INTRODUCTION:

Chemical reactions classified into two types,

1. **Irreversible reaction:**
   
   \[ \text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2 \uparrow \]

2. **Reversible reactions:**
   
   a. **Homogenous reversible reaction**
      
      \[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]
   
   b. **Heterogeneous reversible reaction**
      
      \[ \text{CaCO}_3(s) \rightleftharpoons \text{CaO}_s + \text{CO}_2(g) \]

Here phase rule is used to study the behaviour of heterogeneous reversible reactions.

DEFINITIONS: State phase rule and explain the terms involved in it [June 2014]

The equilibrium reaction is influenced by pressure, temperature, concentration. The phase rule equation is

\[ F = C - P + 2 \]

- **F** = Degree of freedom
- **C** = component
- **P** = Phase

**Phase (P):**

1. Its homogenous and physically distinct
2. It is mechanically separated, it combine with other part of the system by boundaries

**Types:**

1. Gaseous phase
2. Liquid phase
3. Solid phase

**Gaseous phase:**

- All gases are completely miscible
- So there is no boundary

Example: Air with O\(_2\), H\(_2\), N\(_2\), CO\(_2\). So single phase.
**Liquid phase:**

The number of liquid phases depends on the number of liquid present and their miscibilities.

1. If two liquids immiscible, they will form two separate phases i.e two liquid phase.
   
   Example: Benzene – H₂O

2. If two liquids completely miscible, they will form one liquid phase.
   
   Example: Alcohol – H₂O

**Solid Phase:**

Decomposition of CaCO₃

\[
\text{CaCO}_3(s) \rightleftharpoons \text{CaO}_s + \text{CO}_2(g)
\]

It is three phases, 2 solid and gaseous CO₂.

\[
\text{Ice}_s \rightleftharpoons \text{water}_l \rightleftharpoons \text{vapour}_g
\]

Three phases.

It is physically distinct, homogenous and having definite boundary.

**Component (c):**

(i) Smallest number of independent variable.

(ii) Composition of each phase is expressed in the form of chemical equation.

(a) \[
\text{Ice}_s \rightleftharpoons \text{water}_l \rightleftharpoons \text{Vapour}_g
\]

It having three phases.

The chemical composition is H₂O.

But different physical form.

Hence the number of component is one.

(b) Sulphur having 4 phases

1. Rhombic
2. Monoclinic
3. Liquid
4. Vapour

But chemical composition is only sulphur so the component is one.

(c) Thermal decomposition of CaCO₃

\[
\text{CaCO}_3(s) \rightleftharpoons \text{CaO}_s + \text{CO}_2(g)
\]

Three phases, two solid, one gaseous. It is two components. Reason is the chemical composition is different and phase also different. One is (s) and another one is (g)
**Degree of freedom:**

The minimum number of independent variable factors such as temperature, pressure and concentration, it is fixed to define the system completely.

The composition of phase system fixed by using temperature and pressure

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<thead>
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<td>Zero</td>
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<td>Nonvariant</td>
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*Ice₅ ≡ water l ≡ Vapour g*

It is three phases.

It is equal consists in particular pressure & temperature (or) pressure vary any one of the disappear. So it is zero degree of freedom i.e non variant.

**Phase Diagram**

Phase diagram is a graph obtained by plotting one degree of freedom against another. A plot of temperature (T) against pressure (P) it is called P-T diagram. Similarly, a plot of temperature (T) against composition (C) known as T-C diagram. From the diagram we can understand the behaviour of system stability and equilibrium between phases.

Depending on the number of components systems are classified as one component, two components and three components.

**Lecture notes Session No:29**

**APPLICATION OF PHASE RULE**

**One-component system – Water system**

Water exist three phases like, solid, liquid, vapour.

The equilibrium is

- Solid ⇄ Liquid (melting Curve)
- Liquid ⇄ Vapour (Vapour pressure Curve)
- Solid ⇄ Vapour (Sublimation curve)

Then draw the phase diagram,
Explanation for the curves OA, OB, OC

**Curve OA (equilibrium: water ↔ water vapour):** Vapour pressure curve of water. It represents the vapour pressure of liquid water at different temperatures. The two phases water and water vapour coexist in equilibrium along this curve. The curve OA terminates at A, the critical point (218 atm, temp 374°C) when the liquid and vapour are indistinguishable from each other and there is only one phase. When the vapour pressure is equal to one-atmosphere, the corresponding temperature is the boiling point (100°C) of water.

