Chapter10 Gibbs Free Energy-Composition Curves and Binary Phase Diagrams

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§10-1. Introduction

1. At constant T, P

(1) Stable (equilibrium) state $\Leftrightarrow$ $G = G_{min}$

(2) When phases coexist, (a、ß、?…)

$$\overline{G_i}^{\alpha} = \overline{G_i}^{\beta} = \overline{G_i}^{\gamma} = \ldots\ldots$$

2. Isobaric binary phase diagrams can be determined from $\Delta G^M(X_i)$ curves at different T for each phase.

e.g : Si-Ge isomorphous phase diagram.

$T > T_m(Si)$: Liquid

$T \le T_m(Si)$ or liquidus line: solid phase coexists with liquid phase

$X_i^s(T)$、$X_i^\lambda(T)$ can be determined.

§10-2. Gibbs Free Energy Curve, $\triangle G^M(X_B)$

$$\Delta G^M = RT\,(X_A \ln a_A + X_B \ln a_B)$$

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

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

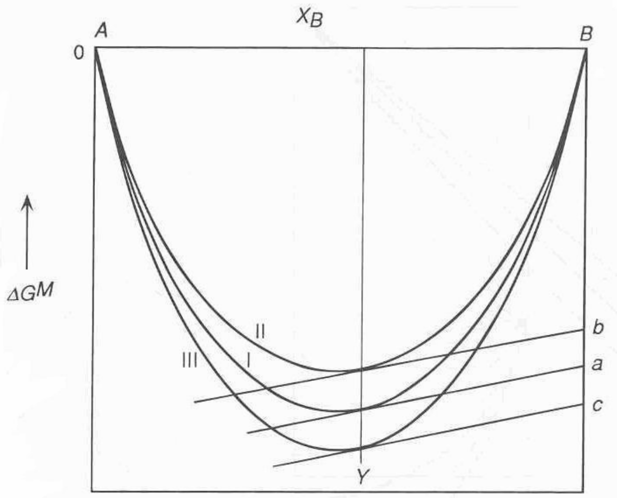

Figure 10.1 The molar Gibbs free energies of mixing in binary systems exhibiting ideal behavior (I), positive deviation from ideal behavior (II), and negative deviation from ideal behavior (III)

Figure 10.1 I. $\Delta G^{M,id} < 0$

II. $\gamma_i > 1$

III. $\gamma_i < 1$

∗When $X_B = X_B^{\circ}$, tangent intercept at $X_B = 1$ is $\Delta\overline{G_B}^M$

$\therefore |\ Bb = \Delta\overline{G_B}^M = RT \ln a_B (II)\ | < |\ Ba = \Delta\overline{G_B}^M = RT \ln a_B (I)\ |$

$< |\ Bc = \Delta\overline{G_B}^M = RT \ln a_B (III)\ |$

$\therefore \gamma_B(II) > \gamma_B^{id} = 1 > \gamma_B(III)$

∗ $X_i \to 0$, $a_i \to 0$, $\Delta\overline{G_i} = RT \ln a_i \to -\infty$

§10-3. $\Delta G^M(X_B)$ of a Regular Solution

$\because$Regular Solution, $S^{xs} = 0$

$$\Delta G^M - \Delta G^{M,id} = G^{xs} = \Delta H^M = RT\alpha X_A X_B = \Omega X_A X_B$$

∗ For $\Delta H^M < 0$, ΔG^M is more negative than $\Delta G^{M,id} < 0$

a homogeneous solution is stable for all X_B.

∗ For $\Delta H^M > 0$, $a > 0$

$$\frac{\Delta G^M}{RT} - \frac{\Delta G^{M,id}}{RT} = \frac{\Delta H^M}{RT} = a X_A X_B$$

ideal solution $\dfrac{\Delta G^{M,id}}{RT} = -\dfrac{\Delta S^{M,id}}{R} = X_A \ln X_A + X_B \ln X_B$

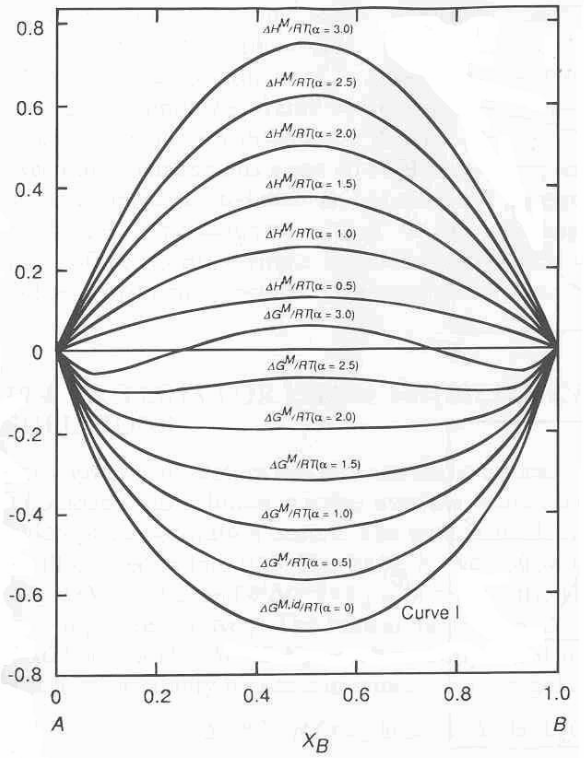

Figure 10.2 The effect of the magnitude of α on the integral molar heats and integral molar Gibbs free energies of formation of a binary regular solution

Figure 10.2 I : $\dfrac{\Delta G^{M,id}}{RT}$ (a=0)

When a ↑ ⇒ part of $\dfrac{\Delta G^M}{RT}$ curve is convex upward.

∗ When all $\Delta G^M(X_B)$ curve is "convex downward" .

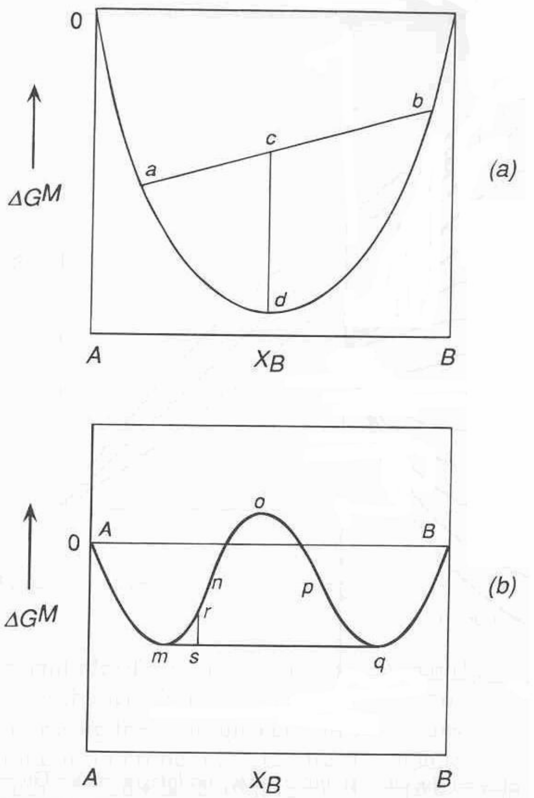

Figure 10.3 (*a*) The molar Gibbs free energies of mixing of binary components which form a complete range of solutions. (*b*) The molar Gibbs free energies of mixing of binary components in a system which exhibits a miscibility gap

Figure 10.3 at any specific X_B°, $\Delta G^M\left(X_B^\circ\right)$=d.

if it is mixed by any other two different compositions $(a+b)\rightarrow c$

$\Delta G^M(c) > \Delta G^M(d)$

i.e. no phase separation.

* When part of $\Delta G^M(X_B)$ curve is "convex upward" .

i. $m < X_B < q$

ΔG^M is minimized when two solutions (m, q) coexist

e.g. $g \rightarrow m + q$

ii. m, q are the common tangent of ΔG^M curve.

$$\therefore \begin{cases} \overline{G}_A(\text{solution} \quad m) = \overline{G}_A(\text{solution} \quad q) \\ \overline{G}_B(\text{solution} \quad m) = \overline{G}_B(\text{solution} \quad q) \end{cases}$$

$\therefore$ subtracting G_A° and G_B°

$$\text{then} \begin{cases} a_A(m) = a_A(q) \\ a_B(m) = a_B(q) \end{cases}$$

i.e. solutions m, q are in equilibrium, they coexist.

a ↑ $\Rightarrow$ clustering causes phase separation
curve AmqB represents the equilibrium state of the system, curve mnopq has no physical significance.

