

Chapter 2.

Phase Diagrams of Pure Fluids

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Equation of state

- The approximate relationship between molar volume and mean intermolecular distance is given by

$$r \sim \left(\frac{V}{N_{AV}} \right)^{\frac{1}{3}}$$

- The packing density of molecules in given volume reflects the strength of the potential interaction.
- The relationship between volume, pressure, and temperature is of fundamental importance and its mathematical form is known as equation of state.
- It is highly required that we examine this relationship in graphical and mathematical form.

Learning Objective

- Using the PVT graph to identify the phase of a pure fluid.
- Working with tabulated values of P, V, T (steam table).
- Identify the region of applicability of the idea-gas law and the truncated virial equation.
- Working with cubic equations of state.
- Working with generalized correlations for the compressibility factor.
- Representing processes on the PV graph.

The PVT Behavior of Pure Fluid

- The relationship between volume, pressure, and temperature is represented graphically by a three-dimensional surface whose general shape is shown.
- The PVT relationship is visualized but it is impractical for routine use. Instead, we work with projections of the PVT surface on one of the three planes, PV, PT, or VT.
- A projection is a view of the three-dimensional surface from an angle perpendicular to the projection plane and reduce the graph into a two-dimensional plot.

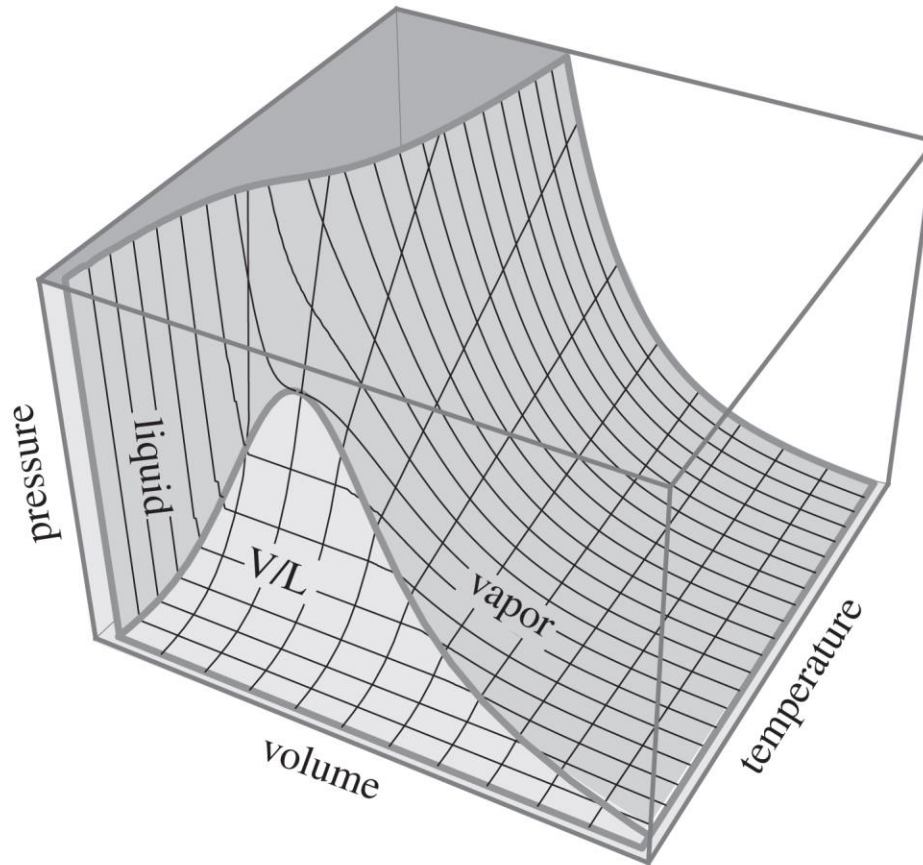


Figure 2-1

The *PVT* surface of a pure fluid.

The PV graph

- The PV graph is the projection on the PV plane.
- Temperature is indicated by contours of constant temperature (isotherms).
- The isotherm that passes through the critical point corresponds to the critical temperature, T_c . This isotherm has an inflection point at the critical point, namely, its first and second derivatives are both zero:

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial^2 V}\right)_T = 0 \quad \text{at } V=V_c, T=T_c$$

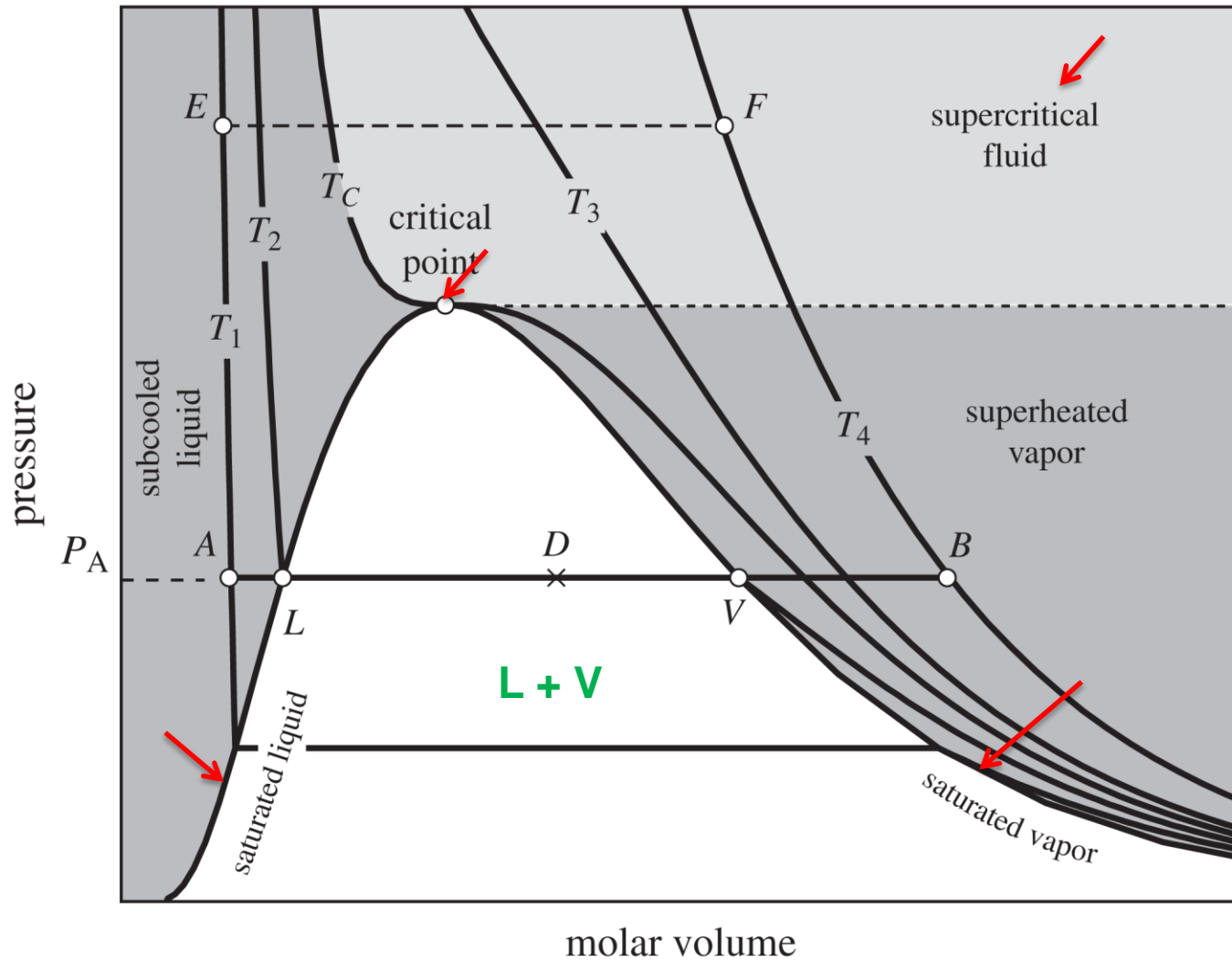


Figure 2-2

The PV graph of pure fluid (the solid phase is not shown).

