University of Washington
Department of Chemistry
Chemistry 453
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Lecture 6. 1/14/15

A. Partition Function & Free Energies

- Here we obtain expressions for the chemical potential and the equilibrium constant in terms of the partition function.
- As stated earlier, with statistical definitions of energy U and entropy S , we can derive other thermodynamic quantities. Consider the Helmholtz free energy defined as A=U-TS. We use the basic definition of A and the statistical definitions of U and S :

$$A = U - TS = U - T\left(k_B \ln Q - \frac{U}{T}\right) = -k_B T \ln Q \qquad (6.1)$$

- Note that like the entropy, the value of A depends upon whether the particles are distinguishable of not. Considering the two cases:

$$Q = \frac{q^N}{N!}\left(indistinguishable)\right) \qquad (6.2)$$

$$A = -k_B T \ln Q = -k_B T\left(\ln q^N - \ln N!\right) = -k_B T\left(N \ln q - N \ln N + N\right)$$

$$= -Nk_B T\left(\ln q - \ln N\right) - Nk_B T = -Nk_B T\left(\ln\left(\frac{q}{N}\right)\right) - Nk_B T$$

$$Q = q^N \left(distinguishable)\right) \qquad (6.3)$$

$$A = -k_B T \ln Q = -k_B T\left(\ln q^N\right) = -Nk_B T \ln q$$

- State variables can also be obtained. The most useful state variable that we can obtain from the expression for the statistical A is pressure. Start with the definition of dA for a reversible process, where the work is pressure-volume work only:

$$dA = -SdT - PdV \qquad (6.4)$$

- Because A is an exact differential

$$dA = -SdT - PdV = \left(\frac{\partial A}{\partial T}\right)_P dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$\therefore -P = \left(\frac{\partial A}{\partial V}\right)_T = \left[\frac{\partial}{\partial V}\left(-k_B T \ln Q\right)\right]_T \Rightarrow \qquad (6.5)$$

$$\therefore P = k_B T\left(\frac{\partial \ln Q}{\partial V}\right)_T = Nk_B T\left(\frac{\partial \ln q}{\partial V}\right)_T = \frac{Nk_B T}{q}\left(\frac{\partial q}{\partial V}\right)_T$$

Not that the state variable pressure does not depend on whether or not the particles are distinguishable.

- With the following statistical definitions, we can obtain definitions for other thermodynamic quantities:

$$Q=\sum_j e^{-E_j/k_BT};U=k_BT^2\left(\frac{\partial\ln Q}{\partial T}\right)_V;\ S=k_B\ln Q+k_BT\left(\frac{\partial\ln Q}{\partial T}\right)_V$$

$$A=-k_BT\ln Q;\ P=k_BT\left(\frac{\partial\ln Q}{\partial V}\right)_T;$$

- Example: With expressions for U and P a statistical expression for the enthalpy H can also be derived

$$\begin{aligned}H&=U+PV=k_BT^2\left(\frac{\partial\ln Q}{\partial T}\right)+Vk_BT\left(\frac{\partial\ln Q}{\partial V}\right)\\&=Nk_BT\left[T\left(\frac{\partial\ln q}{\partial T}\right)+V\left(\frac{\partial\ln q}{\partial V}\right)\right]\end{aligned}\qquad(6.6)$$

B. Partition Function, Chemical Potential and the Equilibrium Constant

- For many applications of the partition function that will follow this lecture, we require a statistical expression for the equilibrium constant K.
- The chemical potential is a key quantity in the thermodynamics of multi-component systems. Recall that the chemical potential and the condition for equilibrium was used to obtain the expression for the equilibrium constant.
- First Step: Obtain an statistical expression for the chemical potential. Starting with the definition of the Helmholtz free energy for a multi-component system:

$$\begin{aligned}&dA=-SdT-PdV+\sum_i\mu_i dN_i\\&\therefore\ \mu_i=\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}}=-k_BT\left(\frac{\partial\ln Q}{\partial N_i}\right)_{T,V,N_{j\neq i}}\end{aligned}\qquad(6.7)$$

