

## Equilibrium Diagrams

When a pure metal solidifies it changes from a liquid to a solid state. An intermediate state of liquid and solid exists (sometimes known as the pasty state). These states are known as *phases*, a phase being defined as regions that differ from one another, either in composition or in structure or in both. In a metal the liquid state consists of atoms randomly arranged whereas in the solid state the atoms are arranged regularly in crystal lattices. Therefore the structure of the two states is different and is referred to as phases.

When a pure metal is cooled from the liquid state it produces a cooling curve as in Figure 1. The change from the liquid to the solid state occurs at a definite temperature. Where solidification begins and finishes at the same temperature but the time increases. Examples of metals that have this are lead, copper, aluminum. A pure metal solidifies at one fixed temperature, a fact which can be checked by plotting a cooling curve. A cooling curve may be obtained by melting a small amount of a metal and recording the temperature drop at suitable time intervals as this metal solidifies (the metal must be allowed to cool very slowly i.e. under equilibrium conditions). We can then plot a graph of temperature against time to give us the cooling curve for that particular metal.

At temperatures above and below the curve falls smoothly without "kinks". When the solidification temperature is reached, the temperature remains CONSTANT for some time thus giving rise to the step in the curve. Down to the temperature of the liquid drops in a regular manner as heat is being lost to the surroundings at a nearly constant rate. The step is due to latent heat. This leads to zero change in temperature until the last drop of liquid has solidified. After no more latent heat is available the solid continues to cool in a regular manner giving the smooth curve.

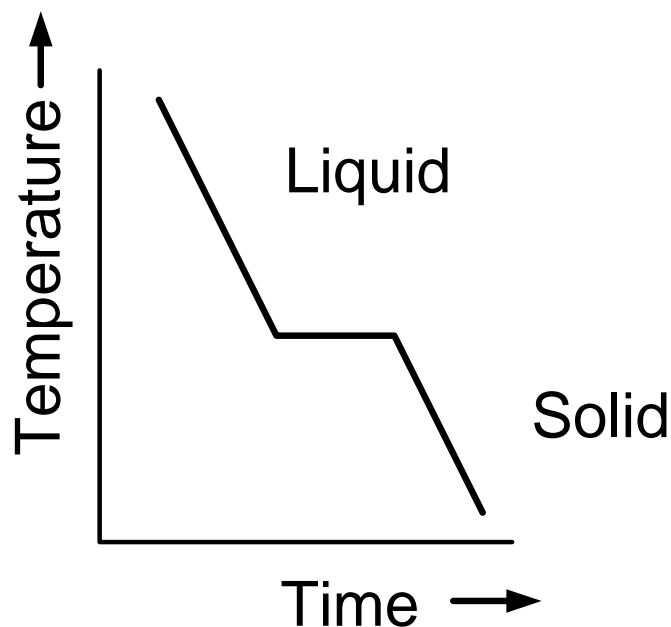


Figure 1 Cooling curve for a pure metal.

However during the cooling of an alloy the solidification occurs gradually during a fall in temperature. An example of this would be Copper Nickel creating a solid solution. This is depicted in Figure 2. Unlike pure metals alloys solidify over a range of temperatures. Below the temperature at which the alloy begins to solidify and the temperature when it is completely solidified the alloy is in a "pasty" state gradually becoming stiffer as the lower limit of the solidification range is approached. Therefore for any alloy there is a definite temperature at which solidification begins and an equally definite point where it ends. These two points are known as the "arrest points". As two metals may be alloyed in many different compositions i.e. you could have 80% A and 20% B or 60%A and 40% B it stands to reason that the cooling curves for all these alloys will be different. Shown here are a selection of cooling curves for an alloy of Lead and Tin. Note that all alloys possess two arrest points with the exception of the 62% TIN alloy (tin mans solder). This alloy has only one single arrest point as the alloy does not go through a pasty state (like a pure metal) it goes directly from a liquid to a solid state .This is called the *EUTECTIC alloy*.

