THERMODYNAMICS I

Third Class

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Thermodynamics Laws and Other Basic Concepts

What is the thermodynamics? Thermodynamic: The science that deals with heat and work and those properties of matter that relate to heat and work, or (Energy differences and transfers between systems).

The First Law of Thermodynamics

In application of the first law to a given process, the sphere of influence of the process is divided into two parts, the system and its surroundings. The region in which the process occurs is set apart as the system; everything with which the system interacts is the surroundings. The system may be of any size depending on the application, and its boundaries may be real or imaginary, rigid or flexible. Frequently a system consists of a single substance; in other cases it may be complex. In any event, the equations of thermodynamics are written with reference to some well-defined system. This focuses attention on the particular process of interest and on the equipment and material directly involved in the process. However, the first law applies to the system and surroundings, and not to the system alone. In its most basic form, the first law requires:

$$\Delta(\textbf{Energy of the system}) + \Delta(\textbf{Energy of surroundings}) = 0$$

Where the difference operator "A" signifies finite changes in the quantities enclosed in parentheses. The system may change in its internal energy, in its potential or kinetic energy, and in the potential or kinetic energy of its finite parts. Since attention is focused on the system, the nature of energy changes in the surroundings is not of interest.

In the thermodynamic sense, heat and work refer to energy in transit across the boundary which divides the system from its surroundings. These forms of energy are not stored, and are never contained in a body or system. Energy is stored in its potential, kinetic, and internal forms; these reside with material objects and exist because of the position, configuration, and motion of matter.

Energy Balance for Closed Systems

If the boundary of a system does not permit the transfer of matter between the system and its surroundings, the system is said to be closed, and its mass is necessarily constant. The development of basic concepts in thermodynamics is facilitated by a careful examination of closed systems, and for this reason they are treated in detail in the following sections.

Far more important for industrial practice are processes in which matter crosses the system boundary as streams that enter and leave process equipment. Such systems are said to be

open, and they are treated later in this chapter, once the necessary foundation material has been presented. Since no streams enter or leave a closed system, no internal energy is transported across the boundary of the system. All energy exchange between a closed system and its surroundings then appears as heat and work, and the total energy change of the surroundings equals the net energy transferred to or from it as heat and work. The second term of Eq. (1.1) may therefore be replaced by

$$\Delta(\textbf{Energy of surroundings}) = \pm Q \pm W$$

The choice of signs used with Q and W depends on which direction of transport is regarded as positive. Heat Q and work W always refer to the system, and the modern sign convention makes the numerical values of both quantities positive for transfer into the system from the surroundings.The corresponding quantities taken with reference to the surroundings, Q_{surr} and W_{surr} have the opposite sign,i.e., $Q_{surr} = -Q$ and $W_{surr} = -W$. With this understanding:

$$\Delta(\textbf{Energy of surroundings}) = Q_{surr} + w_{surr} = -Q - w$$

Equation (1.1) now become:

$$\Delta\,(\textbf{Energy of the system}) = Q + W$$

This equation means that the total energy change of a closed system equals the net energy transferred into it as heat and work.

Closed systems often undergo processes that cause no change in the system other than in its internal energy. For such processes, Eq. (2.2) reduces to:

$$\boxed{\Delta U^t = Q + W}$$

where

U^t : is the total internal energy of the system. Equation (2.3) applies to processes involving finite changes in the internal energy of the system. For diffrentia1 changes:

$$\boxed{dU^t = dQ + dW}$$

For a closed system of (n) moles Eqs . may now be written:

$$\boxed{\Delta(nU) = n\,\Delta U = Q + W} \qquad (2.5)$$

$$\boxed{d(nU) = n\,dU = dQ + dW} \qquad (2.6)$$

The equations of thermodynamics are often written for a representative unit amount material, either a unit mass or a mole. Thus for n = 1 Eqs. (2.5) and (2.6) become:

$$\mathbf{\Delta U = Q + W} \qquad \textbf{and} \qquad \mathbf{dU = dQ + dW}$$

The basis for Q and W is always implied by the quantity appearing on the left side of the energy equation.

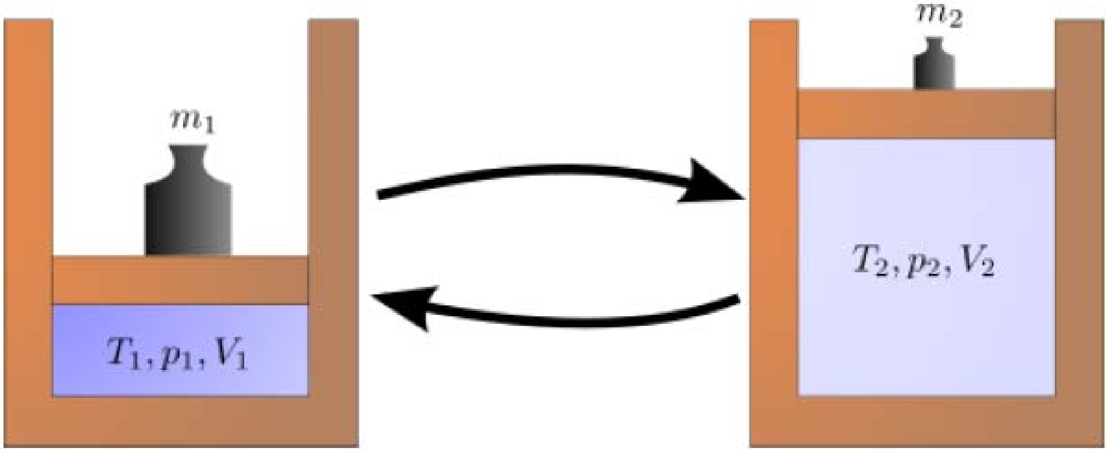
Equilibrium:

Equilibrium is a word denoting a static condition, the absence of change. In thermodynamics it means not only the absence of change but the absence of any tendency toward change on a macroscopic scale. Thus a system at equilibrium exists under conditions such that no change in state can occur. Since any tendency toward change is caused by a driving force of one kind or another, the absence of such a tendency indicates also the absence of any driving force. Hence for a system at equilibrium all forces are in exact balance. Whether a change actually occurs in a system not at equilibrium depends on resistance as well as on driving force. Many systems undergo no measurable change even under the influence of large driving forces, because the resistance to change is very large.

The Reversible Process:

A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions. A reversible process:

- Ideal
- Is frictionless
- Traverses a succession of equilibrium states
- Is driven by forces whose imbalance is differential in magnitude
- Can be reversed at any point by a differential change in external conditions
- When reversed, retraces its forward path, and restores the initial state of system and surroundings



Irreversible process: A process in which it is impossible to return both the system and surroundings to their original states. The work of an irreversible process is calculated by a two-step procedure. First, W is determined for a mechanically reversible process that accomplishes the same change of state as the actual irreversible process. Second, this result is multiplied or divided by an efficiency to give the actual work. If the process produces work, the absolute value for the reversible process is too large and must be multiplied by efficiency. If the process requires work, the value for the reversible process is too small and must be divided by efficiency.

