

Chapter 9

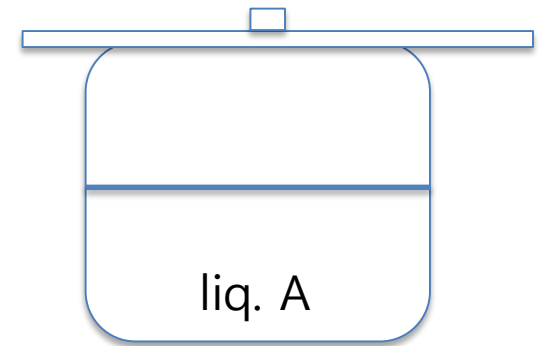
The Behavior of Solutions

9.2 Raoult's Law and Henry's Law

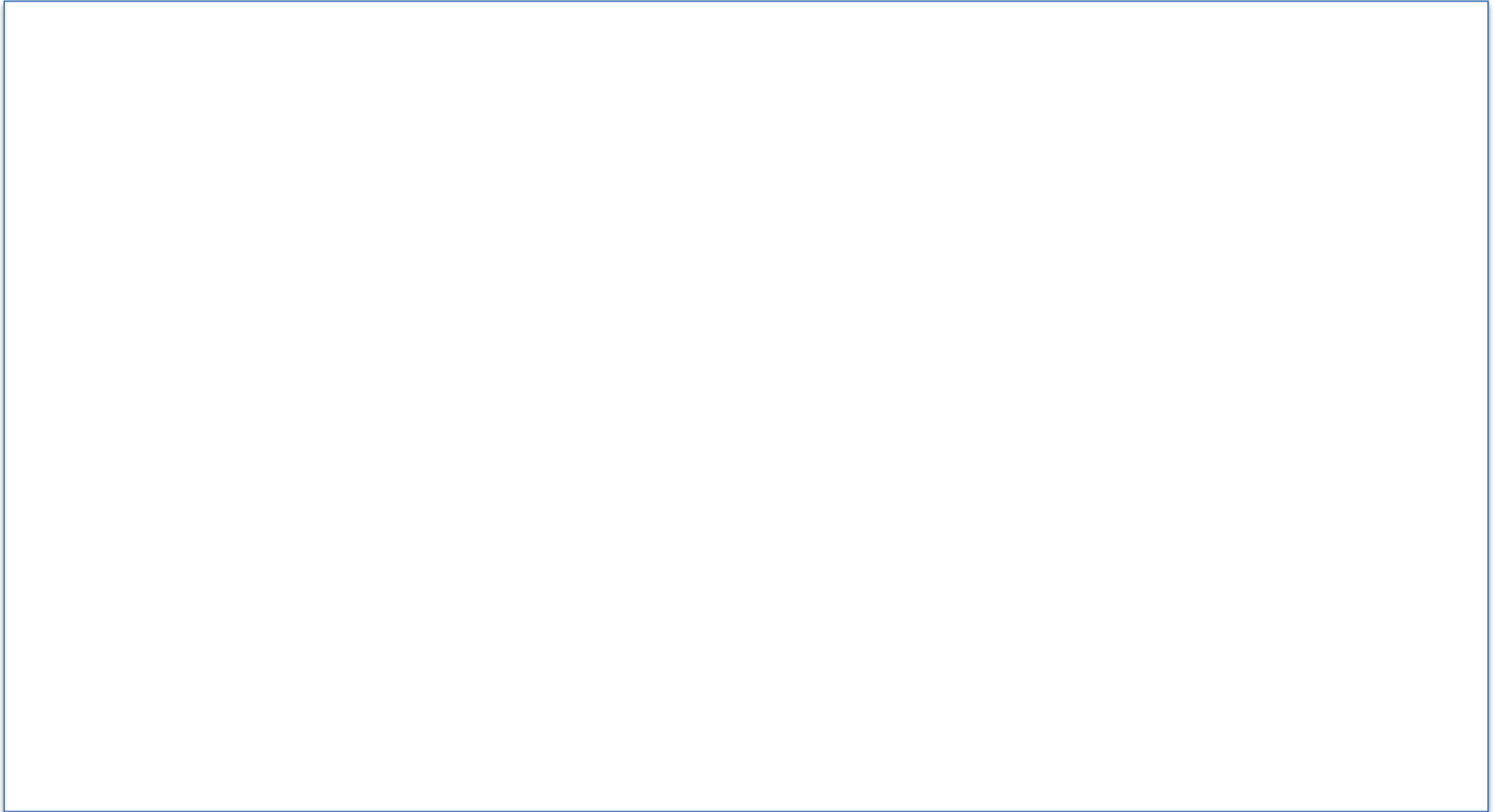
(1) Initially evacuated vessel at T

(2) spontaneously evaporate until P in the vessel reaches the saturated vapor pressure of liq. A, p_A° , at T

(3) a dynamic equilibrium established between the rate of evaporation of liq. A & the rate of condensation of vapor A.



9.2 Raoult's Law and Henry's Law



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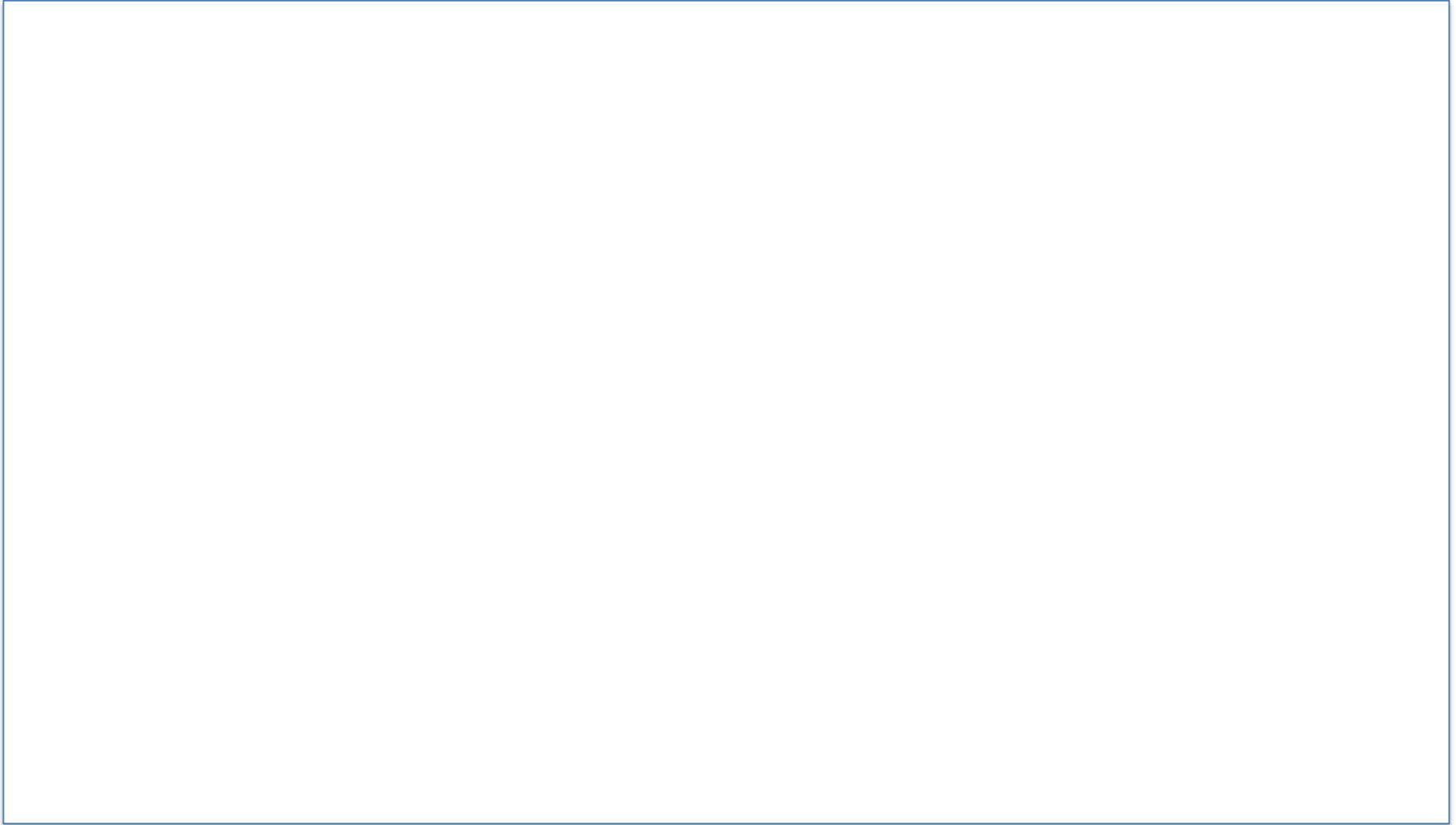
(A) the effect of the small addition of liquid B to liquid A

