

Using the ideal gas equation, we find

$$\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}} = \frac{R}{\bar{V}}$$

$$\Delta \bar{S} = R \ln \frac{V_2}{V_1} = (8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \frac{1.00}{10.0} = -19.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The van der Waals result is smaller than the value obtained with the ideal gas equation.

- 22-56.** Derive an expression for $\Delta \bar{S}$ for the reversible, isothermal expansion of one mole of a gas that obeys the Redlich-Kwong equation (Equation 16.7). Use your result to calculate $\Delta \bar{S}$ for the isothermal compression of ethane from $10.0 \text{ dm}^3 \cdot \text{mol}^{-1}$ to $1.00 \text{ dm}^3 \cdot \text{mol}^{-1}$ at 400 K . Compare your result with the result you would get using the ideal-gas equation.

Because these are the same parameters as those used in the previous problem, the ideal gas equation of state gives a value of $-19.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $\Delta \bar{S}$.

We can use the Maxwell relation (Equation 22.19)

$$\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}}$$

For the Redlich-Kwong equation,

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2} \bar{V}(\bar{V} + B)}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\bar{V}} = \frac{R}{\bar{V} - B} + \frac{A}{2T^{3/2} \bar{V}(\bar{V} + B)}$$

Substituting into the Maxwell equation (Equation 22.19), we find that

$$\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\bar{V}} = \frac{R}{\bar{V} - B} + \frac{A}{2T^{3/2} \bar{V}(\bar{V} + B)}$$

or

$$\Delta \bar{S} = R \ln \frac{\bar{V}_2 - B}{\bar{V}_1 - B} - \frac{A}{2BT^{3/2}} \ln \frac{V_1(V_2 + B)}{V_2(V_1 + B)}$$

For ethane, $A = 98.831 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}$ and $B = 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}$, so

$$\begin{aligned} \Delta \bar{S} &= (0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \ln \frac{1.00 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}}{10.0 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}} \\ &\quad - \frac{98.831 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}}{2(0.045153 \text{ dm}^3 \cdot \text{mol}^{-1})(400 \text{ K})^{3/2}} \ln \frac{(10.0 \text{ dm}^3 \cdot \text{mol}^{-1})(1.045153 \text{ dm}^3 \cdot \text{mol}^{-1})}{(1.00 \text{ dm}^3 \cdot \text{mol}^{-1})(10.045153 \text{ dm}^3 \cdot \text{mol}^{-1})} \\ &= -0.200 \text{ dm}^3 \cdot \text{bar} = -20.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

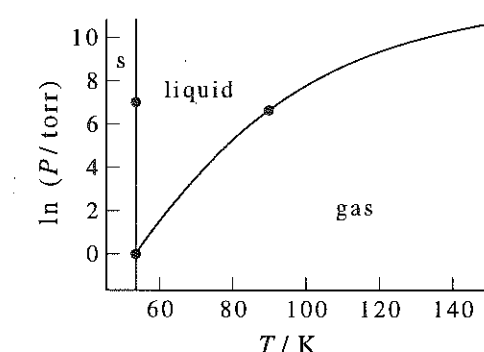
This is smaller than the value obtained with the ideal gas equation.

Phase Equilibria

PROBLEMS AND SOLUTIONS

- 23-1.** Sketch the phase diagram for oxygen using the following data: triple point, 54.3 K and 1.14 torr ; critical point, 154.6 K and 37828 torr ; normal melting point, -218.4°C ; and normal boiling point, -182.9°C . Does oxygen melt under an applied pressure as water does?

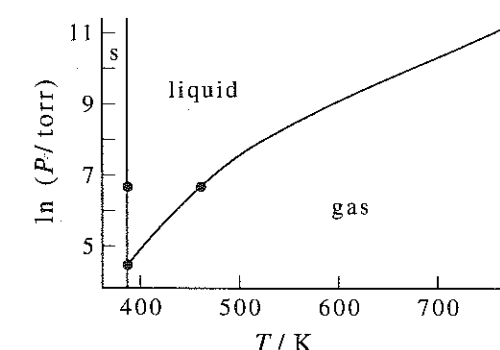
We can use the triple point and the normal melting point to construct the liquid-solid line and the triple point, normal boiling point, and critical point to construct the liquid-gas line. The liquid-gas line stops at the critical point. We produce the diagram



We can see that oxygen does not melt under an applied pressure, because its normal melting point temperature is higher than the triple point temperature.

- 23-2.** Sketch the phase diagram for I_2 given the following data: triple point, 113°C and 0.12 atm ; critical point, 512°C and 116 atm ; normal melting point, 114°C ; normal boiling point, 184°C ; and density of liquid > density of solid.

We use the triple point and normal melting point to construct the liquid-solid line and the triple point, normal boiling point, and critical point to construct the liquid-gas line. Because the density of the liquid is greater than the density of the solid, the solid-liquid line has a positive slope.



23-3. Figure 23.14 shows a density-temperature phase diagram for benzene. Using the following data for the triple point and the critical point, interpret this phase diagram. Why is the triple point indicated by a line in this type of phase diagram?

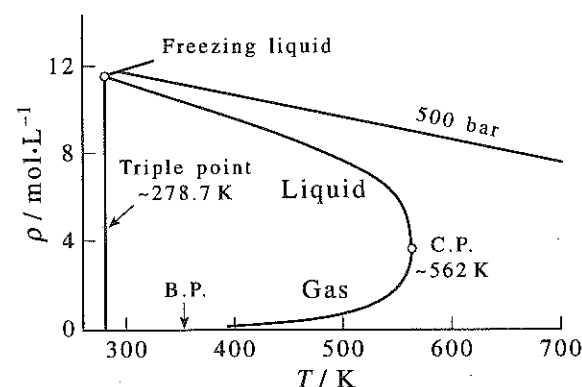
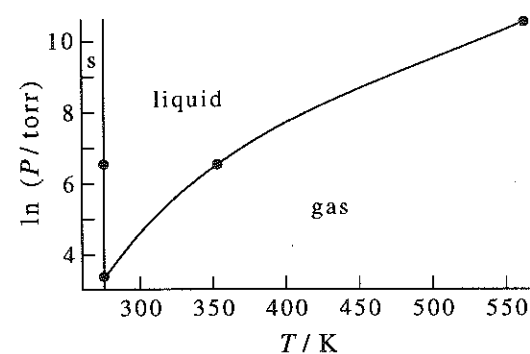


FIGURE 23.14
A density-temperature phase diagram of benzene.

	T/K	P/bar	$\rho/\text{mol}\cdot\text{L}^{-1}$	
			Vapor	Liquid
Triple point	278.680	0.04785	0.002074	11.4766
Critical point	561.75	48.7575	3.90	3.90
Normal freezing point	278.68	1.01325		
Normal boiling point	353.240	1.01325	0.035687	10.4075

The triple point is indicated by a line because it represents a temperature at which the solid, liquid, and gas phases all coexist at equilibrium. The line labelled triple point connects the densities of the liquid and vapor in equilibrium with each other. Notice that the liquid and gaseous densities become equal at the critical point. The line labelled 500 bar represents the density of benzene at 500 bar as a function of temperature. Below the information conveyed by the density-temperature phase diagram is represented in a pressure-temperature phase diagram.



23-4. The vapor pressures of solid and liquid chlorine are given by

$$\ln(P^s/\text{torr}) = 24.320 - \frac{3777 \text{ K}}{T}$$

$$\ln(P^l/\text{torr}) = 17.892 - \frac{2669 \text{ K}}{T}$$

where T is the absolute temperature. Calculate the temperature and pressure at the triple point of chlorine.

This problem is done in the same way as Example 23-1. At the triple point, the two equations for the vapor pressure must be equivalent, since the solid and liquid coexist. Then

$$\begin{aligned} 24.320 - \frac{3777 \text{ K}}{T_{\text{tp}}} &= 17.892 - \frac{2669 \text{ K}}{T_{\text{tp}}} \\ (24.320 - 17.892)T_{\text{tp}} &= -2669 \text{ K} + 3777 \text{ K} \\ T_{\text{tp}} &= 172.4 \text{ K} \end{aligned}$$

We can check this by substituting back into both expressions, and we find $\ln(P^s) = \ln(P^l) = 2.41$ torr and so $P_{\text{tp}} = 11.1$ torr.

23-5. The pressure along the melting curve from the triple-point temperature to an arbitrary temperature can be fit empirically by the Simon equation, which is

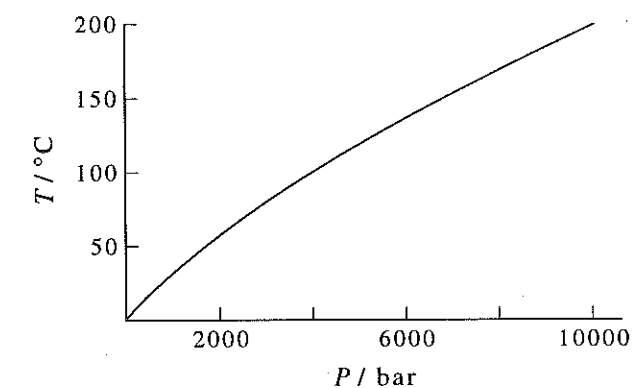
$$(P - P_{\text{tp}})/\text{bar} = a \left[\left(\frac{T}{T_{\text{tp}}} \right)^{\alpha} - 1 \right]$$

where a and α are constants whose values depend upon the substance. Given that $P_{\text{tp}} = 0.04785$ bar, $T_{\text{tp}} = 278.68$ K, $a = 4237$, and $\alpha = 2.3$ for benzene, plot P against T and compare your result with that given in Figure 23.2.

Substituting into this expression, we find that we must plot

$$\begin{aligned} P/\text{bar} &= 0.04785 + 4237 \left[\left(\frac{T/\text{K}}{278.68 \text{ K}} \right)^{2.3} - 1 \right] \\ P/\text{bar} &= 0.04785 - 4237 + \frac{4237}{(278.68)^{2.3}} T^{2.3} \end{aligned}$$

where T is on the y-axis and P is on the x-axis. The result looks very much like Figure 23.2.



23-6. The slope of the melting curve of methane is given by

$$\frac{dP}{dT} = (0.08446 \text{ bar} \cdot \text{K}^{-1.85}) T^{0.85}$$

from the triple point to arbitrary temperatures. Using the fact that the temperature and pressure at the triple point are 90.68 K and 0.1174 bar, calculate the melting pressure of methane at 300 K.

Integrating from the triple point to 300 K gives

$$\int_{0.1174 \text{ bar}}^{P_2} dP = \int_{90.68 \text{ K}}^{300 \text{ K}} 0.08446 \text{ bar} \cdot \text{K}^{-1.85} T^{0.85} dT$$

$$P_2 - 0.1174 \text{ bar} = \frac{0.08446 \text{ bar} \cdot \text{K}^{-1.85}}{1.85} [(300 \text{ K})^{1.85} - (90.68 \text{ K})^{1.85}]$$

$$P_2 = 1556 \text{ bar}$$

This is the melting pressure of methane at 300 K.

23-7. The vapor pressure of methanol along the entire liquid-vapor coexistence curve can be expressed very accurately by the empirical equation

$$\ln(P/\text{bar}) = -\frac{10.752849}{x} + 16.758207 - 3.603425x$$

$$+ 4.373232x^2 - 2.381377x^3 + 4.572199(1-x)^{1.70}$$

where $x = T/T_c$, and $T_c = 512.60 \text{ K}$. Use this formula to show that the normal boiling point of methanol is 337.67 K.

At the normal boiling point, $P = 1 \text{ atm} = 1.01325 \text{ bar}$. If the normal boiling point of methanol is 337.67 K, then the equality below should hold when $x = 337.67/512.60$:

$$\ln(1.01325) \stackrel{?}{=} -\frac{10.752849}{x} + 16.758207 - 3.603425x$$

$$+ 4.373232x^2 - 2.381377x^3 + 4.572199(1-x)^{1.70}$$

$$0.013163 \stackrel{?}{=} -16.323364 + 16.758207 - 2.373719 + 1.897712 - 0.6807220 + 0.735141$$

$$0.013163 \approx 0.0132546$$

23-8. The standard boiling point of a liquid is the temperature at which the vapor pressure is exactly one bar. Use the empirical formula given in the previous problem to show that the standard boiling point of methanol is 337.33 K.

We do this in the same way as the previous problem, but substitute $x = 337.33/512.60$ into

$$\ln(1) \stackrel{?}{=} -\frac{10.752849}{x} + 16.758207 - 3.603425x$$

$$+ 4.373232x^2 - 2.381377x^3 + 4.572199(1-x)^{1.70}$$

$$0 \stackrel{?}{=} -16.339820 + 16.758207 - 2.371329 + 1.893892 - 0.678668 + 0.737572$$

$$0 \approx -0.000143$$

23-9. The vapor pressure of benzene along the liquid-vapor coexistence curve can be accurately expressed by the empirical expression

$$\ln(P/\text{bar}) = -\frac{10.655375}{x} + 23.941912 - 22.388714x$$

$$+ 20.2085593x^2 - 7.219556x^3 + 4.84728(1-x)^{1.70}$$

where $x = T/T_c$, and $T_c = 561.75 \text{ K}$. Use this formula to show that the normal boiling point of benzene is 353.24 K. Use the above expression to calculate the standard boiling point of benzene.

