

5 The Second Law: the machinery

Solutions to exercises

Discussion questions

- E5.1(b)** See the solution to Exercise 3.14(a) and Example 5.1, where it is demonstrated that $\pi_T = a/V_m^2$ for a van der Waals gas. Therefore, there is no dependence on b for a van der Waals gas. The internal pressure results from attractive interactions alone. For van der Waals gases and liquids with strong attractive forces (large a) at small volumes, the internal pressure can be very large.
- E5.2(b)** The relation $(\partial G/\partial T)_p = -S$ shows that the Gibbs function of a system decreases with T at constant p in proportion to the magnitude of its entropy. This makes good sense when one considers the definition of G , which is $G = U + pV - TS$. Hence, G is expected to decrease with T in proportion to S when p is constant. Furthermore, an increase in temperature causes entropy to increase according to

$$\Delta S = \int_i^f dq_{\text{rev}}/T$$

The corresponding increase in molecular disorder causes a decline in the Gibbs energy. (Entropy is always positive.)

- E5.3(b)** The fugacity coefficient, ϕ , can be expressed in terms of an integral involving the compression factor, specifically an integral of $Z - 1$ (see eqn 5.20). Therefore, we expect that the variation with pressure of the fugacity coefficient should be similar, in a very qualitative sense, to the variation with pressure of the compression factor itself. Comparison of figures 1.27 and 5.8 of the text shows this to be roughly the case, though the detailed shapes of the curves are necessarily different because ϕ is an integral function of $Z - 1$ over a range of pressures. So we expect no simple proportionality between ϕ and Z . But we find $\phi < 1$ in pressure regions where attractive forces are expected to predominate and $\phi > 1$ when repulsive forces predominate, which in behavior is similar to that of Z . See Section 5.5(b) for a more complete discussion.

Numerical exercises

- E5.4(b)** $\alpha = \frac{1}{V} \times \left(\frac{\partial V}{\partial T}\right)_p$ $\kappa_T = -\left(\frac{1}{V}\right) \times \left(\frac{\partial V}{\partial p}\right)_T$
- $$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = \boxed{-\alpha V}$$
- E5.5(b)** $\Delta G = nRT \ln\left(\frac{p_f}{p_i}\right)$ at constant temperature, $\frac{p_f}{p_i} = \frac{V_i}{V_f}$
- $$= nRT \ln\left(\frac{V_i}{V_f}\right)$$
- $$= (2.5 \times 10^{-3} \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln\left(\frac{72}{100}\right)$$
- $$= -2.035 = \boxed{-2.0 \text{ J}}$$

$$\begin{aligned}
 \text{E5.6(b)} \quad \left(\frac{\partial G}{\partial T}\right)_p &= -S \quad \left(\frac{\partial G_f}{\partial T}\right)_p = -S_f \quad \text{and} \quad \left(\frac{\partial G_i}{\partial T}\right)_p = -S_i \\
 \Delta S &= S_f - S_i = -\left(\frac{\partial G_f}{\partial T}\right)_p + \left(\frac{\partial G_i}{\partial T}\right)_p \\
 &= -\left\{\frac{\partial(G_f - G_i)}{\partial T}\right\}_p = -\left(\frac{\partial \Delta G}{\partial T}\right)_p \\
 &= -\frac{\partial}{\partial T} \{-73.1 + 42.8 T/\text{K}\} \text{ J} \\
 &= \boxed{-42.8 \text{ J K}^{-1}}
 \end{aligned}$$

E5.7(b) See the solution to Exercise 5.7(a). Without knowledge of the compressibility of methanol we can only assume that $V = V_1(1 - \kappa_T p) \approx V_1$. Then

$$\begin{aligned}
 \Delta G &= V \Delta p \\
 \rho &= \frac{m}{V} \quad \text{so} \quad V = \frac{m}{\rho} = \frac{25 \text{ g}}{0.791 \text{ g cm}^{-3}} = 31.61 \text{ cm}^3 \\
 \Delta G &= (31.61 \text{ cm}^3) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3}\right) \times (99.9 \times 10^6 \text{ Pa}) \\
 &= \boxed{+3.2 \text{ kJ}}
 \end{aligned}$$

$$\text{E5.8(b)} \quad \text{(a)} \quad \Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = nR \ln\left(\frac{p_i}{p_f}\right) \quad [\text{Boyle's Law}]$$