Assume (1) the composition of the surface of the liquid = that of the bulk liquid, X_A , (2) the sizes of A & B atoms comparable

$$r_{e(A)}X_A = k p_A \quad (9.3)$$

$$r_{e(B)}X_B = k' p_B \quad (9.4)$$

9.2 Raoult's Law and Henry's Law



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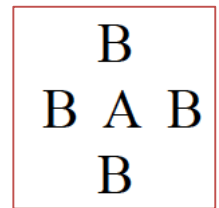
- Requirements:
 - the intrinsic rates of evaporation of A and B
 $\neq f(\text{comp. of the solution})$
 - i.e., the magnitudes of the A-A, B-B, and A-B bond energies in the solution are identical

9.2 Raoult's Law and Henry's Law

(B) If $A-B \gg A-A$ and $B-B$ and a solution of A in B is sufficiently dilute:

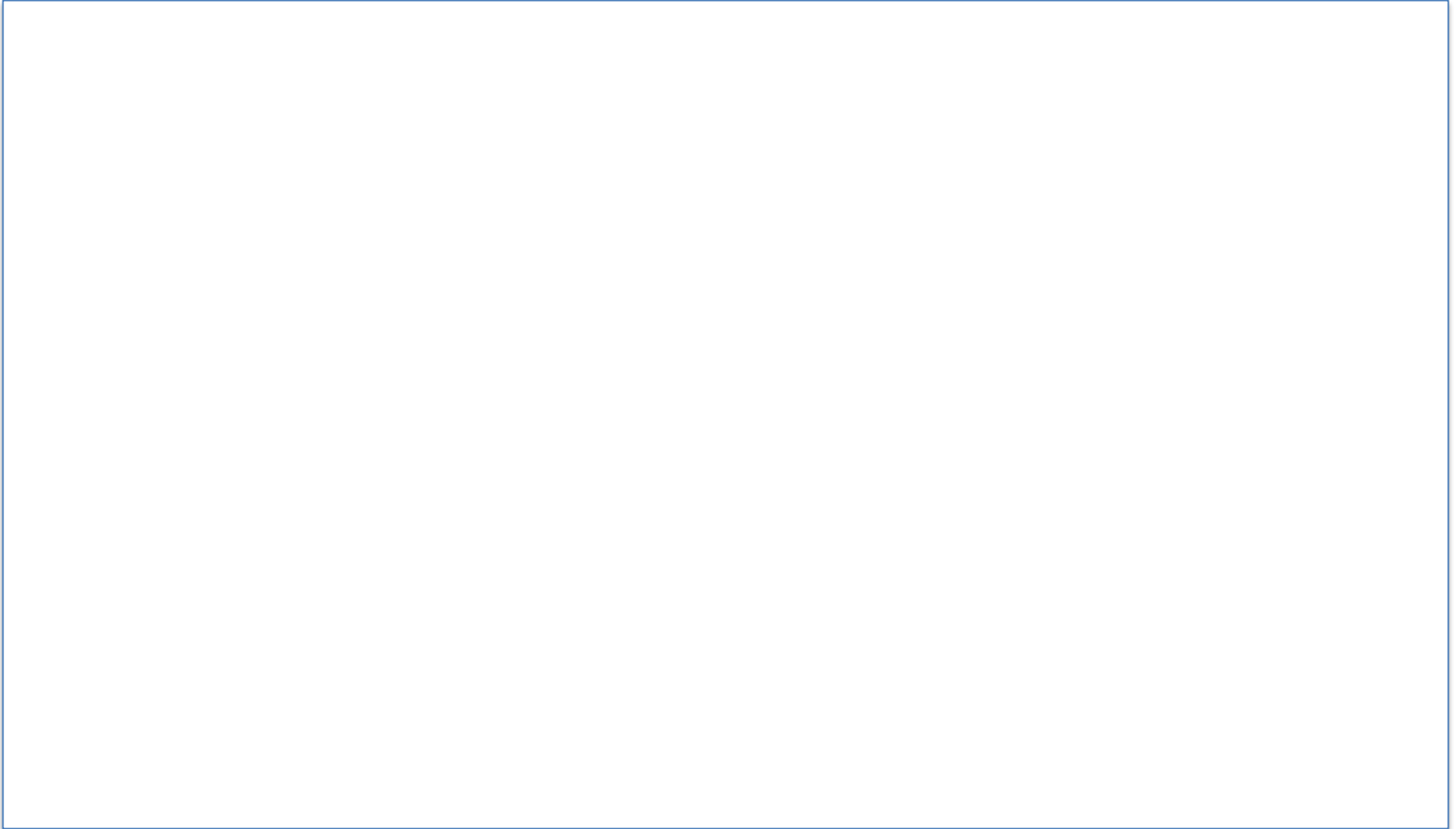
A atom at the surface surrounded only by B,
A in a deeper potential well than are the A
atoms at the surface of pure liq...

