



# Contents of Today

**Review previous**  
Freezing Point Depression  
The lever rule  
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Cooling curves  
Review of today



# Review of Last

- Phase rule : 相律
- Phase diagram : 相图
- One-component systems



# 吉布斯相律

- 吉布斯相律是处于热力学平衡状态的系统中自由度与组元和相数之间关系的规律。
- 基本概念包括相、组元和自由度等。
  - 相为系统中性质与成分均匀的一部分；相平衡指的是在多相体系中所有相的强度性质均相等，体系的性质不会自发地随时间变化的状态即相平衡状态；
  - 组元为决定各平衡相的成分，而且是可以独立变化的组分（元素或化合物）；
  - 自由度是可以在一定范围内任意改变而不引起任何相的产生与消失的最大变量数。

$$F = C - P + 2$$



# 局限性

- 但相律只是对可能存在的平衡状态的一个定性描述。它可以给出一个相图中可能有些什么点、线和区，却不能给出这些点、线和区的具体位置。



# 单组分系统

- 相律分析

$$F = C - P + 2$$

$$C = 1$$

$$P = 1, F = 2$$

$$P \geq 1; F \geq 0$$

$$P = 2, F = 1$$

$$P = 3, F = 0$$

- 物态转变方程式

$$\frac{dP}{dT} = \frac{\Delta_{\alpha}^{\beta} H}{T \Delta_{\alpha}^{\beta} V}$$

$$P = A \exp\left(-\frac{\Delta_{\alpha}^{\beta} H}{RT}\right)$$

气固或气液

$$\Delta P = \frac{\Delta_{\alpha}^{\beta} H}{\Delta_{\alpha}^{\beta} V} \frac{\Delta T}{T_1} = K \cdot \Delta T$$

固液



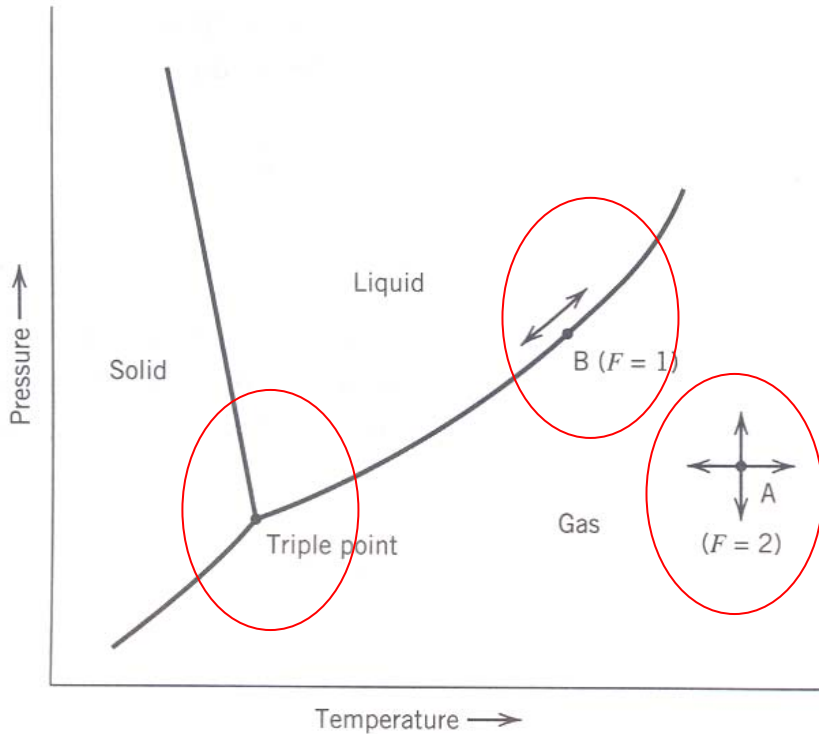
## • 滑冰为何轻快？

[例 6-1] 以往有人以如下方式解释滑冰为何轻快,即在尖锐冰刀的压力下冰在 273K 以下局部融化,形成液体润滑剂。然而根据克-克方程可以计算为使冰的熔点降低几度所需的高压冰是不能承受的,例如:273K 时冰的质量体积  $V_1 = 1.091 \times 10^{-6} \text{ m}^3\text{kg}^{-1}$ , 而水的质量体积  $V_2 = 1 \times 10^{-6} \text{ m}^3\text{kg}^{-1}$ , 冰的熔化热  $\Delta_s^1 H_m = 335 \text{ kJ} \cdot \text{kg}^{-1}$ , 所以

$$\frac{dp}{dT} = \frac{\Delta_s^1 H_m}{T(V_1 - V_2)} = 135 \times 10^5 \text{ Pa} \cdot \text{K}^{-1}。$$

为使冰能在 263K 开始融化,所需增加的压力为 135MPa, 这样大的压强冰是不能承受的,业已证明,滑冰时冰的局部融化主要是由于冰刀与冰之间的滑动摩擦发热所致。

$$\frac{dP}{dT} = \frac{\Delta_{\alpha}^{\beta} H}{T \Delta_{\alpha}^{\beta} V}$$



**Figure 8.1** Phase diagram for water (one component). In the phase diagram for water, the solid–liquid equilibrium line slopes up and to the left from the triple point because the volume change upon solidification is positive. In most materials, the volume change upon solidification is negative, and the solid–liquid equilibrium line slopes up and to the right.

