Chapter 9.   Behavior of Solutions

§ 9-1 Introduction

1. Mixing of real gases:

   T , P , $\Rightarrow$ Ideal gas mixture.

2. Condensed phases (Liquid or Solid solution)
   - Strong interaction between atoms.
   - Solid solubility depends on: 1) atomic size ratio

     2) electronegativity

     3) e/a ratio (valence)

§ 9-2 Raoult's Law and Henry's Law

1. Pure A liquid (solid)

   At temperature T, saturated vapor pressure : p_A^o

   Rate of evaporation : $r_e(A)$

   Condensation rate : $r_c(A) = k\,p_A^o$

   At equilibrium : $r_e(A) = r_c(A) = k\,p_A^o$

2. Pure B liquid or solid: $r_e(B) = r_c(B) = k^{'}\,p_B^o$

3. Liquid + small amount of B

   At T, saturated vapor pressure : p_A , p_B

   Condensation rate of A, B : $r_c(A) = k\,p_A$, $r_c(B) = k^{'}\,p_B$

   Assumptions: evaporation of A, B are independent of composition.

   i.e. same bond energy: $E_{AA} = E_{BB} = E_{AB}$ (ideal case)

   surface composition = bulk composition

   Fraction of surface occupied by A $= X_A$

   Evaporation rate of A: $r_e(A)$ X_A

   At equilibrium : $r_e(A)$ $X_A = r_c(A) = k\,p_A$

   $k\,p_A^o$ $X_A = k\,p_A$

   $$\begin{cases} p_A = X_A p_A^o \\ p_B = X_B p_B^o \end{cases} \Rightarrow \text{Raoult 's Law}$$

4. If E_{AB} is more negative, and A (solute) in B (solvent), A is surrounded by B

$\Rightarrow r_e(A) \qquad r_e^{'}(A)$

$r_e^{'}(A) \qquad r_e(A)$

$r_e^{'}(A) \quad X_A = r_c(A) = k\,p_A$

$$\frac{r_e^{'}(A)\cdot X_A}{r_e(A)} = \frac{k\,p_A}{k\,p_A^o}$$

$$p_A = \frac{r_e^{'}(A)}{r_e(A)} \quad X_A \qquad p_A^o$$

$\begin{cases} p_A = \gamma_A \quad X_A \qquad p_A^o \qquad \text{(eq.1)} \\[2em] p_B = \gamma_B \quad X_B \qquad p_B^o \qquad \text{(eq.2)} \end{cases} \Rightarrow \text{Henry's Law}$

$\gamma_A \quad$ 1 and indep. of comp. $\quad \gamma_A = \text{constant}$

$\gamma_B \quad$ 1 and indep. of comp. $\quad \gamma_B = \text{constant}$

- When X_A ; at same point, A is not only surrounded by B, then

  $r_e^{'}(A)$ varies with composition

  γ_A is not a constant (it depends on composition)

- (eq.1) is obeyed only over an initial range of concentration of A dissolved in B
- (eq.2) is obeyed only over an initial range of concentration of B dissolved in A

  $\gamma_A \quad 1, \quad \gamma_B \quad 1 \quad \Leftrightarrow \quad$ negative deviation

- If E_{AB} is less negative, then $r_e^{'}(A) \qquad r_e(A)$

$$\frac{r_e^{'}(A)}{r_e(A)} = \gamma_A \quad 1 \quad \Leftrightarrow \quad \text{positive deviation.}$$

§ 9-3 Activity of a component in solution

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

If the vapor is ideal gas, $f_i = p_i$

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

Raoult's Law

$$\begin{cases} p_A = X_A \quad p_A^o , \quad a_A = X_A \\ p_B = X_B \quad p_B^o , \quad a_B = X_B \end{cases}$$

Raoult's Law: $a_i = X_i , \quad \gamma_i = 1$

Henry's Law $\begin{cases} p_A = \gamma_A \quad X_A \quad p_A^o, \quad a_A = \gamma_A \quad X_A \\ p_B = \gamma_B \quad X_B \quad p_B^o, \quad a_B = \gamma_B \quad X_B \end{cases}$

Henry's Law: $a_i = \gamma_i X_i \quad \gamma_i \quad 1$

and γ_i is a constant, indep. of composition.

§ 9-4 Gibbs-Duhem Equation

In a solution: ($n_i + n_j + n_k + \ldots\ldots$)

$Q' = Q'(T, P, n_i, n_j, n_k \ldots\ldots..)$, at constant T, P :

$$d\,Q' = \left(\frac{\partial \mathbf{Q}'}{\partial \mathbf{n_i}} \right)_{\mathbf{T,P,n_{j..}\ldots}} \cdot \mathbf{dn_i} + \left(\frac{\partial \mathbf{Q}'}{\partial \mathbf{n_j}} \right)_{\mathbf{n_i,T,P,\ldots}} \cdot \mathbf{dn_j} + \cdots\cdots$$

$$\overline{Q_i} \equiv \left(\frac{\partial Q'}{\partial n_i} \right)_{T,P,n_{j}\ldots} , \quad \text{Partial Molar Quantity}$$

$$d\,Q' = \overline{Q_i}\,dn_i + \overline{Q_j}\,dn_j + \overline{Q_k}\,dn_k + \ldots\ldots\ldots$$

$$Q' = n_i\,\overline{Q_i} + n_j\,\overline{Q_j} + \ldots\ldots\ldots\ldots$$

$$d\,Q' = (\overline{Q_i}\,dn_i + \overline{Q_j}\,dn_j + \ldots\ldots..) + (n_i\,d\overline{Q_i} + n_j\,d\overline{Q_j} + \ldots\ldots..)$$

$$n_i\,d\overline{Q_i} + n_j\,d\overline{Q_j} + \ldots\ldots = 0$$

or $\begin{cases} \sum \mathbf{n_i d\overline{Q_i}} = 0 \\ \sum \mathbf{X_i d\overline{Q_i}} = 0 \end{cases}$ $\Rightarrow$ Gibbs–Duhem Eq.

§ 9-5 Gibbs Free Energy of a Binary Solution

1.

2. $\begin{cases} \text{Molar Gibbs free energy: (G)} \\ \text{Partial molar Gibbs free energy: (} \overline{G_A}, \overline{G_B} \text{)} \end{cases}$

$G' = n_A \overline{G_A} + n_B \overline{G_B}$

or $G = X_A \overline{G_A} + X_B \overline{G_B}$ ....(1)

$dG = (X_A d\overline{G_A} + X_B d\overline{G_B}) + (\overline{G_A} dX_A + \overline{G_B} dX_B)$

$dG = \overline{G_A} dX_A + \overline{G_B} dX_B$

$X_A + X_B = 1 \quad dX_A = - dX_B$

$dG = \overline{G_A} dX_A - \overline{G_B} dX_A = (\overline{G_A} - \overline{G_B}) dX_A$

$\dfrac{dG}{dX_A} = \overline{G_A} - \overline{G_B}$

$X_B \dfrac{dG}{dX_A} = X_B \overline{G_A} - X_B \overline{G_B}$ ....(2)

(1)+(2) $\quad G + X_B \dfrac{dG}{dX_A} = (X_A + X_B)\overline{G_A} = \overline{G_A}$

$\begin{cases} \overline{G_A} = G + (1 - X_A)\dfrac{dG}{dX_A} \\ \overline{G_B} = G + (1 - X_B)\dfrac{dG}{dX_B} \end{cases}$

2. $\Delta G^M (\Delta \overline{G_i^M})$:

change in Gibbs Free Energy due to formation of solution

* one mole pure i (p_i^o) $\Rightarrow$ solution (p_i)

$\Delta G_i = G_{i \ (solution)} - G_{i \ (pure)} = RT \ln\left(\dfrac{p_i}{p_i^o}\right)$

$\therefore \quad \Delta G_i = RT \ln a_i$

$$\begin{cases} \overline{G_i} = G_{i\ (solution)}, \quad G_i^{\,o} = G_{i\ (pure)} \\ \\ \Delta G_i = \Delta \overline{G_i^M} = \overline{G_i} - G_i^{\,o} \end{cases}$$

$$\therefore \quad \boxed{\Delta \overline{G_i^M} = \overline{G_i} - G_i^{\,o} = RT \ln a_i}$$

