Equilibrium Phase Diagram

Contents

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Phase:

Phase is a region of space (a thermodynamic system), throughout which all physical properties of a material are essentially uniform. Examples of physical properties include density, index of refraction, magnetization and chemical composition. A simple description is that a phase is a region of material that is chemically uniform, physically distinct, and (often) mechanically separable. In a system consisting of ice and water in a glass jar, the ice cubes are one phase, the water is a second phase, and the humid air is a third phase over the ice and water. The glass of the jar is another separate phase.

Phase Diagram:

Phase diagram are graphical representations of what phases are present in a materials system at various temperature, pressure, and compositions. Most phase diagrams are constructed by using equilibrium conditions and are used by engineers and scientists to understand and predict many aspects of the behavior of materials.

Necessity of phase diagram (Information obtained from p.d.):

- To show what phases are present at different composition and temperature in equilibrium condition.
- To indicate the equilibrium solid solubility of one element in another
- To indicate the temperature at which an alloy cooled under equilibrium condition starts to solidify and the temp range over which solidify
- To indicate the temperature at which different phases starts to melt.

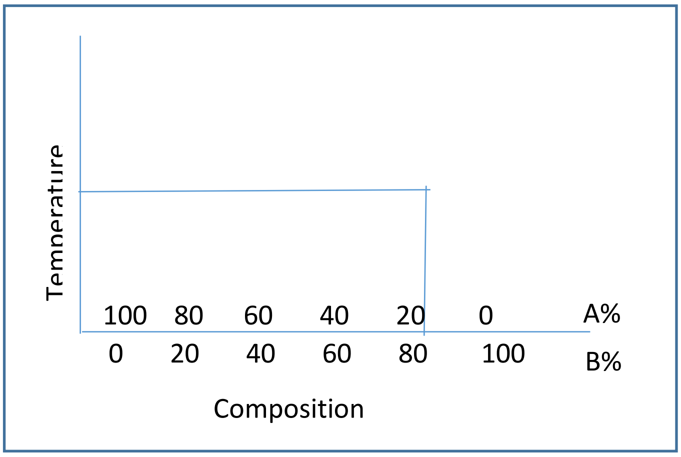


Fig. 1

Solid Solution:

A solid solution is a solid that consists of two or more elements atomically dispersed in a single-phase structure. The solid solution is solid state solution of one or more solutes in a solvent, such a mixture is considered as solution rather than a compound. The crystal structure of the solvent remains unchanged by addition of the solutes. The mixture remains in a single homogeneous phase. A homogeneous mixture of two of more crystalline metals in varying properties is known as solid solution.

$$\text{Solvent + Solute} \longrightarrow \text{Solid Solution}$$

Example: Brass (70% Cu and 30% Zn), Inconel-600, Inconel-617, Inconel-718 (Different percentage of Ni, Cr, Fe, Mo, Nb, Ta, Co, Mn, Cu, Al, Si, C, S, P, B)

In general there are two types of solid solution:

a) **Substitutional solid solution**
b) **Interstitial solid solution**

a) **Substitutional solid solution:** In this solid solution solute atoms of one elements can replace the solvent atom. The crystal structure of the parent element or solvent is unchanged. In this solid solution the crystal structure of both elements must be the same and the atomic size must not differ by more than 15%. Cu (140 pm) and Ni (163 pm) are mutually soluble in all proportion to form substitutional solid solution.

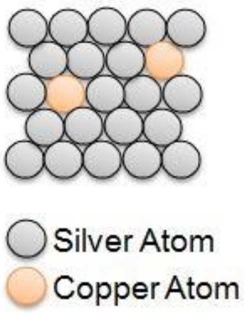


Fig. 2: Substitutional solid solution

Hume-Rothery Rules:

The fraction of atoms of one element that can dissolve in another can vary from a fraction of atomic percent to 100 percent. The following conditions, known as *Hume-Rothery* rules, are favorable for extensive solid solubility of one element in another:

Atomic Size: The diameter of the atoms of the elements must not differ by more than about 15%.

Crystal Structure: The crystal structure of the two elements must be the same.

Electronegativity: There should be no appreciable difference in the electronegativities of the two elements so that compounds will not form.

Valence: The two elements should have the same valence.

b) **Interstitial solid solution:** In this solution the solute atoms take spaces between the atoms of the solvent or parent element. The spaces are called interstices. It can form when one atom is much longer than the other. If the size of solute is 40% less than that of solvent atom then it interstitial solid solution may be formed. Examples of atoms that can form interstitial solid solution due to their small size are H, C, N and O. Carbon (70 pm) in iron (steel) (126 pm) is one example of interstitial solid solution.

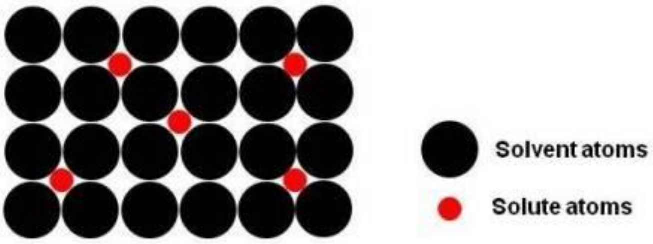


Fig. 3: Interstitial solid solution

Gibbs Phase Rule:

From thermodynamic considerations, J.W. Gibbs derived and equation that computes the number of phases that can coexist in equilibrium in a chosen system. This equation, called Gibbs phase rule, is

$$P + F = C + 2 \tag{1}$$

Where, P= number of phases that coexist in a chosen system

C= number of components in the system

F= degrees of freedom

Usually a component C is the number of element, compound or solution in the system. F is the Degrees of freedom, is the number of variables (pressure, temperature and composition) that can be changed independently without changing the number of phases in equilibrium in the chosen system. The factor 2 comes from the two intensive parameters, temperature and pressure.