The PV graph

- *Subcooled liquid*: its temperature is below the boiling point that corresponds to its pressure.
- *Superheated vapor*: its temperature is higher than the boiling temperature that corresponds to its pressure.
- The organization of information on the PV graph can be better understood by conducting a heating or cooling process and following the path on the graph.

The critical point

- It is an important state and its pressure and temperature have been tabulated for a large number of pure substances.
- In approaching the critical point, the distance between points L and V decreases, indicating that the molar volume of the saturated liquid and saturated vapor come closer together. At the critical point the two saturated phases coincide: vapor and liquid become indistinguishable.
- *Supercritical fluid*: the region of the phase diagram above P_c and T_c ; Other properties, in particular, the solubility of various nonvolatile solutes, are often found to be quite enhanced compared to the supercritical region.

A special limit: the ideal-gas state

- Mathematical specification of the ideal gas state is, $V \rightarrow \infty$ (at constant T), $P \rightarrow 0$ (at constant T).
- On the PV graph, the ideal-gas state is found near the lower-right corner.
- In the ideal-gas state, the PVT relationship is universal for all gases, regardless of chemical composition and this relationship is given by the ideal-gas law, $PV^{ig} = RT$, where V^{ig} is molar volume, T is absolute temperature, and R is a universal constant (ideal-gas constant), 8.314 J/mol K .

Two-phase region—the lever rule

- At point D, a two-phase system that contains portions of liquid and vapor. At the same temperature and pressure but each has its own molar volume.
- Tie line: a line LV connecting the two phases.
- Wet vapor: a vapor-liquid mixture
- Quality of the vapor, x_v : the amount of vapor as a fraction of the total mass

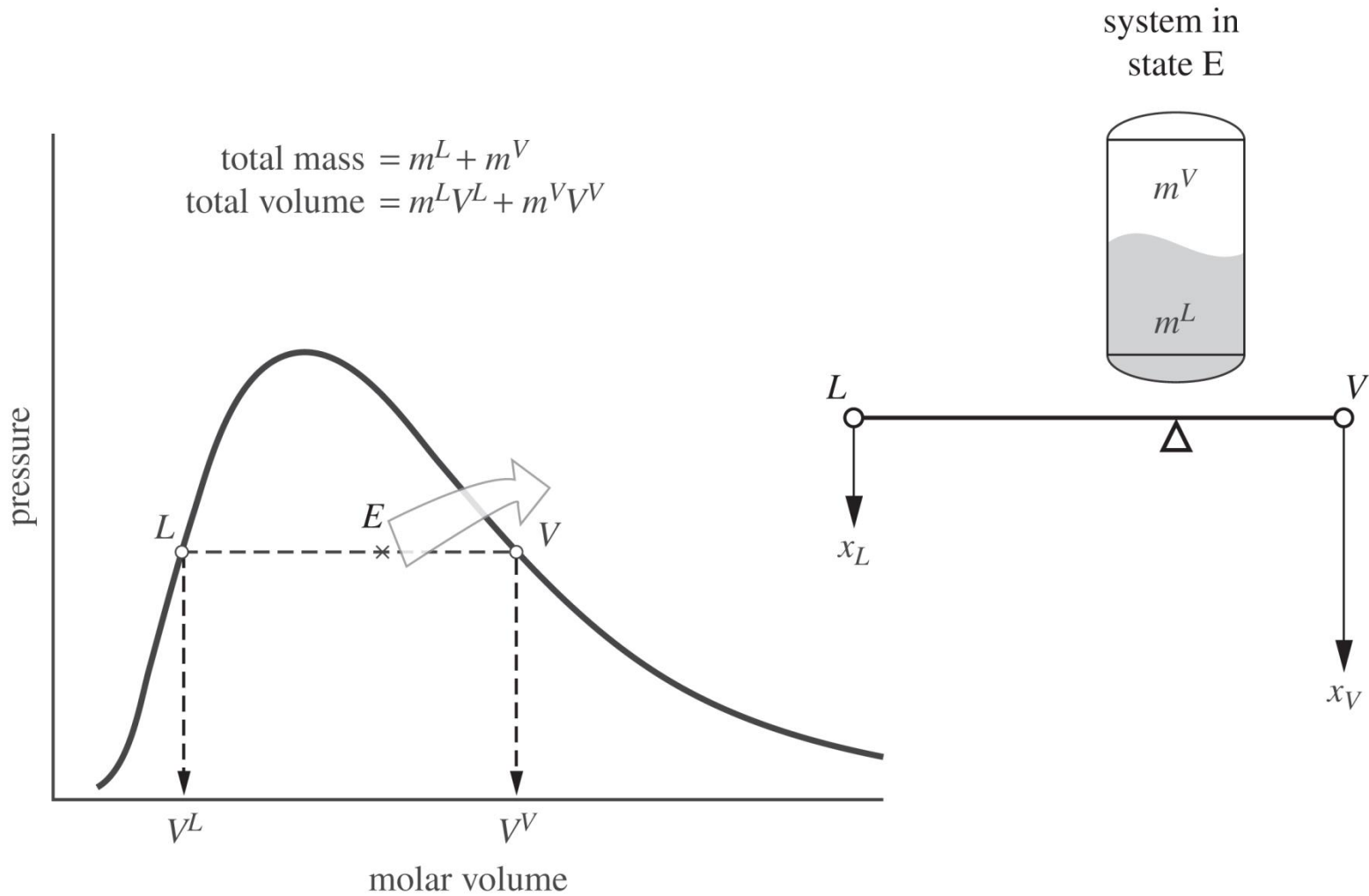


Figure 2-3

Setup for the application of the lever rule on a tie line.

Two-phase region—the lever rule

$$x_v = \frac{n_v}{n_L + n_v}, \quad x_L = \frac{n_L}{n_L + n_v} \quad (\text{molar fractions of vapor and liquid})$$

$$V_{\text{tot}} = n_L V_L + n_v V_v \quad (\text{total volume of the two-phase mixture})$$

$$V = \frac{V_{\text{tot}}}{n_{\text{tot}}} = \frac{n_L V_L}{n_L + n_v} + \frac{n_v V_v}{n_L + n_v} = x_L V_L + x_v V_v \quad (\text{molar volume})$$

$$x_v = \frac{V - V_L}{V_v - V_L}, \quad x_L = \frac{V_v - V}{V_v - V_L}$$

$(x_L + x_v = 1, \text{ fractions of vapor and liquid, the lever rule})$

Example 2.1. Why “Lever” Rule?

If DV , LD , are the distances between points (D, V) and (D, L) respectively, show that the liquid and vapor fractions corresponding to point D satisfy the relationship

$x_V(VD) = x_L(LD)$, where VD and LD are the distance between points V, D , and L, D , respectively.

The PT graph

- Projection of the three-dimensional surface on the pressure/temperature plane.
- Line FC: vapor-liquid boundary
- Line FS: solid-liquid boundary (almost vertical; not affected strongly by pressure; no critical point on the boundary)
- Triple point: intersection between FC and FS (three phases coexist in equilibrium)
- Dotted lines: lines of constant molar volume known as isochores
- Line LL': line at constant volume $V = V_L$, volume of saturated liquid
- Line VV': line at constant volume $V = V_V$, volume of saturated vapor

