduction

Both the general criterion of thermodynamic equilibrium as well as the specific condition of equality of chemical potential of each species which hold at equilibrium was introduced in the last chapter. We now develop the detailed relationships connecting the phase variables (T, P and composition) that originate from the concepts of chemical potential and the fugacity coefficient. The basic principle employed in all separation processes is that under equilibrium the compositions of phases differ from each other, and therefore it is possible to preferentially concentrate one species over another (or others) in one particular phase. This feature of phase equilibria is exploited in a wide variety of process equipments such as distillation, extraction, crystallization, etc.

This chapter focuses on the vapour-liquid equilibria (VLE) problem which is depicted schematically in fig. 7.1. When a multi-component, vapour and liquid phase – each (say) containing N chemical species – co-exist in thermodynamic equilibrium at a temperature T and pressure P, the phase compositions $\left\{y_{1,}\ y_{2,}...y_{N-1}\right\}$ and $\left\{x_{1,}\ x_{2,}...x_{N-1}\right\}$ remain invariant with time, and are related by a unique set of relations. If the relations are known as a function of temperature, pressure and compositions $\left\{y_i\ and\ x_i\right\}$ for each species, then provided some of these variables are specified the rest may be calculated. We will derive such relations for real multi-component systems; but as in all cases of thermodynamic modeling we take the ideal system as our starting point. Next the VLE of systems at moderate pressures are treated. Finally the relations for VLE at high pressures are presented. In the following section we derive the relations that hold for pure component VLE before describing those which apply to multi-component systems.

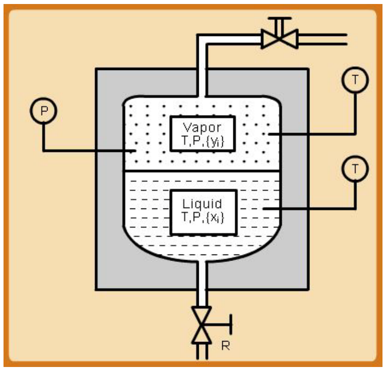


Fig. 7.1 The VLE Problem Description

7.2 Single Component System Phase Equilibria

We start with the general criterion of equality of the chemical potential in the two phases. To generalize the results we assume that any two types of phases α and β of a pure component are at equilibrium. Thus as given by eqn. 6.50:

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad ..(6.50)$$

However, for a pure component the chemical potential is reduces to the pure component molar Gibbs free energy. Therefore:

$\mu_i^{\alpha} = G^{\alpha}$ and, $\mu_i^{\beta} = G^{\beta}$ ..(7.1)

Thus eqn. 6.50 reduces to:

$$G^{\alpha} = G^{\beta} \qquad ..(7.2)$$

On taking a differential:

$$dG^{\alpha} = dG^{\beta} \qquad ..(7.3)$$

Using the generic relationship in eqn. 5.7 we may write in keeping with the fact that for a given equilibrium temperature, the equilibrium pressure corresponds to the saturation vapour pressure P^{sat}:

$$V^{\alpha} dP^{sat} - S^{\alpha} dT = V^{\beta} dP^{sat} - S^{\beta} dT \qquad ..(7.4)$$

On rearranging:

$$\frac{dP^{sat}}{dT} = \frac{S^{\beta} - S^{\alpha}}{V^{\beta} - V^{\alpha}} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}} \qquad ..(7.5)$$

Additionally using the second law we have:

$$dS = dQ/T \qquad ..(7.6)$$

And that for a constant pressure process:

$$dQ = dH \qquad ..(7.7)$$

Using eqns. (7.6) and (7.7) we obtain:

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta} \qquad ..(7.8)$$

Thus, $\Delta S^{\alpha\beta} = \Delta H^{\alpha\beta} / T$, and substitution in eqn.7.5 gives:

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}} \qquad ..(7.9)$$

The last equation is called the *Clapeyron* equation. For the specific case of phase transition from liquid (*l*) to vapor (*v*), it translates into:

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{LV}}{T\Delta V^{LV}} \qquad ..(7.10)$$

Noting that liquid phase molar volumes are relatively much lesser than vapour phase volumes, we may write, $\Delta V^{LV} = V^V - V^V \cong V^v$ ..(7.11)

Further at low to moderate saturation pressures if we assume ideal vapour phase behaviour, then

$$V^v \cong \frac{RT}{P^{sat}} \qquad ..(7.12)$$

Eqn. 7.10 then becomes:

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{LV}}{RT / P^{sat}}$$

Or:

$$\frac{dP^{sat} / P^{sat}}{dT / T^2} = \frac{\Delta H^{LV}}{R} \qquad ..(7.13)$$

Whence, $\Delta H^{LV} = -R[\frac{d \ln P^{sat}}{d(1/T)}]$ ..(7.14)

This approximate equation is known as the *Clausius-Clapeyron equation*. The assumptions used in the above derivations have approximate validity only at low pressures. Integrating eqn. 7.14 we have:

$$\ln P^{sat} = A - \frac{B}{T} \qquad ..(7.15)$$

On comparing eqns. 7.14 and 7.15, it follows that: $B = \Delta H^{LV} / R$, while A is the constant of integration. These are generally regarded as constants for a given species. A plot of experimental values of lnP^{sat} vs. $1/T$ generally yields a line that is nearly straight between the triple and critical points. However, the validity of eqn. 7.15is questionable at relatively high pressures, and certainly in the critical region. Thus the accuracy of the Clausius-Clapeyron equation reduces at higher pressures. A modified form of eqn. 7.15, called the Antoine Equation, has proved to be more accurate (including at higher pressures), has the following form:

$$\ln P^{sat} = A - \frac{B}{T + C} \qquad ..(7.16)$$

A, B, and C are readily available for a large number of species. Appendix VI provides values of Antoine constants for select substances. More complex forms of equations relation temperature and vapour pressure of pure substances have been reported in the literature, which provide even greater accuracy. An example of such an equation is the Wagner equation, which is given by:

$$\ln P_r^{sat} = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{1-\tau}, \text{ where } \tau = 1 - T_r \qquad ..(7.17)$$

The constants for the Wagner equation for specific substances are available in several reference texts (see R.C. Reid, J.M. Prausnitz and B.E. Poling, *Properties of Gases and Liquids*, 4th ed., McGraw-Hill, 1987).

7.3 Derivation of the Phase Rule

The phase rule was introduced in section 1.5 without proof. Here we develop its mathematical form based on the tenets of solution thermodynamics and phase equilibrium criterion presented in the last chapter. Consider a *non-reactive* system under equilibrium, with π phases each containing N independent chemical species. The degrees of freedom for the system, i.e., the number of intensive variables that may vary independently of each other would be given by:

Degrees of freedom = Total number of systemic intensive variables –number of independent equations relating all the variables.

For the system of interest here the above terms are as follows:

I. Total number of systemic intensive variables (also called the phase rule variables)= *T, P and (N-1)* species mole fractions for each of the π phases
II. Number of independent relations connecting the phase rule variables = $(\pi - 1)N$

The second relation above follows from the fact that for each of the *N* species one may use the chemical potential equality relation across all π phases, as described by eqn. 6.52. It follows that for each component there can be only $(\pi - 1)$ independent relations.

Thus the phase rule may be rewritten as:

$$F = \left[2 + (N-1)\pi\right] - \left[(\pi - 1)N\right] = 2 + N - \pi \qquad (7.18)$$

It may be noted that the actual mass of each of the species present are not considered as phase rule variables, as they cannot influence the intensive state of the system. A special case of the phase rule obtains for closed systems for which the initial mass for each species is fixed. Since no mass can enter or leave the system, the extensive state of the system is rendered fixed along with the intensive variables. Therefore, apart from the $(\pi - 1)N$ constraining relations involving the species chemical potentials, there is an additional $\left[(N-1)\pi\right]$ constraint on the mass of each species; this follows from the fact that if a quantum of a species leaves a phase it must reappear in another or more. Thus the phase rule eqn. leads to:

$$F = \left[2 + (N-1)\pi\right] - \left[(\pi - 1)N\right] - \left[(N-1)\pi\right] = 2 \qquad ..(7.19)$$

The above equation is known as the *Duhem's theorem*. It implies that for any closed system formed initially from given masses of a number of chemical species, the equilibrium state is completely determined when any two independent variables are fixed. The two independent variables that one may choose to specify may be either intensive or extensive. However, the number of *independent intensive* variables is given by the phase rule. Therefore, it follows that when F = 1, at least one of the two variables must be extensive, and when F = 0, both must be extensive.

7.4 Description of General VLE Behavior

Before presenting the mathematical formulation of the multi-component VLE problem it is pertinent to discuss some key features of typical vapour liquid phase behaviour. The description of phase behaviour of vapour and liquid phases co-existing under equilibrium can be complex and difficult to visualize for systems containing a large number of chemical species. Thus, to clarify matters it is useful to consider a binary system. The considerations for such a system may, in principle, be generalized to understand the behaviour of multi-component systems. However, we restrict ourselves to description of VLE of multi-component systems to the corresponding mathematical formulation.

When N = 2, the phase rule yields a degree of freedom $F = 4 - \pi$. In the general VLE problem since there are at least two phases, the corresponding number of independent intensive variables become 2. In the case of extractive distillation, there are at least two liquid phases and a vapour phase, whence the degrees of freedom reduce to 1.In the following discussion we present the phase behaviour of the simplest case of a binary VLE. The more volatile of the two is designated as component (1). The phase rule variables for this case are: T, P, y_1 and x_1. Graphical plots of experimentally obtained phase behaviour can then be expressed as a functionof various combinations of these variables. For example at a given temperature one may plot two curves, P *vs.* x_1 (or in short P-x_1) and P *vs.* y_1. Similarly on specifying a certain pressure, one may plot T *vs.* x_1 and T *vs.* y_1. In addition if one fixes either x_1 or y_1 one may plot P-T diagrams. The combination of these diagrams lead to a 3-dimensional surface involving pressure, temperature and phase compositions on the three axes. A typical plot is shown in fig. 7.2.

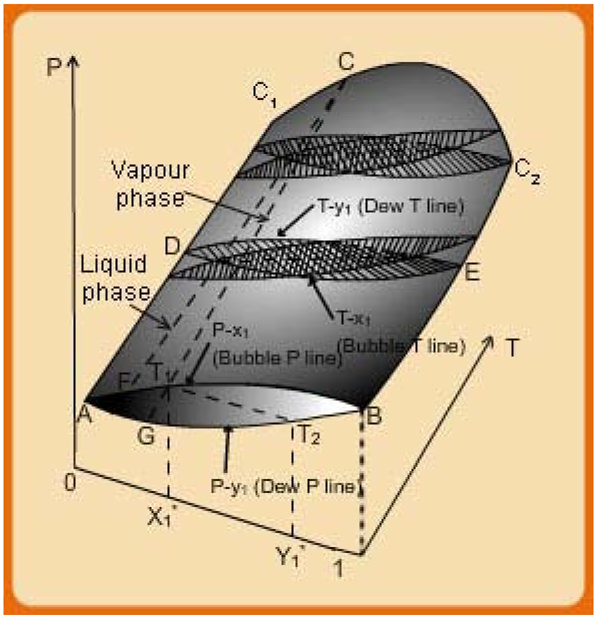


Fig. 7.2 Three dimensional VLE phase diagram for a binary system

Consider first a case of VLE phase behaviour at a constant temperature. This is in shown as the "lens" AB. The lower part of the lens corresponds to P-y_1 while upper curve is the P-x_1 plot. The values of the vapour and liquid compositions at any system equilibrium pressure are found by drawing a line parallel to the $x_1 - y_1$ axis. The point of intersection of this line with the upper curve provides the saturated liquid phase composition (x_1) and is termed the *bubble pressure line*; while that with the lower curve corresponds to the saturated vapour phase composition (y_1) and is termed the *dew pressure line*. Extending the description the entire upper face of the three dimensional surface constitutes the bubble surface. Any point above it corresponds to the state of sub-cooled liquid. In the same manner, the lower face represents the dew surface. For any point below this face the state is that of a superheated vapour. The line that connects the phase compositions (x_1^* *and* y_1^*) is called the *tie line* (shown as T_1-T_2). Such tie lines may be drawn at any other pressure and the same considerations as above are valid.

Similarly, if one considers isobaric plots (shown as the lens DE), for any equilibrium temperature the vapour and liquid phase compositions are found by drawing a line that passes through the specific temperature and is parallel to the $x_1 - y_1$ axis. The upper intersection point provides the vapour phase composition (*dew temperature line*), while the lower one corresponds to the liquid phase composition (*bubble temperature line*). Finally if one fixes the composition at a point on the $x_1 - y_1$ axis the intersection of a vertical plane through the composition point with the 3-dimension surface yields the curve FCG. The upper part of this curve, i.e., FC corresponds to the locus of liquid phase compositions while the lower one (CG) is that of the vapour phase compositions. The point C is the meeting point of the two curves and defines the critical point of the mixture at the composition specified by the original vertical plane at a point on the $x_1 - y_1$ axis. At the two end points of the composition axis are the pure component P-T plots which terminate at the critical points, C_1-C_2, of the two substances.

If one takes a series of varying isothermal or isobaric "lenses", two types of plots result, which are shown in fig. 7.3. Consider the P-x-y plot. The lowest lens (T_X) corresponds to the situation already described in the last paragraph (i.e., the lens MN). However, the one at T_Y corresponds to a case for which $T_{C1} < T_Y$, but $T_{C2} > T_Y$. Thus at this temperature the vapour and liquid phases of the pure component '1' cannot co-exist, and hence the P-x-y plot vanishes as the composition tends to $x_1 \to 1$. If one moves to a still higher temperature say T_Z the P-x-y "hangs" at both ends of the $x_1 - y_1$ as both $T_{C1} < T_Z$, and $T_{C2} < T_Z$. The considerations for the isobaric lenses at P_X, P_Y *and* P_Z are the same as for the isotherms, i,e., for the highest isobar, both $P_{C1} < P_Z$, and $P_{C2} < P_Z$ and so on.

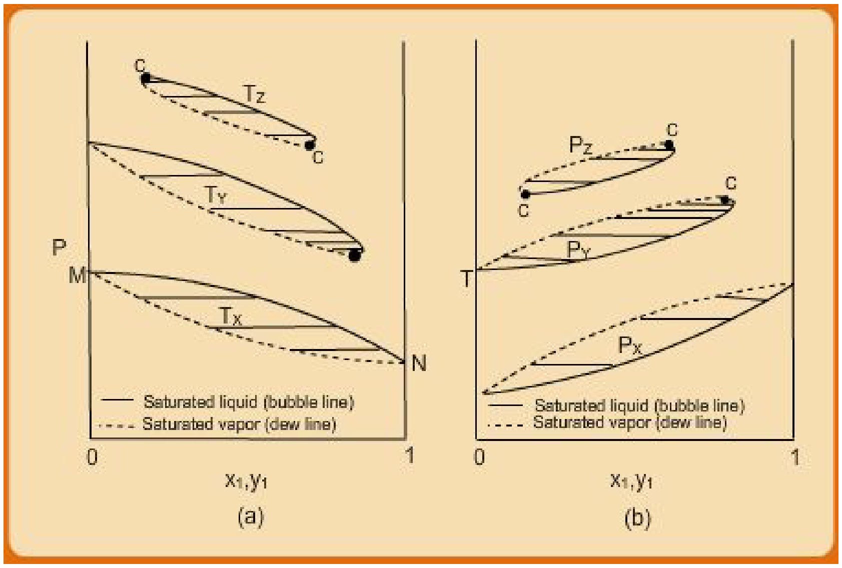


Fig. 7.3 (a) P-x_1–y_1 diagrams for three temperatures. (b) T-x_1-y_1 diagrams for three pressures

If one considers now a series of P-T plots they correspond to the curves shown in fig, 7.4. The lines I-J and K-L which represent the vapour pressure-vs.-T curves for pure species 1 and 2 respectively. At other intermediate compositions the upper and lower plots (obtained by intersection of a vertical plane at constant point on the $x_1 - y_1$ axis, and the P-T-x-y surface of fig. 7.2) constitute a curve that rounds off at the *true* critical point of the mixture (as opposed to the "pseudo-critical" temperature and pressure of mixtures discussed in section 2.4). The critical points of the various mixtures of the two species thus lie along a line on the rounded edge of the surface between J and L; it is, therefore composition dependent. Each interior loop represents the *P-T* behavior of saturated liquid and of saturated vapour for a mixture of *constant composition;* the loops differ from one composition to another. It follows that the *P-T* relation for saturated liquid is different from that for saturated vapour of the same composition. This is in contrast with the behavior of a pure species, for which the bubble and dew lines are the same, as for I-J and K-L.

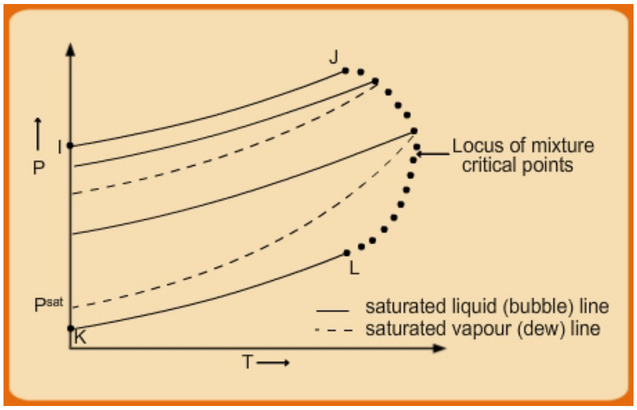


Fig. 7.4 P-T diagram for various compositions

The above discussion suggests that the phase behaviour of even a simple binary can be relatively more difficult to interpret in its complete three-dimensional form. Reducing such behaviour to two-dimensional plots enables easier visualization of the phase behaviour and understanding their features. However, in many instances, even two dimensional plots can be more complex in nature. Examples of such curves (as are often encountered with solvent mixtures in industrial practice) are shown schematically in the form of (*P-x-y)* in fig. 7.5, for systems at relatively low pressures ($\leq 1\,atm$).

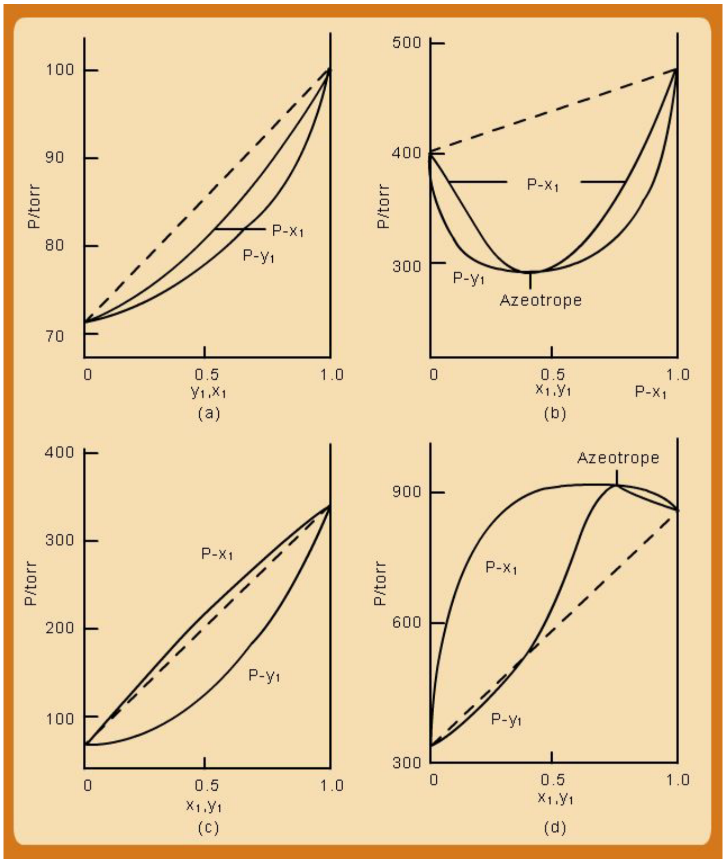


Fig. 7.5 Schematic P-x-y plots showing deviation from ideal VLE behaviour

All the four systemic VLE behaviour exhibits deviation from ideal vapour-liquid systems. As discussed in the next section ideal VLE behaviour is characterized by Raoult's Law (RL). Suffice it mention here that non-ideal VLE systems may exhibit both *negative* (figs. 7.5a & 7.5b) and *positive* deviations (figs. 7.5c and 7.5d) from that which obeys the Raoult's law (RL). The RL behaviour is typified by the dotted $P\text{-}x_1$ lines in each set in fig. 7.5. When the *actual* $P\text{-}x_1$ line lies below the RL-line, the system is said to show negative deviation from RL, while if it lies above it is indicative of a positive deviation.

From a molecular thermodynamic viewpoint, negative deviations occur if the 1-2 type (between unlike species) of molecular interactions (attraction) are *stronger* than 1-1 or 2-2 (between like species) type of interaction. As a result, the molecules of the more volatile component (1) are "constrained" by those of component 2 from transiting to the vapour phase to a *greater* extent than in the case when the former is present in a pure form. This effectively translates into an equilibrium pressure less than the RL system at the same liquid phase composition; hence the actual system displays "negative" deviation in comparison to RL for which 1-1, 2-2, and 1-2 types of interactions are more or less the same. Appreciable negative departures from P-x_1 linearity reflect strong liquid-phase intermolecular interaction. The opposite applies to the case where a system shows a positive deviation from RL; that is, the interaction between the unlike species of molecules is *lower* than that between like molecules.

There is an additional complexity evident in figs. 7.5c and 7.5d. Considering the former we see that it is defined by two distinct types of behaviour on either sides of the point termed as the "azeotrope". At this point the P-x_1 and the P-y_1 curves converge; i.e., the two phases are identical in composition at this point. On left side of the azeotrope $x_1 > y_1$, while on the other side, $x_1 < y_1$. The reverse situation holds for the system depicted in fig. 7.4d. Such systems are not uncommon in the process industry and always pose a difficulty in purifying a mixture to compositions higher than the azeotropic point. This is because during a distillation process when the mixture composition arrives at the azeotropic point the two phases become identical in composition, and the liquid composition does not alter further during evaporation.

The phase behaviour of the same systems as in fig. 7.5 is depicted as *T-x-y* diagrams in fig. 7.6. In particular we refer to the figs 7.6b and 7.6d. As expected the P-x curves *appear inverted* on a T-x diagram. The first kind of system (fig. 7.6b) is said to show a *maximum* boiling point azeotrope, while that depicted by fig. 7.5d shows a *minimum* boiling point azeotropic behaviour.

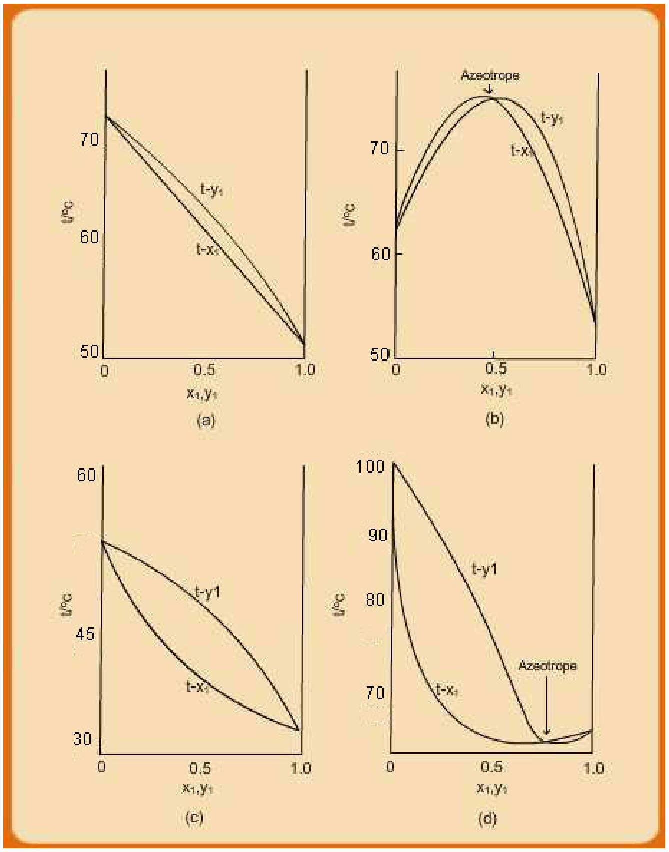


Fig. 7.6 Schematic T-x-y plots showing deviation from ideal VLE behaviour

7.5 Raoult's Law for VLE

As mentioned in the concluding part of the last section, vapour-liquid systems which are *ideal* in nature display a behaviour corresponding to Raoult's Law. In such a system, both the vapour and the liquid phases essentially behave as ideal mixtures. For describing the VLE for such systems we start by applying eqn. 6.50, to the vapour and liquid phases:

$$\mu_i^V = \mu_i^L \qquad ..(7.20)$$

For an ideal vapor mixture by eqn. 6.72 we have:

$$\mu_i^{ig} \equiv G_i^{ig} + RT \ln y_i$$

Similarly for an ideal liquid solution eqn. 6.77 provides:

$$\mu^{id} = G_i^{id} + RT \ln x_i$$

Thus rewriting eqn. 7.20 (using expressions provided by eqns. 6.72 and 6.77):

$$\mu_i^{ig} \equiv \mu_i^{id} \qquad ..(7.21)$$

$$G_i^{ig} + RT \ln y_i = G_i + RT \ln x_i \qquad ..(7.22)$$

Or: $RT \ln(y_i / x_i) = G_i - G_i^{ig}$ ..(7.23)

Since effect of pressure is negligible on liquid properties we assume that:

$$G_i^l (T, P) \simeq G_i^l (T, P_i^S) \qquad ..(7.24)$$

Now for the gas phase: $dG_i^{ig} = V_i^{ig} dP$ (at const T) ..(7.25)

Thus: $G_i^{ig}(T, P_i^s) - G_i^{ig}(T, P) = RT \int_P^{P_i^s} dP / P = RT \ln (P_i^s / P)$ ..(7.26)

Combining eqns. 7.23, 7.24 and 7.26 gives:

$$RT \ln(y_i / x_i) = G_i^l (T, P_i^s) - G_i^{ig}(T, P_i^s) + RT \ln(P_i^s / P) \qquad ..(7.27)$$

The first two terms on the RHS in equation above correspond to the Gibbs free energy of *pure* liquid and vapour phases under equilibrium conditions, i.e., at (T, P_i^s); hence, as shown in section 7.1, these terms equal. Therefore, it follows that:

$$y_i / x_i = P_i^s / P \qquad ..(7.28)$$

Alternately: $y_i P = x_i P_i^s$ ..(7.29)

Equation 7.29 is known as the Raoult's Law.

It may be noted that the conditions for ideal mixture behaviour for the gas and liquid phases are not the same in general. For the gas mixture to be ideal the pressures need to be close to atmospheric or less. While a liquid solution is ideal if the interaction between the *same* molecular species is identical to that between *dissimilar* molecules.

The algorithms needed for generating RL phase diagrams are discussed later in this section. But prior to that, we present examples of *typical* phase diagrams that obtain from the application of the Raoult's law (RL) equations. Consider again a binary system for which a representative *isothermal* plot is depicted in fig. 7.7. (The more volatile of the two components is designated as component '1'). The upper *straight* line represents the saturated liquid compositions, while the lower curve corresponds to the saturated vapour compositions. At any pressure, the phase compositions are found at the intersections of a line parallel to the *x-y* axis with the P-x and P-y curves. The straight line connecting these compositions is the tie line (such as A_1-B_1, A_2-B_2, etc.). The portion of the diagram enclosed by the *P-x-y* curves corresponds to the two phase region where the vapour and liquid phases co-exist. Any point lying outside of this two-phase envelope corresponds to a state where only a single phase is present. Now consider the point L which lies above the phase envelope. At this condition the mixture exists as a *compressed* (or *sub-cooled*) state whose composition corresponds to x_1^*. Lowering the pressure at this fixed composition eventually brings the liquid mixture to the point A_3, where any further reduction of pressure leads to the formation of a vapour phase whose composition is given by B_3. Thus this point is characterized by the formation of the first bubble of vapour, and hence is termed the *bubble point*, the corresponding pressure being the *bubble pressure*, at the given composition.

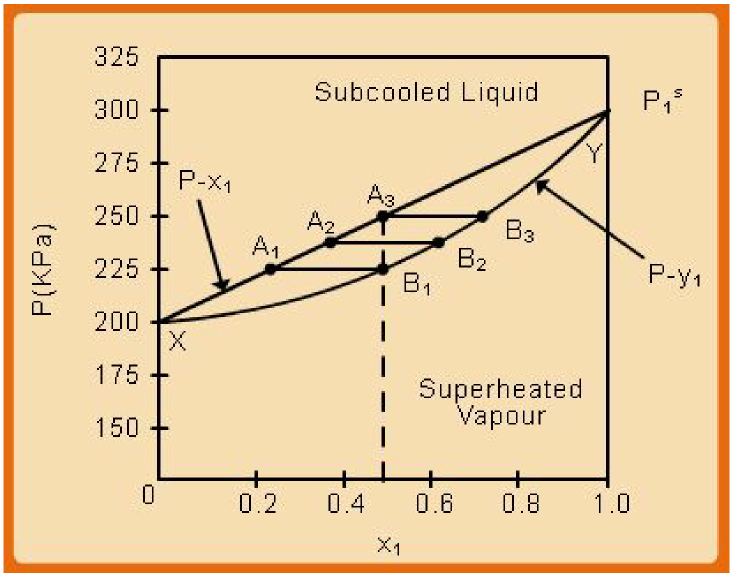


Fig. 7.7 Model P-x-y plot for a system obeying Raoult's Law

Next consider the point V in the above diagram. At this state the mixture is at the same overall composition as at L, but the state is one of single phase, *superheated vapour*. Increasing the pressure at the same composition eventually brings the mixture to the point B_1, where any further increase of pressure leads to the formation of the liquid phase, whose composition is given by the point A_1. Thus this point is said to be the *dew point* corresponding to the vapour phase composition given by y_1^*, while the pressure at this point is termed the dew pressure.

We revert to the discussion on the system state at the bubble point A_3. If one reduces the pressure progressively formation of more bubbles of vapour occurs, which coalesce and lead to the development of a bulk vapour phase. The system eventually reaches the point B_1 where practically the entire mixture exists in the vapour form; further reduction of pressure renders the mixture superheated and finally one reaches the point V (and beyond). Let us focus on what happens as the system transits through the two-phase region defined by the end points A_3 and B_1. Note that the *overall* composition of the system remains invariant as the pressure reduces. However, since now the original amounts of each species need to be distributed across the co-existing vapour and liquid phases the actual composition in each phase must change in accordance with the following mass conservation equation: $z_1(\equiv x_1^* \ or \ y_1^*) = x_1L + y_1V$; where, $z_1 =$ overall composition; x_1 and y_1 are compositions of the liquid and vapour phases at equilibrium, and L and V are the relative amounts of moles (per mole of the original mixture) in the liquid and vapour phases, respectively (thus $L+V=1$). The liquid phase composition progressively changes along the line A_3 to A_1 (*bubble curve*), while the composition of the vapour phase in equilibrium with the liquid phase transits from B_3 to B_1(*dew curve*). At each pressure between the bubble pressure (P_b) and the dew pressure (P_d) the equilibrium vapour and liquid phase compositions, as well as the relative amounts of mass in each phase are constrained by the relations: $z_1(\equiv x_1^* \ or \ y_1^*) = x_1L + y_1V$; and $L+V=1$.

The associated, isobaric T-x-y plots for the same system are shown in fig.7.7. As is expected the dew temperature curve lies *above* the bubble temperature curve. The lens-like region corresponds to the two-phase states of the system. At the point V the system is in a single phase, super-heated state.

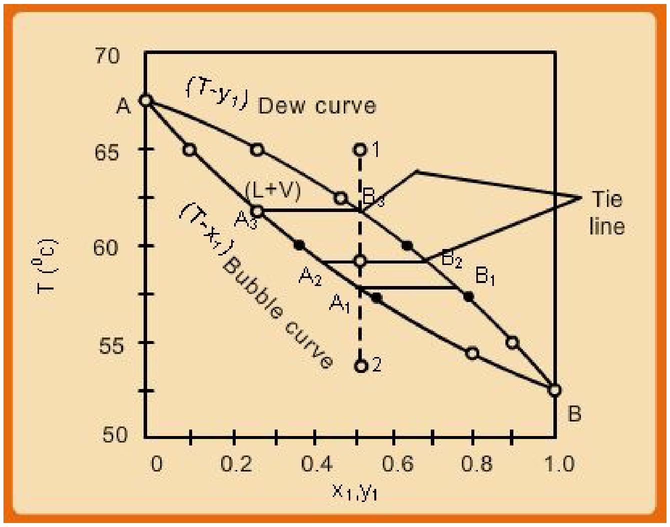


Fig. 7.8 Model T-x-y plot for a system obeying Raoult's Law

Progressive reduction of temperature brings it to the point B_3 where the *first* dew of liquid forms, whose composition is provided by the point A_3. Thus this point is referred to as the *dew point*, and the corresponding temperature called the *dew temperature*(T_d) for the given vapour phase composition (y_1^*). .On the other hand if one starts from the point L (single-phase, compressed liquid state) gradual increase of temperature brings the system to A_1, the *bubble point*, where the first bubble of vapour forms. The associated temperature then is the *bubble temperature* (T_b) for the composition x_1^*. At any other temperature intermediate to T_d and T_b, the system contains co-existing vapour and liquid phases whose compositions are constrained by the same mass conservation relations provided above, i.e., $z_1(\equiv x_1^* \ or \ y_1^*) = x_1 L + y_1 V$; and $L + V = 1$. Note that as in the P-x-y plot the T-x-y plots also are characterized by horizontal tie lines that connect the compositions of the equilibrated vapour and liquid phases.

The data in figures 7.7 and 7.8 may be may be alternately displayed in the form of a *y-x* plot (fig. 7.9). It shows the equilibrium vapour and liquid phase compositions in a more immediate manner. Note that, as required by the phase rule, each pair of equilibrium *y* and *x* values correspond to a different combination of equilibrium temperature and pressure.

