

- b. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$
 $= 2(70.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) + 213.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 2(205.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) - 186.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $= -242.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
- c. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$
 $= 219.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 130.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 200.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $= -112.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

21-48. Use the data in Table 21.2 to calculate the value of $\Delta_r S^\circ$ for the following reactions at 25°C and one bar.

- a. $\text{CO(g)} + 2 \text{H}_2\text{(g)} \longrightarrow \text{CH}_3\text{OH(l)}$
 b. $\text{C(s, graphite)} + \text{H}_2\text{O(l)} \longrightarrow \text{CO(g)} + \text{H}_2\text{(g)}$
 c. $2 \text{CO(g)} + \text{O}_2\text{(g)} \longrightarrow 2 \text{CO}_2\text{(g)}$

- a. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$
 $= 126.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 197.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 2(130.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
 $= -332.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
- b. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$
 $= 130.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} + 197.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 70.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 5.74 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
 $= 252.66 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
- c. $\Delta_r S^\circ = S^\circ[\text{products}] - S^\circ[\text{reactants}]$
 $= 2(213.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) - 205.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - 2(197.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
 $= -173.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

Helmholtz and Gibbs Energies

PROBLEMS AND SOLUTIONS

22-1. The molar enthalpy of vaporization of benzene at its normal boiling point (80.09°C) is 30.72 kJ·mol⁻¹. Assuming that $\Delta_{\text{vap}} \bar{H}$ and $\Delta_{\text{vap}} \bar{S}$ stay constant at their values at 80.09°C, calculate the value of $\Delta_{\text{vap}} \bar{G}$ at 75.0°C, 80.09°C, and 85.0°C. Interpret these results physically.

We can write (as in Section 22-2)

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

At the boiling point of benzene, the liquid and vapor phases are in equilibrium, so $\Delta_{\text{vap}} \bar{G} = 0$. Thus, at 80.09°C,

$$0 = 30.72 \text{ kJ}\cdot\text{mol}^{-1} - (353.24 \text{ K}) \Delta_{\text{vap}} \bar{S}$$

$$\Delta_{\text{vap}} \bar{S} = 86.97 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Since $\Delta_{\text{vap}} \bar{H}$ and $\Delta_{\text{vap}} \bar{S}$ are assumed to stay constant at their boiling-point values, we know their numerical values and can substitute into our first equation:

$$\Delta_{\text{vap}} \bar{G}(75.0^\circ\text{C}) = 30.72 \text{ kJ}\cdot\text{mol}^{-1} - (348.15 \text{ K})(86.97 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = 441.4 \text{ J}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{vap}} \bar{G}(85.0^\circ\text{C}) = 30.72 \text{ kJ}\cdot\text{mol}^{-1} - (358.15 \text{ K})(86.97 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) = -428.3 \text{ J}\cdot\text{mol}^{-1}$$

From these values, we can see that at 75.0°C benzene will spontaneously condense, whereas at 85.0°C it will spontaneously evaporate (just as we would expect).

22-2. Redo Problem 22-1 without assuming that $\Delta_{\text{vap}} \bar{H}$ and $\Delta_{\text{vap}} \bar{S}$ do not vary with temperature. Take the molar heat capacities of liquid and gaseous benzene to be 136.3 J·K⁻¹·mol⁻¹ and 82.4 J·K⁻¹·mol⁻¹, respectively. Compare your results with those you obtained in Problem 22-1. Are any of your physical interpretations different?

We wish to consider the temperature variation of $\Delta_{\text{vap}} \bar{G}$, so we must use Equation 22.31a,

$$\left(\frac{\partial \Delta_{\text{vap}} \bar{G}}{\partial T} \right)_p = -\Delta_{\text{vap}} \bar{S}(T)$$

where (as in Example 20-5)

$$\begin{aligned}\Delta_{\text{vap}}\bar{S}(T) &= \Delta_{\text{vap}}\bar{S}(80.09^\circ\text{C}) + \int_{353.24\text{ K}}^T \frac{\Delta\bar{C}_p}{T} dT \\ &= 86.97\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - (53.9\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \ln \frac{T}{353.24\text{ K}} \\ &= 403.2\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - (53.9\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \ln(T/\text{K})\end{aligned}$$

Substituting into Equation 22.31a, we can write

$$\begin{aligned}\Delta_{\text{vap}}\bar{G}(T) - \Delta_{\text{vap}}\bar{G}(353.24\text{ K}) &= - \int_{353.24\text{ K}}^T [403.2\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ &\quad - (53.9\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \ln(T/\text{K})] dT \\ &= -(403.2\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(T - 353.24\text{ K}) \\ &\quad + (53.9\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) [T \ln(T/\text{K}) - T - 1719.3\text{ K}]\end{aligned}$$

Letting $T = 348.15\text{ K}$ gives

$$\Delta_{\text{vap}}\bar{G}(T) = 2052\text{ J}\cdot\text{mol}^{-1} - 1608\text{ J}\cdot\text{mol}^{-1} = +444\text{ J}\cdot\text{mol}^{-1}$$

and letting $T = 358.15\text{ K}$ gives

$$\Delta_{\text{vap}}\bar{G}(T) = -1980\text{ J}\cdot\text{mol}^{-1} + 1555\text{ J}\cdot\text{mol}^{-1} = -425\text{ J}\cdot\text{mol}^{-1}$$

Notice that taking the temperature variation of $\Delta_{\text{vap}}\bar{H}$ and $\Delta_{\text{vap}}\bar{S}$ into account made little difference over such a small temperature range.

22-3. Substitute $(\partial P/\partial T)_{\bar{V}}$ from the van der Waals equation into Equation 22.19 and integrate from \bar{V}^{id} to \bar{V} to obtain

$$\bar{S}(T, \bar{V}) - \bar{S}^{\text{id}}(T) = R \ln \frac{\bar{V} - b}{\bar{V}^{\text{id}} - b}$$

Now let $\bar{V}^{\text{id}} = RT/P^{\text{id}}$, $P^{\text{id}} = P^\circ = 1\text{ bar}$, and $\bar{V}^{\text{id}} \gg b$ to obtain

$$\bar{S}(T, \bar{V}) - \bar{S}^{\text{id}}(T) = -R \ln \frac{RT/P^\circ}{\bar{V} - b}$$

Given that $\bar{S}^{\text{id}} = 246.35\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for ethane at 400 K, show that

$$\bar{S}(\bar{V})/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 246.35 - 8.3145 \ln \frac{33.258\text{ L}\cdot\text{mol}^{-1}}{\bar{V} - 0.065144\text{ L}\cdot\text{mol}^{-1}}$$

Calculate \bar{S} as a function of $\rho = 1/\bar{V}$ for ethane at 400 K and compare your results with the experimental results shown in Figure 22.2. Show that

$$\begin{aligned}\bar{S}(\bar{V})/\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} &= 246.35 - 8.3145 \ln \frac{33.258\text{ L}\cdot\text{mol}^{-1}}{\bar{V} - 0.045153\text{ L}\cdot\text{mol}^{-1}} \\ &\quad + 13.68 \ln \frac{\bar{V} + 0.045153\text{ L}\cdot\text{mol}^{-1}}{\bar{V}}\end{aligned}$$

for the Redlich-Kwong equation for ethane at 400 K. Calculate \bar{S} as a function of $\rho = 1/\bar{V}$ and compare your results with the experimental results shown in Figure 22.2.

From the van der Waals equation,

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{\bar{V} - b}$$

We can substitute into Equation 22.19 to find an expression for $d\bar{S}$:

$$\begin{aligned}\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_v \\ d\bar{S} &= \frac{R}{\bar{V} - b} d\bar{V}\end{aligned}$$

Integrating both sides of this equation gives

$$\bar{S}(T, \bar{V}) - \bar{S}^{\text{id}}(T) = R \ln \frac{\bar{V} - b}{\bar{V}^{\text{id}} - b}$$

Since \bar{V}^{id} is quite large compared to b , we can neglect b in $\bar{V}^{\text{id}} - b$. Letting $\bar{V}^{\text{id}} = RT/P^{\text{id}}$ and $P^{\text{id}} = P^\circ = 1\text{ bar}$, we find

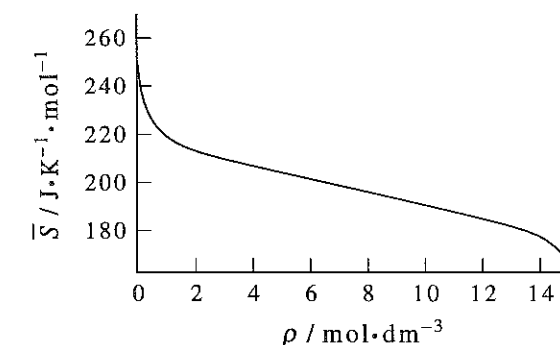
$$\begin{aligned}\bar{S}(T, \bar{V}) - \bar{S}^{\text{id}}(T) &= -R \ln \frac{\bar{V}^{\text{id}}}{\bar{V} - b} \\ &= -R \ln \frac{RT/P^\circ}{\bar{V} - b} \\ \bar{S}(T, \bar{V}) &= \bar{S}^{\text{id}}(T) - R \ln \frac{RT}{\bar{V} - b}\end{aligned}$$

where, in the last equality, the pressure units of R are in bars. For ethane, $a = 5.5818\text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}$ and $b = 0.065144\text{ dm}^3\cdot\text{mol}^{-1}$ (Table 16.3), so

$$\bar{S}(\bar{V}) = 246.35\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} - (8.3145\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \ln \frac{33.258\text{ L}\cdot\text{mol}^{-1}}{\bar{V} - 0.065144\text{ L}\cdot\text{mol}^{-1}}$$

To make graphing entropy vs. density easier, we can break up the logarithmic term and then graph, as shown:

$$\begin{aligned}\bar{S}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} &= 246.35 - (8.3145) \ln 33.258 \\ &\quad + (8.3145) \ln \left(\frac{\text{mol}\cdot\text{dm}^{-3}}{\rho} - 0.065144 \right)\end{aligned}$$



For a Redlich-Kwong gas,

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

and

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

Using Equation 22.19 and integrating (keeping temperature constant) gives

$$\begin{aligned} \left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T &= \frac{R}{\bar{V} - B} + \frac{A}{2\bar{V}(\bar{V} + B)T^{3/2}} \\ \int d\bar{S} &= \int \left[\frac{R}{\bar{V} - B} + \frac{A}{2\bar{V}(\bar{V} + B)T^{3/2}} \right] d\bar{V} \\ \bar{S} - \bar{S}^{\text{id}} &= R \ln \frac{\bar{V} - B}{\bar{V}^{\text{id}} - B} - \frac{A}{2T^{3/2}} \left[-\frac{1}{B} \ln \left(\frac{B + \bar{V}}{\bar{V}} \right) + \frac{1}{B} \ln \left(\frac{B + \bar{V}^{\text{id}}}{\bar{V}^{\text{id}}} \right) \right] \end{aligned}$$

Since for an ideal gas B is negligible compared to \bar{V} ,

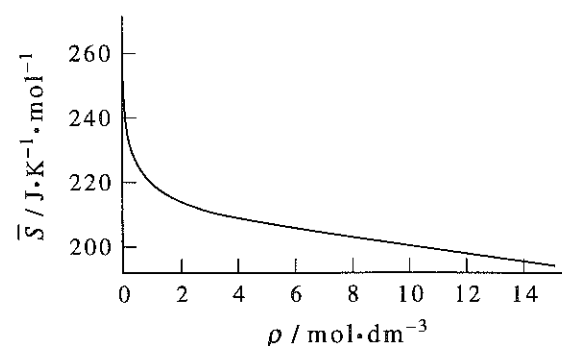
$$\bar{S} - \bar{S}^{\text{id}} = R \ln \frac{\bar{V} - B}{\bar{V}^{\text{id}}} + \frac{A}{2BT^{3/2}} \ln \frac{\bar{V}}{\bar{V} + B}$$

Then, for ethane, since $A = 98.831 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}$ and $B = 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}$ (Table 16.4),

$$\begin{aligned} \bar{S} &= \bar{S}^{\text{id}} - R \ln \frac{\bar{V}^{\text{id}}}{\bar{V} - B} + \frac{A}{2BT^{3/2}} \ln \frac{\bar{V} + B}{\bar{V}} \\ \bar{S} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} &= 246.35 - 8.3145 \ln \frac{33.258 \text{ dm}^3 \cdot \text{mol}^{-1}}{\bar{V} - 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}} \\ &\quad + 13.68 \ln \frac{\bar{V} + 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}}{\bar{V}} \end{aligned}$$

To make graphing entropy vs. density easier, we can break up the logarithmic term and then graph, as shown. We have divided both numerator and denominator of the logarithmic terms in the previous expression by $\text{dm}^3 \cdot \text{mol}^{-1}$.

$$\begin{aligned} \bar{S} / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} &= 246.35 - 8.3145 \left[\ln 33.258 - \ln \left(\frac{1}{\rho} - 0.045153 \right) \right] \\ &\quad + 13.68 \left[\ln \left(\frac{1}{\rho} + 0.045153 \right) - \ln \frac{1}{\rho} \right] \end{aligned}$$



22-4. Use the van der Waals equation to derive

$$\bar{U}(T, \bar{V}) - \bar{U}^{\text{id}}(T) = -\frac{a}{\bar{V}}$$

Use this result along with the van der Waals equation to calculate the value of \bar{U} as a function of \bar{V} for ethane at 400 K, given that $\bar{U}^{\text{id}} = 14.55 \text{ kJ} \cdot \text{mol}^{-1}$. To do this, specify \bar{V} (from $0.0700 \text{ L} \cdot \text{mol}^{-1}$ to $7.00 \text{ L} \cdot \text{mol}^{-1}$, see Figure 22.2), calculate both $\bar{U}(\bar{V})$ and $P(\bar{V})$, and plot $\bar{U}(\bar{V})$ versus $P(\bar{V})$. Compare your result with the experimental data in Figure 22.3. Use the Redlich-Kwong equation to derive

$$\bar{U}(T, \bar{V}) - \bar{U}^{\text{id}}(T) = -\frac{3A}{2BT^{1/2}} \ln \frac{\bar{V} + B}{\bar{V}}$$

Repeat the above calculation for ethane at 400 K.