§10-4. Criteria For Phase Stability in Regular Solutions

∗ Given T, a critical α_{cr} occurs ,

$$\begin{cases} \alpha < \alpha_{cr}, \ \textit{homogeneous solution is stable.} \\ \alpha > \alpha_{cr}, \ \textit{phase separation occurs.} \end{cases}$$

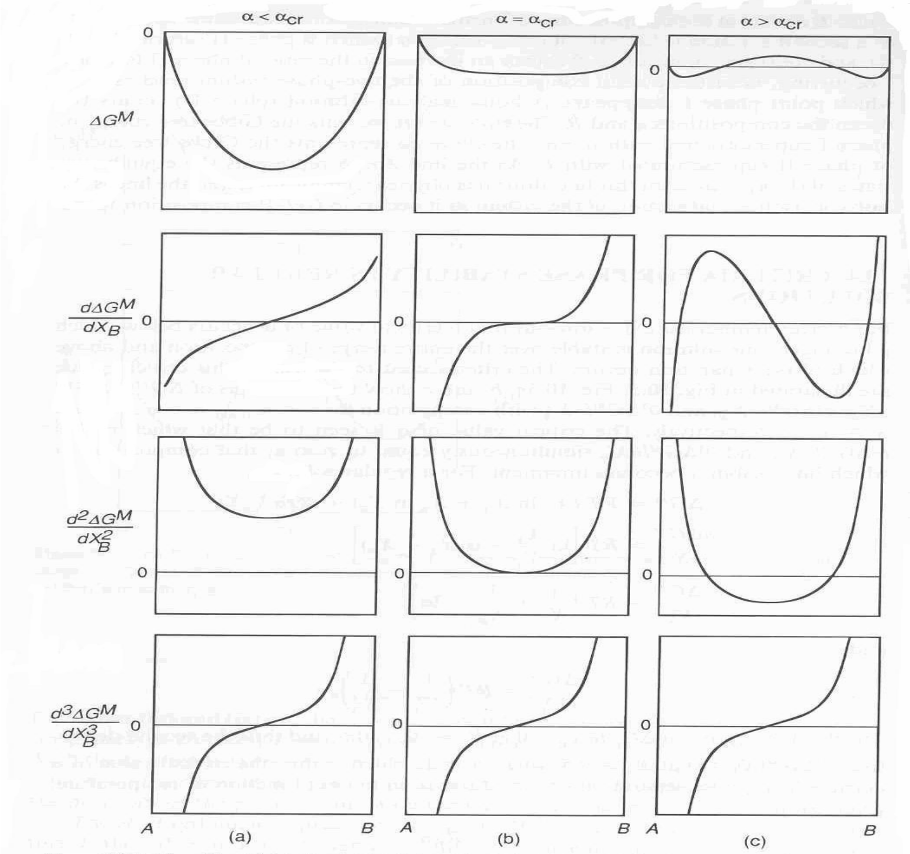

Figure 10.4 The effect of the magnitude of α on the first, second, and third derivatives of the integral Gibbs free energy of mixing with respect to composition

∗ When $\alpha = \alpha_{cr}$, $\dfrac{\partial \Delta G^M}{\partial X_B} = 0$, $\dfrac{\partial^2 \Delta G^M}{\partial X_B{}^2} = 0$, $\dfrac{\partial^3 \Delta G^M}{\partial X_B{}^3} = 0$

Figure 10.4

$$\therefore \Delta G^M = RT(X_A \ln X_A + X_B \ln X_B) + RT\alpha X_A X_B$$

$$\therefore \frac{\partial \Delta G^M}{\partial X_B} = RT\,[\,\ln\frac{X_B}{X_A} + \alpha(X_A - X_B)]$$

$$\frac{\partial^2 \Delta G^M}{\partial {X_B}^2} = RT(\frac{1}{X_A} + \frac{1}{X_B} - 2\alpha)$$

$$\frac{\partial^3 \Delta G^M}{\partial {X_B}^3} = (\frac{1}{{X_A}^2} - \frac{1}{{X_B}^2})$$

From $\frac{\partial^3 \Delta G^M}{\partial {X_B}^3} = 0$, $\therefore X_A = X_B = 0.5$

Then from $\frac{\partial^2 \Delta G^M}{\partial {X_B}^2} = 0$, $\alpha = \boxed{\alpha_{cr} = 2}$

$\because \Omega = RT\alpha$

$\therefore$ For a given positive Ω $(\Omega > 0)$, $\boxed{T_{cr} = \frac{\Omega}{\alpha_{cr} R} = \frac{\Omega}{2R}}$

＊ Given fixed $\Omega > 0$

$$\text{When} \begin{cases} T > T_{cr},\ \alpha < 2,\ \text{homogeneous solution.} \\ T < T_{cr},\ \alpha > 2,\ \text{phase separation occurs.} \end{cases}$$

$$\because \Delta G^M = \underbrace{RT(X_A \ln X_A + X_B \ln X_B)}_{(1)} + \underbrace{RT\alpha X_A X_B}_{(2)}$$

$RT\alpha = \Omega = \text{constant}$

$$\begin{cases} \text{term}(2)\ \text{is indep. of } T \\ \text{term}(1): T \downarrow \Rightarrow \text{term}(1)\ \text{is less negative} \end{cases}$$

$T \le T_{cr} \Rightarrow$ eventually, at $X_B = 0.5$, ΔG^M is positive

$\Delta G^M(X_i)$ is convex upward.

＊ Miscibility curve bounding two-phase region in phase diagram is the locus of common tangent compositions.

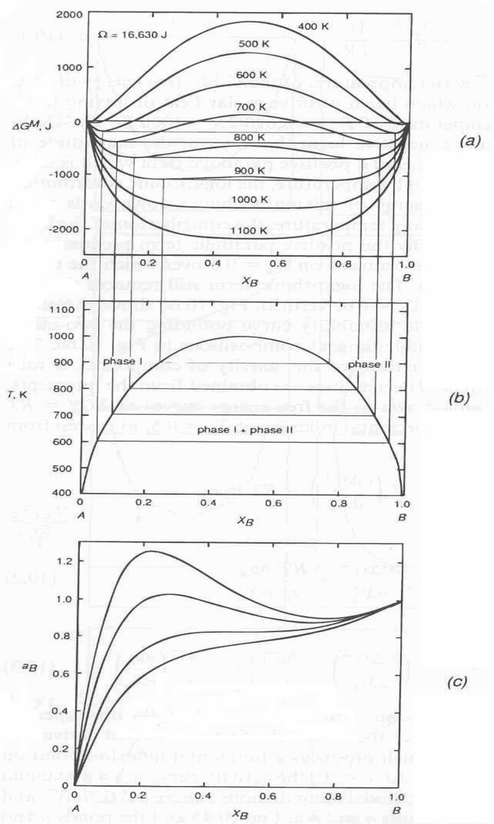

Figure 10.5 (*a*) The effect of temperature on the molar Gibbs free energy of mixing in a binary regular solution for which Ω = 16,630 joules. (*b*) The loci of the double tangent points in Fig. 10.6*a*, which generate the phase diagram for the system. (*c*) The activities of component *B* derived from Fig. 10.6*a*

Figure 10.5 (a),(b) for Ω =16630J , T_{cr} =1000K

∗ a_B (X_B) at different T : **Figure 10.5 (c)**

(1) at T= T_{cr} , $X_B = 0.5$, inflexion occurs (i).

i.e. $\dfrac{\partial a_B}{\partial X_B}$ =0 and $\dfrac{\partial^2 a_B}{\partial {X_B}^2}$ =0

(2) $T < T_{cr}$, a_B (X_B) has a maximum, and minimum point.

