

# Thermodynamics of Materials

14th Lecture  
2007. 4. 28 (Monday)

## *FUGACITY*

$dG = VdP - SdT \rightarrow dG = VdP$  at constant  $T$   
For an ideal gas  $dG = (RT/P)dP = RT \ln P$

*This is true for ideal gases only, but it would be nice to have a similar form for real fluids.*

$dG = RT \ln f$  where  $f$  is the fugacity

$\phi = f/P \rightarrow 1$  as  $P \rightarrow 0$

$\phi$ : the fugacity coefficient,  $f = \phi P$

*Fugacity may be thought of as a thermodynamic pressure; it has units of pressure.*

## NON-IDEAL MIXTURES OF NON-IDEAL GASES

For a perfect gas mixture:

$$\mu_i = \mu_i^\circ + RT \ln P_i = \mu_i^\circ + RT \ln P_T + RT \ln X_i$$

For an ideal mixture of real gases:

$$\mu_i = \mu_i^\circ + RT \ln f_i = \mu_i^\circ + RT \ln f_i^\circ + RT \ln X_i$$

$$f_i = X_i f_i^\circ = X_i \phi_i P_T \quad \text{Lewis Fugacity Rule}$$

For a real mixture of real gases:

$$\mu_i = \mu_i^\circ + RT \ln f_i \quad f_i = X_i \chi_i f_i^\circ = X_i \chi_i \phi_i P_T$$

Correction for  
non-ideal mixing

Correction for  
non-ideal gas

equil. vapor pressure of pure A =  $p_A^\circ$

equil. vapor pressure of pure B =  $p_B^\circ$

mixture  $\rightarrow X_A, X_B$

*What would be the equil. vapor pressure of A and B for the mixture?*

$$p_A = X_A p_A^\circ$$

$\rightarrow$  Raoult's law

$$p_B = X_B p_B^\circ$$

$\rightarrow$  applicable when the magnitudes of the A-A, B-B, and A-B bond energies in the solution are identical.

$\rightarrow$  normally applicable when the concentration is high

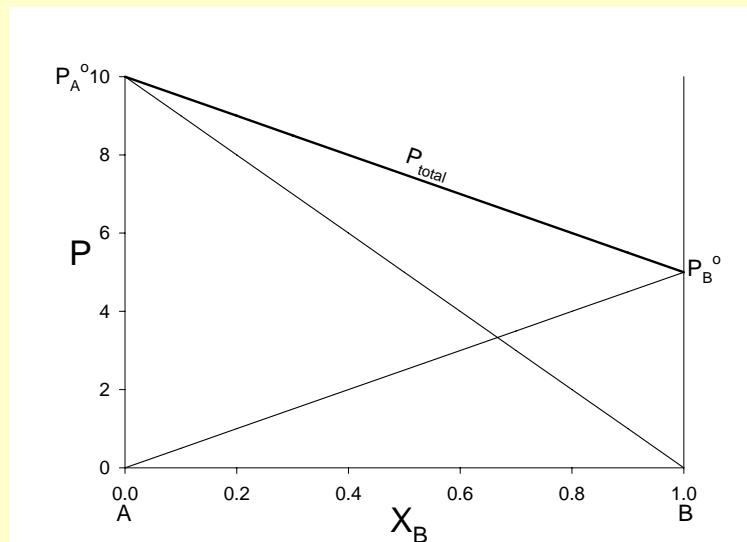
## RAOULT'S LAW

*Raoult (1887) studied vapor-liquid systems in which two or more liquid components were mixed in known proportions and the liquid was equilibrated with its own vapor. The composition of the vapor was then determined.*

*The total vapor pressure of the system was low, so the vapor behaved ideally and conformed to Dalton's law. In such systems, the partial pressures of the gaseous components were found to be a linear function of their mole fraction in the liquid.*

