Four Ways to get Vapor Pressure

Short Cut Method Approximation

$$\boxed{\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right)} \qquad 9.11$$

❗ Shortcut vapor pressure equation. Use care with the shortcut equation below $T_r = 0.5$.

Clausius-Clapyron Equation

$$\ln\left(\frac{P^{sat}}{P_R}\right) = -\frac{\Delta H^{vap}}{R\Delta Z^{vap}}\left(\frac{1}{T}-\frac{1}{T_R}\right) \qquad 9.10$$

Use Peng-Robinson or other EOS and find where the fugacity ratio is 1

Antoine Equation

$$\log_{10} P^{sat} = A - B/(T + C)$$

Which method depends on accuracy needed, availability of parameters, and calculation speed required. For Clausius- Clapron Equation you can use 1) ecentricity, 2) critical point, 3) normal boiling point as reference points.

We want to know the vapor pressure to determine fractionation at vapor/liquid equilibria in Chapter 10 for multicomponent systems

Gibb's Free Energy decides phase equilibria at constant T and P

-SUV
H   A
-pGT

dG=-SdT + VdP   (depends on T and P)

$G^L = G^V$ at equilibrium

dG = VdP (Constant T)

the ratio *f/P* to be the *fugacity coefficient, φ*.

$$\boxed{\frac{(G - G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \ln\varphi} \qquad 9.22$$

$$\frac{(G^L - G^{ig})}{RT} = \frac{(G^V - G^{ig})}{RT} \qquad \ln\left(\frac{f^L}{P}\right) = \ln\left(\frac{f^V}{P}\right) \qquad \boxed{f^L = f^V}$$

Vapor/Liquid Equilibria From EOS

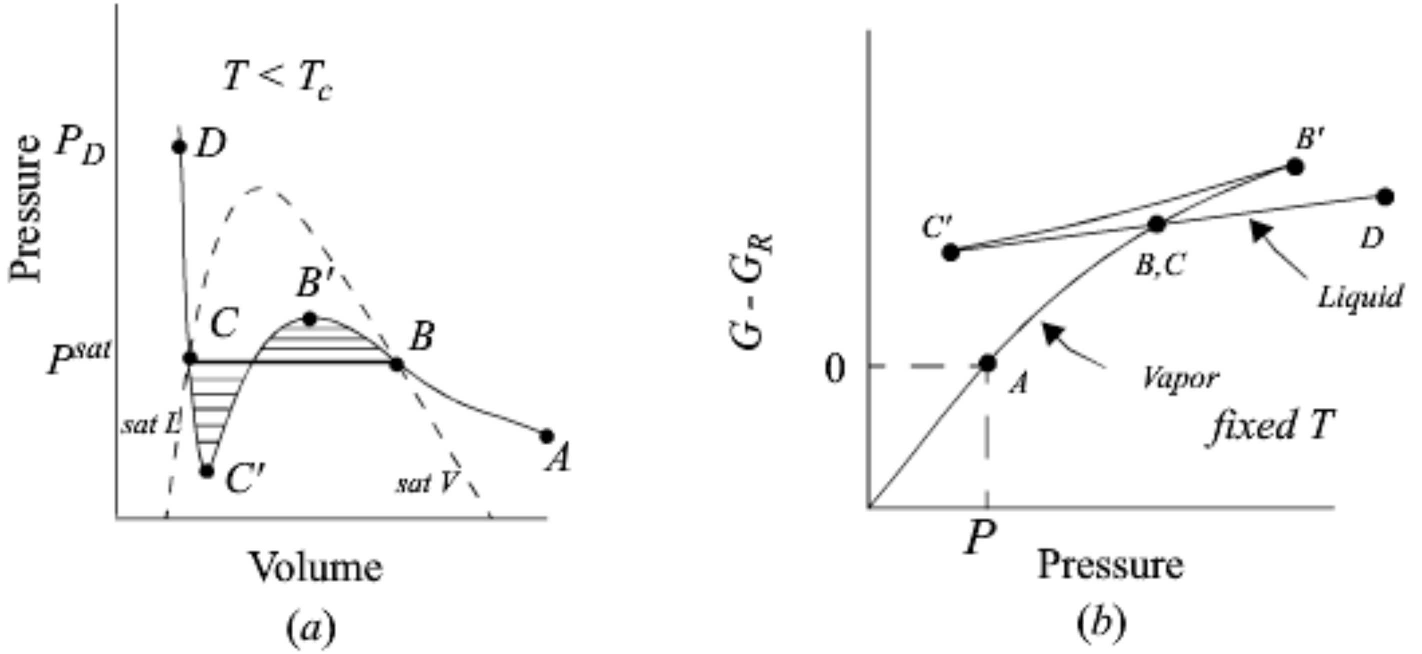


Figure 9.6 *Schematic illustration of the prediction of an isotherm by a cubic equation of state. Compare with Fig. 9.5 on page 350. The figure on the right shows the calculation of Gibbs energy relative to a reference state. The fugacity will have the same qualitative shape.*

CHAPTER

9

PHASE EQUILIBRIUM IN A PURE FLUID

The ability to understand, model, and predict phase equilibria is particularly important for designing separation processes. Typically, these operations comprise the most significant capital costs of plant facilities, and require knowledgeable engineers to design, maintain, and troubleshoot them.

$$G \equiv U + PV - TS \qquad dG = -SdT + VdP \qquad 9.1$$

Phase equilibrium at fixed T and P is most easily understood using G, which is a natural function of P, T.

-SUV
H A
-pGT

9.1 CRITERIA FOR PHASE EQUILIBRIUM

As an introduction to the constraint of phase equilibrium, let us consider an example. A piston/cylinder contains both propane liquid and vapor at −12°C. The piston is forced down a specified distance. Heat transfer is provided to maintain isothermal conditions. Both phases still remain. How much does the pressure increase?

This is a trick question. As long as two phases are present for a single component and the temperature remains constant, then the system pressure remains fixed at the vapor pressure, so the answer is zero increase. The molar volumes of vapor and liquid phases also stay constant since they are state properties. However, as the total volume changes, the quantity of liquid increases, and the quantity of vapor decreases. We are working with a closed system where $n = n^L + n^V$. For the whole system: $\underline{V} = n^L V^{satL} + n^V V^{satV} = n \cdot V^{satL} + q \cdot n \cdot (V^{satV} - V^{satL})$ and since V^{satL} and V^{satV} are fixed and $V^{satL} < V^{satV}$, a decrease in $\underline{V}$ causes a decrease in q.[1]

$$G \equiv U + PV - TS \qquad dG = -SdT + VdP \qquad 9.1$$

$$dG^L = dG^V = 0$$

For the whole system:

$$\underline{G} = n^L G^L + n^V G^V, \text{ by the product rule} \Rightarrow d\underline{G} = n^L dG^L + n^V dG^V + G^L dn^L + G^V dn^V \qquad 9.2$$

But by the mass balance, $dn^L = -dn^V$ which reduces Eqn. 9.2 to $0 = G^L - G^V$ or

$$\boxed{G^L = G^V} \text{ pure fluid phase equilibria} \qquad 9.3$$

As an exercise, select from the steam tables an arbitrary saturation condition and calculate $G = H - TS$ for each phase.

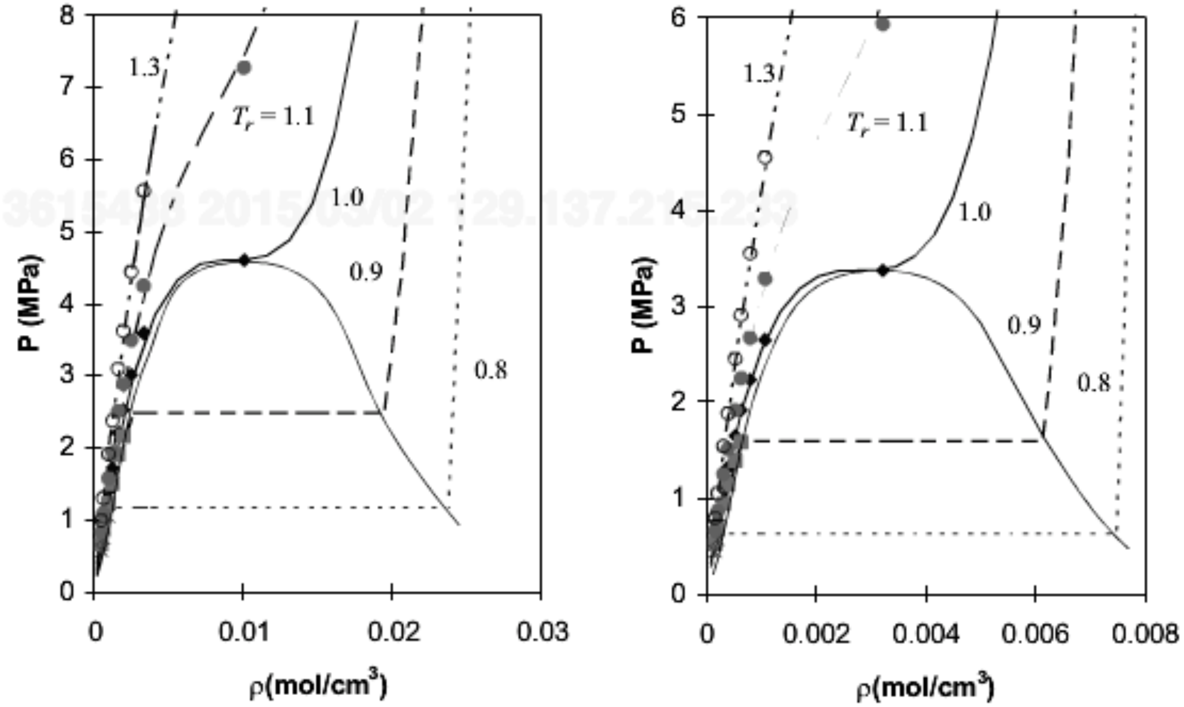
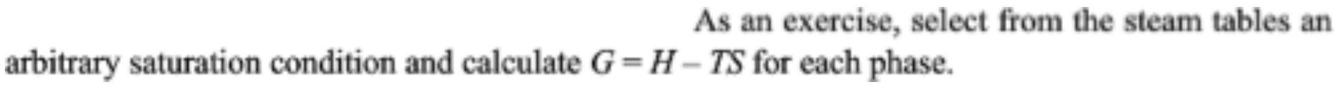
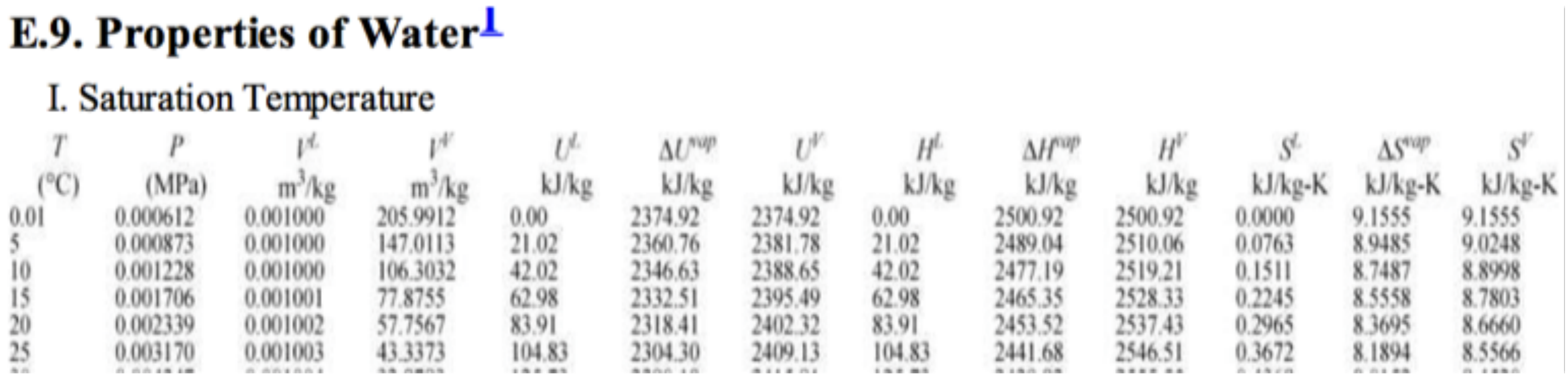


Figure 7.1 *Comparison of the PρT behavior of methane (left) and pentane (right) demonstrating the qualitative similarity which led to corresponding states' treatment of fluids. The lines are calculated with the Peng-Robinson equation to be discussed later. The phase envelope is an approximation sketched through the points available in the plots. The smoothed experimental data are from Brown, G.G., Sounders Jr., M., and Smith, R.L., 1932.* Ind. Eng. Chem., ***24****:513. Although not shown, the Peng-Robinson equation is not particularly accurate for modeling liquid densities.*

9.1 CRITERIA FOR PHASE EQUILIBRIUM



As an exercise, select from the steam tables an arbitrary saturation condition and calculate $G = H - TS$ for each phase.



E.9. Properties of Water[1]

I. Saturation Temperature

T (°C)	P (MPa)	V^L m³/kg	V^V m³/kg	U^L kJ/kg	ΔU^{vap} kJ/kg	U^V kJ/kg	H^L kJ/kg	ΔH^{vap} kJ/kg	H^V kJ/kg	S^L kJ/kg-K	ΔS^{vap} kJ/kg-K	S^V kJ/kg-K
0.01	0.000612	0.001000	205.9912	0.00	2374.92	2374.92	0.00	2500.92	2500.92	0.0000	9.1555	9.1555
5	0.000873	0.001000	147.0113	21.02	2360.76	2381.78	21.02	2489.04	2510.06	0.0763	8.9485	9.0248
10	0.001228	0.001000	106.3032	42.02	2346.63	2388.65	42.02	2477.19	2519.21	0.1511	8.7487	8.8998
15	0.001706	0.001001	77.8755	62.98	2332.51	2395.49	62.98	2465.35	2528.33	0.2245	8.5558	8.7803
20	0.002339	0.001002	57.7567	83.91	2318.41	2402.32	83.91	2453.52	2537.43	0.2965	8.3695	8.6660
25	0.003170	0.001003	43.3373	104.83	2304.30	2409.13	104.83	2441.68	2546.51	0.3672	8.1894	8.5566

At 25°C pure liquid G = 105 kJ/kg – 298°K 0.367 kJ/kg°K = -4 kJ/kg
pure vapor G = 2547 kJ/kg – 298°K 8.56 kJ/kg°K = -4 kJ/kg

-SUV
H A
-pGT

G = H - TS

-SUV
H A
-pGT

$dG = VdP - SdT$

At V/L Equilibria

$dG^L = dG^V$

$V^V dP^{sat} - S^V dT = V^L dP^{sat} - S^L dT$

$(V^V\text{-}V^L)\ dP^{sat} = (S^V\text{-}S^L)\ dT$

Also

$G = H - ST$

At equilibrium $\Delta G^{vap} = 0$

$T^{vap} = \Delta H^{vap} / \Delta S^{vap}$

From above

$dP^{sat}/dT = \Delta H^{vap}/(T(V^V\text{-}V^L))$

9.2 THE CLAUSIUS-CLAPEYRON EQUATION

$$dG^L = dG^V$$

Rewriting the fundamental property relation $\Rightarrow dG = V^V\, dP^{sat} - S^V\, dT = V^L\, dP^{sat} - S^L\, dT$ and rearranging,

$$\Rightarrow (V^V - V^L)dP^{sat} = (S^V - S^L)dT \qquad 9.4$$

Entropy is a difficult property to measure. Let us use a fundamental property to substitute for entropy. By definition of G: $G^V = H^V - TS^V = H^L - TS^L = G^L$