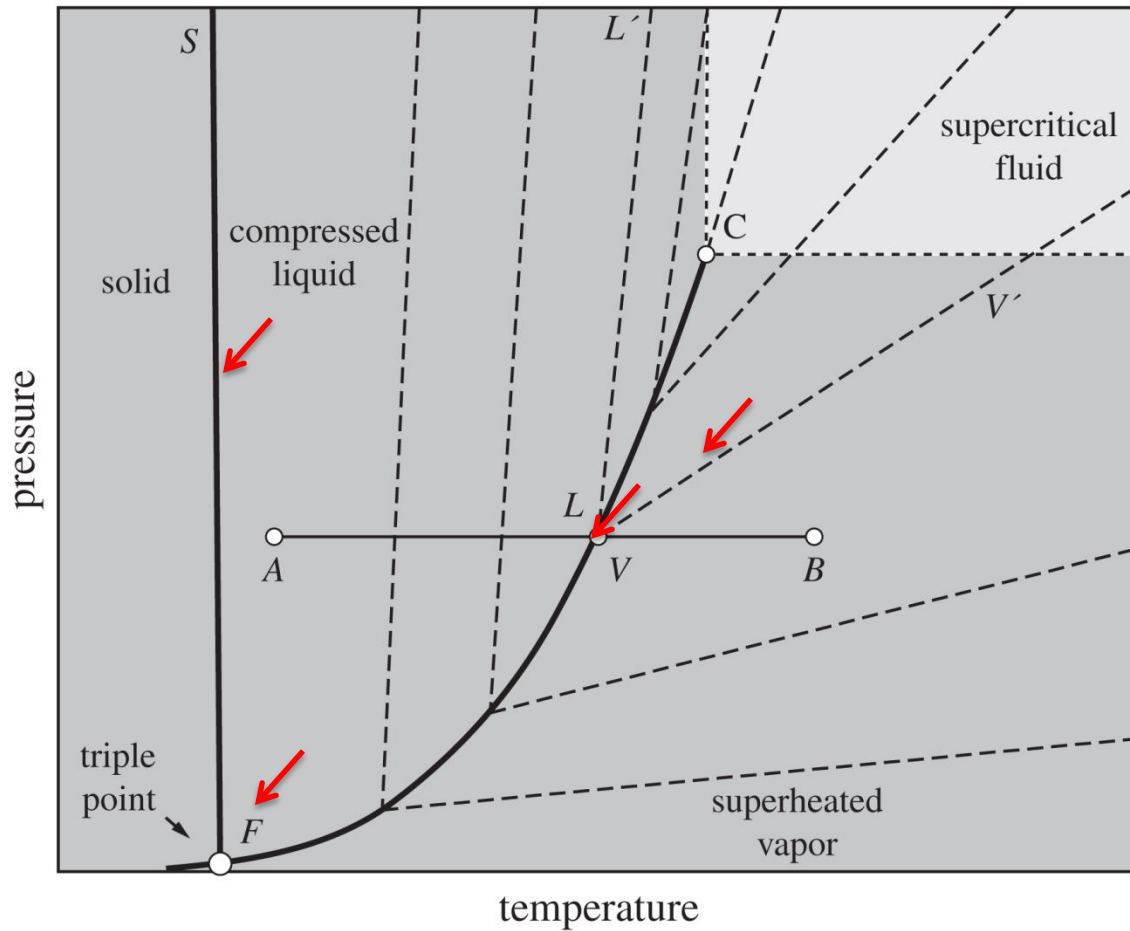


Figure 2-4

Pressure-temperature graph of pure fluid showing the solid, liquid, vapor and supercritical regions. Dotted lines are lines of constant molar volume.

Antoine equation

- Mathematical relationship between saturation pressure and temperature
- $\ln P^{sat} = A - \frac{B}{C+T}$, where A, B, and C are numerical constants specific to the substance. These constants have been obtained by numerical fitting against experimental data and are available for a large number of pure fluids.
- A recommended resource for parameters of the Antoine equation is the *Properties of Gases and Liquids*, by Poling, Prausnitz and O'Connell (5th ed., 2007)

Example 2.2. Determining the phase?

Based only on the Antoine equation given, determine the phase of water at (a) 2 bar, 115 °C, and (b) 20 bar, 300 °C.

Tabulation of properties

- As a state property, the molar(or specific) volume can be determined once as a function of pressure and temperature, and tabulated for future use.
- Tabulations have been compiled for a large number of pure fluids. (e.g., steam table for water)
- American Society of Mechanical Engineers (ASME) published the thermodynamic tables for water.

Interpolation

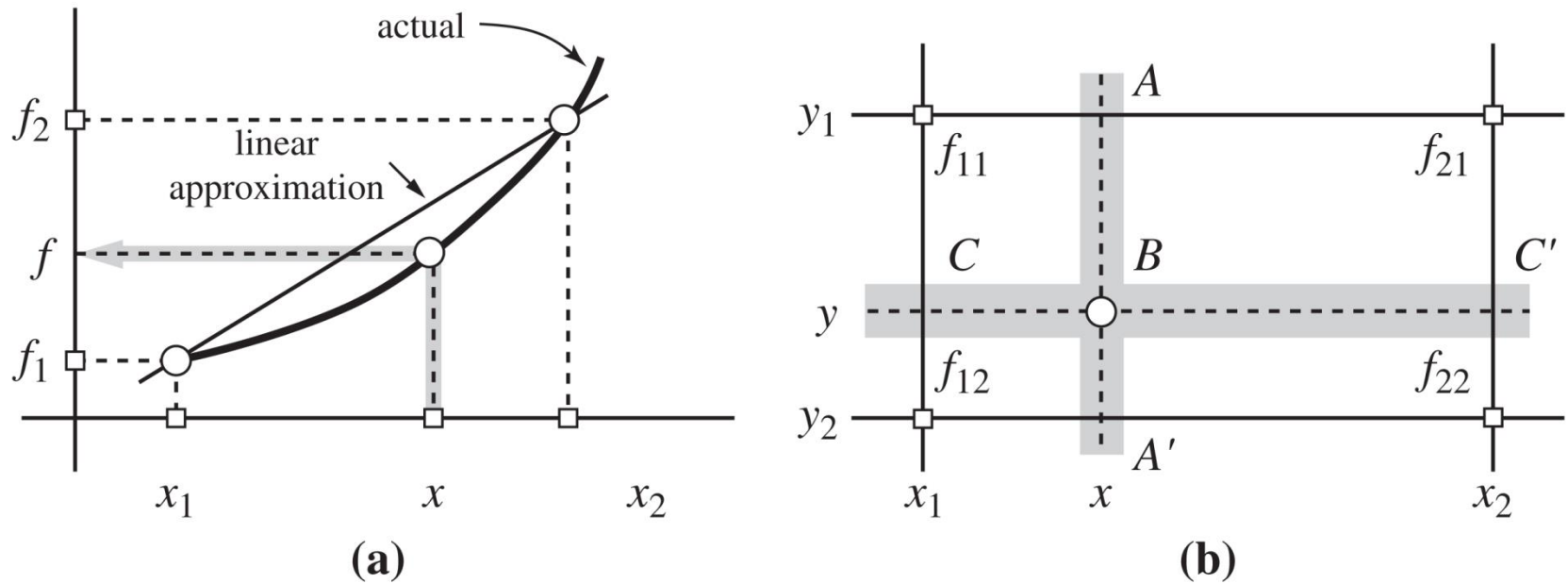


Figure 2-5

Linear interpolation: (a) simple interpolation; (b) double interpolation.

$$f = f_1 + \frac{f_2 - f_1}{x_2 - x_1} (x - x_1)$$

$$f(x, y) = (1 - a)(1 - b)f_{11} + b(1 - a)f_{12} + a(1 - b)f_{21} + abf_{22}$$

$$a = \frac{x - x_1}{x_2 - x_1}, b = \frac{y - y_1}{y_2 - y_1}$$

Compressibility factor and the ZP graph

$$\text{Compressibility factor } Z = \frac{PV}{RT}$$

$$Z^{\text{ig}} = 1 \quad (V^{\text{ig}} = RT/P)$$

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

$V = \frac{ZRT}{P}$ (V , molar volume obtained easily if the compressibility factor is known at a given pressure and temperature)

In the ZP graph, the pressure range over which the approximation of ideal gas state is valid varies with temperature. The isotherm at T_4 closer to 1 over a wider interval of pressures, compared to the isotherm at T_1 , which has a larger negative slope and decreases faster.