Begin with Equation 22.22,

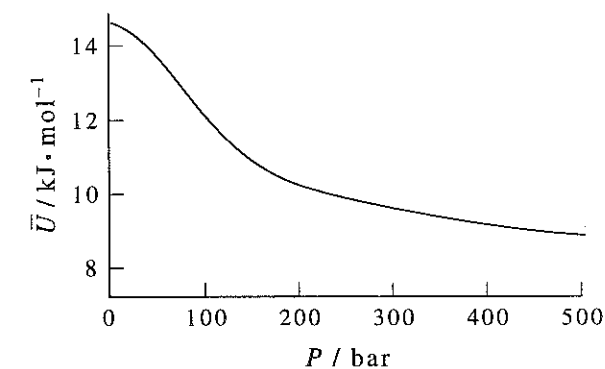
$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_v$$

In Problem 22-3, we found $(\partial P / \partial T)_v$ for the van der Waals and Redlich-Kwong equations. For the van der Waals equation, Equation 22.22 becomes

$$\begin{aligned} \left(\frac{\partial U}{\partial V}\right)_T &= -\frac{RT}{\bar{V} - b} + \frac{a}{\bar{V}^2} + \frac{RT}{\bar{V} - b} = \frac{a}{\bar{V}^2} \\ \int_{\bar{V}^{\text{id}}}^{\bar{V}} dU &= \int_{\bar{V}^{\text{id}}}^{\bar{V}} \frac{a}{\bar{V}^2} d\bar{V} \\ \bar{U} - \bar{U}^{\text{id}} &= -\frac{a}{\bar{V}} \end{aligned}$$

The van der Waals constants for ethane are listed in the previous problem. Substituting, we find that

$$\begin{aligned} \bar{U} &= 14.55 \text{ kJ} \cdot \text{mol}^{-1} - \frac{0.55818 \text{ kJ} \cdot \text{dm}^3 \cdot \text{mol}^{-2}}{\bar{V}} \\ P &= \frac{(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(400 \text{ K})}{\bar{V} - 0.065144 \text{ dm}^3 \cdot \text{mol}^{-1}} - \frac{5.5818 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-1}}{\bar{V}^2} \end{aligned}$$

We can use a parametric plot to plot $\bar{U}(\bar{V})$ vs. $P(\bar{V})$:

For the Redlich-Kwong equation, Equation 22.22 becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{RT}{\bar{V} - B} + \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} + \frac{RT}{\bar{V} - B} + \frac{A}{2T^{1/2}\bar{V}(\bar{V} + B)}$$

$$\int_{\bar{V}^{\text{id}}}^{\bar{V}} dU = \int_{\bar{V}^{\text{id}}}^{\bar{V}} \frac{3A}{2T^{1/2}\bar{V}(\bar{V}+B)} d\bar{V}$$

$$\bar{U} - \bar{U}^{\text{id}} = \frac{3A}{2T^{1/2}} \left(-\frac{1}{B} \ln \frac{\bar{V}+B}{\bar{V}} + \frac{1}{B} \ln \frac{\bar{V}^{\text{id}}+B}{\bar{V}^{\text{id}}} \right)$$

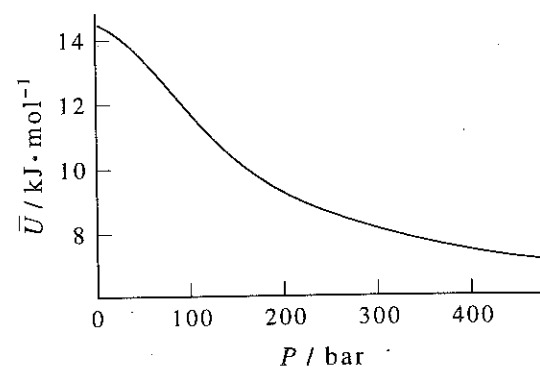
$$\bar{U} = \bar{U}^{\text{id}} - \frac{3A}{2BT^{1/2}} \ln \frac{\bar{V}+B}{\bar{V}}$$

The Redlich-Kwong constants for ethane are listed in the previous problem. Substituting, we find that

$$\bar{U} = 14.55 \text{ kJ} \cdot \text{mol}^{-1} - \frac{3(9.8831 \text{ kJ} \cdot \text{dm}^3 \cdot \text{mol}^{-2} \cdot \text{K}^{1/2})}{2(0.045153 \text{ dm}^3 \cdot \text{mol}^{-1})(400 \text{ K})^{1/2}} \ln \frac{\bar{V} + 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}}{\bar{V}}$$

$$P = \frac{(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(400 \text{ K})}{\bar{V} - 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}} - \frac{98.831 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}}{(400 \text{ K})^{1/2} \bar{V}(\bar{V} + 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1})}$$

Again, use a parametric plot to plot $\bar{U}(\bar{V})$ vs. $P(\bar{V})$:



22-5. Show that $(\partial U / \partial V)_T = 0$ for a gas that obeys an equation of state of the form $Pf(V) = RT$. Give two examples of such equations of state that appear in the text.

We first take the partial derivative of P with respect to T , keeping V constant:

$$Pf(V) = RT$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{f(V)}$$

From Equation 22.22, we can write

$$\left(\frac{\partial U}{\partial V} \right)_T = -P + T \left(\frac{\partial P}{\partial T} \right)_V = -P + \frac{RT}{f(V)} = -P + P = 0$$

Two such equations of state are the ideal gas equation and $P(\bar{V} - b) = RT$.

22-6. Show that

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}} \right)_T = \frac{RT^2}{\bar{V}^2} \frac{dB_{2V}}{dT} + \frac{RT^2}{\bar{V}^3} \frac{dB_{3V}}{dT} + \dots$$

Begin with Equation 22.22,

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}} \right)_T = -P + T \left(\frac{\partial P}{\partial T} \right)_V$$

We can use the virial expansion in the volume to express Z as (Equation 16.22)

$$Z = 1 + B_{2V}\bar{V}^{-1} + B_{3V}\bar{V}^{-2} + O(\bar{V}^{-3})$$

$$P = RT\bar{V}^{-1} + B_{2V}RT\bar{V}^{-2} + B_{3V}RT\bar{V}^{-3} + O(\bar{V}^{-4})$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{\bar{V}} + B_{2V}\frac{R}{\bar{V}^2} + \frac{dB_{2V}}{dT}\frac{RT}{\bar{V}^2} + B_{3V}\frac{R}{\bar{V}^3} + \frac{dB_{3V}}{dT}\frac{RT}{\bar{V}^3} + O(\bar{V}^{-4})$$

Substituting into Equation 22.22 gives

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}} \right)_T = - \left(\frac{RT}{\bar{V}} + B_{2V}\frac{RT}{\bar{V}^2} + B_{3V}\frac{RT}{\bar{V}^3} \right) + \frac{RT}{\bar{V}} + O(\bar{V}^{-4})$$

$$+ B_{2V}\frac{RT}{\bar{V}^2} + \frac{dB_{2V}}{dT}\frac{RT^2}{\bar{V}^2} + B_{3V}\frac{RT}{\bar{V}^3} + \frac{dB_{3V}}{dT}\frac{RT^2}{\bar{V}^3} + O(\bar{V}^{-4})$$

$$= \frac{RT^2}{\bar{V}^2} \frac{dB_{2V}}{dT} + \frac{RT^2}{\bar{V}^3} \frac{dB_{3V}}{dT} + O(\bar{V}^{-4})$$

22-7. Use the result of the previous problem to show that

$$\Delta \bar{U} = -T \frac{dB_{2V}}{dT} (P_2 - P_1) + \dots$$

Use Equation 16.41 for the square-well potential to show that

$$\Delta \bar{U} = -\frac{2\pi\sigma^3 N_A}{3} (\lambda^3 - 1) \frac{\epsilon}{k_B T} e^{\epsilon/k_B T} (P_2 - P_1) + \dots$$

Given that $\sigma = 327.7$ pm, $\epsilon/k_B = 95.2$ K, and $\lambda = 1.58$ for $N_2(g)$, calculate the value of $\Delta \bar{U}$ for a pressure increase from 1.00 bar to 10.0 bar at 300 K.

We integrate the equation we found in the previous problem (keeping T constant):

$$\left(\frac{\partial \bar{U}}{\partial \bar{V}} \right)_T = \frac{RT^2}{\bar{V}^2} \frac{dB_{2V}}{dT} + \frac{RT^2}{\bar{V}^3} \frac{dB_{3V}}{dT} + O(\bar{V}^{-4})$$

$$d\bar{U} = \frac{RT^2}{\bar{V}^2} \frac{dB_{2V}}{dT} d\bar{V} + O(\bar{V}^{-3})$$

$$\Delta \bar{U} = -\frac{RT^2}{\bar{V}} \frac{dB_{2V}}{dT} \Big|_{\bar{V}_1}^{\bar{V}_2}$$

Substitute in for $\bar{V} = RT/P$ to get

$$\Delta \bar{U} = -T(P_2 - P_1) \frac{dB_{2V}}{dT} + \dots$$

Using Equation 16.41,

$$B_{2V}(T) = \frac{2\pi\sigma^3 N_A}{3} [1 - (\lambda^3 - 1)(e^{\epsilon/k_B T} - 1)]$$

$$\frac{dB_{2V}}{dT} = \frac{2\pi\sigma^3 N_A}{3} (\lambda^3 - 1) e^{\epsilon/k_B T} \left(\frac{\epsilon}{k_B T^2} \right)$$

Substitute into the equation for $\Delta\bar{U}$ to find

$$\Delta\bar{U} = -\frac{2\pi\sigma^3 N_A}{3} (\lambda^3 - 1) \frac{\epsilon}{k_B T} e^{\epsilon/k_B T} (P_2 - P_1) + \dots$$

For $N_2(g)$ under the conditions specified,

$$\begin{aligned} \Delta\bar{U} &= -\frac{2\pi\sigma^3 N_A}{3} (\lambda^3 - 1) \frac{\epsilon}{k_B T} e^{\epsilon/k_B T} (P_2 - P_1) + \dots \\ &= -\frac{2\pi(327.7 \times 10^{-12} \text{ m})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{3} (1.58^3 - 1) \left(\frac{95.2}{300} \right) e^{95.2/300} (10.0 - 1.00) \text{ bar} \\ &= -5.13 \times 10^{-4} \text{ bar} \cdot \text{m}^3 \cdot \text{mol}^{-1} \\ &= -51.3 \text{ J} \cdot \text{mol}^{-1} \end{aligned}$$

22-8. Determine $\bar{C}_p - \bar{C}_v$ for a gas that obeys the equation of state $P(\bar{V} - b) = RT$.

We can write, from the equation of state,

$$\begin{aligned} P(\bar{V} - b) &= RT \\ \left(\frac{\partial P}{\partial T} \right)_v &= \frac{R}{\bar{V} - b} \\ \left(\frac{\partial V}{\partial T} \right)_p &= \frac{R}{P} \end{aligned}$$

Now we substitute into Equation 22.23:

$$\bar{C}_p - \bar{C}_v = T \left(\frac{\partial P}{\partial T} \right)_v \left(\frac{\partial \bar{V}}{\partial T} \right)_p = \frac{RT}{\bar{V} - b} \left(\frac{R}{P} \right) = R$$

22-9. The coefficient of thermal expansion of water at 25°C is $2.572 \times 10^{-4} \text{ K}^{-1}$, and its thermal compressibility is $4.525 \times 10^{-5} \text{ bar}^{-1}$. Calculate the value of $C_p - C_v$ for one mole of water at 25°C . The density of water at 25°C is $0.99705 \text{ g} \cdot \text{mL}^{-1}$.

The molar volume of water is

$$\bar{V} = \left(\frac{1}{0.99705 \text{ g} \cdot \text{mL}^{-1}} \right) \left(\frac{18.015 \text{ g}}{1 \text{ mol}} \right) \left(\frac{1 \text{ dm}^3}{1000 \text{ mL}} \right) = 0.018068 \text{ dm}^3 \cdot \text{mol}^{-1}$$

We can now substitute into Equation 22.27 to find $C_p - C_v$. For one mole,

$$\begin{aligned} C_p - C_v &= \frac{\alpha^2 T \bar{V}}{\kappa} \\ &= \frac{(2.572 \times 10^{-4} \text{ K}^{-1})^2 (298.15 \text{ K}) (0.018068 \text{ dm}^3)}{4.525 \times 10^{-5} \text{ bar}^{-1}} \\ &= 7.875 \times 10^{-3} \text{ dm}^3 \cdot \text{bar}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

22-10. Use Equation 22.22 to show that

$$\left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_v$$

Show that $(\partial C_v / \partial V)_T = 0$ for an ideal gas and a van der Waals gas, and that

$$\left(\frac{\partial C_v}{\partial V} \right)_T = -\frac{3A}{4T^{3/2}\bar{V}(\bar{V} + B)}$$

for a Redlich-Kwong gas.

Recall that, by definition, $C_v = (\partial U / \partial T)_v$, so

$$\left(\frac{\partial C_v}{\partial V} \right)_T = \frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V} = \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T$$

Express $(\partial U / \partial V)$ using Equation 22.22 and write

$$\begin{aligned} \left(\frac{\partial U}{\partial V} \right)_T &= -P + T \left(\frac{\partial P}{\partial T} \right)_v \\ \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T &= -\left(\frac{\partial P}{\partial T} \right)_v + \left(\frac{\partial P}{\partial T} \right)_v + T \left(\frac{\partial^2 P}{\partial T^2} \right)_v \\ \left(\frac{\partial C_v}{\partial V} \right)_T &= T \left(\frac{\partial^2 P}{\partial T^2} \right)_v \end{aligned}$$

For an ideal gas and for a van der Waals gas,

$$\begin{aligned} P\bar{V} &= RT & P &= \frac{RT}{\bar{V} - b} + \frac{a}{\bar{V}^2} \\ \left(\frac{\partial^2 P}{\partial T^2} \right)_v &= 0 & \left(\frac{\partial^2 P}{\partial T^2} \right)_v &= 0 \\ T \left(\frac{\partial^2 P}{\partial T^2} \right)_v &= 0 = \left(\frac{\partial C_v}{\partial V} \right)_T & T \left(\frac{\partial^2 P}{\partial T^2} \right)_v &= 0 = \left(\frac{\partial C_v}{\partial V} \right)_T \end{aligned}$$

For a Redlich-Kwong gas,

$$\begin{aligned} P &= \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} \\ \left(\frac{\partial P}{\partial T} \right)_v &= \frac{R}{\bar{V} - B} + \frac{A}{2\bar{V}(\bar{V} + B)T^{3/2}} \\ \left(\frac{\partial^2 P}{\partial T^2} \right)_v &= -\frac{3}{4} \frac{A}{T^{5/2}\bar{V}(\bar{V} + B)} \\ T \left(\frac{\partial^2 P}{\partial T^2} \right)_v &= -\frac{3A}{4T^{3/2}\bar{V}(\bar{V} + B)} = \left(\frac{\partial C_v}{\partial V} \right)_T \end{aligned}$$

22-11. In this problem you will derive the equation (Equation 22.24)

$$C_p - C_v = -T \left(\frac{\partial V}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial V} \right)_T$$

To start, consider V to be a function of T and P and write out dV . Now divide through by dT at constant volume ($dV = 0$) and then substitute the expression for $(\partial P / \partial T)_v$ that you obtain into Equation 22.23 to get the above expression.

The total derivative of $V(T, P)$ is

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

Dividing through by dT at constant volume gives

$$0 = \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

Now substitute for $(\partial P/\partial T)_V$ into Equation 22.23:

$$C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

which is Equation 22.24.

22-12. The quantity $(\partial U/\partial V)_T$ has units of pressure and is called the *internal pressure*, which is a measure of the intermolecular forces within the body of a substance. It is equal to zero for an ideal gas, is nonzero but relatively small for dense gases, and is relatively large for liquids, particularly those whose molecular interactions are strong. Use the following data to calculate the internal pressure of ethane as a function of pressure at 280 K. Compare your values with the values you obtain from the van der Waals equation and the Redlich-Kwong equation.

P/bar	$(dP/dT)/\text{bar}\cdot\text{K}^{-1}$	$\bar{V}/\text{dm}^3\cdot\text{mol}^{-1}$	P/bar	$(dP/dT)/\text{bar}\cdot\text{K}^{-1}$	$\bar{V}/\text{dm}^3\cdot\text{mol}^{-1}$
4.458	0.01740	5.000	307.14	6.9933	0.06410
47.343	4.1673	0.07526	437.40	7.9029	0.06173
98.790	4.9840	0.07143	545.33	8.5653	0.06024
157.45	5.6736	0.06849	672.92	9.2770	0.05882

Use Equation 22.22 to write

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_V$$

To find the experimental values of internal pressure, we can substitute the data given into the above equation. We expressed $(\partial U/\partial V)_T$ for the van der Waals equation in Problem 22-4 as

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{\bar{V}^2}$$

and $(\partial U/\partial V)_T$ for the Redlich-Kwong equation as

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{3A}{2T^{1/2}\bar{V}(\bar{V} + B)}$$

We can use the molar volumes given in the statement of the problem and the constants from Tables 16.3 and 16.4 ($a = 5.5818 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}$, $b = 0.065144 \text{ dm}^3\cdot\text{mol}^{-1}$, $A =$

$98.831 \text{ dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}\cdot\text{K}^{1/2}$, $B = 0.045153 \text{ dm}^3\cdot\text{mol}^{-1}$) to create a table of values of internal pressures for each experimental pressure.