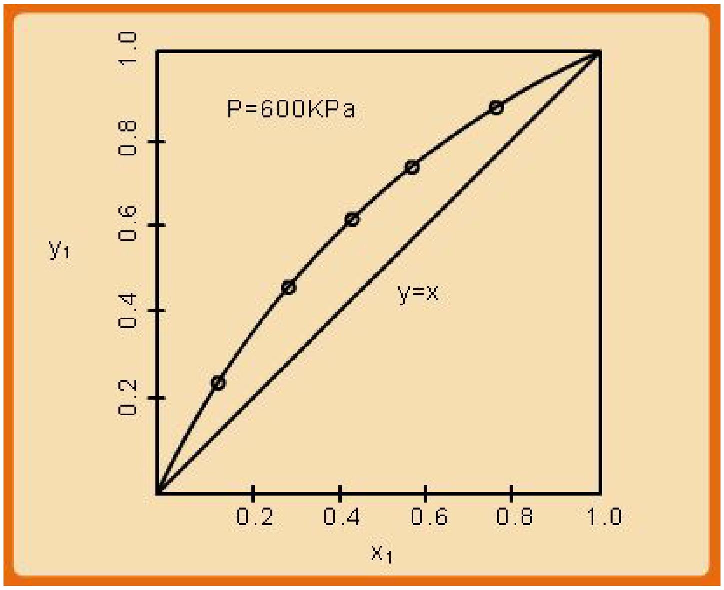


Fig. 7.9 Model y-x plot for a system obeying Raoult's Law

Multi-component VLE calculations using Raoult's Law:

For generality we consider a system containing *N* chemical species. Then by phase rule, for a VLE situation, the degrees of freedom are 2N, the phase rule variables being $\{x_i\},\{y_i\}$, T, and P. The Raoult's Law (eqn. 7.29) provides *N* constraining relations connecting these variables. Thus, for solving the VLE problem, *N* variables need to be specified, so that the values of the other *N* variables may be determined. Five types of VLE computations are commonly encountered in practice. They are enumerated below in table 7.1 first and then the relevant algorithms used are presented.

Table 7.1 Types of VLE calculations

VLE Type	Specified Variables	Computed Variables
Bubble Pressure	T and $\{x_i\}$	P and $\{y_i\}$
Dew Pressure	T and $\{y_i\}$	P and $\{x_i\}$
Bubble Temperature	P and $\{x_i\}$	T and $\{y_i\}$
Dew Temperature	P and $\{y_i\}$	T and $\{x_i\}$
Flash Distillation	T, P and $\{z_i\}$	$L\ or\ V$, $\{x_i\}$ and $\{y_i\}$

In the above table the notations used signify the following:

$\{x_i\} \equiv overall\ liquid\ phase\ compoition \equiv \{x_1, x_2, \dots x_{N-1}\}$

$\{y_i\} \equiv overall\ vapour\ phase\ compoition \equiv \{y_1, y_2, \dots y_{N-1}\}$

$\{z_i\} \equiv overall\ feed\ composition\ to\ flash\ vessel \equiv \{z_1, z_2, \dots z_{N-1}\}$

$L \equiv moles\ of\ liquid\ phase\ formed\ per\ mole\ of\ feed\ to\ flash\ vessel$

In summary, therefore, one specifies either T or P and either the liquid-phase or the vapor-phase composition, thus fixing 1+(N-1) or N phase rule variables as required by the phase rule for VLE calculation. The variants of Raoult's Law (eqn. 7.29) which are used are as follows:

$$y_i = x_i P_i^s / P \qquad ..(7.30)$$

Thus:

$$\sum_i^N x_i P_i^s / P = 1$$

Or:

$$P = \sum_i^N x_i P_i^s \qquad ..(7.31)$$

Also:

$$x_i = y_i P / P_i^s \qquad ..(7.32)$$

Thus:

$$\sum_i^N y_i P / P_i^s = 1$$

Or:

$$P = 1 \Big/ \sum_i^N y_i / P_i^s \qquad ..(7.33)$$

For computation of vapour pressures the Antoine equation (or another suitable equation) may be used:

$$\ln P_i^s = A_i - \frac{B_i}{t + C_i}; \text{ where } t = {}^0K \ (or\ {}^0C) \qquad ..(7.34)$$

Values of Antoine constants for a select group of substances are tabulated in Appendix IV. More exhaustive tabulation is available at:

http://www.eng.auburn.edu/users/drmills/mans486/Diffusion%20Tube/Antoine_coefficient_table.PDF

Bubble Pressure:

Given T and $\{x_i\}$, to calculate P and $\{y_i\}$:

a) Use eqn. 7.31 to compute P

b) Next use eqn. 7.30 to obtain $\{y_i\}$

Dew Pressure:

Given T and $\{y_i\}$, to calculate P and $\{x_i\}$:

a) Use eqn. 7.33 to compute P

b) Use eqn. 7.32 to obtain $\{x_i\}$

Bubble Temperature:

Given P and $\{x_i\}$, to calculate T and $\{y_i\}$

a) For the given pressure compute $\{T_i^s\}$ using the following form of Antoine eqn.

$$T_i^s = \frac{B_i}{A_i - \ln P} - C_i$$

b) Initialize the bubble temperature as: $T_{b(i)} = \sum_i^N x_i T_i^s$

c) Using computed T calculate $\{P_i^s\}$

d) Use equation 7.30 to compute $\{y_i\}$

e) Is $\left|\sum_i y_i - 1\right| < \varepsilon$? ($\varepsilon =$ pre-defined acceptable error for convergence)

f) If yes, $T_{last} = T_{b(f)}$; where $T_{b(f)}$ = final acceptable bubble temperature

g) At $T_{b(f)}$ compute final $\{y_i\}$

h) If $\sum_i y_i - 1 > \varepsilon$, then $T_{last} > T_{b(f)}$; revise to *new* T as: $T_{new} = T_{last}\left(\dfrac{\varepsilon}{\sum_i y_i - 1}\right)$ and return to step (c).

i) If $\sum_i y_i - 1 < -\varepsilon$, then the assumed $T < T_{b(f)}$; where $T_{b(f)}$ = final acceptable bubble temperature

Revise to *new* T using: $T_{new} = T_{last}\left(\dfrac{\left|\sum_i y_i - 1\right|}{\varepsilon}\right)$ and return to step (c).

Dew Temperature:

Given P and $\{y_i\}$, to calculate T and $\{x_i\}$

a) For the given pressure compute $\{T_i^s\}$ using the following form of Antoine eqn.

b) $T_i^s = \dfrac{B_i}{A_i - \ln P} - C_i$

c) Initialize the dew temperature as: $T_{d(i)} = \sum_i^N x_i T_i^s$

d) Using computed T calculate $\{P_i^s\}$

e) Use equation 7.33 to compute $\{x_i\}$

f) Is $\left|\sum_i x_i - 1\right| < \varepsilon$? ($\varepsilon =$ pre-defined acceptable error for convergence)

g) If yes, $T_{last} = T_{d(f)}$; where $T_{d(f)}$ = final acceptable bubble temperature

h) At $T_{d(f)}$ compute final $\{x_i\}$

j) If $\sum_i x_i - 1 > \varepsilon$, then $T_{last} < T_{d(f)}$; revise to *new* T as: $T_{new} = T_{last}\left(\dfrac{\sum_i x_i - 1}{\varepsilon}\right)$ and return to step (c).

k) If $\sum_i x_i - 1 < -\varepsilon$, then $T_{last} > T_{d(f)}$; revise to *new* T as: $T_{new} = T_{last}\left(\frac{\left|\sum_i x_i - 1\right|}{\varepsilon}\right)$ and return to step (c).

Example 7.1

Consider the ternary system: Acetone (1) / Acetonitrile (2) / Nitromethane (3) for which:

$$\ln P_1^S = 14.5463 - \frac{2940.46}{t + 237.22}; \ln P_2^S = 14.5463 - \frac{2940.46}{t + 237.22}; \ln P_3^S = 14.2043 - \frac{2972.64}{t + 209.00}$$

$P_i^S (KPa); t(^0C)$.

Calculate: (a) P, $\{y_i\}$ for a temperature = 80°C, $x_1 = 0.3$, $x_2 = 0.3$ (b) P, $\{x_i\}$, for t = 70°C, $y_1 = 0.5$, $y_2 = 0.3$.

(Click for solution)

Flash Distillation Calculations

This is an operation, often exploited in the chemical industry to achieve the desired enrichment of a feedstock through a one-step distillation process. A schematic of the process is shown in fig. 7.6. A liquid at a pressure equal to or greater than its bubble point pressure is introduced into the flash by passing it through a pressure reduction valve. The abrupt reduction in pressure "flashes" or partially evaporates the feed liquid, which results in the formation of a vapour and a liquid stream which are typically assumed to leave the flash vessel in equilibrium each other.

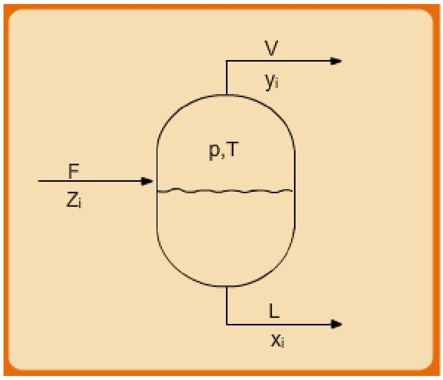


Fig. 7.10 Schematic of Flash Distillation Process

One of the common forms of flash calculation typically involves the determination of the liquid and vapour stream composition that results from process as well also the resultant liquid or vapour phase mole fractions that obtains per mole of feed. Consider a system containing one mole of mixture of chemical species with an *overall* composition represented by the set of mole fractions $\{z_i\}$. Let L and V be the moles of liquid and vapour formed per mole of feed. The corresponding stream compositions are denoted as $\{x_i\}$ and $\{y_i\}$ respectively**.** The material-balance equations are:

$$F = L + V = 1 \qquad ..(7.35)$$

$$z_i F = x_i L + y_i V$$

$$z_i = x_i(1 - V) + y_i V \; ; \qquad ..(7.36)$$

Now: $K_i = y_i / x_i = P_i^s / P$ ..(7.37)

Putting $x_i = y_i / K_i$ and using relations in (7.44) one obtains:

$$y_i = \frac{z_i K_i}{1 + V(K_i - 1)} \qquad ..(7.38)$$

$$\sum_i y_i = 1$$

Using this condition in eqn. 7.38:

$$\sum_i \frac{z_i K_i}{1 + V(K_i - 1)} = 1 \qquad (i = 1, 2\ldots.N) \qquad ..(7.39)$$

Since $x_i = y_i / K_i$, an alternative equation is:

$$x_i = \frac{z_i}{1 + V(K_i - 1)} \qquad (i = 1,2,\ldots.N) \qquad ..(7.40)$$

It follows that: $\sum_i \frac{z_i}{1 + V(K_i - 1)} = 1$ ..(7.41)

Subtracting eqn. 7.41 from 7.39and defining a function φ we get

$$\varphi = \sum_i \frac{z_i(K_i - 1)}{1 + V(K_i - 1)} = 0 \qquad ..(7.42)$$

It follows that: $\frac{d\varphi}{dV} = -\sum_i \frac{z_i(K_i - 1)^2}{[1+V(K_i-1)]^2}$ ..(7.43)

The derivative $\frac{d\varphi}{dV}$ is always negative; in other words the relation between φ vs. V is monotonic, and this makes for convenient application of the well-known Newton-Raphson method of solution (see Appendix VII); this leads to the following equation for the n^{th} iteration:

$$V_{n+1} = V_n - \frac{\varphi_n}{\left(\frac{d\varphi}{dV}\right)_n} \qquad ..(7.44)$$

Where, the values for φ and $\left(\frac{d\varphi}{dV}\right)$ may be computed using eqns. 7.42 and 7.43 respectively.

Example 7.2

A liquid mixture containing equimolar amounts of benzene (1) /toluene (2) and ethylbenzene (3) is flashed to conditions of T = 110°C, P = 90 kPa, determine the equilibrium mole fractions $\{x_i\}$ and $\{y_i\}$ of the liquid and vapor phase formed and the molar fraction V of the vapor formed. Assume that Raoult's law applies. $\ln P^{sat}(Pa) = A - \frac{B}{t(^0K)+C}$

	A	B	C
Benzene	13.8594	2773.78	-53.08
Ethylbenzene	14.0045	3279.47	-59.95
Toluene	14.0098	3103.01	-53.36

(Click for solution)

7.6 VLE Algorithms for Low to Moderate Pressures

The next level of complexity in VLE algorithms arise when one has to account for non-ideal behaviour for both the gas and liquid phases. This may obtain at pressures away from atmospheric and if the constituent molecules form a non-ideal liquid phase. The general approach to VLE of such system involves correcting both sides of the Raoult's law to incorporate the effect of non-ideal behaviour. If the pressures are moderately high the truncated virial EOS may be used to describe the gas phase behaviour, whereas the liquid phase non-ideality is defined by a suitable activity coefficient model. The activity coefficient based approach is preferred for moderate pressures, as under such conditions the liquid phase properties may be conveniently regarded as independent of pressure, hence only temperature effects on the activity coefficients need be accounted for. This approach, of course, is rendered inaccurate at relatively high pressures, where both the gas and liquid phases need to be described using fugacity coefficients derived typically from a cubic (or a higher order) EOS. This is dealt with in the next section. Presently the VLE algorithms for low to moderate pressure range are introduced. The starting point is the eqn. (6.126):

$$\hat{f}_i^{\alpha} = \hat{f}_i^{\psi} \qquad ..(6.126)$$

Applying it to VLE:

$$\hat{f}_i^{V} = \hat{f}_i^{L} \qquad ..(6.127)$$

For gas phase, we use eqn. 6.129:

$$\hat{f}_i^{V} = y_i \hat{\phi}_i P$$

For liquid phase (using eqn. 6.164):

$$\hat{f}_i^{L} = x_i \gamma_i f_i$$

Applying eqn. 6.127:

$$y_i \hat{\phi}_i P = x_i \gamma_i f_i \qquad ..(7.45)$$

From basic fugacity function for liquid phase (eqn.6.119):

$$f_i(T,P) = \phi_i^{sat} P_i^{sat} \exp[\frac{V_i^l (P - P_i^{sat})}{RT}] \qquad ..(6.119)$$

Using eqn. 6.119 in 6.128 we may write the phase equilibria relation as:

$$y_i \Phi_i P = x_i \gamma_i P_i^S \; ; \qquad (i = 1,2,\dots \text{N}) \qquad ..(7.46)$$

Where $\Phi_i = (\hat{\phi}_i / \hat{\phi}_i^s)\exp[-\frac{V_i^L (P - P_i^s)}{RT}]$ ..(7.47)

One may show that the Pontying (exponential factor) in the last equation is usually ~ 1 for low to moderate pressure range, hence one may write:

$$\Phi_i \approx (\hat{\phi}_i / \phi_i^s) \qquad ..(7.48)$$

For a gas mixture obeying the truncated virial EOS (by eqn. 6.98):

$$\phi_i^{sat} = \exp[\frac{B_{ii}P_i^s}{RT}] \qquad ..(7.49)$$

Specifically for a binary using eqns. 6.149 and 6.150:

$$\ln\hat{\phi}_1 = \frac{P}{RT}(B_{11} + y_2^2\delta_{12}) \qquad ..(6.149)$$

$$\hat{\phi}_2 = \exp[\frac{P}{RT}(B_{22} + y_1^2\delta_{12})] \qquad ..(6.150)$$

Using the last four equations it follows that:

$$\Phi_1 = \exp[\frac{B_{11}(P - P_1^s) + Py_2^2\delta_{12}}{RT}] \qquad ..(7.50)$$

And $\Phi_2 = \exp[\frac{B_{22}(P - P_2^s) + Py_1^2\delta_{12}}{RT}]$ ..(7.51)

It may be shown that for a multi-component the general expression for Φ_i is provided by:

$$\Phi_i = \exp\frac{B_{ii}\left(P - P_i^s\right) + \frac{1}{2}P\sum_j\sum_k y_i y_k\left(\delta_{ji} - \delta_{jk}\right)}{RT} \qquad ..(7.52)$$

Now, $\Phi_i = \Phi_i(T, P, y_1, ..., y_{N-1})$

And:

$$\gamma_i = \gamma_i(T, P, x_1, ..., x_{N-1}) \cong \gamma_i(T, x_1, ..., x_{N-1}) \qquad ..(7.53)$$

The approximation made in eqn. 7.53 is a reasonable one, as at low to moderate pressures the dependence of γ_i γ_i on ‘P’ may be neglected (as at such conditions the liquid phase properties are not strongly pressure dependent).

The same five classes as provided in table 7.1 may be solved using this modified form of the Raoult’s law. In all cases eqn. 7.46 provides the starting point for calculation, which may be re-written is two principal alternate forms as follows:

$$y_i = x_i\gamma_i P_i^s / \Phi_i P \qquad ..(7.54)$$

$$x_i = y_i\Phi_i P / \gamma_i P_i^s \qquad ..(7.55)$$

Since $\sum y_i = 1$

$$\sum x_i\gamma_i P_i^s / \Phi_i P = 1$$

Or:

$$P = \sum x_i \gamma_i P_i^s / \Phi_i \quad ..(7.56)$$

Similarly since $\sum x_i = 1 = \sum y_i \Phi_i P / \gamma_i P_i^s$; it follows that:

$$P = 1 / \sum y_i \Phi_i / \gamma_i P_i^s \quad ..(7.57)$$

We may also re-write eqn. 7.46 in terms of the K-factor (as used for Raoult's Law in eqn. 7.37) as follows:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^S}{\Phi_i P} \quad ..(7.58)$$

Accordingly:

$$y_i = K_i x_i \quad ..(7.59)$$

Or:

$$x_i = \frac{y_i}{K_i} \quad ..(7.60)$$

From eqn. 7.59, it follows that:

$$\sum_i K_i x_i = 1 \quad ..(7.61)$$

From eqn. 7.60:

$$\sum_i \frac{y_i}{K_i} = 1$$

Note that when $\Phi_i = \gamma_i = 1$ eqn. 7.46 reduces to the ideal case of Raoult's Law.

Bubble pressure:

Given T and $\{x_i\}$, to calculate P and $\{y_i\}$:

a) Start with given T, $\{x_i\}$, Antoine constants, $\in$ (error value for convergence)

b) Set all $\{\Phi_i\}$ = 1.0, Evaluate $\{P_i^s\}$, $\{\gamma_i\}$, Calculate P using eqn. 7.56

c) Calculate $\{y_i\}$ using eqn.7.54

d) Now evaluate $\{\Phi_i\}$, using eqns. 7.52

e) Calculate P_{new} using eqn. 7.56

f) Is $\delta P < \in$?

g) If ‘No’, go to step ‘c’ and calculate new $\{y_i\}$ with last $\{\Phi_i\}$

h) If ‘Yes’, end at last P, and $\{y_i\}$

Dew Point Pressure:

Given T and $\{y_i\}$, to calculate P and $\{x_i\}$

a) Start with T and $\{y_i\}$; Antoine constants; ε and δ (error values for convergence); start with Raoult’s law by setting all $\{\Phi_i\}$ = 1.0, and all $\{\gamma_i\}$ = 1.0; Evaluate $\{P_i^s\}$, then calculate P using eqn. 7.57; Now evaluate $\{x_i\}$ by eqn. 7.55; Evaluate $\{\gamma_i\}$ using appropriate activity coefficient model Liquid-phase; recalculate P using eqn. (7.65), revise $\{\Phi_i\}$ using given $\{y_i\}$ and last P.

b) Calculate new set $\{x_i\}$ using eqn. 7.55

c) Normalize $\{x_i\}$ using $x_{i(n)} = \dfrac{x_i}{\sum x_i}$, and use normalized $\{x_i\}$ to compute $\{\gamma_i\}$

d) Use last $\{\gamma_i\}$ to calculate P by eqn. 7.57

e) Is $\delta P < \varepsilon$?

f) If ‘Yes’ then $P_{last} = P_{d(f)}$

Bubble Temperature:

Given P and $\{x_i\}$, to calculate T and $\{y_i\}$

a) Solve for T and $\{y_i\}$ first by assuming Raoult’s Law algorithm for bubble temperature

b) Using solution in ‘a’ estimate $\{K_i\}$ using eqn. 7.58 with the given values of P and $\{x_i\}$; latest values of T and $\{y_i\}$

c) Next calculate $\{K_i x_i\}$

d) Calculate all $y_i = K_i x_i \Big/ \sum_i K_i x_i$

e) Using normalized $\{y_i\}$, recalculate $\{K_i\}$ and $\sum_i K_i x_i$

f) Has $\sum_i K_i x_i$ changed? If yes return to step ‘d’

g) If $\sum_i K_i x_i$ has not changed between two successive iterations between steps 'c' and 'd' is $\sum_i K_i x_i = 1$?

h) If *yes*, the last values of T and $\{y_i \equiv K_i x_i\}$ give the final bubble temperature $T_{b(f)}$,and vapour compositions.

i) If *no*, and last $\sum_i K_i x_i > 1$, then $T_{last} > T_{b(f)}$; revise to *new* T as: $T_{new} = T_{last}\left(\dfrac{1}{\sum_i K_i x_i}\right)$ and return to step (c).and return to step 'b'.

j) If *no*, and last $\sum_i K_i x_i < 1$, then $T_{last} < T_{b(f)}$; revise to *new* T as: $T_{new} = T_{last}\sum_i K_i x_i$ and return to step (c).and return to step 'b'.

Dew Temperature:

Given P and $\{y_i\}$, to calculate T and $\{x_i\}$

a) Solve for T and $\{x_i\}$ first by assuming Raoult's Law algorithm for dew temperature

b) Using solution in 'a' estimate $\{K_i\}$ using eqn. 7.58 with the given values of P and $\{y_i\}$; latest values of T and $\{x_i\}$

c) Next calculate $\{y_i / K_i\}$

d) Calculate all $x_i = (y_i / K_i) \Big/ \sum_i (y_i / K_i)$

e) Using normalized $\{x_i\}$, recalculate $\{K_i\}$ and $\sum_i y_i / K_i$

f) Has $\sum_i y_i / K_i$ changed? If yes return to step 'd'

g) If $\sum_i y_i / K_i$ has not changed between two successive iterations between steps 'c' and 'd' is $\sum_i y_i / K_i = 1$?

h) If *yes*, the last values of T and $\{x_i \equiv y_i / K_i\}$ give the *final* dew temperature $T_{d(f)}$,and liquid phase compositions.

i) If *no*, *and* $\sum_i y_i / K_i > 1$, then $T_{last} < T_{d(f)}$; revise to *new* T as: $T_{new} = T_{last} \sum_i x_i / K_i$ and return to step (b).

j) If no, *and* $\sum_i y_i / K_i < 1$, then $T_{last} > T_{d(f)}$; revise to *new* T as: $T_{new} = T_{last} \sum_i x_i / K_i$ and return to step (b).

Example 7.3

Methanol (1)-acetone (2) forms an azeotrope at 760 Torr with x_1= 0.2, T = 55.7^{0}C. Using van Laar model predict the bubble pressure for a system with for x_1 = 0.1 at 55.7^{0}C.

$$\log_{10} P_1^s = 8.0897 - [1582.271/(t+239.726)]; \log_{10} P_2^s = 7.1171 - [1210.595/(t+229.664)]$$

$$P_i^s\,(torr); t(^0C)$$

(Click for solution)

Example 7.4

For a binary, the activity coefficients are $\ln\gamma_1 = Ax_2^2$ and $\ln\gamma_2 = Ax_1^2$. Show that the system forms an azeotrope when $A > \left|\ln\left(P_2^s / P_1^s\right)\right|$

(Click for solution)

Flash Distillation Calculations

The procedure for non-ideal systems takes a form similar to that adopted for systems obeying Raoult's Law except that one needs to additionally check for existence of both liquid and vapour phases following flash. The algorithm comprises the following steps.

a) Start with flash T, P and feed composition $\{z_i\}$

b) At the given T, calculate dew pressure P_d by putting $\{y_i\} = \{z_i\}$

c) Next calculate bubble pressure P_b by putting $\{x_i\} = \{z_i\}$

d) Is $P_d < P < P_b$? If *no*, the vapour phase has not formed.

e) If *yes*, compute $\{\Phi_i\}, \{\gamma_i\}$, and V as $\simeq \dfrac{P_b - P}{P_b - P_d}$

f) Use $\{\Phi_i\},\{\gamma_i\}$, to get $\{K_i\}$ using eqn. 7.58

g) Then use eqn. 7.42 and 7.43 to evaluate φ and $d\varphi / dV$.

h) Using Newton-Raphson method, find V

i) With last V compute $\{x_i\}$ using eqn. 7.40 and $\{y_i\}$ by eqn. 7.38

j) Re-calculate $\{\Phi_i\},\{\gamma_i\}$, and $\{K_i\}$ using eqn. 7.58

k) Check if the change in each parameter x_i, y_i, and V between steps 'e' and 'j' is within pre-defined error values chosen for convergence.

l) If *yes*, then the last values of x_i, y_i, and V constitute the solution

m) If *no*, return to step '*f*' with the last values of x_i, y_i, and V

7.7 High Pressure Vapour Liquid Equilibria

At relatively high pressures the VLE relations used in the last section lose exactness especially with respect to the activity coefficient-based approach for description of the non-ideal behaviour of the liquid phase. This is because the assumption that the activity coefficients are weakly dependent on pressure no longer remains a realistic approximation. In addition, the gas phase *P-V-T* behaviour can no longer be described by the truncated virial EOS. Under such conditions a use of a higher order EOS, which may be applied both to the gas and liquid phase is preferred. As we have seen in chapter 2, the cubic EOS provides just that advantage; besides they offer a reasonable balance between accuracy and computational complexity. We start with the general criterion for phase equilibria as applied to vapour-liquid systems, given by eqn. 6.127:

$$\hat{f}_i^V = \hat{f}_i^L \qquad (i = 1,2, \ldots, N) \qquad ..(7.62)$$

An alternative form of the last equation results from introduction of the fugacity coefficient using eqn. 6.129 and 6.130:

$$y_i\hat{\phi}_i^V P = x_i\hat{\phi}_i^L P \qquad (i = 1,2, \ldots N) \qquad ..(7.63)$$

The last equation reduces to:

$$y_i\hat{\phi}_i^V = x_i\hat{\phi}_i^L \qquad ..(7.64)$$

VLE of pure species

For the special case of pure species *i*, equation 7.64 reduces to:

$\phi_i^V = \phi_i^L$ ..(7.65)

If both ϕ_i^V and ϕ_i^L are expressed in terms of cubic EOS as defined by any of the eqns. 6.104 to 6.107, for a given T one may obtain the saturation vapour pressure by means of suitable algorithm as shown by the worked out example below.

Example 7.5

Estimate the vapour pressure of a substance "A' using PR-EoS, at T = 428^{o}K. For the substance A: T_C = 569.4 K, P_C = 2.497 MPa, = 24.97 bar, $\omega = 0.398$.

(Click for solution)

VLE from K-value Correlations for Hydrocarbon Systems

Using eqn. 7.64 one can write, $K_i = y_i / x_i$

Alternately: $K_i = \hat{\phi}_i^V / \hat{\phi}_i^L$ ..(7.66)

As evident from eqns. 6.155 to 6.157, the expression for species fugacity coefficients for mixtures described by cubic EOS are relatively complex, which in turn makes the estimation of the K-factors difficult as iterative solutions to obtaining T, P and/or compositions are inevitable. As demonstrated in the last section, this is true even for the fugacity and activity coefficient based formulation of the VLE problem. The use of cubic EOS for description of fugacity coefficients of species in both phases poses additional difficulty owing to the intrinsic complexity of the expressions shown in eqns. 6.155 to 6.157.

However, in the case of VLE of light hydrocarbon mixtures a reasonable simplification may be achieved by assuming *ideal solution* behaviour for both the phases. This is a relatively practical approximation as hydrocarbons being non-polar in nature, the intermolecular interactions are generally weaker than amongst polar molecules. In effect in the case of lighter hydrocarbons (C_1-C_{10}) the interactions between the same species and those between dissimilar species are not significantly different. This forms the basis of assuming ideal solution behaviour for such system. It may be noted that since equilibrium pressures in light hydrocarbon systems tend to be 'high' (as they are low-boiling) under practical conditions of distillation processes, ideal solution behaviour yields far more accurate results than would be possible by *ideal gas* assumption.

We develop next the result that obtains owing to the assumption of ideal solution behaviour. The chemical potential of all species in an ideal solution is given by eqn. 6.77:

$$\mu_i^{id} = \bar{G}_i^{id} = G_i + RT\ln x_i \qquad ..(7.67)$$

For a real solution: $d\bar{G}_i = RTd\ln\hat{f}_i$ ..(7.68)

At the same time for pure species at same T&P: $dG_i = RTd\ln f_i$ ..(7.69)

From eqns. (7.68) and (7.69) it follows that:

$$\bar{G}_i - G_i = RT\ln(\hat{f}_i / f_i) \qquad ..(7.70)$$

From (7.67) $\bar{G}_i^{id} - G_i = RT\ln x_i$ ..(7.71)

Thus from eqns. (7.70) and (7.71):

$$\bar{G}_i - \bar{G}_i^{id} = RT\ln(\hat{f}_i / x_i f_i) \qquad ..(7.72)$$

For an ideal solution LHS of (7.72) is identically zero; hence for such a solution:

$$\hat{f}_i = x_i f_i \qquad ..(7.73)$$

For a real gas mixture the fugacity coefficient $\hat{\phi}_i$ is defined by: $\hat{f}_i = y_i\hat{\phi}_i P$

In analogy, for a real solution we define $\hat{\phi}_i$ by: $\hat{f}_i = x_i\hat{\phi}_i P$

Or: $\hat{\phi}_i = \hat{f}_i / x_i P$ ..(7.74)

Using (7.74) for an ideal solution: $\hat{\phi}_i^{id} = \hat{f}_i^{id} / x_i P$ ..(7.75)

Using (7.73) in (7.75) it follows: $\hat{\phi}_i^{id} = x_i f_i / x_i P = f_i / P = \phi_i$

Thus for an ideal solution: $\hat{\phi}_i = \phi_i$ ..(7.76)

Now considering the light hydrocarbon systems, the application of eqn. 7.76 in 7.66 gives:

$$K_i = \frac{\phi_i^L\left(T,P\right)}{\phi_i^V\left(T,P\right)} = \frac{f_i^L(T,P)}{P\phi_i^V(T,P)} \qquad ..(7.77)$$

Using eqn. 6.119 we substitute for the fugacity $f_i^L(T,P)$. Thus:

$$f_i^L = P_i^{sat}\phi_i^{sat}\exp[\frac{V_i^L(P - P_i^{sat})}{RT}]$$

Where, V_i^l is the molar volume of pure species *i* as a saturated liquid. Thus the K-value is given by:

$$K_i = \frac{P_i^{sat}\phi_i^{sat}(T, P_i^{sat})}{P\phi_i^V(T, P)}\exp[\frac{V_i^L(P - P_i^{sat})}{RT}] \qquad ..(7.78)$$

The advantage of eqn. 7.78 is that it is a function of the properties of the pure species only, and therefore its dependence on composition of the vapour and liquid phases is eliminated. The K-factor then is a function of temperature and pressure alone. The terms ϕ_i^{sat} and ϕ_i^V in eqn. 7.78 can in principle be computed using expression provided by cubic EOS (i.e., eqns. 6.104 – 6.107) or a corresponding expression from an higher order EOS, including the generalized correlation (section 6.9). This allows K-factors for light hydrocarbons to be as functions of T and P.

However, it may be noted that the computation of fugacities at high pressures (and/or temperatures) can potentially be rendered difficult as above the critical temperature the liquid state is necessarily hypothetical, while at pressures higher than the saturation pressure the vapour state is hypothetical. This is corrected for by some form of extrapolations to those hypothetical states. Various approaches have been described in the literature (T.E. Daubert, *Chemical Engineering Thermodynamics*, McGraw-Hill, 1985). The nomographs of K-factors (see figs. 7.11 and 7.12) reported by Dadyburjor (D.B. Dadyburjor, *Chem. Eng. Progr.*, vol. 74(4), 85-86, 1978) provide an example of one such approach.

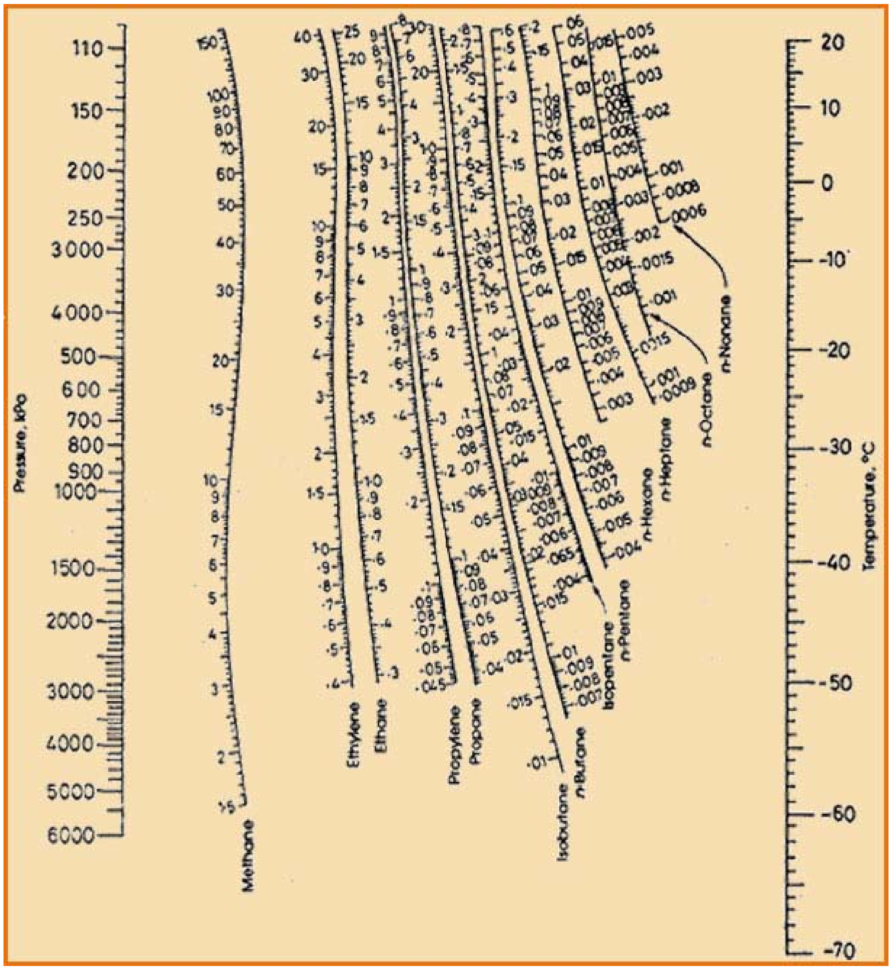


Fig. 7.11 K-factors in light hydrocarbon systems (low temperature range) [Source: Dadyburjor; D.B., *Chem. Eng.Progr.*, Vol. 74 (4) pp.85-86 (1978)].

