

Chapter 9

The Behavior of Solutions

9.7 Nonideal Solutions

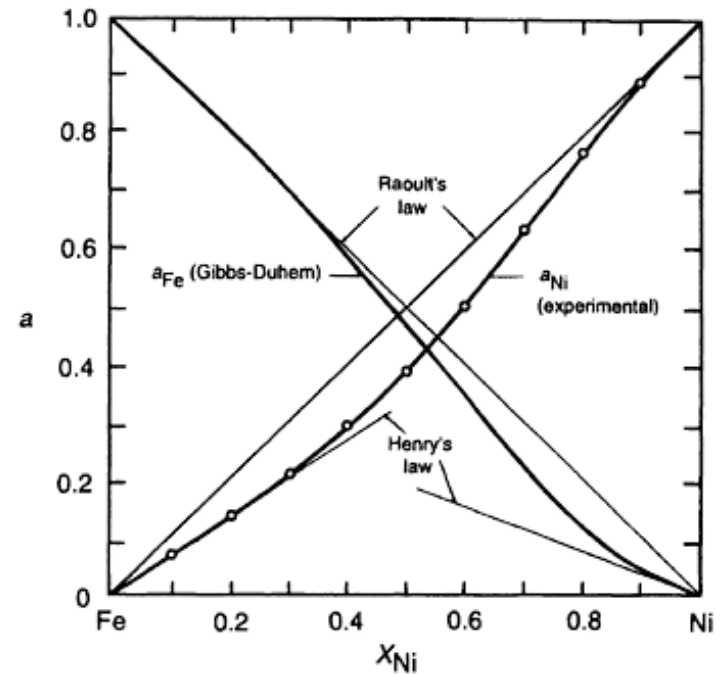


Figure 9.8 Activities in the system iron-nickel at 1600°C. (From G.R.Zellars, S.L.Payne, J.P.Morris, and R.L.Kipp, "The Activities of Iron and Nickel in Liquid Fe-Ni Alloys," *Trans. AIME* (1959), vol. 215, p. 181.)

9.7 Nonideal Solutions

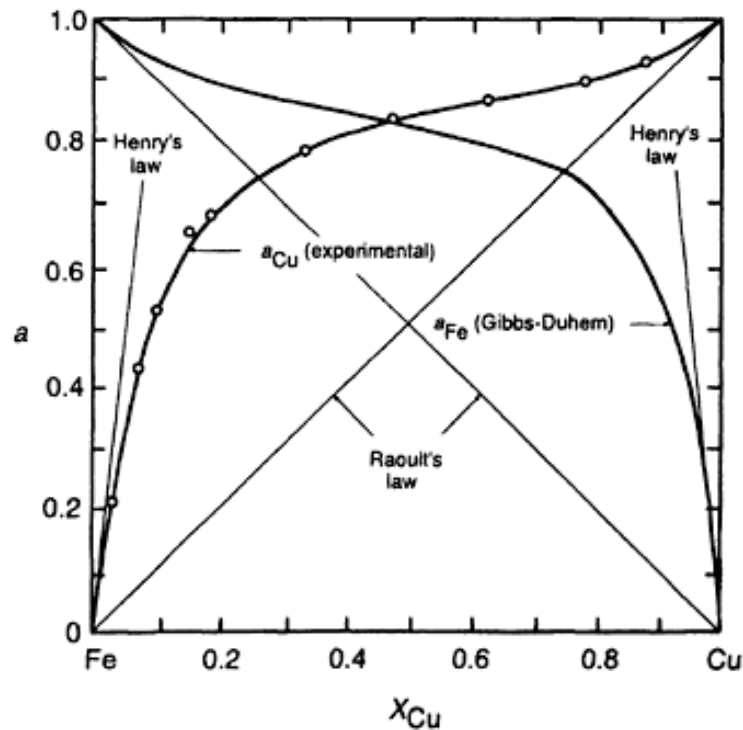


Figure 9.9 Activities in the system iron-copper at 1550°C. (From J.P.Morris and G.R.Zellars, "Vapor Pressure of Liquid Copper and Activities in Liquid Fe-Cu Alloys," *Trans. AIME* (1956), vol. 206, p. 1086.)

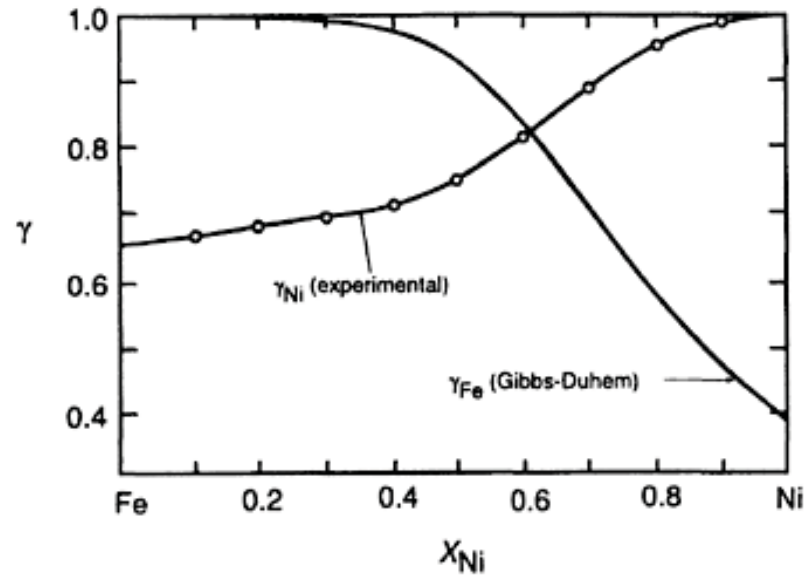


Figure 9.10 Activity coefficients in the system iron-nickel at 1600°C.

9.7 Nonideal Solutions

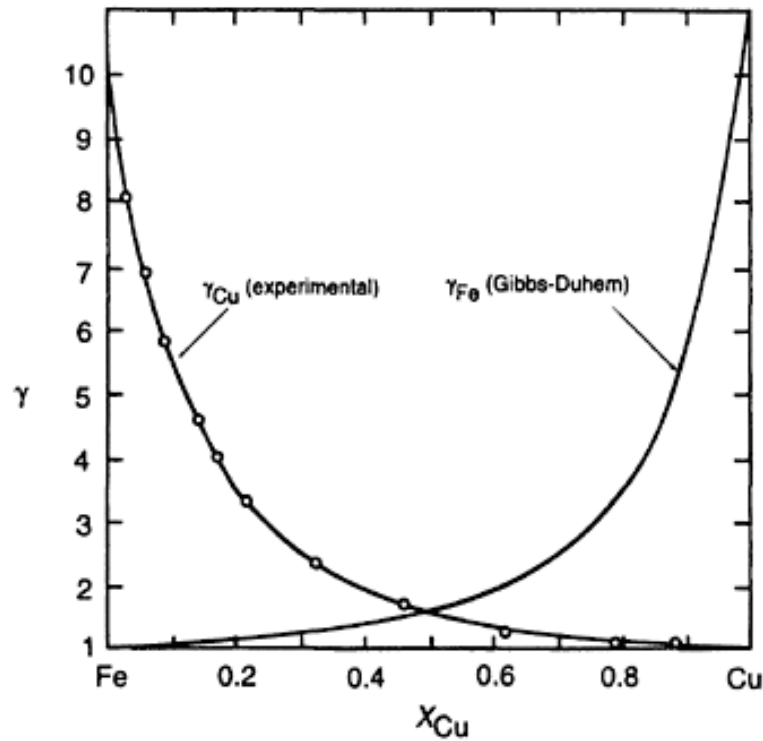
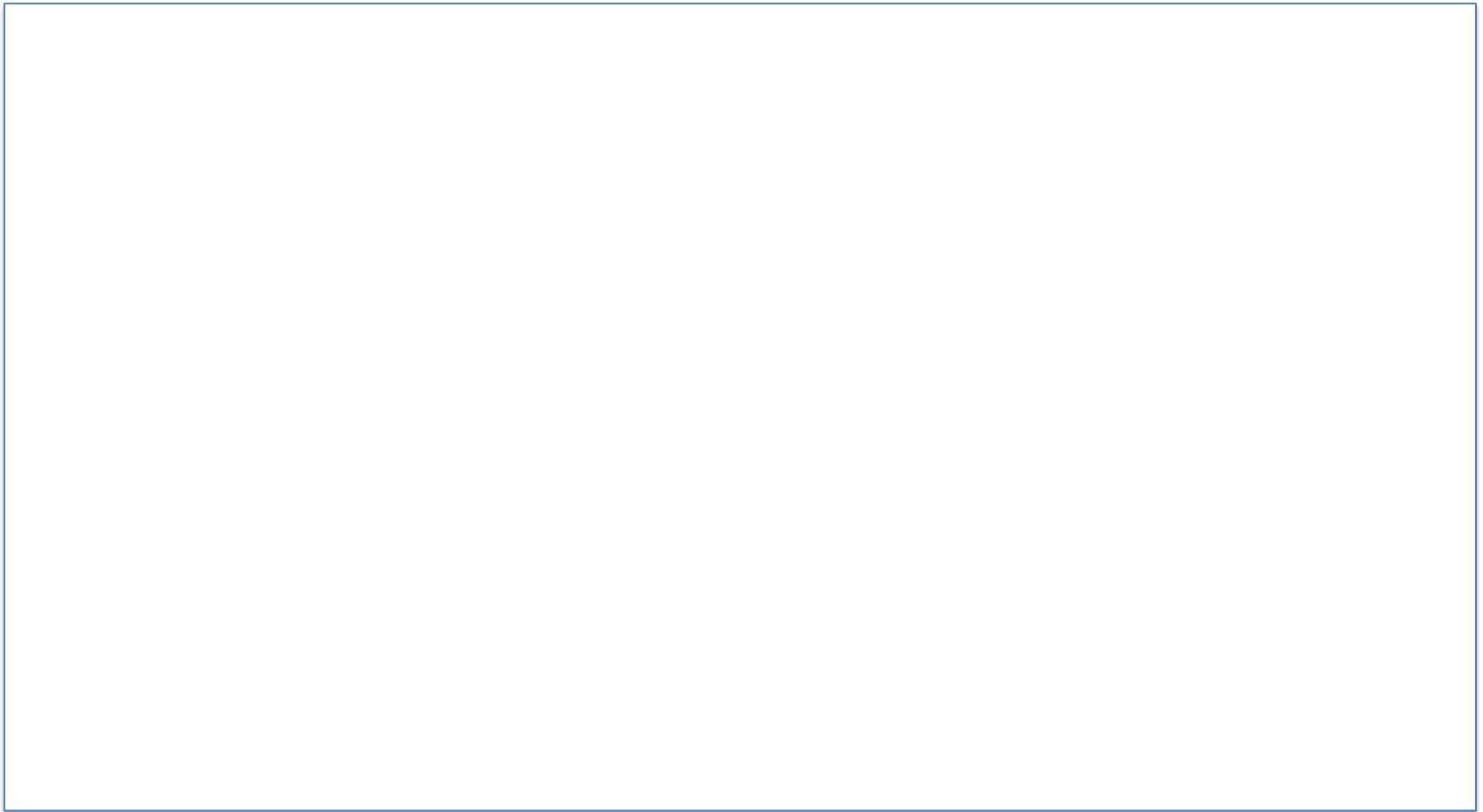


Figure 9.11 Activity coefficients in the system iron-copper at 1550°C.