*For a binary system A-B,*

$$P_A = X_A \cdot P_A^\circ \quad \text{and} \quad P_B = X_B \cdot P_B^\circ$$



*Ideal solution*  $p_A = X_A p_A^\circ$ ,  $p_B = X_B p_B^\circ$

*How about non-ideal solution?*

case 1)  $|E_{A-B}| > |E_{A-A}|$  and  $|E_{A-B}| > |E_{B-B}|$

case 2)  $|E_{A-B}| < |E_{A-A}|$  and  $|E_{A-B}| < |E_{B-B}|$

*What would be the equil. vapor pressure of A and B?*

$$p_A = k_A X_A, p_B = k_B X_B$$

case 1)  $k_A < 1$  and  $k_B < 1 \rightarrow$  negative deviation

case 2)  $k_A > 1$  and  $k_B > 1 \rightarrow$  positive deviation

$\rightarrow$  Henry's law  $\rightarrow$  applicable to dilute solution

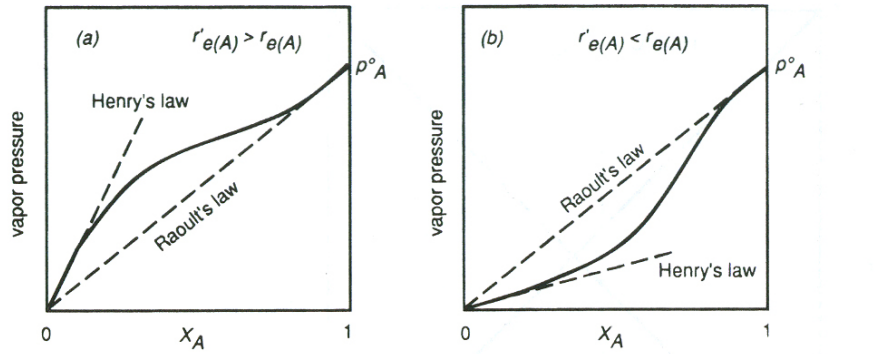
## HENRY'S LAW

Henry (1803) was studying the solubility of gases in liquids. He found that the amount of gas dissolved in a liquid in contact with it was directly proportional to the pressure on the gas, i.e.,

$$P_i = K_i \cdot X_i$$

**$K_i$  is a constant called the Henry's Law constant.**

***This law holds only at relatively low values of  $P_i$ .***



**Figure 9.2** (a) The vapor pressure of a component of a binary solution which exhibits positive deviation from Raoultian behavior. (b) The vapor pressure of a component of a binary solution which exhibits negative deviation from Raoultian behavior.

### Activity

*The activity of a component in any state at T is formally defined as being the ratio of the fugacity of the substance in that state to its fugacity in its standard states, i.e. for the species or substance i,*

$$a_i = \frac{f_i}{f_i^o}$$

*In a condensed solution,  $f_i$  is the fugacity at T and  $f_i^o$  is the fugacity of pure i (the standard state) at T.*

*If the vapor in equilibrium with the condensed solution is ideal, then  $f_i = p_i$*

$$a_i = \frac{p_i}{p_i^o}$$

## Activity

If the vapor in equilibrium with the condensed solution is ideal, then  $f_i = p_i$

$$a_i = \frac{p_i}{p_i^0}$$

If the component  $i$  exhibits Raoultian (ideal) behavior,

$$p_i = X_i p_i^0 \quad a_i = X_i$$

If the component  $i$  exhibits Henryian behavior,

$$a_i = k_i X_i$$

## Activity of Real Systems

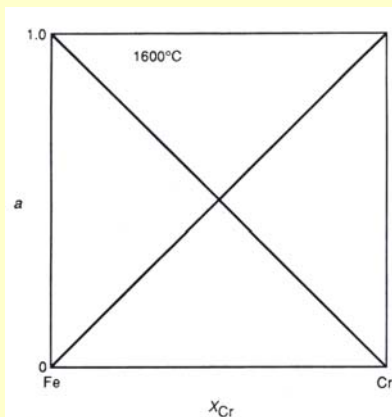


Figure 9.3 Activities in the binary system iron-chromium at 1600°C

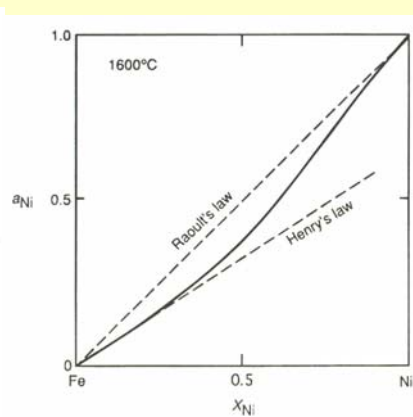
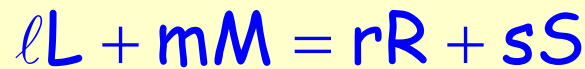