**Curve OB (equilibrium: ice ↔ water vapour):** Sublimation curve of ice. It shows the vapour pressure of solid ice at different temperatures. The two phases solid ice and vapour coexist in equilibrium along this curve. At the lower limit, the curve OB terminates at absolute zero where no vapour exists.

**Curve OC (equilibrium: water ↔ water):** Fusion curve of ice. It depicts the effect of pressure on the melting point of ice. Here ice and water coexist in equilibrium. The fact that OC slopes to the left indicates that the melting point of ice decreases with increase of pressure.
Since ice melts with decrease in volume, by Le Chatelier’s principle the melting point is lowered by an increase of pressure. It may be noted that the 1 atm. line meets the fusion curve at 0˚C which is the normal melting point of ice.

Along the curves OA, OB, OC there are two phases in equilibrium and one component. Apply the phase rule;

\[ F = C - P + 2 ; 1 - 2 + 2 = 1 \text{ (monovariant)} \]

**The Triple point ‘O’:** The curves OA, OB, and OC meet at the triple point ‘O’ where all the three phases liquid water/ice/vapour are in equilibrium. This occurs at 0.0098˚C and vapour pressure 4.58 mm Hg. Since there are three phases and one component, 

\[ F = C - P + 2 ; 1 - 3 + 2 = 0 \text{ (non variant)} \]

If either pressure or temp. is changed, the three phases would not exist and one of the phases would disappear.

**Area AOC, AOB, BOC:**

Area AOC represents conditions for the one-phase system water.

Area AO B represents conditions for the one-phase system water vapour.

Area BOC represents conditions for the one-phase system ice.

In all the three areas there being one-phase and one-component,

\[ F = C - P + 2 ; 1 - 1 + 2 = 2 \text{ (Bi variant)} \]

**Metastable system: supercooled water / vapour**

The vapour pressure curve of water AO continued as dashed line OA’. That is, water can be super-cooled by carefully below its freezing temperature without the separation of Ice. The super-cooled water/vapour system is metastable (unstable), because as soon as small particle of ice is brought in contact with the super-cooled liquid, the entire liquid solidifies.

**Salient features of the water system:**

(i) The curve OA is the vapour pressure curve of water. Hence, water and its vapor co-exist in equilibrium. No. of phases 2, the degree of freedom 1. The system is monovariant.

(ii) The curve OB is the vapour pressure curve of Ice. It is called sublimation curve. Solid is in equilibrium with vapour. The system is monovariant.
(iii) The curve OC is the fusion curve of ice. Ice and water co-exist in equilibrium. The system is monovariant.

(iv) The curve OA’ is vapour pressure curve of the metastable water.

(v) The point O where the three curve OA, OB, OC meet, called as Triple point.

Lecture notes Session No:30

Reduction phase rule (or) condensed phase rule

(i) The degree of freedom of one component system in single phase is,

\[ F = C - P + 2 \]

\[ F = 1 - 1 + 2 \]

\[ F = 2 \]

Degree of freedom is 2.

Here any two factors influence the equilibrium out of three factors (T, P, and C).

Cooling curves / Thermal Analysis

The shape of the freezing point curves for any system, especially those involving metals, can be determined by thermal analysis - a method involving a study of the cooling curves of various compositions of a system during solidification.

Construction of phase diagram by thermal analysis:

When a graph is plot between temperature and time it is called as cooling curve. The thermal analysis involves the study of cooling curve of various compositions of a two component system during solidification.

1. Consider a pure solid substance in fused state is cooled slowly. The temperature is noted at different time interval. Initially the rate of cooling curve is continuous. At the point ‘b’ freezing starts. After this pt. the temperature will remain constant until the liquid melt is completely solidified. This is because the liquid melt and solid crystals are of the same composition. At the horizontal section ‘bc’ the solid crystals and liquid melt are in equilibrium. Thereafter, the temperature of solid will again decrease along the curve ‘cd’.