difficult to be lifted to vapor, evaporation rate is
decreased to $r_e(A)$ to $r_e'(A)$



$$r_e'(A)X_A = kp_A$$

9.2 Raoult's Law and Henry's Law



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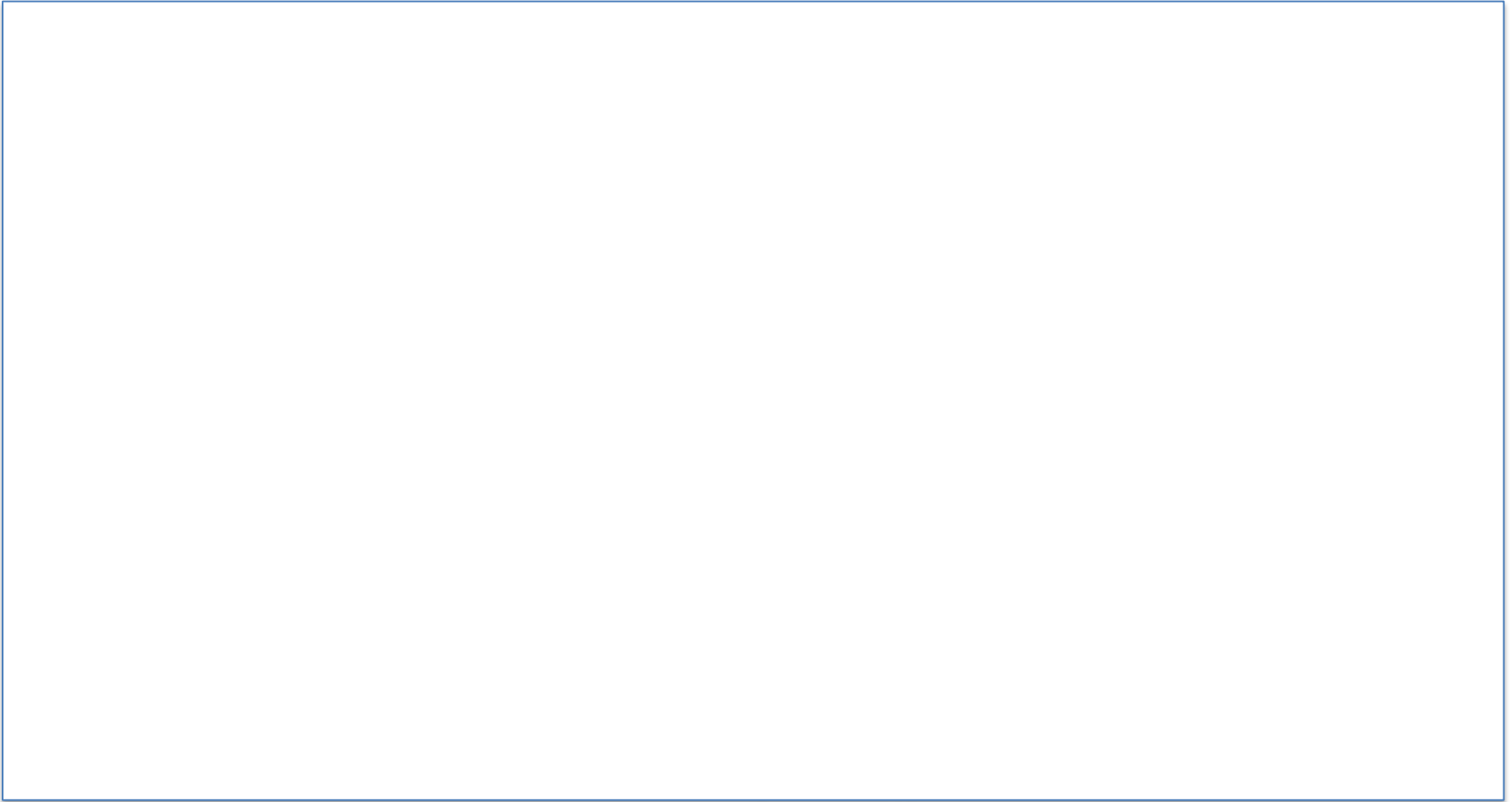


Figure 9.2 (a) The vapor pressure of a component of a binary solution which exhibits positive deviation from Raoultian behavior. (b) The vapor pressure of a component of a binary solution which exhibits negative deviation from Raoultian behavior.

9.3 The Thermodynamic Activity of a Component in Sol'n

$$\text{activity of } i = a_i = \frac{f_i}{f_i^\circ} \quad (9.11)$$

If the vapor above the solution is ideal

$$a_i = \frac{p_i}{p_i^\circ} \quad (9.12)$$

- If the component i exhibits Raoultian behavior, then

$$a_i = X_i \quad (9.13)$$

$$a_i = k_i X_i \quad (9.14)$$

9.3 The Thermodynamic Activity of a Component in Sol'n

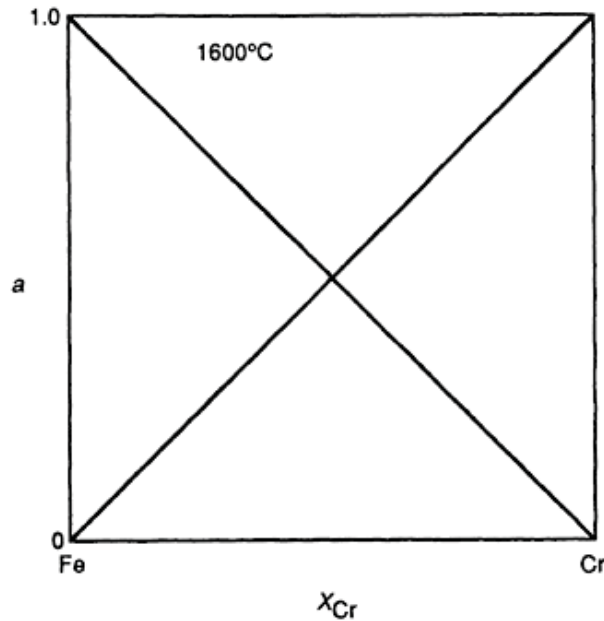


Figure 9.3 Activities in the binary system iron-chromium at 1600°C.

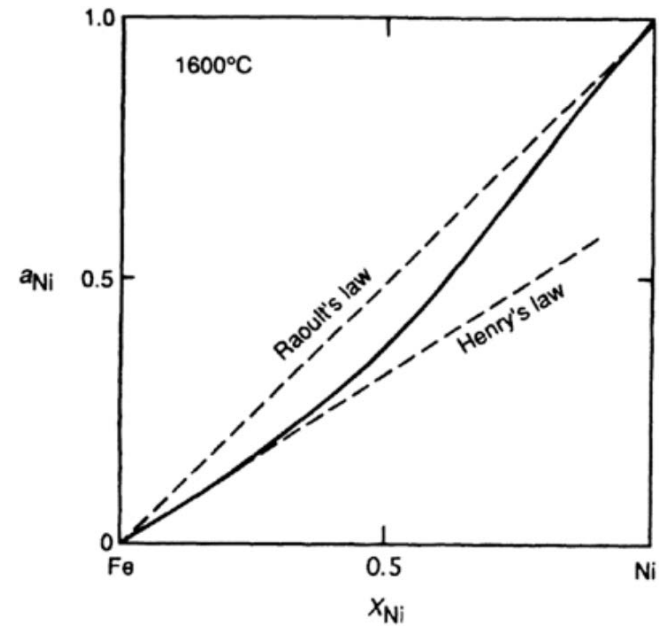


Figure 9.4 The activity of nickel in the system iron-nickel at 1600°C.

