SOLID SOLUTIONS

A homogeneous mixture of atoms of two or more elements in solid state is called as solid solution. It is a single phase system. Atoms of different elements in it cannot be either mechanically separated or physically distinguished. There are two types of solid solutions

a) Interstitial solid solution  
b) Substitutional solid solution

Interstitial Solid Solution

Small solution atoms dissolve in the interstitial space available amongst big solvent atoms and form and interstitial solid solution.

Carbon atoms of atomic radius 0.7 Å form solid solution of this kind in α-iron of atomic radius of 1.24 Å. The arrangement is shown in the following Figure.

Solubility is generally random and limited in nature. Small atoms of hydrogen, carbon, nitrogen and boron, etc., more readily form the interstitial solution in transition metals. This is because of incomplete inner orbitals.
Substitutional Solid Solution

The binary Au-Ag, Ni-Cu, Si-Ge systems showing complete solid solubility are the examples of substitutional solid solution. Such solid solution may be (i) Random or disordered or (ii) Arranged or ordered.

Random or disordered substitutional solid solution

Arranged or Ordered substitutional solid solution

Temperature is the deciding factor in the making of random or ordered solid solutions. Brass, an alloy of Cu-Zn system has ordered arrangement below 450°C.
THE HUME-ROThERY RULES

The Hume-Rothery rules state that two elements must be very similar to each other in order to form a solid solution. The two elements must therefore meet all of the following conditions in order to mix and form a solid solution.

1. **Crystal structure:** The two or more metals should have similar crystal structures such as FCC and FCC or BCC and BCC. Tungsten alloy steel has Fe and W both of BCC structures, while Pt-Ag has FCC structures.

2. **Atomic Size:** Atoms of two metals should have their sizes within 15% of each other. If the size difference is more than 15%, only limited solid solubility will be obtained.

3. **Valency:** The valency of base metal and the alloying element should be the same.

4. **Electronegativity:** The solid solubility will be limited if the two metals possess greater electronegativity. If electronegativity is too high, the two metals will form intermediate phase instead of solid solution.
THE PHASE RULE
SINGLE COMPONENT SYSTEM – ONE-COMPONENT SYSTEM OF IRON

THE PHASE RULE

Phase: A phase is a homogeneous portion of a system that has uniform physical and chemical characteristics. In other words, a phase is a chemically homogeneous, physically distinct and mechanically separable portion of a system. For example, every pure metal forms a phase. Sugar-water solution forms a single phase, since, sugar completely dissolves in water. If sand is suspended in water, it forms two phases, since, sand doesn’t dissolve in water and is distinct.

Component: Components are pure metals or compounds of which the system is made up. For example, in copper-zinc brass, copper and zinc are components. Generally, solute and solvent terms are used. The component, which is in large excess, is called solvent and one, which is in small quantity, is called solute.

System: A system may refer to a specific body of a material under consideration.

Variables: Variables are the external parameters, which can be varied during the study of the system. Example: temperature, pressure, etc.

Composition: Compositions are different quantities of components in a system, expressed in weight percent or atomic percent. The number of variables required to specify completely the composition of the phase is \((C-1)\), where, \(C\) is the number of components in the system.

Degrees of freedom: It is the number of independent variables, which can be varied, without affecting the system. It cannot be more than the total number of variables

The total number of variables is given by \(P(C-1)+2\)

Where, \(P\) – number of phases; \(C\) – number of components;

Gibbs phase rule: It gives the relationship between the number of phases \((P)\), number of components \((C)\) and predicts the number of degrees of freedom \((F)\)
\[ F = C - P + 2 \]

The integer 2 represents external variables, namely temperature and pressure.

The number of degrees of freedom (F) of a system is the number of variables, which can be changed independently without causing a phase to appear or disappear.

When only one phase is present, then \( P = 1 \), degrees of freedom is equal to total number of variables. Thus, when, number of phases increases degrees of freedom decreases. The degrees of freedom cannot be less than zero.