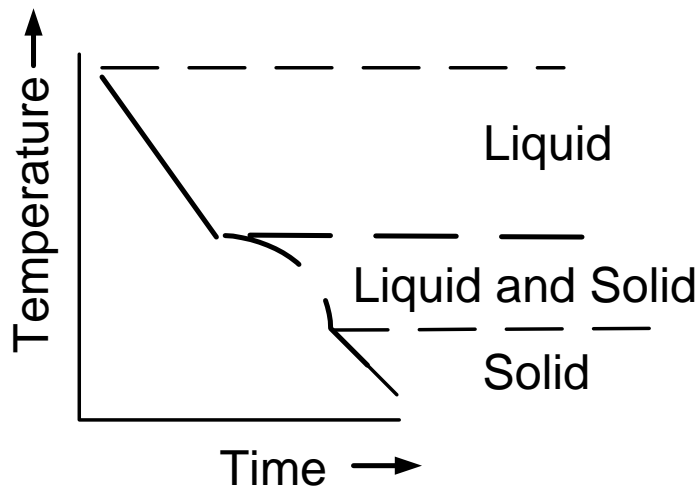
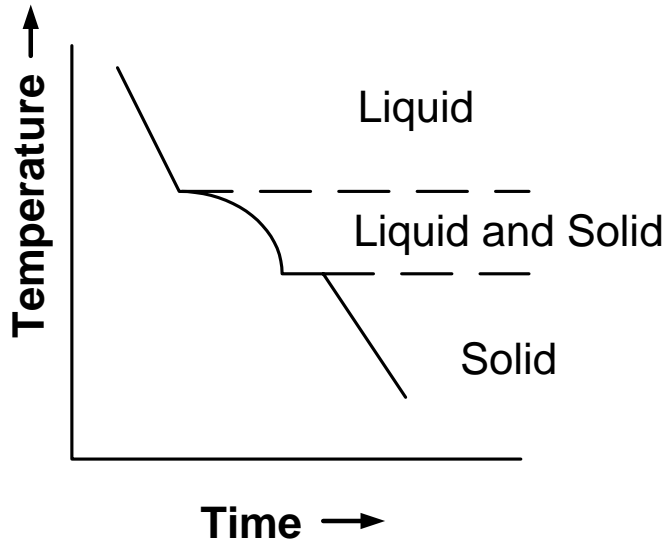


Figure 2 Cooling curve for an alloy.

Some alloys complete their solidification at a constant temperature and a curved temp/time as is shown in Figure 3. Examples are cadmium and bismuth or lead and tin alloys.



**Figure 3** Cooling curves for some alloys

### Alloying metals

Most pure metals are soft and not very useful in their pure state. There are of course exceptions i.e. copper is an excellent electrical conductor in its pure state. Therefore in order to increase properties like strength, hardness and corrosion resistance we mix two or more pure metals together to give us an alloy. Everyday examples of alloys include Bronze which is an alloy of Copper and Tin where the Tin content is usually less than 20%.

### Equilibrium

*Equilibrium may be defined as a state of balance of stability.* When a metal solidifies, equilibrium will occur under conditions of slow cooling where the fall in temperature is small in relation to the time elapsed. To achieve equilibrium it would be necessary, at every stage of cooling, to give the alloy elements time to diffuse (mix through on another) which would lead to a state that each grain of metal would have the same composition throughout. Complete diffusion seldom takes place in casting because solidification usually takes place before diffusion is complete.

### Thermal Equilibrium diagrams.

Instead of dealing with several different cooling curves for any alloy a quicker graph has been created using the various arrest points of all the alloys. When these points are marked on a graph and joined up we get a thermal equilibrium diagram which looks like this in Figure 4.

