Physical metallurgy principles

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Really Weird Author Ranking?!

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The original book (1st and 2nd edition) was written solely by Prof. Robert Reed-Hill. As to the 3rd edition, it is improved, including fracture mechanics, solidification, TEM etc, so it is still good one.
The 3rd edition is written by Professor Robert Reed-Hill (1st author) and the Reza Abbaschian (2nd author), and is also a good book.

However, as to the 4th edition, it is disappointing since it is almost identical to 3rd edition- major change is the removal of 2 chapters and technically it cannot be even regarded as a new edition.

By then, the original author, Professor Reed-Hill has passed away (~2001). However, the 2nd author of 3rd edition, Reza Abbaschian was listed as 1st author. Despite to very little change of 4th edition, there is a 3rd author Lara Abbaschian coming in, and ranked as 2nd author. Thus, the original author Professor Reed-Hill is moved to the place of 3rd author. The 2nd author Ms. Abbaschian, based on the front page of the book, is from an affiliation of business, other than academic institution.

https://www.amazon.com/Physical-Metallurgy-Principles-SI-Version/dp/0495438510

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Physical metallurgy principles

Ch10 Phases

Contents

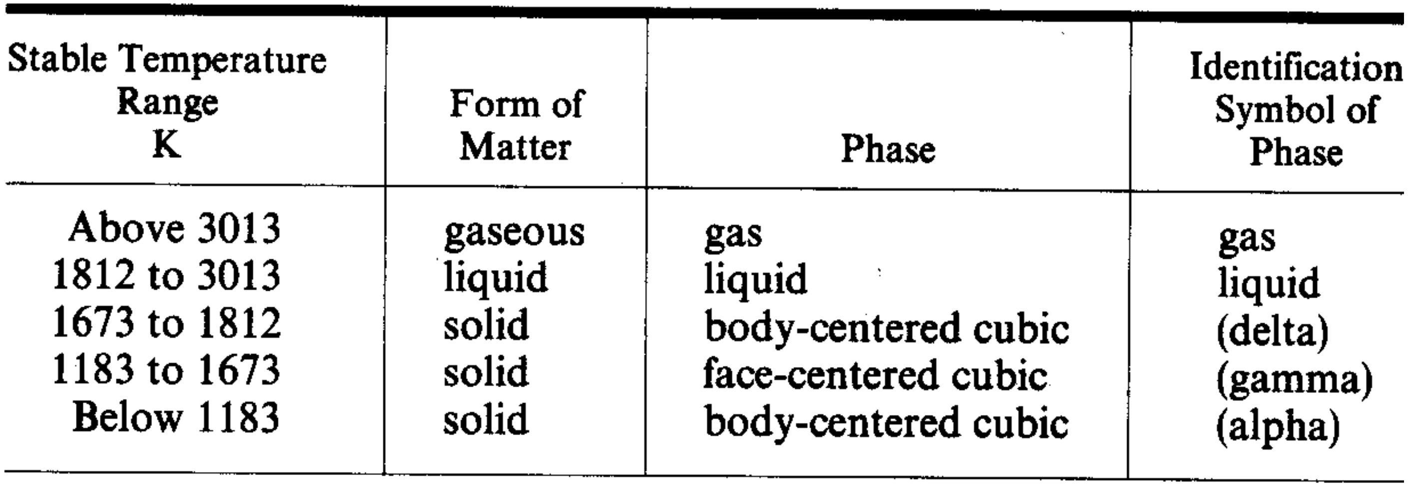
Phases

- A phase is defined as a macroscopically homogeneous body of matter.

  Ex. Three forms of copper—solid, liquid, and gas—constitutes a separate and distinct phases.
- Each crystal structure defines a separate phase, so that polymorphic metals can exist in more than one solid phases.

  Ex. Fe

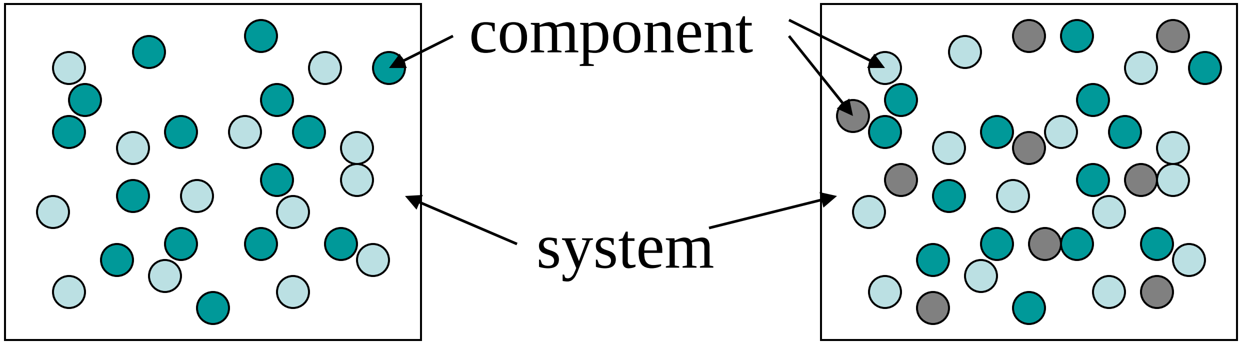
Table 10.1 Phases of Pure Iron



Stable Temperature Range K	Form of Matter	Phase	Identification Symbol of Phase
Above 3013	gaseous	gas	gas
1812 to 3013	liquid	liquid	liquid
1673 to 1812	solid	body-centered cubic	(delta)
1183 to 1673	solid	face-centered cubic	(gamma)
Below 1183	solid	body-centered cubic	(alpha)

definitions

- Binary alloys: two component systems, are mixtures of two metallic elements. Ex. Cu-Zn
- Ternary alloys: three component systems, mixtures of three metallic elements.   Ex. Ag-Ni-Zn
- System: as used in the sense usually employed in thermodynamics, or physical chemistry, is an isolated body of matter.
- Component: often the metallic elements that make up the system.



component

system

Binary alloys

Ternary alloys

- Ex. Pure copper or pure nickel are by themselves one-component systems, while alloys formed by mixing are two component systems.

- Steels are normally considered to be two-component systems consisting of iron and iron carbide(Fe_3C), a compound.

- Terminal solid solution: phases based on the crystal structures of the components.

  Ex. Binary alloys of copper and silver.

  (copper acts as the solvent, with silver the solute; another in which silver is the solvent and copper the solute)

- Intermediate phases: crystal structures different from those of either component may form at certain ratios of the two components. They do not have a fixed composition (ratio of the components) and appear over a range of compositions.

  Ex. Intermediate solid solution: Brass (copper(53-50%)-zinc(47-50%)), intermetallic compound: iron-carbide, Fe_3C.

- In a system, continuous (matrix) phase:the phase that surrounds the other phase ; discontinuous (dispersed) phase: the phase that is surrounded.

- The phases in alloy systems are usually solutions — either liquid, solid or gaseous.
- The free energy of a solution is a thermodynamic property of the solution, or a variable that depends on the thermodynamic state of the solution.

$$G = H(U) + PV - TS$$

- Variables: temperature(T), pressure(P), volume(V), enthalpy(H), entropy(S), and the free energy(G).

- In a one-component system of a given mass and phase, if the two variables temperature and pressure are specified, the volume of the system will have a definite fixed value. At the same time, its free energy, enthalpy, and other properties will also have values that are fixed and determinable.