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

(A) Method 1



9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

(9.51)

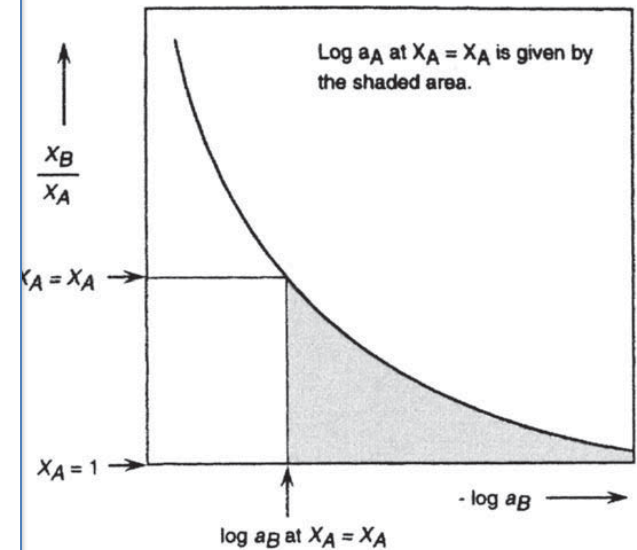


Figure 9.12 A schematic representation of the variation of $\log a_B$ with X_B/X_A in a binary solution, and illustration of the application of the Gibbs-Duhem equation to calculation of the activity of component A .

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

(B) Method 2

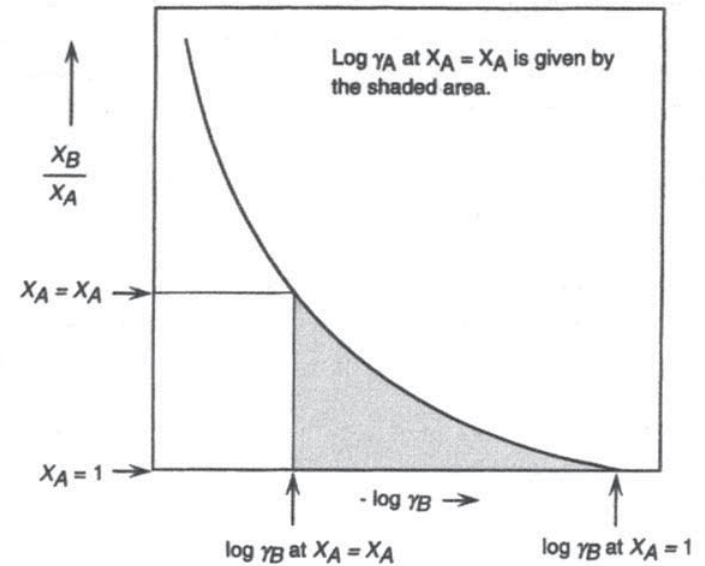


Figure 9.13 A schematic representation of the variation of $\log \gamma_B$ with X_B/X_A in a binary solution, and illustration of the application of the Gibbs-Duhem equation to calculation of the activity coefficient of component A .

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

(C) Method 3

<The α -Function>

$$\alpha_i = \frac{\ln \gamma_i}{(1 - X_i)^2} \quad (9.56)$$

$$\alpha_A = \frac{\ln \gamma_A}{X_B^2} \quad \text{and} \quad \alpha_B = \frac{\ln \gamma_B}{X_A^2}$$

$$\ln \gamma_A = \alpha_A X_B^2 \quad \text{and} \quad \ln \gamma_B = \alpha_B X_A^2 \quad (9.57)$$

$$d \ln \gamma_B = 2\alpha_B X_A dX_A + X_A^2 d\alpha_B \quad (9.58)$$

$$\begin{aligned} d \ln \gamma_A &= -\frac{X_B}{X_A} 2\alpha_B X_A dX_A - \frac{X_B}{X_A} X_A^2 d\alpha_B \\ &= -2X_B \alpha_B dX_A - X_B X_A d\alpha_B \end{aligned} \quad (9.59)$$

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

<The α -Function>

$$\begin{aligned}
 \int d(x,y) &= \int ydx + \int xdy \\
 \int X_B X_A d\alpha_B &= \int d(X_B X_A \alpha_B) - \int \alpha_B d(X_B X_A) \\
 \ln \gamma_A &= - \int 2X_B \alpha_B dX_A - \int d(X_B X_A \alpha_B) + \int \alpha_B d(X_B X_A) \\
 &= - \int 2X_B \alpha_B dX_A - X_B X_A \alpha_B + \int \alpha_B X_B dX_A + \int \alpha_B X_A dX_B \\
 &= - \int 2X_B \alpha_B dX_A - X_B X_A \alpha_B + \int \alpha_B X_B dX_A - \int \alpha_B X_A dX_A \\
 &= -X_B X_A \alpha_B - \int (2X_B - X_B + X_A) \alpha_B dX_A \\
 &= -X_B X_A \alpha_B - \int_{X_A=1}^{X_A=X_A} \alpha_B dX_A
 \end{aligned} \tag{9.61}$$

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

<The α -Function>

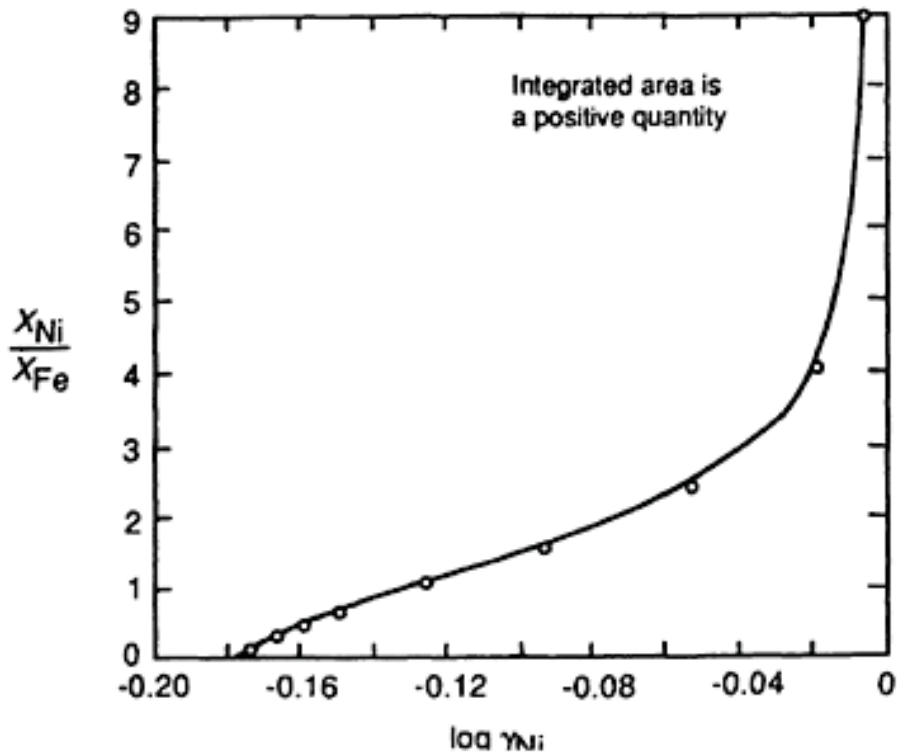


Figure 9.14 Application of the Gibbs-Duhem equation to determination of the activity of iron in the system iron-nickel.

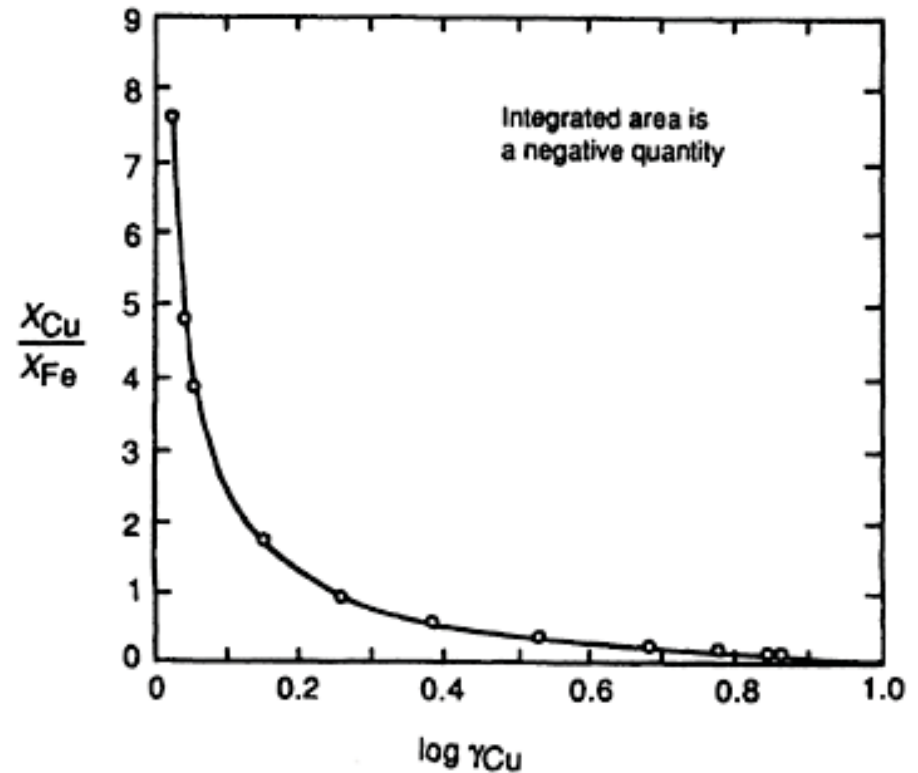


Figure 9.15 Application of the Gibbs-Duhem equation to determination of the activity of iron in the system iron-copper.