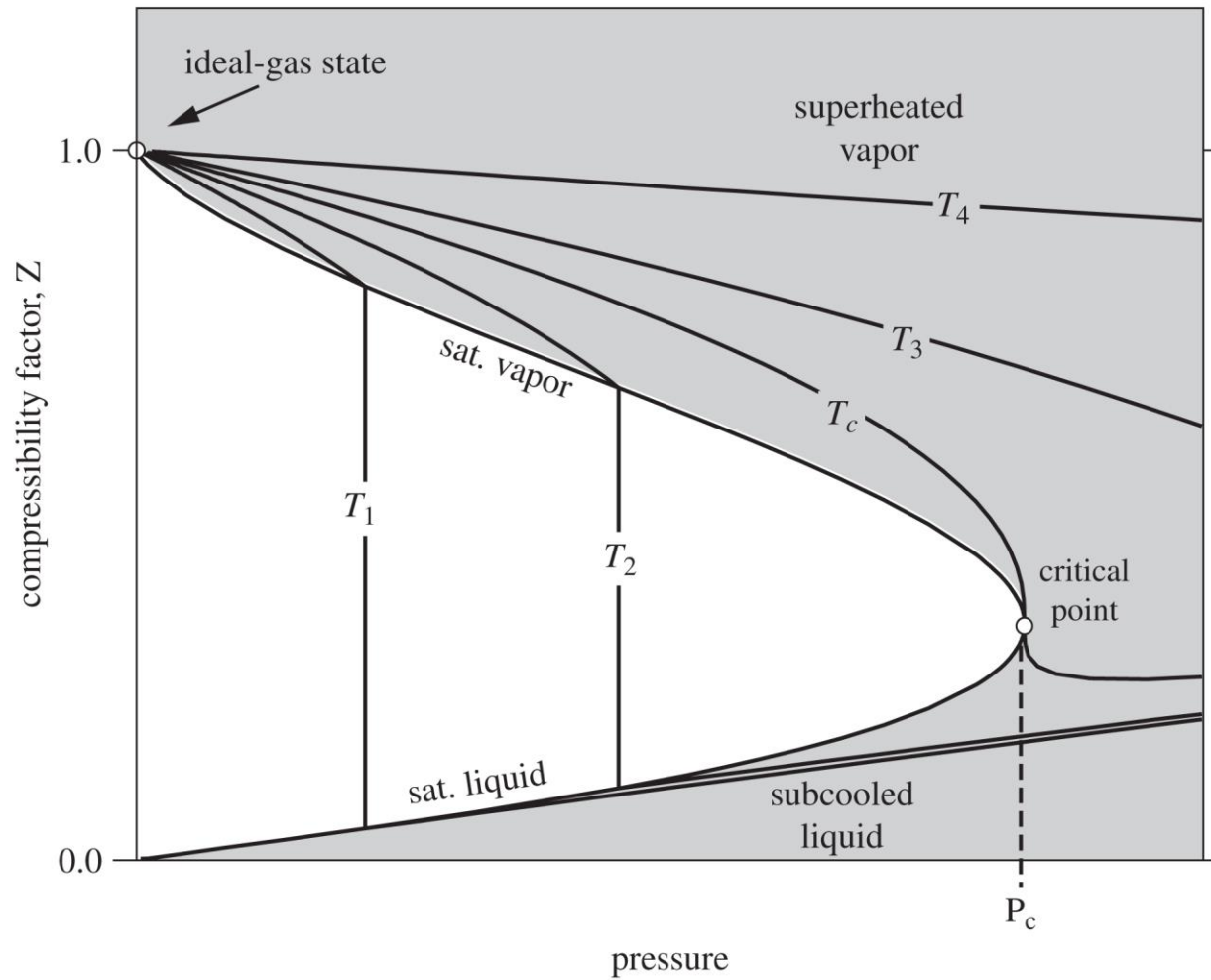


Figure 2-6
The ZP graph of pure fluid.

Corresponding states

- It is found experimentally that the ZP graphs of different fluids look very similar to each other as if they are scaled versions of a single, universal, graph.
- This underlying graph is revealed if pressure and temperature are rescaled by appropriate factors. It is introduced that a set of reduced (dimensionless) variables by scaling pressure and temperature with the corresponding values at the critical point.

$$P_r = \frac{P}{P_c}, T_r = \frac{T}{T_c}$$

- Using the reduced coordinates it is possible to combine ZP data for several compounds on the same graph.

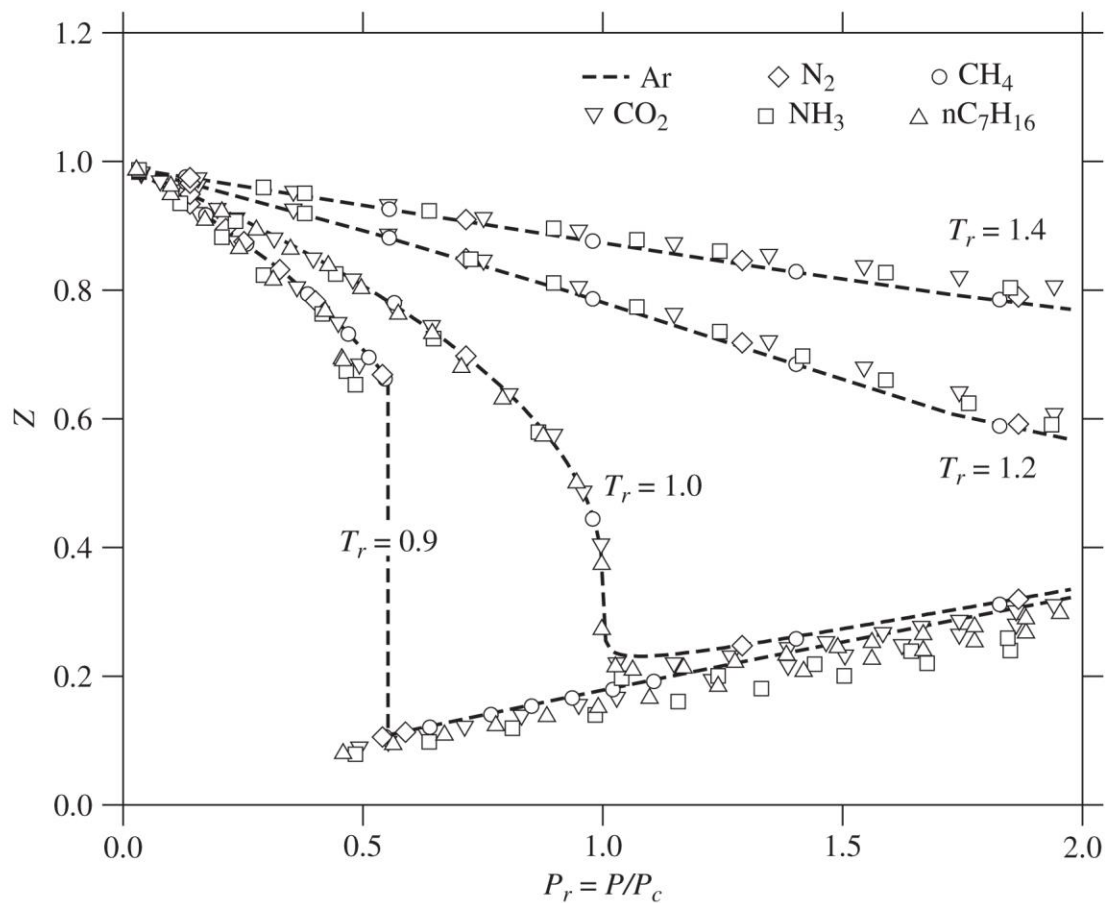


Figure 2-7

The compressibility factor of selected molecules as a function of reduced pressure and temperature. Data compiled from E. W. Lemmon, M. O. McLinden and D. G. Friend, "Thermophysical Properties of Fluid Systems." In *NIST Chemistry WebBook*, NIST Standard Reference Database No. 69, eds. P. J. Linstrom and W. G. Mallard, National Institute of Standards and Technology, Gaithersburg MD, 20899, <http://webbook.nist.gov> (retrieved December 11, 2010).