9.4 The Gibbs-Duhem Equation



9.4 The Gibbs-Duhem Equation

at const. T and P

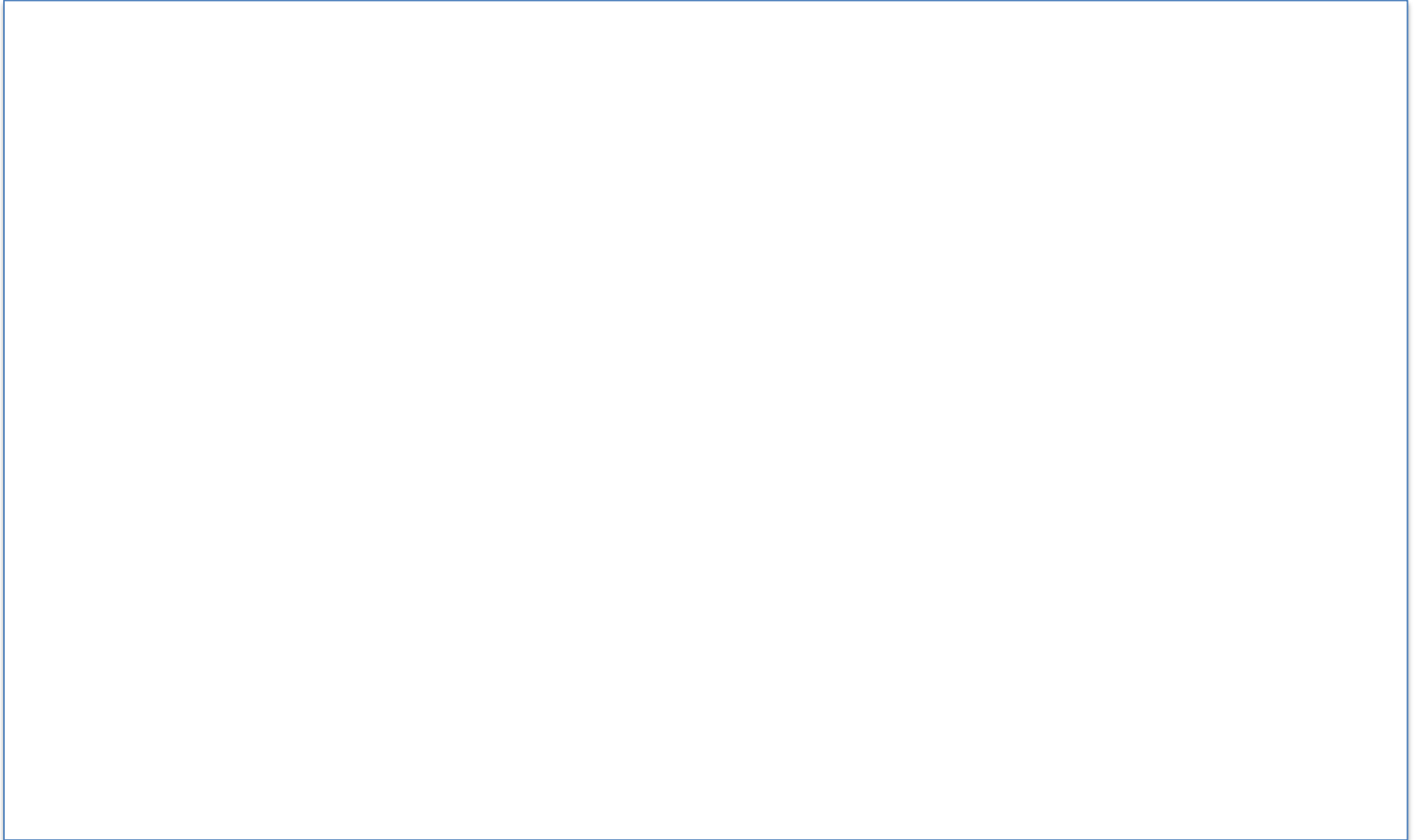
$$dQ' = \left(\frac{\partial Q'}{\partial n_i} \right)_{T,P,n_j,n_k,\dots} dn_i + \left(\frac{\partial Q'}{\partial n_j} \right)_{T,P,n_i,n_k,\dots} dn_j + \left(\frac{\partial Q'}{\partial n_k} \right)_{T,P,n_i,n_j,\dots} dn_k + \dots \quad (9.15)$$

The partial molar value

$$\bar{Q}_i = \left(\frac{\partial Q'}{\partial n_i} \right)_{T,P,n_j,n_k,\dots}$$

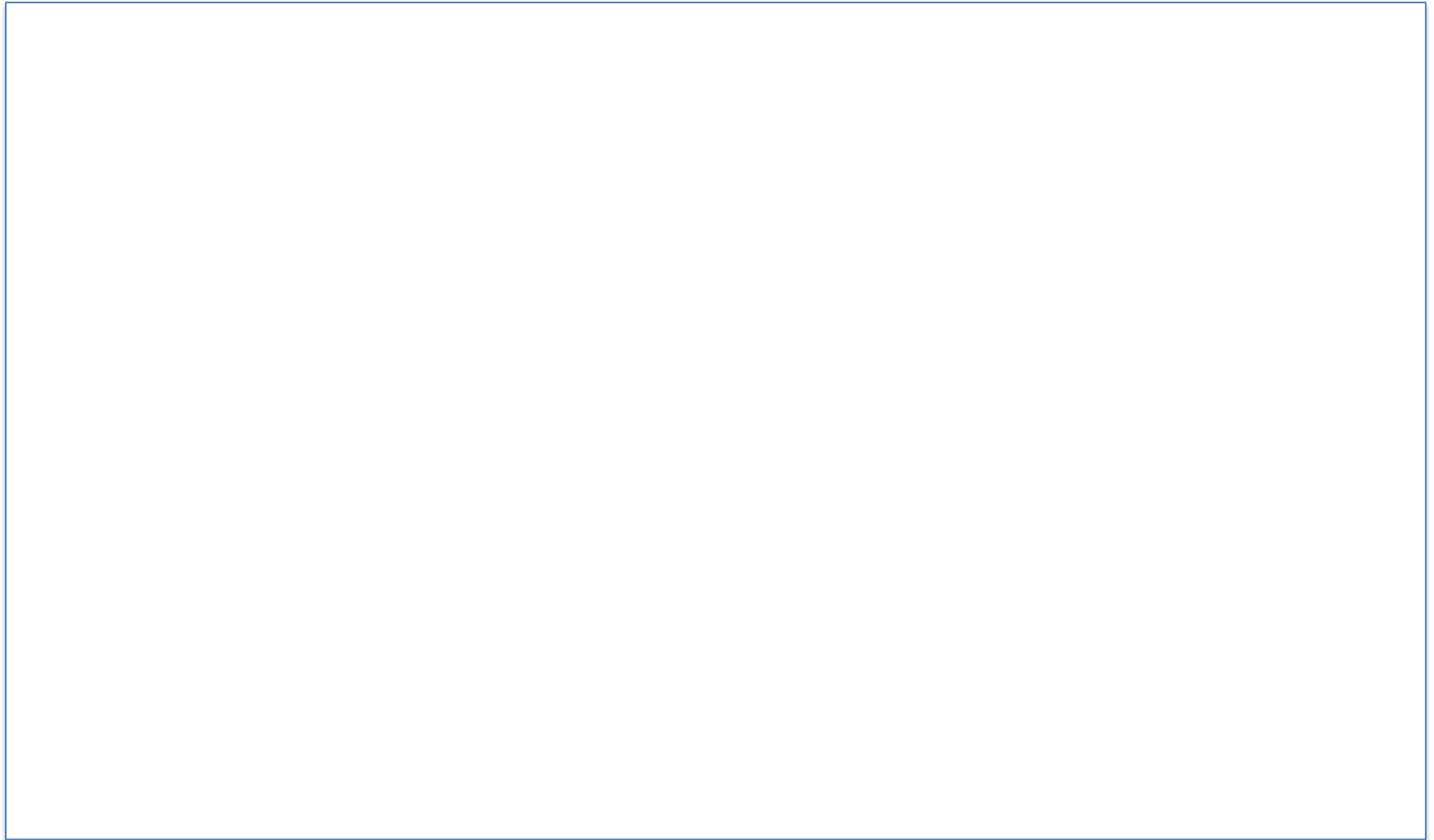
$$dQ' = \bar{Q}_i dn_i + \bar{Q}_j dn_j + \bar{Q}_k dn_k + \dots \quad (9.16)$$