Figure 9.4 The activity of nickel in the system iron-nickel at 1600°C

**Gaskell**

Derive  $\Delta\mu$  for the following reaction in terms of standard Gibbs free energy and activities.



$$\Delta\mu = (r\mu_R + s\mu_S) - (\ell\mu_L + m\mu_M)$$

$$\mu_k = \mu_k^\circ + RT \ln a_k = G_k^\circ + RT \ln a_k$$

$$\Delta\mu = (r(G_R^\circ + RT \ln a_R) + s(G_S^\circ + RT \ln a_S)) - (\ell(G_L^\circ + RT \ln a_L) + m(G_M^\circ + RT \ln a_M))$$

$$\begin{aligned} &= (rG_R^\circ + sG_S^\circ - (\ell G_L^\circ + mG_M^\circ)) + \\ & (rRT \ln a_R + sRT \ln a_S - (\ell RT \ln a_L + mRT \ln a_M)) \\ &= (rG_R^\circ + sG_S^\circ - (\ell G_L^\circ + mG_M^\circ)) + \left( RT \ln \frac{a_R^r a_S^s}{a_L^\ell a_M^m} \right) \end{aligned}$$

$$= \Delta G^\circ + \left( RT \ln \frac{a_R^r a_S^s}{a_L^\ell a_M^m} \right)$$

$$\Delta G^\circ \equiv (rG_R^\circ + sG_S^\circ - (\ell G_L^\circ + mG_M^\circ)) = \Delta\mu^\circ$$

→ standard Gibbs free energy *Gaskell, Table A-1*

⇒ used for irreversibility of chemical reactions

$$\Delta\mu = \Delta G^\circ + \left( RT \ln \frac{a_R^r a_S^s}{a_L^l a_M^m} \right)$$

$$\Delta\mu = \Delta G = \Delta G^\circ + RT \ln Q$$

$$Q \equiv \frac{a_R^r a_S^s}{a_L^l a_M^m} : \text{proper quotient of activities for the reaction}$$

$$Q < \exp\left(-\frac{\Delta G^\circ}{RT}\right) \rightarrow \text{irreversible reaction}$$

$$\Delta\mu = 0 \text{ at equilibrium}$$

$$\Delta\mu = 0 = \Delta G^\circ + RT \ln Q_{\text{equil}}$$

$$Q_{\text{equil}} = \left( \frac{a_R^r a_S^s}{a_L^l a_M^m} \right)_{\text{equil}} \equiv K \rightarrow \text{Equilibrium Constant}$$

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

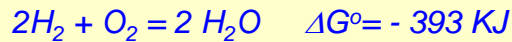
$$\Delta\mu = \Delta G = RT \ln \frac{Q}{K}$$



Ex. A gas mixture at one atmosphere total pressure has the following mole fraction:

$$X_{H_2} = 0.01, X_{O_2} = 0.03, X_{H_2O} = 0.96$$

At 700°C, for the reaction



(a) Determine the direction of spontaneous change for this system

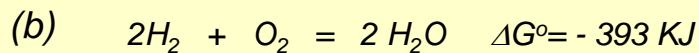
(b) Determine the equilibrium fraction (composition).