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

<The α -Function>

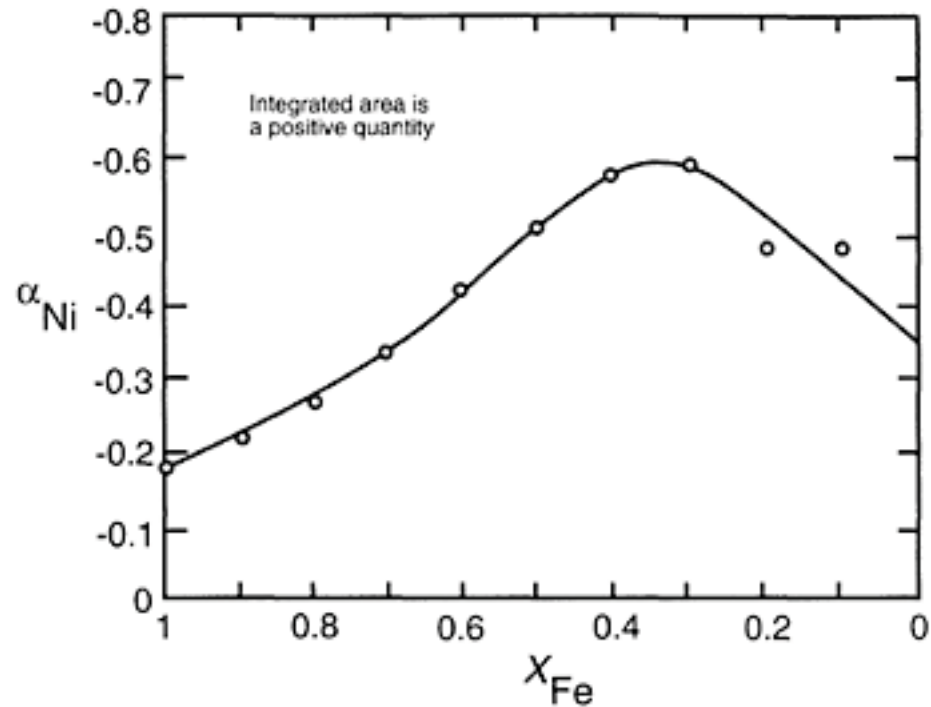


Figure 9.16 The variation of α_{Ni} with composition in the system iron-nickel.

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

<The Relationship between Henry's and Raoult's Laws>

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

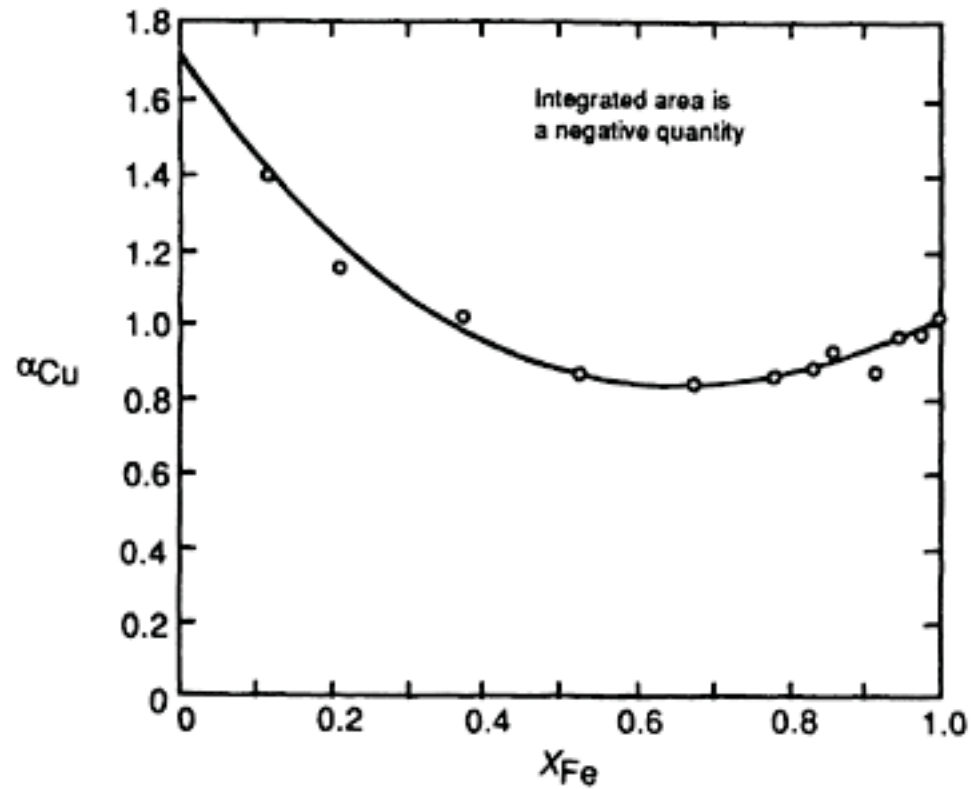
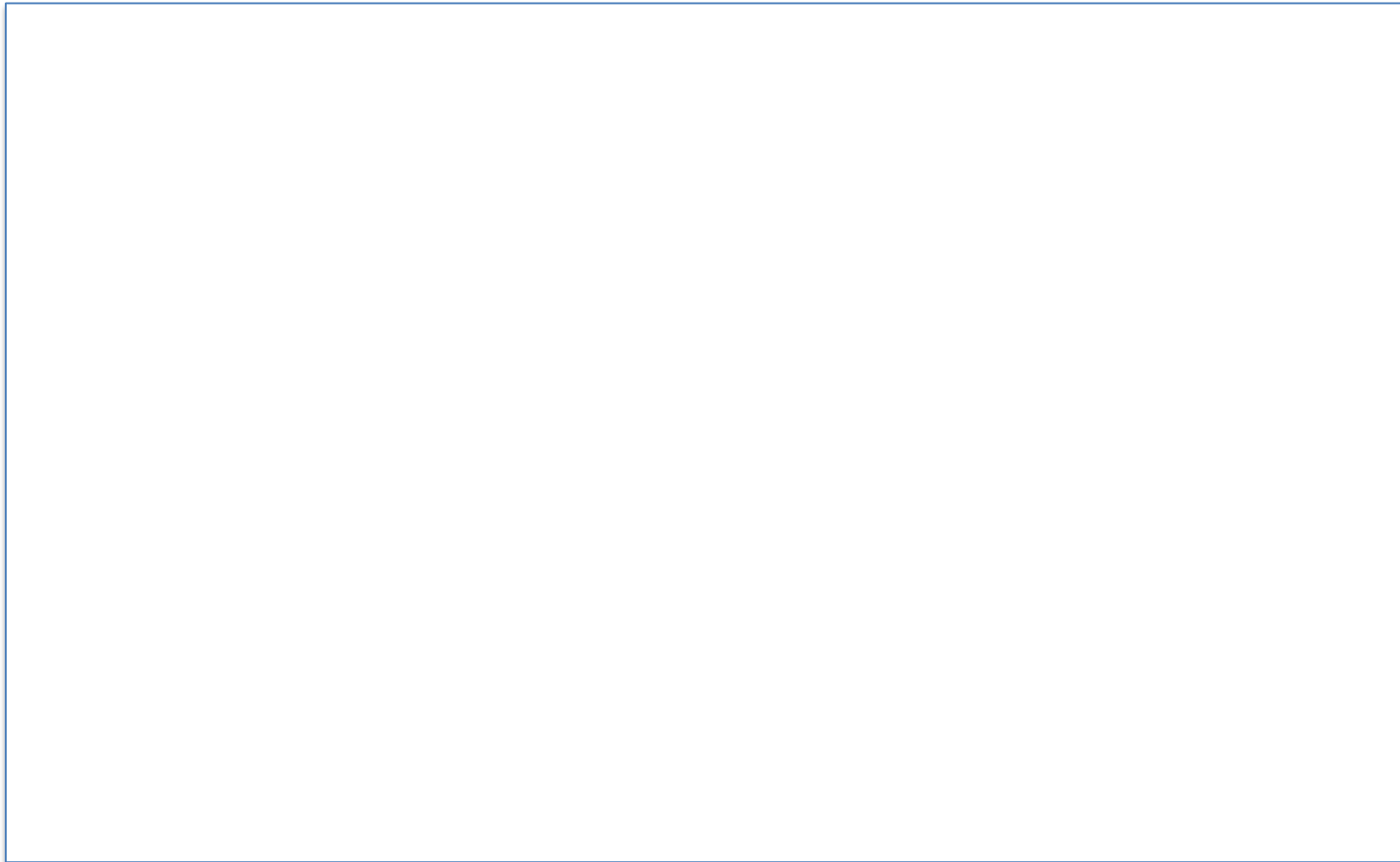


Figure 9.17 The variation of α_{Cu} with composition in the system iron-copper.

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

(D) Method 4

<Direct calculation of the integral molar Gibbs free energy of mixing>



(9.62)

(9.63)

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

<Direct calculation of the integral molar Gibbs free energy of mixing>

$$\Delta G^M \text{ (in the system Fe-Ni)} = RTX_{\text{Fe}} \int_0^{X_{\text{Ni}}} \frac{\ln a_{\text{Ni}}}{X_{\text{Fe}}^2} dX_{\text{Ni}}$$

$$\Delta G^M \text{ (in the system Cu-Fe)} = RTX_{\text{Fe}} \int_0^{X_{\text{Cu}}} \frac{\ln a_{\text{Cu}}}{X_{\text{Fe}}^2} dX_{\text{Cu}}$$

$$\begin{aligned} \Delta G^M &= RT(1 - X_j) \int_0^{X_j} \frac{\ln X_j}{(1 - X_j)^2} dX_j \\ &= RT(1 - X_j) \left[\frac{X_j \ln X_j}{1 - X_j} + \ln(1 - X_j) \right] \\ &= RT \left[X_j \ln X_j + (1 - X_j) \ln(1 - X_j) \right] \end{aligned}$$

$$\Delta H^M = X_B \int_0^{X_A} \frac{\Delta \bar{H}_A^M}{X_B^2} dX_A \quad (9.64)$$

$$\Delta S^M = X_B \int_0^{X_A} \frac{\Delta \bar{S}_A^M}{X_B^2} dX_A \quad (9.65)$$

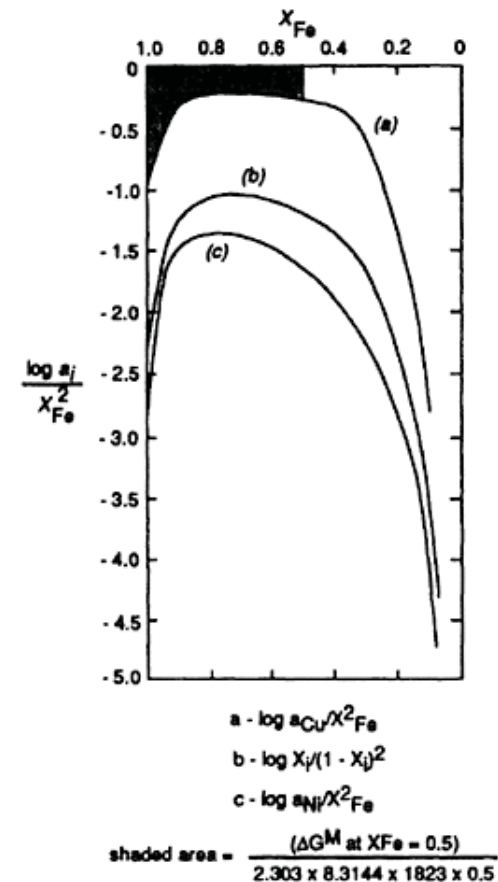


Figure 9.18 Illustration of the direct calculation of the integral molar Gibbs free energies of mixing in the systems iron-copper at 1550°C and iron-nickel at 1600°C.

