HWK #2 , Chs 17+18

17-9

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} V^N$$

$$\langle E\rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

$$\ln Q = \frac{3N}{2}\ln T + \text{ terms not involving } T$$

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3N}{2T}$$

$$\langle E\rangle = k_B T^2\left(\frac{3N}{2T}\right) = \frac{3}{2}Nk_B T$$

17-11

$$Q = \frac{1}{N!}\left(\frac{2\pi m k_B}{h^2}\right)^{3N/2}(V-Nb)^N\, T^{3N/2}\, e^{aN^2/Vk_BT}$$

$$\ln Q = \frac{3N}{2}\ln T + \frac{aN^2}{Vk_BT} + \text{ terms not involving } T$$

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3N}{2T} - \frac{aN^2}{Vk_BT^2}$$

$$\langle E\rangle = k_B T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = k_B T^{\overset{1}{\cancel{2}}}\left(\frac{3N}{2\cancel{T}}\right) - \cancel{k_B T^2}\left(\frac{aN^2}{V\cancel{k_B T^2}}\right)$$

$$= \frac{3}{2}Nk_BT - \frac{aN^2}{V}$$

17-14 $C_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} = \frac{3}{2}Nk_B$ same as monatomic ideal gas

17-17 $$\overline{C}_V = \frac{5}{2}R + R\left(\frac{h\nu}{k_BT}\right)^2 \frac{e^{-h\nu/k_BT}}{(1-e^{-h\nu/k_BT})^2}$$

$\tilde{\nu}_{O_2} = 1556\ \text{cm}^{-1}$ $\frac{hc\tilde{\nu}_{O_2}}{k_B\cancel{T}} = 2240\ \text{K}$ Plug in to eq. + plot

$\nu_{O_2} = c\tilde{\nu}_{O_2}$ (see attached)

17-32

$$Q(N_1, N_2, V, T) = \frac{[q_1]^{N_1}}{N_1!}\frac{[q_2]^{N_2}}{N_2!}$$

$$\ln Q = \ln\left(\frac{q_1^{N_1}}{N_1!}\right) + \ln\left(\frac{q_2^{N_2}}{N_2!}\right)$$

$$= N_1 \ln q_1 + N_2 \ln q_2 - \ln(N_1!) - \ln(N_2!)$$

$$= N_1 \ln\left[\left(\frac{2\pi m_1 k_B T}{h^2}\right)^{3/2} V\right] + N_2 \ln\left[\left(\frac{2\pi m_2 k_B T}{h^2}\right)^{3/2} V\right] - \ln(N_1!$$
$$-\ln$$

$$\langle E\rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3}{2}\frac{N_1}{T} + \frac{3}{2} N_2/T$$

$$\langle E\rangle = k_B T^2 \left(\frac{3}{2}\cdot\frac{1}{T}\right)(N_1 + N_2) = \frac{3}{2}(N_1 + N_2) k_B T$$

$$\langle P\rangle = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = N_1 \cdot \frac{1}{V} + N_2 \cdot \frac{1}{V} = \frac{N_1 + N_2}{V}$$

$$\langle P\rangle = \frac{k_B T\,(N_1 + N_2)}{V} \quad \text{or} \quad PV = (N_1 + N_2) k_B T$$

17-35

$$\text{prob}(v=j) = \frac{e^{-\beta \varepsilon_{vib,j}}}{q_{vib}} \qquad \text{Eq } 17.13$$

$$q_{vib} = \frac{e^{-h\nu/2k_BT}}{1 - e^{-h\nu/k_BT}} \qquad \epsilon_{vib} = \left(v + \frac{1}{2}\right)h\nu$$

$$\text{prob}(v=j) = \frac{e^{-\beta h\nu v}\,\cancel{e^{-\beta h\nu/2}}\left(1 - e^{-h\nu\beta}\right)}{\cancel{e^{-\beta h\nu/2}}}$$

$$= e^{-\beta h\nu v}\left(1 - e^{-h\nu\beta}\right) \qquad \beta = \frac{1}{k_B T}$$

From Table 5.1 $\tilde{\nu}_{HCl} = 2886\ \text{cm}^{-1}$ or $\nu = 8.65 \times 10^{13}\ \frac{1}{s}$

$$h\nu/k_B = \overset{4154}{\cancel{4146}}\ K$$

$$\text{prob}\ (v=0) = 1 - e^{-4154/300} = 0.999999031$$

$$\text{prob}\ (v=1) = e^{-4154/300}\left(1 - e^{-4154/300}\right) = 9.69 \times 10^{-7}$$

$$\text{prob}\ (v=2) = e^{-2(4154/300)}\left(1 - e^{-4154/300}\right) = 9.39 \times 10^{-13}$$