*An **extensive parameter**, like Internal Energy (U), Entropy (S), Volume (V), or Number of Particles (N), are **parameters** that 'scale with the system'. ... An **intensive parameter**, like temperature (T), pressure (P), or chemical potential (μ), are **parameters** that DON'T 'scale with the system'.*

Single Component Phase Diagram:

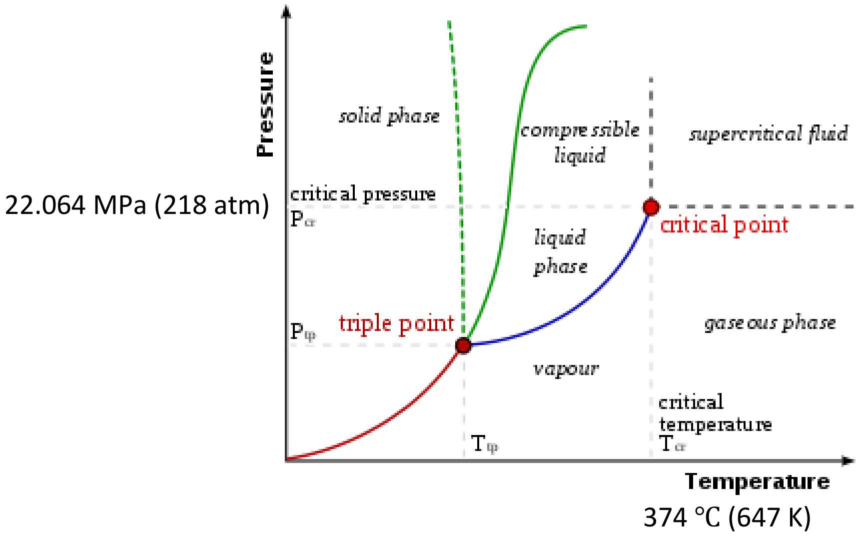


Fig. 4: PT phase diagram of pure water

*A **supercritical fluid** (SCF) is any substance at a temperature and pressure above its critical point, where distinct **liquid** and gas phases do not exist. It can effuse through solids like a gas, and dissolve materials like a **liquid**.*

Let us consider the application of Gibbs phase rule to the PT phase diagram of pure water (Fig. 4) . At the triple point, three phases coexist in equilibrium, and since there is one component in the system (water), the number of degrees of freedom can be calculated as

$$P + F = C + 2$$

$$3 + F = 1 + 2$$

$$F = 0 \qquad \text{(zero degrees of freedom)}$$

Since none of the variables (temperature or pressure) can be changed and still keep the three phases in balance, the triple point is called **invariant point.**

Consider next a point along the liquid-solid freezing curve of the Fig.4. At any point along this line, two phases will coexist. Thus. From the phase rule,

$$2 + F = 1 + 2$$

$$F = 1 \qquad \text{(one degrees of freedom)}$$

This result tells us that there is one degree of freedom, and thus one variable (T or P) can be changed independently and still maintain a system with two coexisting phases. Thus, if a particular pressure is specified, there is only one temperature at which both liquid and solid phases can coexist.

For third case, consider a point on the PT phase diagram inside a single phase. Then there will be only one phase present (p=1), and substituting into the phase-rule equation gives

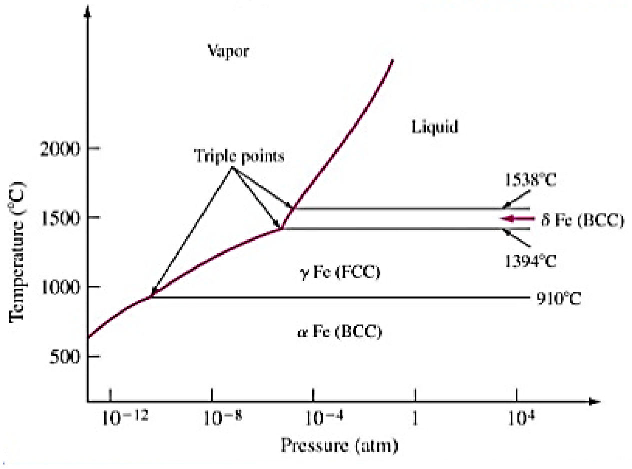
$$1 + F = 1 + 2$$

$$F = 2 \qquad \text{(two degrees of freedom)}$$

This result tells us that two variables (temperature and pressure) can be varied independently and the system will remain in a single phase.

Most binary phase diagrams used in materials science are temperature-composition diagram in which pressure is kept constant, usually at 1 atm. In this case, we have the condensed phase rule, which given by

$$P + F = C + 1$$



3 Solid Phases

1. α Fe (BCC)
2. γ Fe (FCC)
3. δ Fe (BCC)

Fig. 5: PT phase diagram of pure iron

One major characteristic of equilibrium PT phase diagram of pure iron is, there are three separate and distinct solid phases: alpha (α) Fe, gamma (γ) Fe and delta (δ) Fe. Alpha and delta iron have BCC crystal structures whereas gamma iron has an FCC structure. The phase boundaries in the solid state have the same properties as the liquid and solid phase boundaries. For example, under equilibrium conditions, alpha and gamma iron can coexist at a temperature of 910 ℃ and 1 atm pressure and so on. There are also **three** triple points in the iron PT diagram where three different phases coexist: liquid – vapor - δ Fe, vapor - δ Fe - γ Fe, vapor - δ Fe - α Fe.

At atmospheric pressure, three allotropic forms of iron exist: alpha iron (α), gamma iron (γ) (also known as austenite), and delta iron (δ). At very high pressure, a fourth form exists, called epsilon iron (ε) hexaferrum. β-Fe is crystallographically identical to α-Fe, except for magnetic domains and the expanded body-centered cubic lattice parameter as a function of temperature, and is therefore of only minor importance in steel heat treating. For this reason, the beta "phase" is not usually considered a distinct phase but merely the high-temperature end of the alpha phase field.

Binary Isomorphous Phase Diagram (Cu, Ni):

A mixture of two metals is called a binary alloy and constitutes a two-component system since each metallic element in an alloy is considered a separate component. Thus, pure copper is a one-component system, whereas an alloy of copper and nickel is a two-component system. Sometimes a compound in an alloy is also considered a separate component. For example, plain-carbon steels containing mainly iron and iron carbide are considered two-component systems.

In some binary metallic systems, the two elements are completely soluble in each other in both the liquid and solid states. In these systems, only a single type of crystal structure exists for all compositions of the components, and therefore they are called isomorphous systems. In order for the two elements to have complete solid solubility in each other, they usually satisfy one or more of the conditions of the Hume-Rothery solid solubility rules. Though the Hume-Rothery rules are not all applicable for every pair of elements that shows complete solid solubility.

