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Spinodal Points
Compounds
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Conclusion Remarks
Examples

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

- Freezing Point Depression

- The lever rule

- Simple eutectic diagram

- Cooling curves

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

$$C = 2$$

$$P = 1, F = 2$$
$$P = 2, F = 1$$
$$P = 3, F = 0$$

单相区

平衡线包围的两相区

三相平衡线

The liquid solution is in equilibrium with the pure solid,

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

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

If T is close to the T_m

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

Melting point depression

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

$$\Delta T = T_m - T$$
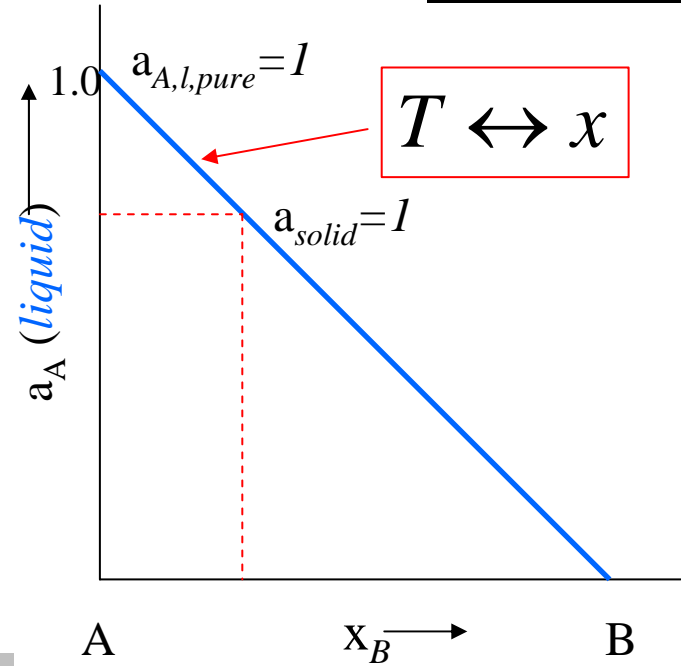
$$\ln(1 - z) = -z \quad \text{small } z$$

稀溶液的依数性

$a_{A,l,pure} = 1$

$T \leftrightarrow x$

$a_{solid} = 1$

a_A (*liquid*)

1.0

A $x_B \longrightarrow$ B

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

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.

$$x_B = F_1 x_{B,l} + F_S x_{B,s}$$

$$F_1(x_{B,l} - x_B) = F_S(x_B - x_{B,s})$$

F_l=fraction liquid
F_S=fraction solid
$F_l + F_S = 1$, and a mass balance

$$\frac{F_1}{F_S} = \frac{x_B - x_{B,s}}{x_{B,l} - x_B} \qquad F_1 = \frac{x_B - x_{B,s}}{x_{B,l} - x_{B,S}}$$
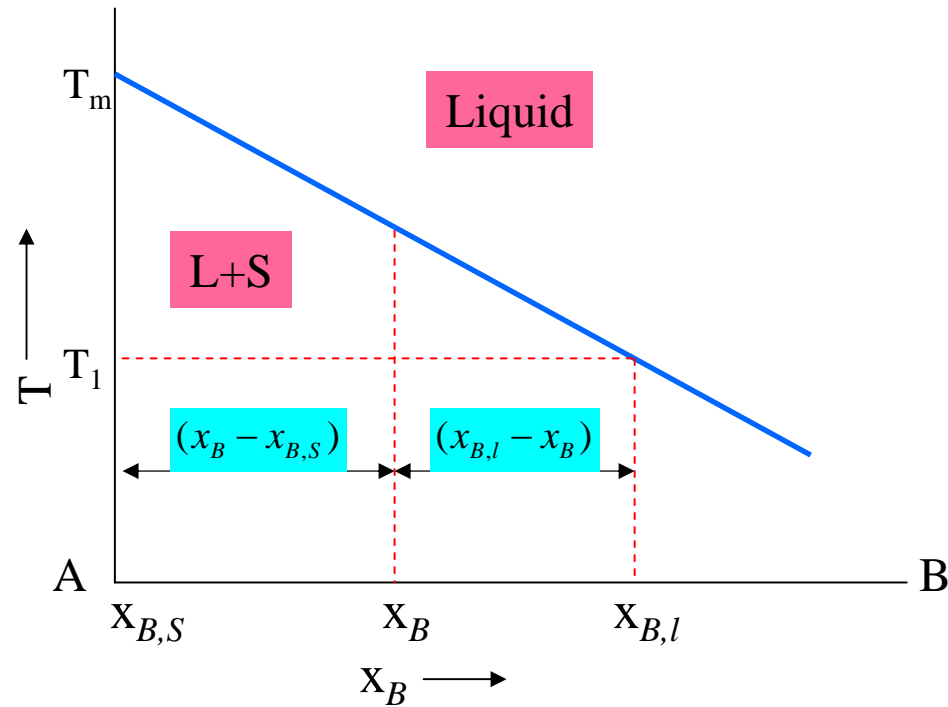
Fig. 9.4 Illustration of the lever rule.

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

$$\text{Liquid} = \text{solid}_A + \text{solid}_B$$

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

If all three phases are present, at equilibrium, the system must at the eutectic temperature and the liquid will have the eutectic composition.
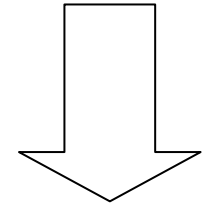
$T_{m,A}$ *Liquid* $T_{m,B}$