Ex. In a three-component system, the mole fraction are:

$$N_A = \frac{n_A}{n_A + n_B + n_C} \quad N_B = \frac{n_B}{n_A + n_B + n_C} \quad N_C = \frac{n_C}{n_A + n_B + n_C}$$

N_A, N_B, N_C :are the mole fractions; n_A, n_B, n_C :are the actual number of moles of the A, B, and C components.

By definition of the mole fraction, then:

$$N_A + N_B + N_C = 1$$

- There are only two independent mole fractions in a ternary system.
- Most metallurgical processes occur at constant temp. and pressure, the state of a solution can be considered to be a function of its composition. Such as free energy can be considered a function of only the composition variables. So, the total free energy (G) of a solution is :

$$G = G(n_A, n_B, n_C)$$ (temp. and pressure constant)

- By partial differentiation, the differential of the free energy of a single solution of three components at constant pressure and temperature is:

$$dG = \frac{\partial G}{\partial n_A} \times dn_A + \frac{\partial G}{\partial n_B} \times dn_B + \frac{\partial G}{\partial n_C} \times dn_C$$

- Where the partial derivatives, such as $\partial G/\partial n_A$, represent the change in the free energy when only one of the components is varied by an infinitesimal amount.
- For a very small variation of component A, while the amounts of the components B and C in the solution are maintained constant, we have $\frac{dG}{dn_A} = \frac{\partial G}{\partial n_A}$
- The partial derivatives are the partial mole free energies of the solution and are designed by the symbols $\overline{G}_A, \overline{G}_B, \overline{G}_C$

$$dG = \overline{G}_A dn_A + \overline{G}_B dn_B + \overline{G}_C dn_C$$

- The total free energy of a solution composed can be obtained by integrating the upper equation. The partial-molar free energies are functions of only the composition of the solution (at constant temperature and pressure), they will also be constant during the formation of the solution.

$$G = n_A \overline{G}_A + n_B \overline{G}_B + n_C \overline{G}_C$$

- Let us differentiate upper equation completely to obtain

$$dG = n_A d\overline{G}_A + \overline{G}_A dn_A + n_B d\overline{G}_B + \overline{G}_B dn_B + n_C d\overline{G}_C + \overline{G}_C dn_C$$

- But we have already seen that the derivative of the free energy is

$$dG = \overline{G}_A dn_A + \overline{G}_B dn_B + \overline{G}_C dn_C$$

$$n_A d\overline{G}_A + n_B d\overline{G}_B + n_C d\overline{G}_C = 0$$

$$\text{..... for three-component solution}$$

$$\text{and, } n_A d\overline{G}_A + n_B d\overline{G}_B + n_C d\overline{G}_C + n_D d\overline{G}_D = 0$$

$$\text{..... for four components}$$

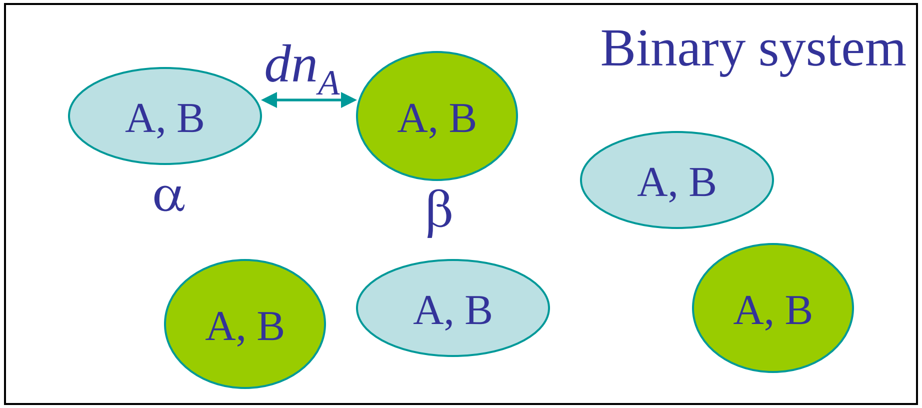
- The significance of these relationships in explaining the phenomena of polyphase systems in equilibrium.

Equilibrium between two phases

- A binary (two-component) system with two phases in equilibrium will now be considered.
- Total energy: α phase $G^{\alpha} = n_A^{\alpha}\overline{G}_A^{\alpha} + n_B^{\alpha}\overline{G}_B^{\alpha}$

  β phase $G^{\beta} = n_A^{\beta}\overline{G}_A^{\beta} + n_B^{\beta}\overline{G}_B^{\beta}$

* A small quantity (dn_A) of component *A*: α phase → transferred to → β phase



$$dG = dG^{\alpha} + dG^{\beta} = \overline{G}_A^{\alpha}(-dn_A) + \overline{G}_A^{\beta}(dn_A)$$

$$\Rightarrow dG = (\overline{G}_A^{\beta} - \overline{G}_A^{\alpha})dn_A$$

- Because we assumed the two phases are at equilibrium. The variation in the free energy for any infinitesimal change inside the system → the shift of a small amount of component A from one phase to the other must be zero.

$$dG = (\overline{G}_A^{\beta} - \overline{G}_A^{\alpha})\,dn_A = 0$$

$$\therefore \overline{G}_A^{\alpha} = \overline{G}_A^{\beta}$$

$$\text{same manner} \qquad \overline{G}_B^{\alpha} = \overline{G}_B^{\beta}$$

$$\text{for M components and } \mu \text{ phase in equilibrium}$$

$$\overline{G}_A^{\alpha} = \overline{G}_A^{\beta} = \overline{G}_A^{\gamma} = \ldots.. = \overline{G}_A^{\mu}$$

$$\overline{G}_B^{\alpha} = \overline{G}_B^{\beta} = \overline{G}_B^{\gamma} = \ldots.. = \overline{G}_B^{\mu}$$

$$\overline{G}_C^{\alpha} = \overline{G}_C^{\beta} = \overline{G}_C^{\gamma} = \ldots.. = \overline{G}_C^{\mu}$$

$$\mathrm{M}$$

$$\overline{G}_M^{\alpha} = \overline{G}_M^{\beta} = \overline{G}_M^{\gamma} = \ldots.. = \overline{G}_M^{\mu}$$

Number of phases in an alloy system

- One-component systems

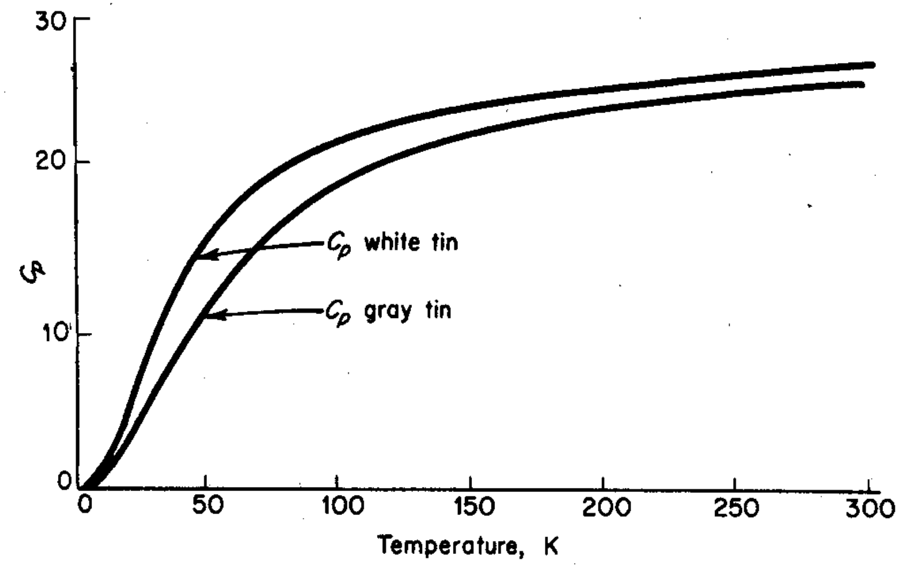
ex. white tin ←→ gray tin

β phase α phase

body-centered diamond cubic

tetragonal large volume expansion (27%)

upper 286.2K below 286.2K



- Gibbs free energy of a pure substance is : $G = H - TS$
- In a reversible process at constant pressure, the heat exchanged between the system and its surrounding equals the enthalpy change of the system.

