



# Contents of Today

热力学研究热功转换的方向、限度以及能量的衡算。

- 热力学基础
  - 可逆过程/熵/判断过程方向性(专题一)
  - 热力学函数关系式(专题二)
- 多相平衡(专题三)
- 溶液/溶体(专题四)
- 相律(专题五)
- 二元、三元相图(专题六)



# 判断过程的方向

孤立体系 ( $dU=0$ ,  $dV=0$ ) , 熵增原理

$(\Delta S)_{U,V} > 0$  表示自发

$(\Delta S)_{U,V} = 0$  表示平衡

$(\Delta S)_{U,V} < 0$  表示不可能

非孤立体系

$\Delta S > \sum \frac{\delta Q}{T}$  表示不可逆

$\Delta S = \sum \frac{\delta Q}{T}$  表示可逆或平衡

$\Delta S < \sum \frac{\delta Q}{T}$  表示不可能进行



# 判断过程的方向

定温定压的体系

$(\Delta G)_{T,p} < 0$  表示自发

$(\Delta G)_{T,p} = 0$  表示平衡

$(\Delta G)_{T,p} > 0$  表示不自发

$(\Delta G)_{T,p} > W'$  表示不可能进行

在定温定压条件下，一个自发过程发生时，系统的Gibbs自由能总要减少，当减少到不能再减少时，系统即达平衡，这是系统的Gibbs自由能应为极小值

**思考题：**试推导在何种条件下，可用U和H来判断过程的方向和限度。

$$TdS - dU - p_{\text{外}}dV \geq -\delta W'$$



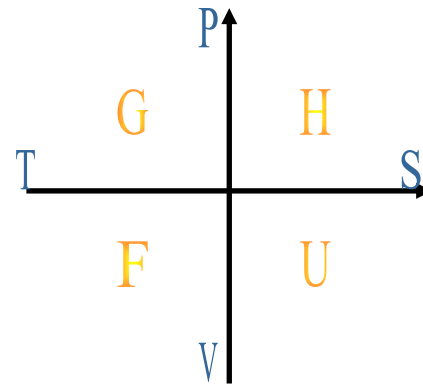
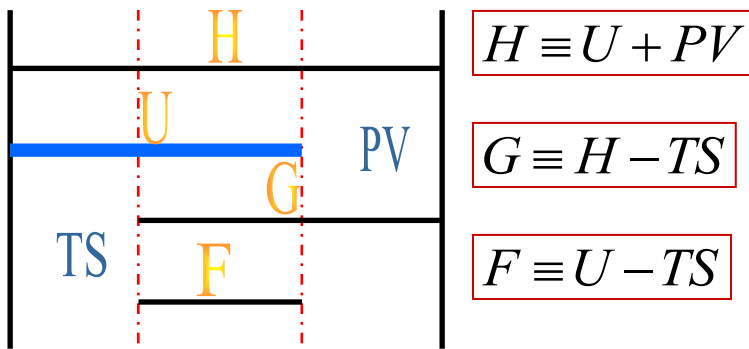
# 专题二、热力学函数关系

## 热力学函数关系及其应用



# Review (2)

当系统由始态I经过某一过程变到终态II后，如能使系统再回到原态，同时也消除了原过程对环境所产生的一切影响，则原来过程称为可逆过程。



$$dU = TdS - PdV$$

$$dF = -SdT - PdV$$

$$dG = -SdT + VdP$$

$$dH = TdS + VdP$$

$\mu_i$  The chemical potential of the component i.

$$\left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j \neq n_i} = \left( \frac{\partial F}{\partial n_i} \right)_{T,V,n_j \neq n_i} = \left( \frac{\partial H}{\partial n_i} \right)_{P,S,n_j \neq n_i} = \left( \frac{\partial U}{\partial n_i} \right)_{V,S,n_j \neq n_i} = \mu_i$$



# 热力学函数关系 (13)

$$dz = Mdx + Ndy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dF = -SdT - PdV$$

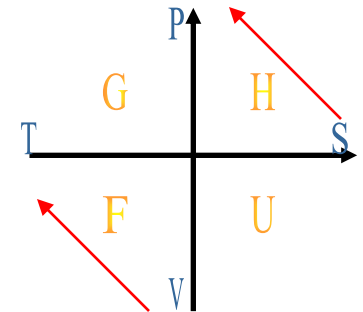
$$dG = -SdT + VdP$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$





# \*专题三、多相平衡

## 多相平衡



# 多相平衡 (1)

- 平衡的概念很重要
- 稳定的、不随时间而变化
- 一些特定的性质在体系中是均匀的
- 从形式上体系不一定是均匀的
  - 冰和水的共存
- 相
  - 物理化学性质均匀的部分
  - 材料的性质取决于一系列材料中的相含量、形态及其分布





## 多相平衡 (2)

- Two states are in equilibrium when no reversible work can be done by having the system change between those two states

$$\delta W_{rev.1 \rightarrow 2} = 0$$

- The temperatures in the two states must be equal
  - A consequence of the second law of thermodynamics



## 多相平衡 (3)

$$\left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,2} dn_i - \left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,1} dn_i = \delta W_{rev}$$

Condition of equilibrium  $\delta W_{rev.1 \rightarrow 2} = 0$

$$\left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,2} dn_i = \left(\overline{G} + \underline{PE} + \underline{KE}\right)_{i,1} dn_i$$

At the same potential energy level and kinetic level

$$\left(\overline{G}_{i,2} - \overline{G}_{i,1}\right) dn_i = \Delta \overline{G}_i = 0 \quad \overline{G}_{i,2} = \overline{G}_{i,1}$$

$$\mu_{i,2} = \mu_{i,1} \quad \text{In term of the chemical potential of } i$$

States 1 and 2 are in equilibrium with respect to material i if the partial molar Gibbs free energy (or chemical potential) of i is the same in both states.



## 例子续2

若上述转移过程可以实现，则

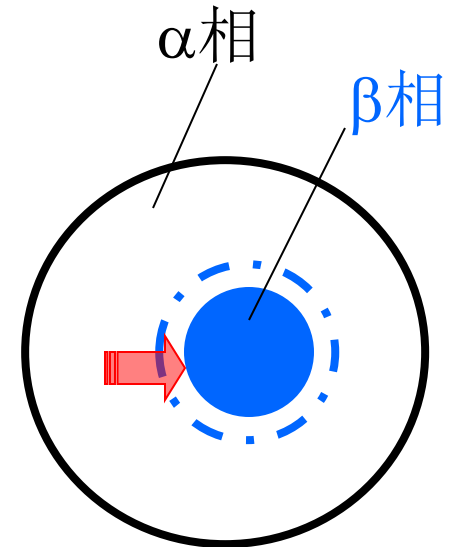
$$dG = (\mu_B^\beta - \mu_B^\alpha)(dn_B) < 0$$