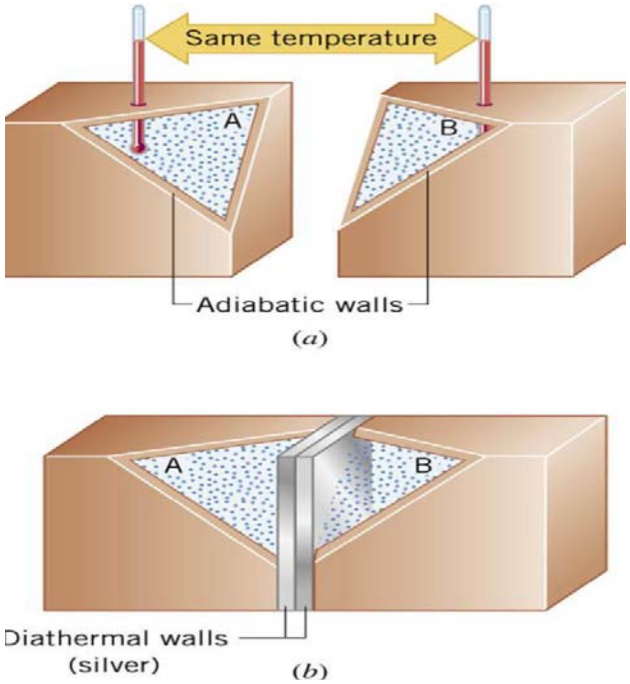
$W_{irr.} = W_{rev.} * efficiency$ if the process produces work

$W_{irr.} = W_{rev.} / efficiency$ if the process requires work

Zeroth Law of Thermodynamics:

- The forgotten Law of Science
- Two systems are said to be in thermal equilibrium if there is no heat flow between them when they are brought into contact.
- Temperature is the indicator of thermal equilibrium in the sense that there is no net flow of heat between two systems in thermal contact that have the same temperature.

Two systems individually in thermal equilibrium with a third system are in thermal equilibrium with each other.



What does steady state process mean?

- The conditions at all points in apparatus are constant with time
- Mass flow rate to the system equal to mass transfer out of the system.
- Rate of work or heat transfer must be constant.

Chapter One
Volumetric properties of pure fluids

The pure substance

We define a
- Pure substance: a material with homogeneous and invariable composition.

To elaborate,
- Pure substances can have multiple phases: an ice-water mixture is still a pure substance.
- An air-steam mixture is not a pure substance.
- Air, being composed of a mixture of N2, O2, and other gases, is formally not a pure substance. However, experience shows that we can often treat air as a pure substance with little error.

We slowly add heat to the cylinder, and observe a variety of interesting phenomena. A sketch of what we observe is given in Fig. below. We notice the following behavior:

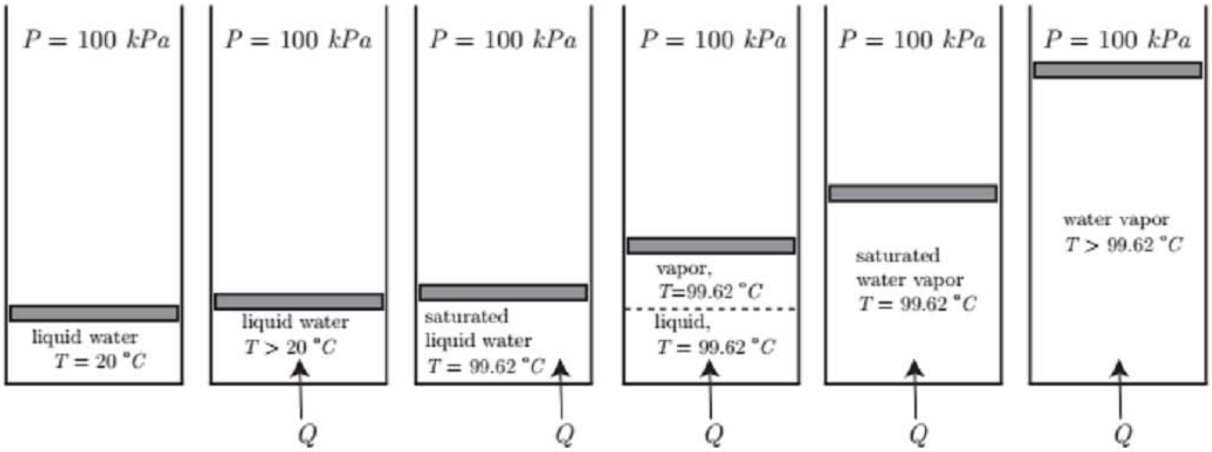


Figure : Sketch of experiment in which heat is added isobarically to water in a closed piston-cylinder arrangement.

The pressure remains at a constant value of 100 kP a. This is an isobaric process.
- The total volume increases slightly as heat is added to the liquid.
- The temperature of the liquid increases significantly as heat is added to the liquid.
- At a special value of temperature, observed to be T = 99.62 ◦C , we have all liquid, but cannot add any more heat and retain all liquid. We will call this state the saturated liquid state. We call T = 99.62°C the saturation temperature at P = 100 kP a. As

we continue to add heat, we have just boiled water! We sketch this process in the temperature-specific volume plane, that is, the T − v plane, in Fig. Note that the mass m of the water is constant in this.

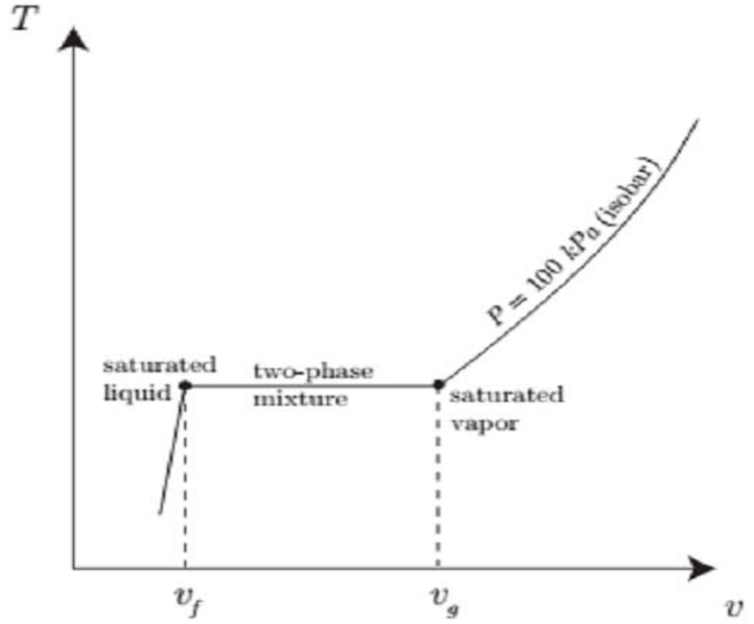


Figure: Isobar in the T − v plane for our thought experiment in which heat is added isobarically to water in a piston-cylinder arrangement.