$*(n_A + n_B)$ at constant T , P

Before mixing , $\quad G'_{before} = n_A G_A^o + n_B G_B^o$

After mixing , $\quad G'_{after} = n_A \overline{G_A} + n_B \overline{G_B}$

$$\Delta G'^M = (n_A \overline{G_A} + n_B \overline{G_B}) \quad (n_A G_A^o + n_B G_B^o)$$

$$= n_A (\overline{G_A} - G_A^o) + n_B (\overline{G_B} - G_B^o)$$

$$\Delta G'^M = n_A \Delta \overline{G_A}^M + n_B \Delta \overline{G_B}^M$$

or $\Delta G'^M = RT(n_A \ln a_A + n_B \ln a_B)$

Total one mole: $\quad X_A + X_B = 1$

$$\begin{cases} \Delta G^M = X_A \Delta \overline{G_A}^M + X_A \Delta \overline{G_B}^M \\ \\ or \quad \Delta G^M = RT(X_A \ln a_A + X_B \ \ln a_B) \end{cases}$$

3. Method of Tangential Intercept ($\quad \Delta \overline{G_A}^M , \Delta \overline{G_B}^M$)

Given $\Delta G^M (X_B) \quad \Rightarrow \quad$ solve $\Delta \overline{G_A}^M$ and $\Delta \overline{G_B}^M$

$\Theta \quad \overline{G_A} = G + (1 - X_A) \dfrac{dG}{dX_A}$

$\quad \overline{G_B} = G + (1 - X_B) \dfrac{dG}{dX_B}$

$\therefore \quad \Delta \overline{G_A} = \Delta G^M + (1 - X_A) \dfrac{d\Delta G^M}{dX_A}$ ....(1)

$\quad \Delta \overline{G_B} = \Delta G^M + (1 - X_B) \dfrac{d\Delta G^M}{dX_B}$ ....(2)
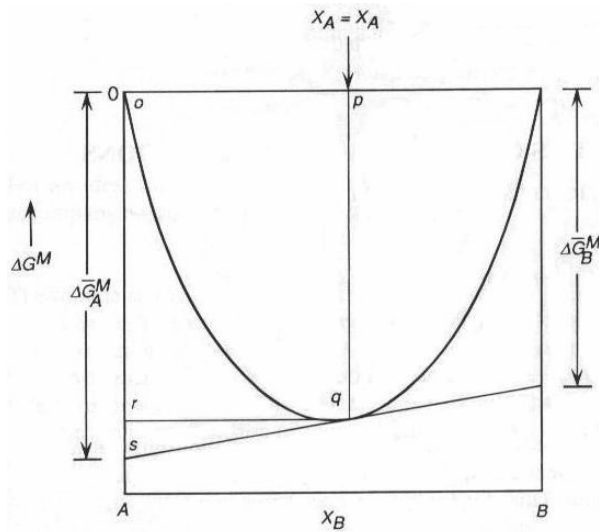
Given $\Delta G^M (X_B)$, Fig . 9-1

Figure 9.1 The variation , with composition , of the molar Gibbs free energy of formation of a binary solution

At composition $X_B = X_B^o = op$, $\Delta G^M = pq = uw$

Tangent at q , slope $= \dfrac{d\Delta G^M}{dX_B} = \dfrac{rs}{rq} = \dfrac{vw}{qw}$

From (2) $\Delta \overline{G}_B = pq + (1 - X_B^o)\dfrac{vw}{qw} = uw + qw\dfrac{vw}{qw} = uw + vw$

$= (uw \quad vw) = uv$

$= $ tangential intercept at $X_B = 1$

From (1) $\Delta \overline{G}_A = pq + (1 - X_A^o)\dfrac{d\Delta G^M}{dX_A} = pq \quad X_B^o \dfrac{d\Delta G^M}{dX_B}$

$= pq \quad rq\dfrac{rs}{rq} = (pq + rs) = (or + rs) = os$

$= $ tangential intercept at $X_A = 1, (X_B = 0)$

§9-6 Properties of Ideal Solution

1. Ideal solution (Raoultian Solution)

$a_i = X_i \quad \gamma_i = 1$

$\Delta G^{M,id} = RT(X_A \ln X_A + X_B \quad \ln X_B)$

$\begin{cases} \overline{\Delta G_A}^{M,id} = RT \ln X_A \\[2em] \overline{\Delta G_B}^{M,id} = RT \ln X_B \end{cases}$

2. $\Delta V^{M,id}=0$, $\Delta\overline{V}_i^{M,id}=0$, $(\overline{V}_i=V_i^o$)

$$\Theta \left(\frac{\partial G}{\partial P}\right)_{T,comp}=V, \qquad \therefore \left(\frac{\partial \overline{G}_i}{\partial P}\right)_{T,comp}=\overline{V}_i$$

$$\therefore \left[\frac{\partial\left(\overline{G}_i-G_i^o\right)}{\partial P}\right]_{T,comp}=(\overline{V}_i-V_i^o$$)

i.e. $$\left[\frac{\partial\Delta\overline{G}_i^M}{\partial P}\right]_{T,comp}=\Delta\overline{V}_i^M$$

$$\Theta \quad \Delta\overline{G}_i^M=RT\ln a_i=RT\ln X_i$$

$$\therefore \Delta\overline{V}_i^M=0, \quad i.e. \quad \overline{V}_i=V_i^o$$

$$\therefore \Delta V^{M,id}=\sum X_i \Delta\overline{V}_i^M=X_A\Delta\overline{V}_A^M+X_B\Delta\overline{V}_B^M=0$$

3. $\Delta H^{M,id}=0$, $\Delta\overline{H}_i^{M,id}=0$ $(\overline{H}_i=H_i^o)$

$$\Theta \quad \left[\frac{\partial(G/T)}{\partial T}\right]_{P,comp}=\frac{H}{T^2}$$

$$\therefore \left[\frac{\partial\left(\overline{G}_i/T\right)}{\partial T}\right]_{P,comp}=\frac{\overline{H}_i}{T^2}$$

$$\therefore \left[\frac{\partial\left(\dfrac{\overline{G}_i-G_i^o}{T}\right)}{\partial T}\right]_{P,comp}=-\frac{\left(\overline{H}_i-H_i^o\right)}{T^2}$$

$$\therefore \left[\frac{\partial\left(\Delta\overline{G}_i^M/T\right)}{\partial T}\right]_{P,comp}=-\frac{\Delta\overline{H}_i^M}{T^2}$$

$$\Theta \quad \Delta\overline{G}_i^M=RT\ln a_i=RT\ln X_i$$

$$\therefore \left[\frac{\partial(R\ln X_i)}{\partial T}\right]_{P,comp}=0$$

$$\Delta\overline{H}_i^M = 0, \quad (\overline{H}_i = H_i^o)$$

$$\therefore \Delta H^{M,id} = \sum X_i \Delta\overline{H}_i^M = 0$$

4. $\left\{\begin{array}{l} \Delta S^{M,id} = R(X_A \ln X_A + X_B \ln X_B) \\ \Delta\overline{S}_i^{M,id} = R \ln X_i \end{array}\right.$

$\Theta \quad \left(\dfrac{\partial G}{\partial T}\right)_{P,comp} = S \qquad \left[\dfrac{\partial(\Delta G^M)}{\partial T}\right]_{P,comp} = \Delta S^M$

$\Theta \quad \Delta G^{M,id} = RT \sum X_i \ln X_i = RT(X_A \ln X_A + X_B \ln X_B)$

$\therefore \Delta S^{M,id} = R \sum X_i \ln X_i = R(X_A \ln X_A + X_B \ln X_B)$

$\Theta \quad \Delta S^M = \sum X_i \Delta\overline{S}_i^M = (X_A \Delta\overline{S}_A^M + X_B \Delta\overline{S}_B^M)$

$\therefore \quad \Delta\overline{S}_A^{M,id} = R \ln X_A \quad , \quad \Delta\overline{S}_B^{M,id} = R \ln X_B$

Notes: (1) $\Delta S^{M,id}$ is indep. of temperature

      (2) $\Delta S^{M,id}$ is the entropy increase due to configurational entropy change