Taking inverse logarithms

$$\begin{aligned}
 p_f &= p_i e^{-\Delta S/nR} = (150 \text{ kPa}) \exp\left(-\frac{-(-15.0 \text{ J K}^{-1})}{(3.00 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})}\right) \\
 &= \boxed{274 \text{ kPa}}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad \Delta G &= nRT \ln\left(\frac{p_f}{p_i}\right) = -T \Delta S \quad [\Delta H = 0, \text{ constant temperature, perfect gas}] \\
 &= -(230 \text{ K}) \times (-15.0 \text{ J K}^{-1}) \\
 &= +3450 \text{ J} = \boxed{3.45 \text{ kJ}}
 \end{aligned}$$

$$\begin{aligned}
 \text{E5.9(b)} \quad \Delta \mu &= \mu_f - \mu_i = RT \ln\left(\frac{p_f}{p_i}\right) \\
 &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (323 \text{ K}) \times \ln\left(\frac{252.0}{92.0}\right) \\
 &= \boxed{2.71 \text{ kJ mol}^{-1}}
 \end{aligned}$$

$$\begin{aligned}
 \text{E5.10(b)} \quad \mu^0 &= \mu^\ominus + RT \ln\left(\frac{p}{p^\ominus}\right) \\
 \mu &= \mu^\ominus + RT \ln\left(\frac{f}{p^\ominus}\right)
 \end{aligned}$$

$$\begin{aligned}\mu - \mu^0 &= RT \ln\left(\frac{f}{p}\right) \quad \left[\frac{f}{p} \equiv \phi\right] \\ \mu - \mu^0 &= RT \ln \phi \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (290 \text{ K}) \times \ln(0.68) \\ &= -929.8 \text{ J mol}^{-1} \\ &= -930 \text{ J mol}^{-1} \quad \text{or} \quad \boxed{-0.93 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\begin{aligned}\text{E5.11(b)} \quad B' &= \frac{B}{RT} = -\frac{(160.0 \text{ cm}^3 \text{ mol}^{-1}) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3}\right)}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (100 \text{ K})} \\ &= \boxed{-1.924 \times 10^{-7} \text{ Pa}^{-1}}\end{aligned}$$

$$\begin{aligned}\phi &= e^{B'p+\dots} \\ &\approx e^{-(1.924 \times 10^{-7} \text{ Pa}^{-1}) \times (62 \times 10^6 \text{ Pa})} \\ &\approx e^{-11.93} \\ &= 7 \times 10^{-6} \quad \text{or} \quad \text{of the order of} \quad \boxed{10^{-6}}\end{aligned}$$

$$\begin{aligned}\text{E5.12(b)} \quad \Delta G &= nV_m \Delta p = V \Delta p \\ &= (1.0 \text{ L}) \times \left(\frac{1 \text{ m}^3}{10^3 \text{ L}}\right) \times (200 \times 10^3 \text{ Pa}) \\ &= 200 \text{ Pa m}^3 = \boxed{200 \text{ J}}\end{aligned}$$

$$\begin{aligned}\text{E5.13(b)} \quad \Delta G_m &= RT \ln\left(\frac{p_f}{p_i}\right) \\ &= (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (500 \text{ K}) \times \ln\left(\frac{100.0 \text{ kPa}}{50.0 \text{ kPa}}\right) \\ &= \boxed{+2.88 \text{ kJ mol}^{-1}}\end{aligned}$$

$$\text{E5.14(b)} \quad V = \left(\frac{\partial G}{\partial p}\right)_T \quad [5.10] = \boxed{\frac{RT}{p} + B' + C'p + D'p^2}$$

which is the virial equation of state.

$$\text{E5.15(b)} \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

For a Dieterici gas

$$\begin{aligned}p &= \frac{RT e^{-a/RTV_m}}{V_m - b} \\ \left(\frac{\partial p}{\partial T}\right)_{V_m} &= \boxed{\frac{R \left(1 + \frac{a}{RV_m T}\right) e^{-a/RTV_m}}{V_m - b}} \\ dS &= \left(\frac{\partial S}{\partial V_m}\right)_T dV_m = \left(\frac{\partial p}{\partial T}\right)_{V_m} dV_m\end{aligned}$$

$$\Delta S = \int_{V_{m,i}}^{V_{m,f}} dS = R \left(1 + \frac{a}{RV_m T} \right) e^{-a/RV_m T} \left(\frac{V_{m,f} - b}{V_{m,i} - b} \right)$$

For a perfect gas $\Delta S = R \ln \left(\frac{V_{m,f}}{V_{m,i}} \right)$

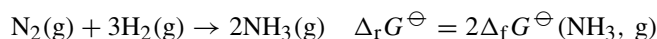
ΔS for a Dieterici gas may be greater or lesser than ΔS for a perfect gas depending on T and the magnitudes of a and b . At very high T , ΔS is greater. At very low T , ΔS is less.