9.8 Application of the Gibbs-Duhem Relation to the Determination of Activity

<Direct calculation of the integral molar Gibbs free energy of mixing>

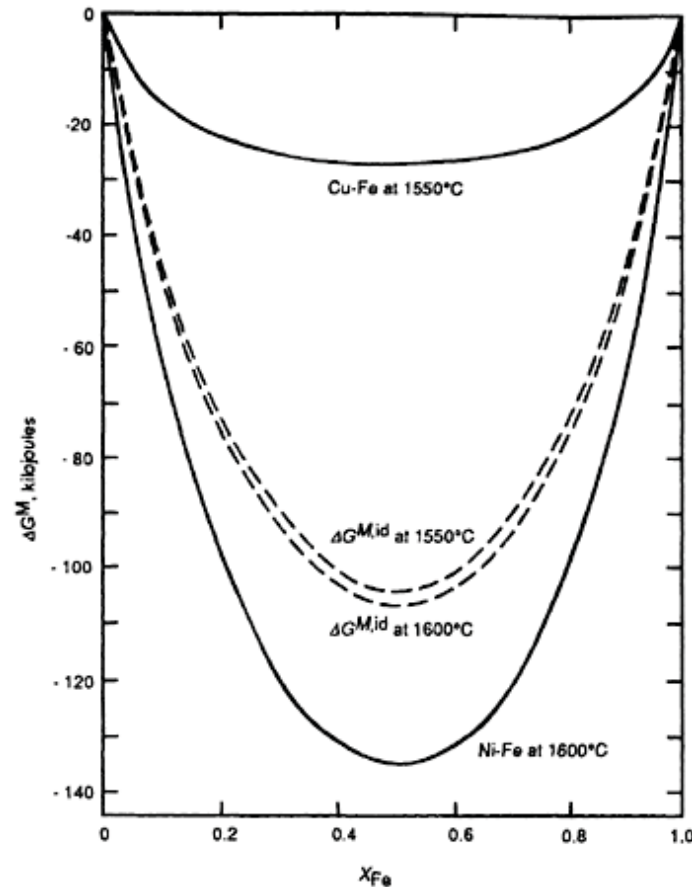


Figure 9.19 The integral molar Gibbs free energies of mixing in the systems iron-copper at 1550°C and iron-nickel at 1600°C.

9.9 Regular Solutions

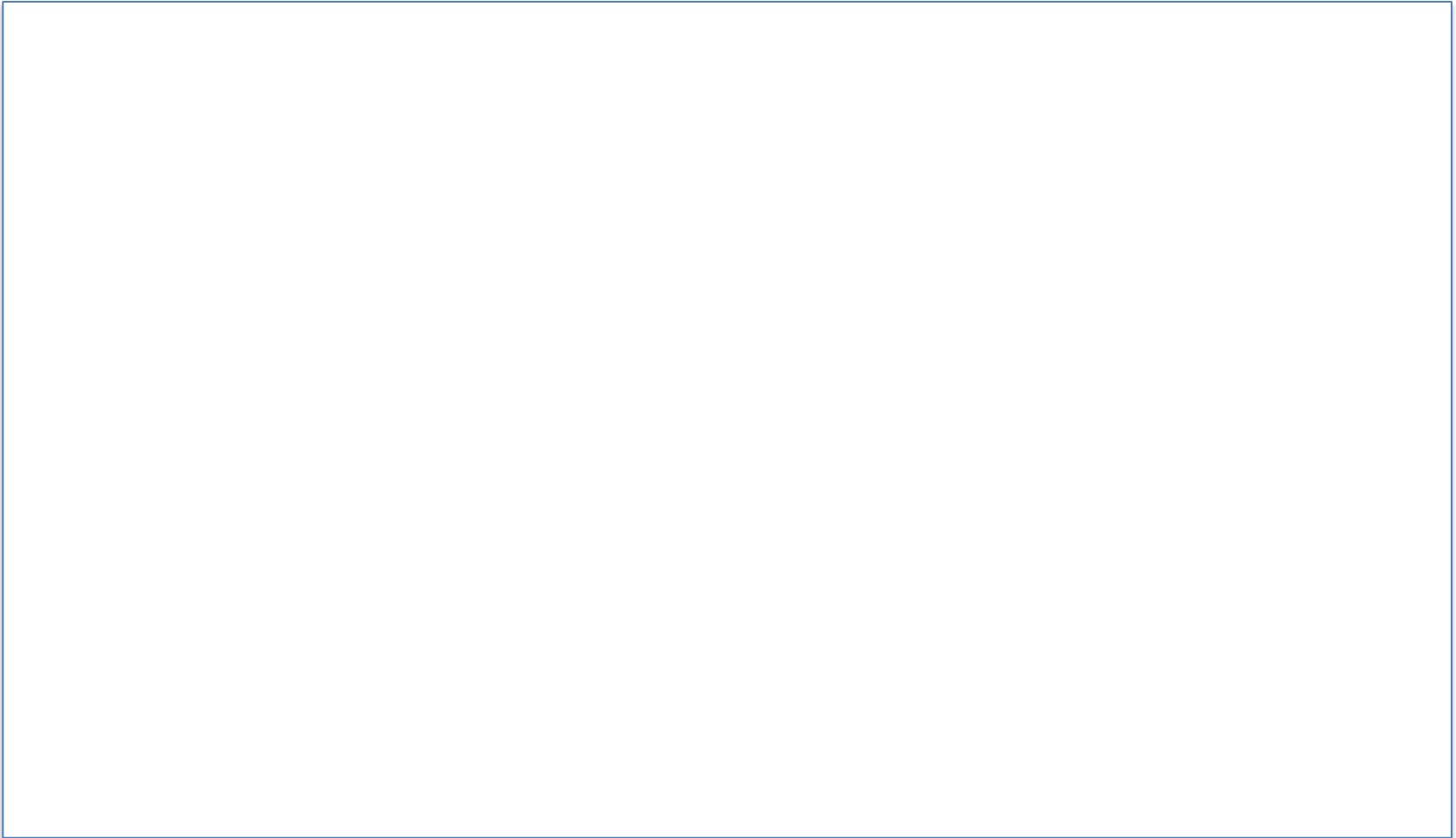
$$\alpha_A = \alpha_B = \alpha$$

$$\alpha = \frac{\alpha'}{RT} \quad (9.69)$$

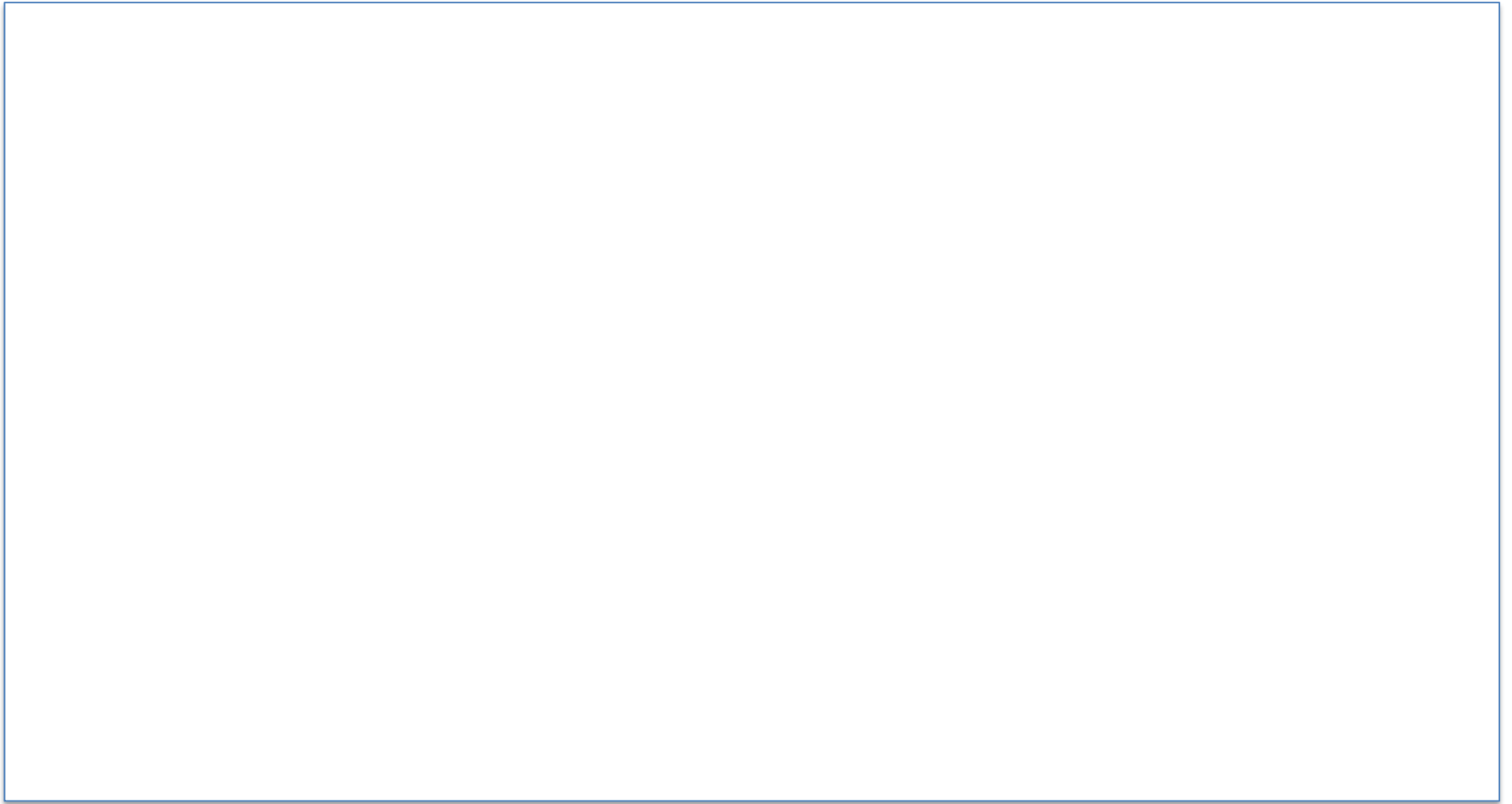
$$\Delta \bar{H}_i^M \neq 0 \quad \text{and} \quad \Delta \bar{S}_i^M = \Delta \bar{S}_i^{M,\text{id}} = -R \ln X_i$$