<table>
<thead>
<tr>
<th>No. of phases</th>
<th>Total number of variables; ( P(C-1)+2 )</th>
<th>Degrees of freedom; ( F = C-P+2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>( 3 ) (T, P, C)</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>( 2 ) (T,P) OR (T,C)</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>( 1 ) (T) OR (P) OR (C)</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>( 0 ) (nil)</td>
</tr>
</tbody>
</table>

Thus, a system cannot have more than four phases in equilibrium.

**PHASE DIAGRAMS**

The pictorial representation of the behavior of two phases or phase structure in a system is called phase diagram. Phase diagrams are helpful in predicting phase transformations and resulting microstructure. The two variables under consideration are only temperature and composition.

The phase diagrams are classified on the basis of the number of components in the system. Single component system has unary diagram, two components system have binary diagram and three-component system give rise to ternary diagram.

**Unary Phase Diagram (one component system of Fe)**

In single component system, there is no composition variable. Only variables are temperature and pressure. Hence, pressure and temperature are plotted. For example, consider the iron phase diagram. The different solid phases formed by the iron is represented by \( \alpha \), \( \delta \) and \( \gamma \).

\[
\begin{align*}
\alpha & \rightarrow \gamma & \gamma & \rightarrow \delta \\
\text{Temperature, } ^\circ\text{C} & 30 & 910 & 1410
\end{align*}
\]

Consider the case of iron (Fe) whose phase diagram is shown below. The diagram indicates different phases as a function of temperature and pressure. The gases, liquids and solid forms of iron are single phases. The boundaries \( \text{AB, } \text{CDE, } \text{FDE, } \text{GHJ and GHK} \) are phase boundaries for two phase equilibrium. Here, \( D=1 \) which implied that either temperature or pressure may be
varied. If we want to maintain two phase equilibrium on these boundaries, then pressure and temperature both are required to be changed accordingly.

![Unary phase diagram of iron](image)

Three phase boundaries meet at points D and H. These points are known and triple points. Here, D=0 and three phase equilibrium exists. As the degree of freedom is zero, i.e., system is constraint, neither pressure nor temperature can be varied. Crystal forms of iron such as \( \alpha \), \( \gamma \) and \( \delta \) are obtained at increasing temperatures. \( \alpha \) form of iron converts to \( \varepsilon \) form near a pressure of about 15 GPa.
BINARY PHASE DIAGRAMS

BINARY PHASE DIAGRAM FOR COMPLETELY SOLUBLE SYSTEM (ISOMORPHOUS SYSTEMS)

Binary phase diagrams involve temperature, pressure and composition as variables. Then, a 3-dimensional representation is required for explaining the system, which is complicated. In order to simplify, the binary phase diagrams are drawn at atmospheric pressure. Also, pressure changes in vapor phase does not affect much the system, where, high melting point components are present, hence, pressure variable can be ignored.

Then, the modified form of the phase rule equation for binary system is

\[ F = C - P + 1 \]

\( \text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3 \), exhibits the simplest binary system where, they are completely soluble with both liquid solubility and solid solubility.

The two components, namely alumina and chromia dissolve each other in all proportions, both in liquid and solid states. There are only two phases in the above phase diagram, liquid phase and solid phase.

The single phase regions are separated by a two-phase region (L+S). in this region, both solid and liquid exist together. In all binary phase diagrams, the two phase region
separates the single phase regions. This is given by “1—2—1” rule, i.e., from single phase (solid) to combined phase (L+S) to liquid phase (single phase).

The phase boundary between liquid phase and the two phase region is called liquidus. The phase boundary between solid and two phase region is called solidus.

When only one phase is present, composition at particular temperature is given by intersecting with composition axis. When two phases are present (L+S region), a horizontal line called tie-line gives both liquid and solid composition.