$L+Solid\ B$

$L+Solid\ A$

T $T_{Eutectic}$

Solid A + Solid B

$x_{Eutectic}$

A $x_B \longrightarrow$ B
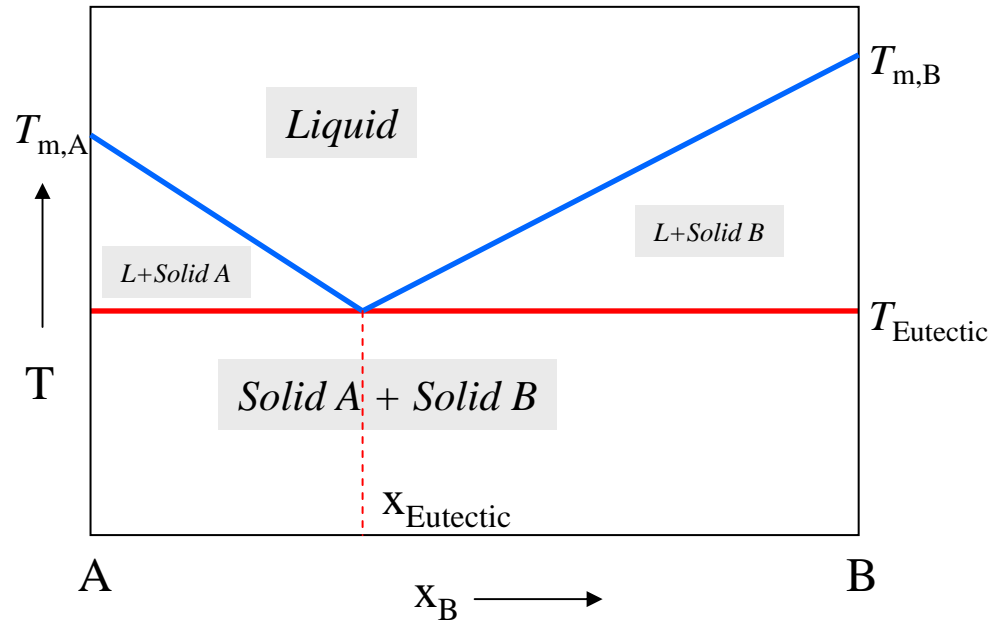
Fig. 9.5 Simple eutectic phase diagram.
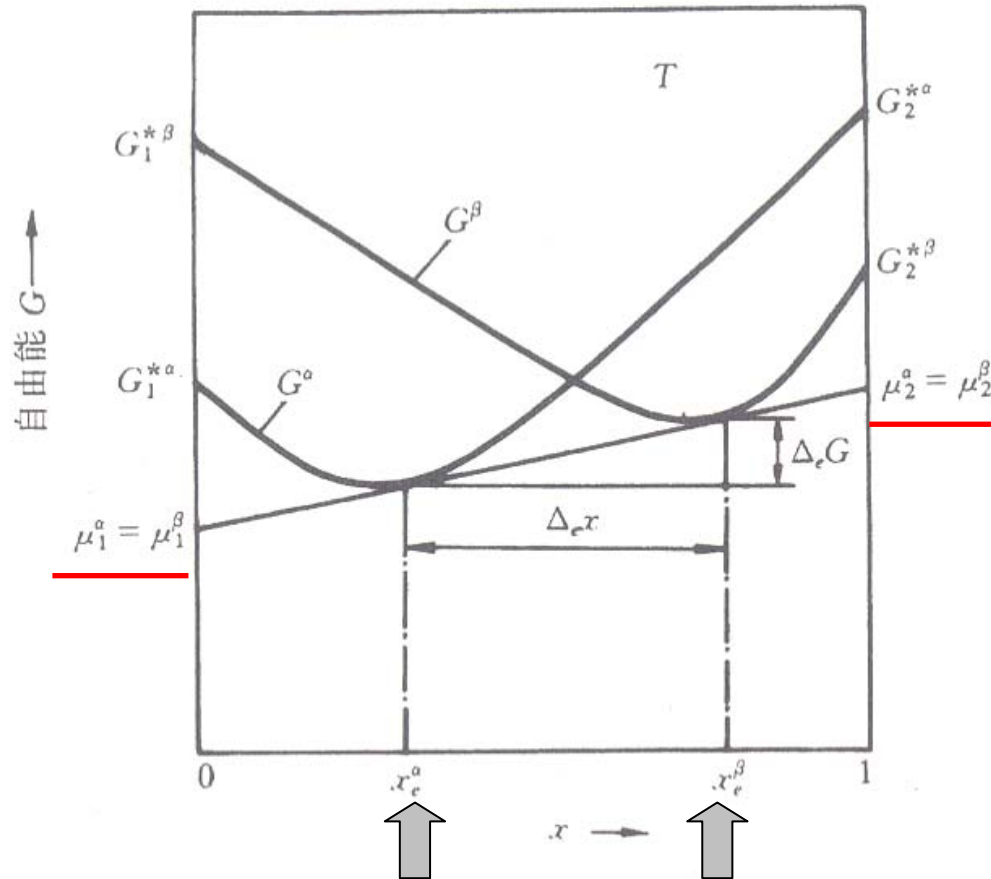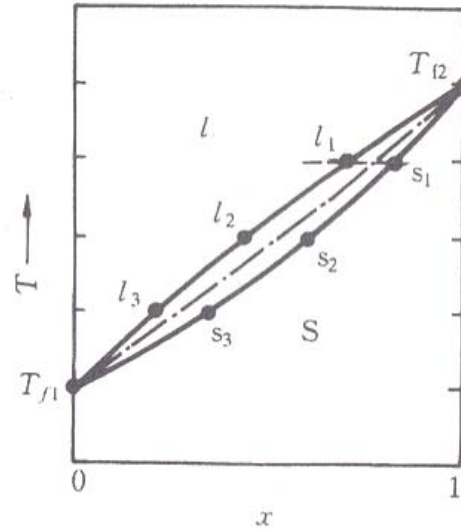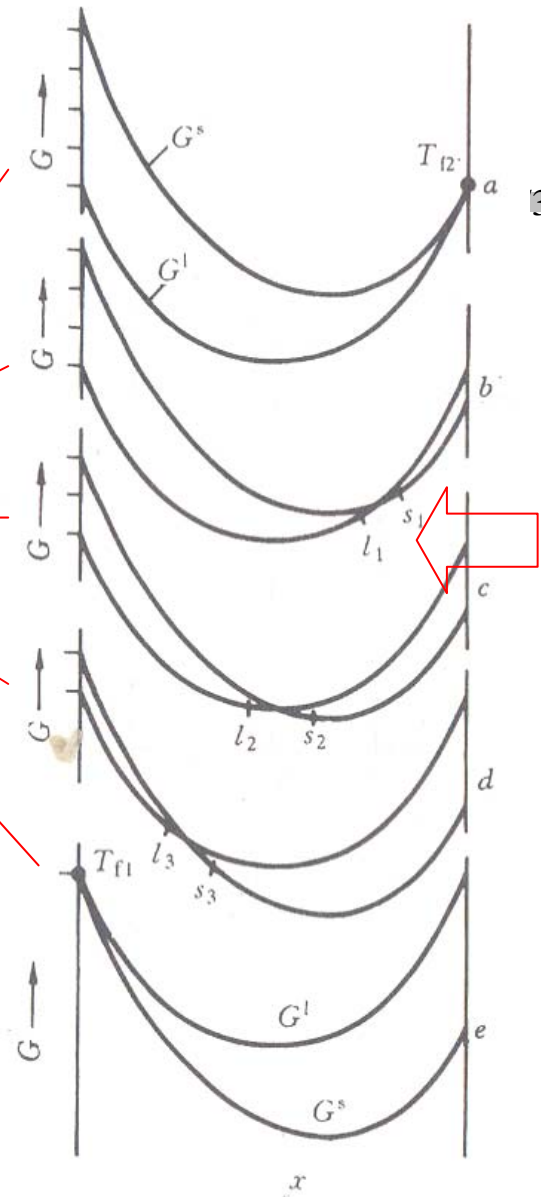
图 6-8 两相平衡时的成分-自由能曲线

公切线符合多相平衡条件

处于平衡条件两相的平衡组成

固液完全互溶
的体系

(a)

(b)

图 6-9　两组元完全互溶的相图

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。

$$F = C - P + 2$$

Nomenclature

Immiscibility：不溶性
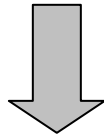Spinodal Points：Spinodal点
Simple Eutectic Diagram：简单共晶相图
Peritectic Phase Diagrams：包晶相图
Ternary Phases Reaction：三相反应
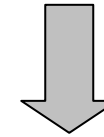
Complete immscibility
Complete miscibility in solid state

Ideality of the mixture

Partial miscibility
Temperature dependence

Non-ideality of the mixture

A regular solid solution of two components

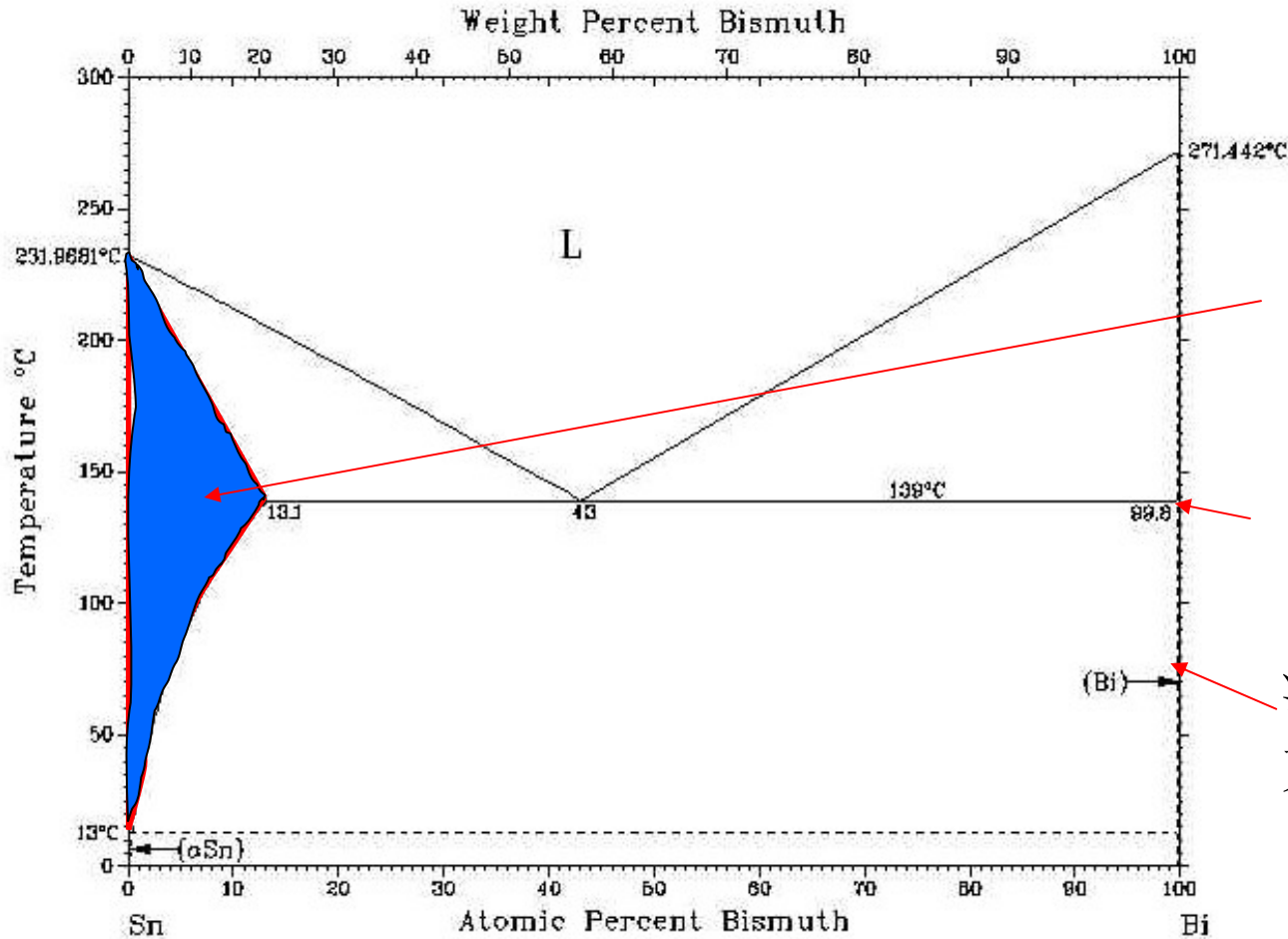$$\underline{G}_M = RT(x_A \ln x_A + x_B \ln x_B) + \omega x_A x_B$$