9.9 Regular Solutions

<The properties of a regular solution>



9.9 Regular Solutions



9.9 Regular Solutions

$$2. G^{XS} = \Delta H^M \neq f(T)$$

It is thus seen that G^{XS} for a regular solution is independent of T

$$\left(\frac{\partial G^{XS}}{\partial T} \right)_{P, \text{comp}} = -S^{XS}$$

S^{XS} for a regular solution is zero,
then G^{XS} , and hence ΔH^M , are independent of T

9.9 Regular Solutions

3. Application of RS

$$\overline{G}_A^{XS} = RT_1 \ln \gamma_{A(T_1)} = RT_2 \ln \gamma_{A(T_2)} = \alpha' X_B^2$$

For a regular solution

$$\frac{\ln \gamma_A \text{ at the temperature } T_2}{\ln \gamma_A \text{ at the temperature } T_1} = \frac{T_1}{T_2} \quad (9.77)$$

Eq. (9.77) is of considerable practical use in converting activity data for a regular solution at one temperature to activity data at another temperature

9.9 Regular Solutions

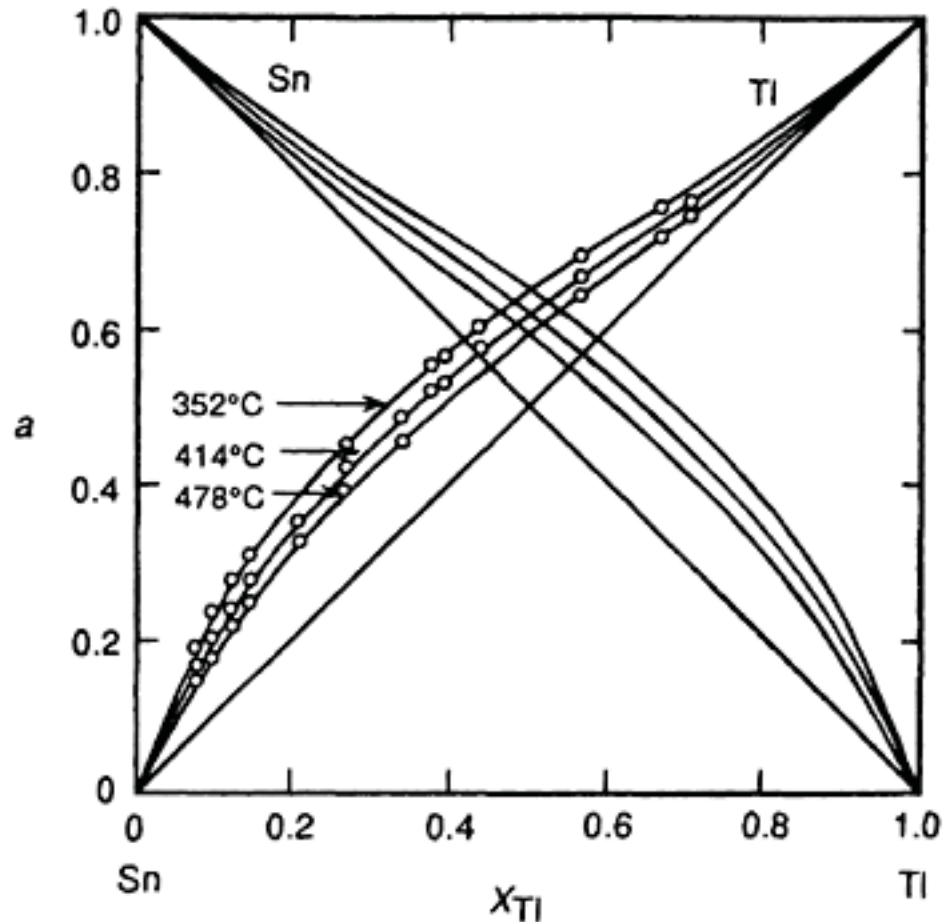


Figure 9.20 Activities in the system thallium-tin. (From J.H.Hildebrand and J.N. Sharma, "The Activities of Molten Alloys of Thallium with Tin and Lead," *J. Am. Chem. Soc.* (1929), vol. 51, p. 462.)

9.9 Regular Solutions

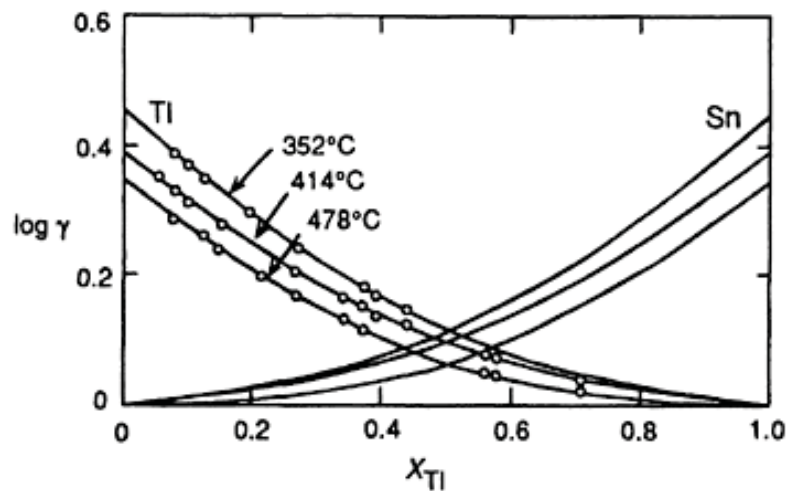


Figure 9.21 Activities coefficients in the system thallium-tin. (From J.H.Hildebrand and J.N.Sharma, "The Activities of Molten Alloys of Thallium with Tin and Lead," *J. Am. Chem. Soc.* (1929), vol. 51, p. 462.)

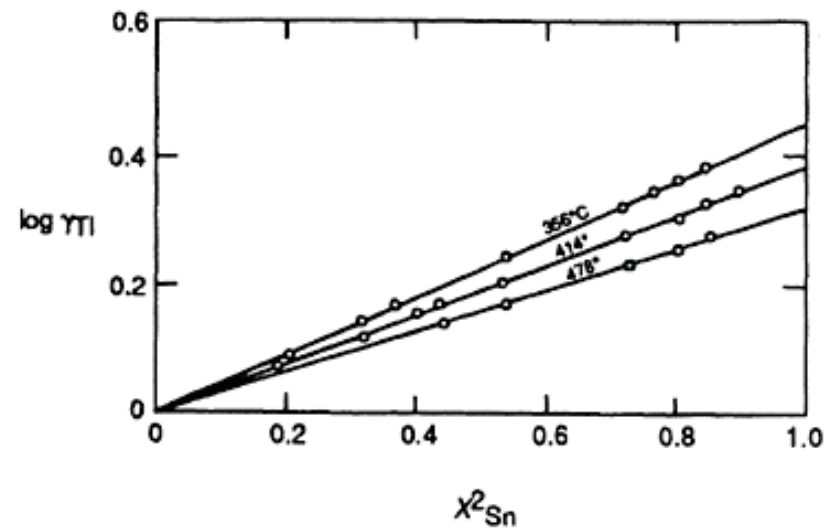


Figure 9.22 $\log \gamma_{Tl}$ vs. X_{Sn}^2 in the system thallium-tin. (From J.H.Hildebrand and J.N.Sharma, "The Activities of Molten Alloys of Thallium with Tin and Lead," *J. Am. Chem. Soc.* (1929), vol. 51, p. 462.)

9.9 Regular Solutions

4. What can we use R.S?

$$\Delta H^M = bX_A X_B \quad \text{or} \quad G^{XS} = b' X_A X_B$$

where b and b' are unequal

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

$$G^{XS} = RTX_B \int_0^{X_A} \frac{\ln \gamma_A}{X_B^2} dX_A$$

$$\gamma_A/X_B^2 = \alpha, \quad G^{XS} = RT\alpha X_A X_B$$

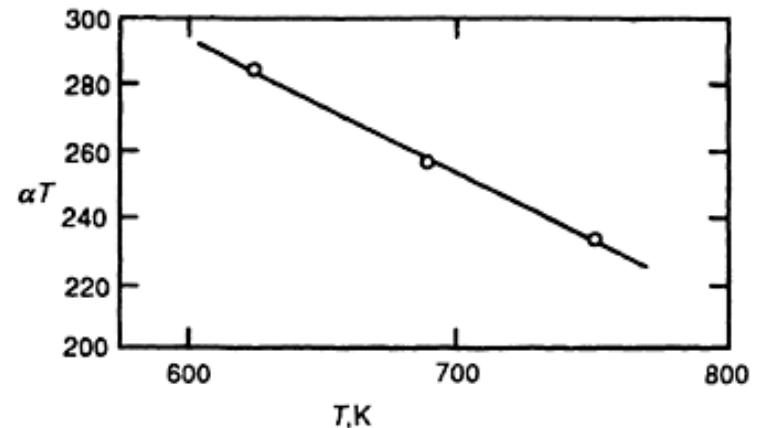


Figure 9.23 The variation of the product αT with T in the system Tl-Sn.