Solutions to problems

Solutions to numerical problem

P5.2

For the reaction



$$(a) \quad \Delta_r G^\ominus(500 \text{ K}) = \tau \Delta_r G^\ominus(T_c) + (1 - \tau) \Delta_r H^\ominus(T_c) \quad \left[\text{Problem 5.1, } \tau = \frac{T}{T_c} \right]$$

$$\begin{aligned} &= \left(\frac{500 \text{ K}}{298.15 \text{ K}} \right) \times (2) \times (-16.45 \text{ kJ mol}^{-1}) \\ &\quad + \left(1 - \frac{500 \text{ K}}{298.15 \text{ K}} \right) \times (2) \times (-46.11 \text{ kJ mol}^{-1}) \\ &= -55.17 + 62.43 \text{ kJ mol}^{-1} = \boxed{+7 \text{ kJ mol}^{-1}} \end{aligned}$$

$$(b) \quad \Delta_r G^\ominus(1000 \text{ K}) = \left(\frac{1000 \text{ K}}{298.15 \text{ K}} \right) \times (2) \times (-16.45 \text{ kJ mol}^{-1}) \\ + \left(1 - \frac{1000 \text{ K}}{298.15 \text{ K}} \right) \times (2) \times (-46.11 \text{ kJ mol}^{-1}) \\ = (-110.35 + 217.09) \text{ kJ mol}^{-1} = \boxed{+107 \text{ kJ mol}^{-1}}$$

Solutions to theoretical problems

P5.5

We start from the fundamental relation

$$dU = T dS - p dV \quad [2]$$

But, since $U = U(S, V)$, we may also write

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV$$

Comparing the two expressions, we see that

$$\left(\frac{\partial U}{\partial S} \right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V} \right)_S = -p$$

These relations are true in general and hence hold for the perfect gas. We can demonstrate this more explicitly for the perfect gas as follows. For the perfect gas at constant volume

$$dU = C_V dT$$

and

$$dS = \frac{dq_{\text{rev}}}{T} = \frac{C_V dT}{T}$$

$$\text{Then } \left(\frac{dU}{dS}\right)_V = \left(\frac{\partial U}{\partial S}\right)_V = \frac{C_V dT}{\left(\frac{C_V dT}{T}\right)} = T$$

For a reversible adiabatic (constant-entropy) change in a perfect gas

$$dU = dw = -p dV$$

$$\text{Therefore, } \left(\frac{\partial U}{\partial V}\right)_S = -p$$

P5.8

$$\begin{aligned} \left(\frac{\partial p}{\partial S}\right)_V &= -\left(\frac{\partial T}{\partial V}\right)_S \quad [\text{Maxwell relation}] \\ &= \frac{1}{\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial V}{\partial S}\right)_T} [\text{chain relation}] = \frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V} [\text{inversion}] \\ &= \frac{\left(\frac{\partial p}{\partial T}\right)_V}{\left(\frac{\partial U}{\partial V}\right)_V \left(\frac{\partial U}{\partial T}\right)_V} [\text{Maxwell relation}] = \frac{-\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V} [\text{chain relation}] \\ &= \frac{-\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial U}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial U}{\partial T}\right)_V} [\text{inversion twice}] = \boxed{\frac{\alpha T}{\kappa_T C_V}} \quad \left[\left(\frac{\partial U}{\partial S}\right)_V = T \right] \end{aligned}$$

P5.10

$$\begin{aligned} \left(\frac{\partial H}{\partial p}\right)_T &= \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_S \quad [\text{Relation 1, Further information 1.7}] \\ dH &= T dS + V dp \quad [\text{Problem 5.6}] \\ dH &= \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \quad (H = H(p, S)) \end{aligned} \left. \vphantom{\begin{aligned} \left(\frac{\partial H}{\partial p}\right)_T &= \left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_S \\ dH &= T dS + V dp \\ dH &= \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \right\} \text{compare}$$

$$\text{Thus, } \left(\frac{\partial H}{\partial S}\right)_p = T, \quad \left(\frac{\partial H}{\partial p}\right)_S = V \quad [dH \text{ exact}]$$

$$\text{Substitution yields, } \left(\frac{\partial H}{\partial p}\right)_T = T \left(\frac{\partial S}{\partial p}\right)_T + V = \boxed{-T \left(\frac{\partial V}{\partial T}\right)_p + V} \quad [\text{Maxwell relation}]$$

(a) For $pV = nRT$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}, \quad \text{hence } \left(\frac{\partial H}{\partial p}\right)_T = \frac{-nRT}{p} + V = \boxed{0}$$

