

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.

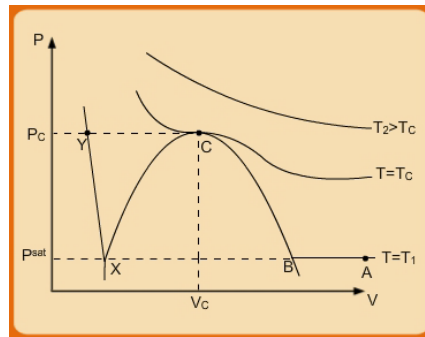
In the following sections we first describe the general nature of the P - V - T behavior of pure substances: in gaseous, liquid and solid forms. The various EOSs available to quantify such real fluid behaviour are then considered. Lastly, generalized correlations to relate gas and liquid behaviour are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

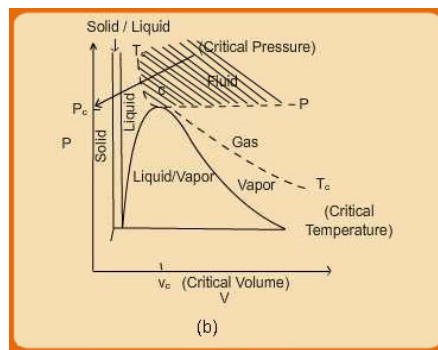
2.1 General P-V-T Behaviour of Real Fluids

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 form. 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_I . 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 behaviour as detailed above may repeat at another temperature T ($>T_I$). 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

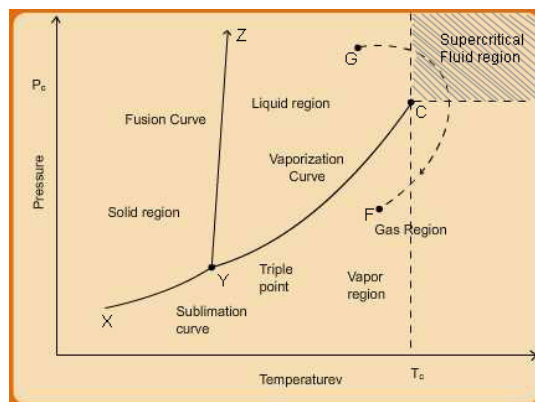


Fig. 2.2 Pressure-Temperature Diagram of a Pure Substance

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

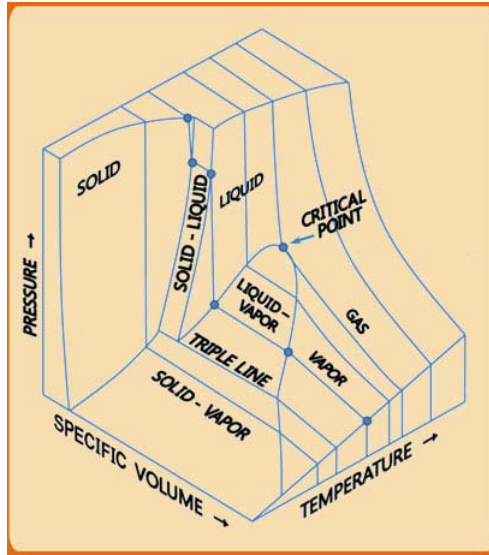


Fig. 2.3 Generalized Three-dimensional P-V-T Surface for a Pure Substance

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

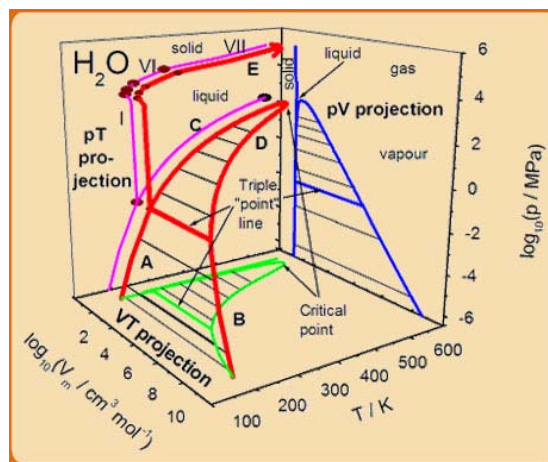


Fig. 2.4 Three-dimensional P-V-T Plot for Water

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 possess 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 ($\sim 5 - 20$ Å (where $1 \text{ Å} = 10^{-8} \text{ m}$)).

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 $\sim 5 \text{ \AA}$ 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.

