Lecture #14
Objectives

1. Notation of chemical reactions
2. General equilibrium
3. Be able to derive the chemical equilibrium constants from statistical mechanics.
4. Identify how nonideal behavior can be accounted for in chemical reactions.

1. Notation of chemical reactions:

   Consider the chemical reaction

   $$\mathrm{Cl_2} + \mathrm{H_2} \rightleftharpoons 2\mathrm{HCl}$$

   The numbers in front of the chemical formulae are the stoichiometric coefficients, which are always positive. We can use the coefficients to define the stoichiometric numbers, ν_i. By convention we take the sign to be positive for products (terms on the right), negative for reactants (terms on the left), and zero for inert species. Hence, $\nu_{\mathrm{Cl_2}} = \nu_{\mathrm{H_2}} = -1$ and $\nu_{\mathrm{HCl}} = 2$. Thus, we can write a single chemical reaction as

   $$\sum_{i=1}^{C} \nu_i M_i = 0$$

   where M_i is the chemical formula for component i. What are the stoichiometric numbers for $3A + 2B \rightleftharpoons 4C$?

   We can write a relationship for the number of moles of a component present at a given time, and the initial number of moles of that component present before the reaction takes place. The relationship is cast in terms of the *extent of reaction*, ξ.

   $$n_i = n_{i0} + \nu_i \xi$$

2. General Equilibrium Formulation:

   At constant pressure and temperature the criterion for general equilibrium is a minimum in the Gibbs free energy:

   $$\min_{n^k, x_i^k} G = \sum_{i=1}^{C} \sum_{k=1}^{\pi} n_i^k \mu_i^k = \sum_{i=1}^{C} \sum_{k=1}^{\pi} n^k x_i^k \mu_i^k$$

   where n^k is the number of moles in phase k, x_i^k is the mole fraction of component i in phase k, and μ_i^k is the chemical potential of component i in phase k. Note that the only variables we have available to manipulate are the total number of moles and mole fractions for each phase. There are also some constraints on the above equation which must be taken into account. The constraints are:

(a) Material balance

$$n_i = \sum_{k=1}^{\pi} n_i^k = \sum_{k=1}^{\pi} n_{i0}^k + \sum_{k=1}^{\pi}\sum_{l=1}^{R} \nu_{il}\xi_l \qquad (i = 1, \ldots, C)$$

(b) Non-negativity

$$\begin{aligned} n^k &\geq 0 \qquad (k = 1, \ldots, \pi) \\ 1 &\geq x_i^k \geq 0 \qquad (i = 1, \ldots, C;\ k = 1, \ldots, \pi) \end{aligned}$$

If we hold the temperature and the volume constant instead then the equilibrium condition is a minimum in the Helmholtz free energy:

$$\min_{n^k, x_i^k} A = \min_{n^k, x_i^k} \{-PV + \sum \mu_i^k n_i^k\}$$

Consider a single phase, single chemical reaction. The Gibbs free energy is given by

$$G = \sum_{i=1}^{C} n_i \mu_i = \sum_{i=1}^{C} n_{i0}\mu_i + \sum_{i=1}^{C} \nu_i \xi \mu_i$$

Then note that

$$dn_i = \nu_i d\xi$$

We want to find

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P} = 0 \quad (i = 1, C)$$

but,

$$dG = -SdT + VdP + \sum_{i=1}^{C} \mu_i dn_i = -SdT + VdP + \sum_{i=1}^{C} \mu_i \nu_i d\xi$$

At constant T, P we have

$$dG = \sum_{i=1}^{C} \mu_i \nu_i d\xi$$

So to find the minimum we need to find

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$$

Hence, the condition for chemical equilibrium is

$$\sum_{i=1}^{C} \nu_i \mu_i = 0.$$

This is true for any chemical reaction at equilibrium.

