

### 3 Deviations from Ideality

- 3/2: 1. An “ideal” rubber band is at 300 K and a mass of 200 g stretches its length by 10 mm. Give the stretch length at 330 K.

*Answer.* We are given that  $L_0 = 10$  mm,  $T_0 = 300$  K, and  $T_1 = 330$  K. It follows since  $L = Nf\ell_0^2/k_B T$  that

$$\frac{Nf\ell_0^2}{k_B} = L_0 T_0$$

Thus,

$$\begin{aligned} L_1 &= \frac{Nf\ell_0^2}{k_B T_1} \\ &= \frac{L_0 T_0}{T_1} \\ \boxed{L_1 = 9.09 \text{ mm}} \end{aligned}$$

□

2. A pill of 0.1 mol of gadolinium (III) sulfate ( $\text{Gd}_2(\text{SO}_4)_3$ ) is used for adiabatic demagnetization.

- (a) Give the molar mass.

*Answer.*

$$\boxed{M = 602.88 \text{ g/mol}}$$

□

- (b) Assuming all electrons unpaired in the  $f$  orbital, give the magnetic moment.

*Answer.*  $\text{Gd}^{3+}$  has the electron configuration  $[\text{Xe}] 4f^7$  since all electrons in higher energy levels are ionized first. Thus, by the spin-only magnetic moment formula,

$$\begin{aligned} \mu &= \sqrt{7(7+2)} \\ \boxed{\mu = 7.94 \mu_B} \end{aligned}$$

□

- (c) Calculate the heat transferred from the lattice to the spin degree of freedom as the field is varied from 1 T to 0 T.

*Answer.* When an external magnetic field is applied to a magnetic dipole, such as  $\text{Gd}_2(\text{SO}_4)_3$ , each molecule can either orient itself parallel or anti to the magnetic field. In other words, a two-state system is created with energies

$$E_1 = -\mu B \qquad E_2 = \mu B$$

where  $\mu$  is the strength of the dipole and  $B$  is the strength of the magnetic field. Thus, the molecular partition function for each particle is

$$q = e^{-E_1/k_B T} + e^{-E_2/k_B T}$$

Additionally, since we are considering a solid lattice, each particle in the lattice is both independent (obviously) and distinguishable (by its position in the lattice). Thus,

$$Q = q^N$$

where  $N = 0.1N_A$  is the number of  $\text{Gd}_2(\text{SO}_4)_3$  particles present. It follows that the magnetic energy of the system is given by

$$\langle E \rangle = k_B T^2 \frac{\partial \ln Q}{\partial T}$$

We are now ready to plug in values. We have that  $\mu = 7.94 \mu_B = 6.36 \times 10^{-23} \text{ J T}^{-1}$  and that  $B = 1 \text{ T}$ . Thus,

$$q = e^{\mu B / k_B T} + e^{-\mu B / k_B T} \approx e^{5.33/T} + e^{-5.33/T}$$

Therefore, we have that

$$\begin{aligned} \langle E \rangle &= N k_B T^2 \frac{\partial \ln q}{\partial T} \\ &= \frac{0.1 N_A k_B T^2}{q} \left[ \frac{\partial}{\partial T} \left( e^{5.33/T} \right) + \frac{\partial}{\partial T} \left( e^{-5.33/T} \right) \right] \\ &= \frac{0.1 R T^2}{q} \left[ e^{5.33/T} \cdot -\frac{5.33}{T^2} + e^{-5.33/T} \cdot \frac{5.33}{T^2} \right] \\ &= \frac{0.533 R}{q} \left[ e^{-5.33/T} - e^{5.33/T} \right] \\ &= 4.43 \cdot \frac{e^{-5.33/T} - e^{5.33/T}}{e^{-5.33/T} + e^{5.33/T}} \\ &= -4.43 \tanh \left( \frac{5.33}{T} \right) \end{aligned}$$

Alternatively, if no external magnetic field is applied, there is only one energy state occupied by every particle with energy that we may take to be 0. It follows that  $q = 1$ ,  $Q = q^N = 1$ ,  $\ln Q = 0$ , and hence the overall magnetic energy  $\langle E \rangle = 0$  (which makes intuitive sense as well).

Thus, assuming that all magnetic energy (i.e., “heat from the lattice”) is transferred to the spin degree of freedom upon demagnetization,

$$\Delta E = 0 - \langle E \rangle$$

$$\Delta E = 4.43 \cdot \tanh \left( \frac{5.33}{T} \right)$$

□

- (d) Estimate the heat capacity of the pill, and determine its lattice temperature if it starts at 4 K.

*Answer.* The internet<sup>[1]</sup> suggests that the Debye temperature  $\Theta_D = 182 \text{ K}$ . Thus, according to Debye theory, we have for  $T = 4 \text{ K}$  that

$$\bar{C}_P(T) = \frac{12\pi^4}{5} R \left( \frac{T}{\Theta_D} \right)^3$$

$$\bar{C}_P(T) = 0.0206 \frac{\text{J}}{\text{mol K}}$$

Additionally, we can relate heat transfer, mass, heat capacity, and change in temperature by  $q = mc\Delta T$  or, with the variables we’ve been using,  $\Delta E = 0.1M\bar{C}_P(T)\Delta T$ . Plugging in  $T = 4 \text{ K}$  and solving yields

$$\begin{aligned} \Delta T &= \frac{\Delta E}{0.1M\bar{C}_P(4)} \\ &= -\frac{44.3}{602.88 \cdot 0.0206} \cdot \tanh \left( \frac{5.33}{T} \right) \\ &= -3.10 \text{ K} \end{aligned}$$

yielding a final lattice temperature of  $\boxed{0.90 \text{ K}}$ .