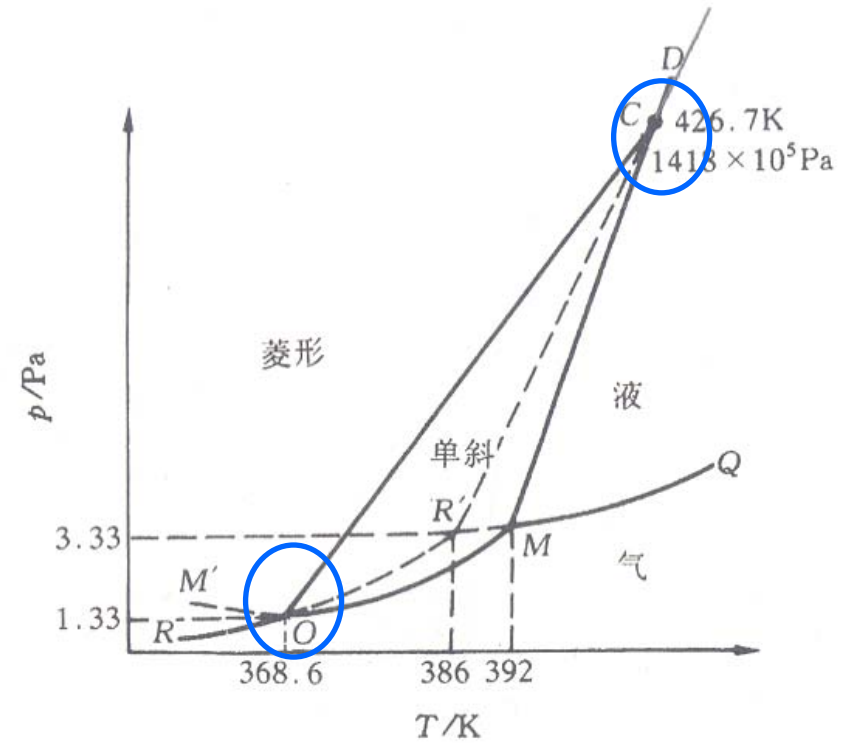


图 6-4 硫系相图

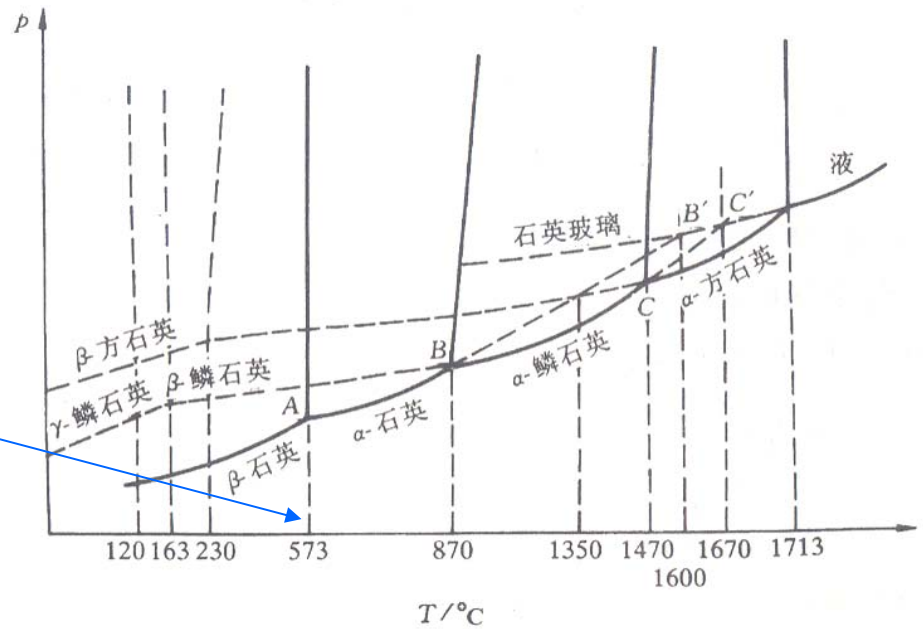
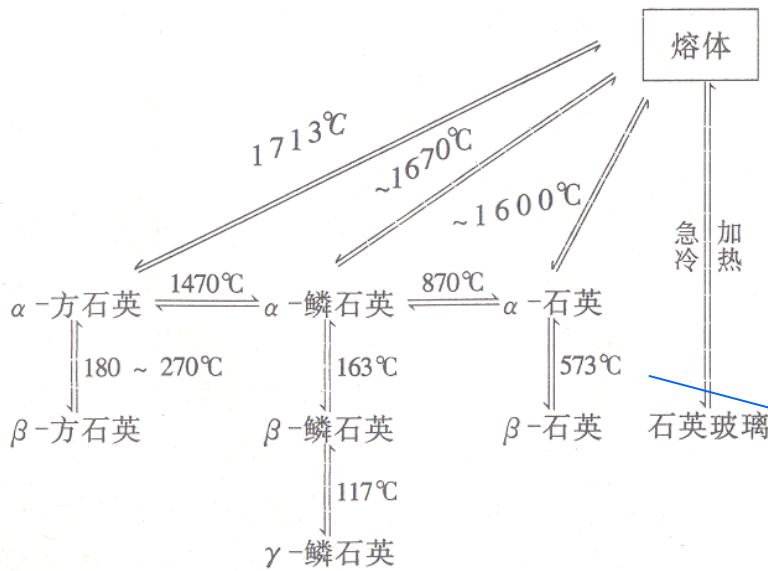


图 6-5 SiO<sub>2</sub> 系相图





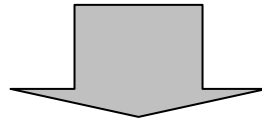
# Nomenclature

- Freezing Point Depression: 凝固点下降
- The lever rule: 杠杆定量
- Simple eutectic diagram: 简单共晶相图
- Cooling curves: 冷却曲线



# Binary Phase Diagrams

In condensed systems, modest variations in pressure do not appreciably alter phase relationship



Phase rule for condensed system

$$F = C - P + 1$$

It is possible to plot phase stability regions for two-component (binary) systems in two dimensions.  $C=2$ ,  $F=3-P$

Composition on abscissa (horizontal axis)  
Temperature on the ordinate (vertical axis)

T - x



# Binary System

Degrees of freedom available in the system (F):

$$F = C - P + 1$$

$$F = C - P + 2$$

F: the number of system variables that we may freely vary, or arbitrarily fix

C: components

P: phase

$$C = 2$$

$$P = 1, F = 2$$

单相区

$$P = 2, F = 1$$

平衡线包围的两相区

$$P = 3, F = 0$$

三相平衡线



- 熔点降低
- 计算完全互溶两相平衡线
- 杠杆定律
- 公切线
- 冷却曲线



# 固态纯A与溶液中A的热力学平衡

- The dissolution of pure, solid A in the liquid solution is the sum of the two processes:
  - The melting of pure A
  - The dissolution of pure liquid A in the liquid solution



# 9.1 Freezing Point Depression (1)

$$A_s = A_l$$

$$\Delta \underline{G} = RT \ln \frac{f_l}{f_s} = RT \ln \left( \frac{a_{l,pure}}{a_{s,pure}} \right)$$

$$\Delta \underline{G} = RT \ln a_{l,pure} \quad \text{if } \underline{a_{s,pure}} = 1$$

$\Delta \underline{G} = 0$  at  $T_m$ , two phases in equilibrium

$$\underline{a_{l,pure}} = 1$$

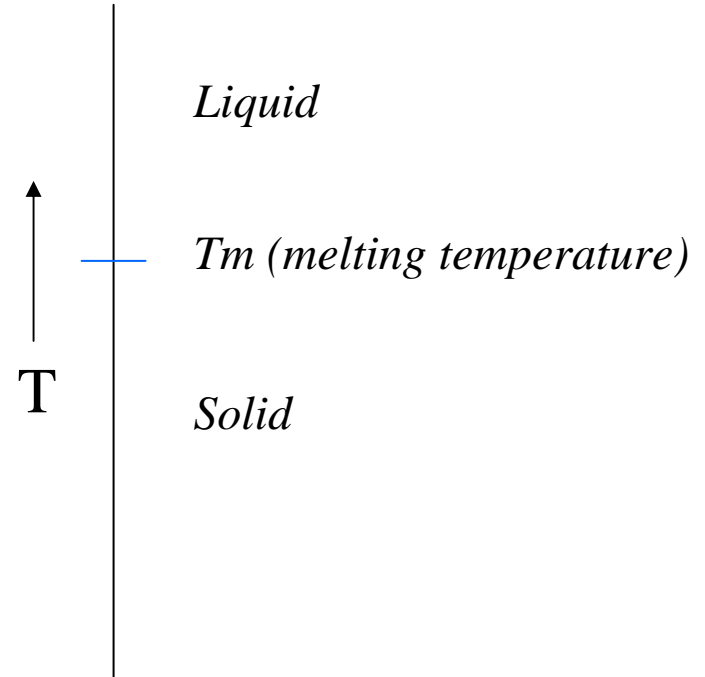


Fig. 9.1 Phase diagram of a single-component system.



# 9.1 Freezing Point Depression (2)

At the **temperature lower than  $T_m$** , the value of Gibbs free energy change for the melting of pure A

$$\Delta G_{melting} = \Delta H_{melting} - T\Delta S_{melting} = L - T\Delta S_{melting}$$

**L**: latent heat of fusion

Assuming no difference in heat capacity between liquid and solid

$$\Delta C_p = 0$$

At melting temperature  **$T_m$**

$$\Delta G_{melting} = 0$$

I. 纯A在**某个温度 $T$** 熔化自由能变化

$$L = T_m \Delta S_{melting} \text{ or } \Delta S_{melting} = \frac{L}{T_m}$$

$$\Delta G_{melting} = L \left( 1 - \frac{T}{T_m} \right) = \frac{L(T_m - T)}{T_m}$$

$$\Delta G_{melting} = RT \ln \frac{a_{l,pure}}{a_{s,pure}} = \frac{L(T_m - T)}{T_m}$$

**At the temperature below  $T_m$** , the activity of pure liquid A is greater than ?



# 9.1 Freezing Point Depression (3)

The case for addition of material B to A  
A and B are immiscible in the solid state  
Form ideal solution in the liquid phase