Sn-Bi

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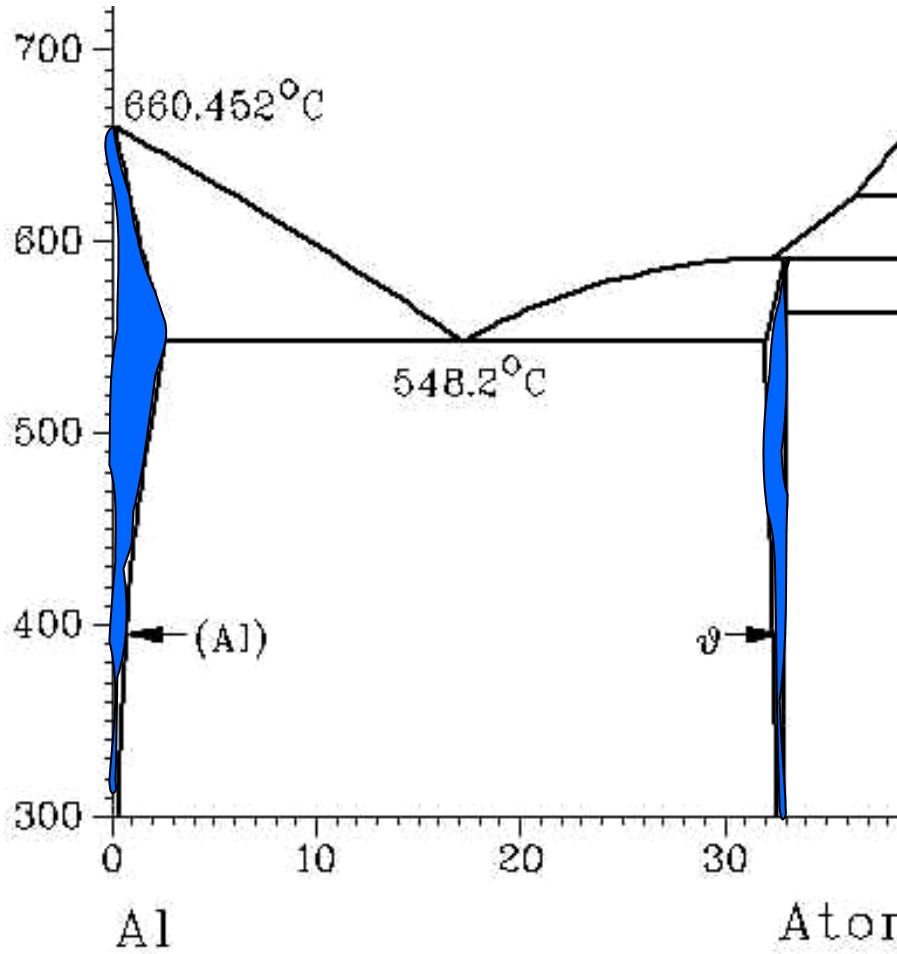

Sn中溶有
Bi形成固
溶体

自由度2

溶解度变化很
大！

Al-Cu phase diagram
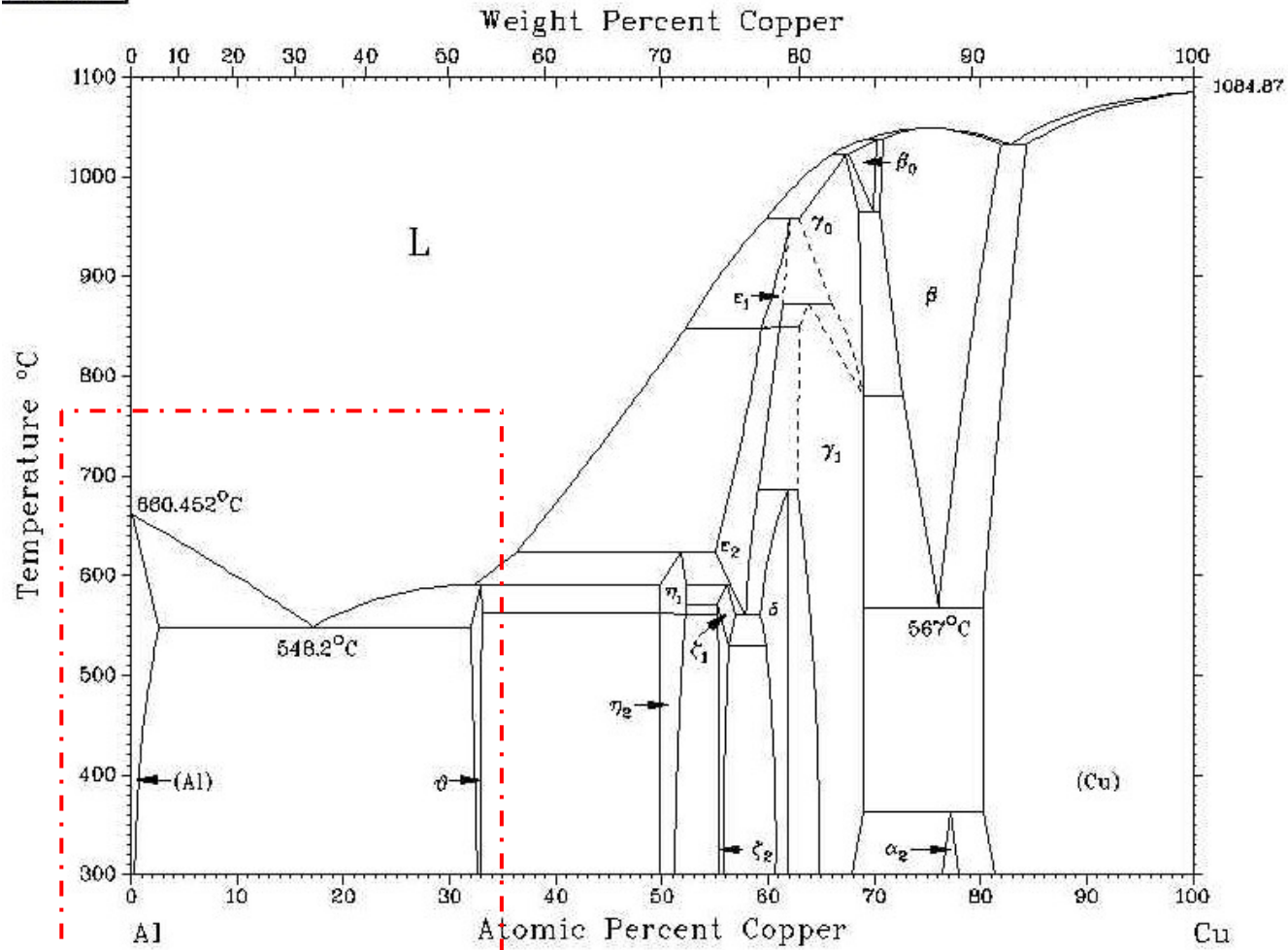
Al-Cu partial phase diagram

溶解度线与纵
轴围成一个单
相区

固溶体

自由度为2

Regular solution 1

Mixtures of A and B, with the overall composition falling between xB1 and xB2 can minimize their molar Gibbs free energies by forming two solutions of composition xB1 and xB2. (i. e., becoming partially immiscible)

Non-ideal !