Corresponding states

- *At the same reduced temperature and pressure, fluids have approximately the same compressibility factor.*
- The compressibility factor of any fluid can be described by a universal equation that is a function of reduced temperature and reduced pressure.

$$Z \approx Z(T_r, P_r)$$

- In general, agreement is very good in the gas phase, where interactions are unimportant.
- The principle of corresponding states should be treated as a working hypothesis that can provide useful but not always highly accurate estimates of the compressibility factor.

Acentric factor and the Pitzer method

- To improve the predictive power of the principle of corresponding state while retaining the simplicity (whatever nonpolar or polar molecule), a third parameter is introduced, the acentric factor.

(where P_r^{sat} is the reduced saturation pressure of the fluid at reduced temperature $Tr = 0.7$. It is a characteristic property of the fluid and is found in tables, usually along with the critical properties of the fluid.)

$$\omega = -1 - \log_{10} P_r^{sat} \Big|_{Tr = 0.7}$$

- Engaged with the Pitzer method, the compressibility factor is expressed in the form.

$$Z = Z^{(0)} + \omega Z^{(1)}$$

(where Z_s are universal functions that depend on Tr and Pr . $Z(0)$ represents the compressibility factor of simple fluids ($\omega=0$) and $Z(1)$ is a correction that is proportional to the acentric factor.)

- Various methodologies have been developed for the calculation of the functions above, the most widely used is that of Lee and Kesler.

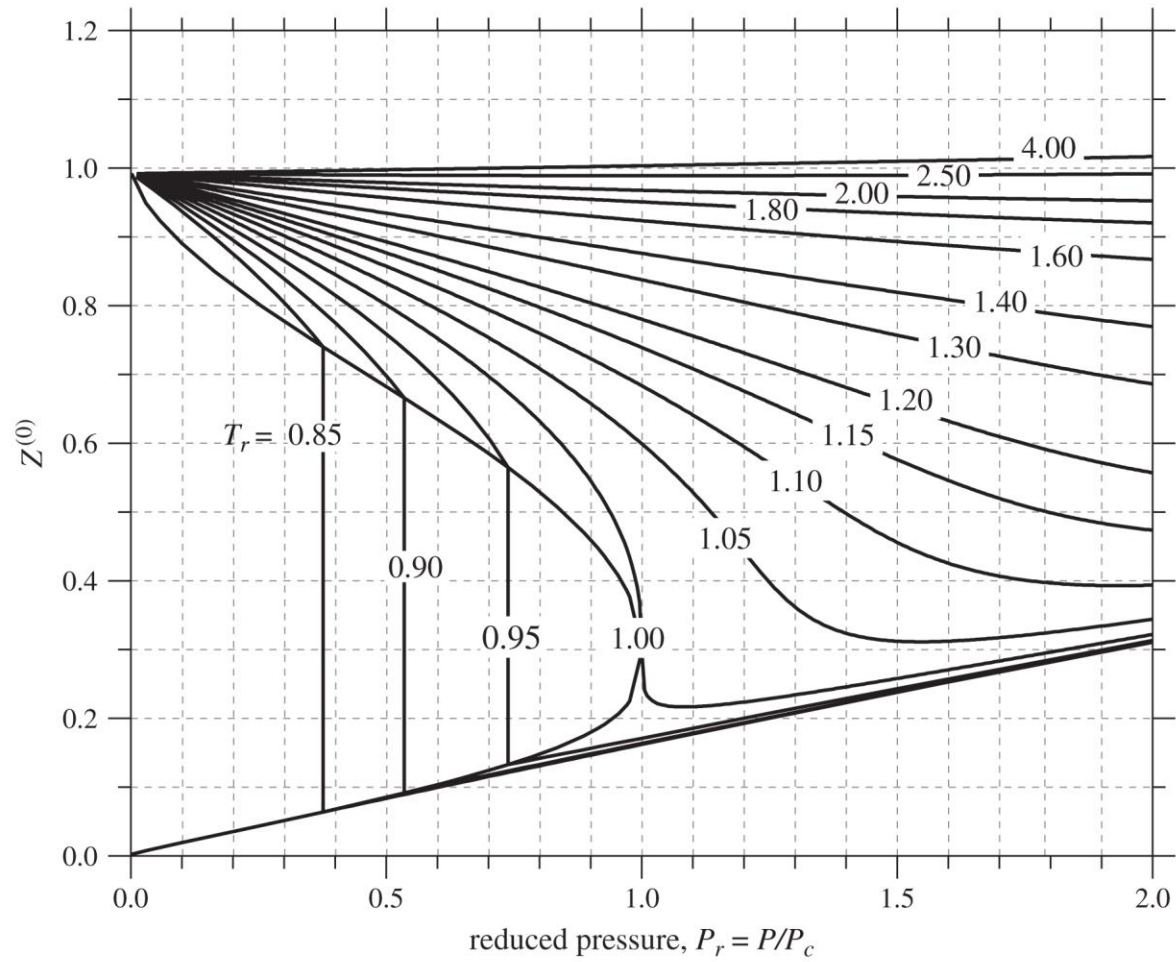


Figure 2-8

Generalized graph of $Z^{(0)}$ based on the Lee-Kesler method.

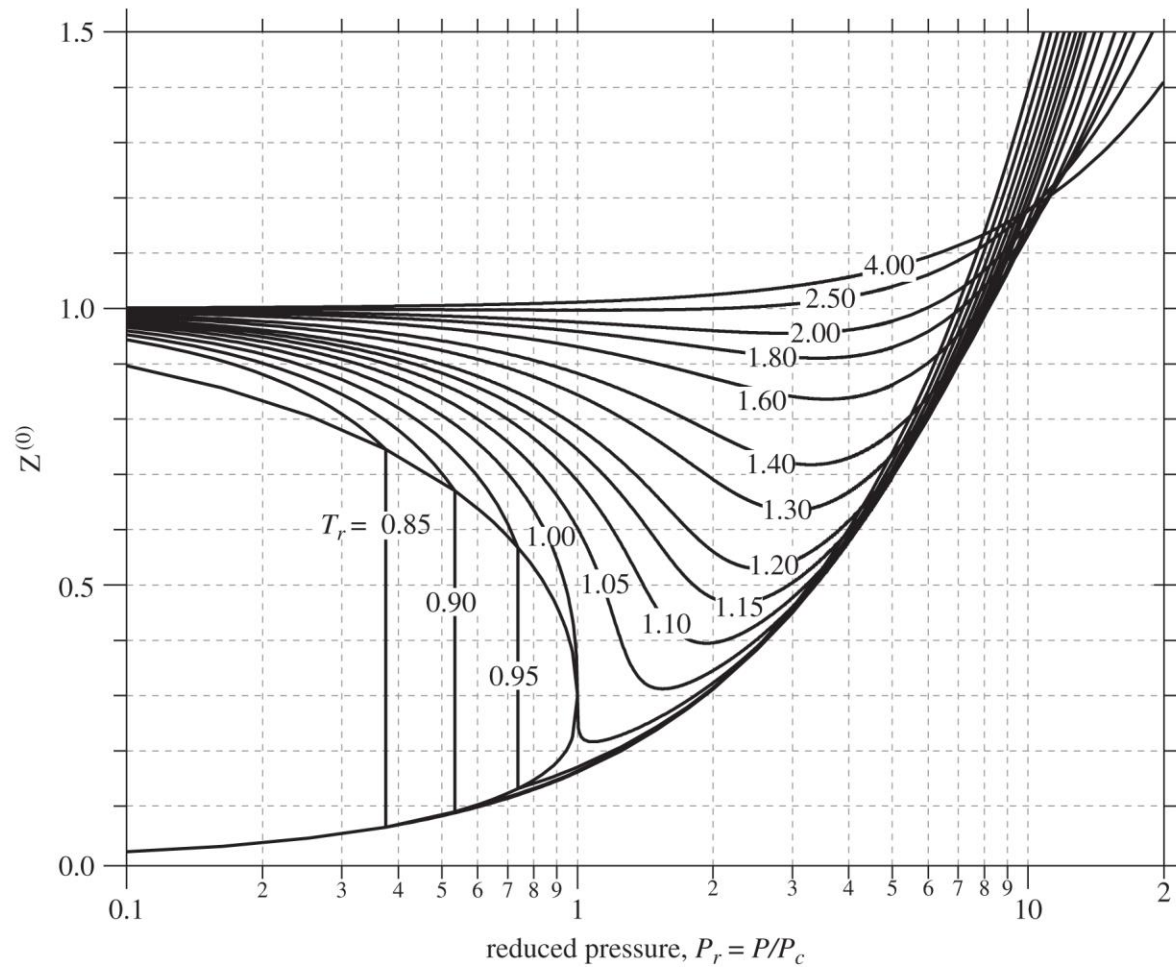


Figure 2-9

Generalized graph of $Z^{(0)}$ based on the Lee-Kesler calculation (extended range of pressures).