Liquid of composition  $x_{A,l}$  in equilibrium with pure solid A at temperature  $T'$  below  $T_m$

$$A_{l,pure} = A_{l,solution}$$

$$\Delta G = RT \ln \frac{a_{l,solution}}{a_{l,pure}}$$

$$A_{s,pure} = A_{l,solution}$$

II. 纯液A进入溶液自由能的变化

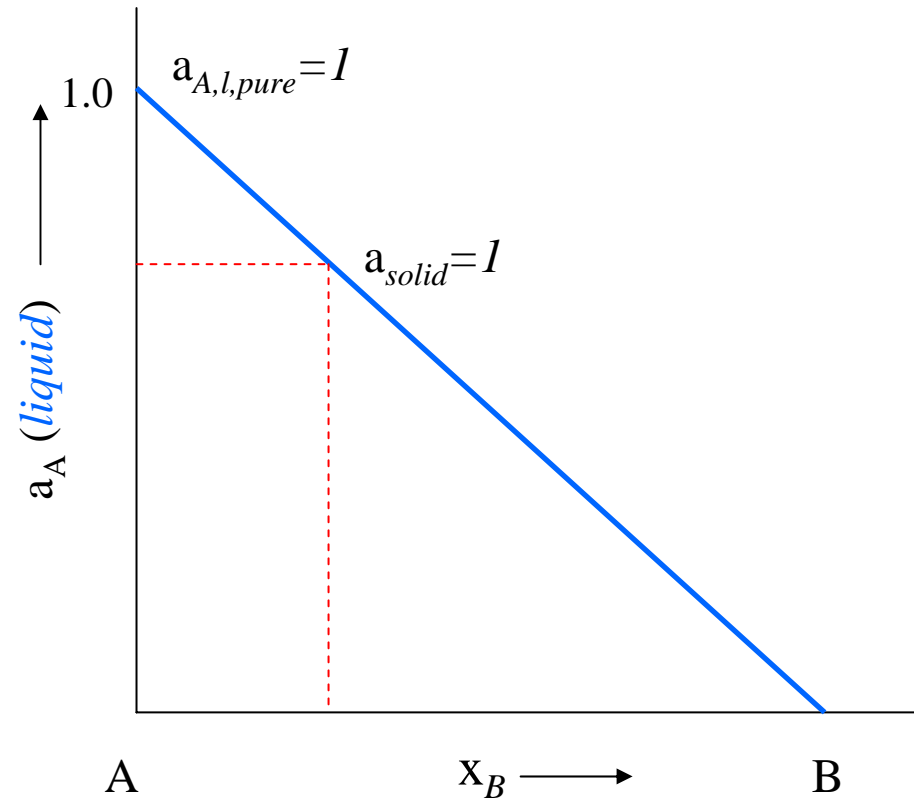


Fig. 9.2 Plot of the activity of  $A_{liquid}$  at  $T < T_{m,A}$  versus composition.





# 9.1 Freezing Point Depression (4)

The liquid solution is in equilibrium with the pure solid,

$$\Delta \underline{G} = \frac{L(T_m - T)}{T_m} + RT \ln \frac{a_{l,solution}}{a_{l,pure}} = 0$$

$$\frac{L(T_m - T)}{T_m} = -RT \ln x_{A,l,solution} \quad \textit{ideal solution}$$

If T is close to the T<sub>m</sub>

$$\ln x_{A,l,solution} = -\frac{L(T_m - T)}{RT_m^2}$$

Melting point depression

$$x_B = \frac{L(T_m - T)}{RT_m^2}$$

$$\Delta T = T_m - T$$

$$\ln(1 - z) = -z \quad \textit{small } z$$

稀溶液的依数性

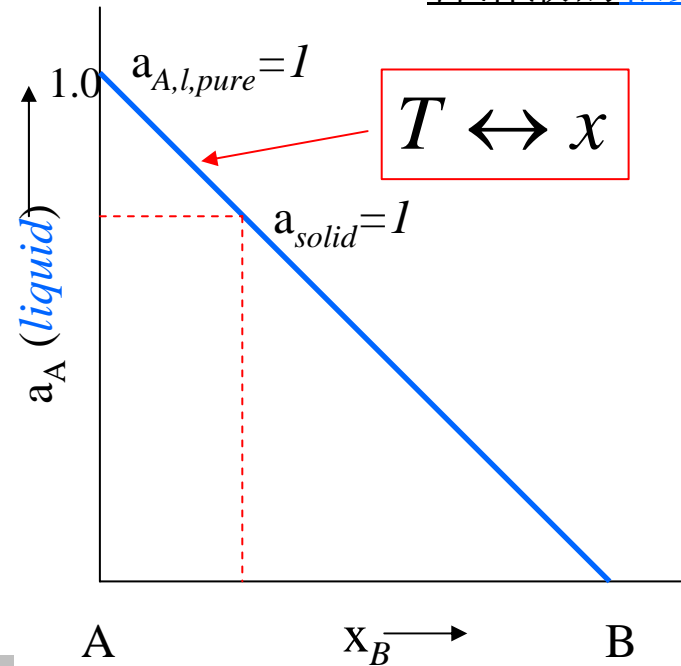


Fig. 9.2 Plot of the activity of A<sub>liquid</sub> at T < T<sub>m,A</sub> versus composition.



## Example

Lowering of the melting point of silver caused by the addition of one mole percent of lead

$$\Delta T = \frac{RT_m^2 x_B}{L} = 11.2 K$$

Provided  $T_m, L$



# 9.1 Freezing Point Depression (5)

Liquid: the equilibrium phase is a liquid A-B solution

Two phase region: L+S, pure solid A is in equilibrium with a liquid solution  
At  $T_1$ , pure solid A is in equilibrium with a liquid solution of composition  $x_{B,l}$ .

Phase rule? For L+S region as a condensed system

$$F = C - P + 1 = 2 - 2 + 1 = 1$$

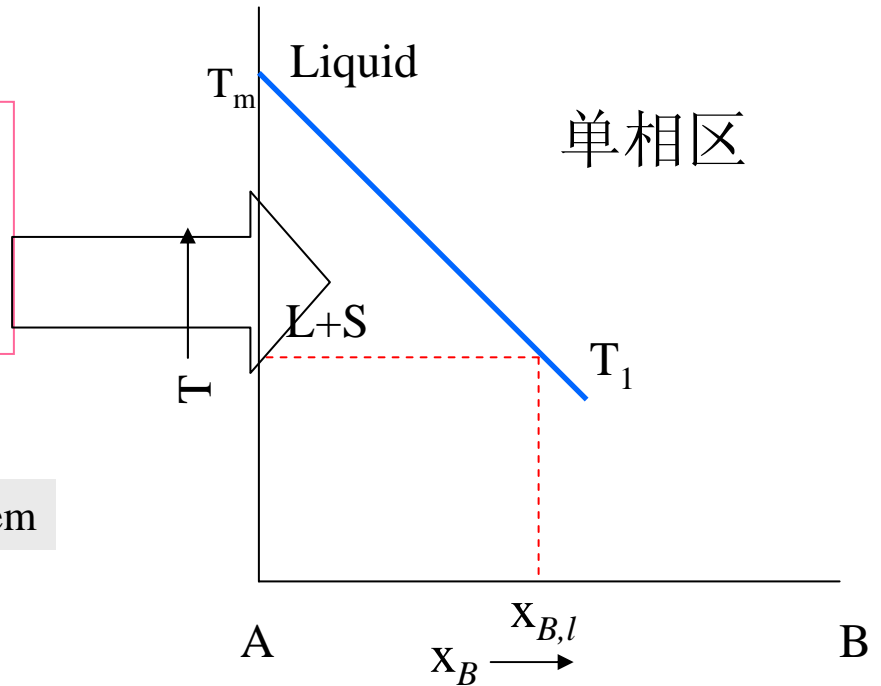


Fig. 9.3 Portion of an A-B phase diagram.

Once T is specified, composition is specified, **not amount**



# 9.2 The Lever Rule (1)

In a two-phase region of a condensed system, if the **overall composition is given**, the **quantities** of the various phases can be calculated, beside to the the **composition**.

