Lecture 12: 10.19.05 Chemical reaction equilibria

Today:

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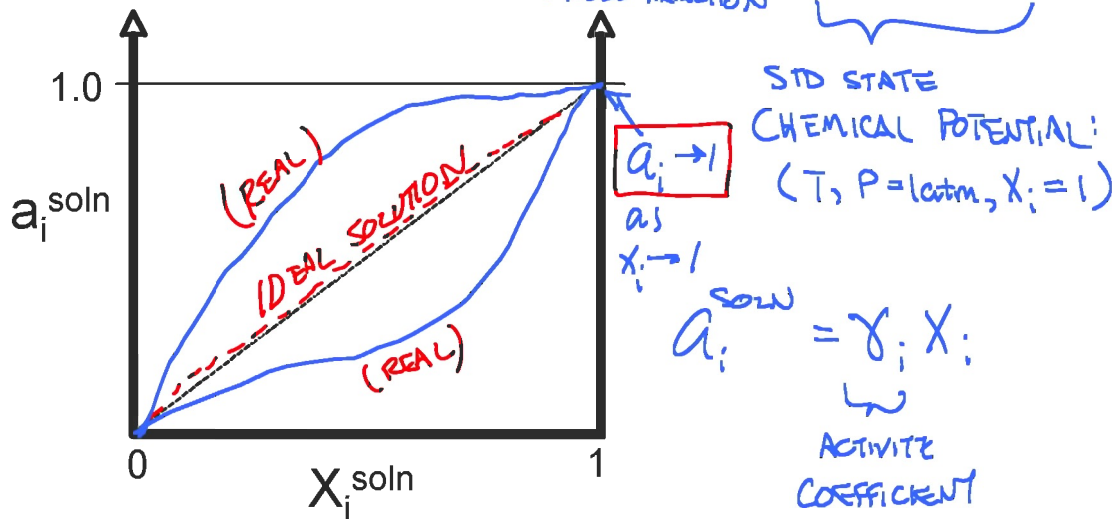
Supplementary Reading:

Last time

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

IDEAL GAS MIXTURE : $\mu_i^{1.6.}(T, P_i) = \mu_i^{0,1.6.}(T, 1atm) + RT \ln\left(\frac{P_i}{P^0}\right)$

$P_i = X_i P$ PARTIAL PRESSURE

GENERAL SOLUTION MODEL ! $\mu_i^{SOLN}(T, P, X_i) = \mu_i^{0,SOLN}(T, \underline{1atm}) + RT \ln a_i^{SOLN}$

$\rightarrow$ MOLE FRACTION

STD STATE CHEMICAL POTENTIAL: $(T, P = 1atm, X_i = 1)$

ACTIVITY

$a_i \rightarrow 1$ as $X_i \rightarrow 1$

$a_i^{SOLN} = \gamma_i X_i$

ACTIVITE COEFFICIENT

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

$\overline{V}_i = \left(\frac{\partial \overline{G}_i}{\partial P}\right)_{T,n} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} = \frac{\partial}{\partial P}\left[\mu_i^0 + RT\ln a_i\right]$

CONSTANT

$\overline{V}_i = 0 + RT \frac{\partial(\ln a_i)}{\partial P}$

$\overline{V}_i dP = RT \, d(\ln a_i)$

PRESSURE HAS SMALL EFFECTS ON a_i OF SOLIDS + LIQUIDS

$\int_{P=1atm}^{P} \overline{V}_i dP \cong \underbrace{\overline{V}_i \Delta P}_{SMALL!} = \int RT\, d(\ln a_i) = RT \ln a_i$