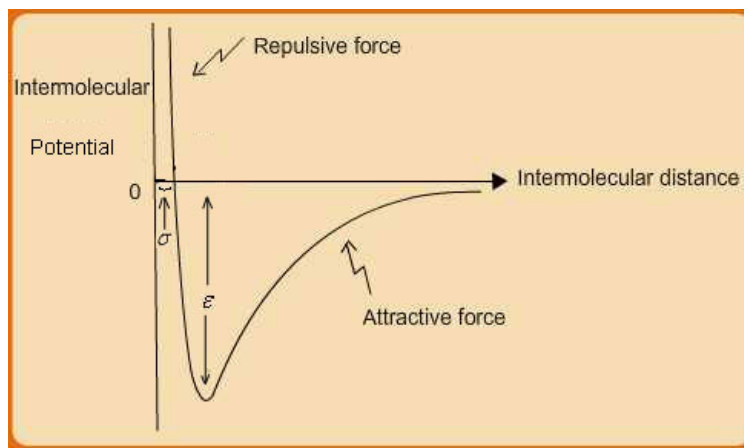


Fig. 2.5 Schematic of Intermolecular potential energy U for a pair of uncharged molecules

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:

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

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 molecules, 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 separations 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:

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

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

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

The generic EOS (2.2) may be written as:

$$\frac{dV}{V} = \beta dT - \kappa dP \quad \text{..(2.5)}$$

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):

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

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.,:

$$V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}; \text{ where } T_r = T / T_c = \text{reduced temperature.} \quad \text{..(2.7)}$$

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

Example 2.1

For a liquid 'A' at 350K and 1 bar, $\kappa = 50 \times 10^{-6} \text{ bar}^{-1}$. (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:

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \quad \text{..(2.8)}$$

Where B , C = second and third virial coefficients

$$\text{Or: } \frac{PV}{RT} = 1 + B'P + C'P^2 + \dots \quad \dots(2.9)$$

It may be shown that the following relations hold further:

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

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:

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

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

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:

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

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

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

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

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):

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

$(P_r^{sat})_{T_r=0.7}$ = 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:

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

where A_0 , B_0 , C_0 , 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:

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

Where, a and b are characteristic constants for a pure substance. For example, for nitrogen the values of a and b are $0.1368 \text{ Pa.m}^6 / \text{mol}^2$ and $3.864 \times 10^{-5} \text{ m}^3 / \text{mol}$ 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:

$$(\partial P / \partial V)_{T_c} = 0 \quad \text{..(2.19)}$$

$$(\partial^2 P / \partial V^2)_{T_c} = 0 \quad \text{..(2.20)}$$

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:

$$a = (27 / 64) R^2 T_c^2 / P_c$$

$$b = (1 / 8) R T_c / P_c$$

$$V_c = (3 / 8) R T_c / P_c$$

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

$$Z_c = P_c V_c / R T_c = 3 / 8 = 0.375$$

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:

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

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:

$$Z = PV/RT \quad \text{..(2.22)}$$

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

$$Z^3 + \alpha Z^2 + \beta Z + \gamma = 0 \quad \text{..(2.23)}$$

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	$-AB$	$\frac{27}{64} \frac{R^2 T_C^2}{P_C}$	$\frac{RT_C}{8P_C}$
RK	1	0	-1	$A - B - B^2$	$-AB$	$\frac{0.42748 R^2 T_C^2 \alpha_{RK}}{P_C}$	$\frac{0.08664 RT_C}{P_C}$
SRK	1	0	-1	$A - B - B^2$	$-AB$	$\frac{0.42748 R^2 T_C^2 \alpha_{SRK}}{P_C}$	$\frac{0.08664 RT_C}{P_C}$
PR	2	-1	$-1 + B$	$A - 2B - 3B^2$	$-AB + B^2 + B^3$	$\frac{0.45724 R^2 T_C^2 \alpha_{PR}}{P_C}$	$\frac{0.07779 RT_C}{P_C}$

The parameters α_{RK} , α_{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:

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

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

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

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:

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

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

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

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

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

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

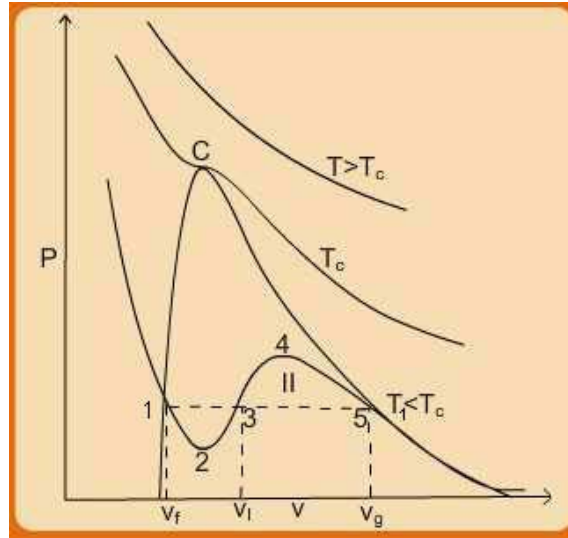


Figure 2.6 P-V plots at constant temperatures (as obtained from a cubic equation of state)

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 .