        $\otimes$ consider: (N_A A atoms + N_B B atoms)

$$\therefore \Delta S'_{conf.} = k \ln \frac{(N_A + N_B)!}{N_A! N_B!}$$

$$= k[\ln(N_A + N_B)! - \ln N_A! - \ln N_B!]$$

$$= k[(N_A + N_B)\ln(N_A + N_B) - (N_A + N_B)]$$

$$(N_A \ln N_A \quad N_A) \quad (N_B \ln N_B \quad N_B)$$

$$= k\left[N_A \ln\left(\frac{N_A}{N_A + N_B}\right) + N_B \ln\left(\frac{N_B}{N_A + N_B}\right)\right]$$

$\Theta \quad \dfrac{N_A}{N_A + N_B} = X_A \quad , \quad \dfrac{N_B}{N_A + N_B} = X_B$

$\therefore \Delta S'_{conf.} = k(N_A + N_B)[X_A \ln X_A + X_B \ln X_B] \qquad \Theta \dfrac{(N_A + N_B)}{N_o} = n$

$$\therefore \Delta S'_{conf.} = nN_o k(X_A \ln X_A + X_B \ln X_B) = nR(X_A \ln X_A + X_B \ln X_B)$$

one mole $\therefore \Delta S_{conf.} = R(X_A \ln X_A + X_B \ln X_B) = \Delta S^{M,id}$

§ 9-7 Nonideal solution

Activity coefficient: $\gamma_i = \dfrac{a_i}{X_i}$

$\begin{cases} \gamma_i = 1 & \text{, ideal solution} \\ \gamma_i \neq 1 & \text{, nonideal solution} \end{cases}$ $\quad \gamma_i \quad 1$: positive deviation

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad \gamma_i \quad 1$: negative deviation

$$\Theta \left[\frac{\partial \left(\Delta \overline{G}_i^M / T \right)}{\partial T} \right]_{P,Comp} = \frac{-\Delta \overline{H}_i^M}{T^2}$$

$$\Delta \overline{G}_i^M = RT \ln a_i = RT \left(\ln \gamma_i + \ln X_i \right)$$

$$d\left(\frac{1}{T} \right) = \frac{-dT}{T^2}$$

$$\therefore \left[\frac{\partial \left(\Delta \overline{G}_i^M / T \right)}{\partial (1/T)} \right]_{P,Comp} = \Delta \overline{H}_i^M$$

$$\therefore \boxed{\left[\frac{\partial \left(R \ln \gamma_i \right)}{\partial (1/T)} \right]_{P,Comp} = \Delta \overline{H}_i^M}$$

Notes : (1) If γ_i = constant (indep. of T) , $\Delta \overline{H}_i^M = 0$

$\qquad$ If $\gamma_i(T) \quad \Delta \overline{H}_i^M \neq 0$

(2) $T \uparrow \Rightarrow$ Nonideal solution $\rightarrow$ ideal solution ($\gamma_i \rightarrow 1$)

(3) $\otimes$ Positive deviation : $\quad \gamma_i \quad 1$

$\qquad$ when $T \uparrow$, $\left(\dfrac{1}{T} \right) \downarrow \Rightarrow \gamma_i \rightarrow 1$, $\quad \therefore \gamma_i \downarrow$

$\qquad \therefore \left(\dfrac{d\gamma_i}{dT} \right) < 0$

$\qquad \therefore \Delta \overline{H}_i^M = \left[\dfrac{\partial \left(R \ln \gamma_i \right)}{\partial (1/T)} \right]_{P,Comp} > 0$

$\therefore$ Mixing process is endothermic.

$\otimes$ negative deviation : $\gamma_i \quad 1$

$$\left(\frac{d\gamma_i}{dT}\right)>0, \qquad \Delta\overline{H}_i^M < 0$$

∴ Mixing process is exothermic.

(4) ⊗ Positive deviation : γ_i 1 , $\left(\dfrac{d\gamma_i}{dT}\right)<0$

endothermic : $\Delta\overline{H}_i^M > 0$

i.e. A-B bond energy is less negative

∴ E_{AA} , E_{BB} more negative ⇒ clustering

⊗ negative deviation : γ_i 1 , $\Delta\overline{H}_i^M < 0$, $\left(\dfrac{d\gamma_i}{dT}\right)>0$

A-B bond energy is more negative

⇒ ordering , (formation of compound)

§ 9-8 Applications of Gibbs-Duhem Equation

1. Given $a_B(X_B)$,   calculate a_A

● In a binary solution , usually only activity of one component is measured , the other can be calculated.

$$\sum X_i d\overline{Q}_i = 0$$

$$X_A d\Delta\overline{G}_A^M + X_B d\Delta\overline{G}_B^M = 0, \qquad \Delta\overline{G}_i^M = RT \ln a$$

∴ $X_A d \ln a_A + X_B d \ln a_B = 0$

$$d \ln a_A = \frac{X_B}{X_A} d \ln a_B$$

∴ $\ln a_A$ (at X_A) $= \displaystyle\int_{\ln a_B \ at \ X_{A=1},X_B=0}^{\ln a_B \ at \ X_A} \left(\frac{X_B}{X_A}\right) d \ln a_B$, Fig . 9-2
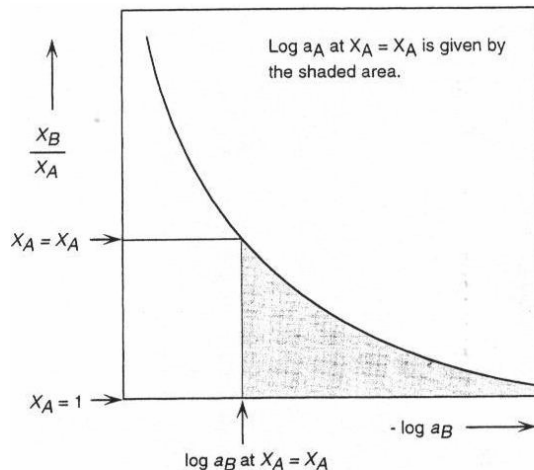

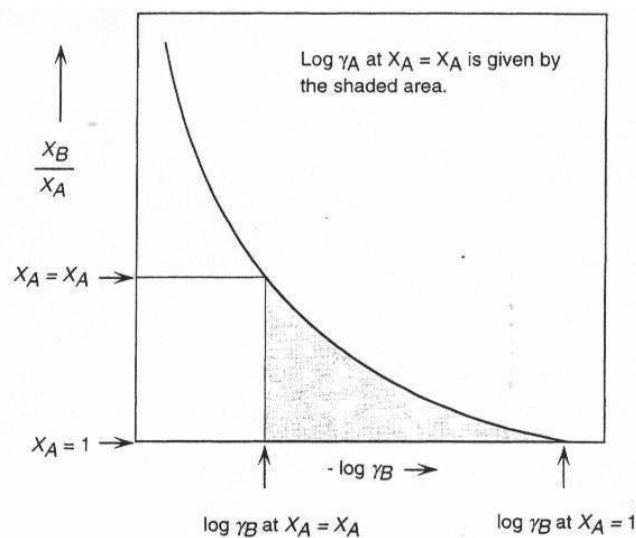Figure 9.2   A schematic representation of the variation of log a_B with X_B/X_A in a binary solution, and illustration of the application of the Gibbs-Duhem equation to calculation of the activity of component A

Note:

$$\text{(1) } X_B \rightarrow 1, \quad \left(\frac{X_B}{X_A}\right) \rightarrow \infty, \quad a_B \rightarrow 1 \quad \therefore \ln a_B \rightarrow 0$$

$$\text{(2) } X_B \rightarrow 0, \quad \left(\frac{X_B}{X_A}\right) \rightarrow 0, \; a_B \rightarrow 0 \quad \therefore \ln a_B \rightarrow \quad \infty, \quad \ln a_B \rightarrow +\infty$$

$\therefore$ two tails exist $\Rightarrow$ error in integrated area $\Rightarrow$ eliminate tail error by using $?_B$

Θ $X_A + X_B = 1$

$dX_A + dX_B = 0$

$$X_A \frac{dX_A}{X_A} + X_B \frac{dX_B}{X_B} = 0$$

$\therefore$ $X_A \, d \ln X_A + X_B \, d \ln X_B = 0$

Θ $X_A \, d \ln a_A + X_B \, d \ln a_B = 0$

$(X_A \, d \ln {}_A + X_B \, d \ln {}_B) + (X_A \, d \ln X_A + X_B \, d \ln X_B) = 0$

$\therefore (X_A \, d \ln {}_A + X_B \, d \ln {}_B) = 0$

$$d \ln {}_A = \left(\frac{X_A}{X_B}\right) d \ln {}_B$$

$$\therefore \ln {}_A (\text{at } X_A) = \int_{\ln r_B \text{ at } X_A=1, X_B=0}^{\ln r_B \text{ at } X_A} \left(\frac{X_B}{X_A}\right) d \ln \gamma_B$$

when $X_B \rightarrow 0$, $\left(\frac{X_B}{X_A}\right) \rightarrow 0$, ${}_B \rightarrow$ constant, $\ln {}_B \rightarrow$ constant, Fig . 9-3.