(a)

$$K = e^{-(\Delta G^\circ / RT)} = e^{-(-393,000 / 8.314 \cdot 973)} = 1.25 \times 10^{21}$$

$$Q = \frac{a_{H_2O}^2}{a_{H_2}^2 a_{O_2}} = \frac{X_{H_2O}^2}{X_{H_2}^2 X_{O_2}} = \frac{(0.96)^2}{(0.01)^2 (0.03)} = 3.1 \times 10^5$$

$$\Delta\mu = \Delta G = RT \ln \frac{Q}{K} \quad \therefore \text{Forward reaction}$$



$$0.01-2x \quad 0.03-x \quad 0.96+2x$$

$$K = \frac{(0.96 + 2x)^2}{(0.01 - 2x)^2 (0.03 - x)} = 1.25 \times 10^{21} \quad x \approx 0.005$$

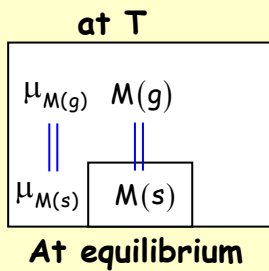
$$X_{H_2} = 0, X_{O_2} = 0.0251, X_{H_2O} = 0.9749$$

**For a system of a condensed phase and a gas phase**

$$\begin{aligned}\mu_{M(s)}(T, P_o) &= \mu_{M(g)}(T, P_{M(g)}^o) + RT \ln(P_{M(g)}/P_{M(g)}^o) \\ &= \mu_{M(g)}(T, P_{M(g)}^o) + RT \ln P_{M(g)} \quad \because P_{M(g)}^o = 1\end{aligned}$$

$$d\mu_i|_{T, n_i} = \bar{V}_i dP \quad \mu_i(T, P) = \mu_i(T, P_o) + \int_{P_o}^P \bar{V}_i dP$$

$\ll 1$



$$\therefore \mu_i(T, P) \cong \mu_i(T, P_o) \quad (+RT \ln a_i = 0, a_i = 1)$$

$T, P_o = 1 \text{ atm} : \text{STD}$

$$\mu_{M(s)}(T, P) = \mu_{M(g)}(T, P)$$

$$\therefore \mu_{M(s)} \cong \mu_{M(s)}^o = \mu_{M(g)}^o + RT \ln P_{M(g)}$$

$$\mu_{M(s)} = \mu_{M(s)}^o + RT \ln a_{M(s)}$$

$$\mu_{M(s)} = \mu_{M(g)}^o + RT \ln P_{M(g)}$$

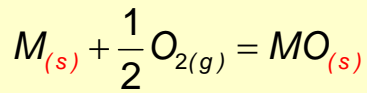
$\mu_{M(s)}^o$  ≡ standard state로 할 때는

→ activity = 1

$\mu_{M(g)}^o$  ≡ standard state로 할 때는

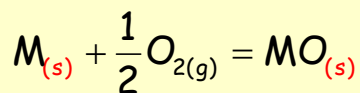
→ activity = equilibrium vapor pressure

Derive the expression for irreversibility in the case of



$$\bar{G}_M(\text{in the gas phase}) = G_M(\text{in the solid metal phase})$$

$$\bar{G}_{MO}(\text{in the gas phase}) = G_{MO}(\text{in the solid oxide phase})$$



$$\Delta G = G_{MO(s)}^\circ + RT \ln a_{MO(s)} - \frac{1}{2} G_{O_2(g)}^\circ - RT \ln P_{O_2}^{1/2} - G_{M(s)}^\circ - RT \ln a_{M(s)} = 0$$

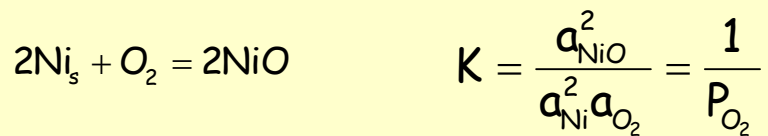
$$\Delta G^\circ = G_{MO(s)}^\circ - \frac{1}{2} G_{O_2(g)}^\circ - G_{M(s)}^\circ = -RT \ln \frac{a_{MO(s)}}{P_{O_2}^{1/2} a_{M(s)}}$$

$$\Delta G^\circ = -RT \ln \frac{1}{P_{O_2}^{1/2}} \quad \because \text{solid를 standard state로 선택할 때는 } a_{MO(s)} = 1, a_{M(s)} = 1$$

$$\Delta G^\circ = -RT \ln \frac{1}{P_{O_2}^{1/2}} = RT \ln P_{O_2} = -RT \ln K$$

Ex) The standard Gibbs free energy change for the reaction of  $2\text{Ni}_s + \text{O}_2 = 2\text{NiO}$  is  
 $\Delta G^\circ = -471,200 + 172 T$  (J)  $298 < T < 1726$ .