SMALL! $\approx -0.74 \frac{J}{mole}$ FOR Fe @ T=1000K

$a_i \cong e^{\Delta \overline{V}_i / RT} \cong e^0 \cong 1$

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:

$$\left[v_A A + v_B B \leftrightarrow v_C C \right. \qquad A + B \rightarrow C$$
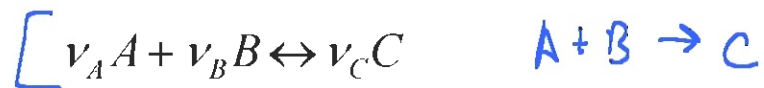
- The v_i are the stoichiometric coefficients for the reactants and products. Equilibrium for this process (the reaction moving left to right as written) is achieved when the Gibbs free energy is minimized:

$$dG_{rxn} = \sum_{i=1}^{C} \mu_i dn_i = 0$$

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

HOW MUCH "C" IS PRESENT AS RXN PROCEEDS?

$$n_C = \underbrace{n_{C,i}}_{\text{INITIAL}} + \underbrace{v_i \xi}_{\text{EXTENT OF REACTION}} = \text{MOLES OF } C$$

differentiate
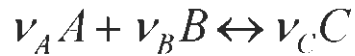
$$dn_C = 0 + v_i d\xi$$

$$\therefore dG_{RXN} = \sum_{i=1}^{C} N_i v_i d\xi$$

↓ MOVE $d\xi$ TO LEFT-HAND SIDE

$$\left(\frac{\partial G_{RXN}}{\partial \xi} \right)_{T,P} = \sum_{i=1}^{C} v_i N_i \equiv \Delta \bar{G}_{RXN}$$

FREE ENERGY CHANGE PER MOLE OF REACTION

- 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:

$$\nu_A A + \nu_B B \leftrightarrow \nu_C C$$

$$\Delta \overline{G}_{RXN} = +\nu_C \underline{N_C} - \nu_B \underline{N_B} - \nu_A \underline{N_A}$$

SIGN TELLS ME IF I HAVE

$$\Delta \overline{G}_{rxn} < 0$$ → A+B→C COMPONENT BEING CREATED OR CONSUMED

SPONTANEOUSLY...

$$\Delta \overline{G}_{rxn} = 0$$ → A + B ⇌ C

$$\Delta \overline{G}_{rxn} > 0$$ → A + B ← C

The simplest case: reacting mixtures of gases[1]

- 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:[1]

$$H_{2(g)} + \frac{1}{2} O_{2(g)} \leftrightarrow H_2O_{(g)}$$
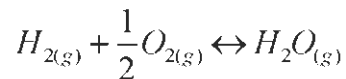
  o The moles of each component present are:

Moles:	H_2	O_2	H_2O
Initially:	1	1	O
During reaction:	$n_{H_2} = 1 - n_{H_2O}$	$n_{O_2} = 1 - \frac{1}{2} n_{H_2O}$	n_{H_2O}
DIFFERENTIATE:	$dn_{H_2} = -dn_{H_2O}$	$dn_{O_2} = -\frac{1}{2} dn_{H_2O}$	dn_{H_2O}
PER MOLE OF REACTION:	$-d\xi$	$-\frac{1}{2} d\xi$	$d\xi$

$$dG_{RXN} = 0 \quad \text{AT EQUILIBRIUM}$$

o   Plugging this information into the equilibrium condition:

AT EQUILIBRIUM
↓

$$dG_{RXN} = -N_{H_2}d\xi - \frac{1}{2}N_{O_2}d\xi + N_{H_2O}d\xi = 0$$

$$\Delta \overline{G}_{RXN} = -N_{H_2} - \frac{1}{2}N_{O_2} + N_{H_2O} = 0$$

IDEAL GASES:

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

$$\underbrace{-N_{H_2}^o - \frac{1}{2}N_{O_2}^o + N_{H_2O}^o}_{\Delta \overline{G}_{RXN}^o} = \overline{R}\overline{T}\ln\frac{\left(\frac{P_{O_2}}{P^o}\right)^{1/2}\left(\frac{P_{H_2}}{P^o}\right)}{\left(\frac{P_{H_2O}}{P^o}\right)}$$

o   The term on the left is the molar change in free energy for reaction of the components in their standard states if H_2 and O_2 react *completely* to become water:

FREE ENERGY CHANGE PER MOLE FOR ALL COMPONENTS IN THEIR STD (REFERENCE) STATES

$$\Delta \overline{G}_{RXN}^o = N_{H_2O}^o - N_{H_2}^o - \frac{1}{2}N_{O_2}^o$$

o   **A convention often used is that $P_i/P_{i,0}$ is implied if we write P_i** (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:

$$-\Delta \overline{G}_{RXN}^o = RT\ln\frac{\left(\frac{P_{H_2O}}{P^o}\right)}{\left(\frac{P_{H_2}}{P^o}\right)\left(\frac{P_{O_2}}{P^o}\right)^{1/2}}$$

DEFINE EQUILIBRIUM CONSTANT:

$$K_p = \frac{\left(\frac{P_{H_2O}}{P^o}\right)}{\left(\frac{P_{H_2}}{P^o}\right)\left(\frac{P_{O_2}}{P^o}\right)^{1/2}} = e^{-\Delta \overline{G}_{RXN}^o/RT}$$

- In general for a reacting ideal gas mixture, we have:

$$aA + bB \rightarrow cC + dD$$

$$K_p(T) = \frac{\left(\frac{P_C}{P^o}\right)^c \left(\frac{P_D}{P^o}\right)^d}{\left(\frac{P_A}{P^o}\right)^a \left(\frac{P_B}{P^o}\right)^b} = e^{-\Delta \overline{G}^o_{RXN}/RT}$$

- o Where ν is the stoichiometric coefficient for the reactant/product. $\Delta \overline{G}^o_{rxn}$ is also referred to as the **molar free energy of formation** for the products C and D.

$$\Delta \overline{G}^o_{RXN} = \underset{i}{\sum} \nu_i N_i \overset{\text{PRODUCTS}}{-} \underset{j}{\sum} \nu_j \mu_j \overset{\text{REACTANTS}}{}$$

$$= c\overline{G}^o_C + d\overline{G}^o_D - a\overline{G}^o_A - b\overline{G}^o_B$$

Reactions of gases with condensed phases[2]