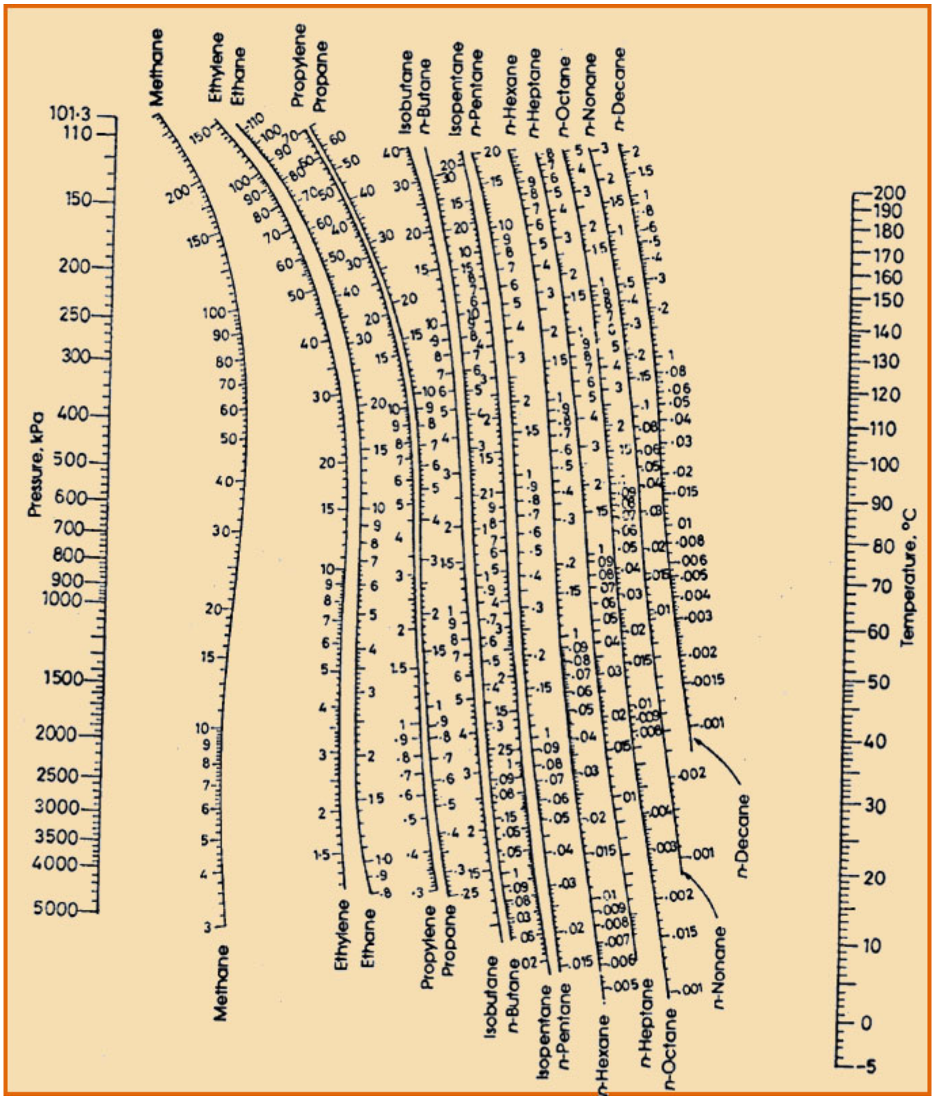


Fig. 7.12 K-factors in light hydrocarbon systems (high temperature range) [Source: Dadyburjor; D.B., *Chem. Eng.Progr.*, Vol. 74 (4) pp.85-86 (1978)].

The nomographs may be conveniently used purpose of VLE calculations in hydrocarbon systems as they the K-factors for each species can be estimated at a given T and P. This is done by drawing a straight line connecting the given temperature and pressure; the corresponding K_i value is read off from the point of intersection of this line with the K_i curve for a particular species. For *bubble point* (either T or P) calculations one uses:

$$\sum_i y_i = \sum_i K_i x_i = 1 \qquad ..(7.79)$$

- For ***pressure*** calculation: If $\sum_i K_i x_i > 1$, assumed pressure is *lower* than the correct value; if $\sum_i K_i x_i < 1$ the assumed pressure is *higher* than the correct pressure. Thus, pressure needs to be revised for the next step of calculation.
- Similarly, for ***temperature*** calculation: if $\sum_i K_i x_i > 1$, assumed temperature is *higher* than the correct value; if $\sum_i K_i x_i < 1$ the assumed temperature is *lower* than the correct value. Thus, temperature needs to be revised for the next step of calculation.

On the other hand the solution for **dew point** calculations derives from:

$$\sum_i x_i = \sum_i \frac{y_i}{K_i} = 1 \qquad ..(7.80)$$

- For ***pressure*** calculation: If, $\sum_i (y_i / K_i) > 1$assumed pressure is *higher* than the correct value; if $\sum_i (y_i / K_i) > 1$the assumed pressure is *lower* than the correct pressure. Thus, pressure needs to be revised for the next step of calculation.
- Similarly, for ***temperature*** calculation: if $\sum_i (y_i / K_i) > 1$, assumed temperature is *lower* than its correct value; if $\sum_i (y_i / K_i) < 1$the assumed temperature is *higher* than its correct value. Thus, temperature needs to be revised for the next step of calculation.

The use of these equations illustrated below using an example.

<u>Example 7.6</u>

A vapour mixture contains 20mol% methane (1), 30mol% ethane (2) , and rest propane (3), at 30^{0}C. Determine the dew composition.

(Click for solution)

High Pressure VLE using cubic EOS

This constitutes a generalized approach without any simplifying assumptions such as employed for light hydrocarbons. The governing relation thus is eqn. 7.66.

$$K_i = \hat{\phi}_i^V / \hat{\phi}_i^L$$

The fugacity of each species, either in vapour or liquid phase, is computed using the expressions that apply to use of cubic EOS (eqns. 6.155 to 6.157). For relevant VLE calculations once again the eqns. 7.79 and 7.80 are employed. The steps for computing (for example) the bubble pressure are enlisted below. The basic principle used for other types of standard calculations (such as discussed for low to moderate pressure VLE systems, table 7.1) remains the same.

Bubble pressure algorithm:

Given T and $\{x_i\}$, to calculate P and $\{y_i\}$

a) Solve for P and $\{y_i\}$ first by assuming Raoult's Law algorithm for bubble pressure

b) Using solution in 'a' estimate $\{K_i\}$ using eqn. 7.66 with the given values of T and $\{x_i\}$; and the latest values of P and $\{y_i\}$

c) Next calculate $\{K_i x_i\}$ and $\sum_i K_i x_i$

d) Calculate all $y_i = K_i x_i \Big/ \sum_i K_i x_i$

e) Using normalized $\{y_i\}$, recalculate $\{K_i\}$ and $\sum_i K_i x_i$

f) Has $\sum_i K_i x_i$ changed between steps 'c' and 'e'? If *yes* return to step 'd'

g) If $\sum_i K_i x_i$ has not changed between two successive iterations between steps 'c' and 'e' is $\sum_i K_i x_i = 1$?

h) If *yes*, the last values of P and $\{y_i \equiv K_i x_i\}$ give the final bubble temperature $P_{b(f)}$,and vapour compositions.

i) If *no*, and last $\sum_i K_i x_i > 1,$ then $P_{last} < P_{b(f)}$; revise to *new P* as: $P_{new} = P_{last} \sum_i K_i x_i$ and return to step (c).and return to step 'b'.

j) If *no*, and last $\sum_i K_i x_i < 1,$ then $P_{last} > P_{b(f)}$; revise to *new P* as: $P_{new} = P_{last} \sum_i K_i x_i$ and return to step (c).and return to step 'b'.

We illustrate the above methodology by a calculation of bubble pressure for an example binary system below.

Example 7.7

For the system of methane (1) and butane (2) compute the bubble pressure for a liquid phase composition of $x_1 = 0.2$ at a temperature of 310K, using the PR-EOS.

(Click for solution)

7.8 Henry's Law

The solubility of gases that are *sparingly* soluble in solvents constitutes a special application of the general VLE relations developed in sections 7.3 and 7.4. There are numerous real-life examples of such situations; for example, the solubilization of oxygen in water, which sustains aqueous life. Similarly, gases such as nitrogen, carbon dioxide, etc., display relatively low solubility (mole fraction: $10^{-5} - 10^{-2}$) in water or many solvents of industrial interest. Further, in many such instances, the solubility of a gas in a solvent is required at temperatures beyond the critical temperature of the gas. Application of vapour-liquid phase equilibria relations given by Raoult's law or its modified versions (discussed in the foregoing sections) to a solute species *i* (in a solvent) requires the saturation vapour pressure P_i^{sat} at the temperature of application. Clearly if the temperature of interest exceeds the critical temperature of the solute, the parameter P_i^{sat} is not definable, and hence such VLE relations presented in sections 7.5 and 7.6 are not appropriate in such cases.

As for any VLE problem the starting point for determining the solubility of a gaseous species 'i' in a liquid is the equality of the fugacity of the solute species and liquid (liq) phases:

$$\hat{f}_i^{gas} = \hat{f}_i^{liq} \qquad ..(7.81)$$

Using eqn. 7.45 (considering low to moderate pressures):

$$y_i\hat{\phi}_i P = x_i\gamma_i f_i \quad ..(7.45)$$

Denoting the gaseous solute as '1' and the solvent as '2', one may write:

$$\hat{f}_1^{gas} = \hat{f}_1^{liq} \quad ..(7.82)$$

And: $\hat{f}_2^{gas} = \hat{f}_2^{liq}$ ..(7.83)

Using eqn. 7.45 the last two equations may be re-written as:

$$y_1\hat{\phi}_1 P = x_1\gamma_1 f_1 \quad ..(7.84)$$

$$y_2\hat{\phi}_2 P = x_2\gamma_2 f_2 \quad ..(7.85)$$

If we further assume that the gas is very sparingly soluble in the solvent, the liquid phase is essentially pure solvent and the following relations derive:

$$\gamma_1 \cong \gamma_1^{\infty}$$

$$\gamma_2 \approx 1$$

Therefore, for component 1 we may rewrite the eqn. 7.84 as:

$$y_1\hat{\phi}_1 P = x_1\gamma_1^{\infty} f_1 \quad ..(7.86)$$

Or alternately:

$$y_1\hat{\phi}_1 P = x_1 H_1 \quad ..(7.87)$$

Where:

$$H_1 = \gamma_1^{\infty} f_1 \quad ..(7.88)$$

Equation 7.88 is termed the Henry's law, and H_1 the Henry's constant, which is defined at the system temperature. If one plots the value of $\hat{f}_1$ as a function of the gas mole fraction x_1 in the solvent phase (as shown schematically in fig. 7.13), the parameter H_1 corresponds to the slope of the tangent drawn on the curve at the limiting condition of $x_1 \to 0$.

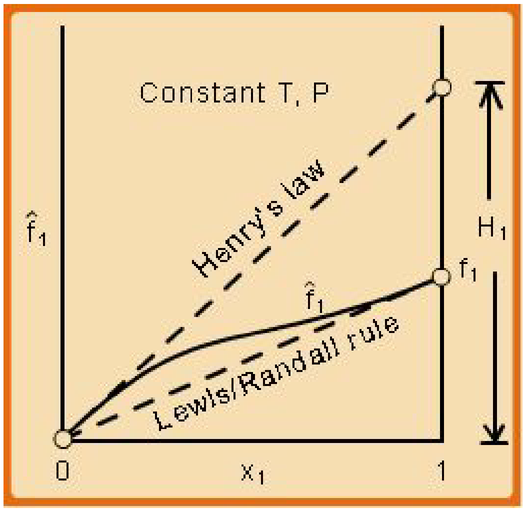


Fig. 7.13 Plot of $\hat{f}_1$ as a function of the gas mole fraction x_1

Similarly for component 2 the phase equilibrium equation 7.85 may be rewritten as:

$$y_2\hat{\phi}_2P \; = \; x_2H_2 \qquad ..(7.89)$$

Where: $H_2 = \gamma_2 f_2$ ..(7.90)

Since $\gamma_2 \approx 1,$ it follows that:

Where: $H_2 \; = \; f_2$ ..(7.91)

Thus: $\hat{f}_2 = \; x_2 f_2$ ..(7.92)

It may be noted that eqn. 7.92 is the same as 6.162 (section 6.15), which describes the Lewis -Randall rule. Thus when Henry's law is applicable for the solute then Lewis-Randall rule is applicable for the solvent. Since for a system temperature $T > T_{c,1}$ the fugacity $\hat{f}_1$ of pure liquid phase for '1' is hypothetical, it follows that the Henry's law constant $H_1 \; (= \gamma_1^{\infty} f_1)$ is necessarily a hypothetical quantity as well. Since solubility of a gas is temperature dependent, it follows that H_i is also a function of temperature. The Henry's law constant for a large number of gases with water as the solvent has been reported in the literature. For example for acetylene the value is 1350bar, for carbon dioxide 1670bar, and for air 72950bar). Fig. 7.14 presents the value of Henry's law constant for a number of gases in water as a function of temperature.

Example 7.8

A concentrated binary solution containing mostly species $2(butX_2 \neq 1)$ 2 (but $x_2 \neq 1$) is in equilibrium with a vapor phase containing both species 1 and 2. The pressure of this two-phase system is 1 bar; the temperature is 298.0K. Determine from the following data good estimates of x_1 and y_1. H_1 = 200 bar; P_2^{sat} = 0.10 bar.

(Click for solution)

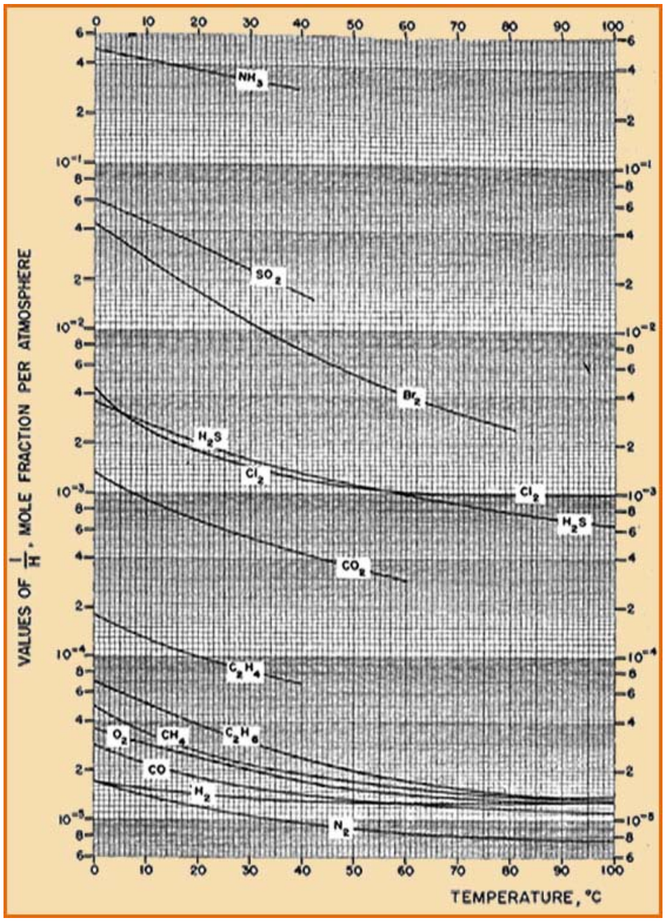


Fig. 7.14 Plot of Henry's Constant vs. Temperature, $\left[(1/H) = N(mole\ \ fraction)/P(atm)\right]$ [Reprinted with permission from O.A. Hougen, K.M. Watson, and R.A. Ragatz (1960), *Chemical Process Principles Charts,* 2nd ed., John Wiley & Sons, New York]

Assignment- Chapter 7

Chapter 8:Chemical Reaction Equilibria

8.1 Introduction

Reaction chemistry forms the essence of chemical processes. The very distinctiveness of the chemical industry lies in its quest for transforming less useful substances to those which are useful to modern life. The perception of old art of ‘alchemy’ bordered on the magical; perhaps in today’s world its role in the form of modern chemistry is in no sense any less. Almost everything that is of use to humans is manufactured through the route of chemical synthesis. Such reactive processes need to be characterized in terms of the maximum possible yield of the desired product at any given conditions, starting from the raw materials (i.e., reactants). The theory of chemical reactions indicates that rates of reactions are generally enhanced by increase of temperature. However, experience shows that the maximum quantum of conversion of reactants to products does not increase monotonically. Indeed for a vast majority the maximum conversion reaches a *maximum* with respect to reaction temperature and subsequently diminishes. This is shown schematically in fig. 8.1.

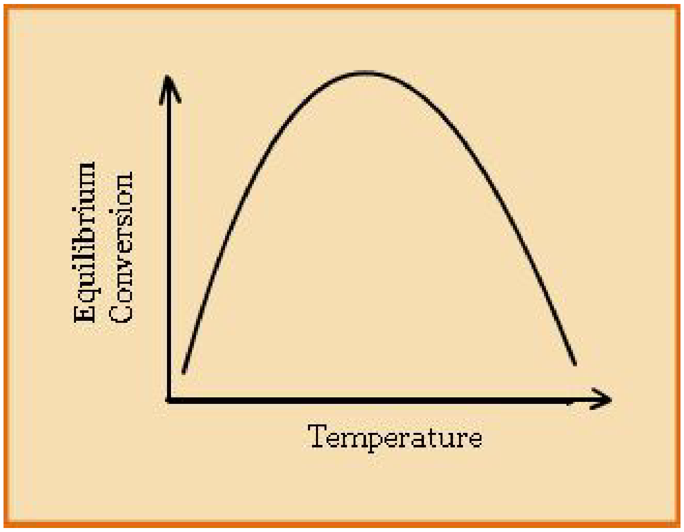


Fig. 8.1 Schematic of Equilibrium Reaction vs. Temperature

The reason behind this phenomenon lies in the molecular processes that occur during a reaction. Consider a typical reaction of the following form occurring in gas phase: $A(g)+B(g)\rightarrow C(g)+D(g)$. The reaction typically begins with the reactants being brought together in a reactor. In the initial phases, molecules of A and B collide and form reactive complexes, which are eventually converted to the products C and D by means of molecular rearrangement. Clearly then the early phase of the reaction process is dominated by the presence and depletion of A and B. However, as the process continues, the fraction of C and D in the reactor increases, which in turn enhances the likelihood of these molecules colliding with each other and undergoing transformation into A and B. Thus, while initially the *forward* reaction dominates, in time the *backward* reaction becomes increasingly significant, which eventually results in the two rates becoming equal. After this point is reached the concentrations of each species in the reactor becomes fixed and displays no further propensity to change unless propelled by any externally imposed "disturbance"(say, by provision of heat). Under such a condition the reaction is said to be in a state of *equilibrium*. The magnitude of all measurable macroscopic variables (T, P and composition) characterizing the reaction remains constant. Clearly under the equilibrium state the percentage conversion of the reactants to products must be the *maximum* possible at the given temperature and pressure. Or else the reaction would progress further until the state of equilibrium is achieved. The principles of chemical reaction thermodynamics are aimed at the prediction of this equilibrium conversion.

The reason why the equilibrium conversion itself changes with variation of temperature may be appreciated easily. The rates of the forward and backward reactions both depend on temperature; however, an increase in temperature will, in general, have different impacts on the rates of each. Hence the extent of conversion at which they become identical will vary with temperature; this prompts a change in the equilibrium conversion. Reactions for which the conversion is 100% or nearly so are termed *irreversible*, while for those which never attains complete conversion are essentially *reversible* in nature. The fact that a maxima may occur in the conversion behaviour (fig. 8.1) suggests that for such reactions while the forward reaction rates dominate at lower temperatures, while at higher temperatures the backward reaction may be predominant.

The choice of the reaction conditions thus depends on the maximum (or equilibrium) conversion possible. Further, the knowledge of equilibrium conversions is essential to intensification of a process. Finally, it also sets the limit that can *never* be crossed in practice regardless of the process strategies. This forms a primary input to the determination of the economic viability of a manufacturing process. If reaction equilibria considerations suggest that the maximum possible conversion over practical ranges of temperature is lower than that required for commercial feasibility no further effort is useful in its further development. On the other hand if the absolute maximum conversion is high then the question of optimizing the process conditions attain significance. Exploration of the best strategy for conducting the reaction (in terms of temperature, pressure, rate enhancement by use of catalytic aids, etc) then offers a critical challenge.

This chapter develops the general thermodynamic relations necessary for prediction of the equilibrium conversion of reactions. As we shall see, as in the case of phase equilibria, the Gibbs free energy of a reaction constitutes a fundamental property in the estimation of equilibrium conversion. The next section presents method of depicting the conversion by the means of the reaction co-ordinate, which is followed by estimation of the heat effects associated with all reactions. The principles of reaction equilibria are then developed.

8.2 Standard Enthalpy and Gibbs free energy of reaction

From the foregoing discussion it may be apparent that a chemical reaction may be carried out in diverse ways by changing temperature, pressure, and feed composition. Each of the different conditions would involve different conversions and heat effects. Thus there is need to define a “standard” way of carrying out a reaction. If all reactions were carried out in the same standard manner, it becomes possible to compare them with respect to heat effects, and equilibrium conversion under the same conditions. In general all reactions are subject to heat effects, whether small or large. A reaction may either release heat (exothermic) or absorb heat (endothermic). However, it is expected that the heat effect will vary with temperature. Thus, there is a need to develop general relations that allow computation of the heat effect associated with a reaction at any temperature.

Consider a reaction of the following form:

$$|\alpha_1| A_1 + |\alpha_2| A_2 \rightarrow |\alpha_3| A_3 + |\alpha_4| A_4 \qquad ..(8.1)$$

The reactants (A_1 and A_2) and products (A_3 and A_4) may be gaseous, liquid or solid. The term $|\alpha_i|$ is the stoichiometric coefficient corresponding to the chemical species A_i. For the purpose of development of the reaction equilibria relations it is convenient to designate the stoichiometric numbers of the reactants as *negative*, while those of the products as *positive*. This is to signify that reactants are *depleted* in proportion to their stoichiometric numbers, while the products are formed in proportion to their stoichiometric numbers. Consider, for example, the following gas-phase reaction:

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

The stoichiometric numbers are written as follows: $\alpha_{CH_4} = -1;\ \alpha_{O_2} = -2;\ \alpha_{CO_2} = 1;\ \alpha_{H_2O} = 2.$

The *standard enthalpy of reaction* $\Delta H^o_{T_0}$ at say at any temperature T is defined in the following manner: it is the *change* in enthalpy that occurs when $|\alpha_1|$ moles of $A_1$and $|\alpha_2|$ moles of B_2 in their *standard states* at temperature T convert *fully* to form $|\alpha_3|$moles of A_3 and $|\alpha_4|$ moles of A_4 in their respective standard states at the same temperature T. The standard states commonly employed are as follows:

— *Gases*: the pure substance in the ideal gas state at 1 bar

— *Liquids and Solids*: the pure liquid or solid at 1 bar

The conceptual schema of a standard reaction is depicted in fig. 8.1. All reactants *enter* and products *leave* the reactor in *pure* component form at the same temperature T, and at their respective standard states. In the literature, data on the standard enthalpy of reaction is typically reported at a

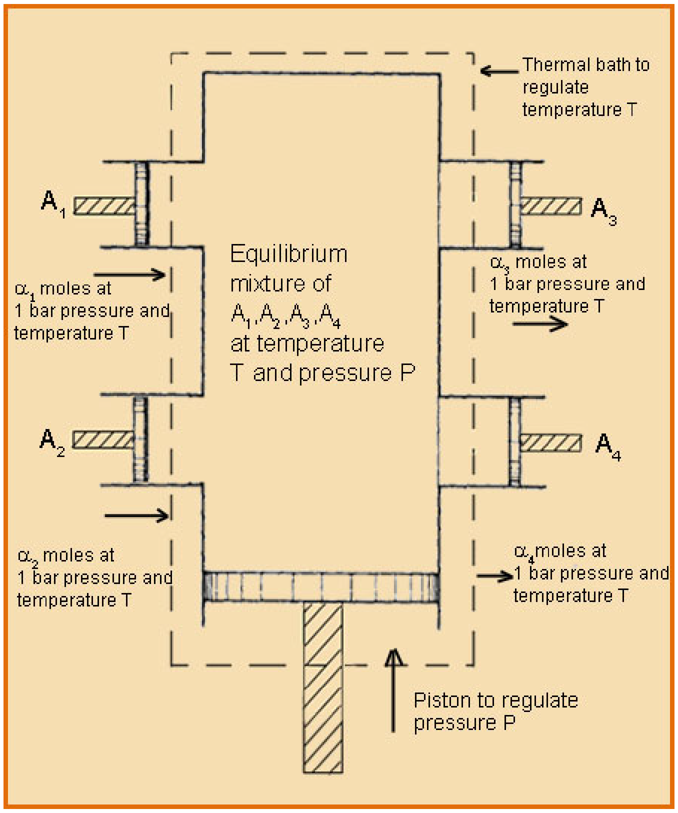


Fig. 8.2 Apparatus in which a gas-phase reaction occurs at equilibrium (van't Hoff equilibrium box)

temperature of 298^0K. Using the sign convention adopted above, the standard enthalpy of reaction at any temperature T may be mathematically expressed as follows:

$$\Delta H_T^0 = \sum_i \alpha_i H_{i,T}^0 \qquad ..(8.2)$$

Where, $H_{i,T}^0$ is the standard state enthalpy of species *'i'* at the temperature *T*, and the summation is over all the reactants and products. For example, on expansion the eqn. 8.2 takes the following form for the reaction depicted in eqn. 8.1:

$$\Delta H_T^0 = \alpha_3 H_{3,T}^0 + \alpha_4 H_{4,T}^0 - \alpha_1 H_{1,T}^0 - \alpha_2 H_{2,T}^0 \qquad ..(8.2)$$

If we further consider that each molecular species '*i*' is formed from *j* elements each, an expression for the standard enthalpy of formation results:

$$\Delta H_{f_i,T}^0 = H_{i,T}^0 - \sum_j \alpha_j H_{j,T}^0 \qquad ..(8.3)$$

Where, the summation is over all *j* constituent elements that make up the i^{th} molecule, $\Delta H_{f_i,T}^0$ is *standard state enthalpy of formation* of the i^{th} molecule at *T*, and $H_{j,T}^0$ the standard state enthalpy of the j^{th} atomic species. If all $H_{j,T}^0$ are *arbitrarily* set to zero as the basis of calculation then eqn. 8.3 simplifies to:

$$H_{i,T}^0 = \Delta H_{f_i,T}^0 \qquad ..(8.4)$$

In such a case eqn. 1 becomes:

$$\Delta H_T^0 = \sum_i \alpha_i \Delta H_{f_i,T}^0 \qquad ..(8.5)$$

Values of Standard Enthalpy of formation of select substances are shown in Appendix VIII.

For simplicity in the subsequent equations we drop the subscript T, but implicitly all terms correspond to temperature *T*. Now writing H_i^0 in a differential form:

$$dH_i^0 = C_{P_i}^0 dT \qquad ..(8.6)$$

Where $C_{P_i}^0$ is the specific heat of the i^{th} species corresponding to its standard state. Note that since the standard state pressure for all substances is 1 bar in terms of pressure, for gases $C_{P_i}^0 = C_{P_i}^{ig}$, while for liquids and solids it is the *actual* value of the specific heat at 1 bar $(C_{P_i}^0 = C_{Pi})$. Since the specific heat of liquids and solids are weakly dependent on pressure, it helps write eqn. 8.6 in the general form shown. The following summation may be applied on eqn. 8.6 to give:

$$\sum_i \alpha_i dH_i^0 = \sum_i \alpha_i C_{P_i}^0 dT \qquad ..(8.7)$$

Since each ξ_i is constant one may write:

$\sum_i d(\alpha_i H_i^0) = d\sum_i \alpha_i H_i^0$ ..(8.8)

Or: $d\sum_i \alpha_i H_i^0 = \sum_i \alpha_i C_{P_i}^0 dT$ ..(8.9)

Thus: $d\Delta H^0 = \sum_i \alpha_i C_{P_i}^0 dT = \Delta C_P^o dT$ ..(8.10)

Where, $\Delta C_P^o = \sum_i \alpha_i C_{P_i}^o$

Thus on integrating eqn. 8.10, between a datum T_0 and any T, we have:

$\Delta H_T^o = \Delta H_0^o + \int_{T_0}^{T} \Delta C_P^o dT$ ..(8.11)

Note that since the standard state pressure is always at 1 bar, for all species one may write the general form of relation for specific heat capacity:

$C_{P_i}^o = A_i + B_i T + C_i T^2 + \ldots$ ..(8.12)

(The values of and $C_{P_i}^o$ thus are those shown in *Appendix III).*

Eqn. 8.12 may be substituted in eqn. 8.11 which leads to:

$\Delta H_T^o = \Delta H_0^o + \int_{T_0}^{T} \left[(\Delta A) + (\Delta B)T + (\Delta C)T^2 + \ldots\right] dT$ ..(8.13)

Where: $\Delta A = \sum_i \alpha_i A_i$; $\Delta B = \sum_i \alpha_i B_i$; $\Delta C = \sum_i \alpha_i C_t$; $\Delta D = \sum_i \alpha_i D_t$; and so on.

The standard enthalpy of reaction is most often reported at 298^0K. Using this value as the datum, the value of the standard heat of reaction at any other temperature can be evaluated using eqn. 8.13. As evident from eqn. 8.5 the enthalpy of a reaction may be recovered from the enthalpy of formation of the individual species for a reaction. Values of standard enthalpy of formation for a select list of compounds are tabulated in Appendix VIII.

In continuance of the foregoing considerations one may also define a standard Gibbs free energy change of a reaction. As we will see in the later sections, this property is essential to computing the equilibrium constant for a reaction at any temperature. As with enthalpy of reaction (eqn. 8.2) the standard Gibbs free energy change at any temperature is given by the function:

$\Delta G_T^0 = \sum_i \alpha_i G_{i,T}^0$ ..(8.14)

Thus, ΔG_T^0 is the difference between the Gibbs energies of the products and reactants when each is in its standard state as a pure substance at the system temperature and at a fixed pressure. Thus, just as the standard enthalpy of reaction is dependent *only* on temperature (the standard state pressure being fixed by definition), so is the Gibbs free energy change of a reaction. It follows that when the temperature is fixed ΔG_T^0 is *independent* of the reaction pressure or composition. Indeed extending the argument, one can define any standard property change of reaction by the same expression; all being functions of temperature alone:

$$\Delta M_T^0 = \sum_i \alpha_i M_{i,T}^0 \qquad ..(8.15)$$

Where: $M \equiv U, H, S, A, G.$

In the context of chemical reaction equlibria the relations between the standard enthalpy of reaction and the standard Gibbs energy change of reaction is of particular significance. Using the form described by eqn. 5.31, since any standard property change of a reaction is only temperature dependent, one may write:

$$H_{i,T}^o = -RT^2 \frac{d\left(G_{i,T}^o / RT\right)}{dT} \qquad ..(8.16)$$

Multiplying of both sides of this equation by α_i and summing over all species one obtains:

$$\sum \alpha_i H_{i,T}^o = -\mathrm{RT}^2 \frac{d\left(\sum \alpha_i G_{i,T}^o / RT\right)}{dT}$$

This may be written as: $\Delta H_T^0 = -RT^2 \frac{d\left(\Delta G_T^0 / RT\right)}{dT}$ ..(8.17)

Or: $\frac{d\left(\Delta G_T^0 / RT\right)}{dT} = -\frac{\Delta H_T^0}{RT^2}$ ..(8.18)

Now substituting eqn. 8.13 in 8.18:

$$\frac{d\left(\Delta G_T^0 / RT\right)}{dT} = -\frac{1}{RT^2}\left[\Delta H_0^o + \left\{(\Delta A) + (\Delta B)T + (\Delta C)T^2 + ...\right\} dT\right]$$

If we know the standard Gibbs free energy change $\Delta G_{T_0}^0$ at a particular temperature T_0 (typically, values are reported at 298^{0}K) the above equation may be integrated as follows:

$$\frac{\Delta G_T^0}{RT} = \frac{\Delta G_{T_0}^0}{RT_0} - \int_{T_0}^{T} \left\langle \frac{1}{RT^2}\left[\Delta H_0^o + \left\{(\Delta A) + (\Delta B)T + (\Delta C)T^2 + ...\right\} dT\right]\right\rangle dT \qquad ..(8.19)$$

Or finally:

$$\frac{\Delta G_T^0}{T} = \frac{\Delta G_{T_0}^0}{T_0} - \int_{T_0}^{T} \left\langle \frac{1}{T^2}\left[\Delta H_0^o + \left\{(\Delta A) + (\Delta B)T + (\Delta C)T^2 + \ldots\right\} dT\right]\right\rangle dT \qquad ..(8.20)$$

<u>Example 8.1</u>

Consider the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the Gibbs free energy of the reaction, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

Species	**a**	**bx10^3**	**cx10^6**	**dx10^9**	**ex10^{-5}**
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

(Click for Solution)

8.3 The Reaction Coordinate

Consider again the general chemical reaction depicted in eqn. 8.1:

$$|\alpha_1|A_1 + |\alpha_2|A_2 = |\alpha_3|A_3 + |\alpha_4|A_4$$

During the progress of the reaction, at each point the extent of depletion of the reactants, and the enhancement in the amount of product is exactly in proportion to their respective stoichiometric coefficients. Thus for any change dn_i in the number of moles of the ith species for a differential progress of the reaction one may write:

$$\frac{dn_1}{\alpha_1} = \frac{dn_2}{\alpha_2} = \ldots = \frac{dn_3}{\alpha_3} = \frac{dn_4}{\alpha_4} \qquad ..(8.21)$$

Since all terms are equal, they can all be set equal to a single quantity $d\xi$, defined to represent *the extent of reaction* as follows:

$$\frac{dn_1}{\alpha_1} = \frac{dn_2}{\alpha_2} = \ldots = \frac{dn_3}{\alpha_3} = \frac{dn_4}{\alpha_4} = d\xi \qquad ..(8.22)$$

The general relation between a differential change dn_i in the number of moles of a reacting species and $d\xi$ is therefore: $dn_i = \alpha_i d\xi \quad (i = 1, 2, \ldots N)$ ..(8.23)

This new variable ξ, called the *reaction coordinate*, describe the extent of conversion of reactants to products for a reaction. Thus, it follows that the value of ξ is zero at the start of the reaction. On the other hand when $\xi = 1$, it follows that the reaction has progressed to an extent at which point each reactant has depleted by an amount equal to its stoichiometric number of moles while each product has formed also in an amount equal to its stoichiometric number of moles. For dimensional consistency one designates such a degree of reaction as corresponding to $\Delta\xi = 1$ mole.