(b) For $p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$ [Table 1.6]

$$T = \frac{p(V - nb)}{nR} + \frac{na(V - nb)}{RV^2}$$

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V-nb)}{RV^3}$$

$$\text{Therefore, } \left(\frac{\partial H}{\partial p}\right)_T = \frac{-T}{\left(\frac{\partial T}{\partial V}\right)_p} + V[\text{inversion}] = \frac{-T}{\frac{p}{nR} + \frac{na}{RV^2} - \frac{2na(V-nb)}{RV^3}} + V$$

which yields after algebraic manipulation

$$\left(\frac{\partial H}{\partial p}\right)_T = \frac{nb - \left(\frac{2na}{RT}\right)\lambda^2}{1 - \left(\frac{2na}{RTV}\right)\lambda^2}, \quad \lambda = 1 - \frac{nb}{V}$$

When $\frac{b}{V_m} \ll 1$, $\lambda \approx 1$ and

$$\frac{2na}{RTV} = \frac{2na}{RT} \times \frac{1}{V} \approx \frac{2na}{RT} \times \frac{p}{nRT} = \frac{2pa}{R^2T^2}$$

$$\text{Therefore, } \left(\frac{\partial H}{\partial p}\right)_T \approx \frac{nb - \left(\frac{2na}{RT}\right)}{1 - \left(\frac{2pa}{R^2T^2}\right)}$$

For argon, $a = 1.337 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 3.20 \times 10^{-2} \text{ L mol}^{-1}$,

$$\frac{2na}{RT} = \frac{(2) \times (1.0 \text{ mol}) \times (1.337 \text{ L}^2 \text{ atm mol}^{-2})}{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = 0.11 \text{ L}$$

$$\frac{2pa}{R^2T^2} = \frac{(2) \times (10.0 \text{ atm}) \times (1.337 \text{ L}^2 \text{ atm mol}^{-2})}{[(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})]^2} = 0.045$$

$$\text{Hence, } \left(\frac{\partial H}{\partial p}\right)_T \approx \frac{\{(3.20 \times 10^{-2}) - (0.11)\} \text{ L}}{1 - 0.045} = -0.0817 \text{ L} = \boxed{-8.3 \text{ J atm}^{-1}}$$

$$\Delta H \approx \left(\frac{\partial H}{\partial p}\right)_T \Delta p \approx (-8.3 \text{ J atm}^{-1}) \times (1 \text{ atm}) = \boxed{-8 \text{ J}}$$

P5.12

$$\pi_T = T \left(\frac{\partial p}{\partial T}\right)_V - p \quad [5.8]$$

$$p = \frac{RT}{V_m} + \frac{BRT}{V_m^2} \quad [\text{The virial expansion, Table 1.6, truncated after the term in } B]$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V_m} + \frac{BR}{V_m^2} + \frac{RT}{V_m^2} \left(\frac{\partial B}{\partial T}\right)_V = \frac{p}{T} + \frac{RT}{V_m^2} \left(\frac{\partial B}{\partial T}\right)_V$$

$$\text{Hence, } \pi_T = \frac{RT^2}{V_m^2} \left(\frac{\partial B}{\partial T}\right)_V \approx \frac{RT^2 \Delta B}{V_m^2 \Delta T}$$

Since π_T represents a (usually) small deviation from perfect gas behaviour, we may approximate V_m .

$$V_m \approx \frac{RT}{p} \quad \boxed{\pi_T \approx \frac{p^2}{R} \times \frac{\Delta B}{\Delta T}}$$

From the data $\Delta B = ((-15.6) - (-28.0)) \text{ cm}^3 \text{ mol}^{-1} = +12.4 \text{ cm}^3 \text{ mol}^{-1}$

Hence,

$$(a) \quad \pi_T = \frac{(1.0 \text{ atm})^2 \times (12.4 \times 10^{-3} \text{ L mol}^{-1})}{(8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (50 \text{ K})} = \boxed{3.0 \times 10^{-3} \text{ atm}}$$

$$(b) \quad \pi_T \propto p^2; \quad \text{so at } p = 10.0 \text{ atm, } \pi_T = \boxed{0.30 \text{ atm}}$$

Comment. In (a) π_T is 0.3 per cent of p ; in (b) it is 3 per cent. Hence at these pressures the approximation for V_m is justified. At 100 atm it would not be.

Question. How would you obtain a reliable estimate of π_T for argon at 100 atm?

