Lecture 17 2/25/13

## A. The Molecular Partition Function for Larger Molecules

- To construct a partition function for molecules, the partition function for translational, rotational, vibrational, and electron motions are combined. For a diatomic molecule this is:

$$q = q_{trans}q_{rot}q_{vib}q_{elec}$$

$$= \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} \times \frac{T}{\sigma\theta_{rot}} \times \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}} \times g_1 e^{D_e/RT} \tag{17.1}$$

- Equation 17.1 is only valid for diatomic molecules. The presence of more bonds complicated the rotational and vibrational partition functions. The simplest polyatomic molecule is carbon dioxide CO_2, which is linear but has two bonds. With two bonds CO_2 has four vibrational modes as shown in Figure 17.1:

Figure 17.1: The vibrational modes of CO_2. a) symmetric bond stretch; b) asymmetric bond stretch; c) two bending modes, one in the page and one out of the page.
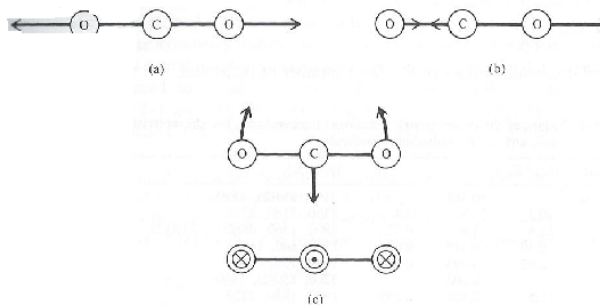
- Each bond vibration mode has a different frequency so each mode has its own vibrational temperature $\theta_{vib,j} = \dfrac{h\nu_j}{k_B}$. For CO2 the vibrational partition function is now

$$q_{vib} = \frac{e^{-\theta_{vib,1}/2T}}{1-e^{-\theta_{vib,1}/T}} \times \frac{e^{-\theta_{vib,2}/2T}}{1-e^{-\theta_{vib,2}/T}} \times \frac{e^{-\theta_{vib,3}/2T}}{1-e^{-\theta_{vib,3}/T}} \times \frac{e^{-\theta_{vib,4}/2T}}{1-e^{-\theta_{vib,4}/T}} = \prod_{j=1}^{4} \frac{e^{-\theta_{vib,j}/2T}}{1-e^{-\theta_{vib,j}/T}} \tag{17.2}$$

- The molecular partition function for CO_2 is now:

$$q = \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} \times \frac{T}{\sigma\theta_{rot}} \times \prod_{j=1}^{4} \frac{e^{-\theta_{vib,j}/2T}}{1-e^{-\theta_{vib,j}/T}} \times g_1 e^{D_e/RT} \tag{17.3}$$

- And the internal energy of CO_2 is from equation 17.3:

$$U = N_A k_B T^2 \frac{\partial \ln q}{\partial T} = \frac{5RT}{2} + \sum_{j=1}^{4}\left[\frac{R\theta_{vib,j}}{2} + \frac{R\theta_{vib,j}}{e^{\theta_{vib,j}/T}-1}\right] - N_A D_e \tag{17.4}$$

- The first term is the total energy from translations and rotations, both in the classical limit.. The summation in the second term is over the four vibrational

modes. The last term is the contribution to the internal energy from electronic motions.

- From equation 17.4 the heat capacity is:

$$C_V = \frac{5R}{2} + \sum_{j=1}^{4} \left(\frac{\theta_{vib,j}}{T} \right)^2 \frac{e^{-\theta_{vib,j}/T}}{\left(1 - e^{-\theta_{vib,j}/T} \right)^2} \tag{17.5}$$

- For linear polyatomic molecules we need the moment of inertia $I = \mu R^2$, the partition function is $q_{rot} = \dfrac{T}{\sigma \theta_{rot}}$ and $U_{rot} = Nk_B T$ or just RT for one mole of rigid rotors. For a non-linear molecule three moments of inertia are required to describe the rotation of the molecule. The three moments of inertia identify the center of mass around which the molecule rotates and are designated I_A, I_B, and I_C. Therefore a non-linear molecule has three rotational temperatures designated θ_A, θ_B, and θ_C. The rotational partition function for a non-linear molecule is

$$q_{rot} = \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\theta_A \theta_B \theta_C} \right)^{1/2} \tag{17.6}$$