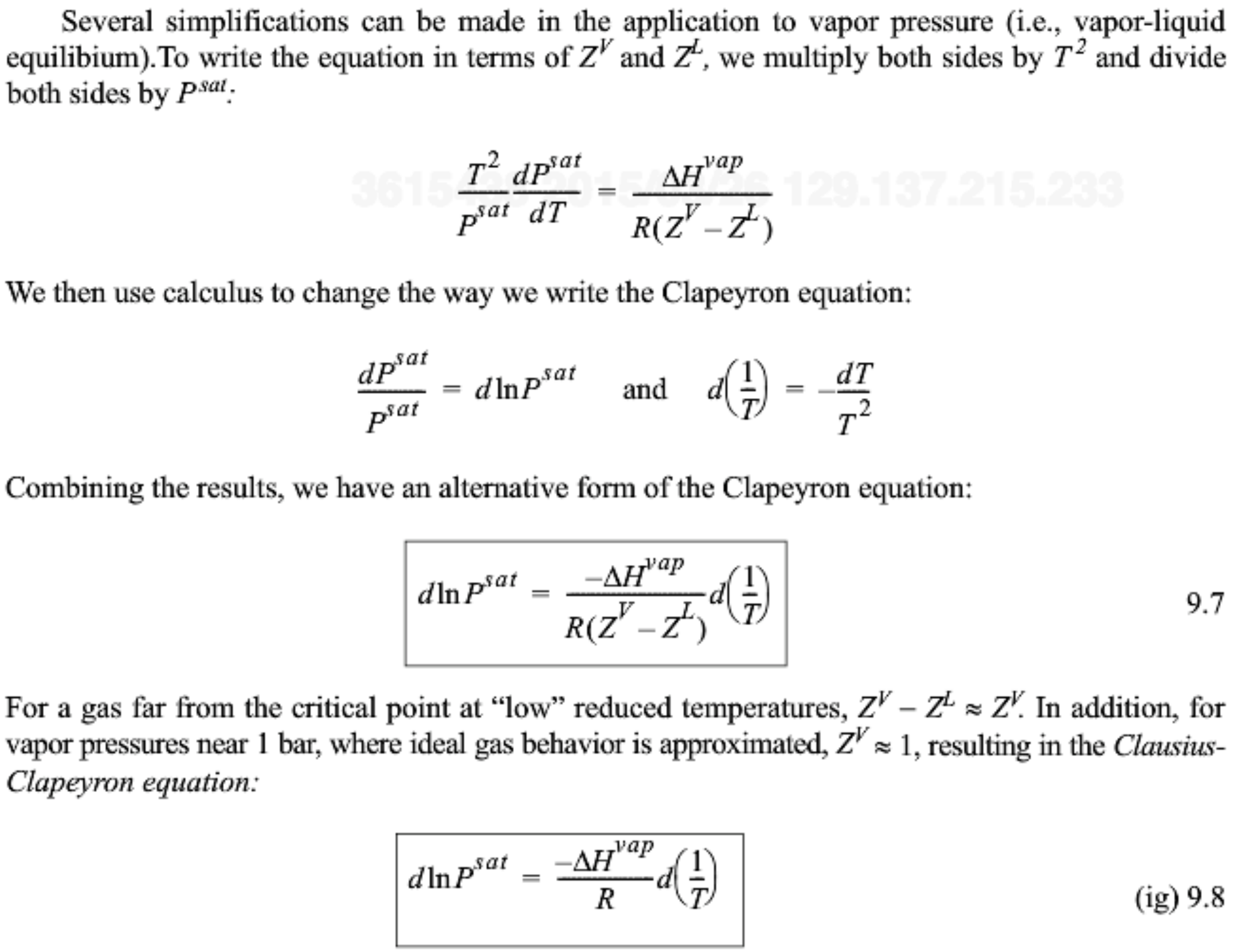
$$\boxed{S^V - S^L = \Delta S^{vap} = \frac{(H^V - H^L)}{T} = \frac{\Delta H^{vap}}{T}} \qquad 9.5$$

Substituting Eqn. 9.5 in for $S^V - S^L$ in Eqn. 9.4, we have the *Clapeyron equation* which is valid for pure fluids along the saturation line:

$$\boxed{\frac{dP^{sat}}{dT} = \frac{\Delta H^{vap}}{T(V^V - V^L)}} \qquad 9.6$$

❗ Clapeyron equation.

> ***Note:*** *This general form of Clapeyron equation can be applied to any kind of phase equilibrium including solid-vapor and solid-liquid equilibria by substituting the alternative sublimation or fusion properties into Eqn. 9.6; we derived the current equation based on vapor-liquid equilibria.*



Several simplifications can be made in the application to vapor pressure (i.e., vapor-liquid equilibium).To write the equation in terms of Z^V and Z^L, we multiply both sides by T^2 and divide both sides by P^{sat}:

$$\frac{T^2}{P^{sat}}\frac{dP^{sat}}{dT} = \frac{\Delta H^{vap}}{R(Z^V - Z^L)}$$

We then use calculus to change the way we write the Clapeyron equation:

$$\frac{dP^{sat}}{P^{sat}} = d\ln P^{sat} \quad \text{and} \quad d\left(\frac{1}{T}\right) = -\frac{dT}{T^2}$$

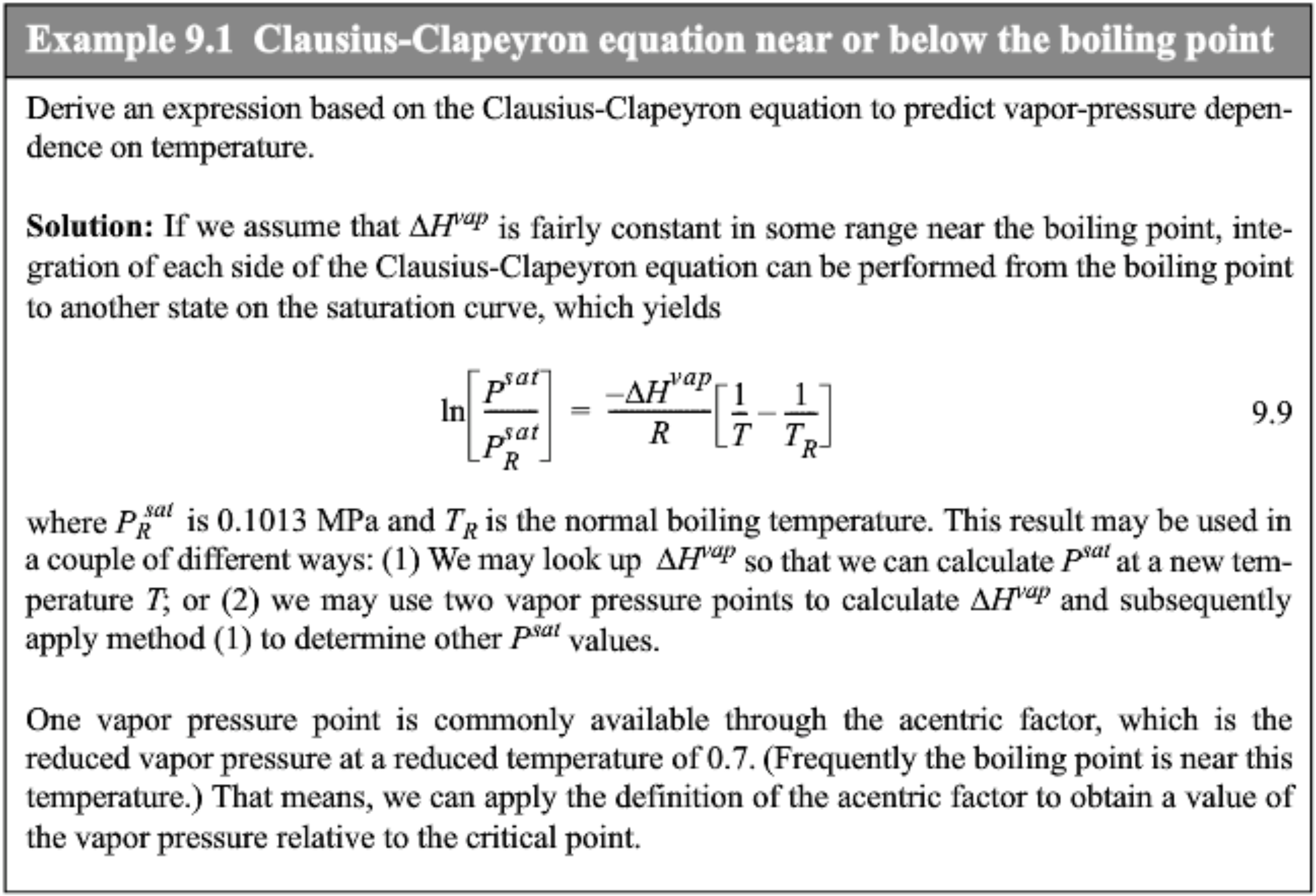
Combining the results, we have an alternative form of the Clapeyron equation:

$$\boxed{d\ln P^{sat} = \frac{-\Delta H^{vap}}{R(Z^V - Z^L)}d\left(\frac{1}{T}\right)} \qquad 9.7$$

For a gas far from the critical point at "low" reduced temperatures, $Z^V - Z^L \approx Z^V$. In addition, for vapor pressures near 1 bar, where ideal gas behavior is approximated, $Z^V \approx 1$, resulting in the *Clausius-Clapeyron equation:*

$$\boxed{d\ln P^{sat} = \frac{-\Delta H^{vap}}{R}d\left(\frac{1}{T}\right)} \qquad \text{(ig) } 9.8$$

The slope of a plot of $\ln P_{sat}$ versus $1/T$ is $-\Delta H_{vap}/R$ (for ideal gas approximation)



Example 9.1 Clausius-Clapeyron equation near or below the boiling point

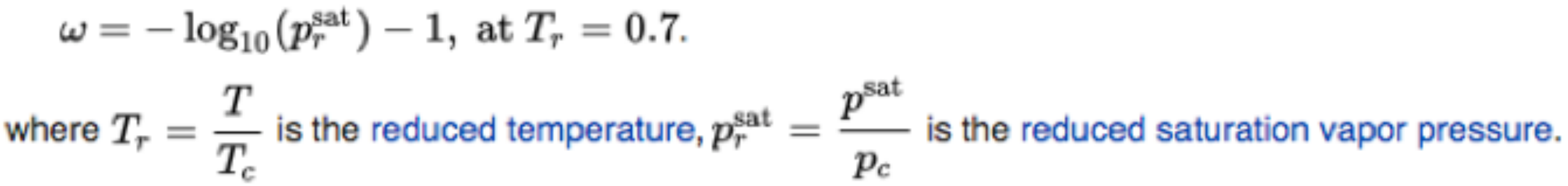
Derive an expression based on the Clausius-Clapeyron equation to predict vapor-pressure dependence on temperature.

Solution: If we assume that ΔH^{vap} is fairly constant in some range near the boiling point, integration of each side of the Clausius-Clapeyron equation can be performed from the boiling point to another state on the saturation curve, which yields

$$\ln\left[\frac{P^{sat}}{P_R^{sat}}\right] = \frac{-\Delta H^{vap}}{R}\left[\frac{1}{T} - \frac{1}{T_R}\right] \qquad 9.9$$

where P_R^{sat} is 0.1013 MPa and T_R is the normal boiling temperature. This result may be used in a couple of different ways: (1) We may look up ΔH^{vap} so that we can calculate P^{sat} at a new temperature T; or (2) we may use two vapor pressure points to calculate ΔH^{vap} and subsequently apply method (1) to determine other P^{sat} values.

One vapor pressure point is commonly available through the acentric factor, which is the reduced vapor pressure at a reduced temperature of 0.7. (Frequently the boiling point is near this temperature.) That means, we can apply the definition of the acentric factor to obtain a value of the vapor pressure relative to the critical point.



$$\omega = -\log_{10}(p_r^{\text{sat}}) - 1, \text{ at } T_r = 0.7.$$

where $T_r = \dfrac{T}{T_c}$ is the reduced temperature, $p_r^{\text{sat}} = \dfrac{p^{\text{sat}}}{p_c}$ is the reduced saturation vapor pressure.

$$\ln\left[\frac{P^{sat}}{P_R^{sat}}\right] = \frac{-\Delta H^{vap}}{R}\left[\frac{1}{T} - \frac{1}{T_R}\right]$$

9.3 SHORTCUT ESTIMATION OF SATURATION PROPERTIES

Clapeyron equation.

$$\boxed{d\ln P^{sat} = \frac{-\Delta H^{vap}}{R(Z^V - Z^L)} d\left(\frac{1}{T}\right)} \qquad 9.7$$

Clausius-Clapeyron equation.

$$\boxed{d\ln P^{sat} = \frac{-\Delta H^{vap}}{R} d\left(\frac{1}{T}\right)} \qquad \text{(ig) } 9.8$$

The conclusion is that setting $\Delta H/\Delta Z$ equal to a constant is a reasonable approximation, especially over the range of $0.5 < T_r < 1.0$. The plot for ethane shows another nearly linear region for $1/T_r > 2$ (temperatures below the normal boiling temperature), with a different slope and intercept. The approach of the previous section should be applied at $T_r < 0.5$. Integrating the Clapeyron equation for vapor pressure, we obtain,

$$\ln\left(\frac{P^{sat}}{P_R}\right) = -\frac{\Delta H^{vap}}{R\Delta Z^{vap}}\left(\frac{1}{T} - \frac{1}{T_R}\right) \qquad 9.10$$

The plot of $\ln P^{sat}$ versus $1/T$ is nearly linear.

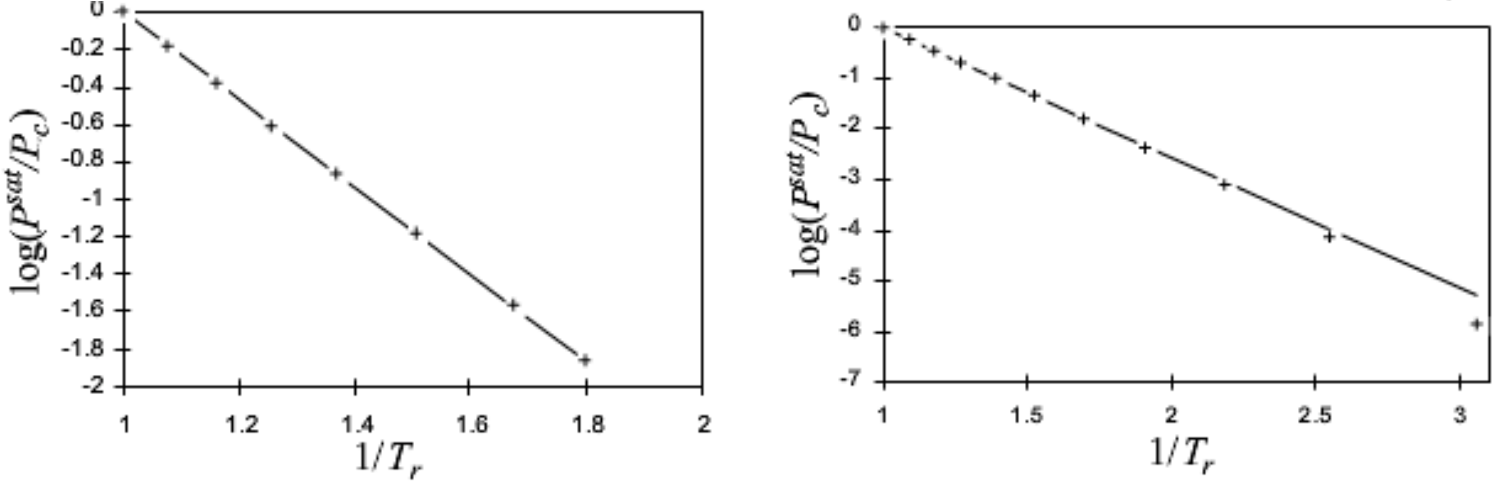
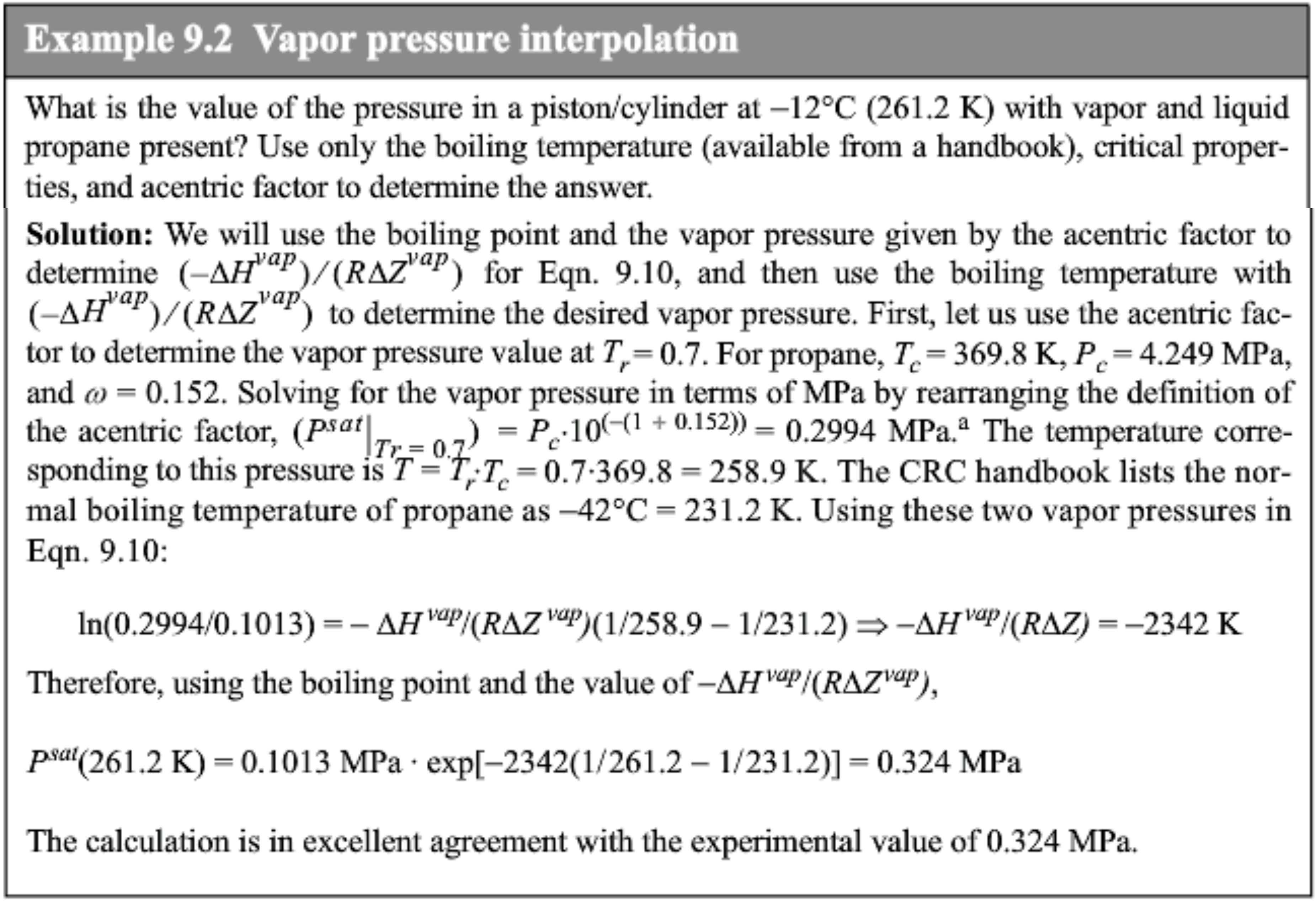


Figure 9.1 *Plot to evaluate Clausius-Clapeyron for calculation of vapor pressures at high pressures, argon (left) and ethane (right).*

$$\omega = -\log_{10}(p_r^{\text{sat}}) - 1, \text{ at } T_r = 0.7$$



Example 9.2 Vapor pressure interpolation

What is the value of the pressure in a piston/cylinder at –12°C (261.2 K) with vapor and liquid propane present? Use only the boiling temperature (available from a handbook), critical properties, and acentric factor to determine the answer.

