

## Problem Set 12

P3

Writing out the expression for the partition function, and recognizing that in the high-temperature limit the partition function can be evaluated by integration:

$$q = \sum_m e^{-\beta \epsilon_m} = \sum_m e^{-\beta \alpha m^2} \cong \int_0^{\infty} e^{-\beta \alpha m^2} dm = \frac{1}{2} \sqrt{\frac{\pi}{\alpha \beta}}$$

$$U = \frac{-N}{q} \left( \frac{\partial q}{\partial \beta} \right)_V = \frac{-N}{q} \left( \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right) \left( \frac{\partial}{\partial \beta} \beta^{-1/2} \right)_V$$

$$= \frac{-N}{q} \left( \frac{1}{2} \sqrt{\frac{\pi}{\alpha}} \right) \left( -\frac{1}{2} \beta^{-3/2} \right) = \frac{1}{2} N \beta^{-1} = \frac{1}{2} N k T$$

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{1}{2} N k$$

P4

The rotational and vibrational temperatures are given by:

$$\theta_r = \frac{B}{k} \quad \theta_v = \frac{\tilde{\nu}}{k}$$

The high-temperature approximation will be valid for rotations or vibrations when the temperature is at least 10-fold greater than the rotational or vibrational temperature, respectively. Using the spectroscopic information provided in the table:

Molecule	$\theta_r$ (K)	High-T for R?	$\theta_v$ (K)	High-T for V?
H <sup>35</sup> Cl	15.3	no	4153	no
<sup>12</sup> C <sup>16</sup> O	2.78	yes	3123	no
<sup>39</sup> KI	0.088	yes	288	no
CsI	0.035	yes	173	no

P10

The total vibrational heat capacity will be equal to the sum of heat capacity contributions from each vibrational degree of freedom. Keeping track of the degeneracy of the 712 cm<sup>-1</sup> mode, the total heat capacity can be written as:

$$C_{V, total} = C_{V, \nu_1} + 2C_{V, \nu_2} + C_{V, \nu_3}$$

where the heat capacity for a specific mode is determined using:

$$C_V = \frac{N}{kT^2} (hc\tilde{\nu})^2 \frac{e^{\frac{hc\tilde{\nu}}{kT}}}{\left( e^{\frac{hc\tilde{\nu}}{kT}} - 1 \right)^2}$$

Evaluating this expression for the 2041 cm<sup>-1</sup> mode at 500 K yields:

$$\begin{aligned}
 C_V &= \frac{N}{kT^2} (hc\tilde{\nu})^2 \frac{e^{-\frac{hc\tilde{\nu}}{kT}}}{\left(e^{-\frac{hc\tilde{\nu}}{kT}} - 1\right)^2} \\
 &= \frac{N}{(1.38 \times 10^{-23} \text{ J K}^{-1})(500 \text{ K})^2} \left( (6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2041 \text{ cm}^{-1}) \right)^2 \\
 &\quad \times \frac{e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2041 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(500 \text{ K})}}}{\left( e^{-\frac{(6.626 \times 10^{-34} \text{ J s})(3.00 \times 10^{10} \text{ cm s}^{-1})(2041 \text{ cm}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(500 \text{ K})}} - 1 \right)^2} \\
 &= N(4.77 \times 10^{-22} \text{ J K}^{-1})(2.81 \times 10^{-3}) \\
 &= nN_A(2.29 \times 10^{-24} \text{ J K}^{-1}) \\
 &= nN_A(2.29 \times 10^{-24} \text{ J K}^{-1}) \\
 &= n(0.811 \text{ J mol}^{-1} \text{ K}^{-1})
 \end{aligned}$$

Similar calculations for the other vibrational degrees of freedom and temperatures of interest yields the following table of molar constant volume heat capacities (units of J mol<sup>-1</sup> K<sup>-1</sup>)

	298 K	500 K	1000 K
2041 cm <sup>-1</sup>	0.042	0.811	4.24
712 cm <sup>-1</sup>	3.37	5.93	7.62
3369 cm <sup>-1</sup>	0.000	0.048	1.56
Total	6.78	12.7	21.0