For example, at particular temperature, T, \(C_l\) gives liquid composition, \(C_s\) gives solid composition and \(C_o\) gives overall composition.
ISOMORPHOUS PHASE DIAGRAMS AND TIE LINE RULE

- A and B must satisfy Flase-Rothney rule for the formation of "extended" solid solution.
- Examples of systems forming isomorphous systems: Cu-Ni, Ag-Au, Ge-Si, Al₂O₃-Cr₂O₃.
- Note the liquidus (the line separating L & L+S regions) and solidus (the line separating L+S and S regions) lines in the figure.

Note that the components in this case are compounds.
Points to be noted:
- Pure components (A, B) melt at a single temperature. (General) Alloys melt over a range of temperatures (we will see some special cases soon).
- Isomorphous phase diagrams form when there is complete solid and liquid solubility.
- Complete solid solubility implies that the crystal structure of the two components have to be same and Hume-Rothery rules have to be followed.
- In some systems (e.g. Au-Ni system) there might be phase separation in the solid state (i.e. the complete solid solubility criterion may not be followed) → these will be considered later in this chapter as a variation of the isomorphous system (with complete solubility in the solid and the liquid state).

- Both the liquid and solid contain the components A and B.
- In Binary phase diagrams between two single phase regions there will be a two phase region → In the isomorphous diagram between the liquid and solid state there is the (Liquid + Solid) state.
- The Liquid + Solid state is NOT a ‘semi-solid’ state → it is a solid of fixed composition and structure, in equilibrium with a liquid of fixed composition.
- In the single phase region the composition of the alloy is ‘the composition’.
  In the two phase region the composition of the two phases is different and is NOT the nominal composition of the alloy (but, is given by the lever rule). Lever rule is considered next.
**Tie line and Lever Rule**

Given a temperature and composition—how do we find the fraction of the phases present along with the composition?

- Say the composition $C_0$ is cooled slowly (*equilibrium*)
- At $T_0$ there is $L + S$ equilibrium
- Solid (crystal) of composition $C_1$ coexists with liquid of composition $C_2$

- We draw a horizontal line (called the **Tie Line**) at the temperature of interest (say $T_0$).
- Tie line is $XY$.
- Note that tie lines can be drawn only in the two phase coexistence regions (*fields*). Though they may be extended to mark the temperature.
- To find the fractions of solid and liquid we use the lever rule.
- We draw a horizontal line (called the **Tie Line**) at the temperature of interest (say $T_0$).
- The portion of the horizontal line in the two phase region is akin to a ‘lever’ with the fulcrum at the nominal composition ($C_0$).
- The opposite arms of the lever are proportional to the fraction of the solid and liquid phases present (this is the lever rule).

At $T_0$:
- The fraction of liquid ($f_L$) is $\propto (C_0 - C_1)$
- The fraction of solid ($f_S$) is $\propto (C_2 - C_0)$

\[
\frac{f_{\text{liquid}}}{{\text{at} \ T_0}} = \frac{C_0 - C_1}{C_2 - C_1} \quad \frac{f_{\text{solid}}}{{\text{at} \ T_0}} = \frac{C_2 - C_0}{C_2 - C_1}
\]

Note: Strictly speaking, cooling curve cannot be overlaid on phase diagram.

```
\frac{f_{\text{liquid}}}{{\text{at} \ T_0}} = \frac{C_0 - C_1}{C_2 - C_1} \quad \frac{f_{\text{solid}}}{{\text{at} \ T_0}} = \frac{C_2 - C_0}{C_2 - C_1}
```

- Tie line: Note that tie line is drawn within the two phase region and is horizontal.
At $T_0$
- The fraction of liquid ($f_l$) is proportional to $(C_0 - C_1) \rightarrow AC$
- The fraction of solid ($f_s$) is proportional to $(C_2 - C_0) \rightarrow CB$

\[ f_{\text{liquid}} = \frac{AC}{AB} = \frac{C_0 - C_1}{C_2 - C_1} \]

\[ f_{\text{solid}} = \frac{CB}{AB} = \frac{C_2 - C_0}{C_2 - C_1} \]
For a composition \( C_0 \):
- At \( T_0 \) → Both the liquid and the solid phases contain both the components A and B
- To reiterate: The state is NOT semi-solid but a mixture of a solid of a definite composition \( C_1 \) with a liquid of definite composition \( C_2 \)
- If the alloy is slowly cooled (maintaining ~equilibrium) then in the two phase region (liquid + solid region) the composition of the solid will move along the brown line and the composition of the liquid will move along the blue line.
- The composition of the solid and liquid are changing as we cool!
THE LEVER RULES, APPLICATION TO ISOMORPHOUS SYSTEM