Find the maximum oxygen partial pressure to avoid the oxidation of nickel at 1500 K.



$$\Delta G^\circ = -RT \ln K = RT \ln P_{\text{O}_2}$$

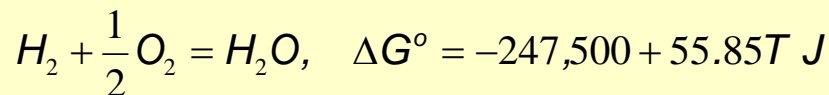
$$\Delta G_{1500\text{K}}^\circ = -213200 \text{ (J)} = RT \ln P_{\text{O}_2} = 8.314 \cdot 1500 \ln P_{\text{O}_2}$$

$$P_{\text{O}_2} = 3.76 \times 10^{-8} \text{ (atm)}$$

*How can we make  $P_{\text{O}_2} < 10^{-10}$  atm or  $10^{-20}$  atm?  
 How can we control  $P_{\text{O}_2}$ ?*

*→ Equilibrium in  $\text{H}_2\text{O}-\text{H}_2$  and  $\text{CO}_2-\text{CO}$  Mixtures*

*Determine the ratio of  $P_{\text{H}_2\text{O}}$  to  $P_{\text{H}_2}$  to make  
 $P_{\text{O}_2} = 10^{-10}$  atm at 2000 K.*



$$\ln K = \frac{247,500}{8.3144T} - \frac{55.85}{8.3144} = 8.167 \text{ at } 2000 \text{ K}$$

$$K = 3.521 \times 10^3 = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}} \quad \text{with } P_{O_2} = 10^{-10} \text{ atm,}$$

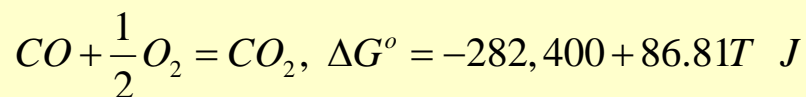
$$\frac{P_{H_2O}}{P_{H_2}} = 3.521 \times 10^3 \times 10^{-5} = 3.521 \times 10^{-2}$$

*How can you prepare this condition in the laboratory?*

*If  $P_{H_2} = 1 \text{ atm}$ ,  $P_{H_2O}$  must be  $0.0352 \text{ atm}$ .  
 $0.0352 \text{ atm}$  is the saturated vapor pressure  
of water at  $27.0^\circ\text{C}$ .*

*→ bubbling hydrogen gas at  $1 \text{ atm}$  pressure  
through pure liquid water at  $27^\circ\text{C}$ .*

*How can you make  $P_{O_2} = 10^{-20} \text{ atm}$  at  $1000 \text{ K}$ ?*



*Determine the ratio of  $P_{CO_2}$  to  $P_{CO}$  to make  
 $P_{O_2} = 10^{-20} \text{ atm}$  at  $1000 \text{ K}$ .*

$$\ln K = \frac{282,400}{8.3144T} - \frac{86.81}{8.3144} = 23.52 \text{ at } 1000 \text{ K}$$

with  $P_{O_2} = 10^{-20}$  atm,

$$K = 1.646 \times 10^{10} = \frac{P_{CO_2}}{P_{CO} P_{O_2}^{1/2}} = \frac{P_{CO_2}}{P_{CO} \times 10^{-10}}$$

$$\frac{P_{CO_2}}{P_{CO}} = 1.646 \quad P = 1 \text{ atm} = P_{CO_2} + P_{CO}$$

$$P_{CO_2} = 0.622 \text{ atm}, P_{CO} = 0.378 \text{ atm}$$

## Thermodynamics of Chemical Vapor Deposition

**How do we define the irreversibility  
criterion for deposition in CVD?**

**How about in PVD?**