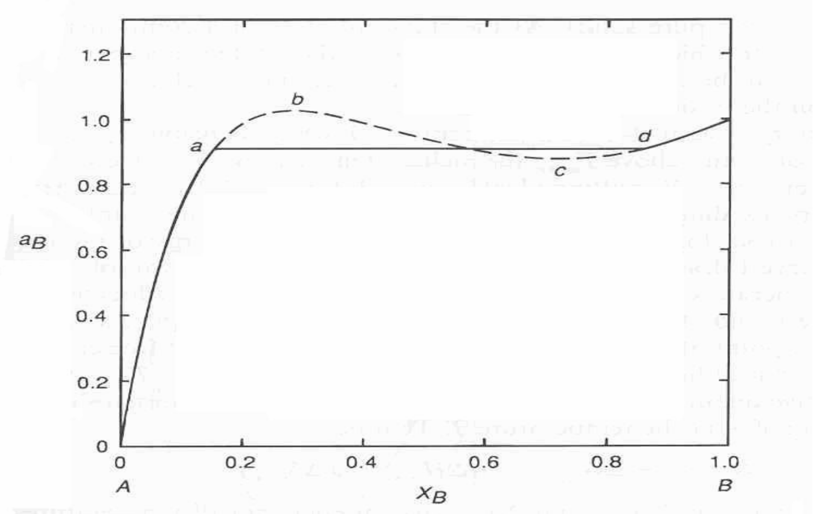

Figure 10.6 The activity of *B* at 800 K derived from Fig. 10.6*a*

e.g. **Figure 10.6** points b, c where $\frac{\partial a_B}{\partial X_B}=0$ and $\frac{\partial^2 \Delta\overline{G}_B^M}{\partial X_B{}^2}=0$

$\Rightarrow$ spinodal compositions.

∗ $a_B(X_B)$ curve between $\overset{\frown}{bc}$, $\left(\frac{\partial a_B}{\partial X_B}\right)<0$,

this violates the stability criterion : $X_B \uparrow, \left(\frac{\partial a_B}{\partial X_B}\right)\uparrow$

$\Rightarrow$ curve $\overset{\frown}{bc}$ has no physical significance.

$\Rightarrow$ horizontal $\overline{ad}$ is actual constant activity in the two-phase region.

Points a, d are the common tangent of the $\Delta G^M(X_B)$ curve.

§10-5. Standard States and Two-Phase Equilibrium

1. Standard states: pure component in its stable state at specific T, P.

∗ ∵ Standard state changes with T.

∴ Choice of standard state is based on convenience.

2. Consider phase diagram in **Figure 10.7** and $T_{m(A)} < T < T_{m(B)}$

Choose standard states: $G^o_{A(\lambda)} = 0$, $G^o_{A(S)} = 0$

$$\therefore G^{o}_{A(S)} - G^{o}_{A(\lambda)} = -\Delta G^{o}_{m(A)} = -(\Delta H^{o}_{m(A)} - T\Delta S^{o}_{m(A)})$$

$$\Delta H = \Delta H_{o} + \int \Delta C_{P} dT \quad , \quad \Delta S = \Delta S_{o} + \int \frac{\Delta C_{P}}{T} dT$$

$$\begin{cases} \text{at } T = T_{m(A)},\ \Delta G^{o}_{m(A)} = 0 \quad \therefore \Delta H^{o}_{m(A)} = T_{m}\Delta S^{o}_{m(A)} \\ \text{if } C_{P,A(S)} = C_{P,A(\lambda)},\ \Delta H^{o}_{m(A)},\ \Delta S^{o}_{m(A)} \text{ are indep. of } T. \end{cases}$$

$$\therefore \Delta G^{o}_{m(A)} = \Delta H^{o}_{m(A)} \left[\frac{T_{m(A)} - T}{T_{m(A)}} \right]$$

$\therefore$point c, $G^{o}_{A(s)}$ is more positive, when T↑ ($T > T_{m(A)}$)

line $\overline{cb}$ is Gibbs free energy of unmixed $\begin{cases} \text{solid A} \\ \text{solid B} \end{cases}$

$$\Delta G = -X_{A} \cdot \Delta G^{o}_{m(A)}$$

similarly, $G^{o}_{B(\lambda)} - G^{o}_{B(S)} = \Delta G^{o}_{m(B)} = \Delta H^{o}_{m(B)} - T\Delta S^{o}_{m(B)} \cong \Delta H^{o}_{m(B)} \left[\frac{T_{m(A)} - T}{T_{m(A)}} \right]$

line $\overline{ab}$, $\Delta G = X_{B} \cdot \Delta G^{o}_{m(B)}$

$$\begin{cases} \text{curve } \overset{\frown}{aed} \text{ is the liguid solution }, \Delta G^{M}_{(\lambda)} \\ \text{curve } \overset{\frown}{cfb} \text{ is solid solution }, \Delta G^{M}_{(S)} \end{cases}$$

✻ Assume : Ideal solution for solid and liquid solutions.

$$\therefore \begin{cases} \Delta G^{M}_{(\lambda)} = RT(X_{A} \ln X_{A} + X_{B} \ln X_{B}) + X_{B}\Delta G^{o}_{m(B)} \text{......(1)} \\ \Delta G^{M}_{(S)} = RT(X_{A} \ln X_{A} + X_{B} \ln X_{B}) - X_{A}\Delta G^{o}_{m(A)} \text{......(2)} \end{cases}$$

✻ Common tangent positions e, f are the compositions of liquid and solid solutions in equilibrium.

✻ When T↓, $\overline{\mathbf{ca}}$↓ and $\overline{\mathbf{bd}}$↑, positions of common tangent shift to left.

$X_{A(\lambda)}(T) = ?$, $X_{A(s)}(T) = ?$

For equilibrium between solid and liquid

$$\begin{cases}\Delta\overline{G}^{M}_{A(s)} = \Delta\overline{G}^{M}_{A(\lambda)} \text{......(3)}\\ \Delta\overline{G}^{M}_{B(s)} = \Delta\overline{G}^{M}_{B(\lambda)} \text{......(4)}\end{cases}$$

$$\because\ \Delta\overline{G}^{M}_{A(\lambda)} = \Delta G^{M}_{A(\lambda)} + X_{B(\lambda)}\,\frac{\partial\Delta G^{M}_{(\lambda)}}{\partial X_{A(\lambda)}}$$

From (1) $$\frac{\partial\Delta G^{M}_{(\lambda)}}{\partial X_{A(\lambda)}} = RT(\ln X_{A(\lambda)} - \ln X_{B(\lambda)}) - \Delta G^{o}_{m(B)}$$

$$\therefore\ \Delta\overline{G}^{M}_{A(\lambda)} = RT\ln X_{A(\lambda)} \text{......(5)}$$

Similarly, $$\Delta\overline{G}^{M}_{A(S)} = \Delta G^{M}_{(S)} + X_{B(S)}\,\frac{\partial\Delta G^{M}}{\partial X_{A(S)}}$$

From (2) : $$\therefore\ \Delta\overline{G}^{M}_{A(S)} = RT\ln X_{A(S)} - \Delta G^{o}_{m(A)} \text{......(6)}$$

From (3),(5),(6), $$\therefore RT\ln X_{A(\lambda)} = RT\ln X_{A(S)} - \Delta G^{o}_{m(A)}$$

From (1),(2),(4), $$RT\ln X_{B(S)} = RT\ln X_{B(\lambda)} + \Delta G^{o}_{m(B)}$$

$$\therefore \begin{cases} X_{A(\lambda)} = X_{A(S)}\cdot\exp(-\dfrac{\Delta G^{o}_{m(A)}}{RT})\text{......(7)}\\ X_{B(\lambda)} = X_{B(S)}\cdot\exp(-\dfrac{\Delta G^{o}_{m(B)}}{RT})\end{cases}$$

or $$(1 - X_{A(\lambda)}) = (1 - X_{A(S)})\exp(-\frac{\Delta G^{o}_{m(B)}}{RT})\text{......(8)}$$

From (7),(8)

$$\begin{cases} X_{A(S)} = \dfrac{1-\exp(-\dfrac{\Delta G^{o}_{m(B)}}{RT})}{\exp(-\dfrac{\Delta G^{o}_{m(A)}}{RT}) - \exp(-\dfrac{\Delta G^{o}_{m(B)}}{RT})}\\[2ex] X_{A(\lambda)} = \dfrac{[1-\exp(-\dfrac{\Delta G^{o}_{m(B)}}{RT})]\cdot\exp(-\dfrac{\Delta G^{o}_{m(A)}}{RT})}{\exp(-\dfrac{\Delta G^{o}_{m(A)}}{RT}) - \exp(-\dfrac{\Delta G^{o}_{m(B)}}{RT})}\end{cases}$$

If $C_{P,i(\lambda)} = C_{P,i(S)}$

$$\Delta G^{o}_{m(i)} \cong \Delta H^{o}_{m(i)} \left[\frac{T_{m(i)} - T}{T_{m(i)}} \right]$$

∴Given $T_{m(A)}$, $T_{m(A)}$, $\Delta H^{o}_{m(A)}$, $\Delta H^{o}_{m(B)}$ and

assuming ideal solution model for both liquid and solid solutions.