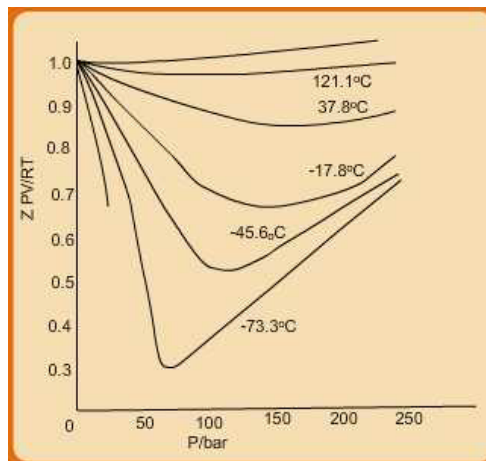


Fig. 2.7 Variation of Compressibility-factor with pressure and temperature (Source: J.M. Smith, H.C. Van Ness and M.M. Abbott, *Introduction to Chemical Engineering Thermodynamics*, 6th ed., McGraw-Hill, 2001)

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.

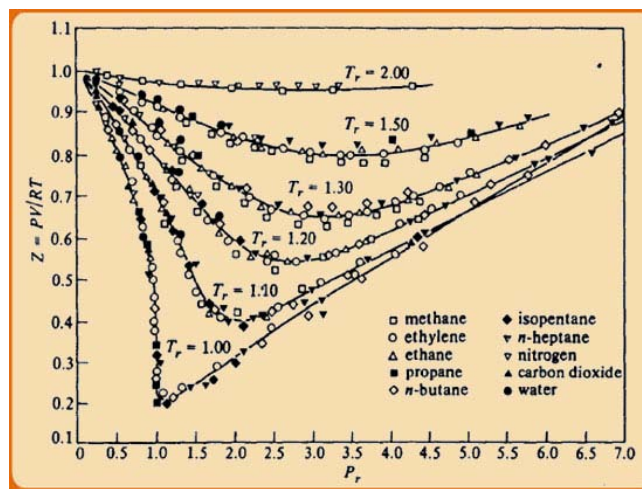


Fig. 2.8 Experimental compressibility factors for different fluids as a function of the reduced temperature and pressure. [Source: H. C.Van Ness and M.M Abbott (1982) based on data from G.-J. Su (1946). *Ind. Engr. Chem.* 38, p 803.]

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 simple 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 a very 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:

$$Z = Z^0 + \omega Z^1 \quad \text{..(2.24)}$$

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:

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

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 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