因为  $dn_B > 0$

所以

$$\mu_B^\beta < \mu_B^\alpha$$

组分B有 $dn_B$ 由 $\alpha$ 相  
进入 $\beta$ 相



上式表明物质总是由化学势较高的相自发转移到化学势较低的相，直到该物质在两相中的化学势相等。

对比水与水位、电流与电势的关系，也有某种“势”的意思，所以称为化学势



# 化学势判据

$$\sum_B \mu_B dn_B \leq 0$$

$$\sum_i \mu_i dn_i \leq 0$$

这一判据式讨论具体的平衡规律、过程的方向与限度



# P, V, Xi影响化学势

## 1, 温度的影响

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

$$\underline{S}_{298}^0 = \int_0^{298} \frac{C_P}{T} dT$$

## 2, 压力的影响

气相

$$\left(\frac{\partial G}{\partial P}\right)_{T, x_i} = V$$

$$\underline{V} = \frac{RT}{P}$$

$$d\underline{G} = RT d \ln P$$

## 3, 组成的影响: 偏摩尔Gibbs自由能



# Enthalpy/Entropy/Gibbs

$$G = H - TS = H_0 + \int_0^T C_P dT - T \int_0^T \frac{C_P}{T} dT$$

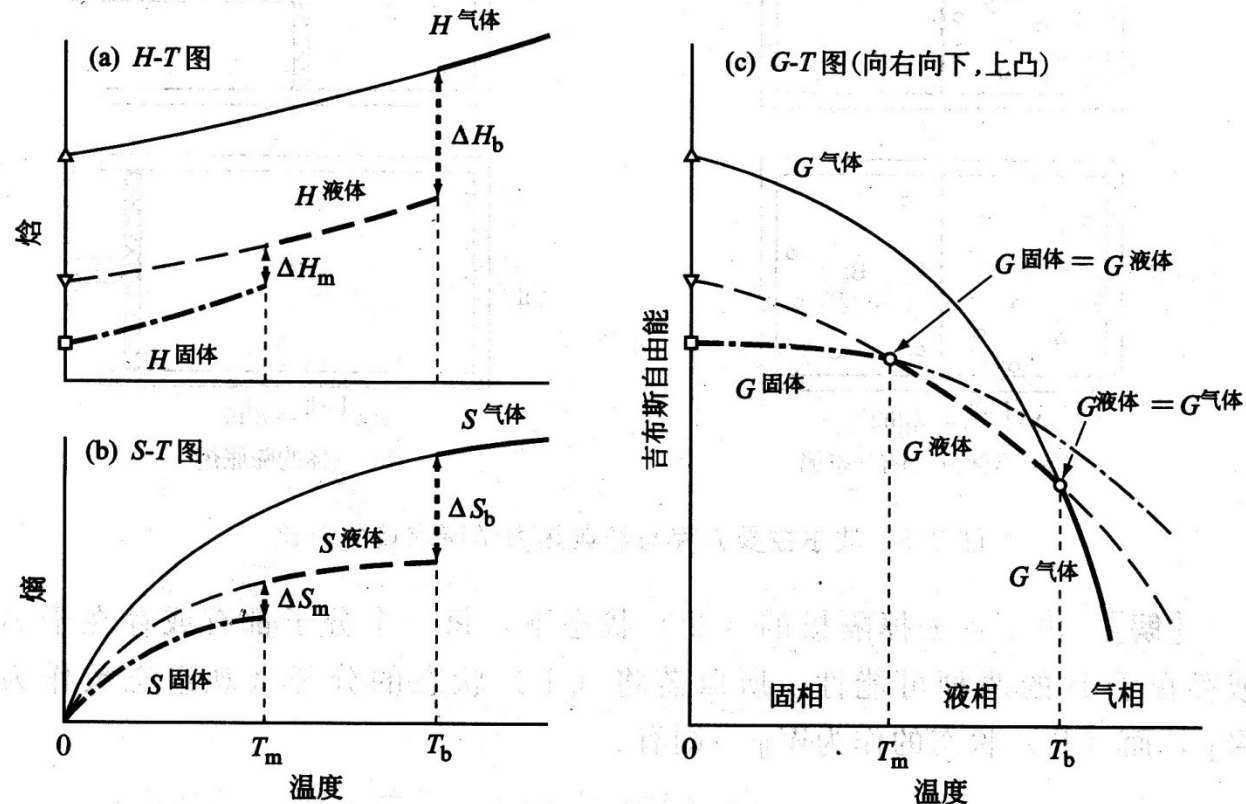


图 2.7 纯物质的 (a) 焓、(b) 熵、(c) 自由能  
(图中的粗线为稳定相, 细线为亚稳相)



# 专题四、溶液

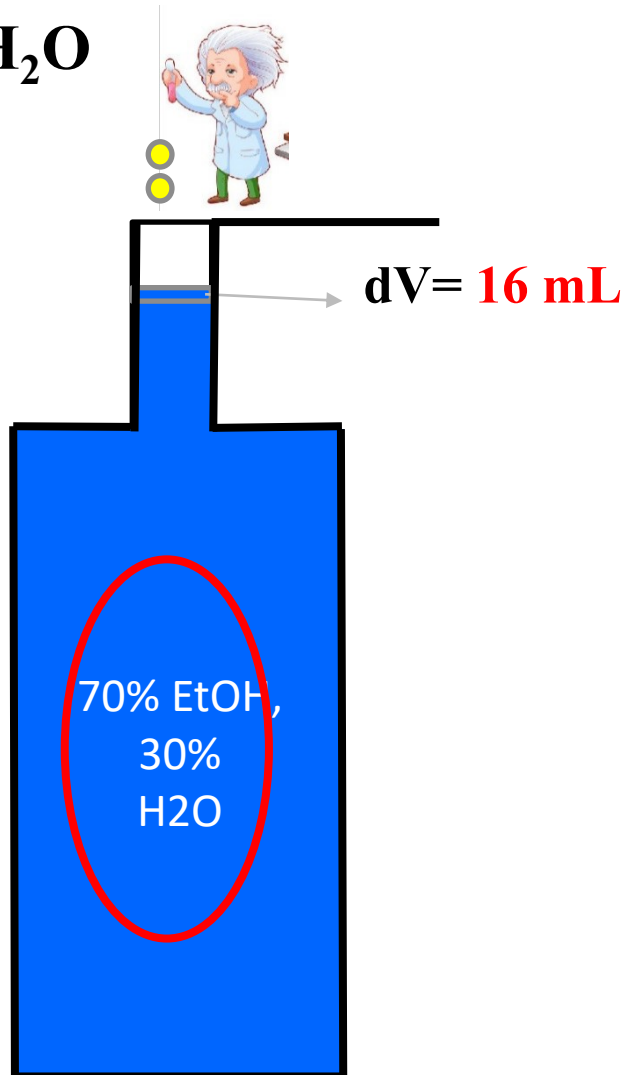
## 溶液



# Partial Molar Quantities 偏摩尔量

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Phase Transformation and Applications

1 mol H<sub>2</sub>O  
18 mL



Definition of partial molar volume

$$\bar{V}_A = \left( \frac{\partial V}{\partial n_A} \right)_{T, P, n_B}$$

$$dV = 16 \text{ mL}$$

$$dn_A = 1 \text{ mol}$$

EtOH/H<sub>2</sub>O solution:

*Partial molar volume of water*

$$\bar{V}_A = \frac{\partial V}{\partial n_A} = 16 \text{ mL/mol}$$

Pure water:

$$\underline{V}_A = 18 \text{ mL/mol}$$

$$\bar{V}_A^{rel} = \bar{V}_A - \underline{V}_A = -2 \text{ mL/mol}$$





# Raoult's law and Henry's law

S. J. T. U.

Phase Transformation and Applications

## Raoult's law

1887年, 经验定律,  $P_A = P_A^* x_A \Rightarrow a_A = x_A$

“溶液中溶剂的蒸气压 $P_A$ 等于同一温度下纯溶剂的蒸气压 $P_A^*$ 与溶液中溶剂的摩尔分数 $x_A$ 的乘积”

## Henry's law

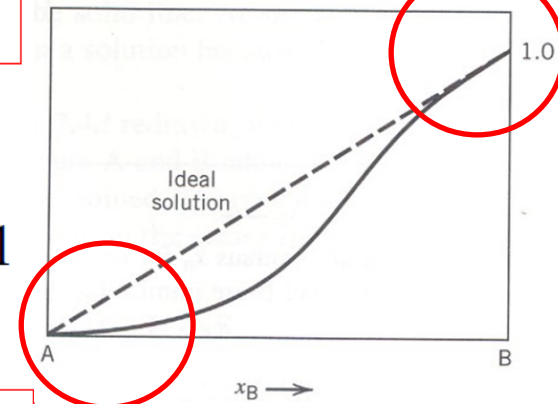
1803年, 经验定律

$$x_B = k_{x,B} P_B \Rightarrow P_B = k_{x,B} x_B \rightarrow \gamma_B = 1$$

$k_{x,B} ? P_B^*$

“在一定温度下微溶气体在溶液中的平衡组成与该气体的平衡气相分压成正比”

## Raoult's law



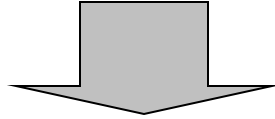
## Henry's law

$$f_B = c^* x_B$$



# 溶液 (1)

Chemical changes among pure components and compounds



**Solutions:** elements or compounds dissolved in one another

Many of the interesting properties of materials and many important chemical reactions take place

Thermodynamics of these solutions



## 溶液 (2)

Fugacity is defined for gases:

$$d\bar{G}_i = RTd(\ln f_i)$$

Thermodynamic activity of a component, i, is defined as:

$$\alpha_i \equiv \frac{f_i}{f_i^\circ}$$

$f_i^\circ$  The fugacity of the component i in its standard state.

The fugacity of a condensed phase is equal to the fugacity of the vapor phase in equilibrium with it.

The fugacity of the vapor is equal to the pressure of the vapor, if the vapor in equilibrium with the condensed phase is ideal.



# Entropy of Mixing: Ideal Solution

For an ideal solution,

$$\overline{G}_i^{rel} = RT \ln x_i \quad a_i = x_i$$

The relative partial entropy of component A,

$$\overline{S}_A^{rel} = -\frac{\partial}{\partial T} \left( \overline{G}_A^{rel} \right)_{P, n_B} = \frac{\partial}{\partial T} (RT \ln x_A)_{P, x_B}$$

$$\overline{S}_A^{rel} = -R \ln x_A$$

The molar entropy of mixing for a solution of A + B,

$$\underline{S}_M = x_A \overline{S}_A^{rel} + x_B \overline{S}_B^{rel}$$

$$\underline{S}_M = -R[x_A \ln x_A + x_B \ln x_B]$$

For **ideal solution** with many components,

$$\underline{S}_M = -R \sum_i x_i \ln x_i$$



# Enthalpy of Mixing: Ideal Solution (1)

The enthalpy of mixing of a solution,

$$\frac{d\left(\frac{\overline{G}_A^{rel}}{T}\right)}{d\left(\frac{1}{T}\right)} = \overline{H}_A^{rel} \quad \leftarrow \quad d\left(\frac{\Delta G}{T}\right)_P = \Delta H d\left(\frac{1}{T}\right)_P$$

For an ideal solution:  $\overline{G}_A^{rel} = RT \ln \alpha_A = RT \ln x_A$

$$\frac{d(R \ln x_A)}{dT} = \overline{H}_A^{rel} = 0 = \overline{H}_A - \underline{H}_A$$

The enthalpy of mixing of an ideal solution is zero:

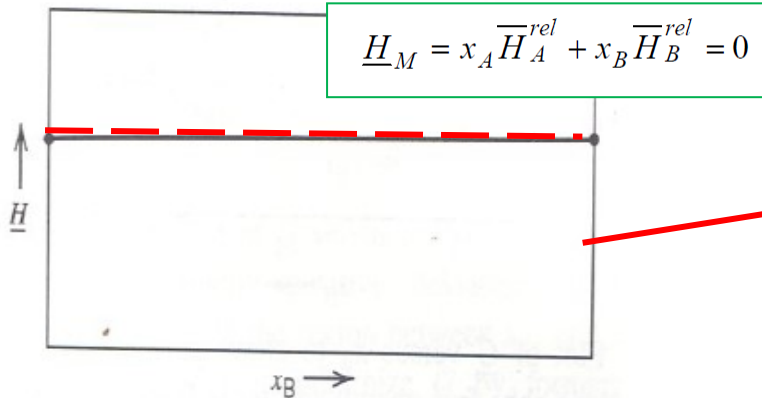
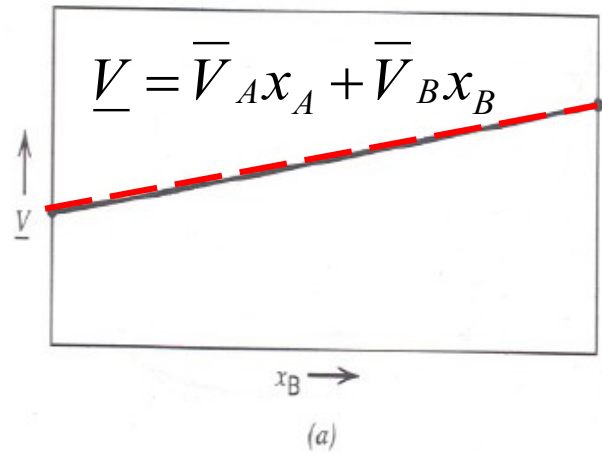
$$\underline{H}_M = x_A \overline{H}_A^{rel} + x_B \overline{H}_B^{rel} = 0 \quad (\text{ideal solution})$$



# 7.6 Graphical Representation (理想溶液)

S. J. T. U.

Phase Transformation and Applications



$$\overline{H}_A^{rel} = 0 = \overline{H}_A - \underline{H}_A$$

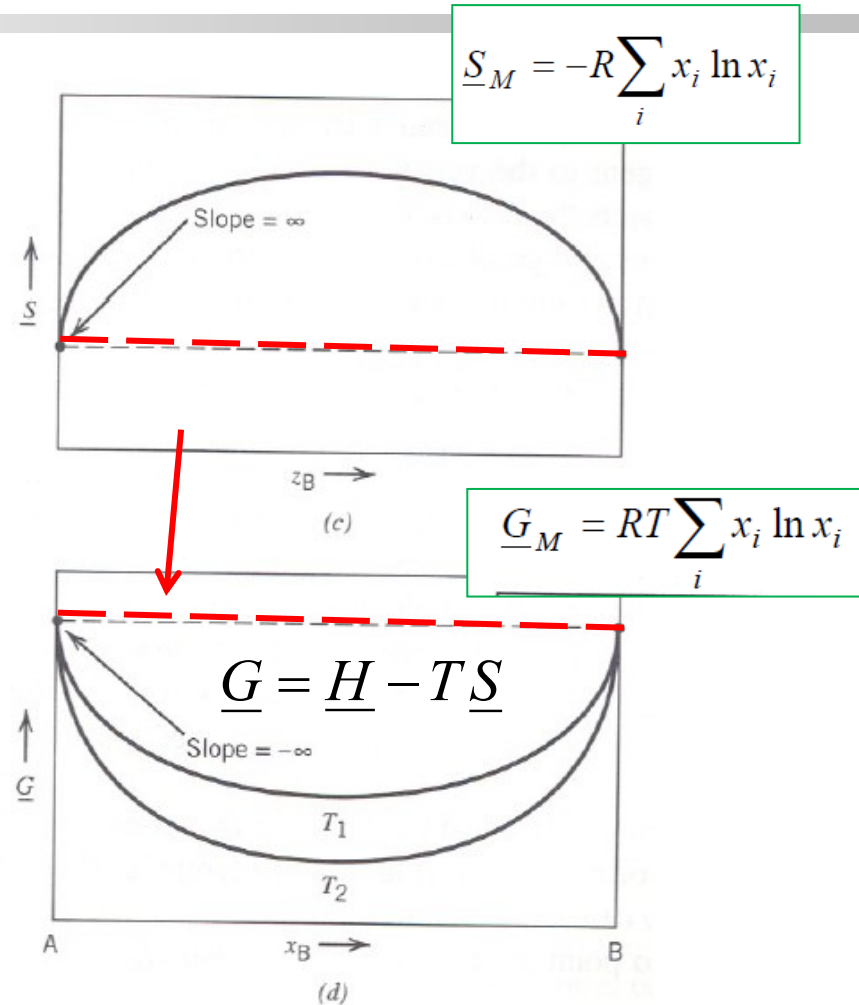
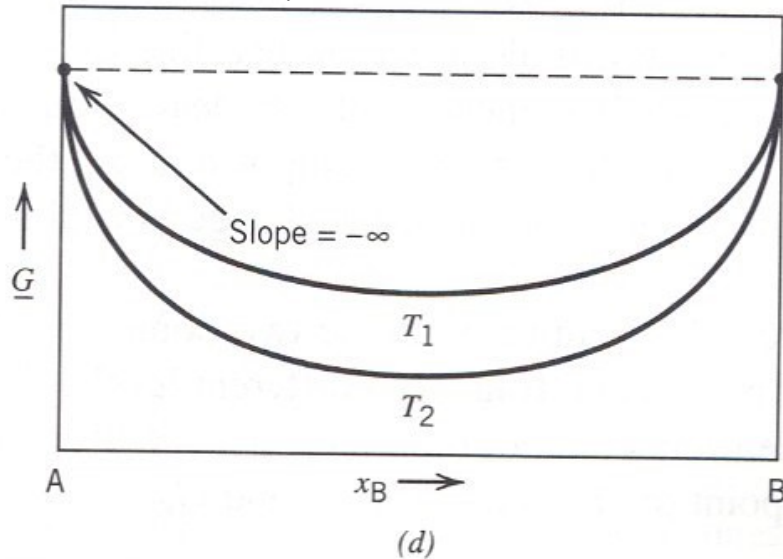


Figure 7.4 Molar properties for an ideal solution A-B: (a) volume of mixing, (b) enthalpy of mixing, (c) entropy of mixing, and (d) Gibbs free energy of mixing.



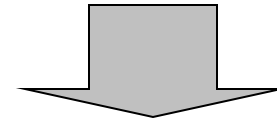
# Introduction

$$\underline{G}_M = RT \sum_i x_i \ln x_i$$



**Figure 7.4** Molar properties for an ideal solution A–B: (a) volume of mixing, (b) enthalpy of mixing, (c) entropy of mixing, and (d) Gibbs free energy of mixing.

Ideal solution



Non-ideal solution: practical solution

Many forms

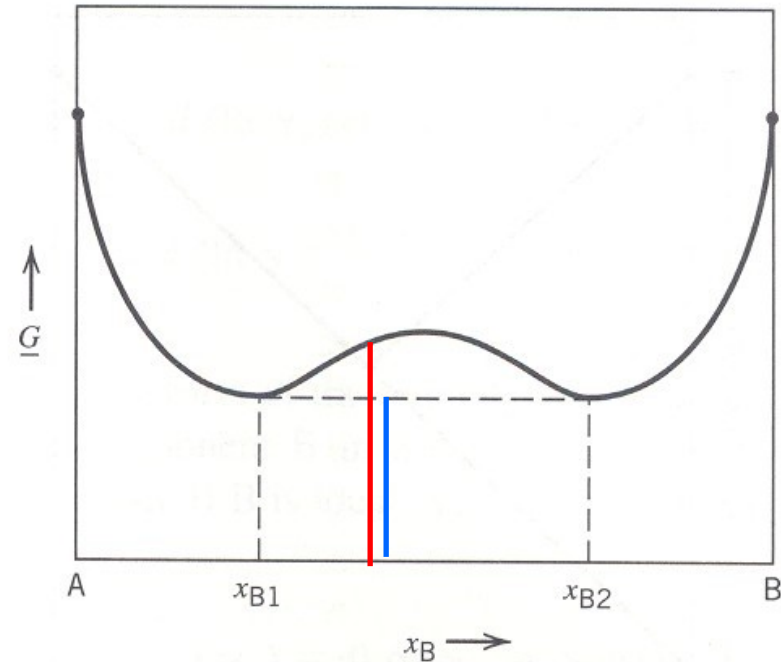


# Non-ideal Solution (1)

A single solution in this region is unstable relative to the mixture of solutions of  $x_{B1}$  and  $x_{B2}$ .

If equilibrium were attained, the single solution would decompose into two solutions because the Gibbs free energy change associated with such a decomposition is negative.

$$\underline{G}_M \neq RT \sum_i x_i \ln x_i$$



**Figure 7.6** Plot of  $\underline{G}$  versus  $x_B$  for a nonideal solution, showing positive deviations from Raoult's law. (In the region between  $x_{B1}$  and  $x_{B2}$ , the system can minimize  $G$  by forming mixtures of two solutions,  $x_{B1}$  and  $x_{B2}$ .)