The relative quantities or fractions of liquid and solid using a mass balance.

$$x_B = F_l x_{B,l} + F_s x_{B,s}$$

$$F_l (x_{B,l} - x_B) = F_s (x_B - x_{B,s})$$

$F_l$ =fraction liquid

$F_s$ =fraction solid

$F_l + F_s = 1$ , and a mass balance

$$\frac{F_l}{F_s} = \frac{x_B - x_{B,s}}{x_{B,l} - x_B}$$

$$F_l = \frac{x_B - x_{B,s}}{x_{B,l} - x_{B,s}}$$

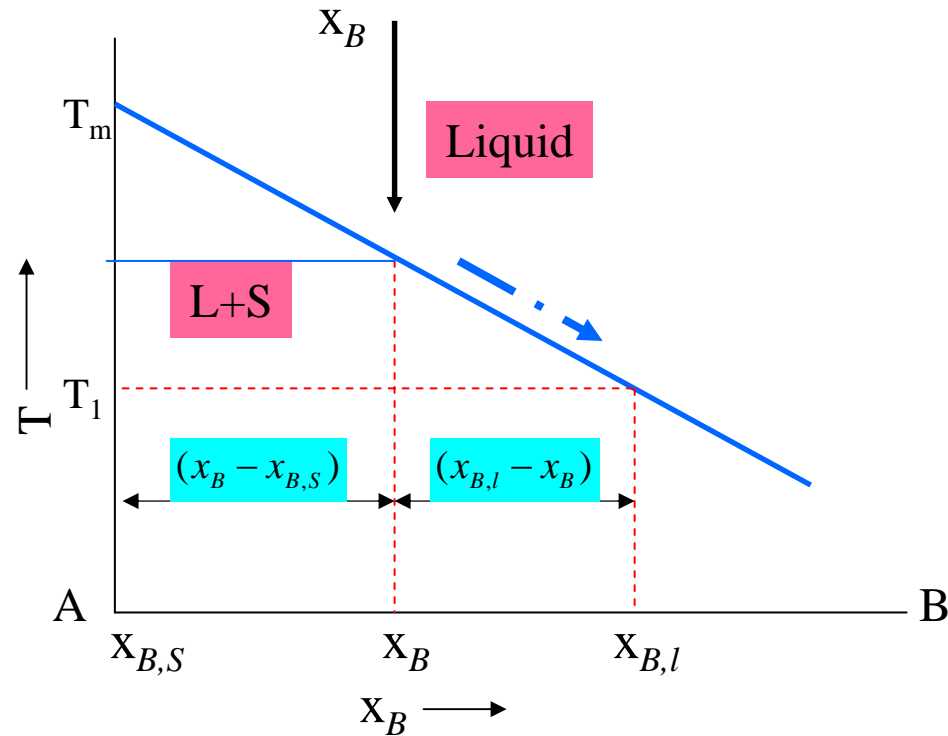


Fig. 9.4 Illustration of the lever rule.



## 9.2 The Lever Rule (2)

### Example

500K, a **lead-tin** binary alloy containing 50 mol % tin, at 500 K,  
the equilibrium composition of the liquid 59 mol % tin,  
the composition of the solid is 24 mol % tin.

The fraction of liquid at 500 K ?

$$F_1 = \frac{x_B - x_{B,s}}{x_{B,l} - x_{B,s}} = \frac{0.50 - 0.24}{0.59 - 0.24} = 0.74$$

**At equilibrium, the alloy will be 74 % liquid at 500 K, on a mass basis.**

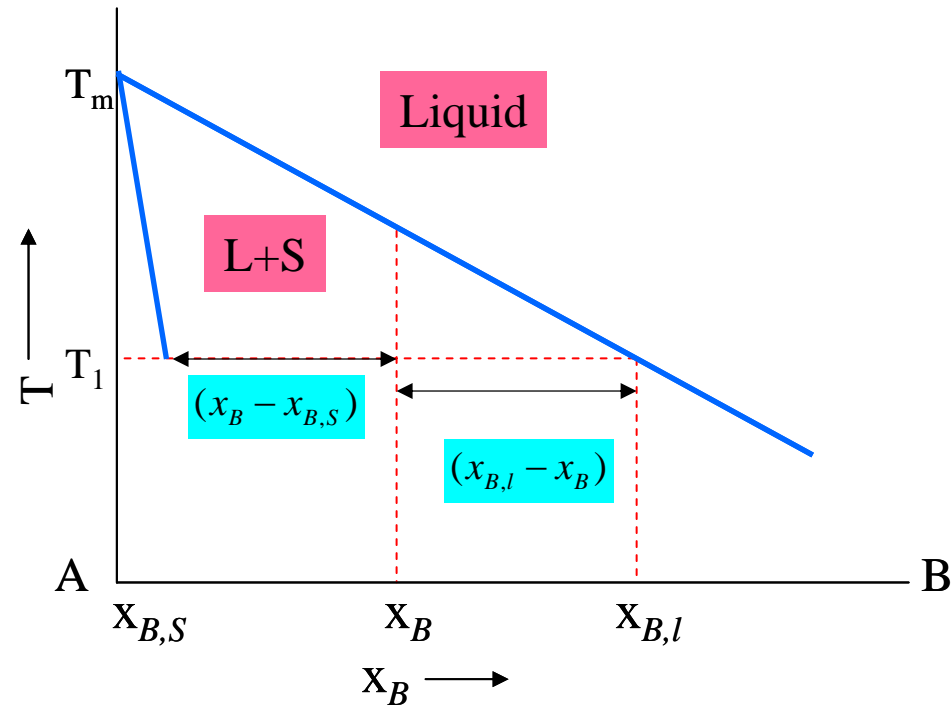


Fig. 9.4 Illustration of the lever rule.



# 9.3 Simple Eutectic Diagram

A-B system, A and B are immiscible in the solid state, but completely miscible in the liquid state.

When the melting point depression lines intersect, the material will solidify totally into solid A and solid B, *eutectic temperature*. The lowest temperature at which a liquid solution of A and B may exist at equilibrium with solid A and B. *eutectic composition*. At *eutectic point*: / phase rule



$$F = C - P + 1 = 2 - 3 + 1 = 0$$

If all three phases are present, at equilibrium, the system must at the *eutectic temperature* and the liquid will have the *eutectic composition*.

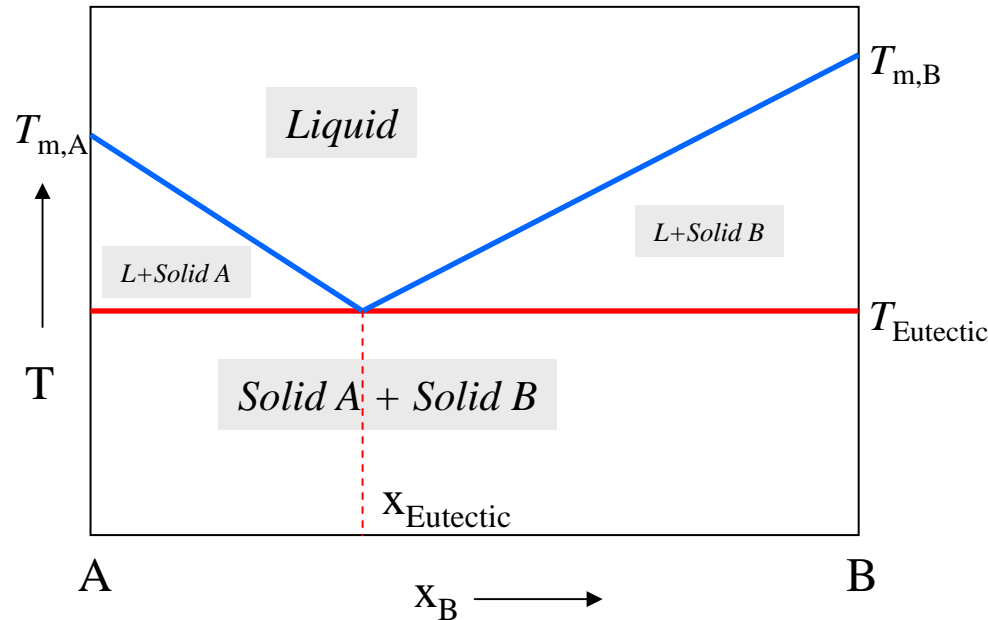


Fig. 9.5 Simple eutectic phase diagram.