9.4 The Gibbs-Duhem Equation

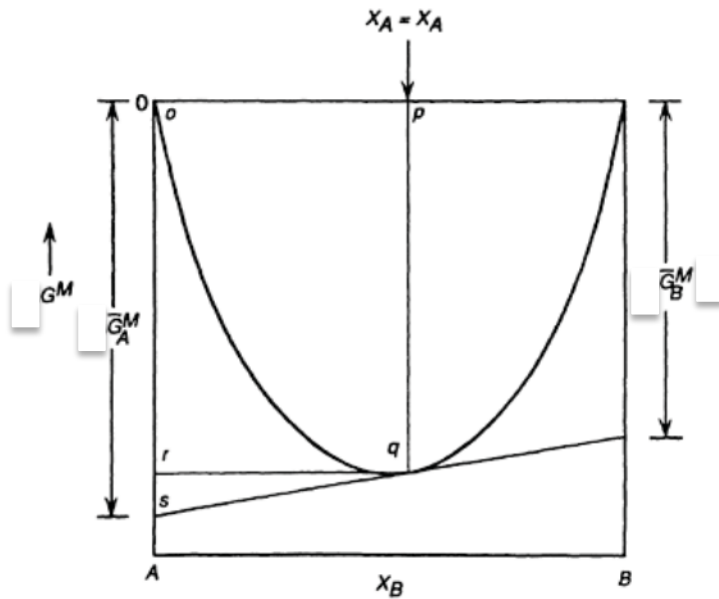


9.5 The Gibbs Free Energy of Formation of a Solution

* Molar free E of a solution & partial molar f.e. of solution of components



9.5 The Gibbs Free Energy of Formation of a Solution



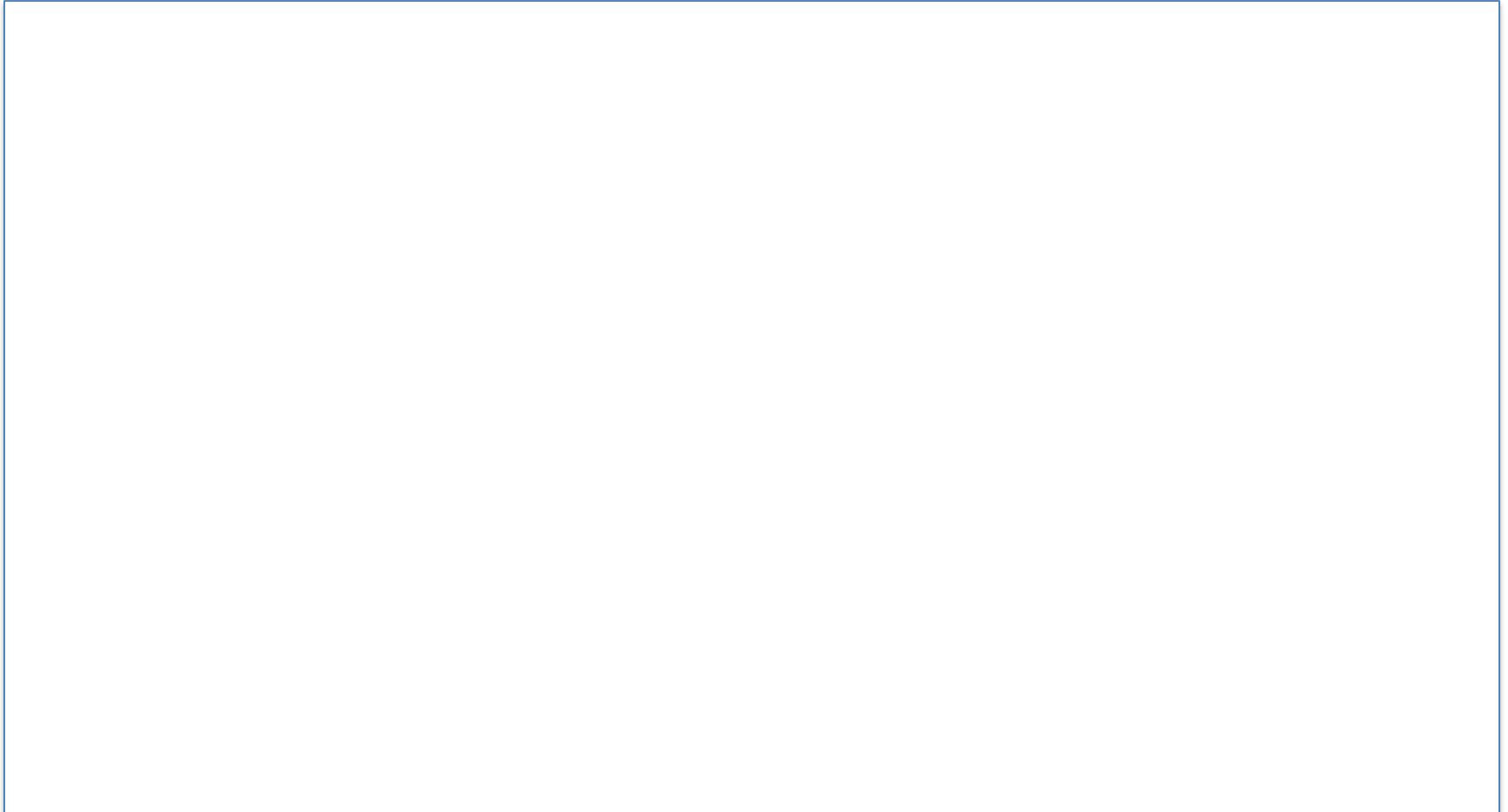
$$\bar{G}_A = G + X_B \frac{dG}{dX_A}$$

$$\bar{G}_B = G + X_A \frac{dG}{dX_B}$$

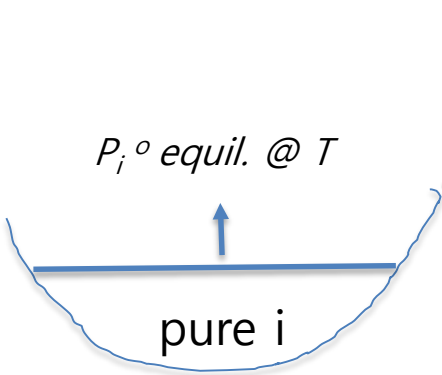
(9.27b)