P5.13

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad \text{and} \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

$$(a) \quad \left(\frac{\partial C_V}{\partial V} \right)_T = \frac{\partial^2 U}{\partial V \partial T} = \frac{\partial^2 U}{\partial T \partial V} = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \right)_V = 0 \quad [\pi_T = 0]$$

$$\begin{aligned} \left(\frac{\partial C_V}{\partial p} \right)_T &= \frac{\partial^2 U}{\partial p \partial T} = \frac{\partial^2 U}{\partial T \partial p} = \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial p} \right)_T \right)_V \\ &= \left(\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial p} \right)_T \right)_V = 0 \quad (\pi_T = 0) \end{aligned}$$

$$\text{Since } C_p = C_V + R, \quad \left(\frac{\partial C_p}{\partial x} \right)_T = \left(\frac{\partial C_V}{\partial x} \right)_T \quad \text{for } x = p \text{ or } V$$

C_V and C_p may depend on temperature. Since $\frac{dC_V}{dT} = \frac{d^2 U}{dT^2}$, $\frac{dC_V}{dT}$ is nonzero if U depends on T through a nonlinear relation. See Chapter 20 for further discussion of this point. However, for a perfect monatomic gas, U is a linear function of T ; hence C_V is independent of T . A similar argument applies to C_p .

(b) This equation of state is the same as that of Problem 5.12.

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V} \right)_T &= \frac{\partial^2 U}{\partial T \partial V} = \left(\frac{\partial \pi_T}{\partial T} \right)_V \quad [\text{Part (a)}] \\ &= \left(\frac{\partial}{\partial T} \frac{RT^2}{V_m^2} \left(\frac{\partial B}{\partial T} \right)_V \right)_V \quad [\text{Problem 5.12}] \\ &= \frac{2RT}{V_m^2} \left(\frac{\partial B}{\partial T} \right)_V + \frac{RT^2}{V_m^2} \left(\frac{\partial^2 B}{\partial T^2} \right)_V \\ &= \boxed{\frac{RT}{V_m^2} \left(\frac{\partial^2 (BT)}{\partial T^2} \right)_V} \end{aligned}$$

P5.15

$$\pi_T = T \left(\frac{\partial p}{\partial T} \right)_V - p \quad [5.8]$$

$$p = \frac{nRT}{V - nb} \times e^{-an/RTV} \quad [\text{Table 1.6}]$$

$$T \left(\frac{\partial p}{\partial T} \right)_V = \frac{nRT}{V - nb} \times e^{-an/RTV} + \frac{na}{RTV} \times \frac{nRT}{V - nb} \times e^{-an/RTV} = p + \frac{nap}{RTV}$$

Hence, $\pi_T = \frac{nap}{RTV}$

$\pi_T \rightarrow 0$ as $p \rightarrow 0$, $V \rightarrow \infty$, $a \rightarrow 0$, and $T \rightarrow \infty$. The fact that $\pi_T > 0$ (because $a > 0$) is consistent with a representing attractive contributions, since it implies that $\left(\frac{\partial U}{\partial V}\right)_T > 0$ and the internal energy rises as the gas expands (so decreasing the average attractive interactions).

P5.17

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp = V dp$$

$$G(p_f) - G(p_i) = \int_{p_i}^{p_f} V dp$$

In order to complete the integration, V as a function of p is required.

$$\left(\frac{\partial V}{\partial p}\right)_T = -\kappa_T V \text{ (given), so } d \ln V = -\kappa dp$$

Hence, the volume varies with pressure as

$$\int_{V_0}^V d \ln V = -\kappa_T \int_{p_i}^p dp$$

or $V = V_0 e^{-\kappa_T(p-p_i)}$ ($V = V_0$ when $p = p_i$)

Hence, $\int_{p_i}^{p_f} dG = \int_{p_i}^{p_f} V dp = V_0 \int_{p_i}^{p_f} e^{-\kappa_T(p-p_i)} dp$

$$G(p_f) = G(p_i) + (V_0) \times \left(\frac{1 - e^{-\kappa_T(p_f-p_i)}}{\kappa_T}\right) = G(p_i) + (V_0) \times \left(\frac{1 - e^{-\kappa_T \Delta p}}{\kappa_T}\right)$$

If $\kappa_T \Delta p \ll 1$, $1 - e^{-\kappa_T \Delta p} \approx 1 - (1 - \kappa_T \Delta p + \frac{1}{2} \kappa_T^2 \Delta p^2) = \kappa_T \Delta p - \frac{1}{2} \kappa_T^2 \Delta p^2$

Hence, $G' = G + V_0 \Delta p \left(1 - \frac{1}{2} \kappa_T \Delta p\right)$

For the compression of copper, the change in molar Gibbs function is

$$\begin{aligned} \Delta G_m &= V_m \Delta p \left(1 - \frac{1}{2} \kappa_T \Delta p\right) = \left(\frac{M \Delta p}{\rho}\right) \times \left(1 - \frac{1}{2} \kappa_T \Delta p\right) \\ &= \left(\frac{63.54 \text{ g mol}^{-1}}{8.93 \times 10^6 \text{ g m}^{-3}}\right) \times (500) \times (1.013 \times 10^5 \text{ Pa}) \times \left(1 - \frac{1}{2} \kappa_T \Delta p\right) \\ &= (360.4 \text{ J}) \times \left(1 - \frac{1}{2} \kappa_T \Delta p\right) \end{aligned}$$