$$q = dH = \int C_p dT$$

q : a small transfer of heat into or out of the system

dH : accompanying enthalpy change of the system

C_p : the specific heat at a constant pressure

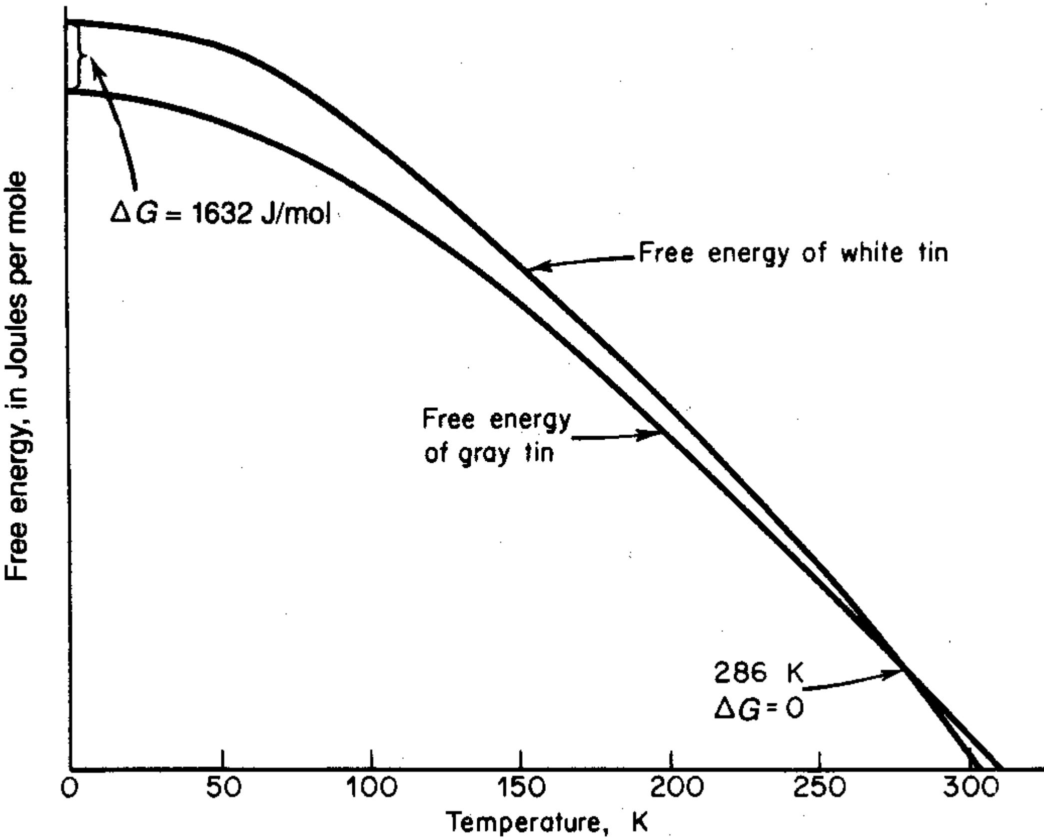
$$\Rightarrow H = H_0 + \int_0^T C_p dT$$

Simlarly, a reversible process for entropy

$$dS = \frac{dq}{T} = \frac{C_p dT}{T} \qquad \Rightarrow \quad S = S_0 + \int_0^T \frac{C_p dT}{T} = \int_0^T \frac{C_p dT}{T}$$

$$(0\text{K} \Rightarrow S_0 = 0)$$

- The free energy of both the white and gray tin:



$$G^{\alpha} = H_0^{\alpha} + \int_0^T C_p^{\alpha} dT - T\int_0^T \frac{C_p^{\alpha} dT}{T}$$

$$G^{\beta} = H_0^{\beta} + \int_0^T C_p^{\beta} dT - T\int_0^T \frac{C_p^{\beta} dT}{T}$$

$$286.2\text{K} \Rightarrow \Delta G = 0 \text{ (gray and white tin are coexists)}$$

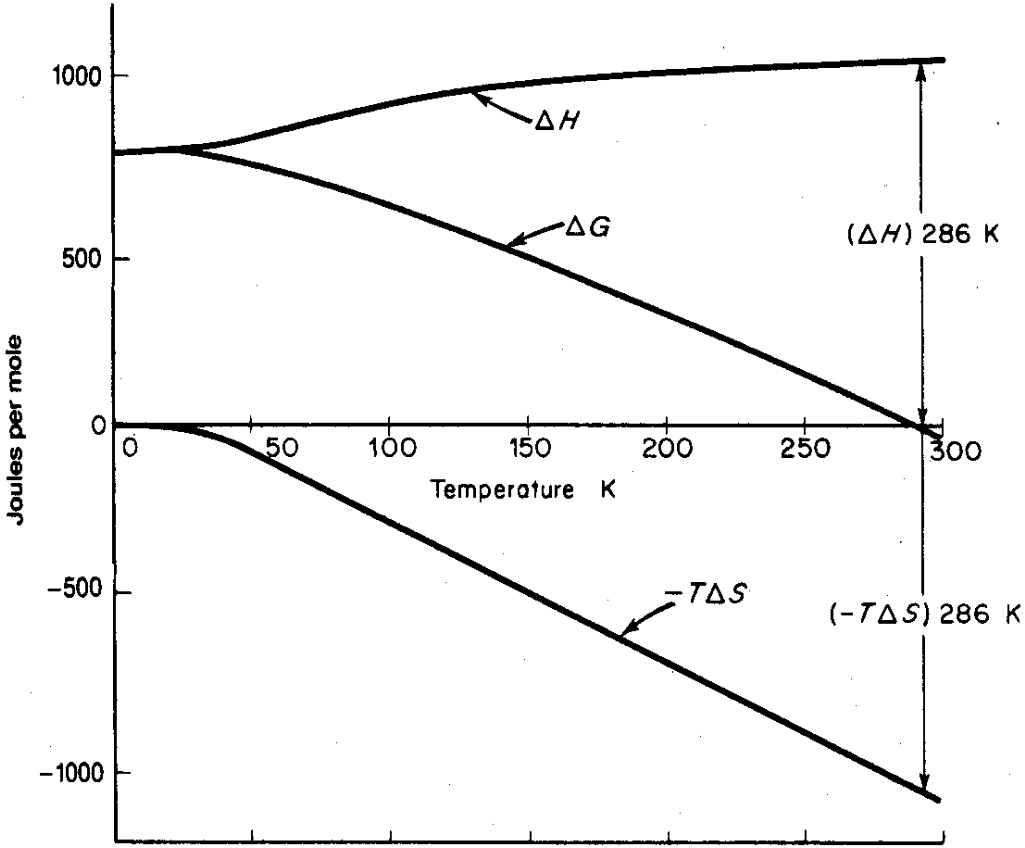
$$\text{below } 286.2\text{K} \Rightarrow \text{gray tin has the lowest free energy}$$

$$\Rightarrow \text{gray tin is the most stable phase}$$

$$\text{above } 286.2\text{K} \Rightarrow \text{white tin has the lowest free energy}$$

$$\Rightarrow \text{white tin is the most stable phase}$$

$$\text{T} \uparrow \Rightarrow \text{G} \downarrow \text{(TS term is importance in the free energy equation)}$$



the closest packing structure
→More closely bound phase

More open structure → the greatest entropy of vibration

High-T stable phase is BCC;
Low-T phase has a close-packed structure (FCC, HCP)
Ex. Li, Na, Ca, Ti….