9.5 The Gibbs Free Energy of Formation of a Solution

* The free E change due to the formation of a solution



9.5 The Gibbs Free Energy of Formation of a Solution

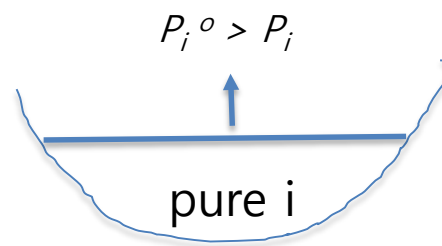


$$\Delta G_{(b)} = RT \ln \left(\frac{p_i}{p_i^o} \right)$$

the Gibbs free energy after mixing = $n_A \bar{G}_A + n_B \bar{G}_B$

$$\Delta \bar{G}_i^M = \bar{G}_i - G_i^o = RT \ln a_i$$

(9.28)



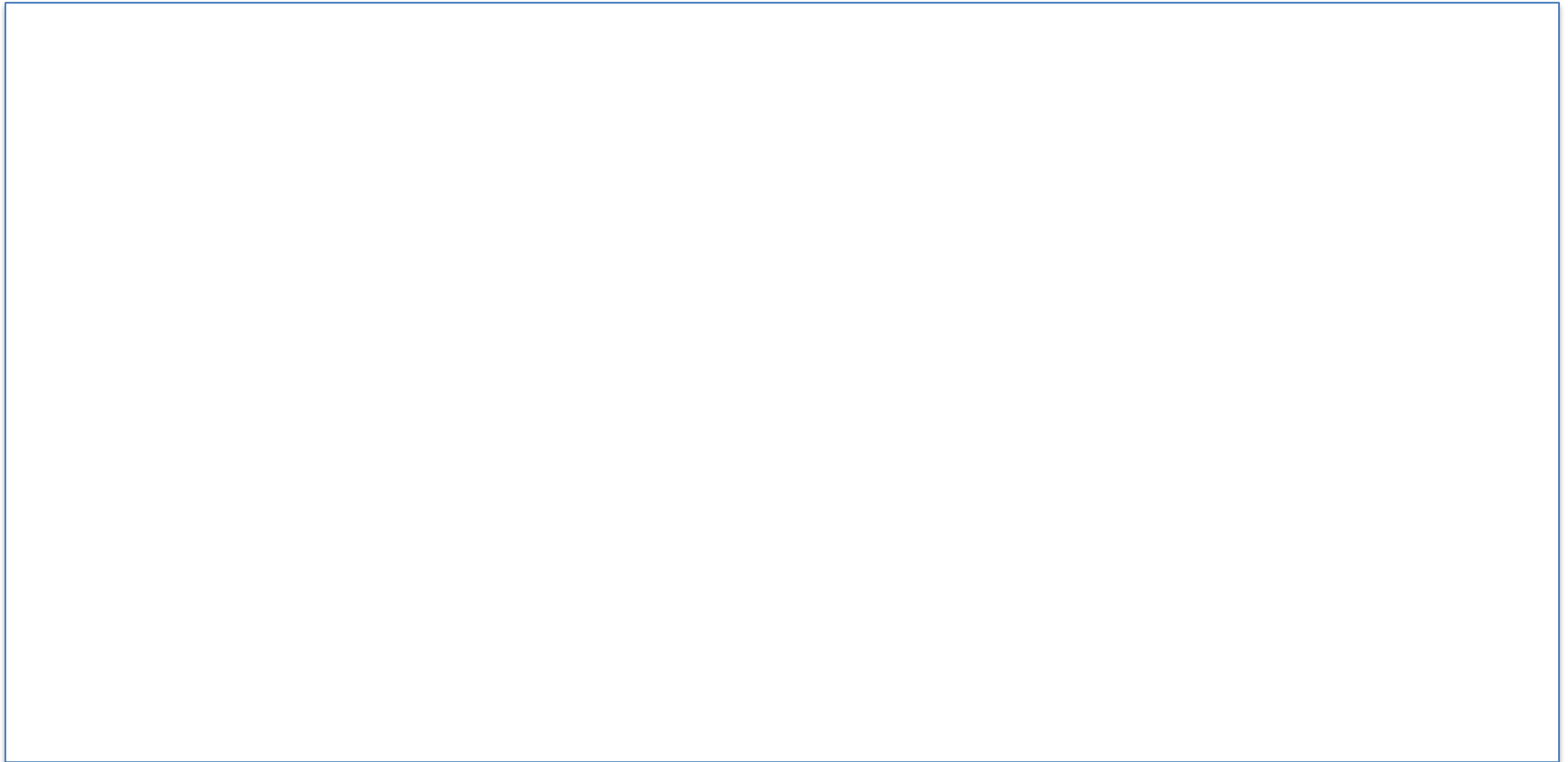
the Gibbs free energy before mixing = $n_A G_A^o + n_B G_B^o$

$$\begin{aligned} \Delta G'^M &= (n_A \bar{G}_A + n_B \bar{G}_B) - (n_A G_A^o + n_B G_B^o) \\ &= n_A (\bar{G}_A - G_A^o) + n_B (\bar{G}_B - G_B^o) \end{aligned}$$

$$\Delta G_{(b)} = G_i(\text{in solution}) - G_i(\text{pure}) - RT \ln a_i$$

9.5 The Gibbs Free Energy of Formation of a Solution

The Change in Gibbs Free Energy Due to the Formation of a Solution



9.5 The Gibbs Free Energy of Formation of a Solution



(9.33a)

(9.33b)

$\frac{d\Delta G^M}{dX_A}$ = the slope of the tangent to the ΔG^M curve at the composition X_A

$$= \frac{rs}{rq}$$

$$\Delta \bar{G}_A^M = pq + rq \frac{rs}{rq} = pq + rs = or + rs = os$$

= the tangential intercept at $X_A = 1$

9.6 The Properties of Raoultian Ideal Solutions

- Raoultian : $a_i = X_i$
- For an ideal binary A-B solution

$$\Delta G^{M,\text{id}} = RT(X_A \ln X_A + X_B \ln X_B) \quad (9.34)$$

$$\Delta \bar{G}_A^{M,\text{id}} = RT \ln X_A \quad \text{and} \quad \Delta \bar{G}_B^{M,\text{id}} = RT \ln X_B$$