P13

a) The Dulong–Petit law is applicable to atomic crystals. KCl is a molecular crystal where vibrational degrees of freedom will also contribute to  $C_V$ .

b)

$$C_V = 3Nk \left( \frac{\theta_V}{T} \right)^2 \frac{e^{\frac{\theta_V}{T}}}{\left( e^{\frac{\theta_V}{T}} - 1 \right)^2}$$

$$21.0 \text{ J mol}^{-1} \text{ K}^{-1} = 3 \left( 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) \left( \frac{\theta_V}{50 \text{ K}} \right)^2 \frac{e^{\frac{\theta_V}{50 \text{ K}}}}{\left( e^{\frac{\theta_V}{50 \text{ K}}} - 1 \right)^2}$$

$$0.841 = \left( \frac{\theta_V}{50 \text{ K}} \right)^2 \frac{e^{\frac{\theta_V}{50 \text{ K}}}}{\left( e^{\frac{\theta_V}{50 \text{ K}}} - 1 \right)^2}$$

$$\theta_V = 71.4 \text{ K (determined using Excel)}$$

Using the vibrational temperature, the predicted heat capacity at 175 K can be determined:

$$C_V = 3Nk \left( \frac{\theta_V}{T} \right)^2 \frac{e^{\frac{\theta_V}{T}}}{\left( e^{\frac{\theta_V}{T}} - 1 \right)^2}$$

$$C_{V,m} = 3 \left( 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \right) \left( \frac{71.4 \text{ K}}{175 \text{ K}} \right)^2 \frac{e^{\frac{71.4 \text{ K}}{175 \text{ K}}}}{\left( e^{\frac{71.4 \text{ K}}{175 \text{ K}}} - 1 \right)^2}$$

$$= 24.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

P18

$$U_m^o = U_{T,m}^o + U_{R,m}^o + U_{V,m}^o + U_{E,m}^o$$

$$= \frac{3}{2} RT + \frac{3}{2} RT + N_A hc \left[ \left( \frac{\tilde{\nu}_1}{e^{\beta hc \tilde{\nu}_1} - 1} \right) + \left( \frac{\tilde{\nu}_2}{e^{\beta hc \tilde{\nu}_2} - 1} \right) + \left( \frac{\tilde{\nu}_3}{e^{\beta hc \tilde{\nu}_3} - 1} \right) \right] + 0$$

$$= 3R(298.15 \text{ K}) + 479 \text{ J mol}^{-1} = 7.92 \text{ kJ mol}^{-1}$$

$$S_m^\circ = \frac{U_m^\circ}{T} + k \ln Q = \frac{U_m^\circ}{T} + k \ln \left( \frac{q_{total}^N}{N!} \right) = \frac{U_m^\circ}{T} + Nk \ln(q_{total}) - k \ln(N!)$$

$$= \frac{7.92 \text{ kJ mol}^{-1}}{298.15 \text{ K}} + R \ln(q_r q_R q_V q_E) - R \ln((1 \text{ mol}) N_A) + R$$

$$= -420 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln(q_r q_R q_V q_E)$$

$$q_r = \left( \frac{V}{\Lambda^3} \right) = \frac{0.0245 \text{ m}^3}{1.89 \times 10^{-33} \text{ m}^3} = 1.30 \times 10^{31}$$

$$q_R = \frac{\sqrt{\pi}}{\sigma} \left( \frac{kT}{B_A} \right)^{1/2} \left( \frac{kT}{B_B} \right)^{1/2} \left( \frac{kT}{B_C} \right)^{1/2}$$

$$= \frac{\sqrt{\pi}}{2} \left( \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{1.60 \text{ cm}^{-1}} \right)^{1/2} \left( \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{0.31 \text{ cm}^{-1}} \right)^{1/2}$$

$$\times \left( \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{0.29 \text{ cm}^{-1}} \right)^{1/2}$$

$$= 6.98 \times 10^3$$

$$q_V = \left( \frac{1}{1 - e^{-\beta \epsilon_1}} \right) \left( \frac{1}{1 - e^{-\beta \epsilon_2}} \right) \left( \frac{1}{1 - e^{-\beta \epsilon_3}} \right)$$

$$= \left( \frac{1}{1 - e^{-\frac{938 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}}} \right) \left( \frac{1}{1 - e^{-\frac{450 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}}} \right) \left( \frac{1}{1 - e^{-\frac{1100 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}}} \right)$$

$$= 1.14$$

$$q_E = 2$$

$$S_m^\circ = -420 \text{ J mol}^{-1} \text{ K}^{-1} + R \ln(q_r q_R q_V q_E) = -424 \text{ J mol}^{-1} \text{ K}^{-1} + 676 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$S_m^\circ = 256 \text{ J mol}^{-1} \text{ K}^{-1}$$