Solution: We will use the boiling point and the vapor pressure given by the acentric factor to determine $(-\Delta H^{vap})/(R\Delta Z^{vap})$ for Eqn. 9.10, and then use the boiling temperature with $(-\Delta H^{vap})/(R\Delta Z^{vap})$ to determine the desired vapor pressure. First, let us use the acentric factor to determine the vapor pressure value at $T_r = 0.7$. For propane, $T_c = 369.8$ K, $P_c = 4.249$ MPa, and $\omega = 0.152$. Solving for the vapor pressure in terms of MPa by rearranging the definition of the acentric factor, $(P^{sat}|_{Tr\,=\,0.7}) = P_c \cdot 10^{(-(1\,+\,0.152))} = 0.2994$ MPa.[a] The temperature corresponding to this pressure is $T = T_r \cdot T_c = 0.7 \cdot 369.8 = 258.9$ K. The CRC handbook lists the normal boiling temperature of propane as –42°C = 231.2 K. Using these two vapor pressures in Eqn. 9.10:

$$\ln(0.2994/0.1013) = -\Delta H^{vap}/(R\Delta Z^{vap})(1/258.9 - 1/231.2) \Rightarrow -\Delta H^{vap}/(R\Delta Z) = -2342 \text{ K}$$

Therefore, using the boiling point and the value of $-\Delta H^{vap}/(R\Delta Z^{vap})$,

$$P^{sat}(261.2 \text{ K}) = 0.1013 \text{ MPa} \cdot \exp[-2342(1/261.2 - 1/231.2)] = 0.324 \text{ MPa}$$

The calculation is in excellent agreement with the experimental value of 0.324 MPa.

$$\ln\left(\frac{P^{sat}}{P_R}\right) = -\frac{\Delta H^{vap}}{R\Delta Z^{vap}}\left(\frac{1}{T}-\frac{1}{T_R}\right) \qquad 9.10$$

$$\omega = -\log_{10}(p_r^{\text{sat}}) - 1, \text{ at } T_r = 0.7$$

Since the linear relationship of Eqn. 9.10 applies over a broad range of temperatures, we can derive an approximate general estimate of the saturation pressure based on the critical point as the reference and acentric factor as a second point on the vapor pressure curve.

Setting $P_R = P_c$ and $T_R = T_c$,

$$\ln(P_r^{sat}) \approx \frac{-\Delta H^{vap}}{R\Delta Z^{vap} T_c}\left(\frac{T_c}{T}-\frac{T_c}{T_c}\right) = \frac{\Delta H^{vap}}{R\Delta Z^{vap} T_c}\left(1-\frac{1}{T_r}\right)$$

Common logarithms are conventional for shortcut estimation, possibly because they are more convenient to visualize orders of magnitude.

$$\log_{10} P_r^{sat} = \frac{1}{2.303}\frac{\Delta H}{R\Delta Z T_c}\left(1-\frac{1}{T_r}\right) \equiv A\left(1-\frac{1}{T_r}\right)$$

Relating this equation to the acentric factor defined by Eqn. 7.2,

$$\log_{10} P_r^{sat}\Big|_{T_r = 0.7} \equiv -(\omega+1) = A\left(1-\frac{1}{0.7}\right) = -\frac{3}{7}A \Rightarrow A = \frac{7}{3}(1+\omega)$$

which results in a **shortcut vapor pressure** equation,

$$\boxed{\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right)} \qquad 9.11$$

❗ Shortcut vapor pressure equation. Use care with the shortcut equation below $T_r = 0.5$.

> ***Note:*** *The shortcut vapor pressure equation must be regarded as an approximation for rapid estimates. The approximation is generally good above $P = 0.5$ bar; the percent error can become significant at lower pressures (and temperatures). Keep in mind that its estimates are based on the critical pressure which is generally 40–50 bar and acentric factor (at $T_r = 0.7$).*

$$\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right) \qquad 9.11$$

Example 9.3 Application of the shortcut vapor pressure equation

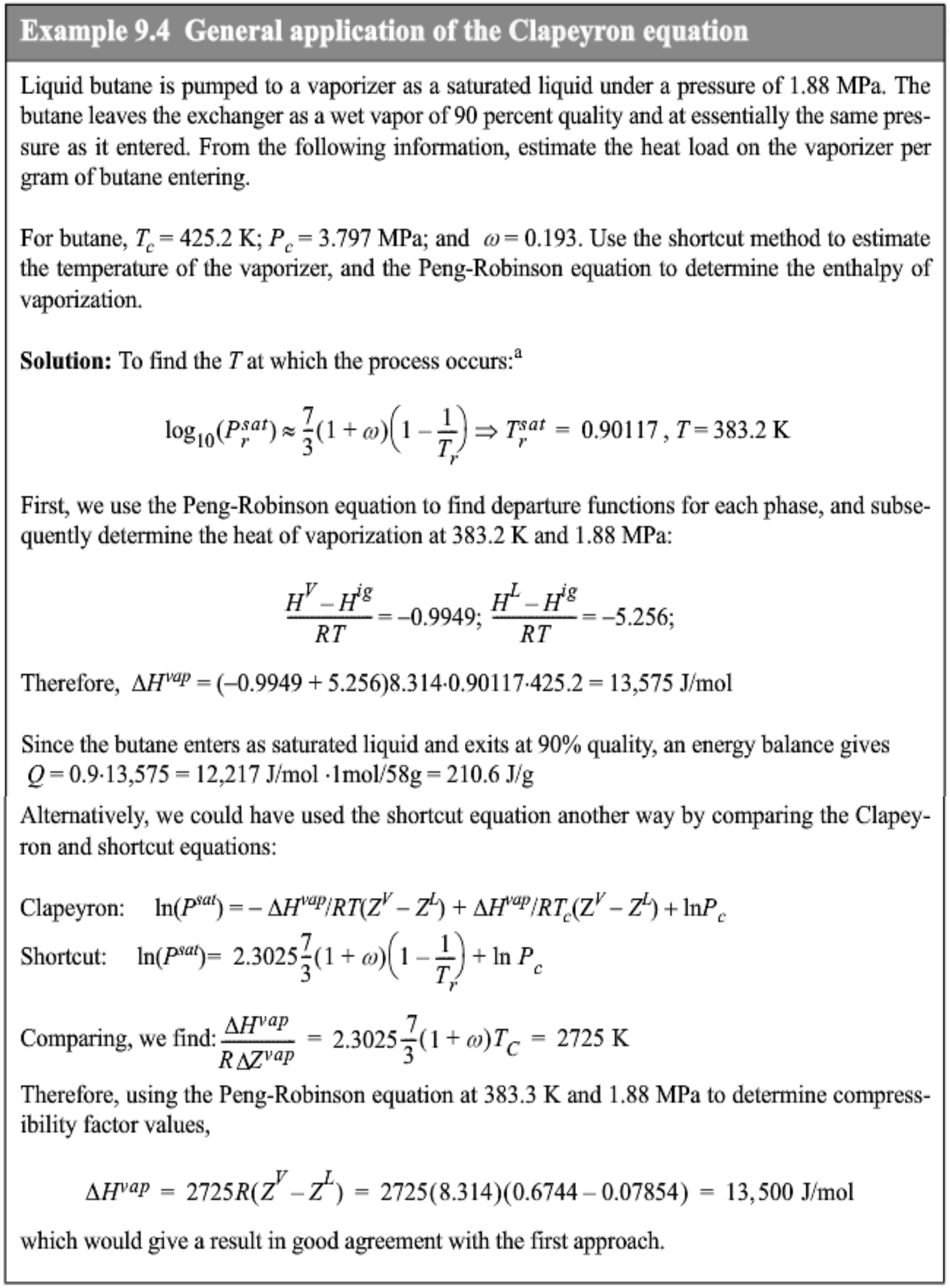
Use the shortcut vapor pressure equation to calculate the vapor pressure of propane at −12°C, and compare the calculation with the results from Example 9.2.

Solution: For propane at −12°C, $T_r = 261.2/369.8 = 0.7063$,

$$P^{sat}(-12°\mathrm{C}) \approx P_c \cdot 10^{\frac{7(1+\omega)}{3}\left(1-\frac{1}{0.7063}\right)} = 0.324\ \mathrm{MPa}$$

This is in excellent agreement with the result of Example 9.2, with considerably less effort.

$$d\ln P^{sat} = \frac{-\Delta H^{vap}}{R(Z^V - Z^L)} d\left(\frac{1}{T}\right)$$



Example 9.4 General application of the Clapeyron equation

Liquid butane is pumped to a vaporizer as a saturated liquid under a pressure of 1.88 MPa. The butane leaves the exchanger as a wet vapor of 90 percent quality and at essentially the same pressure as it entered. From the following information, estimate the heat load on the vaporizer per gram of butane entering.

For butane, $T_c = 425.2$ K; $P_c = 3.797$ MPa; and $\omega = 0.193$. Use the shortcut method to estimate the temperature of the vaporizer, and the Peng-Robinson equation to determine the enthalpy of vaporization.

Solution: To find the T at which the process occurs:[a]

$$\log_{10}(P_r^{sat}) \approx \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right) \Rightarrow T_r^{sat} = 0.90117\,,\ T = 383.2\text{ K}$$

First, we use the Peng-Robinson equation to find departure functions for each phase, and subsequently determine the heat of vaporization at 383.2 K and 1.88 MPa:

$$\frac{H^V - H^{ig}}{RT} = -0.9949;\ \frac{H^L - H^{ig}}{RT} = -5.256;$$

Therefore, $\Delta H^{vap} = (-0.9949 + 5.256)8.314 \cdot 0.90117 \cdot 425.2 = 13{,}575$ J/mol

Since the butane enters as saturated liquid and exits at 90% quality, an energy balance gives $Q = 0.9 \cdot 13{,}575 = 12{,}217$ J/mol $\cdot$1mol/58g $= 210.6$ J/g

Alternatively, we could have used the shortcut equation another way by comparing the Clapeyron and shortcut equations:

Clapeyron: $\ln(P^{sat}) = -\Delta H^{vap}/RT(Z^V - Z^L) + \Delta H^{vap}/RT_c(Z^V - Z^L) + \ln P_c$

Shortcut: $\ln(P^{sat}) = 2.3025\frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right) + \ln P_c$

Comparing, we find: $\frac{\Delta H^{vap}}{R\Delta Z^{vap}} = 2.3025\frac{7}{3}(1+\omega)T_C = 2725\text{ K}$

Therefore, using the Peng-Robinson equation at 383.3 K and 1.88 MPa to determine compressibility factor values,

$$\Delta H^{vap} = 2725R(Z^V - Z^L) = 2725(8.314)(0.6744 - 0.07854) = 13{,}500\text{ J/mol}$$

which would give a result in good agreement with the first approach.

The Antoine Equation

The simple form of the shortcut vapor-pressure equation is extremely appealing, but there are times when we desire greater precision than such a simple equation can provide. One obvious alternative would be to use the same form over a shorter range of temperatures. By fitting the local slope and intercept, an excellent fit could be obtained. To extend the range of applicability slightly, one modification is to introduce an additional adjustable parameter in the denominator of the equation. The resultant equation is referred to as the **Antoine equation**:

$$\log_{10} P^{sat} = A - B/(T + C) \qquad 9.12$$

$$\log_{10} P_r^{sat} = \frac{7}{3}(1 + \omega)\left(1 - \frac{1}{T_r}\right) \qquad 9.11$$

Four Ways to get Vapor Pressure

Short Cut Method Approximation

$$\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right) \quad 9.11$$

Shortcut vapor pressure equation. Use care with the shortcut equation below $T_r = 0.5$.

Clausius-Clapyron Equation

$$\ln\left(\frac{P^{sat}}{P_R}\right) = -\frac{\Delta H^{vap}}{R\Delta Z^{vap}}\left(\frac{1}{T}-\frac{1}{T_R}\right) \quad 9.10$$

Use Peng-Robinson or other EOS and find where the fugacity ratio is 1

Antoine Equation

$$\log_{10} P^{sat} = A - B/(T + C)$$

Which method depends on accuracy needed, availability of parameters, and calculation speed required. For Clausius- Clapron Equation you can use 1) ecentricity, 2) critical point, 3) normal boiling point as reference points.

9.4 CHANGES IN GIBBS ENERGY WITH PRESSURE

$$dG = -SdT + VdP,$$

$$dG = VdP(\text{const. } T)$$

$$G_2 - G_1 = \int_{P_1}^{P_2} VdP(\text{const. } T) \qquad 9.14$$

Gibbs Energy in the Low-Pressure Limit

The calculation of ΔG is illustrated in Fig. 9.2, where the shaded area represents the integral. The slope of a G versus P plot at constant temperature is equal to the molar volume. For a real fluid, the ideal-gas approximation is valid only at low pressures. The volume is given by $V = ZRT/P$; thus,

$$dG = -SdT + VdP,$$

$$dG = RTZ\frac{dP}{P} \qquad 9.15$$

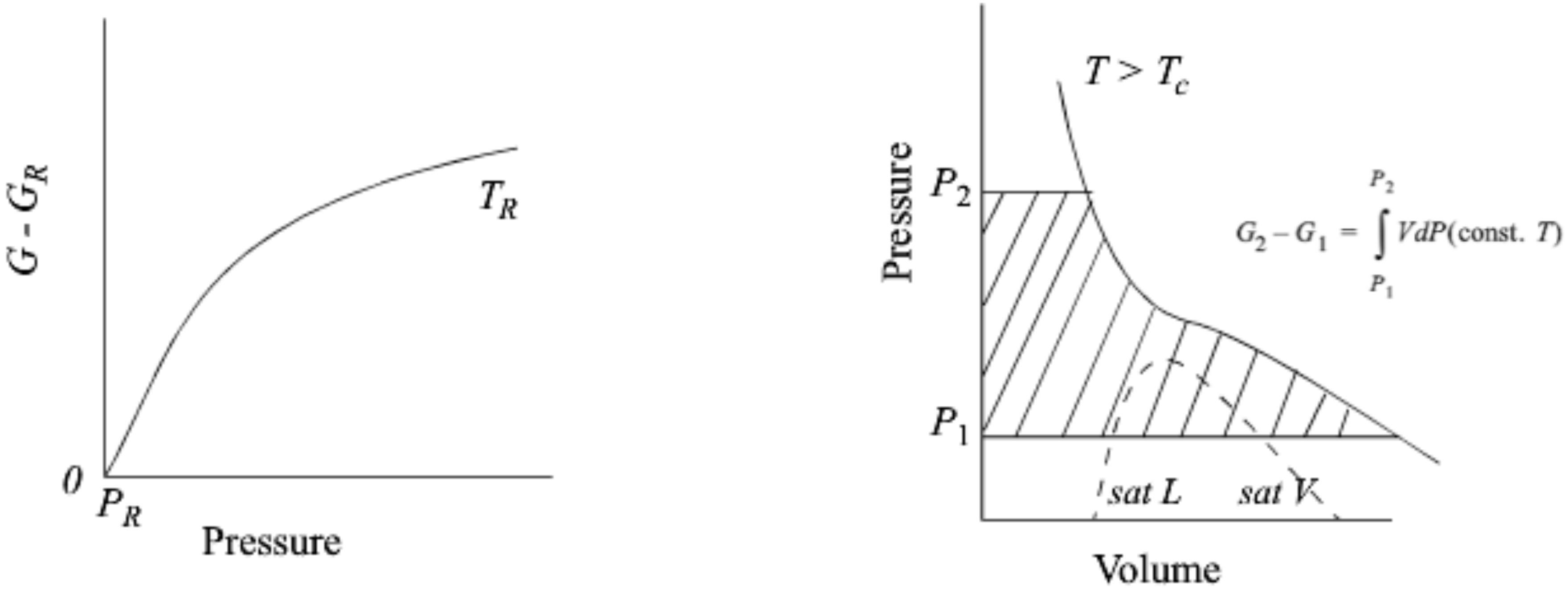


Figure 9.2 *Schematic of dependence of G on pressure for a real fluid at T_R, and an isothermal change on a P-V diagram for a change from P_1 to P_2.*