This problem is essentially the same as Problem 23-7. We must substitute $x = 353.24/561.75$ into the equation

$$\ln(1.01325) \stackrel{?}{=} -\frac{10.655375}{x} + 23.941912 - 22.388714x$$

$$+ 20.2085593x^2 - 7.219556x^3 + 4.84728(1-x)^{1.70}$$

$$0.013163 \stackrel{?}{=} -16.945014 + 23.941912 - 14.078486 + 7.990776 - 1.795109 + 0.899064$$

$$0.013163 \approx 0.0131423$$

To calculate the standard boiling point of benzene, we must solve the polynomial equation for x when $P = 1 \text{ bar}$, or when $\ln P/\text{bar} = 0$:

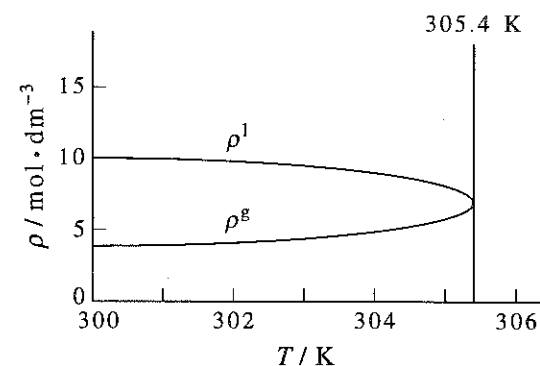
$$0 = -\frac{10.655375}{x} + 23.941912 - 22.388714x$$

$$+ 20.2085593x^2 - 7.219556x^3 + 4.84728(1-x)^{1.70}$$

Inputting this formula into a computational mathematics program such as *Mathematica* (or using the Newton-Raphson method) gives $x = 0.62806$, so the standard boiling point is $T = (561.75 \text{ K})x = 352.8 \text{ K}$.

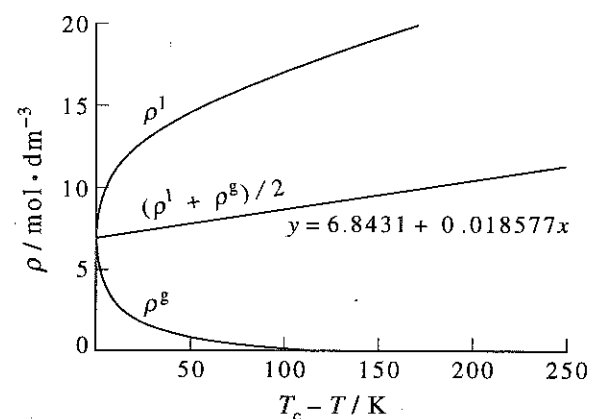
23-10. Plot the following data for the densities of liquid and gaseous ethane in equilibrium with each other as a function of temperature, and determine the critical temperature of ethane.

T/K	$\rho^l/\text{mol} \cdot \text{dm}^{-3}$	$\rho^g/\text{mol} \cdot \text{dm}^{-3}$	T/K	$\rho^l/\text{mol} \cdot \text{dm}^{-3}$	$\rho^g/\text{mol} \cdot \text{dm}^{-3}$
100.00	21.341	1.336×10^{-3}	283.15	12.458	2.067
140.00	19.857	0.03303	293.15	11.297	2.880
180.00	18.279	0.05413	298.15	10.499	3.502
220.00	16.499	0.2999	302.15	9.544	4.307
240.00	15.464	0.5799	304.15	8.737	5.030
260.00	14.261	1.051	304.65	8.387	5.328
270.00	13.549	1.401	305.15	7.830	5.866



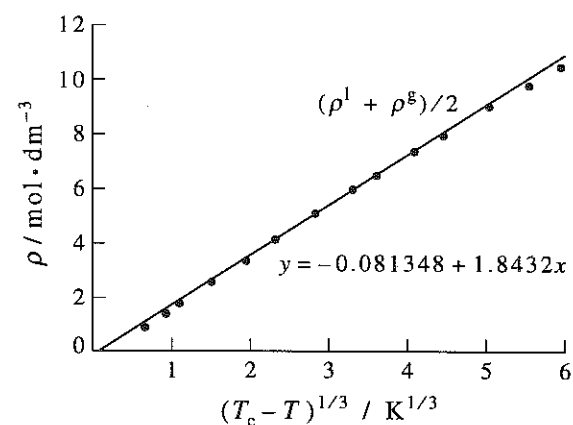
The critical temperature of ethane is about 305.4 K.

- 23-11.** Use the data in the preceding problem to plot $(\rho^l + \rho^g)/2$ against $T_c - T$, with $T_c = 305.4$ K. The resulting straight line is an empirical law called the *law of rectilinear diameters*. If this curve is plotted on the same figure as in the preceding problem, the intersection of the two curves gives the critical density, ρ_c .



The critical density ρ_c is about $6.84 \text{ mol} \cdot \text{dm}^{-3}$.

- 23-12.** Use the data in Problem 23-10 to plot $(\rho^l - \rho^g)$ against $(T_c - T)^{1/3}$ with $T_c = 305.4$ K. What does this plot tell you?



The linear nature of this plot tells us that $(\rho^l - \rho^g)$ varies as $(T - T_c)^{1/3}$ near the critical point.

- 23-13.** The densities of the coexisting liquid and vapor phases of methanol from the triple point to the critical point are accurately given by the empirical expressions

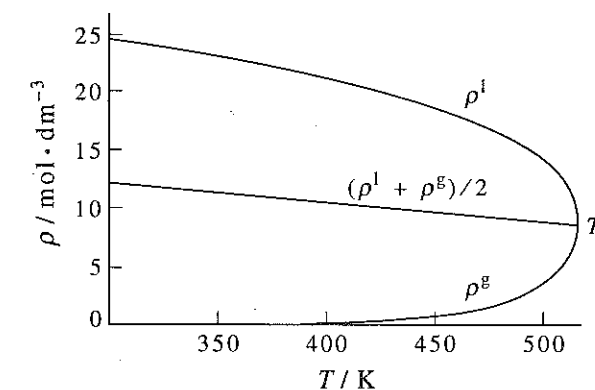
$$\frac{\rho^l}{\rho_c} - 1 = 2.51709(1-x)^{0.350} + 2.466694(1-x) - 3.066818(1-x^2) + 1.325077(1-x^3)$$

and

$$\ln \frac{\rho^g}{\rho_c} = -10.619689 \frac{1-x}{x} - 2.556682(1-x)^{0.350} + 3.881454(1-x) + 4.795568(1-x)^2$$

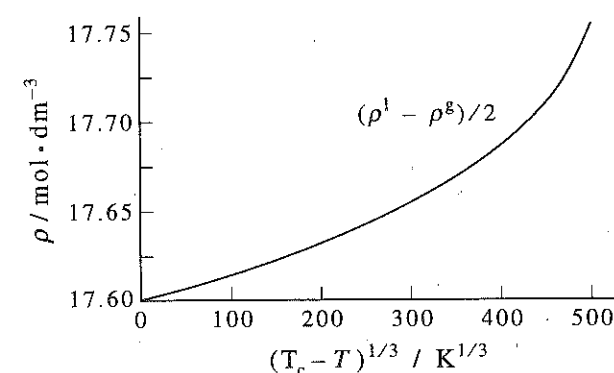
where $\rho_c = 8.40 \text{ mol} \cdot \text{L}^{-1}$ and $x = T/T_c$, where $T_c = 512.60$ K. Use these expressions to plot ρ^l and ρ^g against temperature, as in Figure 23.7. Now plot $(\rho^l + \rho^g)/2$ against T . Show that this line intersects the ρ^l and ρ^g curves at $T = T_c$.

In this graph, the highest line represents ρ^l , the lowest line represents ρ^g , and the dashed line which comes between the two represents $(\rho^l + \rho^g)/2$. At $T = T_c$, $\rho^l = \rho^g$, and so $(\rho^l + \rho^g)/2 = \rho^l = \rho^g$. Therefore, the lines all meet at $T = T_c$.



- 23-14.** Use the expressions given in the previous problem to plot $(\rho^l - \rho^g)/2$ against $(T_c - T)^{1/3}$. Do you get a reasonably straight line? If not, determine the value of the exponent of $(T_c - T)$ that gives the best straight line.

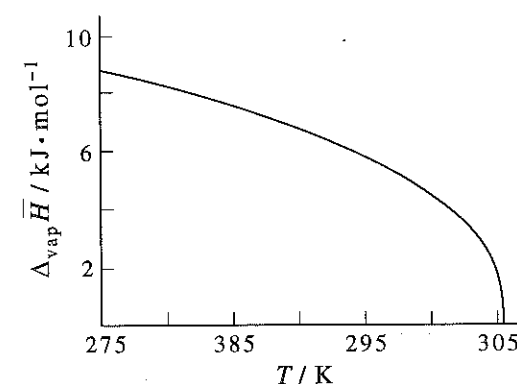
We find a line which is reasonably straight (although the curvature shown here is marked, note the scale of the y-axis).



23–15. The molar enthalpy of vaporization of ethane can be expressed as

$$\Delta_{\text{vap}} \bar{H}(T) / \text{kJ} \cdot \text{mol}^{-1} = \sum_{j=1}^6 A_j x^j$$

where $A_1 = 12.857$, $A_2 = 5.409$, $A_3 = 33.835$, $A_4 = -97.520$, $A_5 = 100.849$, $A_6 = -37.933$, and $x = (T_c - T)^{1/3} / (T_c - T_p)^{1/3}$ where the critical temperature $T_c = 305.4$ K and the triple point temperature $T_p = 90.35$ K. Plot $\Delta_{\text{vap}} \bar{H}(T)$ versus T and show that the curve is similar to that of Figure 23.8.



23–16. Fit the following data for argon to a cubic polynomial in T . Use your result to determine the critical temperature.

T/K	$\Delta_{\text{vap}} \bar{H} / \text{J} \cdot \text{mol}^{-1}$	T/K	$\Delta_{\text{vap}} \bar{H} / \text{J} \cdot \text{mol}^{-1}$
83.80	6573.8	122.0	4928.7
86.0	6508.4	126.0	4665.0
90.0	6381.8	130.0	4367.7
94.0	6245.2	134.0	4024.7
98.0	6097.7	138.0	3618.8
102.0	5938.8	142.0	3118.2
106.0	5767.6	146.0	2436.3
110.0	5583.0	148.0	1944.5
114.0	5383.5	149.0	1610.2
118.0	5166.5	150.0	1131.5

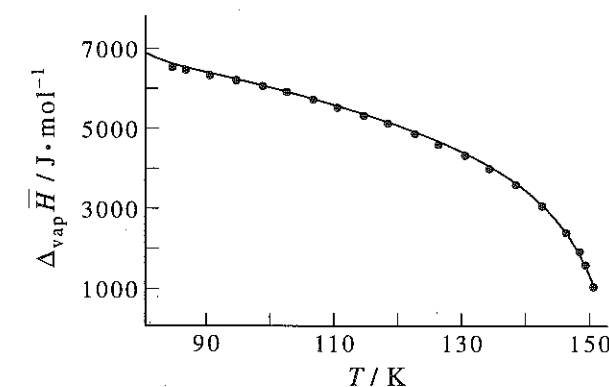
Fitting the data to a cubic polynomial in T gives the expression

$$\Delta_{\text{vap}} \bar{H} / \text{J} \cdot \text{mol}^{-1} = 39458.8 - (912.758 \text{ K}^{-1})T + (8.53681 \text{ K}^{-2})T^2 - (0.0276089 \text{ K}^{-3})T^3$$

Solving for T when $\Delta_{\text{vap}} \bar{H} = 0$ (at the critical temperature) gives a critical temperature of $T_c = 156.0$ K. A better fit is to a fifth-order polynomial in T , which gives the expression

$$\Delta_{\text{vap}} \bar{H} / \text{J} \cdot \text{mol}^{-1} = 474232 - (21594.6 \text{ K}^{-1})T + (396.54 \text{ K}^{-2})T^2 - (3.61587 \text{ K}^{-3})T^3 + (1.63603 \times 10^{-2} \text{ K}^{-4})T^4 - (2.94294 \times 10^{-5} \text{ K}^{-5})T^5$$

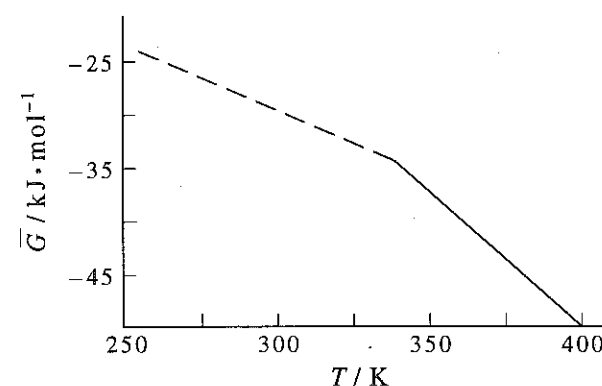
We can solve this fifth-order equation for T when $\Delta_{\text{vap}} \bar{H} = 0$ by using a computational mathematics program or the Newton-Raphson method, which both give a critical temperature of $T_c = 153.2$ K.