# 稀溶液及其依数性

- 稀溶液

溶剂符合Raoult定量，即理想溶液

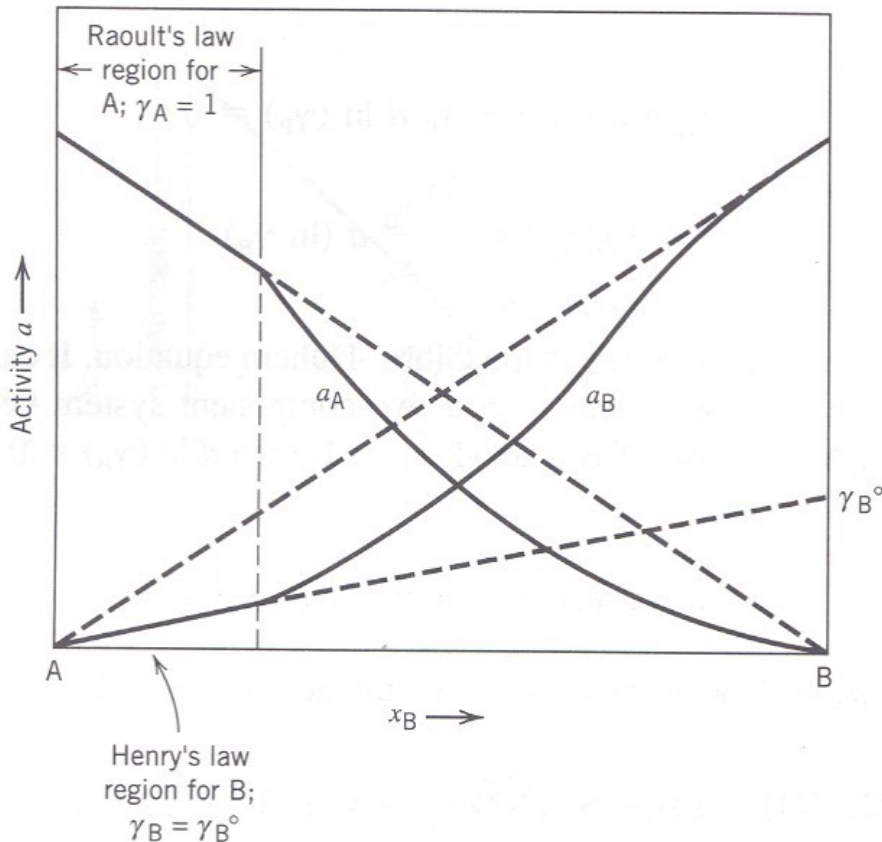
溶质符合Henry定量，非理想，活度系数为常数



# Dilute Solution and Colligative Properties (1)

S. J. T. U.

Phase Transformation and Applications



**Figure 7.11** Henry's law and Raoult's law regions for the nonideal solution.

Henry's law region:

$$\gamma_B = \gamma_B^\circ \quad d(\ln \gamma_B^\circ) = 0$$

$$\gamma_B^\circ = \text{Constant}$$

Raoult's law region:

$$\gamma_A^\circ = 1$$

$$x_A = 1, a_A = 1$$



# Raoult's law and Henry's law

## Raoult's law

1887年，经验定律，  $P_A = P_A^* x_A \Rightarrow a_A = x_A$

“溶液中溶剂的蒸气压 $P_A$ 等于同一温度下纯溶剂的蒸气压 $P_A^*$ 与溶液中溶剂的摩尔分数 $x_A$ 的乘积”

## Henry's law

1803年，经验定律  $x_B = k'_{x,B} P_B \Rightarrow P_B = k_{x,B} x_B \not\rightarrow \gamma_B = 1$

$$k_{x,B} ? P_B^*$$

“在一定温度下微溶气体在溶液中的平衡组成与该气体的平衡气相分压成正比”



# Dilute Solution and Colligative Properties (2)

S. J. T. U.

Phase Transformation and Applications

The vapor pressure of the solvent is reduced.

$$P_S = P_S^\circ x_S = P_S^\circ (1 - x_U)$$

依数性：？

The boiling point of the solvent is elevated.

$$\ln x_S = \ln(1 - x_U) = \frac{\Delta H_{vap}^\circ}{R} \left[ \frac{1}{T_B} - \frac{1}{T_B^\circ} \right]$$

The freezing point of the solvent is lowered.

The solvent will display an osmotic pressure.



S. J. T. U.

Phase Transformation and Applications

# Dilute Solution and Colligative Properties (3)

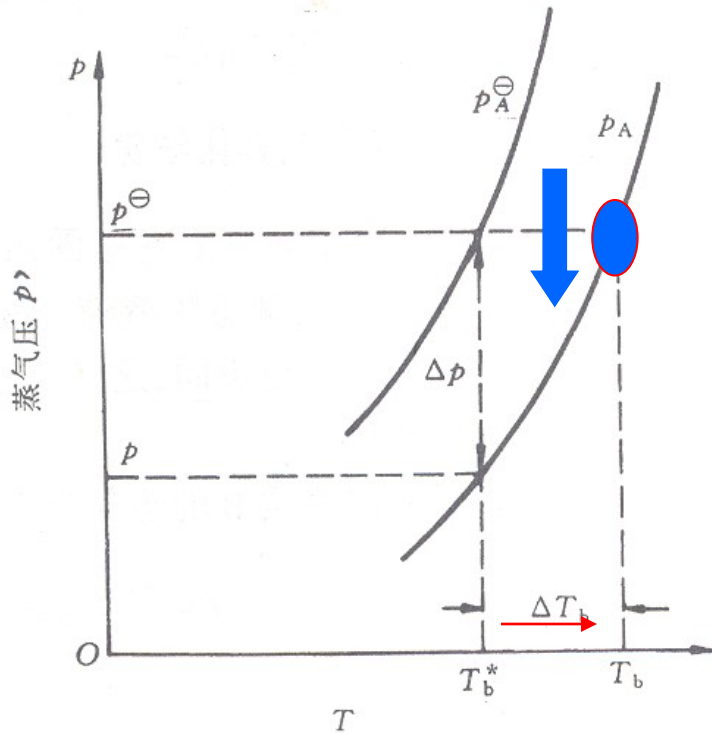


图 5-6 稀溶液中溶液的沸点升高

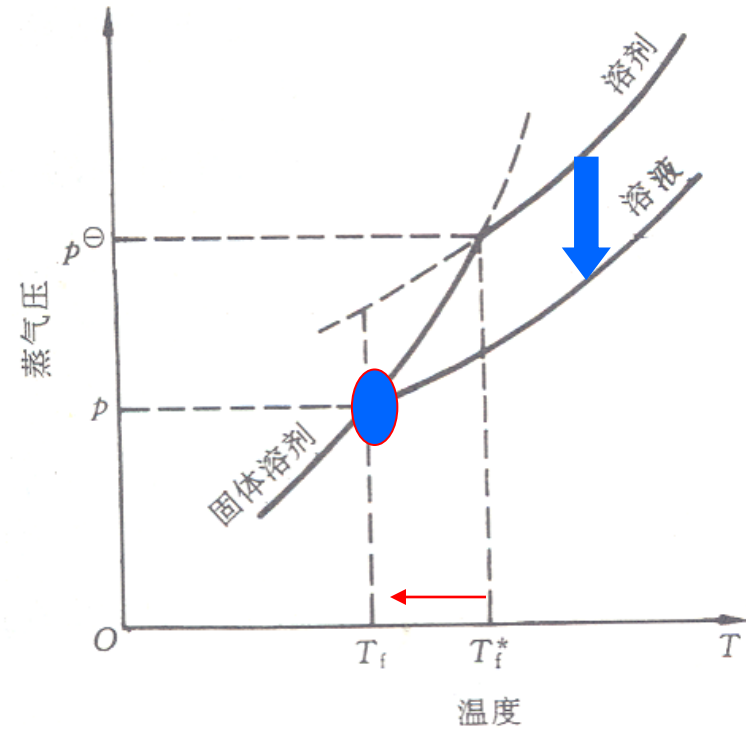


图 5-7 稀溶液的凝固点下降

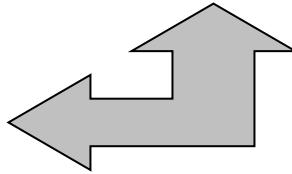


# Osmotic Pressure (1)

$$\mu_A - \mu_A^\circ = RT \ln x_A \quad \text{Raoult's law}$$

$$\mu_A - \mu_A^\circ = RT \ln(1 - x_B) = -RTx_B$$

$$\mu_A - \mu_A^\circ = \int_{P+\Pi}^P \underline{V}_A dP = -\underline{V}_A \Pi$$



$$\Pi = RT \frac{x_B}{\underline{V}_A}$$

半透膜!

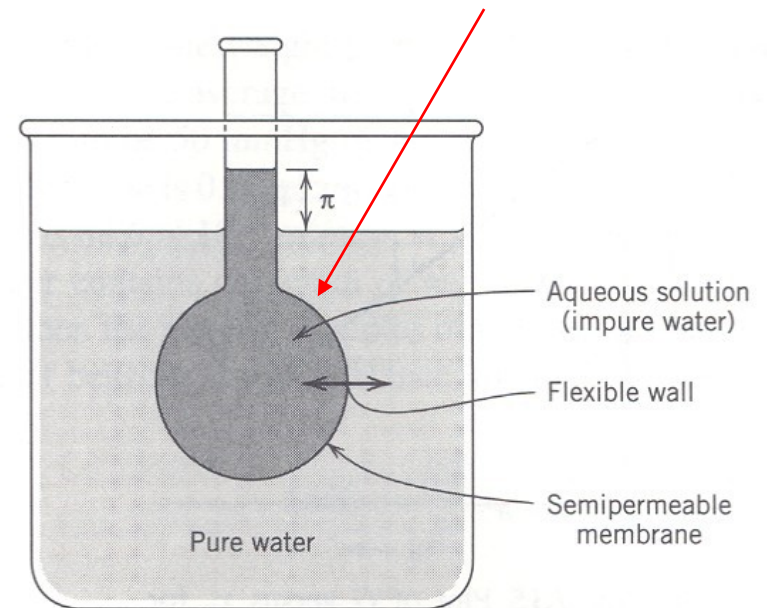


Figure 7.14 Osmotic pressure.