Now, considering that at the point where the reaction has proceeded to an arbitrary extent characterized by ξ (such that $\xi > 0$), the number of moles of i^{th} species is n_i we obtain the following relation:

$\int_{n_{i0}}^{n_i} dn_i = \alpha_i \int_0^{\xi} d\eta$; where, η is a dummy variable and n_{i0} = initial number of moles of '*i*'. Thus:

$$n_i = n_{i_o} + \alpha_i \xi \text{ ;(i = 1,2,...,N)} \qquad ..(8.24)$$

Thus the *total* number of moles of all species corresponding to ξ extent of reaction**:**

$$n = \sum n_i = \sum n_{i_o} + \xi \sum \alpha_i \qquad ..(8.25)$$

Or: $n = n_0 + \alpha\xi$ ..(8.26)

Where:

$$n_0 = \sum n_{i_o} \qquad ..(8.27)$$

$$\alpha = \sum \alpha_i \qquad ..(8.28)$$

Thus, $y_i = \dfrac{n_i}{n} = \dfrac{n_{i_{io}} + \alpha_i \xi}{n_o + \alpha\xi}$ ..(8.29)

Example 8.2

Consider the following reaction: A(g) + B(g) = C(g) + 3D(g).

Intially the following number of moles are introduced in the reactor. Obtain the mole fraction expressions in terms of reaction coordinate.

$n_{0,A}$ = 2 mol, $n_{0,B}$ = 1 mol, $n_{0,C}$ = 1 mol $n_{0,D}$ = 4 mol

(Click for Solution)

The foregoing approach may be easily extended to develop the corresponding relations for a set of multiple, independent reactions which may occur in a thermodynamic system. In such a case each reaction is assigned an autonomous reaction co-ordinate ξ_j **(**to represent the *j*th reaction**).** Further the stoichiometric coefficient of the *i*th species as it appears in the *j*th reaction is designated by $\alpha_{i,j}$. Since a species may participate in more than a single reaction, the change in the total number of moles of the species at any point of time would be the sum of the change due each independent reaction; thus, in general:

$$dn_i = \sum_j \alpha_{i,j} d\xi_j \qquad (i = 1,2,...N) \qquad ..(8.30)$$

On integrating the above equation starting from the initial number of moles n_{i_o} to n_i corresponding to the reaction coordinate ξ_j of each reaction:

$$\int_{n_{i0}}^{n_i} dn_i = \int_0^{\xi_i} \sum_j \alpha_{i,j} d\xi_j \ (i = 1,2,...,N) \qquad ..(8.31)$$

Or: $n_i = n_{i_o} + \sum_j \alpha_{i,j}\xi_j$ ..(8.32)

Summing over all species gives:

$$\sum_i n_i = \sum_i n_{i_o} + \sum_i \sum_j \alpha_{i,j} d\xi_j \qquad ..(8.33)$$

Now: $\sum_i n_i = n$ and, $\sum_i n_{i_o} = n_0$ ..(8.34)

We may interchange the order of the summation on the right side of eqn. (8.33); thus:

$$\sum_i \sum_j \alpha_{i,j} d\xi_j = \sum_j \sum_i \alpha_{i,j} d\xi_j \qquad ..(8.35)$$

Thus, using eqns. 8.34 and 8.35, eqn. 8.33 may be written as:

$$n = n_0 + \sum_j \left(\sum_i \alpha_{i,j} \right) \xi_j \qquad ..(8.36)$$

In the same manner as eqn. 8.28, one may write: .

$$\alpha_j = \sum_i \alpha_{i,j} \qquad ..(8.37)$$

Thus eqn. 8.33 becomes: $n = n_0 + \sum_j \alpha_j \xi_j$ ..(8.38)

Using eqns. 8.32 and 8.38 one finally obtains:

$$y_i = \frac{n_{i_o} + \sum_j \alpha_{i,j}\xi_j}{n_o + \sum_j \alpha_j \xi_j} \qquad (i = 1,2,....,N) \qquad ..(8.39)$$

Example 8.3

Consider the following simultaneous reactions. Express the reaction mixture composition as function of the reaction co-ordinates. All reactants and products are gaseous.

A + B = C + 3D ..(1)

A + 2B = E + 4D ..(2)

Initial number of moles: $n_{0,A}$ = 2 mol; $n_{0,B}$ = 3 mol

(Click for Solution)

8.4 Criteria for Chemical Reaction Equilibrium

The general criterion for thermodynamic equilibrium was derived in section 6.3 as:

$$(dG^t)_{T,P} \le 0 \qquad ..(6.36b)$$

As already explained, the above equation implies that if a closed system undergoes a process of change while being under thermal and mechanical equilibrium, for all incremental changes associated with the compositions of each species, the total Gibbs free energy of the system would decrease. At complete equilibrium the equality sign holds; or, in other words, the Gibbs free energy of the system corresponds to the minimum value possible under the constraints of constant (and uniform) temperature and pressure. Since the criterion makes no assumptions as to the nature of the system in terms of the number of species or phases, or if reactions take place between the species, it may also be applied to determine a specific criterion for a reactive system under equilibrium.

As has been explained in the opening a paragraph of this chapter, at the initial state of a reaction, when the reactants are brought together a state of non-equilibrium ensues as reactants begin undergoing progressive transformation to products. However, a state of equilibrium must finally attain when the rates of forward and backward reactions equalize. Under such a condition, no further change in the composition of the residual reactants or products formed occurs. However, if we consider this particular state, we may conclude that while in a macroscopic sense the system is in a state of *static* equilibrium, in the microscopic sense there is dynamic equilibrium as reactants convert to products and vice versa. Thus the system is subject to minute fluctuations of concentrations of each species.

However, by the necessity of maintenance of the dynamic equilibrium the system always returns to the state of stable thermodynamic equilibrium. In a macroscopic sense then the system remains under the under equilibrium state described by eqn. 6.36b. It follows that in a reactive system at the state of chemical equilibrium the Gibbs free energy is minimum subject to the conditions of thermal and mechanical equilibrium.

The above considerations hold regardless of the number of reactants or the reactions occurring in the system. Since the reaction co-ordinate is the single parameter that relates the compositions of all the species, the variation of the total Gibbs free energy of the system as a function of the reaction co-ordinate may be shown schematically as in fig. 8.3; here ξ_e is the value of the reaction co-ordinate at equilibrium.

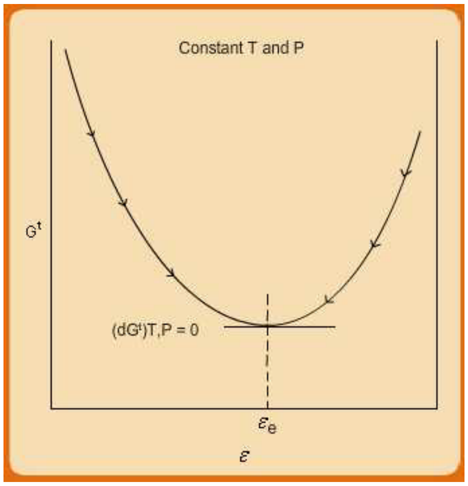


Fig. 8.3 Variation of system Gibbs free energy with equilibrium conversion

8.5 The Equilibrium Constant of Reactions

Since chemical composition of a reactive system undergoes change during a reaction, one may use the eqn. 6.41 for total differential of the Gibbs free energy change (for a single phase system):

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i dn_i \qquad ..(6.41)$$

For simplicity considering a single reaction occurring in a closed system one can rewrite the last equation using eqn. 8.3:

$$d(nG) = (nV)dP - (nS)dT + \sum \mu_i \alpha_i d\xi \qquad ..(8.40)$$

It follows that: $\sum \alpha_i \mu_i = \left[\frac{\partial(nG)}{\partial \xi}\right]_{T,P}$ ..(8.41)

On further applying the general condition of thermodynamic equilibrium given by eqn. 6.36b it follows that:

$$\left[\frac{\partial(nG)}{\partial\xi}\right]_{T,P} \equiv \left[\frac{\partial G^t}{\partial\xi}\right]_{T,P} = 0 \qquad ..(8.42)$$

Hence by eqn. 8.41 and 8.42:

$$\sum \alpha_i \mu_i = 0 \qquad ..(8.43)$$

Since the reactive system is usually a mixture one may use the eqn. 6.123:

$d\mu_i = d\overline{G}_i = RTd\ln \hat{f}_i$; at constant T ..(6.123)

Integration of this equation at constant T from the standard state of species *i* to the reaction pressure:

$$\mu_{i,T} = G^o_{i,T} + RT\ ln\frac{\hat{f}_i}{f^o_i} \qquad ..(8.44)$$

The ratio $\hat{f}_i/f^o_i$ is called the activity $\hat{a}_i$ of species *i* in the reaction mixture, i.e.:

$$\hat{a}_i = \frac{\hat{f}_i}{f^o_i} \qquad ..(8.45)$$

Thus, the preceding equation becomes: $\mu_{i,T} = G^0_{i,T} + RT\ln\hat{a}_i$ ..(8.46)

Using eqns. 8.46 and 8.44 in eqn. 8.43 to eliminate μ_i gives:

$$\sum \alpha_i (G^o_{i,T} + RT\ ln\ \hat{a}_i) = 0 \qquad ..(8.47)$$

On further re-organization we have:

$$\sum \nu_i G^o_{i,T} + RT\sum \ln(\hat{a}_i)^{\alpha_i} = 0$$

$$\ln\left[\prod(\hat{a}_i)^{\alpha_i}\right] = -\frac{\sum \alpha_i G^o_{i,T}}{RT} \qquad ..(8.48)$$

Where, $\prod$ signifies the product over all species *i*. Alternately:

$$\prod(\hat{a}_i)^{\alpha_i} = exp\left(-\frac{\sum \alpha_i G^o_{i,T}}{RT}\right) \qquad ..(8.49)$$

$$\prod(\hat{a}_i)^{\alpha_i} = \Pi\left(\hat{f}_i / f^0_i\right)^{\alpha_i} = K_T \qquad ..(8.50)$$

On comparing eqns. 8.49 and 8.50 it follows: $K_T = exp\left(-\frac{\sum \alpha_i G^o_{i,T}}{RT}\right)$ ..(8.51)

The parameter K_T is defined as the equilibrium constant for the reaction at a given temperature. Since the standard Gibbs free energy of pure species, $G_{i,T}^o$, depends only on temperature, the equilibrium constant K_T is also a function of temperature alone. On the other hand, by eqn. 8.50 K_T is a function of $\hat{f}_i$, which is in turn a function of composition, temperature and pressure. Thus, it follows that since temperature fixes the equilibrium constant, any variation in the pressure of the reaction must lead to a change of equilibrium composition subject to the constraint of K_T remaining constant. Equation (8.51) may also be written as:

$$-RT\ln K_T = \sum \alpha_i G_{i,T}^o = \Delta G_T^0 \qquad ..(8.52)$$

$$\ln K_T = -\frac{\Delta G_T^0}{RT} \qquad ..(8.53)$$

Taking a differential of eqn. 8.53:

$$\frac{d\ln K_T}{dT} = -\frac{d\left(\Delta G_T^0/RT\right)}{dT} \qquad ..(8.53)$$

Now using eqn. 8.18:

$$\frac{d\ln K_T}{dT} = \frac{\Delta H_T^0}{RT^2} \qquad ..(8.54)$$

On further use of eqn. 8.13:

$$\frac{d\ln K_T}{dT} = \frac{\Delta H_0^o + \int_{T_0}^{T}\left[(\Delta A) + (\Delta B)T + (\Delta C)T^2 + ...\right]}{RT^2}$$

Lastly, upon integration one obtains the following expression:

$$\ln K_T = \ln K_{T_0} - \frac{\Delta H_0^o + \int_{T_0}^{T}\left[(\Delta A) + (\Delta B)T + (\Delta C)T^2 + ...\right]dT}{RT^2} \qquad ..(8.55)$$

Where, K_{T_0} is the reaction equilibrium constant at a temperature T_0.

If ΔH_T^0, is assumed independent of T (i.e. ΔH_{avg}^0, over a given range of temperature $(T_2 - T_1)$, a simpler relationship follows from eqn. 8.54:

$$\ln\frac{K_{T2}}{K_{T1}} = -\frac{\Delta H_{avg}^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad ..(8.55)$$

The above equation suggests that a plot of $\ln K_T$ vs. $1/T$ is expected to approximate a straight line. It also makes possible the estimation of the equilibrium constant at a temperature given its values at another temperature. However, eqn. 8.55 provides a more rigorous expression of the equilibrium constant as a function of temperature.

Equation 8.54 gives an important clue to the variation of the equilibrium constant depending on the heat effect of the reaction. Thus, if the reaction is exothermic, i.e., $\Delta H_T^0 < 0,$ the equilibrium constant decreases with increasing temperature. On the other hand, if the reaction is endothermic, i.e., $\Delta H_T^0 > 0,$ equilibrium constant increases with increasing temperature. As we shall see in the following section, the equilibrium conversion also follows the same pattern.

Example 8.4

Consider again the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the equilibrium constant, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

Species	a	bx10^3	cx10^6	dx10^9	ex10^{-5}
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

(Click for solution)

8.6 Reactions involving gaseous species

We now consider eqn. 8.50 that represents a relation that connects equilibrium composition with the equilibrium constant for a reaction. The activities $\hat{a}_i$ in eqn. 8.50 contains the standard state fugacity of each species which – as described in section 8.1 – is chosen as that of pure species at 1 bar pressure. The assumption of such a standard state is necessarily arbitrary, and any other standard state may be chosen. But the specific assumption of 1 bar pressure is convenient from the point of calculations. Obviously the value of the state Gibbs free energy G_i^o of the species needs to correspond to that at the standard state fugacity. In the development that follows we first consider the case of reactions where all the species are gaseous; the case of liquids and solids as reactants are considered following that.

For a gas the standard state is the *ideal-gas state* of pure *i* at a pressure of 1 bar. Since a gaseous species at such a pressure is considered to be in an ideal gas state its fugacity is equal to its pressure; hence at the standard state assumed at the present, f_i^o = 1 bar for each species of a gas-phase reaction. Thus, the activity and hence eqn. 8.50 may be re-written as follows:

$$\hat{a}_i = \hat{f}_i / f_i^o = \hat{f}_i \qquad ..(8.56)$$

$$K = \prod \left(\hat{f}_i \right)^{\alpha_i} \qquad ..(8.57)$$

For the use of eqn. 8.57, the fugacity $\hat{f}_i$ must be specified in bar [or (atm)] because each $\hat{f}_i$ is implicitly divided by f_i^o 1 bar [or 1(atm)]. It follows that the equilibrium constant K_T is dimensionless. This is true also for the case of liquid and/or solid reactive species, though, as is shown later, the standard state fugacity is not necessarily 1 bar, since for condensed phases the fugacity and pressure need not be identical at low pressures.

By eqn. 6.129, for gaseous species, $\hat{f}_i = \hat{\phi}_i y_i P.$ Thus eqn. 8.57 may be rewritten as:

$$K_T = \prod \left(\hat{\phi}_i y_i P \right)^{\alpha_i} \qquad ..(8.58)$$

On further expanding the above equation:

$$K_T = \left\{ \prod \left(\hat{\phi}_i \right)^{\alpha_i} \right\} \left\{ \prod \left(y_i \right)^{\alpha_i} \right\} \left\{ \prod \left(P \right)^{\alpha_i} \right\} \qquad ..(8.59)$$

Or:

$$K_T = K_\phi K_y P^\alpha \qquad ..(8.60)$$

Where:

$$K_\phi = \left\{ \prod \left(\hat{\phi}_i \right)^{\alpha_i} \right\} \qquad ..(8.61)$$

$$K_y = \left\{ \prod \left(y_i \right)^{\alpha_i} \right\} \qquad ..(8.62)$$

$$\left\{ \prod \left(P \right)^{\alpha_i} \right\} = P^{\sum_i \alpha_i} = P^\alpha \qquad ..(8.63)$$

An alternate from of eqn. 8.60 is:

$$K_\phi K_y = K_T P^{-\alpha} \qquad ..(8.64)$$

Both the terms K_ϕ and K_y contain the mole fraction y_i of each species. As given by eqn. 8.29 or 8.39, all the mole fractions may be expressed as a function of the reaction co-ordinate ξ of the reaction(s). Hence, for a reaction under equilibrium at a given temperature and pressure the only unknown in eqn. 8.64 is the equilibrium reaction co-ordinate ξ_e. An appropriate model for the fugacity coefficient (based on an EOS: virial, cubic, etc.) may be assumed depending on the pressure, and eqn. 8.64 may then solved using suitable algorithms to yield the equilibrium mole fractions of each species. A relatively simple equation ensues in the event the reaction gas mixture is assumed to be ideal; whence $\hat{\phi}_i = 1$. Thus, eqn. 8.64 simplifies to:

$$K_y = K_T P^{-\alpha} \qquad ..(8.65)$$

Or:

$$\Pi\left(y_i\right)^{\alpha_i} = P^{-\alpha} K \qquad ..(8.66)$$

Yet another simplified version of eqn. 8.64 results on assuming *ideal solution* behavior for which (by eqn.7.84): $\hat{\phi}_i = \phi_i$. Thus:

$$K_\phi = \left\{\Pi\left(\phi_i\right)^{\alpha_i}\right\} \qquad ..(8.67)$$

This simplification renders the parameter K_ϕ independent of composition. Once again a suitable model for fugacity coefficient (using an EOS) may be used for computing each ϕ_i and eqn. 8.64 solved for the equilibrium conversion.

Example 8.5

Consider the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

Species	**a**	**$bx10^3$**	**$cx10^6$**	**$dx10^9$**	**$ex10^{-5}$**
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

(Click for solution)

8.7 Reaction equilibria for simultaneous reactions

While we have so far presented reaction equlibria for single reactions, the more common situation that obtains in industrial practice is that of multiple, simultaneous reactions. Usually this occurs due to the presence of 'side' reactions that take place in addition to the main, desired reaction. This leads to the formation of unwanted side products, necessitating additional investments in the form of purification processes to achieve the required purity of the product(s). An example of such simultaneously occurring reaction is:

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

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

Clearly the challenge in such cases is to determine the reaction conditions (of temperature, pressure and feed composition) that maximize the conversion of the reactants to the desired product(s). Essentially there are two methods to solve for the reaction equilibria in such systems.

Method 1: Use of reaction-co-ordinates for each reaction

This is an extension of the method already presented in the last section for single reactions. Consider, for generality, a system containing *i* chemical species, participating in *j* *independent* parallel reactions, each defined by a reaction equilibrium constant K_j and a reaction co-ordinate ξ_j. One can then write a set of *j* equations of the type 8.64 as follows:

$$(K_\phi)_j (K_y)_j = K_{T,j} P^{-\alpha_j} \qquad ..(8.68)$$

Where, α_j and y_i are given by eqns. 8.37 and 8.39 respectively (as follows):

$$\alpha_j = \sum_i \alpha_{i,j} \qquad ..(8.37)$$

And, $$y_i = \frac{n_{i_o} + \sum_j \alpha_{i,j}\xi_j}{n_o + \sum_j \alpha_j \xi_j} \qquad (i = 1,2,....,N) \qquad ..(8.39)$$

Therefore there are *j* unknown reaction co-ordinates which may be obtained by solving simultaneously *j* equations of the type 8.68.

Example 8. 6

The following two independent reactions occur in the steam cracking of methane at 1000 K and 1 bar: $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$; and $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$. Assuming ideal gas behaviour 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, and that at 1000K, the equilibrium constants for the two reactions are 30 and 1.5 respectively.

(Click for solution)

Method 2: Use of Lagrangian Undetermined Multipliers

This method utilizes the well-known Lagrangian method of undetermined multipliers typically employed for optimizing an objective function subject to a set of constraints. As outlined in section 8.3 at the point of equilibrium in a reactive system, the total Gibbs free energy of the system is a minimum. Further, during the reaction process while the total number of moles may not be conserved, the total mass of each atomic species remains constant. Thus, in mathematical terms, the multi-reaction equilibria problem amounts to minimizing the total Gibbs free energy of the system subject to the constraint of conservation of total atomic masses in the system. The great advantage that this approach offers over the previous method is that one does not need to explicitly determine the set of independent chemical reactions that may be occurring in the system.

We formulate below the set of equations that need to be solved to obtain the composition of the system at equilibrium. Let there be N chemical (reactive) species and p (corresponding) elements in a system; further, n_i= initial no of moles of species i; β_{ik} = number of atoms of k^{th} element in the i^{th} chemical species; β_k = total number of atomic masses of k^{th} element as available in the initial feed composition.

$$\sum_i n_i \beta_{ik} = \beta_k; \ (k = 1, 2\ldots, p) \qquad ..(8.69)$$

Or: $$\sum_i n_i \beta_{ik} - \beta_k = 0; \ (k = 1, 2\ldots, p) \qquad ..(8.70)$$

Use of *p* number of Lagrangian multipliers (one for each element present in the system) give:

$$\lambda_k\left(\sum_i n_i\beta_{ik}-\beta_k\right)=0;\quad (k\ =\ 1,2\ldots,\ p) \qquad ..(8.71)$$

These equations are summed over *p*, giving:

$$\sum_p \lambda_k\left(\sum_i n_i\beta_{ik}\text{ - }\beta_k\right)=0 \qquad ..(8.72)$$

Let G^t be the total Gibbs free energy of the system. Thus, incorporating p equations of the type 8.72 one can write the total Lagrangian *L* for the system as follows:

$$L=G^t+\sum_p \lambda_k\left(\sum_i n_i\beta_{ik}-\beta_k\right) \qquad ..(8.73)$$

It may be noted that in eqn. 8.73, *L* always equals G^t as the second term on the RHS is identically zero. Therefore, *minimum* values of both *L*and G_t occur when the partial derivatives of *L* with respect to all the n_i and λ_k are zero.

Thus: $$\left(\frac{\partial F}{\partial n_i}\right)_{T,P,n_{j\neq i}}=\left(\frac{\partial G^t}{\partial n_i}\right)_{T,P,n_{j\neq i}}+\sum_k \lambda_k\beta_{ik}=0;\quad (i\ =\ 1,2,\ldots,N) \qquad ..(8.74)$$

However, the first term on the RHS is the chemical potential of each reactive species in the system; thus eqn. 8.74 may be written as:

$$\mu_i+\sum_k \lambda_k\beta_{ik}=0;\quad (i\ =\ 1,2,\ldots,N) \qquad ..(8.75)$$

But by eqn. 8.44:

$$\mu_{i,T}=G^o_{i,T}+RTln\left(\hat{f}_i/f_i^o\right) \qquad ..(8.44)$$

Once again, we consider, for illustration, the case of gaseous reactions for which the standard state pressure for each species is 1 bar, whence, $f_i^0=1bar$.

$$\mu_{i,T}=G^o_{i,T}+RTln\left(\hat{f}_i\right) \qquad ..(8.76)$$

$$\mu_{i,T}=\Delta G^o_{f_i,T}+RT\ln\left(y_i\hat{\phi}_iP\right) \qquad ..(8.77)$$

In the above equation $G^o_{i,T}$ may be equated to $\Delta G^o_{f_i,T}$, the latter being the standard Gibbs free energy of formation of the '*i*' species (at temperature *T*). In arriving at this relation, the standard Gibbs free energy of formation of the elements comprising the i^{th} species are arbitrarily set to zero (for convenience of calculations). Thus combining eqns. 8.75 and 8.77 one obtains:

$$\Delta G^o_{f_i,T} + RT\ln\left(y_i\hat{\phi}_i P\right) + \sum_k \lambda_k \beta_{ik} = 0; \quad \left(i \ = \ 1,2,\ldots,N\right); \qquad ..(8.78)$$

In eqn. 8.78, the reaction pressure *P* needs to be specified in bar (as $f_i^0 = 1bar$). Also, if the i^{th} species is an element, the corresponding $\Delta G^0_{f_i,T} = 0$

Further taking the *partial* derivative of the Lagrangian *L* (of eqn. 8.73) $(\partial L/\partial \lambda_k)_{n_i,\lambda_{n\neq k}}$ with respect to each of the *p* undetermined multipliers, an additional set of *p* equations of type 8.70 obtains. Thus there are a total of $(N+p)$ equations which may be solved simultaneously to obtain the complete set of equilibrium mole fractions of *N* species.

Example 8.7

The gas n-pentane (1) is known to isomerise into neo-pentane (2) and iso-pentane (3) according to the following reaction scheme: $P_1 \rightleftharpoons P_2; P_2 \rightleftharpoons P_3; P_3 \rightleftharpoons P_1$. 3 moles of pure n-pentane is fed into a reactor at 400°K and 0.5 atm. Compute the number of moles of each species present at equilibrium.

Species	ΔG_f^0 at 400°K (Cal/mol)
P_1	9600
P_2	8900
P_3	8200

8.8 Reactions involving Liquids and Solids

In many instances of industrially important reactions, the reactants are not only gaseous but are also liquids and / or solids. Such reactions are usually *heterogeneous* in nature as reactants may exist in separate phases. Some examples include:

- Removal of CO_2 from synthesis gas by aqueous solution of potassium carbonate
- Removal of H_2S by ethanolamine or sodium hydroxide
- Air oxidation of aldehydes to acids
- Oxidation of cyclohexane to adipic acid
- Chlorination of benzene

- Decomposition of $CaCO_3$ to CaO and CO_2

In all such instances some species need to dissolve and then diffuse into another phase during the process of reaction. Such reactions therefore require not only reaction equilibria considerations, but that of phase equilibria as well. For simplicity, however we consider here only reaction equilibria of instances where liquid or solid reactive species are involved. The thermodynamic treatment presented below may easily be extended to describe any heterogeneous reaction. The basic relation for the equilibrium constant remains the starting point. By eqn. 8.50 we have:

$$K_T = \prod \left(\hat{a}_i\right)^{\alpha_i} \qquad ..(8.50)$$

On expanding (by eqn. 6.171):

$$\hat{a}_i = \hat{f}_i\left(T, P,\ x_i\right) / \ f_i^0 \qquad ..(8.79)$$

As already mentioned in section 8.1 above, for solids and liquids the usual standard state is the *pure* solid or liquid at 1 bar [or 1(atm)] and at the temperature (T) of the system. However, unlike in the case of gaseous species, the value of f_i^o for such a state cannot be 1 bar (or 1 atm), and eqn.(8.50) cannot be reduced to the form simple form of eqn. 8.57.

Liquid-phase reactants

On rewriting eqn. 8.79:

$$\hat{f}_i\left(T, P,\ x_i\right) = x_i \gamma_i f_i$$

Thus:

$$\hat{a}_i = x_i \gamma_i f_i(T, P) / \ f_i^0(T, 1bar) \qquad ..(8.80)$$

By eqn. 6.115:

$$RTdlnf_i = V_i dP$$

Thus on integrating:

$$\int_{f_i^0(T,1bar)}^{f_i(T,P)} d\ln f_i = \int_1^P \frac{V_i}{RT} dP \qquad ..(8.81)$$

As we have already seen in section 6.10, the liquid phase properties, such as molar volume, are weakly dependent on pressure; hence their variation with respect to pressure may be, for most practical situations, considered negligible. Thus, if one considers that in the last equation the molar volume V_i is constant over the range 1 – P bar, one obtains:

$$\ln\left[\frac{f_i}{f_i^0}\right]=\frac{V_i(P-1)}{RT}$$ ..(8.82)

$$\therefore\ f_i\,/\,f_i^o=\exp\ \left\{\frac{V_i(P-1)}{RT}\right\}$$ ..(8.83)

Thus, using eqn. 8.53 in 8.50:

$$K_T=\Pi\left(\hat{a}_i\right)^{\alpha_i}=\left[\pi\left(x_i\gamma_i\right)^{\alpha_i}\right]\ \left[\Pi\left(f_i\,/\,f_i^o\right)^{\alpha_i}\right]$$ ..(8.84)

Or: $\Pi\left(f_i\,/\,f_i^o\right)^{\alpha_i}=\exp\ \left[\left(\frac{P\text{-}1}{RT}\right)\sum\alpha_iV_i\right]$

Thus:

$$K_T=\left[\Pi\left(x_i\gamma_i\right)^{\alpha_i}\right]\ \exp\ \left[\frac{(P\text{-}1)\sum\alpha_iV_i}{RT}\right]$$ ..(8.85)

Except for very high pressure the exponential term on the right side of the above equation: $(P\text{-}1)\sum\alpha_iV_i << RT$.

Thus one may approximate:

$$\exp\ \left[\frac{(P\text{-}1)\sum\alpha_iV_i}{RT}\right]\approx 1.0$$

Whence:

$$K_T\simeq\prod\left(x_i\gamma_i\right)^{\alpha_i}$$ ..(8.86)

To use the above equation for prediction of the equilibrium composition one needs to employ a suitable activity coefficient model. The activity coefficient models described in section 6.18 are based on physical interactions between molecules. Hence, their use is not expected to be adequately representative of a situation where molecules are subject to specific chemical forces and are chemically transformed due to formation of intermediate reactive complexes. While it is possible to write models for physical interactions it is generally not feasible to establish quantitative relations that describe the microscopic-level interactions between reactive molecular species. Discussions on approaches to solve such problems may be found elsewhere (J.M. Prausnitz, R.N. Lichtenthaler and E.G. Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria,* 3rd ed., Prentice Hall, 1998). Nevertheless, for the purpose of illustrating an approximate solution, one may simplify eqn. 8.86 by assuming ideal solution behavior, wherein $\gamma_i = 1.0$. Hence:

$$K = \prod (x_i)^{\alpha_i} \qquad ..(8.87)$$

However, since reactive solutions can never be ideal, one way to overcome the difficulty is by defining a reaction equilibrium constant based on molar concentration (say in moles/m^3), rather than in terms of mole fractions. Thus:

$$K_c = \prod (C_i)^{\alpha_i} \qquad ..(8.88)$$

Where, C_i = molar concentration of each species.

It is generally difficult to predict the equilibrium constant K_C, and one needs to use experimentally determine values of such constants in order to predict equilibrium compositions.

Example 8.8

Consider the liquid phase reaction: A(l) + B(l) → C(l) + D(l). At 50^{o}C, the equilibrium constant is 0.09. Initial number of moles, $n_{A,0}$ = 1 mole; $n_{B,0}$ = 1 mol Find the equilibrium conversion. Assume ideal solution behaviour.

(Click for solution)

Solid-phase reactants

Consider a solid reactive species now, for which one again starts from eqn. 8.80:

$$\hat{a}_i = \hat{f}_i(T, P, x_i) / f_i^0 \qquad ..(8.80)$$

Thus as for a liquid reactant one has

$$\hat{a}_i = (x_i\gamma_i)\left(f_i / f_i^0\right) = \hat{a}_i = (x_i\gamma_i)\exp\left[\frac{(P-1)V_i}{RT}\right]$$

As it is for liquid species, V_i for solids is also small and remains practically constant with pressure, thus:

$$\exp\left[\frac{(P\text{-}1)\sum \alpha_i V_i}{RT}\right] \approx 1.0$$

In addition, the solid species is typically ‘pure’ as any dissolved gas or liquid (for a multi-phase reaction) is negligible in amount.

Thus $x_i \sim 1.0, \rightarrow \gamma_i = 1.$

Therefore, for solids $\hat{a}_i = (x_i \gamma_i)\exp\left[\frac{(P-1)V_i}{RT}\right] \approx 1.0$ ..(8.89)

<u>Example 8.9</u>

Consider the following reaction: A(s) + B(g) → C(s) + D(g). Determine the equilibrium fraction of B which reacts at 500^{o}C if equal number of moles of A and B are introduced into the reactor initially. The equilibrium constant for the reaction at 500^{o}C is 2.0.

Assignment- Chapter 8

Example 2.1

For a liquid 'A' at 350K and 1 bar, κ = $50 x 10^{-6}$ bar^{-1}. To what pressure must water be compressed at 350 K to change its density by 0.5%? Assume that κ is independent of P.