$$\underline{S}^{xs}_{M} = 0$$

$$\underline{G}^{xs}_{M} = \underline{H}^{xs}_{M} = \omega x_A x_B$$

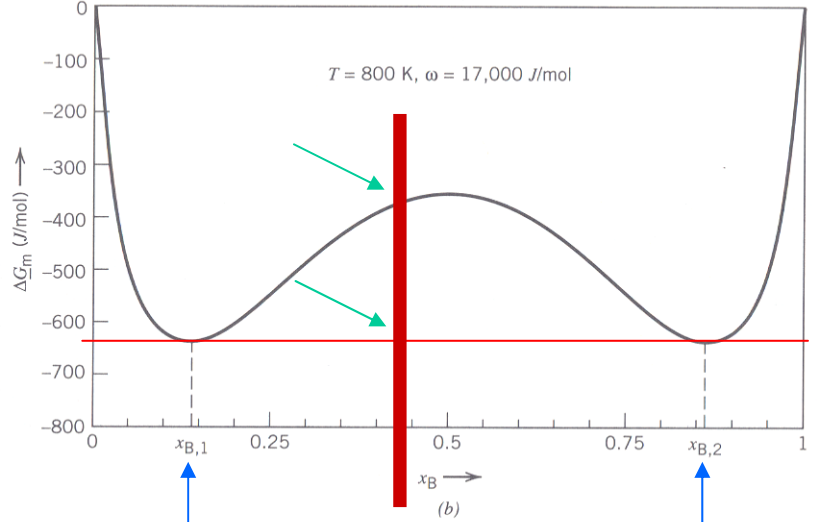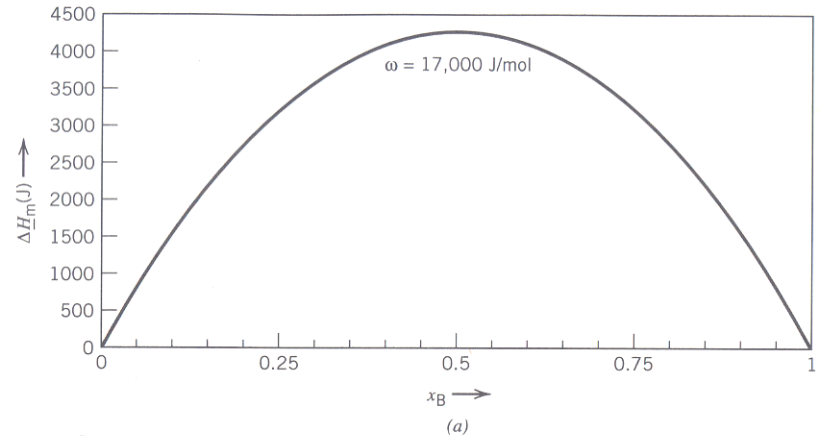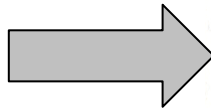$$\boxed{\underline{G}_M = \underline{G}^{ideal}_M + \underline{G}^{xs}_M}$$

Figure 9.13 Plots of properties of mixing versus composition for regular solutions: (a) molar enthalpy and (b) molar Gibbs free energy.

Regular solution 2

In the case of regular solutions

Gibbs free energy of mixing is symmetrical
around the mid-point composition

$$\left(\frac{\partial \underline{G}_M}{\partial x_B}\right)_T = RT\ln\left(\frac{x_B}{1-x_B}\right) + \varpi(1-2x_B) = 0$$

$$\boxed{T \leftrightarrow x_B}$$

$$T_C = \varpi\big/2R$$

Above Tc
The A and B are completely miscible

Below Tc
The solution separates into two separate phases
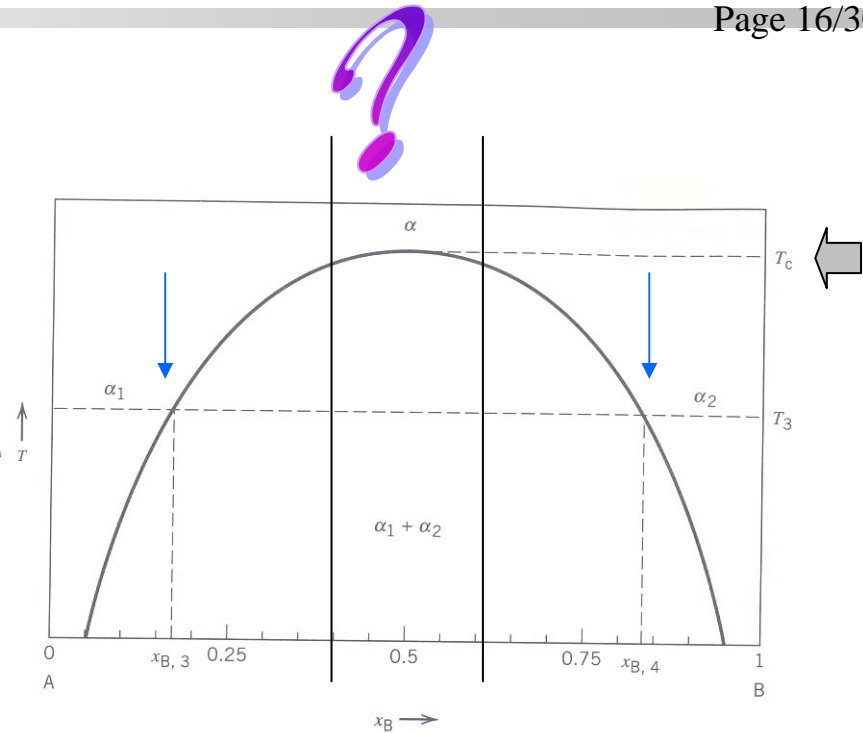At points under the miscibility gap, the phase
compositions vary with temperature

Figure 9.14 The miscibility gap in solid A–B solutions.

Spinodal points

A special significance in the study of phase transformations

$$\left(\frac{\partial^2 \underline{G}_M}{\partial x_B^2}\right)_T = RT(\frac{1}{x_A} + \frac{1}{x_B}) - 2\varpi = 0$$
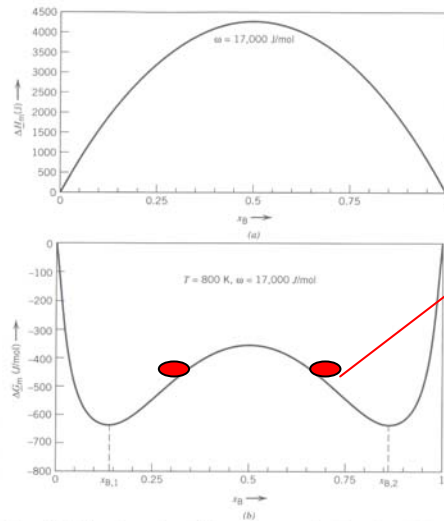
$$x_A x_B = \frac{RT}{2\varpi}$$

Figure 9.15 The miscibility gap, showing spinodal line.

Figure 9.13 Plots of properties of mixing versus composition for regular solutions: (a) molar enthalpy and (b) molar Gibbs free energy.
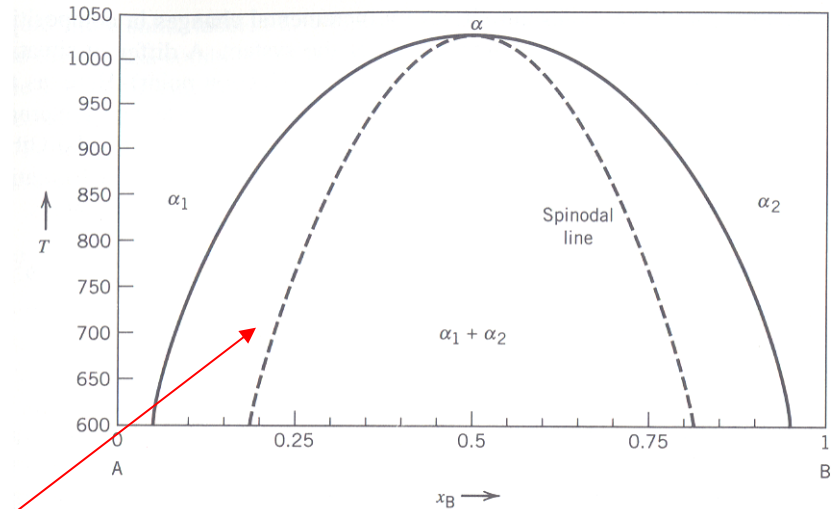
Gibbs free energy of mixing curve is concave downward
In this region the solution may begin the process of decomposition into the equilibrium phases by incremental changes in composition without increasing the total Gibbs free energy of the system.
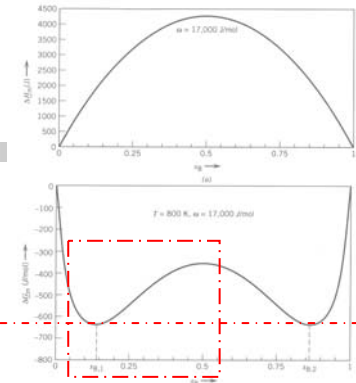
Figure 9.13 Plots of properties of mixing versus composition for regular solutions: (a) molar enthalpy and (b) molar Gibbs free energy.
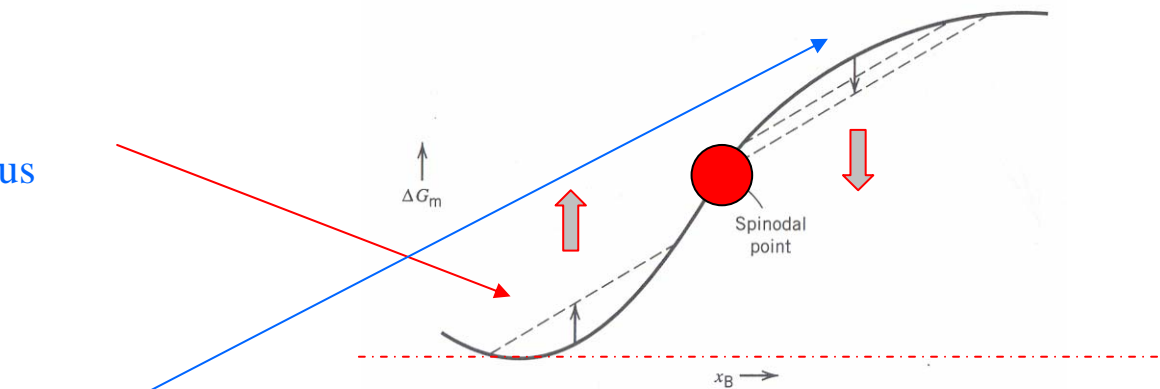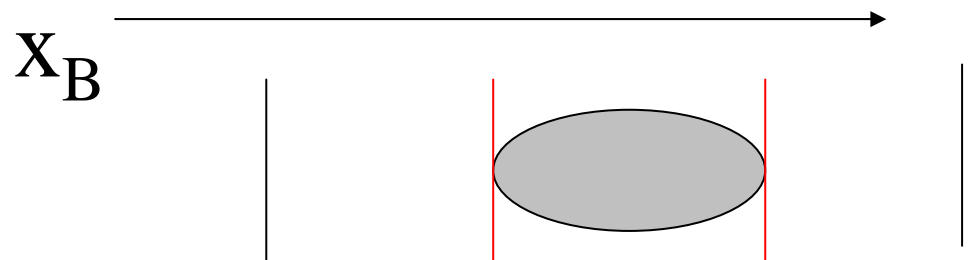
To the left of the spinodal point
The transformation is discontinuous

