Lecture 12: 10.19.05 Chemical reaction equilibria

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Reading: Engel and Reid 6.7-6.9, 6.11, 6.12, 9.11-9.13

Supplementary Reading:
Last time we introduced models for the chemical potential of materials:

**Ideal Gas Mixture:**

\[ N_i^{\text{ideal}}(T, p_i) = N_i^{\text{ideal}}(T, \text{latm}) + RT \ln \left( \frac{p_i}{p_0} \right) \]

\[ p_i = x_i \cdot P \quad \text{Partial Pressure} \]

**General Solution Model:**

\[ N_i^{\text{soln}}(T, P, x_i) = N_i^{\text{soln}}(T, \text{latm}) + RT \ln a_i^{\text{soln}} \]

\[ a_i^{\text{soln}}(T, P, x_i = 1) \]

**Activity Coefficient:**

\[ \gamma_i = \frac{a_i}{x_i} \]

**Standard State Chemical Potential:**

\[ \mu_i = \gamma_i \cdot x_i \cdot \mu^{\text{soln}} \]

\[ \mu_i \rightarrow \gamma_i \rightarrow x_i \rightarrow 1 \]

\[ \frac{dG}{dP} = V_i dP - S_i dT + \sum_{i} x_i \frac{d}{dn_i} \]

\[ \bar{V}_i = \left( \frac{\partial \bar{V}_i}{\partial P} \right)_{T, N} = \left( \frac{\partial N_i}{\partial P} \right)_{T, N} = \frac{\partial}{\partial P} \left[ N_i^{\text{soln}} + RT \ln a_i^{\text{soln}} \right] \]

\[ \bar{V}_i = 0 + RT \frac{d(\ln a_i)}{dP} \]

\[ \int \bar{V}_i dP = RT \int d(\ln a_i) \]

\[ P = \text{latm} \quad \text{Small!} \]

\[ a_i = e \quad e^0 = 1 \]

\[ \Delta P / RT \]
Equating chemical potentials during reactions

- We already know the chemical potential dictates mass flow—driving molecules from one phase into another in closed systems, or driving the addition/subtraction of molecules in open systems. But what about the case where two components can chemically react and be consumed to create a 3rd, completely new component? The chemical potential again controls the outcome.

The extent of reaction

- When components of a closed system can react, they must still obey the Gibbs condition to reach equilibrium. Consider a generic simple reaction:

\[ v_A A + v_B B \leftrightarrow v_C C \]

\[ \Delta G_{\text{rxn}} = \sum_{i=1}^{C} n_i d\mu_i = 0 \]

- The \( v_i \) are the stoichiometric coefficients for the reactants and products. Equilibrium for this process (the reaction moving left to right as written) is achieved when the Gibbs free energy is minimized:

**equilibrium condition at constant (T,P) for a closed system**

**How much "C" is present as reaction proceeds?**

\[ n_C = n_{C_i} + \sum_{i} v_i \xi \]

\[ \begin{align*}
\text{INITIAL} & \quad \text{EXTENT OF REACTION} \\
\text{Differentiate} & \\
\text{d}n_C &= 0 + \sum_{i} v_i \text{d}\xi \\
\therefore \text{d}G_{\text{rxn}} &= \sum_{i} v_i n_i \text{d}\xi
\end{align*} \]

\[ \text{Move } \text{d}\xi \text{ to left-hand side} \\
\left( \frac{\Delta G_{\text{rxn}}}{\text{d}\xi} \right)_{T,P} = \sum_{i} v_i n_i \equiv \Delta \overline{G}_{\text{rxn}} \]
- The value of the free energy per mole of reaction determines the direction of a reaction, just as free energy determines the direction of any other process. For example, for a simple generic reaction:

\[ n_A A + n_B B \leftrightarrow n_C C \]

\[ \Delta G_{rxn} = n_C U_C - n_B U_B - n_A U_A \]

- \( \Delta G_{rxn} < 0 \) \( \Rightarrow A + B \rightarrow C \) \( \text{COMPONENT BEING CREATED OR CONSUMED SPONTANEOUSLY...} \)

- \( \Delta G_{rxn} = 0 \) \( \Rightarrow A + B \rightleftharpoons C \)

- \( \Delta G_{rxn} > 0 \) \( \Rightarrow A + B \leftarrow C \)

---

The simplest case: reacting mixtures of gases

- We can use the equilibrium condition to predict how far chemical reactions will proceed before coming to equilibrium. Let's go through a simple example: the reaction of hydrogen and oxygen to form water vapor:

\[ H_2(g) + \frac{1}{2} O_2(g) \leftrightarrow H_2O(g) \]

- The moles of each component present are:

<table>
<thead>
<tr>
<th>Moles:</th>
<th>H(_2)</th>
<th>O(_2)</th>
<th>H(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initially:</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>During reaction:</td>
<td>( n_{H_2} = 1 - n_{H_2O} )</td>
<td>( n_{O_2} = 1 - \frac{1}{2} n_{H_2O} )</td>
<td>( n_{H_2O} )</td>
</tr>
<tr>
<td>DIFFERENTIATE:</td>
<td>( \frac{dn_{H_2}}{dt} = -\frac{dn_{H_2O}}{dt} )</td>
<td>( \frac{dn_{O_2}}{dt} = -\frac{1}{2} \frac{dn_{H_2O}}{dt} )</td>
<td>( \frac{dn_{H_2O}}{dt} )</td>
</tr>
<tr>
<td>PER MOLE OF REACTION:</td>
<td>(-\delta\xi)</td>
<td>(-\frac{1}{2}\delta\xi)</td>
<td>(\delta\xi)</td>
</tr>
</tbody>
</table>

\[ \Delta G_{rxn} = 0 \text{ AT EQUILIBRIUM} \]
Plugging this information into the equilibrium condition:

\[ dG_{\text{RN}} = -N_{H_2} d\chi - \frac{1}{2} N_{NO_2} d\chi + N_{H_2O} d\chi = 0 \]

\[ \Delta G_{\text{RN}} = -N_{H_2} - \frac{1}{2} N_{NO_2} + N_{H_2O} = 0 \]

**Ideal Gases:**

\[ -[N_{H_2}^o + R\ln\left(\frac{P_{H_2}}{P^o}\right)] - \frac{1}{2} N_{NO_2}^o - R\ln\left(\frac{P_{O_2}}{P^o}\right) + N_{H_2O}^o + R\ln\left(\frac{P_{H_2O}}{P^o}\right) = 0 \]

\[ \Delta G_{\text{RN}}^o = R\ln\left(\frac{P_{H_2}^{1/2}}{P_{O_2}}\right) \left(\frac{P_{H_2O}}{P^o}\right) \]

The term on the left is the molar change in free energy for reaction of the components in their standard states if H₂ and O₂ react completely to become water:

\[ \Delta G_{\text{RN}}^o = N_{H_2O}^o - N_{H_2}^o - \frac{1}{2} N_{NO_2}^o \]

A convention often used is that \( P/P^o \) is implied if we write \( P_r \) (confusing, but this is the historical convention). Note that our text is quite good about ‘keeping’ the reference pressure in the equations for ideal gas reactions. It’s a good habit for you as well. Thus the term on the right re-arranges to:

\[ -\Delta G_{\text{RN}}^o = R\ln\left(\frac{P_{H_2O}}{P^o}\right) \left(\frac{P_{H_2}}{P^o}\right) \left(\frac{P_{O_2}}{P^o}\right)^{1/2} \]

**Define Equilibrium Constant:**

\[ K_P = \frac{\left(\frac{P_{H_2O}}{P^o}\right)}{\left(\frac{P_{H_2}}{P^o}\right)\left(\frac{P_{O_2}}{P^o}\right)^{1/2}} = e^{\frac{-\Delta G_{\text{RN}}^o}{RT}} \]
• In general for a reacting ideal gas mixture, we have:

\[
K_p(T) = \frac{\left(\frac{P_C}{P^0}\right)^c \left(\frac{P_D}{P^0}\right)^d}{\left(\frac{P_A}{P^0}\right)^a \left(\frac{P_B}{P^0}\right)^b} = e^{-\frac{\Delta G_{\text{RXN}}^o}{kT}}
\]

○ Where ν is the stoichiometric coefficient for the reactant/product. \(\Delta G_{\text{RXN}}^o\) is also referred to as the **molar free energy of formation** for the products C and D.

\[
\Delta G_{\text{RXN}}^o = \sum_i ν_i \mu_i - \sum_j ν_j \mu_j
\]

\[
= c \mu_C^o + d \mu_D^o - a \mu_A^o - b \mu_B^o
\]
Reactions of gases with condensed phases

An example: oxidation of a metal

- Suppose we wish to consider now a reaction between a gas and a solid or liquid. An example of great practical significance is the oxidation of a metal:

\[ \text{M}_\text{(s)} + \frac{1}{2} \text{O}_2 \rightarrow \text{MO}_\text{(s)} \]

(Figure modified from Dill and Bromberg)

- There are two key simplifying assumptions we will make to determine the equilibrium state of such reactions that are valid for most real materials:

**Approximation 1:** The first we will make is that the oxygen is insoluble in the metal (i.e. no molecules of oxygen diffuse into the bulk of the metal lattice).