P/bar	Experimental	$(\partial U/\partial V)_T/\text{bar}$ van der Waals	Redlich-Kwong
4.458	0.4140	0.2233	0.3512
47.343	1119.5	972.5	967.1
98.790	1296.7	1094	1064
157.45	1431.2	1190	1138
307.14	1651.0	1359	1265
437.40	1775.4	1465	1343
545.33	1853.0	1538	1395
672.92	1924.6	1613	1449

22-13. Show that

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = -RT^2 \left(\frac{dB_{2P}}{dT} + \frac{dB_{3P}}{dT} P + \dots \right)$$

$$= B_{2V}(T) - T \frac{dB_{2V}}{dT} + O(P)$$

Use Equation 16.41 for the square-well potential to obtain

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \frac{2\pi\sigma^3 N_A}{3} \left[\lambda^3 - (\lambda^3 - 1) \left(1 + \frac{\varepsilon}{k_B T} \right) e^{\varepsilon/k_B T} \right]$$

Given that $\sigma = 327.7 \text{ pm}$, $\varepsilon/k_B = 95.2 \text{ K}$, and $\lambda = 1.58$ for $\text{N}_2(\text{g})$, calculate the value of $(\partial \bar{H}/\partial P)_T$ at 300 K. Evaluate $\Delta \bar{H} = \bar{H}(P = 10.0 \text{ bar}) - \bar{H}(P = 1.0 \text{ bar})$. Compare your result with $8.724 \text{ kJ}\cdot\text{mol}^{-1}$, the value of $\bar{H}(T) - \bar{H}(0)$ for nitrogen at 300 K.

Use the virial expansion in the pressure (Equation 16.23):

$$Z = 1 + B_{2P}P + B_{3P}P^2 + O(P^3)$$

$$\bar{V} = \frac{RT}{P} + RTB_{2P} + PRTB_{3P} + O(P^2)$$

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{R}{P} + RB_{2P} + RT \frac{dB_{2P}}{dT} + PRB_{3P} + PRT \frac{dB_{3P}}{dT} + O(P^2)$$

Substitute into Equation 22.34:

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \bar{V} - T \left(\frac{\partial \bar{V}}{\partial T}\right)_P$$

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \left[\frac{RT}{P} + RTB_{2P} + PRTB_{3P} \right] - \left[\frac{RT}{P} + RTB_{2P} + RT^2 \frac{dB_{2P}}{dT} + PRTB_{3P} + PRT^2 \frac{dB_{3P}}{dT} \right] + O(P^2)$$

$$= -RT^2 \left[\frac{dB_{2P}}{dT} + \frac{dB_{3P}}{dT} P + O(P^2) \right] \quad (1)$$

Since $B_{2V} = RT B_{2P}$ (Equation 16.24),

$$\begin{aligned}\frac{dB_{2V}}{dT} &= RB_{2P} + RT \frac{dB_{2P}}{dT} \\ \frac{dB_{2V}}{dT} \frac{1}{RT} &= \frac{B_{2V}}{RT^2} + \frac{dB_{2P}}{dT} \\ \frac{dB_{2P}}{dT} &= \frac{1}{RT} \frac{dB_{2V}}{dT} - \frac{B_{2V}}{RT^2}\end{aligned}$$

Then Equation 1 becomes

$$\begin{aligned}\left(\frac{\partial \bar{H}}{\partial P}\right)_T &= -RT^2 \left[\frac{dB_{2P}}{dT} + O(P) \right] \\ &= B_{2V} - T \frac{dB_{2V}}{dT} + O(P)\end{aligned}\quad (2)$$

Start with Equation 16.41 and find $-T dB_{2V}/dT$:

$$\begin{aligned}B_{2V}(T) &= \frac{2\pi\sigma^3 N_A}{3} [1 - (\lambda^3 - 1)(e^{\epsilon/k_B T} - 1)] \\ \frac{dB_{2V}}{dT} &= \frac{2\pi\sigma^3 N_A}{3} (\lambda^3 - 1) e^{\epsilon/k_B T} \left(\frac{\epsilon}{k_B T^2} \right) \\ -T \frac{dB_{2V}}{dT} &= -\frac{2\pi\sigma^3 N_A}{3} (\lambda^3 - 1) e^{\epsilon/k_B T} \left(\frac{\epsilon}{k_B T} \right)\end{aligned}$$

Substituting this value into Equation 2 and ignoring terms of P or higher, we find

$$\begin{aligned}\left(\frac{\partial \bar{H}}{\partial P}\right)_T &= \frac{2\pi\sigma^3 N_A}{3} \left[1 - (\lambda^3 - 1)(e^{\epsilon/k_B T} - 1) - e^{\epsilon/k_B T} \left(\frac{\epsilon}{k_B T} \right) (\lambda^3 - 1) \right] \\ &= \frac{2\pi\sigma^3 N_A}{3} \left[1 - (\lambda^3 e^{\epsilon/k_B T} + 1 - \lambda^3 - e^{\epsilon/k_B T}) - \lambda^3 \frac{\epsilon}{k_B T} e^{\epsilon/k_B T} + \frac{\epsilon}{k_B T} e^{\epsilon/k_B T} \right] \\ &= \frac{2\pi\sigma^3 N_A}{3} \left[\lambda^3 - e^{\epsilon/k_B T} \left(\lambda^3 - 1 - \frac{\epsilon}{k_B T} + \lambda^3 \frac{\epsilon}{k_B T} \right) \right] \\ &= \frac{2\pi\sigma^3 N_A}{3} \left[\lambda^3 - (\lambda^3 - 1) \left(1 + \frac{\epsilon}{k_B T} \right) e^{\epsilon/k_B T} \right]\end{aligned}$$

Using the parameters provided for nitrogen, this expression becomes

$$\begin{aligned}\left(\frac{\partial \bar{H}}{\partial P}\right)_T &= \frac{2\pi(327.7 \times 10^{-12} \text{ m})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{3} \left[1.58^3 - (1.58^3 - 1) \left(1 + \frac{95.2}{300} \right) e^{95.2/300} \right] \\ &= -6.138 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}\end{aligned}$$

Then

$$\Delta \bar{H} = (-6.138 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}) \Delta P = -5.52 \times 10^{-4} \text{ m}^3 \cdot \text{bar} \cdot \text{mol}^{-1} = -55.2 \text{ J} \cdot \text{mol}^{-1}$$

- 22-14. Show that the enthalpy is a function of only the temperature for a gas that obeys the equation of state $P(\bar{V} - bT) = RT$.

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \bar{V} - T \left(\frac{\partial \bar{V}}{\partial T}\right)_P \quad (22.34)$$

For a gas obeying the equation of state $P(\bar{V} - bT) = RT$,

$$\begin{aligned}\bar{V} &= \frac{RT}{P} + bT \\ \left(\frac{\partial \bar{V}}{\partial T}\right)_P &= \frac{R}{P} + b\end{aligned}$$

Substituting into Equation 22.34, we find

$$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = \frac{RT}{P} + bT - T \left(\frac{R}{P} + b \right) = 0$$

and so enthalpy does not depend on pressure for a gas with this equation of state.

- 22-15. Use your results for the van der Waals equation and the Redlich-Kwong equation in Problem 22-4 to calculate $\bar{H}(T, \bar{V})$ as a function of volume for ethane at 400 K. In each case, use the equation $\bar{H} = \bar{U} + P\bar{V}$. Compare your results with the experimental data shown in Figure 22.5.

$$\bar{H} = \bar{U}(T, \bar{V}) + P\bar{V}$$

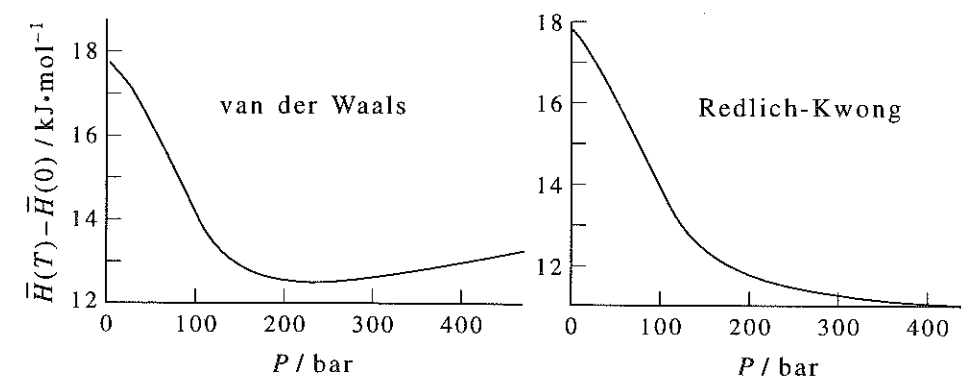
From Problem 22-4, for a van der Waals gas

$$\begin{aligned}\bar{U} &= 14.55 \text{ kJ} \cdot \text{mol}^{-1} - \frac{0.55818 \text{ kJ} \cdot \text{dm}^3 \cdot \text{mol}^{-2}}{\bar{V}} \\ P &= \frac{(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(400 \text{ K})}{\bar{V} - 0.065144 \text{ dm}^3 \cdot \text{mol}^{-1}} - \frac{5.5818 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-1}}{\bar{V}^2}\end{aligned}$$

and for a Redlich-Kwong gas

$$\begin{aligned}\bar{U} &= 14.55 \text{ kJ} \cdot \text{mol}^{-1} - \frac{3(9.8831 \text{ kJ} \cdot \text{dm}^3 \cdot \text{mol}^{-2} \cdot \text{K}^{1/2})}{2(0.045153 \text{ dm}^3 \cdot \text{mol}^{-1})(400 \text{ K})^{1/2}} \ln \frac{\bar{V} + 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}}{\bar{V}} \\ P &= \frac{(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(400 \text{ K})}{\bar{V} - 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}} - \frac{98.831 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}}{(400 \text{ K})^{1/2} \bar{V}(\bar{V} + 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1})}\end{aligned}$$

Note that in using these values, we find \bar{U} in terms of $\text{kJ} \cdot \text{mol}^{-1}$ and $P\bar{V}$ in terms of $\text{dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1}$. Dividing $P\bar{V}$ by 10 will result in values of enthalpy given in $\text{kJ} \cdot \text{mol}^{-1}$. Using these values, we can produce plots of \bar{H} vs. P .



22-16. Use Equation 22.34 to show that

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Use a virial expansion in P to show that

$$\left(\frac{\partial \bar{C}_p}{\partial P}\right)_T = -T \frac{dB_{2V}}{dT} + O(P)$$

Use the square-well second virial coefficient (Equation 16.41) and the parameters given in Problem 22-13 to calculate the value of $(\partial \bar{C}_p / \partial P)_T$ for $N_2(g)$ at 0°C . Now calculate \bar{C}_p at 100 atm and 0°C , using $\bar{C}_p^{\text{id}} = 5R/2$.

We define C_p as $(\partial H / \partial T)_P$ (Equation 19.40). Starting with Equation 22.34,

$$\begin{aligned} \left(\frac{\partial H}{\partial P}\right)_T &= V - T \left(\frac{\partial V}{\partial T}\right)_P \\ \frac{\partial}{\partial T} \left(\frac{\partial H}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P - T \frac{\partial}{\partial T} \left(\frac{\partial V}{\partial T}\right)_P \\ \frac{\partial}{\partial P} \left(\frac{\partial H}{\partial T}\right)_P &= -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \\ \left(\frac{\partial C_p}{\partial P}\right)_T &= -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \end{aligned} \quad (1)$$

Using a virial expansion in P , we find

$$\begin{aligned} \bar{V} &= \frac{RT}{P} + RTB_{2P} + PRTB_{3P} + O(P^2) \\ \left(\frac{\partial \bar{V}}{\partial T}\right)_P &= \frac{R}{P} + RB_{2P} + RT \frac{dB_{2P}}{dT} + O(P) \\ \left(\frac{\partial^2 \bar{V}}{\partial T^2}\right)_P &= R \frac{dB_{2P}}{dT} + R \frac{dB_{2P}}{dT} + RT \frac{d^2 B_{2P}}{dT^2} + O(P) \\ &= 2R \frac{dB_{2P}}{dT} + RT \frac{d^2 B_{2P}}{dT^2} + O(P) \end{aligned}$$

Now, since $B_{2V} = RTB_{2P}$ (Equation 16.24),

$$\begin{aligned} B_{2P} &= \frac{B_{2V}}{RT} \\ \frac{dB_{2P}}{dT} &= \frac{1}{RT} \frac{dB_{2V}}{dT} - \frac{B_{2V}}{RT^2} \\ \frac{d^2 B_{2P}}{dT^2} &= \frac{1}{RT} \frac{d^2 B_{2V}}{dT^2} - \frac{1}{RT^2} \frac{dB_{2V}}{dT} - \frac{1}{RT^2} \frac{dB_{2V}}{dT} + \frac{2B_{2V}}{RT^3} \\ &= \frac{1}{RT} \frac{d^2 B_{2V}}{dT^2} - \frac{2}{RT^2} \frac{dB_{2V}}{dT} + \frac{2B_{2V}}{RT^3} \end{aligned}$$

Now we solve Equation 1 for $(\partial \bar{C}_p / \partial P)_T$ in terms of B_{2V} :

$$\begin{aligned} \left(\frac{\partial \bar{C}_p}{\partial P}\right)_T &= -T \left(\frac{\partial^2 \bar{V}}{\partial T^2}\right)_P \\ &= -T \left[2R \frac{dB_{2P}}{dT} + RT \frac{d^2 B_{2P}}{dT^2} + O(P) \right] \\ &= -T \left[2R \left(\frac{1}{RT} \frac{dB_{2V}}{dT} - \frac{B_{2V}}{RT^2} \right) + RT \left(\frac{1}{RT} \frac{d^2 B_{2V}}{dT^2} - \frac{2}{RT^2} \frac{dB_{2V}}{dT} + \frac{2B_{2V}}{RT^3} \right) \right] + O(P) \\ &= -\frac{2dB_{2V}}{dT} + \frac{2B_{2V}}{T} - T \frac{d^2 B_{2V}}{dT^2} + \frac{2dB_{2V}}{dT} - \frac{2B_{2V}}{T} + O(P) \\ &= -T \frac{d^2 B_{2V}}{dT^2} + O(P) \end{aligned}$$

Using Equation 16.41,

$$\begin{aligned} B_{2V}(T) &= \frac{2\pi\sigma^3 N_A}{3} [1 - (\lambda^3 - 1)(e^{\epsilon/k_B T} - 1)] \\ \frac{dB_{2V}}{dT} &= \frac{2\pi\sigma^3 N_A}{3} (\lambda^3 - 1) e^{\epsilon/k_B T} \left(\frac{\epsilon}{k_B T^2} \right) \\ \frac{d^2 B_{2V}}{dT^2} &= -\frac{2\pi\sigma^3 N_A}{3} (\lambda^3 - 1) e^{\epsilon/k_B T} \frac{\epsilon}{k_B T^3} \left(\frac{\epsilon}{k_B T} + 2 \right) \\ \left(\frac{\partial \bar{C}_p}{\partial P}\right)_T &= -T \frac{d^2 B_{2V}}{dT^2} = \frac{2\pi\sigma^3 N_A}{3} (\lambda^3 - 1) e^{\epsilon/k_B T} \frac{\epsilon}{k_B T^2} \left(\frac{\epsilon}{k_B T} + 2 \right) \end{aligned}$$

For nitrogen at 298.15 K,

$$\begin{aligned} \left(\frac{\partial \bar{C}_p}{\partial P}\right)_T &= \frac{2\pi(327.7 \times 10^{-12} \text{ m})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{3} (1.58^3 - 1) e^{95.2/298.15} \frac{95.2}{(298.15)^2 \text{ K}} \left(\frac{95.2}{298.15} + 2 \right) \\ &= 4.467 \times 10^{-7} \text{ m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 4.47 \times 10^{-4} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

Finally,

$$\begin{aligned} \bar{C}_p - \bar{C}_p^{\text{id}} &= (4.467 \times 10^{-4} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(P - P^{\text{id}}) \\ \bar{C}_p &= \frac{5R}{2} + (4.467 \times 10^{-4} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(99 \text{ atm}) \\ &= (2.5)(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) + 4.42 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &= 25.21 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

22-17. Show that the molar enthalpy of a substance at pressure P relative to its value at one bar is given by

$$\bar{H}(T, P) = \bar{H}(T, P = 1 \text{ bar}) + \int_1^P \left[\bar{V} - T \left(\frac{\partial \bar{V}}{\partial T} \right)_P \right] dP'$$

Calculate the value of $\bar{H}(T, P) - \bar{H}(T, P = 1 \text{ bar})$ at 0°C and 100 bar for mercury given that the molar volume of mercury varies with temperature according to

$$\bar{V}(t) = (14.75 \text{ mL} \cdot \text{mol}^{-1})(1 + 0.182 \times 10^{-3}t + 2.95 \times 10^{-9}t^2 + 1.15 \times 10^{-10}t^3)$$

where t is the Celsius temperature. Assume that $\bar{V}(0)$ does not vary with pressure over this range and express your answer in units of $\text{kJ} \cdot \text{mol}^{-1}$.