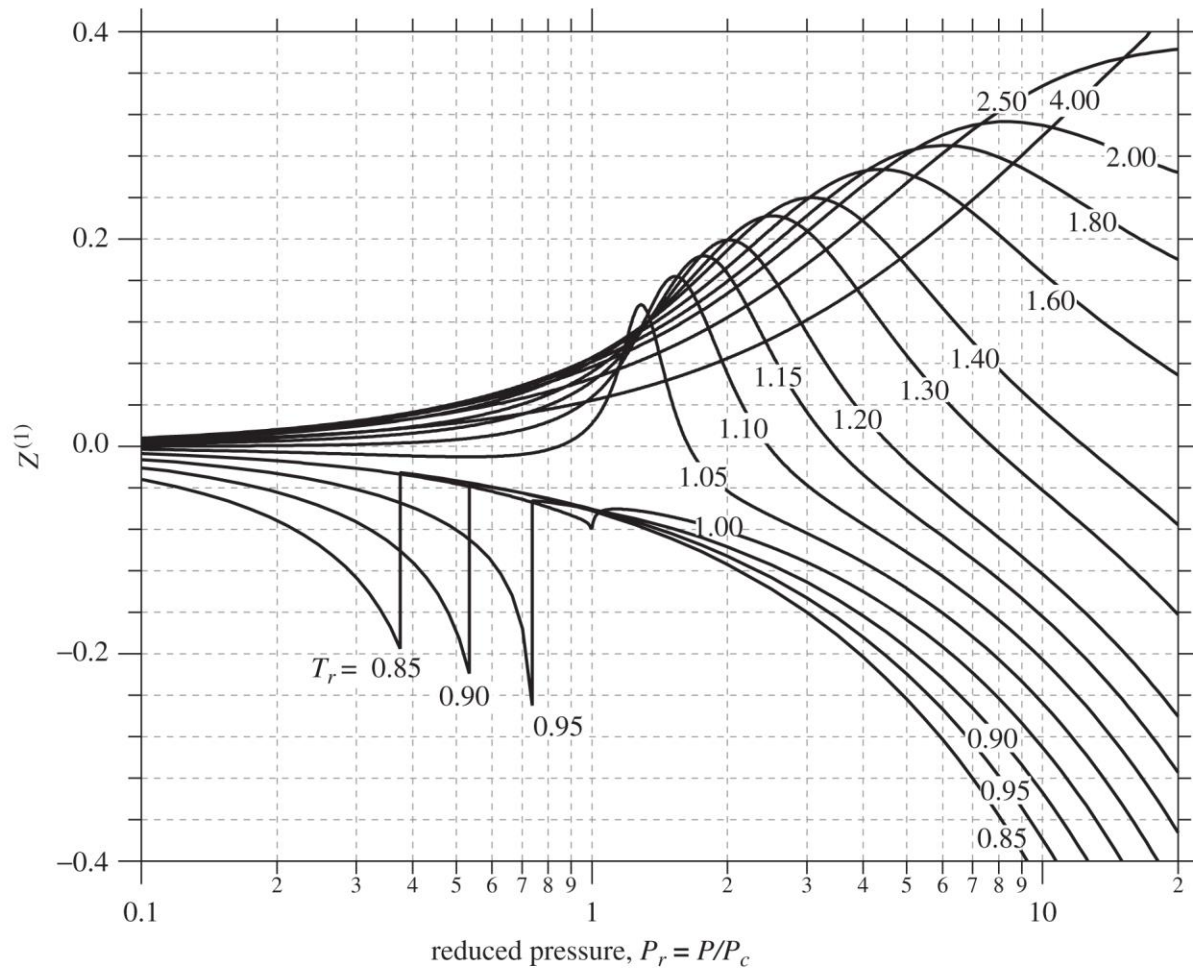


Figure 2-10

Generalized graph of $Z^{(1)}$ based on the Lee-Kesler calculation.

Example 2.3. Corresponding states?

Use the Pitzer correlation with the Lee-Kesler graphs to estimate the density of carbon dioxide at 35 bar, 75 °C.

Example 2.4. Corresponding states?

Estimate the density of carbon dioxide at 35 bar, 75 °C using data only from the steam tables.

Virial equation

- All isotherms on the ZP graphs begin at $P = 0$, $Z = 1$, and grow outward with pressure. This behavior can be described mathematically as power series in P :

$$Z = 1 + b(T)P + c(T)P^2 + \dots$$

- In this region isotherms are fairly linear in P . Upon further increasing pressure, the quadratic and then other higher-order terms become increasingly more important and isotherms are no longer linear. Instead of P and T , with V and T as the state variables, a similar series expansion can be constructed in terms of volume:

$$Z = 1 + B(T)/V + C(T)/V^2 + \dots$$

Truncated virial equation

- If all the coefficients of the expansion were known, the virial equation would provide complete description of the vapor isotherm up to the point it intersects the saturated vapor line.

$$Z = 1 + BP/RT$$

- Pitzer method for the second virial coefficient:

$$BP_c/RT_c = B^0 + \omega b^1$$

$$B^0 = 0.083 - 0.422/Tr^{1.6}$$

$$B^1 = 0.139 - 0.172/Tr^{4.2}$$

Example 2.5. Comparison of Methods?

Calculate the molar volume of ethylene at 40 °C, 90 bar, using the (a) ideal-gas law, (b) the truncated virial equation, and (c) the Pitzer correlation with the Lee-Kesler values for $Z^{(0)}$, $Z^{(1)}$.

Method	Z	V(10^{-4} m ³ /mol)
Ideal gas	1	2.893
Virial	0.5619	1.626
Lee Kesler	0.4305	1.245
literature	0.4216	1.220