# 9.4 Cooling Curves (1)

Pure A, cooled below  $T_m$  by removing thermal energy at a constant rate, assuming the equilibrium is maintained at all times.

### Liquid or solid state

The removal of thermal energy lowers its temperature.

### Melting point

The removal of thermal energy results in solidification.

The temperature does not change, *a thermal arrest* in the cooling curve.

### Pure material

$$F = C - P + 1 = 1 - 2 + 1 = 0$$

### Eutectic composition binary material

$$F = C - P + 1 = 2 - 3 + 1 = 0$$

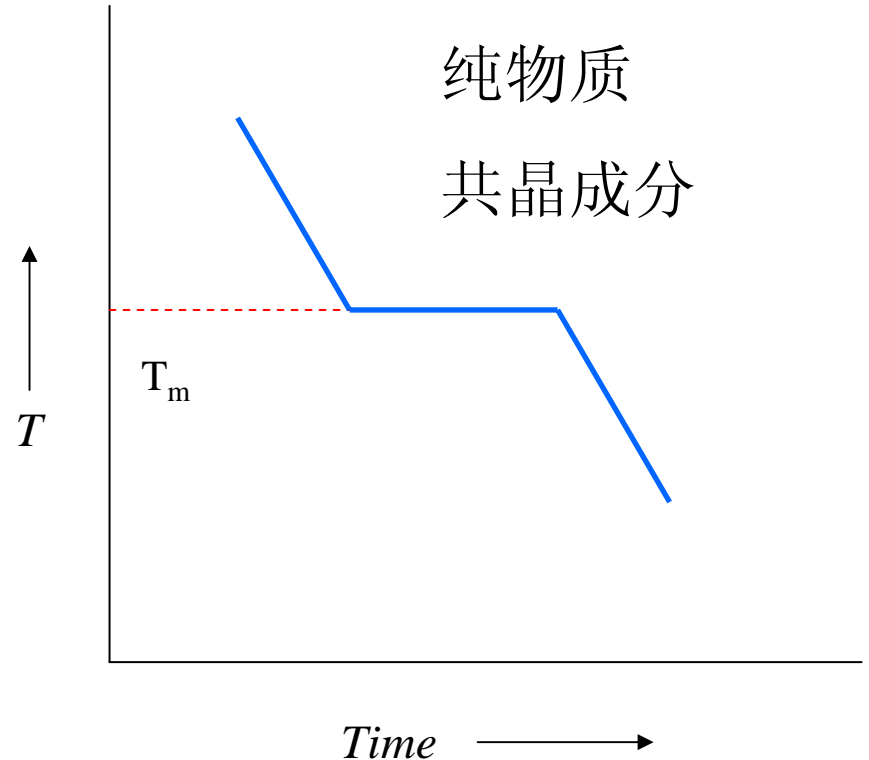


Fig. 9.6 Cooling curve for a pure material (or eutectic).



# 9.4 Cooling Curves (2)

Composition other than eutectic composition, cooled below  $T_m$  by removing thermal energy at a constant rate, assuming the equilibrium is maintained at all times.

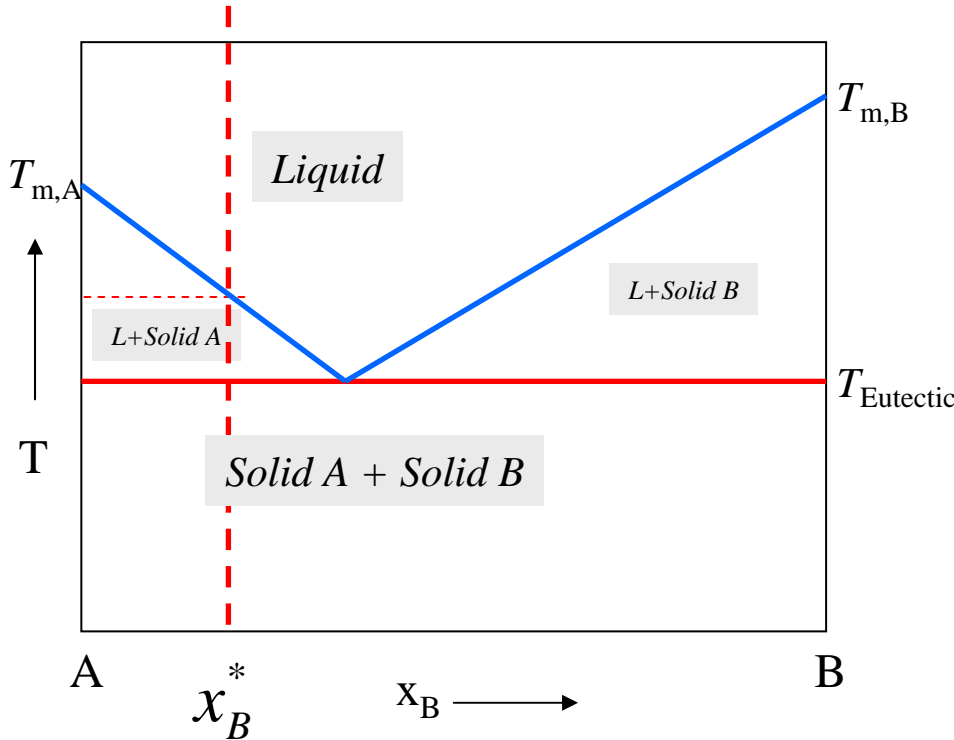


Fig. 9.7 Phase diagram for a system A-B.

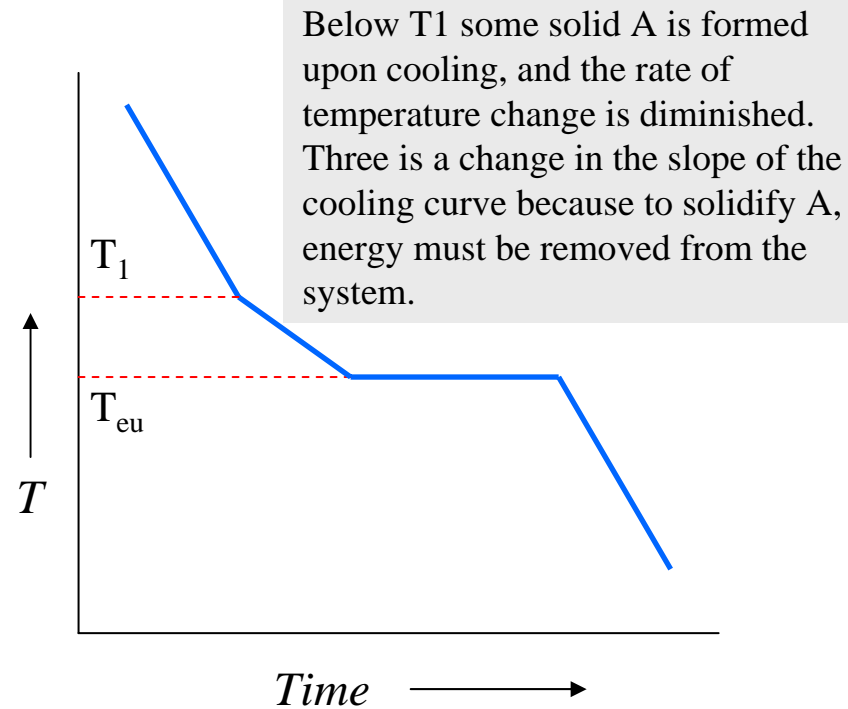
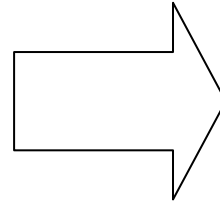


Fig. 9.8 Cooling curve for alloy  $x_B^*$





- 简单共晶
- 液态完全互溶
- 固态完全不溶



- 固液均完全互溶

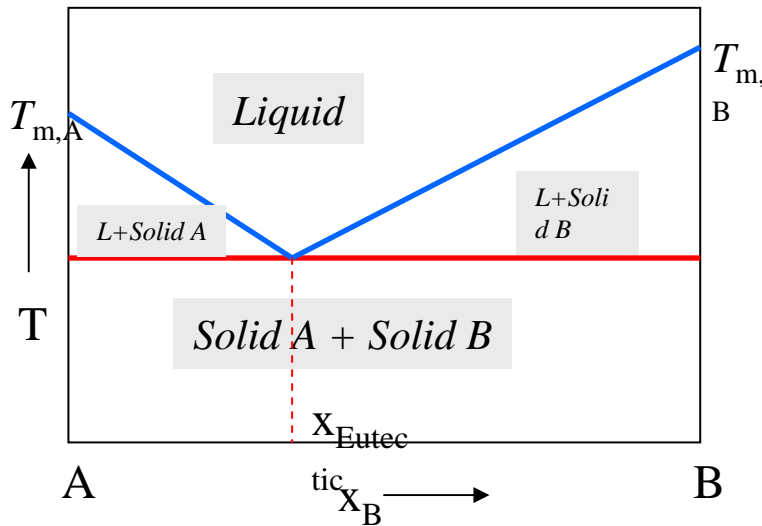


Fig. 9.5 Simple eutectic phase diagram.