The Lever Rule

The lever rule helps to calculate the relative proportions of solid and liquid material present in the mixture at any given temperature.

For example consider $\text{Al}_2\text{O}_3-\text{Cr}_2\text{O}_3$ system

The horizontal line passing through the solidus-liquidus curve at temperature $T$, is known as lever arm $(A-B)$ or tie line.

\[
\text{Weight fraction of liquid} = \frac{\text{CB}}{\text{AB}} = \frac{C_s - C_0}{C_s - C_l}
\]

\[
\text{Weight fraction of liquid} = \frac{\text{AC}}{\text{AB}} = \frac{C_0 - C_l}{C_s - C_l}
\]
Then, the lever rule states that, to determine the overall composition of solid and liquid fractions at point C (Temperature T), consider that point as fulcrum and ends as weights (weight fraction of solid and liquid). At temperature T, at particular composition of chromia at C₀ (point C), the fraction of liquid (point A, C₁) and weight fraction of solid (point B, C₃) is given by the above equation.

The lever rule is not applicable at eutectic or peritectic points as three phases exist in equilibrium at these temperatures. It can be applied just below or just above the invariant line. The lever rule may be used to calculate

i) The fraction of a proeutectic phase
ii) The fraction of an eutectic mixture, and
iii) The fraction of phase of an eutectic mixture.

Applications of isomorphous systems (phase diagrams)

Alloy phase diagrams are useful to metallurgists, materials engineers, and materials scientists in the following major areas:
- Development of new alloys for specific applications,
- Fabrication of these alloys into useful configurations,
- Design and control of heat treatment procedures for specific alloys that will produce the required mechanical, physical, and chemical properties, and
- Solving problems that arise with specific alloys in their performance in commercial applications, thus improving product predictability
- Predict the temperature at which freezing or melting begins or ends for any specific alloy composition in an alloy system.
- Predict the safe temperature for hot working or heat treatment
- Determine the number of phases, type of phases, and composition of phases present in any given alloy at a specific temperature.
- Predict possible heat treatments.
- Alloy Design in age-hardening alloys, forming pure austenite steel phase, to get permanent magnetic phase
EUTECTIC PHASE DIAGRAM

Binary phase diagram of partial soluble system (Eutectic Phase Diagram)

A eutectic phase diagram is obtained when the melting points of the two components of phase diagram are neither very close nor much different. Only liquid solubility exists in such cases. The solid solubility may be negligible or partial. Solid solubility is never zero even in an unfavourable conditions. Thus, there are two cases of eutectic phase diagrams, viz.

i) Complete liquid solubility with negligible solubility – Cd-Bi system

ii) Complete liquid solubility with partial solid solubility – Pb-Sn system.

The phase diagram of Pb-Sn alloy system is shown below. Melting points of Pb and Sn are 327°C and 232°C, respectively. In the solid α-phase, a very small amount of Sn in dissolved in Pb. The other solid phase is β in which very small quantity of lead is dissolved in tin. Both the components dissolve in each other sufficiently in (α+β) phase. Two-phase regions (α+β) and (α+L), (α+β) and L; (α+β) and (β+L) are separated by a horizontal line BDE. This line corresponds to a temperature T, known as eutectic temperature. Composition at point D is called eutectic composition. At this point, the liquid phase L transforms to (α+β) phase during cooling and vice-versa during heating.
Composition of Sn and Pb at points B, D and E are shown at eutectic temperature. These cannot be varied because degree of freedom for three phases in equilibrium is zero.

