

## Homework 3 key

1.

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

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

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

$$\begin{aligned} \langle E \rangle &= k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} = k_B T^2 \left( \frac{3N}{2T} - \frac{aN^2}{Vk_B T^2} \right) \\ &= \frac{3}{2} N k_B T - \frac{aN^2}{V} \end{aligned}$$

$$C_V = \left( \frac{\partial \langle E \rangle}{\partial T} \right)_{N,V} = \frac{3}{2} N k_B \quad \text{Same as } \overset{\text{monatomic}}{\text{ideal gas}}$$

2.

$$P_j = \frac{e^{-\beta \epsilon_{vib,j}}}{q_{vib}} \quad q_{vib} = \frac{e^{-h\nu/2k_B T}}{1 - e^{-h\nu/k_B T}} = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

$$\epsilon_{vib} = (v + 1/2)h\nu \quad \beta = \frac{1}{k_B T}$$

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

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

$$P_j = e^{-\beta v h\nu} (1 - e^{-\beta h\nu})$$

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

$$\tilde{\nu} = 2886 \text{ cm}^{-1} \quad \text{or} \quad \nu = 8.65 \times 10^{13} \text{ 1/s}$$

$$\frac{h\nu}{k_B} = 4154 \text{ K} = \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s}) (8.65 \times 10^{13} \text{ 1/s})}{1.38 \times 10^{-23} \text{ J/K}}$$

$$P_0 = e^0 (1 - e^{-4154/300}) = 0.999999031$$

$$P_1 = e^{-(4154/300)} (1 - e^{-4154/300}) = 9.69 \times 10^{-7}$$

$$P_2 = e^{-2(4154/300)} (1 - e^{-4154/300}) = 9.39 \times 10^{-13}$$

majority of HCl molecules are in ground state at room temperature

3.

use partition function for levels.  $P_2 = 0.02$ 

$$P_2 = \frac{g_2 e^{-\epsilon_2/k_B T}}{g_1 e^0 + g_2 e^{-\epsilon_2/k_B T}}$$

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

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

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

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

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

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

$$T = 3420 \text{ K}$$

much higher temperature  
than typically reached  
in lab or average situations