At T = constant (using expression for κ)

$$\frac{dP}{P} = \kappa dP$$

$$Or : \ln\frac{P_2}{P_1} = \kappa\Delta P$$

Now $P_2 = 1.005P_1$

$$\Delta P = \frac{\ln(1.005)}{K} = \frac{\ln(1.005)}{50\times10^{-6}}\text{bar} = 100\text{bar}$$

$P_2 = P_1 + \Delta P$ = 100 bar

Example 2.2

Calculate the molar volume for butane at 2.5bar and 298 K using the truncated virial EOS using the following data: $T_C = 425.1K;\ P_C = 37.96bar;\ \omega = 0.2.$

T = 298 K, T_c = 425.1 K, $T_r = T/T_c$ = 0.701

P = 2.93 bar, P_c = 37.96 bar, $P_r = P/P_c$ = 0.069

ω = 0.200, Mol. Wt. = 58

Using truncated viral EOS

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.661$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = -0.624$$

$$V = \frac{RT}{P} + (B^0 + wB^1)\frac{RT_c}{P_c} = 9.4\times10^3\text{cm}^3/\text{mol}$$

Example 2.3

For methane at 298K and 2 MPa compute the molar volume using SRK equation.

T_c = 190.7 K, P_c = 46.41 bar, ω = 0.011, $T_r = T/T_c = 1.56395$

$$Let\ S = 0.48 + 1.574\omega - 0.176\omega^2 = 0.48 + 1.574X0.011 - 0.176(0.011)^2 = 0.4972$$

$$\alpha(SRK) = \left[1 - S\left(1 - \sqrt{T_r}\right)\right]^2 = 0.07664$$

$$a = \frac{0.42748R^2T_C^2\alpha(SRK)}{P_c} = 0.1774\,Pa.(m^3/mol)^2$$

$b = 0.08664 \frac{RT_c}{P_c} = 2.9598\, X\, 10^{-5}\, m^3 / mol$

$\therefore A = \frac{aP}{(RT)^2} = 5.7765\, X\, 10^{-2}, B = \frac{bP}{RT} = 2.3881\, X\, 10^{-2}$

The SRK EOS can be expressed as: $Z^3 + \alpha Z^2 + \beta Z + \gamma = 0$

Here, $\alpha = -1$; $\beta = A - B - B^2 = 3.3813\, X\, 10^{-2}, \gamma = -AB = -1.3510\, X\, 10^{-2}$

Refer to method of solution for cubic equation and solving the cubic equation yields Z = 0.9665. Thus, the molar volume is given as follows.

V = ZRT/P = (0.9665)(83.14cm^{3}bar/molK)(298K)/20bar = 1197.3 cm^3/mol

Example 2.4

A rigid 0.5-m^3 vessel at 25^{o}C and 2500kPa holds ethane; compute the number of moles of ethane in the vessel. For ethane: T_c = 305 K; P_c = 48.72 bar, ω = 0.1.

T = 298 K, T_c = 305 K; T_r = 0.977

P = 220 KPa, P_c = 48.72 bar, P_r = 0.452

V_{total} = 0.5 m^3, ω = 0.1

Using plots for Z^0 and Z^1, at given T, P we have: Z^0 = 0.8105, Z^1 = -0.0479

Thus: $Z = Z_0 + \omega Z^1 = 0.806$

$V_1 = Z_1 RT_1 / P_1 = 798.8 cm^3 mol^{-1}$

Moles of ethane in vessel $= 0.5x10^6 cm^3 / 798.7 cm^3 mol^{-1} \approx 626\, moles.$

Example 2.5

Compute the saturate liquid phase molar volume for methane at 150K. For methane T$_c$= 190.7 K, P$_c$= 46.41 bar, V$_C$ = 98.6cm^3/mol, Z$_C$ = 0.286, ω = 0.011.

At the given condition: $T_r = T/T_c \sim 0.8$

Using Rakectt Equation: $V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$; where $T_r = T / T_C$ = reduced temperture.

Thus:

$V^{sat} = (98.6)(0.286)^{(1-0.8)^{0.2857}} = 44.7 cm^3 / mol.$

Example 2.6

Estimate the second virial coefficient for an equimolar mixture of propane and n-pentane at 500K and 10 bar.

	T_c (K)	**P_c (bar)**	**V_c x 10^3 (m^3/mol)**	**Z_c**	**ω**	**y_i**
Propane (1)	369.9	42.57	0.2	0.271	0.153	0.5
Pentane (2)	469.8	33.75	0.311	0.269	0.269	0.5

$$K_{12} = 1 - \frac{8(V_{c1}V_{c2})^{0.5}}{\left(V_{c1}^{\frac{1}{3}} + V_{c2}^{\frac{1}{3}}\right)^3} = 8.902\, X\, 10^{-3}$$

$$T_{c12} = \sqrt{T_{c1}T_{c2}}(1 - K_{12}) = 413.2\, K$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} = 0.202$$

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2} = 0.27$$

$$V_{c12} = \left(\frac{V_{c1}^{\frac{1}{3}} + V_{c2}^{\frac{1}{3}}}{2}\right)^3 = 0.2516\, X\, 10^{-3}\, m^3/mol$$

$$P_{c12} = \frac{Z_{c12}KT_{c12}}{V_{c12}} = 3.6866\, MPa$$

$$T_{r12} = \frac{500}{T_{c12}} = \frac{500}{413.2} = 1.21$$

$$\therefore B_{12}{}^{0} = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.2281$$

$$B_{12}{}^{1} = 0.139 - \frac{0.172}{T_r^{4.2}} = 6.1762\, X\, 10^{-2}$$

$$\therefore\ \frac{B_{12}P_{c12}}{RT_{c12}} = B_{12}^{0} + \omega_{12}B_{12}^{1} = -0.2156 \therefore B_{12} = -2.0091\, X\, 10^{-4}\, m^3/mol$$

Similarly, for pure components $T_{r1} = \frac{500}{369.9} = 1.3571,\ T_{r2} = 1.0643$

Following the same procedure above (K_{11} = K_{22}= 0), [K_{ij} = 0 where i = j]

B_{11} = - 1.1833×10^{-4} m^3/mol, B_{22} = - 3.4407×10^{-4} m^3/ mol

$$\therefore B_{mix} = y_1^2 B_{11} + 2y_1y_2B_{12} + y_2^2B_{22} = -2.16\ x\ 10^{-4}\ m^3/mol$$

Example 2.7

Calculate the molar volume of an ethylene and propylene mixture comprising 70 mole percent ethylene and 30 mole percent propylene at 600 K and 60 bar. Assume that the mixture follows the Redlich-Kwong equation of state.

	T$_c$ (K)	**P$_c$ (bar)**
Ethylene (1)	283.1	51.17
Propylene (2)	365.1	46.0

R-K parameters for pure species and mixture are obtained first

$$a_1 = \frac{0.42748R^2T_{c1}^2}{P_cT^{0.5}} = \frac{0.42748\ X\ (8.314)^2\ X\ (283.1)^2}{51.17\ X\ 10^5\ X\ \sqrt{600}} = 0.3179\ Pa\left(\frac{m^3}{mol}\right)^2$$

$$b_1 = \frac{0.08664RT_c}{P_c} = \frac{0.08664\ X\ 8.314\ X\ 283.1}{51.17\ X\ 10^5} = 3.9852\ X\ 10^{-5}\ \frac{m^3}{mol}$$

Similarly, $a_2 = 0.6679\ Pa\left(\frac{m^3}{mol}\right)^2, b_2 = 5.7172\ X\ 10^{-5}\ m^3/mol$

$$\therefore a_m = y_1^2a_1 + 2y_1y_2\sqrt{a_1a_2} + y_2^2a_2^2 = 0.4094\ Pa\left(\frac{m^3}{mol}\right)^2$$

$$b_m = y_1b_1 + y_2b_2 = 4.5048\ X\ 10^{-5}\ m^3/mol$$

$$\therefore \frac{b_1}{b_m} = 0.8847; \frac{b_2}{b_m} = 1.2691$$

Now, solve for Z from cubic EOS,

$$A = \frac{aP}{(RT)^2} = \frac{a_mP}{(RT)^2} = \frac{0.4094\ X\ 60\ X\ 10^5}{(8.314\ X\ 600)^2} = 9.8713\ X\ 10^{-2}$$

$$B = \frac{bP}{RT} = \frac{b_mP}{RT} = \frac{4.5048\ X\ 10^{-5}}{8.314\ X\ 600} = 5.4183\ X\ 10^{-2}$$

It follows, $\alpha = -1, \beta = A - B - B^2 = 4.1594\ X\ 10^{-2}$

$$\gamma = -AB = -9.8713\ X\ 10^{-2}\ X\ 5.4183\ X\ 10^{-2} = -5.3486\ X\ 10^{-3}$$

$$\therefore p = \beta - \frac{\alpha^2}{3} = -0.2917; q = \frac{2\alpha^3}{27} - \frac{\alpha\beta}{3} + \gamma = -6.5558\ X\ 10^{-2}$$

$$D = \frac{q^2}{4} + \frac{p^3}{27} = 1.5519\ X\ 10^{-4};\ \sqrt{D} = 1.2457\ X\ 10^{-2}$$

Since $D > 0$, one real root only exists,

$$Z = \left\{-\frac{q}{2}+\sqrt{D}\right\}^{1/3} + \left\{-\frac{q}{2}-\sqrt{D}\right\}^{1/3} - \frac{\alpha}{3} = 0.9626$$

The mixture molar volume = $V = Z_m RT / P = (0.9626)(83.14)(600)/60 \approx 800 cm^3 / mol$

Example 2.8

Find the molar volume and internal energy of a system containing water and steam at 50% quality at 200^{0}C.

From saturated steam tables one has the following data at 200^{0}C.

$V^V = 0.13 m^3 / kg; V^L = 0.0012 m^3 / kg; U^V = 2593 kJ / kg; U^L = 851 kJ / kg$

System molar volume: $V = V^L + x^V (V^V - V^L) = 0.065 m^3 / kg$

System molar internal energy: $U = U^L + x^V (U^V - U^L) = 1722.0 kJ / kg$

Example 9

Using Riedel's correlation, estimate the enthalpy of vaporization of water at its normal boiling point and compare the result with that given in steam tables.

Solution: For water, P_c = 221.2 bar, T_c = 647.3 K and T_{br} = 373.15/647.3 = 0.5765.

$$\Delta H_n^{vap} = 1.093 RT_c \left[T_{br} \frac{\ln P_c - 1.013}{0.930 - T_{br}} \right] = 1.093 \text{ x } 8.314 \text{ x } 647.3 \left[0.5765 \frac{(\ln 221.2 - 1.013)}{0.930 - 0.5765} \right]$$

= 42.075 kJ/mol = 2337.5 kJ/kg

We get from steam tables = 2256.94 kJ/kg and error = $\frac{(2337.5 - 2256.94)}{2256.94}$ x 100 = 3.57%

Example 2.10

The enthalpy of vaporization of water at 100^{o}C is 2256.94 kJ/kg. Determine the value at 150^{o}C, and compare the value with that listed in the steam tables.

Solution: For water, T_c = 647.3 K.

$$T_{r1} = \frac{373.15}{647.3} = 0.5765; \quad T_{r2} = \frac{423.15}{647.3} = 0.6537$$

$$\Delta H_2^{vap} = \Delta H_1^{vap} \left(\frac{1 - T_{r2}}{1 - T_{r2}} \right)^{0.38} \quad \text{or} \quad \Delta H_2^{vap} = 2256.94 \left(\frac{1 - 0.6537}{1 - 0.5765} \right)^{0.38} = 2090.78 \; kJ / kg$$

ΔH^{vap} from steam tables = 2113.25 kJ/kg

Example 3.1

A gas initially at 1 MPa, 500°C is contained in a piston-cylinder arrangement of initial volume of 0.1 m^3. The gas expanded isothermally to a final pressure of 100 kPa. Determine the work.

$$PV = \text{Constant};\ V_2 = \frac{P_1V_1}{P_2}$$

$$W = \int PdV = \int \frac{C}{V}dV$$

$$W = P_1V_1 \ln\frac{V_2}{V_1}$$

Putting all relevant data, W = 230.3 KJ

Example 3.2

Helium gas expands from 125 kPa, 350 K and 0.25 m^3 to 100 kPa in a polytropic process with $\delta = 1.667$. How much work does it give out?

PV^{δ} = Constant

$$V_2 = V_1\left(\frac{P_1}{P_2}\right)^{1/\delta} = 0.2852\,\text{m}^3$$

$$W_2 = \frac{P_2V_2 - P_1V_1}{1-n} = 4.09\ \text{KJ}$$

Example 3.3

A chiller cools liquid water (Sp. Ht = 4.2 J/gmK) for air-conditioning purposes. Assume 2.5 kg/s water at 20°C and 100 kPa is cooled to 5°C in a chiller. How much heat transfer (kW) is needed?

Heat transferred needed = Q_{out}

$$\dot{Q}_{out} = \dot{m}\,\dot{q}_{out}$$

$$Q_{\text{out}} = \dot{m}\,C_p\,\Delta T = \dot{m}\,(H_i - H_e) = 156.75\ \text{KW}$$

Example 3.4

A piston-cylinder assembly contains 0.1 kg wet steam of quality 0.75 at 100 kPa. If 150 kJ energy is added as heat while the pressure of the steam is held constant determine the final state of steam.

From saturated steam tables one has the following data at 100kPa.

$V^V = 1.694 m^3/kg; V^L = 10^{-3} m^3/kg; H^V = 2675 kJ/kg; H^L = 417.5 kJ/kg$

System molar volume: $V = V^L + x^V (V^V - V^L) = 1.27 m^3/kg$

System molar internal energy: $H = H^L + x^V (H^V - H^L) = 2110.0 kJ/kg$

Total enthalpy at state 1= $H_1^t = mH_1$

By first law: $Q^t = H_2^t - H_1^t = 150 kJ$

Thus $H_2 = (Q^t + H_1^t)/m = 3610.\ 9 KJ/kg$

It may be seen that at 100kPa, the saturated steam enthalpy $H_2 > H^V \Rightarrow$ hence the state 2 is *superheated steam* at 100 kPa & H = 3610.9 KJ/kg.

Example 3.5

An adiabatic compressor operating under steady-state conditions receives air (ideal gas) at 0.1 MPa and 300 K and discharges at 1 MPa. If the flow rate of air through the compressor is 2 mol/s, determine the power consumption of the compressor. Constant pressure specific heat for air = 1kJ/kg.

For compressor $\dot{Q} = 0$

Let 'i' and 'e' denote the inlet and exit streams respectively.

We assume that: $u_i = u_e = 0$ and that $z_i - z_e = 0$.

Thus, the 1st law becomes,

$$\dot{m}(H_e - H_i) = -\dot{W}_S \quad ..(1)$$

$$But, H_e - H_i = C_P(T_e - T_i) \quad ..(2)$$

$$C_P - C_V = R$$

$$C_P / C_V = \gamma$$

$$\text{Thus, } C_P = \frac{\gamma R}{\gamma - 1}$$

It follows that from the given data $\gamma = 1.4$

$$H_e - H_i = \frac{\gamma R}{\gamma - 1}(T_e - T_i) \quad ..(3)$$

Also for adiabatic operation of the compressor:

$$T_e = T_i \left[\frac{P_e}{P_i}\right]^{\frac{\gamma-1}{\gamma}} \cong 580^0 K$$

$$\overset{\bullet}{m} = 2mol/s = 0.058kg/s$$

Substituting the relevant data: $-\overset{\bullet}{W}_S = \overset{\bullet}{m}\left[\frac{\gamma R}{\gamma - 1}\right](T_e - T_i) = 16.25kW$ = 16.25

Example 3.6

An insulated piston-cylinder system has air at 400kPa & 600K. Through an inlet pipe to the cylinder air at certain temperature T(K) and pressure P (kPa) is supplied reversibly into the cylinder till the volume of the air in the cylinder is 4 times the initial volume. The expansion occurs isobarically at 400kPa. At the end of the process the air temperature inside the cylinder is 450K. Assume ideal gas behaviour compute the temperature of the air supplied through the inlet pipe.

Applying the first law (Δ PE = Δ KE = 0)

$$\frac{d(mU_{cv})}{dt} + \Delta(H\dot{m}) = \dot{Q} + \dot{W}$$

$$\frac{d(mU_{cv})}{dt} + \Delta\left(H\frac{dm}{dt}\right) = \frac{\delta Q}{dt} + \frac{\delta W}{dt}$$

Or $d(mU_{cv}) + \Delta(Hdm) = \delta Q + \delta W$ ..(1)

For change of state from 1 – 2

$$\int_1^2 (mU_{cv}) + \Delta\int_1^2 Hdm = \int_1^2 \delta Q + \int_1^2 \delta W$$

Or $\Delta U^{t2}_1 + \int_1^2 H_e dm_e - \int_1^2 H_i dm_i = Q_{12} + W_{12}$

Here $Q_{12} = 0$, $\int_1^2 H_e dm_e = 0$ as there is no exit

Equation (1) may be expanded into:

$(m_2U_2 - m_1U_1)_{cv} - H_i(m_2 - m_1) = -P(V_2^t - V_1^t)$ …………………..(2)

For ideal gas $m = PV^t / R_m T$……………………… (3);

$R_m = R$/Mol. Wt.

Since incoming fluid and system fluid are same we can write (by ideal gas assumption): $H = C_p T$; $U = C_V T$ (ideal gas assumption) ………….(4)

Putting relations (3) and (4) in (2) and simplifying we finally obtain

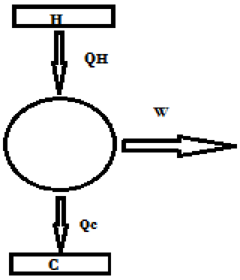
$$T_i = \frac{V_2^t}{\left\{ \frac{V_1^t}{T_1} + \frac{V_2^{\,t} - V_1^t}{T_2} \right\}}$$

Now $V_2^t = 4V_1^t$, $T_1 = 600$ K, $T_2 = 450$ K, to calculate T_i

Thus $T_\mathrm{i} = 480$ K.

Example 4.1

An inventor claims to have devised a cyclic engine which exchanges heat with reservoirs at 27°C and 327°C, and which produces 0.6 kJ of work for each kJ of heat extracted from the hot reservoir. Is the claim believable? If instead he claimed that the delivered work would be 0.25kJ / kJ of extracted heat, would the engine be feasible?



Q_H = 1KJ, W= 0.6KJ, T_H = 600K, T_c = 300K

Efficiency:

$$\eta_{actual} = \frac{|W|}{|Q_H|} = 0.6$$

$$\eta_{ideal(Carnot)} = 1 - \frac{T_c}{T_H} = 0.5$$

Since $\eta_{actual} > \eta_{ideal}$ the engine is not possible.

However for a delivered work of 0.25kJ / kJ of extracted heat the $\eta_{actual} < \eta_{ideal}$; hence the engine is feasible.

Example 4.2

A rigid vessel of 0.06 m^3 volume contains an ideal gas, C_V = (5/2)R, at 500 K and 1 bar. (a) If 15 kJ of heat is transferred to the gas, determine its entropy change. (b) If the vessel is fitted with a stirrer that is rotated by a shaft so that work in the amount of 15 kJ is done on the gas, what is the entropy change of the gas if the process is adiabatic? What is ΔS^{total}?

$$n = P_1 V_t / RT_1 = 1.443 mole$$

$$\Delta U = Q + W = Q = 15000J = nC_V(T_2 - T_1)$$ [W=0]

Hence T_2 = 1000K

$$\Delta S^t = n\left[C_P \ln T_2 / T_1 - R \ln P_2 / P_1\right]; \text{ but } \frac{P_2}{P_1} = \frac{T_2}{T_1}$$

Hence $\Delta S^t = 20.8 J/K$

For second case, the since change of state of the gas is same as in part 'a'

$\Delta S_{system} = 20.8 J / K$;

$\Delta S_{surr} = 0$ (as there is no heat effect on the surrounding)

$\Delta S^t_{universe} = \Delta S^t_{system} + \Delta S^t_{surr} = 20.8 J / K$; (Hence stirring process is irreversible)

Example 4.3

An ideal gas, Cp = (7/2)R, is heated in a steady-flow heat exchanger from 70°C to 190°C by another stream of the same ideal gas which enters at 320°C. The flow rates of the two streams are the same, and heat losses from the exchanger are negligible. Calculate the molar entropy changes of the two gas streams for both parallel and countercurrent flow in the exchanger. What is ΔS^{total} in each case?

Temperature drop of stream 'B' in either case of flow is the same as the temperature rise of first stream 'A' = 120^{o}C. Thus, exit temperture of stream 'B' = 200^{o}C

Thus in both cases:

$$\Delta S_A = C_P \ln\left(\frac{463}{343}\right) = 8.726 J / molK$$

$$\Delta S_B = C_P \ln\left(\frac{473}{593}\right) = -6.58 J / molK$$

$\therefore \Delta S^{total}$ (in both types of flow) = $\Delta S_A + \Delta S_B = 2.15 J / molK$

Example 4.4

Ten kmol per hour of air is throttled from upstream conditions of 25°C and 10 bar to a downstream pressure of 1.2 bar. Assume air to be an ideal gas with C_P = (7/2)R. (a) What is the downstream temperature? (b) What is the entropy change of the air in J/molK? (c) What is the rate of entropy generation in W/K?

$\dot{m}$ = 10Kmol /hr.

Since Q, W_S = 0, the process is isenthalpic

$\Delta H_{12} = C_P(T_2 - T_1) = 0; \quad \Rightarrow T_2 = T_1 = 298K$

$\Delta S = C_P \ln(T_2 / T_1) - R \ln(P_2 / P_1) = 17.63 \; J / molK$

Rate of entropy generation:

$\dot{S}_G = \dot{m} \Delta S$ = 48.97 W/K

Example 4.5

A steady-flow adiabatic turbine (expander) accepts gas at conditions T_1 = 500 K, P_1 = 6 bar, and discharges at conditions T_2 = 371 K, P_2 = 1.2 bar. Assuming ideal gases, determine (per mole of gas) W_{actual}, W_{ideal}, W_{lost}, and entropy generation rate. T_{surr} = 300 K, C_P/R = 7/2.

$$\Delta H = nC_p(T_2 - T_1);\ W_S = \Delta H \Rightarrow W_S = -3753.85\ J$$

$$\Delta S = n\left[C_P \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}\right] = 4.698 J/K$$

$W_{ideal} = \Delta H - T_\sigma \Delta S = -5163J$

$$W_{lost} = \left| W_{ideal} - W_{S,actual} \right| = 1409.3\ J$$

$S_G = W_{lost} / T_\sigma = 4.698J/K$

Example 4.6

A steam turbine operates adiabatically at a power level of 3500 kW. Steam enters the turbine at 2400 kPa and 500°C and exhausts from the turbine at 20 kPa. What is the steam rate through the turbine, and what is the turbine efficiency?

$\dot{W}_S$ = - 3500KW, H_2= 2609.9 KJ/Kg, S_1= 7.3439 KJ/Kg^{0}K, H_1=3462.9 KJ/Kg

$\dot{m} = \dot{W}_S / \Delta H$ = 4.1 Kg/s;

Since the process is adiabatic for a reversible process: $S_1 = S_2$

Thus S_2 = 7.3439 KJ/Kg^{0}K

At 20kPa checking the steam table we find that at the exit the steam is 'wet', since the following condition holds at 20kPa:

$$S_{liq}(= 0.8321 kJ/kg\,^0K) < S_2 < S_{vap}(= 7.9094 kJ/kg\,^0K)$$

Thus: $S_2 = S_{liq} + x(S_{vap} - S_{liq})$

On substituting the values of all the parameters we get:

x = 0.92.

Thus for reversible and adiabatic process:

$$H_2^{id} = H_{liq} + x(H_{vap} - H_{liq}) \simeq 2.421\times10^3 \frac{KJ}{Kg}$$

$$\eta = (H_2 - H_1)/(H^{id}{}_2 - H_1) \simeq 0.82$$

Example 5.1

Derive an expression for enthalpy change of a gas during an isothermal process assuming using the following EOS: $P(V-b) = RT$

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

$$P\ (V\text{-}b) = RT \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$dH = C_\mathrm{p} dT + \left(V - \frac{RT}{P}\right) dP = C_p dT + b dP$$

$$\Delta H = \int C_P dT + b(P_2 - P_1)$$

Example 5.2

Derive an expression for enthalpy change of a gas during an isothermal process assuming using the following EOS: $Z = 1 + AP_\mathrm{r} / T_\mathrm{r}$

$$\frac{H^R}{RT_c} = -T_r^{\,2} \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r}\right)_{P_r} \frac{dP_r}{P_r}$$

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(-\frac{AP_r}{T_r^{\,2}}\right) \frac{dP_r}{P_r} = AP_r$$

$$\Delta H = \Delta H^{ig} + H_2^R - H_1^R$$

$$= \Delta H^{ig} + A(P_{r2} - P_{r1}) RT_c$$

Example 5.3

Derive expressions for H^R, S^R from RK-EOS.

General expressions are:

$$H^R = RT\left(Z - 1\right) + \int_{V=\infty}^{V} \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \qquad ..(1)$$

$$S^R = R \ln Z + \int_{V=\infty}^{V} \left[\left(\frac{\partial P}{\partial T}\right)_V - \frac{R}{V}\right] dV \qquad ..(2)$$

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} = \frac{RT}{V-b} - \frac{a'}{V(V+b)\sqrt{T}} \qquad ..(3)$$

Where, $a' = \frac{0.42748 R^2 T_C^{2.5}}{P_C}; b = \frac{0.08664}{P_C} RT_C$

$$\therefore \quad T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left[\frac{R}{V-b} + \frac{a'}{2V(V+b)T^{3/2}}\right]$$

$\therefore$

$$- \quad \left[\frac{RT}{V-b} - \frac{a'}{V(V+b)T^{1/2}}\right] = \frac{3a'}{2V(V+b)T^{1/2}}$$

$$\therefore \; H^R = RT\;(Z-1) + \frac{3a'}{2\sqrt{T}} \int_{V=\infty}^{V} \frac{dV}{V(V+b)}$$

Putting $Z = PV/RT$ $\qquad \sqrt{}$

$$H^R = PV - RT \; - \frac{3a}{2b}\ln\left[\frac{V+b}{V}\right]$$

Replacing P we get: $H^R = \frac{bRT}{(V-b)} - \frac{a}{(V+b)} - \frac{3a}{2b}\ln\left[\frac{V+b}{V}\right]$

Similarly using (2) and (3) one may show:

$$S^R = R\;\ln\frac{(PV)}{RT} + R\ln\left(\frac{V-b}{V}\right) - \frac{a}{2bT}\ln\left(\frac{V+b}{V}\right)$$

Example 5.4

Carbon dioxide at upstream conditions $T_1 = 350$ K and $P_1 = 80$ bar is throttled to a downstream pressure of 1.2 bar. Estimate the downstream temperature and ΔS of the gas.

For CO_2: $C_p^{ig}/R = 5.457 + 1.045\times10^{-3}T - \frac{1.157}{T^2}\times10^5$

$T_1 = 350$K, $P_1 = 80$ bar, $T_C = 304.2$K, $P_C = 73.8$ bar and $\omega = 0.224$

For the process $H_2 - H_1 = 0$ (Isenthalpic, from energy balance)

Now $H_2 - H_1 = H_2^R - H_1^R + \Delta H^{ig}$...........$(A)$

$Tr_1 = T_1/T_c = 1.151$, $Pr_1 = P_1/P_c = 1.084$

If one assume that at 1.2 bar (at exit), the gas is ideal, then:

$H_2^R \simeq 0$; then $\Delta H^{ig} = \int_{T_1}^{T_2} C_p{}^{ig} dT = H_1^R$ ….. (B)

Use generalized correlations for residual properties, and read from relevant figures for residual properties to find H_1^R at given Tr$_1$, & Pr$_1$ and then solve Equation (B) by trial & error to get T$_2 \simeq$ 280K

Thus: $\Delta S = S_2^R - S_1^R + \Delta S^{ig} \simeq -S_1^R + \left[C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \right] \simeq 31.5 J / molK$

Example 5.5

Estimate the final temperature and the work required when 1 mol of n-butane is compressed isentropically in a steady-flow process from 1 bar and 50°C to 7.8 bar.

ω = 0.2, T_c = 425.1 K, P_c = 37.96 bar

T_1 = 323 K, P_1 = 1 bar, P_2 = 7.8 bar

For the process, $\Delta S = 0$

T_{r2} = 0.76017, P_{r2} = 0.2052,

P_{r1} = 0.02639; hence we assume that at state 1 the residual properties are zero as the gas is at ideal state.

For n-butane: $C_p^{ig} / R = 1.9 + 36.9 \times 10^{-3} T - 11.4 \times 10^{-6} T^2$

Using generalized correlations for state 2 and reading from relevant figures for residual properties one finally obtains the following residual property values at ‘2’:

From generalized correction at point ‘2’ $\frac{\left(H^R\right)^o}{RT_C} = -0.5679$, $\frac{\left(S^R\right)^o}{RT_C} = -0.05210$

$$\Delta S = \int_{T_1}^{T_2} C_p \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R$$

Assume T_2 and solve iteratively with ΔS = 0 to obtain the final value of T_2 which is = 381K.

Next use generalized correlation figures for residual enthalpies; whereby at point ‘2’:

$$\frac{H^R}{RT_c} = -0.30330$$

$$W = \Delta H = \Delta H^{ig} + RT_c (H_2^R - H_1^R)$$

$$= \int_{T_1}^{T_2} C_p{}^{ig} dT + RT_c (H_2^R - H_1^R)$$

Finally, $W = 5678$ J/mol

Example 5.6

Calculate the changes in enthalpy and entropy per mole when a mixture of 70 mole % ethylene (1) and 30 mole% propylene (2) at 323K and 10 bar is taken to 60 bar and 600 K using the generalized compressibility factor approach.

$$C_{p1}^{ig} = 4.196 + 154.565x10^{-3}T - 81.076x10^{-6}T^2 + 16.813x10^{-9}T^3;$$

$$C_{p2}^{ig} = 3.305 + 235.821x10^{-3}T - 117.58x10^{-6}T^2 + 22.673x10^{-9}T^3$$

Use pure species data to compute those of mixture.

Thus, $T_{c,mix} = \sum y_i T_{ci} = y_i T_{ci} + y_2 T_{c2} = 307.7\ K$

(1 = ethylene, 2 = Propylene)

Similarly $P_{c,mix} = \sum y_i P_{ci} = 46.619\ bar$

$$\omega_{mix} = \sum y_i \omega_i = 0.1055$$

At state 1, $T_{r,mix} = \frac{323}{307.7} = 1.05; P_{r,mix} = \frac{10}{49.619} = 0.2$

Now, $\frac{H^R}{RT_c} = \left(\frac{H^R}{RT_c}\right)^0 + \omega\left(\frac{H^R}{RT_c}\right)^1$; $\frac{S^R}{R} = \left(\frac{S^R}{R}\right)^0 + \omega\left(\frac{S^R}{R}\right)^1$

From Tables at given $T_{r,mix}$ and $P_{r,mix}$

$$\left(\frac{H^R}{RT_c}\right)^0 = -0.205; \left(\frac{H^R}{RT_c}\right)^1 = -0.16$$

$$\left(\frac{S^R}{R}\right)^0 = -0.125, \left(\frac{S^R}{R}\right)^1 = -0.145$$

$$\therefore \frac{H^R}{RT_{c,mix}} = -\{0.205 + 0.1055\ X\ 0.16\} = -0.222$$

$\therefore$ At state 1 $(H^R)_1 = -0.222\ X\ 8.314\ X\ 307.7 = -0.568\ \frac{KJ}{mol}$

and $\frac{S^R}{R} = -\{0.125 + 0.145\ X\ 0.1055\} = -0.14$

Thus, $(S^R)_1 = -0.14\ X\ 8.314 = -1.164 \frac{J}{mol\ K}\ at\ state\ 1$

Similarly on repeating the calculation for state 2, T = 600K, P = 60 bar, we obtain

$$(H^R)_2 = -0.874 \frac{kJ}{mol}; (S^R)_2 = -1.3 \frac{J}{mol\ K}$$

Now, $H_2 - H_1 = (H^R)_2 - (H^R)_1 + \Delta H^{ig}$

$\Delta H^{ig} = \int_{T_1}^{T_2} \left(\sum y_i C_{pi}^{ig}\right) dT\ ; where\ C_{pi}^{ig} = a + bT + cT^2 + dT^3 (\frac{kJ}{mol})$

Thus, $\Delta H^{ig} = \int_{T_1}^{T_2} (\Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3) dT$

Where, $\Delta a = \sum y_i a_i$; $\Delta b = \sum y_i b_i$; $\Delta c = \sum y_i c_i$; $\Delta d = \sum y_i d_i$

For component 1,

$$C_{P_1}^{ig} = 4.196 + 154.565\, X\, 10^{-3}\, T - 81.076\, X\, 10^{-6} T^2 + 16.183\, X\, 10^{-9}\, T^3$$

Similarly,

$$C_{P_2}^{ig} = 3.305 + 235.821\, X\, 10^{-3}\, T - 117.58\, X\, 10^{-6} T^2 + 22.673\, X\, 10^{-9}\, T^3$$

$\therefore \Delta a = 0.7\, X\, 4.196 + 0.3\, X\, 3.305 = 3.9287$

Similarly, $\Delta b = 70.7463\, X\, 10^{-3}$; $\Delta c = -92.0272\, X\, 10^{-6}$ and $\Delta d = 18.571\, X\, 10^{-9}$

Hence, $\Delta H^{ig} = \int_{T_1}^{T_2} (\Delta a + \Delta b T + \Delta c T^2 + \Delta d T^3) dT = 5.091\ kJ/mol$

$$\therefore H_2 - H_1 = (H^R)_2 - (H^R)_1 + \Delta H^{ig} = -0.874 - (-0.568) + 5.091 = 4.785\ kJ/mol$$

$$S_2 - S_1 = S_2^R - S_1^R + \Delta S^{ig}$$

Now, $\Delta S^{ig} = \int_{T_1}^{T_2} C_{p,mix} dT/T - Rln\ P_2/P_1$

$$= \int_{T_1}^{T_2} (\Delta a + \Delta b T + \Delta c T^2 + \Delta d T^3) \frac{dT}{T} - Rln(\frac{60}{10})$$

Final answer on substitution of all parameters

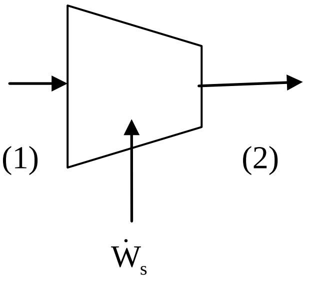
$$\Delta S^{ig} = -3.502 \frac{J}{mol\ K}$$

$$S_2 - S_1 = S_2^R - S_1^R + \Delta S^{ig} = -1.3 - (-1.164) - 3.502 = -3.638 \frac{J}{mol\ K}$$

Example 5.7

A certain gas is compressed adiabatically from 293 K and 135 KPa to 550 KPa. What is the work needed? What is the final T_2? Assume ideal gas behavior. Compressor $\eta = 0.8$.

