Homework 3 key

1.

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

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

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

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

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

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

2.

$$P_j = \frac{e^{-\beta \varepsilon_{vib,j}}}{q_{vib}}$$

$$q_{vib} = \frac{e^{-h\nu/2k_BT}}{1-e^{-h\nu/k_BT}} = \frac{e^{-\frac{\beta h\nu}{2}}}{1-e^{-\beta h\nu}}$$

$$\varepsilon_{vib} = (v+\tfrac{1}{2})h\nu \qquad \beta = \frac{1}{k_BT}$$

$$P_j = \frac{e^{-\beta(v+\frac{1}{2})h\nu}}{\dfrac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}} = \frac{e^{-\beta v h\nu}\,\cancel{e^{-\beta h\nu/2}}}{\cancel{e^{-\beta h\nu/2}}}\cdot\left(1-e^{-\beta h\nu}\right)$$

recall: $e^{a+b} = e^a e^b$

$$P_j = e^{-\beta v h\nu}\left(1-e^{-\beta h\nu}\right)$$
$$= e^{-\frac{v h\nu}{k_BT}}\left(1-e^{-h\nu/k_BT}\right)$$

$\tilde{\nu} = 2886\ cm^{-1}$ or $\nu = 8.65\times10^{13}\ 1/s$

$$h\nu/k_B = 4154\,K = \frac{(6.626\times10^{-34}\ J\cdot s)(8.65\times10^{13}\ 1/s)}{1.38\times10^{-23}\ J/K}$$

$$P_0 = e^0\left(1-e^{-4154/300}\right) = 0.999999031$$
$$P_1 = e^{1(4154/300)}\left(1-e^{-4154/300}\right) = 9.69\times10^{-7}$$
$$P_2 = e^{2(4154/300)}\left(1-e^{-4154/300}\right) = 9.39\times10^{-13}$$

majority of HCl molecules are in ground state at room temperature

3. use partition function for levels. $P_2 = 0.02$

$$P_2 = \frac{g_2 e^{-\varepsilon_2/k_B T}}{g_1 e^0 + g_2 e^{-\varepsilon_2/k_B T}}$$

$$0.02 = \frac{2e^{-7603.2/0.695T}}{4 + 2e^{-7603.2/0.695T}}$$

$$0.02\left(4 + 2e^{-7603.2/0.695T}\right) = 2e^{-7603.2/0.695T}$$

$$0.08 + 0.04e^{-7603.2/0.695T} = 2e^{-7603.2/0.695T}$$

$$0.08 = 1.96e^{-7603.2/0.695T}$$

$$\frac{0.08}{1.96} = e^{-7603.2/0.695T}$$

$$\ln\left(\frac{0.08}{1.96}\right) = -7603.2/0.695T$$

$$T = 3420\ K$$

much higher temperature than typically reached in lab or average situations