□

<sup>1</sup><https://www.knowledgedoor.com/2/elements.handbook/debye.temperature.html>

3. A Joule-Thomson expansion is an adiabatic and reversible expansion from a pressure  $P_1$  to a pressure  $P_2$ , made closer to reversible by having a porous section that slows down the gas.

- (a) Show that the Joule-Thomson expansion conserves enthalpy.

*Answer.* We have from the first law of thermodynamics that

$$\begin{aligned} dU &= \delta q + \delta w \\ &= dw \\ \int_1^2 dU &= \int_1^2 dw \\ U_2 - U_1 &= P_1 V_1 - P_2 V_2 \\ U_2 + P_2 V_2 &= U_1 + P_1 V_1 \\ H_1 &= H_2 \end{aligned}$$

as desired. □

- (b) Show that an ideal gas's temperature is unchanged during a Joule-Thomson expansion.

*Answer.* We know that enthalpy is conserved. Thus,

$$\begin{aligned} H_1 &= H_2 \\ U_1 + P_1 V_1 &= U_2 + P_2 V_2 \\ U_1(T_1) + nRT_1 &= U_2(T_2) + nRT_2 \end{aligned}$$

It follows since the above equation depends entirely on temperature that for equality to hold,  $T_1 = T_2$  necessarily. □

- (c) Argue why a real gas can cool (or heat up) during a Joule-Thomson expansion.

*Answer.* For a real gas, the internal energy is a function of both temperature and intermolecular forces, so some energy could be transferred from one “reservoir” to the other. □

- (d) Show that the temperature change is given by  $(\partial T / \partial P)_H$ .

*Answer.* The total differential of  $H(P, T)$  is

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

It follows by the definition of  $C_P$  that

$$\begin{aligned} dH &= \left( \frac{\partial H}{\partial P} \right)_T dP + C_P dT \\ dH - C_P dT &= \left( \frac{\partial H}{\partial P} \right)_T dP \\ \left( \frac{\partial H}{\partial P} \right)_H - C_P \left( \frac{\partial T}{\partial P} \right)_H &= \left( \frac{\partial H}{\partial P} \right)_T \\ 0 - C_P \left( \frac{\partial T}{\partial P} \right)_H &= \left( \frac{\partial H}{\partial P} \right)_T \\ \left( \frac{\partial T}{\partial P} \right)_H &= -\frac{1}{C_P} \left( \frac{\partial H}{\partial P} \right)_T \end{aligned}$$

Since  $H$  is conserved and hence constant, the right side of the equation equals zero, and hence  $T$  is unchanged even as pressure varies. □

(e) Problem 22-48: Show that

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(\alpha T - 1)$$

where  $\alpha$  is the coefficient of thermal expansion.

*Answer.* At constant temperature, we have

$$dG = d(H - TS)$$

$$dG = dH - T dS - S dT$$

$$dG = dH - T dS$$

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

It follows by the Maxwell relation

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

that

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

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

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

Therefore, from part (d),

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_H &= -\frac{1}{C_P} \left(\frac{\partial H}{\partial P}\right)_T \\ &= -\frac{1}{C_P} \left[ V - T \left(\frac{\partial V}{\partial T}\right)_P \right] \\ &= \frac{1}{C_P} \left[ T \left(\frac{\partial V}{\partial T}\right)_P - V \right] \\ &= \frac{V}{C_P} (\alpha T - 1) \end{aligned}$$

□

(f) Problem 22-49: Show that a gas with only excluded volume cools upon expansion.

*Answer.* The equation of state for only excluded volume is  $P(V - nb) = nRT$ . Solving for  $V$  yields  $n(RT + bP)/P$ . Thus,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P}$$

Consequently, since  $1 - nb/V = nRT/PV$ , we have that

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_H &= \frac{1}{C_P} \left[ T \left(\frac{\partial V}{\partial T}\right)_P - V \right] \\ &= \frac{V}{C_P} \left[ \frac{nRT}{PV} - 1 \right] \\ &= -\frac{V}{C_P} \frac{nb}{V} \\ dT &= -\frac{nb}{C_P} dP \end{aligned}$$

Since  $n, b, C_P > 0$  and  $dP < 0$ , we have that  $dT > 0$ , as desired.

□

- (g) Problem 22-51: Give the sign and estimate the magnitude of  $(\partial T/\partial P)_H$  for  $\text{N}_2$  gas around 300 K from 100 atm to 1 atm based on van der Waals parameters.

*Answer.* For  $\text{N}_2$ , we have that  $b_0 = 45.29 \text{ cm}^3 \text{ mol}^{-1}$ ,  $\lambda = 1.87$ ,  $\varepsilon/k_B = 53.7$ ,  $C_P = 7R/2$ , and  $T = 300 \text{ K}$ . Therefore,

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

$$\left(\frac{\partial T}{\partial P}\right)_H = +1.97$$

□