Figure 9.3   A schematic representation of the variation of log γ_B with X_B/X_A in a binary solution, and illustration of the application of the Gibbs-Duhem equation to calculation of the activity coefficient of component A

- The 2nd tail is eliminated by a-function

Define $\quad a_i \equiv \dfrac{\ln \gamma_i}{(1-X_i)^2}$

When $X_B \to 1$, $\quad_B \to 1$, $\ln \quad_B \to 0$ and $(1\text{-}X_B)\quad 0 \Rightarrow a_B$ is finite.

$\therefore$ Given $a_B \Rightarrow$ calculate $\quad_A$, a_A

$\ominus \quad a_B = \dfrac{\ln \gamma_B}{X_A^{\,2}}$

$\therefore \quad \ln \gamma_B = a_B X_A^2$

$d \ \ln \gamma_B = 2 a_B \ X_A d X_A + X_A^2 d a_B$

$\therefore \quad d \ \ln \gamma_A = \left(\dfrac{X_B}{X_A}\right) d \ \ln \gamma_B$

$\qquad = \left(\dfrac{X_B}{X_A}\right)(2 a_B \ X_A d X_A + X_A^2 d a_B \ )$

$\qquad = 2 X_B \ a_B d X_A \quad X_B \ X_A d a_B$

$\therefore \quad \ln \gamma_A = \displaystyle\int_{X_A=1}^{X_A} 2 X_B \ a_B d X_A \quad \int_{a_B \ at \ X_A=1}^{a_B} X_B X_A d a_B$

$\ominus \displaystyle\int d(xy) = \int y dx + \int x dy$

$\Rightarrow \displaystyle\int X_B X_A d X_B = \int d(X_B X_A \alpha_B) - \int \alpha_B d(X_B X_A)$

$\Rightarrow \ln \gamma_A = \displaystyle\int 2 X_B \ a_B d X_A \quad [\int d(X_B X_A \alpha_B) - \int \alpha_B d(X_A X_B)]$

$\qquad = \displaystyle\int 2 X_B \ \alpha_B d X_A \quad \int d(X_B X_A \alpha_B) + \int \alpha_B d(X_A X_B)$

$\qquad = \displaystyle\int 2 X_B \ a_B d X_A \quad X_B X_A \ a_B + \int \alpha_B X_A d X_A + \int \alpha_B X_A d X_B$

$\therefore \ln \gamma_A = \displaystyle\int 2 X_B \ a_B d X_A \quad X_B X_A \ a_B + \int \alpha_B X_B d X_A \quad \int \alpha_B X_A d X_A$

$\qquad = X_B X_A \ \alpha_B \quad \displaystyle\int (2 X_B a_B - a_B X_B + a_B X_A) d X_A$

$\qquad = X_B X_A \ \alpha_B \quad \displaystyle\int (2 X_B - X_B + X_A) \alpha_B d X_A$

$\therefore \ \ln \gamma_A = X_B X_A \ a_B \quad \displaystyle\int_{X_A=1}^{X_A} \alpha_B d X_A$
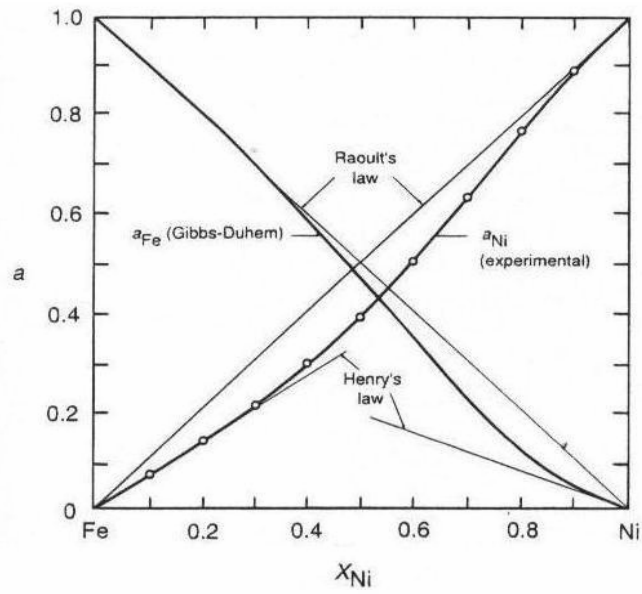
Figure 9.4 Activities in the system iron-copper at 1550 C (From J.P.Morris
and G.R.Zellars , "Vapor Pressure of Liquid Copper and Activities in Liquid
Fe-Cu Alloys," Trans. AIME (1956), vol. 206 , p.1086)
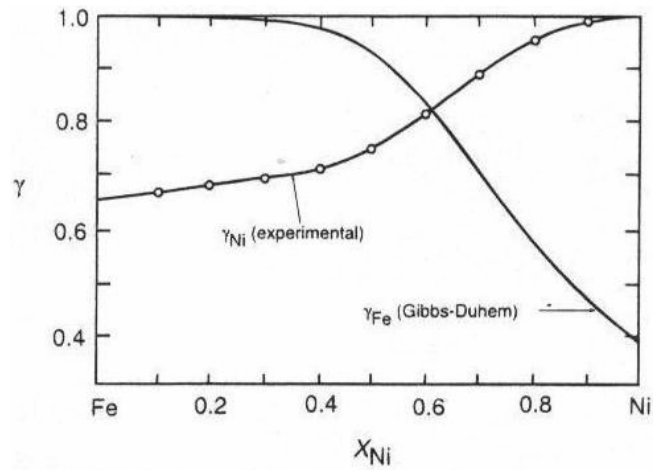

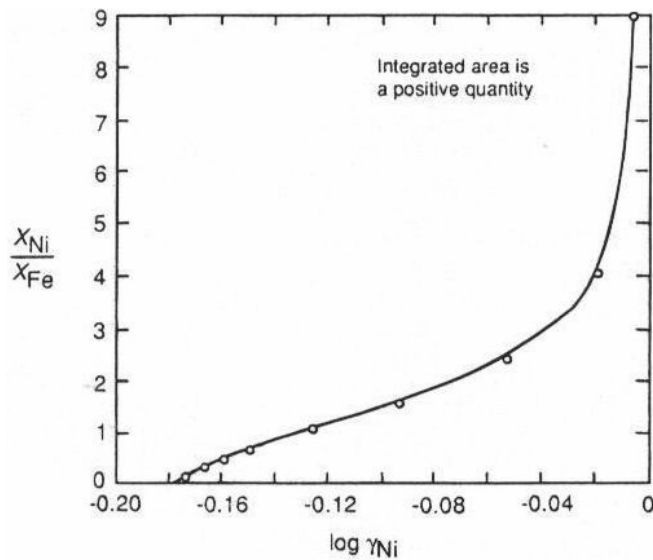Figure 9.5 Activity coefficients in the system iron-nickel at 1600°C

Figure 9.6   Application of the Gibbs-Duhem equation to determination of the activity of iron in the
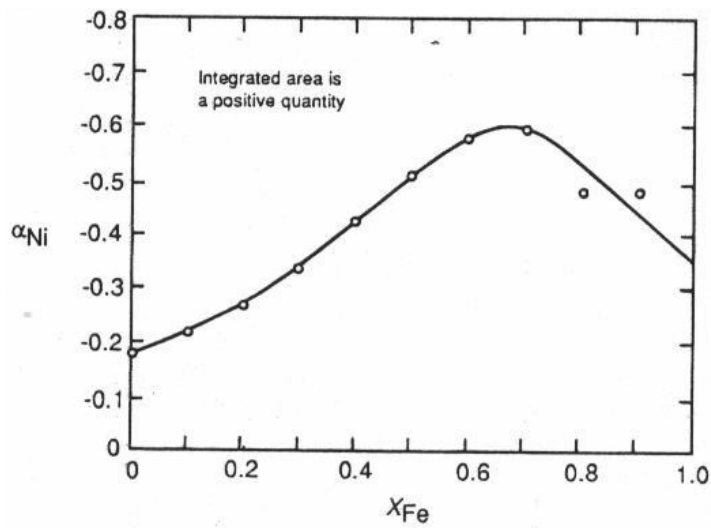system iron-nickel