ΔG_m

Spinodal point

x_B

Figure 9.16 The relation between Gibbs free energy of mixing and composition on either side of spinodal point.

To the right of the spinodal point
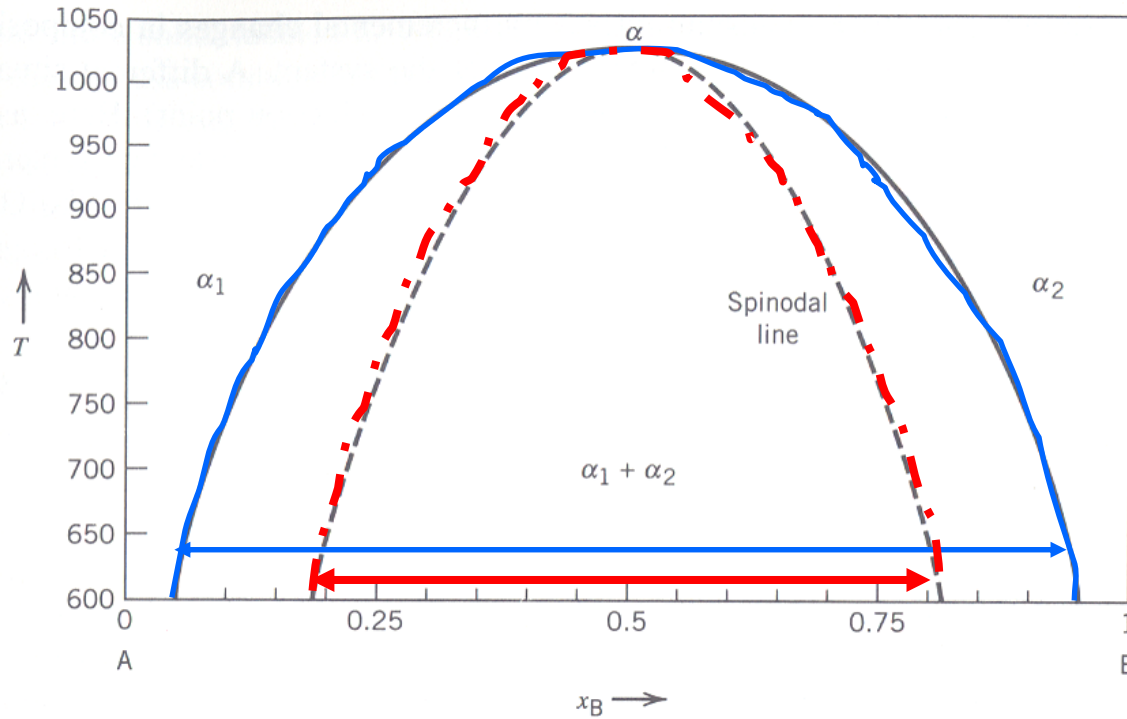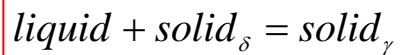The transformation is continuous

X_B

非理想

规则溶液

相律

Figure 9.15 The miscibility gap, showing spinodal line.

Peritectic Phase Diagrams

Peritectic transformation
A liquid phase and a solid phase can combine to
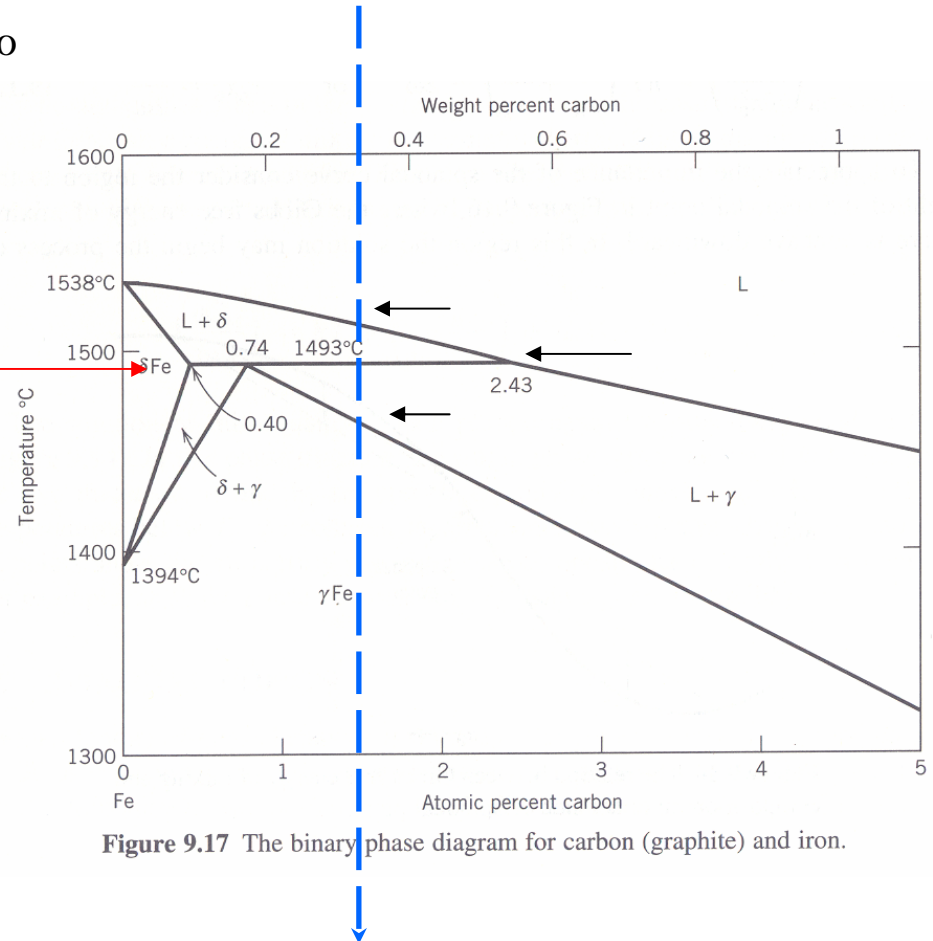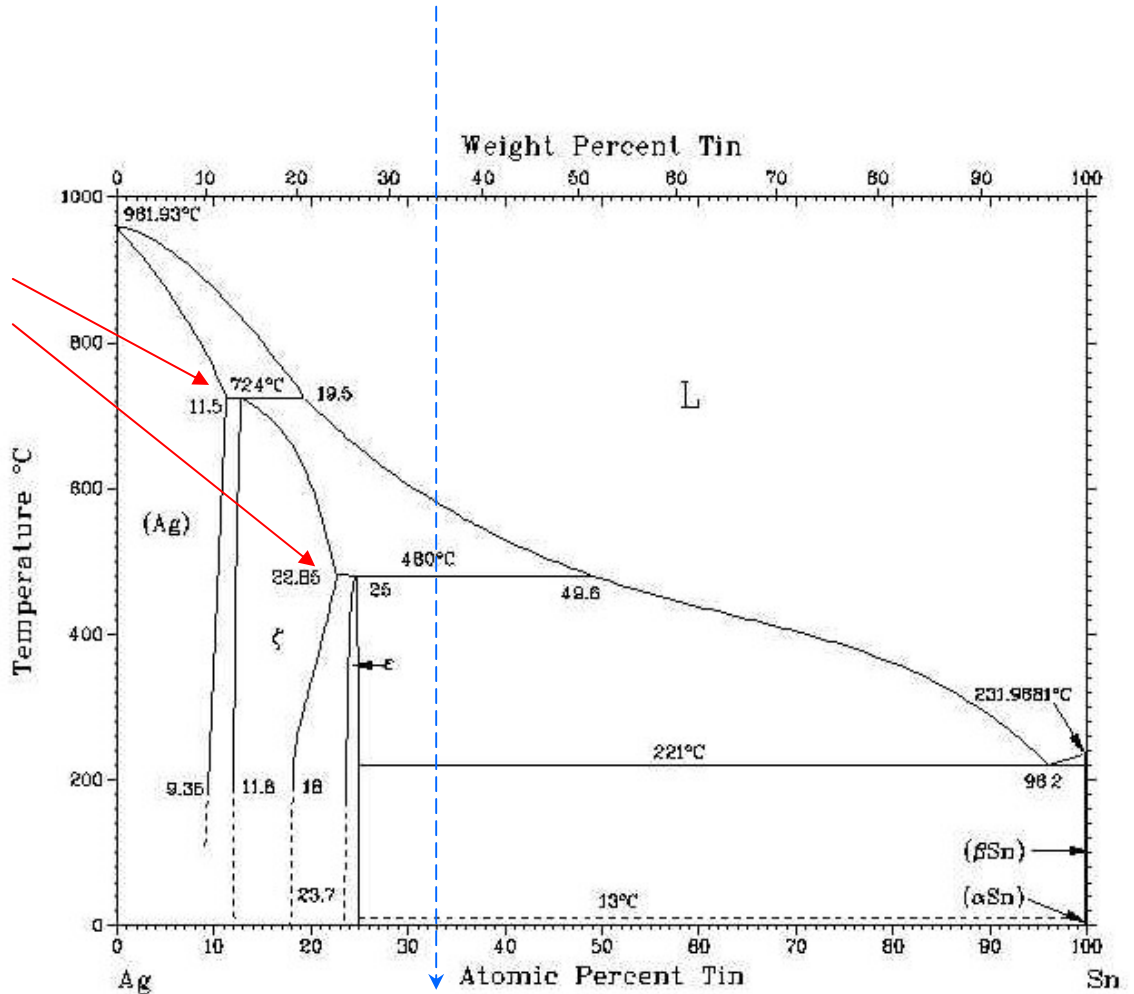form an entirely new solid phase