Begin with Equation 22.34:

$$\begin{aligned}\left(\frac{\partial \bar{H}}{\partial P}\right)_T &= \bar{V} - T \left(\frac{\partial \bar{V}}{\partial T}\right)_P \\ d\bar{H} &= \left[\bar{V} - T \left(\frac{\partial \bar{V}}{\partial T}\right)_P\right] dP \\ \bar{H}(T, P) - \bar{H}(T, 1 \text{ bar}) &= \int_{1 \text{ bar}}^P \left[\bar{V} - T \left(\frac{\partial \bar{V}}{\partial T}\right)_P\right] dP'\end{aligned}$$

where we have begun using P' as the quantity integrated over in order to distinguish it from P , the final pressure of the substance.

Using the values given for mercury,

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = (14.75 \text{ mL} \cdot \text{mol}^{-1})(0.182 \times 10^{-3} + 5.90 \times 10^{-9}t + 3.45 \times 10^{-10}t^2)$$

Then at 0°C and 100 bar,

$$\begin{aligned}\bar{H}(T, 100 \text{ bar}) - \bar{H}(T, 1 \text{ bar}) &= (14.75 \text{ mL} \cdot \text{mol}^{-1}) \int_{1 \text{ bar}}^{100 \text{ bar}} [1 - T(0.182 \times 10^{-3})] dP' \\ &= (14.75 \text{ mL} \cdot \text{mol}^{-1})(99 \text{ bar})[1 - (298.15)(0.182 \times 10^{-3})] \\ &= 1381 \text{ mL} \cdot \text{bar} \cdot \text{mol}^{-1} = 138.1 \text{ J} \cdot \text{mol}^{-1}\end{aligned}$$

22-18. Show that

$$dH = \left[V - T \left(\frac{\partial V}{\partial T}\right)_P\right] dP + C_P dT$$

What does this equation tell you about the natural variables of H ?

Write the total derivative of $H(P, T)$:

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

We can now use Equation 22-34 and the definition of C_P to write this as

$$dH = \left[V - T \left(\frac{\partial V}{\partial T}\right)_P\right] dP + C_P dT$$

Since the coefficients of dP and dT are not simple, this tells us that the natural variables of H are not P and T .

22-19. What are the natural variables of the entropy?

$$dS = PdV + \frac{1}{T}dU \quad (22.39)$$

Because the coefficients of dV and dU are simple thermodynamic quantities, we say that V and U are the natural variables of entropy.

22-20. Experimentally determined entropies are commonly adjusted for nonideality by using an equation of state called the (modified) Berthelot equation:

$$\frac{P\bar{V}}{RT} = 1 + \frac{9}{128} \frac{PT_c}{P_c T} \left(1 - 6 \frac{T_c^2}{T^2}\right)$$

Show that this equation leads to the correction

$$S^\circ(\text{at one bar}) = \bar{S}(\text{at one bar}) + \frac{27}{32} \frac{RT_c^3}{P_c T^3} (1 \text{ bar})$$

This result needs only the critical data for the substance. Use this equation along with the critical data in Table 16.5 to calculate the nonideality correction for $\text{N}_2(\text{g})$ at 298.15 K. Compare your result with the value used in Table 21.1.

$$S^\circ(1 \text{ bar}) - \bar{S}(1 \text{ bar}) = \int_{P^{\text{id}}}^{1 \text{ bar}} \left[\left(\frac{\partial \bar{V}}{\partial T}\right)_P - \frac{R}{P} \right] dP \quad (22.54)$$

We find $(\partial \bar{V}/\partial T)$ from the modified Berthelot equation:

$$\begin{aligned}\frac{P\bar{V}}{RT} &= 1 + \frac{9}{128} \frac{PT_c}{P_c T} \left(1 - 6 \frac{T_c^2}{T^2}\right) \\ \bar{V} &= \frac{RT}{P} + \frac{9R}{128} \frac{T_c}{P_c} - \frac{9 \cdot 6}{128} \frac{RT_c^3}{P_c T^2} \\ \left(\frac{\partial \bar{V}}{\partial T}\right)_P &= \frac{R}{P} + \frac{9 \cdot 6 \cdot 2}{128} \frac{RT_c^3}{P_c T^3}\end{aligned}$$

Now substitute into Equation 22.54 to find $S^\circ(1 \text{ bar}) - \bar{S}(1 \text{ bar})$, neglecting P^{id} with respect to 1 bar:

$$\begin{aligned}S^\circ(1 \text{ bar}) - \bar{S}(1 \text{ bar}) &= \int_{P^{\text{id}}}^{1 \text{ bar}} \left[\frac{R}{P} + \frac{27}{32} \frac{RT_c^3}{P_c T^3} - \frac{R}{P} \right] dP \\ &= \frac{27}{32} \frac{RT_c^3}{P_c T^3} (1 \text{ bar})\end{aligned}$$

For N_2 at 298.15 K, $T_c = 126.2 \text{ K}$ and $P_c = 34.00 \text{ bar}$. Then the nonideality correction (the difference between the two values of S) is

$$\begin{aligned}S^\circ(1 \text{ bar}) - \bar{S}(1 \text{ bar}) &= \frac{27 (8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) (126.2 \text{ K})^3}{32 (34.00 \text{ bar}) (298.15 \text{ K})^3} (1 \text{ bar}) \\ &= 0.0156 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\end{aligned}$$

This is essentially the value used in Table 21.1 ($0.02 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$).

22-21. Use the result of Problem 22-20 along with the critical data in Table 16.5 to determine the nonideality correction for $\text{CO}(\text{g})$ at its normal boiling point, 81.6 K. Compare your result with the value used in Problem 21-24.

$$\begin{aligned}
 S^\circ(1 \text{ bar}) - \bar{S}(1 \text{ bar}) &= \frac{27}{32} \frac{RT_c^3}{P_c T^3} (1 \text{ bar}) \\
 &= \frac{27}{32} \frac{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(132.85 \text{ K})^3}{(34.935 \text{ bar})(81.6 \text{ K})^3} (1 \text{ bar}) \\
 &= 0.867 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
 \end{aligned}$$

This is comparable to the value used in Problem 21–24 ($0.879 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$).

22–22. Use the result of Problem 22–20 along with the critical data in Table 16.5 to determine the nonideality correction for $\text{Cl}_2(\text{g})$ at its normal boiling point, 239 K. Compare your result with the value used in Problem 21–16.

$$\begin{aligned}
 S^\circ(1 \text{ bar}) - \bar{S}(1 \text{ bar}) &= \frac{27}{32} \frac{RT_c^3}{P_c T^3} (1 \text{ bar}) \\
 &= \frac{27}{32} \frac{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(416.9 \text{ K})^3}{(79.91 \text{ bar})(239 \text{ K})^3} (1 \text{ bar}) \\
 &= 0.466 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
 \end{aligned}$$

This is comparable to the value of $0.502 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ used in Problem 21–16.

22–23. Derive the equation

$$\left(\frac{\partial(A/T)}{\partial T} \right)_v = -\frac{U}{T^2}$$

which is a Gibbs-Helmholtz equation for A .

Begin with the definition of A (Equation 22.4):

$$\begin{aligned}
 A &= U - TS \\
 \frac{\partial}{\partial T} \left(\frac{A}{T} \right) &= \frac{\partial}{\partial T} \left[\frac{U}{T} - S \right] \\
 \left[\frac{\partial(A/T)}{\partial T} \right]_v &= -\frac{U}{T^2} + \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_v - \left(\frac{\partial S}{\partial T} \right)_v
 \end{aligned}$$

Now, by the definition of C_v ,

$$\frac{C_v}{T} = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_v$$

From Equation 21.2, we also know that

$$\frac{C_v}{T} = \left(\frac{\partial S}{\partial T} \right)_v$$

Therefore,

$$\left(\frac{\partial(A/T)}{\partial T} \right)_v = -\frac{U}{T^2} + \frac{C_v}{T} - \frac{C_v}{T} = -\frac{U}{T^2}$$

22–24. We can derive the Gibbs-Helmholtz equation directly from Equation 22.31a in the following way. Start with $(\partial G/\partial T)_p = -S$ and substitute for S from $G = H - TS$ to obtain

$$\frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p - \frac{G}{T^2} = -\frac{H}{T^2}$$

Now show that the left side is equal to $(\partial[G/T]/\partial T)_p$ to get the Gibbs-Helmholtz equation.

Begin with the equality in the statement of the problem and substitute for S as suggested (from Equation 22.13):

$$\begin{aligned}
 \left(\frac{\partial G}{\partial T} \right)_p &= -S = \frac{G}{T} - \frac{H}{T} \\
 \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p - \frac{G}{T^2} &= -\frac{H}{T^2} \quad (1)
 \end{aligned}$$

Taking the partial derivative of G/T with respect to T gives

$$\frac{\partial}{\partial T} \left(\frac{G}{T} \right) = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_p - \frac{G}{T^2}$$

so we can write Equation 1 as

$$\frac{\partial}{\partial T} \left(\frac{G}{T} \right) = -\frac{H}{T^2}$$

which is the Gibbs-Helmholtz equation.

22–25. Use the following data for benzene to plot $\bar{G}(T) - \bar{H}(0)$ versus T . [In this case we will ignore the (usually small) corrections due to nonideality of the gas phase.]

$$\bar{C}_p^s(T)/R = \frac{12\pi^4}{5} \left(\frac{T}{\Theta_D} \right)^3 \quad \Theta_D = 130.5 \text{ K} \quad 0 \text{ K} < T < 13 \text{ K}$$

$$\bar{C}_p^l(T)/R = -0.6077 + (0.1088 \text{ K}^{-1})T - (5.345 \times 10^{-4} \text{ K}^{-2})T^2 + (1.275 \times 10^{-6} \text{ K}^{-3})T^3 \quad 13 \text{ K} < T < 278.6 \text{ K}$$

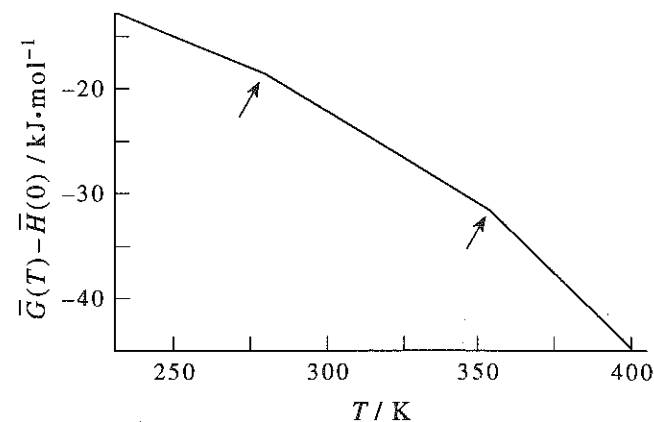
$$\bar{C}_p^l(T)/R = 12.713 + (1.974 \times 10^{-3} \text{ K}^{-1})T - (4.766 \times 10^{-5} \text{ K}^{-2})T^2 \quad 278.6 \text{ K} < T < 353.2 \text{ K}$$

$$\bar{C}_p^g(T)/R = -4.077 + (0.05676 \text{ K}^{-1})T - (3.588 \times 10^{-5} \text{ K}^{-2})T^2 + (8.520 \times 10^{-9} \text{ K}^{-3})T^3 \quad 353.2 \text{ K} < T < 1000 \text{ K}$$

$$T_{\text{fus}} = 278.68 \text{ K} \quad \Delta_{\text{fus}} \bar{H} = 9.95 \text{ kJ} \cdot \text{mol}^{-1}$$

$$T_{\text{vap}} = 353.24 \text{ K} \quad \Delta_{\text{vap}} \bar{H} = 30.72 \text{ kJ} \cdot \text{mol}^{-1}$$

Use the Equation $\bar{G}(T) - \bar{H}(0) = \bar{H}(T) - \bar{H}(0) - T\bar{S}(T)$ (as in Section 22–7) and Equations 22.62 and 22.63 for $\bar{H}(T) - \bar{H}(0)$ and $\bar{S}(T)$ to plot. (See Problem 21.15 for an explanation of how to assign the values of entropy and enthalpy as functions of temperature.)



The discontinuities in the slope at the melting and boiling points are difficult to see and so are highlighted with arrows.

22-26. Use the following data for propene to plot $\bar{G}(T) - \bar{H}(0)$ versus T . [In this case we will ignore the (usually small) corrections due to nonideality of the gas phase.]

$$\bar{C}_p^s(T)/R = \frac{12\pi^4}{5} \left(\frac{T}{\Theta_D} \right)^3 \quad \Theta_D = 100 \text{ K} \quad 0 \text{ K} < T < 15 \text{ K}$$

$$\bar{C}_p^s(T)/R = -1.616 + (0.08677 \text{ K}^{-1})T - (9.791 \times 10^{-4} \text{ K}^{-2})T^2 + (2.611 \times 10^{-6} \text{ K}^{-3})T^3$$

$$15 \text{ K} < T < 87.90 \text{ K}$$

$$\bar{C}_p^l(T)/R = 15.935 - (0.08677 \text{ K}^{-1})T + (4.294 \times 10^{-4} \text{ K}^{-2})T^2 - (6.276 \times 10^{-7} \text{ K}^{-3})T^3$$

$$87.90 \text{ K} < T < 225.46 \text{ K}$$

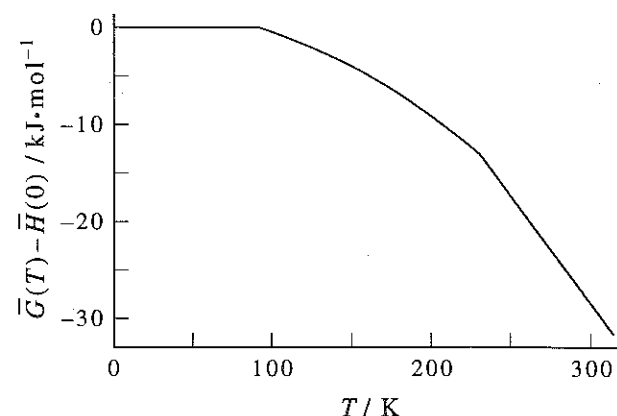
$$\bar{C}_p^g(T)/R = 1.4970 + (2.266 \times 10^{-2} \text{ K}^{-1})T - (5.725 \times 10^{-6} \text{ K}^{-2})T^2$$

$$225.46 \text{ K} < T < 1000 \text{ K}$$

$$T_{\text{fus}} = 87.90 \text{ K} \quad \Delta_{\text{fus}} \bar{H} = 3.00 \text{ kJ} \cdot \text{mol}^{-1}$$

$$T_{\text{vap}} = 225.46 \text{ K} \quad \Delta_{\text{vap}} \bar{H} = 18.42 \text{ kJ} \cdot \text{mol}^{-1}$$

This is done in the same way as Problem 22-25.