If we take $\kappa_T = 0$ (incompressible), $\Delta G_m = +360 \text{ J}$. For its actual value

$$\begin{aligned} \frac{1}{2} \kappa_T \Delta p &= \left(\frac{1}{2}\right) \times (0.8 \times 10^{-6} \text{ atm}^{-1}) \times (500 \text{ atm}) = 2 \times 10^{-4} \\ 1 - \frac{1}{2} \kappa_T \Delta p &= 0.9998 \end{aligned}$$

Hence, ΔG_m differs from the simpler version by only 2 parts in 10^4 (0.02 per cent)

$$\text{P5.19} \quad \kappa_S = - \left(\frac{1}{V} \right) \times \left(\frac{\partial V}{\partial p} \right)_S = - \frac{1}{V \left(\frac{\partial p}{\partial V} \right)_S}$$

The only constant-entropy changes of state for a perfect gas are reversible adiabatic changes, for which

$$pV^\gamma = \text{const}$$

$$\text{Then, } \left(\frac{\partial p}{\partial V} \right)_S = \left(\frac{\partial}{\partial V} \frac{\text{const}}{V^\gamma} \right)_S = -\gamma \times \left(\frac{\text{const}}{V^{\gamma+1}} \right) = \frac{-\gamma p}{V}$$

$$\text{Therefore, } \kappa_S = \frac{-1}{V \left(\frac{-\gamma p}{V} \right)} = \frac{+1}{\gamma p}$$

$$\text{Hence, } \boxed{p\gamma\kappa_S = +1}$$

P5.21

$$S = S(T, p)$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp$$

$$T dS = T \left(\frac{\partial S}{\partial T} \right)_p dT + T \left(\frac{\partial S}{\partial p} \right)_T dp$$

$$\text{Use } \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial S}{\partial H} \right)_p \left(\frac{\partial H}{\partial T} \right)_p = \frac{1}{T} \times C_p \quad \left[\left(\frac{\partial H}{\partial S} \right)_p = T, \text{ Problem 5.6} \right]$$

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \quad [\text{Maxwell relation}]$$

$$\text{Hence, } T dS = C_p dT - T \left(\frac{\partial V}{\partial T} \right)_p dp = \boxed{C_p dT - \alpha TV dp}$$

For reversible, isothermal compression, $T dS = dq_{\text{rev}}$, $dT = 0$; hence

$$dq_{\text{rev}} = -\alpha TV dp$$

$$q_{\text{rev}} = \int_{p_i}^{p_f} -\alpha TV dp = \boxed{-\alpha TV \Delta p} \quad [\alpha \text{ and } V \text{ assumed constant}]$$

For mercury

$$q_{\text{rev}} = (-1.82 \times 10^{-4} \text{ K}^{-1}) \times (273 \text{ K}) \times (1.00 \times 10^{-4} \text{ m}^{-3}) \times (1.0 \times 10^8 \text{ Pa}) = \boxed{-0.50 \text{ kJ}}$$

P5.25

When we neglect b in the van der Waals equation we have

$$p = \frac{RT}{V_m} - \frac{a}{V_m^2}$$

and hence

$$Z = 1 - \frac{a}{RTV_m}$$

Then substituting into eqn 5.20 we get

$$\ln \phi = \int_o^p \left(\frac{Z-1}{p} \right) dp = \int_o^p \frac{-a}{pRTV_m} dp$$

In order to perform this integration we must eliminate the variable V_m by solving for it in terms of p . Rewriting the expression for p in the form of a quadratic we have

$$V_m^2 - \frac{RT}{p}V_m + \frac{a}{p} = 0$$

The solution is

$$V_m = \frac{1}{2} \left(\frac{RT}{p} \pm \frac{1}{p} \sqrt{(RT)^2 - 4ap} \right)$$

applying the approximation $(RT)^2 \gg 4ap$ we obtain

$$V_m = \frac{1}{2} \left(\frac{RT}{p} \pm \frac{RT}{p} \right)$$

Choosing the + sign we get

$$V_m = \frac{RT}{p} \text{ which is the perfect volume}$$

Then

$$\ln \phi = \int_0^p -\frac{a}{RT^2} dp = \boxed{-\frac{ap}{(RT)^2}}$$

For ammonia $a = 4.169 \text{ atm L}^2 \text{ mol}^{-2}$

$$\begin{aligned} \ln \phi &= -\frac{4.169 \text{ atm L}^2 \text{ mol}^{-2} \times 10.00 \text{ atm}}{(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K})^2} \\ &= -0.06965 \\ \phi &= 0.9237 = \frac{f}{p} \end{aligned}$$