The eutectic temperature and eutectic reaction are called *invariant temperature* and *invariant reactions*.

In the above phase diagram the different boundaries separating different phases are given below:

Boundary CD between L and α+L phases is liquidus I
Boundary DF between L and β+L phases is liquidus II
Boundary BC between α and α+L phases is solidus I
Boundary EF between β and β+L phases is solidus II
Boundary AB between α and α+β phases is solvus I
Boundary EG between β and α+β phases is solvus II

Composition of alloys left to the point D are called *hypoeutectic alloys*, and those to the right are known as *hypereutectic alloys*.

**Eutectic characteristics:**

Eutectic temperature = 183°C
Eutectic composition = 62% Sn; 38% Pb
Eutectic reaction = \[ L \xrightarrow{\text{cooling}} \alpha + \beta \]
Degrees of freedom, F = 0

This means the composition, temperature are fixed. Any change in the above parameters, the equilibrium is disturbed. This is Invariant Reaction. The eutectic temperature is called Invariant temperature (F = 0).
Eutectoid Phase Diagram

The eutectoid reaction involves transformation of solid phase into two other solid phases on cooling and vice-versa. This is also an invariant reaction. The corresponding temperature is called *eutectoid temperature* and the corresponding composition is called *eutectoid composition*.

\[
\text{cooling} \\
\gamma \rightleftharpoons \alpha + \beta \\
\text{heating}
\]
PERITECTIC PHASE DIAGRAM, OTHER INVARIANT REACTIONS

Peritectic Phase Diagram

Partial miscibility & the melting points of the two pure components (Ag & Pt) are vastly different. The melting points of At & Pt differ by more than 800°C. Here, also no pure components exist in any of the composition. The phase which first solidifies is called $\alpha$ phase. Here, $\alpha$ phase represents Pt in Ag. The phase which solidifies latter is called $\beta$ phase, where, $\beta$ phase represents Ag in Pt.

This phase diagram is similar to that of binary system, with components with close melting points. But, in contrast to the eutectic reaction, Peritectic reaction takes place between liquid and solid phase to yield single solid phase on cooling.

The peritectic composition ($C_p$) is the composition and the product solid phase.

The peritectic horizontal line is the tie-line which defines the composition of liquid phase and the $\beta$ phase and the corresponding temperature is called peritectic temperature ($T_p$). This reaction is similar to eutectic reaction, and can be given as.

$$\text{cooling} \quad \text{Peritectic reaction} \quad = \quad L + \beta \quad \Leftrightarrow \quad \alpha \quad (\text{invariant reaction})$$

$$\text{heating}$$

when the liquid phase is replaced by another third solid phase, the resulting reaction is called peritectoid reaction. The temperature at which peritectoid reaction takes place is called peritectoid temperature.

$$\text{cooling} \quad \text{Peritectoid reaction} \quad = \quad \gamma + \beta \quad \Leftrightarrow \quad \alpha \quad (\text{invariant reaction})$$

$$\text{heating}$$
Binary Ag-Pt peritectic phase diagram

Invariant reactions

Eutectic reaction

\[ \text{cooling} \quad L \xleftrightarrow{\ } \alpha + \beta \]

Eutectoid reaction

\[ \text{heating} \quad \gamma \xleftrightarrow{\ } \alpha + \beta \]

Peritectic reaction

\[ \text{heating} \quad L + \beta \xleftrightarrow{\ } \alpha \]

\[ \text{cooling} \quad \beta \xleftrightarrow{\ } \alpha + \beta \]
Peritectoid reaction

\[ \gamma + \beta \rightleftharpoons \alpha \]

The temperature at which the above reaction takes place is called invariant temperature. The meeting point of three phases (eutectic point or peritectic point) is called invariant point.