## 7.13 Osmotic pressure (2)

### Application of Osmotic effect

As an example, 0.6mol/L NaCl:

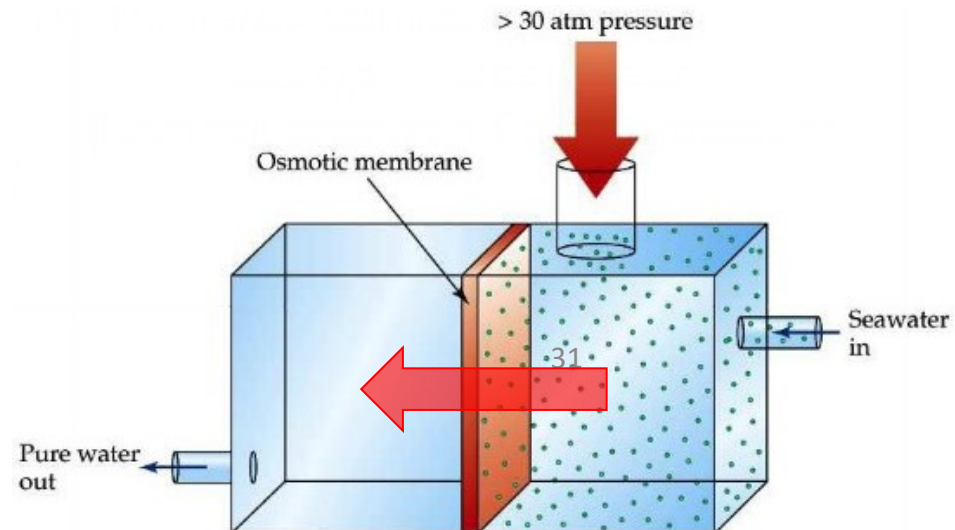
$$x_B = \frac{0.6}{1000/18} = 0.0108$$



$$\Pi = \frac{2(0.0108)(8.314)(298)}{18 \times 10^{-6}} = 29.7 \times 10^5 \text{ N/m}^2 = 29.7 \text{ atm}$$

$$\Pi = RT \frac{x_B}{V_A}$$

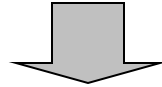
m<sup>3</sup>/mol





# Graphical Representation (1)

If we know a property of a two-component solution as a function of composition



We can determine the partial molar values of that property.

The molar volume of a solution can be determined simply by forming solutions of A and B with different compositions and measuring the resulting specific volume.





## Graphical Representation (2)

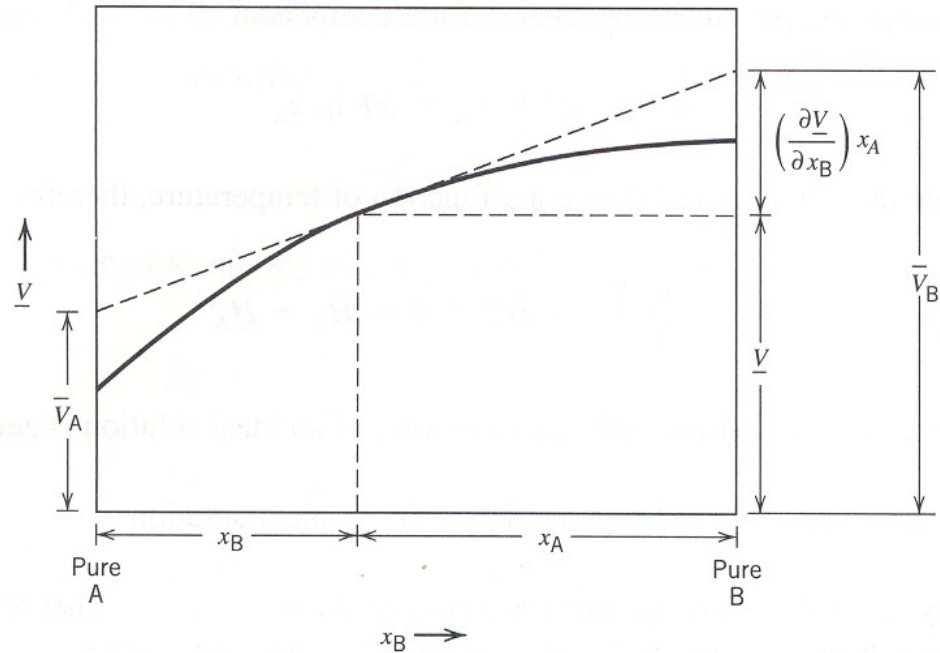
$$d\underline{V} = \bar{V}_A dx_A + \bar{V}_B dx_B$$

$$x_A + x_B = 1$$

$$dx_A + dx_B = 0$$

$$dx_A / dx_B = -1$$

$$\left( \frac{\partial \underline{V}}{\partial x_B} \right)_{T,P} = \bar{V}_B - \bar{V}_A$$



**Figure 7.3** Plot of  $\underline{V}$  versus  $x_B$  to show geometrical relationships in an A-B solution.



# 7.6 Graphical Representation (一般溶液)

S. J. T. U.  
Phase Transformation and Applications

**What is the slope?**

$$d\underline{V} = \bar{V}_A dx_A + \bar{V}_B dx_B$$

$$x_A + x_B = 1$$

$$dx_A + dx_B = 0$$

$$dx_A / dx_B = -1$$

$$\left( \frac{\partial \underline{V}}{\partial x_B} \right)_{T,P} = \bar{V}_B - \bar{V}_A$$

$$\underline{V} = \bar{V}_A x_A + \bar{V}_B x_B$$

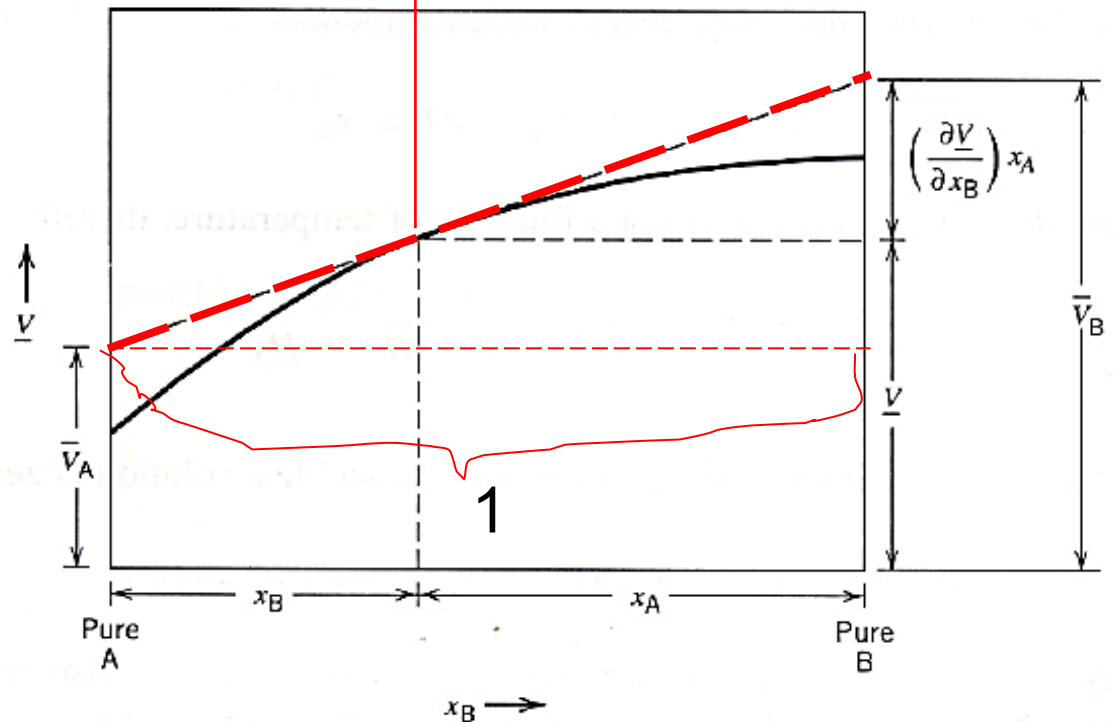


Figure 7.3 Plot of  $\underline{V}$  versus  $x_B$  to show geometrical relationships in an A-B solution.

$$\left( \frac{\partial \underline{V}}{\partial x_B} \right)_{T,P} = \text{Slope} = \Delta y / \Delta x = \Delta y = \bar{V}_B - \bar{V}_A$$



# 7.6 Graphical Representation (3)

S. J. T. U.  
Phase Transformation and Applications

$$d\underline{V} = \bar{V}_A dx_A + \bar{V}_B dx_B$$

$$\left( \frac{\partial \underline{V}}{\partial x_B} \right)_{T,P} = \bar{V}_B - \bar{V}_A$$

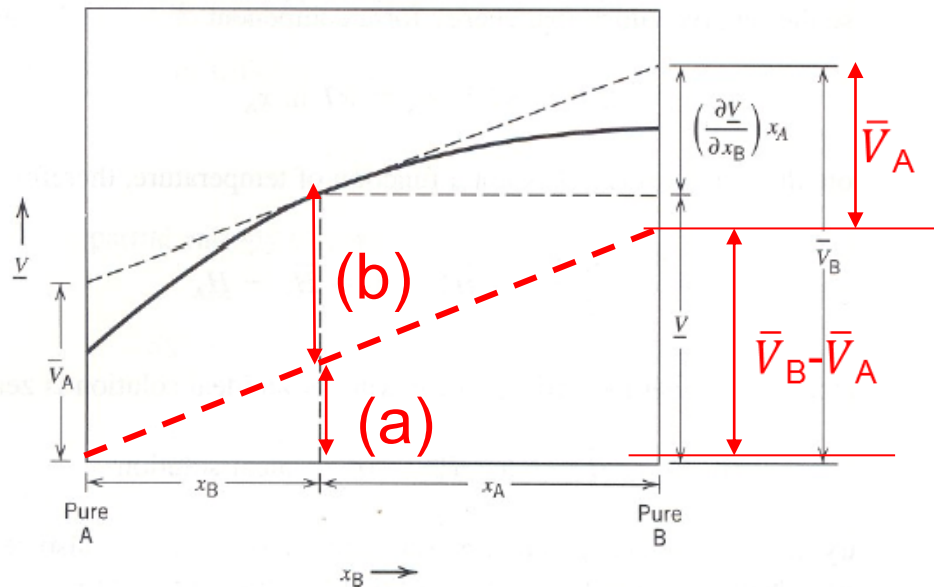


Figure 7.3 Plot of  $\underline{V}$  versus  $x_B$  to show geometrical relationships in an A-B solution.