$$f = \phi p = 0.9237 \times 10.00 \text{ atm} = \boxed{9.237 \text{ atm}}$$

P5.27

The equation of state $\frac{pV_m}{RT} = 1 + \frac{qT}{V_m}$ is solved for $V_m = \left(\frac{RT}{2p}\right) \left[1 + \left(1 + \frac{4pq}{R}\right)^{1/2}\right]$ so

$$\begin{aligned} \frac{Z-1}{p} &= \frac{\frac{pV_m}{RT} - 1}{p} = \frac{qT}{pV_m} = \frac{\frac{2q}{R}}{1 + \left(1 + \frac{4pq}{R}\right)^{1/2}} \\ \ln \phi &= \int_0^p \left(\frac{Z-1}{p}\right) dp [24] = \frac{2q}{R} \int_0^p \frac{dp}{1 + \left(1 + \frac{4pq}{R}\right)^{1/2}} \end{aligned}$$

Defining, $a \equiv 1 + \left(1 + \frac{4pq}{R}\right)^{1/2}$, $dp = \frac{R(a-1)}{2q} da$, gives

$$\begin{aligned} \ln \phi &= \int_2^a \left(\frac{a-1}{a}\right) da \quad [a=2, \text{ when } p=0] \\ &= a - 2 - \ln \frac{1}{2}a = \left(1 + \frac{4pq}{R}\right)^{1/2} - 1 - \ln \left\{ \frac{1}{2} \left(1 + \frac{4pq}{R}\right)^{1/2} + \frac{1}{2} \right\} \end{aligned}$$

$$\text{Hence, } \phi = \boxed{\frac{2e^{\{(1+4pq/R)^{1/2}-1\}}}{1 + \left(1 + \frac{4pq}{R}\right)^{1/2}}}$$

This function is plotted in Fig. 5.1(a) when $\frac{4pq}{R} \ll 1$, and using the approximations

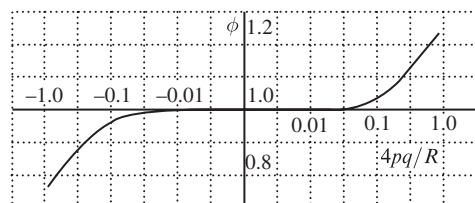


Figure 5.1(a)

$$e^x \approx 1 + x, \quad (1+x)^{1/2} \approx 1 + \frac{1}{2}x, \quad \text{and} \quad (1+x)^{-1} \approx 1 - x \quad [x \ll 1]$$

$$\phi \approx 1 + \frac{pq}{R}$$

When ϕ is plotted against $x = 4pq/R$ on a linear rather than exponential scale, the apparent curvature seen in Fig. 5.1(a) is diminished and the curve seems almost linear. See Fig. 5.1(b).

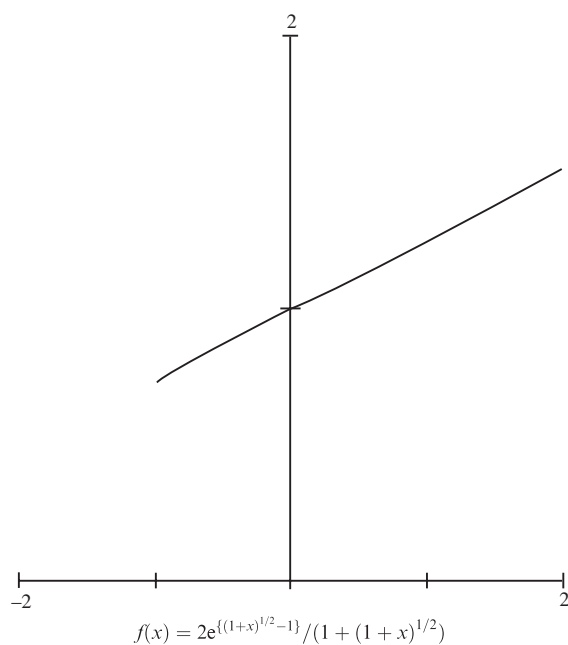


Figure 5.1(b)