\[
\begin{align*}
C &= 2; \quad P = 3; \quad F = C - P + 1 = 0; \\
F &= 0
\end{align*}
\]
FREE ENERGY COMPOSITION CURVES FOR BINARY SYSTEMS

Free energy composition curves for binary systems

Consider the Gibbs free energy of one mole of atoms (molar gibbs free energy), some of which are A atoms and some of which are B atoms. Consider \( G(X_B) \), that is, resultant ‘G’ as we change the relative amounts of A and B.

\[
G = H - TS
\]

\( H = \) enthalpy  
\( T = \) temperature  
\( S = \) entropy

Define \textit{molar} quantities:

\[
g = \frac{G}{\text{mole}}  
\]

\[
h = \frac{H}{\text{mole}}  
\]

\[
s = \frac{S}{\text{mole}}
\]

\[
X_i = \text{mole fraction of } i = \frac{N_i}{\sum N_i}
\]

0% B (100% A)

\[
\begin{array}{cccccccc}
\end{array}
\]

33% B

\[
\begin{array}{cccccccc}
\end{array}
\]

67% B

\[
\begin{array}{cccccccc}
B & B & B & B & A & A \\
B & B & B & B & A & A \\
B & B & B & B & A & A \\
\end{array}
\]

100% B

\[
\begin{array}{cccccccc}
B & B & B & B & B & B \\
B & B & B & B & B & B \\
B & B & B & B & B & B \\
\end{array}
\]
If the (molar) Gibbs free energy of pure A is $G_A$, and that of pure B is $G_B$, then the (molar) Gibbs free energy for the combination of pure components is

$$G_{\text{pure, combined}} = G_A \cdot X_A + G_B \cdot X_B$$

As a function of composition, the Gibbs free energy for the combination of pure A and pure B is a straight line connecting $G_A$ and $G_B$, as shown below:

Now, let us remove the imaginary partition and let the A and B atoms mix. There should be some change in $g$ due to this mixing, and it is given by

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

The enthalpy term, $\Delta H_{\text{mix}}$, represents the nature of the chemical bonding, or, put in different words, the extent to which A prefers B, or A prefers A as a neighbor. The entropy term, $\Delta S_{\text{mix}}$, signifies the increase in disorder in the system as we let the A and B atoms mix. It is independent of the nature of the chemical bonding. We can approximate our isomorphous, binary system as an ideal solution, therefore

$$\Delta H_{\text{mix}} = 0.$$  

Let us qualitatively examine the entropy of mixing. If we have a system of pure A, and let the A atoms “mix” with one another, there is no increase in entropy because they were mixed to begin with. The same holds true for a system of pure B. If we have just one atom of B in a mole of A, removing the invisible partition hardly changes the amount of disorder. But, as we get to a 50:50 composition of A:B, the increase in entropy as we allow the system to mix is enormous. Therefore, $\Delta S_{\text{mix}}$ has the following dependence on composition.
From that we can easily get the change in Gibbs free energy due to mixing:

Now we sum $G(\text{pure, combined})$ and $\Delta G_{\text{mix}}$ to get the total Gibbs free energy of the solution as a function of composition:

At this point we have the general shape of the $G(X_B)$ curves for phases in a binary system. This overall shape holds for both the solid and liquid phases, so long as both make ideal (or close to ideal) solutions.
MICROSTRUCTURAL CHANGE DURING COOLING

Microstructural changes during phase transformation

Liquid phase first changes to solid-liquid phase and finally to solid phase during cooling. If variation in the rate of cooling is slow to fast, for example from 3.3°C per minute to 12,000°C per minute, different microstructures will develop. Microstructure of single phase above the liquidus is shown below:

![Liquid phase](image)

On cooling below we obtain two phase co-existing solid-liquid phase. The solid crystals float on the liquid phase.

![Solid in liquid phase](image)

However, for eutectic solid solutions, the β crystals float in the liquid of eutectic composition below eutectic temperature.
On further cooling, the system cross the solidus and crystallizes into poly crystalline solid. The changes are true for the cases when two components have almost similar melting points.