9.9 Regular Solutions

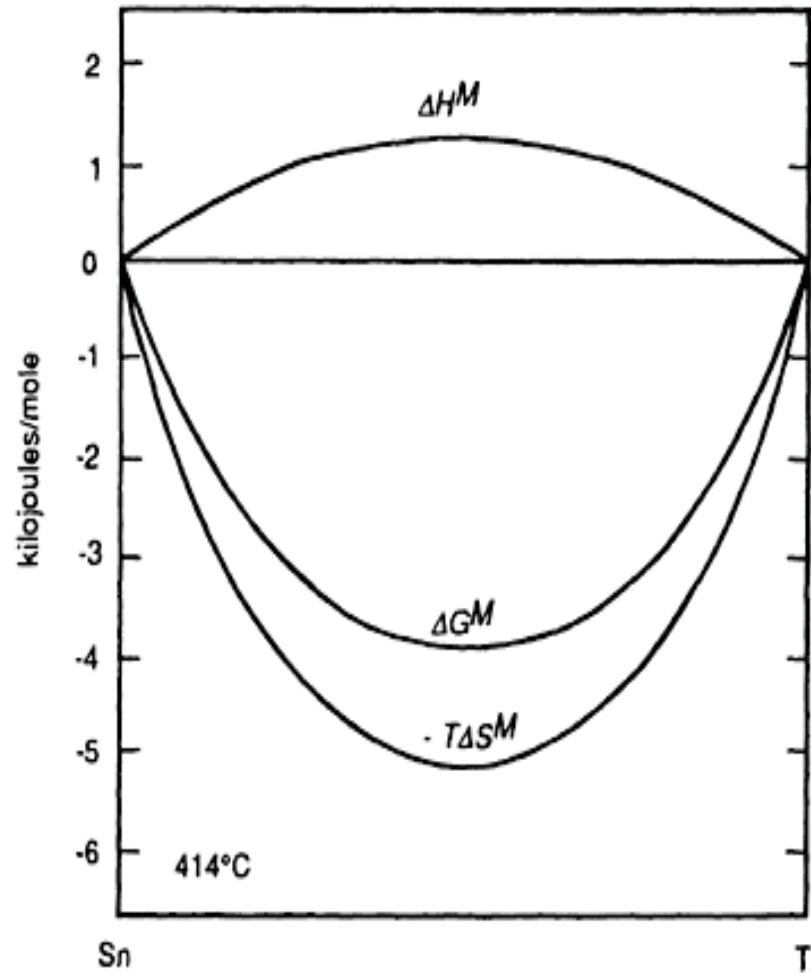


Figure 9.24 The molar enthalpy, entropy, and Gibbs free energy of mixing of thallium and tin at 414°C.

9.10 A Statistical Model of Solutions

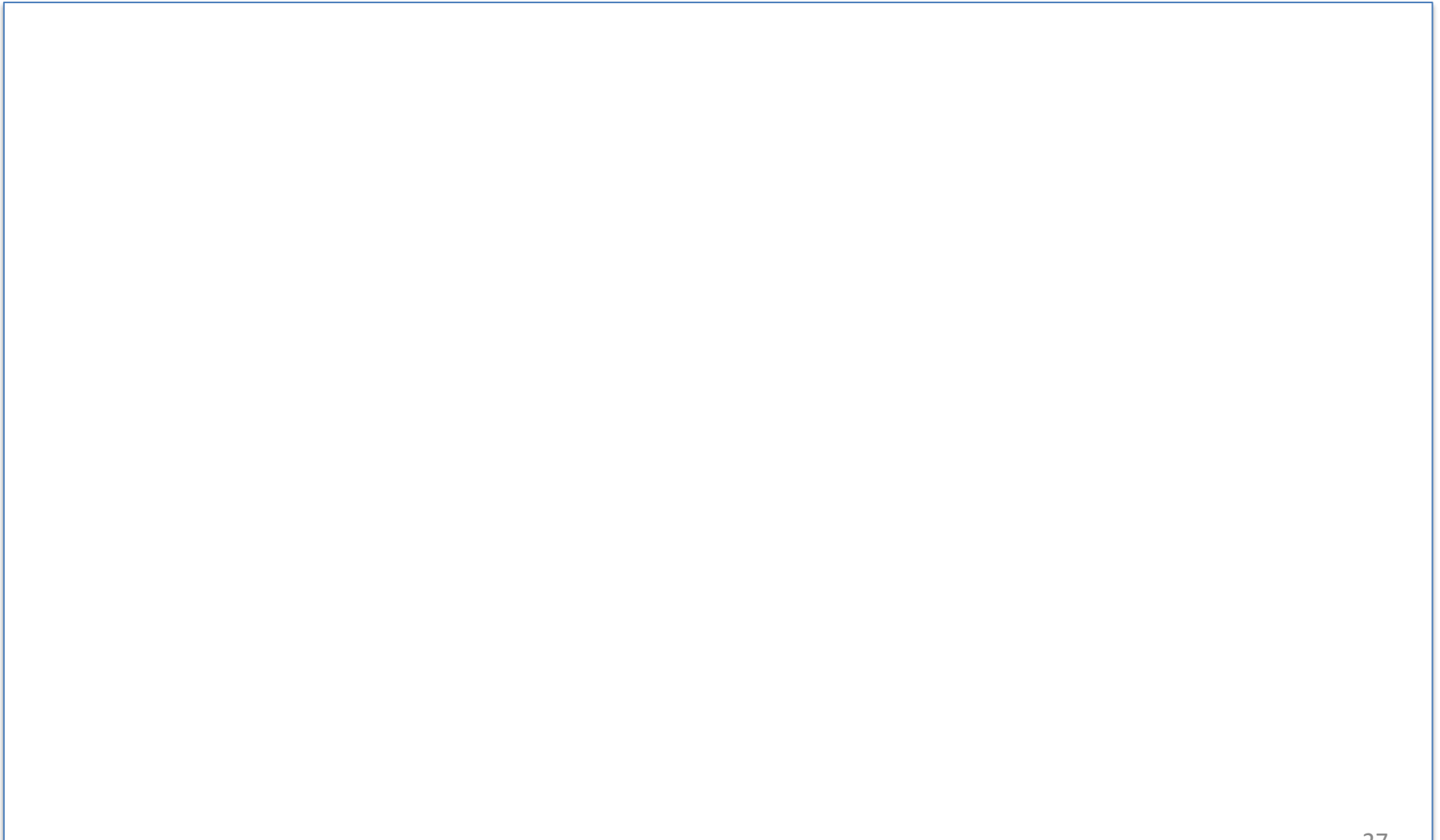
- Application of the statistical mixing model to two components which have equal molar volumes
- In solution the interatomic forces exist only between neighboring atoms
- The energy of the solution is the sum of the interatomic bond energies
- Consider 1 mole of a mixed crystal containing N_A atoms of A and N_B atoms of B

$$X_A = \frac{N_A}{N_A + N_B} = \frac{N_A}{N_O} \quad \text{and} \quad X_B = \frac{N_B}{N_O} \quad N_O \text{ is Avogadro's number}$$

1. A-A bonds the energy of each of which is E_{AA}
2. B-B bonds the energy of each of which is E_{BB}
3. A-B bonds the energy of each of which is E_{AB}

9.10 A Statistical Model of Solutions

<Quasi-Chemical Model>



9.10 A Statistical Model of Solutions

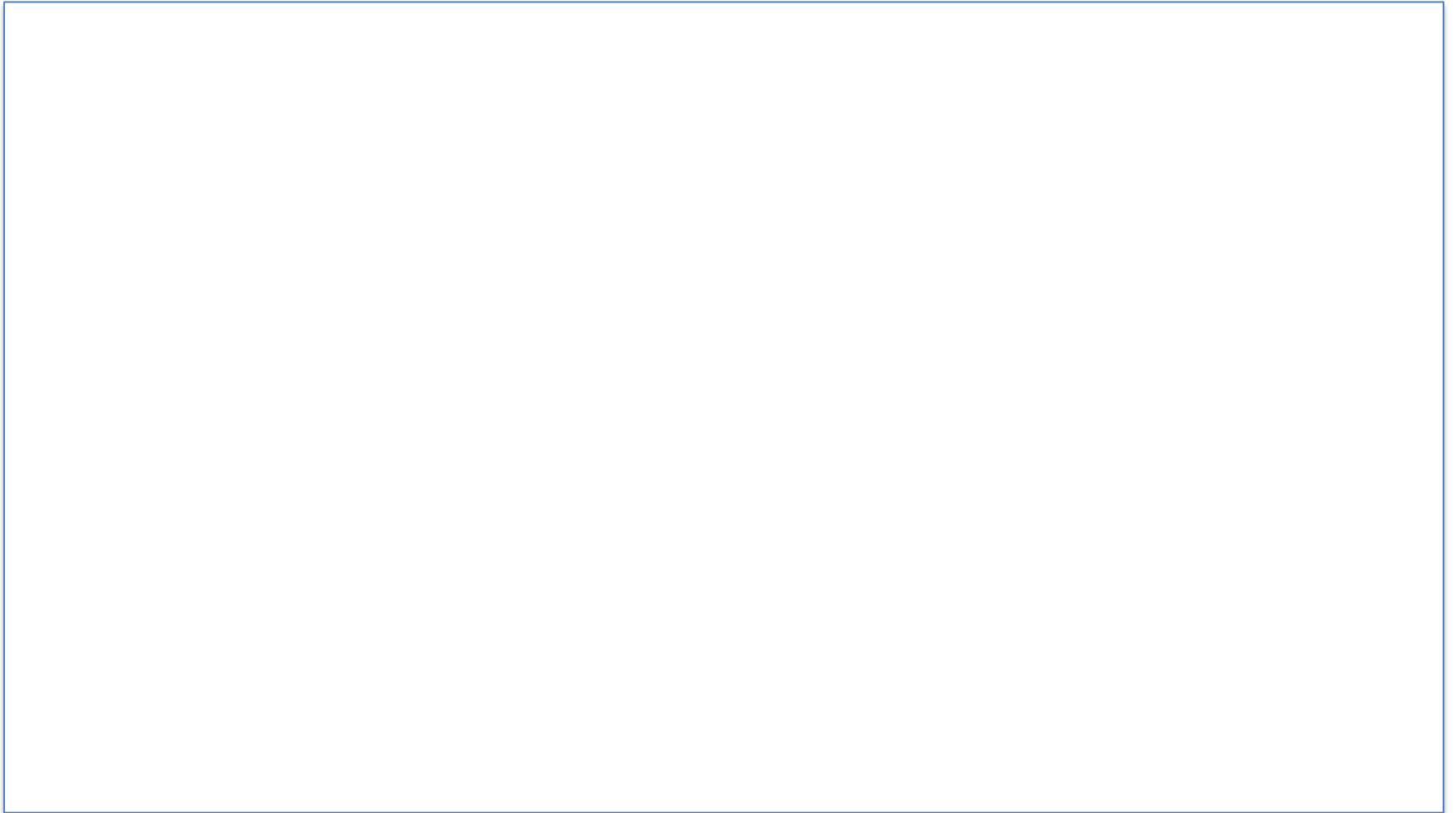
- N_A atoms in pure A

$2 \times$ the number of A–A bonds
= the number of atoms \times the number of bonds per atom

$$P_{AA} = \frac{1}{2} N_A z$$

$$P_{BB} = \frac{1}{2} N_B z$$

9.10 A Statistical Model of Solutions



9.10 A Statistical Model of Solutions

- If $\Delta H^M = 0$, then the mixing of the N_A atoms with the N_B atoms of B is random \leftarrow random mixing