23-17. Use the following data for methanol at one atm to plot \bar{G} versus T around the normal boiling point (337.668 K). What is the value of $\Delta_{\text{vap}}\bar{H}$?

T/K	$\bar{H}/\text{kJ}\cdot\text{mol}^{-1}$	$\bar{S}/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
240	4.7183	112.259
280	7.7071	123.870
300	9.3082	129.375
320	10.9933	134.756
330	11.8671	137.412
337.668	12.5509	139.437
337.668	47.8100	243.856
350	48.5113	245.937
360	49.0631	247.492
380	50.1458	250.419
400	51.2257	253.189

We can use the formula $\bar{G} = \bar{H} - T\bar{S}$ to find \bar{G} from this data and then plot \bar{G} vs. T :



The line of best fit for the gaseous phase is $\bar{G}^g/\text{kJ}\cdot\text{mol}^{-1} = 49.57 - 0.249T$ and the line of best fit for the liquid phase is $\bar{G}^l/\text{kJ}\cdot\text{mol}^{-1} = 8.1913 - 0.126T$. $\Delta_{\text{vap}}\bar{H}$ will simply be the change in enthalpy when going from a liquid to a gas:

$$\Delta_{\text{vap}}\bar{H}/\text{kJ}\cdot\text{mol}^{-1} = 47.8100 - 12.5509 = 35.2591$$

23-18. In this problem, we will sketch \bar{G} versus P for the solid, liquid, and gaseous phases for a generic ideal substance as in Figure 23.11. Let $\bar{V}^s = 0.600$, $\bar{V}^l = 0.850$, and $RT = 2.5$, in arbitrary units. Now show that

$$\bar{G}^s = 0.600(P - P_0) + \bar{G}_0^s$$

$$\bar{G}^l = 0.850(P - P_0) + \bar{G}_0^l$$

and

$$\bar{G}^g = 2.5 \ln(P - P_0) + \bar{G}_0^g$$

where $P_0 = 1$ and \bar{G}_0^s , \bar{G}_0^l , and \bar{G}_0^g are the respective zeros of energy. Show that if we (arbitrarily) choose the solid and liquid phases to be in equilibrium at $P = 2.00$ and the liquid and gaseous phases to be in equilibrium at $P = 1.00$, then we obtain

$$\bar{G}_0^s - \bar{G}_0^l = 0.250$$

and

$$\bar{G}_0^l = \bar{G}_0^g$$

from which we obtain

$$\bar{G}_0^s - \bar{G}_0^g = 0.250$$

Now we can express \bar{G}^s , \bar{G}^l , and \bar{G}^g in terms of a common zero of energy, \bar{G}_0^g , which we must do to compare them with each other and to plot them on the same graph. Show that

$$\bar{G}^s - \bar{G}_0^g = 0.600(P - 1) + 0.250$$

$$\bar{G}^l - \bar{G}_0^g = 0.850(P - 1)$$

$$\bar{G}^g - \bar{G}_0^g = 2.5 \ln P$$

Plot these on the same graph from $P = 0.100$ to 3.00 and compare your result with Figure 23.11.

We know from Chapter 22 that $(\partial\bar{G}/\partial P)_T = \bar{V}$. This means that (for an ideal gas)

$$\bar{G} - \bar{G}_0 = \int_{P_0}^P \bar{V} dP = RT \ln \frac{P}{P_0}$$

For the solid and liquid phases, \bar{V} is essentially constant with respect to pressure, and so $\bar{G} - \bar{G}_0 = \bar{V}(P - P_0)$. Therefore, we have

$$\bar{G}^s = 0.600(P - 1) + \bar{G}_0^s$$

$$\bar{G}^l = 0.850(P - 1) + \bar{G}_0^l$$

$$\bar{G}^g = RT \ln \frac{P}{P_0} + \bar{G}_0^g = 2.5 \ln P + \bar{G}_0^g$$

where the units are arbitrary. Now, at equilibrium, $\bar{G}^l = \bar{G}^g$. Since the solid and liquid are in equilibrium at $P = 2.00$ and the liquid and gas are in equilibrium at $P = 1.00$,

$$\bar{G}^s(P = 2.00) = \bar{G}^l(P = 2.00)$$

$$0.600 + \bar{G}_0^s = 0.850 + \bar{G}_0^l$$

$$\bar{G}_0^s - \bar{G}_0^l = 0.250$$

$$\bar{G}^l(P = 1.00) = \bar{G}^g(P = 1.00)$$

$$\bar{G}_0^l = \bar{G}_0^g$$

and so $\bar{G}_0^s - \bar{G}_0^g = 0.250$. Now substitute into the first equations we found:

$$\bar{G}^s = 0.600(P - 1) + \bar{G}_0^s = 0.600(P - 1) + 0.250 + \bar{G}_0^g$$

$$\bar{G}^s - \bar{G}_0^g = 0.600(P - 1) + 0.250$$

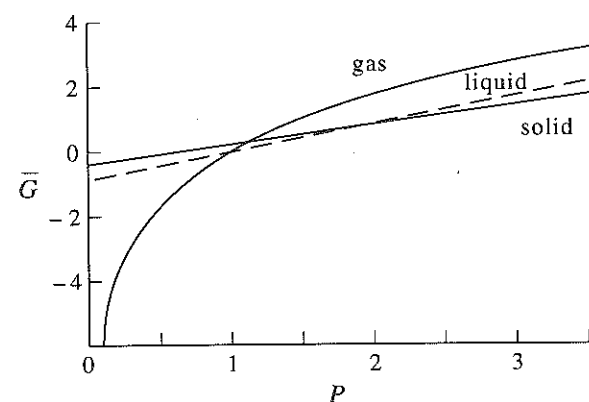
Also

$$\bar{G}^l - \bar{G}_0^g = 0.850(P - 1)$$

and

$$\bar{G}^g - \bar{G}_0^g = 2.5 \ln P$$

A plot of the Gibbs energies of the gas, liquid, and solid using \bar{G}_0^g as the zero of energy is shown:



Since we see a gas-liquid-solid progression, we are looking at a temperature less than the triple point temperature (as explained in the caption of Figure 23.11).

23-19. In this problem, we will demonstrate that entropy always increases when there is a material flow from a region of higher concentration to one of lower concentration. (Compare with Problems 22-41 and 22-42.) Consider a two-compartment system enclosed by rigid, impermeable, adiabatic walls, and let the two compartments be separated by a rigid, insulating, but permeable wall. We assume that the two compartments are in equilibrium but that they are not in equilibrium with each other. Show that

$$U_1 = \text{constant}, \quad U_2 = \text{constant}, \quad V_1 = \text{constant}, \quad V_2 = \text{constant},$$

and

$$n_1 + n_2 = \text{constant}$$

for this system. Now show that

$$dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dn$$

in general, and that

$$\begin{aligned} dS &= \left(\frac{\partial S_1}{\partial n_1}\right)dn_1 + \left(\frac{\partial S_2}{\partial n_2}\right)dn_2 \\ &= dn_1 \left(\frac{\mu_2}{T} - \frac{\mu_1}{T}\right) \geq 0 \end{aligned}$$

for this system. Use this result to discuss the direction of a (isothermal) material flow under a chemical potential difference.

The volume of each compartment cannot change, since the walls of the compartments are rigid. Thus $V_1 = \text{constant}$ and $V_2 = \text{constant}$. Since the walls are adiabatic, $\delta q = 0$ for the gases in each compartment. For both components of the system $\delta w = 0$, since there is no change in volume, so $dU = 0$ for both compartments. Thus $U_1 = \text{constant}$ and $U_2 = \text{constant}$. Finally, since the entire system is surrounded by impermeable walls, the total number of moles of gas in the system must remain constant, so $n_1 + n_2 = \text{constant}$.

We have defined $\mu = (\partial G/\partial n)_{P,T}$ (Equation 23.3), so $\mu dn = dG$. Now recall (Equation 22.13) that

$$G = U - TS + PV$$

$$dG = dU - TdS + PdV$$

$$\frac{\mu dn}{T} = \frac{dU}{T} - dS + \frac{P}{T}dV$$

$$dS = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dn$$

For this system, since $dU = dV = 0$,

$$dS_1 = -\frac{\mu_1}{T}dn_1, \quad dS_2 = -\frac{\mu_2}{T}dn_2$$

Then

$$\begin{aligned} dS_{\text{system}} &= dS_1 + dS_2 \\ &= \left(\frac{\partial S_1}{\partial n_1}\right)dn_1 + \left(\frac{\partial S_2}{\partial n_2}\right)dn_2 \\ &= -\frac{\mu_1}{T}dn_1 - \frac{\mu_2}{T}(-dn_1) \\ &= dn_1 \left(\frac{\mu_2}{T} - \frac{\mu_1}{T}\right) \end{aligned}$$

If molecules are flowing into compartment 1, then dn_1 is positive and $\mu_2 > \mu_1$ (since transfer occurs from the system with higher chemical potential to the system with lower chemical potential). Then both terms in the expression above are positive and $dS_{\text{system}} > 0$. If molecules are flowing into compartment 2, then dn_1 is negative and $\mu_2 < \mu_1$, making both terms negative and $dS_{\text{system}} > 0$. If dn_1 is 0 (no transfer occurs), then the two compartments are in equilibrium with respect to material flow, and $dS_{\text{system}} = 0$.

23-20. Determine the value of dT/dP for water at its normal boiling point of 373.15 K given that the molar enthalpy of vaporization is 40.65 kJ·mol⁻¹, and the densities of the liquid and vapor are 0.9584 g·L⁻¹ and 0.6010 g·mL⁻¹, respectively. Estimate the boiling point of water at 2 atm.

First find $\bar{V}^g - \bar{V}^l$:

$$\begin{aligned} \bar{V}^g - \bar{V}^l &= \left(\frac{1}{0.6010 \text{ g} \cdot \text{dm}^{-3}} - \frac{1}{958.4 \text{ g} \cdot \text{dm}^{-3}} \right) (18.015 \text{ g} \cdot \text{mol}^{-1}) \\ &= 29.96 \text{ dm}^3 \cdot \text{mol}^{-1} \end{aligned}$$

Now use Equation 23.10 to write

$$\begin{aligned} \frac{dT}{dP} &= \frac{T \Delta_{\text{vap}} \bar{V}}{\Delta_{\text{vap}} \bar{H}} \\ &= \frac{(373.15 \text{ K})(\bar{V}^g - \bar{V}^l)}{40\,650 \text{ J} \cdot \text{mol}^{-1}} \\ &= \left[\frac{(373.15 \text{ K})(29.96 \text{ dm}^3 \cdot \text{mol}^{-1})}{40\,650 \text{ J} \cdot \text{mol}^{-1}} \right] \left(\frac{8.314 \text{ J}}{0.08206 \text{ dm}^3 \cdot \text{atm}} \right) \\ &= 27.9 \text{ K} \cdot \text{atm}^{-1} \end{aligned}$$

To estimate the boiling point of water at 2 atm, we can find the change in temperature which accompanies a change in pressure of 1 atm (since we know the boiling point of water at 1 atm). That is $\Delta T = (27.9 \text{ K} \cdot \text{atm}^{-1})(1 \text{ atm}) = 27.9 \text{ K}$. Therefore, the boiling point of water at 2 atm is about 127.9°C .

- 23-21.** The orthobaric densities of liquid and gaseous ethyl acetate are $0.826 \text{ g} \cdot \text{mL}^{-1}$ and $0.00319 \text{ g} \cdot \text{mL}^{-1}$, respectively, at its normal boiling point (77.11°C). The rate of change of vapor pressure with temperature is $23.0 \text{ torr} \cdot \text{K}^{-1}$ at the normal boiling point. Estimate the molar enthalpy of vaporization of ethyl acetate at its normal boiling point.