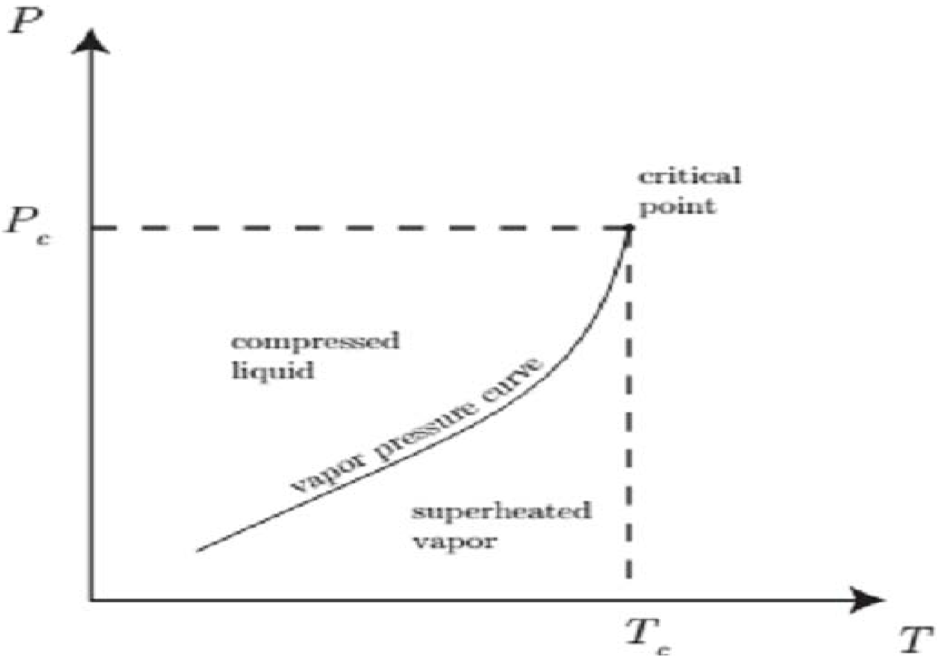


Figure: Saturation pressure versus saturation temperature sketch.

- Saturated liquid: the material is at T_{sat} and is all liquid.
- Saturated vapour: the material is at T_{sat} and is all vapour.
- Compressed (subcooled) liquid: the material is liquid with $T < T_{sat}$.
- Superheated vapor: the material is vapor with T > Tsat .

- Two-phase mixture: the material is composed of co-existing liquid and vapor with both at T^{sat} .

Some Definitions

Triple point: triple point of a substance is the temperature and pressure at which the three phases (gas, liquid, and solid) of that substance coexist in thermodynamic equilibrium. Also it is the point at wich three curves are met (sublimation, fusion and vaporization).

Critical point: The point at highest temp. (Tc) and Pressure (Pc) at which a pure chemical species can exist in vapour/liquid equilibrium. The point critical is the point at which the liquid and vapour phases are not distinguishable; because of the liquid and vapour having same properties.

Fluid region: it is a region of higher temperature and pressure than Tc and Pc, and it is termed supercritical.

PVT Behavior of Pure Substances

The P-T or Phase Change Diagram

This is called phase diagram since all three phases are separated from each other by three lines. Most pure substances exhibit the same behavior

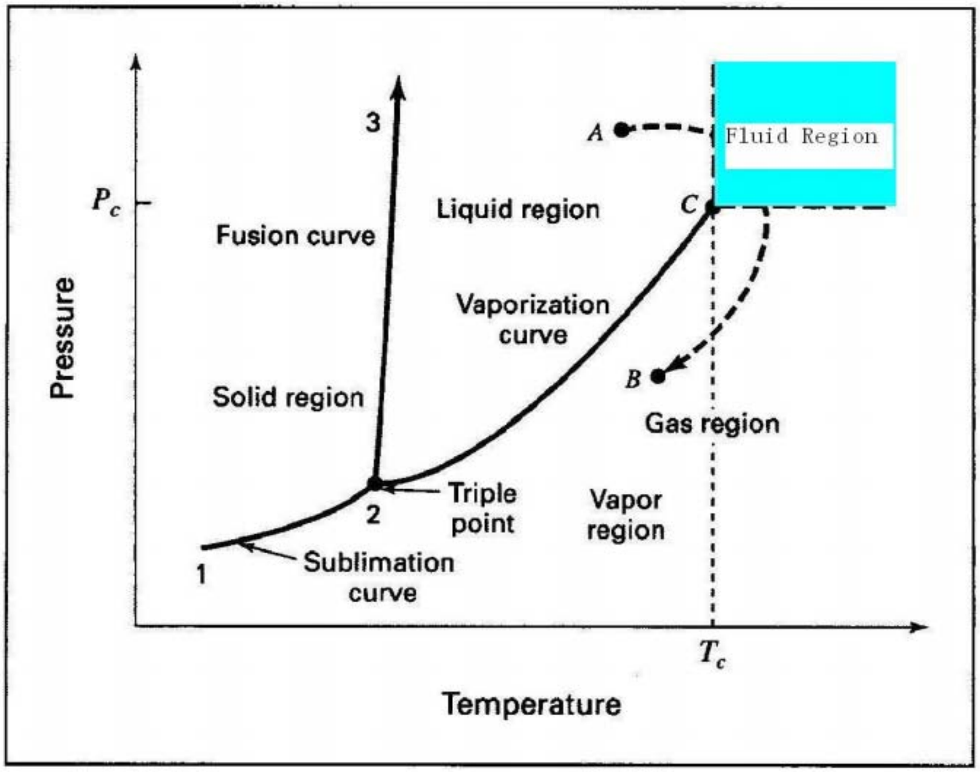


Figure : PT digram for pure substance

There are two ways that a substance can pass from solid phase to vapour phase i) it melts first into a liquid and subsequently evaporates, ii) it evaporates directly without melting (sublimation).

- The sublimation line (1-2) separates the solid and the vapor.
- The vaporization line (2-C) separates the liquid and vapour regions .
- The melting or fusion line (2-3) separates the solid and liquid and gives the solid /liquid equilibrium relationship.
- These three lines meet at the triple point, where the three phases coexist in Equilibrium.
- From A to B lead from the liquid region to the gas region without crossing a phase boundary. The transition from liquid to gas is gradual. On the other hand, paths which cross phase boundary 2-C include a vaporization step, where an abrupt change from liquid to gas occurs.

if $P<P_{TP}$, the solid phase can change directly to a vapour phase.

at $P<P_{TP}$ the pure substance cannot exist in the liquid phase. Normally ($P>P_{TP}$) the substance melts into a liquid and then evaporates.

The triple point is invariant (F = 0). If the system exists along any of the two-phase lines of Fig. 3.4, it is univariant (F = 1), whereas in the single-phase regions it is divariant (F = 2).

The gas region is sometimes divided into two parts, as indicated by the dotted vertical line of Fig. 3.4. A gas to the left of this line, which can be condensed either by compression at constant temperature or by cooling at constant pressure, is called a vapor. The region everywhere to the right of this line, where T > Tc including the fluid region, is termed supercritical.

P-V Diagram

Figure 3.5shows the liquid, liquid/vapour, and vapour regions of the P V diagram, with four isotherms superimposed. Isotherms on Fig. 3.4 are vertical lines, and at temperatures greater than Tc, do not cross a phase boundary. On Fig. 3.5 the isotherm labelled T > Tc is therefore smooth.

The lines labelled T_1 and T_2 are for subcritical temperatures, and consist of three segments. The horizontal segment of each isotherm represents all possible mixtures of liquid and vapours in equilibrium, ranging from 100% liquid at the left end to 100% vapours at the right end.

The locus of these end points is the dome-shaped curve labelled BCD, the left half of which (from B to C) represents single-phase (saturated) liquids at their vaporization (boiling) temperatures, and the right half (from C to D), single-phase (saturated) vapours at their condensation temperatures.