Gibbs Energy in the Low-Pressure Limit

The calculation of ΔG is illustrated in Fig. 9.2, where the shaded area represents the integral. The slope of a G versus P plot at constant temperature is equal to the molar volume.For a real fluid, the ideal-gas approximation is valid only at low pressures. The volume is given by $V = ZRT/P$; thus,

$$dG = -SdT + VdP,$$

$$dG = RTZ\frac{dP}{P} \qquad 9.15$$

$$dG^{ig} = RT\frac{dP}{P} = RTd\ln P \qquad \text{(ig) } 9.16$$

$$G_2 - G_1 = \int_{P_1}^{P_2} VdP(\text{const. } T)$$

$$\Delta G^{ig} = \int_{P_1}^{P_2} \frac{RT}{P}\,dP = RT\ln\frac{P_2}{P_1} \qquad \text{(ig) } 9.17$$

Both dG and dG^{ig} become infinite as pressure approaches zero. This means that both Eqns. 9.15 and 9.16 are difficult to use directly at low pressure. However, as a real fluid state approaches zero pressure, Z will approach the ideal gas limit and dG approaches dG^{ig}. Thus, the difference $dG - dG^{ig}$ will remain finite, and goes to zero as P goes to zero. Thus,

$$dG - dG^{ig} = d(G - G^{ig})$$

$$d(G - G^{ig})/RT = (Z - 1)/P\, dP \qquad 9.18$$

Pressure Dependent Formulas

$$\left(\frac{H-H^{ig}}{RT}\right) = -\int_0^P T\left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \qquad 8.29$$

$$\left(\frac{S-S^{ig}}{R}\right) = -\int_0^P \left[(Z-1) + T\left(\frac{\partial Z}{\partial T}\right)_P\right]\frac{dP}{P} \qquad 8.30$$

-SUV
H A
-pGT

G = H - ST

$$d(G-G^{ig})/RT = (Z-1)/P\, dP \qquad 9.18$$

9.5 FUGACITY AND FUGACITY COEFFICIENT

In principle, all pure-component, phase-equilibrium problems could be solved using Gibbs energy. Historically, however, an alternative property has been applied in chemical engineering calculations, the *fugacity*. The fugacity has one advantage over the Gibbs energy in that its application to mixtures is a straightforward extension of its application to pure fluids. It also has some empirical appeal because the fugacity of an ideal gas equals the pressure and the fugacity of a liquid equals the vapor pressure under common conditions, as we will show in Section 9.8. The vapor pressure was the original property used for characterization of phase equilibrium by experimentalists.

$$dG = RTZ\frac{dP}{P} \qquad 9.15$$

$$dG^{ig} = RT\frac{dP}{P} = RTd\ln P \qquad \text{(ig) } 9.16$$

$$dG = VdP \equiv RTd\ln f \qquad 9.19$$

$$d(G - G^{ig})/RT = d\ln(f/P) \qquad 9.20$$

the ratio f/P to be the *fugacity coefficient,* φ.

$$\boxed{\frac{(G - G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \ln\varphi} \qquad 9.22$$

$$\boxed{\frac{(G-G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \ln\varphi}$$

Arrhenius (1859-1927) Function:

Probability = $\exp(-\Delta E/kT)$ or = $\exp(-\Delta E/RT)$
Gives the probability of an event happening if the event is thermally activated; i.e. if the probability changes with the temperature.

Viscosity = $\text{Viscosity}_0 \exp(-\Delta E_a/kT)$ Flow happens when atoms thermally move out of the way with an activation energy ΔE_a

Vapor Pressure = $P_0 \exp(-\Delta E_{vap}/kT)$ Antoine equation

$\Delta E_{vap} = \Delta H_{vap} - T\,\Delta S_{vap}$

$P_{sat} = P_0 \exp(A - B/(T+C))$ $A = -\Delta S_{vap}/R$ $B = \Delta H_{vap}$ C = Temp for no P_{sat}

Entropy prob. = $\exp(S/R)$ Energy with no enthalpy (Boltzman equation)

Fugacity

$f/P = \exp((G-G^{ig})/RT)$ = probability of a molecule escaping from a phase

$G = H - TS$ is a measure of the balance between enthalpic attractions and thermally driven dispersion of the molecules. So f is a measure of the dispersibility of a phase, the more dispersible the less stable. Lower fugacity is the more stable phase.

Arrhenius accurately predicted global warming due to CO_2 in a paper published in 1896 which was widely read. His calculations were within 10% of current global temperature rises.

$$\boxed{\frac{(G-G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \ln\varphi = \frac{1}{RT}\int_0^P (V-V^{ig})dP = \int_0^P \frac{(Z-1)}{P}dP} \qquad 9.23$$

$$\boxed{\frac{(G-G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \int_0^\rho \frac{(Z-1)}{\rho}d\rho + (Z-1) - \ln Z} \qquad 9.24$$

Note: *In practice, we do not evaluate the fugacity of a substance directly. Instead, we evaluate the fugacity coefficient, and then calculate the fugacity by*

$$\boxed{f = \varphi P} \qquad 9.25$$

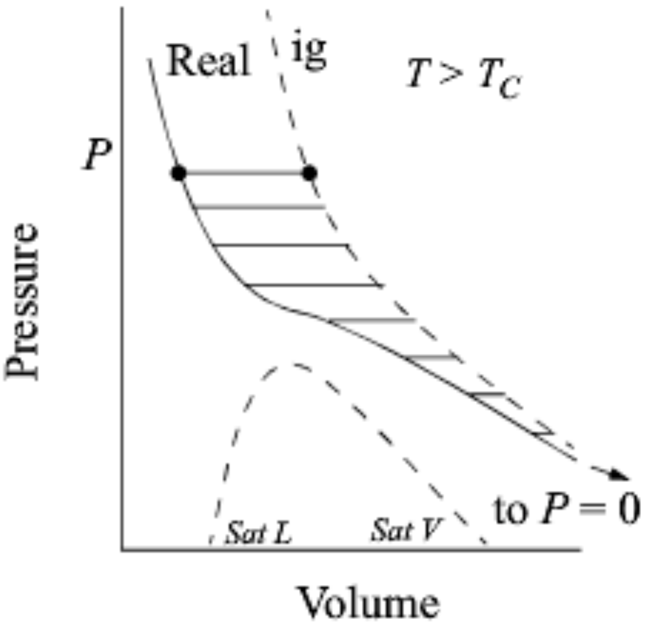


Figure 9.3 *Illustration of RT* ln *φ as a departure function.*

$$\boxed{\frac{(G - G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \ln\varphi = \frac{1}{RT}\int_0^P (V - V^{ig})dP = \int_0^P \frac{(Z-1)}{P}dP} \qquad 9.23$$

A graphical interpretation of the fugacity coefficient can be seen in Fig. 9.3. The integral of Eqn. 9.23 is represented by the negative value of the shaded region between the real gas isotherm and the ideal gas isotherm. The fugacity coefficient is a measure of non-ideality. *Under most common conditions, the fugacity coefficient is less than one.* At very high pressures, the fugacity coefficient can become greater than one.

9.6 FUGACITY CRITERIA FOR PHASE EQUILIBRIA

We began the chapter by showing that Gibbs energy was equivalent in phases at equilibrium. Here we show that equilibrium may also be described by equivalence of fugacities. Since

$$G^L = G^V \qquad 9.3$$

we may subtract G^{ig} from both sides and divide by RT, giving

$$\frac{(G^L - G^{ig})}{RT} = \frac{(G^V - G^{ig})}{RT} \qquad 9.26$$

Substituting Eqn. 9.22, $\frac{(G - G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \ln\varphi$

$$\ln\left(\frac{f^L}{P}\right) = \ln\left(\frac{f^V}{P}\right)$$

which becomes

$$\boxed{f^L = f^V} \qquad 9.27$$

9.7 CALCULATION OF FUGACITY (GASES)

$$\boxed{\frac{(G-G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \ln\varphi = \frac{1}{RT}\int_0^P (V-V^{ig})dP = \int_0^P \frac{(Z-1)}{P}dP} \qquad 9.23$$

Ideal Gas

$$\varphi^{ig} = 1 \text{ and } f^{ig} = P \qquad \text{(ig) } 9.29$$

The Virial Equation

The virial equation may be used to represent the compressibility factor in the *low-to-moderate pressure region* where Z is linear with pressure at constant temperature. Eqn. 7.10 should be used to evaluate the appropriateness of the virial coefficient method. Substituting $Z = 1 + BP/RT$, or $Z - 1 = BP/RT$ into Eqn. 9.23,

$$\ln\varphi = \int_0^P \frac{B}{RT}dP = \frac{BP}{RT} \qquad 9.30$$

Thus,

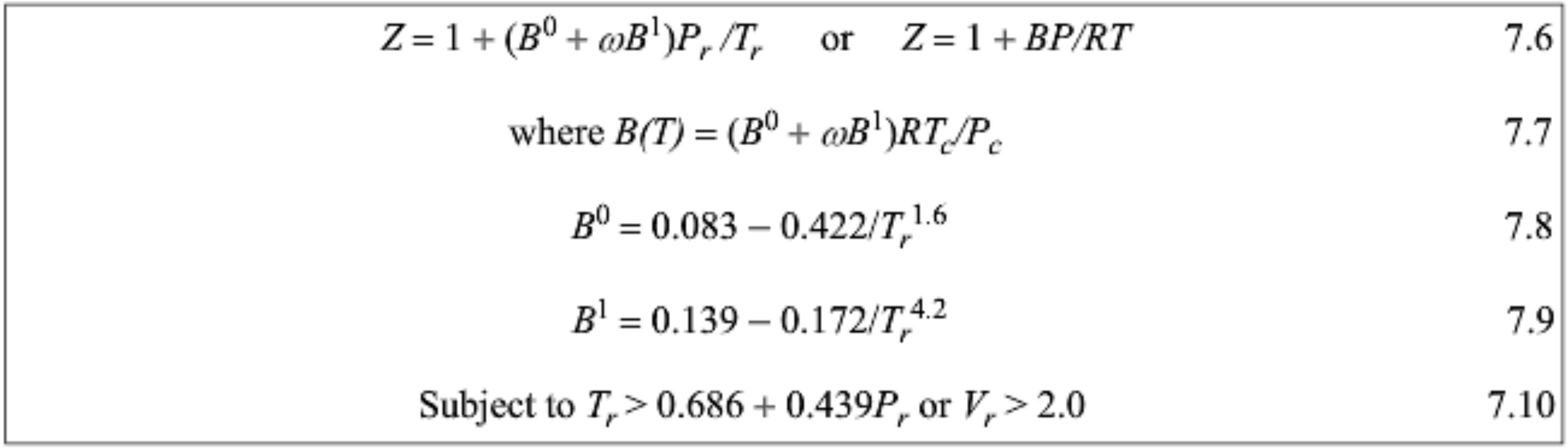
$$\ln\varphi = \frac{BP}{RT} \qquad 9.31$$

Writing the virial coefficient in reduced temperature and pressure,

$$\ln\varphi = \frac{P_r}{T_r}(B^0 + \omega B^1) \qquad 9.32$$

where B^0 and B^1 are the virial coefficient correlations given in Eqns. 7.8 and 7.9 on page 259.

The Virial Equation



$$Z = 1 + (B^0 + \omega B^1)P_r/T_r \quad \text{or} \quad Z = 1 + BP/RT \tag{7.6}$$

$$\text{where } B(T) = (B^0 + \omega B^1)RT_c/P_c \tag{7.7}$$

$$B^0 = 0.083 - 0.422/T_r^{1.6} \tag{7.8}$$

$$B^1 = 0.139 - 0.172/T_r^{4.2} \tag{7.9}$$

$$\text{Subject to } T_r > 0.686 + 0.439P_r \text{ or } V_r > 2.0 \tag{7.10}$$

9.7 CALCULATION OF FUGACITY (GASES)

The Peng-Robinson Equation

or the equivalent form for *P-V-T* data in the form $Z = f(T,V)$, which is essentially Eqn. 8.26,

$$\boxed{\frac{(G - G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \int_0^{\rho} \frac{(Z-1)}{\rho} d\rho + (Z-1) - \ln Z} \qquad 9.24$$

which is the form used for cubic equations of state.

$$Z = \frac{1}{(1 - b\rho)} - \frac{a\rho/RT}{(1 + 2b\rho - b^2\rho^2)}$$

$$\ln\varphi = -\ln(Z - B) - \frac{A}{B\sqrt{8}}\ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right] + Z - 1 \qquad 9.33$$

To apply, the technique is analogous to the calculation of departure functions. At a given *P, T,* the cubic equation is solved for *Z,* and the result is used to calculate φ and then fugacity is calculated, $f = \varphi P$. This method has been programmed into Preos.xlsx and Preos.m.

Example 8.6 Gibbs departure for the Peng-Robinson equation

Obtain a general expression for the Gibbs energy departure function of the Peng-Robinson equation.

$$Z = \frac{1}{(1-b\rho)} - \frac{a\rho/RT}{(1+2b\rho-b^2\rho^2)}$$

$$\boxed{\frac{(G-G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \int_0^{\rho}\frac{(Z-1)}{\rho}d\rho + (Z-1) - \ln Z}$$

Solution: The answer is obtained by evaluating Eqn. 8.26. The argument for the integrand is

$$Z-1 = \frac{1}{1-b\rho} - \frac{1-b\rho}{1-b\rho} - \frac{(a\rho)/RT}{(1+2b\rho-b^2\rho^2)} = \frac{b\rho}{(1-b\rho)} + \frac{a\rho/RT}{(1+2b\rho-b^2\rho^2)}$$

Evaluating the integral (similar to the integral in Example 8.5), noting again the change in integration variables,

$$\int_0^{b\rho}(Z-1)\frac{d(b\rho)}{b\rho} = \int_0^{b\rho}\frac{d(b\rho)}{(1-b\rho)} + \frac{a}{bRT}\int_0^{b\rho}\frac{d(b\rho)}{(1+2b\rho-b^2\rho^2)}$$

$$\frac{(A-A^{ig})_{T,V}}{RT} = -\ln(1-b\rho) - \frac{a}{bRT\sqrt{8}}\ln\left[\frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho}\right]$$

Making the result dimensionless,

$$\boxed{\frac{(G-G^{ig})}{RT} = Z-1-\ln(Z-B) - \frac{A}{B\sqrt{8}}\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right]} \quad 8.36$$

9.7 CALCULATION OF FUGACITY (GASES)

Generalized Charts

$$\ln\varphi = \ln\varphi^0 + \omega\ln\varphi^1$$

Fig. 9.4 can be useful for hand calculation, if you do not have a computer. A sample calculation for propane at 463.15 and 2.5 MPa gives

$$\ln(f/P) = \frac{G-G^{ig}}{RT} = -0.1 + 0.152(0.05) = -0.09$$

compared to the value of –0.112 from the Peng-Robinson equation.