First find $\bar{V}^g - \bar{V}^l$:

$$\bar{V}^g - \bar{V}^l = \left(\frac{1}{0.00319 \text{ g} \cdot \text{mL}^{-1}} - \frac{1}{0.826 \text{ g} \cdot \text{mL}^{-1}} \right) (88.102 \text{ g} \cdot \text{mol}^{-1})$$

$$\Delta_{\text{vap}} \bar{V} = 27\,510 \text{ cm}^3 \cdot \text{mol}^{-1} = 275.10 \text{ dm}^3 \cdot \text{mol}^{-1}$$

Now use Equation 23.10 to write

$$\Delta_{\text{vap}} \bar{H} = T \Delta_{\text{vap}} \bar{V} \left(\frac{dP}{dT} \right)$$

$$= (350.26 \text{ K})(275.10 \text{ dm}^3 \cdot \text{mol}^{-1})(23.0 \text{ torr} \cdot \text{K}^{-1}) \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{8.314 \text{ J}}{0.08206 \text{ L} \cdot \text{atm}} \right)$$

$$= 29.5 \text{ kJ} \cdot \text{mol}^{-1}$$

- 23-22.** The vapor pressure of mercury from 400°C to 1300°C can be expressed by

$$\ln(P/\text{torr}) = -\frac{7060.7 \text{ K}}{T} + 17.85$$

The density of the vapor at its normal boiling point is $3.82 \text{ g} \cdot \text{L}^{-1}$ and that of the liquid is $12.7 \text{ g} \cdot \text{mL}^{-1}$. Estimate the molar enthalpy of vaporization of mercury at its normal boiling point.

If we express P using the above equation, we find that

$$\frac{dP}{dT} = P \left(\frac{7060.7 \text{ K}}{T^2} \right)$$

At the boiling point and one atmosphere of pressure,

$$\frac{dP}{dT} = (760 \text{ torr}) \left[\frac{7060.7 \text{ K}}{(629.88 \text{ K})^2} \right] = 13.52 \text{ torr} \cdot \text{K}^{-1}$$

We find $\Delta_{\text{vap}} \bar{V}$ by subtracting \bar{V}^l from \bar{V}^g :

$$\bar{V}^g - \bar{V}^l = \left(\frac{1}{3.82 \text{ g} \cdot \text{dm}^{-3}} - \frac{1}{12700 \text{ g} \cdot \text{dm}^{-3}} \right) (200.59 \text{ g} \cdot \text{mol}^{-1})$$

$$\Delta_{\text{vap}} \bar{V} = 52.49 \text{ dm}^3 \cdot \text{mol}^{-1}$$

Now we use Equation 23.10 to estimate $\Delta_{\text{vap}} \bar{H}$.

$$\Delta_{\text{vap}} \bar{H} = T \Delta_{\text{vap}} \bar{V} \frac{dP}{dT}$$

$$= (629.88 \text{ K})(52.49 \text{ dm}^3 \cdot \text{mol}^{-1})(13.52 \text{ torr} \cdot \text{K}^{-1})$$

$$= 447\,200 \text{ dm}^3 \cdot \text{torr} \cdot \text{mol}^{-1} \left(\frac{1 \text{ atm}}{760 \text{ torr}} \right) \left(\frac{8.314 \text{ J}}{0.08206 \text{ dm}^3 \cdot \text{atm}} \right)$$

$$= 59.62 \text{ kJ} \cdot \text{mol}^{-1}$$

- 23-23.** The pressures at the solid-liquid coexistence boundary of propane are given by the empirical equation

$$P = -718 + 2.38565T^{1.283}$$

where P is in bars and T is in kelvins. Given that $T_{\text{fus}} = 85.46 \text{ K}$ and $\Delta_{\text{fus}} \bar{H} = 3.53 \text{ kJ} \cdot \text{mol}^{-1}$, calculate $\Delta_{\text{fus}} \bar{V}$ at 85.46 K .

At 85.46 K , the empirical equation gives

$$\frac{dP}{dT} = 3.06079(85.46)^{0.283} = 10.778 \text{ bar} \cdot \text{K}^{-1}$$

We substitute into Equation 23.10 to find

$$\Delta_{\text{fus}} \bar{V} = \frac{\Delta_{\text{fus}} \bar{H}}{T} \left(\frac{dP}{dT} \right)^{-1}$$

$$= \frac{35\,300 \text{ J} \cdot \text{mol}^{-1}}{85.46 \text{ K}} (10.778 \text{ bar} \cdot \text{K}^{-1}) \left(\frac{10 \text{ bar} \cdot \text{cm}^3}{1 \text{ J}} \right)$$

$$= 383 \text{ cm}^3 \cdot \text{mol}^{-1}$$

- 23-24.** Use the vapor pressure data given in Problem 23-7 and the density data given in Problem 23-13 to calculate $\Delta_{\text{vap}} \bar{H}$ for methanol from the triple point (175.6 K) to the critical point (512.6 K). Plot your result.

We are given ρ in units of $\text{mol} \cdot \text{dm}^{-3}$ in Problem 23-13 and P in units of bars in Problem 23-7. We want to find $\Delta_{\text{vap}} \bar{H}$ using Equation 23.10:

$$\Delta_{\text{vap}} \bar{H} = T \Delta_{\text{vap}} \bar{V} \frac{dP}{dT}$$

Taking the derivative of the expression for P given in Problem 23-7 gives us

$$\frac{dP}{dT} / \text{bar} \cdot \text{K}^{-1} = P \left[-0.0070297 - 0.0151634(1 - 0.00195084T)^{0.7} \right. \\ \left. + \frac{5511.91}{T^2} + 3.32871 \times 10^{-5}T - 5.30412 \times 10^{-8}T^2 \right]$$

Using $1/\rho^l$ for \bar{V}^l and $1/\rho^g$ for \bar{V}^g gives

$$\Delta_{\text{vap}} \bar{V} / \text{dm}^3 \cdot \text{mol}^{-1} = \frac{1}{\rho^g} - \frac{1}{\rho^l}$$

or (where $\Delta_{\text{vap}} \bar{V}$ is in units of $\text{dm}^3 \cdot \text{mol}^{-1}$)

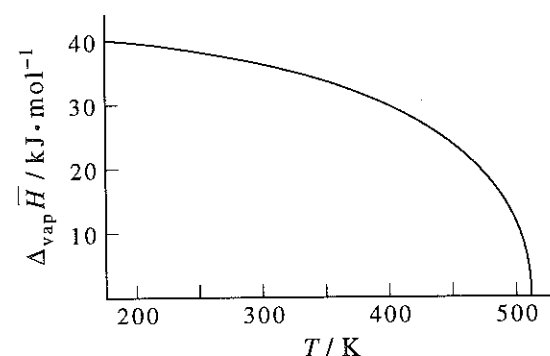
$$\Delta_{\text{vap}} \bar{V} = 0.119048 \exp \left[2.55668(1 - 0.0019508T)^{0.35} - 3.88145(1 - 0.0019508T) - 4.79557(1 - 0.0019508T)^2 + \frac{5443.65(1 - 0.0019508)}{T} \right] - 0.119048 \left[1 + 2.5171(1 - 0.0019508T)^{0.35} + 2.46669(1 - 0.0019508T) - 3.06682(1 - 0.0019508T)^2 + 1.32508(1 - 0.0019508T)^3 \right]^{-1}$$

Substituting these expressions into Equation 23.10 gives $\Delta_{\text{vap}} \bar{H}$ in units of $\text{dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1}$. To convert this to $\text{kJ} \cdot \text{mol}^{-1}$ we must divide by 10.

Now graph

$$\Delta_{\text{vap}} \bar{H} / \text{kJ} \cdot \text{mol}^{-1} = \frac{\Delta_{\text{vap}} \bar{V}}{10} \frac{dP}{dT} T$$

using the expressions found above for $\Delta_{\text{vap}} \bar{V}$ and dP/dT :

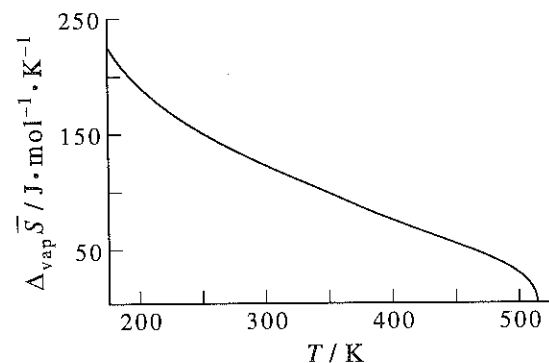


23-25. Use the result of the previous problem to plot $\Delta_{\text{vap}} \bar{S}$ of methanol from the triple point to the critical point.

Since at a transition point $\Delta_{\text{tr}} \bar{G} = 0$,

$$\frac{\Delta_{\text{vap}} \bar{H}}{T} = \Delta_{\text{vap}} \bar{S}$$

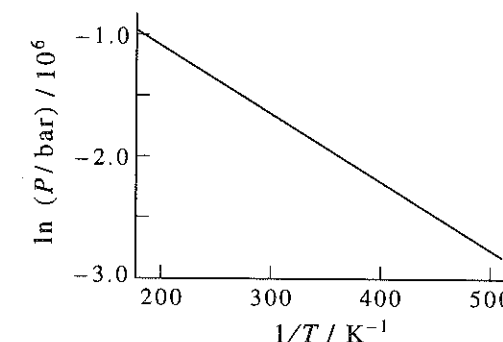
We can use the expression for $\Delta_{\text{vap}} \bar{H}$ given in Problem 23-24 (converting it to $\text{J} \cdot \text{mol}^{-1}$, since these are the usual units of entropy) to graph $\Delta_{\text{vap}} \bar{S}$.



Notice that $\Delta_{\text{vap}} \bar{S} \rightarrow 0$ as $T \rightarrow T_c$.

23-26. Use the vapor pressure data for methanol given in Problem 23-7 to plot $\ln P$ against $1/T$. Using your calculations from Problem 23-24, over what temperature range do you think the Clausius-Clapeyron equation will be valid?

Use the formula for $\ln P$ given in Problem 23-7 to plot $\ln P$ vs. $1/T$.



The slope of the line plotted should be constant for the Clausius-Clapeyron equation to be valid. It appears that the Clausius-Clapeyron equation is valid over the range plotted in Problem 23-31.

23-27. The molar enthalpy of vaporization of water is $40.65 \text{ kJ} \cdot \text{mol}^{-1}$ at its normal boiling point. Use the Clausius-Clapeyron equation to calculate the vapor pressure of water at 110°C . The experimental value is 1075 torr.

Assuming $\Delta_{\text{vap}} \bar{H}$ remains constant with respect to temperature over this ten-degree temperature range, we can use Equation 23.13:

$$\begin{aligned} \ln \frac{P_2}{P_1} &= \frac{\Delta_{\text{vap}} \bar{H}}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \\ \ln \frac{P_2}{1 \text{ atm}} &= \frac{40650 \text{ J} \cdot \text{mol}^{-1}}{8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} \left[\frac{10 \text{ K}}{(373.15 \text{ K})(383.15 \text{ K})} \right] \\ \ln (P_2 / \text{atm}) &= 0.342 \\ P_2 &= 1.408 \text{ atm} = 1070 \text{ torr} \end{aligned}$$

23-28. The vapor pressure of benzaldehyde is 400 torr at 154°C and its normal boiling point is 179°C . Estimate its molar enthalpy of vaporization. The experimental value is $42.50 \text{ kJ} \cdot \text{mol}^{-1}$.

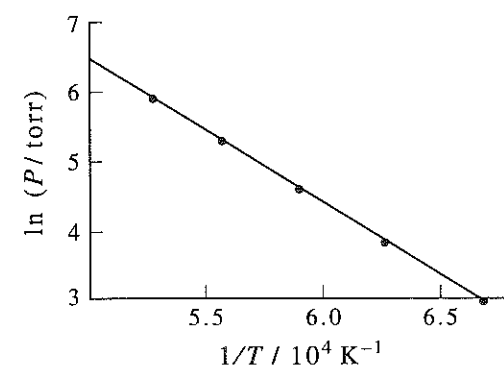
Again, assuming $\Delta_{\text{vap}} \bar{H}$ does not vary over this temperature range, we can use Equation 23.13.

$$\begin{aligned} \ln \frac{P_2}{P_1} &= \frac{\Delta_{\text{vap}} \bar{H}}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \\ \Delta_{\text{vap}} \bar{H} &= \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{P_2}{P_1} \\ &= \frac{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(427.15 \text{ K})(452.15 \text{ K})}{25 \text{ K}} \ln \frac{760}{400} \\ &= 41.2 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

23–29. Use the following data to estimate the normal boiling point and the molar enthalpy of vaporization of lead.