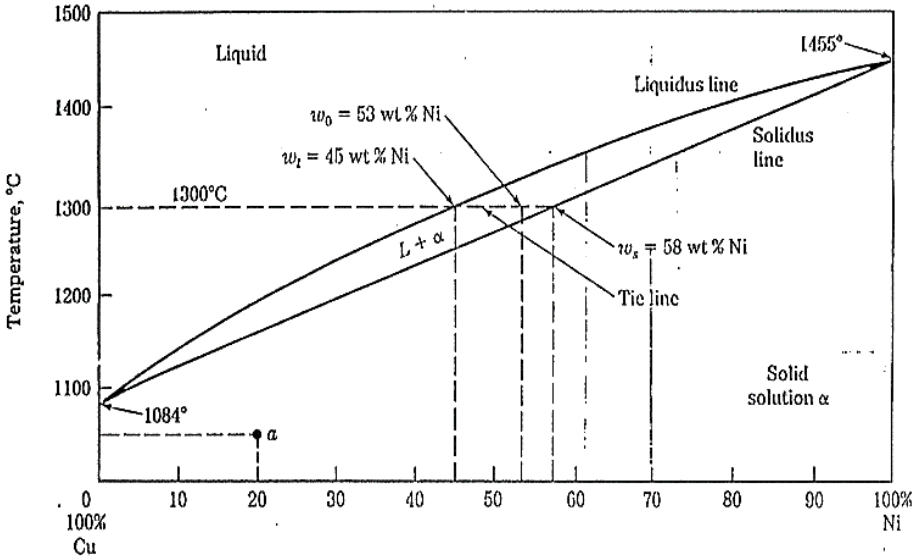


Fig. 6: The copper-nickel phase diagram.

An important example of an isomorphous binary alloy system is the copper-nickel system. A phase diagram of this system with temperature as the ordinate and chemical composition in weight percent as the abscissa is shown in Fig. 6. This diagram has been determined for slow cooling or equilibrium conditions at atmospheric pressure and does not apply to alloys that have been rapidly cooled through the solidification temperature range. The area above the upper line in the diagram, called the **liquidus**, corresponds to the region of stability of the liquid phase, and the area below the lower line, or **solidus**, represents the region of stability for the solid phase. The region between the liquidus and solidus represents a two-phase region where both the liquid and solid phases coexist. For the binary isomorphous phase diagram of Cu and Ni, according to the Gibbs phase rule ($F = C - P + 1$), at the melting point of the pure components, the number of components C is 1 (either Cu or Ni) and the number of phases available P is 2 (liquid or solid), resulting in a degree of freedom of 0 ($F = 1-2 + 1 = 0$). These points are referred to as invariant points ($F = 0$). This means that any change in temperature will change the microstructure either into solid or liquid. Accordingly, in the single-phase regions (liquid or solid), the number of components, C, is 2 and the number of phases available, P, is 1, resulting in a degree of freedom of 2 ($F = 2 - 1 + 1 = 2$). This means that we can maintain the microstructure of the system in this region by varying either the temperature or composition independently. In the two-phase region, the number of components, C, is 2 and the number of phases available, P, is 2, resulting in a degree of freedom of 1 ($F = 2 - 2 + 1 = 1$). This means that only one variable (either temperature or composition) can be changed independently while maintaining the two-phase structure of the system. If the temperature is changed, the phase composition will also change.

In the single-phase region of solid solution α, both the temperature and the composition of the alloy must be specified in order to locate a point on the phase diagram. For example, the temperature 1050°C and 20 percent Ni specify the point a on the Cu-Ni phase diagram of Fig. 6. The microstructure of solid solution α at this temperature and composition appears the same as that of a pure metal, i.e., the only observable feature in the optical microscope will be grain boundaries. However, because the alloy is a solid solution of 20 percent Ni in copper, the alloy will have higher strength and electrical resistivity than pure copper.

In the region between the liquidus and solidus lines, both liquid and solid phases exist. The amount of each phase present depends on the temperature and chemical composition of the alloy. Let us consider an alloy of 53 wt % Ni-47 wt % Cu at 1300°C in Fig. 6. Since this alloy contains both liquid and solid phases at 1300°C, neither of these phases can have the average composition of 53% Ni-47% Cu. The compositions of the liquid and solid phases at 1300°C can be determined by drawing a horizontal **tie line** at 1300°C from the liquidus line to the solidus line and then dropping vertical lines to the horizontal composition axis. The composition of the liquid phase (w_l) at 1300°C is 45 wt % Ni and that of the solid phase (w_s) is 58 wt % Ni, as indicated by the intersection of the dashed vertical lines with the composition axis.

Binary equilibrium phase diagrams for components that are completely soluble in each other in the solid state can be constructed from a series of liquid-solid cooling curves, as shown for the Cu-Ni system in Fig. 7. As discussed in the previous section, the cooling curves for pure metals show horizontal thermal arrests at their freezing points, as shown for pure copper and nickel in Fig. 7a at AB and CD. Binary solid solutions exhibit slope changes in their cooling curves at the liquidus and

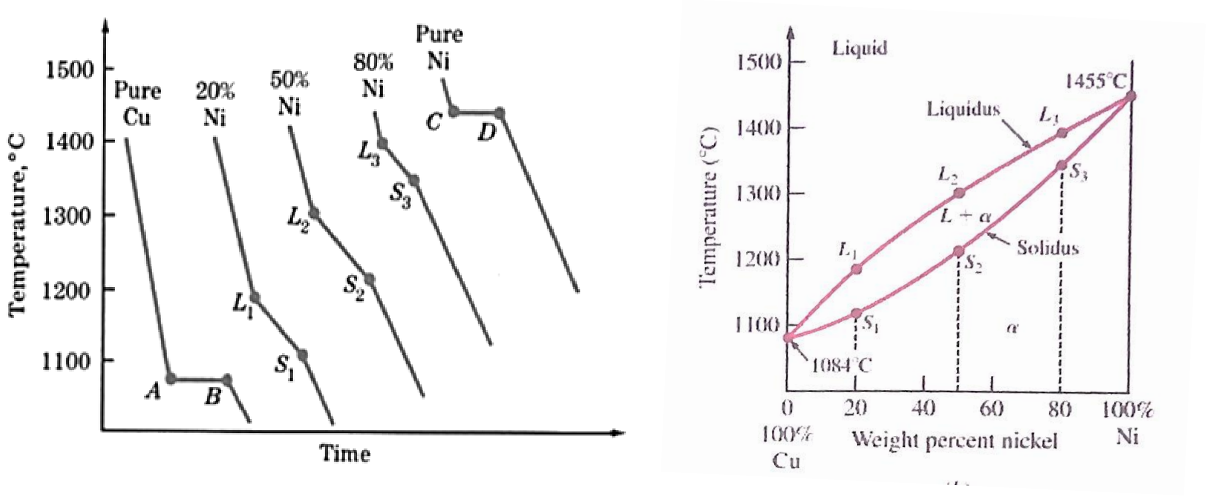


Fig. 7: Construction of the Cu-Ni equilibrium phase diagram from liquid-solid cooling curves.