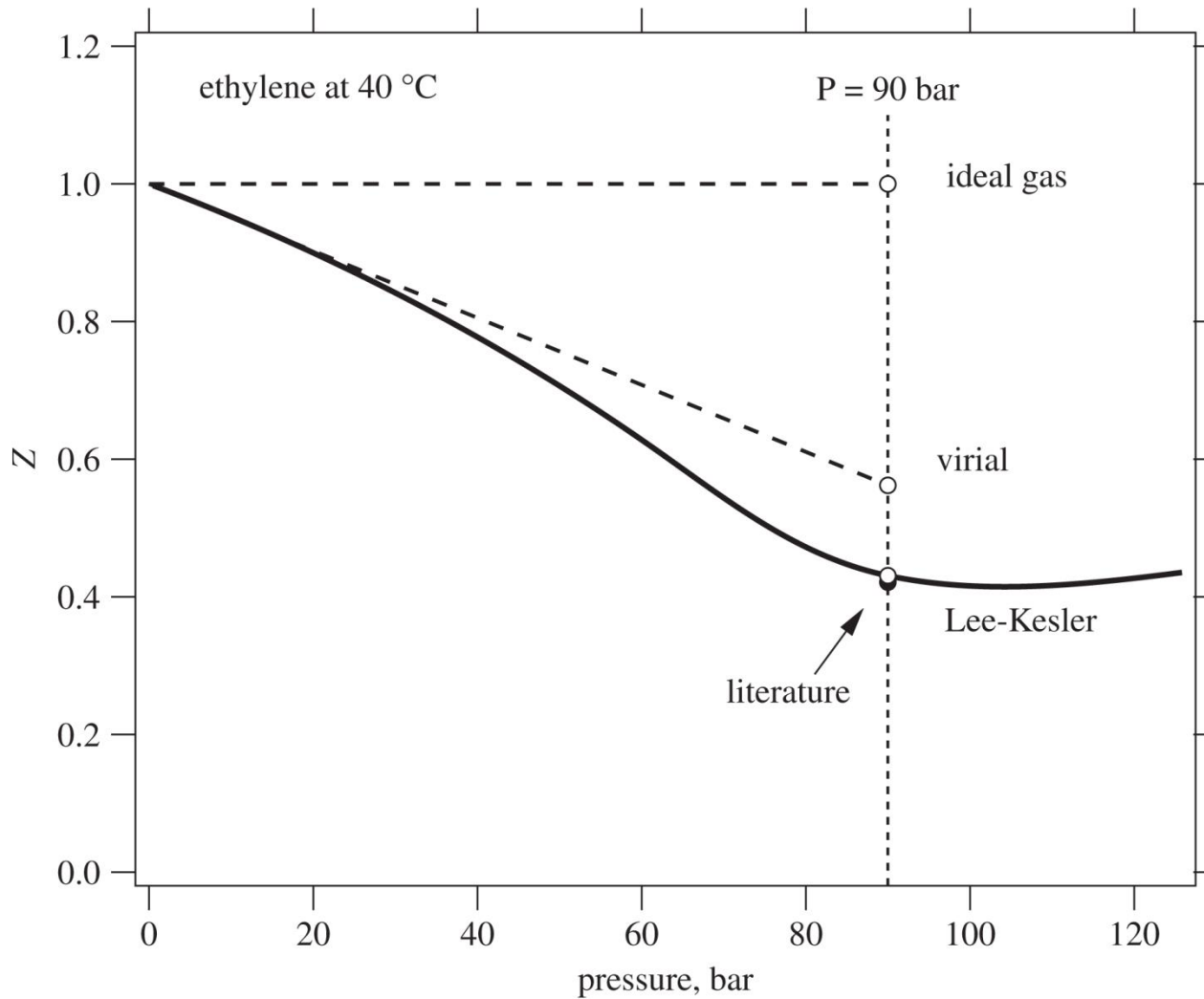


Figure 2-11

Calculated isotherms of ethylene at 40 °C using the ideal-gas law, the truncated virial equation, and the Pitzer method with the Lee-Kesler values of $Z^{(0)}$ and $Z^{(1)}$ (see Example 2.9).

Cubic equations of state

- For engineering calculations it is important to have equations of state that are accurate over a wide range of pressures and temperatures.
- Ideal gas law: very simple to use but restricted to gases at low pressures.
- Truncated virial equation: applicable over a somewhat wider range of pressures but only for gases.
- *What if the pressure is high or the phase liquid?: The cubic equations of state are useful because they are capable of handling both liquids and gases.*

Cubic equations of state

- Van der Waals equation of state:

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

- Soave-Redlich-Kwong (SRK) equation of state:

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

- Peng-Robinson(PR) equation of state:

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

PVT behavior of cubic equations of state

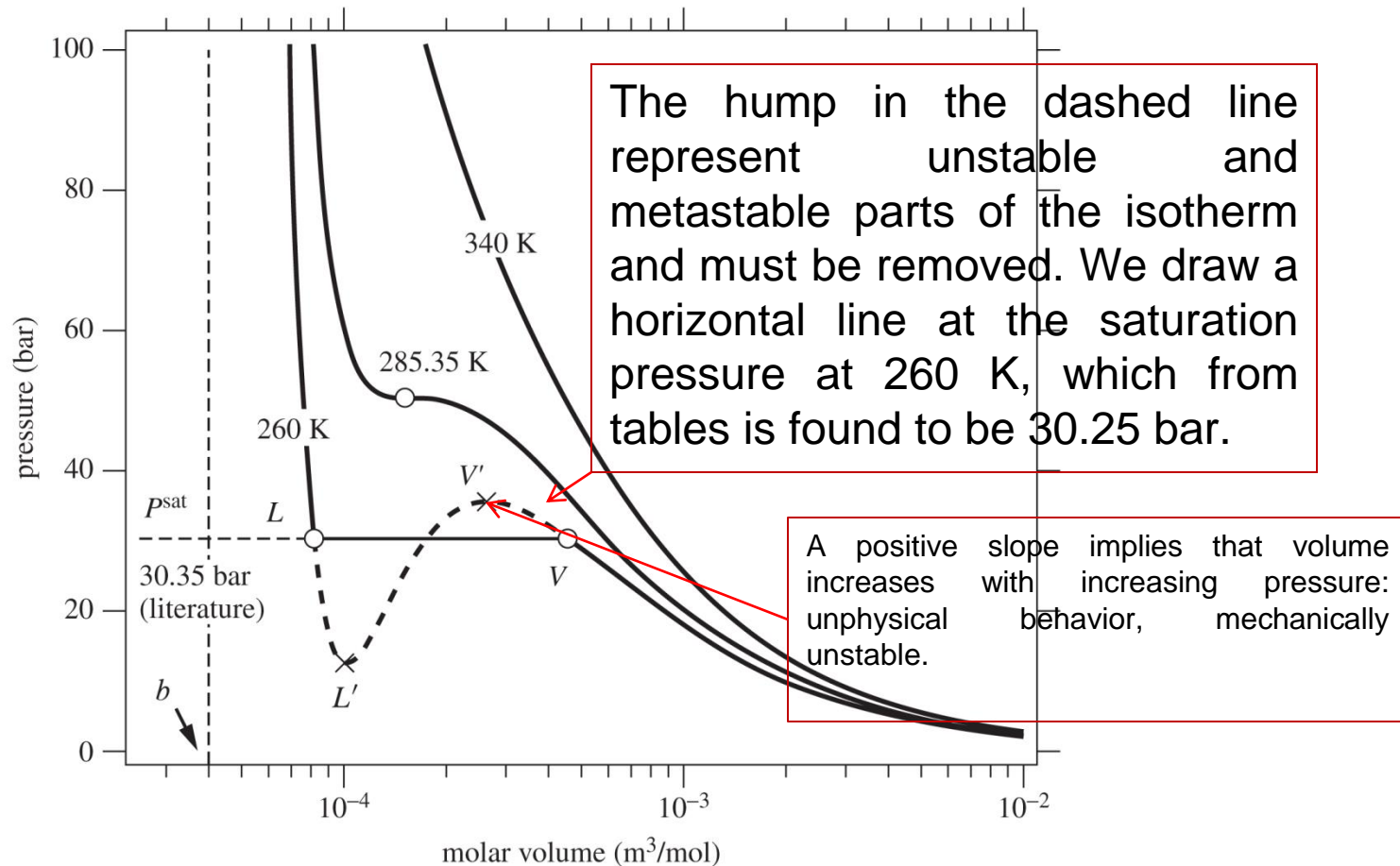


Figure 2-12

Isotherms of ethylene calculated by the Soave-Redlich-Kwong equation.

Working with cubic equations

- The molar volume at given pressure and temperature can be calculated by solving *the equation of state or the cubic equation for V* .
- Compared to the Z equations which is dimensionless, the cubic equations reduces the chances of errors involving units.
- As a cubic equation, its roots can be computed using standard formulas described in other references.

Other equations of state

Benedict-Webb-Rubin equation of state:

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

- It is getting birth with any mathematical requirements at the point that subcritical isotherms must exhibit the characteristic h-shaped portion, with an unstable part between the liquid and vapor branches.
- It requires eight parameters (A_0 , B_0 , C_0 , a , b , c , α , and γ) that are specific to the fluid.
- A modified form of this equation was used by Lee and Kesler in the calculation of $Z(0)$ and $Z(1)$.

Example 2.6. Calculation of Lee-Kesler factors, $Z^{(0)}$, $Z^{(1)}$

Lee and Kesler computed the values of $Z^{(0)}$ and $Z^{(1)}$ using a modification of the BWR equation of state.