The solidus and liquidus lines in isomorphous phase diagram can be calculated.

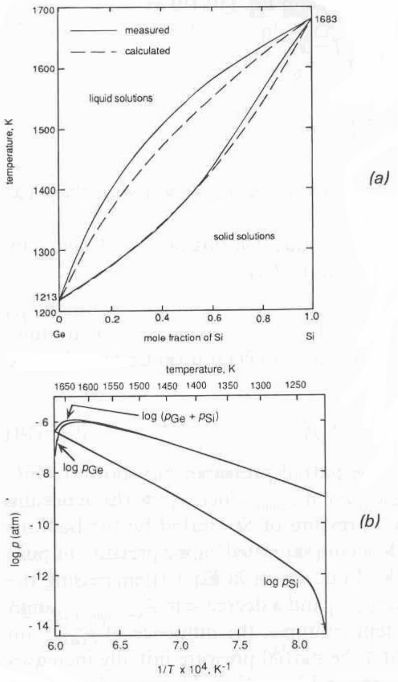

Figure 10.8 (*a*) The calculated phase diagram for the system Ge–Si assuming Raoultian behavior of the solid and liquid solutions. (*b*) The variations, with temperature, of the partial pressures of Ge and Si (and their sum) with composition along the liquidus line

Example: Ge-Si **Figure 10.8**

*Positions of points of double tangency are not influenced by choice of standard states; they are determined only by T, $\Delta G^{o}_{m(A)}$, $\Delta G^{o}_{m(B)}$.

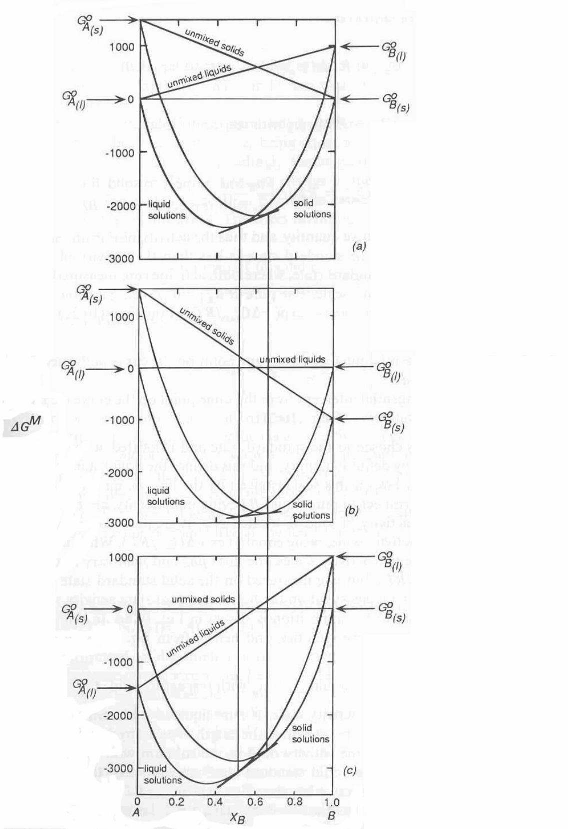

Figure 10.9 The Gibbs free energy of mixing curves for a binary system A–B which forms ideal solid solutions and ideal liquid solutions, at a temperature which is higher than $T_{m(A)}$ and lower than $T_{m(B)}$. (a) Liquid A and solid B chosen as standard states located at $\Delta G^M = 0$. (b) Liquid A and liquid B chosen as standard states located at $\Delta G^M = 0$. (c) Solid A and solid B chosen as standard states located at $\Delta G^M = 0$. The positions of the points of double-tangency are not influenced by the choice of standard state.

See. Eq.(1),(2) and **Figure 10.9**

∗Values of activity, a_i , will depend on the choice of standard state of i and T.

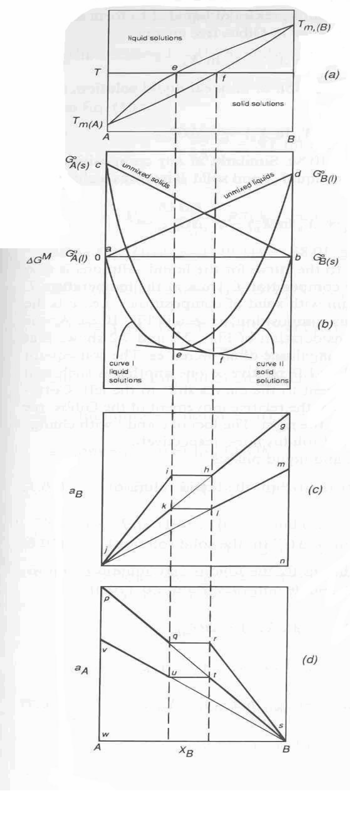

Figure 10.7 (a) The phase diagram for the system A–B. (b) The Gibbs free energies of mixing in the system A–B at the temperature T. (c) The activities of B at the temperature T and comparison of the solid and liquid standard states. (d) The activities of A at the temperature T, and comparison of the solid and liquid standard states.

See. **Figure 10.7 (a)(b)(c)**:

Consider $a_B : \mathrm{T_{m(A)}} < \mathrm{T} < \mathrm{T_{m(B)}}$

If pure B(s) is chosen as standard state,

i.e. $\mathrm{G^o_{B(s)}} = 0$, $\mathrm{G^o_{B(\lambda)}} > 0$

$\therefore a_{B(s)} = 1$, at $\mathrm{X_B} = 1$. i.e. gn =1

point m is $a_{B(\lambda)}$ of pure liquid B

$$\therefore a_{B(\lambda)} = \frac{\mathrm{mn}}{\mathrm{qn}} < 1$$

$$\because \begin{cases} \overline{G}_B = G^o_{B(s)} + RT\ ln(a_B\ \ w.r.t.\ \ B_{(S)}) \\ \overline{G}_B = G^o_{B(\lambda)} + RT\ ln(a_B\ \ w.r.t.\ \ B_{(\lambda)}) \end{cases}$$

But $\mathrm{\overline{G}_B}$ should be independent of choice of standard state.

$$\therefore \mathrm{G^o_{B(\lambda)}} - \mathrm{G^o_{B(s)}} = \Delta \mathrm{G^o_{m(B)}} = \mathrm{RT\ ln}\left[\frac{a_B\ \ w.r.t.\ \ B_{(s)}}{a_B\ \ w.r.t.\ \ B_{(\lambda)}} \right]$$

Since $\mathrm{T} < \mathrm{T_{m(B)}}$, $\therefore \Delta \mathrm{G^o_{m(B)}} > 0$, $\therefore \left[\frac{a_B\ \ w.r.t.\ \ B_{(s)}}{a_B\ \ w.r.t.\ \ B_{(\lambda)}} \right] > 1$

$$\therefore \frac{a_B\ \ w.r.t.\ \ B_{(s)}}{a_B\ \ w.r.t.\ \ B_{(\lambda)}} > 1$$

i.e. $a_{B(s)} > a_{B(\lambda)}$

$$\frac{a_B\ \ w.r.t.\ \ B_{(s)}}{a_B\ \ w.r.t.\ \ B_{(\lambda)}} = \exp\left(\frac{\Delta \mathrm{G^o_{m(B)}}}{\mathrm{RT}}\right)$$

Similarly, $$\frac{a_i\ \ w.r.t.\ \ solid\ \ i}{a_i\ \ w.r.t.\ \ liquid\ \ i} = \exp\left(\frac{\Delta \mathrm{G^o_{m(i)}}}{\mathrm{RT}}\right) = \exp\left[\Delta \mathrm{H^o_{m(i)}} \left(\frac{\mathrm{T_{m(i)}} - \mathrm{T}}{\mathrm{RTT_{m(i)}}}\right)\right]$$

$\therefore$ In **Figure 10.7(c)** , $a_B(\mathrm{X_B})$

$$\begin{cases} \text{line } \overline{\text{jihg}} \text{ is based on B(s) as standard state} \\ \text{line } \overline{\text{jklm}} \text{ is based on B}(\lambda) \text{ as standard state} \end{cases}$$

these two lines vary in a constant ratio of $\exp\left(\frac{\Delta G^{o}_{m(B)}}{RT}\right)$

∗ Similar discussions can be applied to a_A, **Figure 10.7(d)**

∗ When $T\downarrow$, since $T < T_{m(B)}$

$\therefore \Delta G^{o}_{m(B)} > 0$, and $\Delta G^{o}_{m(B)} \uparrow$

$[\frac{a_{B(s)}}{a_{B(\lambda)}}]\uparrow$, i.e. $\left(\frac{gn}{mn}\right)\uparrow$ or $\left(\frac{mn}{gn}\right)\downarrow$

When $T\uparrow$, $\Delta G^{o}_{m(B)}\downarrow$; at $T = T_{m(B)}$, $\Delta G^{o}_{m(B)} = 0$, $a_{B(s)} = a_{B(\lambda)}$

Point g and point m coincide.