T/K	1500	1600	1700	1800	1900
P/torr	19.72	48.48	107.2	217.7	408.2

Plot $\ln P$ vs. $1/T$:



The equation for the line of best fit is $y = 17.3799 - 21597.6x$. At 1 atm (the normal boiling point pressure), $\ln 760 = y$ and so

$$17.3799 = 6.6333 + \frac{21597.6}{T}$$

$$T = 2010 \text{ K}$$

The normal boiling point is about 2010 K. Now recall that the slope of the plot we have created should be $-\Delta_{\text{vap}}\bar{H}/R$ (Equation 23.14). Then

$$\Delta_{\text{vap}}\bar{H} = (8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(21597.6 \text{ K}) = 179.6 \text{ kJ}\cdot\text{mol}^{-1}$$

23–30. The vapor pressure of solid iodine is given by

$$\ln(P/\text{atm}) = -\frac{8090.0 \text{ K}}{T} - 2.013 \ln(T/\text{K}) + 32.908$$

Use this equation to calculate the normal sublimation temperature and the molar enthalpy of sublimation of $\text{I}_2(\text{s})$ at 25°C . The experimental value of $\Delta_{\text{sub}}\bar{H}$ is $62.23 \text{ kJ}\cdot\text{mol}^{-1}$.

The sublimation temperature is found by setting $P = 1 \text{ atm}$ in the above equation:

$$0 = -\frac{8090.0 \text{ K}}{T_{\text{sub}}} - 2.013 \ln(T_{\text{sub}}/\text{K}) + 32.908$$

We can solve this equation for T using the Newton-Raphson method, and we find that $T_{\text{sub}} = 386.8 \text{ K}$.

We can now use the equation provided and Equation 23.12 to find the molar enthalpy of sublimation:

$$\frac{\Delta_{\text{sub}}\bar{H}}{RT^2} = \frac{d \ln P}{dT} = \frac{8090.0 \text{ K}}{T^2} - \frac{2.013}{T}$$

$$\Delta_{\text{sub}}\bar{H} = R(8090.0 \text{ K} - 2.013T)$$

At 25°C ,

$$\Delta_{\text{sub}}\bar{H} = (8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})[8090.0 \text{ K} - 2.013(298.15 \text{ K})] = 62.27 \text{ kJ}\cdot\text{mol}^{-1}$$

23–31. Fit the following vapor pressure data of ice to an equation of the form

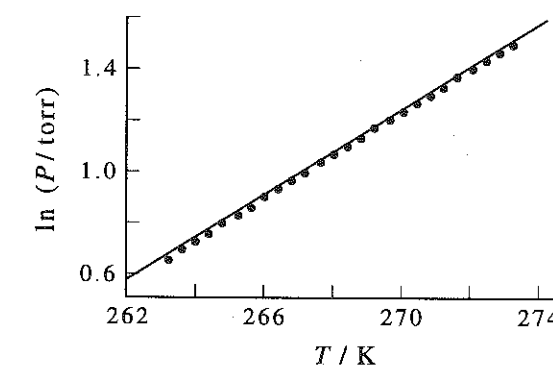
$$\ln P = -\frac{a}{T} + b \ln T + cT$$

where T is temperature in kelvins. Use your result to determine the molar enthalpy of sublimation of ice at 0°C .

$t/^\circ\text{C}$	P/torr	$t/^\circ\text{C}$	P/torr
-10.0	1.950	-4.8	3.065
-9.6	2.021	-4.4	3.171
-9.2	2.093	-4.0	3.280
-8.8	2.168	-3.6	3.393
-8.4	2.246	-3.2	3.509
-8.0	2.326	-2.8	3.630
-7.6	2.408	-2.4	3.753
-7.2	2.493	-2.0	3.880
-6.8	2.581	-1.6	4.012
-6.4	2.672	-1.2	4.147
-6.0	2.765	-0.8	4.287
-5.6	2.862	-0.4	4.431
-5.2	2.962	0.0	4.579

Fitting the data to an equation of this form gives

$$\ln P = -\frac{5686.7 \text{ K}}{T} + 4.4948 \ln T - (0.010527 \text{ K}^{-1}T)$$



Using this equation and Equation 23.12, we find that

$$\frac{\Delta_{\text{sub}}\bar{H}}{RT^2} = \frac{d \ln P}{dT} = \frac{5686.7 \text{ K}}{T^2} + \frac{4.4948}{T} - 0.010527 \text{ K}^{-1}$$

$$\Delta_{\text{sub}}\bar{H} = R[5686.7 \text{ K} + 4.4948T - (0.010527 \text{ K}^{-1})T^2]$$

At 0°C ,

$$\Delta_{\text{sub}}\bar{H} = (8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})[5686.7 \text{ K} + 4.4948(273.15 \text{ K}) - (0.010527 \text{ K}^{-1})(273.15 \text{ K})^2]$$

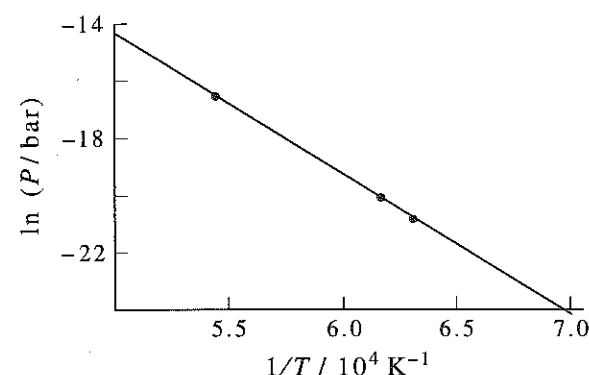
$$= 50.96 \text{ kJ}\cdot\text{mol}^{-1}$$

23–32. The following table gives the vapor pressure data for liquid palladium as a function of temperature:

T/K	P/bar
1587	1.002×10^{-9}
1624	2.152×10^{-9}
1841	7.499×10^{-8}

Estimate the molar enthalpy of vaporization of palladium.

Plot $\ln P$ vs. $1/T$:



The line of best fit is $y = 10.4359 - 49407x$. Since the slope of this line is equal to $-\Delta_{\text{vap}}\bar{H}/R$,

$$\Delta_{\text{vap}}\bar{H} = (49407 \text{ K})(8.31451 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) = 410.8 \text{ kJ}\cdot\text{mol}^{-1}$$

23–33. The sublimation pressure of CO_2 at 138.85 K and 158.75 K is 1.33×10^{-3} bar and 2.66×10^{-2} bar, respectively. Estimate the molar enthalpy of sublimation of CO_2 .

Substitute into Equation 23.13:

$$\begin{aligned} \ln \frac{P_2}{P_1} &= \frac{\Delta_{\text{sub}}\bar{H}}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right) \\ \Delta_{\text{sub}}\bar{H} &= (8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \ln \left(\frac{2.66 \times 10^{-2}}{1.33 \times 10^{-3}} \right) \left[\frac{(138.85 \text{ K})(158.75 \text{ K})}{19.9 \text{ K}} \right] \\ &= 27.6 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

23–34. The vapor pressures of solid and liquid hydrogen iodide can be expressed empirically as

$$\ln(P^s/\text{torr}) = -\frac{2906.2 \text{ K}}{T} + 19.020$$

and

$$\ln(P^l/\text{torr}) = -\frac{2595.7 \text{ K}}{T} + 17.572$$

Calculate the ratio of the slopes of the solid-gas curve and the liquid-gas curve at the triple point.

We can write the slopes of the solid-gas and liquid-gas curves as

$$\frac{dP^s}{dT} = P^s \left(\frac{2906.2 \text{ K}}{T^2} \right) \quad \text{and} \quad \frac{dP^l}{dT} = P^l \left(\frac{2595.7 \text{ K}}{T^2} \right)$$

where pressures are in units of torr. Since $P^s = P^l$ at the triple point, the ratio of the slopes at the triple point is

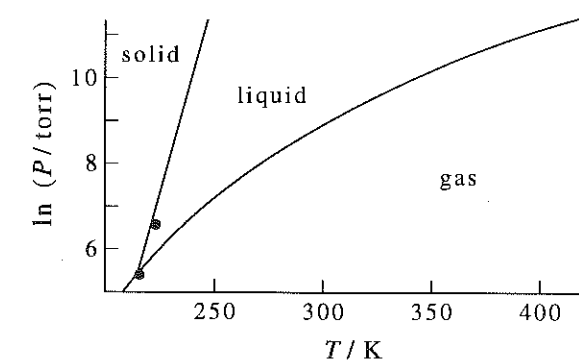
$$\frac{dP^s/dT}{dP^l/dT} = \frac{2906.2 \text{ K}}{2595.7 \text{ K}} = 1.120$$

23–35. Given that the normal melting point, the critical temperature, and the critical pressure of hydrogen iodide are 222 K, 424 K and 82.0 atm, respectively, use the data in the previous problem to sketch the phase diagram of hydrogen iodide.

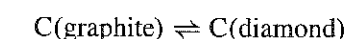
The triple point is located where the solid and liquid vapor pressures are the same, so at the triple point

$$\begin{aligned} 19.020 - \frac{2906.2 \text{ K}}{T_{\text{tp}}} &= 17.572 - \frac{2595.7 \text{ K}}{T_{\text{tp}}} \\ 1.448 T_{\text{tp}} &= 310.5 \text{ K} \\ T_{\text{tp}} &= 214.43 \text{ K} \end{aligned}$$

Substituting to solve for P_{tp} , we find that $P_{\text{tp}} = 236.8$ torr. We also know that the normal melting point of HI is 222 K, so we can produce a phase diagram of hydrogen iodide by plotting the line between the solid and gas, the line between the vapor and gas, the critical point, the triple point, and the normal melting point. Note that the equation for the liquid-gas line is not completely accurate at high temperatures and pressures (it does not intersect the critical point).



23–36. Consider the phase change



Given that $\Delta_r G^\circ/\text{J}\cdot\text{mol}^{-1} = 1895 + 3.363T$, calculate $\Delta_r H^\circ$ and $\Delta_r S^\circ$. Calculate the pressure at which diamond and graphite are in equilibrium with each other at 25°C . Take the density of diamond and graphite to be $3.51 \text{ g}\cdot\text{cm}^{-3}$ and $2.25 \text{ g}\cdot\text{cm}^{-3}$, respectively. Assume that both diamond and graphite are incompressible.

To find the standard molar Gibbs entropy, we use the Maxwell relation (Equation 22.46)

$$\Delta_r \bar{S}^\circ = - \left(\frac{\partial \Delta_r \bar{G}^\circ}{\partial T} \right)_P = -3.363 \text{ J} \cdot \text{mol}^{-1}$$

Substituting into $\Delta_r \bar{G}^\circ = \Delta_r \bar{H}^\circ - T \Delta_r \bar{S}^\circ$ (Equation 22.13), we find that $\Delta_r \bar{H}^\circ = 1895 \text{ J} \cdot \text{mol}^{-1}$. Because both graphite and diamond are incompressible, we can write (as in Problem 23-18)

$$\bar{G}_{\text{graph}}^\circ = \bar{G}_{\text{graph}}^\circ + \bar{V}_{\text{graph}}(P - P_0)$$

and

$$\bar{G}_{\text{diam}}^\circ = \bar{G}_{\text{diam}}^\circ + \bar{V}_{\text{diam}}(P - P_0)$$

Combining these two equations gives

$$\Delta_r \bar{G}^\circ = \Delta_r \bar{G}^\circ + (\bar{V}_{\text{diam}} - \bar{V}_{\text{graph}})(P - P_0)$$

When graphite and diamond are in equilibrium, $\Delta_r \bar{G}^\circ = 0$. Substituting into the equation given in the problem, we see that at 25°C, $\Delta_r \bar{G}^\circ = 2898 \text{ J} \cdot \text{mol}^{-1}$. Then

$$\begin{aligned} 0 &= \Delta_r \bar{G}^\circ + \left(\frac{1}{3510 \text{ g} \cdot \text{dm}^{-3}} - \frac{1}{2250 \text{ g} \cdot \text{dm}^{-3}} \right) (12.01 \text{ g} \cdot \text{mol}^{-1})(P - 1 \text{ bar}) \\ &= 2898 \text{ J} \cdot \text{mol}^{-1} - (1.916 \times 10^{-3} \text{ dm}^3 \cdot \text{mol}^{-1})(P - 1 \text{ bar}) \\ P &= \frac{1}{1.916 \times 10^{-3} \text{ dm}^3 \cdot \text{mol}^{-1}} (2898 \text{ J} \cdot \text{mol}^{-1}) \left(\frac{0.08206 \text{ dm}^3 \cdot \text{bar}}{8.3145 \text{ J}} \right) + 1 \text{ bar} \\ &= 15\,000 \text{ bar} \end{aligned}$$

23-37. Use Equation 23.36 to calculate $\mu^\circ - E_0$ for Kr(g) at 298.15 K. The literature value is $-42.72 \text{ kJ} \cdot \text{mol}^{-1}$.

$$\mu^\circ - E_0 = -RT \ln \left[\left(\frac{q^0}{V} \right) \frac{k_B T}{P^\circ} \right] \quad (23.36)$$

We do this in the same way we found $\mu^\circ - E_0$ for Ar(g) in Section 23-5. First,

$$\begin{aligned} \frac{q^0(V, T)}{V} &= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \\ &= \left[\frac{(2\pi)(1.391 \times 10^{-25} \text{ kg} \cdot \text{mol}^{-1})(1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(298.15 \text{ K})}{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \\ &= 7.422 \times 10^{32} \text{ m}^{-3} \\ \frac{k_B T}{P^\circ} &= \frac{(1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(298.15 \text{ K})}{1.0 \times 10^5 \text{ Pa}} = 4.116 \times 10^{-26} \text{ m}^{-3} \end{aligned}$$

Substituting into Equation 23.34 gives

$$\begin{aligned} \mu^\circ - E_0 &= -RT \ln \left[\left(\frac{q^0}{V} \right) \frac{k_B T}{P^\circ} \right] \\ &= -R(298.15 \text{ K}) \ln[(7.422 \times 10^{32} \text{ m}^{-3})(4.116 \times 10^{-26} \text{ m}^{-3})] \\ &= -4.272 \times 10^4 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

23-38. Show that Equations 23.30 and 23.32 for $\mu(T, P)$ for a monatomic ideal gas are equivalent to using the relation $\bar{G} = \bar{H} - T\bar{S}$ with $\bar{H} = 5RT/2$ and \bar{S} given by Equation 20.45.