solidus lines, as shown in Fig. 7 at compositions of 80% Cu-20% Ni, 50% Cu-50% Ni, and 20% Cu-80% Ni. The slope changes at L_1, L_2, and L_3 in Fig. 7a correspond to the liquidus points L_1, L_2, and L_3 of Fig. 7b. Similarly, the slope changes of S_1, S_2, and S_3 of Fig. 7a correspond to the points of S_1, S_2, and S_3 on the solidus line of Fig. 7b. Further accuracy in the construction of the Cu-Ni phase diagram can be attained by determining more cooling curves at intermediate alloy compositions. The cooling curve for metal alloys in an isomorphous system does not contain the thermal arrest region that one observes in the solidification of a pure metal. Instead, solidification begins at a specific temperature and ends at a lower temperature as presented by L and S symbols in Fig. 7. As a result, unlike pure metals, alloys solidify over a range of temperatures. Thus, when we refer to the freezing temperature of a metal alloy, we are speaking of the temperature at which the solidification process is complete.

Tie Line:

An isothermal (constant temperature) line through the alloy's position on the phase diagram when it is in a two phase field, intersecting the two adjacent solubility curves, is called a tie line.

The Lever Rule

The weight percentages of the phases in any two-phase region of a binary equilibrium phase diagram can be calculated by using the lever rule. For example, by using the lever rule, the weight percent liquid and weight percent solid for any particular temperature can be calculated for any average alloy composition in the two-phase liquid-plus-solid region of the binary copper-nickel phase diagram of Fig. 6.

The fraction of a phase having a composition indicated by one end of the lever is equal to the ratio of the length of the lever of the other side of the fulcrum to the total length of the lever.

wt fraction of solid phase = ` $\mathbf{X_S} = \frac{w_0 - w_l}{w_s - w_l}$

wt fraction of liquid phase = $\mathbf{X_l} = \frac{w_s - w_o}{w_s - w_l}$

To derive the lever-rule equations, let us consider the binary equilibrium phase diagram of two elements A and B that are completely soluble in each other, as shown in Fig. 8. Let x be the alloy composition of interest and its weight fraction of B in A be w_0. Let T be the temperature of interest, and let us construct a tie line (LS) at temperature T from the liquidus at point L to the solidus line at point S, forming the tie line LOS. At temperature T, the alloy x consists of a mixture of liquid of w_l weight fraction of B and solid of w_s weight fraction of B.

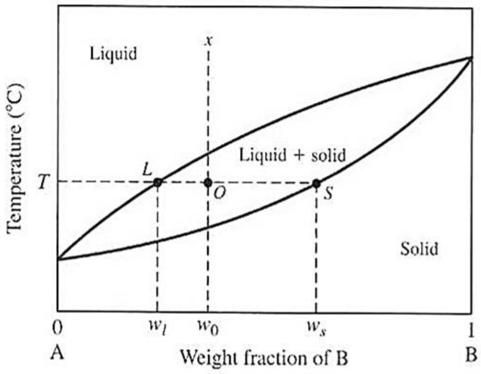


Fig. 8: Binary phase diagram of two metals A and B completely soluble in each other being used to derive the lever-rule equations. At temperature T, the composition of the liquid phase is w_l and that of the solid is w_s.

The lever-rule equations can be derived by using weight balances. One equation for the derivation of the lever-rule equations is obtained from the fact that the sum of the weight fraction of the liquid phase, X_l, and the weight fraction of the solid phase, X_S must equal 1. Thus,

$$X_l + X_S = 1$$

$$\text{or } X_l = 1 - X_S$$

$$\text{and } X_S = 1 - X_l$$

A second equation for the derivation of the lever rule can be obtained by a weight balance of B in the alloy as a whole and the sum of B in the two separate phases. Let us consider 1 g of the alloy, and make this weight balance:

$$\begin{matrix}\text{Grams of B in} & & \text{Grams of B in} & & \text{Grams of B in}\\ \text{two-phase mixture} & = & \text{liquid phase} & + & \text{solid phase}\end{matrix}$$

$$\overbrace{(1\text{ g})}^{\substack{\text{Grams of two-}\\ \text{phase mixture}}}\ \underbrace{(1)}_{\substack{\text{wt fraction of}\\ \text{phase mixture}}}\ \underbrace{\left(\frac{\%\,w_0}{100}\right)}_{\substack{\text{Average wt fraction of B}\\ \text{in phase mixture}}} \qquad \overbrace{(1\text{ g})}^{\substack{\text{Grams of liquid}\\ \text{phase}}}\ \underbrace{(X_l)}_{\substack{\text{wt fraction of}\\ \text{liquid phase}}}\ \underbrace{\left(\frac{\%\,w_l}{100}\right)}_{\substack{\text{wt fraction of B in liquid}\\ \text{phase}}} \qquad \overbrace{(1\text{ g})}^{\substack{\text{Grams solid}\\ \text{phase}}}\ \underbrace{(X_S)}_{\substack{\text{wt fraction of}\\ \text{solid phase}}}\ \underbrace{\left(\frac{\%\,w_s}{100}\right)}_{\substack{\text{wt fraction of B in}\\ \text{solid phase}}}$$

Thus, $w_0 = X_l w_l + X_S w_s$

combined with $X_l = 1 - X_S$

gives $w_0 = (1 - X_S) w_l + X_S w_s$

Or $w_0 = w_l - X_S w_l + X_S w_s$

Rearranging, $X_S w_s - X_S w_l = w_0 - w_l$

wt fraction of solid phase = `

$$\mathbf{X_S} = \frac{\boldsymbol{w_0 - w_l}}{\boldsymbol{w_s - w_l}} \qquad (1)$$

Similarly, $w_0 = X_l w_l + X_S w_s$

combined with $X_S = 1 - X_l$

gives, wt fraction of liquid phase =

$$\mathbf{X_l} = \frac{\boldsymbol{w_s - w_o}}{\boldsymbol{w_s - w_l}} \qquad (2)$$

Equations 1 and 2 are the lever-rule equations. Effectively, the lever-rule equations state that to calculate the weight fraction of one phase of a two-phase mixture, one must use the segment of the tie line that is on the opposite side of the alloy of interest and is farthest away from the phase for which the weight fraction is being calculated. The ratio of this line segment of the tie line to the total tie line provides the weight fraction of the phase being determined. Thus, in Fig. 8, the weight fraction of the liquid phase is the ratio OS/LS, and the weight fraction of the solid phase is the ratio LO/LS. Weight fractions can he converted to weight percentages by multiplying by 100 percent

Problem: A copper-nickel alloy contains 47 wt % Cu and 53 wt % Ni and is at 1300 ℃. Use Fig. 6 and answer the following:

a. What is the weight percent of copper in the liquid and solid phase at this temperature e?
b. What weight percent of this alloy is liquid and what weight percent is solid?