22-27. Use a virial expansion for Z to prove (a) that the integrand in Equation 22.74 is finite as $P \rightarrow 0$, and (b) that $(Z - 1)/P = 0$ for an ideal gas.

a. Use the virial expansion $Z = 1 + B_{2P}P + B_{3P}P^2 + O(P^3)$. Then

$$\frac{Z - 1}{P} = \frac{1 + B_{2P}P + B_{3P}P^2 + O(P^3) - 1}{P}$$

$$= B_{2P} + B_{3P}P + O(P^2)$$

As $P \rightarrow 0$, then, the integrand approaches B_{2P} , which is finite.

b. For an ideal gas, $Z = P\bar{V}/RT$ and $P\bar{V} = RT$, so

$$\frac{Z - 1}{P} = \frac{1 - 1}{P} = 0$$

22-28. Derive a virial expansion in the pressure for $\ln \gamma$.

Begin with Equation 22.74 and expand Z as in Problem 22-27(a):

$$\ln \gamma = \int_0^P \frac{Z - 1}{P'} dP'$$

$$= \int_0^P (B_{2P} + B_{3P}P' + O(P'^2)) dP'$$

$$= B_{2P}P + \frac{B_{3P}P^2}{2} + O(P^3)$$

22-29. The compressibility factor for ethane at 600 K can be fit to the expression

$$Z = 1.0000 - 0.000612(P/\text{bar}) + 2.661 \times 10^{-6}(P/\text{bar})^2$$

$$- 1.390 \times 10^{-9}(P/\text{bar})^3 - 1.077 \times 10^{-13}(P/\text{bar})^4$$

for $0 \leq P/\text{bar} \leq 600$. Use this expression to determine the fugacity coefficient of ethane as a function of pressure at 600 K.

Substitute into Equation 22.74:

$$\ln \gamma = \int_0^P \frac{Z - 1}{P'} dP'$$

$$= \int_0^P [-6.12 \times 10^{-4} \text{ bar}^{-1} + (2.661 \times 10^{-6} \text{ bar}^{-2})P'$$

$$- (1.390 \times 10^{-9} \text{ bar}^{-3})P'^2 - (1.077 \times 10^{-13} \text{ bar}^{-4})P'^3] dP'$$

$$= -(6.12 \times 10^{-4} \text{ bar}^{-1})P + \frac{1}{2}(2.661 \times 10^{-6} \text{ bar}^{-2})P^2$$

$$- \frac{1}{3}(1.390 \times 10^{-9} \text{ bar}^{-3})P^3 - \frac{1}{4}(1.077 \times 10^{-13} \text{ bar}^{-4})P^4$$

$$\gamma = \exp[-(6.12 \times 10^{-4} \text{ bar}^{-1})P + (1.3305 \times 10^{-6} \text{ bar}^{-2})P^2$$

$$- (4.633 \times 10^{-10} \text{ bar}^{-3})P^3 - (2.693 \times 10^{-14} \text{ bar}^{-4})P^4]$$

22-30. Use Figure 22.11 and the data in Table 16.5 to estimate the fugacity of ethane at 360 K and 1000 atm.

From Table 16.5, $T_c = 305.34$ K and $P_c = 48.077$ atm. Then at 360 K and 1000 atm, $T/T_c = 1.18$ and $P/P_c = 20.8$. Using Figure 22.11, it appears that $\gamma \approx 0.63$.

22-31. Use the following data for ethane at 360 K to plot the fugacity coefficient against pressure.

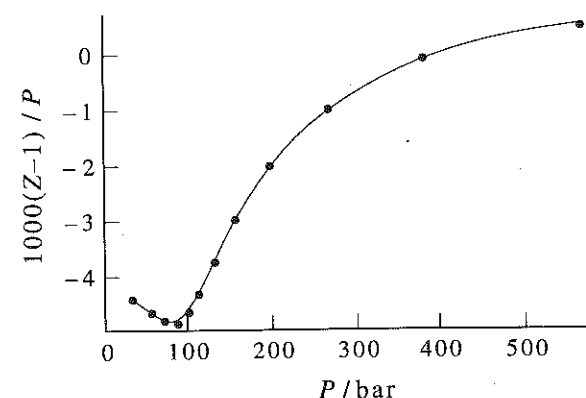
$\rho/\text{mol}\cdot\text{dm}^{-3}$	P/bar	$\rho/\text{mol}\cdot\text{dm}^{-3}$	P/bar	$\rho/\text{mol}\cdot\text{dm}^{-3}$	P/bar
1.20	31.031	6.00	97.767	10.80	197.643
2.40	53.940	7.20	112.115	12.00	266.858
3.60	71.099	8.40	130.149	13.00	381.344
4.80	84.892	9.60	156.078	14.40	566.335

Compare your result with the result you obtained in Problem 22-30.

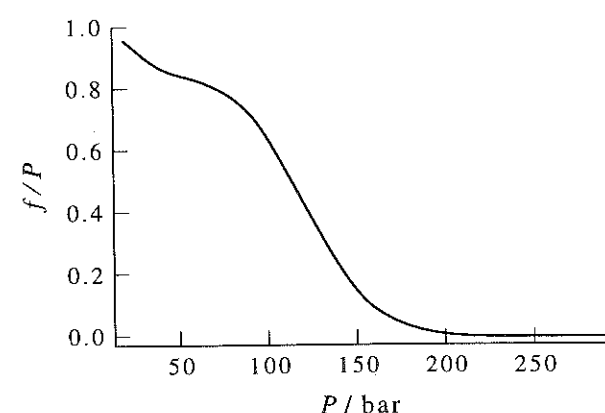
By definition,

$$\frac{(Z-1)}{P} = \frac{1}{\rho RT} - \frac{1}{P} = y$$

Now we can plot $(Z-1)/P$ vs. P :



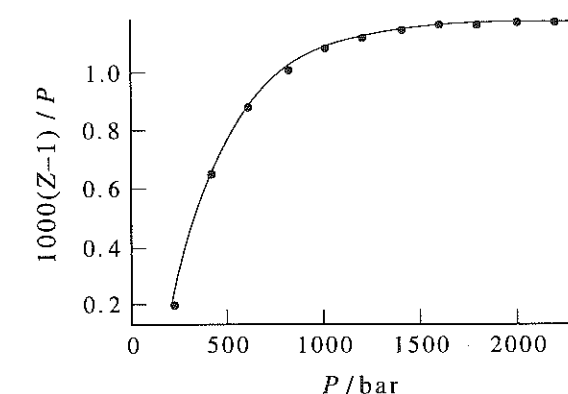
Numerical integration using the trapezoidal approximation allows us to graph f/P vs. P , in the same way that Figure 22.10 was created from Figure 22.9.



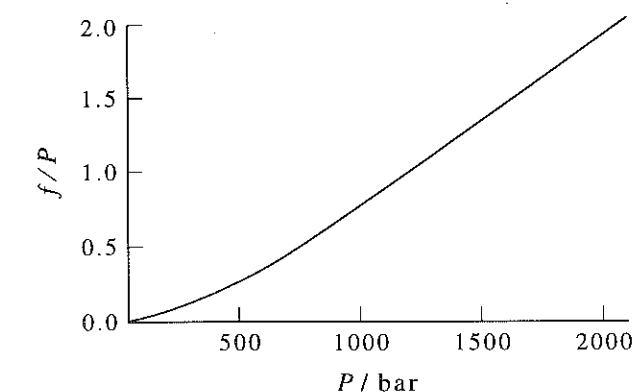
22-32. Use the following data for $\text{N}_2(\text{g})$ at 0°C to plot the fugacity coefficient as a function of pressure.

P/atm	$Z = P\bar{V}/RT$	P/atm	$Z = P\bar{V}/RT$	P/atm	$Z = P\bar{V}/RT$
200	1.0390	1000	2.0700	1800	3.0861
400	1.2570	1200	2.3352	2000	3.3270
600	1.5260	1400	2.5942	2200	3.5640
800	1.8016	1600	2.8456	2400	3.8004

Again, plot $(Z-1)/P$ vs. P :



Then do numerical integration with the trapezoidal approximation to graph f/P vs. P :



22-33. It might appear that we can't use Equation 22.72 to determine the fugacity of a van der Waals gas because the van der Waals equation is a cubic equation in \bar{V} , so we can't solve it analytically for \bar{V} to carry out the integration in Equation 22.72. We can get around this problem, however, by integrating Equation 22.72 by parts. First show that

$$RT \ln \gamma = P\bar{V} - RT - \int_{\bar{V}^{\text{id}}}^{\bar{V}} P d\bar{V}' - RT \ln \frac{P}{P^{\text{id}}}$$

where $P^{\text{id}} \rightarrow 0$, $\bar{V}^{\text{id}} \rightarrow \infty$, and $P^{\text{id}}\bar{V}^{\text{id}} \rightarrow RT$. Substitute P from the van der Waals equation into the first term and the integral on the right side of the above equation and integrate to obtain

$$RT \ln \gamma = \frac{RT\bar{V}}{\bar{V}-b} - \frac{a}{\bar{V}} - RT - RT \ln \frac{\bar{V}-b}{\bar{V}^{\text{id}}-b} - \frac{a}{\bar{V}} - RT \ln \frac{P}{P^{\text{id}}}$$

Now use the fact that $\bar{V}^{\text{id}} \rightarrow \infty$ and that $P^{\text{id}}\bar{V}^{\text{id}} = RT$ to show that

$$\ln \gamma = -\ln \left[1 - \frac{a(\bar{V} - b)}{RT\bar{V}^2} \right] + \frac{b}{\bar{V} - b} - \frac{2a}{RT\bar{V}}$$

This equation gives the fugacity of a van der Waals gas as a function of \bar{V} . You can use the van der Waals equation itself to calculate P from \bar{V} , so the above equation, in conjunction with the van der Waals equation, gives $\ln \gamma$ as a function of pressure.

First we integrate Equation 22.72 by parts:

$$\begin{aligned} \ln \gamma &= \int_{P^{\text{id}}}^P \left(\frac{\bar{V}}{RT} - \frac{1}{P'} \right) dP' \\ RT \ln \gamma &= \int_{P^{\text{id}}}^P \bar{V} dP' - \int_{P^{\text{id}}}^P \frac{RT}{P'} dP' \\ &= P\bar{V} \Big|_{P^{\text{id}}}^P - \int_{\bar{V}^{\text{id}}}^{\bar{V}} P' d\bar{V} - RT \ln \frac{P}{P^{\text{id}}} \\ &= P\bar{V} - (P\bar{V})^{\text{id}} - \int_{\bar{V}^{\text{id}}}^{\bar{V}} P' d\bar{V} - RT \ln \frac{P}{P^{\text{id}}} \\ &= P\bar{V} - RT - \int_{\bar{V}^{\text{id}}}^{\bar{V}} P' d\bar{V} - RT \ln \frac{P}{P^{\text{id}}} \end{aligned}$$

Substituting P from the van der Waals equation, we find that this equation becomes

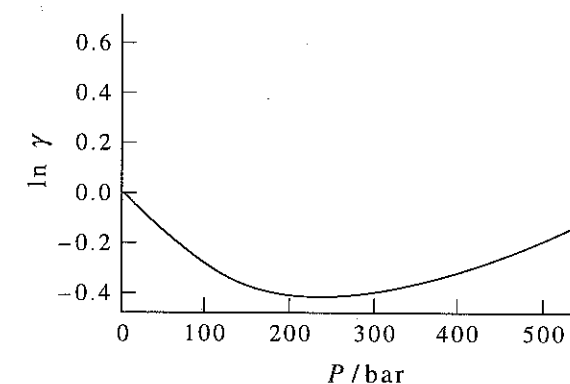
$$\begin{aligned} RT \ln \gamma &= \bar{V} \left[\frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \right] - RT - \int_{\bar{V}^{\text{id}}}^{\bar{V}} \left[\frac{RT}{\bar{V}' - b} - \frac{a}{\bar{V}'^2} \right] d\bar{V}' - RT \ln \frac{P}{P^{\text{id}}} \\ &= \frac{RT\bar{V}}{\bar{V} - b} - \frac{a}{\bar{V}} - RT - RT \ln \frac{\bar{V} - b}{\bar{V}^{\text{id}} - b} - \frac{a}{\bar{V}} + \frac{a}{\bar{V}^{\text{id}}} - RT \ln \frac{P}{P^{\text{id}}} \\ &= \frac{RT\bar{V}}{\bar{V} - b} - \frac{a}{\bar{V}} - RT - RT \ln \frac{\bar{V} - b}{\bar{V}^{\text{id}} - b} - \frac{a}{\bar{V}} + \frac{a}{\bar{V}^{\text{id}}} - RT \ln \frac{P}{P^{\text{id}}} \end{aligned}$$

Now, since $\bar{V}^{\text{id}} \rightarrow \infty$, we can neglect b in the denominator of the logarithmic term and consider the a/\bar{V}^{id} term negligible. Also, since $P^{\text{id}}\bar{V}^{\text{id}} = RT$, we write the above expression as

$$\begin{aligned} RT \ln \gamma &= \frac{RT\bar{V}}{\bar{V} - b} - \frac{2a}{\bar{V}} - RT - RT \left(\ln \frac{\bar{V} - b}{\bar{V}^{\text{id}}} + \ln \frac{P}{P^{\text{id}}} \right) \\ \ln \gamma &= \frac{\bar{V}}{\bar{V} - b} - \frac{2a}{\bar{V}RT} - 1 + \ln \bar{V}^{\text{id}} P^{\text{id}} - \ln P(\bar{V} - b) \\ &= \frac{\bar{V} - (\bar{V} - b)}{\bar{V} - b} - \frac{2a}{RT\bar{V}} - \ln \frac{P(\bar{V} - b)}{RT} \\ &= \frac{b}{\bar{V} - b} - \frac{2a}{RT\bar{V}} - \ln \left[\frac{(\bar{V} - b)}{RT} \left(\frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \right) \right] \\ &= \frac{b}{\bar{V} - b} - \frac{2a}{RT\bar{V}} - \ln \left[1 - \frac{a(\bar{V} - b)}{RT\bar{V}^2} \right] \end{aligned}$$

22-34. Use the final equation in Problem 22-33 along with the van der Waals equation to plot $\ln \gamma$ against pressure for CO(g) at 200 K. Compare your result with Figure 22.10.

From Table 16.3, $a = 1.4734 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $b = 0.039523 \text{ dm}^3 \cdot \text{mol}^{-1}$ for CO. We are given $\ln \gamma$ as a function of \bar{V} in Problem 22-33, and the van der Waals equation gives P as a function of \bar{V} . Therefore, we can choose values of \bar{V} and calculate the corresponding values of $\ln \gamma$ and P . Then we can plot $\ln \gamma$ against P . The result is



22-35. Show that the expression for $\ln \gamma$ for the van der Waals equation (Problem 22-33) can be written in the reduced form

$$\ln \gamma = \frac{1}{3V_R - 1} - \frac{9}{4V_R T_R} - \ln \left[1 - \frac{3(3V_R - 1)}{8T_R V_R^2} \right]$$

Use this equation along with the van der Waals equation in reduced form (Equation 16.19) to plot γ against P_R for $T_R = 1.00$ and 2.00 and compare your results with Figure 22.11.