- Note there are three degrees of rotational freedom for a non-linear molecule and according to equation 17.6 the internal energy and heat capacity associated with this rotation are

$$U_{rot} = \frac{3RT}{2}; C_{V,rot} = \frac{3R}{2} \tag{17.7}$$

B. Statistical Description of Equilibria

- Here we learn how to use statistical principles to calculate equilibrium constants for gas phase chemical reactions. Consider a gas phase reaction of the following general form:

$$v_A A + v_B B \rightleftharpoons v_C C + v_D D \tag{17.8}$$

- Now the condition for equilibrium is

$$v_A \mu_A + v_B \mu_B = v_C \mu_C + v_D \mu_D \tag{17.9}$$

where the chemical potentials are $\mu = \left(\dfrac{\partial A}{\partial N} \right)_{V,T}$. We have already shown that using the statistical definition of the Helmholtz energy $A = -k_B T \ln Q$ and the definition of the partition function for a gas $Q = \dfrac{q^N}{N!}$ the statistical definition of the chemical potential is:

$$\mu = -k_B T \ln \left(\frac{q}{N} \right) \tag{17.10}$$

- Now putting the statistical expression for the chemical potential from equation 17.10 into equation 17.9 we get

$$v_A \ln\left(\frac{q_A}{N_A}\right) + v_B \ln\left(\frac{q_B}{N_B}\right) = v_C\left(\frac{q_C}{N_C}\right) + v_D\left(\frac{q_D}{N_D}\right) \tag{17.11}$$

- We can remove the logarithms, rearrange equation 17.11 and divide all terms by the volume V to get:

$$K_C = \frac{\left(\frac{N_D}{V}\right)^{v_D}\left(\frac{N_C}{V}\right)^{v_C}}{\left(\frac{N_A}{V}\right)^{v_A}\left(\frac{N_B}{V}\right)^{v_B}} = \frac{[D]^{v_D}[C]^{v_D}}{[A]^{v_A}[B]^{v_B}} = \frac{\left(\frac{q_D}{V}\right)^{v_D}\left(\frac{q_C}{V}\right)^{v_C}}{\left(\frac{q_A}{V}\right)^{v_A}\left(\frac{q_B}{V}\right)^{v_B}} \tag{17.12}$$

- Equation 17.12 is the statistical expression for the equilibrium constant. Using the ideal gas law we can expression the equilibrium constant in terms of pressures

$$K_C = \frac{\left(\frac{N_D}{V}\right)^{v_D}\left(\frac{N_C}{V}\right)^{v_C}}{\left(\frac{N_A}{V}\right)^{v_A}\left(\frac{N_B}{V}\right)^{v_B}} = \frac{\left(\frac{P_D}{k_B T}\right)^{v_D}\left(\frac{P_C}{k_B T}\right)^{v_C}}{\left(\frac{P_A}{k_B T}\right)^{v_A}\left(\frac{P_B}{k_B T}\right)^{v_B}} = \frac{\left(\frac{q_D}{V}\right)^{v_D}\left(\frac{q_C}{V}\right)^{v_C}}{\left(\frac{q_A}{V}\right)^{v_A}\left(\frac{q_B}{V}\right)^{v_B}} \tag{17.13}$$

- We now define the equilibrium constant KP as the ratio of equilibrium pressures:

$$K_C = \frac{P_D^{v_D} P_C^{v_C}}{P_A^{v_A} P_B^{v_B}}(k_B T)^{v_A + v_B - v_C - v_D} = K_P (k_B T)^{v_A + v_B - v_C - v_D} = \frac{\left(\frac{q_D}{V}\right)^{v_D}\left(\frac{q_C}{V}\right)^{v_C}}{\left(\frac{q_A}{V}\right)^{v_A}\left(\frac{q_B}{V}\right)^{v_B}} \tag{17.14}$$