![Cooling curve diagram](image)
(2) Considering a mixture of two solids A and B is in fused state. Allow to cool slowly. Initially the rate of cooling curve will be continuous (ab), when the crystals of either A or B is formed from the liquid melt, which is indicated by break in continuity of the cooling curve. Now the temperature again decreases with time but at a different rate, because the solid-crystal and liquid melt are not of the same composition. The slope ‘be’ of the curve represents a continuous and progressive change in composition of liquid melt.

Finally the liquid melt reaches the point ‘c’ at which it separates as solid A and solid B. Now the temperature will remain constant until the liquid melt is completely solidified. Point ‘c’ called eutectic point a minimum freezing point corresponding to eutectic mixture. Thereafter temperature remain constant till solidification up to ‘d’.

Lecture notes Session No:31
Explain phase diagram of Pb-Ag system.[ June 2014]

**Eutectic:**

A binary system consisting of two components, which are completely miscible with one another in liquid state but they do not form any compound and on solidification they give rise merely to an intimate mixture known as eutectic (easy melting) (Pb-Ag, Pb-Sb, KI-H₂O)

**Eutectic point:** Two solid substances capable of forming solid solutions having the properties of lowering each others freezing point. The minimum freezing point corresponding to eutectic mixture is eutectic point.

**Eutectic mixture:** It is a solid solution of two or more substances having the lowest freezing point of all the possible mix of components.
This system has two components and four phases. The phases are (a) solid Ag (b) solid Pb (c) solution of molten Ag and Pb and (d) vapour. The boiling points of silver and lead being considerably high, the vapour phase is practically absent.

**Simple eutectic systems (Pb-Ag system)**

The salient features of the diagram are:

(a) Two curves, AC and BC
(b) Eutectic point C
(c) Three areas (i) above ACB (ii) below AC (iii) below BC

**Curve AC** (the freezing point curve of Ag) shows the effect on freezing point of Ag on addition of lead in small quantities. The curve starts A (961°C), the melting point of Ag, where pure Ag co-exists as solid and liquid (vapour being neglected). This curve indicates that the melting point of Ag falls gradually on adding Pb, along AC, till the lowest point C (303°C) is reached, where the solution gets saturated with respect to lead. At C, no more lead can go in solution and consequently, melting point of Ag does not fall any further; and if any lead is added, it separates as the solid phase. Along this curve, solid Ag and solution co-exist and hence, according to reduced phase rule equation: \( F = 3-P = 3-2 = 1 \), i.e., the system is univariant. The point C (303°C) corresponds to a fixed composition of 2.6% Ag and 97.4% Pb and is known as eutectic composition. On cooling, the whole mass crystallizes out as such.
**Curve BC (freezing point curve of Pb)** represents the effect on freezing point of Pb on gradual addition of small amounts of Ag to it. Point B is the melting point of pure lead (327°C). Along BC, the melting point gradually falls on the addition of Ag, till lowest point O is reached, where the solution gets saturated with respect to Ag and the melting point of lead does not fall any more. On cooling, the whole mass (having eutectic composition) crystallizes out. The system is monovariant.

**Eutectic point C**: The curve AC and BC intersect at C, which is called the eutectic point. Here three phases solid Ag, solid Pb, and solution are in equilibrium. Applying the reduced phase rule;

\[ F = C - P + 1 = 2 - 3 + 1 = 0 \] (nonvariant)

Both variables temperature (303°C) and composition (97.4 % Pb, 2.6% Ag: eutectic composition) are fixed. If the temperature is raised above the eutectic temperature, the solid phases Ag and Pb disappear. No mixture of lead and silver has a melting point lower than the eutectic temperature.

Below the temperature line of eutectic, there are two regions viz.,

(i) the region marked eutectic + solid Ag, in which crystalline silver and solid eutectic are stable, and

(ii) the region marked eutectic + solid Pb, in which crystalline lead and solid eutectic are stable.