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:
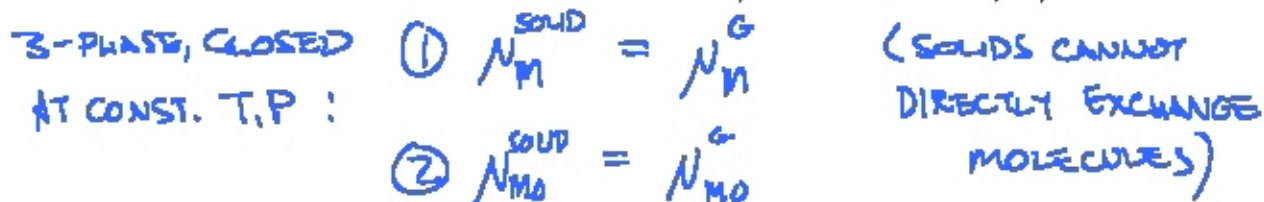
$$M_{(s)} + \tfrac{1}{2}O_{2(g)} \rightleftharpoons MO_{(s)}$$
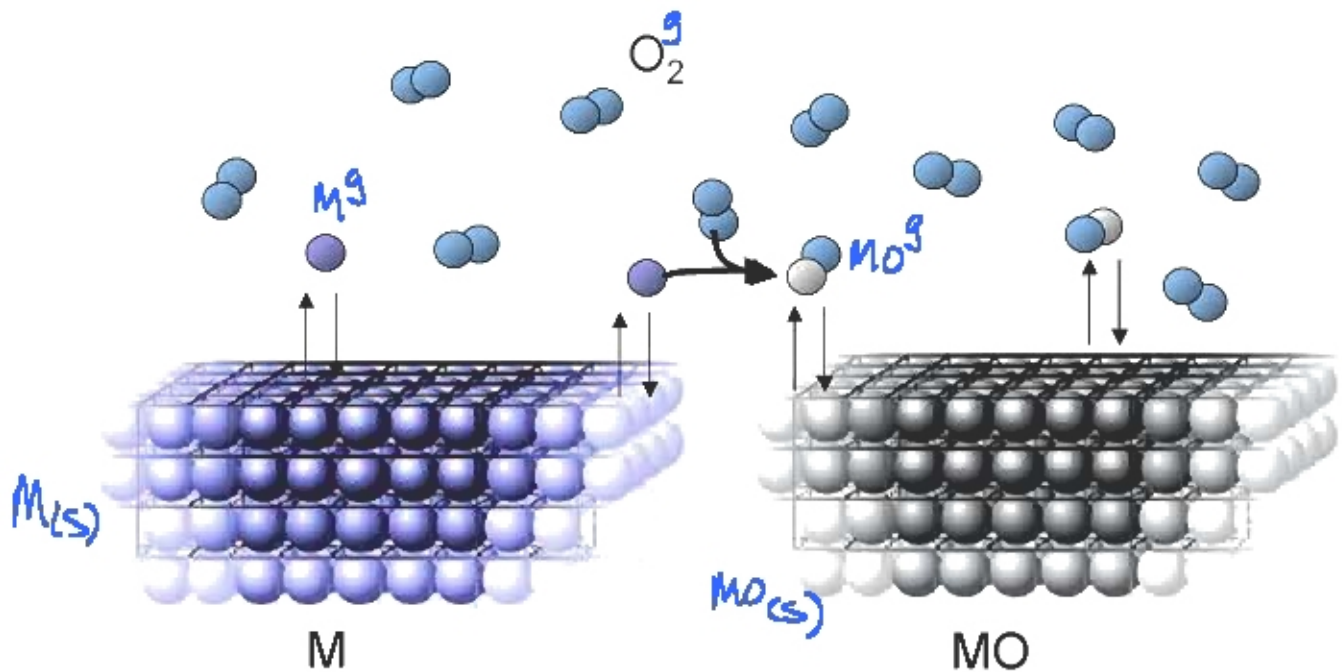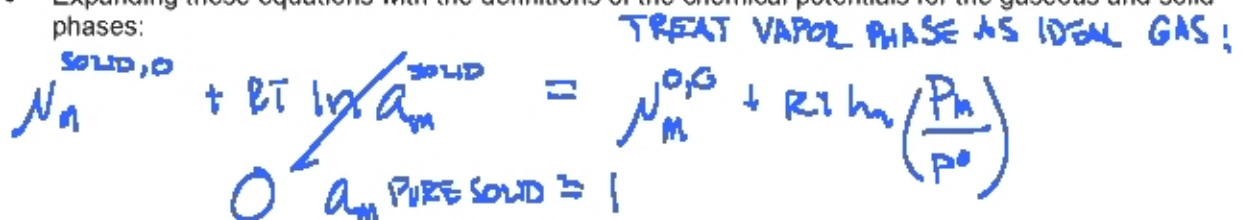

(Figure modified from Dill and Bromberg[3])

- **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:

3-PHASE, CLOSED
AT CONST. T,P :

$$① \quad \mu_M^{SOLID} = \mu_M^{G}$$

(SOLIDS CANNOT
DIRECTLY EXCHANGE
MOLECULES)

$$② \quad \mu_{MO}^{SOLID} = \mu_{MO}^{G}$$

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

TREAT VAPOR PHASE AS IDEAL GAS!

$$\mu_M^{SOLID,0} + RT \ln a_M^{SOLID} = \mu_M^{0,G} + RT \ln\left(\frac{P_M}{P^0}\right)$$

$$0 \quad a_M \text{ PURE SOLID} \approx 1$$

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:

$$① \quad \mu_M^{o,g} + RT \ln \frac{P_M}{p^o} = \mu_M^{o,\text{solid M}}$$

$$② \quad \mu_{MO}^{o,g} + RT \ln \frac{P_{MO}}{p^o} = \mu_{MO}^{o,\text{solid MO}}$$