- We can finally write out the equilibrium constant in terms of pressure

$$K_P = \frac{\left(\frac{q_D}{V}\right)^{v_D}\left(\frac{q_C}{V}\right)^{v_C}}{\left(\frac{q_A}{V}\right)^{v_A}\left(\frac{q_B}{V}\right)^{v_B}}(k_B T)^{v_C + v_D - v_A - v_B} \tag{17.15}$$

Example: For the equilibrium $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ calculate the equilibrium constant KP at T=1000K. Calculate ΔG^o and determine if the formation of water is thermodynamically favorable at this temperature. Assume V=1m³. The following data are available:

- For H₂: $\theta_{vib} = 6215K$, $\theta_{rot} = 85.3K$, $D_e = 457.6 kJmol^{-1}$, $g_1 = 1$.

- For O₂: $\theta_{vib} = 2256K$, $\theta_{rot} = 2.07K$, $D_e = 503 kJmol^{-1}$, $g_1 = 3$.

- For H₂O there are three vibrational motions shown to the right. The three vibrational temperatures are: $\theta_{vib,1} = 5360K$, $\theta_{vib,2} = 5160K$, $\theta_{vib,3} = 2290K$.

Because water is non-linear the three rotational temperatures are: $\theta_{rot,1} = 40.1K$, $\theta_{vib,2} = 20.9K$, $\theta_{vib,3} = 13.4K$

For water also: D_e=940kJmol⁻¹, g_1=1, and σ=2.
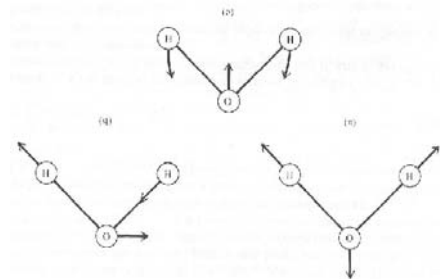
Solution: $K_P = \dfrac{1}{(k_B T)^{1/2}} \dfrac{(q_{H_2O}/V)}{(q_{H_2}/V)(q_{O_2}/V)^{1/2}}$

$q_{H_2} = q_{trans}q_{vib}q_{rot}q_{elec} = \dfrac{V}{h^3}(2\pi k_B T)^{3/2}\left(\dfrac{M}{N_A}\right)^{3/2}\dfrac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}}\dfrac{T}{\sigma\theta_{rot}}g_1 e^{D_e^{H_2}/RT}$

$\therefore q_{H_2} = \dfrac{(1m^3)(6.28\times1.38\times10^{-20}J)^{3/2}}{(6.62\times10^{-34}Js)^3}\left(\dfrac{0.002kgmol^{-1}}{6.02\times10^{23}mol^{-1}}\right)^{3/2}\dfrac{e^{-3.11}}{1-e^{-6.215}}\dfrac{1000K}{(2)(85.3K)}e^{D_e^{H_2}/RT}$

$= \dfrac{2.55\times10^{-29}J^{-3/2}m^3 s^{-3}}{2.90\times10^{-100}}(33.2\times10^{-28}kg)^{3/2}(0.045)(5.86) = 4.44\times10^{30}e^{D_e^{H_2}/RT}$

$q_{O_2} = q_{trans}q_{vib}q_{rot}q_{elec} = \dfrac{V}{h^3}(2\pi k_B T)^{3/2}\left(\dfrac{M}{N_A}\right)^{3/2}\dfrac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}}\dfrac{T}{\sigma\theta_{rot}}g_1 e^{D_e^{O_2}/RT}$

$\therefore q_{O_2} = \dfrac{(1m^3)(6.28\times1.38\times10^{-20}J)^{3/2}}{(6.62\times10^{-34}Js)^3}\left(\dfrac{0.032kgmol^{-1}}{6.02\times10^{23}mol^{-1}}\right)^{3/2}\dfrac{e^{-1.128}}{1-e^{-2.256}}\dfrac{1000K}{(2)(2.07K)}(3)e^{D_e^{O_2}/RT}$