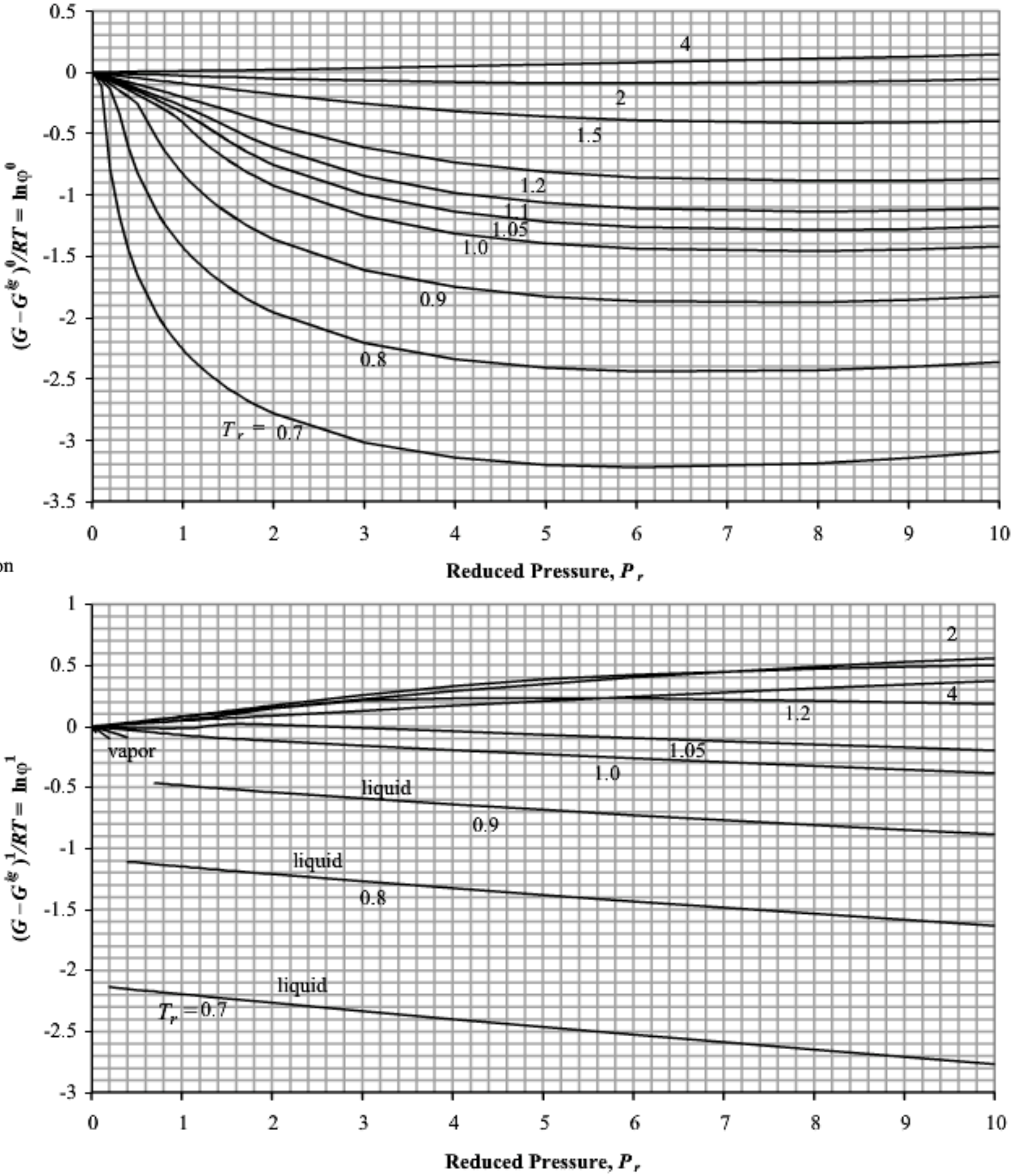


Figure 9.4 *Generalized charts for estimating the Gibbs departure function using the Lee-Kesler equation of state.* $(G-G^{ig})^0/RT$ *uses* $\omega = 0.0$*, and* $(G-G^{ig})^1/RT$ *is the correction factor for a hypothetical compound with* $\omega = 1.0$*.*

9.8 CALCULATION OF FUGACITY (LIQUIDS)

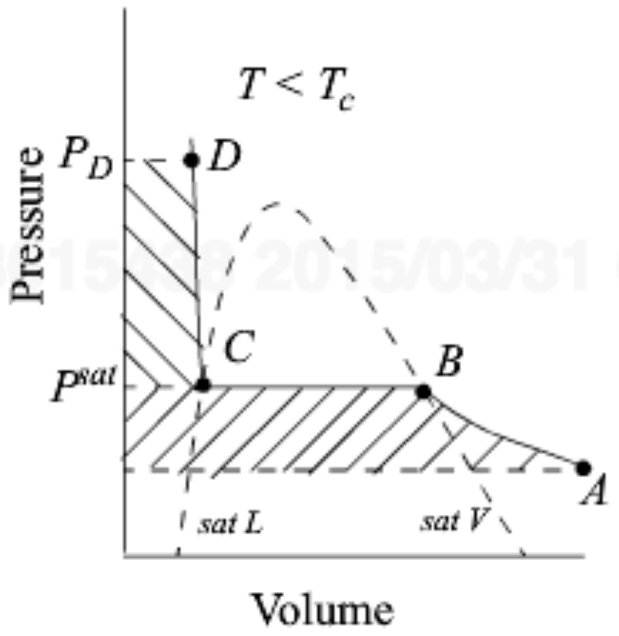
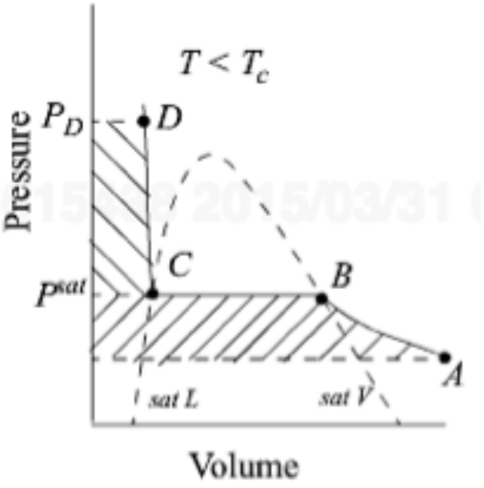


Figure 9.5 *Schematic for calculation of Gibbs energy and fugacity changes at constant temperature for a pure liquid.*

$$f_C = f_B = f^{sat} \tag{9.36}$$

9.8 CALCULATION OF FUGACITY (LIQUIDS)

Poynting Method



$$dG = VdP \equiv RTd\ln f \qquad 9.19$$

$$RT\ln\frac{f_D}{f^{sat}} = \int_{P^{sat}}^{P_D} VdP \qquad 9.37$$

Since liquids are fairly incompressible for $T_r < 0.9$, the volume is approximately constant, and may be removed from the integral, with the resultant Poynting correction becoming

$$\frac{f}{f^{sat}} = \exp\left(\frac{V^L(P-P^{sat})}{RT}\right) \qquad 9.38$$

Poynting method for liquids.

$$\boxed{f = \varphi^{sat}P^{sat}\exp\left(\frac{V^L(P-P^{sat})}{RT}\right)} \qquad 9.39$$

Saturated liquid volume can be estimated within a slight percent error using the **Rackett** equation

$$V^{satL} = V_c Z_c^{(1-T_r)^{0.2857}} \qquad 9.40$$

The Poynting correction, Eqn. 9.38, is essentially unity for many compounds near room T and P; thus, it is frequently ignored.

$$\boxed{f^L \approx \varphi^{sat} P^{sat}} \text{ or commonly } \boxed{f^L \approx P^{sat}} \qquad 9.41$$

❗ Frequent approximation.

$$\frac{f}{f^{sat}} = \exp\left(\frac{V^L(P - P^{sat})}{RT}\right) \qquad 9.38$$

9.8 CALCULATION OF FUGACITY (LIQUIDS)

Equation of State Method

$$\boxed{\frac{(G-G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \int_0^{\rho}\frac{(Z-1)}{\rho}d\rho + (Z-1) - \ln Z} \qquad 9.24$$

$$\ln\varphi = -\ln(Z-B) - \frac{A}{B\sqrt{8}}\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right] + Z - 1 \qquad 9.33$$

$$G_2 - G_1 = \int_{P_1}^{P_2} VdP(\text{const. } T) \qquad 9.14$$

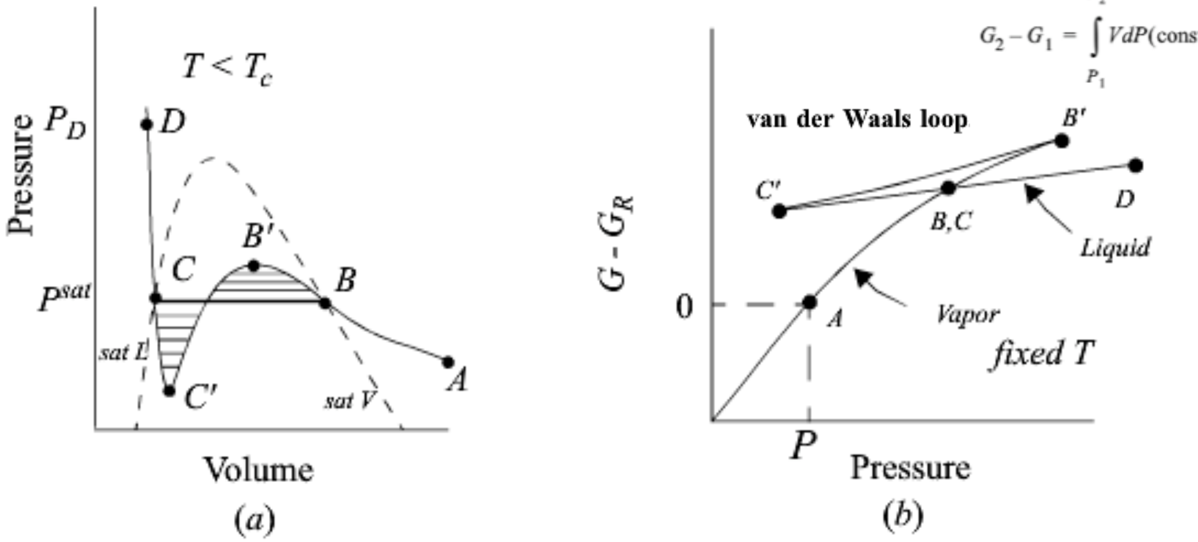
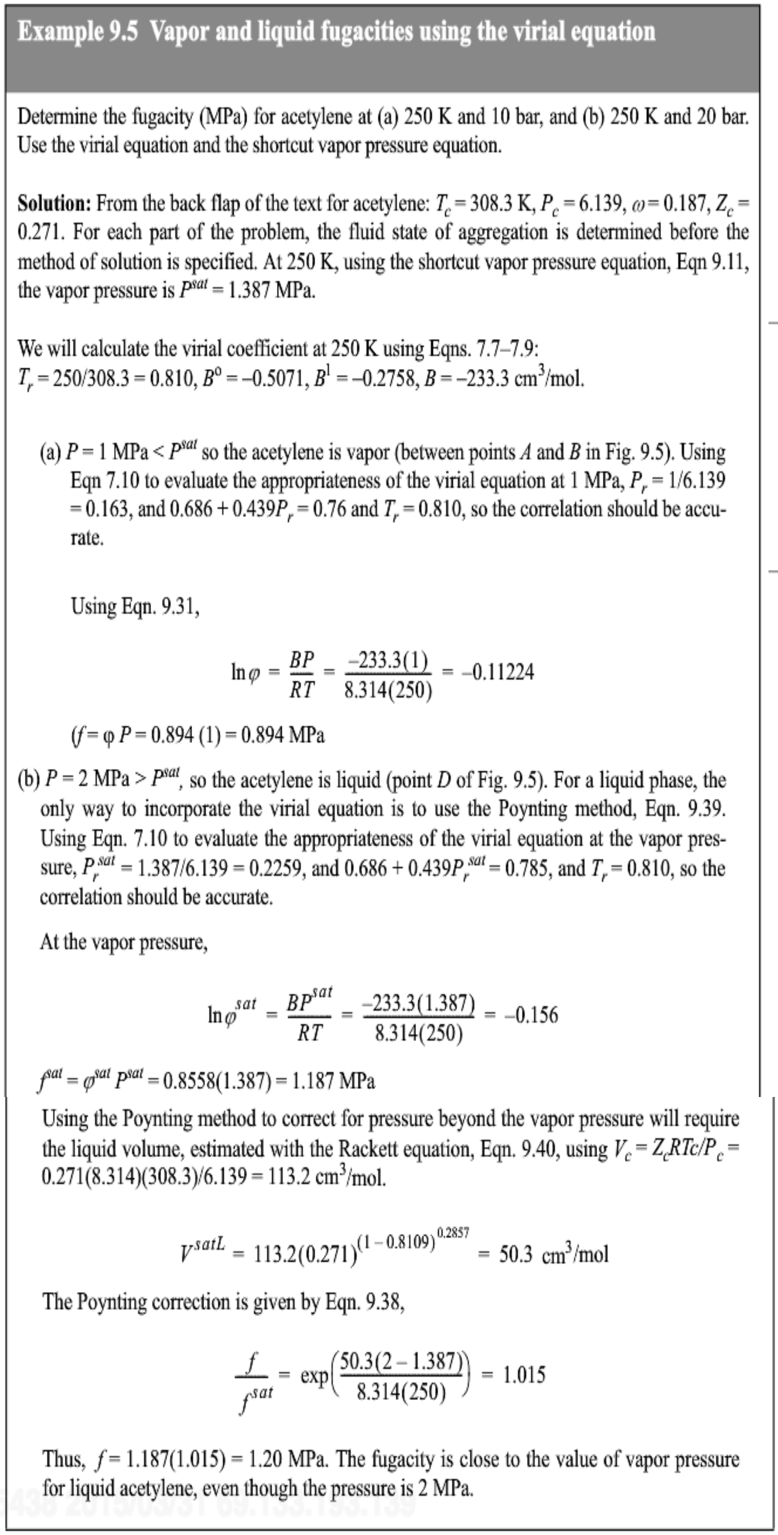


Figure 9.6 *Schematic illustration of the prediction of an isotherm by a cubic equation of state. Compare with Fig. 9.5 on page 350. The figure on the right shows the calculation of Gibbs energy relative to a reference state. The fugacity will have the same qualitative shape.*



Example 9.5 Vapor and liquid fugacities using the virial equation

Determine the fugacity (MPa) for acetylene at (a) 250 K and 10 bar, and (b) 250 K and 20 bar. Use the virial equation and the shortcut vapor pressure equation.

Solution: From the back flap of the text for acetylene: $T_c = 308.3$ K, $P_c = 6.139$, $\omega = 0.187$, $Z_c = 0.271$. For each part of the problem, the fluid state of aggregation is determined before the method of solution is specified. At 250 K, using the shortcut vapor pressure equation, Eqn 9.11, the vapor pressure is $P^{sat} = 1.387$ MPa.

We will calculate the virial coefficient at 250 K using Eqns. 7.7–7.9:
$T_r = 250/308.3 = 0.810$, $B^0 = -0.5071$, $B^1 = -0.2758$, $B = -233.3$ cm^3/mol.

(a) $P = 1$ MPa $< P^{sat}$ so the acetylene is vapor (between points A and B in Fig. 9.5). Using Eqn 7.10 to evaluate the appropriateness of the virial equation at 1 MPa, $P_r = 1/6.139 = 0.163$, and $0.686 + 0.439P_r = 0.76$ and $T_r = 0.810$, so the correlation should be accurate.

Using Eqn. 9.31,

$$\ln\varphi = \frac{BP}{RT} = \frac{-233.3(1)}{8.314(250)} = -0.11224$$

($f = \varphi P = 0.894$ (1) = 0.894 MPa

(b) $P = 2$ MPa $> P^{sat}$, so the acetylene is liquid (point D of Fig. 9.5). For a liquid phase, the only way to incorporate the virial equation is to use the Poynting method, Eqn. 9.39. Using Eqn. 7.10 to evaluate the appropriateness of the virial equation at the vapor pressure, $P_r^{sat} = 1.387/6.139 = 0.2259$, and $0.686 + 0.439P_r^{sat} = 0.785$, and $T_r = 0.810$, so the correlation should be accurate.