Recall that μ for a pure substance is \bar{G} . Equation 20.45 is

$$\bar{S} = \frac{5}{2}R + R \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{\bar{V}}{N_A} \right]$$

Therefore,

$$\begin{aligned} \bar{G} &= \bar{H} - T\bar{S} = \frac{5RT}{2} - TS \\ &= \frac{5RT}{2} - \frac{5RT}{2} - RT \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P} \right] \\ &= -RT \ln \left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P} \right] + RT \ln P \\ &= -RT \ln \left[\left(\frac{q^0}{V} \right) k_B T \right] + RT \ln P \end{aligned}$$

This is Equation 23.30. Equation 23.32 appears when we substitute $P^\circ = 1 \text{ bar}$ into this equation.

23-39. Use Equation 23.37 and the molecular parameters in Table 18.2 to calculate $\mu^\circ - E_0$ for $\text{N}_2(\text{g})$ at 298.15 K. The literature value is $-48.46 \text{ kJ} \cdot \text{mol}^{-1}$.

$$\begin{aligned} \frac{q^0}{V} &= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} \\ &= \left[\frac{2\pi(4.65 \times 10^{-26} \text{ kg} \cdot \text{mol}^{-1})k_B(298.15 \text{ K})}{h^2} \right]^{3/2} \frac{298.15 \text{ K}}{2(2.88 \text{ K})} \frac{1}{1 - e^{-3374/298.15}} \\ &= 7.42 \times 10^{33} \text{ m}^{-3} \\ \frac{RT}{N_A P^\circ} &= 4.116 \times 10^{-26} \text{ m}^3 \end{aligned}$$

where use the value of $RT/N_A P^\circ$ from Problem 23-36, since the fraction $RT/N_A P^\circ$ is independent of the substance. Now, substituting, we see that

$$\begin{aligned} \mu^\circ - E_0 &= -RT \ln \left[\left(\frac{q^0}{V} \right) \frac{RT}{N_A P^\circ} \right] \\ &= -R(298.15 \text{ K}) \ln[(7.42 \times 10^{33} \text{ m}^{-3})(4.116 \times 10^{-26} \text{ m}^3)] \\ &= -48.43 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

23-40. Use Equation 23.37 and the molecular parameters in Table 18.2 to calculate $\mu^\circ - E_0$ for $\text{CO}(\text{g})$ at 298.15 K. The literature value is $-50.26 \text{ kJ} \cdot \text{mol}^{-1}$.

23-40. Use Equation 23.37 and the molecular parameters in Table 18.2 to calculate $\mu^\circ - E_0$ for CO(g) at 298.15 K. The literature value is $-50.26 \text{ kJ} \cdot \text{mol}^{-1}$.

$$\begin{aligned} \frac{q^0}{V} &= \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} \\ &= \left[\frac{2\pi (4.65 \times 10^{-26} \text{ kg} \cdot \text{mol}^{-1}) k_B (298.15 \text{ K})}{h^2} \right]^{3/2} \frac{298.15 \text{ K}}{2(2.77 \text{ K})} \frac{1}{1 - e^{-3103/298.15}} \\ &= 1.54 \times 10^{34} \text{ m}^{-3} \\ \frac{RT}{N_A P^\circ} &= 4.116 \times 10^{-26} \text{ m}^3 \end{aligned}$$

Now, substituting, we see that

$$\begin{aligned} \mu^\circ - E_0 &= -RT \ln \left[\left(\frac{q^0}{V} \right) \frac{RT}{N_A P^\circ} \right] \\ &= -R(298.15 \text{ K}) \ln[(1.54 \times 10^{34} \text{ m}^{-3})(4.116 \times 10^{-26} \text{ m}^3)] \\ &= -50.25 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

23-41. Use Equation 18.60 [without the factor of $\exp(D_e/k_B T)$] and the molecular parameters in Table 18.4 to calculate $\mu^\circ - E_0$ for CH₄(g) at 298.15 K. The literature value is $-45.51 \text{ kJ} \cdot \text{mol}^{-1}$.

$$\frac{q}{V} = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{\text{rot,A}} \Theta_{\text{rot,B}} \Theta_{\text{rot,C}}} \right)^{1/2} \left[\prod_{j=1}^9 \frac{e^{-\Theta_{\text{vib},j}/2T}}{(1 - e^{-\Theta_{\text{vib},j}/T})} \right] \quad (18.60)$$

The ground-state energy must be considered for each vibrational state, so, in analogy to the derivation of q^0 in Section 23-5,

$$\begin{aligned} \frac{q^0}{V} &= \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{\text{rot,A}} \Theta_{\text{rot,B}} \Theta_{\text{rot,C}}} \right)^{1/2} \left[\prod_{j=1}^9 \frac{1}{(1 - e^{-\Theta_{\text{vib},j}/T})} \right] \\ &= 2.30 \times 10^{33} \text{ m}^{-3} \\ \frac{RT}{N_A P^\circ} &= 4.116 \times 10^{-26} \text{ m}^3 \\ \mu^\circ - E_0 &= -RT \ln \left[\left(\frac{q^0}{V} \right) \frac{RT}{N_A P^\circ} \right] \\ &= -R(298.15 \text{ K}) \ln[(2.30 \times 10^{33} \text{ m}^{-3})(4.116 \times 10^{-26} \text{ m}^3)] \\ &= -45.53 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

23-42. When we refer to the equilibrium vapor pressure of a liquid, we tacitly assume that some of the liquid has evaporated into a vacuum and that equilibrium is then achieved. Suppose, however, that we are able by some means to exert an additional pressure on the surface of the liquid. One way to do this is to introduce an insoluble, inert gas into the space above the liquid. In this problem, we will investigate how the equilibrium vapor pressure of a liquid depends upon the total pressure exerted on it.

Consider a liquid and a vapor in equilibrium with each other, so that $\mu^l = \mu^g$. Show that

$$\bar{V}^l dP^l = \bar{V}^g dP^g$$

because the two phases are at the same temperature. Assuming that the vapor may be treated as an ideal gas and that \bar{V}^l does not vary appreciably with pressure, show that

$$\ln \frac{P^g(\text{at } P^l = P)}{P^g(\text{at } P^l = 0)} = \frac{\bar{V}^l P^l}{RT}$$

Use this equation to calculate the vapor pressure of water at a total pressure of 10.0 atm at 25°C. Take $P^g(\text{at } P^l = 0) = 0.0313 \text{ atm}$.

We start with the fact that $\mu^l = \mu^g$. Since μ can be written as a function of T and P , and since the temperature does not change, we can write

$$d\mu^l = \left(\frac{\partial \bar{G}}{\partial P} \right) dP^l = \bar{V}^l dP^l$$

Likewise, $d\mu^g = \bar{V}^g dP^g$, and so

$$\bar{V}^l dP^l = \bar{V}^g dP^g$$

follows naturally from the initial assumption. Now we assume that the vapor can be treated as an ideal gas and that \bar{V}^l does not vary with respect to pressure, so

$$\begin{aligned} \bar{V}^l dP^l &= \frac{RT}{P^g} dP^g \\ \frac{\bar{V}^l}{RT} dP^l &= \frac{dP^g}{P^g} \\ \frac{\bar{V}^l}{RT} \int_0^P dP^l &= \int_{P^g(P^l=0)}^{P^g(P^l=P)} \frac{dP^g}{P^g} \\ \frac{\bar{V}^l P}{RT} &= \ln \frac{P^g(P^l = P)}{P^g(P^l = 0)} \end{aligned}$$

The specific density of water is $1 \text{ g} \cdot \text{cm}^{-3}$, so $\bar{V} = 0.018 \text{ dm}^3 \cdot \text{mol}^{-1}$. For water at a total pressure of 10.0 atm at 298.15 K, since the vapor pressure of water expanding into a vacuum is 0.0313 atm at 298.15 K,

$$\begin{aligned} \ln \frac{P^g(P^l = P)}{0.0313 \text{ atm}} &= \frac{\bar{V}^l P^l}{R(298.15 \text{ K})} \\ \ln \frac{P^g(P^l = P)}{0.0313 \text{ atm}} &= \frac{(0.018 \text{ dm}^3 \cdot \text{mol}^{-1})(10.0 \text{ atm})}{(0.082058 \text{ dm}^3 \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})} \\ \frac{P^g}{0.0313 \text{ atm}} &= 1.007 \\ P^g &= 0.0315 \text{ atm} \end{aligned}$$

The vapor pressure of water at a total pressure 10.0 atm at 298.15 K is 0.0315 atm, or a change of $2 \times 10^{-4} \text{ atm}$.

23-43. Using the fact that the vapor pressure of a liquid does not vary appreciably with the total pressure, show that the final result of the previous problem can be written as

$$\frac{\Delta P^g}{P^g} = \frac{\bar{V}^l P^l}{RT}$$

Hint: Let $P^g(\text{at } P = P^l) = P^g(\text{at } P = 0) + \Delta P$ and use the fact that ΔP is small. Calculate ΔP for water at a total pressure of 10.0 atm at 25°C. Compare your answer with the one you obtained in the previous problem.

$$\ln \frac{P^g(P^l = P)}{P^g(P^l = 0)} = \frac{\bar{V}^l P^l}{RT}$$

$$\ln \frac{P^g(P^l = 0) + \Delta P^g}{P^g(P^l = 0)} = \frac{\bar{V}^l P^l}{RT}$$

Use the relation $\ln(1+x) \approx x$ when x is small to obtain

$$\ln \left(1 + \frac{\Delta P^g}{P^g} \right) = \frac{\bar{V}^l P^l}{RT}$$

$$\ln \frac{\Delta P^g}{P^g} = \frac{\bar{V}^l P^l}{RT}$$

Again, the vapor pressure of water expanding into a vacuum is 0.0313 atm at 298.15 K and $\bar{V} = 0.018 \text{ dm}^3 \cdot \text{mol}^{-1}$, so

$$\frac{\Delta P^g}{P^g} = \frac{\bar{V}^l P^l}{RT}$$

$$\Delta P^g = \frac{(0.0313 \text{ atm})(0.018 \text{ dm}^3 \cdot \text{mol}^{-1})(10.0 \text{ atm})}{(0.082058 \text{ dm}^3 \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})}$$

$$= 2.30 \times 10^{-4} \text{ atm}$$

This would give a vapor pressure of 0.0315 atm, as in the previous problem.

23–44. In this problem, we will show that the vapor pressure of a droplet is not the same as the vapor pressure of a relatively large body of liquid. Consider a spherical droplet of liquid of radius r in equilibrium with a vapor at a pressure P , and a flat surface of the same liquid in equilibrium with a vapor at a pressure P_0 . Show that the change in Gibbs energy for the isothermal transfer of dn moles of the liquid from the flat surface to the droplet is

$$dG = dnRT \ln \frac{P}{P_0}$$

This change in Gibbs energy is due to the change in surface energy of the droplet (the change in surface energy of the large, flat surface is negligible). Show that

$$dnRT \ln \frac{P}{P_0} = \gamma dA$$

where γ is the surface tension of the liquid and dA is the change in the surface area of a droplet. Assuming the droplet is spherical, show that

$$dn = \frac{4\pi r^2 dr}{\bar{V}^l}$$

$$dA = 8\pi r dr$$

and finally that

$$\ln \frac{P}{P_0} = \frac{2\gamma \bar{V}^l}{rRT} \quad (1)$$

Because the right side is positive, we see that the vapor pressure of a droplet is greater than that of a planar surface. What if $r \rightarrow \infty$?