P21

$$\begin{aligned}
 S &= \frac{U}{T} + k \ln Q = \frac{U}{T} + k \ln \left( \frac{q_{\text{total}}^N}{N!} \right) = \frac{U_m}{T} + Nk \ln(q_{\text{total}}) - k \ln(N!) \\
 &= nR + nR \ln(q_r) - nR \ln(nN_A) + nR \\
 &= 2nR + nR \ln(q_r) - nR \ln(nN_A)
 \end{aligned}$$

$$q_r = \frac{A}{\Lambda^2} \quad \text{where } \Lambda = \left( \frac{h^2}{2\pi mkT} \right)^{1/2} \quad \text{and } A = \text{area}$$

$$\begin{aligned}
 S &= 2nR + nR \ln \left( \frac{A}{\Lambda^2} \right) - nR \ln(nN_A) \\
 &= nR \left[ \ln(e^2) + \ln \left( \frac{A}{\Lambda^2} \right) - \ln(nN_A) \right]
 \end{aligned}$$

$$S_m = R \ln \left( \frac{e^2 A}{nN_A \Lambda^2} \right)$$

P28

$$\begin{aligned}
 A &= -kT \ln(q_v)^N = -NkT \ln q_v \\
 &= -nRT \ln(1 - e^{-\beta h\nu})^{-1} \\
 A_m &= RT \ln(1 - e^{-\beta h\nu})
 \end{aligned}$$

$$G = -kT \left[ \ln(q_v)^N - V \left( \frac{\partial \ln(q_v)^N}{\partial V} \right)_T \right]$$

$$G = -kT \ln(q_v)^N = -NkT \ln q_v$$

$$G_m = RT \ln(1 - e^{-\beta h\nu})$$

The vibrational contribution to the molar Helmholtz and Gibbs energies are equivalent.

P30

$$G_R = -NkT \ln q_R$$

$$G_{R,m} = -RT \ln q_R$$

$$q_R = \frac{kT}{\sigma B} = \frac{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}{(2)(0.42 \text{ cm}^{-1})} = 493$$

$$G_{R,m}^{\circ} = -(8.134 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \ln(493) = -15.4 \text{ kJ mol}^{-1}$$

$$G_Y = -NkT \ln q_Y$$

$$G_{Y,m} = -RT \ln q_Y$$

$$q_Y = \left( \frac{1}{1 - e^{-\beta \tilde{\nu}_1}} \right) \left( \frac{1}{1 - e^{-\beta \tilde{\nu}_2}} \right)^2 \left( \frac{1}{1 - e^{-\beta \tilde{\nu}_3}} \right)$$

$$= \left( \frac{1}{1 - e^{-\frac{1285 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}}} \right) \left( \frac{1}{1 - e^{-\frac{589 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}}} \right)^2 \left( \frac{1}{1 - e^{-\frac{2224 \text{ cm}^{-1}}{(0.695 \text{ cm}^{-1} \text{ K}^{-1})(298.15 \text{ K})}}} \right)$$
$$= 1.13$$

$$G_{Y,m}^{\circ} = -(8.134 \text{ J mol}^{-1} \text{ K}^{-1})(298.15 \text{ K}) \ln(1.13) = -0.30 \text{ kJ mol}^{-1}$$

