Lecture 7. 1/21/15

A. Partition Function & Equilibrium

- In the last lecture we found that for a chemical reaction
  \[ \nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \] (7.1)
  the equilibrium criterion is
  \[ \nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D \] (7.2)

- Substituting the statistical expression for the chemical potential
  \[ \mu_i = -k_B T \ln \left( \frac{q_i}{N} \right) \] (7.3)
  into equation 7.2 we obtain
  \[ \Delta \mu = -k_B T \ln K = \nu_C \mu_C + \nu_D \mu_D - \nu_A \mu_A - \nu_B \mu_B \]
  \[ = -k_B T \left( -\nu_A \ln \left( \frac{q_A}{N} \right) - \nu_B \ln \left( \frac{q_B}{N} \right) + \nu_C \ln \left( \frac{q_C}{N} \right) + \nu_D \ln \left( \frac{q_D}{N} \right) \right) \] (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:
  \[ K_p = \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} N^{\nu_C + \nu_D - \nu_A - \nu_B} = \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} N^{-\Delta \nu} \] (7.5)
  \[ \Delta \nu = \nu_C + \nu_D - \nu_A - \nu_B \]

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

- Let us consider the simplest possible equilibrium
  \[ A \rightleftharpoons B \ldots K = \frac{q_B}{q_A} \] (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
  \[ \epsilon_{B,0} = \epsilon_{A,0} + \Delta \epsilon \] (7.7)
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:

\[
q_A^* = \sum_j e^{-\varepsilon_{A,j}/k_BT} \quad \text{and} \quad q_B^* = \sum_j e^{-\varepsilon_{B,j}+\Delta\varepsilon}/k_BT = e^{-\Delta\varepsilon/k_BT} \sum_j e^{-\varepsilon_{B,j}}/k_BT
\]  

(7.8)

Note in equation 7.8 the energies \( \varepsilon_{A,j} \) for \( i>0 \) are referenced to \( \varepsilon_{A,0} = 0 \). Also, in equation 7.8 the energies \( \varepsilon_{B,j} \) 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:

\[
K = \frac{q_B^*}{q_A^*} = e^{-\Delta\varepsilon/k_BT} \sum_j e^{-\varepsilon_{B,j}/k_BT}/\sum_j e^{-\varepsilon_{A,j}/k_BT} 
\]  

(7.9)

At low T such that \( \Delta\varepsilon \gg k_B T \), 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 \( \Delta\varepsilon \ll k_B T \) 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
\[
\ln K = \frac{-\Delta G^*}{RT} = \frac{-\Delta H^*}{RT} + \frac{\Delta S^*}{R} \tag{7.10}
\]

- At low T the \(\frac{-\Delta H^*}{RT}\) dominates so \(\ln K \approx \frac{-\Delta H^*}{RT}\). Because \(\Delta H^* > 0\) \(\ln K\) 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 \(\ln K \approx \frac{\Delta S^*}{RT}\). In this case the equilibrium is dominated by entropic effects. If \(\Delta S^* > 0\) the B form will be favored at high T.

- In fact we have set up the problem so that \(\Delta S^* > 0\). Note the energy level spacing for the B form is smaller than for the A form. This means at high T where \(\Delta \epsilon \ll k_B T\) 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 \(\Delta H^* \approx 0\) the equilibrium would be driven by entropy alone. This is the case in homework set 3 problem 3.