## 9.5 Complete Miscibility (1)

A two-component system A-B in which A and B are completely miscible in both solid and liquid states, and form ideal solutions in both.

Given the information about the **melting temperatures and the enthalpies of melting** of the two components, the equilibrium phase diagram can be **predicted**.

$$\Delta \underline{G}_{\text{melting}} = \frac{L(T_m - T)}{T_m} = \mu_l^p - \mu_s^p$$

$T_m$  Melting temperature

$L$  Enthalpy of melting

$\mu_l^p, \mu_s^p$  Chemical potentials of pure liquid and pure solid, respectively

Chemical potential of A in liquid solution

$$\begin{aligned}\mu_{A,l} &= \mu_{A,l}^p + RT \ln a_{A,l} \quad \textit{ideal solution} \\ &= \mu_{A,l}^p + RT \ln x_{A,l}\end{aligned}$$

Molar Gibbs free energy of the liquid solution

$$\begin{aligned}\underline{G}_l &= x_A \mu_A + x_B \mu_B \\ &= x_A \mu_{A,l}^p + x_B \mu_{B,l}^p + RT(x_{A,l} \ln x_{A,l} + x_{B,l} \ln x_{B,l})\end{aligned}$$

Similar for the solid solution



## 9.5 Complete Miscibility (2)

The pure liquids A and B are chosen as the standard states.

$$\underline{G}_l = x_A \mu_{A,l}^P + x_B \mu_{B,l}^P + RT(x_{A,l} \ln x_{A,l} + x_{B,l} \ln x_{B,l}) = RT(x_{A,l} \ln x_{A,l} + x_{B,l} \ln x_{B,l})$$

$$\underline{G}_s = RT(x_{A,S} \ln x_{A,S} + x_{B,S} \ln x_{B,S}) - x_{A,S} \left[ \frac{L}{T_{m,A}} (T_{m,A} - T) \right] - x_{B,S} \left[ \frac{L}{T_{m,B}} (T_{m,B} - T) \right]$$

Assuming the melting temperatures for A and B are 900 K and 1300 K respectively. The value of  $L/T_m$  was assumed to be 9 J/K (Trouton's rule).

纯A在某个温度熔化自由能变化

$$\Delta \underline{G}_{melting} = RT \ln \frac{a_{l,pure}}{a_{s,pure}} = \frac{L(T_m - T)}{T_m}$$



# 9.5 Complete Miscibility (3)

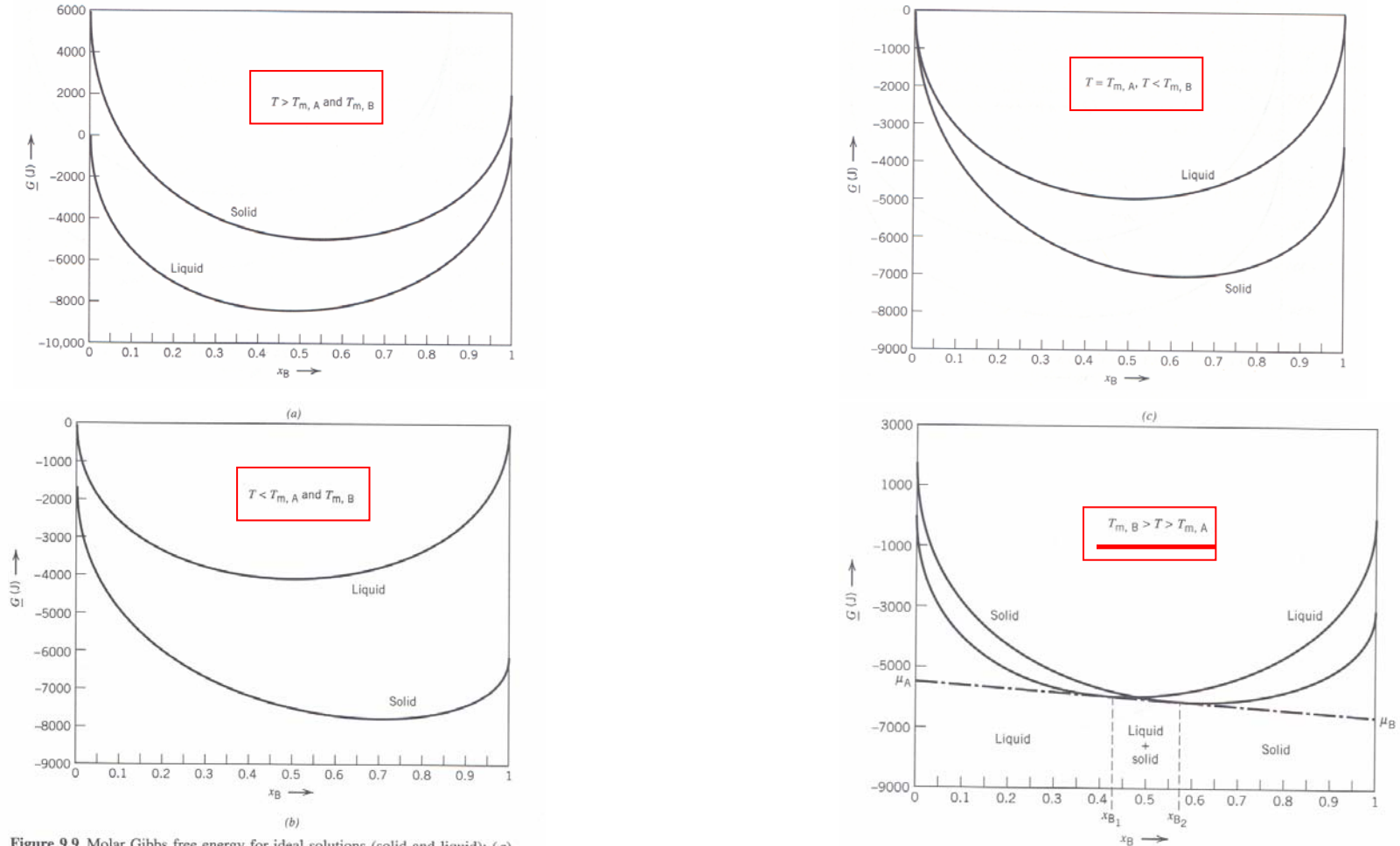
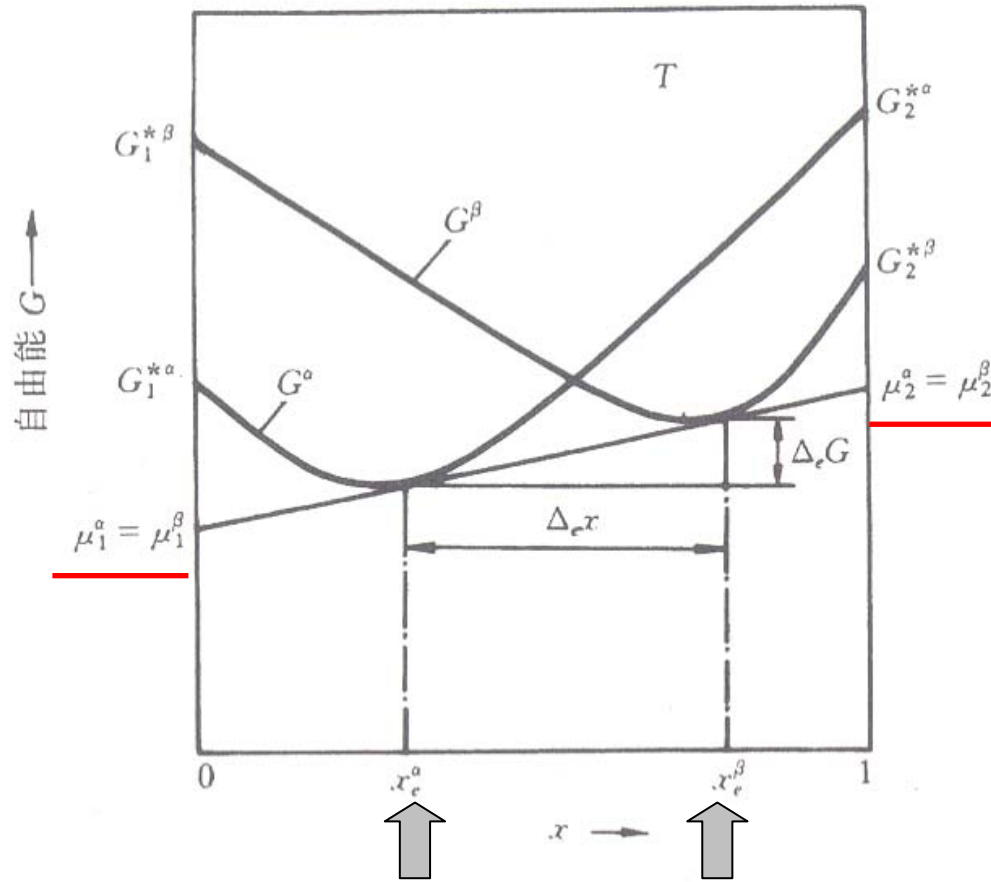
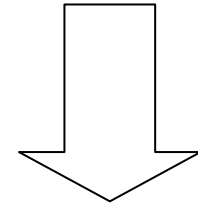