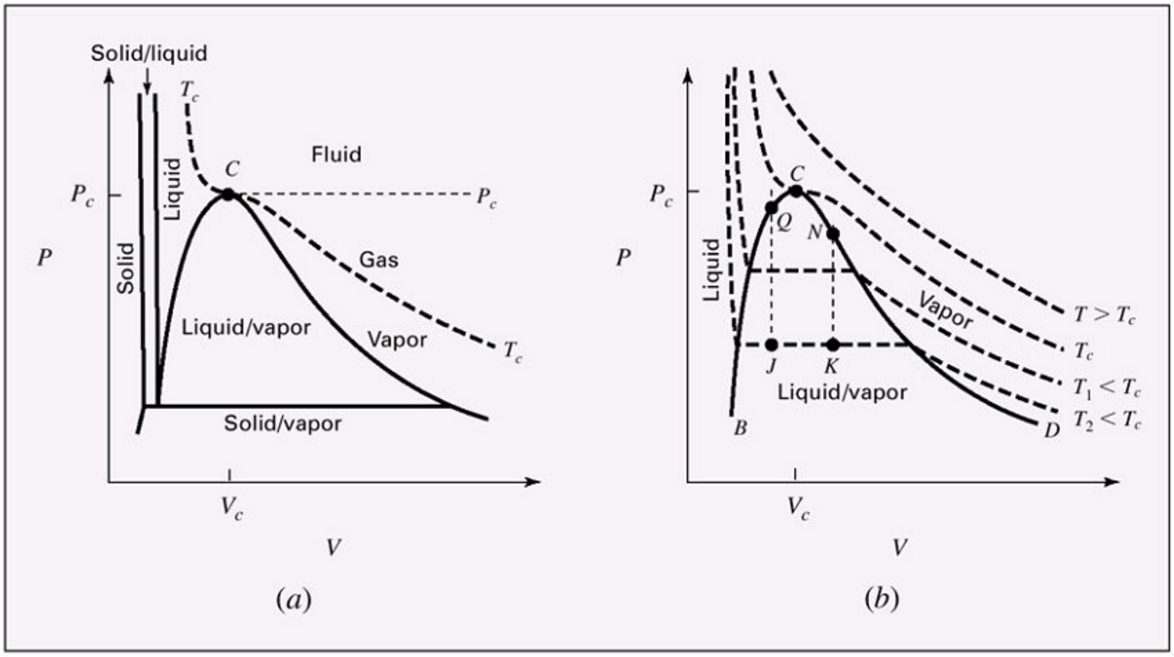


Figure : PV diagrams for a pure substance.
(a) Showing solid,liquid and gas regions.(b) Showing liquid, liquid/vapour, and vapour regions with isotherms

Single-Phase Region

For the regions of the diagram where a single phase exists, Fig. 5 implies a relation connecting P, V, and T which may be expressed by the functional equation:

$$f(P, V, T) = 0$$

The simplest equation of state is for an ideal gas, P V = RT a relation which has approximate validity for the low- pressure gas region of Fig. 5 if V is considered a function of T and P, then V = f(T, P), and

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

The partial derivatives in this equation have definite physical meanings, and are related to two properties, commonly tabulated for liquids, and defined as follows:

Volume expansivity (expansion factor):

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

Isothermal compressibility (compressibility factor):

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

Combination of Eqs. (1) through (3) provides the equation:

$$\frac{dV}{V} = \beta\, dT - \kappa\, dP$$

a. β and k are function of T, P they increased as T increased.
b. For real liquid β and k are constant when change in T,P is relative small
c. When a fluid is incompressible β and k are zero

Thus for small changes in T and P little error is introduced if they are assumed constant.

Integration of Eq. then yields:

$$\ln \frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1)$$

This is a less restrictive approximation than the assumption of an incompressible fluid.

Example 3.1

For liquid acetone at 20°C and 1 bar,

$$\beta = 1.487 \times 10^{-3}\ {}^\circ\mathrm{C}^{-1} \qquad \kappa = 62 \times 10^{-6}\ \mathrm{bar}^{-1} \qquad V = 1.287\ \mathrm{cm}^3\ \mathrm{g}^{-1}$$

For acetone, find:

(*a*) The value of $(\partial P/\partial T)_V$ at 20°C and 1 bar.

(*b*) The pressure generated by heating at constant V from 20°C and 1 b
30°C.

(*c*) The change in volume for a change from 20°C and 1 bar to 0°C and 10 b

Solution 3.1

(*a*) The derivative $(\partial P/\partial T)_V$ is determined by application of Eq. (3.4) to the case for which V is constant and $dV = 0$:

$$\beta\, dT - \kappa\, dP = 0 \qquad (\text{const } V)$$

or

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{\kappa} = \frac{1.487 \times 10^{-3}}{62 \times 10^{-6}} = 24\ \mathrm{bar}\ {}^\circ\mathrm{C}^{-1}$$

(*b*) If β and κ are assumed constant in the 10°C temperature interval, then the equation derived in (*a*) may be written (V = const):

$$\Delta P = \frac{\beta}{\kappa}\Delta T = (24)(10) = 240\ \mathrm{bar}$$

and

$$P_2 = P_1 + \Delta P = 1 + 240 = 241\ \mathrm{bar}$$

(*c*) Direct substitution into Eq. (3.5) gives:

$$\ln\frac{V_2}{V_1} = (1.487 \times 10^{-3})(-20) - (62 \times 10^{-6})(9) = -0.0303$$

$$\frac{V_2}{V_1} = 0.9702 \qquad \text{and} \qquad V_2 = (0.9702)(1.287) = 1.249\ \mathrm{cm}^3\ \mathrm{g}^{-1}$$

Then,

$$\Delta V = V_2 - V_1 = 1.249 - 1.287 = -0.038\ \mathrm{cm}^3\ \mathrm{g}^{-1}$$

Virial Equations of State

For example, PV along an isotherm may be expressed as a function of P by a power series:

$$PV = a + bP + cP^2 + \cdots$$

If b = aB', c = aC', etc., then,

$$PV = a(1 + B'P + C'P^2 + D'P^3 + \ldots)$$

where a, B', C', etc., are constants for a given temperature and a given chemical species.

In principle, the right side of Eq. (3.6) is an infinite series. However, in practice a finite number of terms is used. In fact, P VT data show that at low pressures truncation after two terms usually provides satisfactory results.

Two Forms of the Virial Equation:

A useful auxiliary thermodynamic property is defined by the equation:

$$\boxed{Z \equiv \frac{PV}{RT}}$$

This dimensionless ratio is called the compressibility factor. With this definition and with a = RT [Eq. (3.7)], Eq. (3.6) becomes:

$$\boxed{Z = 1 + B'P + C'P^2 + D'P^3 + \cdots}$$

An alternative expression for Z is also in common use

$$\boxed{Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots}$$

Both of these equations are known as virial expansions, and the parameters B', C', D', etc., and B, C, D, etc., are called virial coefficients. Parameters B' and B are second virial coefficients; C' and C are third virial coefficients; etc. For a given gas the virial coefficients are functions of temperature only.