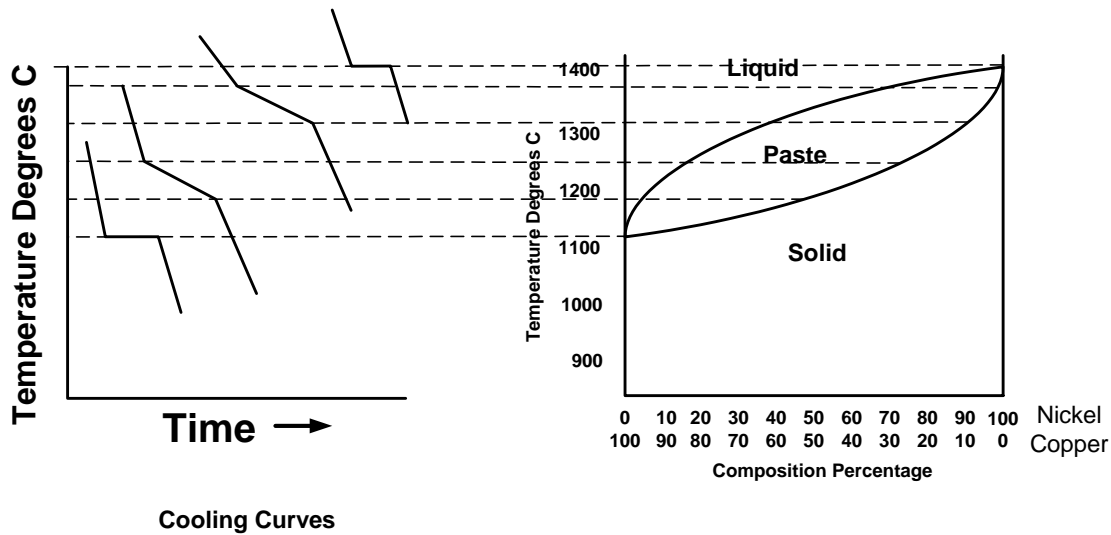


Figure 4 Creating a thermal equilibrium diagram.

As you can see there are three areas the liquid state, the solid state and the pasty state which consists of a solid phase and a liquid phase. A very important point to note is that the line joining all the points where the liquid begins to solidify is known as the *Liquidus* line while the line joining all the points where solidification is just complete is known as the *Solidus* line.

If we want to find out what temperature 60% Copper is fully solidifies at in an alloy of Copper and Nickel. Firstly we need the thermal equilibrium diagram for the alloy of Copper and Tin. This is the thermal equilibrium diagram for the alloy of Copper and Nickel. In order to find what temperature 60% copper solidifies at we simply draw a vertical line from 60% copper until it hits the solidus line and at this is the point where 60% Copper has fully solidified.

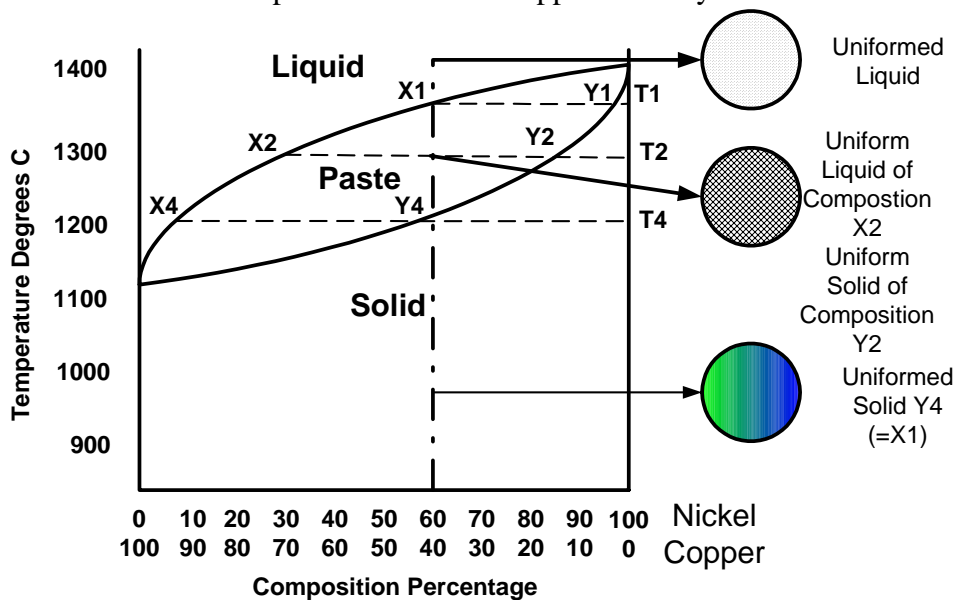


Figure 5 Nickel/Copper thermal equilibrium diagram

Thermal equilibrium diagrams are the metallurgist's maps. Just as a person considering climbing or walking in a new area would obtain and study an Ordnance Survey map, in order to fully plan the outdoor pursuit.

