1) McQuarrie 7-16

a) Prove that the most probably molecular speed is $v = \sqrt{\frac{2kT}{m}}$, the average speed is $< v >= \sqrt{\frac{8kT}{\pi m}}$, and the rms speed is $\sqrt{< v^2 >} = \sqrt{\frac{3kT}{m}}$.

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$E = \frac{1}{2}mv^2$$

rms speed:

$$< v^2 >= \sum_{i=x,y,z} < v_i^2 >= 3 < v_i^2 >$$

$$< v^2 >= \frac{3 \int v_i^2 exp(-E\beta)di}{\int exp(-E\beta)di}$$

Using integral tables,

$$\int exp(-ax^2)dx = \sqrt{\frac{\pi}{4a}}$$

$$\int x^2 exp(-ax^2)dx = \frac{1}{4a}\sqrt{\frac{\pi}{a}}$$

let $a = \frac{1}{2}m\beta$

$$< v^2 >= \frac{3\sqrt{4}}{4a}$$

$$< v^2 >= \frac{3}{m\beta} = \frac{3kT}{m}$$

$$\sqrt{< v^2 >} = \sqrt{\frac{3kT}{m}}$$

average speed:

$$< v >=< \sqrt{v_x^2 + v_y^2 + v_z^2} >$$

$$< v >= \frac{\iiint \sqrt{v_x^2 + v_y^2 + v_z^2} exp(-E\beta)dv_x dv_y dv_z}{\iiint exp(-E\beta)dv_x dv_y dv_z}$$

To simplify the integrals, convert the Boltzmann distribution, p, to spherical polar and normalize the probability function.

$$p(v) = \frac{4\pi m^{3/2}}{(2\pi kT)^{3/2}} v^2 exp(-E\beta)$$

$$< v >= \int vp(v)dv = \int \frac{4\pi m^{3/2}}{(2\pi kT)^{3/2}} v^3 exp(-E\beta)dv$$

$$\int x^3 exp(-ax^2)dx = \frac{1}{2a^2}$$

$$< v >= \frac{16\pi m^{3/2}}{2(m\beta)^2(2\pi kT)^{3/2}} = \frac{8\pi(kT)^2 m^{3/2}}{m^2(2\pi kT)^{3/2}}$$

$$< v >= \frac{8\pi\sqrt{kT}}{\sqrt{m}(2\pi)^{3/2}} = \frac{\sqrt{64kT}}{\sqrt{8m\pi}}$$

$$< v >= \sqrt{\frac{8kT}{m\pi}}$$

most probable speed:

$$\frac{dp(v)}{dv} = 0$$

$$\frac{dp(v)}{dv} = \frac{8\pi m^{3/2}}{(2\pi kT)^{3/2}} vexp(-E\beta) - \frac{4m\pi m^{3/2}}{kT(2\pi kT)^{3/2}} v^3 exp(-E\beta)$$

$$\frac{dp(v)}{dv} = (\frac{8\pi m^{3/2}}{(2\pi kT)^{3/2}} v - \frac{4m\pi m^{3/2}}{kT(2\pi kT)^{3/2}} v^3) exp(-E\beta) = 0$$

$$\frac{dp(v)}{dv} = \frac{8\pi m^{3/2}}{(2\pi kT)^{3/2}} v - \frac{4m\pi m^{3/2}}{kT(2\pi kT)^{3/2}} v^3 = 0$$

$$\frac{8\pi m^{3/2}}{(2\pi kT)^{3/2}} v = \frac{4m\pi m^{3/2}}{kT(2\pi kT)^{3/2}} v^3$$

$$8\pi = \frac{4m\pi}{kT} v^2$$

$$v^2 = \frac{8\pi kT}{4m\pi} = \frac{2kT}{m}$$

$$v = \sqrt{\frac{2kT}{m}}$$

b) Evaluate these quantities for H_2 and N_2

H_2:

$$< v >= 1.57x10^3 m/s$$

$$v = 1.92x10^3 m/s$$

$$\sqrt{< v^2 >} = 1.77x10^3 m/s$$

N_2:

$$< v >= 4.21x10^2 m/s$$

$$v = 5.15x10^2 m/s$$

$$\sqrt{< v^2 >} = 4.75x10^2 m/s$$

2) What are the vibrational and rotational contributions to C_v for ND_3?