The two sets of coefficients in Eqs. (3.1 1) and (3.12) are related as follows:

$$B' = \frac{B}{RT} \qquad C' = \frac{C - B^2}{(RT)^2} \qquad D' = \frac{D - 3BC + 2B^3}{(RT)^3} \qquad \text{etc.}$$

The Ideal Gas

Table 3.1 shows the differences between the ideal gas and the real gas

Ideal gas	Real gas
1. No attraction between the molecules	There is an attraction force between molecules
2. Volume of molecules is negligible	Volume of molecules is not negligible
3. Equation of state is PV=nRT, Z=1 when P=0 Vg=∞	Equation of state is PV=ZnRT, Z≠1 , depend on (T,P)

Application of The Virial Equations

The two forms of the virial expansion are infinite series. For engineering purposes their use is practical only where convergence is very rapid, that is, where two or three terms suffice for reasonably close approximations to the values of the series. This is realized for gases and vapours at low to moderate pressures.

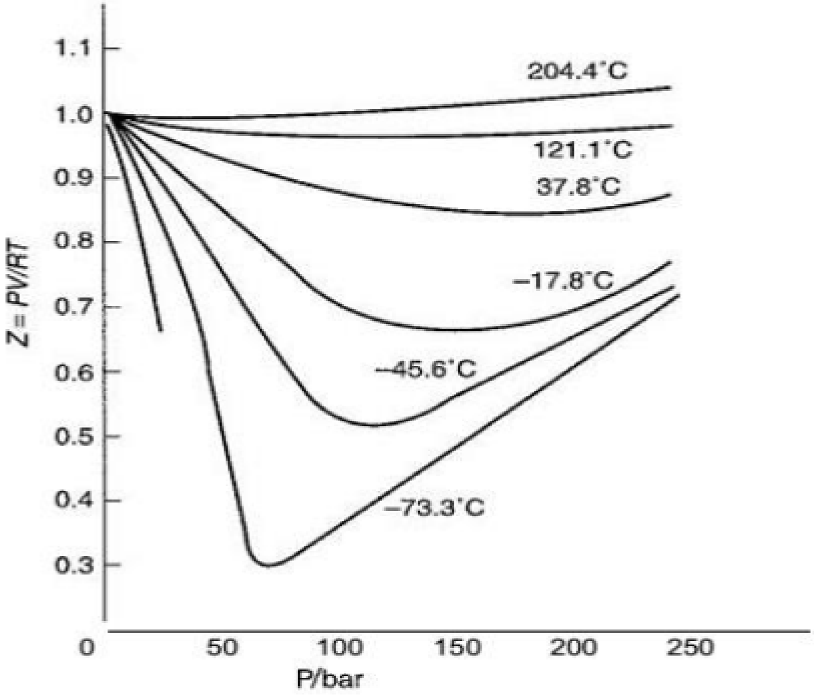


Fig.: Compressibility factor for methan

Values of the compressibility factor Z (as calculated from P VT data for methane by the defining equation Z = P V/ RT) are plotted vs. pressure for various constant temperatures. All isotherms originate at the value Z = 1 for P = 0. In addition the isotherms are nearly straight lines at low pressures. Thus the tangent to an isotherm at P = 0 is a good approximation of the isotherm from P ¬ 0 to some finite pressure. Differentiation of Eq. for a given temperature gives:

$$\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \cdots$$

from which, $$\left(\frac{\partial Z}{\partial P}\right)_{T;P=0} = B'$$

Thus the equation of the tangent line is:

$$Z = 1 + B'P$$

a result also given by truncating Eq. (3.11) to two terms. A more common form of this equation results from the substitution (Sec. 3.2), B' = B/RT:

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

Equation (3.12) may also be truncated to two terms for application at low pressures:

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

However, this Eq. is more convenient in application and is more accurate . Thus when the virial equation is truncated to two terms, Eq. is preferred. This equation is satisfactory of pressure about up to 5 bar. The second virial coefficient B is substance dependent and a function of temperature.

For pressures above the range of applicability of Eq. above but below the critical pressure, the virial equation truncated to three terms often provides excellent results. In this case the appropriate form is:

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

This equation can be solved directly for pressure, but is cubic in volume. Solution for V is easily done by an iterative scheme with a calculator.

Example 3.8

Reported values for the virial coefficients of isopropanol vapor at 200°C are:

$$B = -388 \text{ cm}^3 \text{ mol}^{-1} \qquad C = -26{,}000 \text{ cm}^6 \text{ mol}^{-2}$$

Calculate V and Z for isopropanol vapor at 200°C and 10 bar by:

(*a*) The ideal-gas equation; (*b*) Equation (3.38); (*c*) Equation (3.40).

Solution 3.8

The absolute temperature is $T = 473.15$ K, and the appropriate value of the gas constant is $R = 83.14 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$.

(*a*) For an ideal gas, $Z = 1$, and

$$V = \frac{RT}{P} = \frac{(83.14)(473.15)}{10} = 3{,}934 \text{ cm}^3 \text{ mol}^{-1}$$

(*b*) Solving Eq. (3.38) for V gives:

$$V = \frac{RT}{P} + B = 3{,}934 - 388 = 3{,}546 \text{ cm}^3 \text{ mol}^{-1}$$

Whence,

$$Z = \frac{PV}{RT} = \frac{V}{RT/P} = \frac{3{,}546}{3{,}934} = 0.9014$$

(*c*) To facilitate iteration, write Eq. (3.40) as:

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

where subscript i denotes the iteration number. For the first iteration, $i = 0$, and

$$V_1 = \frac{RT}{P}\left(1 + \frac{B}{V_0} + \frac{C}{V_0^2}\right)$$

where $V_0 = 3{,}934$, the ideal-gas value. Numerically,

$$V_1 = 3{,}934\left[1 - \frac{388}{3{,}934} - \frac{26{,}000}{(3{,}934)^2}\right] = 3{,}539$$

The second iteration depends on this result:

$$V_2 = \frac{RT}{P}\left(1 + \frac{B}{V_1} + \frac{C}{V_1^2}\right) = 3{,}934\left[1 + \frac{388}{3{,}539} - \frac{26{,}000}{(3{,}539)^2}\right] = 3{,}495$$

Iteration continues until the difference $V_{i+1} - V_i$ is insignificant, and leads after five iterations to the final value,[7]

$$V = 3{,}488 \text{ cm}^3 \text{ mol}^{-1}$$

from which $Z = 0.8866$. In comparison with this result, the ideal-gas value is 13% too high and Eq. (3.38) gives a value 1.7% too high.

Cubic Equations of State

If an equation of state is to represent the PVT behaviour of both liquids and vapours, it must encompass a wide range of temperatures and pressures. Yet it must not be so complex as to present excessive numerical or analytical difficulties in application. Polynomial equations that are cubic in molar volume offer a compromise between generality and simplicity that is suitable to many purposes. Cubic equations are in fact the simplest equations capable of representing both liquid and vapour behaviour.

The van der Waals Equation of State

The first practical cubic equation of state was proposed by J. D. van der waals6 in 1873:

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

Here, a and b are positive constants; when they are zero, the ideal-gas equation is recovered. Given values of a and b for a particular fluid, one can calculate P as a function of V for various values of T.