There are a number of different types of thermal equilibrium diagrams

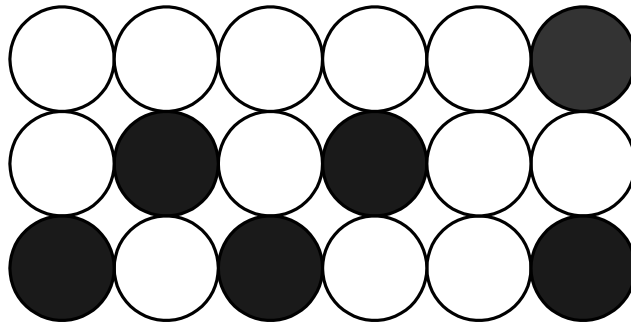
1. An alloy system in which the two metals are soluble in each other in all proportions in both liquid and solid state.
2. An alloy system in which the two metals are soluble in each other in all proportions in the liquid but not in the solid state.
3. An alloy system in which the two metals are soluble in each other in all proportions in the liquid but only partially in the solid state.
4. Iron/Carbon equilibrium diagram.

### 1. Solid Solution Alloys

A solid solution occurs when we alloy two metals and they are completely soluble in each other. If a solid solution alloy is viewed under a microscope only one type of crystal can be seen just like a pure metal. Solid solution alloys have similar properties to pure metals but with greater strength but are not good electrical conductors.

#### A. Substitutional solid solution

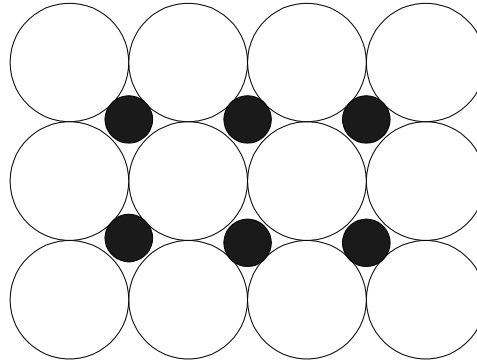
The name of this solid solution tells you exactly what happens as atoms of the parent metal ( or solvent metal) are replaced or substituted by atoms of the alloying metal (solute metal) In this case, the atoms of the two metals in the alloy, are of similar size. Here we see the brown atoms have been replaced or substituted by the blue atoms. Depicted in Figure 6.



**Figure 6 Substitutional Solid Solution**

#### B. Interstitial solid solution

In interstitial solid solutions the atoms of the parent or solvent metal are bigger than the atoms of the alloying or solute metal. In this case, the smaller atoms fit into interstices i.e spaces between the larger atoms. The smaller atoms are small enough to fit into the spaces between the larger solvent atoms. Shown below in Figure 7.



**Figure 7 Interstitial solid solution**

In both substitutional and interstitial solid solutions the overall atomic structure is virtually unchanged. Examples of solid solution alloys include Copper- Nickel, Gold- Silver all whom has an F.C.C structure. Molybdenum- Tungsten is an example of an solid solution with a B.C.C structure. Thermal diagrams created using solid solution alloys are given the name binary alloys and examples of these diagrams are shown below. One final thing we must deal with before we move on to the next type of alloy combination is the lever rule.

### C. The Lever Rule

The equilibrium diagram for a solid solution alloy that we have just been dealing with contains two distinct phases, liquid and solid solutions. Between the liquidus and solidus lines these two phases exist together in equilibrium and hence the area between the curves is known as the two phase region. If a horizontal line is drawn through the two phase region, such a line is called a *tie line*. We see a tie line drawn in this equilibrium diagram. The lever rule may be introduced by considering the simple see - saw. For the see- saw to be balanced, i.e in equilibrium, without movement up or down on either side, (weight W1) ( distance X1) = (weight W2) (distance X2).

This is the lever rule and in metallurgy the horizontal constant temperature tie-line represents the see - saw with the fulcrum at the alloy composition under consideration. Therefore if we take the diagram for the Copper -Nickel alloy as above and we take the composition of 60% copper and 40% Nickel the lever rule will apply like this.