9.6 The Properties of Raoultian Ideal Solutions

- For the species i occurring in a solution

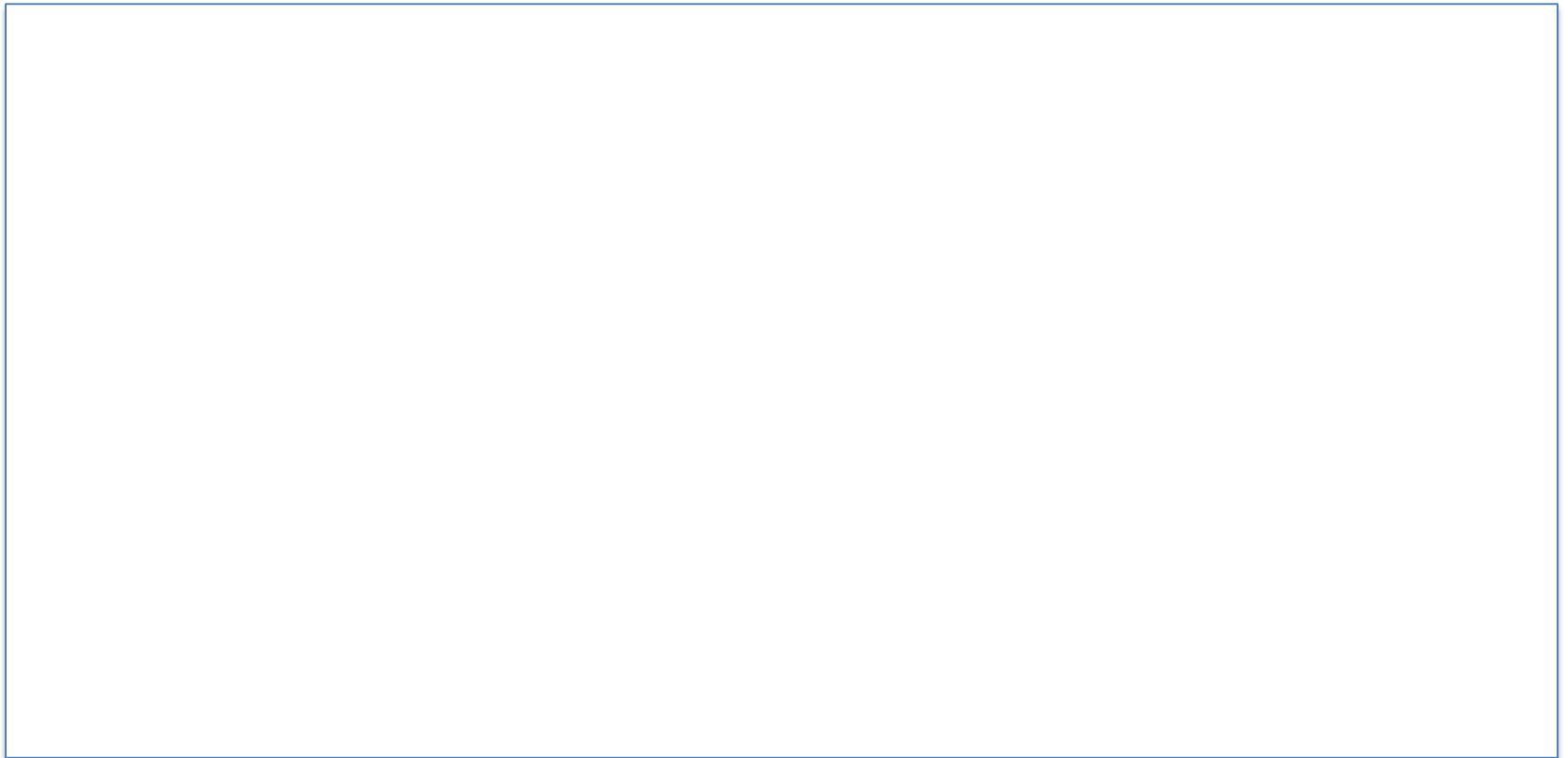
$$\left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,\text{comp}} = \bar{V}_i \quad (9.35)$$

- For pure i

$$\left(\frac{\partial G_i^\circ}{\partial P}\right)_{T,\text{comp}} = V_i^\circ \quad (9.36)$$

9.6 The Properties of Raoultian Ideal Solutions

(i) The Change in Volume Accompanying the Formation of an Ideal Solution



9.6 The Properties of Raoultian Ideal Solutions

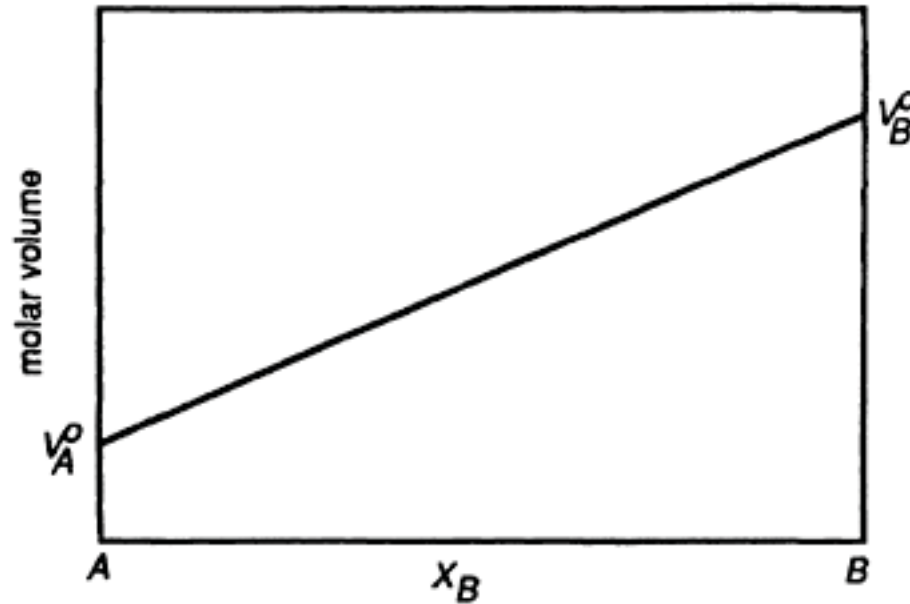


Figure 9.6 The variation, with composition, of the molar volume of a binary Raoultian solution.

9.6 The Properties of Raoultian Ideal Solutions

(ii) The Heat of Formation of an Ideal Solution



9.6 The Properties of Raoultian Ideal Solutions

(iii) The Heat of Formation of an Ideal Solution

$$\frac{d(R \ln X_i)}{dT} = -\frac{\Delta \bar{H}_i^M}{T^2}$$

$$\Delta \bar{H}_i^{M,\text{id}} = \bar{H}_i - H_i^\circ = 0$$

$$\bar{H}_i = H_i^\circ \quad (9.42)$$

$$\begin{aligned} \Delta H'^M &= (n_A \bar{H}_A + n_B \bar{H}_B) - (n_A H_A^\circ + n_B H_B^\circ) \\ &= n_A (\bar{H}_A - H_A^\circ) + n_B (\bar{H}_B - H_B^\circ) \\ &= n_A \Delta \bar{H}_A^M + n_B \Delta \bar{H}_B^M \end{aligned}$$