Sol^n:

a) From Fig. 6, at 1300 ℃, the intersection of 1300 ℃ tie line with the liquidus line gives 55 wt % Cu in the liquid phase and intersection of the solidus line of the given temp gives the 42 wt % Cu in the solid phase.
b) From Fig. 6 and using the lever rule on the 1300 ℃ tie line,

$w_o = 53$ % Ni $\qquad$ $w_l = 45$ % Ni $\qquad$ $w_s = 58$ % Ni

wt fraction of solid phase = $X_s = \frac{53 - 45}{58 - 45} = 0.62 = 62\ \%$

wt fraction of liquid phase = $X_l = \frac{58-53}{58-45} = 0.38 = 38\%$

Binary Eutectic Alloy Systems

When two substances forming the solid solution are soluble in liquid phase and insoluble in solid phase then it is found that, the freezing point of one substance is lowered by addition of other substance to the mixture. The minimum freezing point for a composition is called eutectic point and a composition at this point is called eutectic composition.

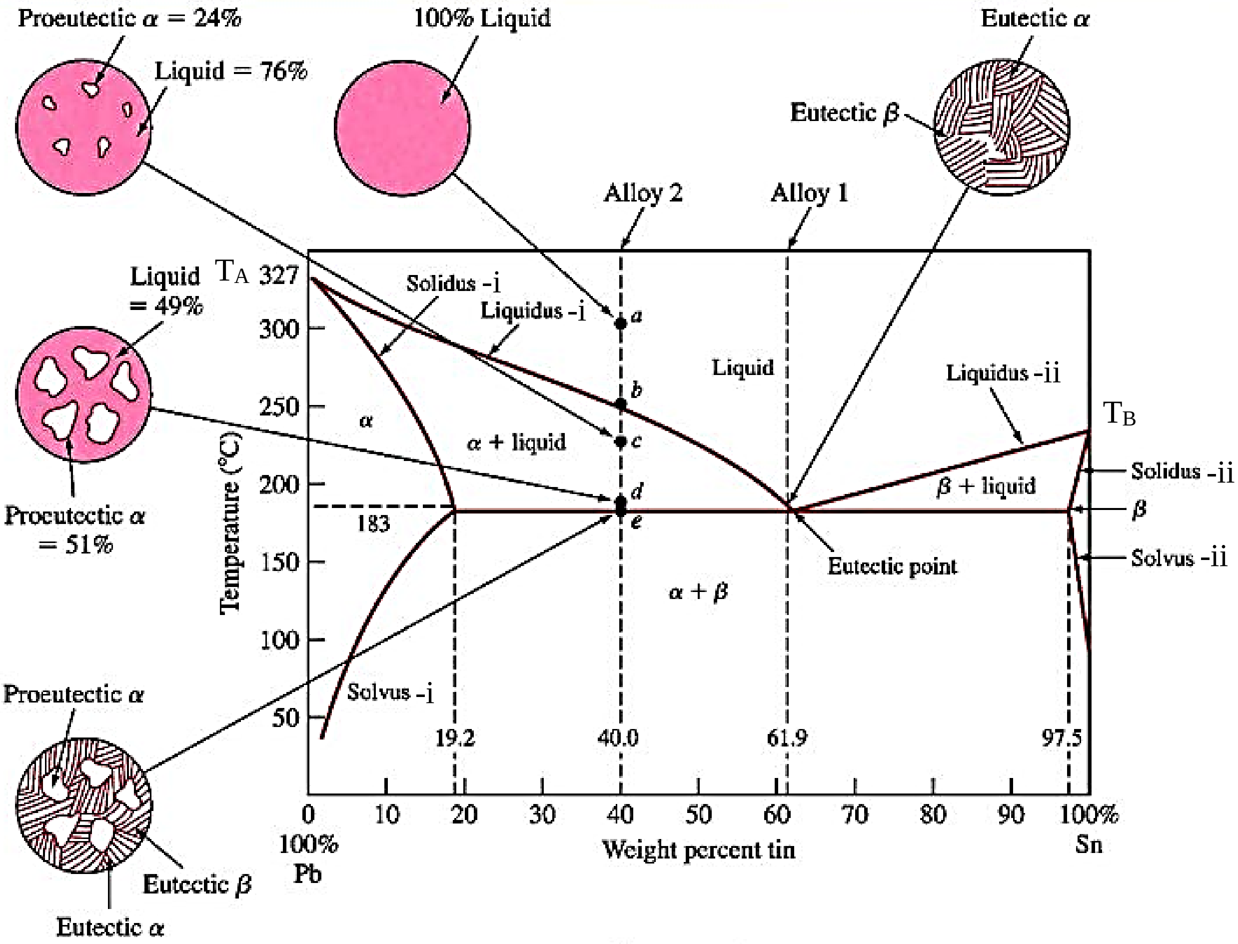


Fig. 9: The lead-tin equilibrium phase diagram. This diagram is characterized by the limited solid solubility of each terminal phase (α and β). The eutectic invariant reaction at 61.9% Sn and 183 °C is the most important feature of this system.

As there is complete liquid solubility, the liquid phase extends overall composition above the melting temperatures, T_A and T_B of the components A (Pb) and B (Sn). The solid phase at the left end is A-rich, designated by α, which dissolves only in a limited amount of B. This solubility decreases with decreasing temperature. The solid solution at the right end is B-rich, designated by β, which dissolves only a very small amount of A in it.

The phase boundaries between α and $\alpha + \beta$ regions and between β and $\alpha + \beta$ regions are called solvus lines.