-0.8
-0.7   Integrated area is
-0.6   a positive quantity
α_{Ni}

Figure 9.7 The variation of α_{Ni} with composition in the system iron-nickel

Ex 1:   Fe-Ni alloy   (γ_{Ni} < 1) T = 1600

$a_{Ni}(X_{Ni})$ is measured   Fig . 9.4

$\gamma_{Ni}(X_{Ni})$ can be calculated   Fig . 9.5

$\left(\dfrac{X_{Ni}}{X_{Fe}}\right)$ v.s.   log γ_{Ni} Fig. 9.6

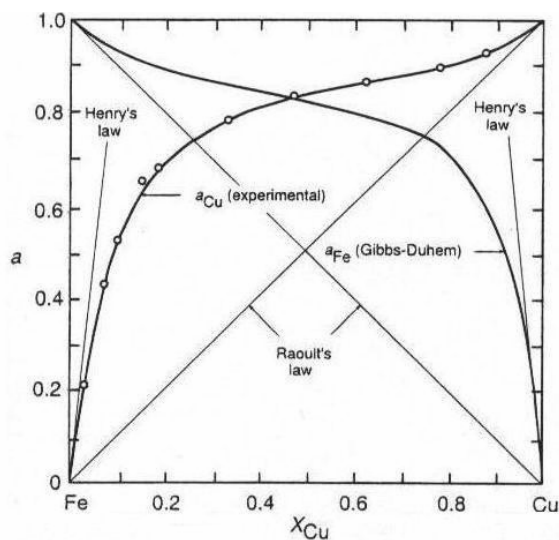$\alpha_{Ni}(X_{Fe})$ Fig. 9.7 } calculate γ_{Fe}

Figure 9.8 Activities in the system iron-copper at 1550 C (From J.P.Morris and G.R. Zellars,"Vapor Pressure of Liquid Copper and Activities in Liquid Fe-Cu Alloys," Trans. AIME (1956) , vol. 206, p.1086)
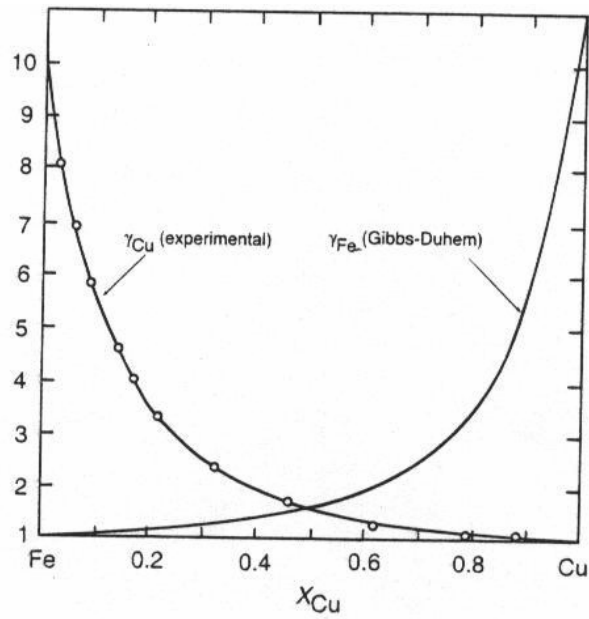
Figure 9.9 Activity coefficients in the system iron-copper at 1550°C
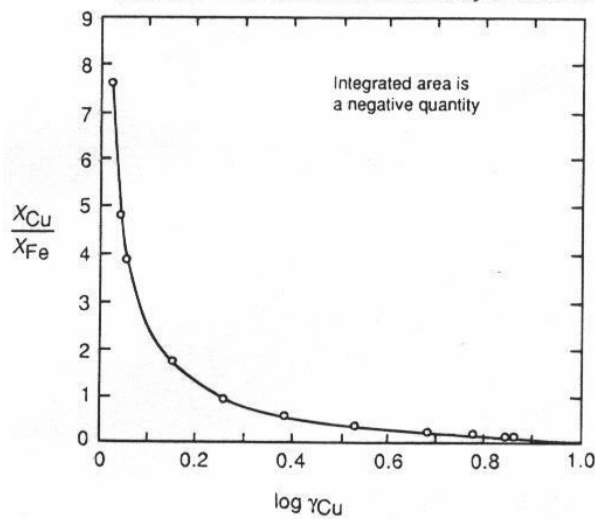

Figure 9.10 Application of the Gibbs-Duhem equation to determination of the activity of iron in the system iron-copper
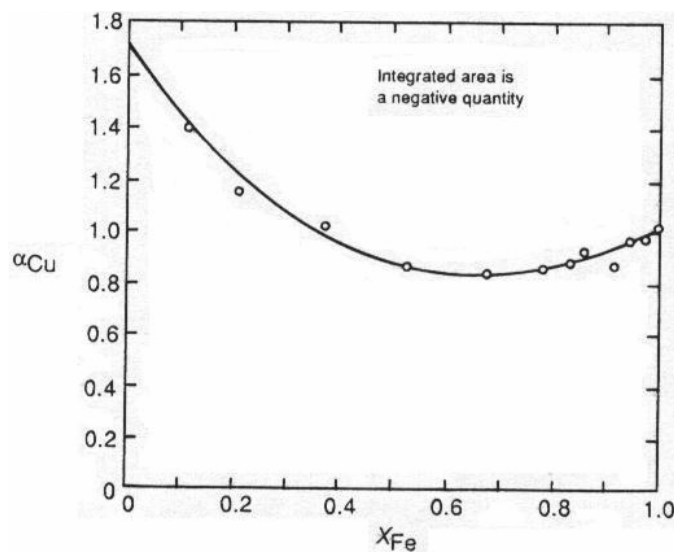

Figure 9.11 The variation of $\alpha\text{-}_{Cu}$ with composition in the system iron-copper

Ex 2 :   Fe-Cu alloy   ($\gamma_{Cu} > 1$)   T=1550

$a_{Cu}(X_{Cu})$ is   measured   Fig . 9.8

$\gamma_{Cu}(X_{Cu})$ can be calculated   Fig . 9.9

$\left(\dfrac{X_{Cu}}{X_{Fe}}\right)$ v.s.   log γ_{Cu} Fig . 9.10

$\alpha_{Cu}(X_{Fe})$ Fig . 9.11 $\Bigg\}$ calculate γ_{Fe}

2. solute B obeys Henry's Law $\Leftrightarrow$ solvent A obeys Raoult's Law

$a_B = \gamma_B X_B$, γ_B =constant $a_A = X_A$

proof: Θ $a_B = \gamma_B X_B$

$\therefore \ \ln a_B = \ln \gamma_B + \ln X_B$

$\therefore \ d \ln a_B = d \ln X_B$

Gibbs-Duhem eq. $d \ln a_A = (\dfrac{X_B}{X_A}) d \ln a_B$

$\therefore \ d \ln a_A = \dfrac{X_B}{X_A} d \ln X_B$

$= \dfrac{X_B}{X_A} \dfrac{dX_B}{X_B}$

$= \dfrac{dX_B}{X_A}$

$= \dfrac{dX_A}{X_A}$

$= d \ln X_A$

$\therefore \ \ln a_A = \ln X_A + c'$

$a_A = c X_A$

But X_A =1 (pure material)

a_A =1 , c=1

$a_A = X_A$ (Raoult's Law)

3. Given $a_A(X_A)$,   calculate ΔG^M

$\overline{\Delta G_A}^M = \Delta G^M + X_B \dfrac{d\Delta G^M}{dX_A}$

$\dfrac{\overline{\Delta G_A}^M dX_A}{X_B^2} = \dfrac{-\Delta G^M dX_B + X_B d\Delta G^M}{X_B^2} = d\left(\dfrac{\Delta G^M}{X_B}\right)$