$= \dfrac{2.55\times10^{-29}J^{-3/2}m^3 s^{-3}}{2.90\times10^{-100}}(5.31\times10^{-26}kg)^{3/2}(0.362)(242)(3)e^{D_e^{O_2}/RT} = 8.20\times10^{35}e^{D_e^{O_2}/RT}$

$q_{H_2O} = q_{trans}q_{vib}q_{rot}q_{elec} = \dfrac{V}{h^3}(2\pi k_B T)^{3/2}\left(\dfrac{M}{N_A}\right)^{3/2}\dfrac{e^{-\theta_{vib1}/2T}}{1-e^{-\theta_{vib1}/T}}\dfrac{e^{-\theta_{vib2}/2T}}{1-e^{-\theta_{vib2}/T}}\dfrac{e^{-\theta_{vib3}/2T}}{1-e^{-\theta_{vib3}/T}}\dfrac{\pi^{1/2}}{\sigma}\left(\dfrac{T^3}{\theta_{rot1}\theta_{rot2}\theta_{rot3}}\right)^{1/2}g_1 e^{D_e^{H_2O}/RT}$

$\therefore q_{H_2O} = \dfrac{(1m^3)(6.28\times1.38\times10^{-20}J)^{3/2}}{(6.62\times10^{-34}Js)^3}\left(\dfrac{0.018kgmol^{-1}}{6.02\times10^{23}mol^{-1}}\right)^{3/2}\dfrac{e^{-2.680}}{1-e^{-5.360}}\dfrac{e^{-2.580}}{1-e^{-5.160}}\dfrac{e^{-1.145}}{1-e^{-2.290}}\times$

$\dfrac{(3.14)^{1/2}}{(2)}\left(\dfrac{10^9}{(40.1)(20.9)(13.4)}\right)^{1/2}e^{D_e^{H_2O}/RT}$

$= \dfrac{2.55\times10^{-29}J^{-3/2}m^3 s^{-3}}{2.90\times10^{-100}}(3.00\times10^{-26}kg)^{3/2}(0.069)(0.076)(0.354)(0.886)(2221)^{1/2}e^{D_e^{H_2O}/RT}$

$= 3.46\times10^{31}e^{D_e^{H_2O}/RT}$

$K_P = \dfrac{1}{(k_B T)^{1/2}}\dfrac{(q_{H_2O}/V)}{(q_{H_2}/V)(q_{O_2}/V)^{1/2}} = \left(\dfrac{1}{1.38\times10^{-20}J}\right)^{1/2}\dfrac{3.46\times10^{31}e^{D_e^{H_2O}/RT}m^{-3}}{(4.44\times10^{30}e^{D_e^{H_2}/RT}m^{-3})(82.0\times10^{34}e^{D_e^{O_2}/RT}m^{-3})^{1/2}}$

$(0.851\times10^{20}J^{-1})^{1/2}8.61\times10^{-2+31-30-17}m^{3/2}e^{(D_e^{H_2O}-D_e^{H_2}-D_e^{O_2}/2)/RT} = 7.94\times10^{-8}J^{-1/2}m^{3/2}e^{(940-458-252)/8.31}$

$= 7.94\times10^{-8}e^{27.7}Pa^{-1/2} = 8.51\times10^4 Pa^{-1/2}\left(\dfrac{1Pa}{9.88\times10^{-6}atm}\right)^{1/2} = 27.1 atm^{-1/2}$

- This problem is far more challenging than anything you will encounter in regular course work. However, given the right data, obtaining an equilibrium constant is simply a two stage process. First, you calculate the relevant partition function for each molecule. Then you plug these values into the equilibrium constant equation.
- Be careful not to let the big numbers scare you into thinking you have made a mistake. Partition functions for molecules are large numbers due to the translational degrees of freedom.
- Be careful with the dissociation energy exponent. If you use values of D_e in kJ per mole be sure to divide by RT not k_BT. And convert the kJ to Joules because R uses Joules.
- The equilibrium constant has units because I did not divide by a standard state pressure. If I had done that the equilibrium constant would be unitless.