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

$$\Delta H = H_0^{\beta} + \int_0^T C_p^{\beta} dT - H_0^{\alpha} - \int_0^T C_p^{\alpha} dT$$

and $$T\Delta S = T\int_0^T \frac{C_p^{\beta} dT}{T} - T\int_0^T \frac{C_p^{\alpha} dT}{T}$$

at the temperature of transformation (286.2K)

$$\Delta H = T\Delta S \Rightarrow \Delta G = 0$$

Two-component systems

-- single phase binary systems

- Ideal solutions: no tendency for either A atoms or for B atoms to cluster together or for opposite types of atoms to attract each other.

free energy of mixing N_A moles of A atoms and N_B moles of B atoms

$$G = G_A^0 N_A + G_B^0 N_B + T\Delta S_M$$

G_A^0 : free energy per mole of pure A

G_B^0 : free energy per mole of pure B

T : the absolute temperature

ΔS_M : the entropy of mixing

$$G = G_A^0 N_A + G_B^0 N_B + RT(N_A \ln N_A + N_B \ln N_B)$$

$$G = N_A(G_A^0 + RT \ln N_A) + N_B(G_B^0 + RT \ln N_B)$$

if $\overline{G}_A = G_A^0 + RT \ln N_A$

$\overline{G}_B = G_B^0 + RT \ln N_B$

$$\Delta\overline{G}_A = \overline{G}_A - G_A^0 = RT \ln N_A$$

$$\Delta\overline{G}_B = \overline{G}_B - G_B^0 = RT \ln N_B$$

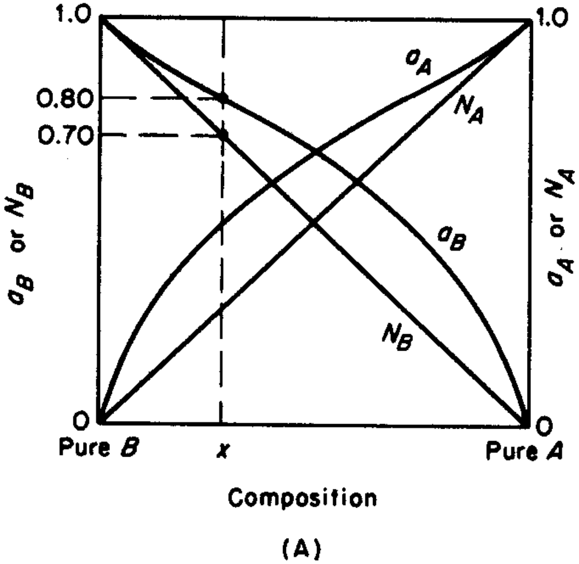
$\Delta\overline{G}_A and \Delta\overline{G}_B$: the quantities of the increase in free energy when one mole (A or B) is dissolved at constant temperature in a very large quantity of the solution.

- Nonideal solutions: in most liquid and solid solutions, no preference either for their own or for their opposites.

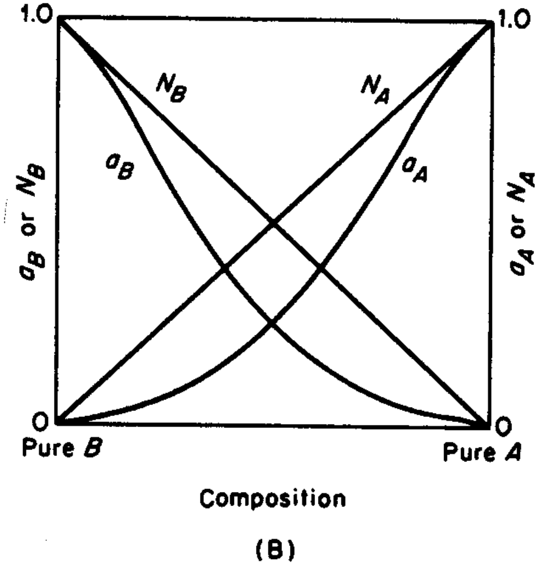
$$\Delta\overline{G}_A = RT \ln a_A$$

$$\Delta\overline{G}_B = RT \ln a_B$$

- a_A is the activity of component A: indicate the extent to which a solution departs from an ideal solution.



Positive deviation



Negative deviation

Ideal solution:

$$\Delta\overline{G_i} = RT \ln 0.70 = -0.356RT$$

nonideal solution:

$$\Delta\overline{G_n} = RT \ln 0.80 = -0.223RT$$

positive deviation:

$a_A > N_A$ and $a_B > N_B$

$\Delta\overline{G_i} < \Delta\overline{G_n}$

attraction between same atoms

> attraction between dissimilar atoms

if a_A and $a_B = 1 \Rightarrow$ two components were completely insoluble

negative deviation:

$a_A < N_A$ and $a_B < N_B$

$\Delta\overline{G_i} > \Delta\overline{G_n}$

attraction between same atoms

< attraction between dissimilar atoms

- Activity coefficients: the ratios of the activities to their respective atom fractions.

$$\gamma_A = \frac{a_A}{N_A} \quad \text{and} \quad \gamma_B = \frac{a_B}{N_B}$$

- The free energy of a mole of ideal solution should given by:

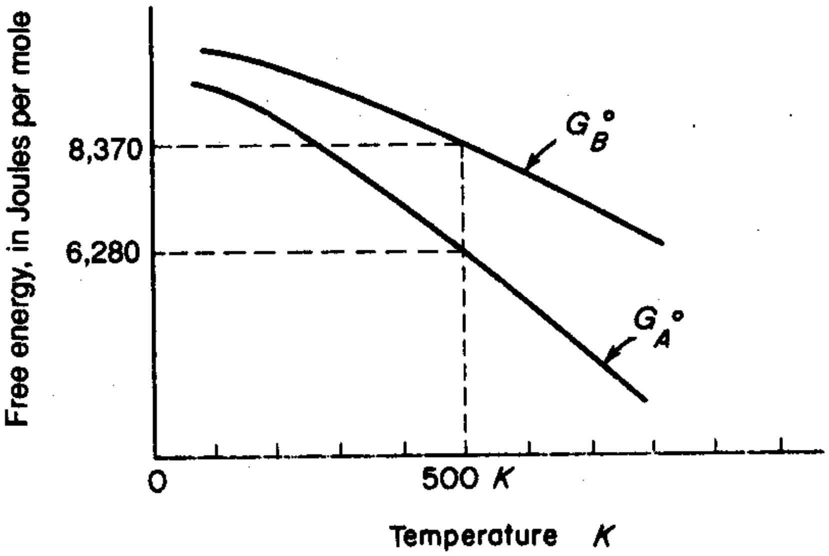
$$G = N_A G_A^0 + N_B G_B^0 + RT(N_A \ln N_A + N_B \ln N_B)$$