Liquidus-i: Boundary between L and L+ α
Liquidus-ii: Boundary between L and L+ β

Solidus-i: Boundary between α and L+ α
Solidus-ii: Boundary between β and L+ β

Solvus-i: Boundary between α and $\alpha + \beta$
Solvus-ii: Boundary between β and $\alpha + \beta$

In simple binary eutectic systems like the Pb-Sn one, there is a specific alloy composition known as the eutectic composition that freezes at a lower temperature than all other compositions. This low temperature, which corresponds to the lowest temperature at which the liquid phase can exist when cooled slowly, is called the eutectic temperature. In the Pb-Sn system, the eutectic composition (61.9 percent Sn and 38.1 percent Pb) and the eutectic temperature (183°C) determine a point on the phase diagram called the eutectic point. When liquid of eutectic composition is slowly cooled to the eutectic temperature, the single liquid phase transforms simultaneously into two solid forms (solid solutions α and β). This transformation is known as the eutectic reaction and is written as

$$\text{Liquid} \xrightarrow[\text{Cooling}]{} \alpha \text{ solid solution} + \beta \text{ solid solution}$$

The eutectic reaction is called an invariant reaction since it occurs under equilibrium conditions at a specific temperature and alloy composition that cannot be varied (according to Gibbs rule, F = 0). During the progress of the eutectic reaction, the liquid phase is in equilibrium with the two solid solutions α and β, thus during a eutectic reaction, three phases coexist and are in equilibrium. Since three phases in a binary phase diagram can only be in equilibrium at one temperature, a horizontal thermal arrest appears at the eutectic temperature in the cooling curve of an alloy of eutectic composition.

Compositions to the left of the eutectic point arc called **hypoeutectic**, Fig. 9. Conversely, compositions to the right of the eutectic point are called **hypereutectic**.

Consider the slow cooling of a 40% Sn-60% Pb alloy from the liquid state at 300°C to room temperature. As the temperature is lowered from 300°C (point a), the alloy will remain liquid until the liquidus line is intersected at point b at about 245°C. At this temperature, solid solution a containing 12 percent Sn will begin to precipitate from the liquid. The first solid to form in this type of alloy is called **primary** or **proeutectic** alpha. The term proeutectic alpha is used to distinguish this constituent from the alpha that forms later by the eutectic reaction.

Hume-Rothery electron compounds:

Hume-Rothery pointed out that, the number of electron to number of atom ratio is approximately the same for a given phase of different alloy. For elements excepting the transition metals (Fe, Co, Ni) the number of valence electrons are counted. Valence electron for transition metals are not counted but only their number of atoms are taken into consideration. For example, Fe-Al will give β phase with Hume-Rothery ration 3:2. In Fe-Ni alloy both are transition metals and the ration cannot be calculated.

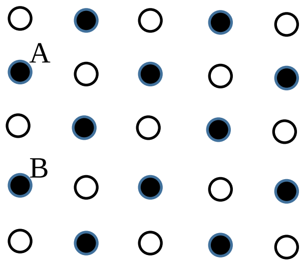
Table-1: Compositon and electron to atom ratio for structurally analogous phases

Electron to atom ratio 3:2 β structure (bcc)	Electron to atom ratio 21:13 γ structure (complex cubic)	Electron to atom ratio 7:4 ϵ structure (hcp)
CuZn	Cu_5Zn_8	$CuZn_3$
CuBe	Cu_5Cd_8	$CuCd_3$
Cu_3Al	Cu_9Al_4	Cu_3Ge
Cu_5Sn	Au_5Cd_8	$AgZn_3$
AgCd	Ag_5Cd_8	Ag_3Sn
AgMg	Cu_3Si_8	$AuZn_3$

Since the phases have a certain range of composition over which they are stable, the chemical formulas and the electron to atom ratios given in the table are approximate. For the alloy given in the table the electron to atom ratios are calculated on the basis of the normal number of valence electrons associated with the atoms involved.

Ordered and Disordered Phases of a Cyrstal:

Let us consider an alloy composed of equal numbers of A-atoms and B-atoms. This alloy is said to be ordered if the A-atoms and B-atoms have a regular periodic arrangement with respect to one another.



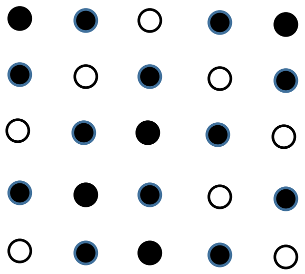
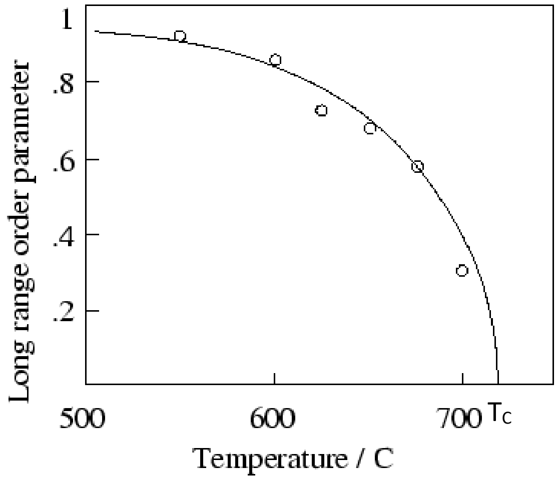


Fig. 10: Ordered AB alloy **Fig. 11:** Disordered AB alloy

An ordered phase means long range order and is spread up to several interatomic distances in the lattice. Disordered means disappearance of long range order, although there may be still some short range order in a disordered lattice. In the common ordered arrangement of an A-B alloy with a bcc structure all the nearest neighbors of a B-atoms are A-atoms and vice-versa. Temperature may be the principle factor which may make the crystal disordered from an ordered state. The crystal is completely ordered at absolute zero. As the temperature increase the orderedness decreases and at above certain transition temperature T_c the crystal is fully disordered.