We can use Equations 16.12 to express a and b in terms of T_c and \bar{V}_c :

$$3\bar{V}_c = b + \frac{RT_c}{P_c} \quad 3\bar{V}_c^2 = \frac{a}{P_c} \quad \bar{V}_c^3 = \frac{ab}{P_c}$$

Combining the first and the second, and the second and the third, equations gives

$$\begin{aligned} 3\bar{V}_c &= b + \frac{\bar{V}_c^3 RT_c}{ab} & 3\bar{V}_c^2 &= \frac{a\bar{V}_c^3}{ab} \\ 3\bar{V}_c &= \frac{\bar{V}_c}{3} + \frac{3\bar{V}_c^2 RT_c}{a} & b &= \frac{\bar{V}_c}{3} \\ a &= \frac{9}{8} \bar{V}_c RT_c \end{aligned}$$

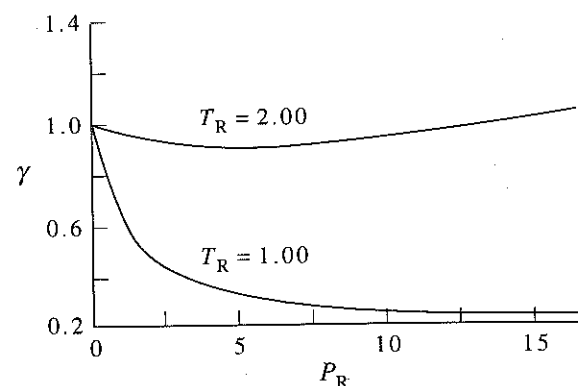
Now we can substitute into the expression for $\ln \gamma$ we found in the previous problem:

$$\begin{aligned} \ln \gamma &= \frac{b}{\bar{V} - b} - \frac{2a}{RT\bar{V}} - \ln \left[1 - \frac{a(\bar{V} - b)}{RT\bar{V}^2} \right] \\ &= \frac{\bar{V}_c}{3\bar{V} - \bar{V}_c} - \frac{2}{RT\bar{V}} \left(\frac{9}{8} \bar{V}_c RT_c \right) - \ln \left[1 - \frac{9}{8} \bar{V}_c RT_c \frac{(\bar{V} - \bar{V}_c)}{3RT\bar{V}^2} \right] \\ &= \frac{1}{3\bar{V}_R - 1} - \frac{9}{4T_R \bar{V}_R} - \ln \left[1 - \frac{3(3\bar{V}_R - 1)}{8T_R \bar{V}_R^2} \right] \end{aligned}$$

Equation 16.19 gives

$$P_R = \frac{8}{3} T_R \left(\bar{V}_R - \frac{1}{3} \right)^{-1} - \frac{3}{\bar{V}_R^2}$$

We have now found expressions for both $\ln \gamma$ and P as functions of \bar{V}_R and T_R . We can therefore choose values of \bar{V}_R for a specific value of T_R and calculate the corresponding values of $\ln \gamma$ and P , and plot γ against P . The result is



This looks very much like the experimental curves plotted in Figure 22.11.

22-36. Use the method outlined in Problem 22-33 to show that

$$\ln \gamma = \frac{B}{\bar{V} - B} - \frac{A}{RT^{3/2}(\bar{V} + B)} - \frac{A}{BRT^{3/2}} \ln \frac{\bar{V} + B}{\bar{V}} - \ln \left[1 - \frac{A(\bar{V} - B)}{RT^{3/2}\bar{V}(\bar{V} + B)} \right]$$

for the Redlich-Kwong equation. You need to use the standard integral

$$\int \frac{dx}{x(ax + b)} = -\frac{1}{a} \ln \frac{a + bx}{x}$$

For a Redlich-Kwong gas,

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

We can still use the first equation in Problem 22-43, since it was independent of the equation of state chosen. Also, realize that as $\bar{V}^{\text{id}} \rightarrow \infty$, B becomes negligible with respect to \bar{V}^{id} .

$$\begin{aligned} RT \ln \gamma &= P\bar{V} - RT - \int_{\bar{V}^{\text{id}}}^{\bar{V}} P' d\bar{V} - RT \ln \frac{P}{P^{\text{id}}} \\ &= \frac{RT\bar{V}}{\bar{V} - B} - \frac{A}{T^{1/2}(\bar{V} + B)} - RT - \int_{\bar{V}^{\text{id}}}^{\bar{V}} \left[\frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} \right] d\bar{V} - RT \ln \frac{P}{P^{\text{id}}} \\ &= RT \left(\frac{\bar{V}}{\bar{V} - B} - 1 \right) - \frac{A}{T^{1/2}(\bar{V} + B)} - RT \ln \frac{\bar{V} - B}{\bar{V}^{\text{id}} - B} \\ &\quad - \frac{A}{T^{1/2}B} \left[\ln \frac{\bar{V} + B}{\bar{V}} - \ln \frac{\bar{V}^{\text{id}} + B}{\bar{V}^{\text{id}}} \right] - RT \ln \frac{P}{P^{\text{id}}} \\ \ln \gamma &= \frac{B}{\bar{V} - B} - \frac{A}{RT^{3/2}(\bar{V} + B)} - \frac{A}{BRT^{3/2}} \ln \frac{\bar{V} + B}{\bar{V}} - \ln \frac{P(\bar{V} - B)}{P^{\text{id}}\bar{V}^{\text{id}}} \end{aligned}$$

$$\begin{aligned} &= \frac{B}{\bar{V} - B} - \frac{A}{RT^{3/2}(\bar{V} + B)} - \frac{A}{BRT^{3/2}} \ln \frac{\bar{V} + B}{\bar{V}} \\ &\quad - \ln \left\{ \frac{(\bar{V} - B)}{RT} \left[\frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} \right] \right\} \\ &= \frac{B}{\bar{V} - B} - \frac{A}{RT^{3/2}(\bar{V} + B)} - \frac{A}{BRT^{3/2}} \ln \frac{\bar{V} + B}{\bar{V}} - \ln \left[1 - \frac{A(\bar{V} - B)}{RT^{3/2}\bar{V}(\bar{V} + B)} \right] \end{aligned}$$

22-37. Show that $\ln \gamma$ for the Redlich-Kwong equation (see Problem 22-36) can be written in the reduced form

$$\begin{aligned} \ln \gamma &= \frac{0.25992}{\bar{V}_R - 0.25992} - \frac{1.2824}{T_R^{3/2}(\bar{V}_R + 0.25992)} \\ &\quad - \frac{4.9340}{T_R^{3/2}} \ln \frac{\bar{V}_R + 0.25992}{\bar{V}_R} - \ln \left[1 - \frac{1.2824(\bar{V}_R - 0.25992)}{T_R^{3/2}\bar{V}_R(\bar{V}_R + 0.25992)} \right] \end{aligned}$$

From Problem 16-26, we can express A and B in terms of T_c and \bar{V}_c :

$$3\bar{V}_c = \frac{RT_c}{P_c} \quad B = 0.25992\bar{V}_c \quad A = 0.42748 \frac{R^2 T_c^{5/2}}{P_c}$$

Then

$$A = 0.42748 \frac{R^2 T_c^{5/2} 3\bar{V}_c}{RT_c} = 1.2824 R \bar{V}_c T_c^{3/2}$$

Now we can substitute into our expression for $\ln \gamma$ in the previous problem:

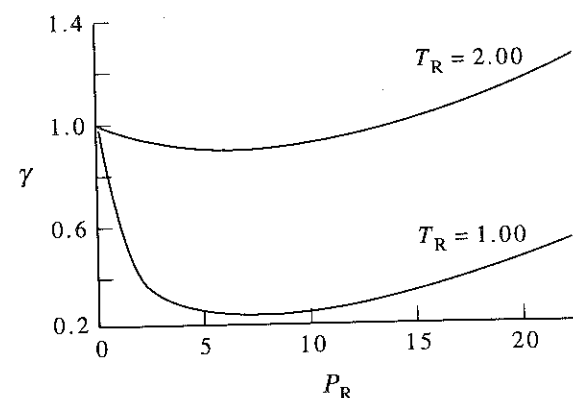
$$\begin{aligned} \ln \gamma &= \frac{B}{\bar{V} - B} - \frac{A}{RT^{3/2}(\bar{V} + B)} - \frac{A}{BRT^{3/2}} \ln \frac{\bar{V} + B}{\bar{V}} - \ln \left[1 - \frac{A(\bar{V} - B)}{RT^{3/2}\bar{V}(\bar{V} + B)} \right] \\ &= \frac{0.25992\bar{V}_c}{\bar{V} - 0.25992\bar{V}_c} - \frac{1.2824 R \bar{V}_c T_c^{3/2}}{RT^{3/2}(\bar{V} + 0.25992\bar{V}_c)} - \frac{1.2824 R \bar{V}_c T_c^{3/2}}{RT^{3/2}(0.25992\bar{V}_c)} \ln \frac{\bar{V} + 0.25992\bar{V}_c}{\bar{V}} \\ &\quad - \ln \left[1 - \frac{1.2824 R \bar{V}_c T_c^{3/2}(\bar{V} - 0.25992\bar{V}_c)}{RT^{3/2}(\bar{V} + 0.25992\bar{V}_c)\bar{V}} \right] \\ &= \frac{0.25992}{\bar{V}_R - 0.25992} - \frac{1.2824}{T_R^{3/2}(\bar{V}_R + 0.25992)} \\ &\quad - \frac{4.9340}{T_R^{3/2}} \ln \frac{\bar{V}_R + 0.25992}{\bar{V}_R} - \ln \left[1 - \frac{1.2824(\bar{V}_R - 0.25992)}{T_R^{3/2}\bar{V}_R(\bar{V}_R + 0.25992)} \right] \end{aligned}$$

22-38. Use the expression for $\ln \gamma$ in reduced form given in Problem 22-37 along with the Redlich-Kwong equation in reduced form (Example 16-7) to plot $\ln \gamma$ versus P_R for $T_R = 1.00$ and 2.00 and compare your results with those you obtained in Problem 22-35 for the van der Waals equation.

From Example 16-7, we have an expression for P_R as a function of T_R and \bar{V}_R :

$$P_R = \frac{3T_R}{\bar{V}_R - 0.25992} - \frac{3.8473}{T_R^{1/2}\bar{V}_R(\bar{V}_R + 0.25992)}$$

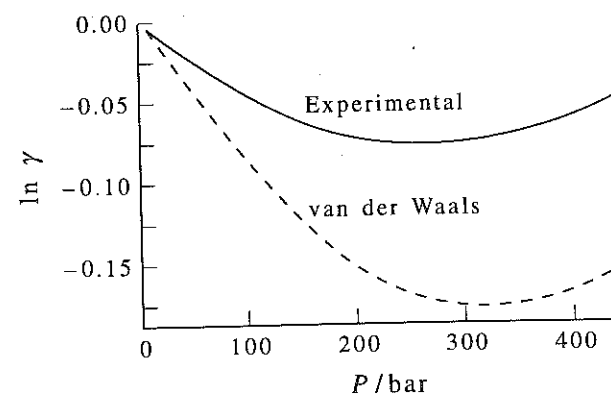
and from the previous problem we have an expression for $\ln \gamma$ as a function of T_R and \bar{V}_R . We can therefore choose values of \bar{V}_R for a specific value of T_R and calculate the corresponding values of $\ln \gamma$ and P , and then plot γ against P . The result is



The upward curvature observed here is more marked than that in the plot we obtained from the van der Waals equation.

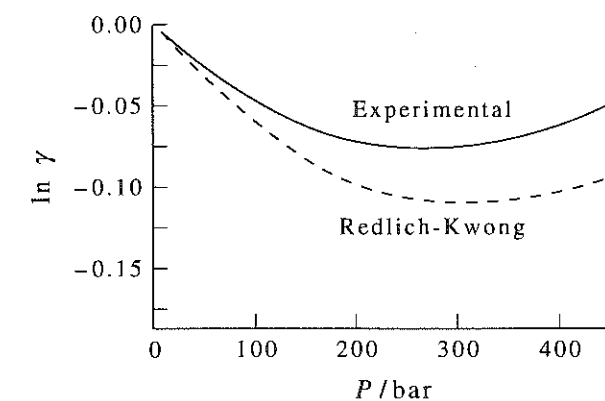
- 22-39. Compare $\ln \gamma$ for the van der Waals equation (Problem 22-33) with the values of $\ln \gamma$ for ethane at 600 K (Problem 22-29).

We can graph both the experimental and van der Waals $\ln \gamma$ vs. P , using $a = 5.5818 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-2}$ and $b = 0.065144 \text{ dm}^3 \cdot \text{mol}^{-1}$. This is only a good fit at extremely low pressures.



- 22-40. Compare $\ln \gamma$ for the Redlich-Kwong equation (Problem 22-36) with the values of $\ln \gamma$ for ethane at 600 K (Problem 22-29).

We can graph both the experimental and Redlich-Kwong $\ln \gamma$ vs. P , using $A = 98.831 \text{ dm}^3 \cdot \text{bar} \cdot \text{K}^{-1/2} \cdot \text{mol}^{-2}$ and $B = 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}$. The Redlich-Kwong equation provides a markedly better description of the behavior of $\ln \gamma$ than the van der Waals equation does.



- 22-41. We can use the equation $(\partial S / \partial U)_V = 1/T$ to illustrate the consequence of the fact that entropy always increases during an irreversible adiabatic process. Consider a two-compartment system enclosed by rigid adiabatic walls, and let the two compartments be separated by a rigid heat-conducting wall. We assume that each compartment is at equilibrium but that they are not in equilibrium with each other. Because no work can be done by this two-compartment system (rigid walls) and no energy as heat can be exchanged with the surroundings (adiabatic walls),

$$U = U_1 + U_2 = \text{constant}$$

Show that

$$dS = \left(\frac{\partial S_1}{\partial U_1} \right) dU_1 + \left(\frac{\partial S_2}{\partial U_2} \right) dU_2$$

because the entropy of each compartment can change only as a result of a change in energy. Now show that

$$dS = dU_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \geq 0$$

Use this result to discuss the direction of the flow of energy as heat from one temperature to another.

We know that $U_1 + U_2$ is a constant, so $dU_1 = -dU_2$. Since the change of entropy of each compartment is dependent only on the energy change of each compartment (using the fact that we can express dS in terms of dU and dV , its natural variables), we can write

$$dS(U_1, U_2) = \left(\frac{\partial S_1}{\partial U_1} \right) dU_1 + \left(\frac{\partial S_2}{\partial U_2} \right) dU_2$$

Notice that this is a constant-volume process, so we use the expression $(\partial S / \partial U)_V = 1/T$ to write

$$\left(\frac{\partial S_1}{\partial U_1} \right)_V = \frac{1}{T_1} \quad \text{and} \quad \left(\frac{\partial S_2}{\partial U_2} \right)_V = \frac{1}{T_2}$$

Substituting into the expression for dS gives

$$dS = \frac{dU_1}{T_1} + \frac{dU_2}{T_2} = dU_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \geq 0$$

where the inequality holds because entropy always increases in an irreversible adiabatic process. If the energy flows from compartment 2 into compartment 1, dU_1 must be positive, and so $T_1 < T_2$ in order for the inequality to hold. Likewise, if the energy flows from compartment 2

into compartment 1, dU_1 is negative and so $T_1 > T_2$. The energy always flows from the higher temperature to the lower temperature.

22-42. Modify the argument in Problem 22-41 to the case in which the two compartments are separated by a nonrigid, insulating wall. Derive the result

$$dS = \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1$$

Use this result to discuss the direction of a volume change under an isothermal pressure difference.

Since the entire system is isolated, we know

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

This means that $dU_1 = -dU_2$ and $dV_1 = -dV_2$. Now entropy depends on the energy and the volume, so

$$dS = \left(\frac{\partial S_1}{\partial U_1} \right) dU_1 + \left(\frac{\partial S_1}{\partial V_1} \right) dV_1 + \left(\frac{\partial S_2}{\partial U_2} \right) dU_2 + \left(\frac{\partial S_2}{\partial V_2} \right) dV_2$$

From Equation 22.40, $(\partial S/\partial U)_V = 1/T$ and $(\partial S/\partial V)_U = P/T$, so

$$\begin{aligned} dS &= \frac{dU_1}{T_1} - \frac{dU_1}{T_2} + \frac{P_1}{T_1} dV_1 - \frac{P_2}{T_2} dV_1 \\ &= dU \left(\frac{1}{T_1} - \frac{1}{T_2} \right) + dV_1 \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) \end{aligned}$$

For an isothermal process, this expression becomes

$$dS = \frac{dV_1}{T} (P_1 - P_2)$$

If the volume of compartment 1 increases, dV_1 is positive and so $P_1 > P_2$ in order for dS to be positive. If the volume of compartment 1 decreases, dV_1 is negative and $P_2 > P_1$. The higher pressure compartment will expand under an isothermal pressure difference.