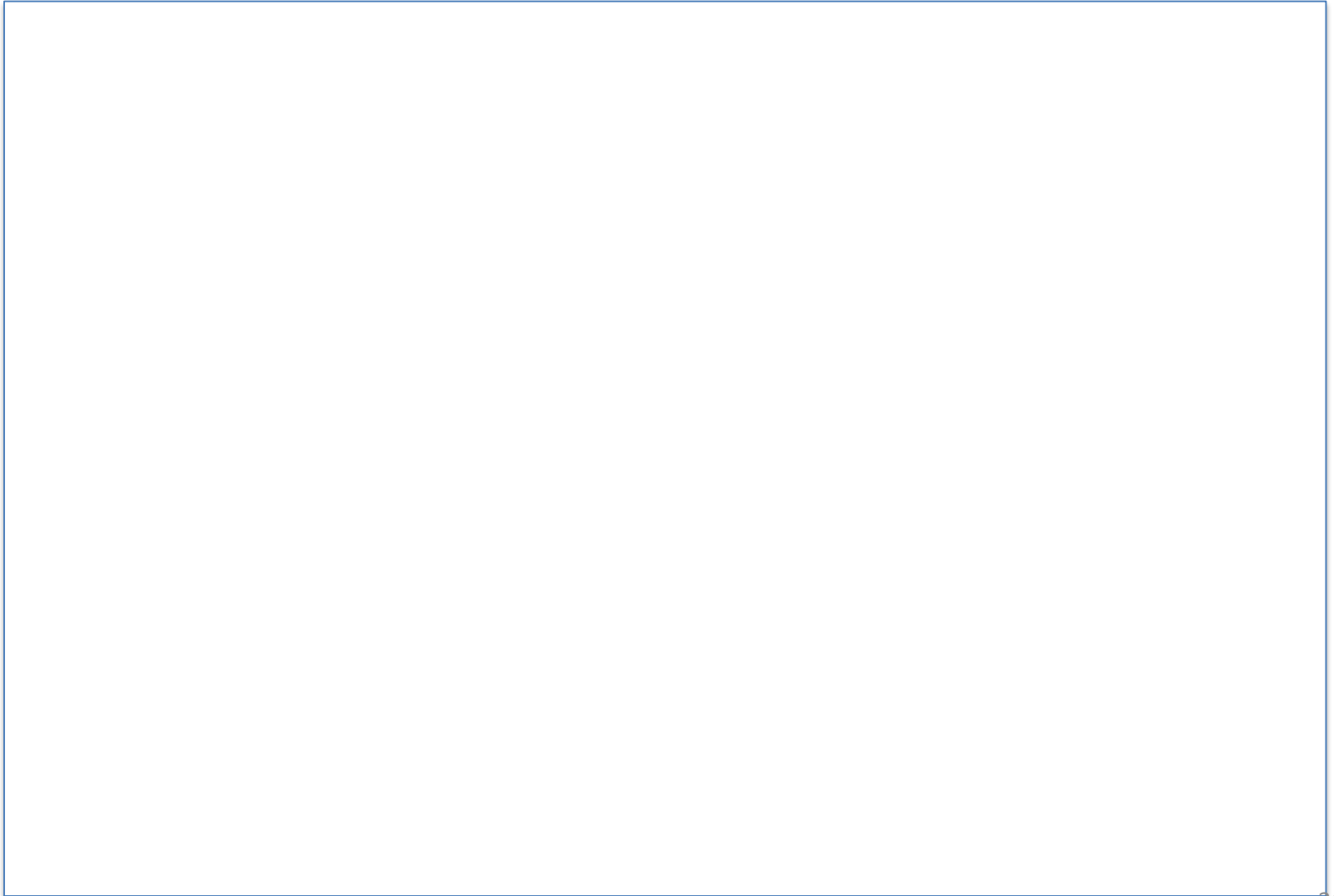
$$\Delta S^M = \Delta S^{M.id} = -R(X_A \ln X_A + X_B \ln X_B)$$

- $|\Delta H^M| \leq RT$
The mixing of the atoms is also approximately random
- Consider two neighboring lattice sites in the crystal
The probability that site 1 is occupied by an A atom is

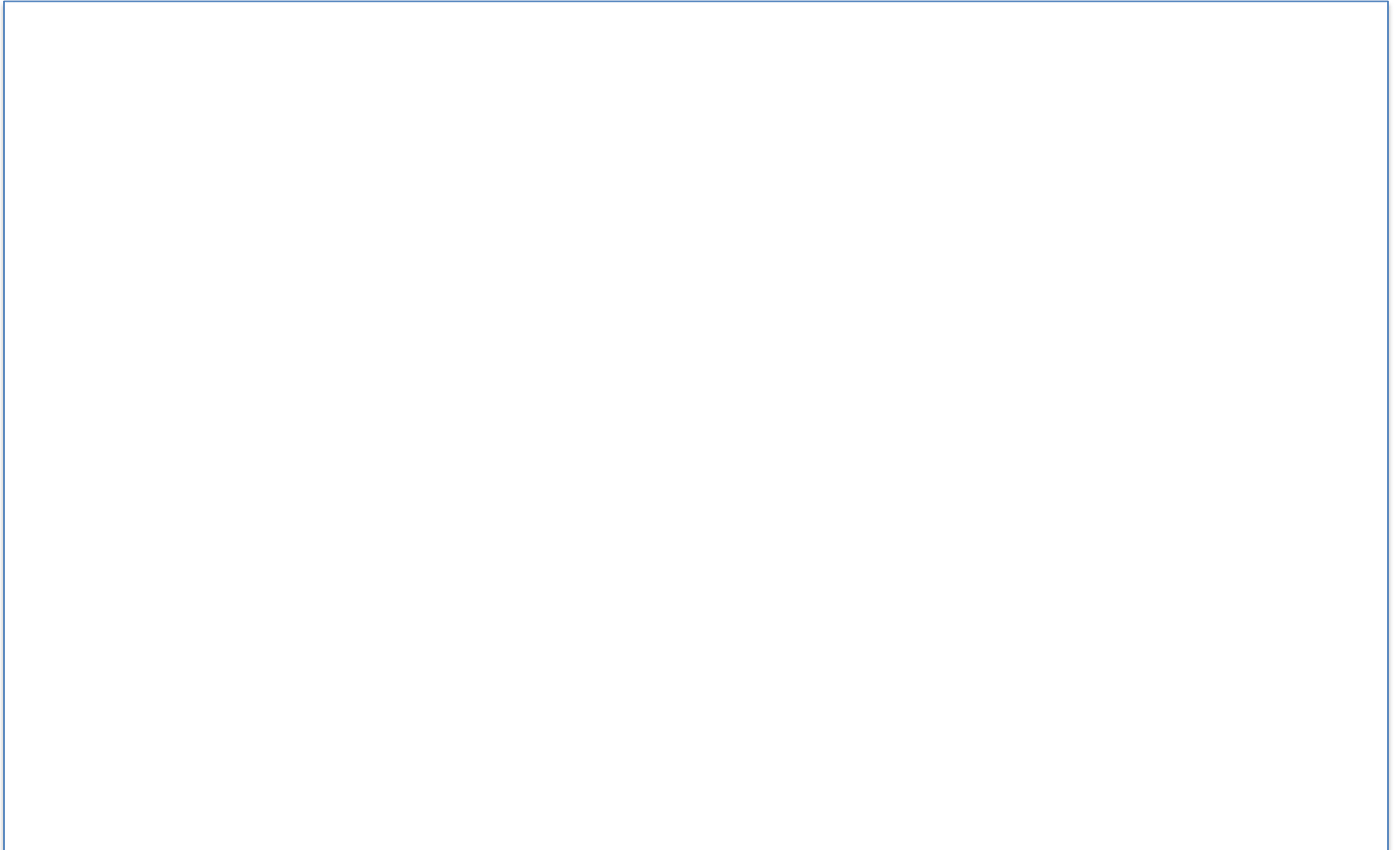
$$\frac{\text{the number of A atoms in the crystal}}{\text{the number of lattice sites in the crystal}} = \frac{N_A}{N_O} = X_A$$

- The probability that site 2 is occupied by a B atom is X_B
- Thus the probability of A-B pair is $2X_A X_B$, A-A pair is X_A^2 , B-B pair is X_B^2