$$Q = q^N$$

$$C_v = \frac{dU}{dT}$$

$$U = kT^2 \frac{dln(Q)}{dT} = NkT^2 \frac{dln(q)}{dT}$$

From equipartition of the rotational levels (or by taking the derivatives of the partition function), each degree for freedom gives $U_i = \frac{NkT}{2}$

$$U = \sum_i U_i = \frac{3NkT}{2}$$

$$C_v = \frac{3Nk}{2}$$

$$C_v = 12.47 J/moleK$$

For each vibration in ND_3,

$$C_v = Nk\frac{\Theta_v^2}{T^2}\frac{exp(\Theta_v/T)}{(exp(\Theta_v/T)-1)^2}$$

$$\Theta_v = \frac{hc\omega}{k}$$

From NIST,

$$\omega_1 = 2420.1cm^{-1}$$

$$\omega_2 = 2420.6cm^{-1}$$

$$\omega_3 = 745.7cm^{-1}$$

$$\omega_4 = 749.4cm^{-1}$$

$$\omega_5 = 2564cm^{-1}$$

$$\omega_6 = 1191cm^{-1}$$

$$C_v = 7.10J/moleK$$

Total for vibrations and rotations:

$$C_v = 19.58J/moleK$$

3) McQuarrie 9-10

Calculate K_p for CO_2 <=> $CO + \frac{1}{2}O_2$ at 3000K. The experimental value is $0.378\sqrt{atm}$

$$K_p = \frac{q'_{CO}\sqrt{q'_{O2}}}{q'_{CO2}}$$

$$q' = \frac{q}{V} = q'' exp(D_0\beta)$$

$$q = \frac{(2\pi mkT)^{3/2}}{h^3}V\frac{T}{\sigma\Theta_r}g_0 exp(D_0\beta)\prod^{3N-5}(1-exp(-\Theta_v\beta))^{-1}$$

From Atkins, O_2:

$$m = 5.314x10^{-26}kg$$

$$\sigma = 2$$

$$\Theta_r = 2.08K$$

$$\Theta_v = 2274K$$

$$D_0 = 118.0kcal/mole$$

$$g_0 = 3$$

CO:

$$m = 4.651x10^{-26}kg$$

$$\sigma = 1$$

$$\Theta_r = 2.78K$$

$$\Theta_v = 3122K$$

$$D_0 = 255.8kcal/mole$$

$$g_0 = 1$$

CO_2:

$$m = 7.308x10^{-26}kg$$

$$\sigma = 2$$

$$\Theta_r = 0.561K$$

$$\Theta_v = 1997, 3380, 960, 960K$$

$$D_0 = 381.5kcal/mole$$

$$g_0 = 1$$

The values of the partition functions without including $exp(D_0\beta)$, q'',

$$q''_{CO2} = 3.141x10^{38}$$

$$q''_{O2} = 1.596x10^{37}$$

$$q''_{CO} = 4.747x10^{36}$$

$$K_p = \frac{(4.747x10^{36})\sqrt{1.596x10^{37}}}{3.141x10^{38}} exp((118/2+255.8-381.5)*1000/(3000*1.9858775)) \frac{\sqrt{atm}}{\sqrt{101325Pa}}$$

$$K_p = 0.327\sqrt{atm}$$

4) McQuarrie 10-7

The density of Na is 0.95 g/cm^3 at room temperature. Assuming there is one conduction electron per atom, calculate the Fermi energy and Fermi temperature.

$$E_f = \frac{h^2}{2m_e}\frac{3^{2/3}}{(8\pi)^{2/3}}\frac{N^{2/3}}{V^{2/3}}$$

$$T_f = E_f/k$$

$$E_f = (2.4098x10^{-37})(0.242)\rho^{2/3}$$

$$\rho = \frac{0.95g/cm^3}{22.98976928g/mole}\frac{6.022x10^{23}e^-}{mole}\frac{100^3cm^3}{m^3} = 8.5235x10^{18}e^-/m^3$$

$$E_f = 4.9796x10^{-19}J = 3.108eV$$

$$T_f = 36066.8K$$