$$\frac{\text{Weight of solid solution of composition } q}{\text{Weight of liquid of composition } m} = \frac{bm}{qb}$$

$$\text{Ratio} = bm/pb$$

## 2. Eutectic Alloys

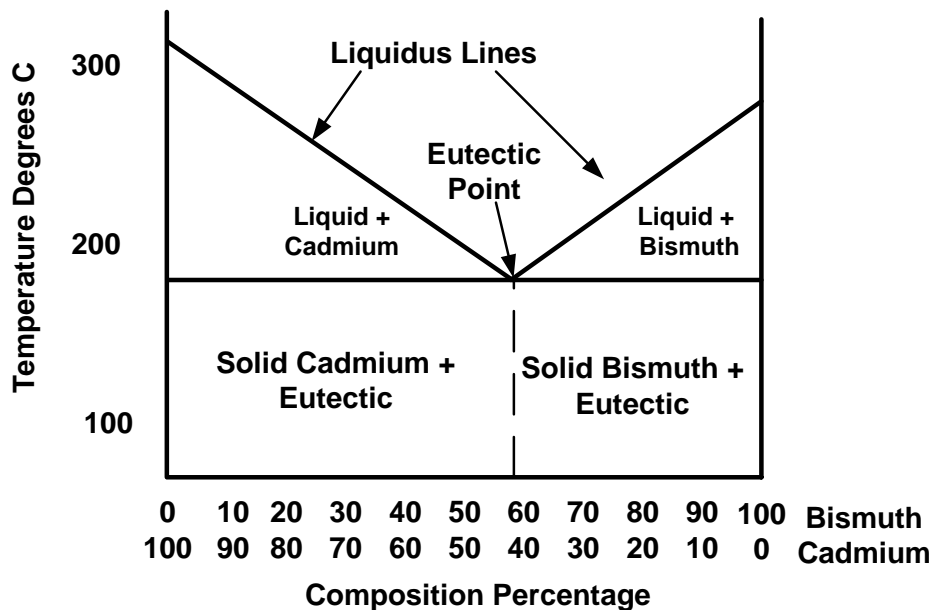
Eutectic

A eutectic is an alloy of lowest melting point in that alloy system and is formed when two distinct solid phases separate simultaneously at constant temperature from a single liquid phase (i.e.) changing from a solid to a liquid at a constant temperature.

Note: under the microscope it is possible to see the two pure metals as separate constituents (complete insolubility in solid state)

The solid solution equilibrium diagram discussed was formed by two metals being totally soluble in both the liquid and solid states. A Eutectic equilibrium diagram results when the two metals are soluble in the liquid state but insoluble in the solid state. In the liquid state the two metals are soluble in each other but when cooling is complete, the grain of the solid alloy consist of two distinguishable metals which can be seen under a microscope to be like a layer of one metal on top of a layer of the other metal. This situation is completely different where the cooled solid grains look just like one metal when viewed under a microscope. In order to fully understand this type of alloy combination we will look at the Cadmium/ Bismuth eutectic thermal equilibrium diagram. Cadmium and Bismuth are completely soluble in the liquid state, but are completely insoluble in the solid state. See Figure 8.

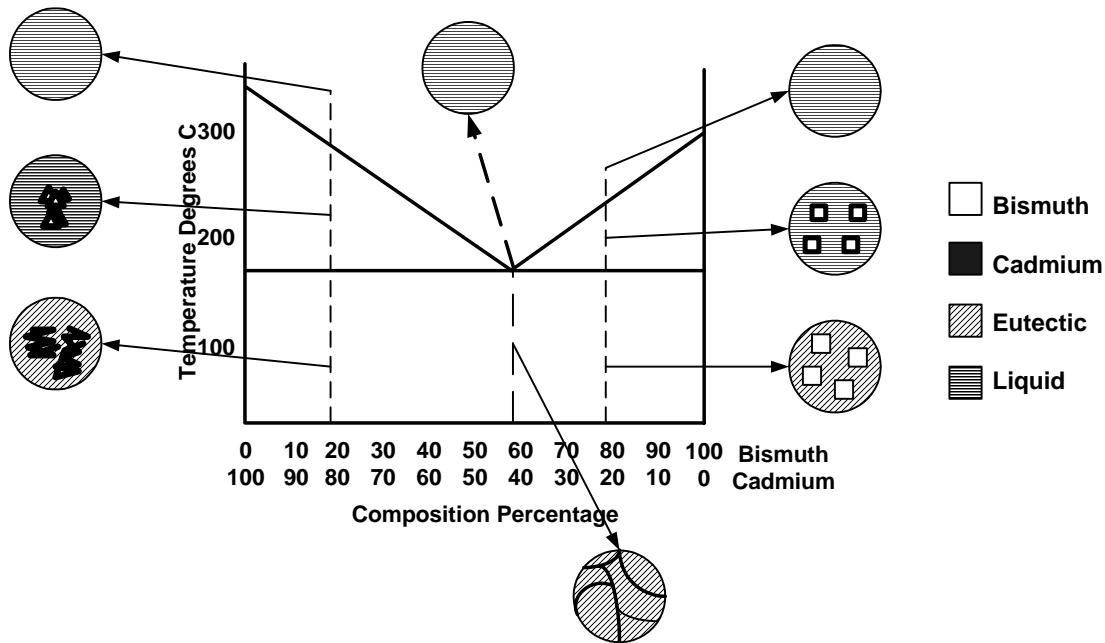
The first and most noticeable point on this diagram is the Eutectic point. The eutectic point as can be seen above is a point in the diagram where the liquid alloy changes to a solid without going through a pasty state. This is the lowest melting point of any composition for the alloy.