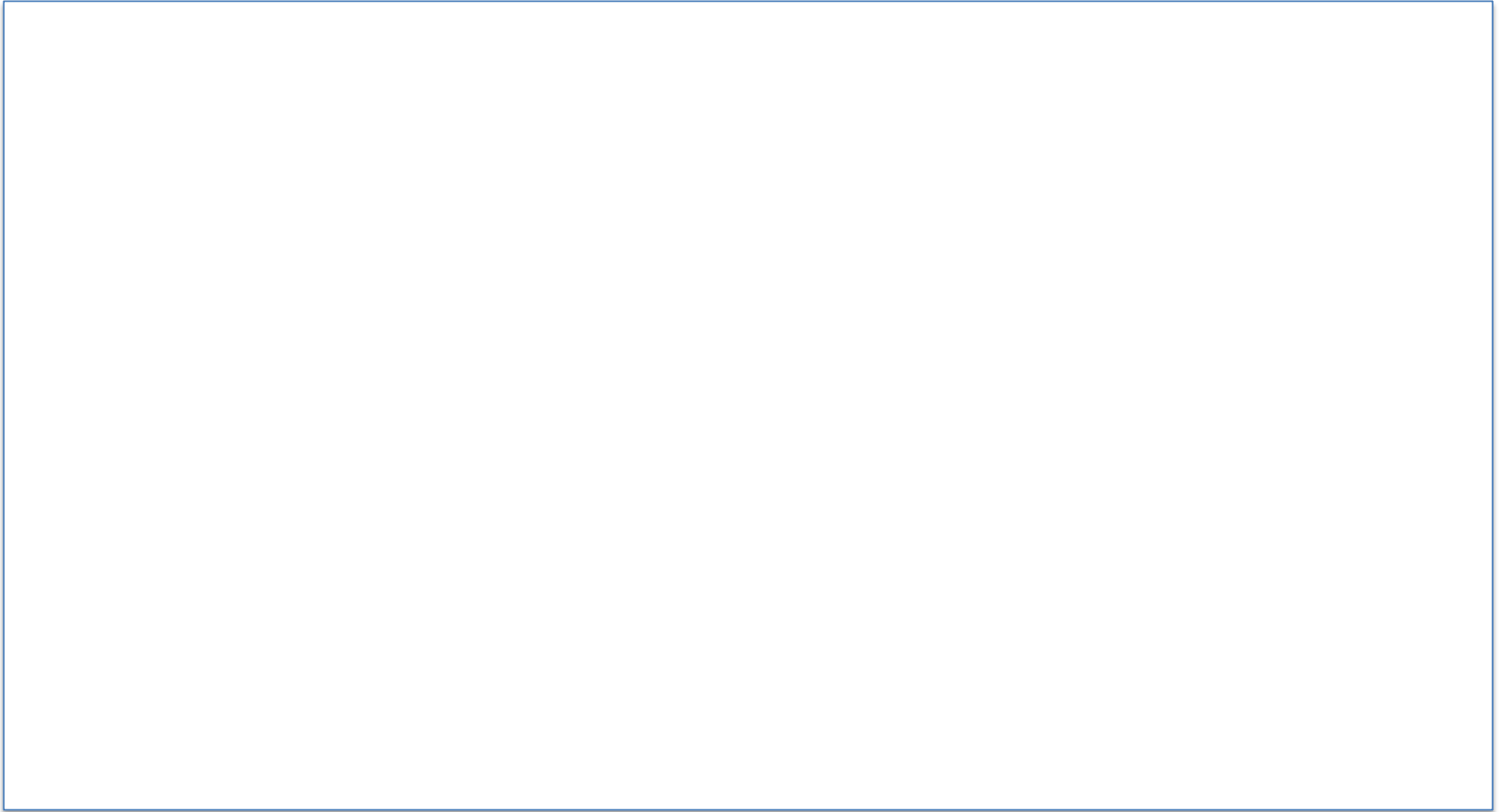
9.10 A Statistical Model of Solutions



9.10 A Statistical Model of Solutions



A Statistical Model of Solutions



9.10 A Statistical Model of Solutions

- Henry's law requires that γ_A , and hence $\ln\gamma_A$, approach a constant value as X_B approaches unity

Thus,

$$\gamma_A \rightarrow \ln\gamma_A^\circ = \Omega/RT$$

- The applicability of the statistical model to real solutions decreases as the magnitude of Ω increases, i.e., if the magnitude of EAB is significantly greater or less than the average of EAA and EBB then random mixing of the A and B atoms cannot be assumed

9.10 A Statistical Model of Solutions

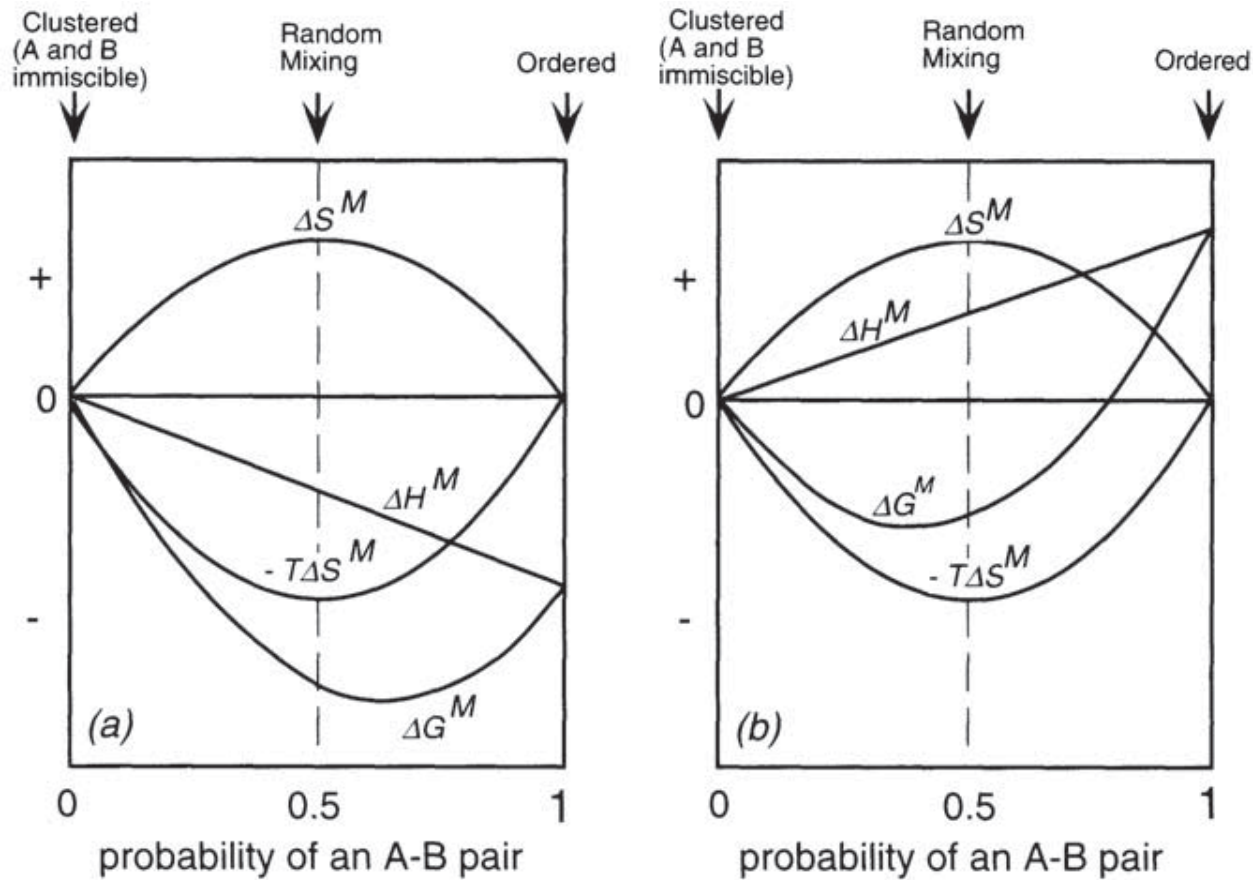


Figure 9.25 Illustration of the origins of deviation from regular solution behavior

9.11 Subregular Solutions

$$\Omega = a + bX_B + cX_B^2 + dX_B^3 + \dots \quad (9.92)$$

$$G^{XS} = (a + bX_B)X_A X_B \quad (9.93)$$

$$\overline{G}_A^{XS} = aX_B^2 + bX_B^2(X_B - X_A) \quad (9.94a)$$

$$\overline{G}_B^{XS} = aX_A^2 + 2bX_A^2 X_B \quad (9.94b)$$

$$\frac{dG^{XS}}{dX_B} = 0$$

$$G^{XS} = aX_B + 2(b - a)X_B^2 - bX_B^3$$

$$\frac{dG^{XS}}{dX_B} = a + 2(b - a)X_B - 3bX_B^2 = 0$$

$$X_B = \frac{2(b - a) \pm 2\sqrt{b^2 + ab + a^2}}{6b}$$

9.10 Subregular Solutions

$$G^{XS} = (a_0 + b_0 X_B) X_A X_B \left(1 - \frac{T}{\tau}\right) \quad (9.95)$$

$$\begin{aligned} S^{XS} &= -\frac{\partial G^{XS}}{\partial T} \\ &= \frac{(a_0 + b_0) X_A X_B}{\tau} \end{aligned} \quad (9.96)$$

$$\begin{aligned} \Delta H^M &= G^{XS} + TS^{XS} \\ &= (a_0 + b_0 X_B) X_A X_B \left(2 - \frac{T}{\tau}\right) \end{aligned} \quad (9.97)$$

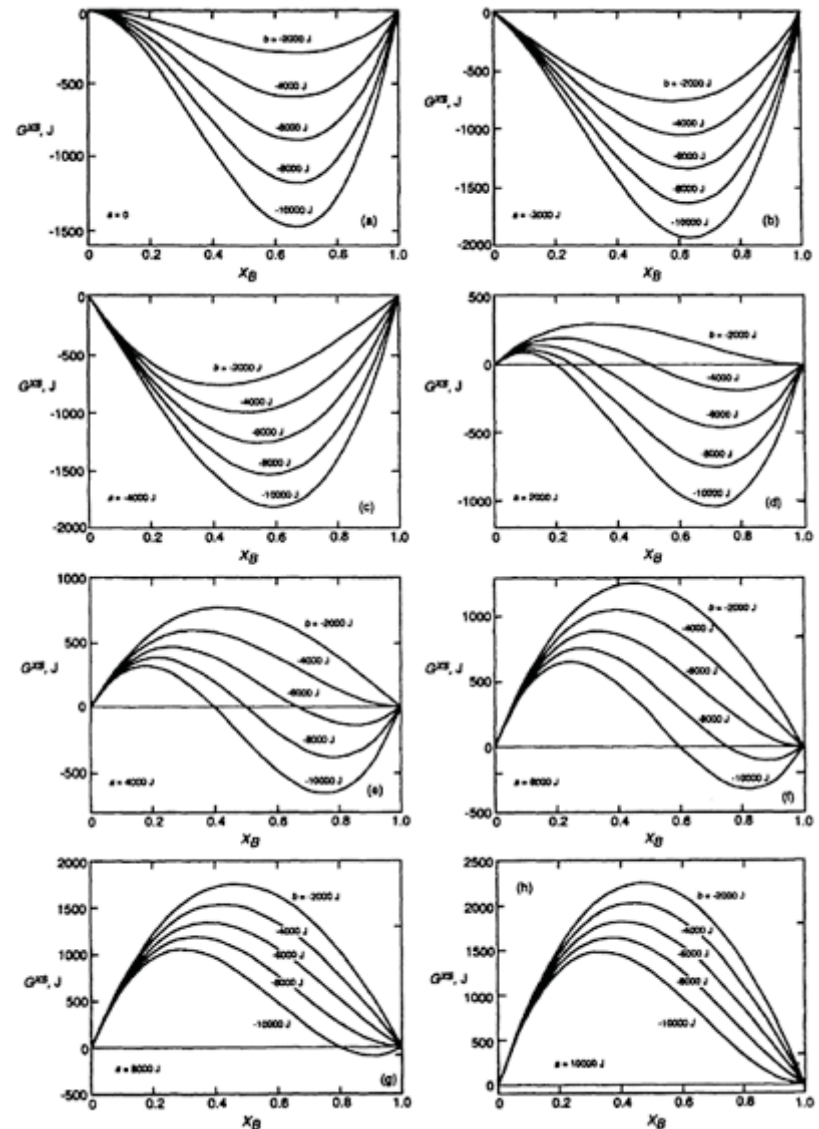


Figure 9.26 Excess molar Gibbs free energy curves generated by the subregular solution model.