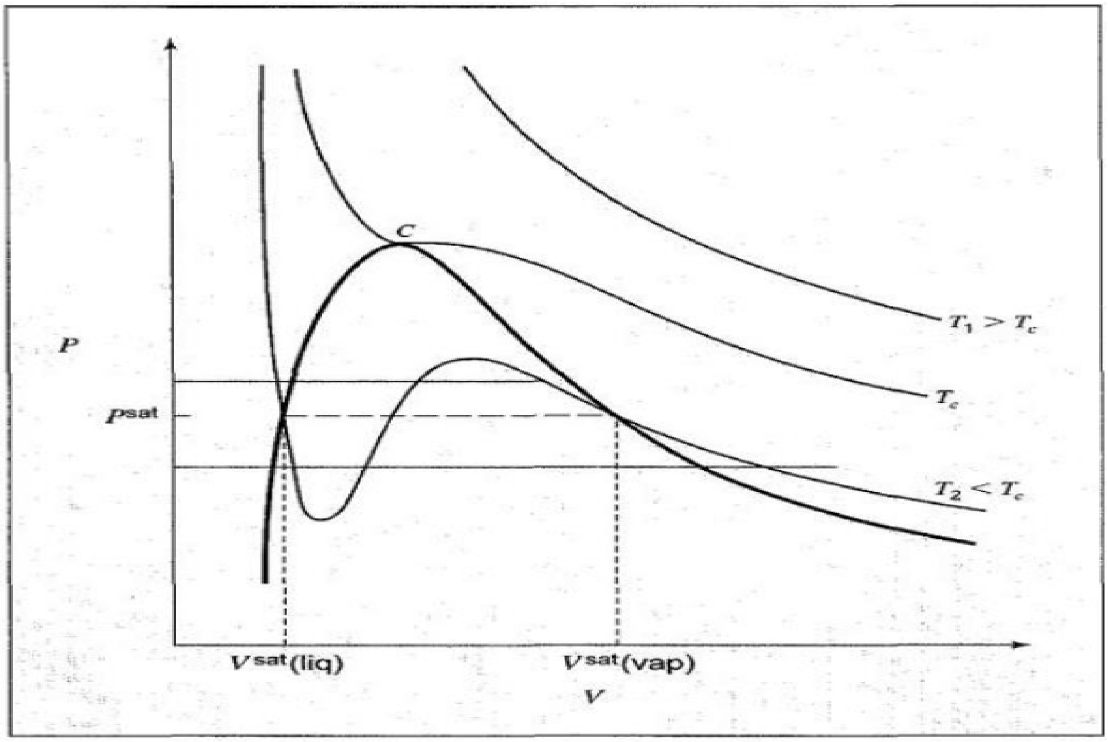


Fig.: Isotherms as given by a cubic equation of state

Figure 3.12 is a schematic P V diagram showing three such isotherms. Superimposed is the "dome" representing states of saturated liquid and saturated vapor. For the isotherm $T_1 > T_c$.

pressure is a monotonically decreasing function with increasing molar volume. The critical isotherm (labeled Tc) contains the horizontal inflection at C characteristic of the critical point. For the isotherm T2 < Tc the pressure decreases rapidly in the subcooled-liquid region with increasing V; after crossing the saturated-liquid line, it goes through a minimum, rises to a maximum, and then decreases, crossing the saturated-vapor line and continuing downward into the superheated-vapor region.

Saturated liquid and saturated vapor coexist in varying proportions at the saturation or vapor pressure. This behavior, shown by the dashed line in Fig. 3.12, is nonanalytic, and we accept as inevitable the unrealistic behavior of equations of state in the two-phase region.

Cubic equations of state have three volume roots, of which two may be complex. Physically meaningful values of V are always real, positive, and greater than constant b.

1. For an isotherm at T > Tc at any positive value of P yields only one such root.
2. For the critical isotherm (T = Tc), this is also true, except at the critical pressure, where there are three roots, all equal to Vc.
3. For isotherms at T < Tc the equation may exhibit one or three real roots, depending on the pressure. Although these roots are real and positive, they are not physically stable states for the portion of an isotherm lying between saturated liquid and saturated vapor (under the "dome"). Only the roots for $P = P_{Sat}$, namely $V_{sat}(liq)$ and $V_{sat}(vap)$, are stable states.

For other pressures below P_{Sat}, the smallest root is a liquid or "liquid-like" volume, and the largest is a vapor or "vapor-like" volume. The third root, lying between the other values, is of no significance.

$$a = \frac{27}{64}\frac{R^2T_c^2}{P_c} \qquad b = \frac{1}{8}\frac{RT_c}{P_c}$$

Soave-Redlick-Kwong (SRK) Equation

The Soave-Redlick-Kwong (SRK) equation belongs to a class of cubic equations of state because, when expanded, they yield third-degree equations for the specific volume. The SRK equation of state is:

In physics and thermodynamics, the Redlich–Kwong equation of state is an equation that is derived from the van der Waals equation. It is generally more accurate than the van der

Waals equation and the ideal gas equation, but not used as frequently because the increased difficulty in its derivatives and overall use.

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}\,V_m\,(V_m + b)},$$

where:
■P is the gas pressure
■R is the gas constant,
■T is temperature,
■V_m is the molar volume (V/n),
■a is a constant that corrects for attractive potential of molecules, and
■b is a constant that corrects for volume.

The constants are different depending on which gas is being analyzed. The constants can be calculated from the critical point data of the gas:
Let P be pressure in atm, Tbe temperature in K and V_m be molar volume in lit/gmol.The RedlichKwong equation is given by:

$$P = \frac{RT}{\hat{V} - b} - \frac{a}{\hat{V}(\hat{V} + b)\sqrt{T}}$$

$$a = 0.42747\left(\frac{R^2 T_c^{\frac{5}{2}}}{P_c}\right)$$

$$b = 0.08664\left(\frac{RT_c}{P_c}\right)$$

1) Vapor Volume:

The equation above was multiplied through by (V-b) /P to give:

$$\boldsymbol{V - b = \frac{R.T}{P} - \frac{a(V - b)}{T^{0.5}\,.P\,.V.\,(V + b)}}$$

For iteration, write:

$$\boldsymbol{Vi+1 = \frac{R.T}{P} + b - \frac{a(Vi-b)}{T^{0.5}\,.P\,.Vi.(Vi+b)}}$$

The initial value for $\boldsymbol{V}$ **i** is obtained from ideal gas law:

$$\bar{v}_{\text{ideal}} = \frac{\bar{R}T}{p}$$

2) Liquid Volume:

$$\boldsymbol{Vi+1 = \frac{1}{C}\left(V_i^3 - \frac{R\,.T}{P}\,V_i^2 - \frac{a\,.b}{P\,.T^{0.5}}\right)}$$

For iteration, The initial value for $\boldsymbol{V}$ **i** take $\mathbf{V_O = b}$.

$$a = 0.42747\left(\frac{R^2T_c^{\frac{5}{2}}}{P_c}\right)$$

$$b = 0.08664\left(\frac{RT_c}{P_c}\right)$$

$$\boldsymbol{C = b^2 + \frac{b\,.R.T}{P} - \frac{a}{P\,.\,T^{0.5}}}$$

The values of **Tc** & **Pc** are available into appendix B, from book (Smith).

Generalized Correlations for Gases and for Liquid

Generalized correlations find widespread use. Most popular are correlations of the kind developed by Pitzer and coworkers for the compressibility factor Z and for the second virial coefficient B.