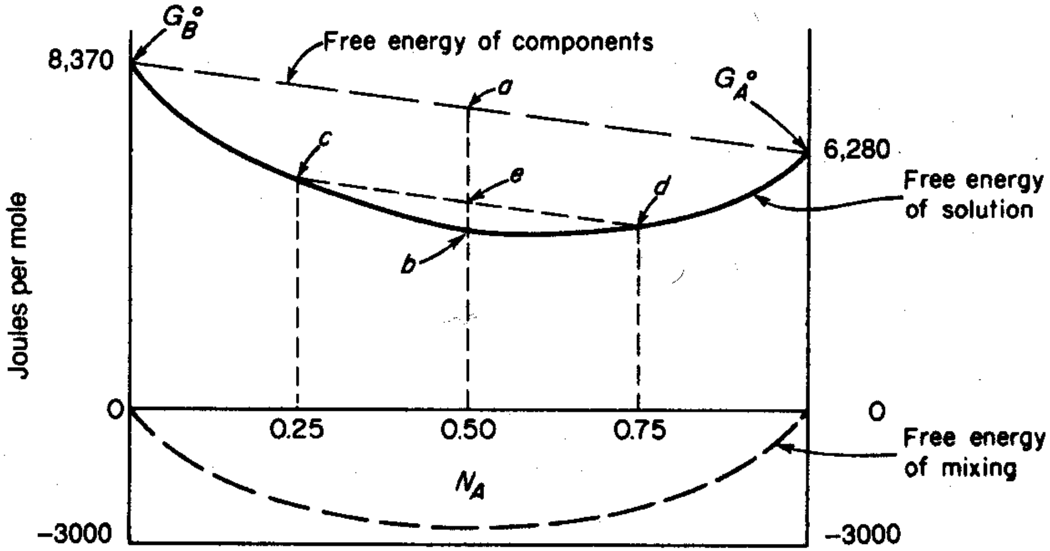
$$N_A G_A^0 + N_B G_B^0 : \text{free energy of one total mole of the two components (not mixed)}$$

$$RT(N_A \ln N_A + N_B \ln N_B) : \text{the contribution of the entropy of mixing to the free energy of the solution, and directly proportional to the temperature}$$

- The homogeneous solid solution has the lower free energy and represents the stable state.

$$G = N_A G_A^0 + N_B G_B^0 + RT(N_A \ln N_A + N_B \ln N_B)$$





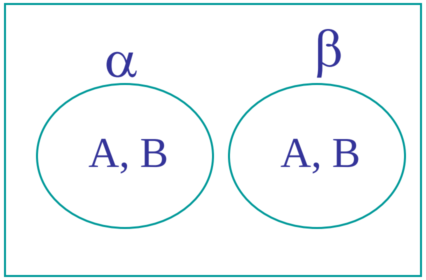
At 500K temperature

Table 10.2 Data for Computing the Entropy of Mixing Contribution to the Free Energy of an Ideal Solution

Atom Fraction, N_A	$(N_A \ln N_A + N_B \ln N_B)$	$RT(N_A \ln N_A + N_B \ln N_B)$ for Temperature 500 K
0.00	0.000	000 J/mol
0.10	−0.325	−1,351
0.20	−0.500	−2,079
0.30	−0.611	−2,540
0.40	−0.673	−2,798
0.50	−0.690	−2,868
0.60	−0.673	−2,798
0.70	−0.611	−2,540
0.80	−0.500	−2,079
0.90	−0.325	−1,351
1.00	−0.000	000

Two-component systems

-- two phases binary systems



- Two-component (A, B) systems containing two phases (α, β)

$$n_A d\overline{G}_A + n_B d\overline{G}_B = 0 \;\Rightarrow\; N_A d\overline{G}_A + N_B d\overline{G}_B = 0$$

$$\alpha \text{ phase}: N_A^{\alpha} d\overline{G}_A + N_B^{\alpha} d\overline{G}_B = 0$$

$$\beta \text{ phase}: N_A^{\beta} d\overline{G}_A + N_B^{\beta} d\overline{G}_B = 0$$

- Restrictive equations: restricts the values of the mole fractions of the components in the solutions.

- Ex.

α phase	β phase
$N_{Ag} = 0.86$	$N_{Ag} = 0.05$
$N_{Cu} = 0.14$	$N_{Cu} = 0.95$

$$0.86 d\overline{G}_{Ag} + 0.14 d\overline{G}_{Cu} = 0$$

$$0.05 d\overline{G}_{Ag} + 0.95 d\overline{G}_{Cu} = 0$$

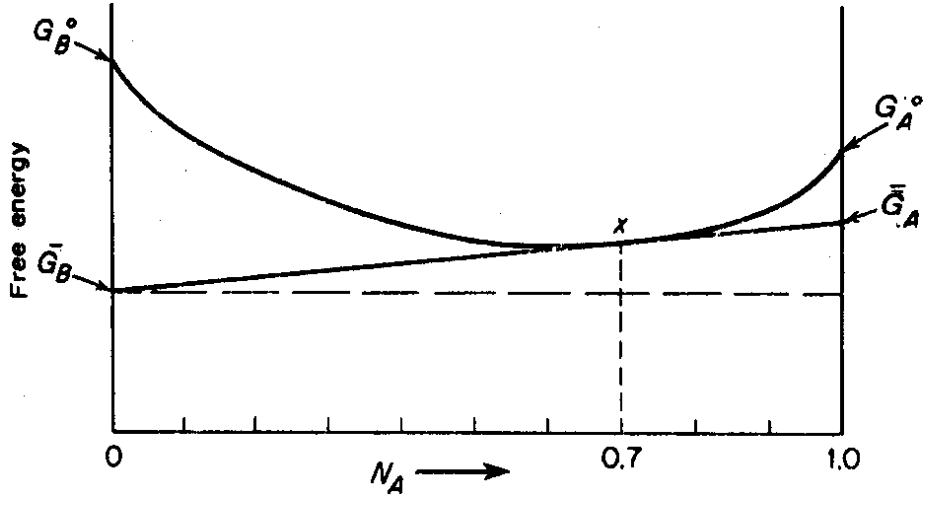
$$\frac{0.86 d\overline{G}_{Ag}}{0.05 d\overline{G}_{Ag}} = \frac{-0.14 d\overline{G}_{Cu}}{-0.95 d\overline{G}_{Cu}}$$

$$\frac{0.86}{0.05} \neq \frac{0.14}{0.95} \quad \text{so, } d\overline{G}_{Ag} = d\overline{G}_{Cu} = 0$$

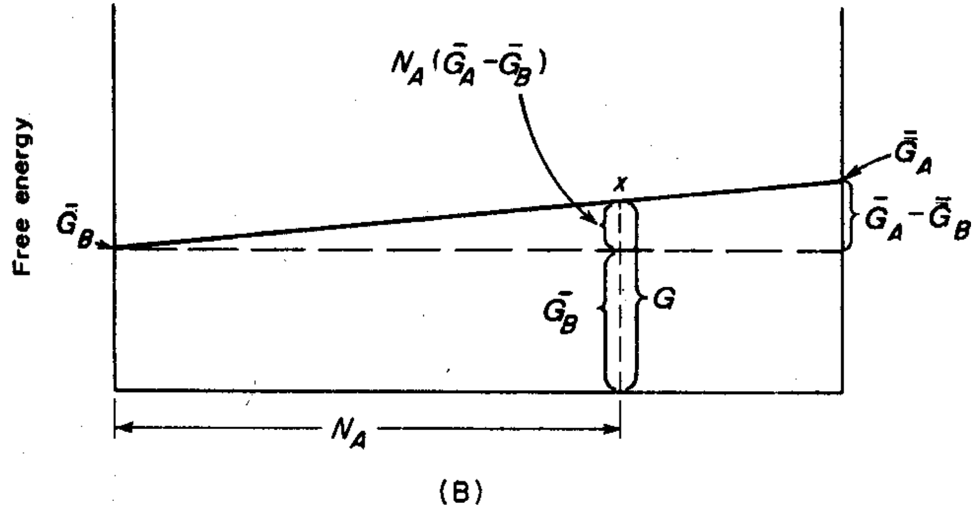
Which means that at a constant temperature and a constant pressure there can be no change in the partial-molal free energies when the two phases are in equilibrium.