Majority of HCl molecules are in ground state @ Room temp

17-43

$$\text{prob} = \frac{g_e e^{-\varepsilon_e/k_BT}}{\sum_e g_e e^{-\varepsilon_e/k_BT}} \qquad g_e = \text{degeneracy}$$

$$0.02 = \frac{2e^{-\frac{7603.2\ \text{cm}^{-1}}{0.69509\ \text{cm}^{-1}\ T}}}{4 + 2e^{-\frac{7603.2}{0.69509T}}}$$

$$0.02\left(4 + 2e^{-\frac{7603.2}{0.69509T}}\right) = 2e^{-\frac{7603.2}{0.69509T}}$$

$$0.08 + 0.04e^{-\frac{7603.2}{0.69509T}} = 2e^{-\frac{7603.2}{0.69509T}}$$

$$0.08 = 1.96e^{-\frac{7603.2}{0.69509T}}$$

$$\ln\left(\frac{0.08}{1.96}\right) = \frac{-7603.2}{0.69509T}$$

$T = 3420\ k$ much higher than that reached in typical lab situations

18-6

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_{N,V} = N\left(\frac{\partial \langle \varepsilon \rangle}{\partial T}\right)_{N,V}$$

$$q_{trans} = \left(\frac{2\pi m k_B T}{h^2}\right)^{1/2} a \qquad \ln q_{trans} = \frac{1}{2}\ln T + \text{terms n involvin } T$$

$$\langle \varepsilon_{trans} \rangle = k_B T^2 \left(\frac{\partial \ln q_{trans}}{\partial T}\right)_V$$

$$= k_B T^2 \left(\frac{1}{2}\frac{1}{T}\right) = \frac{1}{2}k_B T$$

$$C_V = N\left(\frac{\partial\left(\frac{1}{2}k_B T\right)}{\partial T}\right)_{N,V} = \frac{1}{2}k_B N = \boxed{\frac{R}{2}} \qquad R = Nk_B$$

18-11 $f_0 = 1 - e^{-\Theta_{vib}/T}$ ground state

$f = e^{-\Theta_{vib}/T}$ <u>all</u> excited states

[See attached]

Part d

18-21

Eq 18.48

$$\frac{C_{V,vib}}{R} = \sum_{j=1}^{d}\left[\left(\frac{\Theta_{vib,j}}{T}\right)^2 \frac{e^{-\Theta_{vib,j}/T}}{\left(1 - e^{-\Theta_{vib,j}/T}\right)^2}\right]$$

each term of sum represents contribution from each normal mode

$\Theta_{vib}^{H_2O} = \underset{①}{5360}, \underset{②}{5160}, \underset{③}{2290}$ $T = 600\,K$

① $\frac{C_V}{R} = 1.05 \times 10^{-2}$

② $C_V/R = 1.36 \times 10^{-2}$

③ $C_V/R = 0.335$ ← largest contribution; $\boxed{\text{bending mode}}$

↑ from NIST webbook

$\frac{C_{V,vib}}{R}$ (total) $= 0.359$

18-30 Eq 18.62 $\frac{\overline{C}_V}{R} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{6}\left(\frac{\Theta_{vib,j}}{T}\right)^2 \frac{e^{-\Theta_{vib,j}/T}}{\left(1 - e^{-\Theta_{vib,j}/T}\right)^2}$

For NH_3... $\Theta_{vib,1} = 4800\,K$ $\Theta_{vib,2} = 1360\,K$, $\Theta_{vib,3} = \Theta_{vib,4} = 4880\,K$

$\Theta_{vib,5} = \Theta_{vib,6} = 2330\,K$

see attached {
① Plug $\Theta_{vib,j}$ into Eq. 18.62 and plot as function of T
② Plot empirical formula as function of T

18-37

$$\frac{f_v}{f_0} = \left(\frac{e^{-\beta h\nu(v+1/2)}}{q_{vib}}\right)\left(\frac{q_{vib}}{e^{-\beta h\nu/2}}\right) = e^{-\beta h\nu v}$$

slope $= -\beta h\nu$
(see attached)

$\ln(f_v/f_0) = -\beta h\nu\, v$ or

$y = m x + b$

slope = −1.5797 (after forcing intercept = 0)

$-1.5797 = -\beta h\nu$ $\qquad \tilde{\nu}_{N_2} = 2330\ \text{cm}^{-1}$

$\nu_{N_2} = 6.985 \times 10^{13}\ 1/s$

$\beta = \frac{1}{k_B T} = 3.413 \times 10^{19}$

$T = \frac{1}{k_B (3.413 \times 10^{19})} = 2120\ K$

Questions

1. Since $\ln(f_\nu / f_0)$ vs ν gave a straight line ($R^2 = .9991$), the system is in thermodynamic equilibrium with respect to vibrational energy.
2. $T_{vib} = 2120\ K$
3. The vibrational + translational temperatures need not equal because the time scale of energy transfer between vibrational states + between translational states are different (vibrational is slower).

Part b 18-9

$$\frac{\bar{C}_{V,vib}}{R} = \left(\frac{\Theta_{vib}}{T}\right)^2 \frac{e^{-\Theta_{vib}/T}}{\left(1 - e^{-\Theta_{vib}/T}\right)^2} \qquad \Theta_{vib,Cl_2} = 805\ K$$

See attached (#1 + #2 on graph)

#3 ~100% @ $2\Theta_{vib}$
~92% @ Θ_{vib}
~72% @ $\frac{1}{2}\Theta_{vib}$

18-17 $\quad f_J = (2J+1)\left(\frac{\Theta_{rot}}{T}\right) e^{-\Theta_{rot} J(J+1)/T} \qquad \Theta_{rot,NO} = 2.39\ K$

See plot attached

$J_{mp,300} \cong \left(\frac{300}{2\Theta_{rot}}\right)^{1/2} - \frac{1}{2} \cong 7 \qquad J_{mp,1000} \cong \left(\frac{1000}{2\Theta_{rot}}\right)^{1/2} - \frac{1}{2} \cong 14$

matches plot