For an isothermal process involving an ideal gas,

$$\Delta G = nRT \ln \frac{P_2}{P_1} \quad (22.58)$$

When a small amount of Gibbs energy goes from the flat surface (of vapor pressure P_0) to the droplet (with vapor pressure P), corresponding to adding dn moles to the droplet from the flat surface, the change in Gibbs energy dG is

$$G(\text{droplet}) - G(\text{surface}) = dnRT \ln \frac{P}{P_1} - dnRT \ln \frac{P_0}{P_1}$$

where P_1 is an arbitrary reference pressure. Therefore, we have

$$dG = dnRT \ln \frac{P}{P_0}$$

This change in surface energy is equal to γdA , so

$$dnRT \ln \frac{P}{P_0} = \gamma dA$$

If a spherical droplet contains n moles, then

$$n\bar{V}^l = \frac{4}{3}\pi r^3$$

$$dn = \frac{4\pi r^2 dr}{\bar{V}^l}$$

$$A = 4\pi r^2$$

$$dA = 8\pi r dr$$

Substituting these expressions back into $dnRT \ln(P/P_0) = \gamma dA$, we find that

$$\frac{4\pi r^2 dr}{\bar{V}^l} RT \ln \frac{P}{P_0} = \gamma 8\pi r dr$$

$$\ln \frac{P}{P_0} = \frac{2\gamma \bar{V}^l}{rRT}$$

If $r \rightarrow \infty$, then $\ln(P/P_0) \rightarrow 0$: the spherical droplet becomes more and more like the flat surface.

23–45. Use Equation 1 of Problem 23–44 to calculate the vapor pressure at 25°C of droplets of water of radius $1.0 \times 10^{-5} \text{ cm}$. Take the surface tension of water to be $7.20 \times 10^{-4} \text{ J} \cdot \text{m}^{-2}$.

$$\ln \frac{P}{P_0} = \frac{2\gamma \bar{V}^l}{rRT}$$

$$\ln \frac{P}{0.0313 \text{ atm}} = \frac{2(7.20 \times 10^{-4} \text{ J} \cdot \text{m}^{-2})(18.0 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1})}{(1.0 \times 10^{-7} \text{ m})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})} = 1.046 \times 10^{-4}$$

Solving for P , we find that

$$P = (0.0313 \text{ atm})e^{1.046 \times 10^{-4}} = 0.0313 \text{ atm}$$

The vapor pressure of these droplets of water is not significantly different from the vapor pressure of water in a surface.

23-46. Figure 23.15 shows reduced pressure, P_R , plotted against reduced volume, \bar{V}_R , for the van der Waals equation at a reduced temperature, T_R , of 0.85. The so-called van der Waals loop apparent in the figure will occur for any reduced temperature less than unity and is a consequence of the simplified form of the van der Waals equation. It turns out that any analytic equation of state (one that can be written as a Maclaurin expansion in the reduced density, $1/\bar{V}_R$) will give loops for subcritical temperatures ($T_R < 1$). The correct behavior as the pressure is increased is given by the path abdfg in Figure 23.15. The horizontal region bdf, not given by the van der Waals equation, represents the condensation of the gas to a liquid at a fixed pressure. We can draw the horizontal line (called a *tie line*) at the correct position by recognizing that the chemical potentials of the liquid and the vapor must be equal at the points b and f. Using this requirement, Maxwell showed that the horizontal line representing condensation should be drawn such that the areas of the loops above and below the line must be equal. To prove *Maxwell's equal-area construction rule*, integrate $(\partial\mu/\partial P)_T = \bar{V}$ by parts along the path bcdef and use the fact that μ^l (the value of μ at point f) $= \mu^g$ (the value of μ at point b) to obtain

$$\begin{aligned}\mu^l - \mu^g &= P_0(\bar{V}^l - \bar{V}^g) - \int_{bcdef} P d\bar{V} \\ &= \int_{bcdef} (P_0 - P) d\bar{V}\end{aligned}$$

where P_0 is the pressure corresponding to the tie line. Interpret this result.

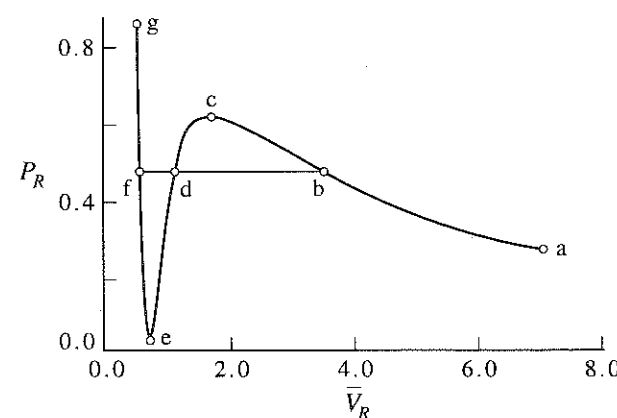


FIGURE 23.15

A plot of reduced pressure, P_R , versus reduced volume, \bar{V}_R , for the van der Waals equation at a reduced temperature, T_R , of 0.85.

Start with the equation

$$\int_{bcdef} d\mu = \int_{bcdef} \bar{V} dP$$

and integrate by parts to obtain

$$\mu^l - \mu^g = P_0(\bar{V}^l - \bar{V}^g) - \int_{bcdef} P d\bar{V}$$

Now combine the two terms on the right to get

$$\mu^l - \mu^g = \int_{bcdef} (P_0 - P) d\bar{V}$$

Now $\mu^l = \mu^g$, so

$$\int_{bcdef} (P_0 - P) d\bar{V} = 0$$

or the specified area in a plot of P against \bar{V} is equal to zero.

23-47. The isothermal compressibility, κ_T , is defined by

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

Because $(\partial P/\partial V)_T = 0$ at the critical point, κ_T diverges there. A question that has generated a great deal of experimental and theoretical research is the question of the manner in which κ_T diverges as T approaches T_c . Does it diverge as $\ln(T - T_c)$ or perhaps as $(T - T_c)^{-\gamma}$ where γ is some *critical exponent*? An early theory of the behavior of thermodynamic functions such as κ_T very near the critical point was proposed by van der Waals, who predicted that κ_T diverges as $(T - T_c)^{-1}$. To see how van der Waals arrived at this prediction, we consider the (double) Taylor expansion of the pressure $P(\bar{V}, T)$ about T_c and \bar{V}_c :

$$\begin{aligned}P(\bar{V}, T) &= P(\bar{V}_c, T_c) + (T - T_c) \left(\frac{\partial P}{\partial T} \right)_c + \frac{1}{2} (T - T_c)^2 \left(\frac{\partial^2 P}{\partial T^2} \right)_c \\ &\quad + (T - T_c)(\bar{V} - \bar{V}_c) \left(\frac{\partial^2 P}{\partial V \partial T} \right)_c + \frac{1}{6} (\bar{V} - \bar{V}_c)^3 \left(\frac{\partial^3 P}{\partial \bar{V}^3} \right)_c + \dots\end{aligned}$$

Why are there no terms in $(\bar{V} - \bar{V}_c)$ or $(\bar{V} - \bar{V}_c)^2$? Write this Taylor series as

$$P = P_c + a(T - T_c) + b(T - T_c)^2 + c(T - T_c)(\bar{V} - \bar{V}_c) + d(\bar{V} - \bar{V}_c)^3 + \dots$$

Now show that

$$\left(\frac{\partial P}{\partial \bar{V}} \right)_T = c(T - T_c) + 3d(\bar{V} - \bar{V}_c)^2 + \dots \quad \left(\begin{matrix} T \rightarrow T_c \\ \bar{V} \rightarrow \bar{V}_c \end{matrix} \right)$$

and that

$$\kappa_T = \frac{-1/\bar{V}}{c(T - T_c) + 3d(\bar{V} - \bar{V}_c)^2 + \dots}$$

Now let $\bar{V} = \bar{V}_c$ to obtain

$$\kappa_T \propto \frac{1}{T - T_c} \quad T \rightarrow (T_c)$$

Accurate experimental measurements of κ_T as $T \rightarrow T_c$ suggest that κ_T diverges a little more strongly than $(T - T_c)^{-1}$. In particular, it is found that $\kappa_T \rightarrow (T - T_c)^{-\gamma}$ where $\gamma = 1.24$. Thus, the theory of van der Waals, although qualitatively correct, is not quantitatively correct.

The Taylor expansion of $P(\bar{V}, T)$ about T_c and \bar{V}_c is

$$\begin{aligned}P(\bar{V}, T) &= P(\bar{V}_c, T_c) + (T - T_c) \left(\frac{\partial P}{\partial T} \right)_c + (\bar{V} - \bar{V}_c) \left(\frac{\partial P}{\partial \bar{V}} \right)_c \\ &\quad + \frac{1}{2} (T - T_c)^2 \left(\frac{\partial^2 P}{\partial T^2} \right)_c + (T - T_c)(\bar{V} - \bar{V}_c) \left(\frac{\partial^2 P}{\partial \bar{V} \partial T} \right)_c \\ &\quad + \frac{1}{2} (\bar{V} - \bar{V}_c)^2 \left(\frac{\partial^2 P}{\partial \bar{V}^2} \right)_c + \frac{1}{6} (\bar{V} - \bar{V}_c)^3 \left(\frac{\partial^3 P}{\partial \bar{V}^3} \right)_c + \dots\end{aligned}$$

However, recall from Section 16-3 that, at the critical point, $(\partial P / \partial \bar{V})_c = (\partial^2 P / \partial \bar{V}^2)_c = 0$. Thus, the Taylor expansion becomes

$$\begin{aligned} P &= P(\bar{V}_c, T_c) + (T - T_c) \left(\frac{\partial P}{\partial T} \right)_c + \frac{1}{2} (T - T_c)^2 \left(\frac{\partial^2 P}{\partial T^2} \right)_c \\ &\quad + (T - T_c)(\bar{V} - \bar{V}_c) \left(\frac{\partial^2 P}{\partial \bar{V} \partial T} \right)_c + \frac{1}{6} (\bar{V} - \bar{V}_c)^3 \left(\frac{\partial^3 P}{\partial \bar{V}^3} \right)_c + \dots \\ &= P_c + a(T - T_c) + b(T - T_c)^2 + c(T - T_c)(\bar{V} - \bar{V}_c) \\ &\quad + d(\bar{V} - \bar{V}_c)^3 + \dots \\ \left(\frac{\partial P}{\partial \bar{V}} \right)_T &= c(T - T_c) + 3d(\bar{V} - \bar{V}_c)^2 + \dots \end{aligned}$$

Note that in differentiating, we truncated our expansion and dropped terms of $O[(\bar{V} - \bar{V}_c)^4]$, $O[(T - T_c)^3]$, and third-order terms of $O[(\bar{V} - \bar{V}_c)^3(T - T_c)]$. Our partial derivative is thus accurate to $O[(\bar{V} - \bar{V}_c)^4]$ and $O[(T - T_c)^3]$. We can truncate these terms because when $\bar{V} \rightarrow \bar{V}_c$ and $T \rightarrow T_c$ the higher-order terms become negligible, so we find

$$\begin{aligned} \kappa_T &= -\frac{1}{\bar{V}} \left(\frac{\partial P}{\partial \bar{V}} \right)_T^{-1} \\ &= -\frac{1}{\bar{V}} \left[\frac{1}{c(T - T_c) + 3d(\bar{V} - \bar{V}_c)^2 + \dots} \right] \quad T \rightarrow T_c, \quad \bar{V} \rightarrow \bar{V}_c \end{aligned}$$

Letting $\bar{V} = \bar{V}_c$, we find that

$$\begin{aligned} \kappa_T &= -\frac{1}{\bar{V}_c c(T - T_c)} \\ \kappa_T &\propto \frac{1}{(T - T_c)} \quad T \rightarrow T_c \end{aligned}$$

Again, this expression is only accurate to $O[(T - T_c)^2]$.