Graphical determinations of partial-molal free energies

$$G = \overline{G}_B + N_A(\overline{G}_A - \overline{G}_B)$$
$$G = N_A\overline{G}_A + (1 - N_A)\overline{G}_B$$
$$(1 - N_A) = N_B$$
$$G = N_A\overline{G}_A + N_B\overline{G}_B$$



(A)



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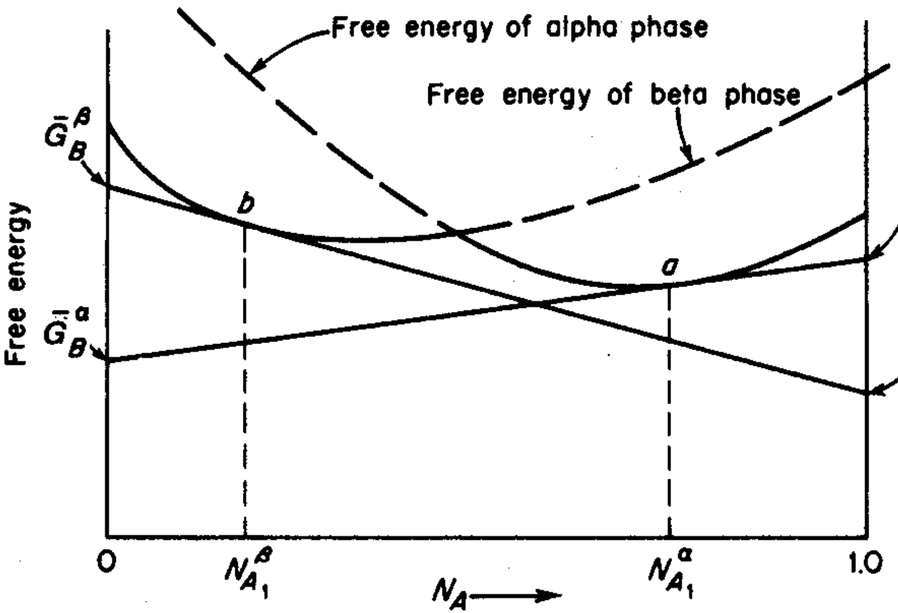
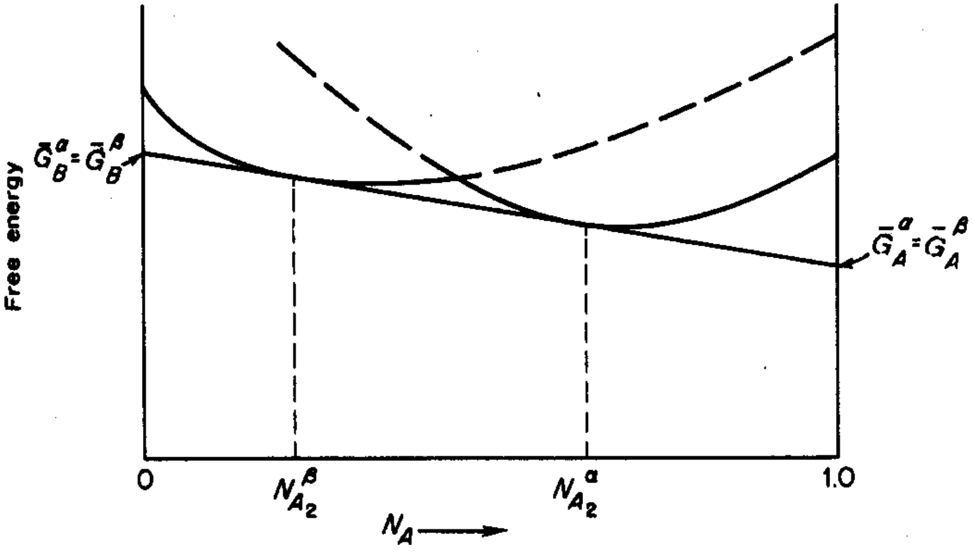




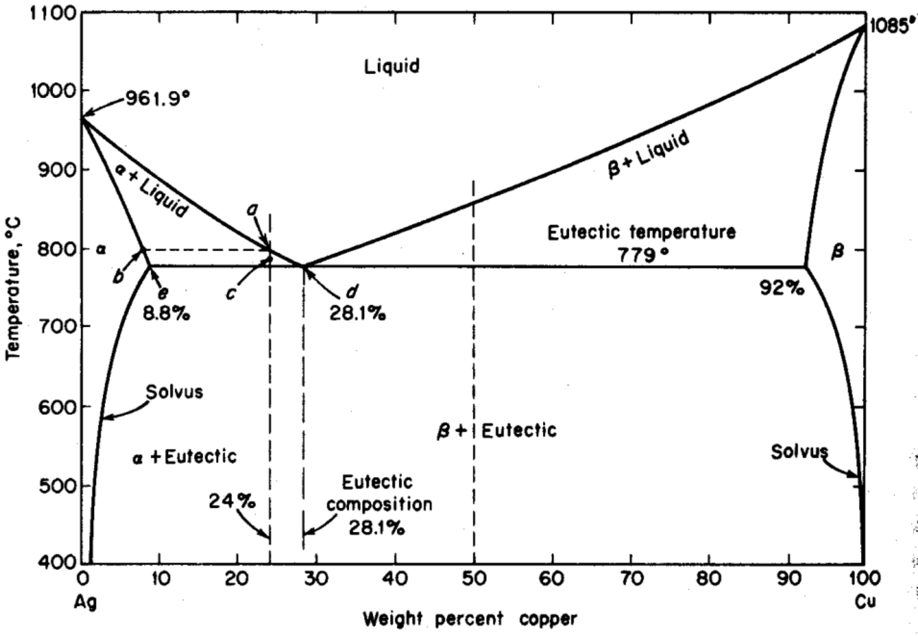
- At constant pressure and temp. the compositions of the phases are fixed.
- The partial-molal free energies of each component be the same in both phases at equilibrium.

$$\overline{G}_A^\alpha = \overline{G}_A^\beta$$

$$\overline{G}_B^\alpha = \overline{G}_B^\beta$$

Two-components systems with three phases in equilibrium

- In two-component systems, three phases in equilibrium occur only under constant temp., pressure, and compositions.
- Ex. Three-phase reaction: Cu-Ag alloy phase diagrams