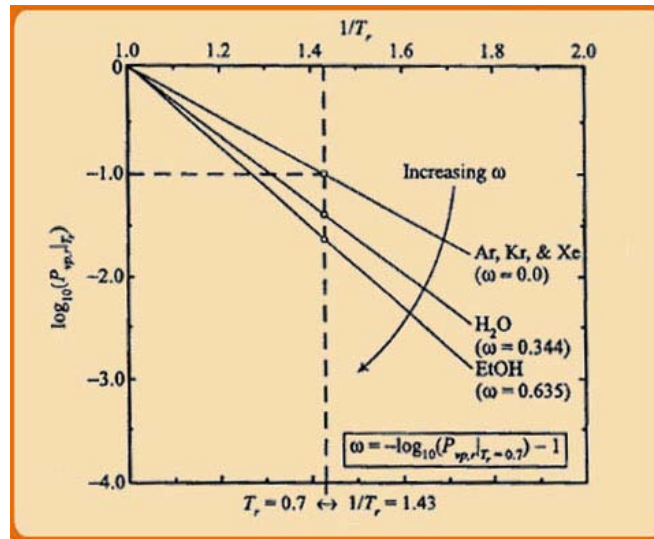
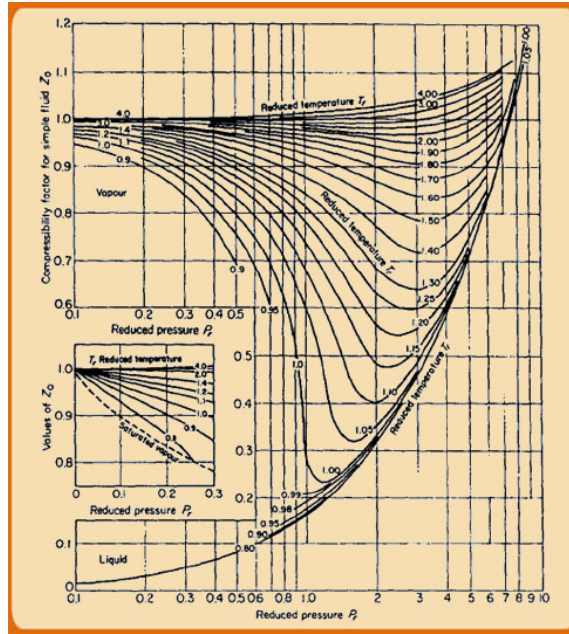
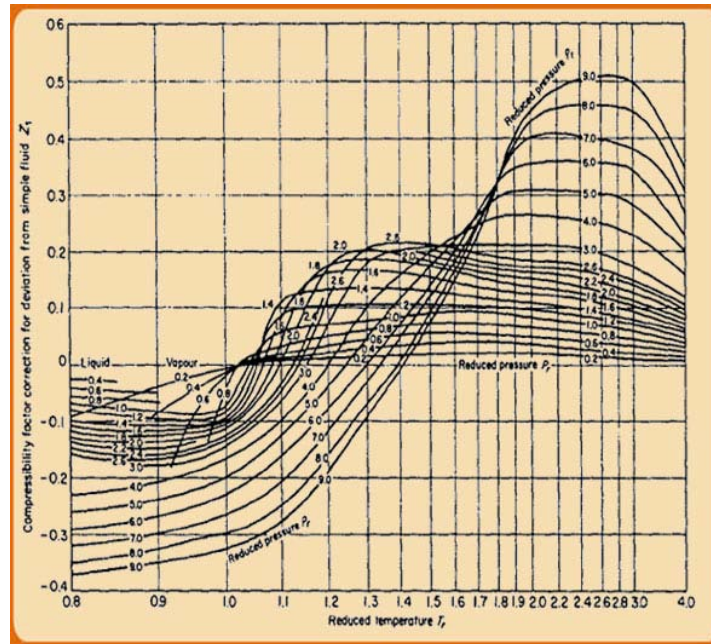


Fig. 2.9 Plot of P_r vs. T_r for select substances of varying polarity (Source: J.W. Tester and M. Modell, *Thermodynamics and its Applications*, 3rd ed., Prentice Hall, 1999).

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 Appendix 1.1 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-m³ vessel at 25°C and 2500kPa holds ethane; compute the number of moles of ethane in the vessel. For ethane: $T_c = 305 \text{ K}$; $P_c = 48.72 \text{ bar}$, $\omega = 0.1$

[\(Click for solution\)](#)

Example 2.5

Compute the saturate liquid phase molar volume for methane at 150K. For methane $T_c = 190.7 \text{ K}$, $P_c = 46.41 \text{ bar}$, $V_c = 98.6 \text{ cm}^3/\text{mol}$, $Z_c = 0.286$, $\omega = 0.011$.

[\(Click for solution\)](#)

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:

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \quad \dots(2.26)$$

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 $i = 1$ and $j = 2$; the expansion of eqn.2.23 yields:

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

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

$$P_{cij} = Z_{cij} R T_{cij} / V_{cij}$$

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

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

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

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

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

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 10³ (m³/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
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[\(Click for solution\)](#)

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):

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

$$b_m = y_1 b_1 + y_2 b_2 \quad \text{..(2.30)}$$

$$\omega_m = y_1 \omega_1 + y_2 \omega_2 \quad \text{..(2.31)}$$

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:

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

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

$$\text{following equation: } Z_m = Z_m^0 + \omega Z_m^1 \quad \text{..(2.33)}$$

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

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

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

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 is called the ‘quality’.

Example 2.8

Find the molar volume and internal energy of a system containing water and steam at 50% quality at 200°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 solid to liquid the effect is termed heat of fusion. Such enthalpy changes typically quantify the amount of heat needed 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 boiling point (ΔH_n^{vap}) of a pure substance:

$$\frac{\Delta H_n^{vap}}{T_n} = \frac{1.092(\ln P_C - 1.013)}{(0.093 - T_m)} \quad \dots(2.36)$$

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:

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

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.

[\(Click for solution\)](#)

Example 2.10

The enthalpy of vaporization of water at 100°C is 2256.94 kJ/kg. Determine the value at 150°C, 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 Benedict-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 ($\omega = 0$) and those of a *reference* fluid; for the latter *n-Octane* is used... The compressibility factor Z for the fluid is given by:

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

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):

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

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

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

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

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

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

$$\text{Further, } V_r^0 = P_c V^0 / RT_c \quad \text{..(A.2.7)}$$

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	0.048736
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
$$Z^R = P_r V_r^R / T_r \quad (\text{A.2.8})$$
- 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:

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

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