$\left(\dfrac{\Delta G^M}{X_B}\right) = \int_0^{X_A} \dfrac{\overline{\Delta G_A}^M dX_A}{X_B^2}$ ……….Eq(1)

$$\Delta \overline{G}_A^M = RT \ln a_A$$

$$\Delta G^M = RT\, X_B \int_0^{X_A} \frac{\ln a_A\, dX_A}{X_B^2} \quad\ldots\ldots\ldots..Eq(2)$$
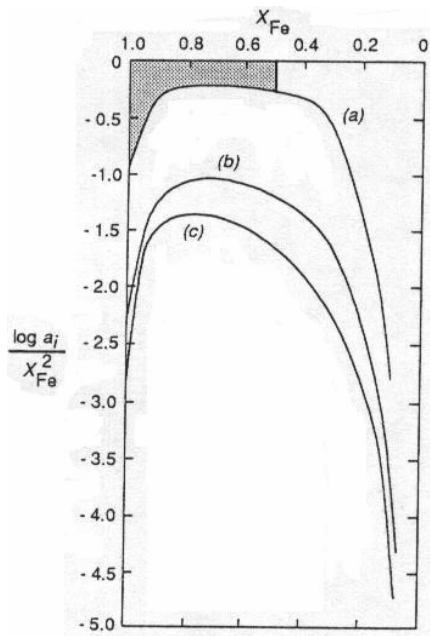
Ex 1: Fe-Ni alloy a_{Ni} measured

$$\Delta G^M = RT\, X_{Fe} \int_0^{X_{Ni}} \frac{\ln a_{Ni} dX_{Ni}}{X_{Fe}^2}$$

Ex 2: Fe-Cu alloy

$$\Delta G^M = RT\, X_{Fe} \int_0^{X_{Cu}} \frac{\ln a_{Cu}\, dX_{Cu}}{X_{Fe}^2}$$

Fig. 9-12,   Fig. 9-13

a - log a_{Cu}/X^2_{Fe}

b - log $X_i/(1 - X_i)^2$

c - log a_{Ni}/X^2_{Fe}

shaded area = $\dfrac{(\Delta G^M \text{ at } XFe = 0.5)}{2.303 \times 8.3144 \times 1823 \times 0.5}$

Figure 9.12 Illustration of the direct calculation of the integral molar Gibbs free energies of mixing in the systems iron-copper at 1550°C and iron-nickel at 1600°C
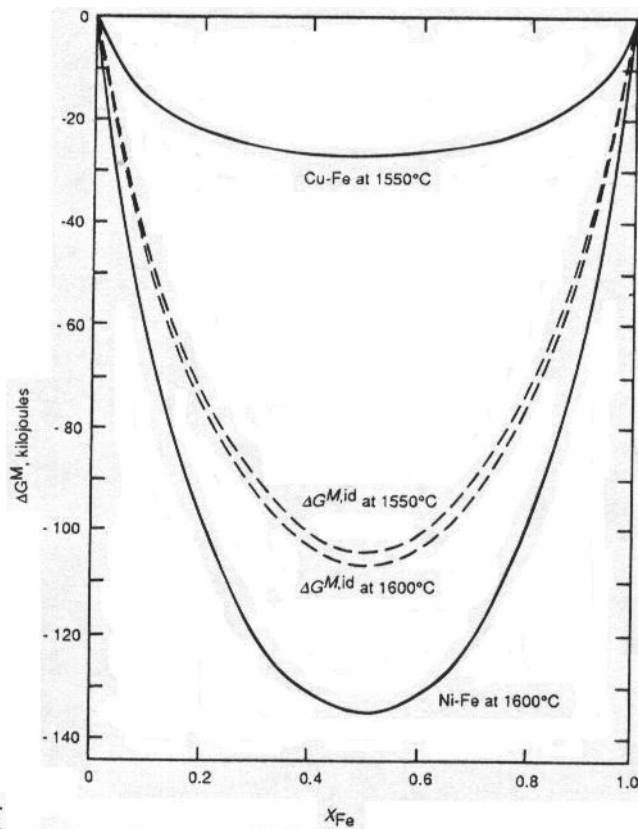
Figure 9.13 The integral molar Gibbs free energies of mixing in the systems iron-copper at 1550°C and iron-nickel at 1600°C

Notes:

1. when $X_i \to 0$ $\left[\dfrac{\ln a_i}{(1-X_i)^2} \right] \to \infty$ $\therefore$ error exists

2. For ideal solution : $a_i = X_i$

$$\Delta G^M = RT(1 \quad X_i) \int_0^{X_i} \frac{\ln X_i}{(1-X_i)^2} dX_i$$

$$= RT(1 \quad X_i) \left[\frac{X_i \ln X_i}{(1-X_i)} + \ln(1-X_i) \right]$$

$$= RT \left[X_i \ln X_i + (1-X_i) \ln(1-X_i) \right]$$

3. Eq.(1) can be used for any extensive properties

$$\left\{ \begin{array}{l} \Delta H^M = X_B \int_0^{X_A} \frac{\Delta \overline{H}_A^M}{X_B^2} dX_A \\[4mm] \Delta S^M = X_B \int_0^{X_A} \frac{\Delta \overline{S}_A^M}{X_B^2} dX_A \end{array} \right.$$

4. $\Delta G^{XS} = RT \quad X_B \int_0^{X_A} \frac{\ln \gamma_A}{X_B^2} dX_A$

when $X_i \to 0, \quad \gamma_i \to \text{const}.$

$\therefore \quad \dfrac{\ln \gamma_i}{(1-X_i)^2}$ is finite

$\Delta G^M = \Delta G^{M,id} + \Delta G^{XS}$, error can be eliminated.

$\Delta G^{M,id} = RT(X_A \ln X_A + X_B \ln X_B)$

§ 9-9 Regular Solution

1. Ideal solution $\left\{ \begin{array}{l} a_i = X_i \\[3mm] \gamma_i = 1 \end{array} \right.$ $\left\{ \begin{array}{l} \Delta \overline{H}_i^M = 0 \\[3mm] \Delta \overline{S}_i^M = -R \ln X_i \end{array} \right.$

Nonideal solution : $\left\{ \begin{array}{l} a_i \neq X_i \qquad \Delta \overline{H}_i^M \neq 0 \\[3mm] \gamma_i \neq 1 \end{array} \right.$

2. The Simplist Mathematical Form of a nonideal solution is "Regular solution".

⊗ Definition

$$\begin{cases}(1) \quad \Delta\overline{S}_i^{M} = \Delta\overline{S}_i^{M,id} = -R\ln X_i \\[2em] (2) \quad \Delta\overline{H}_i^{M} \text{ is a function of composition only. It is indep. of } T.\end{cases}$$

Consider that: $X_A \to 0$, $X_B \to 0$, then $H^M \to 0$

Since H^M is a function of composition only, $H^M(X_B)$.

$$H^M = X_A X_B(\text{'}+bX_B+cX_B^2+dX_B^3+\ldots..)$$

The simplest mathematical form of regular solution is $H^M = \text{'}X_A X_B$

If

$$\begin{cases} RT\ln\gamma_B = \boldsymbol{a}\,'X_A^2 \\[2em] RT\ln\gamma_A = \boldsymbol{a}\,'X_B^2 , \qquad \boldsymbol{a}\,' \text{ is constant}\end{cases}$$

From eq(9.61) $\ln\boldsymbol{g}_A = X_A X_B \boldsymbol{a}_B \int_{X_A=1}^{X_A} \boldsymbol{a}_B dX_A$

If $\boldsymbol{a}_B$ is indep. of composition

$$\Rightarrow \quad \ln\boldsymbol{g}_A = X_A X_B \boldsymbol{a}_B \quad \boldsymbol{a}_B(X_A-1)$$
$$= X_A X_B \boldsymbol{a}_B + \boldsymbol{a}_B X_B$$
$$= \boldsymbol{a}_B X_B(1 \quad X_A)$$
$$= \boldsymbol{a}_B X_B^2$$

By definition: $\boldsymbol{a}_A = \dfrac{\ln\boldsymbol{g}_A}{X_B^2}$

$\therefore \boldsymbol{a}_B = \boldsymbol{a}_A = \boldsymbol{a}$

If $RT\ln\boldsymbol{g}_A = \boldsymbol{a}\,'X_B^2$

$$\Rightarrow \quad \boldsymbol{a} = \dfrac{\boldsymbol{a}'}{RT}$$

i.e. $\boldsymbol{a}$ function is an inverse function of temperature for the simplest regular solution