22-43. In this problem, we will derive virial expansions for \bar{U} , \bar{H} , \bar{S} , \bar{A} , and \bar{G} . Substitute

$$Z = 1 + B_{2P}P + B_{3P}P^2 + \dots$$

into Equation 22.65 and integrate from a small pressure, P^{id} , to P to obtain

$$\bar{G}(T, P) - \bar{G}(T, P^{\text{id}}) = RT \ln \frac{P}{P^{\text{id}}} + RT B_{2P}P + \frac{RT B_{3P}}{2} P^2 + \dots$$

Now use Equation 22.64 (realize that $P = P^{\text{id}}$ in Equation 22.64) to get

$$\bar{G}(T, P) - G^\circ(T) = RT \ln P + RT B_{2P}P + \frac{RT B_{3P}}{2} P^2 + \dots \quad (1)$$

at $P^\circ = 1$ bar. Now use Equation 22.31a to get

$$\bar{S}(T, P) - S^\circ(T) = -R \ln P - \frac{d(RT B_{2P})}{dT} P - \frac{1}{2} \frac{d(RT B_{3P})}{dT} P^2 + \dots \quad (2)$$

at $P^\circ = 1$ bar. Now use $\bar{G} = \bar{H} - T\bar{S}$ to get

$$\bar{H}(T, P) - H^\circ(T) = -RT^2 \frac{dB_{2P}}{dT} P - \frac{RT^2}{2} \frac{dB_{3P}}{dT} P^2 + \dots \quad (3)$$

Now use the fact that $\bar{C}_P = (\partial \bar{H}/\partial T)_P$ to get

$$\bar{C}_P(T, P) - C_P^\circ(T) = -RT \left[2 \frac{dB_{2P}}{dT} + T \frac{d^2 B_{2P}}{dT^2} \right] P - \frac{RT}{2} \left[2 \frac{dB_{3P}}{dT} + T \frac{d^2 B_{3P}}{dT^2} \right] P^2 + \dots \quad (4)$$

We can obtain expansions for \bar{U} and \bar{A} by using the equation $\bar{H} = \bar{U} + P\bar{V} = \bar{U} + RTZ$ and $\bar{G} = \bar{A} + P\bar{V} = \bar{A} + RTZ$. Show that

$$\bar{U} - U^\circ = -RT \left(B_{2P} + T \frac{dB_{2P}}{dT} \right) P - RT \left(B_{3P} + \frac{T}{2} \frac{dB_{3P}}{dT} \right) P^2 + \dots \quad (5)$$

and

$$\bar{A} - A^\circ = RT \ln P - \frac{RT B_{3P}}{2} P^2 + \dots \quad (6)$$

at $P^\circ = 1$ bar.

We can use the virial expansion in pressure to write

$$\begin{aligned} Z &= 1 + B_{2P}P + B_{3P}P^2 + \dots \\ \bar{V} &= \frac{RT}{P} + B_{2P}RT + B_{3P}RTP + \dots \end{aligned}$$

Now substitute into Equation 22.65:

$$\begin{aligned} \left(\frac{\partial \bar{G}}{\partial P} \right)_T &= \bar{V} \\ \int_{P^{\text{id}}}^P d\bar{G} &= \int_{P^{\text{id}}}^P \left[\frac{RT}{P} + B_{2P}RT + B_{3P}RTP + O(P^2) \right] dP \\ \bar{G}(T, P) - \bar{G}(T, P^{\text{id}}) &= RT \ln \frac{P}{P^{\text{id}}} + RT B_{2P}(P - P^{\text{id}}) + \frac{RT B_{3P}}{2} (P^2 - P^{\text{id}2}) + O(P^3) \end{aligned}$$

Since P^{id} is very small, we can neglect it with respect to P in the last two terms and find

$$\bar{G}(T, P) - \bar{G}(T, P^{\text{id}}) = RT \ln \frac{P}{P^{\text{id}}} + RT B_{2P}P + \frac{RT B_{3P}}{2} P^2 + O(P^3)$$

Equation 22.64 states that

$$\bar{G}(T, P^{\text{id}}) = G^\circ(T) + RT \ln \frac{P^{\text{id}}}{P^\circ}$$

Substituting,

$$\bar{G}(T, P) - G^\circ(T) = RT \ln \frac{P}{P^\circ} + RT B_{2P}P + \frac{RT B_{3P}}{2} P^2 + O(P^3)$$

which is Equation 1 when $P^\circ = 1$ bar. Now

$$\begin{aligned}\bar{S} &= -\left(\frac{\partial \bar{G}}{\partial T}\right)_P \\ \bar{S}(T, P) - S^\circ(T) &= -\left(\frac{\partial [\bar{G}(T, P) - G^\circ(T)]}{\partial T}\right)_P \\ &= -R \ln P - \frac{d(RTB_{2P})}{dT}P - \frac{1}{2} \frac{d(TRB_{3P})}{dT}P^2 + O(P^3)\end{aligned}$$

which is Equation 2. Since $\bar{G} = \bar{H} - T\bar{S}$, we can now write

$$\begin{aligned}\bar{G}(T, P) - G^\circ(T) &= \bar{H}(T, P) - H^\circ(T) - T[\bar{S}(T, P) - S^\circ(T)] \\ \bar{H}(T, P) - H^\circ(T) &= RT \ln P + RTB_{2P}P + \frac{RTB_{3P}}{2}P^2 + T[-R \ln P \\ &\quad - \frac{d(RTB_{2P})}{dT}P - \frac{1}{2} \frac{d(TRB_{3P})}{dT}P^2 + O(P^3)] \\ &= -RT^2 \frac{dB_{2P}}{dT}P - \frac{RT^2}{2} \frac{dB_{3P}}{dT}P^2 + O(P^3)\end{aligned}$$

This is Equation 3. Now we can take the partial derivative of enthalpy with respect to temperature to find \bar{C}_p :

$$\begin{aligned}\bar{C}_p &= \left(\frac{\partial \bar{H}}{\partial T}\right)_P \\ \bar{C}_p(T, P) - C_p^\circ(T) &= \left(\frac{\partial [\bar{H}(T, P) - H^\circ(T)]}{\partial T}\right)_P \\ &= \left(-2RT \frac{dB_{2P}}{dT} - RT^2 \frac{d^2B_{2P}}{dT^2}\right)P - \left(RT \frac{dB_{3P}}{dT} + \frac{RT^2}{2} \frac{d^2B_{3P}}{dT^2}\right)P^2 + O(P^3) \\ &= -RT \left(2 \frac{dB_{2P}}{dT} + T \frac{d^2B_{2P}}{dT^2}\right)P - \frac{RT}{2} \left(2 \frac{dB_{3P}}{dT} + T \frac{d^2B_{3P}}{dT^2}\right)P^2 + O(P^3)\end{aligned}$$

This is Equation 4. Now use the fact that $\bar{U} = \bar{H} - P\bar{V}$:

$$\begin{aligned}\bar{U}(T, P) - U^\circ(T) &= \bar{H}(T, P) - H^\circ(T) - P[\bar{V}(T, P) - V^\circ(T)] \\ &= \left[-RT^2 \frac{dB_{2P}}{dT}P - \frac{RT^2}{2} \frac{dB_{3P}}{dT}P^2\right] - P\left[\frac{ZRT}{P} - \frac{RT}{P}\right] + O(P^3) \\ &= -RT^2 \frac{dB_{2P}}{dT}P - \frac{RT^2}{2} \frac{dB_{3P}}{dT}P^2 - ZRT - RT + O(P^3) \\ &= -RT^2 \frac{dB_{2P}}{dT}P - \frac{RT^2}{2} \frac{dB_{3P}}{dT}P^2 - [1 + B_{2P}P + B_{3P}P^2]RT - RT + O(P^3) \\ &= -RT \left(B_{2P} + T \frac{dB_{2P}}{dT}\right)P - RT \left(B_{3P} + \frac{T}{2} \frac{dB_{3P}}{dT}\right)P^2 + O(P^3)\end{aligned}$$

In the above derivation, we realized that $PV^\circ = RT$, or $Z = 1$ for these conditions. We can similarly use the fact that $\bar{G} = \bar{A} + RTZ$, and write

$$\begin{aligned}\bar{A} - A^\circ &= \bar{G} - G^\circ - RT(Z - 1) \\ &= \left[RT \ln P + RTB_{2P}P + \frac{RTB_{3P}}{2}P^2\right] - RT(1 + B_{2P}P + B_{3P}P^2 - 1) + O(P^3)\end{aligned}$$

$$\begin{aligned}&= RT \ln P + PRTB_{2P} + \frac{RTB_{3P}}{2}P^2 - PRTB_{2P} - RTB_{3P}P^2 + O(P^3) \\ &= RT \ln P - \frac{RTB_{3P}}{2}P^2 + O(P^3)\end{aligned}$$

22-44. In this problem, we will derive the equation

$$\bar{H}(T, P) - H^\circ(T) = RT(Z - 1) + \int_{V^{\text{id}}}^{\bar{V}} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] dV'$$

where \bar{V}^{id} is a very large (molar) volume, where the gas is sure to behave ideally. Start with $dH = TdS + VdP$ to derive

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

and use one of the Maxwell relations for $(\partial S/\partial V)_T$ to obtain

$$\left(\frac{\partial H}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V + V \left(\frac{\partial P}{\partial V}\right)_T$$

Now integrate by parts from an ideal-gas limit to an arbitrary limit to obtain the desired equation.

Start with Equation 22.49 and take the partial derivative of both sides with respect to V :

$$\begin{aligned}dH &= TdS + VdP \\ \left(\frac{\partial H}{\partial V}\right)_T &= T \left(\frac{\partial S}{\partial V}\right)_T + V \left(\frac{\partial P}{\partial V}\right)_T\end{aligned}$$

Now use Equation 22.19 to write this as

$$\left(\frac{\partial H}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V + V \left(\frac{\partial P}{\partial V}\right)_T$$

We now integrate the above equation. Recall that $PV = nZRT$, and for an ideal gas $Z = 1$.

$$\begin{aligned}\int_{H^{\text{id}}}^H dH &= \int_{V^{\text{id}}}^V \left[T \left(\frac{\partial P}{\partial T}\right)_V + V \left(\frac{\partial P}{\partial V}\right)_T\right] dV' \\ H - H^\circ &= \int_{V^{\text{id}}}^V \left[T \left(\frac{\partial P}{\partial T}\right)_V - V \left(\frac{nZRT}{V^2}\right) + nRT \left(\frac{\partial Z}{\partial V}\right)_T\right] dV' \\ H - H^\circ &= \int_{V^{\text{id}}}^V \left[T \left(\frac{\partial P}{\partial T}\right)_V - \frac{nZRT}{V}\right] dV' + \int_1^Z nRT dZ' \\ &= nRT \int_1^Z dZ' + \int_{V^{\text{id}}}^V \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] dV' \\ &= nRT(Z - 1) + \int_{V^{\text{id}}}^V \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] dV'\end{aligned}$$

Dividing both sides of the above equation by n gives the desired equation.

22-45. Using the result of Problem 22-44, show that H is independent of volume for an ideal gas. What about a gas whose equation of state is $P(\bar{V} - b) = RT$? Does U depend upon volume for this equation of state? Account for any difference.

For an ideal gas,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \quad \text{and} \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{V^2}$$

Substituting into the equation from the previous problem,

$$\left(\frac{\partial H}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V + V \left(\frac{\partial P}{\partial V}\right)_T = \frac{nRT}{V} - \frac{nRT}{V^2} = 0$$

For the second equation of state given in the problem,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \quad \text{and} \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{(V-b)^2}$$

$$\begin{aligned} \left(\frac{\partial \bar{H}}{\partial V}\right)_T &= T \left(\frac{\partial P}{\partial T}\right)_V + V \left(\frac{\partial P}{\partial V}\right)_T \\ &= \frac{RT}{V-b} - \frac{VRT}{(V-b)^2} = \frac{RT}{V-b} \left[1 - \frac{V}{V-b}\right] \end{aligned}$$

Remember that $\bar{U} = \bar{H} - P\bar{V}$, so

$$\begin{aligned} \left(\frac{\partial \bar{U}}{\partial V}\right)_T &= \left(\frac{\partial \bar{H}}{\partial V}\right)_T - P - V \left(\frac{\partial P}{\partial V}\right)_T \\ &= \frac{RT}{V-b} \left[1 - \frac{V}{V-b}\right] - \frac{RT}{V-b} + V \frac{RT}{(V-b)^2} = 0 \end{aligned}$$

Therefore \bar{U} does not depend on volume for a gas that obeys the equation of state $P(\bar{V} - b) = RT$.

22-46. Using the result of Problem 22-44, show that

$$\bar{H} - H^\circ = \frac{RTb}{\bar{V} - b} - \frac{2a}{\bar{V}}$$

for the van der Waals equation.

For the van der Waals equation of state,

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \quad \text{and} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V} - b}$$

Also,

$$Z = \frac{P\bar{V}}{RT} = \left[\frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \right] \frac{\bar{V}}{RT}$$

Now we substitute these values into the equation from Problem 22-44:

$$\begin{aligned} \bar{H} - \bar{H}^\circ &= ZRT - RT + \int_{\bar{V}^\text{id}}^{\bar{V}} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] d\bar{V} \\ &= \bar{V} \left[\frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \right] - RT + \int_{\bar{V}^\text{id}}^{\bar{V}} \left[\frac{RT}{\bar{V} - b} - \frac{RT}{\bar{V} - b} + \frac{a}{\bar{V}^2} \right] d\bar{V} \end{aligned}$$

$$\begin{aligned} &= RT \frac{\bar{V} - (\bar{V} - b)}{\bar{V} - b} - \frac{a}{\bar{V}} - \frac{a}{\bar{V}} \Big|_{\bar{V}^\text{id}}^{\bar{V}} \\ &= \frac{RTb}{\bar{V} - b} - \frac{2a}{\bar{V}} + \frac{a}{\bar{V}^\text{id}} \\ &= \frac{RTb}{\bar{V} - b} - \frac{2a}{\bar{V}} \end{aligned}$$

because \bar{V}^id is very large compared to \bar{V} .

22-47. Using the result of Problem 22-44, show that

$$\bar{H} - H^\circ = \frac{RTB}{\bar{V} - B} - \frac{A}{T^{1/2}(\bar{V} + B)} - \frac{3A}{2BT^{1/2}} \ln \frac{\bar{V} + B}{\bar{V}}$$

for the Redlich-Kwong equation.

For the Redlich-Kwong equation of state,

$$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V} - B} + \frac{A}{2T^{3/2}\bar{V}(\bar{V} + B)}$$

Also, we write Z as

$$Z = \left[\frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} \right] \frac{\bar{V}}{RT}$$

Now we substitute these values into the equation from Problem 22-44:

$$\begin{aligned} \bar{H} - \bar{H}^\circ &= ZRT - RT + \int_{\bar{V}^\text{id}}^{\bar{V}} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] d\bar{V} \\ &= \bar{V} \left[\frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)} \right] - RT + \int_{\bar{V}^\text{id}}^{\bar{V}} \left[\frac{RT}{\bar{V} - B} + \frac{A}{2T^{1/2}\bar{V}'(\bar{V}' + B)} \right. \\ &\quad \left. - \frac{RT}{\bar{V} - B} + \frac{A}{T^{1/2}\bar{V}'(\bar{V}' + B)} \right] d\bar{V}' \\ &= \frac{\bar{V}RT - RT(\bar{V} - B)}{\bar{V} - B} - \frac{A}{T^{1/2}(\bar{V} + B)} + \int_{\bar{V}^\text{id}}^{\bar{V}} \frac{3A}{2T^{1/2}\bar{V}'(\bar{V}' + B)} d\bar{V}' \\ &= \frac{BRT}{\bar{V} - B} - \frac{A}{T^{1/2}(\bar{V} + B)} - \frac{3A}{2BT^{1/2}} \left(\ln \frac{\bar{V} + B}{\bar{V}} - \ln \frac{\bar{V}^\text{id} + B}{\bar{V}^\text{id}} \right) \\ &= \frac{BRT}{\bar{V} - B} - \frac{A}{T^{1/2}(\bar{V} + B)} - \frac{3A}{2BT^{1/2}} \ln \frac{\bar{V} + B}{\bar{V}} \end{aligned}$$

because \bar{V}^id is very large compared to \bar{V} .