$$\Delta H^{M,\text{id}} = 0 \quad (9.43)$$

9.6 The Properties of Raoultian Ideal Solutions

(iv) The Entropy of Formation of an Ideal Solution

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

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

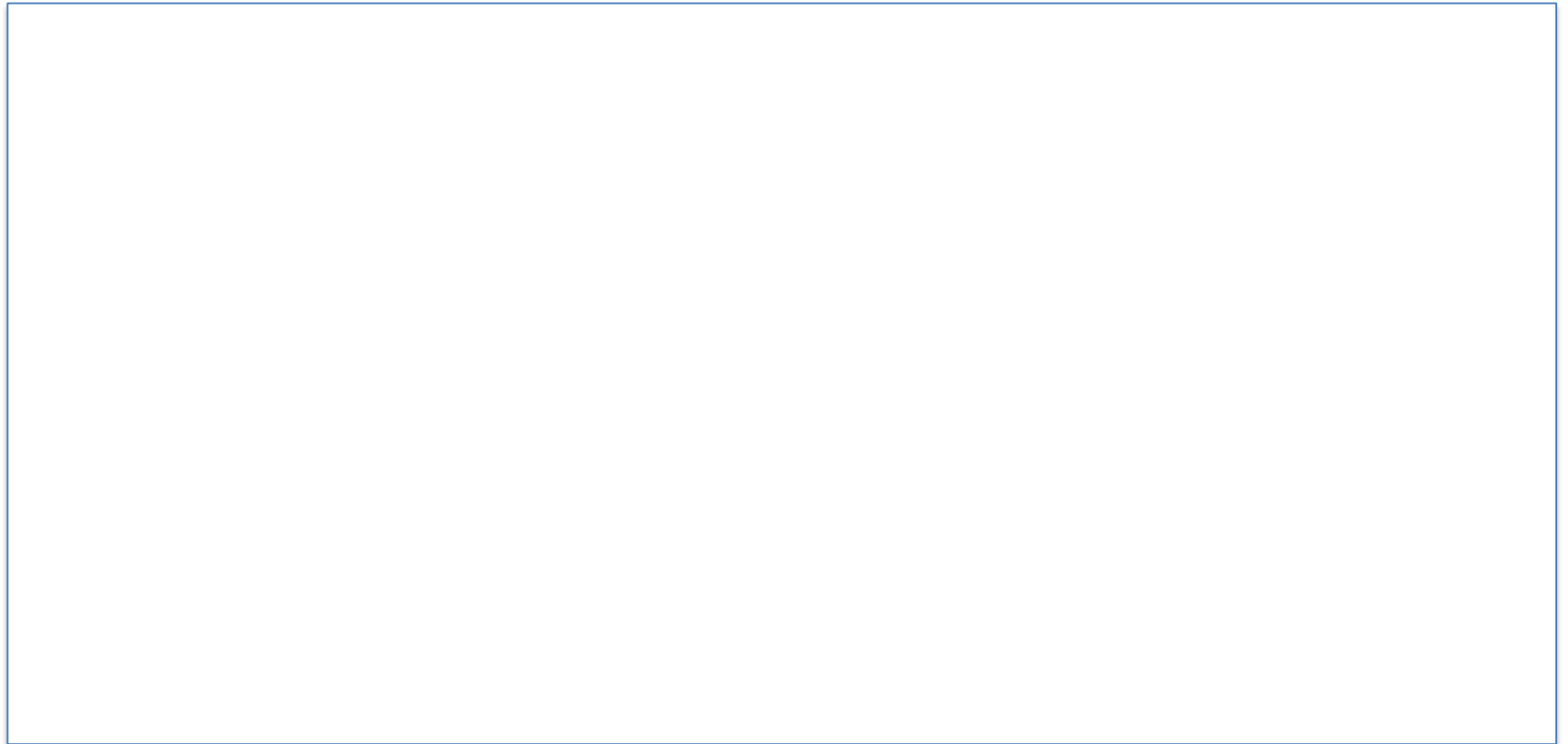
Eq. (9.44) shows that the entropy of formation of an ideal binary solution is independent of temperature

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

$$\begin{aligned}\Delta S^{M,\text{id}} &= -\left(\frac{\partial \Delta G^{M,\text{id}}}{\partial T}\right)_{P,\text{comp}} \\ &= -R(X_A \ln X_A + X_B \ln X_B)\end{aligned}\tag{9.44}$$

9.6 The Properties of Raoultian Ideal Solutions

(v) The Entropy of Formation of an Ideal Solution



9.6 The Properties of Raoultian Ideal Solutions

(vi) The Entropy of Formation of an Ideal Solution

$$N_A \text{ particles of } A = \frac{N_A}{N_O} \text{ moles of } A = n_A \text{ moles of } A$$

$$N_B \text{ particles of } B = \frac{N_B}{N_O} \text{ moles of } B = n_B \text{ moles of } B$$

$$\Delta S'_{\text{conf}} = -kN_O(n_A \ln X_A + n_B \ln X_B)$$

$$\Delta S'_{\text{conf}} = -R(n_A \ln X_A + n_B \ln X_B)$$

$$\Delta S_{\text{conf}} = -R(X_A \ln X_A + X_B \ln X_B) \quad (9.45)$$

9.6 The Properties of Raoultian Ideal Solutions

(vii) The Entropy of Formation of an Ideal Solution

$$\Delta S^M = X_A \Delta \bar{S}_A^M + X_B \Delta \bar{S}_B^M$$

$$\Delta \bar{S}_A^{M,id} = -R \ln X_A \quad \text{and} \quad \Delta \bar{S}_B^{M,id} = -R \ln X_B$$

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

$$\Delta G^{M,id} = -T \Delta S^{M,id}$$

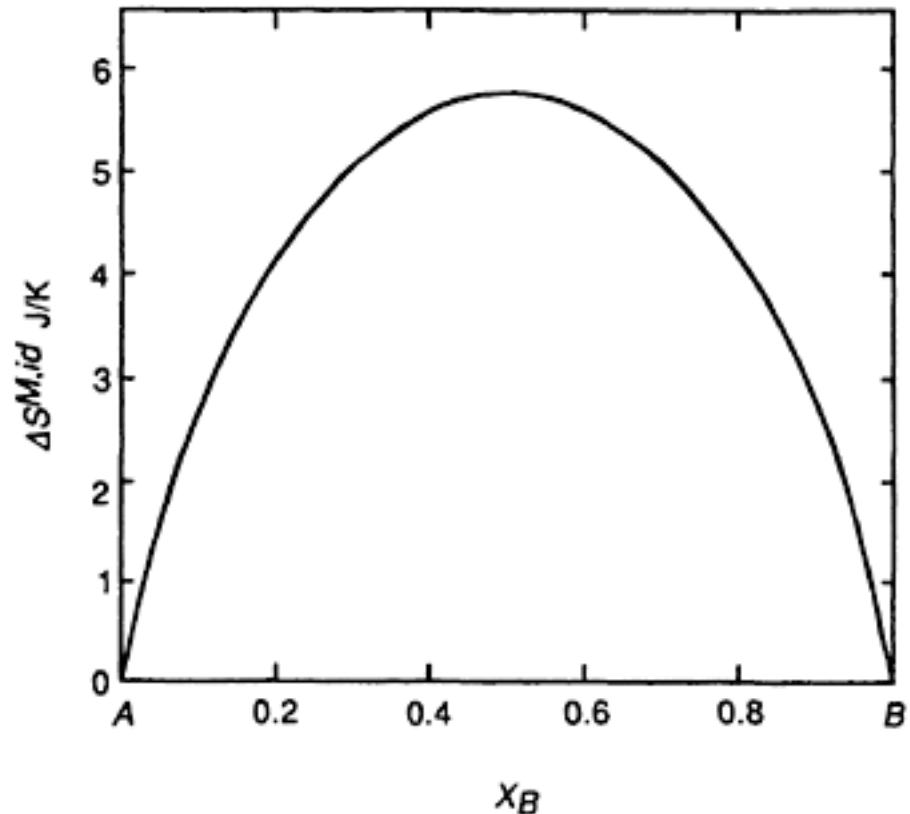


Figure 9.7 The variation, with composition, of the molar entropy of formation of a binary Raoultian solution.