Pitzer Correlations for the Compressibility Factor :

The correlation for Z takes the form:

$$Z = Z^0 + \omega Z^1$$

where

Z^O and Z' are functions of both T_r and P_r.

$$Z^O = F^o(T_r, P_r)$$

$$Z' = F'(T_r, P_r)$$

and ω :is the centric factor depend on of (T_c , P_c and V_c).

$$T_r = T / T_c$$

$$P_r = P / Pc$$

Equation of state that represents “Z” above is said to be generalized because of their general applicability to all gases.

A disadvantage of the generalized compressibility factor correlation is its graphical nature, thus figures may be used for quick estimates of Z^O and Z' verses P_r and T_r.

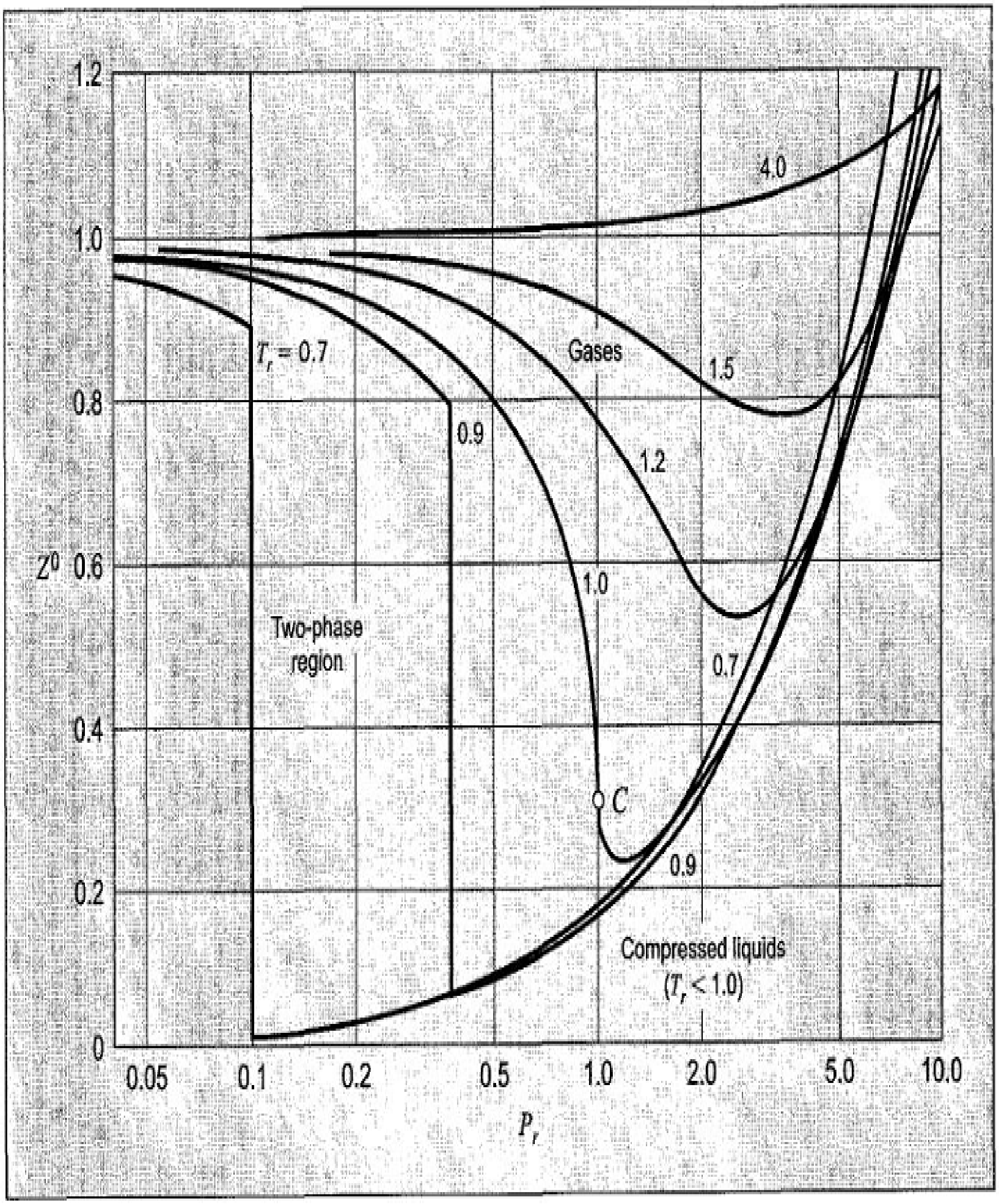


Figure 3.14 The Lee/Kesler correlation for $Z^0 = F^0(T_r, P_r)$

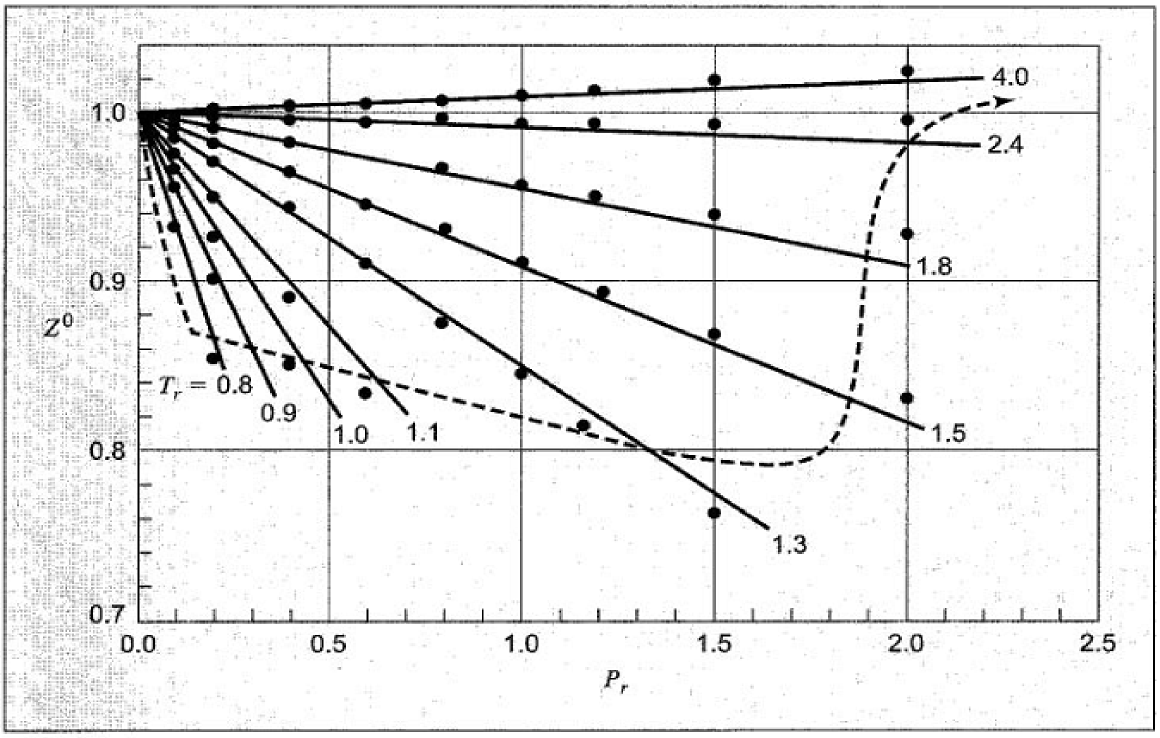


Figure 3.15 Comparison of correlations for Z^0. The virial-coefficient correlation is represented by the straight lines; the Lee/Kesler correlation, by the points. In the region above the dashed line the two correlations differ by less than 2%