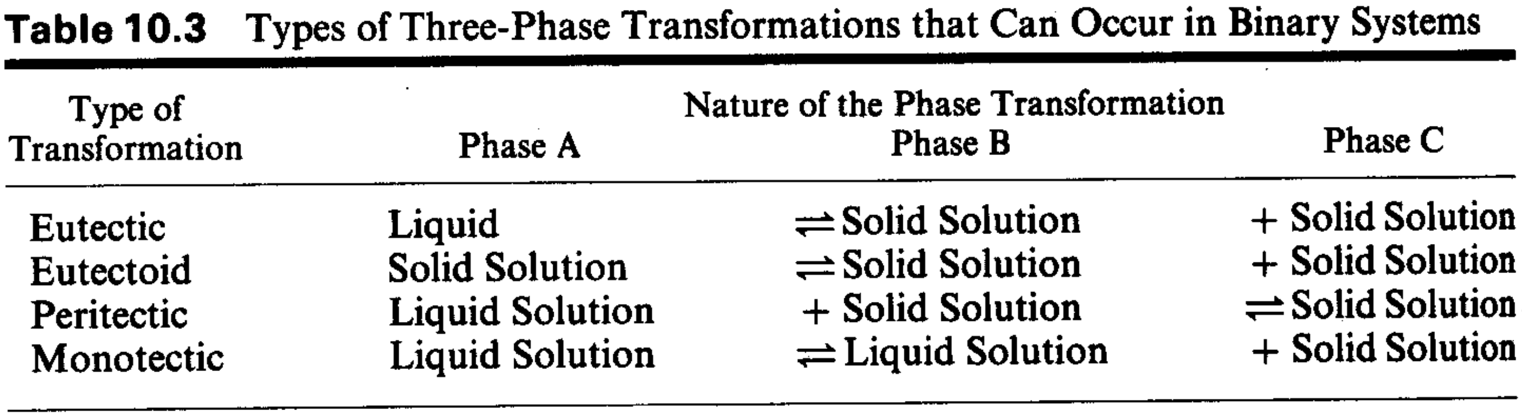
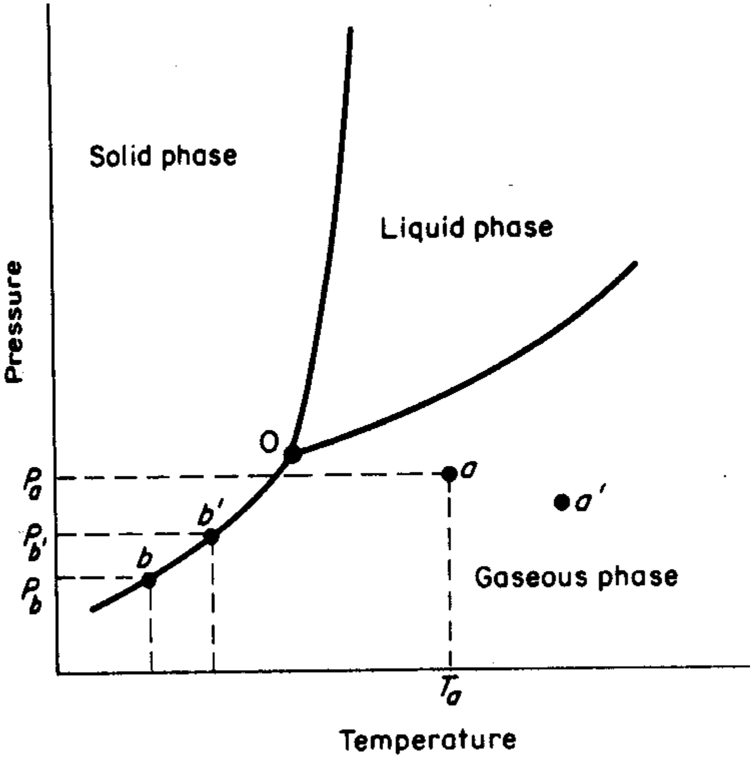


Table 10.3 Types of Three-Phase Transformations that Can Occur in Binary Systems

Type of Transformation	Nature of the Phase Transformation Phase A	Phase B	Phase C
Eutectic	Liquid	⇌ Solid Solution	+ Solid Solution
Eutectoid	Solid Solution	⇌ Solid Solution	+ Solid Solution
Peritectic	Liquid Solution	+ Solid Solution	⇌ Solid Solution
Monotectic	Liquid Solution	⇌ Liquid Solution	+ Solid Solution

Phase rule

$$P + F = C + 2$$



A single-component phase diagram

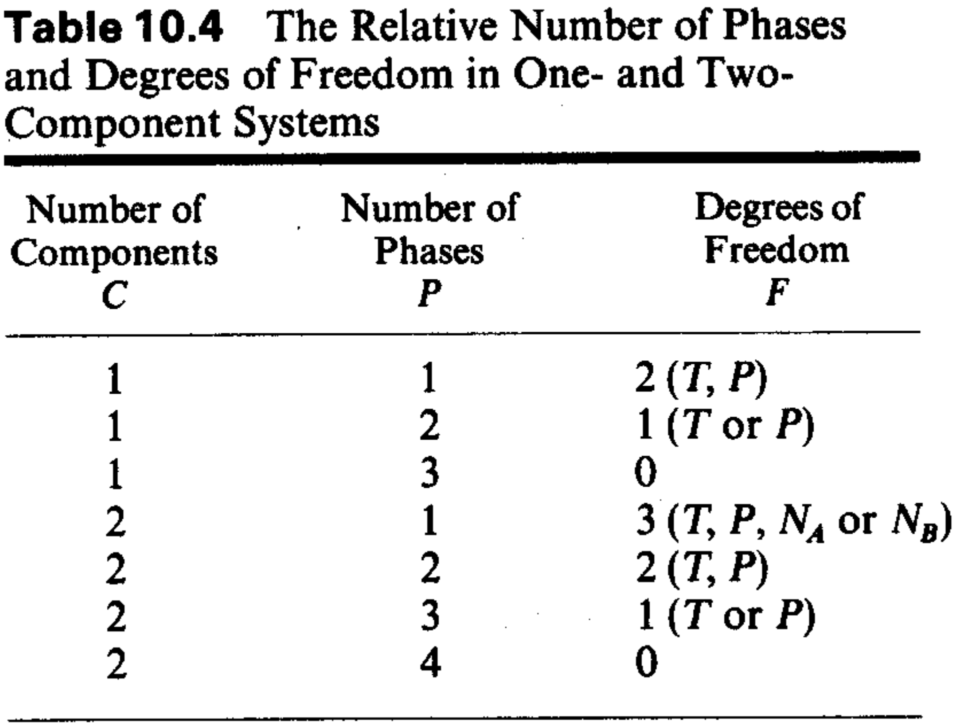
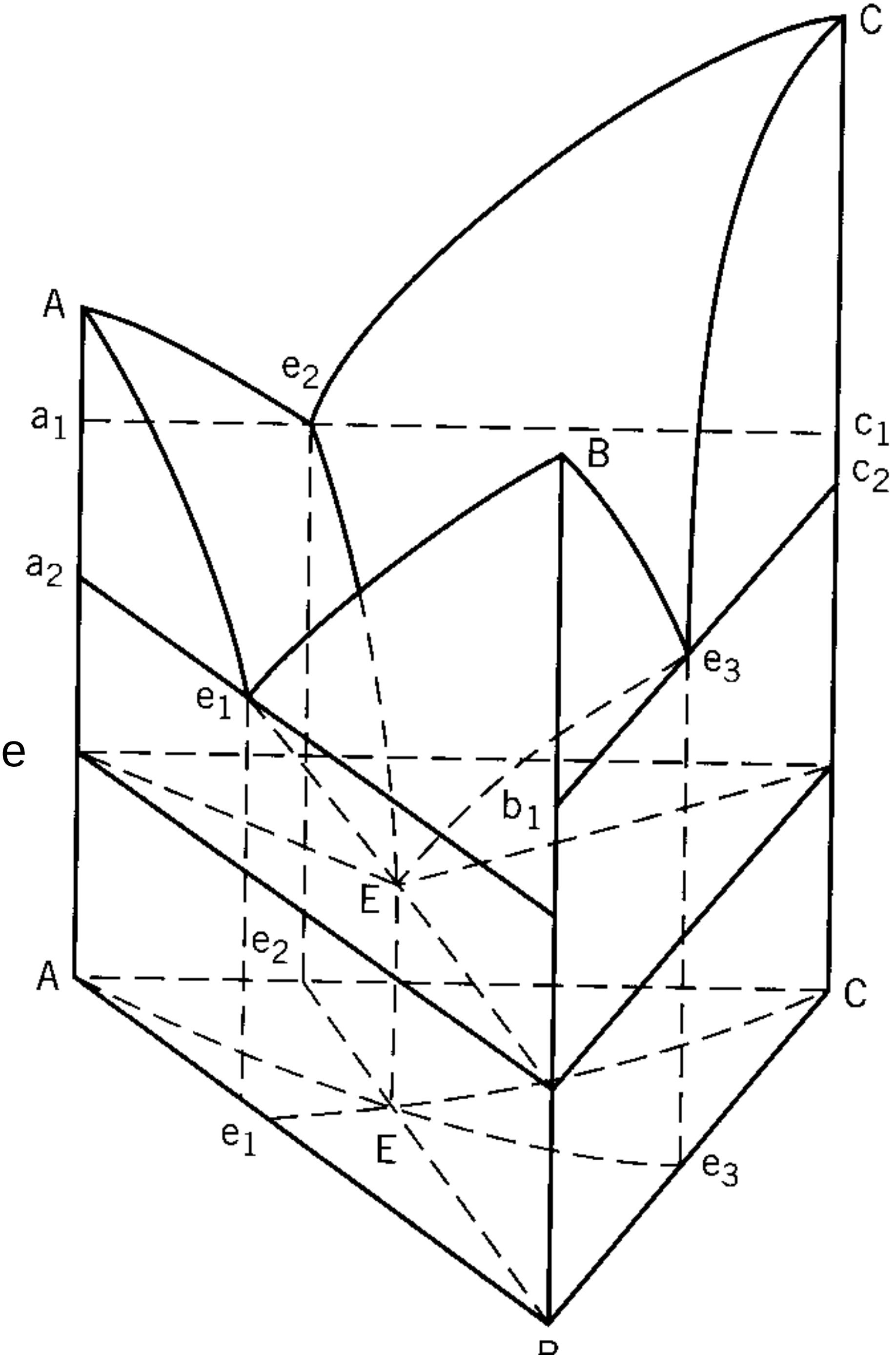