For the gas: $C_p^{ig} = 1.65 + 8.9 \text{ x } 10^{-3} T - 2.2 \text{ x } 10^{-6}\, T^2$



For rev. process $\Delta S = S_2 - S_1 = 0$

Flow process thus lead to:

$$\Delta S = \int_{T_1}^{T_2} C_p^{ig} \frac{dT}{T} - R \int_{P_1}^{P_2} \frac{dP}{P} \therefore \Delta$$

$$\therefore \int_{293}^{T_2} (1.65 + 8.9 \text{ x } 10^{-3}\, T - 2.2 \text{ x } 10^{-6}\, T^2) \frac{dT}{T} = 8.314 \ln\left(\frac{550}{135}\right)$$

$\Rightarrow T_2^{\text{reversible}}$ (by iteration) $\simeq$ 395 K

By first Law Q (=0) + $W_s = \Delta H$

$$\therefore W_s \text{ (isentropic, reversible)} = H_2 - H_1 = \int_{T_1}^{T_2} C_p^{ig}\, dT$$

$$\therefore W_S^{reversible} = \int_{293}^{395} [1.65 + 8.9 \text{ x } 10^{-3} T - 2.2 \text{ x } 10^{-6} T^2)\, dT \underset{\sim}{} 3960 \text{ J/mol.}$$

$\therefore$ Thus actual work needed = W_S^{rev} / η

= 3960/0.8 = 4950 J/mol

$$\therefore W_S^{rev} = \Delta H = \int_{T_1}^{T_2} C_p^{ig} dT$$

$$\therefore 4950 = \int_{293}^{T_2^{irrev}} [1.65 + 8.9\, x\, 10^{-3} T - 2.2\, x 10^{-6} T^2]\, dT$$

$$\Rightarrow T_2 \text{ (actual)} \underset{\sim}{} 420^o K \Rightarrow 147^o C$$

Example 6.1

Consider a solution of two species S1/S2 at 25°C such that x_1 = 0.4. If $\overline{V}_1$ = 40 x 10^{-6} m^3/mol, find $\overline{V}_2$. The solution specific gravity is = 0.90 and the molecular weights of the species are 32 and 18 respectively.

Molar mass of solution = $x_1M_1 + x_2M_2$ (M = MW)

= 0.4 x 32 + 0.6 x 18

= 23.433 gm/mol = 23.6 x 10^{-3} kg/mol

Solution molar volume = $\frac{\text{Molar mass}}{\text{Density}} \Rightarrow$

$$= \frac{23.6x10^{-3} kg/mol}{900 kg/m^3} = 26.2 \text{ x } 10^{-6} \text{ m}^3\text{/mol}$$

Now V = $x_1 \overline{V}_1 + x_2 \overline{V}_2$

$$\Rightarrow \overline{V}_2 = (V - x_1\overline{V}_1)/x_2 = \frac{(26.2\ -\ 0.4\ x\ 40)\ x10^{-6}}{0.6}$$

= 17.0 x 10^{-6} m^3/mol.

Example 6.2

The molar enthalpy of a binary solution is given by:

V = 500 x_1 + 1000 x_2 + x_1x_2 (50 x_1+40x_2) cm^3/mol. Find the expressions for

$\overline{V}_1$, and $\overline{V}_1^{\infty}$.

Putting x_1 = 1- x_2; it follows:

V = 500 + 550 x_2 – 60 x_2^2 + 10 x_2^3

$$\frac{dV}{dx_2} = 550 - 120\ x_2 + 30\ x_2^2$$

$$\overline{V}_1 = V - x_2 \frac{dV}{dx_2}$$

= 500 x_1 + 1000 x_2 + x_1x_2 (500x_1 + 40 x_2) -x_2 [550 – 120 x_2 + 30 x_2^2]

Putting x_2 = 1-x_1; and simplifying:

$$\overline{V}_1 = 540 - 60\ \text{x}_1 + 20\ \text{x}_1^3$$

$$\overline{V}_1^{\infty} = \lim_{x_1 \to 0} \overline{V}_1 = 540 \text{ J / mol}$$

Alternately one may also use the generic definitions:

$$\overline{V}_1 = \left.\frac{\partial nV}{\partial n_1}\right|_{n_2,T,P}$$

$V = 500 + 550\ x_2 - 60\ x_2^2 + 10\ x_2^3$

Putting $x_2 = 1 - x_1$ and simplifying:

$V = 1000 - 460\ x_1 - 30\ x_1^2 - 10\ x_1^3$

$$V = 1000 - 460\ \frac{n_1}{n} - 30\frac{n_1^2}{n^2} - 10\frac{n_1^3}{n^3}$$

Where, $n = n_1 + n_2$ (moles of mixture)

$$\overline{V}_1 = \left.\frac{\partial nV}{\partial n_1}\right|_{n_2} \quad ; \quad \text{note that:} \quad \left.\frac{\partial nV}{\partial n_1}\right|_{n_2} = 1$$

$$\overline{V}_1 = \frac{\partial}{\partial n_1}\left[\left(1000 - 460\ \frac{n_1}{n} - 30\ \frac{n_1^2}{n^2} - \frac{10\ n_1^3}{n^3}\right) n\right]_{n_2}$$

$$= \frac{\partial}{\partial n_1}\left[\ 1000\ n - 460\ n_1 - 30\ \frac{n_1^2}{n} - \frac{10\ n_1^3}{n^2}\right]_{n_2}$$

$$= 640 - 60\ \frac{n_1^2}{n^2} + 20\frac{n_1^3}{n^3}$$

$= 640 - 60\ x_1^2 + 20\ x_1^3$ … [same as the earlier expression]

The same exercises may be carried for obtaining $\overline{V}_2$.

Example 6.3

What is the change in entropy when 0.6 m^3 of CO_2 and 0.4 m^3 of N_2, each at 1 bar and 25°C blend to form a gas mixture at the same conditions? Assume ideal gases.

For an ideal gas, mole fraction = volume fraction

CO_2 (1) / N_2(2); $y_1 = 0.6$, $y_2=0.4$

$$(\Delta S)_{mix} = -R\sum y_i \ln y_i = 5.5 J / molK$$

Example 6.4

Estimate the fugacity of ethane at 122.2 K and 5 bar using the truncated virial EOS.

For ethane $T_c = 305.4K$, $P_c = 48.84$ bar, $\omega = 0.099$

$$\therefore T_r = \frac{122.2}{305.4} = 0.4,\ P_r = \frac{2}{48.84} = 0.041$$

Now, $B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} = -1.7452$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} = -7.9311$$

$$\ln\phi = (B^0 + \omega B^1)\frac{P_r}{T_r} = -0.25936 \to \ \phi = 0.7715$$

$$\therefore f = \phi P = 3.9\ bar$$

Example 6.5

Estimate the fugacity of ammonia vapor at 4.0 MPa and 321K assuming that it obeys the RK equation of state.

$$a = 0.42748\frac{R^2T_c^{2.5}}{P_cT^{0.5}} = \frac{0.42748 * (8.314)^2 * (405.5)^{2.5}}{112.77 * 10^5 * (321.55)^{0.5}} = 4.8383\ X\ 10^{-1}\ Pa\left(\frac{m^3}{mol}\right)^2$$

$$b = \frac{0.08664RT_c}{P_c} = \frac{0.08664 * 8.314 * 405.5}{112.77 * 10^5} = 2.5902 * 10^{-5}m^3/mol$$

Now,

$$\ln\phi = \frac{b}{V-b} - \frac{a}{RT(V+b)} - \frac{a}{bRT}ln\left(\frac{V+b}{V}\right) - ln\left(\frac{V-b}{V}\right) - ln\left[\frac{V}{V-b} - \frac{a}{RT(V+b)}\right]$$

In the above equation T = 321.55K, V is not known.

So solve RK-EOS for V_{vapour} at the given temperature and pressure, i.e., at P =1.95 MPa, T = 321.55 K (see example 2.3)

V_{vapour} turns out to be ≈ 1.1987 * 10^{-3} m^3/mol

Thus on substitution in eq. (1) ln φ = -0.1189 → φ = 0.888

$$\therefore f = \phi P = 0.888 * 5.0 = 4.4\ MPa$$

Example 6.6

Estimate the fugacity of methane at 32C and 9.28 bar. Use the generalized correlation approach.

For methane T_c = 190.7 K, P_c = 46.41 bar, ω = 0.011

$$\therefore T_r = \frac{305}{190.7} = 1.6, P_r = \frac{9.28}{46.41} = 0.9$$

For given T_r and P_r, read off φ^0 and φ^1 from figures of fugacity coefficients.

Then $\phi = (\phi^0)(\phi^1)^\omega = 0.9865$

$$\therefore f = \phi P = 9.155\ bar$$

Example 6.7

Estimate the fugacity of cyclopentane at 110 C and 275 bar. At 110 C the vapor pressure of cyclopentane is 5.267 bar.

For cyclopentane T_c = 511.8 K, P_c = 45.02 bar, ω = 0.196, Z_c = 0.273, V_c = 258 cm/mol, T_n = 322.4 K

T = 383K, P = 275 bar, P^3(383K) = 5.267 bar

T_r = 0.7486, $P_r^{sat} = P^{sat}/P_C = 0.117$

Calculate f^{sat} at the given Vapour pressure by

Virial EOS $\Rightarrow \ln \phi^{sat} = BP^{sat}/RT \Rightarrow f^{sat} = \phi^{sat} P^{sat}$

Here T = 383K, B is obtained as in problem 18, by B^0, B^1 .

Final φ^S = 0.9

Now by Rackett equation $V^{sat} = V_C Z_C^{\ (1-T_{nbr})^{0.2857}}$

$$T_{nbr} = 322.4/54.8 = 0.63 \Rightarrow V^{sat} = 97.092\frac{cm^3}{mol}$$

$$\therefore f^{sat} = \phi^{sat} P^{sat}.\exp\left[V^{sat}\left(P - P^{sat}\right)/RT\right] = 10.79 bar$$

Example 6.8

For the following system compute the species fugacity coefficients for an equimolar mixture at 20 bar and 500K.

	T_c (K)	**P_c (bar)**	**V_c X 10^3 (m^3/mol)**	**Z_c**	**ω**	**y_i**
Propane (1)	369.9	42.57	0.2	0.271	0.153	0.4
Pentane (2)	469.8	33.75	0.311	0.269	0.269	0.6

P = 20 bar, T = 500 K, $y_1 = y_2 = 0.5$

$$K_{12} = 1 - \frac{8(V_{c1}V_{c2})^{0.5}}{\left(V_{c1}^{\frac{1}{3}} + V_{c2}^{\frac{1}{3}}\right)^3} = 8.902\ X\ 10^{-3}$$

$$T_{c12} = \sqrt{T_{c1}T_{c2}}(1 - K_{12}) = 413.2\ K$$

$$\omega_{12} = \frac{\omega_1 + \omega_2}{2} = 0.202$$

$$Z_{c12} = \frac{Z_{c1} + Z_{c2}}{2} = 0.27$$

$$V_{c12} = \left(\frac{V_{c1}^{\frac{1}{3}} + V_{c2}^{\frac{1}{3}}}{2} \right)^3 = 0.2516\,X\,10^{-3}\,m^3/mol$$

$$P_{c12} = \frac{Z_{c12}KT_{c12}}{V_{c12}} = 3.6866\,MPa$$

$$T_{r12} = \frac{500}{T_{c12}} = \frac{500}{413.2} = 1.21$$

$$\therefore B_{12}{}^{0} = 0.083 - \frac{0.422}{T_r^{1.6}} = -0.2281$$

$$B_{12}{}^{1} = 0.139 - \frac{0.172}{T_r^{4.2}} = 6.1762\,X\,10^{-2}$$

$$\therefore\ \frac{B_{12}P_{c12}}{RT_{c12}} = B_{12}^0 + \omega_{12}B_{12}^1 = -0.2156$$

$$\therefore B_{12} = -2.0091\,X\,10^{-4}\,m^3/mol$$

Similarly, for pure components $T_{r1} = \frac{500}{369.9} = 1.3571,\ T_{r2} = 1.0643$

Following the same procedure above ($K_{11} = K_{22}= 0$), [$K_{ij} = 0$ if i = j] it may be shown that:

B_{11} = - 1.1833×10^{-4} m^3/mol, B_{22} = - 3.4407×10^{-4} m^3/ mol

Thus:

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} = 1.5665\,X\,10^{-4}\,m^3/mol$$

$$\ln \widehat{\phi_1} = \frac{P}{RT}[B_{11} + y_2^2\delta_{12}] = \left\{ \frac{20\,bar}{83.14\frac{cm^3bar}{mol\,K}.500\,K}[-1.1833 + 0.25(1.5665)] \right\}$$

$$x10^{-4}X10^{-6}cm^3/mol$$

$$\ln \widehat{\phi_1} = -0.03808 \rightarrow \widehat{\varphi_1} = 0.9626$$

Similarly,

$$\ln \widehat{\phi_2} = \frac{20}{83.14\,X\,500}[-2.3923 + 0.25\,X\,1.5665]X10^{-4}X10^{6}\frac{cm^3}{mol} = -0.9625$$

$$\therefore\ \widehat{\phi_2} = 0.9082$$

Example 6.9

Calculate the fugacities of ethylene and propylene in a mixture of 70 mole percent ethylene and 30 mole percent propylene at 600 K and 60 bar. Assume that the mixture follows the Redlich-Kwong equation of state.

	T_c (K)	**P_c (bar)**
Ethylene (1)	283.1	51.17
Propylene (2)	365.1	46.0

R-K parameters for pure species and mixture are obtained first

$$a_1 = \frac{0.42748R^2T_{c1}^2}{P_cT^{0.5}} = \frac{0.42748\ X\ (8.314)^2\ X\ (283.1)^2}{51.17\ X\ 10^5\ X\ \sqrt{600}} = 0.3179\ Pa\left(\frac{m^3}{mol}\right)^2$$

$$b_1 = \frac{0.08664RT_c}{P_c} = \frac{0.08664\ X\ 8.314\ X\ 283.1}{51.17\ X\ 10^5} = 3.9852\ X\ 10^{-5}\ \frac{m^3}{mol}$$

Similarly, $a_2 = 0.6679\ Pa\left(\frac{m^3}{mol}\right)^2, b_2 = 5.7172\ X\ 10^{-5}\ m^3/mol$

$$\therefore a_m = y_1^2a_1 + 2y_1y_2\sqrt{a_1a_2} + y_2^2a_2^2 = 0.4094\ Pa\left(\frac{m^3}{mol}\right)^2$$

$$b_m = y_1b_1 + y_2b_2 = 4.5048\ X\ 10^{-5}\ m^3/mol$$

$$\therefore \frac{b_1}{b_m} = 0.8847; \frac{b_2}{b_m} = 1.2691$$

Now, solve for Z from cubic EOS,

$$A = \frac{aP}{(RT)^2} = \frac{a_mP}{(RT)^2} = \frac{0.4094\ X\ 60\ X\ 10^5}{(8.314\ X\ 600)^2} = 9.8713\ X\ 10^{-2}$$

$$B = \frac{bP}{RT} = \frac{b_mP}{RT} = \frac{4.5048\ X\ 10^{-5}}{8.314\ X\ 600} = 5.4183\ X\ 10^{-2}$$

It follows, $\alpha = -1, \beta = A - B - B^2 = 4.1594\ X\ 10^{-2}$

$$\gamma = -AB = -9.8713\ X\ 10^{-2}\ X\ 5.4183\ X\ 10^{-2} = -5.3486\ X\ 10^{-3}$$

$$\therefore p = \beta - \frac{\alpha^2}{3} = -0.2917; q = \frac{2\alpha^3}{27} - \frac{\alpha\beta}{3} + \gamma = -6.5558\ X\ 10^{-2}$$

$$D = \frac{q^2}{4} + \frac{p^3}{27} = 1.5519\ X\ 10^{-4};\ \sqrt{D} = 1.2457\ X\ 10^{-2}$$

Since $D > 0$, one real root only exists,

$$Z = \left\{-\frac{q}{2} + \sqrt{D}\right\}^{1/3} + \left\{-\frac{q}{2} - \sqrt{D}\right\}^{1/3} - \frac{\alpha}{3} = 0.9626$$

$$\ln(Z - B) = -9.6052\ X\ 10^{-2}; ln\left(\frac{Z + B}{Z}\right) = 5.4761\ X\ 10^{-2}$$

$$2\sqrt{\frac{a_1}{a_m}} = 1.7624; 2\sqrt{\frac{a_2}{a_m}} = 2.5546$$

$$\frac{a}{bRT} = 1.8218$$

$$\ln \widehat{\phi_1} = \frac{b_1}{b_m}(Z-1) - \ln(Z-B) + \frac{a_m}{b_m RT}\left(\frac{b_1}{b_m} - 2\sqrt{\frac{a_1}{a_m}}\right)\ln\left(\frac{Z+B}{Z}\right) = -0.0246$$

$$\therefore \widehat{\phi_1} = 0.9757;\ \widehat{f_1} = \widehat{\phi_1} y_1 P = 40.98\ bar$$

$$\ln \widehat{\phi_2} = \frac{b_2}{b_m}(Z-1) - \ln(Z-B) + \frac{a_m}{b_m RT}\left(\frac{b_2}{b_m} - 2\sqrt{\frac{a_2}{a_m}}\right)\ln\left(\frac{Z+B}{Z}\right) = -0.07965$$

$$\therefore \widehat{\phi_2} = 0.9234;\ \widehat{f_2} = \widehat{\phi_2} y_2 P = 16.62\ bar$$

Example 6.10

Methanol (1)-acetone (2) system is described by the Van Laar activity coefficient model. At 60^0C, the model parameters are $A_{12} = 0.47;\ A_{21} = 0.78$. Estimate the activity coefficients for a solution containing 10mole% of methanol.

$$\ln \gamma_1 = \frac{A_{12}}{\left(1 + \frac{A_{12}x_1}{A_{21}x_2}\right)^2};\ln \gamma_2 = \frac{A_{21}}{\left(1 + \frac{A_{21}x_2}{A_{12}x_1}\right)^2}$$

For $x_1 = 0.1$, $\gamma_1 = 1.5219$, $\gamma_2 = 1.0032$

Example 6.11

Use of Regular Solution Model to estimate activity coefficients for an equimolar benzene (1) / cyclohexane (2) solution 350^oK. The solubility parameters are: $\delta_1 = 9.2\ (\text{cal/cm}^3)^{1/2}$; $\delta_2 = 8.2\ (\text{cal/cm}^3)^{1/2}$. The molar volumes: $V_1^L = 88\ \text{cm}^3/\text{mol}$; $V_2^L = 107\ \text{cm}^3/\text{mol}$

Volume fraction $= \Phi_1 = x_1V_1^L / \left(x_1V_1^L + x_2V_2^L\right)$ = 88 / (88 + 107) = 0.45

$$\Phi_2 = 1 - \Phi_1 = 0.55$$

$$RT \ \ln \gamma_1 = V_1^L \Phi_2^{\,2} (\delta_1 - \delta_2)^2 = 88\ x\ 0.55^2 \left[9.2\ -\ 8.2\right]^2$$

R = 1.987 cal/mol, T = 350^oK

Hence $\ln \gamma_1 = 0.038 \Rightarrow \gamma_1 = 1.04$

Similarly RT ln $\gamma_2 = V_2^L \Phi_1^{\,2} (\delta_1 - \delta_2)^2$

Hence $\gamma_2 = 1.03$

Example 6.12

Use UNIFAC model to estimate activity coefficients for an equimolar n-pentane (1) /acetone (2) solution 350^{o}K.

$$B_{11} = -963, B_{22} = -1523, B_{12} = 52 cm^3 / mol$$

$$\therefore \delta_{12} = 2B_{12} - B_{11} - B_{22} =$$

$$\Phi_1 = \exp\left[\frac{B_{11}\left(P - P_1^S\right) + Py_2^2\delta_{12}}{RT}\right]$$

$$\Phi_2 = \exp\left[\frac{B_{22}\left(P - P_2^S\right) + Py_1^2\delta_{12}}{RT}\right]$$

Follow the algorithm provided in the text for bubble pressure calculation.

Final Answer: $P_b = 85.14 KPa, y_1 = 0.812, y_2 = 0.188$

Example 7.1

Consider the ternary system: Acetone (1) / Acetonitrile (2) / Nitromethane (3) for which:

$$\ln P_1^S = 14.5463 - \frac{2940.46}{t + 237.22};\ \ln\ P_2^S = 14.5463 - \frac{2940.46}{t + 237.22};\ \ln P_3^S = 14.2043 - \frac{2972.64}{t + 209.00}$$

$P_i^S (KPa); t(^0C).$

Calculate: (a) P, $\{y_i\}$ for a temperature = 80^{o}C, x_1 = 0.3, x_2 = 0.3 (b) P, $\{x_i\}$, for t = 70^{o}C, y_1 = 0.5, y_2 = 0.3.

(a) For 80^{o}C, P_1^S = 195.75, P_2^S = 97.84, P_3^S = 50.32 KPa. Thus:

$$P = \sum x_i P_i^S = 108.3 KPa$$

Next:

$$y_i = x_i P_i^S / P$$

Thus:

$$y_1 = 0.54,\ y_2 = 0.27,\ y_3 = 0.19$$

(b) For 70^{o}C, P_1^S = 144.77, P_2^S = 70.37, P_3^S = 43.80 KPa

$$P = 1 / \sum y_k / P_k^S = 81.4 \text{ KPa}$$

Next:

$$x_i = y_i P / P_i^S$$

Thus:

$$x_1 = 0.28,\ x_2 = 0.34,\ x_3 = 0.38$$

Example 7.2

A liquid mixture containing equimolar amounts of benzene (1) /toluene (2) and ethylbenzene (3) is flashed to conditions of T = 110^{o}C, P = 90 kPa, determine the equilibrium mole fractions $\{x_i\}$ and $\{y_i\}$ of the liquid and vapor phase formed and the molar fraction V of the vapor formed. Assume that Raoult's law applies. $\ln P^{sat}(Pa) = A - \frac{B}{t(^0K) + C}$

	A	B	C
Benzene	13.8594	2773.78	-53.08
Ethylbenzene	14.0045	3279.47	-59.95
Toluene	14.0098	3103.01	-53.36

At T = 383K, the saturation vapour pressures are: $P_1^S = 233.2;\ P_2^S = 99.1;\ P_3^S = 47.1 kPa$

Thus: $K_1 = P_1^S / P = 2.6$; similarly $K_2 = 1.1; K_3 = 0.52$

For flash $\sum_{i=1}^{n}\frac{Z_iK_i}{1\ +V(K_i-1)}=1$

Thus: $\frac{Z_1K_1}{1\ +V(K_1-1)}+\frac{Z_2K_2}{1\ +V(K_2-1)}+\frac{Z_3K_3}{1\ +V(K_3-1)}=1$ ..(1)

$Z_1=Z_2=Z_3=0.33$

On substituting the values of K_i and Z_i by solving eqn. (1) on obtains: V = 0.834

Example 7.3

Methanol (1)-acetone (2) forms an azeotrope at 760 Torr with x_1= 0.2, T = 55.7^{0}C. Using van Laar model predict the bubble pressure for a system with for x_1 = 0.1 at 55.7^{0}C.

$\log_{10}P_1^S=8.0897-[1582.271/(t+239.726)];\log_{10}P_2^S=7.1171-[1210.595/(t+229.664)]$

$P_i^S(torr);t(^0C)$

At 55.7^{0}C $P_1^s=541.75torr;P_2^s=745.5torr$

We assume that the vapour phase is ideal. Hence the VL equation is given by:

$y_iP=x_i\gamma_iP_i^S$

At the azeotropic condition: $y_i=x_i$

Hence,

$\gamma_i=P/P_i^S$

Thus $\gamma_1=\ 1.4313,\ln\gamma_1=\ 0.3607$ and $\gamma_2=1.0318,\ln\gamma_2=\ 0.0137$

The Van Laar parameters are estimated next using the azeotropic composition given by $x_1=0.2$ and $x_2=0.8$:

$$A_{12}=\ln\gamma_1\left(1+\frac{x_2\ln\gamma_2}{x_1\ln\gamma_1}\right)^2=0.4786$$

$$A_{21}=\ln\gamma_2\left(1+\frac{x_1\ln\gamma_1}{x_2\ln\gamma_2}\right)^2=0.7878$$

Thus $\ln\gamma_1=\frac{A_{12}}{\left(1+\frac{A_{12}x_1}{A_{21}x_2}\right)^2};\ln\gamma_2=\frac{A_{21}}{\left(1+\frac{A_{21}x_2}{A_{12}x_1}\right)^2}$

For x_1 = 0.1, γ_1 = 1.5219, γ_2 = 1.0032

$\therefore P=\sum x_i\gamma_iP_i^s=757.62$ torr, $y_1=\gamma_1x_1P_1^s/P=0.1067$

Example 7.4

For a binary, the activity coefficients are $\ln\gamma_1 = Ax_2^2$ and $\ln\gamma_2 = Ax_1^2$. Show that the system forms an azeotrope when $A > \left|\ln\left(P_2^s / P_1^s\right)\right|$

Again $\gamma_1 = P/P_1^s\,, \gamma_2 = P/P_2^s$

$$\ln\gamma_1 = Ax_2^2 = P/P_1^s\,; \ln\gamma_2 = Ax_1^2 = P/P_2^s$$

$$\therefore A\left(x_2^2 - x_1^2\right) = \ln\left(P_2^s/P_1^s\right)$$

or $A\left(x_2 - x_1\right) = A\left(1 - 2x_1\right) = \ln\left(P_2^s/P_1^s\right)$

or $x_1 = \dfrac{1}{2}\left[1 - \dfrac{1}{A}\ln\left(P_2^s/P_1^s\right)\right]$

For azeotropy $0 < x_1 < 1$

If $x_1 = 0$, then $A = \ln\left(P_2^s/P_1^s\right)$

If $x_1 = 1$, then $A = -\ln\left(P_2^s/P_1^s\right)$

Thus for azeotropy to exist $A > \left|\ln P_2^s/P_1^s\right|$

Example 7.5

Estimate the vapour pressure of a substance "A' using PR-EoS, at T = 428°K. For the substance A: T_C = 569.4 K, P_C = 2.497 MPa, = 24.97 bar ω = 0.398.

T_r = 0.7514

At this temperature for starting the iteration, assume P^{sat} = 0.215 MPa

$f_\omega = 0.37464 + 1.54226\omega - 0.26992\,\omega^2 = 0.94570$

$\alpha_{PR} = \left[1 + f_\omega\left(1 - \sqrt{T_r}\right)\right]^2 = 1.2677$

$$a = \frac{0.45724 R^2 T_C^2 \alpha_{PR}}{P_C} = \frac{0.45724\ x\ \left(8.314\ Pa.m^3/mol^oK\ x\ 569.4\right)^2\ x1.2677}{24.97\ x\ 10^5}$$

$$= 5.2024\ \text{Pa.m}^6/\text{mol}^2$$

$$b = \frac{0.07780\ RT_C}{P_C} = \frac{0.07780\ x\ 8.314\ x\ 569.4}{24.97\ x10^5} = 1.4750 \times 10^{-4}\ \text{m}^3/\text{mol}$$

$$A = aP/\left(RT\right)^2 = \frac{5.2024\ x\ 0.215\ x\ 10^6}{\left(8.314\ x\ 428.0\right)^2} = 8.8398 \times 10^{-2}$$

Assuming $P = P^{sat}$:

$B = bP/RT = \dfrac{1.4750\ x\ 10^{-4}\ x\ 0.215\ x\ 10^{6}}{8.314\ x\ 428}$ = 8.9151 x 10^{-3}

$Z^3 + \alpha Z^2 + \beta Z + \gamma\gamma = 0$

α = -1+B = -0.9911

β = A-2B-3B^2 = 7.0329 x 10^{-2}

γ = -AB + B^2+B^3 = -7.0789 x 10^{-4}

On solving Z_1 = 0.9151, Z_2 = 1.2106 x 10^{-2}, Z_3 = 6.39 x 10^{-2}

Thus Z^V = 0.9151, Z^L = 1.2106 x 10^{-2}.

Now by PR-EoS: $\ln\phi = (Z - 1) - \ln\ (Z - B) - \dfrac{a}{2\sqrt{2}\,bRT}\ln\left\{\dfrac{Z + B(1+\sqrt{2})}{Z + B(1-\sqrt{2})}\right\}$

∴ ∴ Putting Z = Z^L

$\ln\ \phi^L\ \phi^L$ = (1.2106 x 10^{-2}) -1-ln [1.2106 – 8.9151 x 10^{-3}]

$$-\frac{5.2024}{2\sqrt{2}\ x\ 1.475\ x\ 10^{-4}\ x\ 8.314\ x\ 428}\ x\ \ln\ \left\{\frac{0.9151\ +\ 8.9151\ x\ 10^{-3}(1+\sqrt{2})}{0.9151\ +\ 8.9151\ x\ 10^{-3}(1+\sqrt{2})}\right\}$$

$= -0.0978 \Rightarrow \phi^L = 0.90 \Rightarrow f^L = \phi^L P = 0.19 MPa$ = –0.0978 ⇒ ϕ^L = 0.90 ⇒ $f^L = \phi^L P$ = 0.19 MPa

Similarly putting Z = Z^V gives ln ϕ^V = -0.0821 ⇒⇒ ϕ^V = 0.9212

or f^V = 0.1981

→→ If $f^L > f^V$, assumed value of P (=P^{sat}) < actual P^{sat}

→ If $f^L < f^V$, assumed value of P (=$P^{sat)}$ > actual P_{sat}

$P_{(revised)} = P\ \dfrac{f^L}{f^V}$

For the present case $P_{revised}$ = 0.215 x $\dfrac{0.195}{0.1981}$ = 0.2116 MPa

Use revised ‘P’ to recalculate A, B, {Z_i}; thus:

A = aP/(RT)^2 = 8.6999 x 10^{-2} ; B = bP/RT = 8.7742 x 10^{-3}

∴ α = -6.8568 x 10^{-4}; β = 6.922 x 10^{-2}; γ = -6.8568 x 10^{-4}

Resolving f(z) = 0 ⇒ Z_1 = 0.9166; Z_2 = 6.2907 x 10^{-4}; Z_3 = 1.1711 x 10^{-2}

Hence new Z^V = 0.9166; Z^L = 1.1711 x 10^{-2}

Using Z = Z^V and Z = Z^L respectively

New $\phi\,\phi^V$ = 0.9225 ⇒ f^V = (0.9225 x 0.2116) = 0.1952 MPa

Similarly ϕ^L = 0.9224 ⇒ $f^L \simeq$ 0.1952 MPa

Thus $P^{sat} \simeq 0.2116$ MPa (at 428^oK).

Example 7.6

A vapour mixture contains 20mol% methane (1), 30mol% ethane (2) , and rest propane (3), at 30^0C. Determine the dew composition.

Assume $P = 2.15\ MPa$

$At\ 30°C, and\ 2.15\ MPa$ read off the K factors from the charts.

$K_1 = 8.1,\ K_2 = 1.82,\ K_3 = 0.62$

$$x_1 = \frac{y_1}{K_1} = \frac{0.2}{8.1} = 0.0247$$

$$x_2 = \frac{y_2}{K_2} = \frac{0.3}{1.82} = 0.1648$$

$$x_3 = \frac{y_3}{K_3} = \frac{0.5}{0.62} = 0.8065$$

$$\sum x_i = 0.9960 \sim 1$$

Hence dew pressure = 2.15 MPa. The dew composition therefore corresponds to the values of x_i computed above.

Example 7.7

For the system of methane (1) and butane (2) compute the bubble pressure for a liquid phase composition of $x_1 = 0.2$ at a temperature of 310K, using the PR-EOS.

P (guessed): 40.8 bar

y_1 (guessed) = 0.85; $y_2 = 0.15$;

First consider calculation of the species fugacity coefficients for the liquid phase as T, P and x_1 (=0.2) are all know. For this one needs to solve for the cubic EOS with *liquid phase compositions.*

T = 310K, P = 40.8bar

For each species the following estimates are made:

Table 1

Parameter	**Methane (1)**	**Butane (2)**
f_ω	3.9310×10^{-3}	6.7229×10^{-3}

a (Pa.m^{-6}/mol^{2})	0.198207	1.811717
b (m^{3}/mol)	0.000027	0.000072

With x_1 = 0.2, it follows that

$$a_m = x_1^2 a_1 + 2x_1 x_2 (a_1 a_2)^{1/2} + x_2^2 a_2 = 1.3592\, Pa.m^{-6} / mol^2$$

$$b_m = x_1 b_1 + x_2 b_2 = 0.000063\, m^3 / mol$$

$$A_m = \frac{a_m P}{R^2 T^2} = 0.8304$$

$$B_m = \frac{b_m P}{RT} = 0.10$$

With the above values of A and B solve the cubic PR-EOS. The roots are as:

$$Z_1 = 0.1471$$
$$Z_2 = 0.3764 + 0.5899i$$
$$Z_3 = 0.3764 - 0.5899i$$

The feasible root for the liquid phase is: Z^L = 0.1471

Now using the generalized expression for species fugacity coefficients for PR-EOS:

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z-1) - \ln(Z-B) + \frac{a_m}{2\sqrt{2} b_m RT}\left[\frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}}\right]\ln\left[\frac{Z + B(1+\sqrt{2})}{Z + B(1-\sqrt{2})}\right]$$

Using: Z= Z^L = 0.1471; $B = B_m$

$$\ln \hat{\phi}_1 = \frac{b_1}{b_m}(Z^L - 1) - \ln(Z^L - B_m) + \frac{a_m}{2\sqrt{2} b_m RT}\left[\frac{b_1}{b_m} - 2\sqrt{\frac{a_1}{a_m}}\right]\ln\left[\frac{Z^L + B_m(1+\sqrt{2})}{Z^L + B_m(1-\sqrt{2})}\right]$$

$$\text{whence}: \hat{\phi}_1^L = 4.0271$$

$$\text{Similarly}: \hat{\phi}_2^L = 0.0932$$

Next compute the fugacity coefficients for the vapour phase. The calculations are the same as above except that x_i is replaced with y_i. (Note that the pure component properties remain the same as in Table 1, since the T and R are the same, i.e, 310K and 40.8bar, respectively.