I.  $x_A \left( \frac{\partial \underline{V}}{\partial x_B} \right)_{T,P} = x_A \bar{V}_B - x_A \bar{V}_A$

II.  $x_B \left( \frac{\partial \underline{V}}{\partial x_B} \right)_{T,P} = x_B \bar{V}_B - x_B \bar{V}_A$

III.  $\underline{V} = \bar{V}_A x_A + \bar{V}_B x_B$

$$\begin{aligned} \underline{V} &= (a) + (b) \\ &= x_B (\bar{V}_B - \bar{V}_A) + \bar{V}_A \\ &= x_B \bar{V}_B + x_A \bar{V}_A \end{aligned}$$



# 7.6 Graphical Representation (3)

S. J. T. U.  
Phase Transformation and Applications

$$d\underline{V} = \bar{V}_A dx_A + \bar{V}_B dx_B$$

$$\left( \frac{\partial \underline{V}}{\partial x_B} \right)_{T,P} = \bar{V}_B - \bar{V}_A$$

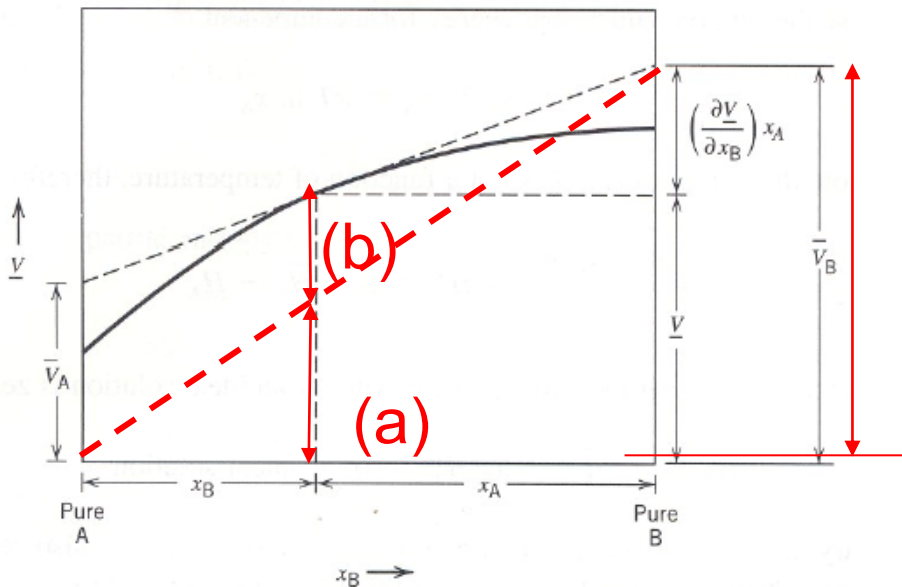


Figure 7.3 Plot of  $\underline{V}$  versus  $x_B$  to show geometrical relationships in an A-B solution.

I.  $x_A \left( \frac{\partial \underline{V}}{\partial x_B} \right)_{T,P} = x_A \bar{V}_B - x_A \bar{V}_A$

II.  $x_B \left( \frac{\partial \underline{V}}{\partial x_B} \right)_{T,P} = x_B \bar{V}_B - x_B \bar{V}_A$

III.  $\underline{V} = \bar{V}_A x_A + \bar{V}_B x_B$

$$\underline{V} = (a) + (b)$$

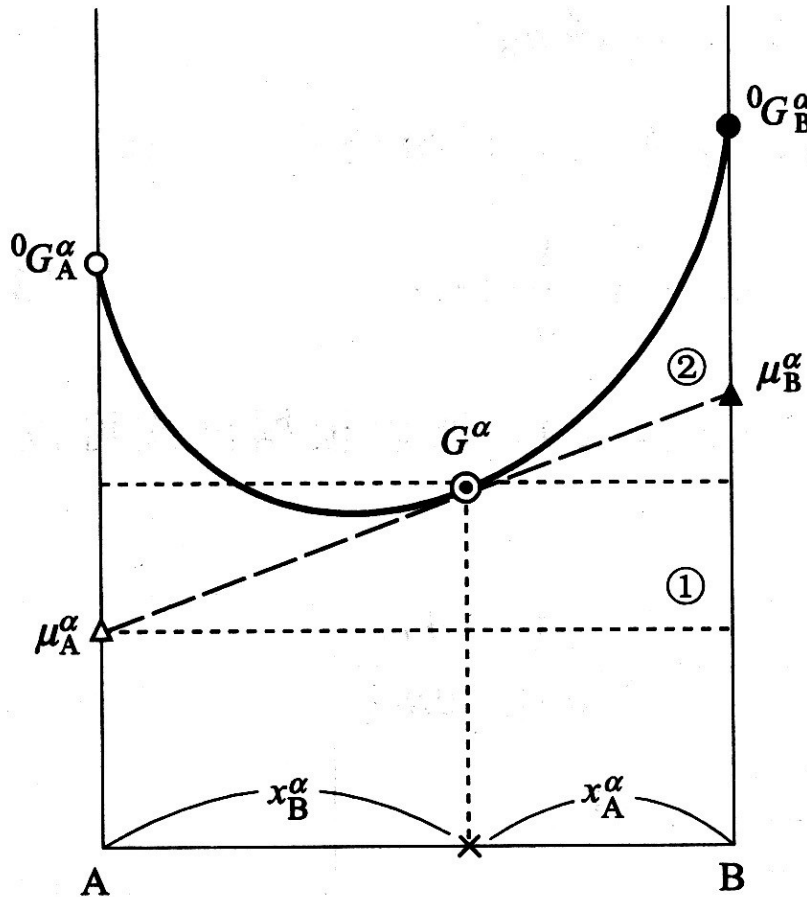
$$= x_B \bar{V}_B + x_A \bar{V}_A$$

[illegible]

elective topics



# Binary



(a) A-B系

A-B二元自由能和化学势之间的关系

$$G^{\alpha} = \mu_A^{\alpha} \cdot x_A + \mu_B^{\alpha} \cdot x_B$$

$$\left. \begin{aligned} \mu_A^{\alpha} &= G^{\alpha} - \left( \frac{\partial G^{\alpha}}{\partial x_B} \right) \cdot x_B \\ \mu_B^{\alpha} &= G^{\alpha} - \left( \frac{\partial G^{\alpha}}{\partial x_B} \right) \cdot x_B + \left( \frac{\partial G^{\alpha}}{\partial x_B} \right) \end{aligned} \right\}$$



## Example 3.7

【例题 3.7】 试根据正规溶体模型，求出 A-B 二元系  $\alpha$  溶体中组元 A 和 B 的化学势表达式。

【解】 根据式 (3.15)，A-B 二元系  $\alpha$  溶体自由能的正规溶体近似表达式为

$$G^{\alpha} = {}^0G_A^{\alpha}(1-x_B) + {}^0G_B^{\alpha}x_B + \Omega_{AB}^{\alpha}(1-x_B)x_B \\ + RT[(1-x_B)\ln(1-x_B) + x_B\ln x_B]$$

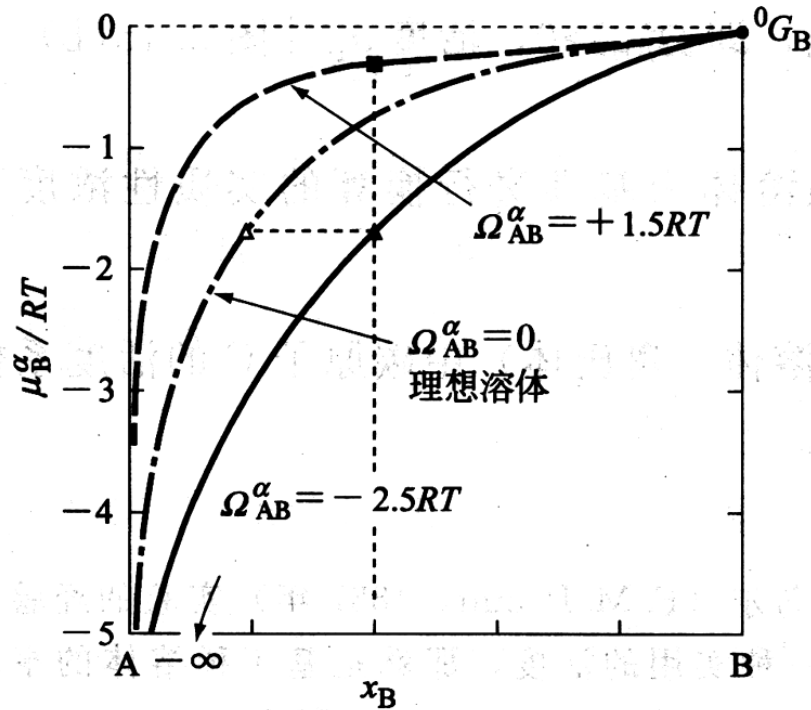
将上式求  $(\partial G^{\alpha}/\partial x_B)$ ，并代入式 (3.39) 中，可得式 (3.43)。

$$\left. \begin{aligned} \mu_A^{\alpha} &= {}^0G_A^{\alpha} + \Omega_{AB}^{\alpha} \cdot x_B^2 + RT\ln(1-x_B) \\ \mu_B^{\alpha} &= {}^0G_B^{\alpha} + \Omega_{AB}^{\alpha} \cdot (1-x_B)^2 + RT\ln x_B \end{aligned} \right\} \quad (3.43)$$