**Figure 8 Bismuth / Cadmium (Eutectic Alloy)**

As you would expect everything above the liquidus line is in the liquid state and in this state the two metals are totally soluble in each other. In the eutectic point region (represented by the green line) there is only the eutectic composition alloy. If you look at 100% Cadmium you will see that there is a large amount of solid Cadmium while this decreases in the alloys found nearer to the eutectic. The same applies for Bismuth. Therefore we can say that as the composition of the alloy moves away from the eutectic composition, grains of either Cadmium or Bismuth appear in the *eutectic matrix*.

### Microstructures



An examination at 80% Cadmium and 20% Bismuth. As the temperature falls crystal nuclei of pure cadmium begin to form. The temperature cuts the liquidus line at 80/20% and the other phase boundary is the 100% Cadmium ordinate. Dendrites of cadmium are deposited and the remaining liquid becomes increasingly richer in bismuth. Therefore the composition of the liquid moves to the right. As the temperature decreases more cadmium deposition takes place. The growth of cadmium dendrites and consequent enriching of the remaining liquid is bismuth.

The changing properties depending on metal composition are shown in Figure 9.



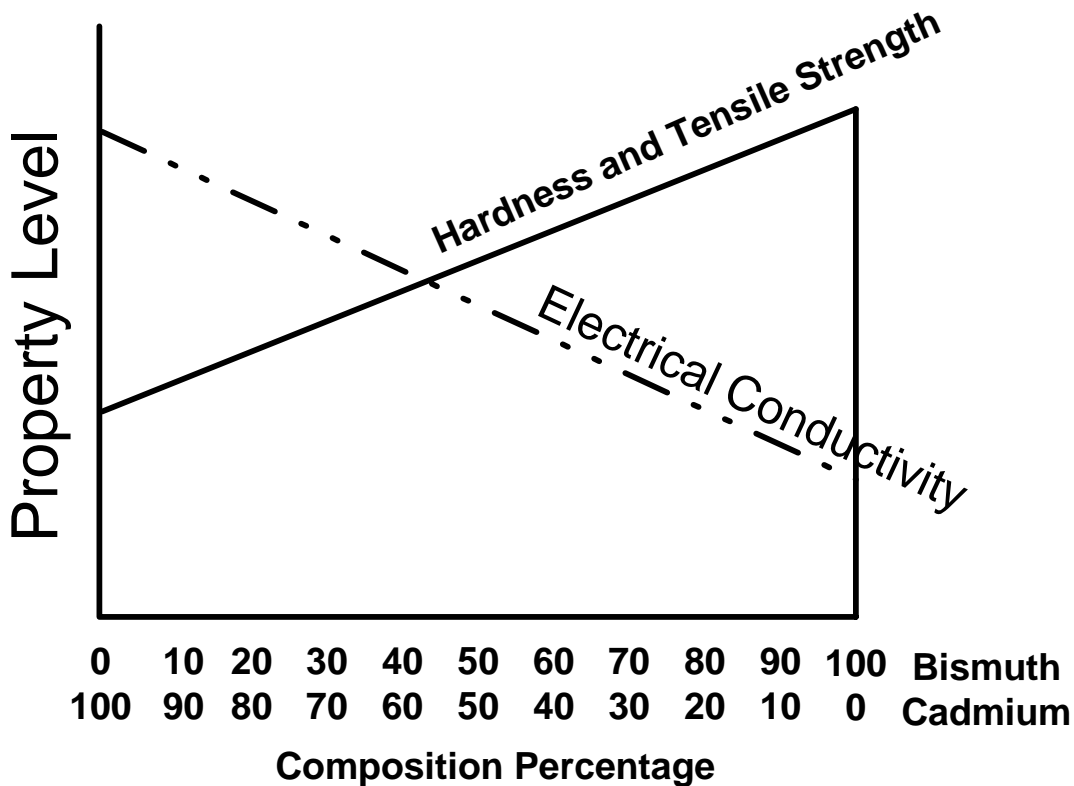


Figure 9 Metal Properties

### 3. Partial solubility

The partial solubility equilibrium diagram is derived from the previous two diagrams that indicated soluble and insoluble states. Few alloys exhibit total insolubility or total solubility and many metals combine to form a partial solubility system. The ends of the totally soluble system are amalgamated with the central portion of the insoluble or eutectic system to form the partially soluble in the solid state equilibrium diagram as shown here. The partial solubility diagram looks very different to what we have encountered so far so we will work on its various components before we move on to seeing its uses. Lines "ae" and "eb" (grey) are the liquidus lines. Lines "ac" and "bd" (maroon) are the Solidus lines. Two new lines exist in this diagram "cf" and "dg" (in blue) and these are the Solvus lines which show the solubility of the two metals in each other. Lead and Tin combine to form solder and the equilibrium diagram is shown below. On this diagram I have included drawing of a typical microstructure for six different alloys of Lead and Tin these microstructures are fairly self explanatory further explanations can be gotten by clicking on the relevant microstructure in Figure 10.