3. Excess Quantity

Θ $\quad \Delta\overline{G}_i = RT\ln a_i = RT\ln\boldsymbol{g}_i + RT\ln X_i$

$\therefore \quad \Delta\overline{G}_i = \Delta\overline{G}_i^{id} + \Delta\overline{G}_i^{xs}$

or $G = G^{id} + G^{xs}$ (one mole) , $\Delta G^M = \Delta G^{M,id} + G^{xs}$

$$\Delta G^M = \Delta H^M - T \Delta S^M$$

ideal solution : $\Delta H^{M,id} = 0$, $\Delta G^{M,id} = T \Delta S^{M,id}$

$\therefore$ $G^{xs} = \Delta G^M$ $\Delta G^{M,id}$

$= (\Delta H^M \quad T \Delta S^M) \quad (\quad T \Delta S^{M,id})$

$= \Delta H^M \quad T(\Delta S^M \quad \Delta S^{M,id})$

since for a regular solution $\Delta S^M = \Delta S^{M,id}$

$\Rightarrow$ $G^{xs} = \Delta H^M$

$$\Delta G^M = \sum X_i \Delta \overline{G}_i^M = X_A \ (RT \ln a_A + RT \ln a_B)$$

$$\Delta G^M = RT(X_A \ln X_A + X_B \ln X_B) + RT(X_A \ln g_A + X_B \ln g_B)$$

Θ $\Delta G^{M,id} = RT(X_A \ln X_A + X_B \ln X_B)$

$\therefore$ $G^{xs} = RT(X_A \ln g_A + X_B \ln g_B)$

$\therefore$ $G^{xs} = X_A \overline{G_A}^{xs} + X_B \overline{G_B}^{xs}$

For the simplest regular solution: $a_B = a_A = a$

$\Rightarrow$ $\ln g_A = a \ X_B^2$, $\ln g_B = a \ X_A^2$

$\Rightarrow G^{xs} = RT(X_A \ a \ X_B^2 + X_B \ a \ X_A^2)$

$$= a \ RT \ X_A X_B = a' \ X_A X_B$$

For the simplest regular solution:

$G^{xs} = \Delta H^M = a \ RT \ X_A X_B = a' \ X_A X_B$

$G^{xs} = \Delta H^M$ is indep. of T

$$\left(\frac{\partial G^{xs}}{\partial T} \right)_{P,comp} = S^{xs} = 0$$

at a fixed composition

$$\overline{G_A}^{xs} = RT_1 \ \ln g_{A(T_1)} = RT_2 \ \ln g_{A(T_2)} = a' X_B^2$$

$\therefore$ $\dfrac{\ln g_{A(T_2)}}{\ln g_{B(T_1)}} = \dfrac{T_1}{T_2}$

Notes : (1) For the simplest regular solution

$$G^{xs} = \Delta H^M = a \ RT \ X_A X_B = a' \ X_A X_B$$

$\therefore$ $a \ T$ is indep. of T

(2) If $\Delta H^M = b \ X_A X_B$, $G^{xs} = b' X_A X_B$, $b \neq b'$

$$\Rightarrow \Delta S^M \neq \Delta S^{M,id}$$

$$\Rightarrow \text{ Nonregular}$$

e.g. (1) Au-Cu, 1550K $\begin{cases} G^{xs} = 24060\, X_{Cu} X_{Au} \\ \\ \Delta H^M \text{ is asymmertric} \Rightarrow S^{xs} \neq 0 \end{cases}$

(2) Au-Ag, 1350K $\begin{cases} \Delta H^M = 20590\, X_{Ag} X_{Au} \\ \\ G^{xs} \text{ is asymmertric} \Rightarrow S^{xs} \neq 0 \end{cases}$

§ 9-10 Statistical (Quasi-chemical) Model of Solution

- Physical significance of a regular solution

- Assumptions : $\overline{V_A} = V_A^O = V_B^O = \overline{V_B}$, $\Delta V^M = 0$

∴ Energy of solution $\Leftrightarrow$ sum of interatomic bond energies.

Consider : (N_A A atoms + N_B B atoms)

$N_A + N_B = N_o$ (1 mole)

$$\Rightarrow \quad X_A = \frac{N_A}{N_A + N_B} = \frac{N_A}{N_o} , \quad X_B = \frac{N_B}{N_o}$$

∴ $E = P_{AA} E_{AA} + P_{BB} E_{BB} + P_{AB} E_{AB}$

E_{AA}, E_{BB}, E_{AB} are bond energies of A-A ,B-B, A-B, respectively.

P_{AA}, P_{BB}, P_{AB} are bond numbers of A-A ,B-B, A-B, respectively.

$N_A Z = P_{AB} + 2 P_{AA}$

∴ $P_{AA} = \dfrac{1}{2}(N_A Z - P_{AB})$, similarly $P_{BB} = \dfrac{1}{2}(N_B Z - P_{AB})$

∴ $E = \dfrac{1}{2} N_A Z E_{AA} + \dfrac{1}{2} Z N_B E_{BB} + P_{AB}[E_{AB} - \dfrac{1}{2}(E_{AA} + E_{BB})]$

For pure N_A A atoms : $N_A Z = 2 P_{AA}$

Pure N_B B atoms: $Z N_B = 2 P_{BB}$

Before mixing : $E_o = \dfrac{1}{2} N_A Z E_{AA} + \dfrac{1}{2} Z N_B E_{BB}$

$\Delta E^M = E - E_o = P_{AB}[E_{AB} - \dfrac{1}{2}(E_{AA} + E_{BB})]$

$\Theta \quad \Delta H^M = \Delta E^M + P \Delta V^M = \Delta E^M \quad (\Delta V^M = 0)$

$$\therefore \quad \Delta H^M = \Delta E^M = P_{AB}[E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})]$$

For solutions which exhibit relatively small deviations from ideal behavior,

i.e. $\left| \Delta H^M \right| \leq RT$

$\therefore$ mixing of atoms can be assumed to be random

P_{AB} can be calculated.

Consider two neighboring lattice sites **a b**

Probability that $\left\{ \begin{array}{l} \textbf{\textit{a}} \text{ occupied by A and} \\ \textbf{\textit{b}} \text{ occupied by B} \end{array} \right\}$ $X_A X_B$

Probability that $\left\{ \begin{array}{l} \textbf{\textit{a}} \text{ occupied by B and} \\ \textbf{\textit{b}} \text{ occupied by A} \end{array} \right\}$ $X_B X_A$

$\therefore$ Probability that a neighboring pair of sites contains A-B pair is $2 X_A X_B$

$\therefore$ (number of A-B bonds)=(number of neighboring pair of sites)×(Probability of A-B pair)

$$\therefore \quad P_{AB} = (\frac{1}{2} Z N_o) \times (2 X_A X_B) = Z N_o X_A X_B$$

i.e. $\Delta H^M = Z N_o X_A X_B [E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})]$

define $\boxed{\Omega \equiv Z N_o [E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})]}$

$\Rightarrow \Delta H^M = \Omega X_A X_B$

Since random mixing is assumed, statistical model $\Leftrightarrow$ regular solution model

$\therefore \Delta H^M = G^{xs} = \Omega X_A X_B = RT a X_A X_B$

$\Rightarrow \boxed{a = \frac{\Omega}{RT}}$ i.e. $\boxed{a' = \Omega}$

$\Theta \quad \Delta \overline{H_A}^M = \Delta H^M + (1 - X_A) \frac{d \Delta H^M}{d X_A}$

$\qquad = \Omega X_A X_B + X_B \Omega (X_B - X_A) = \Omega X_B^2$

similarly, $\Delta \overline{H_B}^M = \Omega X_A^2$

$\Theta \quad$ Mixing is random $\therefore \left\{ \begin{array}{l} \Delta \overline{S_A}^M = R \ln X_A \\ \\ \Delta \overline{S_B}^M = R \ln X_B \end{array} \right.$