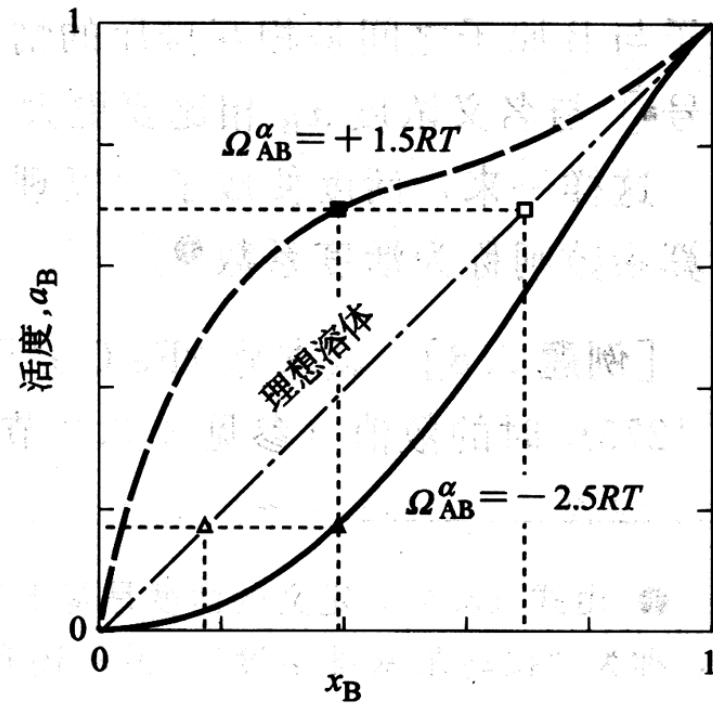




## Example 3.7



(a) 化学势



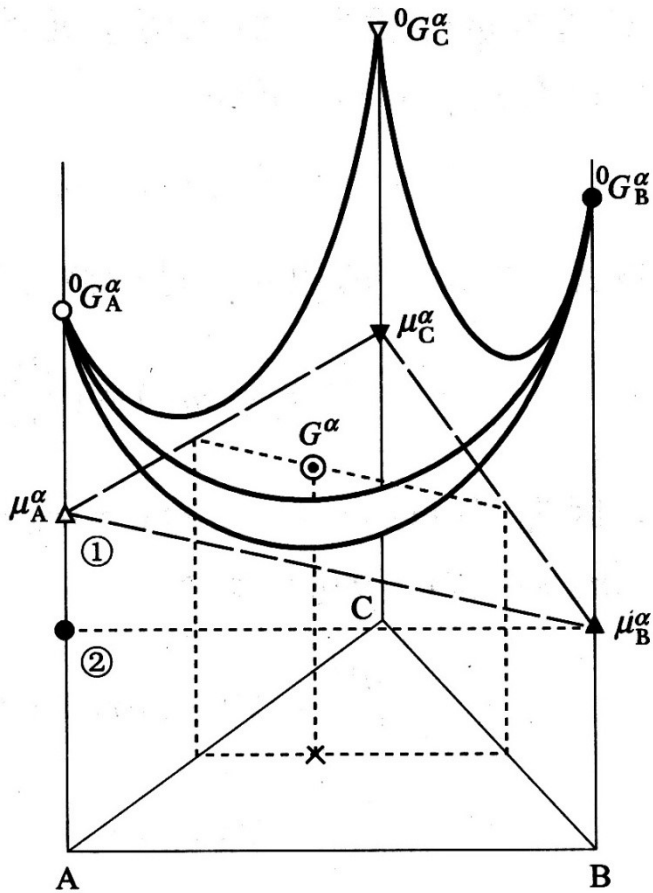
(b) 活度(拉乌尔基准)

图 3.15 A-B 系正规溶体 B 组元的化学势 ( $\mu_B^\alpha$ ) 和活度 ( $a_B$ ), 其中  $\mu_B^\alpha$  的数值是令  ${}^0G_B^\alpha = 0$  并除以  $RT$  时的数值





# Ternary



(b) A-B-C系

A-B-C三元系自由能和化学势之间的关系

$$\left. \begin{aligned} \mu_1^a &= G^a - \sum_{i=2}^n \left( \frac{\partial G^a}{\partial x_i} \right) \cdot x_i \\ \mu_j^a &= \mu_1^a + \left( \frac{\partial G^a}{\partial x_j} \right) \end{aligned} \right\}$$

$$G^a = \sum_{i=1}^n \mu_i^a \cdot x_i = \mu_1^a + \sum_{i=2}^n (\mu_i^a - \mu_1^a) \cdot x_i$$

$$\mu_i^a - \mu_1^a = \left( \frac{\partial G^a}{\partial x_i} \right)$$



# One-component System / $\text{H}_2\text{O}$

- 有趣的 “凉快的开水”
- 三相点温度0.01摄氏度 (**纯水**在**611 Pa**外压下的凝固点)
  - $0.00747 + 0.00242 = 0.00989$  (思考题/程 Page 153)
  - 冰点0.00摄氏度 (溶解空气水在1大气压下的凝固点)

## 水三相点的实验测定

1938年所发表的论文“水的三相点温度”，其测定数值( $0.00980^\circ\text{C}$ )被国际温标会议采纳。

1956年编著出版的《物理化学》是第一部高水平的中文物理化学教科书。



黄子卿



# 水的三相平衡点

1 大气压于101325Pa, 已知水的冰点为0.00摄氏度 (即溶解空气杂质水在1大气压下的凝固点), 摄氏零度水中空气杂质的含量约为  $0.0013 \text{ mol/kg}$ 。水与冰的摩尔体积和水凝固焓变值(这些值对于纯水与含空气杂质水没有区别)分别为:

$$V_l = 0.019 \times 10^{-3} \text{ m}^3 \cdot \text{mol}^{-1} \quad \text{纯水凝固点随空气杂质变化可表为:}$$

$$V_s = 0.02063 \times 10^{-3} \text{ m}^3 \cdot \text{mol}^{-1} \quad \Delta T_f = -K_f \cdot \Delta b_B$$

$$\Delta H_{fus} = -5.99 \text{ KJ} / \text{mol} \quad 1.86 \text{ K} \cdot \text{kg} \cdot \text{mol}^{-1} \quad K_f \text{ 凝固点降低系数}$$

- ① 推导水与冰两相平衡温度与压力关系的克拉佩龙方程;
- ② 如果把水中的空气杂质排掉, 纯水与含空气杂质水 (视作稀溶液) 的凝固点相比是上升了还是下降了? 为什么?
- ③ 纯水的三相 (水冰汽) 点平衡压力为611Pa, 计算纯水三相点的平衡温度是多少? (精确到小数点后面4位)



解：1) 在一定温度  $T$  及压力  $P$  下，纯水仅液态和固态两种形式平衡共存，则该物质在两相中的化学势相等  $\mu_l = \mu_s$ ，亦即  $G_l = G_s$ ，

当温度从  $T$  改变到  $T + dT$ ，根据相律，压力必须相应地改变到  $P + dP$ ，两相吉布斯自由能分别变为  $G_l + dG_l$ ， $G_s + dG_s$ ，

在新的平衡情况下： $G_l + dG_l = G_s + dG_s$ ，

由此可得  $dG_l = dG_s$ ，根据热力学基本公式  $dG = -SdT + VdP$

所以  $-S_l dT + V_l dP = -S_s dT + V_s dP$

$$\text{整理得 } \frac{dT}{dP} = \frac{T \cdot \Delta V_{l \rightarrow s}}{\Delta H_{fus}}$$

2) 若把水中杂质除去，凝固点升高

由于  $\Delta T_f = -K_f \cdot \Delta b_B$ ，把水中杂质去除， $\Delta b_B < 0$ ， $\Delta T_f > 0$ ，所以水的凝固点升高。



3) 纯水三相点变化来源于两方面: i) 压力变化引起的凝固点变化; ii) 除去杂质后引起的凝固点变化.

i) 根据(1)中所得的公式在凝固点温度, 压力从 1atm 降到 611Pa 时引起的凝固点温度变化为

$$dT = \frac{T \cdot \Delta V_{l \rightarrow s}}{\Delta H_{fus}} \cdot dP = \frac{273.15 \times (0.02063 \times 10^{-3} - 0.019 \times 10^{-3})}{-5990} \times (611 - 101325) = 0.00749^\circ\text{C}$$

所以水在 611Pa 压力下的凝固点为  $0.00749^\circ\text{C}$

ii) 由于杂质去除, 凝固点的变化

$$\Delta T_f = -K_f \cdot \Delta b_B = -1.86 \text{K} \cdot \text{kg} \cdot \text{mol}^{-1} \times (-0.0013 \text{mol} / \text{Kg}) = 0.002418^\circ\text{C}$$

所以纯水的三相点温度为  $0.00749^\circ\text{C} + 0.002418^\circ\text{C} = 0.009908^\circ\text{C}$