The following six problems involve the Joule-Thomson coefficient.

22-48. We introduced the Joule-Thomson effect and the Joule-Thomson coefficient in Problems 19-52 through 19-54. The Joule-Thomson coefficient is defined by

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = -\frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$$

and is a direct measure of the expected temperature change when a gas is expanded through a throttle. We can use one of the equations derived in this chapter to obtain a convenient working equation for μ_{JT} . Show that

$$\mu_{JT} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

Use this result to show that $\mu_{JT} = 0$ for an ideal gas.

Start with

$$\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P \quad (22.34)$$

Substitute this into the expression for μ_{JT} to obtain

$$\mu_{JT} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]$$

For an ideal gas, $(\partial V/\partial T)_P = nR/P$, so

$$\mu_{JT} = \frac{1}{C_p} \left[\frac{nRT}{P} - V \right] = 0$$

since $PV = nRT$.

22-49. Use the virial equation of state of the form

$$\frac{P\bar{V}}{RT} = 1 + \frac{B_{2V}(T)}{RT}P + \dots$$

to show that

$$\mu_{JT} = \frac{1}{C_p} \left[T \frac{dB_{2V}}{dT} - B_{2V} \right] + O(P)$$

It so happens that B_{2V} is negative and dB_{2V}/dT is positive for $T^* < 3.5$ (see Figure 16.15) so that μ_{JT} is positive for low temperatures. Therefore, the gas will cool upon expansion under these conditions. (See Problem 22-48.)

Use the virial equation of state to express V :

$$\begin{aligned} \frac{P\bar{V}}{RT} &= 1 + \frac{B_{2V}(T)}{RT}P + O(P^2) \\ \bar{V} &= \frac{RT}{P} + B_{2V}(T) + O(P) \\ \left(\frac{\partial \bar{V}}{\partial T} \right)_P &= \frac{R}{P} + \frac{dB_{2V}}{dT} + O(P) \end{aligned}$$

Substituting into the equation for μ_{JT} from Problem 22-48,

$$\begin{aligned} \mu_{JT} &= \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] \\ &= \frac{1}{C_p} \left[\frac{RT}{P} + T \frac{dB_{2V}}{dT} - \frac{RT}{P} - B_{2V} + O(P) \right] \\ &= \frac{1}{C_p} \left[T \frac{dB_{2V}}{dT} - B_{2V} \right] + O(P) \end{aligned}$$

22-50. Show that

$$\mu_{JT} = -\frac{b}{C_p}$$

for a gas that obeys the equation of state $P(\bar{V} - b) = RT$. (See Problem 22-48.)

For such a gas,

$$\left(\frac{\partial \bar{V}}{\partial T} \right)_P = \frac{R}{P} \quad \text{and} \quad \bar{V} = \frac{RT}{P} + b$$

Substituting into the equation for μ_{JT} from Problem 22-48,

$$\mu_{JT} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right] = \frac{1}{C_p} \left[\frac{RT}{P} - \frac{RT}{P} - b \right] = -\frac{b}{C_p}$$

22-51. The second virial coefficient for a square-well potential is (Equation 16.41)

$$B_{2V}(T) = b_0[1 - (\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1)]$$

Show that

$$\mu_{JT} = \frac{b_0}{C_p} \left[(\lambda^3 - 1) \left(1 + \frac{\varepsilon}{k_B T} \right) e^{\varepsilon/k_B T} - \lambda^3 \right]$$

where $b_0 = 2\pi\sigma^3 N_A/3$. Given the following square-well parameters, calculate μ_{JT} at 0°C and compare your values with the given experimental values. Take $C_p = 5R/2$ for Ar and $7R/2$ for N_2 and CO_2 .

Gas	$b_0/\text{mL}\cdot\text{mol}^{-1}$	λ	ε/k_B	$\mu_{JT}(\text{exptl})/\text{K}\cdot\text{atm}^{-1}$
Ar	39.87	1.85	69.4	0.43
N_2	45.29	1.87	53.7	0.26
CO_2	75.79	1.83	119	1.3

From Problem 22-49, we have

$$\mu_{JT} = \frac{1}{C_p} \left[T \frac{dB_{2V}}{dT} - B_{2V} \right] + O(P)$$

Now we find dB_{2V}/dT from Equation 16.41:

$$B_{2V} = b_0 [1 - (\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1)]$$

$$\frac{dB_{2V}}{dT} = \frac{\varepsilon b_0}{k_B T^2} (\lambda^3 - 1) e^{\varepsilon/k_B T}$$

Substituting into the expression for μ_{JT} , we find

$$\begin{aligned} \mu_{JT} &= \frac{1}{C_p} \left[T \frac{dB_{2V}}{dT} - B_{2V} \right] + O(P) \\ &= \frac{1}{C_p} \left[\frac{b_0 \varepsilon}{k_B T} (\lambda^3 - 1) e^{\varepsilon/k_B T} - b_0 + b_0 (\lambda^3 - 1)(e^{\varepsilon/k_B T} - 1) \right] \\ &= \frac{b_0}{C_p} \left\{ e^{\varepsilon/k_B T} \left[\frac{\varepsilon}{k_B T} (\lambda^3 - 1) \right] - 1 + \lambda^3 e^{\varepsilon/k_B T} - e^{\varepsilon/k_B T} - \lambda^3 + 1 \right\} \\ &= \frac{b_0}{C_p} \left\{ e^{\varepsilon/k_B T} \left[\frac{\varepsilon}{k_B T} (\lambda^3 - 1) + (\lambda^3 - 1) \right] - \lambda^3 \right\} \\ &= \frac{b_0}{C_p} \left[(\lambda^3 - 1) \left(1 + \frac{\varepsilon}{k_B T} \right) e^{\varepsilon/k_B T} - \lambda^3 \right] \end{aligned}$$

We can now use the given values of λ , b_0 , and ε/k_B to calculate μ_{JT} (theoretical) for Ar, N₂, and CO₂. We use $\bar{C}_p = 5R/2$ for argon and $\bar{C}_p = 7R/2$ for N₂ and CO₂.

Gas	Ar	N ₂	CO ₂
$\mu_{JT}(\text{theor.})/\text{K} \cdot \text{atm}^{-1}$	0.44	0.24	1.39
$\mu_{JT}(\text{exp.})/\text{K} \cdot \text{atm}^{-1}$	0.43	0.26	1.3
Percent Difference	3.4	7.3	6.6

22-52. The temperature at which the Joule-Thomson coefficient changes sign is called the *Joule-Thomson inversion temperature*, T_i . The low-pressure Joule-Thomson inversion temperature for the square-well potential is obtained by setting $\mu_{JT} = 0$ in Problem 22-51. This procedure leads to an equation for $k_B T/\varepsilon$ in terms of λ^3 that cannot be solved analytically. Solve the equation numerically to calculate T_i for the three gases given in the previous problem. The experimental values are 794 K, 621 K, and 1500 K for Ar, N₂, and CO₂, respectively.

$$0 = \frac{b_0}{C_p} \left[(\lambda^3 - 1) \left(1 + \frac{\varepsilon}{k_B T} \right) e^{\varepsilon/k_B T} - \lambda^3 \right]$$

$$\lambda^3 = (\lambda^3 - 1) \left(1 + \frac{\varepsilon}{k_B T} \right) e^{\varepsilon/k_B T}$$

We can use the experimental values as initial values and then use the Newton-Raphson method to find T_i . The inversion temperatures found are tabulated below.

Gas	Ar	N ₂	CO ₂
$T_i(\text{theor.})/\text{K}$	791	634	1310
$T_i(\text{exp.})/\text{K}$	794	621	1500
Percent Difference	0.378	2.09	12.7

22-53. Use the data in Problem 22-51 to estimate the temperature drop when each of the gases undergoes an expansion for 100 atm to one atm.

By definition, $\mu_{JT} = (\partial T/\partial P)_H$, so

$$\frac{1}{\mu_{JT}} = \left(\frac{\partial P}{\partial T} \right)_H$$

$$\int \mu_{JT} dP = \int dT$$

Let us assume that μ_{JT} does not change significantly over the pressure range. Then

$$\Delta T = \mu_{JT} \Delta P$$

Using the experimental values of μ_{JT} , we see that Ar(g) experiences a temperature drop of 42.6 K, N₂(g) has a temperature drop of 25.7 K, and CO₂(g) drops in temperature by 129 K.

22-54. When a rubber band is stretched, it exerts a restoring force, f , which is a function of its length L and its temperature T . The work involved is given by

$$w = \int f(L, T) dL \quad (1)$$

Why is there no negative sign in front of the integral, as there is in Equation 19.2 for P - V work? Given that the volume change upon stretching a rubber band is negligible, show that

$$dU = TdS + fdL \quad (2)$$

and that

$$\left(\frac{\partial U}{\partial L} \right)_T = T \left(\frac{\partial S}{\partial L} \right)_T + f \quad (3)$$

Using the definition $A = U - TS$, show that Equation 2 becomes

$$dA = -SdT + fdL \quad (4)$$

and derive the Maxwell relation

$$\left(\frac{\partial f}{\partial T} \right)_L = - \left(\frac{\partial S}{\partial L} \right)_T \quad (5)$$

Substitute Equation 5 into Equation 3 to obtain the analog of Equation 22.22

$$\left(\frac{\partial U}{\partial L} \right)_T = f - T \left(\frac{\partial f}{\partial T} \right)_L$$

For many elastic systems, the observed temperature-dependence of the force is linear. We define an *ideal rubber band* by

$$f = T\phi(L) \quad (\text{ideal rubber band}) \quad (6)$$

Show that $(\partial U/\partial L)_T = 0$ for an ideal rubber band. Compare this result with $(\partial U/\partial V)_T = 0$ for an ideal gas.

Now let's consider what happens when we stretch a rubber band quickly (and, hence, adiabatically). In this case, $dU = dw = fdL$. Use the fact that U depends upon only the temperature for an ideal rubber band to show that

$$dU = \left(\frac{\partial U}{\partial T} \right)_L dT = fdL \quad (7)$$

The quantity $(\partial U/\partial T)_L$ is a heat capacity, so Equation 7 becomes

$$C_L dT = f dL \quad (8)$$

Argue now that if a rubber band is suddenly stretched, then its temperature will rise. Verify this result by holding a rubber band against your upper lip and stretching it quickly.

There is no negative sign in front of the integral because the force the rubber band exerts is a restoring force, which means that it is acting to contract the rubber band.

Since $dU = \delta q + \delta w$ and $\delta q = T dS$,

$$dU = T dS + f dL \quad (2)$$

Taking the partial derivative of both sides with respect to L at constant T gives

$$\left(\frac{\partial U}{\partial L}\right)_T = T \left(\frac{\partial S}{\partial L}\right)_T + f \quad (3)$$

Then, since $A = U - TS$, $U = A + TS$ and

$$\begin{aligned} dU &= T dS + f dL \\ dA + T dS + S dT &= T dS + f dL \\ dA &= -S dT + f dL \end{aligned} \quad (4)$$

We can also write dA as the total derivative of $A(T, L)$:

$$dA = \left(\frac{\partial A}{\partial T}\right)_L dT + \left(\frac{\partial A}{\partial L}\right)_T dL$$

Comparing the above equation and Equation 4, we see that

$$\left(\frac{\partial A}{\partial T}\right)_L = -S \quad \text{and} \quad \left(\frac{\partial A}{\partial L}\right)_T = f$$

and equating the second cross partial derivatives gives

$$-\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial f}{\partial T}\right)_L \quad (5)$$

Substituting into Equation 3 gives

$$\left(\frac{\partial U}{\partial L}\right)_T = -T \left(\frac{\partial f}{\partial T}\right)_L + f$$

For an ideal rubber band,

$$f = T\phi(L) \quad \text{and so} \quad \left(\frac{\partial f}{\partial T}\right)_L = \phi_L$$

Then

$$\left(\frac{\partial U}{\partial L}\right)_T = -T \left(\frac{\partial f}{\partial T}\right)_L + f = -T\phi + T\phi = 0$$

Both this result and the result $(\partial U/\partial V)_T = 0$ essentially state that the energy of the system is independent of the length of the rubber band or the volume of the gas at constant temperature.

Now define $C_L = (\partial U/\partial T)_L$. For the ideal rubber band, U depends only on temperature, so we can write

$$\begin{aligned} U &= \int \left(\frac{\partial U}{\partial T}\right)_L dT \\ dU &= \left(\frac{\partial U}{\partial T}\right)_T dT = C_L dT \end{aligned}$$

We know that $dU = f dL$ from the problem text, so we can now write

$$C_L dT = f dL$$

If we suddenly stretch a rubber band, we are applying force f over the distance we stretch the rubber band. Then

$$\int f dL = C_L \int dT$$

which is approximately

$$f \Delta L = C_L \Delta T$$

If ΔL is positive (we are stretching the rubber band), then ΔT must also be positive, and the rubber band heats up when we stretch it.

22-55. Derive an expression for ΔS for the reversible, isothermal expansion of one mole of a gas that obeys van der Waals equation. Use your result to calculate ΔS 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 to what you would get using the ideal-gas equation.

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 van der Waals equation,

$$\begin{aligned} P &= \frac{RT}{\bar{V} - b} - \frac{a}{\bar{V}^2} \\ \left(\frac{\partial P}{\partial T}\right)_{\bar{V}} &= \frac{R}{\bar{V} - b} \end{aligned}$$

Substituting into the Maxwell equation above, we find that

$$\left(\frac{\partial \bar{S}}{\partial \bar{V}}\right)_T = \frac{R}{\bar{V} - b}$$

or

$$\Delta \bar{S} = R \ln \frac{\bar{V}_2 - b}{\bar{V}_1 - b}$$

For ethane, $b = 0.065144 \text{ dm}^3 \cdot \text{mol}^{-1}$, so

$$\begin{aligned} \Delta \bar{S} &= (8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \frac{1.00 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.065144 \text{ dm}^3 \cdot \text{mol}^{-1}}{10.0 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.065144 \text{ dm}^3 \cdot \text{mol}^{-1}} \\ &= -19.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

Using the ideal gas equation, we find

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

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

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

- 22-56. Derive an expression for ΔS 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 ΔS 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 ΔS .

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

$$\Delta \bar{S} = (0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \ln \frac{1.00 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}}{10.0 \text{ dm}^3 \cdot \text{mol}^{-1} - 0.045153 \text{ dm}^3 \cdot \text{mol}^{-1}}$$

$$- \frac{98.831 \text{ dm}^6 \cdot \text{bar} \cdot \text{mol}^{-2} \cdot \text{K}^{1/2}}{2(0.045153 \text{ dm}^3 \cdot \text{mol}^{-1})(400 \text{ K})^{3/2}} \ln \frac{(10.0 \text{ dm}^3 \cdot \text{mol}^{-1})(1.045153 \text{ dm}^3 \cdot \text{mol}^{-1})}{(1.00 \text{ dm}^3 \cdot \text{mol}^{-1})(10.045153 \text{ dm}^3 \cdot \text{mol}^{-1})}$$

$$= -0.200 \text{ dm}^3 \cdot \text{bar} = -20.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

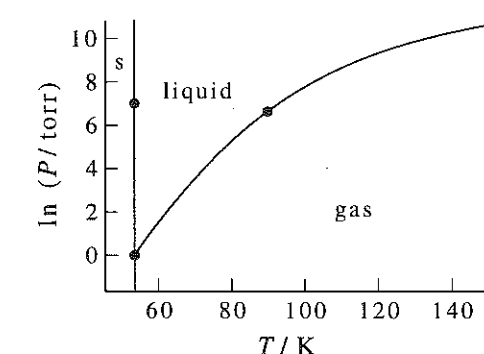
This is smaller than the value obtained with the ideal gas equation.

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.

