University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 21 2/6/15:
Example of Statistical Equilibrium Constants and Partition Functions for Larger Molecules;

A. Statistical Expression for Equilibrium Constants

- It is also possible to calculate the equilibrium constant for reactions between atoms and molecules and to understand why equilibria favor products or reactants based on the partition function properties. Recall for the equilibrium:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \tag{21.1}$$

The equilibrium constant is in terms of partition functions

$$K_P = \frac{q_C^{\circ,\nu_C} q_D^{\circ,\nu_D}}{q_A^{\circ,\nu_A} q_B^{\circ,\nu_B}} N^{\nu_A+\nu_B-\nu_C-\nu_D} = \frac{q_C^{\circ,\nu_C} q_D^{\circ,\nu_D}}{q_A^{\circ,\nu_A} q_B^{\circ,\nu_B}} N^{-\Delta\nu} \tag{21.2}$$

$$\Delta\nu = \nu_C + \nu_D - \nu_A - \nu_B \tag{21.3}$$

- For dissociation of $H_2 \rightleftarrows H + H$ $\Delta\nu=+1$ The equilibrium constant K for the reaction is

$$K = \frac{q_H^2}{q_{H_2}} N^{-1} \tag{21.4}$$

- For a hydrogen atom:

$$q_H = q_{trans} q_{elec} = \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2}\left(g_1 + g_2 e^{-\Delta E_{2,1}/k_B T} + \dots\right) \approx \frac{V}{\Lambda^3} g_1 \tag{21.5}$$

...and for hydrogen atoms $g_1=2$.

$$\Lambda^{-3} = \frac{\left(2\pi m_H k_B T\right)^{3/2}}{h^3} = \frac{\left((6.28)\left(1.66\times10^{-27} kg\right)\left(1.38\times10^{-20} J\right)\right)^{3/2}}{\left(6.626\times10^{-34} Js\right)^3}$$

$$= \frac{1.73\times10^{-69}}{2.91\times10^{-100}} m^{-3} = 0.595\times10^{31} m^{-3}$$

$$\therefore q_H = g_1 \frac{V}{\Lambda^3} = 2V\left(0.595\times10^{31} m^{-3}\right) = 1.19\times10^{31}\left(\frac{V}{m^3}\right)$$

- For the partition function of H_2 from Table 20.1:

$\sigma = 2, \quad \theta_{vib} = 6215K, \theta_{rot} = 85.3K, D_e = 457.6kJmol^{-1}, g_1 = 1$

$$
\begin{aligned}
q_{H_2} &= q_{trans}q_{vib}q_{rot}q_{elec} = \frac{V}{h^3}\left(2\pi m_{H_2}k_BT\right)^{3/2} \times \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}} \times \frac{T}{\sigma\theta_{rot}} \times g_{1,H_2}e^{D_e/RT} \\
&= \frac{2^{3/2}V}{h^3}\left(2\pi m_H k_BT\right)^{3/2} \times \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}} \times \frac{T}{\sigma\theta_{rot}} \times g_{1,H_2}e^{D_e/RT} \\
&= \left(2^{3/2}V\right)\left(0.595\times10^{31}m^{-3}\right) \times \frac{e^{-6215/2000}}{1-e^{-6215/1000}} \frac{\left(1000K\right)e^{457600/8310}}{\left(2\right)\left(85.3K\right)} \qquad (21.6) \\
&= \left(\frac{V}{m^3}\right)\left(9.85\times10^{31}m^{-3}\right) \times \frac{e^{-3.11}}{1-e^{-6.215}} \times e^{55.1} \approx \left(\frac{V}{m^3}\right)\left(9.85\times10^{31}m^{-3}\right)e^{52} \\
&= 3.77\times10^{54}\left(\frac{V}{m^3}\right)
\end{aligned}
$$

- Now put the partition functions for H and H_2 into equation 21.2:

$$
K = \frac{q_H^2}{q_{H_2}}N^{-1} = \frac{\left(1.19\times10^{31}\right)^2}{3.77\times10^{54}}\left(\frac{Nm^3}{V}\right)^{-1} = 3.85\times10^{7}\left(\frac{Nm^3}{V}\right)^{-1} \qquad (21.7)
$$