# Regular Solution (1)

$$\underline{G}_M = x_A \overline{G}_A^{rel} + x_B \overline{G}_B^{rel}$$

$$\overline{G}_A^{rel} = \overline{G}_A - \underline{G}_A^\circ = RT \ln \alpha_A$$

$$\underline{G}_M = x_A RT \ln(\gamma_A x_A) + x_B RT \ln(\gamma_B x_B)$$

$$\underline{G}_M = \underline{RT(x_A \ln x_A + x_B \ln x_B)} + RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

$$\underline{G}_M = \underline{G}_M^{ideal} + \underline{G}_M^{xs}$$

$$\underline{G}_M^{ideal} = RT(x_A \ln x_A + x_B \ln x_B)$$

$$\underline{G}_M^{xs} = RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$



# Regular Solution (2)

$$\ln \gamma_A = \frac{\omega}{RT} x_B^2 = \frac{\omega}{RT} (1 - x_A)^2$$

$$\underline{G}^{xs} = \underline{H}^{xs} \quad \text{regular solution}$$

$$\underline{G}_M = RT(x_A \ln x_A + x_B \ln x_B) + RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

$$\underline{G}_M = RT(x_A \ln x_A + x_B \ln x_B) + \underbrace{x_A \omega x_B^2 + x_B \omega x_A^2}_{\substack{(x_A + x_B)(\omega x_A x_B) \\ \omega x_A x_B}}$$

$$\underline{G}_M = RT(x_A \ln x_A + x_B \ln x_B) + \omega x_A x_B$$

$$\underline{H}_M = \omega x_A x_B$$

$$\underline{G}_M = \underline{G}_M^{ideal} + \underline{G}_M^{xs}$$

$$\underline{H}_M = \underline{H}_M^{ideal} + \underline{H}_M^{xs}$$

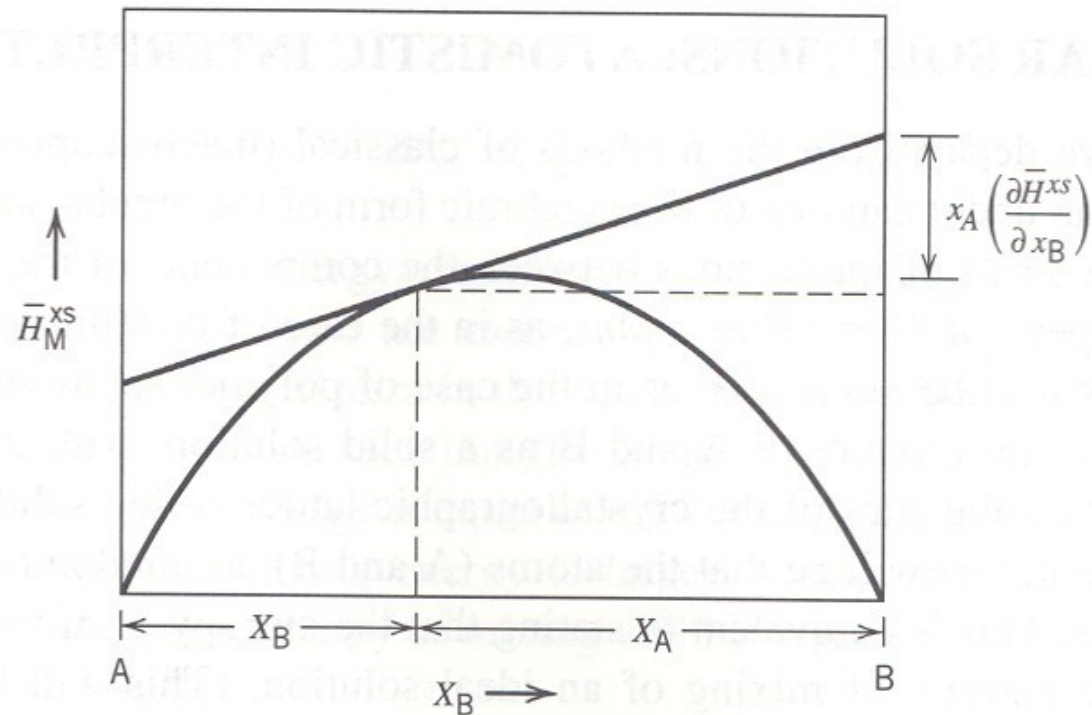
$$\underline{H}_M^{ideal} = 0$$



## Regular Solution (3)

For the regular solution:  $\underline{S}_M^{xs} = 0$      $\underline{G}_M^{xs} = \underline{H}_M^{xs} = \omega x_A x_B$

$$\bar{H}_B^{xs} = \underline{H}_M^{xs} + x_A \left( \frac{\partial \underline{H}_M^{xs}}{\partial x_B} \right)_T$$



**Figure 7.13** Plot of excess enthalpy of mixing versus composition for a nonideal solution.





## Regular Solution (4)

For the regular solution:  $\underline{S}_M^{xs} = 0$   $\underline{G}_M^{xs} = \underline{H}_M^{xs} = \omega x_A x_B$

$$\boxed{\overline{H}_B^{xs} = \underline{H}_M^{xs} + x_A \left( \frac{\partial \underline{H}_M^{xs}}{\partial x_B} \right)_T} \quad \overline{H}_B^{xs} = \omega x_A x_B + x_A \left( \frac{\partial (\omega x_A x_B)}{\partial x_B} \right)_T$$

$$\overline{H}_B^{xs} = \omega x_A x_B + x_A \omega (x_A - x_B)$$

$$\overline{H}_B^{xs} = \omega x_A^2 \quad \boxed{\overline{G}_B^{xs} = RT \ln \gamma_B} \quad \leftarrow \underline{G}_M^{xs} = RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

$$\ln \gamma_B = \frac{\omega}{RT} x_A^2$$

Justify the algebraic form of the activity coefficient in a regular solution.



# Regular Solution: Atomistic Interpretation (1)

S. J. T. U.  
Phase Transformation and Applications

A,B二元完全无序分布

只考虑最近邻原子间的相互作用

Random distribution

Z: coordination number

$E_{AA}$ : bonding energy

$N_A$ 个A原子与 $N_B$ 个B原子混合形成规则溶液

**Table 7.1** Bond Energies After Mixing Atoms A and B in a Solid Solution

	Number of Bonds	Energy per Bond	Energy
$N_{AB}$	$N_A \frac{N_B}{N_T} Z$	$E_{AB}$	$\frac{N_A N_B}{N_T} Z E_{AB}$
$N_{AA}$	$\frac{1}{2} \frac{N_A^2}{N_T} Z$	$E_{AA}$	$\frac{1}{2} \frac{N_A^2}{N_T} Z E_{AA}$
$N_{BB}$	$\frac{1}{2} \frac{N_B^2}{N_T} Z$	$E_{BB}$	$\frac{1}{2} \frac{N_B^2}{N_T} Z E_{BB}$



# Regular Solution: Atomistic Interpretation (2)

S. J. T. U.

Phase Transformation and Applications

$$\frac{N_A Z}{2} \times \frac{N_A}{N_T}$$

$$E_M = Z \left[ \frac{N_A^2}{2N_T} E_{AA} + \frac{N_B^2}{2N_T} E_{BB} + \frac{N_A N_B}{N_T} E_{AB} - \frac{N_A}{2} E_{AA} - \frac{N_B}{2} E_{BB} \right]$$

$$E_M = ZN_T \left\{ \frac{[x_A^2 - x_A]E_{AA} + [x_B^2 - x_B]E_{BB}}{2} \right\} + x_A x_B E_{AB}$$

$E_{AA}$ : bonding energy

$$E_M = ZN_T x_A x_B [E_{AB} - 1/2(E_{AA} + E_{BB})]$$

$\varpi = 0$ , ideal

$\varpi \neq 0$ ,  $\underline{S}_M^{xs} = 0$ , regular

$$E_M = \omega x_A x_B \quad \text{where} \quad \omega = ZN_T [E_{AB} - 1/2(E_{AA} + E_{BB})]$$

$$\underline{G}_M^{xs} = \underline{H}_M^{xs} - T \underline{S}_M^{xs} = \varpi x_A x_B$$

$$H = U + PV = E + PV$$

$$\underline{S}_M^{xs} = 0$$



# Regular Solution Atomistic Interpretation (3)

S. J. T. U.  
Phase Transformation and Applications

For the regular solution:  $\underline{S}_M = 0$   $\underline{G}_M^{xs} = \underline{H}_M^{xs} = \omega x_A x_B$

$$\overline{H}_B^{xs} = \underline{H}_M^{xs} + x_A \left( \frac{\partial \underline{H}_M^{xs}}{\partial x_B} \right)_T \quad \overline{H}_B^{xs} = \omega x_A x_B + x_A \left( \frac{\partial (\omega x_A x_B)}{\partial x_B} \right)_T$$

$$\overline{H}_B^{xs} = \omega x_A x_B + x_A \omega (x_A - x_B)$$

$$\overline{H}_B^{xs} = \omega x_A^2$$

$$\overline{G}_B^{xs} = RT \ln \gamma_B$$

$$\ln \gamma_B = \frac{\omega}{RT} x_A^2$$

Justify the algebraic form c  
in a regular solution.

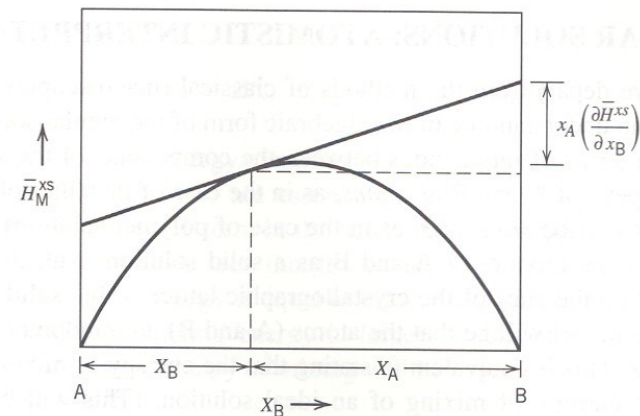


Figure 7.13 Plot of excess enthalpy of mixing versus composition for a nonideal solution.