1. (10 pts) Calculate the equilibrium constant for the following reaction at 300 K.

$H_2 + D_2$ <==> 2HD

(For molecular data of H_2 and D_2, refer to Table 16.2, P.C23 in Atkins. You can assume that the bond length and the force constant of HD are the averages of those in H_2 and D_2. However, you should then calculate B and ν for HD). You have to determine the value of ΔE_o from the ZPEs of these three species.

$$H_2 + D_2 \rightleftharpoons 2HD \quad @ \ 300\,^\circ K.$$

$$K_p(T) = \frac{(q^t q^r q^v q^e)^2_{HD}}{(q^t q^r q^v q^e)_{H_2}(q^t q^r q^v q^e)_{D_2}} e^{-\Delta E_0/RT}$$

Since there are equal #s of molecules in the reactants and products, it is more convenient to calculate the ratios of each individual types of q.

Translational: $q^t = 2.561\times10^{-2}\, T^{5/2} M^{3/2}$

$$\text{ratio of } q^t = \frac{(q^t)^2_{HD}}{(q^t)_{D_2}(q^t)_{H_2}} = \frac{(M_{HD}^{3/2})^2}{M_{H_2}^{3/2} M_{D_2}^{3/2}} = \frac{(3)^3}{(2)^{3/2}(4)^{3/2}} = 1.19$$

Rotational $$q^r = \frac{8\pi^2 \mu r^2 kT}{\sigma h} = \frac{8\pi^2 I kT}{\sigma h}$$

$\sigma(H_2) = \sigma(D_2) = 2 \qquad \sigma(HD) = 1$

$$\text{ratio of } q^r = \frac{(I/\sigma)^2_{HD}}{(I/\sigma)_{H_2}(I/\sigma)_{D_2}} = 3.56$$

$I_{H_2} = 4.56\times10^{-48}$ kg m^2

$I_{D_2} = 9.13\times10^{-48}$ kg m^2

$I_{HD} = 6.09\times10^{-48}$ kg m^2

Vibrational $q^V = (1 - e^{-hc\bar{\nu}/kT})^{-1}$

$\bar{\nu}(H_2) = 4400.4\ cm^{-1}$; $\bar{\nu}(D_2) = 3118.4\ cm^{-1}$

$k(HD) = \frac{1}{2}(574.9 + 577.0) = 576\ N\ m^{-1}$

$\bar{\nu}(HD) = 3828.6\ cm^{-1}$

$$\text{ratio of } q^V = \frac{[1 - e^{-hc(3828.6)/kT}]^{-2}}{[1 - e^{-hc(4400.4)/kT}][1 - e^{-hc(3118.4)/kT}]}$$

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Electronic $g_0 = 1$ for all species $\Rightarrow q^e = 1$ for all species

$$\Delta E_0 = \frac{N_A}{2} hc [2 \times 3828.6 - 4400.4 - 3118.4]$$

$= 8.28 \times 10^2\ J\ mol^{-1}$

$$K_p(T) = \left(\frac{q_{HD}^2}{q_{H_2} q_{D_2}}\right)^{trans} (\quad)^{rot} (\quad)^{vib} (\quad)^{elec} e^{-\Delta E_0/RT}$$

$= (1.19)(3.56)(1)(1)\, e^{-8.28 \times 10^2 / 8.314 \times 300}$

$= 3.04$.