- Second Step: Let's assume a gas phase reaction and so the particles are indistinguishable so that Q=q^N/N!. Putting the expression for Q into equation 6.7

$$\mu_i=\left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_{j\neq i}}=-k_BT\left(\frac{\partial\ln Q}{\partial N_i}\right)_{T,V,N_{j\neq i}}=-k_BT\left(\frac{\partial\ln\left(q_i^{N_i}/N_i!\right)}{\partial N_i}\right)_{T,V,N_{j\neq i}}=-k_BT\ln\left(\frac{q_i}{N_i}\right)$$

(6.8)

- Step 3: Combine the criterion for equilibrium with equation 6.8. For a chemical reaction

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D \tag{6.9}$$

the equilibrium condition is

$$\nu_A \mu_A + \nu_B \mu_B = \nu_C \mu_C + \nu_D \mu_D \tag{6.10}$$

so that

$$\begin{aligned}\Delta\mu^\circ &= -k_B T \ln K = \nu_C \mu_C^\circ + \nu_D \mu_D^\circ - \nu_A \mu_A^\circ - \nu_B \mu_B^\circ \\ &= -k_B T \left(-\nu_A \ln\left(\frac{q_A^\circ}{N}\right) - \nu_B \ln\left(\frac{q_B^\circ}{N}\right) + \nu_C \ln\left(\frac{q_C^\circ}{N}\right) + \nu_D \ln\left(\frac{q_D^\circ}{N}\right) \right)\end{aligned} \tag{6.11}$$

- 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:

$$\begin{aligned}K_P &= \frac{q_C^{\circ,\nu_C} q_D^{\circ,\nu_D}}{q_A^{\circ,\nu_A} q_B^{\circ,\nu_B}} N^{\nu_A+\nu_B-\nu_C-\nu_D} = \frac{q_C^{\circ,\nu_C} q_D^{\circ,\nu_D}}{q_A^{\circ,\nu_A} q_B^{\circ,\nu_B}} N^{-\Delta\nu} \\ \Delta\nu &= \nu_C + \nu_D - \nu_A - \nu_B\end{aligned} \tag{6.12}$$

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

- Let us consider the simplest possible equilibrium

$$A \rightleftarrows B \ldots K = \frac{q_B^\circ}{q_A^\circ} \tag{6.13}$$

- The equilibrium expressed in equation 6.13 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 6.1 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

$$\varepsilon_{B,0} = \varepsilon_{A,0} + \Delta\varepsilon \tag{6.14}$$

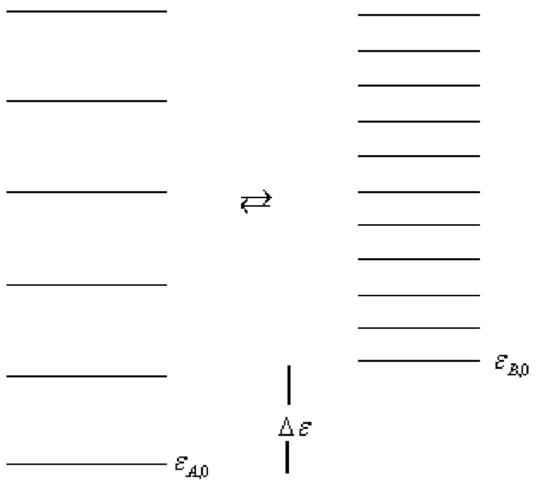

Figure 6.1: Two molecular systems with different energy spacings and different ground state energies in equilibrium

- 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 6.14 . Then the partition functions are:

$$q_A^\circ = \sum_j e^{-\varepsilon_{A,j}/k_BT} \quad and \quad q_B^\circ = \sum_j e^{-\left(\varepsilon_{B,j}+\Delta\varepsilon\right)/k_BT} = e^{-\Delta\varepsilon/k_BT}\sum_j e^{-\left(\varepsilon_{B,j}\right)/k_BT} \qquad (6.15)$$

- Note in equation 6.15 the energies $\varepsilon_{A,i}$ for i>0, are referenced to $\varepsilon_{A,0} = 0$.
- Also, in equation 6.15 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 6.13 is now:

$$K = \frac{q_B^\circ}{q_A^\circ} = e^{-\Delta\varepsilon/k_BT}\frac{\sum_j e^{-\varepsilon_{B,j}/k_BT}}{\sum_j e^{-\varepsilon_{A,j}/k_BT}} \qquad (6.16)$$

- 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

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (6.17)$$

  - 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 partiton 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.