§10-6. Binary Phase Diagrams with Liquid and Solid Exhibiting Regular Solution.

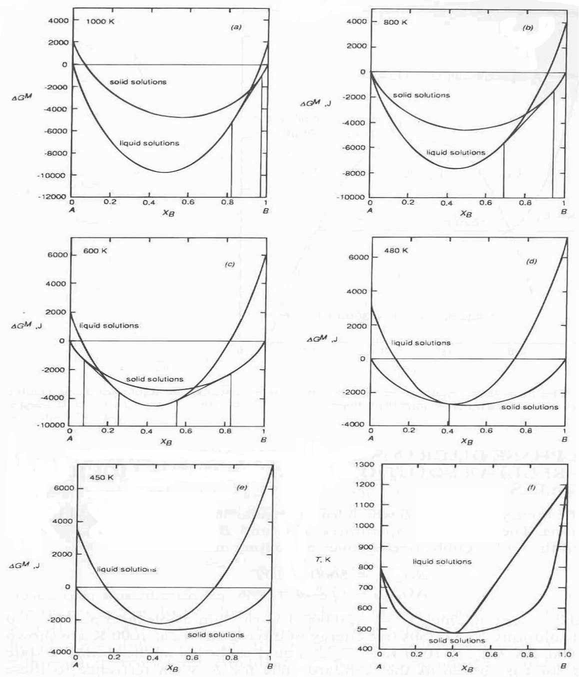

Figure 10.10 The Gibbs free energy of mixing curves at various temperatures, and the phase diagram for a binary system which forms regular solid solutions in which $\Omega_s = 0$ and regular liquid solutions in which $\Omega_l = -20{,}000$ J

1. $T_{m(A)} = 800K$, $T_{m(B)} = 1200K$ **Figure 10.10**

$$\begin{cases} \Delta G_{m(A)} = 8000 - 10T \\ \Delta G_{m(B)} = 12000 - 10T \end{cases} \qquad \begin{matrix} \Omega_\lambda = -20KJ \ (\text{Regular}) \\ \Omega_s = 0 \ (\text{ideal}) \end{matrix}$$

(1) $T_{m(A)} < T = 1000K < T_{m(B)}$

Standard states : $G^o_{B(s)} = 0$, $G^o_{A(\lambda)} = 0$

$$\therefore \begin{cases} \Delta G^M_\lambda = X_B \cdot \Delta G^o_{m(B)} + RT(X_A \ln X_A + X_B \ln X_B) + \Omega_\lambda X_A X_B \\ \Delta G^M_S = -X_A \cdot \Delta G^o_{m(A)} + RT(X_A \ln X_A + X_B \ln X_B) + \Omega_S X_A X_B \end{cases}$$

(2) T= $T_{m(A)}$ =800K , **Figure 10.10(b)**

(3) 480K<T=600K< $T_{m(A)}$ =800K , **Figure 10.10(c)**

Standard states : $G^o_{A(s)}$, $G^o_{B(s)}$

$$\therefore \begin{cases} \Delta G^M_\lambda = X_B \Delta G^o_{m(B)} + X_A \Delta G^o_{m(A)} + RT(X_A \ln X_A + X_B \ln X_B) + \Omega_\lambda X_A X_B \\ \Delta G^M_S = RT(X_A \ln X_A + X_B \ln X_B) \end{cases}$$

(4) T=480K , $\Delta G^M_S = \Delta G^M_\lambda$ at $X_B = 0.41$

(5) T<480K , $\Delta G^M_S < \Delta G^M_\lambda$

2. $$\begin{cases} T_{m(A)} = 800K \\ T_{m(B)} = 1200K \end{cases} \qquad \begin{matrix} \Delta G_{m(A)} = 800 - 10T \\ \Delta G_{m(B)} = 12000 - 10T \end{matrix}$$

$$\begin{cases} \Omega_\lambda = -20KJ \ (\text{Regular}) \\ \Omega_S = +10KJ \ (\text{Regular}) \end{cases}$$

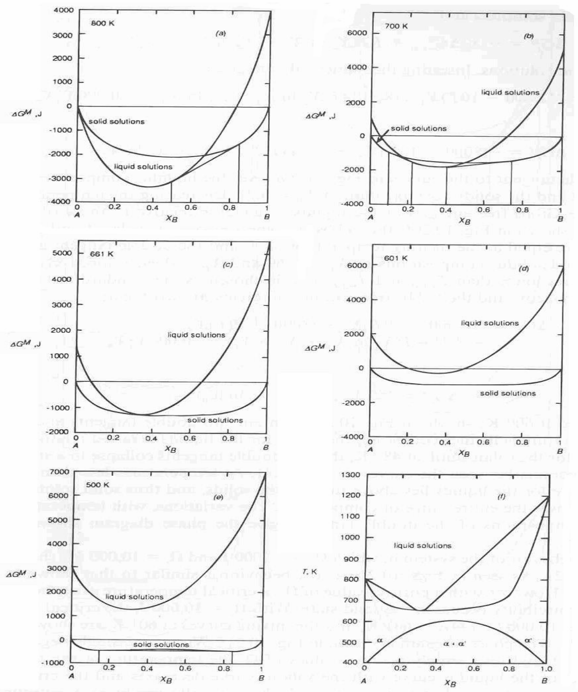

Figure 10.11 The Gibbs free energy of mixing curves at various temperatures, and the phase diagram for a binary system which forms regular solid solutions in which $\Omega_s = 10{,}000$ J and regular liquid solutions in which $\Omega_l = -2000$ J

Figure 10.11

$*$ For solid solution : $T_{cr} = \frac{\Omega_S}{2R} = \frac{10000}{2 \times 8.314} = 601(K)$

But $\Delta G_S^M = \Delta G_\lambda^M$, at T=661K , $X_B = 0.35$

$*$ When $\Omega_\lambda \downarrow$ and $\Omega_S \uparrow$

$T_{cr} \uparrow$ and point ($\Delta G_S^M = \Delta G_\lambda^M$) $\downarrow$

Eventually, these two points merge, then eutectic system occurs.

3. Same conditions , but $\begin{cases} \Omega_\lambda = +20KJ \ \ (\text{Re gular}) \\ \Omega_S = +30KJ \ \ (\text{Re gular}) \end{cases}$

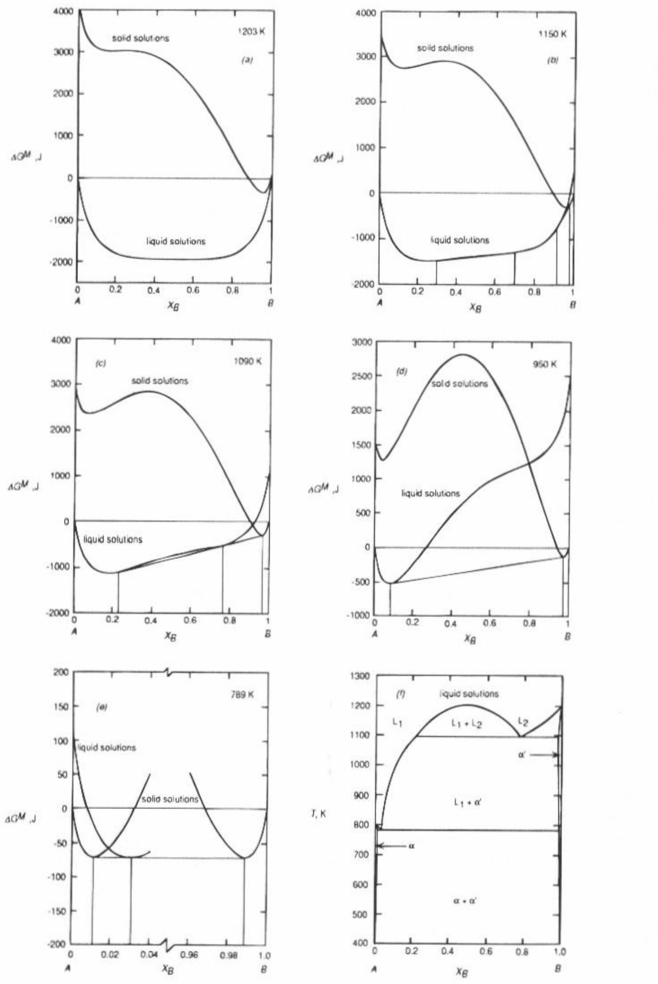

Figure 10.12 The Gibbs free energy of mixing curves at various temperatures, and the phase diagram for a binary system which forms regular solid solutions in which $\Omega_s = 30{,}000$ J and regular liquid solutions in which $\Omega_l = 20{,}000$ J