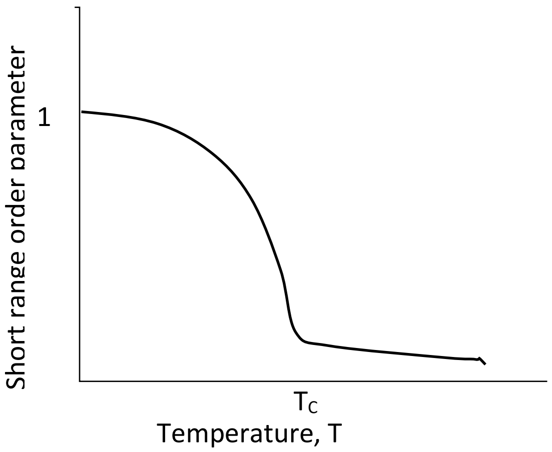


Fig. 12: Long-range order in A-B alloy **Fig. 13:** Long-range order in A-B alloy

The ordered structure may be viewed as being made up of two interpenetrating sublattices, on one of which, called the α sublattice, on which the A atoms reside and on the other hand the β sublattice, on which the B atoms reside. Each site is surrounded by eight equidistant sites. If this ordered arrangement of the atoms extends over thousands of atom diameters, it represents perfect long-range order. It should be noted that in the perfectly ordered condition the space lattice is no longer bcc, since the positions occupied by the A atoms no longer have surroundings equivalent to those occupied by the B atoms. In fact the structure shown in fig bellow is characterized by a simple cubic space lattice with an AB atom pair with each lattice point

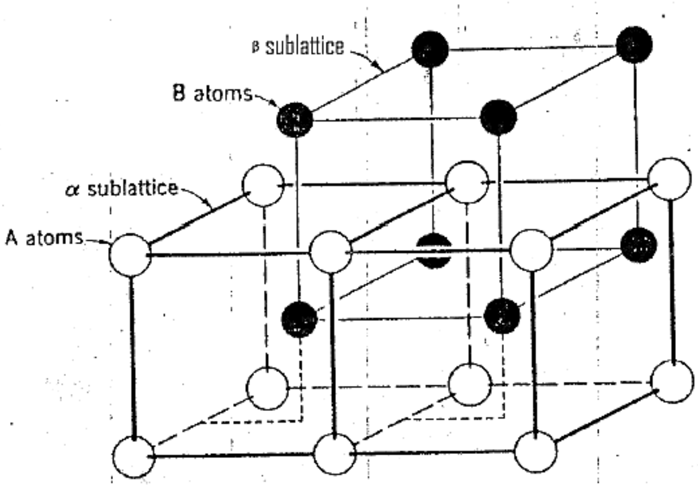
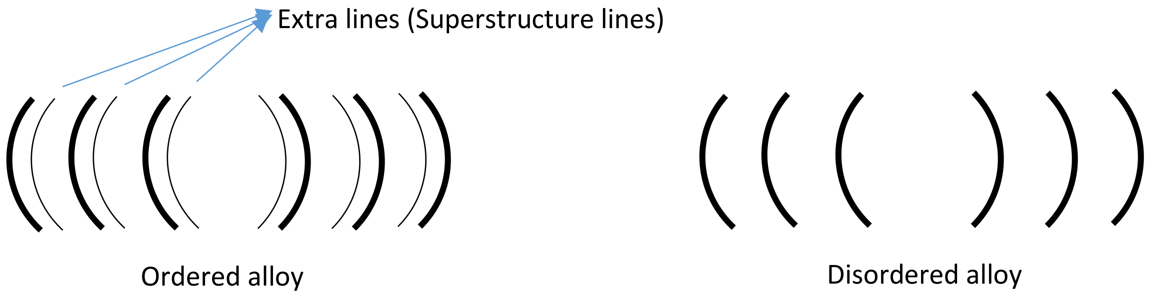
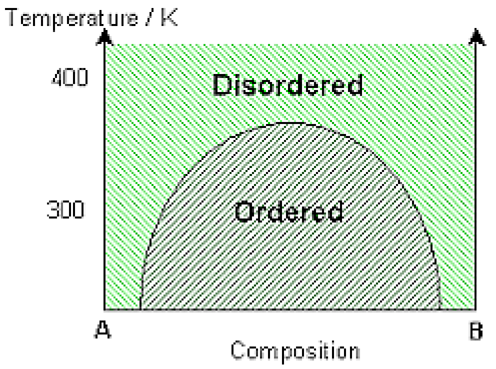


Fig.14: The order arrangement in a 50:50 alloy

The degree of order is detected by x-ray diffraction studies. In certain direction of an ordered alloy two types of atoms have separate atomic planes and produce extra diffraction lines which are not present in the disordered structure. The extra lines are called super structure lines.



There is a dependency of order parameter on both temperature and composition of elements of the alloy system. The variation of orderedness with temperature and composition is shown below:



Bragg-Williams theory of order-disorder phase transformation of an AB alloy

It has been conceived that, when the temperature is increased it bring about the order phase of an alloy into disordered phase. This type of phase transition is a 2nd order phase transition, which does not involved any latent heat capacity at the transition temperature.

If there are N atoms A and N atoms B in the alloy then a long range order parameter P is defined such that, The no of ‘A’ in ‘a’ lattice is equal to ½(1+P)N

The no of ‘B’ in ‘b’ lattice is equal to ½(1+P)N

The no of ‘A’ in ‘b’ lattice is equal to ½((1-P)N

When $P=\pm 1$, then the order is perfect and each lattice contains only one type of atoms.

When P=0, each lattice contains equal no of A and B atoms and there is no long range order.

In an over simplified way, a part of the internal energy of the lattice to be associated with the bond energy like AA, BB, AB between the nearest neighbor pairs. The total bond energy is therefore,

$$E=N_{AA}U_{AA} + N_{BB}U_{BB} + N_{AB}U_{AB} \tag{1}$$

Where N_{ij} is the no of nearest neighbors of i,j bonds and U_{ij} is the energy of an i,j bond.

If there is an A atom in lattice ‘a’ and there is another A atom in the nearest site of ‘b’ then there is a probability that an AA bond will form. Existence of these two atoms is dependent on their probabilities of existence at those sites and these probabilities are independent.