- Note we can finish the calculation depending on what additional information we have. Assume ideal gas conditions and $N=nN_A$ so that $PV=Nk_BT$. Assume P=101325 Pa. Then

$$
K = 3.85\times10^{7} \times \frac{V}{N} = 3.85\times10^{7} \times \frac{k_BT}{P} = \left(3.85\times10^{7}\right) \times \frac{1.38\times10^{-20}}{101325} = 5.26\times10^{-18} \qquad (21.8)
$$

Hydrogen does not dissociate appreciably at T=1000K.

- Now we can also calculate the standard free energy for the dissociation of H_2:

$$
\begin{aligned}
&\Delta G^0 = -RT\ln K = -\left(8.31JK^{-1}mol^{-1}\right)\left(1000K\right)\ln\left(5.26\times10^{-18}\right) \\
&= \left(-8310Jmol^{-1}\right)\left[\ln 5.26 - 18\ln 10\right] = \left(-8310Jmol^{-1}\right)\left[1.66-41.5\right] = 331kJmol^{-1} \qquad (21.9)
\end{aligned}
$$

A. The Molecular Partition Function for Larger Molecules

- The partition function expression :

$$
\begin{aligned}
q &= q_{trans}q_{rot}q_{vib}q_{elec} \\
&= \frac{V}{h^3}\left(2\pi mk_BT\right)^{3/2} \times \frac{T}{\sigma\theta_{rot}} \times \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}} \times g_1e^{D_e/RT}
\end{aligned}
\qquad (21.10)
$$

is only valid for diatomic molecules.

- The presence of more bonds complicates the rotational and vibrational partition functions. The simplest polyatomic molecule is carbon dioxide CO_2, which is linear but has two bonds.

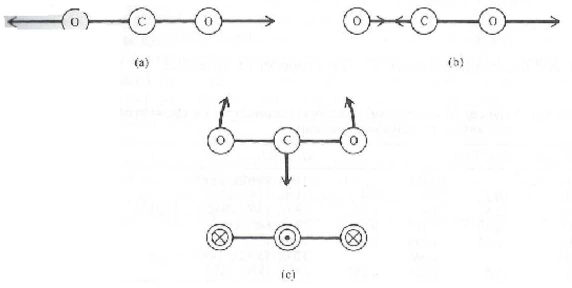


Figure 21.1: The vibrational modes of CO_2. a) symmetric bond stretch; b) asymmetric bond stretch; c) two bending modes, one in the page and one out of the page.

- For linear polyatomic molecules with N atoms the number of vibrational modes is 3N-5. With three atoms CO_2 has four vibrational modes (i.e. 3N-5=9-5=4)for its two bonds as shown in Figure 21.1 Each bond vibration mode has a different frequency so each mode has its own vibrational temperature $\theta_{vib,j} = \frac{h\nu_j}{k_B}$. For CO_2 the vibrational partition function is now

$$q_{vib} = \frac{e^{-\theta_{vib,1}/2T}}{1-e^{-\theta_{vib,1}/T}} \times \frac{e^{-\theta_{vib,2}/2T}}{1-e^{-\theta_{vib,2}/T}} \times \frac{e^{-\theta_{vib,3}/2T}}{1-e^{-\theta_{vib,3}/T}} \times \frac{e^{-\theta_{vib,4}/2T}}{1-e^{-\theta_{vib,4}/T}} = \prod_{j=1}^{4} \frac{e^{-\theta_{vib,j}/2T}}{1-e^{-\theta_{vib,j}/T}} \qquad (21.11)$$

- The molecular partition function for CO_2 is now:

$$q = \frac{V}{h^3}\left(2\pi m k_B T\right)^{3/2} \times \frac{T}{\sigma\theta_{rot}} \times \prod_{j=1}^{4} \frac{e^{-\theta_{vib,j}/2T}}{1-e^{-\theta_{vib,j}/T}} \times g_1 e^{D_e/RT} \qquad (21.12)$$