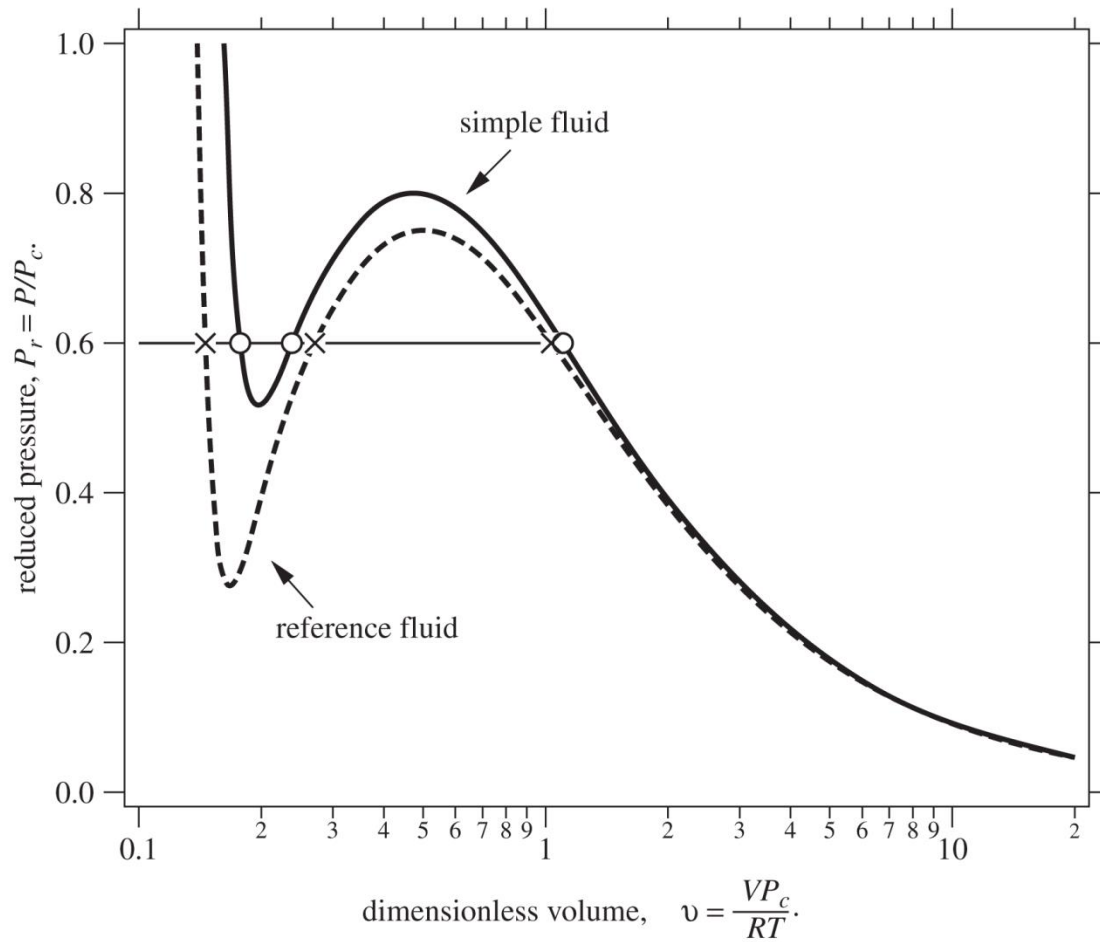


Figure 2-13

Isotherms of the modified BWR equation for the simple and reference fluid at $T_r = 0.95$ (see Example 2.12).

Thermal Expansion and Isothermal Compression

- The effect of temperature and pressure on volume is quantified by two coefficients, *the volumetric coefficient of thermal expansion and the coefficient of isothermal compression*.

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

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

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

Empirical equations for density

- A useful and accurate method for the calculation of liquid molar volumes at saturation is the *Rackett equation*.

Rackett equation:

$$V_L = \frac{RT_c}{P_c} Z_R^{1 + (1 - T_r)^{2/7}}$$

$$v^{l,\text{sat}} = \frac{RT_c}{P_c} (0.29056 - 0.08775\omega)[1 + (1 - T_r)^{2/7}]$$

Example 2.7. Constant-volume heating of liquid

A glass container is filled with acetone at 25 °C and sealed, leaving no air inside. Determine the pressure that develops in the container when it is heated to 35 °C. The isothermal compressibility of acetone is as shown in Table 2-188 in Perry's Chemical Engineer's Handbook).

$$\kappa = 52 \times 10^{-6} \text{ bar}^{-1}$$

You may ignore the expansion of the container.

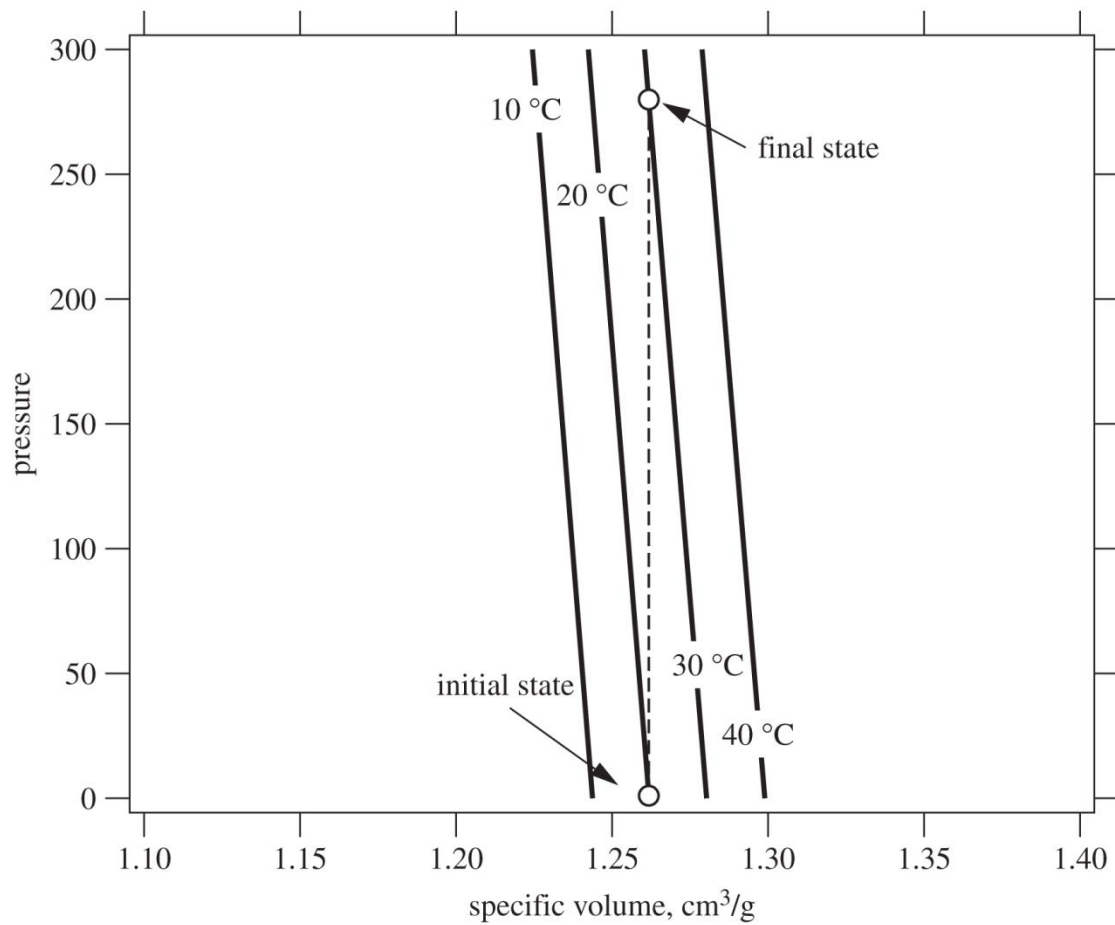


Figure 2-14

Pressure-volume isotherms of acetone (see Example 2.14).