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

$$M_{(g)} + \tfrac{1}{2}O_{2(g)} \rightleftharpoons MO_{(g)}$$
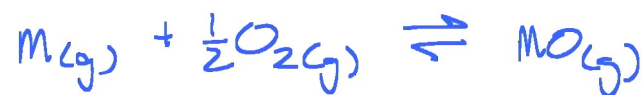
- Just as the case for the ideal gas reaction, we start with the Gibbs condition for equilibrium:

$$\Delta \overline{G}_{rxn} = \overset{products}{\sum_{i=1}} \mu_i v_i - \overset{reac\tan ts}{\sum_{j=1}} \mu_j v_j = 0$$

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

$$N_{MO}^{o,g} + RT\ln\frac{P_{mo}}{P^o} - \tfrac{1}{2}N_{O_2}^{o,g} - RT\ln\left(\frac{P_{O_2}}{p^o}\right)^{1/2} - N_m^{o,g} - RT\ln\left(\frac{P_m}{p^o}\right) = 0$$

$$\boxed{3} \; \Delta\overline{G}_{RXN}^o = RT\ln\left(\frac{\left(\frac{P_{O_2}}{p^o}\right)^{1/2}\left(\frac{P_m}{p^o}\right)}{\left(\frac{P_{mo}}{p^o}\right)}\right)$$

← RATIO OF 2 VERY TINY #'S!

- $\Delta \overline{G}_{rxn}^{o}$ 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:

$$\text{①} \quad N_M^{o,g} = N_M^{o,\text{SOLID }M} - RT \ln \frac{P_M}{P^o}$$

$$\text{②} \quad N_{MO}^{o,g} = N_{MO}^{o,\text{SOLID }MO} - RT \ln \frac{P_{MO}}{P^o}$$

PLUGGING INTO ③ !

$$N_{MO}^{o,\text{SOLID }MO} - RT \ln \frac{P_{MO}}{P^o} - \frac{1}{2} N_{O_2}^{o,g} - N_M^{o,\text{SOLID }M} + RT \ln \frac{P_M}{P^o} =$$

$$-RT \ln \frac{\left(\frac{P_{MO}}{P^o}\right)}{\left(\frac{P_M}{P^o}\right)\left(\frac{P_{O_2}}{P^o}\right)^{1/2}}$$

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_{O2} = 1 atm pressure), $\Delta \overline{G}_{rxn} = \Delta \overline{G}_{rxn,o}$. A plot of $\Delta \overline{G}_{rxn}$ vs. temperature, called an Ellingham diagram, can be used to predict the outcome of the reaction.

$$\Delta \overline{G}_{RXN}^o = N_{MO}^{o,\text{SOLID }MO} - \frac{1}{2} N_{O_2}^{o,g} - N_M^{o,\text{SOLID }M} = -RT \ln \frac{1}{\left(\frac{P_{O_2}}{P^o}\right)^{1/2}} = -RT \ln K_p$$

ONLY TRUE AT EQUILIBRIUM !

$$\Delta \overline{G}_{RXN} = \Delta \overline{G}_{RXN}^o + RT \ln \frac{1}{\left(\frac{P_{O_2}}{P^o}\right)^{1/2}}$$

An example calculation

- 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:
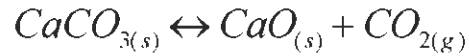
$$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$$

- 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:

$$\Delta \overline{G}^o_{f,CaCO_{3(s)}} = \mu^o_{CaCO_{3(s)}} = -1,084 kJ/mole \qquad \Delta \overline{G}^o_{f,CaO_{(s)}} = \mu^o_{CaO_{(s)}} = -603.3 kJ/mole$$

$$\Delta \overline{G}^o_{f,CO_{2(g)}} = \mu^o_{CO_{2(g)}} = -394.4 kJ/mole$$

- (Modified from Example 6.11 in Engel and Reid)

References

1.   Carter, W. C. (2002).
2.   Gaskell, D. R. Introduction to Metallurgical Thermodynamics (Hemisphere, New York, 1981).
3.   Dill, K. & Bromberg, S. Molecular Driving Forces (New York, 2003).