- And the internal energy of CO_2 is from equation 21.12:

$$U = N_A k_B T^2 \frac{\partial \ln q}{\partial T} = \frac{5RT}{2} + \sum_{j=1}^{4}\left[\frac{R\theta_{vib,j}}{2} + \frac{R\theta_{vib,j}}{e^{\theta_{vib,j}/T}-1}\right] - D_e \qquad (21.13)$$

- 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 21.13 the heat capacity is:

$$C_V = \frac{5R}{2} + R\sum_{j=1}^{4}\left(\frac{\theta_{vib,j}}{T}\right)^2 \frac{e^{-\theta_{vib,j}/T}}{\left(1-e^{-\theta_{vib,j}/T}\right)^2} \qquad (21.14)$$

  - For linear polyatomic molecules we need the moment of inertia $I = \mu R^2$, the partition function is $q_{rot} = \frac{T}{\sigma\theta_{rot}}$ and $U_{rot} = Nk_BT$ 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

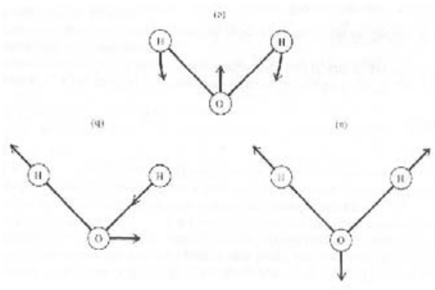
$$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\theta_A\theta_B\theta_C}\right)^{1/2} \qquad (21.15)$$

  - Note there are three degrees of rotational freedom for a non-linear molecule and according to equation 21.15 the internal energy and heat capacity associated with this rotation are

$$U_{rot} = \frac{3RT}{2}; C_{V,rot} = \frac{3R}{2} \qquad (21.16)$$

Example of Non-linear Molecule: Calculate the molecular partition function for H_2O

- For a non-linear molecule with N atoms the number of vibrational modes is 3N-6.
- For H_2O N=3, so 3N-6=3. 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:

$$q_{H_2O} = q_{trans}q_{vib}q_{rot}q_{elec} = \frac{V}{h^3}\left(2\pi k_B T\right)^{3/2}\left(\frac{M}{N_A}\right)^{3/2} \frac{e^{-\theta_{vib1}/2T}}{1-e^{-\theta_{vib1}/T}} \frac{e^{-\theta_{vib2}/2T}}{1-e^{-\theta_{vib2}/T}} \frac{e^{-\theta_{vib3}/2T}}{1-e^{-\theta_{vib3}/T}} \times$$

$$\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\theta_{rot1}\theta_{rot2}\theta_{rot3}}\right)^{1/2} g_1 e^{D_e^{H2O}/RT}$$

$$\therefore q_{H_2O} = \frac{\left(1m^3\right)\left(6.28\times 1.38\times 10^{-20} J\right)^{3/2}}{\left(6.62\times 10^{-34} Js\right)^3}\left(\frac{0.018kgmol^{-1}}{6.02\times 10^{23} mol^{-1}}\right)^{3/2} \frac{e^{-2.680}}{1-e^{-5.360}} \frac{e^{-2.580}}{1-e^{-5.160}} \frac{e^{-1.145}}{1-e^{-2.290}} \times$$

$$\frac{\left(3.14\right)^{1/2}}{\left(2\right)}\left(\frac{10^9}{\left(40.1\right)\left(20.9\right)\left(13.4\right)}\right)^{1/2} e^{D_e^{H2O}/RT}$$

$$= \frac{2.55\times 10^{-29} J^{-3/2} m^3 s^{-3}}{2.90\times 10^{-100}}\left(3.00\times 10^{-26} kg\right)^{3/2}\left(0.069\right)\left(0.076\right)\left(0.354\right)\left(0.886\right)\left(2221\right)^{1/2} e^{D_e^{H2O}/RT}$$

$$= 3.46\times 10^{31} e^{D_e^{H2O}/RT}$$