23-48. We can use the ideas of the previous problem to predict how the difference in the densities (ρ^l and ρ^g) of the coexisting liquid and vapor states (*orthobaric densities*) behave as $T \rightarrow T_c$. Substitute

$$P = P_c + a(T - T_c) + b(T - T_c)^2 + c(T - T_c)(\bar{V} - \bar{V}_c) + d(\bar{V} - \bar{V}_c)^3 + \dots \quad (1)$$

into the Maxwell equal-area construction (Problem 23-46) to get

$$\begin{aligned} P_0 &= P_c + a(T - T_c) + b(T - T_c)^2 + \frac{c}{2}(T - T_c)(\bar{V}^l + \bar{V}^g - 2\bar{V}_c) \\ &\quad + \frac{d}{4}[(\bar{V}^g - \bar{V}_c)^2 + (\bar{V}^l - \bar{V}_c)^2](\bar{V}^l + \bar{V}^g - 2\bar{V}_c) + \dots \quad (2) \end{aligned}$$

For $P < P_c$, Equation 1 gives loops and so has three roots, \bar{V}^l , \bar{V}_c , and \bar{V}^g for $P = P_0$. We can obtain a first approximation to these roots by assuming that $\bar{V}_c \approx \frac{1}{2}(\bar{V}^l + \bar{V}^g)$ in Equation 2 and writing

$$P_0 = P_c + a(T - T_c) + b(T - T_c)^2$$

To this approximation, the three roots to Equation 1 are obtained from

$$d(\bar{V} - \bar{V}_c)^3 + c(T - T_c)(\bar{V} - \bar{V}_c) = 0$$

Show that the three roots are

$$\begin{aligned} \bar{V}_1 &= \bar{V}^l = \bar{V}_c - \left(\frac{c}{d} \right)^{1/2} (T_c - T)^{1/2} \\ \bar{V}_2 &= \bar{V}_c \\ \bar{V}_3 &= \bar{V}^g = \bar{V}_c + \left(\frac{c}{d} \right)^{1/2} (T_c - T)^{1/2} \end{aligned}$$

Now show that

$$\bar{V}^g - \bar{V}^l = 2 \left(\frac{c}{d} \right)^{1/2} (T_c - T)^{1/2} \quad \left(\begin{array}{l} T < T_c \\ T \rightarrow T_c \end{array} \right)$$

and that this equation is equivalent to

$$\rho^l - \rho^g \rightarrow A(T_c - T)^{1/2} \quad \left(\begin{array}{l} T < T_c \\ T \rightarrow T_c \end{array} \right)$$

Thus, the van der Waals theory predicts that the critical exponent in this case is 1/2. It has been shown experimentally that

$$\rho^l - \rho^g \rightarrow A(T_c - T)^\beta$$

where $\beta = 0.324$. Thus, as in the previous problem, although qualitatively correct, the van der Waals theory is not quantitatively correct.

We start with the result of Problem 23-46,

$$\begin{aligned} \mu^l - \mu^g &= \int_{\text{bdef}} (P_0 - P) d\bar{V} \\ 0 &= \int [P_0 - P_c - a(T - T_c) - b(T - T_c)^2 - c(T - T_c)(\bar{V} - \bar{V}_c) \\ &\quad - d(\bar{V} - \bar{V}_c)^3 - \dots] d\bar{V} \\ &= [P_0 - P_c - a(T - T_c) - b(T - T_c)^2] (\bar{V}^l - \bar{V}^g) - \frac{1}{2} c(T - T_c) [(\bar{V}^l - \bar{V}_c)^2 - (\bar{V}^g - \bar{V}_c)^2] \\ &\quad - \frac{1}{4} d [(\bar{V}^l - \bar{V}_c)^4 - (\bar{V}^g - \bar{V}_c)^4] \\ P_0 &= P_c + a(T - T_c) + b(T - T_c)^2 \\ &\quad + \frac{c}{2} \left[\frac{(\bar{V}^l)^2 - 2\bar{V}_c \bar{V}^l + \bar{V}_c^2 - (\bar{V}^g)^2 + 2\bar{V}_c \bar{V}^g - \bar{V}_c^2}{\bar{V}^l - \bar{V}^g} \right] \\ &\quad + \frac{d}{4} \left[\frac{(\bar{V}^l - \bar{V}_c)^2 - (\bar{V}^g - \bar{V}_c)^2}{\bar{V}^l - \bar{V}^g} \right] [(\bar{V}^l - \bar{V}_c)^2 + (\bar{V}^g - \bar{V}_c)^2] \\ &= P_c + a(T - T_c) + b(T - T_c)^2 \\ &\quad + \frac{c}{2} \left[\frac{(\bar{V}^l + \bar{V}^g)(\bar{V}^l - \bar{V}^g) - 2\bar{V}_c(\bar{V}^l - \bar{V}^g)}{\bar{V}^l - \bar{V}^g} \right] \\ &\quad + \frac{d}{4} \left[\frac{(\bar{V}^l + \bar{V}^g)(\bar{V}^l - \bar{V}^g) - 2\bar{V}_c(\bar{V}^l - \bar{V}^g)}{\bar{V}^l - \bar{V}^g} \right] [(\bar{V}^l - \bar{V}_c)^2 + (\bar{V}^g - \bar{V}_c)^2] \\ &= P_c + a(T - T_c) + b(T - T_c)^2 + \frac{c}{2} [\bar{V}^l + \bar{V}^g - 2\bar{V}_c] \\ &\quad + \frac{d}{4} [\bar{V}^l + \bar{V}^g - 2\bar{V}_c] [(\bar{V}^l - \bar{V}_c)^2 + (\bar{V}^g - \bar{V}_c)^2] \end{aligned}$$

Now assume that $\bar{V}_c \approx \frac{1}{2}(\bar{V}^g + \bar{V}^l)$ to get

$$P_0 = P_c + a(T - T_c) + b(T - T_c)^2$$

To this approximation, the three roots to Equation 1 are given by

$$\begin{aligned} d(\bar{V} - \bar{V}_c)^3 + c(T - T_c)(\bar{V} - \bar{V}_c) &= 0 \\ (\bar{V} - \bar{V}_c)[d(\bar{V} - \bar{V}_c)^2 + c(T - T_c)] &= 0 \end{aligned}$$

This expression is accurate only to $O(T - T_c)$. We then find the three roots

$$\begin{aligned} \bar{V} - \bar{V}_c &= 0 \\ \bar{V}_2 &= \bar{V}_c \\ \bar{V} - \bar{V}_c &= \left[-\frac{c(T - T_c)}{d} \right]^{1/2} \\ \bar{V}_3 &= \bar{V}_c + \left(\frac{c}{d} \right)^{1/2} (T_c - T)^{1/2} \\ \bar{V} - \bar{V}_c &= - \left[-\frac{c(T - T_c)}{d} \right]^{1/2} \\ \bar{V}_1 &= \bar{V}_c - \left(\frac{c}{d} \right)^{1/2} (T_c - T)^{1/2} \end{aligned}$$

These values are only accurate to $O[(T - T_c)^{1/2}]$. We know that the largest root is the value of \bar{V}^g and that the smallest root is the value of \bar{V}^l . Then, to the correct accuracy,

$$\begin{aligned} \bar{V}^g - \bar{V}^l &= \bar{V}_c + \left(\frac{c}{d} \right)^{1/2} (T_c - T)^{1/2} - \left[\bar{V}_c - \left(\frac{c}{d} \right)^{1/2} (T_c - T)^{1/2} \right] \\ &= 2 \left(\frac{c}{d} \right)^{1/2} (T_c - T)^{1/2} \end{aligned}$$

where $T \rightarrow T_c$, but $T < T_c$ (in order for the quantity $T_c - T$ to be real). Notice that the $(T - T_c)$ term in the product of the molar volumes drops out, since we have been truncating our expressions. The difference in densities is then

$$\begin{aligned} \rho^l - \rho^g &= \frac{1}{\bar{V}^l} - \frac{1}{\bar{V}^g} \\ &= \frac{\bar{V}^g - \bar{V}^l}{\bar{V}^l \bar{V}^g} \\ &= 2 \left(\frac{c}{d} \right)^{1/2} (T_c - T)^{1/2} \bar{V}_c^2 \\ &= A(T_c - T)^{1/2} \end{aligned}$$

23-49. The following data give the temperature, the vapor pressure, and the density of the coexisting vapor phase of butane. Use the van der Waals equation and the Redlich-Kwong equation to calculate the vapor pressure and compare your result with the experimental values given below.

T/K	P/bar	$\rho^g/\text{mol}\cdot\text{L}^{-1}$
200	0.0195	0.00117
210	0.0405	0.00233
220	0.0781	0.00430
230	0.1410	0.00746
240	0.2408	0.01225
250	0.3915	0.01924
260	0.6099	0.02905
270	0.9155	0.04239
280	1.330	0.06008

For butane, from Tables 16.3 and 16.4, $a = 13.888 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2}$, $b = 0.11641 \text{ dm}^3 \cdot \text{mol}^{-1}$, $A = 290.16 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}$, and $B = 0.080683 \text{ dm}^3 \cdot \text{mol}^{-1}$. We can substitute the given density and temperature into the van der Waals and Redlich-Kwong equations and thus find the vapor pressure P that is given by each equation.

For the van der Waals approximation,

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \quad (16.5)$$

and for the Redlich-Kwong approximation

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2} \bar{V}(\bar{V} + B)} \quad (16.8)$$

T/K	$P(\text{van der Waals})/\text{bar}$	$P(\text{Redlich-Kwong})/\text{bar}$
200	0.0194	0.0194
210	0.0406	0.0406
220	0.0784	0.0783
230	0.1420	0.1417
240	0.2427	0.2419
250	0.3957	0.3938
260	0.6184	0.6143
270	0.9314	0.9233
280	1.3584	1.3432

23-50. The following data give the temperature, the vapor pressure, and the density of the coexisting vapor phase of benzene. Use the van der Waals equation and the Redlich-Kwong equation to calculate the vapor pressure and compare your result with the experimental values given below.

Use Equations 16.17 and 16.18 with $T_c = 561.75$ K and $P_c = 48.7575$ bar to calculate the van der Waals parameters and the Redlich-Kwong parameters.

T/K	P/bar	$\rho^g/\text{mol}\cdot\text{L}^{-1}$
290.0	0.0860	0.00359
300.0	0.1381	0.00558
310.0	0.2139	0.00839
320.0	0.3205	0.01223
330.0	0.4666	0.01734
340.0	0.6615	0.02399
350.0	0.9161	0.03248

We can do this in the same way as the previous problem after finding a , b , A , and B using Equations 16.17 and 16.18:

$$a = \frac{27(RT_c)^2}{64P_c} = \frac{27[(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1})(561.75)]^2}{64(48.7575 \text{ bar})} = 18.876 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}$$

$$b = \frac{RT_c}{8P_c} = \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1})(561.75)}{8(48.7575 \text{ bar})} = 0.11974 \text{ dm}^3\cdot\text{mol}^{-1}$$

$$A = 0.42748 \frac{R^2 T_c^{5/2}}{P_c} = 0.42748 \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})^2 (561.75 \text{ K})^{5/2}}{48.7575 \text{ bar}} \\ = 453.21 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{1/2}$$

$$B = 0.086640 \frac{RT_c}{P_c} = 0.086640 \frac{(0.083145 \text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1})(561.75)}{48.7575 \text{ bar}} = 0.082996 \text{ dm}^3\cdot\text{mol}^{-1}$$

Now substitute into the appropriate equations to find the vapor pressure P for each temperature and density:

T/K	$P(\text{van der Waals})/\text{bar}$	$P(\text{Redlich-Kwong})/\text{bar}$
290	0.00842	0.00757
300	0.13869	0.13843
310	0.21514	0.21459
320	0.32305	0.32194
330	0.47109	0.46897
340	0.66927	0.66541
350	0.92897	0.92225

Solutions I Liquid-Liquid Solutions

PROBLEMS AND SOLUTIONS

24-1. In the text, we went from Equation 24.5 to 24.6 using a physical argument involving varying the size of the system while keeping T and P fixed. We could also have used a mathematical process called *Euler's theorem*. Before we can learn about Euler's theorem, we must first define a *homogeneous function*. A function $f(z_1, z_2, \dots, z_N)$ is said to be homogeneous if

$$f(\lambda z_1, \lambda z_2, \dots, \lambda z_N) = \lambda f(z_1, z_2, \dots, z_N)$$

Argue that extensive thermodynamic quantities are homogeneous functions of their extensive variables.

If we change extensive variables by a factor of λ , then we change an extensive function of these variables by a factor of λ .

24-2. Euler's theorem says that if $f(z_1, z_2, \dots, z_N)$ is homogeneous, then

$$f(z_1, z_2, \dots, z_N) = z_1 \frac{\partial f}{\partial z_1} + z_2 \frac{\partial f}{\partial z_2} + \dots + z_N \frac{\partial f}{\partial z_N}$$

Prove Euler's theorem by differentiating the equation in Problem 24-1 with respect to λ and then setting $\lambda = 1$.

Apply Euler's theorem to $G = G(n_1, n_2, T, P)$ to derive Equation 24.6. (*Hint:* Because T and P are intensive variables, they are simply irrelevant variables in this case.)

Start with

$$\lambda f(z_1, z_2, \dots, z_N) = f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)$$

differentiate with respect to λ to obtain

$$f(z_1, z_2, \dots, z_N) = \frac{\partial f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)}{\partial \lambda z_1} \frac{\partial \lambda z_1}{\partial \lambda} + \dots + \frac{\partial f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)}{\partial \lambda z_N} \frac{\partial \lambda z_N}{\partial \lambda} \\ = z_1 \frac{\partial f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)}{\partial \lambda z_1} + \dots + z_N \frac{\partial f(\lambda z_1, \lambda z_2, \dots, \lambda z_N)}{\partial \lambda z_N}$$

Now set $\lambda = 1$

$$f(z_1, z_2, \dots, z_N) = z_1 \frac{\partial f}{\partial z_1} + \dots + z_N \frac{\partial f}{\partial z_N}$$