For a bcc lattice there are 8 nearest neighbors of a given A atom. Now considering the above probabilities the no of bonds for N number of A atoms and N no of B atoms are

$$\left.\begin{aligned} N_{AA} &= 8N\left[\frac{1}{2}(1+P)\frac{1}{2}(1-P)\right] = 2(1-P^2)N \\ N_{BB} &= 8N\left[\frac{1}{2}(1+P)\frac{1}{2}(1-P)\right] = 2(1-P^2)N \\ N_{AB} &= 8N\left[\frac{1}{2}(1+P)\right]^2 + 8N\left[\frac{1}{2}(1-P)\right]^2 = 4N(1+P^2) \end{aligned}\right\} \tag{2}$$

Putting the values of (2) in (1) we obtain

$$\begin{aligned} E &= 2(1-P^2)N\, U_{AA} + 2(1-P^2)N\, U_{BB} + 4N(1+P^2)U_{AB} \\ &= 2N\, U_{AA} - 2N\, P^2U_{AA} + 2N\, U_{BB} - 2N\, P^2\, U_{BB} + 4N\, U_{AB} - 4NP^2U_{AB} \\ &= 2N(U_{AA} + U_{BB} + 2U_{AB}) + 2NP^2\,(2U_{AB} - U_{AA} - U_{BB}) \\ &= E_0 + 2NP^2U \end{aligned} \tag{3}$$

$$\left.\begin{aligned} &\text{Where, } E_0 = 2N(U_{AA} + U_{BB} + 2U_{AB}) \\ &\text{And } U = 2U_{AB} - U_{AA} - U_{BB} \end{aligned}\right\} \tag{4}$$

Now we calculate the entropy of these distribution of atom. The thermodynamic probability of the distribution of these atoms w is

$$W = \left[\frac{N!}{\left(\frac{1}{2}(1+P)N\right)!\left(\frac{1}{2}(1-P)N\right)!}\right]^2 \tag{5}$$

The relation between entropy and probability from Boltzmann distribution

$$S = K_B log W \tag{6}$$

Using Stirling’s approximation ($\log_e n! = n\log_e n - n$) for high values of N in (5) to calculate logW, and putting this in (6) we get

$$S = K_B log\left[\frac{N!}{\left(\frac{1}{2}(1+P)N\right)!\,\left(\frac{1}{2}(1-P)N\right)!}\right]^2$$

$$S = 2K_B log\left\{\frac{N!}{\left(\frac{1}{2}(1+P)N\right)!\,\left(\frac{1}{2}(1-P)N\right)!}\right\}$$

$$S = 2K_B\left[logN!\, - \left\{log\left(\frac{1}{2}(1+P)N\right)! + log\left(\frac{1}{2}(1-P)N\right)!\right\}\right]$$

$$S = 2K_B\left[NlogN - N\, - \left(\frac{1}{2}(1+P)N\right)log\left(\frac{1}{2}(1+P)N\right) + \left(\frac{1}{2}(1+P)N\right) - \left(\frac{1}{2}(1-P)N\right)log\left(\frac{1}{2}(1-P)N\right) + \left(\frac{1}{2}(1-P)N\right)\right]$$

$$S = 2K_B\left[NlogN - N\, - \left(\frac{1}{2}(1+P)N\right)log\left(\frac{1}{2}(1+P)N\right) + \frac{N}{2}(1+P+1-P) - \left(\frac{1}{2}(1-P)N\right)log\left(\frac{1}{2}(1-P)N\right)\right]$$

$$S = 2K_B\left[NlogN\, - \left(\frac{N}{2}(1+P)\right)log\left(\frac{N}{2}(1+P)\right) - \left(\frac{N}{2}(1-P)\right)log\left(\frac{N}{2}(1-P)\right)\right]$$

$$S = 2K_BNlogN\, - K_BN(1+P)log\left(\frac{N}{2}(1+P)\right) - K_BN(1-P)log\left(\frac{N}{2}(1-P)\right)$$

$$S = 2K_BNlogN\, - K_BN(1+P)\{logN + log(1+P) - log2\} - K_BN(1-P)\{logN + log(1-P) - log2\}$$

$$\begin{aligned}S = 2K_BNlogN &- K_BN(1+P)logN - K_BN(1+P)log(1+P) + K_BN(1+P)log2 - K_BN(1-P)logN \\ &- K_BN(1-P)log(1-P) + K_BN(1-P)log2\end{aligned}$$

$$S = K_BNlogN(2-1-P-1+P)\, - K_BN(1+P)log(1+P) + K_BNlog2(1+P+1-P) - K_BN(1-P)log(1-P)$$

$$S = \, 2K_BNlog2 - K_BN(1+P)log(1+P) - K_BN(1-P)log(1-P)$$

$$S = \, 2K_BNlog2 - K_BN[(1+P)log(1+P) + (1-P)log(1-P)] \tag{7}$$

Now for P = ±1, S = 0 and for P=0, S=2NK$_B$log2

The equilibrium order is determined by the requirement that the free energy F= E – TS is minimum w.r.t P. Using (7) for S and (3) for E and differentiating (7) w.r.to P and equating the result to zero we get,

$$4NPU + NK_BT[log(1+P)/(1-P)]=0$$

This should be solved graphically, we may find a smooth varying curve shown in fig. 15. (8)

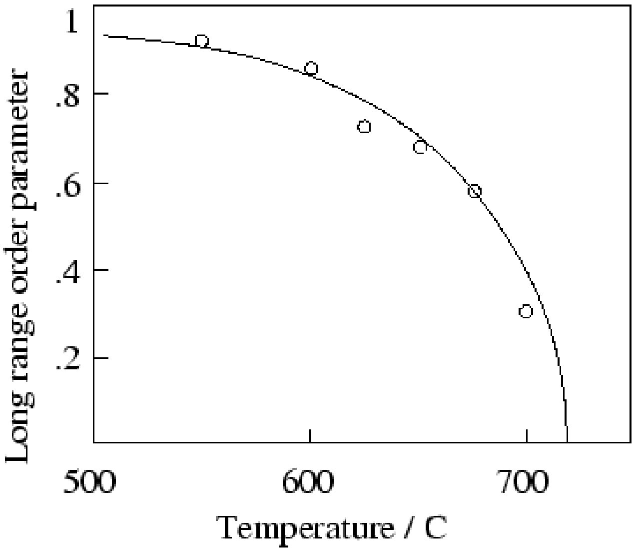


Fig. 15. Long range order parameter

When $P \approx 0$, we may expand eqn (8) to find

$$4NPU + 2K_BNTP = 0$$

$$2NK_BTP = -4NPU$$

$$T = T_C = -\frac{2U}{K_B} \qquad (9)$$

T_C is the transition temperature at which the long range order P becomes zero. Above this temp the long range order parameter vanishes and the system becomes disordered. This should be keep in mind that in equation (9) the effective interaction U is negative means an attraction between A and B atoms. If the dominant interaction is repulsive then a two phase structure is formed without the expected phase transformation.