$$liquid + solid_\alpha = solid_\beta$$

$$liquid + solid_\delta = solid_\gamma$$

相律？

Figure 9.17 The binary phase diagram for carbon (graphite) and iron.

Peritectic Phase Diagrams 2

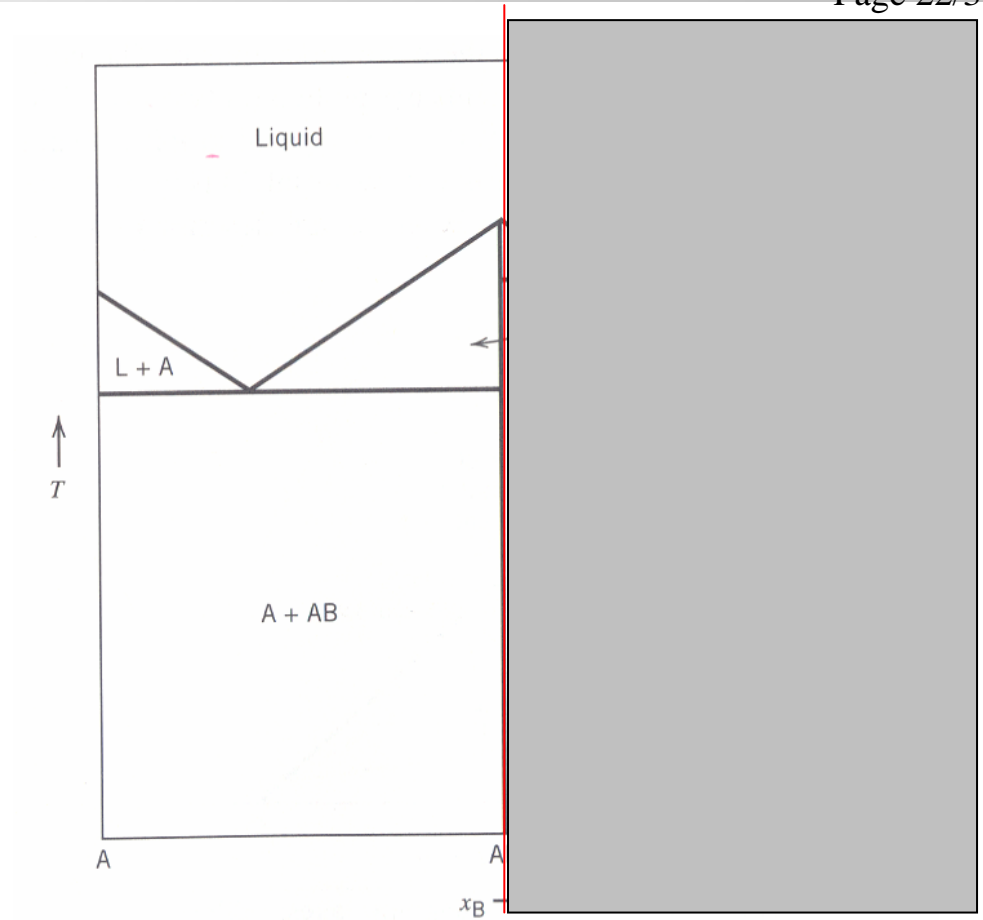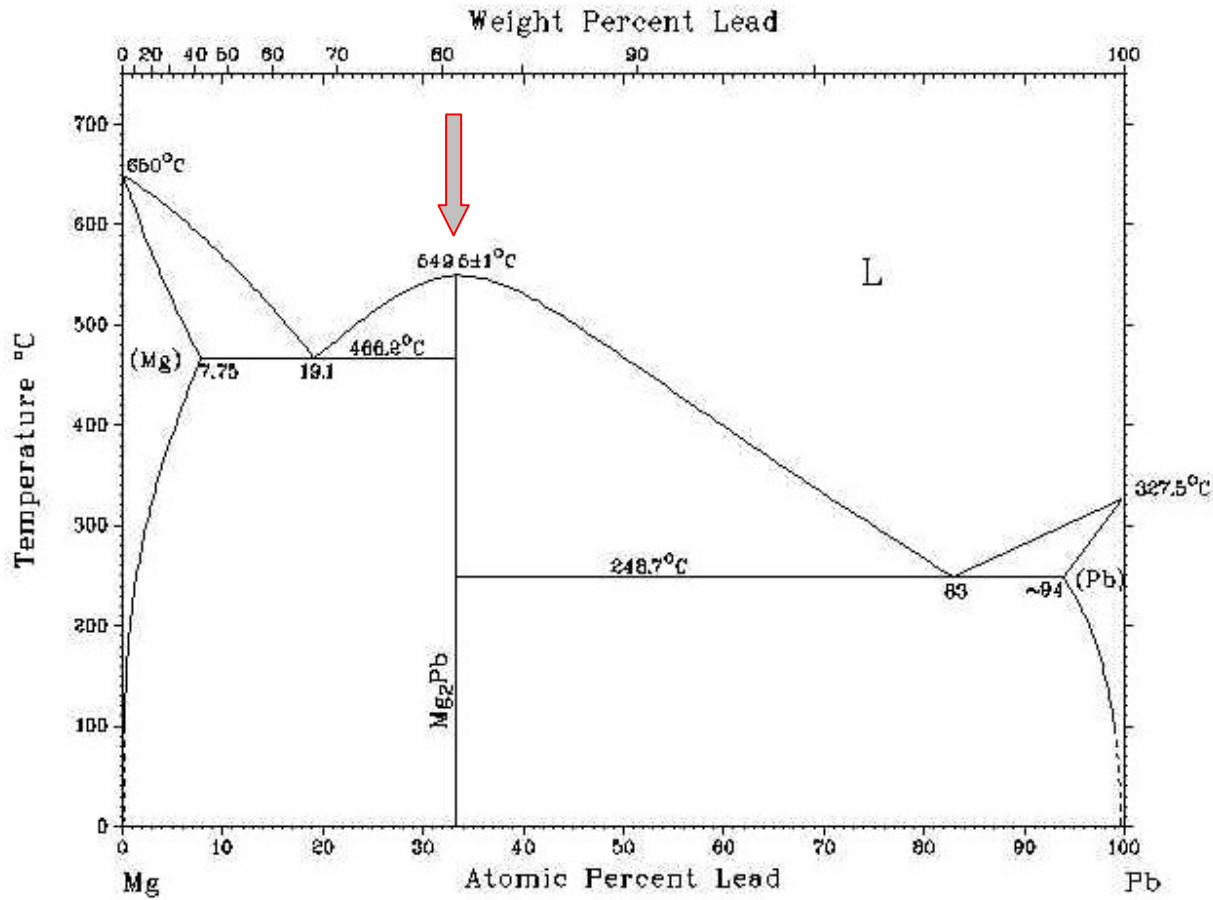$$liquid + solid_{\alpha} = solid_{\beta}$$