With y_1 = 0.85, it follows that

$$a_m = y_1^2 a_1 + 2y_1 y_2 (a_1 a_2)^{1/2} + y_2^2 a_2 = 0.3323\, Pa.m^{-6} / mol^2$$

$$b_m = y_1 b_1 + y_2 b_2 = 0.000033\, m^3 / mol$$

$$A_m = \frac{a_m P}{R^2 T^2} = 0.2030$$

$$B_m = \frac{b_m P}{RT} = 0.0528$$

With the above values of A and B solve the cubic PR-EOS. The roots are as:

$$Z_1 = 0.8537$$
$$Z_2 = 0.0467 + 0.0833i$$
$$Z_3 = 0.0467 - 0.0833i$$

The feasible root for the liquid phase is: Z^V = 0.8537

Now using the generalized expression for species fugacity coefficients for PR-EOS:

$$\ln \hat{\phi}_i = \frac{b_i}{b_m}(Z-1) - \ln(Z-B) + \frac{a_m}{2\sqrt{2}b_m RT}\left[\frac{b_i}{b_m} - 2\sqrt{\frac{a_i}{a_m}}\right]\ln\left[\frac{Z+B(1+\sqrt{2})}{Z+B(1-\sqrt{2})}\right]$$

Using: Z= Z^V = 0.8537; $B = B_m$

$$\ln \hat{\phi}_1 = \frac{b_1}{b_m}(Z^V-1) - \ln(Z^V-B_m) + \frac{a_m}{2\sqrt{2}b_m RT}\left[\frac{b_1}{b_m} - 2\sqrt{\frac{a_1}{a_m}}\right]\ln\left[\frac{Z^V+B_m(1+\sqrt{2})}{Z^V+B_m(1-\sqrt{2})}\right]$$

$$\text{whence}: \hat{\phi}_1^V = 0.9399$$

$$\text{Similarly}: \hat{\phi}_2^V = 0.5184$$

Therefore:

$$K_1 = \frac{y_1}{x_1} = \frac{\hat{\phi}_1^L}{\hat{\phi}_1^V} = \frac{4.0271}{0.9399} = 4.2846$$

$$y_1 = K_1 x_1 = 0.8569$$

$$K_2 = \frac{y_2}{x_2} = \frac{\hat{\phi}_2^L}{\hat{\phi}_2^V} = \frac{0.0932}{0.5184} = 0.1798$$

$$y_2 = K_2 x_2 = 0.1438$$

$$\text{Thus}: \sum_i y_i = 1.0007$$

Therefore we may terminate the iteration at this point.

Bubble Pressure = 40.8bar

y_1 = 0.8569

Example 7.8

A concentrated binary solution containing mostly species 2 (but $x_2 \neq 1$) is in equilibrium with a vapor phase containing both species 1 and 2. The pressure of this two-phase system is 1 bar; the temperature is 298.0K. Determine from the following data good estimates of x_1 and y_1.

H_1 = 200 bar; P_2^{sat} = 0.10 bar.

H_1= 200 bar, P_2^s= 0.1 bar, P = 1 bar

Assume that vapor phase is ideal at P = 1 bar. Assume Lewis - Randall rule applies to concentrated species and Henry's law to dilute species then:

$y_1P = H_1x_1$ And $y_2P = x_2P_2^s$

Now $P = (y_1 + y_2)P = y_1P + y_2P = H_1x_1 + x_2P_2^s$

Or $P = H_1x_1 + (1 - x_1)P_2^s$ → Solving gives, $x_1 = 4.5 \times 10^{-3}$ and $y_1 = 0.9$

Example 8.1

Consider the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

Species	**a**	**bx10^3**	**cx10^6**	**dx10^9**	**ex10^{-5}**
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

From standard tables $\Delta H^0_{R,298} \approx -52.7$ KJ; $\Delta G^0_{R,298} = 14.5$ KJ

Now $\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta C_P^0 dT$ ---------------------- (A)

$\Delta C_P^0 = \sum \alpha_i C_{P,i}^0 = \Delta a + \Delta bT + \Delta CT^2 + \Delta dT^3 + \Delta e / T^2$ ------------- (B)

Where:

$\Delta a = \sum \alpha_i a_i, \Delta b = \sum \alpha_i b_i, etc$

For example $\Delta a = 20.691 - 4.196 - 28.850 = -12.355$

$\Delta b = (205.346 - 154.565 - 12.055) \times 10^{-3} = 3.8726 \times 10^{-2}$

Similarly $\Delta c = -1.8717 \times 10^{-5}$; $\Delta d = 2.012 \times 10^{-9}$; $\Delta e = -1.006 \times 10^{5}$

Putting B in A and integrating A we get:

$$\Delta H_T^0 = -50.944(KJ) - 12.355T + \frac{3.8726 \times 10^{-2}}{2} T^2 - \frac{1.8717 \times 10^{-5}}{3} T^3 + \frac{2.012 \times 10^{-9}}{4} T^4 + 1.006 \times 10^5 / T \quad \text{…………..(C)}$$

By Vant Hoff equation: $\frac{d(\Delta G_T^0 / RT)}{dT} = -\frac{\Delta H_T^0}{RT^2}$

$$\therefore \frac{\Delta G_T^0}{RT} - \frac{\Delta G_{298}^0}{R(298)} = -\int_{298}^{T} \frac{\Delta H_T^0}{RT^2} dT \quad \text{-- D}$$

We already know ΔH_T^0 from (C); putting C in D and integrating we obtain:

$$\Delta G_T^0 = -50.944 + 12.355T \ln T - \frac{3.8726 \times 10^{-2}}{2} T^2 + \frac{1.8718 \times 10^{-5}}{6} T^3 - \frac{2.012 \times 10^{-9}}{12} T^4 + \frac{1.006 \times 10^5}{2T} + 56.681T$$

Putting T=500k, ΔG_T^0 = 11.43kJ

Example 8.2

Consider the following reaction: A(g) + B(g) = C(g) + 3D(g) $CH_4 + H_2O \rightarrow CO + 3H_2$

Intially the following number of moles are introduced in the reactor. Obtian the mole fraction expressions in terms of reaction coordinate.

$n_{0,A}$ = 2 mol, $n_{0,B}$ = 1 mol, $n_{0,C}$ = 1 mol $n_{0,D}$ = 4 mol

$\alpha \sum \alpha_i$ = -i = -1-1+1+3 = 2

$n_o = \sum_i n_{i_o}$ = 2+ 1 +1 + 4 = 8

$$y_i = \frac{n_i}{n} = \frac{n_{i_o} + \alpha_i \xi}{n_o + \alpha \xi}$$

$$\therefore \therefore \; y_A = \frac{2-\xi}{8+2\xi}; \quad y_B = \frac{1-\xi}{8+2\xi}; \quad y_C = \frac{1+\xi}{8+2\xi}; \quad y_{H_2} = \frac{4+\xi}{8+2\xi}$$

Example 8.3

Consider the following simultaneous reactions. Express the reaction mixture composition as function of the reaction co-ordinates. All reactants and products are gaseous.

A + B = C + 3D ..(1)

A + 2B = E + 4D ..(2)

Initial number of moles:

$n_{0,A}$ = 2 mol; $n_{0,B}$ = 3 mol

Let the reaction co-ordinates for each reaction be ξ_1 *and* ξ_2 respectively.

j	A	B	C	D	E	$\alpha_j = \Sigma \alpha_{i,j}$
1	- 1	-1	1	3	0	2
2	-2	-2	0	4	1	2

$$y_i = \frac{n_{io} + \sum_j \alpha_{i,j}\xi_j}{n_o + \sum_j \alpha_j \xi_j};$$

n_o = 2+3 = 5

$$\therefore \; y_A = \frac{2-\xi_1-\xi_2}{5+2\xi_1+2\xi_2}; \; y_B = \frac{3-\xi_1-2\xi_2}{5+2\xi_1+2\xi_2}; \; y_C = \frac{\xi_1}{5+ 2\xi_1+2\xi_2}$$

$$y_D = \frac{3\xi_1 + 4\xi_2}{5 + 2\xi_1 + 2\xi_2};\ y_E = \frac{\xi_2}{5 + 2\xi_1 + 2\xi_2}$$

Example 8.4

Consider the reaction : $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the equilibrium constant, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

Species	**a**	**bx10^3**	**cx10^6**	**dx10^9**	**ex10^{-5}**
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

From standard tables $\Delta H^0_{R,298} \approx -52.7$ KJ; $\Delta G^0_{R,298} = 14.5$ KJ

$$\text{Now } \Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta C_P^0 dT \text{ ---------------------- (A)}$$

$$\Delta C_P^0 = \sum \alpha_i C_{P,i}^0 = \Delta a + \Delta bT + \Delta CT^2 + \Delta dT^3 + \Delta e/T^2 \text{ ------------- (B)}$$

Where:

$$\Delta a = \sum \alpha_i a_i, \Delta b = \sum \alpha_i b_i, etc$$

For example $\Delta a = 20.691 – 4.196 - 28.850 = -12.355$

$\Delta b = (205.346 – 154.565 – 12.055) \times 10^{-3} = 3.8726 \times 10^{-2}$

Similarly $\Delta c = -1.8717 \times 10^{-5}$; $\Delta d = 2.012 \times 10^{-9}$; $\Delta e = -1.006 \times 10^5$

Putting B in A and integrating A we get:

$$\Delta H_T^0 = -50.944(KJ) - 12.355T + \frac{3.8726\times10^{-2}}{2}T^2 - \frac{1.8717\times10^{-5}}{3}T^3 + \frac{2.012\times10^{-9}}{4}T^4 + 1.006\times10^5/T \qquad \ldots\ldots\ldots\ldots.(C)$$

By Vant Hoff equation: $\dfrac{d(\Delta G_T^0/RT)}{dT} = -\dfrac{\Delta H_T^0}{RT^2}$

$$\therefore \frac{\Delta G_T^0}{RT} - \frac{\Delta G_{298}^0}{R(298)} = -\int_{298}^{T} \frac{\Delta H_T^0}{RT^2} dT \text{ --- D}$$

We already know ΔH_T^0 from (C); putting C in D and integrating we obtain:

$$\Delta G_T^0 = -50.944 + 12.355T\ln T - \frac{3.8726\times10^{-2}}{2}T^2 + \frac{1.8718\times10^{-5}}{6}T^3 - \frac{2.012\times10^{-9}}{12}T^4$$
$$+\frac{1.006\times10^5}{2T} + 56.681T$$

Putting T=500k, ΔG_T^0 = 11.43kJ

Hence K_{500} = exp [-1143/8.314 x 1000] = 0.064

Example 8.5

Consider the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$. If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 500 K and 40 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal gas. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K).

Species	**a**	**bx10^3**	**cx10^6**	**dx10^9**	**ex10^{-5}**
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

From standard tables $\Delta H^0_{R,298} \approx$ -52.7 KJ; $\Delta G^0_{R,298}$ = 14.5 KJ

Now $\Delta H_T^0 = \Delta H_{298}^0 + \int_{298}^{T} \Delta C_P^0 dT$ ---------------------- (A)

$\Delta C_P^0 = \sum \alpha_i C_{P,i}^0 = \Delta a + \Delta bT + \Delta CT^2 + \Delta dT^3 + \Delta e / T^2$ ------------ (B)

Where:

$\Delta a = \sum \alpha_i a_i, \Delta b = \sum \alpha_i b_i, etc$

For example Δa = 20.691 – 4.196 -28.850 = -12.355

Δb = (205.346 – 154.565 – 12.055) x 10^{-3} = 3.8726 x 10^{-2}

Similarly Δc = -1.8717 x 10^{-5} ; Δd = 2.012 x 10^{-9} ; Δe = -1.006 x 10^5

Putting B in A and integrating A we get:

$$\Delta H_T^0 = -50.944(KJ) - 12.355T + \frac{3.8726\times10^{-2}}{2}T^2 - \frac{1.8717\times10^{-5}}{3}T^3 +$$
$$\frac{2.012\times10^{-9}}{4}T^4 + 1.006\times10^5/T \qquad \text{…………..(C)}$$

By Vant Hoff equation: $\frac{d(\Delta G_T^0/RT)}{dT} = -\frac{\Delta H_T^0}{RT^2}$

$$\therefore \frac{\Delta G_T^0}{RT} - \frac{\Delta G_{298}^0}{R(298)} = -\int_{298}^{T} \frac{\Delta H_T^0}{RT^2} dT \qquad \text{--} \quad D$$

We already know ΔH_T^0 from (C); putting C in D and integrating we obtain:

$$\Delta G_T^0 = -50.944 + 12.355T\ln T - \frac{3.8726\times10^{-2}}{2}T^2 + \frac{1.8718\times10^{-5}}{6}T^3 - \frac{2.012\times10^{-9}}{12}T^4$$

$$+\frac{1.006\times10^5}{2T} + 56.681T$$

Putting T=500k, ΔG_T^0 = 11.43kJ

Hence K_{500} = exp [-1143/8.314 x 1000] = 0.064

$\alpha = \Sigma\alpha_i = 1\text{-}1\text{-}1 = -1$

$\therefore$ K = $K_\varphi K_y P^\alpha$; K_φ=1(since ideal gas assumption is made)

P = 40bar

Component	**n_{i0}**	**n(exit)**	**y_i(exit)**
C2H4	1	1-ε	(1-ε)/(2-ε)
H2O	1	1-ε	(1-ε)/(2-ε)
C2H5OH	0	ε	(ε)/(2-ε)

n_t (at exit) = 2-ε

$$\therefore K = K_y = y_{C_2H_5OH} / y_{C_2H_4} y_{H_2O} = \frac{\xi/(2-\xi)}{\{(1-\xi)/(2-\xi)\}^2} = \frac{\xi(2-\xi)}{(1-\xi)^2}$$

Now K = $K_\varphi K_y P^\alpha$ = (1) K_y P^{-1}

$$\therefore K_y = 40K; K_y = \xi(2-\xi)/(1-\xi)^2$$

$$\therefore K_y = \frac{\xi(2-\xi)}{(1-\xi)^2} = 40\times K_{500} = 40\times0.064 = 2.56$$

On solving ξ = 0.47

Thus $y_{C_2H_4} = (1-\xi)/(2-\xi) = 0.3464 = y_{H_2O}$

$$y_{C_2H_5OH} = \xi/(2-\xi) = 0.3072$$

Example 8. 6

The following two independent reactions occur in the steam cracking of methane at 1000 K and 1 bar: $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$; and $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$. Assuming ideal gas behaviour 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, and that at 1000K, the equilibrium constants for the two reactions are 30 and 1.5 respectively.

Let ξ_1 and ξ_2 be the reaction co-ordinate for the two reactions, we have

Comp	$\mathbf{n_{i0}}$	$\mathbf{n_{exit}}$	$\mathbf{y_{exit}}$
CH_4	1	$1 - \xi_1$	$(1 - \xi_1) / 2(1 + \xi_1)$
H_2O	1	$1 – \xi_1 – \xi_2$	$(1 – \xi_1 – \xi_2) / 2(1 + \xi_1)$
CO	0	$\xi_1 – \xi_2$	$(\xi_1 – \xi_2) / 2(1 + \xi_1)$
CO_2	0	ξ_2	$\xi_2 / 2(1 + \xi_1)$
H_2	0	$3\xi_1 + \xi_2$	$(3\xi_1 + \xi_2) / 2(1 + \xi_1)$

Total moles at equilibrum: $2(1 + \xi_1)$

$K = K_\varphi K_y P^\alpha$ (for each reaction); $K_\varphi = 1.0$ (ideal gas assumption); P = 1 bar

Thus $K_1 = \left[\frac{(\xi_1-\xi_2)}{2(1+\xi_1)}\right]\left[\frac{(3\xi_1+\xi_2)}{2(1+\xi_1)}\right]^3 \Big/ \left[\frac{(\varepsilon_1-\xi_2)}{2(1+\xi_1)}\right]\left[\frac{(3\xi_1+\xi_2)}{2(1+\xi_1)}\right]$

$$= \frac{(\xi_1-\xi_2)(3\xi_1+\xi_2)^3}{4(1+\xi_1)^2(1-\xi_1)(1-\xi_1-\xi_2)} = 30 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad A$$

Similarly $K_2 = \frac{(3\xi_1+\xi_2)\xi_2}{(\xi_1-\xi_2)(1-\xi_1-\xi_2)} = 1.5 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad B$

A and B needs to be solved simultaneously; a simple way to do this is to

(i) Assume ε_2 , calculate ε_1 using B

(ii) Use ξ_2 and ξ_1 in A to check if $K_1 = 30$

(iii) If $K_1 \neq 30,$ assume new ε_2 and go to step 1

Using the above algorithm, one finally obtains: $\xi_1 = 0.7980$, $\xi_2 = 0.0626$.

Thus: $y_{CO_2} = 0.0174, y_{CH_4} = 0.0562, y_{H_2O} = 0.0388, y_{CO} = 0.2045, y_{H_2} = 0.6831$

<u>Example 8.7</u>

The gas n-pentane (1) is known to isomerise into neo-pentane (2) and iso-pentane (3) according to the following reaction scheme: $P_1 \rightleftharpoons P_2; P_2 \rightleftharpoons P_3; P_3 \rightleftharpoons P_1$. 3 moles of pure n-pentane is fed into a reactor at 400°K and 0.5 atm. Compute the number of moles of each species present at equilibrium.

Species	ΔG_f^0 at 400°K (Cal/mol)
P_1	9600
P_2	8900
P_3	8200

We use here the method of undetermined Lagrangian Multipliers.

The set of equation to be solved are:

$A_C = 15, A_H = 36$

For P_1: $\frac{9600}{RT} + \ln\left(\frac{n_1}{\sum n_i}\right) + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0$

For P_2: $\frac{8900}{RT} + \ln\left(\frac{n_2}{\sum n_i}\right) + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0$

For P_3: $\frac{8200}{RT} + \ln\left(\frac{n_3}{\sum n_i}\right) + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0$

Atomic mass balance for C: $5(n_1 + n_2 + n_3) = 15$

For H: $12(n_1 + n_2 + n_3) = 36$

$n_1 + n_2 + n_3 = 10$

Alternately: $\frac{9600}{RT} + \ln y_1 + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0$ …………………. (A)

$\frac{8900}{RT} + \ln y_2 + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0$ …………………. (B)

T = 400K

$\frac{8200}{\mathrm{RT}} + \ln y_3 + \frac{5\lambda_C}{RT} + \frac{12\lambda_H}{RT} = 0$ …………………. (C)

and $y_1 + y_2 + y_3 = 1$ …………………. (D)

It follows from (A) – (C), $y_2 / y_1 = 2.41$; $y_3 / y_2 = 2.41$

Using eqn. (D) $y_1 = 0.108$, $y_2 = 0.29$, $y_3 = 0.63$

Example 8.8

Consider the liquid phase reaction: A(l) + B(l) → C(l) + D(l). At 50^{o}C, the equilibrium constant is 0.09. Initial number of moles, $n_{A,0}$ = 1 mole; $n_{B,0}$ = 1 mol Find the equilibrium conversion. Assume ideal solution behaviour.

$$\therefore \mathrm{K} = \therefore \left(x_i \ \gamma_i\right)^{\gamma_i} \ \underbrace{\left[\exp\left\{\frac{(P\text{-}1)\sum \gamma_i V_i}{RT}\right\}\right]}_{1.0}$$

Also, $\gamma_i = 1$ (ideal solution)

Hence $\mathrm{K} = \pi \ \left(x_i\right)^{\gamma_i}$

$x_A = x_B = (1\text{-}\xi)/2$; $\quad x_C = x_D = \xi / 2$

$\therefore$ $K = x_C \ x_D / x_A \ x_B = [\xi/(1\text{-} \ \xi)]^2$

$\Rightarrow 0.09 = [\xi/(1\text{-} \ \xi)]^2$

Thus, $\xi_e = 0.23$

Example 8.9

Consider the following reaction: A(s) + B(g) → C(s) + D(g). Determine the equilibrium fraction of B which reacts at 500^{o}C if equal number of moles of A and B are introduced into the reactor initially. The equilibrium constant for the reaction at 500^{o}C is 2.0.

The reaction is:

$A(s) + B(g) \rightarrow C(s) + D(g)$; basis 1 mole of A & B each initially

$$K = \hat{a}_C \hat{a}_D \Big/ \hat{a}_A \hat{a}_B$$

For solids: $\hat{a} = 1$

Thus:

$$K = \hat{a}_D \Big/ \hat{a}_B = K_\phi K_y P^\alpha \ ; \alpha = 0, \ and \ K_\phi = 1$$

$$\therefore K = K_y$$

If one assumes equimolar feed of reactants:

$y_B = (1-\xi); \ y_D = \xi$

$$\therefore K = K_y = 2.0 = \frac{\xi}{1-\xi} \Rightarrow \xi = 0.67$$

Thus 67% of B reacts.

Example 9.1

Use the van Laar activity coefficient expression to predict the compositions of co-existing liquid phases (I and II) comprised of two partially miscible liquids (1) and (2) at 50^{o}C and 4 bar. At these conditions the van Laar equations are given by:

$$\ln\gamma_1 = \frac{A_{12}}{[1+\frac{A_{12}x_1}{A_{21}x_2}]^2}; \ln\gamma_2 = \frac{A_{21}}{[1+\frac{A_{21}x_2}{A_{12}x_1}]^2}; A_{12} = 2.5; A_{21} = 3.5$$

Solution:

This system is a binary; however, there are 2 phases since ‘1’ and ‘2’ are partially miscible. One of the phases (I) is rich in component ‘1’ (with some ‘2’ dissolved in it); while the second phase (II) is rich in component ‘2’ (with some ‘1’ dissolved in it). Estimates of the composition of both phases are required. We use two equations of type 9.34 as there are 2 components.

For component 1:

$$x_1^I\gamma_1^I = x_1^I \exp(\frac{\alpha}{[1+\frac{\alpha x_1^I}{\beta(1-x_1^I)}]^2}) = x_1^{II} \exp(\frac{\alpha}{[1+\frac{\alpha x_1^{II}}{\beta(1-x_1^{II})}]^2}) = x_1^{II}\gamma_1^{II} \quad ..(a)$$

For component 2:

$$x_2^I\gamma_2^I = x_2^I \exp(\frac{\beta}{[1+\frac{\beta x_2^I}{\alpha(1-x_2^I)}]^2}) = x_2^{II} \exp(\frac{\beta}{[1+\frac{\beta x_2^{II}}{\alpha(1-x_2^{II})}]^2}) = x_2^{II}\gamma_2^{II} \quad ..(b)$$

Lastly $x_1^I + x_2^I = 1$ ..(c)

And: $x_1^{II} + x_2^{II} = 1$ ..(d)

Equations I – IV need to be solved simultaneously using a suitable algorithm to obtain the final solution: $x_1^I = 0.12$, $x_1^{II} = 0.85$; and $x_2^I = 0.88$, $x_2^{II} = 0.15$

Example 9.2

Estimate solubility of a solid A in a liquid B at 300°K, using (i) ideal solution assumption, (ii) regular solution model for liquid-phase. The following data are available: $V_A^L = 100 cm^3/mol; V_B^L = 125 cm^3/mol; \delta_A = 9.5(\text{cal/cc})^{1/2}; \delta_B = 7.5(\text{cal/cc})^{1/2}$. Heat of fusion for A: 17.5 kJ/mol. Melting point for A = 350°K.

Assuming that solid-phase is pure naphthalene (which is in equilibrium with solution of naphthalene in hexane), $z_1 = 1, \gamma_1^S = 1$, we start with the simplified equation:

$$\ln x_A = -\ln \gamma_A - \left[\frac{\Delta H^{fus}_{T_m,A}}{R}\left(\frac{1}{T} - \frac{1}{T_{m,A}}\right)\right]$$

For ideal solution the above equation reduces to:

$$\ln x_A = -\left[\frac{\Delta H^{fus}_{T_{m,A}}}{R}\left(\frac{1}{T} - \frac{1}{T_{m,A}}\right)\right]$$

Using the data provided: $\ln x_A = -\left[\frac{17500}{8.314}\left(\frac{1}{300} - \frac{1}{350}\right)\right]$

Thus, the ideal solubility $x_A = 0.38$.

By Regular solution theory: $RT \ \ln \gamma_A = V_A^L(\delta_A - \delta_A)^2 \Phi_B^2$

$$\therefore \ \ln \ x_A = -\frac{V_A^L \Phi_B^2 (\delta_A - \delta_B)^2}{RT} - \frac{\Delta H^{fus}}{RT}\left[1 - \frac{T}{T_{m_A}}\right] \quad ..(1)$$

$$\text{Also } \Phi_B = \frac{x_B V_b^L}{x_A V_A^L + x_B V_B^L} \quad ..(2)$$

T = 300 K, T_{m_1} = 350°K

$V_A^L = 100 cm^3/mol; V_B^L = 125 cm^3/mol; \delta_A = 9.5(\text{cal/cc})^{1/2}; \delta_B = 7.5(\text{cal/cc})^{1/2}$. Solution algorithm:

(1) Assume x_A (to start with assume $x_A = 0$)

(2) Calculate Φ_B from eqn 2

(3) Use equation (1) to calculate new x_A

(4) If $x_{A,i+1} - x_{A,i} < 0.01$, $x_{A,i+1}$ is the solution or else, return to step '1'.

The final converged value for $x_A \approx 0.08$

Note that the result differs significantly from that obtained by assuming ideal solution behaviour for the liquid phase.

Example 9.3

Compute the eutectic composition and temperature for a mixture of two substances A and B using the following data:

Property	**A**	**B**
Normal T_m (^oK)	180	181
ΔH^{fus} (J/mol)	6600	9075

We use the ideal solution behaviour for the liquid phase. The following equation then holds at the eutectic point:

$$\exp\left[\frac{\Delta H_A^{fus}}{RT_{m,A}}\left(\frac{T-T_{m,A}}{T}\right)\right]+\exp\left[\frac{\Delta H_B^{fus}}{RT_{m,B}}\left(\frac{T-T_{m,B}}{T}\right)\right]=1$$

On substituting all relevant data:

$$\exp\left[\frac{6600}{8.314x180}\left(\frac{T-180}{T}\right)\right]+\exp\left[\frac{9075}{8.314x181}\left(\frac{T-180}{T}\right)\right]=1$$

On solving by trial and error, $T\left(eutectic\right)\approx 150\,^0K$

The eutectic composition is found from the following equation:

$$x_A=\exp\left[\frac{\Delta H_A^{fus}}{RT_{m_A}}\left(\frac{T-T_{m_A}}{T}\right)\right]$$

Substituting all the available data with T = 150^0K, the eutectic composition is found to be: $x_A \approx 0.5$.

Example 9.4

A certain solid A has a vapour pressure of 0.01 bar at 300^0K. Compute its solubility at the same temperature in a gas B at a pressure of 1.0bar. The molar volume of the solid is 125cc/mol.

We start with the following equation:

$$P_A^{sat}\phi_A^{sat}\exp\left[\frac{V_A^S\left(P-P_A^{sat}\right)}{RT}\right]=y_A\hat{\phi}_A P$$

Since $P_A^{sat}=10^{-2}bar, \phi_A^{sat}\approx 1.0$

Further as the total system pressure is 1.0bar, it follows that

$\hat{\phi}_A \cong 1.0$

Thus the solubility of the solid at the system pressure is given by:

$$y_A=(P_A^{sat}/P)\exp\left[\frac{V_A^S\left(P-P_A^{sat}\right)}{RT}\right]$$

Substituting all relevant data the solubility is:

$y_A = 1.05x10^{-2}.$

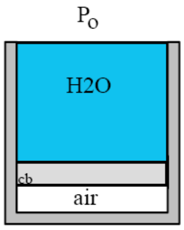
Assignment for Chapter 2
(Answers are in parenthesis)

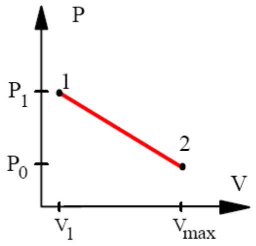
1. Express the volume expansivity and the isothermal compressibility as functions of density ρ and its partial derivatives. For water at 323K (50^{o}C) and 1 bar, $\kappa = 44.18x10^{-6}$ bar^{-1}. To what pressure must water be compressed at 323 K (50^{o}C) to change its density by 1%? Assume that κ is independent of P. **[226.2 bar]**
2. For liquid water the isothermal compressibility is given by: $\kappa = \frac{c}{V(P+b)}$

   where c, b are functions of temperature only. If 1 kg of water is compressed isothermally and reversibly from 1 to 500 bars at 333K, how much work is required? At 333K, b = 2700 bar and c = 0.125 cm^{-3} g^{-1}. **[0.516 J/gm]**
3. Calculate the reversible work done in compressing 0.0283 m^{3} of mercury at a constant temperature of 0^{o}C from 1 atm to 3000 atm. The isothermal compressibility of mercury at 0^{o}C is: $\kappa = 3.9 \text{ x } 10^{-6} - 0.1 \text{ x } 10^{-9} P$; where P is in atm and κ is in atm^{-1}. **[0.52J]**
4. A substance for which κ is a constant undergoes an isothermal, mechanically reversible process from initial state (P_1, V_1) to final state (P_2, V_2), where V is molar volume. (a) Starting with the definition of κ, show that the path of the process is described by: V = A(T) exp(-κP); (b) Determine an exact expression which gives the isothermal work done on 1 mol of this constant -κ substance. [$P_1V_1 - P_2V_2 + (V_1 - V_2)/\kappa$]
5. For methyl chloride at 373.15 K (100^{o}C) the second and third virial coefficient s are: B = -242.5 cm^{3} mol^{-1}; C = 25 200 cm^{6} mol^{-2}. Calculate the work of mechanically reversible, isothermal compression of 1 mol of methyl chloride 1 bar to 55 bars at 100^{o}C. Base calculations on the following form of the virial equation: $Z = 1 + \frac{B}{V} + \frac{C}{V^2}$ **[12.62 kJ/mol, 12.596 kJ/mol]**
6. Calculate V for sulfur hexafluoride at 75^{o}C and 15 bar by the following equations: (a) The truncated virial equation with the following experimental values of virial coefficients: B = -194 cn^{3} mol^{-1}; C = 15300 cm^{6} mol^{-2} (b) The truncated virial equation, with a value of B from the generalized Pitzer correlation. (c) The Redlich/Kwong equation (d) The Soave/Redlich/Kwong equation (e) The Peng/Robinson equation. **[1722, 1734, 1714, 1727, 1701cm3/mol];** For sulfur hexafluoride, T_c = 318.7 K, P_c = 37.6 bar, V_c = 198 cm^{3} mol^{-1}, and $\omega = 0.286$.
7. Use the Soave/Redlich/Kwong equation to calculate the molar volumes of saturated liquid and saturated vapor for propane at 40C for which the vapour pressure is 13.71 bar. **[104.7, 1480.7 cm3/mol]**
8. A 30-m^{3} tank contains 14 m^{3} of liquid n-butane in equilibrium with its vapor at 298.15 K (25^{o}C). Estimate the mass of n-butane vapor in the tank. The vapor pressure of n-butane at the given temperature is 2.43 bar. **[98.2 kg]**
9. A rigid 0.35-m^{3} vessel at 25^{o}C and 2200kpa holds ethane; what pressure develops if it is heated to 220^{o}C? **[42.7 bar]**
10. To what pressure does one fill a 0.15-m^{3} vessel at 25^{o}C for storing 40 kg of ethylene in it? **[79.7 bar]**
11. Liquid water at 25^{o}C and 1 bar fills a rigid vessel. If heat is added to the water until its temperature reaches 50^{o}C, what pressure is developed? The average value of β between 25 and 50^{o}C is 36.2 x 10^{-5} K^{-1}. The value of κ at 1 bar and 50^{o}C is 4.42 x 10^{-5} bar^{-1}, and may be assumed independent of P. The specific volume of liquid water at 25^{o}C is 1.0030 cm^{3} g^{-1}. **[206 bar]**
12. A two-phase system of liquid water and water vapor in equilibrium at 8000 kPa consists of equal volumes of liquid and vapor. If the total volume is 0.15 m^{3}, what is the total enthalpy H^{t} and what is the total entropy S^{t}? **[80173.5kJ, 192.15 kJ/K]**

Assignment on Chapter 3
(Note: Answers are given in the square brackets)