Figure 10.12

∗ Critical temperatures for solid and liquid solutions.

$$T_{cr(\lambda)} = \frac{\Omega_\lambda}{2R} = 1203\text{K}$$

$$T_{cr(S)} = \frac{\Omega_S}{2R} = 1804\text{K} > T_{cr(\lambda)}$$

$$* \begin{cases} \text{Monotectic} \ : \lambda_2 \rightarrow \lambda_1 + \alpha^{/} \\ \text{Eutectic} \ : \lambda \rightarrow \alpha + \alpha^{/} \end{cases} \qquad \text{are shown.}$$

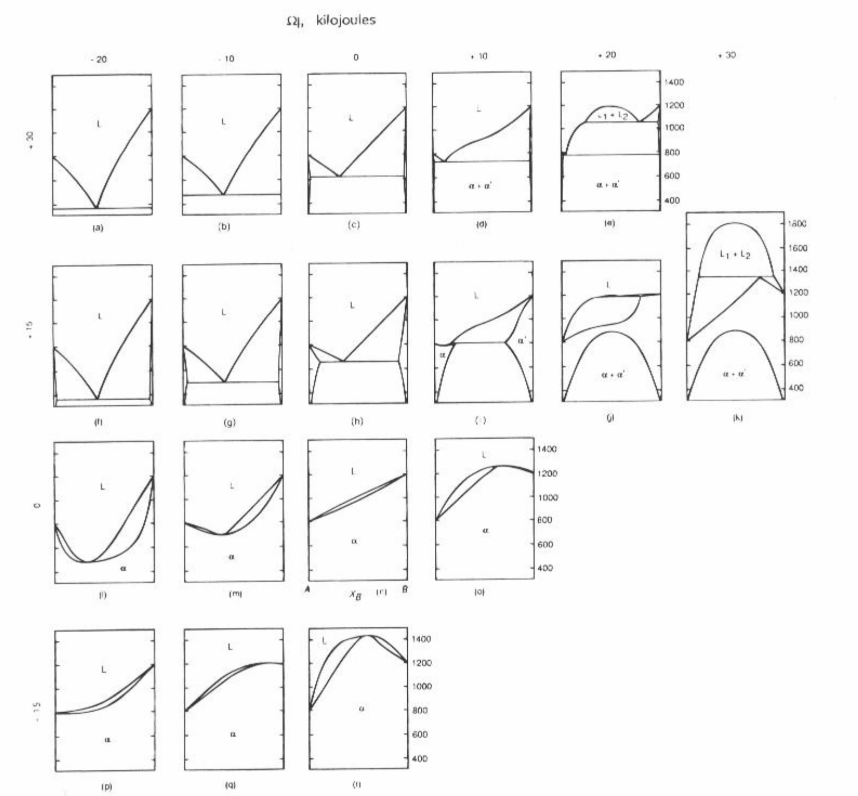

Figure 10.13 Topological changes in the phase diagram for a system *A–B* with regular solid and liquid solutions, brought about by systematic changes in the values of Ω_s and Ω_l. The melting temperatures of *A* and *B* are, respectively, 800 and 1200 K, and the molar entropies of melting of both components are 10 J/K (From A. D. Pelton and W. T. Thompson, *Prog. Solid State Chem.* (1975), vol. 10, part 3, p. 119)

4. **Figure 10.13** Different Ω_λ, Ω_S

∗ (a) → (d), $\Omega_\lambda \uparrow \Rightarrow T_{eutectic} \uparrow$, (e) liquid is unstable ⇒ monotectic.

§7. Eutectic Phase Diagrams and Monotectic Phase Diagram

1. Complete solid solubility of components A, B:

$$\begin{cases}(1)\text{Same crystal structure}\\(2)\text{Comparable atomic size}\\(3)\text{Similar electronegativity}\\(4)\text{Similar valence}\end{cases}$$

if any one condition is not met ⇒ miscibility gap.

2. A-B system with two terminal solid solutions. (α,β)

   e.g. eutectic phase diagram. **Figure 10.14**

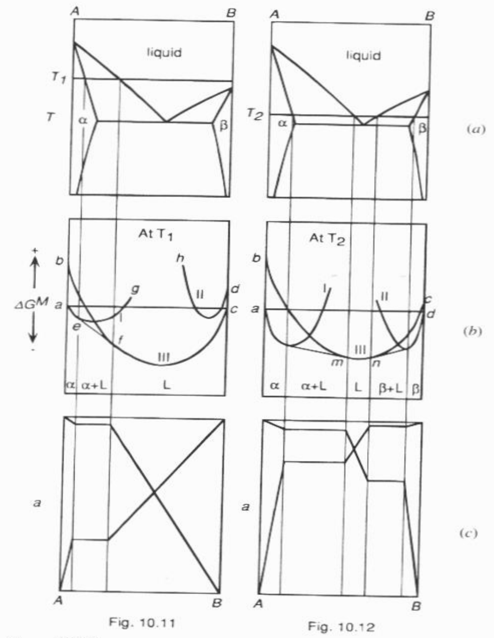

Figure 10.14 The effect of temperature on the molar Gibbs free energies of mixing and the activities of the components of the system A–B

3. Solid solubility in α, β phases are extremely small.

$\ast$ When solid solubility$\downarrow$ $\Rightarrow \Delta G_{\alpha}^{M}$ is compressed toward $X_A = 1$

i.e. it coincides with vertical axis.

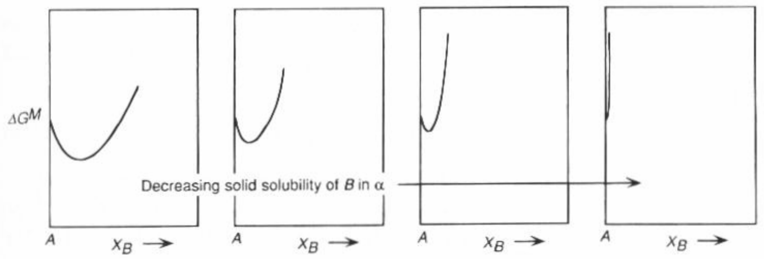

Figure 10.15 The effect of decreasing solid solubility on the molar Gibbs free energy of mixing curve

Figure 10.15 $\ast\begin{cases}\text{Complete miscibility in liquid state}\\ \text{Complete immiscibility in solid state}\end{cases}$

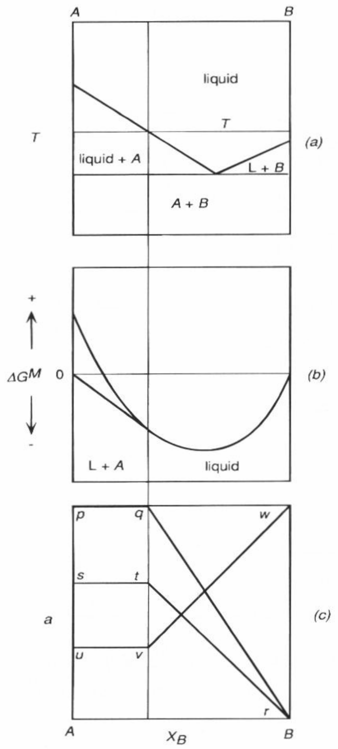

Figure 10.16 The molar Gibbs free energy of mixing and the activities in a binary eutectic system that exhibits complete liquid miscibility and vitual complete solid immiscibility

Figure 10.16 Liquidus curves can be calculated assuming that liquid solution is an ideal solution.

a_A w.r.t. $A_{(S)}$ at $X_A = 1$ $\quad a_A = 1$

Consider at $T < T_{m(A)}$, (pure $A_{(s)}$ + liquid) coexist.