Compounds

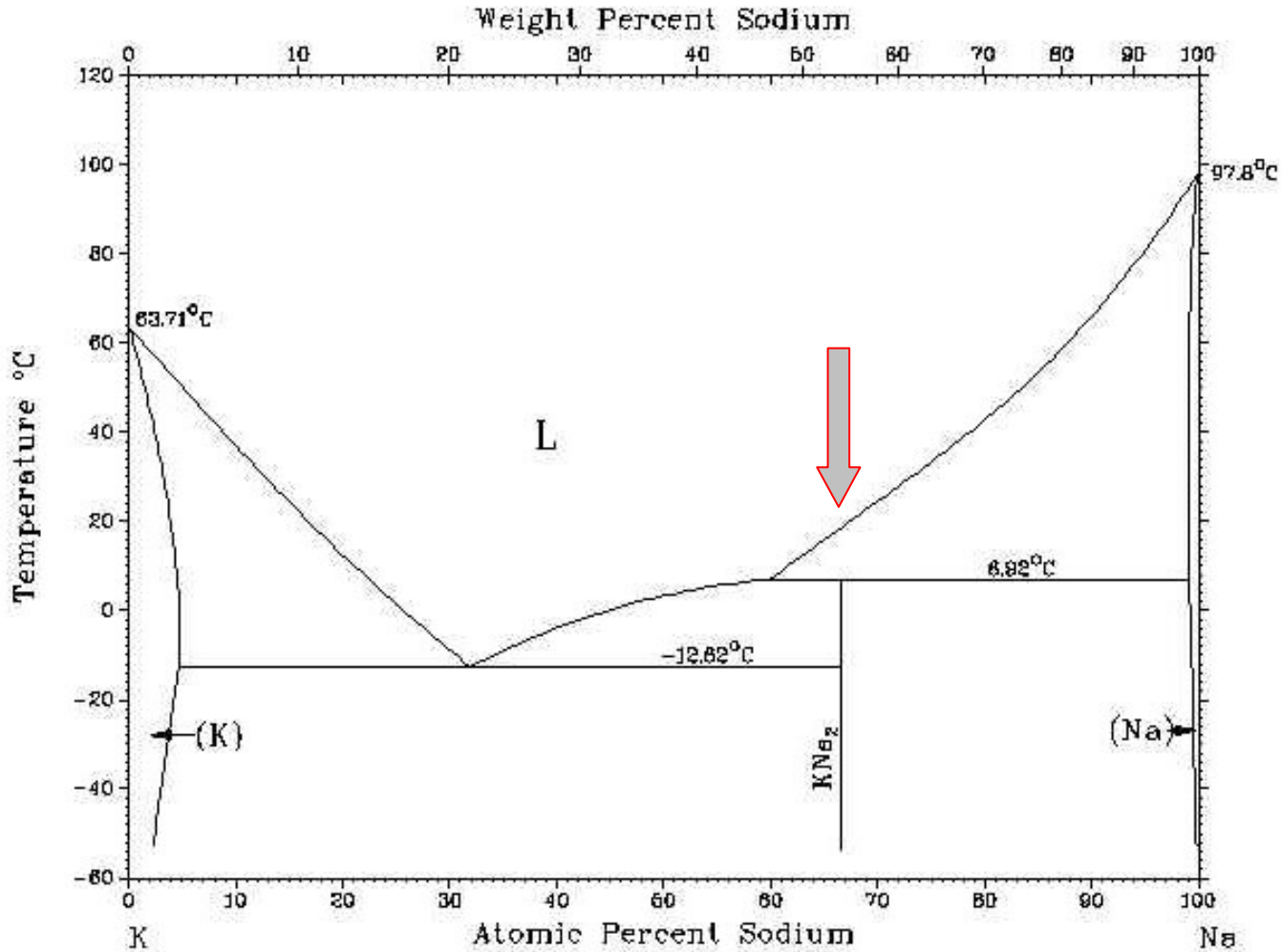**Figure 9.18** Schematic phase diagram for a system A–B containing compounds AB and AB$_2$.

Mg-Pb

形成稳定化合物

具有不
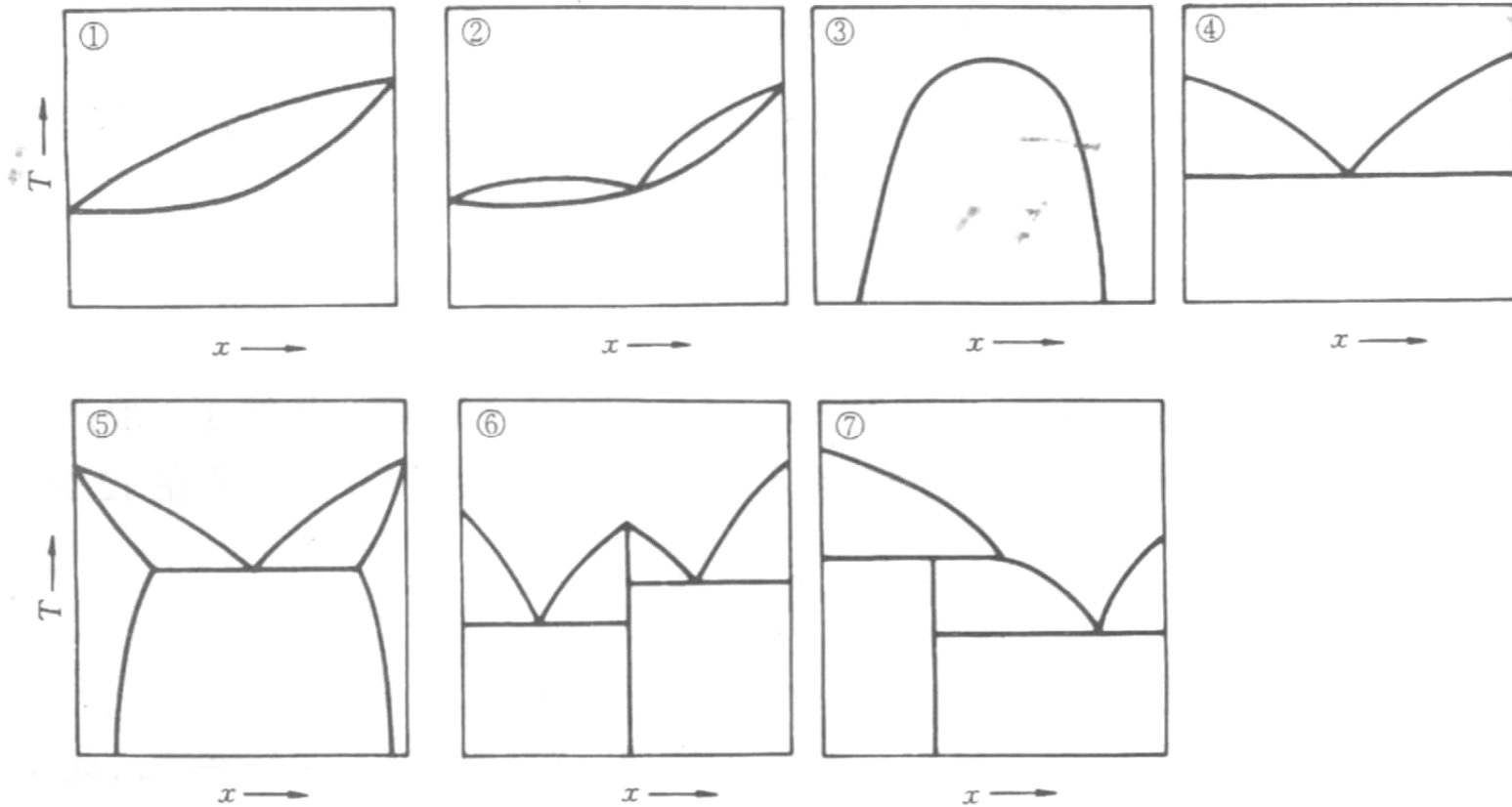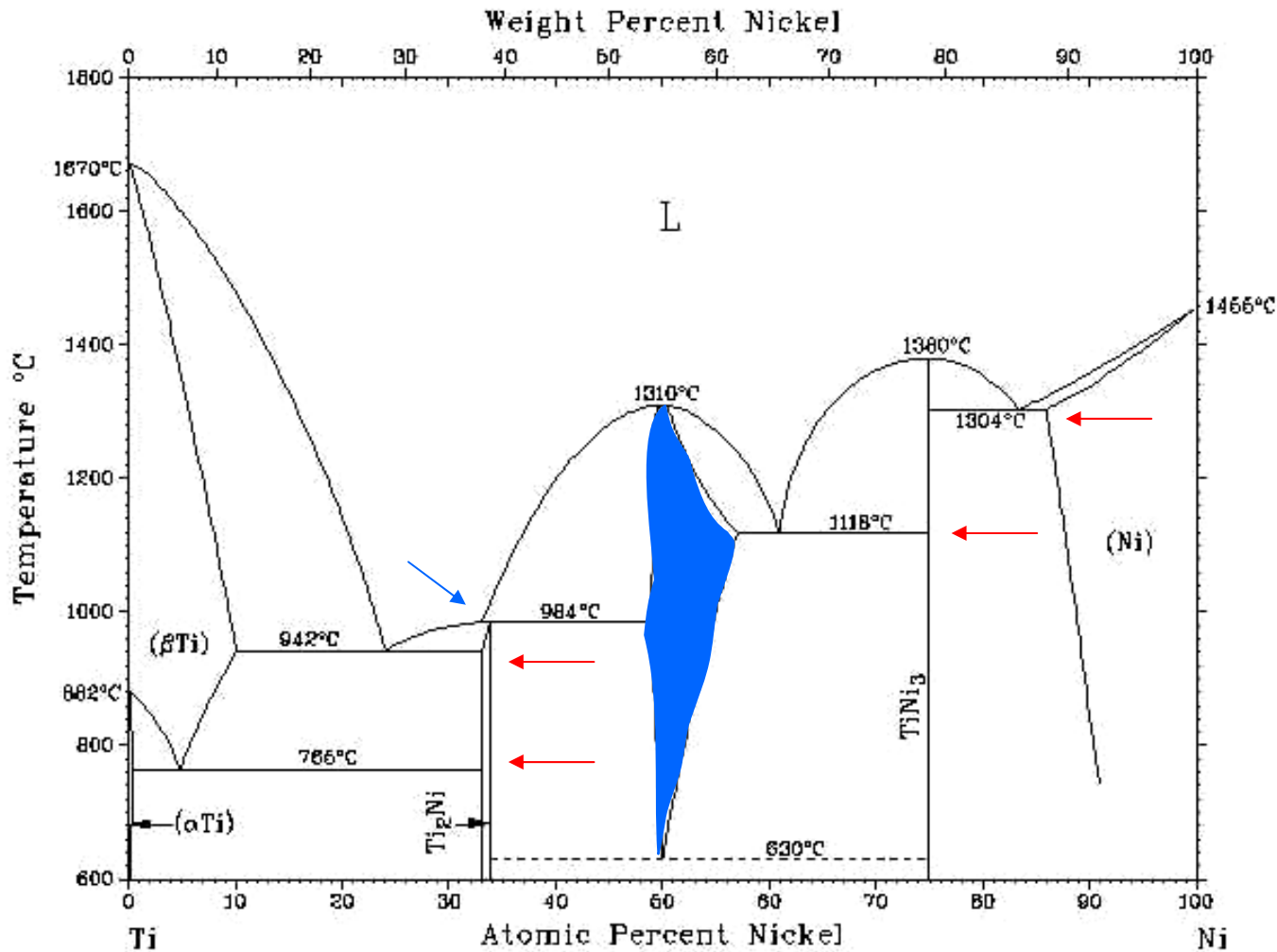稳定化
合物

