University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Lecture 7. 1/21/15

A. Partition Function & Equilibrium

- In the last lecture we found that for a chemical reaction

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \tag{7.1}$$

the equilibrium criterion is

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D \tag{7.2}$$

- Substituting the statistical expression for the chemical potential

$$\mu_i = -k_B T \ln\left(\frac{q_i}{N}\right) \tag{7.3}$$

into equation 7.2 we obtain

$$\begin{aligned}\Delta\mu^\circ = -k_B T \ln K &= \nu_C \mu_C^\circ + \nu_D \mu_D^\circ - \nu_A \mu_A^\circ - \nu_B \mu_B^\circ \\ &= -k_B T\left(-\nu_A \ln\left(\frac{q_A^\circ}{N}\right) - \nu_B \ln\left(\frac{q_B^\circ}{N}\right) + \nu_C \ln\left(\frac{q_C^\circ}{N}\right) + \nu_D \ln\left(\frac{q_D^\circ}{N}\right)\right)\end{aligned} \tag{7.4}$$

- Note we use N in each denominator because we assume the chemical potential of each species is per mole and scale the number of moles with the stoichiometric coefficients. The equilibrium constant is:

$$\begin{aligned}K_P &= \frac{q_C^{\circ,\nu_C} q_D^{\circ,\nu_D}}{q_A^{\circ,\nu_A} q_B^{\circ,\nu_B}} N^{\nu_A+\nu_B-\nu_C-\nu_D} = \frac{q_C^{\circ,\nu_C} q_D^{\circ,\nu_D}}{q_A^{\circ,\nu_A} q_B^{\circ,\nu_B}} N^{-\Delta\nu} \\ \Delta\nu &= \nu_C + \nu_D - \nu_A - \nu_B\end{aligned} \tag{7.5}$$

B. Enthalpically Driven vs. Entropically Driven Reactions: Correspondence of Classical and Statistical Thermodynamics

- Let us consider the simplest possible equilibrium

$$A \rightleftarrows B \ldots K = \frac{q_B^\circ}{q_A^\circ} \tag{7.6}$$

- The equilibrium expressed in equation 7.6 could be the gas phase isomerization equilibrium between butane (A) and isobutene (B) or it could express the equilibrium between the structured form of a protein (A=N) and the unstructured or denatured form (B=D).
- As shown in Figure 7.1 let us represent the energies of A and B as energy ladders with different energy level spacings. For generality we also assume the ground state energies are different such that

$$\varepsilon_{B,0} = \varepsilon_{A,0} + \Delta\varepsilon \tag{7.7}$$

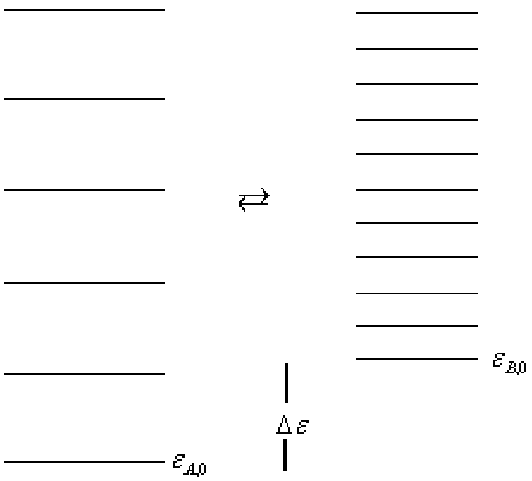

Figure 7.1: Two molecular systems with different energy spacings and different ground state energies in equilibrium

- We need to define the partition functions for A and B relative to a common reference. We chose this to be the A ground state so we use equation 7.7. Then the partition functions are:

$$q_A^\circ = \sum_j e^{-\varepsilon_{A,j}/k_BT} \quad and \quad q_B^\circ = \sum_j e^{-\left(\varepsilon_{B,j}+\Delta\varepsilon\right)/k_BT} = e^{-\Delta\varepsilon/k_BT}\sum_j e^{-\left(\varepsilon_{B,j}\right)/k_BT} \qquad (7.8)$$

- Note in equation 7.8 the energies $\varepsilon_{A,i}$ for i>0, are referenced to $\varepsilon_{A,0} = 0$.
- Also, in equation 7.8 the energies $\varepsilon_{B,i}$ for i>0 are referenced to $\varepsilon_{B,0} = 0$, The B referencing is OK IF the B molecule is viewed in isolation. But in an endothermic chemical reaction, we must take into account that $\varepsilon_{B,0} - \varepsilon_{A,0} = \Delta\varepsilon$ >0. Therefore, when partition functions are combined into the expression for K, all energies must be referenced to a common ground state. In this case we use $\varepsilon_{A,0} = 0$ as the reference state.
- The equilibrium constant in equation 7.6 is now:

$$K = \frac{q_B^\circ}{q_A^\circ} = e^{-\Delta\varepsilon/k_BT}\,\frac{\sum_j e^{-\varepsilon_{B,j}/k_BT}}{\sum_j e^{-\varepsilon_{A,j}/k_BT}} \qquad (7.9)$$

- At low T such that $\Delta\varepsilon \gg k_BT$, the term $e^{-\Delta\varepsilon/k_BT}$ <<1 and so K<<1. This means at low temperature, the A form is favored. This means that at low temperature molecules will congregate in the lowest energies available, which is in the A energy manifold.
- At high T such that $\Delta\varepsilon \ll k_BT$ the term $e^{-\Delta\varepsilon/k_BT}$ >>1 and so K>>1. This means at high temperature the B form is favored even though at low T the B form is not favored.
- In classical thermodynamics this result is obtained from the equation

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (7.10)$$

- At low T the $\frac{-\Delta H^\circ}{RT}$ dominates so $\ln K \approx \frac{-\Delta H^\circ}{RT}$.. Because $\Delta H^\circ > 0$ lnK is large and negative meaning K is very small. The endothermic conversion of A to B is disfavored and the A form dominates
- At high T $\ln K \approx \frac{\Delta S^\circ}{RT}$. In this case the equilibrium is dominated by entropic effects. If ΔS°>0 the B form will be favored at high T.
- In fact we have set up the problem so that ΔS°>0. Note the energy level spacing for the B form is smaller than for the A form. This means at thigh T where $\Delta\varepsilon \ll k_B T$ the partition function for the B form will be higher than the partition function for the A form.

- If the reaction were thermo-neutral such that $\Delta H^\circ \approx 0$ the equilibrium would be driven by entropy alone. This is the case in homework set 3 problem 3.