**Area ACB**: This region represents the single phase system, the solution of molten Ag and Pb. Applying the reduced phase rule;

\[ F = C - P + 1 = 2 - 1 + 1 = 2 \] (Bivariant)

**Lecture notes Session No:32**

**Application of reduced phase rule to the above systems Pattinson’s Process for the Desilverisation of Argentiferrous lead:**

The argentiferous lead containing small amount of silver is melted well above the melting temperature of pure lead (327°C). Let the point X represent the system ‘molten lead’ on the diagram. It is then allowed to cool when the temperature of the melt falls along the dashed line XY. As the temperature corresponding to Y on the curve BC is reached, solid lead begins to separate and the solution would contain relatively larger amount of silver. On further cooling, more of lead separates along the curve BC until the eutectic point C is
reached. Lead is continuously removed by means of ladles and the percentage of silver in the melt goes on increasing. At C, an alloy containing 2.6% Ag and 97.4% Pb is obtained.

**ZINC-MAGNESIUM ALLOY SYSTEM**: In this system, the components form one or more compounds in some stoichiometric proportions. These compounds melt into the liquid state having the same composition as the solid. Such compounds are called compounds with congruent melting points. Thus, a compound is said to possess congruent melting point, if it melts sharply at a constant temperature into a liquid, having the same composition as that of the solid.

Let us illustrate such a system by Zn-Mg binary alloys (figure). Zinc and magnesium melt at 419.5 and 650°C respectively and they form a compound MgZn₂ in which the ratio of Mg and Zn is 1:2. This compound melts at B (590°C). This phase diagram may be considered as equivalent to two phase diagrams of Pb-Ag type placed side-by-side. The one on the left consists of Zn and MgZn₂ system while the other on the right is formed by the MgZn₂ and Mg. The curve AE₁ and CE₂ represent the compositions of liquids in equilibrium with solid Zn and solid Mg respectively. The central portion of curve E₁BE₂ has maxima at B (590°C). This gives the conditions of equilibrium of liquid with solid compound, MgZn₂. At B, the liquid has the same composition as the solid in equilibrium. Thus, the temperature at B represents the melting point of the compound MgZn₂. As MgZn₂ can co-exist as solid and liquid of same composition, MgZn₂ is said to have congruent melting point. The composition corresponding to point B is 33.3% Mg and 66.7% Zn in the ratio of 1:2. The sharpness of maxima (point B) gives the information about the stability of the compound formed. A sharp maxima indicates that the compound does not dissociate appreciably whereas a flat maxima indicates an appreciable dissociation as in this system.

There are two eutectic points, E₁ and E₂. At E₁ the solid Zn and MgZn₂ deposits; while at E₂ Mg and MgZn₂ are the two phases.
Lecture notes Session No:33

Alloy is a combination of two (or) more difference elements

Properties of alloy:

1. Alloys are hard material.
2. Alloy posses low electrical conductivity.
3. Alloys resist corrosion.

IMPORTANCE (OR) NEED OF MAKING ALLOY:

(i) To increase the hardness of the metal:
   Pure metals are soft but by adding other metals it becomes harders.
   Eg: Gold and silver are soft but by adding copper to give hardness.

(ii) To lower the melting point of the metal:
   By adding alloy substance, the metal make easily fusible
   Eg: Alloy of lead, bismuth having lower melting point

(iii) To increase the corrosion resistance of the metal:
   Metal in pure form it is quite reactive and easily corroded by surroundings
   Eg: Pure iron get corroded but it alloy with carbon (or) chromium it resist corrosion.

(iv) To modify chemical activity of the metal:
   Chemical activity of the metal can be increased (or) decreased by alloying.
   Eg: Sodium amalgam is less reactive than sodium. Aluminium amalgam is more reactive than Al.

(v) To modify the colour of the metal:
   Metal make the alloy, the colour of the metal is changed
   Eg: silver and zinc are white but it make alloy it becomes pink

Preparation of alloys

Two component or binary are manufactured as follows (i) Fusion method (ii) electro-deposition (iii) reduction method (iv) powder metallurgy.