Summary of Binary Phase Diagrams

图 6-25 二元相图的 7 种基本类型

Ternary Phases Reaction in Binary Systems

表 6-1　二元系的各种三相平衡反应

转　变　类　型		反　应　式	图　型　特　征
共晶型	共晶转变	$l \rightleftharpoons \alpha + \beta$	
	共析转变	$\gamma \rightleftharpoons \alpha + \beta$	
	偏晶转变	$l_1 \rightleftharpoons l_2 + \alpha$	
	熔晶转变	$\delta \rightleftharpoons l + \gamma$	
包晶型	包晶转变	$l + \beta \rightleftharpoons \alpha$	
	包析转变	$\gamma + \beta \rightleftharpoons \alpha$	
	合晶转变	$l_1 + l_2 \rightleftharpoons \alpha$	

二元相图构成的规则

- 相图中所有的线条都代表发生相转变的温度和平衡相的成分，相界线是相平衡的体现，平衡成分必沿着相界线随温度变化；

- 两个单相区之间必有一个由这两个相组成的两相区隔开，而不能以一条线接界；两个两相区必须以单相区或三相水平线隔开。相区接触法则：在二元相图中，相邻相区的相数差为**1**，相数差大于**1**的相区只能相交于一点；

- 二元相图中，三相平衡必为一水平线，表示恒温反应，三个单相区分别交于水平线上的三个点，其中两点在水平线的两端，另一点在端点之间。

- 与三相线相接的两相区与单相区的相界线的延长线必须进入两相区，而不能进入单相区。

T_1
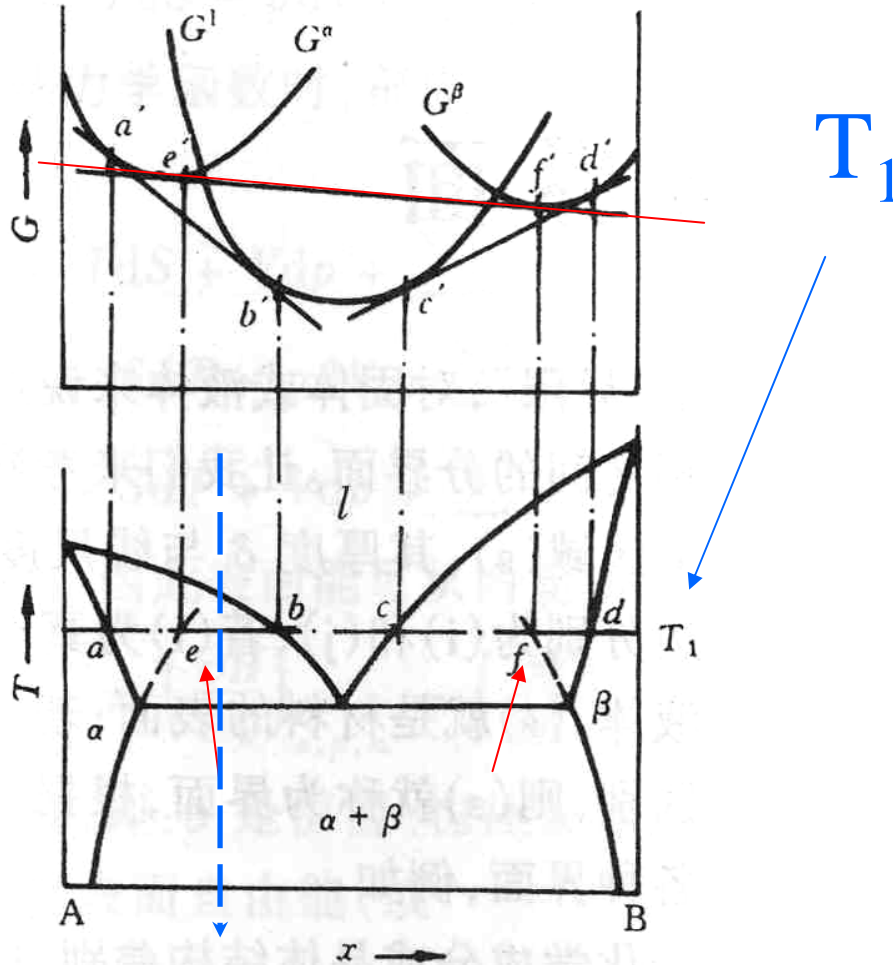
相图的测定

通过实验测量和观察材料中的某个或某些性质的变化来确定材料中的相平衡关系，并绘制出相图。

动态法/静态法
测定手段
样品的合成方式

相图集

至今，人们已积累了大量珍贵的实测相图数据，大部分被汇编成册并得到广泛应用。

M. Hansen，1936年，二元合金相图

T. B. Massalski，1986年，二元合金相图

印度金属学会，三元铁合金相图集，四元铁合金相图集，三元镍合金相图集

俄巴依科夫研究所，三元合金状态图集

德国金属学会，三元合金相图集

我国昆明贵金属研究所，贵金属合金相图集

美国国家标准研究所，陶瓷学家用相图

Review of Today

- Immiscibility

- Spinodal Points

- Compounds

- Summary of Binary Phase

- Ternary Phases Reaction in Binary Systems

- 二元相图构成的规则

Homework

- Exercises in Chap 6

  P 234, 9.6, 9.9, 9.13