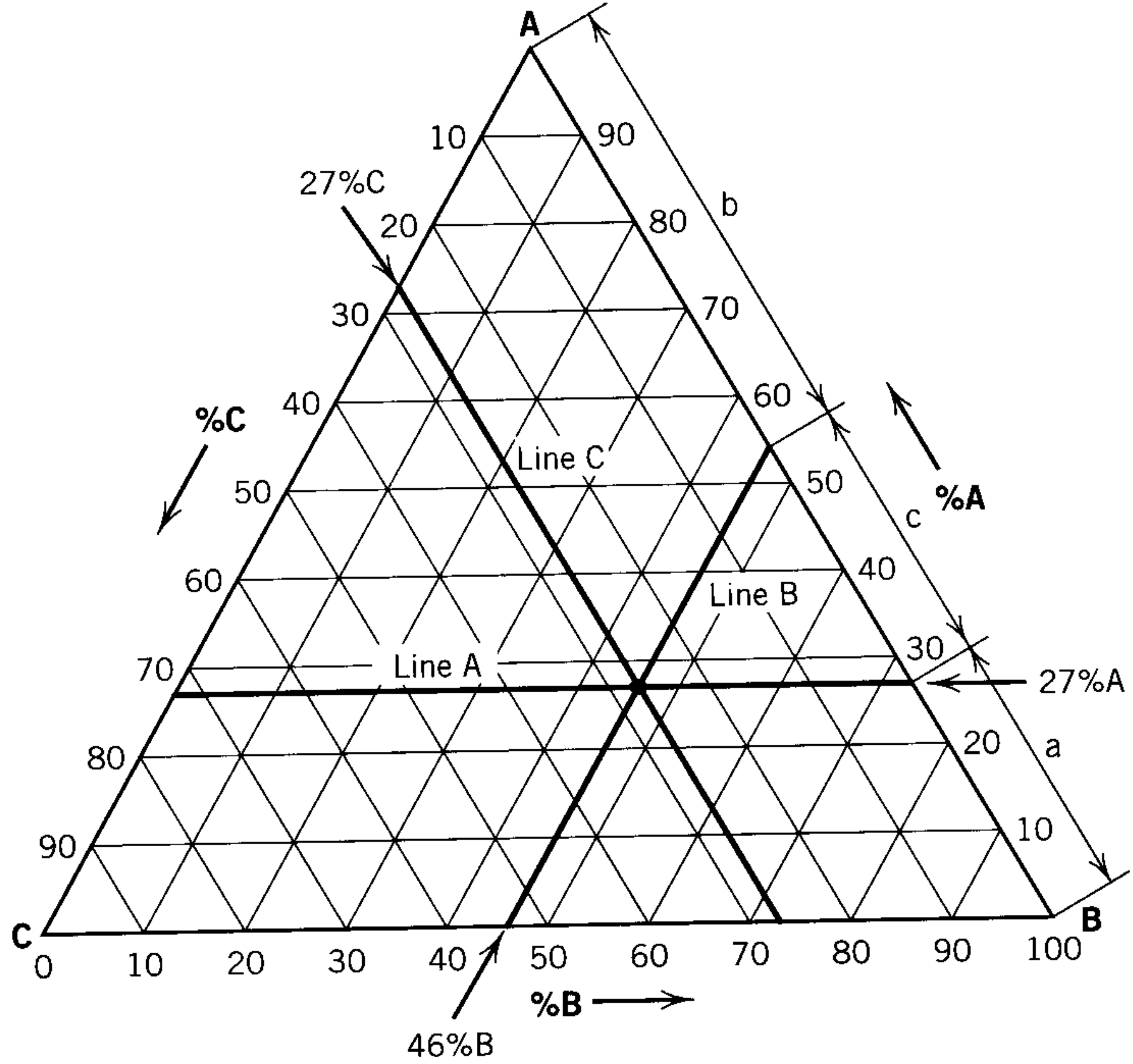
Table 10.4 The Relative Number of Phases and Degrees of Freedom in One- and Two-Component Systems

Number of Components C	Number of Phases P	Degrees of Freedom F
1	1	2 (T, P)
1	2	1 (T or P)
1	3	0
2	1	3 (T, P, N_A or N_B)
2	2	2 (T, P)
2	3	1 (T or P)
2	4	0

Ternary phase diagram



The vertical axis is temperature


A
B
C
10
20
30
40
50
60
70
80
90
100
0
27%C
27%A
46%B
%A
%B
%C
b
c
a
Line A
Line B
Line C

27%A – 46%B – 27%C

Crystalline Phases

Notation	Oxide Formula
Cristobalite Tridymite	SiO_2
Fayalite	$2FeO \cdot SiO_2$
Wüstite	"FeO"
Hercynite	$FeO \cdot Al_2O_3$
Corundum	Al_2O_3
Mullite	$3Al_2O_3 \cdot 2SiO_2$
Iron Cordierite	$2FeO \cdot 2Al_2O_3 \cdot 5SiO$

Temperatures up to approximately 1550° (are on the Geophysical Laboratory Scale; those above 1550° C are on the 1948 International Scale.