Solution to applications

P5.28

$$w_{\text{add,max}} = \Delta_r G \quad [4.38]$$

$$\begin{aligned} \Delta_r G^\ominus(37^\circ\text{C}) &= \tau \Delta_r G^\ominus(T_c) + (1 - \tau) \Delta_r H^\ominus(T_c) \quad \left[\text{Problem 5.1, } \tau = \frac{T}{T_c} \right] \\ &= \left(\frac{310 \text{ K}}{298.15 \text{ K}} \right) \times (-6333 \text{ kJ mol}^{-1}) + \left(1 - \frac{310 \text{ K}}{298.15 \text{ K}} \right) \times (-5797 \text{ kJ mol}^{-1}) \\ &= -6354 \text{ kJ mol}^{-1} \end{aligned}$$

The difference is $\Delta_r G^\ominus(37^\circ\text{C}) - \Delta_r G^\ominus(T_c) = \{-6354 - (-6333)\} \text{ kJ mol}^{-1} = \boxed{-21 \text{ kJ mol}^{-1}}$
Therefore, an additional 21 kJ mol^{-1} of non-expansion work may be done at the higher temperature.

Comment. As shown by Problem 5.1, increasing the temperature does not necessarily increase the maximum non-expansion work. The relative magnitude of $\Delta_r G^\ominus$ and $\Delta_r H^\ominus$ is the determining factor.

P5.31 The Gibbs–Helmholtz equation is

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

so for a small temperature change

$$\Delta \left(\frac{\Delta_r G^\ominus}{T} \right) = \frac{\Delta_r H^\ominus}{T^2} \Delta T \quad \text{and} \quad \frac{\Delta_r G_2^\ominus}{T_2} = \frac{\Delta_r G_1^\ominus}{T_1} - \frac{\Delta_r H^\ominus}{T^2 \Delta T}$$

$$\text{so } \int d \frac{\Delta_r G^\ominus}{T} = - \int \frac{\Delta_r H^\ominus}{T^2} dT \quad \text{and} \quad \frac{\Delta_r G_{190}^\ominus}{T_{190}} = \frac{\Delta_r G_{220}^\ominus}{T_{220}} + \Delta_r H^\ominus \left(\frac{1}{T_{190}} - \frac{1}{T_{220}} \right)$$

$$\Delta_r G_{190}^\ominus = \Delta_r G_{220}^\ominus \frac{T_{190}}{T_{220}} + \Delta_r H^\ominus \left(1 - \frac{T_{190}}{T_{220}} \right)$$

For the monohydrate

$$\Delta_r G_{190}^\ominus = (46.2 \text{ kJ mol}^{-1}) \times \left(\frac{190 \text{ K}}{220 \text{ K}} \right) + (127 \text{ kJ mol}^{-1}) \times \left(1 - \frac{190 \text{ K}}{220 \text{ K}} \right),$$

$$\Delta_r G_{190}^\ominus = \boxed{57.2 \text{ kJ mol}^{-1}}$$

For the dihydrate

$$\Delta_r G_{190}^\ominus = (69.4 \text{ kJ mol}^{-1}) \times \left(\frac{190 \text{ K}}{220 \text{ K}} \right) + (188 \text{ kJ mol}^{-1}) \times \left(1 - \frac{190 \text{ K}}{220 \text{ K}} \right),$$

$$\Delta_r G_{190}^\ominus = \boxed{85.6 \text{ kJ mol}^{-1}}$$

For the monohydrate

$$\Delta_r G_{190}^\ominus = (93.2 \text{ kJ mol}^{-1}) \times \left(\frac{190 \text{ K}}{220 \text{ K}} \right) + (237 \text{ kJ mol}^{-1}) \times \left(1 - \frac{190 \text{ K}}{220 \text{ K}} \right),$$

$$\Delta_r G_{190}^\ominus = \boxed{112.8 \text{ kJ mol}^{-1}}$$

P5.32 The change in the Helmholtz energy equals the maximum work associated with stretching the polymer. Then

$$dw_{\max} = dA = -f dl$$

For stretching at constant T

$$f = - \left(\frac{\partial A}{\partial l} \right)_T = - \left(\frac{\partial U}{\partial l} \right)_T + T \left(\frac{\partial S}{\partial l} \right)_T$$

assuming that $(\partial U/\partial l)_T = 0$ (valid for rubbers)

$$\begin{aligned} f &= T \left(\frac{\partial S}{\partial l} \right)_T = T \left(\frac{\partial}{\partial l} \right)_T \left\{ -\frac{3k_B l^2}{2Na^2} + C \right\} \\ &= T \left\{ -\frac{3k_B l}{Na^2} \right\} = - \left(\frac{3k_B T}{Na^2} \right) l \end{aligned}$$

This tensile force has the Hooke's law form $f = -k_H l$ with $k_H = 3k_B T/Na^2$.