Figure 9.9 Molar Gibbs free energy for ideal solutions (solid and liquid): (a) at temperatures above the melting points of A and B, (b) at temperatures below the melting points of A and B, (c) at the melting point of A, and (d) at temperatures between the melting points of A and B.



公切线符合多相平衡条件



处于平衡条件两相的平衡组成

图 6-8 两相平衡时的成分-自由能曲线



## 9.5 Complete Miscibility (4)

If, at a given temperature, the molar Gibbs free energy curves for two phases intersect, there is a range of compositions over which the two may exist at equilibrium,  $x_{B,1}$  and  $x_{B,2}$ .

The extent of this region can be determined by drawing the common tangent line between the two curves.

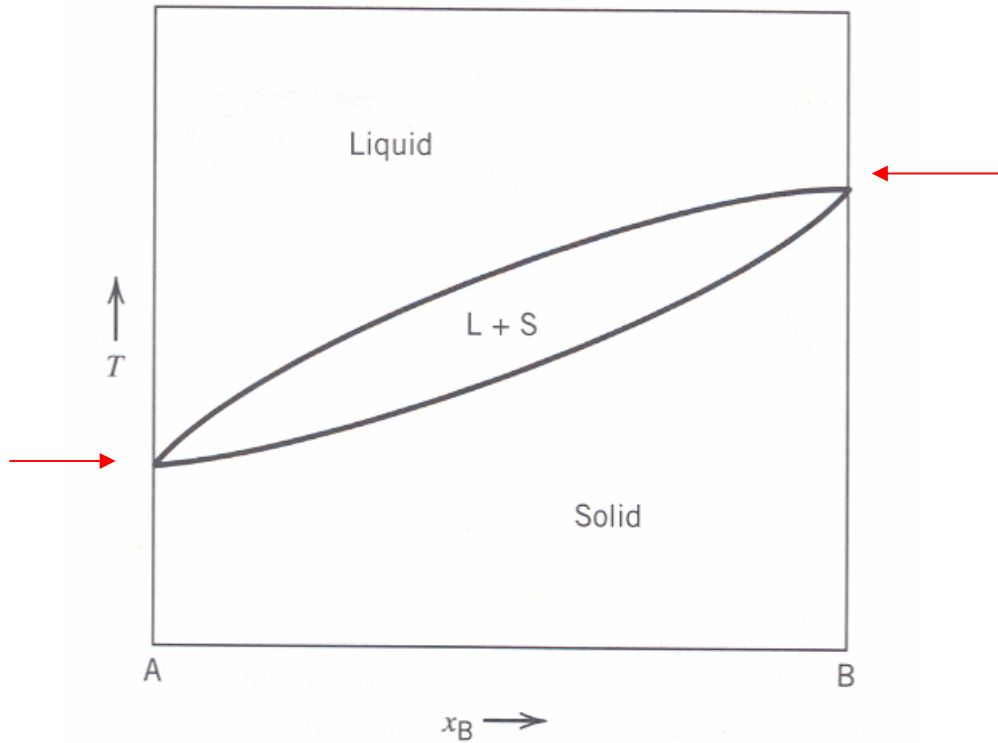
The intercepts of the tangent to a Gibbs free energy of mixing curve on the vertical axes are the chemical potentials of both A and B.

The intercepts of the common tangent indicate that the chemical potentials of A in both phases are equal; hence the two phases are in equilibrium.

The result of a calculation based on this principle is a phase diagram, with a lens-like stability region for the coexistence of liquid and solid.

