Chemistry 562 **Fall 2012**

Problem Set 11

Due beginning of class on Wednesday, May 2nd

(Make your reasoning clear. We need to understand your reasoning, not just see the final result.)

1. (a) Write out the equation for the canonical partition function Q in terms of the molecular translational, rotational, and vibrational partition functions of an HCN gas.

   (b) Find the equation for E for the HCN gas in terms of molecular parameters. (recall $E=U-U(0)$). Use the equation for the rotational molecular partition function in the high temperature limit. (*Note: HCN has 4 normal modes: the CH stretch, the CN stretch, and a doubly degenerate bend.*)

   (c) Find the equation for the molar heat capacity C_p of HCN in terms of molecular parameters and calculate it at 298 K. The normal modes for HCN are at 3311 cm^{-1} (CH stretch), 712 cm^{-1} (doubly degenerate bend), and 2097 cm^{-1} (CN stretch). You may use $C_p = C_v + R$. How does your value of C_p compare to the experimental value of 35.9 J/(mole K)?

2. For the reaction:

$$A_2 + B_2 \Leftrightarrow 2AB$$

   where A and B are different isotopes of the same atom:

   (a) Find the ratio $\dfrac{\left(q^T_{AB}\right)^2}{q^T_{A_2} q^T_{B_2}}$ in terms of m_{A_2}, m_{B_2}, and m_{AB}. (T refers to the translational partition function.)

   (b) Find the ratio $\dfrac{\left(q^R_{AB}\right)^2}{q^R_{A_2} q^R_{B_2}}$ in terms of m_{A_2}, m_{B_2}, and m_{AB}. Use the high temperature limit for the rotational partition functions. Don't forget to include the symmetry number.

   (c) Using the results of parts (a) and (b), and assuming the vibrational and electronic partition functions are 1, show that the equilibrium constant is equal to: $4\dfrac{m_{AB}}{\sqrt{m_{A_2} m_{B_2}}} e^{-\beta(2\varepsilon^0_{AB} - \varepsilon^0_{A_2} - \varepsilon^0_{B_2})}$.

   (ε^0_{AB}, $\varepsilon^0_{A_2}$, *and* $\varepsilon^0_{B_2}$ *are the zero point energies of AB,* A_2, *and* B_2 *respectively*)

1 a) $q_{HCN} = q_T q_R q_V$

$q_V = q_{\nu_1} q_{\nu_2} q_{\nu_3} q_{\nu_4}$

$$Q = \frac{q^N}{N!} = \frac{(q_T q_R q_V)^N}{N!}$$

b) $$E = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_V = -\left(\frac{\partial \ln\left[(q_T q_R q_V)^N / N!\right]}{\partial \beta}\right)_V$$

$$= -N\left[\underset{①}{\left(\frac{\partial \ln q_T}{\partial \beta}\right)_V} + \underset{②}{\left(\frac{\partial \ln q_R}{\partial \beta}\right)_V} + \underset{③}{\left(\frac{\partial \ln q_V}{\partial \beta}\right)_V}\right] + \cancelto{0}{\left(\frac{\partial \ln N!}{\partial \beta}\right)_V}$$

① $$\left(\frac{\partial \ln q_T}{\partial \beta}\right)_V = \left(\frac{\partial \ln\left[\left(\frac{2\pi m}{\beta h^2}\right)^{3/2} V\right]}{\partial \beta}\right)_V = \frac{3}{2}\frac{d\ln(2\pi m/\beta h^2)}{d\beta} + \cancelto{0}{\left(\frac{\partial \ln V}{\partial \beta}\right)_V}$$

$$= -\frac{3}{2}\frac{d\ln\beta}{d\beta} = -\frac{3}{2}\frac{1}{\beta} = -\frac{3}{2}kT$$

② $$\left(\frac{\partial \ln q_R}{\partial \beta}\right)_V = \frac{d\ln\left(\frac{1}{\sigma hcB\beta}\right)}{d\beta} = -\frac{d\ln\beta}{d\beta} = -kT$$

1 b) (cont)

③ $$\left(\frac{\partial \ln q_v}{\partial \beta}\right)_V = \frac{d \ln (1-e^{-\beta hc\tilde{\nu}})^{-1}}{d\beta} = \frac{1}{(1-e^{-\beta hc\tilde{\nu}})^{-1}} \frac{d(1-e^{-\beta hc\tilde{\nu}})^{-1}}{d\beta}$$

$$= \cancel{(1-e^{-\beta hc\tilde{\nu}})}(-1)(1-e^{-\beta hc\tilde{\nu}})^{\overset{-1}{\cancel{-2}}}(+hc\tilde{\nu})(+e^{-\beta hc\tilde{\nu}})$$

$$= \frac{-hc\tilde{\nu}\, e^{-\beta hc\tilde{\nu}}}{1-e^{-\beta hc\tilde{\nu}}} \frac{e^{\beta hc\tilde{\nu}}}{e^{\beta hc\tilde{\nu}}} = \frac{-hc\tilde{\nu}}{e^{\beta hc\tilde{\nu}}-1}$$