$\therefore G^o_{A(s)} = \overline{G}_{A(\lambda)} = G^o_{A(\lambda)} + RT \ln a_A$ w.r.t. $A_{(\lambda)}$

$\therefore G^o_{A(\lambda)} - G^o_{A(s)} = \Delta G^o_{m(A)} = -RT \ln a_A$

assuming ideal liquid solution $a_A = X_{A(\lambda)}$

$\therefore \Delta G^o_{m(A)} = -RT \ln X_{A(\lambda)}$

i.e. $X_{A(\lambda)} = \exp(-\dfrac{\Delta G^o_{m(A)}}{RT})$

If $\Delta G^o_{m(A)} = f$ (T) is known $\Rightarrow X_{A(\lambda)} = g$ (T) can be obtained.

e.g. Bi-Cd phase diagram **Figure 10.17**

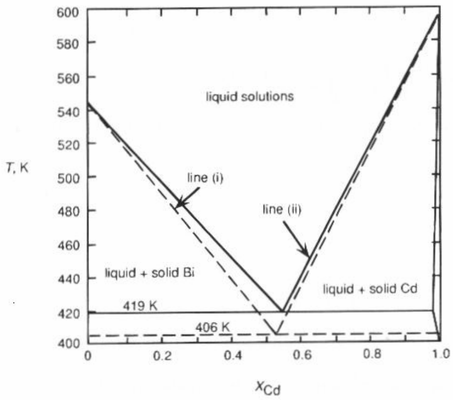

Figure 10.17 The phase diagram for the system Bi–Cd. The full lines are the measured liquidus lines, and the broken lines are calculated assuming no solid solution and ideal mixing in the liquid solutions.

$$(3.1)\ \mathrm{Bi}\begin{cases} T_{m(Bi)} = 544\ \ K \\ \Delta H^{o}_{m(Bi)} = 10900\ \ (J) \\ C_{P,Bi(s)} = 18.8 + 22.6\times10^{-3}T\ \ (J/K) \\ C_{P,Bi(\lambda)} = 20 + 6.15\times10^{-3}T + 21.1\times10^{5}T^{-2}\ \ (J/K) \end{cases}$$

$$\therefore\ \text{At } T = T_{m(Bi)} = 544K,\ \ \Delta G^{o}_{m(Bi)} = 0 = \Delta H^{o}_{m(Bi)} - T_m \cdot \Delta S^{o}_{m(Bi)}$$

$$\therefore \Delta S^{o}_{m(Bi)} = \frac{\Delta H^{o}_{m(Bi)}}{T_{m(Bi)}} = 20.0\ (J/K)$$

$$\Delta G^{o}_{m(Bi)}(T) = ? \qquad T \neq T_{m(Bi)}$$

$$\therefore \Delta C_{P,Bi} = C_{P,Bi(\lambda)} - C_{P,Bi(s)} = 1.2 - 16.45\times10^{-3}T + 21.1\times10^{5}T^{-2}$$

$$\Delta G^{o}_{m(Bi)} = \Delta H^{o}_{m(Bi),544} + \int_{544}^{T}\Delta C_{P,Bi}\,dT - T\left(\Delta S^{o}_{m(Bi),544} + \int_{544}^{T}\frac{\Delta C_{P,Bi}}{T}\,dT\right)$$

$$= 16560 - 23.79T - 1.2T\ \ln T + 8.225\times10^{-3}T^{2} - 10.55\times10^{5}T^{-1}$$

$$\text{ideal solution}:\ -RT\ln X_{Bi(\lambda)} = \Delta G^{o}_{m(Bi)}$$

$\therefore$

$$\ln X_{Bi(\lambda)} = \frac{-1992}{T} + 2.861 + 0.144\ln T - 9.892\times10^{-4}T + \frac{1.269\times10^{5}}{T^{2}} \ldots\ldots(1)$$

$\therefore X_{Bi(\lambda)}(T)$ is line(i) in **Fig. 10.17**

$$(3.2)\ \mathrm{Cd}\begin{cases} T_{m(d)} = 594\ \ \mathrm{K} \\ \Delta H^{o}_{m(Cd)} = 6400\ \ \mathrm{J},\ \ \Delta S^{o}_{m(Cd)} = 10.77\ \ \mathrm{J/K} \\ C_{P,Cd(s)} = 22.2 + 12.3\times 10^{-3}\,T\ \ (\mathrm{J/K}) \\ C_{P,Cd(\lambda)} = 29.7\ \ (\mathrm{J/K}) \end{cases}$$

$$\therefore\ \ \Delta G^{o}_{m(Cd)} = \Delta H^{o}_{m(Cd)} + \int_{594}^{T}\Delta C_{P,Cd}\,dT - T\left(\Delta S^{o}_{m(Cd)} + \int_{594}^{T}\frac{\Delta C_{P,(Cd)}}{T}\,dT\right)$$

$$\Delta G^{o}_{m(Cd)} = -RT\ln X_{Cd(\lambda)}\,,\ \ \begin{cases} *\ \text{assume ideal liquid solution} \\ *\ \text{neglect solid solubility} \end{cases}$$

$$\therefore\ \ \ln X_{Cd(\lambda)} = \frac{-495}{T} - 4.489 + 0.90\ \ln T - 7.397\times 10^{-4}\,T\ \ldots\ldots(2)$$

$$(3.3)\ \ \therefore\ \text{Eutectic temperature:}\begin{cases} *\,(1)\ \ X_{Bi(\lambda)} = f(T) \\ *\,(2)\ \ 1 - X_{Bi(\lambda)} = g(T) \end{cases}$$

$$\therefore\ \ 1 - f(T) = g(T)\ \ \Rightarrow\ \ T = T_e = 406\ \mathrm{K}$$

$$\text{Actual}\ :\ \ T_e = 419\mathrm{K} > (T_e = 406\mathrm{K})_{cal.}$$

$\because$ Caculation is based on “ideal” solution.

$$\text{At}\ \ T=419\mathrm{K}\ ,\ \ \begin{cases} \text{from}\ \ (1): \Delta G^{o}_{m(Bi)} = 2482\mathrm{J} \\ \text{from}\ \ (2): \Delta G^{o}_{m(Cd)} = 1898\mathrm{J} \end{cases}$$

$$\because\begin{cases} \Delta G^{o}_{m(Bi)} = RT\ln\ a_{Bi} \\ \Delta G_{m(Cd)} = RT\ln\ a_{Cd} \end{cases}$$

$$\therefore\begin{cases} a_{Bi} = 0.49 \\ a_{Cd} = 0.58 \end{cases}\ \ \text{, Actual eutectic composition is}\ \ X_{Cd} = 0.55,\ \ X_{Bi} = 0.45$$

$$\therefore\begin{cases} \gamma_{Bi} = \dfrac{a_{Bi}}{X_{Bi}} = 1.09 \\ \gamma_{Cd} = \dfrac{a_{Cd}}{X_{Cd}} = 1.05 \end{cases} > 1.0$$

$\therefore$ positive deviation from ideality ! $\Rightarrow T_e > T_{e(cal.)}$

4. When positive deviation from ideal liquid solution increase , $G^{XS} > 0$, $G^{XS}\uparrow$ $\Rightarrow \Omega > \Omega_{cr}$ (1) Liquidus curve is not a monotonic. Max. and min. of curve forms.

(2) Liquid miscibility gap forms.

$\Rightarrow$ as conditions (1),(2) merge, monotectic system appears.