(i) Fusion method: The component metal of the alloy with higher melting point is melted in a refractory bricks lined crucible or melting pot. This is followed by the addition of the component with lower melting point to the melt. Uniform mixing is done using graphite rods. The surface of the mixed molten metals is usually covered with a layer of powdered carbon to prevent the oxidation of the molten mass. Solid alloy will be obtained on cooling the molten mass.
(ii) Electro-deposition method: Here simultaneous electrolytic deposition of different mixed electrolytes by passing direct current that will result in the formation of the alloy at the cathode. Brass is obtained by the electrolysis of mixed solution of copper and zinc cyanides dissolved in KCN.

(iii) Reduction method: In this method a suitable composition of one component of the alloy is reduced in the presence of the other component metal. Al-Bronze is prepared by reducing alumina (Al2O3) in the presence of Cu in an electric furnace.

(iv) Powder metallurgy: A finely divided powdered metals are intimately mixed and subjected to great pressure and temperature.

**Lecture notes Session No:34 &35**

**CLASSIFICATION (OR) TYPES OF ALLOYS**

- **Ferrous alloy**
  - Example:  
    1. Nichrome  
    2. Stainless steel  
    3. Alnico

- **Non-ferrous alloy**
  - Example:  
    1. Brass  
    2. Bronze  
    3. Solder

**Discuss the composition prop and uses of any two ferrous alliys?[June 2014]**

**Ferrous alloys**: Steel is an alloy of iron and carbon. Also addition of small amount of one or more metals like Cr, Ni, Mo etc. imparts special properties to steel.

a) **Nichrome**: Ni-60% and Cr-12% called Nichrome. It give resistant to chemicals and heat, high melting point and high electrical resistance. Used for making resistance coils, heating elements in iron box and other electrical appliances.

b) **Alnico**: Aluminum – Nickel – Cobalt has the composition of Al-12%; Ni-20%,Co-6% and remaining iron. It is highly magnetic. Used for making powerful magnets, used in generators, motors, microphones, speakers etc.

c) **Stainless steel**: These are alloy steels containing Cr with other elements such as Ni and Mo. Cr is effective if its content is 16 % or more. Carbon content ranges from 0.3 – 1.5 % stainless steel resists corrosion by atmospheric gases and other chemicals.

Classified as
(i) Heat treatable (Martensitic) Stainless steel: Contains 12-14% Cr and 0.12-0.35% C.

Properties:
- Magnetic, tough and can be worked in old condition.
- Used upto temperatures 800 °C
- Resistant towards weather and water

Used in making surgical instruments, scissors, blades etc.

(ii) Ferritic Stainless steel: Cr 16-18% and C-0.12%.

Properties:
- Magnetic, better corrosion resistance, ductility and easily machine able.
- Used to make pump shafts, valves etc.,

(iii) Austenitic Stainless steel: 18% Cr, 8% Ni and some Mo.

Properties: Maximum resistant to corrosion

Used in making household utensils, dental and surgical instruments.

Non-Ferrous alloys:
Non-ferrous alloys do not contain iron as the major element. Some of the important non-ferrous alloys have the major element Cu, Al, Ni, Zn, Sn and Pb. The important properties of non-ferrous alloys: high corrosion resistance, strength and workability, good machinability, appearance and colour.

a) Solders:
Joining two metal piece by means of heat and filler alloy at comparatively lower temperature (400C) is known as soldering. The filler alloy is known as solder. Usually Pb and Sn are used.

i) Soft solder: 37-67% Pb; 31-61% Sn and 0.12-2% Antimony; Used for soldering electrical connections.

ii) Brazing alloy: 92% Sn; Sb-5.5% and Cu-2.5%; Used for soldering steel joints.

iii) Tinman’s Solder: 66% Sn and 34% Pb; Used for general soldering and tinning.

b) Copper alloys: Brass and Bronze
Brass: Alloy of Cu and Zinc containing more than 5% Zinc.

i) Commercial Brass / French Gold: 90% Cu and 10% Zn; Stronger and harder; Used for making rivets, screws, jewellery etc.

ii) Cartridge brass: 70% Cu and 30% Zn; soft alloy; Used for making cartridge cases, household articles, condenser tubes etc.
iii) Dutch metal / low brass: 80% Cu and 20% Zn; Used for making musical instruments, flexible hoses, name plate etc.