At the vapor pressure,

$$\ln\varphi^{sat} = \frac{BP^{sat}}{RT} = \frac{-233.3(1.387)}{8.314(250)} = -0.156$$

$f^{sat} = \varphi^{sat} P^{sat} = 0.8558(1.387) = 1.187$ MPa

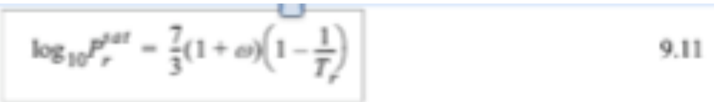
Using the Poynting method to correct for pressure beyond the vapor pressure will require the liquid volume, estimated with the Rackett equation, Eqn. 9.40, using $V_c = Z_cRTc/P_c = 0.271(8.314)(308.3)/6.139 = 113.2$ cm^3/mol.

$$V^{satL} = 113.2(0.271)^{(1-0.8109)^{0.2857}} = 50.3 \text{ cm}^3\text{/mol}$$

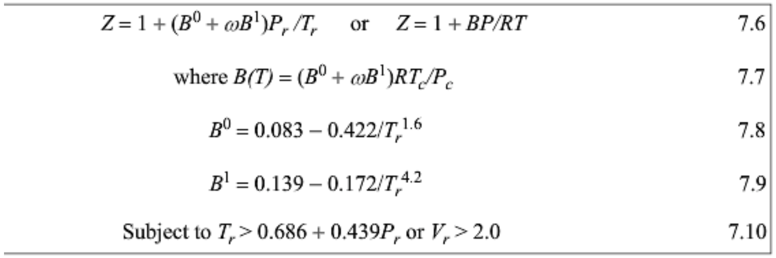
The Poynting correction is given by Eqn. 9.38,

$$\frac{f}{f^{sat}} = \exp\left(\frac{50.3(2-1.387)}{8.314(250)}\right) = 1.015$$

Thus, $f = 1.187(1.015) = 1.20$ MPa. The fugacity is close to the value of vapor pressure for liquid acetylene, even though the pressure is 2 MPa.



$$\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right) \qquad 9.11$$



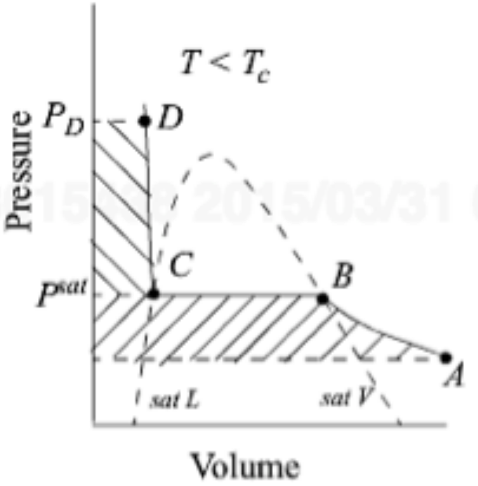
$$Z = 1 + (B^0 + \omega B^1)P_r/T_r \quad \text{or} \quad Z = 1 + BP/RT \qquad 7.6$$

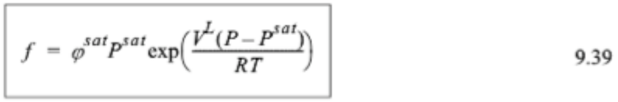
$$\text{where } B(T) = (B^0 + \omega B^1)RT_c/P_c \qquad 7.7$$

$$B^0 = 0.083 - 0.422/T_r^{1.6} \qquad 7.8$$

$$B^1 = 0.139 - 0.172/T_r^{4.2} \qquad 7.9$$

$$\text{Subject to } T_r > 0.686 + 0.439P_r \text{ or } V_r > 2.0 \qquad 7.10$$





$$f = \varphi^{sat}P^{sat}\exp\left(\frac{V^L(P-P^{sat})}{RT}\right) \qquad 9.39$$

$$V^{satL} = V_cZ_c^{(1-T_r)^{0.2857}} \qquad 9.40$$

9.9 CALCULATION OF FUGACITY (SOLIDS)

Fugacities of solids are calculated using the Poynting method, with the exception that the volume in the Poynting correction is the volume of the solid phase.

$$\boxed{f^S = \varphi^{sat} P^{sat} \exp\left(\frac{V^S(P - P^{sat})}{RT}\right)} \tag{9.42}$$

Poynting method for solids.

$$\boxed{f^S \approx \varphi^{sat} P^{sat}} \text{ or commonly } \boxed{f^S \approx P^{sat}} \tag{9.43}$$

Frequent approximation.

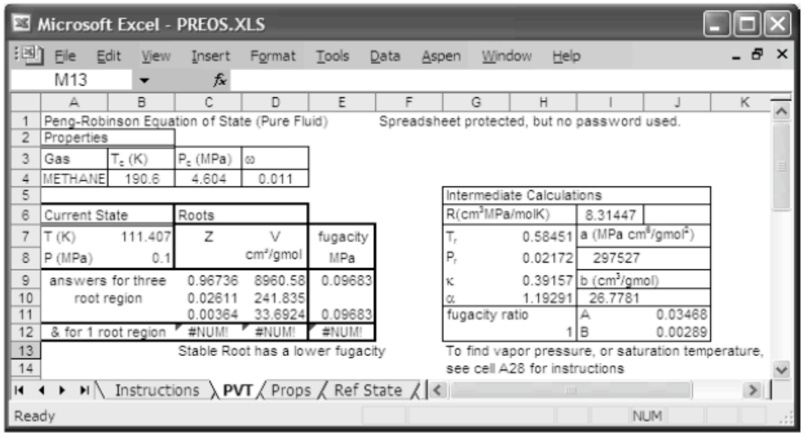
9.10 SATURATION CONDITIONS FROM AN EQUATION OF STATE

The only thermodynamic specification that is required for determining the saturation temperature or pressure is that the Gibbs energies (or fugacities) of the vapor and liquid be equal. *This involves finding the pressure or temperature where the vapor and liquid fugacities are equal*. The interesting part of the problem comes in computing the saturation condition by iterating on the temperature or pressure.

Example 9.6 Vapor pressure from the Peng-Robinson equation

Use the Peng-Robinson equation to calculate the normal boiling point of methane.

Solution: Vapor pressure calculations are available in Preos.xlsx and PreosPropsmenu.m. Let us discuss Preos.xlsx first. The spreadsheet is more illustrative in showing the steps to the calculation. Computing the saturation temperature or pressure in Excel is rapid using the Solver tool in Excel.

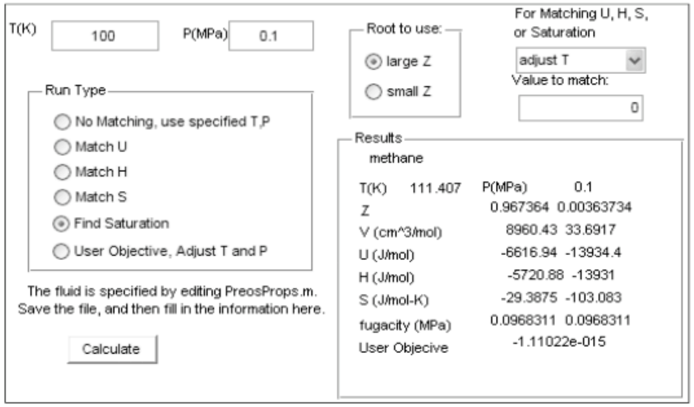


	A	B	C	D	E	F	G	H	I	J	K
1	Peng-Robinson Equation of State (Pure Fluid)					Spreadsheet protected, but no password used.					
2	Properties										
3	Gas	T_c (K)	P_c (MPa)	ω							
4	METHANE	190.6	4.604	0.011							
5							Intermediate Calculations				
6	Current State		Roots				R(cm³MPa/molK)		8.31447		
7	T (K)	111.407	Z	V	fugacity		T_r	0.58451	a (MPa cm⁶/gmol²)		
8	P (MPa)	0.1		cm³/gmol	MPa		P_r	0.02172	297527		
9	answers for three		0.96736	8960.58	0.09683		κ	0.39157	b (cm³/gmol)		
10	root region		0.02611	241.835			α	1.19291	26.7781		
11			0.00364	33.6924	0.09683		fugacity ratio		A	0.03468	
12	& for 1 root region		#NUM!	#NUM!	#NUM!			1	B	0.00289	
13			Stable Root has a lower fugacity				To find vapor pressure, or saturation temperature,				
14							see cell A28 for instructions				

Figure 9.7 *Example of Preos.xlsx used to calculate vapor pressure.*

On the spreadsheet shown in Fig. 9.7, cell H12 is included with the fugacity ratio of the two phases; the cell can be used to locate a saturation condition. Initialize Excel by entering the desired P in cell B8, in this case 0.1 MPa. Then, adjust the temperature to provide a guess in the two-phase (three-root) region. Then, instruct Solver to set the cell for the fugacity ratio (H12) to a value of one by adjusting temperature (B7), subject to the constraint that the temperature (B7) is less than the critical temperature.

In MATLAB, the initial guess is entered in the upper left. The “Run Type” is set as a saturation calculation. The “Root to use” and “Value to match” are not used for a saturation calculation. The drop-down box “For Matching...” is set to adjust the temperature. The results are shown in Fig. 9.8.



T(K) 100
P(MPa) 0.1

Root to use:
● large Z
○ small Z

For Matching U, H, S, or Saturation: adjust T
Value to match: 0

Run Type
○ No Matching, use specified T,P
○ Match U
○ Match H
○ Match S
● Find Saturation
○ User Objective, Adjust T and P

The fluid is specified by editing PreosProps.m.
Save the file, and then fill in the information here.

```
Results
  methane

T(K)     111.407   P(MPa)       0.1
Z                  0.967364  0.00363734
V (cm^3/mol)        8960.43  33.6917
U (J/mol)          -6616.94  -13934.4
H (J/mol)          -5720.88  -13931
S (J/mol-K)        -29.3875  -103.083
fugacity (MPa)    0.0968311  0.0968311
User Objecive        -1.11022e-015
```

Figure 9.8 *Example of PreosPropsMenu.m used to calculate vapor pressure.*

For methane the solution is found to be 111.4 K which is very close to the experimental value used in Example 8.9 on page 320. Saturation pressures can also be found by adjusting pressure at fixed temperature.

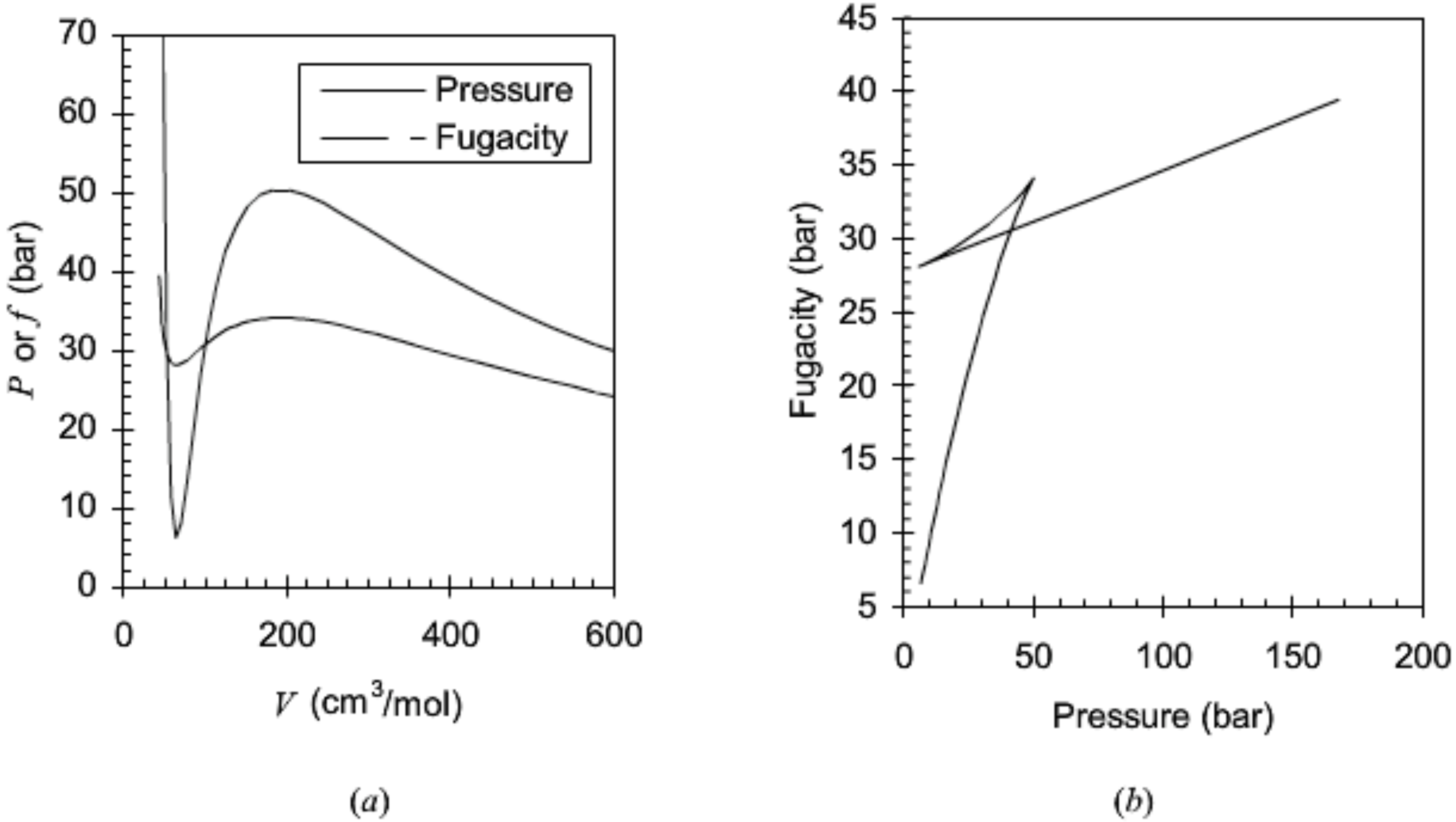


Figure 9.9 *Predictions of the Peng-Robinson equation of state for CO_2: (a) prediction of the P-V isotherm and fugacity at 280 K; (b) plot of data from part (a) as fugacity versus pressure, showing the crossover of fugacity at the vapor pressure. Several isotherms for CO_2 are shown in Fig. 7.5 on page 264.*

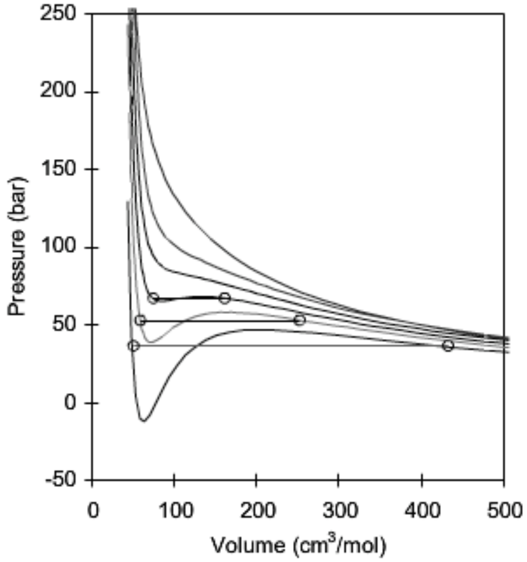


Figure 7.5 *Illustration of the prediction of isotherms by the Peng-Robinson equation of state for CO_2 ($T_c = 304.2$ K) at 275 K, 290 K, 300 K, 310 K, 320 K, and 350 K. Higher temperatures result in a high pressure for a given volume. The "humps" are explained in the text. The calculated vapor pressures are 36.42 bar at 275 K, 53.2 bar at 290 K, and 67.21 bar at 300 K.*