∗ Assuming liquid solution is regular.

$$\therefore -\Delta G^{o}_{m(A)} = RT\ \ln a_A = RT\ \ln X_A + RT\ \ln \gamma_A$$

$$\because \text{regular solution}: \quad \alpha = \frac{\ln \gamma_A}{(1-X_A)^2} = \frac{\Omega}{RT}$$

$$\therefore \Delta G^{o}_{m(A)} = RT\ \ln X_A + RT\,\alpha\,(1-X_A)^2$$

$$\Delta G^{o}_{m(A)} = RT\ \ln X_A + \Omega\ (1-X_A)^2$$

e.g. $T_{m(A)} = 2000K$, $\Delta H^{o}_{m(A)} = 10KJ$

$$\therefore -\Delta G^{o}_{m(A)} = 10000+5T = RT\ \ln X_A + \Omega\ (1-X_A)^2$$

Liquidus curve $X_{A(\lambda)}$ for different Ω is shown in **Figure 10.18**

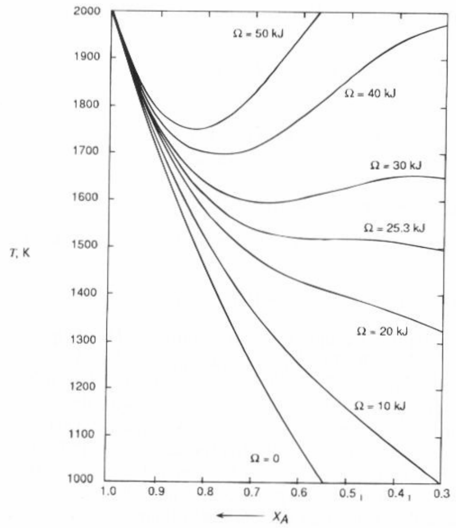

Figure 10.18 Calculated liquidus lines assuming regular solution behavior in the liquid solutions and no solid solubility

∴

$\Omega > \Omega_{cr} = 25.3KJ$

max. and min. appears $\Rightarrow$ part of curve has no physical meaning.

$$\text{At}\ \ \Omega = \Omega_{cr} \quad \begin{cases} T_{cr} = 1413K \\ X_A = 0.5 \end{cases}$$

$$\left(\frac{dT}{dX_A}\right) = 0, \quad \frac{d^2T}{dX_A^2} = 0$$

Proof :

$$\because \frac{a_A \text{ w.r.t. } A_{(S)}}{a_A \text{ w.r.t. } A_{(\lambda)}} = \exp[\frac{\Delta G^o_{m(A)}}{RT}] = \exp[\frac{\Delta H^o_{m(A)}}{RT}(\frac{T_{m(A)} - T}{T_{m(A)}})]$$

pure $A_{(S)}$ is standard state. $\therefore a_A = 1$ w.r.t. $A_{(S)}$

$$\therefore \frac{1}{a_{A(l)}} = \exp[\frac{\Delta H^o_{m(A)}}{RT} - \frac{\Delta H^o_{m(A)}}{RT_{m(A)}}]$$

$$\therefore \ln a_A = -\frac{\Delta H^o_{m(A)}}{RT} + \frac{\Delta H^o_{m(A)}}{RT_{m(A)}}$$

$$\frac{d\ln a_A}{dT} = \frac{\Delta H^o_{m(A)}}{RT^2}, \quad \therefore d\ln a_A = \frac{da_A}{a_A} = \frac{\Delta H^o_{m(A)}}{RT^2} dT$$

$$\frac{dT}{dX_A} = \frac{RT^2}{\Delta H^o_{m(A)} \cdot a_A} \cdot \frac{da_A}{dX_A}$$

$$\frac{d^2T}{dX_A^2} = (\frac{2RT}{\Delta H^o_{m(A)} \cdot a_A} \cdot \frac{da_A}{dX_A})\frac{dT}{dX_A} - (\frac{RT^2}{\Delta H^o_{m(A)}} \cdot \frac{da_A}{dX_A}). \frac{1}{a_A^2}. (\frac{da_A}{dX_A})$$

$$+ \frac{RT^2}{\Delta H^o_{m(A)} \cdot a_A}. \frac{d^2a_A}{dX_A^2}$$

$$\because \Omega = \Omega_{cr}, T = T_{cr}, \frac{da_A}{dX_A} = 0 \text{ and } \frac{d^2a_A}{dX_A^2} = 0$$

$$\therefore \frac{dT}{dX_A} = 0 \text{ and } \frac{d^2T}{dX_A^2} = 0$$

* When $\Omega = 30KJ$, for regular liquid solution

$$T_{cr} = \frac{\Omega}{2R} = \frac{30000}{8.31 \times 2} = 1804K$$

Figure 10.19.

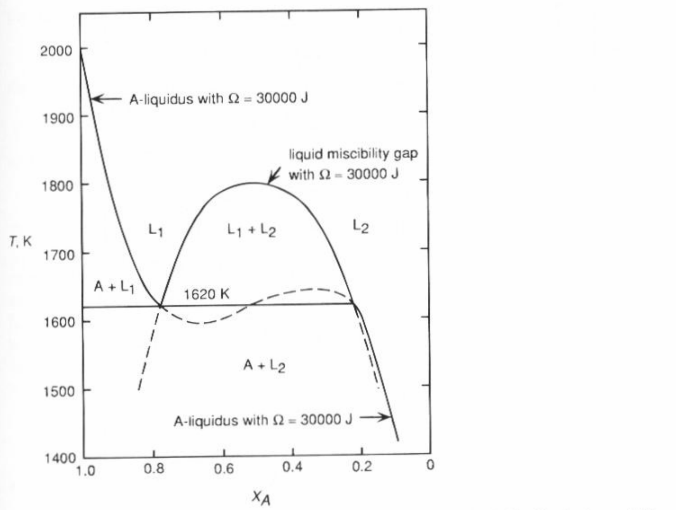

Figure 10.19 The monotectic equilibrium in a binary system in which the liquid solutions exhibit regular solution behavior with Ω = 30,000 J

Ex: Cs-Rb phase diagram, **Figure 10.20**

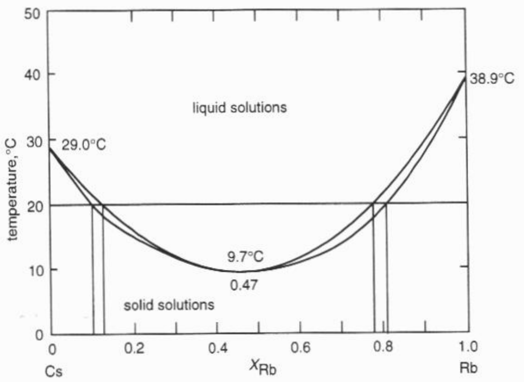

Figure 10.20 The phase diagram for the system Cs–Rb

$$\begin{cases} T_{m(Cs)} = 28.4^{o}C \\ T_{m(Rb)} = 39.5^{o}C \end{cases}, \quad \begin{cases} \Delta G^{o}_{m(Cs)} = 2100 - 6.95T \ \ (J) \\ \Delta G^{o}_{m(Rb)} = 2200 - 7.05T \ \ (J) \end{cases}$$

Compare with theory assuming: $\begin{cases} \text{liquid solution : ideal} \\ \text{solid solution : regular}, \Omega_S = ? \end{cases}$

Sol: From phase diagram : liquidus and solidus curves touch each other

$$\text{at} \begin{cases} X_{Rb} = 0.47 \\ T = 9.7^{o}C \end{cases}$$

$$\text{when} \begin{cases} T < T_{m(Cs)} \\ T < T_{m(Rb)} \end{cases}$$

Standard states : $G^{o}_{Cs(s)}=0$, $G^{o}_{Rb(s)}=0$

$$\therefore \begin{cases} \Delta G^{M}_{(\lambda)} = RT(X_{Rb}\ln X_{Rb} + X_{Cs}\ln X_{Cs}) + X_{Rb}\cdot\Delta G^{o}_{m(Rb)} + X_{Cs}\cdot\Delta G^{o}_{m(Cs)} \\ \Delta G^{M}_{(s)} = RT(X_{Rb}\ln X_{Rb} + X_{Cs}\ln X_{Cs}) + \Omega_S X_{Rb} X_{Cs} \end{cases}$$

at $\begin{cases} T = 9.7^{o}C = 282.7K \\ X_{Rb} = 0.47, X_{Cs} = 0.53 \end{cases}$ $\Delta G^{M}_{(\lambda)} = \Delta G^{M}_{(s)}$, $\therefore \Omega_s = 668(J)$

c.p. When $T=20\,^{o}C=293K$

common tangents to $\Delta G^{M}_{(\lambda)}$ and $\Delta G^{M}_{(s)}$

$\begin{cases} X_{Rb(s)} = 0.10 \\ X_{Rb(\lambda)} = 0.13 \end{cases}$ $\begin{cases} X_{Rb(\lambda)} = 0.75 \\ X_{Rb(s)} = 0.81 \end{cases}$

Very good fitting!! **Figure 10.21**