We will need one of these for each vibrational mode

$$E = \frac{3}{2}NkT + NkT + \sum_{i=1}^{4} \frac{Nhc\tilde{\nu}_i}{e^{\beta hc\tilde{\nu}_i}-1}$$

c) $C_p = C_v + R$ $\qquad$ $C_v = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$

$$C_v = \frac{3}{2}Nk + Nk + \frac{d}{dT}\left(\sum_{i=1}^{4} \frac{Nhc\tilde{\nu}_i}{e^{\beta hc\tilde{\nu}_i}-1}\right)$$

doing one of the vib terms

$$\frac{df}{dT} = \frac{df}{d\beta}\frac{d\beta}{dT} = -kT^{-2}\frac{d}{d\beta}\left(\frac{Nhc\tilde{\nu}}{e^{\beta hc\tilde{\nu}}-1}\right) = \frac{-kNhc\tilde{\nu}}{T^2}(-1)(e^{\beta hc\tilde{\nu}}-1)^{-2}\left(\frac{hc\tilde{\nu}}{k}\right)e^{\beta hc\tilde{\nu}}$$

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

1 c) (cont)

$$C_p = \frac{3}{2}Nk + Nk + \frac{Nk}{T^2}\sum_{i=1}^{4}(hc\tilde{\nu}_i/k)^2 e^{\beta hc\tilde{\nu}_i}(e^{\beta hc\tilde{\nu}_i}-1)^{-2} + R$$

$$C_p = \frac{7}{2}R + \frac{R}{T^2}\sum_{i=1}^{4}\left(\frac{hc\tilde{\nu}_i}{k}\right)^2(e^{\beta hc\tilde{\nu}_i-1})^{-2}e^{\beta hc\tilde{\nu}_i}$$

see Mathcad sheet for calculation

2) a) $A_2 + B_2 \rightleftarrows 2AB$

$$q_x^T = \left(\frac{2\pi m_x}{\beta h^2}\right)^{3/2} V$$

$$\frac{(q_{AB}^T)^2}{q_{A_2}^T q_{B_2}^T} = \frac{(2\pi/\beta h^2)^{6/2}V^2 \quad m_{AB}^{6/2}}{(2\pi/\beta h^2)^{3/2}V\, m_{A_2}^{3/2}\ (2\pi/\beta h^2)^{3/2}V m_{B_2}^{3/2}} = \frac{m_{AB}^3}{m_{A_2}^{3/2}\, m_{B_2}^{3/2}} = \left(\frac{m_{AB}}{m_{A_2}^{1/2}\, m_{B_2}^{1/2}}\right)^3$$

b) $q_x^R = \frac{kT}{\sigma hcB}$

$$\frac{(q_{AB}^R)^2}{q_{A_2}^R\, q_{B_2}^R} = \frac{\cancel{\left(\frac{kT}{hc}\right)^2}\ \frac{1}{1\,B_{AB}^2}}{\cancel{\left(\frac{kT}{hc}\right)}\frac{1}{2B_{A_2}}\cancel{\left(\frac{kT}{hc}\right)}\frac{1}{2B_{B_2}}}$$

assume

$R_{AB} = R_{A2} = R_{B_2}$

because we're only exchanging isotopes

2) b) (cont)

$$B = \frac{\hbar}{4\pi c \mu R^2} \qquad m_A + m_A = m_{AA}$$

$$= \frac{4\, B_{A_2} B_{B_2}}{B_{AB}^2} = \frac{4\, \cancel{\mu}_{AB}^2}{\cancel{\mu}_{AA} \cancel{\mu}_{BB}} = \frac{4\left(\frac{\cancel{m}_A \cancel{m}_B}{m_{AB}}\right)^2}{\frac{\cancel{m_A^2}}{m_{AA}} \frac{\cancel{m_B^2}}{m_{BB}}} = 4\, \frac{m_{AA} m_{BB}}{m_{AB}^2}$$

c) $$K = \frac{q_{AB}^2}{q_{A_2} q_{B_2}} e^{-\Delta_r \varepsilon_0 \beta} = \frac{m_{AB}^{\overset{1}{\cancel{3}}}}{m_{A_2}^{\overset{1}{\cancel{3}}/2} m_{B_2}^{\overset{1}{\cancel{3}}/2}} \cdot 4\, \frac{\cancel{m}_{A_2} \cancel{m}_{B_2}}{\cancel{m}_{AB}^2} e^{-\Delta_r \varepsilon_0 \beta}$$

$$\Delta_r \varepsilon_0 = -\left[D_0(\text{prod}) - D_0(\text{react})\right] = \left[2\varepsilon_{AB}^{\circ} - \varepsilon_{A_2}^{\circ} - \varepsilon_{B_2}^{\circ}\right]$$