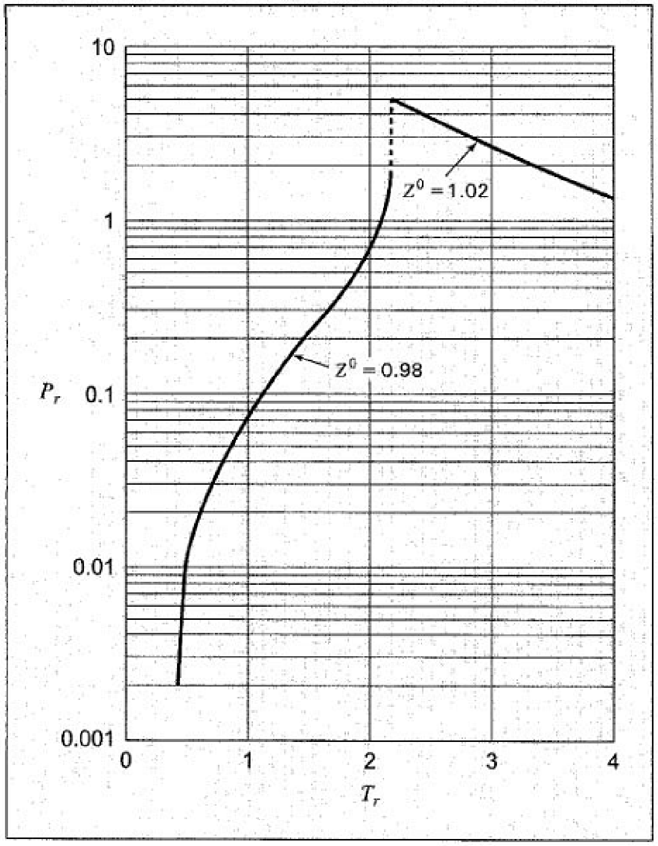


Figure 3.16 Region where Z^0 lies between 0.98 and 1.02, and the ideal-gas equation is a reasonable approximation

Pitzer Correlations for the Second Virial Coefficient

Pitzer correlation provide reliable results for gases which are nonpolar or only slightly polar ; for these errors of no more than 2-3 % are indicated.A disadvantage of generalized compressibility factor correlation is its graphical nature. The simplest form of the Virial equation has validity only at low to moderate pressures where Z is linear in pressure .The generalized Virial-coefficient correlation is therefore useful only where Z^0 and Z ' are at least approximately linear functions of reduced pressure.The simplest form is:

$$Z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_C}{RT_C}\right)\frac{P_r}{T_r}$$

Pitzer proposed a second correlation , which expressed the quantity as BP_C/RT_C

$$\left(\frac{BP_C}{RT_C}\right) = B^\circ + B\omega'$$

Together, these two equations become:

$$Z = 1 + B^\circ \frac{P_r}{T_r} + \omega B' \frac{P_r}{T_r}$$

Comparison of this equation with generalized compressibility factor :

$$Z = Z^0 + \omega Z^1$$

Provides the following identifications:

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

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

Second Virial coefficients are functions of temperature only, and similarly B0 and B' are functions of reduced temperature only. They are well represented by the following equations:

$$B^\circ = 0.083 - \frac{0.422}{T_r^{1.6}}$$

$$B' = 0.139 - \frac{0.172}{T_r^{4.2}}$$

Generalized Correlations for Liquids:

Although the molar volumes of liquids can be calculated by means of generalized cubic equations of state, the results are often not of high accuracy. In addition, generalized equations are available for the estimation of molar volumes of saturated liquids. The simplest equation, proposed by Rackett,

$$V^{sat} = V_c Z_c^{(1-T_r)^{0.2857}}$$

The only data required are the critical constants, given in App. B. from Smith thermodynamics book.

Lydersen, and Hougen developed a two-parameter corresponding-states correlation for estimation of liquid volumes. It provides a correlation of reduced density p, as a function of reduced temperature and pressure. By definition,

$$\rho_r \equiv \frac{\rho}{\rho_c} = \frac{V_c}{V}$$

Where

ρ_c : is the density at the critical point.

A better procedure is to make use of a single known liquid volume (state 1) by the identity,

$$V_2 = V_1 \frac{\rho_{r_1}}{\rho_{r_2}}$$

where

V_2 = required volume

V_I = known volume

P_{r1} , P_{r2} = reduced densities read from Fig. 3.17

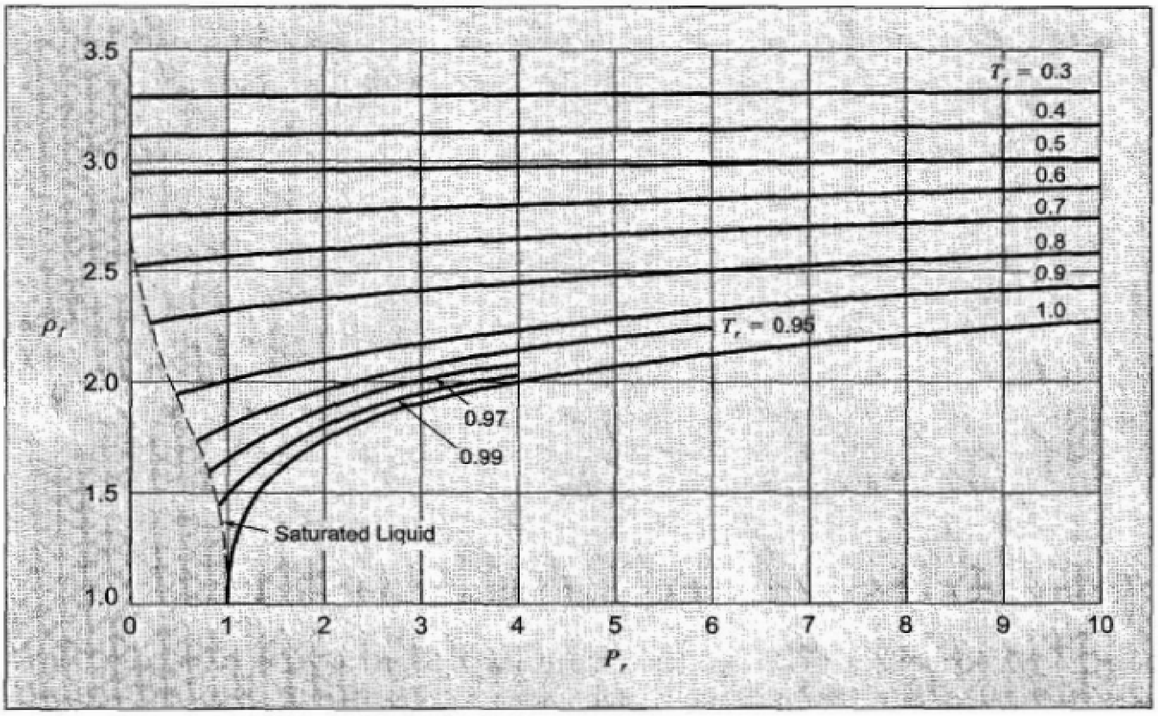


***Figure* 3.17** Generalized density correlation for liquids

EXAMPLES

TUTORIALS SHEET NO.(1)