iv) Aluminum brass: 76% Cu, 22% Zn and 2% Al; better corrosion resistance; used for marine works.

v) Special brasses:
   a) German silver: 25-50% Cu, 10-35% Zn and 5-35% Sn; Ductile, malleable; used in making utensils, bolts, screws etc.,
   b) Admirely brass / Tobin brass: 59-62% Cu, 0.5-1.5% Sn rest Zn; high corrosion resistance; Used in propellers and marine works

**Bronze:**

i) Coinage bronze / Common bronze: 89-92% Cu and 11-8% Sn; soft, ductile and durable; Used for making pump, valves, coins, statues etc.

ii) Gun metal: 85% Cu, 8% Sn, 4% Zn and 3% Pb; Hard, tough; Used for foundry works, water fittings, marine pump etc.

iii) High phosphorous bronze: 10-13% Sn, 0.4% P and rest is Cu; hard and brittle; Used for making bearings, gears, taps, springs etc.

iv) Aluminum bronze: 90-93% Cu and 7-10% Al; corrosion resistance; Used for making bushes, bearings, utensils, etc.

v) Nickel bronze: 90% Cu, 9% Ni and 1% Fe; hard, corrosion resistance; Used for rolling purpose.

vi) Beryllium copper: 97.4% Cu and 2.6% Be; quite hard; used for making springs.

**Lecture notes Session No:36**

**Discuss any four heat treatment of steel in detail [June2014]**

**Heat treatment of alloys:**

The process of heating and cooling of solid steel under controlled condition.

At the time of heat treatment, only change physical properties of metal (or) alloy but not chemical properties.

**Types of heat treatment of alloy:**

(i) **Annealing:**

   Annealing means softening i.e the metal heated to high temperature and slowly cooling in a furnace (absence of air).

**Types of annealing:**

1. Low temperature annealing.
2. High temperature annealing.

**Low temperature annealing:**
The steel heated to below the critical temperature and followed by slow cooling in furnace.

**High temperature annealing:**
The steel heated to above the critical temperature and followed by slow cooling in furnace.

**Purpose:**
1. Increase the ductility and machinability.
2. Reduce the hardness.

(ii) **Hardening (or) Quenching:**
The steel heated to beyond the critical temperature and then suddenly dipped into oil (or) fluid.

**Purpose:**
1. Increase resistance to wear.
2. Increase abrasion resistance.
3. Increase the strength.

(iii) **Tempering:**
The already hardened steel heated to lower the critical temperature (or) own hardening temperature and slowly cooled (Blow redness).

**Purpose:**
1. It reduces the brittleness.
2. Increase the ductility and malleability.
3. Increase the strength and hardness.

(iv) **Normalising:**
The steel heated to above the critical temperature and followed by slow cooling in air.

**Purpose:**
1. Increase the toughness.
2. Recover the uniform of the steel.
3. It removes the internal stresses.

(v) **Carburizing:**
1. The steel article taken in a iron box.
2. Iron box consist of charcoal.
3. Then Iron box heated about 950°C.
4. Then slowing cooled.
5. The steel article absorbed charcoal in the outer layer.
6. The outer layer of steel article converted into high carbon steel.

**Purpose:**
To produce hard wearing surface on steel article.

**(vi) Nitriding:**
Heating the metal in presence of NH₃ at 550°C. The nitrogen dissociated from ammonia and combine with surface of the metal to form hard nitride.

**Purpose:**
To get very hard surface

**6. Flame hardening:** This is a method for localized hardening. The area to be surface-hardened is heated in an oxy-acetylene or oxy-hydrogenated flame. This is then abruptly cooled by spraying water on it.

**7. Gas carburizing:** Here the metal is treated with a gas rich in hydrocarbon at high temperature. This will produce a hard wearing surface containing a tough and relatively soft core inside.

**8. Cyaniding:** A layer of hard surface is produced on low or medium carbon steel. This is done by immersing the metal ina molten salt containing KCN or NaCN at a temperature of about 870°C followed by quenching in oil or water.

**9. Induction Hardening:** In this process the hardening of steel is done by heating using a high frequency current of about 2000 hertz. The heated surface is quenched by using water spray.