- The metal and metal oxide solids must be in equilibrium with their vapor phases:

\[ N_M^{\text{solid}} = N_M^{G} \]

\[ N_{\text{MO}}^{\text{solid}} = N_{\text{MO}}^{G} \]

- Expanding these equations with the definitions of the chemical potentials for the gaseous and solid phases:

\[ N_M + B_T \ln \frac{a_m^{\text{solid}}}{a_m^{\text{pure solid}}} = N_M^{\text{G}} + R T \ln \left( \frac{P}{P_0} \right) \]

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Approximation 2: The vapor pressure of most solids ($P_m$ in the chemical potential expression) is so small that the last term on the left-hand side of the equation above is negligible. This is typically a very good approximation. In other words, the activity of the solid in equilibrium with its vapor phase may be taken as unity. This leaves us with:

1. $\mu_{M}^{o,g} + RT \ln \frac{P_m}{P_0} = \mu_{M}^{o,solid\ M}$
2. $\mu_{MO}^{o,g} + RT \ln \frac{P_m}{P_0} = \mu_{MO}^{o,solid\ MO}$

- Assume the reaction equilibrium is established in the gas phase:

$$\text{M}_2\text{O}_3\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightleftharpoons \text{MO}_2\text{(g)}$$

- Just as the case for the ideal gas reaction, we start with the Gibbs condition for equilibrium:

$$\Delta G_{\text{rxn}} = \sum_{i=1}^{products} \mu_i v_i - \sum_{j=1}^{reactant} \mu_j v_j = 0$$

$$N_{MO}^{(g)} - \frac{1}{2} N_{O_2}^{(g)} - N_{M}^{(g)} = 0$$

$$N_{MO}^{o,g} + RT \ln \frac{P_m}{P_0} - \frac{1}{2} N_{O_2}^{o,g} - RT \ln \left( \frac{P_{O_2}}{P_0} \right) = 0$$

$$\Delta G_{\text{rxn}}^o = RT \ln \left( \frac{P_{O_2}^{1/2}}{P_0} \right) - \mu_{MO}^{o,solid\ MO} - RT \ln \left( \frac{P_m}{P_0} \right) = 0$$
- $\Delta G^\circ_{\text{roa}}$ is the difference in free energy between 1 mole of gaseous MO at $P = 1$ atm and the sum of the free energies of 1/2 mole of $O_2 (g)$ at $P = 1$ atm and 1 mole of gaseous $M$ at $P = 1$ atm, all at temperature $T$. (Exactly analogous to the standard state free energy of reaction we derived for the pure gas reaction).

- The expression above is the same result we obtained for simple reactions between gases. However, we can utilize the solid-vapor equilibrium expressions to further simplify the result:

\[
N^0_{O_m} = N^0_{M} - RT \ln \frac{P_m}{P_o} \\
N^0_{O_{2d}} = N^0_{M} - RT \ln \frac{P_{O_2}}{P_o}
\]

Plugging into \[3\]!

\[
N^0_{M2d} - RT \ln \frac{P_{M2}}{P_o} - \frac{1}{2} N^0_{O_2} - N^0_{M} + RT \ln \frac{P_m}{P_o} = \\
- RT \ln \left( \frac{P_{M2}}{P_o} \right) \left( \frac{P_{O_2}^{1/2}}{P_o} \right)
\]

**Implications of the final result**

- Our equilibrium expression states that there is only one unique oxygen partial pressure at a given temperature that will cause the reaction to be in equilibrium (i.e. reversible formation and dissolution of MO).

- When an oxidation/reduction reaction is carried out in a pure oxygen atmosphere (at $P_{O_2} = 1$ atm pressure), $\Delta G^\circ_{\text{roa}} = \Delta G^\circ_{\text{roa},o}$. A plot of $\Delta G^\circ_{\text{roa}}$ vs. temperature, called an Ellingham diagram, can be used to predict the outcome of the reaction.

\[
\Delta G^\circ_{\text{rxn}} = N^0_{M2d} - \frac{1}{2} N^0_{O_2} - N^0_{M} = -RT \ln \frac{1}{\left( \frac{P_{O_2}^{1/2}}{P_o} \right)} = -RT \ln K^\circ
\]

**ONLY TRUE AT EQUILIBRIUM!**

\[
\Delta G_{\text{rxn}} = \Delta G^\circ_{\text{rxn}} + RT \ln \frac{1}{\left( \frac{P_{O_2}^{1/2}}{P_o} \right)}
\]
Calcium carbonate is a major component of many biological hard materials such as seashells, and is often studied to learn how organisms build materials via ‘bottom up’ molecular assembly (a process called biomineralization). It undergoes thermal decomposition on heating according to the reaction:

\[ \text{CaCO}_3(s) \leftrightarrow \text{CaO}(s) + \text{CO}_2(g) \]

Given the standard state free energies (free energies of formation) for each component, calculate the pressure of CO\(_2\) in equilibrium with one mole of calcium carbonate at 2000 K:

\[ \Delta G_f^{\circ} = \mu_{\text{CaCO}_3}^{\circ} = -1,084 \text{ kJ/mole} \quad \Delta G_f^{\circ} = \mu_{\text{CaO}}^{\circ} = -603.3 \text{ kJ/mole} \]

\[ \Delta G_f^{\circ} = \mu_{\text{CO}_2}^{\circ} = -394.4 \text{ kJ/mole} \]

(Modified from Example 6.11 in Engel and Reid)
References