P32

$$K = \frac{\left(\frac{q}{N_A}\right)_{35/37}^2}{\left(\frac{q}{N_A}\right)_{35/35} \left(\frac{q}{N_A}\right)_{37/37}} e^{-\beta \epsilon_0} = \frac{(q)_{35/37}^2}{(q)_{35/35} (q)_{37/37}}$$

$$q_{35/37} = q_T q_R = \left(\frac{V}{\Lambda_{35/37}^3}\right) \left(\frac{1}{\sigma \beta B_{35/37}}\right)$$

$$q_{35/35} = q_T q_R = \left(\frac{V}{\Lambda_{35/35}^3}\right) \left(\frac{1}{\sigma \beta B_{35/35}}\right)$$

$$q_{37/37} = q_T q_R = \left(\frac{V}{\Lambda_{37/37}^3}\right) \left(\frac{1}{\sigma \beta B_{37/37}}\right)$$

$$K = \frac{(q)_{35/37}^2}{(q)_{35/35} (q)_{37/37}} = \frac{\left(\left(\frac{V}{\Lambda_{35/37}^3}\right) \left(\frac{1}{\sigma_{35/37} \beta B_{35/37}}\right)\right)^2}{\left(\left(\frac{V}{\Lambda_{35/35}^3}\right) \left(\frac{1}{\sigma_{35/35} \beta B_{35/35}}\right)\right) \left(\left(\frac{V}{\Lambda_{37/37}^3}\right) \left(\frac{1}{\sigma_{37/37} \beta B_{37/37}}\right)\right)}$$

$$\cong \frac{\sigma_{37/37} \sigma_{35/35}}{\sigma_{35/37}^2} = \frac{(2)(2)}{(1)^2} = 4$$

P33

a) Since the helium is  $^4\text{He}$ , only even  $J$  states are allowed; therefore, the first excited rotational state is  $J = 2$ .

$$I = \mu r^2 = \left(\frac{m_{\text{He}}}{2}\right) (65 \times 10^{-10} \text{ m})^2 = \left(\frac{0.004 \text{ kg mol}^{-1}}{2(N_A)}\right) (4.23 \times 10^{-17} \text{ m}^2)$$

$$= 1.40 \times 10^{-48} \text{ kg m}^2$$

$$B = \frac{h}{8\pi^2 c I} = \frac{6.626 \times 10^{-34} \text{ J s}}{8\pi^2 (3.00 \times 10^{10} \text{ cm s}^{-1}) (1.40 \times 10^{-48} \text{ kg m}^2)}$$

$$= 0.002 \text{ cm}^{-1} = 23.9 \text{ mJ mol}^{-1}$$

$$E_{J=2} = BJ(J+1) = 23.9 \text{ mJ mol}^{-1} (6) = 143.4 \text{ mJ mol}^{-1}$$

b)

$$K = \frac{\left(\frac{q}{N_A}\right)_{\text{He}}^2 e^{-\beta \epsilon_0}}{\left(\frac{q_T}{N_A}\right)_{\text{He}_2}} = \frac{\left(\frac{q_T}{N_A}\right)_{\text{He}}^2 e^{-\beta(0.083 \text{ J mol}^{-1}/N_A)}}{\left(\frac{q_T}{N_A}\right)_{\text{He}_2}}$$

$$q_{T,\text{He}} = \frac{V}{\Lambda_{\text{He}}^3} = \left(\frac{0.001 \text{ m}^3}{2.11 \times 10^{-29} \text{ m}^3}\right) = 4.75 \times 10^{25}$$

$$q_{T,\text{He}_2} = \frac{V}{\Lambda_{\text{He}_2}^3} = \left(\frac{0.001 \text{ m}^3}{7.45 \times 10^{-30} \text{ m}^3}\right) = 1.34 \times 10^{26}$$

$$K = \frac{\left(\frac{q_T}{N_A}\right)_{\text{He}}^2 e^{-\beta(0.083 \text{ J mol}^{-1}/N_A)}}{\left(\frac{q_T}{N_A}\right)_{\text{He}_2}} = \frac{\left(\frac{4.75 \times 10^{25}}{N_A}\right)_{\text{He}}^2 e^{-\frac{(0.083 \text{ J mol}^{-1}/N_A)}{(1.38 \times 10^{-23} \text{ J K}^{-1})(10 \text{ K})}}}{\left(\frac{1.34 \times 10^{26}}{N_A}\right)_{\text{He}_2}}$$

$$K = (28.0)(0.999) \cong 28.0$$

Even at this low temperature, equilibrium favors dissociation.