3. Reactions in ideal gases

The standard free energy equilibrium constant in classical thermodynamics is

$$-RT \ln K_{eq} = \sum_i \nu_i \mu_i^\circ = \Delta \tilde{G}^\circ_{rxn}$$

where superscript $\circ$ refers to the chemicals in their *standard states.* What is meant by *standard states*? it is generally taken to refer to unit pressure (i.e., 1 bar) or unit fugacity at the temperature of the reaction. $\Delta \tilde{G}^\circ_{rxn}$ is the change in free energy of reaction per mole of the molecules in their standard states,

$$\Delta \tilde{G}^\circ_{rxn} = \sum_i \nu_i \tilde{G}_i^\circ = \sum_i \nu_i \mu_i^\circ,$$

where we have used the fact that for a pure fluid $\tilde{G}_i = \mu_i$.

Recall that in classical thermodynamics we define K_{eq} in terms of fugacities,

$$K_{eq} = \prod_i \left(\frac{\hat{f}_i}{f_i^\circ} \right)^{\nu_i}$$

where f° is the standard state fugacity. For an ideal gas the equilibrium constant gives a direct measure of the equilibrium conversion through the mole fractions.

$$K_{eq} = \prod_i \left(\frac{y_i p}{P^\circ} \right)^{\nu_i}$$

The goal is to compute K_{eq} from statistical mechanics. To do this we need an expression for μ_i° from statistical mechanics. Recall that

$$\mu = -kT \left(\frac{\partial \ln Q}{\partial N} \right)_{V,T}$$

Invoking the semi-classical partition function,

$$Q = \frac{Z q_{\text{int}}^N}{\Lambda^{3N} N!}$$

where

$$q_{\text{int}} = q_e q_v q_r$$

Assume that at the standard state the molecules are ideal gases. This is usually a good approximation at high temperatures and pressures of 1 bar. Then $Z = V^N$ and we can write

$$\mu_i^\circ = -kT \ln \left(\frac{V^\circ q_{\text{int},i}}{N \Lambda_i^3} \right),$$

where V° is the volume in the standard state. Recognizing that $V^\circ/N = kT/P^\circ$ we have

$$\tilde{G}_i^\circ = N_\mathrm{A}\mu_i^\circ = -RT\ln\left(\frac{kTq_{\mathrm{int},i}}{P^\circ\Lambda_i^3}\right),$$

where N_A is Avogadro's number and we have recognized that the molar Gibbs free energy is just N_A times the molecular (not molar) chemical potential of the pure fluid.

Thus,

$$K_{eq} = \prod_i \left(\frac{q_{\mathrm{int},i}kT}{P^\circ\Lambda_i^3}\right)^{\nu_i} = \left(\frac{kT}{P^\circ}\right)^{\Delta\nu}\prod_i\left(\frac{q_{\mathrm{int},i}}{\Lambda_i^3}\right)^{\nu_i}$$

where $\Delta\nu = \sum_i \nu_i$ and $P^\circ = 1$ bar.

4. Example: Association in sodium vapor.
   Consider the gas phase association reaction

   $$2\mathrm{Na} \rightleftharpoons \mathrm{Na}_2$$

   The equilibrium constant can be written as

   $$K(T) = \frac{P_{\mathrm{Na}_2}P^\circ}{P_{\mathrm{Na}}^2} = \frac{P^\circ}{kT}\frac{(q_{\mathrm{int,Na}_2}/\Lambda^3_{\mathrm{N}a_2})}{(q_{\mathrm{int,Na}}/\Lambda^3_{\mathrm{N}a})^2}$$

   The electronic ground state of Na is doubly degenerate ($\omega = 2$).

   $$\frac{q_{\mathrm{int,Na}_2}}{\Lambda^3_{\mathrm{N}a_2}} = \left(\frac{2\pi m_{\mathrm{Na}_2}kT}{h^2}\right)^{3/2}\left(\frac{T}{2\Theta_r}\right)\frac{\exp(D_0/kT)}{1-\exp(-\Theta_v/T)}$$

   $$\frac{q_{\mathrm{int,Na}}}{\Lambda^3_{\mathrm{N}a}} = \left(\frac{2\pi m_{\mathrm{Na}}kT}{h^2}\right)^{3/2} q_{\mathrm{elec}}$$

   Plugging in the numbers and using $T = 1000$ K we get

   $$K(T = 1000) = 0.493$$

   The experimental value is 0.469.