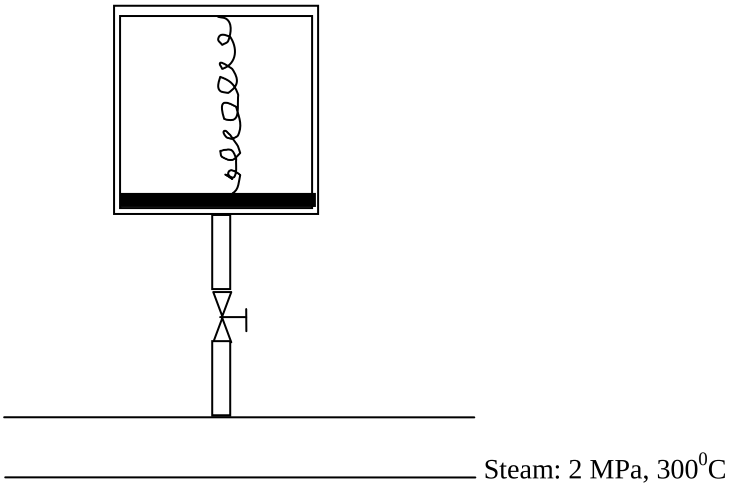
1. 2.5 kJ of work must be delivered isobarically on a rod from a piston/cylinder containing air at at 500 kPa. What is value of diameter cylinder needed to restrict the rod motion to maximum 0.5 m? **[0.113 m]**
2. A gas initially at 1 MPa, 500°C is contained in a piston-cylinder arrangement of initial volume of 0.1 m^3. The gas expanded isothermally to a final pressure of 100 kPa. Determine the work. **[230.3 kJ]**
3. A cylinder has 0.1kg of air with a 5 kg piston on top. A valve at the bottom of cylinder is opened to let out the air out and the piston (dia = 2.5cm) drops by 0.25m. What is the work involved in the process? **[– 0.0245kJ]**
4. A chiller cools liquid water (Sp. Ht = 4.2 J/gmK) for air-conditioning purposes. Assume 2.5 kg/s water at 20^oC and 100 kPa is cooled to 5^oC in a chiller. How much heat transfer (kW) is needed? **[156.75 kW]**
5. Helium gas expands from 125 kPa, 350 K and 0.25 m^3 to 100 kPa in a polytropic process with γ = 1.667. How much work does it give out? **[4.09 kJ]**
6. For the following conditions of water determine the state: (i) T=60C; V=5000cm^3/gm (ii) T=60C; V=10000cm^3/gm (iii) T=80C; V=0.5cm^3/gm (iv) T=90C; P= 200kPa (v) P = 100 kPa, T = 150C (vi) U = 2000kJ /kg, T=40C (vii) U = 2500kJ /kg, T=70C (viii) U = 3000kJ /kg, V=240cm^3/gm (ix) H = 3500kJ /kg, V=240cm^3/gm (x) H = 3300kJ /kg, P=1300kPa. *(Use P-V diagrams to arrive at the answer).*
7. A piston-cylinder assembly contains 0.1 kg wet steam of quality 0.75 (X) at 100 kPa. If 150 kJ energy is added as heat while the pressure of the steam is held constant determine the final state of steam and work done by the steam. **[State of steam: Superheated; W = 25.567 kJ]**
8. In a particular engine cylinder one mole of an ideal gas (γ=1.4) is compressed from 25^oC 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. **[T_2 = 554.7 K, Q = -3.201 kJ]**
9. An adiabatic compressor operating under steady-state conditions receives air (ideal gas) at 0.1 MPa and 300 K and discharges at 1 MPa. If the flow rate of air through the compressor is 2 mol/s, determine the power consumption of the compressor. **[16.25 kW]**
10. 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. **[T_f = 550 K, P_f = 0.55 MPa]**
11. A 10 m high cylinder, cross-sectional area 0.1 m^2, has a mass less piston at the bottom with water at 20°C on top of it, shown in figure below. Air at 300 K, volume 0.3 m^3, under the piston is heated so that the piston moves up, spilling all the water out. Find the total heat transfer to the air needed. **[220.7 kJ]**





12. A piston/cylinder contains 0.001 m^3 air at 300 K, 150 kPa. The air is now compressed in a process in which $PV^{12.5}$ = C to a final pressure of 600 kPa. Find the work performed by the air and the heat transfer. **[W = -0.192 kJ, Q = -0.072 kJ]**
13. A nozzle receives 0.1 kg/s steam at 1 MPa, 400^oC with negligible velocity. The exit is at 500 kPa, 350^oC and the flow is adiabatic. Find the nozzle exit velocity and the exit area. **[u_e = 438.7 m/s, A = 1.3 cm^2]**
14. A diffuser has air entering at 100 kPa, 300 K, with a velocity of 200 m/s. The inlet cross-sectional area of the diffuser is 100 mm^2. At the exit, the area is 860 mm^2, and the exit velocity is 20 m/s. Determine the exit pressure and temperature of the air. **[P_e = 123.92 kPa, T_e = 319.74 K]**

15. An exhaust fan in a building should be able to move 2.5 kg/s air at 98 kPa, 20^{o}C through a 0.4 m diameter vent hole. How high a velocity must it generate and how much power is required to do that? **[V = 17.1 m/s, W = 0.366 kW]**
16. Helium in a steel tank is at 250 kPa, 300 K with a volume of 0.1 m^3. It is used to fill a balloon. When the tank pressure drops to 150 kPa the flow of helium stops by itself. If all the helium still is at 300 K how big a balloon can one get? Assume the pressure in the balloon varies linearly with volume from 100 kPa (V = 0) to the final 150 kPa. How much heat transfer did take place? **[V=0.0667m^3; Q = 13.334 kJ]**
17. In a steam generator, compressed liquid water at 10 MPa, 30°C, enters a 30-mm diameter tube @ 3 L/s. Steam at 9 MPa, 400°C exits a tube of same diameter. Find heat transfer rate to the water. **[8973 kW]**
18. An insulated tank of volume 1 m^3 contains saturated steam at 1 bar. This tank is connected to a line carrying superheated steam at 2 MPa and 300^{0}C and filled to a pressure of 2 MPa. Determine the state and quantity of steam in the tank at the end of the filling operation. **[6.43 kg; P = 2 MPa, T = 418 ^{0}C]**
19. Consider a piston-cylinder containing 0.2m^3 of gas at 0.3MPa. Atmospheric pressure (0.1MPa) and an external spring holds the piston at equilibrium initially. The gas is heated to a state P=0.6MPa, V^t=0.5m^3. Assuming ideal gas, calculate work needed and the potential energy change for the spring. **[0.135MJ]**
20. An insulated piston-cylinder system has air at 400kPa & 500K. Through an inlet pipe to the cylinder air at certain temperature T(K) and pressure P (kPa) is supplied reversibly into the cylinder till the volume of the air in the cylinder is 3 times the initial volume. The expansion occurs isobarically at 400kPa. At the end of the process the air temperature inside the cylinder is 400K. Assume ideal gas behaviour compute the temperature of the air supplied through the inlet pipe. **[91^{0}C]**
21. An adiabatic air compressor takes in air at 25C and 0.1MPa and discharges at 1MPa. If the compressor efficiency is 80% find the exit air temperature, assuming ideal gas behaviour. **[372^{o}C].**
22. An insulated & evacuated tank has a piston and spring as shown in the figure; it is connected to a steam line carrying steam at 2 MPa and 300^{0}C. Initially the spring is just touching the piston exerting no force. When the valve is opened steam enters the tank till the pressure rises to 2.0 MPa. Determine the state of steam inside the tank. Chose the tank, the piston and spring as the control volume. **[364 ^{0}C]**



23. A closed system containing an ideal gas initially at a temperature T_1 is compressed adiabatically till its temperature rises to T_2. At this temperature the gas receives heat Q_2 from a hot reservoir under isothermal conditions. Next it undergoes an adiabatic expansion till its temperature returns to T_1. At this temperature the gas releases Q_1 heat to another reservoir under isothermal conditions so that the gas returns to its initial state. If the efficiency of the cycle is defines as the ratio of the net work output to the net heat absorbed, show that it is = 1 – (T_1/ T_2).
24. A cylinder (volume 0.1m^3) contains nitrogen at 14.0MPa and 300K. The cylinder outlet valve develops a minute leak allowing the gas to escape slowly to the ambient atmosphere (pressure = 0.1MPa), till the gas cylinder pressure reduces to 2.0MPa, and a low-pressure alarm fitted to the

cylinder sounds. Determine the amount of gas that escapes the cylinder during the process. For simplification assume ideal gas behaviour and that the gas escaping from the cylinder has a constant temperature of $(T_i + T_f)/2$, where T_i and T_f are the initial and final temperatures of gas within the cylinder. For the gas $\gamma = 1.4$. **[428.5moles]**

25. An insulated gas cylinder containing N_1 moles of gas initially at P_1 and T_1 is filled with the same gas from a high pressure source at a constant pressure P_{in} and temperature T_{in}. Assuming ideal gas behaviour show that at any time during the filling process the cylinder pressure P and the temperature T are related by the following equation form: $P(t)/[\alpha + \beta P(t)] = T$; where T(^{0}K). Determine the actual expressions for the constants in the above equation. $[\alpha = (P_1/T_1) - (P_1/\gamma T_i); \beta = 1/\gamma T_i]$
26. A water tank of volume 1.0m^3 (with an inlet and an outlet) contains a substance whose concentration needs to be reduced to 1% of its initial concentration by allowing pure water to flow steadily through the tank. Assuming that the tank water is perfectly mixed, calculate the mass of water that needs to flow through the tank (Sp. Gravity = 1.0). **[4605kg]**

Chapter 4 Assignment
(Answers are in parenthesis)

1. A rigid vessel of 0.06 m^3 volume contains an ideal gas, $C_V = (5/2)R$, at 500 K and 1 bar. (a) If 15 kJ of heat is transferred to the gas, determine its entropy change. (b) If the vessel is fitted with a stirrer that is rotated by a shaft so that work in the amount of 15 kJ is done on the gas, what is the entropy change of the gas if the process is adiabatic? What is ΔS^{total} ? **(20.8J/k, 20.8J/K)**
2. An ideal gas, $Cp = (7/2)R$, is heated in a steady-flow heat exchanger from 70°C to 190°C by another stream of the same ideal gas which enters at 320°C. The flow rates of the two streams are the same, and heat losses from the exchanger are negligible. Calculate the molar entropy changes of the two gas streams for both parallel and countercurrent flow in the exchanger. What is ΔS^{total} in each case? **(2.15J/molK, same in both cases)**
3. One mole of an ideal gas, $C_P = (7/2)R$ and $C_V = (5/2)R$, is compressed adiabatically in a piston cylinder device from 2 bar and 25°C to 7 bar. The process is irreversible and requires 35% more work than a reversible, adiabatic compression from the same initial state to the same final pressure. What is the entropy change of the gas? **(2.914J/molK)**
4. A mass m of liquid water at temperature T_1 is mixed adiabatically and isobarically with an equal mass of liquid water at temperature T_2. Assuming constant C_P, show that: $\Delta S^{total} = S_G = 2mC_P \ln\left[\frac{(T_1+T_2)/2}{\sqrt{T_1T_2}}\right]$ and prove that this is positive. What would be the result if the masses of the water were different, say, m_1 and m_2?
5. A reversible cycle executed by 1 mol of an ideal gas for which $C_P = (5/2)R$ and $C_V = (3/2)R$ consists of the following: Starting at $T_1 = 700$ K and $P_1 = 1.5$ bar, the gas is cooled at constant pressure to $T_2 = 350$ K. From 350 K and 1.5 bar, the gas is compressed isothermally to pressure P_2. The gas returns to its initial state along a path for which PT = constant. What is the thermal efficiency of the cycle? **(0.07)**
6. One mole of an ideal gas is compressed isothermally but irreversibly at 130°C from 2.5 bar to 6.5 bar in a piston cylinder device. The work required is 30% greater than the work of reversible, isothermal compression. The heat transferred from the gas during compression flows to a heat reservoir at 25°C. Calculate the entropy changes of the gas, the heat reservoir, and ΔS^{total}. **(–7.94J/molK, 13.96J/molK, 6.02J/molK)**
7. Ten kmol per hour of air is throttled from upstream conditions of 25°C and 10 bar to a downstream pressure of 1.2 bar. Assume air to be an ideal gas with $C_P = (7/2)R$. (a) What is the downstream temperature? (b) What is the entropy change of the air in J/molK? (c) What is the rate of entropy generation in W/K? (d) If the surroundings are at 20°C, what is the lost work? **(298K, 17.63J/molK, 48.9W/K, 5.2kJ/mol)**
8. A steady-flow adiabatic turbine (expander) accepts gas at conditions $T_1 = 500$ K, $P_1 = 6$ bar, and discharges at conditions $T_2 = 371$ K, $P_2 = 1.2$ bar. Assuming ideal gases, determine (per mole of gas) W_{actual}, W_{ideal}, W_{lost}, and entropy generation rate.$T_{surrounding}$, = 300 K, $C_P/R = 7/2$. **(3753.8J, –5163J, 1409J, 4.7J/K)**
9. An ideal gas at 2500 kPa is throttled adiabatically to 150 kPa at the rate of 20 mol/s. Determine rates of entropy generation and lost work if $T_{surrounding} = 300$ K **(0.468kW/K, 140.3kW)**
10. A vessel, divided into two parts by a partition, contains 4 mol of nitrogen gas at 75°C and 30 bar on one side and 2.5 mol of argon gas at 130°C and 20 bar on the

other. If the partition is removed and the gases mix adiabatically and completely, what is the change in entropy? Assume nitrogen to be an ideal gas with $C_v = (5/2)R$ and argon to be an ideal gas with $C_v = (3/2)R$. **[38.3J/K]**

11. A stream of nitrogen flowing at the rate of 2 kg s^{-1} and a stream of hydrogen flowing at the rate of 0.5 kgs^{-1} mix adiabatically in a steady-flow process. If the gases are assumed ideal, what is the rate of entropy increase as a result of the process? **[1411W/K]**

Chapter 5 Assignment
(Answers are in parenthesis)

1. Steam expands isentropically in a converging-diverging nozzle from inlet conditions of 1400 kPa, 598K, and negligible velocity to a discharge pressure of 140 kPa. At the throat the cross-sectional area is 6 cm^2. Determine the mass flow rate of the steam and the state of the steam at the exit of the nozzle. **(1.08kg/s, 0.966)**
2. Steam expands adiabatically in a nozzle from inlet conditions of 9 bar, 488K, and a velocity of 70m/s to a discharge pressure of 2.4bar where its velocity is 609.6 m/s. What is the state of the steam at the nozzle exit? **(0.987)**
3. Carbon dioxide at upstream conditions T_1 = 350 K and P_1 = 80 bar is throttled to a downstream pressure of 1.2 bar. Estimate the downstream temperature and ΔS of the gas. **(280K, 31.5J/molK)**
4. A steam turbine operates adiabatically at a power level of 3500 kW. Steam enters the turbine at 2400 kPa and 500°C and exhausts from the turbine as saturated vapor at 20 kPa. What is the steam rate through the turbine, and what is the turbine efficiency? **(4.1kg/s, 0.819)**
5. Isobutane expands adiabatically in a turbine from 5000 kPa and 250°C to 500 kPa at the rate of 0.7 kmol/s. If the turbine efficiency is 0.80, what is the power output of the turbine and what is the temperature of the isobutane leaving the turbine? (**4663kW, 458K**)
6. Saturated steam at 125 kPa is compressed adiabatically in a centrifugal compressor to 700 kPa at the rate of 2.5 kg/s. The compressor efficiency is 78%. What is the power requirement of the compressor and what are the enthalpy and entropy of the steam in its final state? **(3156.6kJ/kg, 7.45kJ/kgK, 1173kW).**
7. Derive an expression for enthalpy change of a gas during an isothermal process assuming that: $\left(P+\frac{a}{TV^2}\right)(V-b)=RT$ **[** $Ans:(3a)(\frac{1}{V_1}-\frac{1}{V_2})+RTb(\frac{1}{V_2-b}-\frac{1}{V_1-b})$ **]**

Chapter 6 Assignment
(Answers are in parenthesis)

1. The molar volume (cm^3 mol^1) of a binary liquid mixture at T and P is given by: V = 120x_1 + 70x_2 + (15x_1 + 8x_2)x_1x_2 cm^3/mol (a) Find expressions for the partial molar volumes of species 1 and 2 at T and P. (b) (c) Show that these expressions satisfy the Gibbs/Duhem equation. (d) Show that $(d\overline{V_1}/dx_1)_{x_1=1} = (d\overline{V_2}/dx_1)_{x_1=0} = 0$ (e) Calculate V_1, V_2, $\overline{V}_1^{\infty}$, and $\overline{V}_2^{\infty}$. [$\overline{V_1} = 128 - 2x_1 - 20x_1^2 + 14x_1^3$; $\overline{V_2} = 70 + x_1^2 + 14x_1^3$; $V_1 = 120; V_2 = 70$ $\overline{V_1^{\infty}} = 128; \overline{V_2^{\infty}} = 84$, all in cm^3/mol]

2. For a ternary solution at constant T and P, the composition dependence of molar property M is given by: M = x_1M_1 + x_2M_2 + x_3M_3 + $x_1x_2x_3C$; where M_1, M_2,and M_3 are the values of M for pure species 1, 2, and 3, and C is a parameter independent of composition. Determine expressions for $\overline{M}_1$, $\overline{M}_2$, and $\overline{M}_3$. As a partial check on your results, verify that they satisfy the summability relation. For this correlating equation, what are the $\overline{M}_i$ at infinite dilution? **[**$\overline{M_i} = M_i + Cx_jx_k(1-2x_i)$ **;** $\overline{M_i^{\infty}} = M_i + Cx_jx_k$ **]**

3. For a particular binary liquid solution at constant T and P, the molar enthalpies of mixtures are represented by the equation: H = $x_1(a_1+b_1x_1)$ + $x_2(a_2+b_2x_2)$; where the a_i and b_i are constants. Since the equation has the form of $H = \Sigma \overline{H}_i x_i$; it might be that $\overline{H}_i$ = $a_i+b_ix_i$. Show whether this is true.

4. Say that for a binary solution the heat (enthalpy of mixing) data is available in the form ΔH_{mix} *vs.* x_1. Show that the partial molar enthalpies are given by the following equations: $\overline{H}_1 - H_1 = \Delta H_{mix} - x_2 \dfrac{d(\Delta H_{mix})}{dx_2}$; and, $\overline{H}_2 - H_2 = \Delta H_{mix} + (1-x_2)\dfrac{d(\Delta H_{mix})}{dx_2}$

5. Show that: $\overline{H}_1 = -x_2^2 \left.\dfrac{\partial(H_{mix}/x_2)}{\partial x_2}\right|_{T,P}$

6. For a ternary system (containing A, B, and C) show that:

   (i) $\overline{M}_A = M + (1-x_A)\left(\dfrac{\partial M}{\partial x_A}\right)_{T,P,x_B} - x_B\left(\dfrac{\partial M}{\partial x_B}\right)_{T,P,x_A}$

   (ii) $\overline{M}_A = M + (1-x_A)\left(\dfrac{\partial M}{\partial x_A}\right)_{T,P,x_C} - x_C\left(\dfrac{\partial M}{\partial x_C}\right)_{T,P,x_A}$

7. Prove the following identities: (a) $\overline{A}_i = \mu_i - P\left(\dfrac{\partial \mu_i}{\partial P}\right)_{T,n}$, (b) $\overline{U}_i = \mu_i - P\left(\dfrac{\partial \mu_i}{\partial P}\right)_{T,n} - T\left(\dfrac{\partial \mu_i}{\partial T}\right)_{P,n}$

$\overline{A}_i$ = partial molar Helmholtz's free energy

$\overline{U}_i$ = partial molar internal energy

μ_i = partial molar Gibss free energy (chemical potential)

8. When one mole of sulphuric acid (1) is added to ‘n’ moles of water at 25^0C the heat evolved is calculated according to the equation: $Q(cal) = \dfrac{17860n}{n+1.7893}$. Assuming that the molar enthalpies of both the components are zero at 25^0C, compute the partial molar enthalpies for a mixture containing 1 mole of sulphuric acid and three moles of water. $[\bar{H}_1 = -6981.5 cal/mol; \bar{H}_2 = -1395.0 cal/mol]$

9. The heat of mixing for octanol(1)/decane(2) is given by: $\Delta H_{mix} = x_1 x_2 \left[A + B(x_1 - x_2)\right] J/mol$

   Where, $A = -12974 + 51.05T; B = 8728.8 - 34.13T; T(^0K)$. (i) Compute the partial molar enthalpies of each component for an equi-molar solution at 300K (assuming pure component enthalpies to be zero). (ii) A mixture containing 20mol% of octanol is mixed with another containing 80mol% octanol in a steady flow isothermal mixer. How much heat needs to be added or removed from the mixer? $[\bar{H}_1 = 917.8 J/mol;\ \bar{H}_2 = 257.7 J/mol; 211.4 J/mol\ of\ mixture]$

10. The Berthelot EOS is given by: $\left(P + \dfrac{a}{TV^2}\right)\left(V-b\right) = RT$; Show that the fugacity coefficient is: $\ln\phi = \dfrac{b}{V-b} - \dfrac{2a}{RT^2V} - \ln\left(\dfrac{V-b}{V}\right) - \ln\left[\dfrac{V}{V-b} - \dfrac{a}{RT^2V}\right]$
11. Estimate the fugacity of methane at 32C and 9.28 bar. Use the generalized compressibility factor correlation. **[9.15bar]**
12. Determine the ratio of the fugacity in the final state to that in the initial state for steam undergoing the isothermal change of state: from 9000 kPa and 400 C to 300 kPa. **[0.04]**
13. Estimate the fugacity of n-Pentane at its normal-boiling point temperature and 200 bar. **[2.4bar]**

Chapter 7 Assignment
(Answers are in parenthesis)

VLE by Raoult's Law

1. Assuming the validity of Raoult's law, do the following calculations for the benzene(1)/toluene(2) system: (a) Given x_1 = 0.33 and T = 100^{o}C, find y_1 and P [P= 109.12kPa, $y_1 = 0.545$]; $y_1 = 0.545$ (b) Given y_1 = 0.33 and T = 100^{o}C, find x_1 and P [T= 92.04kPa, $x_1 = 0.169$]; (c) Given x_1 = 0.33 and P= 120kPa, find y_1 and T [T= 103.4C, $y_1 = 0.542$] (d) Given y_1 = 0.33 and P = 120kPa, find x_1 and T. [T= 109.16C, $x_1 = 0.173$] (e) Given T = 105^{o}C and P = 120kPa, find x_1 and y_1**[x_1 = 0.33, y_1 = 0.485]** (f) For part (e) if the overall mole fraction of benzene is z_1=0.3685, what molar fraction of the system is vapour? **[V=0.231]**

2. Assuming Raoult's law to apply to the system n-pentane(1)/n-heptane(2). (a) What are the values of x_1 and $y_1$at T = 55^{o}C and P=$\frac{1}{2}\left(P_1^{sat} + P_2^{sat}\right)$? [x_1 = 0.5, y_1 = 0.915] (b) If we plot vapor molar fraction V vs. overall composition z_1, is the plot linear / non-linear? [Linear] (c) For T = 55^{o}C and z_1 = 0.5, If V = 0.5 find: P, x_1, and y_1.[**Approximate values are P ~ 50kPa, x_1 ~ 0.2 and y_1 = 0.8]**

3. A single-stage liquid/vapor separation for the benzene(1)/ethylbenzene(2) system must produce phases of the following equilibrium compositions. For x_1 = 0.35, y_1 = 0.70, determine the T and P in the separator. What additional information is needed to compute the relative molar amounts of liquid and vapor leaving the separator? Assume that Raoult's law applies.**[T=134C, P=207kPa, need z_i]**

4. A liquid mixture containing equimolar amounts of benzene(1)/toluene(2) and ethylbenzene(3) is flashed to conditions T and P. For T = 110^{o}C, P = 90 kPa, determine the equilibrium mole fractions {x_i} and {y_i} of the liquid and vapor phase formed and the molar fraction V of the vapor formed. Assume that Raoult's law applies.**[V=0.834, x_1 = 0.143, y_1 = 0.371, x_2 = 0.306, y_1 =0.339].**

5. A liquid mixture of 25mol% pentane(1), 45mol% hexane(2) and 30mol% heptane(3) initially at high pressure and 69^{0}C is partially vaporized by isothermally lowering the pressure to 1atm. Find the relative amounts of liquid and vapour in the system and the compositions. **[L=0.564, x_1= 0.142, x_2= 0.448, y_1= 0.390, y_2= 0.453]** The vapour pressure relations are $\{\ln P_1^S(bar); t(^0K)\}$: $\ln P_1^S = 10.422 - 26799/RT; \ln P_2^S = 10.456 - 29676/RT; \ln P_3^S = 11.431 - 35200/RT$

Non-ideal System VLE

6. For the system ethyl ethanoate(1)/n-heptane(2) at 70^{o}C, ln γ_1 = $0.95\,x_2^2$;ln γ_2 = $0.95\,x_1^2$; P_1^{sat} = 79.80 kPa; P_2^{sat} = 40.50 kPa, (a) Make a BUBL P calculation for T = 70^{o}C, x_1 = 0.05. [P=47.97kPa, y_1 = 0.196] (b) Make a DEW P calculation for T = 70^{o}C, y_1 = 0.05. [P=42.19kPa, x_1 = 0.0104], (c) What is the azeotrope composition and pressure at T = 70^{o}C? **[P^{az} =47.97kPa, x_1^{az} = y_1^{az} = 0.857]**

7. A liquid mixture of cyclohexanone(1)/phenol(2) for which x_1 = 0.6 is in equilibrium with its vapor at 144^{o}C. Determine the equilibrium pressure P and vapor composition y_1 from the following information: ln γ_1 = $A\,x_2^2$; ln γ_2 = $A\,x_1^2$ At 417.15 K (144^{o}C), P_1^{sat}= 75.20 and P_2^{sat}= 31.66 kPa. The system forms an azeotrope at 417.15 K (144^{o}C) for which x_1^{az} = y_1^{az} = 0.294. **[P=38.19kPa, y_1 = 0.844]**

8. For the acetone (1)/methanol (2) system a vapor mixture for which z_1 = 0.25 is cooled to temperature T in the two-phase region and flows into a separation chamber at a pressure of 1 bar. If the composition of the liquid product is to be x_1 = 0.175, what is the required value of T, and what is the value of y_1? For liquid mixtures of this system to a good approximation: ln γ_1 = $0.64\,x_2^2$; ln γ_2 = $0.64\,x_1^2$ **[T =59.4C, y_1 = 0.307]**

9. The following is a rule of thumb: For a binary system in VLE at low pressure, the equilibrium vapor-phase mole fraction y_1 corresponding to an ***equimolar*** liquid mixture is approximately y_1 = $P_1^{sat}/(P_1^{sat}+P_2^{sat})$; where P_i^{sat} is a pure-species vapor pressure. Clearly, this equation is valid if Raoult's law applies. Prove that it is also valid for VLE described by with: ln γ_1 = $A\,x_2^2$ and ln γ_2 = $A\,x_1^2$

10. For a distillation column separating ethyl-ether(1)/ ethanol(2) into essentially pure components at 1atm, find the range of values of α_{12} (relative volatility).

    Data: ln P_1^s = 9.25-2420.72 /(T-45.72), lnP_2^s = 12.17 - 3737.60 / (T-44.17), where P (bar), T(K), For the liquid phase, $G^E/x_1x_2RT = A_{21}x_1 + A_{12}x_2$, A_{12}= 0.1665+233.74/T;A_{21} = 0.5908+197.55/T.

    [$\alpha_{12}(x_1 \rightarrow 1)$ = 2.2, $\alpha_{12}(x_2 \rightarrow 1)$ = 8.64]

11. Find if Benzene(1)/Cyclohexane(2) forms an azeotrope at 77.6°C. The following data are available for use of Regular Solution theory. At 77.6°C, P_1^s = 745 mm Hg, P_2^s = 735 mm Hg. **[$(x_1)^{az} = 0.525$]**

Species(i)	**V_i(cc/mole)**	**δ_i(cal/cc)$^{1/2}$**
Benzene	89	9.2
Cyclohexane	109	8.2

High Pressure VLE and Henry's Law

12. A vapour mixture contains 20mol% methane, 30mol% ethane, and rest propane, at 30°C. Determine the dew composition. **[$x_1 = 0.0247$, $x_2 = 0.1648$]**

13. A liquid mixture of 50mol% pentane and 50mol% heptane initially at low temperature is heated at a constant pressure of 1 atm until 50mol% of the liquid is vapourized. Calculate the relevant compositions and the temperature.[**x_1= 0.274, y_1= 0.726, T = 341.7°K]**

14. A vapor mixture of 40 mole percent ethylene and 60 mole percent propylene at 40C and 500 kPa is isothermally compressed. Determine the pressure at which condensation begins and the composition of the first drop of liquid that forms. **[2.65MPa]**

15. A liquid mixture of 25 mole percent ethylene and 75 mole percent propylene at -40C is kept in a piston-cylinder assembly. The piston exerts a constant pressure of 1 MPa. Compute the bubble temperature and composition. **[– 8.5°C]**

16. A system formed of methane (1) and a light oil(2) at 200 K and 30 bar consists of a vapour phase containing 95 mol-% methane and a liquid phase containing oil and dissolved methane. The fugacity of the methane is given by Henry's law, and at the temperature of interest Henry's constant is H_1 = 200 bar. Assuming **ideal solution** in gas phase estimate the equilibrium mole fraction of methane in the liquid phase. Use virial EOS for gas phase. **[0.118]**

17. Using PR-EOS: Compute the dew pressure for methane (1) / butane (2) system at 310K with y_1=0.80 **[Dew P=23.6 bar, x_1=0.1094]**

Chapter 8 Assignment
(Answers are in parenthesis)

1. Calculate the standard Gibbs free energy change and the equilibrium constant at 298K for the following reaction: $C_2H_5OH(g) + (1/2)O_2(g) \rightarrow CH_3CHO(g) + H_2O(g)$. **[– 188.9kJ; 1.4x10^{38}]**

2. Assuming that ΔH^o is constant in the temperature range 298 – 800 K, estimate the equilibrium constant at 800 K for the reaction of Problem 1. **[4.3x10^{14}]**

3. Ethanol can be produced according to the reaction: $C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$
   If an equimolar mixture of ethylene and water vapor is fed to a reactor which is maintained at 1000 K and 1 bar determine the degree of conversion, assuming that the reaction mixture behaves like an ideal solution. Assume the following ideal gas specific heat data: $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K) **[0.5]**

Species	**a**	**bx10^3**	**cx10^6**	**dx10^9**	**ex10^{-5}**
C_2H_4	20.691	205.346	– 99.793	18.825	-
H_2O	4.196	154.565	– 81.076	16.813	-
C_2H_5OH	28.850	12.055	-	-	1.006

4. Calculate the degree of conversion and the composition of the reaction mixture if $N_2(g)$ and $H_2(g)$ are fed in the mole ratio of 1:5 at 800 K and 100 bar for the synthesis of ammonia. Assume that equilibrium is established and the reaction mixture behaves like an ideal gas. $C_p^{ig} = a + bT + cT^2 + dT^3 + eT^{-2}$ (J/mol); T(K) **[0.2356]**

Species	**a**	**bx10^3**	**cx10^6**	**dx10^9**	**ex10^{-5}**
N_2	20.270	4.930	-	-	0.333
H_2	27.012	3.509	-	-	0.690
NH_3	29.747	25.108	-	-	– 1.546

5. Calculate the degree of conversion if the feed to an ammonia synthesis reactor is a mixture of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ in the mole ratio 1:3:0.1 at 800 K and 100 bar. Assume that the reaction mixture behaves like an ideal gas. **[0.1235]**

6. The following two independent reactions occur in the steam cracking of methane at 1000 K and 1 bar: $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$; and $CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$. Assuming ideal gas behaviour 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, and that at 1000K, the equilibrium constants for the two reactions are 30 and 1.5 respectively. **[$\varepsilon_1 = 0.8$; $\varepsilon_2 = 0.06$]**

7. Consider the following reaction: $Fe(s) + H_2O(g) \rightarrow FeO(s) + H_2(g)$. Assuming that equilibrium is achieved, determine the fraction of H_2O which decomposes at 1000°C. The equilibrium constant for the reaction at 1000°C is 1.6. **[61.5%]**

8. Show that:

$$\left(\frac{\partial \varepsilon_e}{\partial T}\right)_P = \frac{K_y}{RT^2}\frac{d\varepsilon_e}{dK_y}\Delta H^0 \qquad \text{and} \qquad \left(\frac{\partial \varepsilon_e}{\partial P}\right)_T = \frac{K_y}{P}\frac{d\varepsilon_e}{dK_y}(-\nu)$$

9. The gas stream from a sulfur burner is composed of 15-mol-% SO_2, 20-mol-% O_2, and 65-mol-% N_2. This gas stream at 1 bar and 480°C enters a catalytic converter, where the SO_2 is further oxidized to SO_3. Assuming that the reaction reaches equilibrium, how much heat must be removed from the converter to maintain isothermal conditions? Base your answer on 1 mol of entering gas. **[Ans: ε_e = 0.1455, Q = – 14314 J/mol]**

10. For the cracking reaction: $C_3H_8(g) \rightarrow C_2H_4(g) + CH_4(g)$; the equilibrium conversion is negligible at 300 K, but becomes appreciable at temperatures above 500 K. For a pressure of 1 bar, determine (a) The fractional conversion of propane at 625 K. (b) The temperature at which the fractional conversion is 85%. **[Ans: ε_e = 0.777, T = 647K]**

11. The following isomerization reaction occurs in the liquid phase: A → B; where A and B are miscible liquids for which: $G^E / RT = 0.1x_Ax_B$. (a) If $\Delta G^o_{298} = -1000$ J/mol, what is the equilibrium composition of the mixture at 298°K? **[x_A = 0.3955]** (b) What is the answer for 'a' if one assumes that A and B form an ideal solution? **[x_A = 0.4005].**

12. Feed gas to a methanol synthesis reactor is: 75-mol-% H_2, 15-mol-% CO, 5-mol-% CO_2, and 5-mol-% N_2. The system comes to equilibrium at 550 K and 100 bar with respect to the following reactions: $2H_2(g) + CO(g) \rightarrow CH_3OH(g)$; and $H_2(g) + CO_2(g) \rightarrow CO(g) + H_2O(g)$. Assuming ideal gases, determine the composition of the equilibrium mixture. **[Ans: $K_1 = 6.749\text{x}10^{-4}$; $K_2 = 1.726\text{x}10^{-2}$; $\varepsilon_1 = 0.1186$; $\varepsilon_2 = 8.8812\text{x}10^{-3}$].**