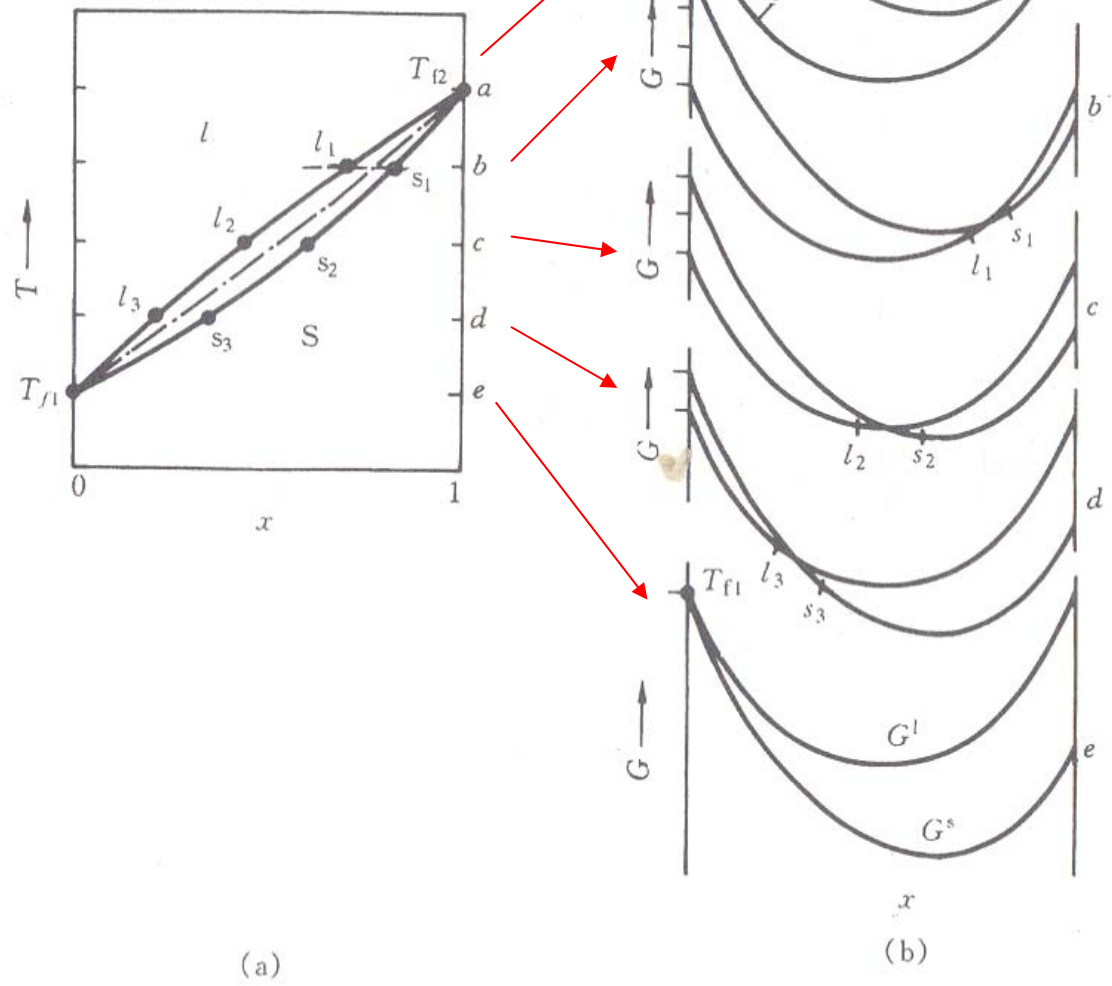


# 9.5 Complete Miscibility (5)



- 点
- 单相区
- 平衡线/两相平衡区

Figure 9.10 Phase diagram for a system A-B: ideal solutions, solid and liquid.

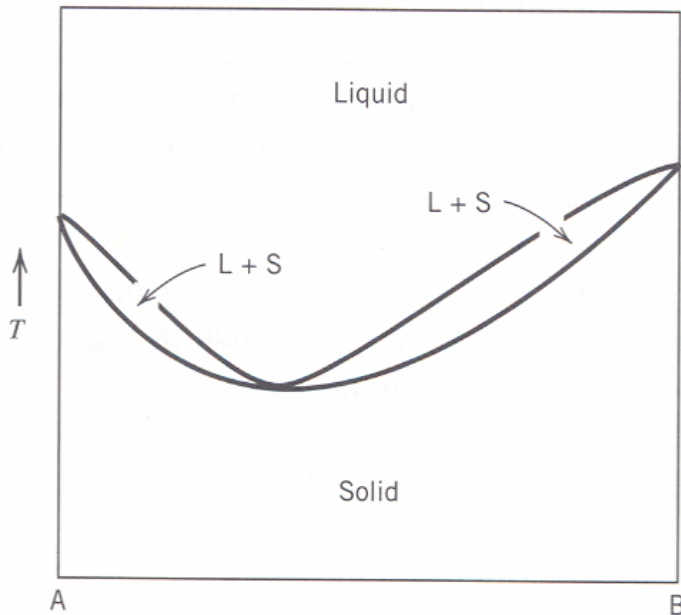




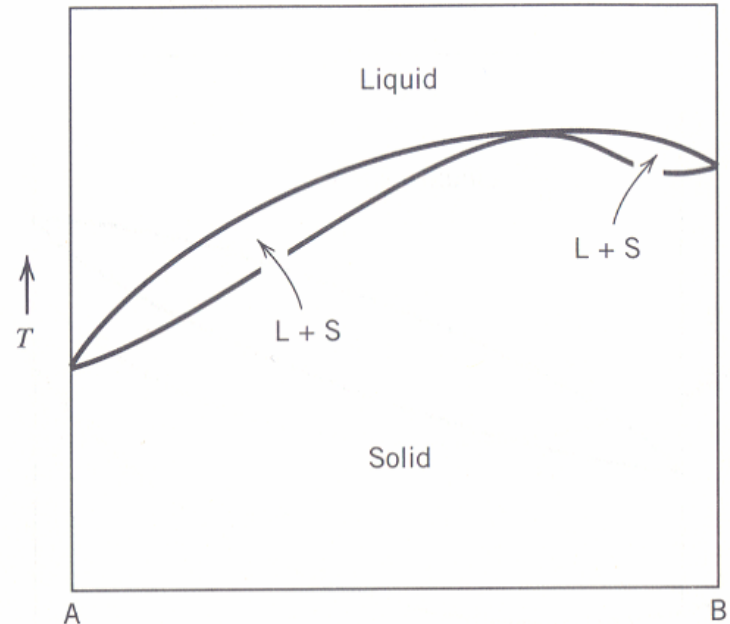


# 9.5 Complete Miscibility (6)

If the solid and liquid solutions of A and B are **non-ideal**, then the lens-like liquid-solid phase region can have other forms.



**Figure 9.11** Possible phase diagram for a system A–B with complete miscibility of the components in liquid and solid but nonideal behavior.



**Figure 9.12** Another possible phase diagram for the system A–B described in Figure 9.11.

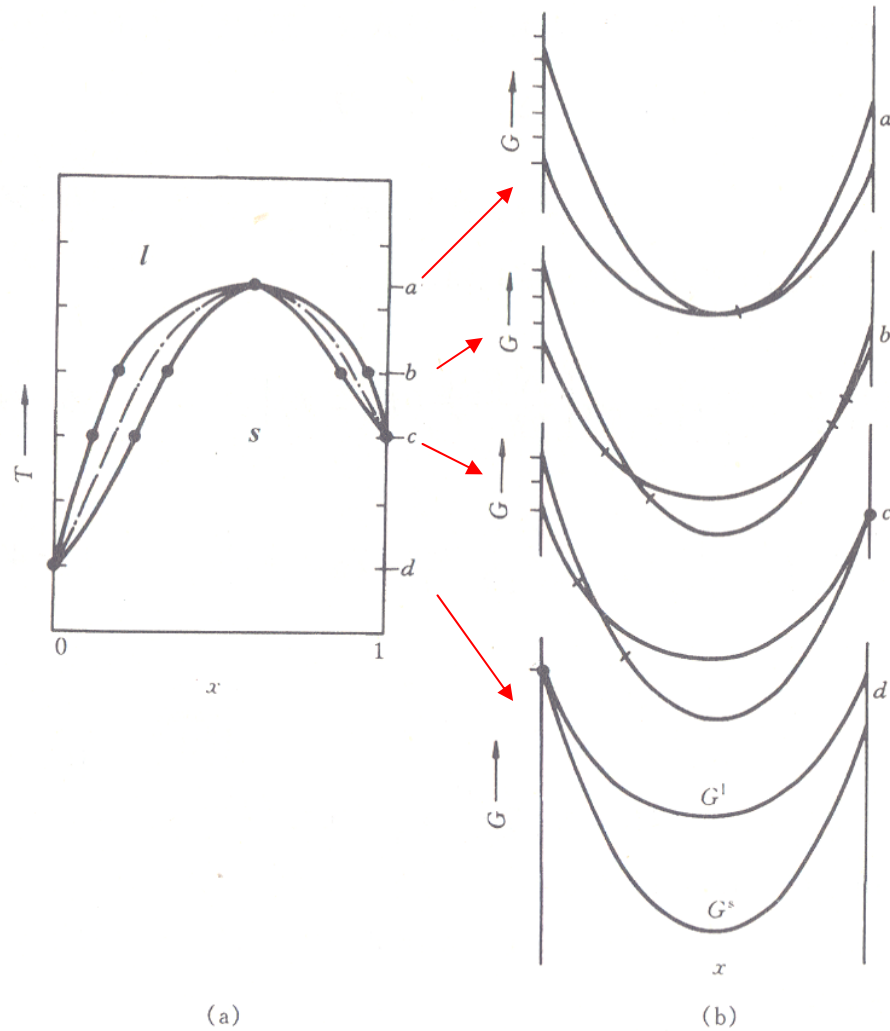


图 6-12 具有最高熔点的完全互溶相图  
(a)  $T-x$  图 (b)  $G-x$  图



# Review of Today

- Freezing Point Depression
- The lever rule
- Simple eutectic diagram
- Cooling curves



# Homework

- Exercises in Chap 6  
P 234, 9.4