$\therefore \quad \Delta \overline{G_A}^M = \Delta \overline{H_A}^M \quad T \Delta \overline{S_A}^M$

$$= \Omega X_B^2 + RT \ln X_A$$

But $\quad \Delta \overline{G_A}^M = RT \ln a_A = RT \ln g_A + RT \ln X_A$

$\Rightarrow \quad RT \ln g_A = \Omega X_B^2$

$\Rightarrow \quad \ln g_A = \dfrac{\Omega}{RT} X_B^2 = a X_B^2, \quad$ similarly $\quad \ln g_B = \dfrac{\Omega}{RT} X_A^2 = a X_A^2$

Note: (1) Ideal solution ,

$$\Delta H^M = 0 \text{ , i.e. } \Omega = 0 \text{ , } E_{AB} = \frac{1}{2}(E_{AA} + E_{BB})$$

(2) Negative deviation

$$\Delta H^M < 0 \text{ , i.e. } \Omega < 0 \text{ , } \quad \mid E_{AB} \mid > \frac{1}{2}(E_{AA} + E_{BB}), \quad g_i < 1$$

(3) Positive deviation

$$\Delta H^M > 0 \text{ , i.e. } \Omega > 0 \text{ , } \mid E_{AB} \mid < \frac{1}{2}(E_{AA} + E_{BB}), \quad g_i > 1$$

(4) Henry's Law : $X_B \to 1 \quad X_A \to 0$

$$\ln g_A \to \ln g_A^o = \frac{\Omega}{RT} \quad \text{or} \quad g_A^o = e^{\frac{\Omega}{RT}}$$

(5) when $\quad \mid E_{AB} \mid$ is significantly greater or less than $\dfrac{1}{2} \mid E_{AA} + E_{BB} \mid$

$$\Rightarrow \mid \Omega \mid \text{ increases}$$

$\Rightarrow$ Random mixing cannot be assumed.

$\Rightarrow$ Applicability of statistical model decreases .

(6) Equilibrium configuration of a solution at constant T, P $\Leftrightarrow$ G=G$_{min}$

Θ G = H TS $\quad \therefore$ G$_{min}$ $\Leftrightarrow$ H$_{min}$ and S$_{max}$

$\otimes$ If $\quad \mid E_{AB} \mid > \dfrac{1}{2} \mid E_{AA} + E_{BB} \mid \quad$ (Negative deviation)

$$\Omega < 0, \quad \Delta H^M < 0, \quad H < 0$$
$$H_{min} \Leftrightarrow P_{AB} \to (P_{AB})_{max}$$

i.e. $\mid \Omega \mid$ increases $\Rightarrow$ P$_{AB}$ increases (ordering)

$\otimes$ If $S \to S_{max}$, completely random mixing

T increases $\Rightarrow (TS) \uparrow \Rightarrow G \downarrow$

$\therefore$ G $\to$ G$_{min}$ is compromised between Ω and T

$\therefore$ when T is not too high and Ω is appreciably negative

$\Rightarrow \quad P_{AB} > P_{AB}$(random)

$\Rightarrow \quad$ Assumption of random mixing is not valid

$\otimes$ For a given Ω: T $\uparrow$ $\Rightarrow$ more nearly random mixing

For a given T : $|\Omega|\downarrow$ $\Rightarrow$ more nearly random mixing

$\otimes$ only when $\Delta H^M = 0$, random configuration is the equilibrium

i.e. $\Delta G^M = \Delta G^M_{\min}$ (random)

$\otimes$ At constant T, as $|\Omega|\uparrow\Rightarrow$ $\Delta G^M_{\min}$ moves far away from random

if $\Delta H^M < 0$, $\Delta G^M_{\min}$ $\rightarrow$ ordered

if $\Delta H^M > 0$, $\Delta G^M_{\min}$ $\rightarrow$ clustered

$\otimes$ At constant $|\Omega|$, as $T\uparrow\Rightarrow$ $|T\Delta S^M|\uparrow$

$\Rightarrow \Delta G^M_{\min}$ moves toward center (random)

§ 9-11 Subregular Solution

$\otimes$ Simplest regular solution :

$$\Omega = \boldsymbol{a}' = \frac{\boldsymbol{a}}{RT} = ZN_o\,[\,E_{AB} - \frac{1}{2}(E_{AA} + E_{BB})\,] = \text{constant}$$

and $G^{xs} = \Delta H^M = \boldsymbol{a}'\,X_A X_B = \Omega\,X_A X_B$

$\therefore$ parabolic function , symmetric about $X_A = X_B = 0.5$

$\otimes$ Subregular Solution

$G^{xs} = \Delta H^M = (a + b\,X_B)\,X_A X_B$

constants a, b have no physical meaning, they are parameters adjusted to fit

equation to experimentally measured data

e.g. Ag-Au at T=1350 K

data fitting a= 11320 J , b=1940 J

$\otimes$ Non-regular Solution

G^{xs} is a function of X_B , T

ΔH^M is also a function of X_B , T

$\Delta S^M \neq \Delta S^{M,id}$ ($S^{xs} \neq 0$)

e.g. $G^{xs} = (a_o + b_o\,X_B)\,X_A X_B\left(1 - \frac{T}{t}\right)$

$\therefore S^{xs} = \left(\frac{\partial G^{xs}}{\partial T}\right) = \frac{(a_o + b_o X_B)X_A X_B}{t}$

$\Delta H^M = G^{xs} + T\,S^{xs} = (a_o + b_o\,X_B)\,X_A X_B$

EX1.   Cu-Au solid solution at T=600 °C =873 K

Solution is regular with $G^{xs} = 28280 X_{Au} X_{Cu}$ J

For pure Cu and Au

$$\ln p_{Cu}^{o} (atm)= \frac{40920}{T} \quad 0.86 \ln T+21.67$$

$$\ln p_{Au}^{o} (atm)= \frac{45650}{T} \quad 0.306 \ln T+10.81$$

calculate p_{Cu} and p_{Au} over Cu-Au solid solution at $X_{Cu} =0.6$, T=873 K

Sol: Θ Regular solution $\therefore \Omega = 28280$ J

$$\ln g_{Cu} =\frac{\Omega}{RT}X_{Au}^{2}, \qquad \ln g_{Au}=\frac{\Omega}{RT}X_{Cu}^{2}$$

$\therefore$ $g_{Cu} =0.536$, $g_{Au}=0.246$

$$\begin{cases} a_{Cu} = g_{Cu} X_{Cu} =0.322 \\ a_{Au} = g_{Au} X_{Au} =0.098 \end{cases}$$

By definition:

$$a_{Cu} \equiv \frac{p_{Cu}}{p_{Cu}^{o}}$$

$$a_{Au} \equiv \frac{p_{Au}}{p_{Au}^{o}}$$

at T=873 K $p_{Cu}^{o} =3.35\times10^{-14}$ atm

$$p_{Au}^{o} =1.52\times10^{-16} \text{ atm}$$

$\therefore$ $p_{Cu} =1.08 \times10^{-14}$ atm

$p_{Au} =1.50\times 10^{-16}$ atm

EX2.   Ga-Cd Liquid solution at T=700K
Regular solution , $X_{Ga} = 0.5$ $a_{Ga} =0.79$

$\Delta H_{evap,Ga} =270,000$ J/mole $Z_{Ga} =11$

$\Delta H_{evap,Cd} =100,000$ J/mole $Z_{Cd} =8$

Calculate $E_{Ga-Cd} =?$

Sol: Θ $g_{Ga} = \dfrac{a_{Ga}}{X_{Ga}} = 1.59$

$\ln g_{Ga} = \dfrac{\Omega}{RT} X_{Cd}^2$

∴ $\Omega = 10795$ J/mole

$\Omega = ZN_o \left[E_{Ga-Cd} \quad \dfrac{1}{2}(E_{Ga-Ga} + E_{Cd-Cd}) \right]$

Θ liquid Ga : $\Delta H_{evap,Ga} \cong \quad \dfrac{1}{2} Z_{Ga} \quad N_o \ E_{Ga-Ga}$

liquid Cd : $\Delta H_{evap,Cd} \cong \quad \dfrac{1}{2} Z_{Cd} \quad N_o \ E_{Cd-Cd}$

∴ $E_{Ga-Ga} = \quad 8.15 \times 10^{-20}$ J

$E_{Cd-Cd} = \quad 4.15 \times 10^{-20}$ J

Assume : Ga-Cd liquid $Z = \dfrac{1}{2}\left(Z_{Ga} + Z_{Cd}\right) = 9.5$

∴ $E_{Ga-Cd} = \quad 5.96 \times 10^{-20}$ J