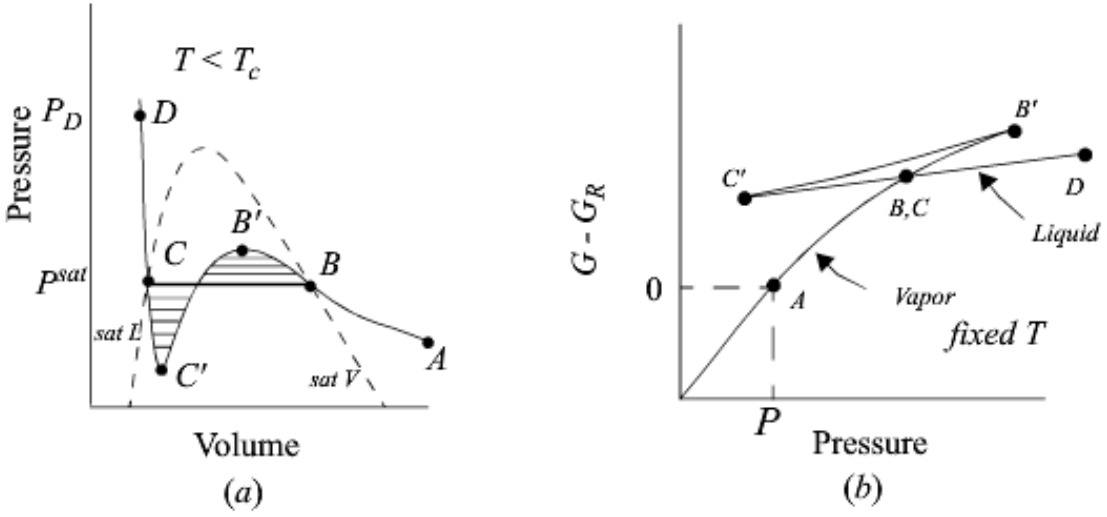
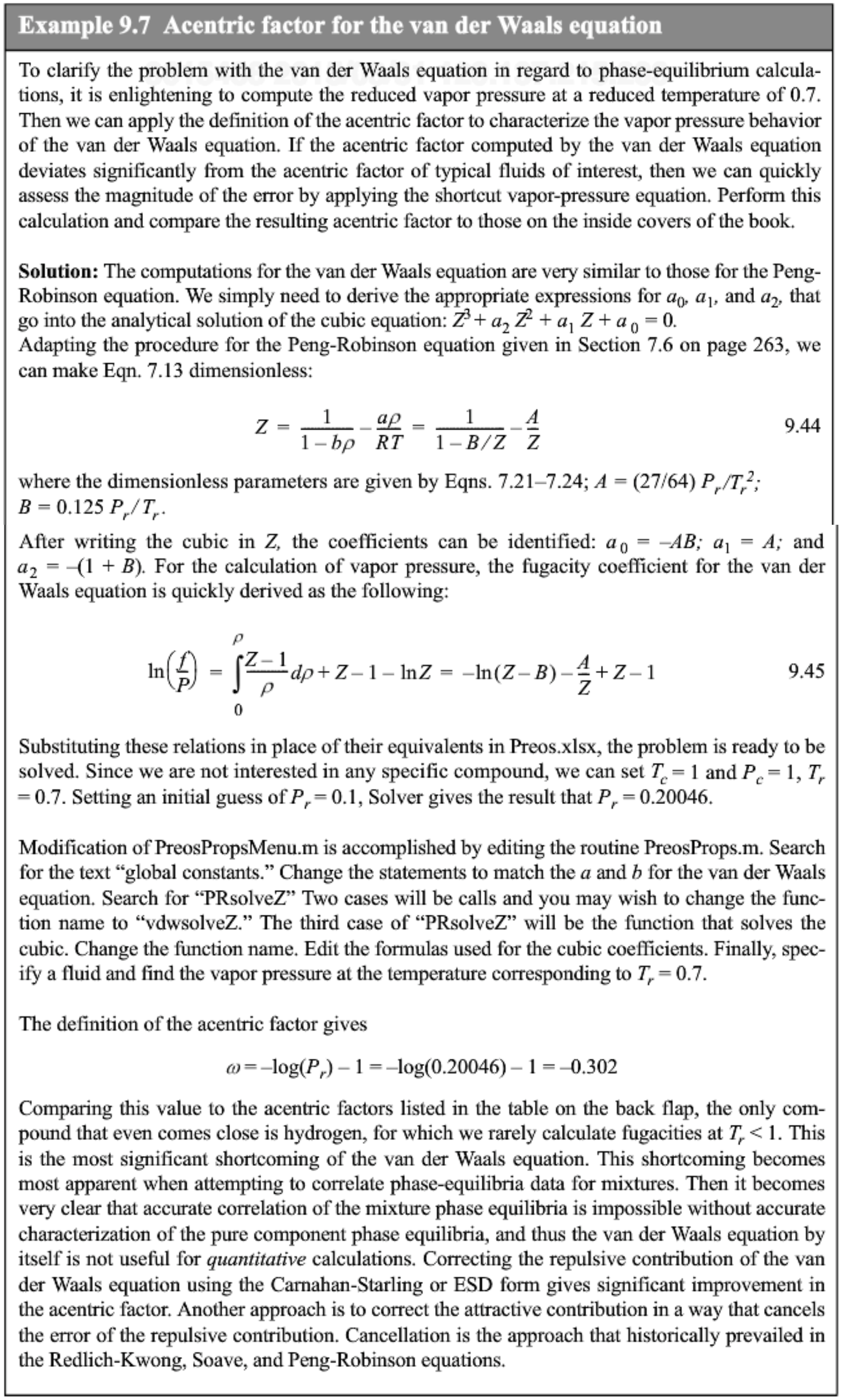


Figure 9.6 *Schematic illustration of the prediction of an isotherm by a cubic equation of state. Compare with Fig. 9.5 on page 350. The figure on the right shows the calculation of Gibbs energy relative to a reference state. The fugacity will have the same qualitative shape.*



Example 9.7 Acentric factor for the van der Waals equation

To clarify the problem with the van der Waals equation in regard to phase-equilibrium calculations, it is enlightening to compute the reduced vapor pressure at a reduced temperature of 0.7. Then we can apply the definition of the acentric factor to characterize the vapor pressure behavior of the van der Waals equation. If the acentric factor computed by the van der Waals equation deviates significantly from the acentric factor of typical fluids of interest, then we can quickly assess the magnitude of the error by applying the shortcut vapor-pressure equation. Perform this calculation and compare the resulting acentric factor to those on the inside covers of the book.

Solution: The computations for the van der Waals equation are very similar to those for the Peng-Robinson equation. We simply need to derive the appropriate expressions for a_0, a_1, and a_2, that go into the analytical solution of the cubic equation: $Z^3 + a_2 Z^2 + a_1 Z + a_0 = 0$.
Adapting the procedure for the Peng-Robinson equation given in Section 7.6 on page 263, we can make Eqn. 7.13 dimensionless:

$$Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT} = \frac{1}{1-B/Z} - \frac{A}{Z} \qquad 9.44$$

where the dimensionless parameters are given by Eqns. 7.21–7.24; $A = (27/64)\,P_r/T_r^2$; $B = 0.125\,P_r/T_r$.

After writing the cubic in Z, the coefficients can be identified: $a_0 = -AB$; $a_1 = A$; and $a_2 = -(1 + B)$. For the calculation of vapor pressure, the fugacity coefficient for the van der Waals equation is quickly derived as the following:

$$\ln\left(\frac{f}{P}\right) = \int_0^\rho \frac{Z-1}{\rho}d\rho + Z - 1 - \ln Z = -\ln(Z-B) - \frac{A}{Z} + Z - 1 \qquad 9.45$$

Substituting these relations in place of their equivalents in Preos.xlsx, the problem is ready to be solved. Since we are not interested in any specific compound, we can set $T_c = 1$ and $P_c = 1$, $T_r = 0.7$. Setting an initial guess of $P_r = 0.1$, Solver gives the result that $P_r = 0.20046$.

Modification of PreosPropsMenu.m is accomplished by editing the routine PreosProps.m. Search for the text "global constants." Change the statements to match the *a* and *b* for the van der Waals equation. Search for "PRsolveZ" Two cases will be calls and you may wish to change the function name to "vdwsolveZ." The third case of "PRsolveZ" will be the function that solves the cubic. Change the function name. Edit the formulas used for the cubic coefficients. Finally, specify a fluid and find the vapor pressure at the temperature corresponding to $T_r = 0.7$.

The definition of the acentric factor gives

$$\omega = -\log(P_r) - 1 = -\log(0.20046) - 1 = -0.302$$

Comparing this value to the acentric factors listed in the table on the back flap, the only compound that even comes close is hydrogen, for which we rarely calculate fugacities at $T_r < 1$. This is the most significant shortcoming of the van der Waals equation. This shortcoming becomes most apparent when attempting to correlate phase-equilibria data for mixtures. Then it becomes very clear that accurate correlation of the mixture phase equilibria is impossible without accurate characterization of the pure component phase equilibria, and thus the van der Waals equation by itself is not useful for *quantitative* calculations. Correcting the repulsive contribution of the van der Waals equation using the Carnahan-Starling or ESD form gives significant improvement in the acentric factor. Another approach is to correct the attractive contribution in a way that cancels the error of the repulsive contribution. Cancellation is the approach that historically prevailed in the Redlich-Kwong, Soave, and Peng-Robinson equations.

$$\omega = -\log_{10}(p_r^{\text{sat}}) - 1, \text{ at } T_r = 0.7$$

$$\boxed{\log_{10} P_r^{sat} = \frac{7}{3}(1+\omega)\left(1-\frac{1}{T_r}\right)} \qquad 9.11$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2 \quad \text{or} \quad Z = \frac{1}{(1-b\rho)} - \frac{a\rho}{RT} \qquad 7.12$$

❶ Van der Waals EOS.

where ρ = molar density = $n/\underline{V}$.

$$a \equiv \frac{27}{64}\frac{R^2T_c^2}{P_c} \quad ; \quad b \equiv \frac{RT_c}{8P_c} \qquad 7.13$$

$$\boxed{Z = 1 + Z^{rep} + Z^{att} = 1 + \frac{b\rho}{1-b\rho} - \frac{a\rho}{RT}} \qquad 7.14$$

❶ The van der Waals equation

$$A \equiv aP/R^2T^2 \qquad 7.21$$

$$B \equiv bP/RT \qquad 7.22$$

$$\boxed{\frac{(G-G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \int_0^\rho \frac{(Z-1)}{\rho}d\rho + (Z-1) - \ln Z} \qquad 9.24$$

The Equal Area Rule

$$\frac{(G^L - G^{ig})}{RT} = \frac{(G^V - G^{ig})}{RT} \tag{9.26}$$

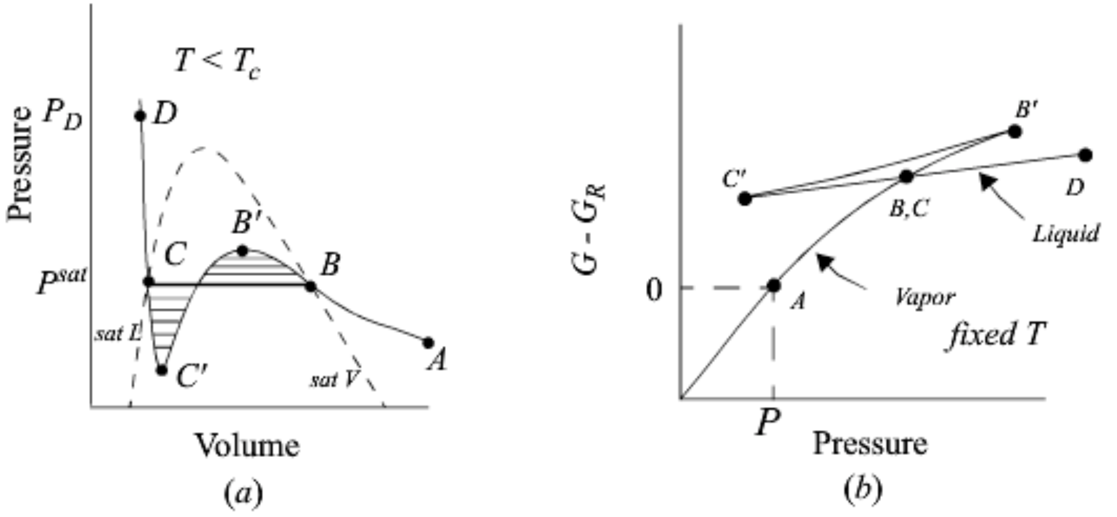
$$\boxed{\frac{(G - G^{ig})}{RT} = \ln\left(\frac{f}{P}\right) = \int_0^{\rho} \frac{(Z-1)}{\rho} d\rho + (Z-1) - \ln Z} \tag{9.24}$$

$$\frac{G^L - G^V}{RT} = \frac{G^L - G^{ig}}{RT} - \frac{G^V - G^{ig}}{RT} = \int_{\rho^V}^{\rho^L} \frac{Z-1}{\rho} d\rho + Z^L - Z^V - \ln(Z^L/Z^V) \tag{9.46}$$

$$\frac{G^L - G^V}{RT} = -\int_{V^V}^{V^L} \left(\frac{P}{RT} - \frac{1}{V}\right) dV + \frac{1}{RT}(PV^L - PV^v) - \ln\left(\frac{PV^L/RT}{PV^V/RT}\right) \tag{9.47}$$

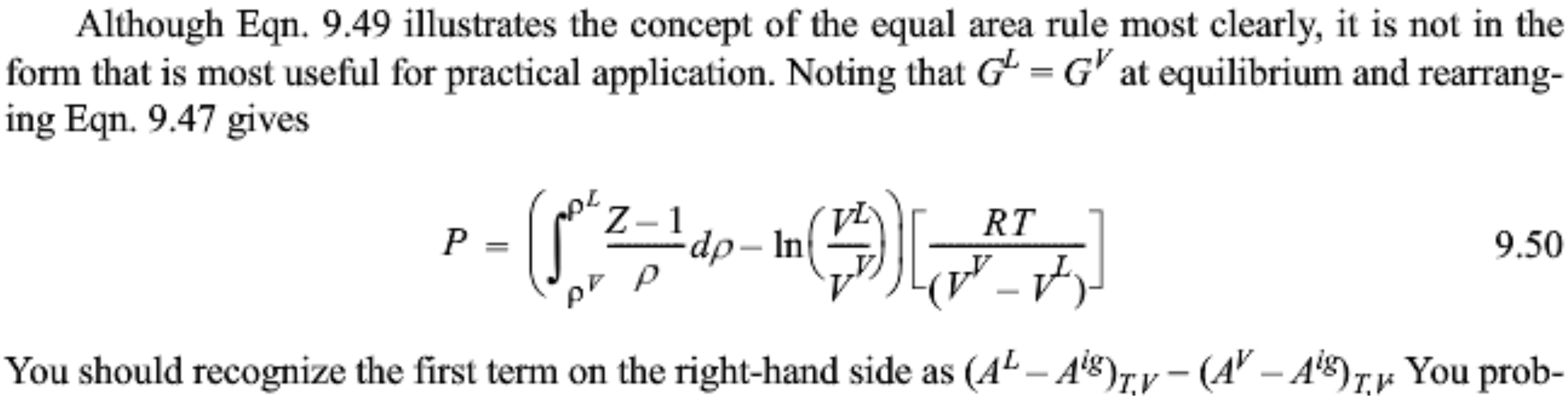
$$\frac{G^L - G^V}{RT} = \frac{1}{RT}(PV^L - PV^V) - \int_{V^V}^{V^L} \left(\frac{P}{RT}\right) dV + \int_{V^V}^{V^L} \left(\frac{1}{V}\right) dV - \ln\left(\frac{V^L}{V^V}\right) \tag{9.48}$$

$$\frac{G^L - G^V}{RT} = \frac{-1}{RT}\left\{ -[PV]_{V^V}^{V^L} + \int_{V^V}^{V^L} P dV \right\} \tag{9.49}$$



(*a*) (*b*)

Figure 9.6 *Schematic illustration of the prediction of an isotherm by a cubic equation of state. Compare with Fig. 9.5 on page 350. The figure on the right shows the calculation of Gibbs energy relative to a reference state. The fugacity will have the same qualitative shape.*

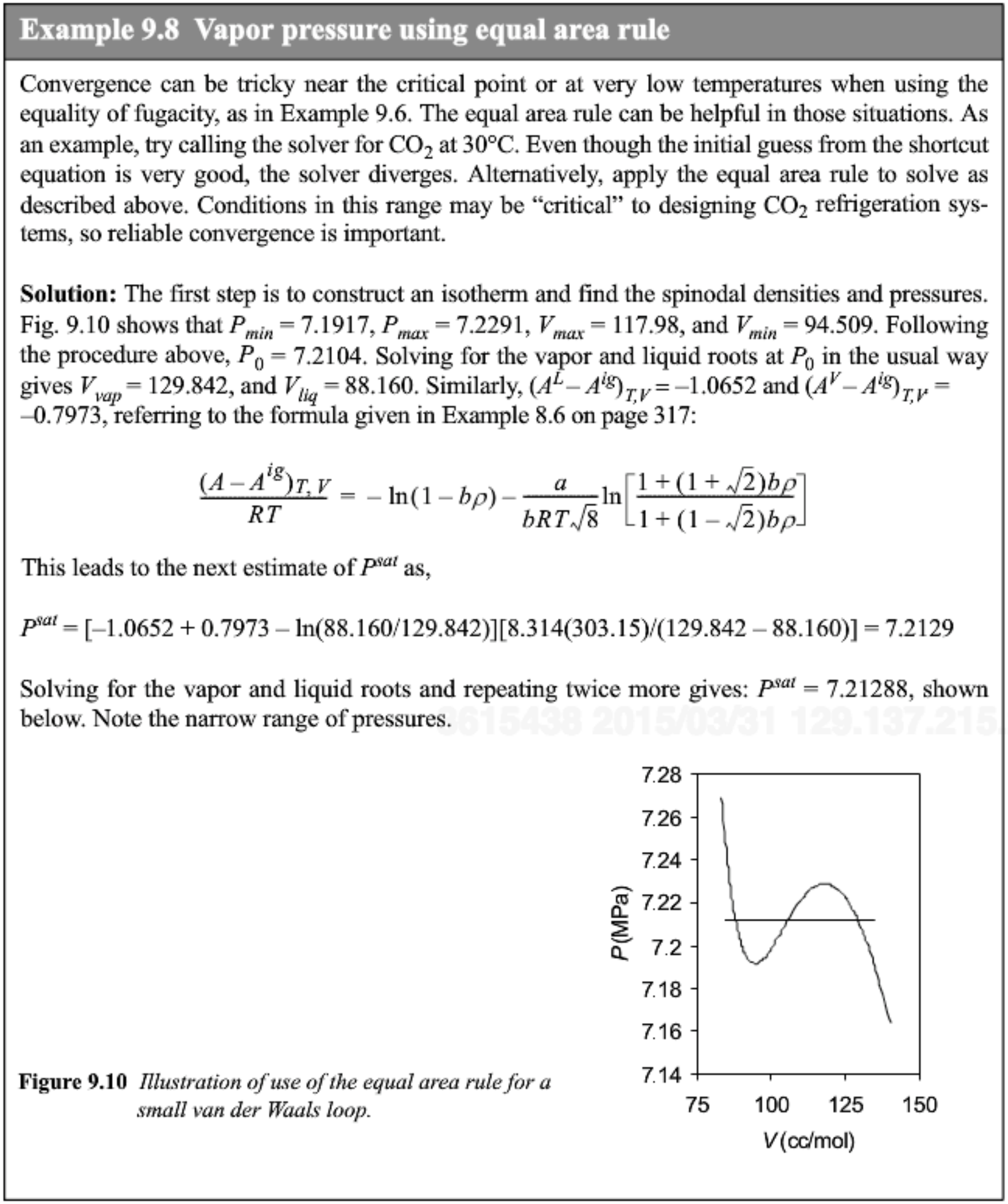


Although Eqn. 9.49 illustrates the concept of the equal area rule most clearly, it is not in the form that is most useful for practical application. Noting that $G^L = G^V$ at equilibrium and rearranging Eqn. 9.47 gives

$$P = \left(\int_{\rho^V}^{\rho^L} \frac{Z-1}{\rho} d\rho - \ln\left(\frac{V^L}{V^V}\right)\right)\left[\frac{RT}{(V^V - V^L)}\right] \tag{9.50}$$

You should recognize the first term on the right-hand side as $(A^L - A^{ig})_{T,V} - (A^V - A^{ig})_{T,V}$. You prob-

$P_0 = (P_{max}+P_{min})/2$



Example 9.8 Vapor pressure using equal area rule

Convergence can be tricky near the critical point or at very low temperatures when using the equality of fugacity, as in Example 9.6. The equal area rule can be helpful in those situations. As an example, try calling the solver for CO_2 at 30°C. Even though the initial guess from the shortcut equation is very good, the solver diverges. Alternatively, apply the equal area rule to solve as described above. Conditions in this range may be "critical" to designing CO_2 refrigeration systems, so reliable convergence is important.