5. Nonideal mixture behavior in fluid phase reactions.

   (a) Recall that at equilibrium

   $$\sum_{i=1}^{C}\nu_i\mu_i = 0.$$

This expression is valid for ideal and nonideal solutions. For any real (or ideal) fluid we can write the chemical potential as

$$\mu_i = \mu_i^\circ + RT \ln\left(\frac{\hat{f}_i}{f_i^\circ}\right) = \mu_i^\circ + RT\ln a_i,$$

where μ_i° is a function of temperature only and $a_i = x_i\gamma_i$ and γ_i is the activity coefficient. Let μ_i° on a per mole basis be given by

$$\mu_i^\circ = -RT\ln\left(\frac{kTq_{\text{int},i}}{P^\circ\Lambda_i^3}\right)$$

Then the equilibrium equation becomes

$$\sum_{i=1}^{C}\nu_i(\mu_i^\circ + RT\ln a_i) = \sum_{i=1}^{C}\nu_i\mu_i^\circ + \sum_{i=1}^{C}\nu_i RT\ln a_i = 0$$

$$\sum_{i=1}^{C}\nu_i\mu_i = -RT\sum_{i=1}^{C}\nu_i\ln\left(\frac{kTq_{\text{int},i}}{P^\circ\Lambda_i^3}\right) + RT\sum_{i=1}^{C}\nu_i\ln a_i = 0$$

$$\sum_{i=1}^{C}\ln\left(\frac{kTq_{\text{int},i}}{P^\circ\Lambda_i^3}\right)^{\nu_i} = \sum_{i=1}^{C}\ln\left(a_i\right)^{\nu_i}$$

$$\ln\left[\prod_{i=1}^{C}\left(\frac{kTq_{\text{int},i}}{P^\circ\Lambda_i^3}\right)^{\nu_i}\right] = \ln\left(\prod_{i=1}^{C}a_i^{\nu_i}\right)$$

$$K(T) = \prod_{i=1}^{C}a_i^{\nu_i}$$

Now you can calculate $K(T)$ from statistical mechanics as before, but use some liquid phase activity coefficient model for a_i to correct for nonideal behavior to find the composition.

6. Gas phase nonidealities.

For reactions in nonideal gases we use the fugacity to relate the equilibrium constant to the compositions:

$$K = \prod_i\left(\frac{\hat{f}_i}{f_i^\circ}\right)^{\nu_i}$$

If we assume unit fugacity as the reference state this becomes

$$K = \prod_i\left(\hat{f}_i\right)^{\nu_i} = K_f$$

Introducing the fugacity coefficients we have

$$K = \prod_i\left(\hat{\phi}_i y_i P\right)^{\nu_i} = K_{\hat{\phi}}K_y P^{\Delta\nu}$$

where

$$K_{\hat{\phi}} = \prod_i \hat{\phi}_i^{\nu_i}$$

7. Condensed phases:

   Substitute $a_i = \gamma_i x_i$ to get

   $$K_{eq} = \prod_i (\gamma_i x_i)^{\nu_i} = \prod_i \gamma_i^{\nu_i} \prod_i x_i^{\nu_i} = K_\gamma K_x$$

   If you know K_{eq} and have an expression for γ_i you can use this equation to solve for the equilibrium composition in a nonideal liquid phase reaction. The problem is nonlinear in the mole fractions and must be solved numerically.

   If on the other hand you know the equilibrium constant and can measure several equilibrium compositions you can fit the parameters for an activity coefficient model. Walas shows how to do this.