$$\begin{cases} D_0 = D_e - \varepsilon_0 \\ D_e(\text{prod}) = D_e(\text{react}) \\ D_0(\text{prod}) \neq D_0(\text{react}) \end{cases}$$

$$K = 4\, \frac{m_{AB}}{\sqrt{m_{A_2} m_{B_2}}} e^{-\beta[2\varepsilon_{AB}^{\circ} - \varepsilon_{A_2}^{\circ} - \varepsilon_{B_2}^{\circ}]}$$

d) i) $$q_v = \frac{1}{1 - e^{-\beta h c \tilde{\nu}}} = \frac{1}{1 - e^{-\left(\frac{3113\ \text{cm}^{-1}}{300\text{K}\ 0.695\ \text{cm}^{-1}/\text{K}}\right)}} = 1.0000003$$

This is well within the sig figs given. Virtually no D_2 molecules are in $v = 1$

This number will only get closer to 1 for H_2 and HD, their energy level spacings are even greater. $\omega = \sqrt{k/\mu}$, k will be constant, μ will decrease, ω will increase

2 d) ii) See Mathcad

iii) "   "

iv) Again, see $\omega = \sqrt{\frac{k}{\mu}}$

The fractional difference between $\mu_{^{37}Cl\,^{37}Cl}$ and $\mu_{^{35}Cl\,^{35}Cl}$ will be much less than that between μ_{HH} and μ_{DD}. This will keep the exponential term much closer to 1, decreasing the effect in the Cl isomerization relative to H isomerization.

$$q_H := \frac{k \cdot T}{B}$$

$$q_H = 3.475$$

This answer is off by nine percent. This isn't as good as last week's rotator (HCl), because the rotational constant for H2 is so large due to its small moment of inertia.

$$\frac{q_9 - q_H}{q_9} = 0.092$$

2 d) iii)

$m_H := 1.00782$ $\qquad \varepsilon_{HD} := \frac{3813 \cdot cm^{-1}}{2}$ $\quad \varepsilon_{HH} := \frac{4401 cm^{-1}}{2}$ $\quad \varepsilon_{DD} := \frac{3113 cm^{-1}}{2}$

$m_D := 2.01410$

$e^{-\beta \cdot (2 \cdot \varepsilon_{HD} - \varepsilon_{HH} - \varepsilon_{DD})} = 0.764$ $\qquad 4 \cdot \frac{(m_H + m_D)}{\sqrt{(m_H + m_H) \cdot (m_D + m_D)}} = 4.242$

$$K := 4 \cdot \frac{(m_H + m_D)}{\sqrt{(m_H + m_H) \cdot (m_D + m_D)}} \cdot e^{-\beta \cdot (2 \cdot \varepsilon_{HD} - \varepsilon_{HH} - \varepsilon_{DD})}$$

$K = 3.243$

HW #11

1 c)

$h := 6.626068 \cdot 10^{-34} \text{J} \cdot \text{s}$

$c := 2.997924 \cdot 10^{10} \dfrac{\text{cm}}{\text{s}}$

$k := 1.38065 \cdot 10^{-23} \dfrac{\text{J}}{\text{K}}$

$R := 8.314472 \dfrac{\text{J}}{\text{mol} \cdot \text{K}}$

$$\nu := \begin{pmatrix} \dfrac{3311}{\text{cm}} \\ \dfrac{2094}{\text{cm}} \\ \dfrac{712}{\text{cm}} \\ \dfrac{712}{\text{cm}} \end{pmatrix}$$

$$C_p(T) := \frac{7}{2} \cdot R + \frac{R}{T^2} \cdot \sum_{i=0}^{3} \left(\frac{h \cdot c \cdot \nu_i}{k} \right)^2 \cdot \left(e^{\frac{h \cdot c}{k \cdot T} \cdot \nu_i} - 1 \right)^{-2} \cdot e^{\frac{h \cdot c \cdot \nu_i}{k \cdot T}}$$

$C_p(298\text{K}) = 35.878 \dfrac{\text{J}}{\text{mol} \cdot \text{K}}$

This result agrees very well with the experimental value. It is within the significant figures of the cited result.

2 d) ii)

This is the same calculation that we did last week.

$T := 300\text{K}$ $\quad k := 0.6950687 \dfrac{\text{cm}^{-1}}{\text{K}}$

$\beta := \dfrac{1}{k \cdot T}$ $\quad \beta = 4.796 \times 10^{-3} \text{cm}$ $\quad B := 60\text{cm}^{-1}$

$i := 0 .. 99$

$\varepsilon_i := B \cdot i \cdot (i + 1)$ $\quad g_i := 2 \cdot i + 1$

$$q_i := \sum_{J=0}^{i} g_J \cdot e^{-\beta \cdot \varepsilon_J}$$

$q_0 = 1$

$q_9 = 3.829$

$q_{20} = 3.829$

$q_{99} = 3.829$