Solution: The first step is to construct an isotherm and find the spinodal densities and pressures. Fig. 9.10 shows that $P_{min} = 7.1917$, $P_{max} = 7.2291$, $V_{max} = 117.98$, and $V_{min} = 94.509$. Following the procedure above, $P_0 = 7.2104$. Solving for the vapor and liquid roots at P_0 in the usual way gives $V_{vap} = 129.842$, and $V_{liq} = 88.160$. Similarly, $(A^L - A^{ig})_{T,V} = -1.0652$ and $(A^V - A^{ig})_{T,V} = -0.7973$, referring to the formula given in Example 8.6 on page 317:

$$\frac{(A-A^{ig})_{T,V}}{RT} = -\ln(1-b\rho) - \frac{a}{bRT\sqrt{8}}\ln\left[\frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho}\right]$$

This leads to the next estimate of P^{sat} as,

$$P^{sat} = [-1.0652 + 0.7973 - \ln(88.160/129.842)][8.314(303.15)/(129.842 - 88.160)] = 7.2129$$

Solving for the vapor and liquid roots and repeating twice more gives: $P^{sat} = 7.21288$, shown below. Note the narrow range of pressures.

Figure 9.10 *Illustration of use of the equal area rule for a small van der Waals loop.*

9.11 STABLE ROOTS AND SATURATION CONDITIONS

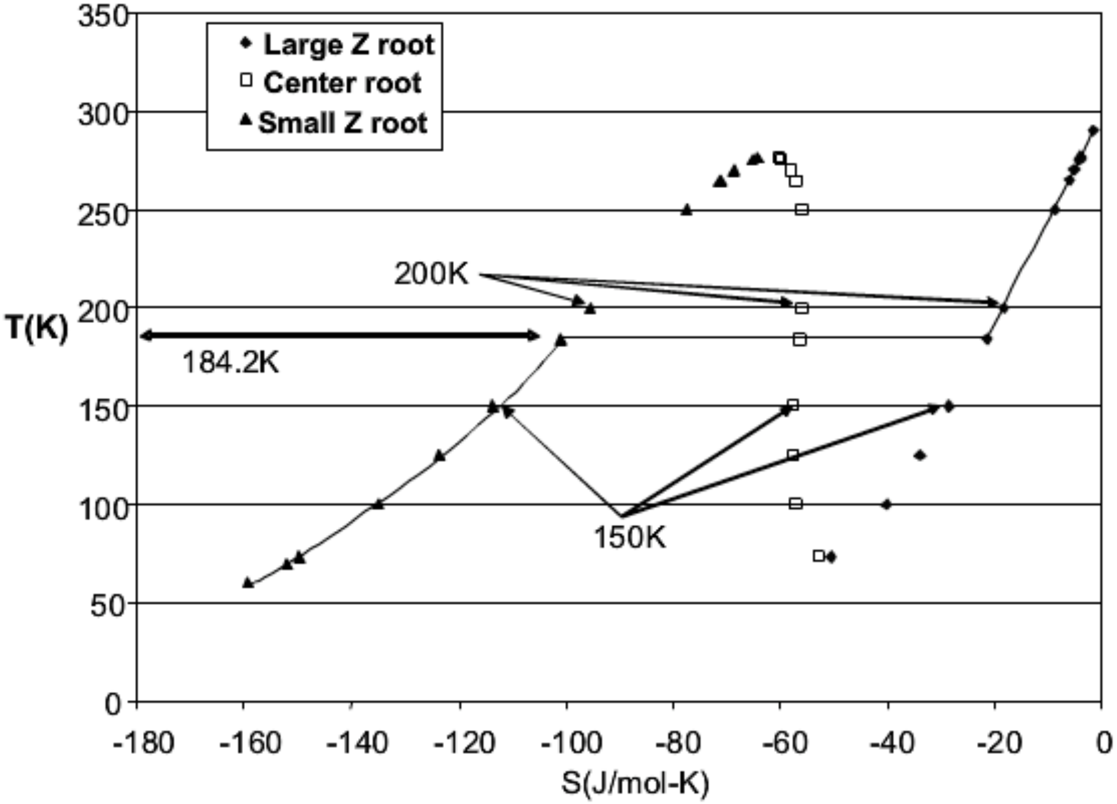


Figure 9.11 *Entropy values for ethane calculated from the Peng-Robinson equation along an isobar at 0.1 MPa. The largest Z root is shown as diamonds, the smallest Z root is shown as triangles, and the center root is shown as open squares. The stable behavior is indicated by the solid line.*

Suppose a process problem requires a state with $S = -18.185$ J/mol-K. At 200 K, the largest Z root has this value. The corresponding values of the fugacities from largest to smallest Z are 0.0976 MPa, 0.652 MPa, and 0.206 MPa, indicating that the largest root is most stable, so the largest root will give the remainder of the state variables.

9.11 STABLE ROOTS AND SATURATION CONDITIONS

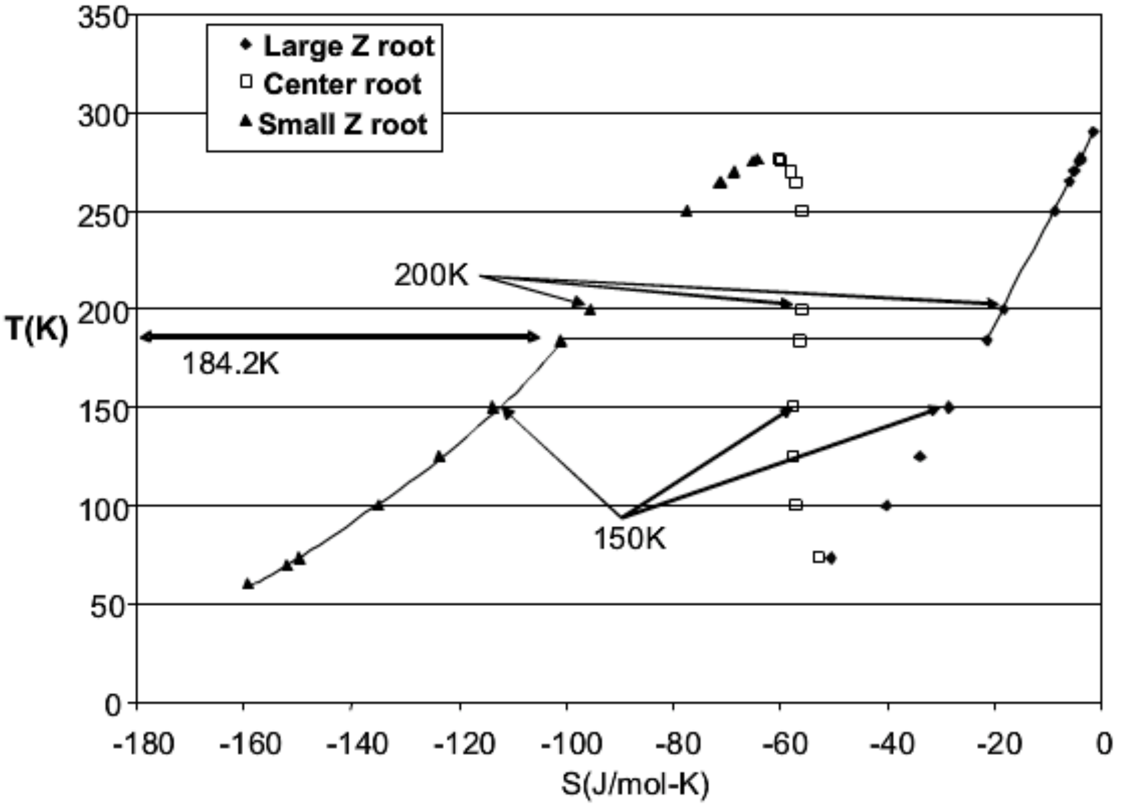


Figure 9.11 *Entropy values for ethane calculated from the Peng-Robinson equation along an isobar at 0.1 MPa. The largest Z root is shown as diamonds, the smallest Z root is shown as triangles, and the center root is shown as open squares. The stable behavior is indicated by the solid line.*

Suppose a process problem requires a state with *S* = –28.35 J/mol-K. At 150 K, the largest *Z* root has this value. The corresponding values of the fugacities from largest to smallest *Z* are 0.0951 MPa, 0.313 MPa, and 0.0099 MPa, indicating that the smallest root is most stable. Even though the largest *Z* root has the correct value of *S*, the root is not the most stable root, and must be discarded.

9.11 STABLE ROOTS AND SATURATION CONDITIONS

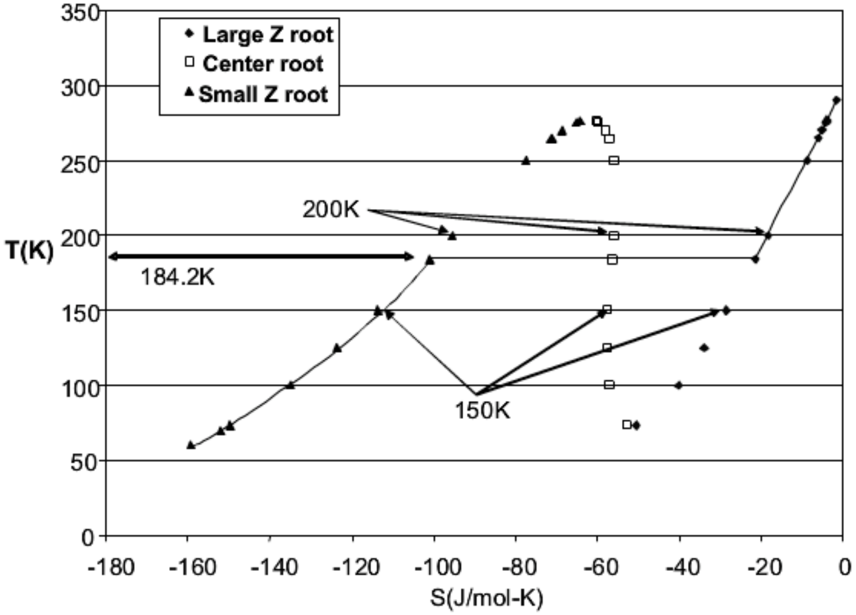


Figure 9.11 *Entropy values for ethane calculated from the Peng-Robinson equation along an isobar at 0.1 MPa. The largest Z root is shown as diamonds, the smallest Z root is shown as triangles, and the center root is shown as open squares. The*

Further exploration of roots would show that the desired value of S cannot be obtained by the middle or smallest roots, or any most stable root. Usually if this behavior is suspected, it is quickest to determine the saturation conditions for the given pressure and compare the saturation values to the specified value. (Think about how you handled saturated steam calculations from a turbine using the steam tables and used the saturation values as a guide.) The saturation conditions at 0.1 MPa can be found by adjusting the T until the fugacities become equal for the large Z and small Z roots, which is found to occur at 184.2 K. At this condition, the corresponding values of the fugacities from largest to smallest Z are 0.0971 MPa, 0.524 MPa, and 0.0971 MPa, indicating that largest and smallest Z roots are in phase equilibrium, and the center root is discarded as before. The corresponding values for saturated entropy are $S = -21.3021$ J/mol-K for the vapor phase and -100.955 J/mol-K for the liquid phase. For any condition at 0.1 MPa, any value of S between these two values will fall in the two-phase region. Therefore, the desired state of $S = -28.35$ J/mol-K is two-phase, with a quality calculated using the saturation values,

$$S = S^{satL} + q\,(S^{satV} - S^{satL})$$

-28.35 J/mol-K $= -100.955 + q(-21.3021 + 100.955)$. Solving, $q = 0.912$

9.12 TEMPERATURE EFFECTS ON *G* AND *f*

The effect of temperature at fixed pressure is

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad 9.51$$

The Gibbs energy change with temperature is then dependent on entropy. Gibbs energy will decrease with increasing temperature. Since the entropy of a vapor is higher than the entropy of a liquid, the Gibbs energy will change more rapidly with temperature for vapor. Since the Gibbs energy is proportional to the log of fugacity, the fugacity dependence will follow the same trends. Similar statements are valid comparing liquids and solids.[7]

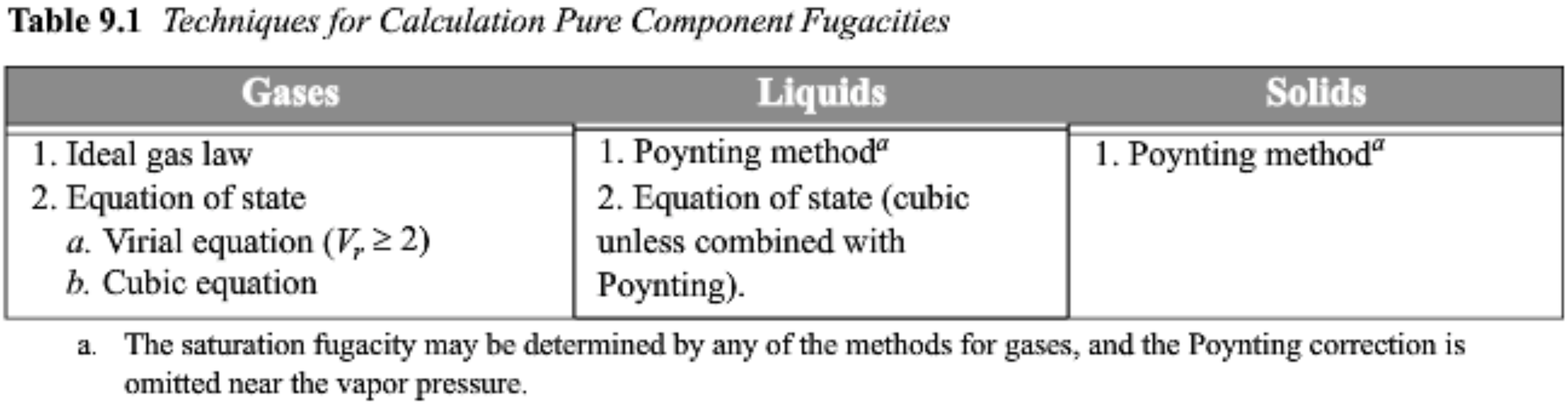


Table 9.1 *Techniques for Calculation Pure Component Fugacities*

Gases	Liquids	Solids
1. Ideal gas law 2. Equation of state *a.* Virial equation ($V_r \geq 2$) *b.* Cubic equation	1. Poynting method[a] 2. Equation of state (cubic unless combined with Poynting).	1. Poynting method[a]

[a] The saturation fugacity may be determined by any of the methods for gases, and the Poynting correction is omitted near the vapor pressure.