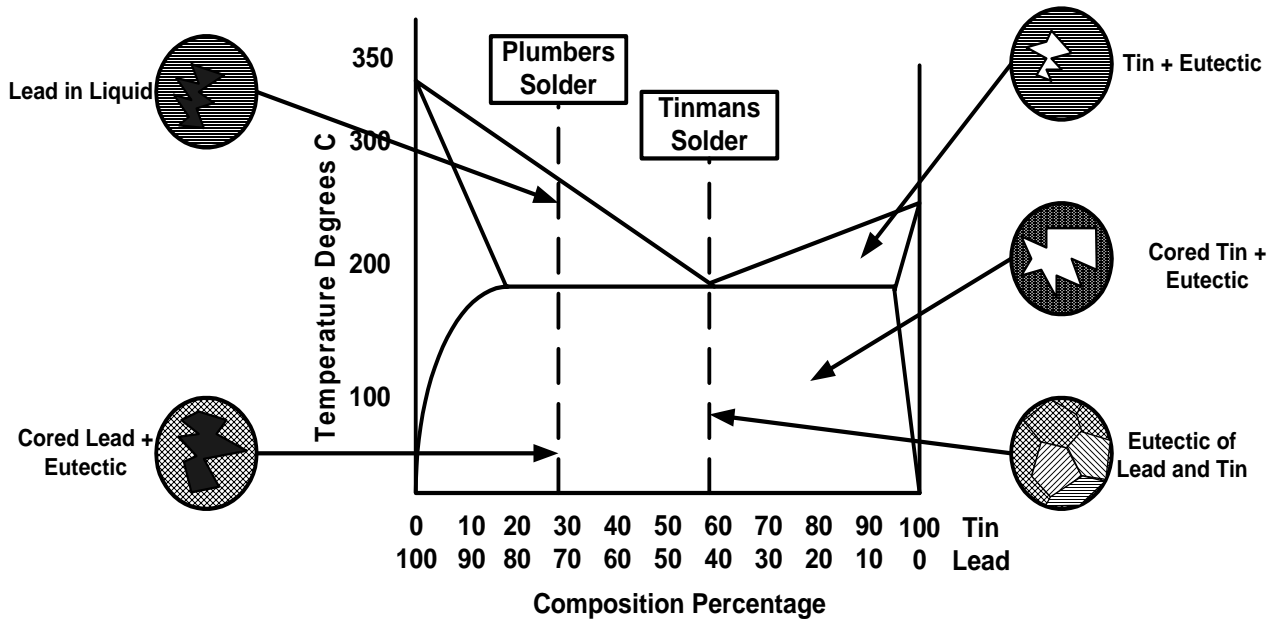
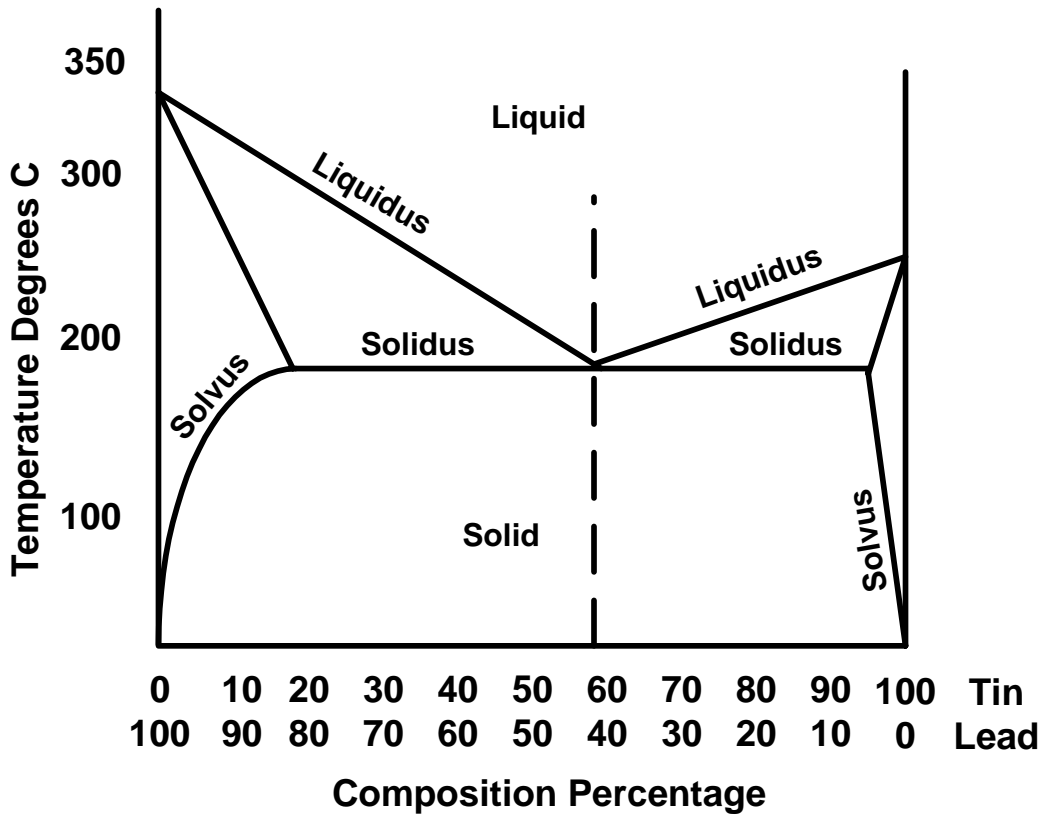


Figure 10 Lead/Tin (solder) partial solubility



**Figure 11 Liquidus and Solidus**Inter-metallic Compounds

Whilst some metal alloy systems exhibit total or partial solubility and others are insoluble in the solid state, a number of metals combine together to form an intermediate phase or intermediate compounds. There are two types of inter-metallic compounds which are often encountered in metallurgy.

Electron compounds

These compounds are of definite chemical crystal structure and arise if the two alloying metals are of different crystal structure, valency, and if one of these metals is electro- positive with the other being electro- negative an example of this type of electron compound would be an alloy of the elements Magnesium and Tin which combine to form an inter-metallic compound  $Mg_2Sn$ . The composition of the compound is fixed and consists of two atoms of Magnesium combining with one atom of Tin. Metallic compounds form a crystal lattice with the atoms of the alloying metals taking up specific positions within the lattice. These compounds are usually hard and brittle.

Interstitial compounds

Interstitial compounds, as the name suggests form between metals, or metals and non- metallic elements, with atom sizes very similar to those that form interstitial solid solution. One set of atoms fit into the spaces, or interstices, between the larger atoms. Iron Carbide ( $Fe_3C$ ) or cementite which is important in the study of Iron- Carbon diagrams is an example of an interstitial compound. As the chemical symbol for Cementite is  $Fe_3C$  we know that Cementite is an interstitial compound containing 3 iron atoms for every 1 atom of Carbon.

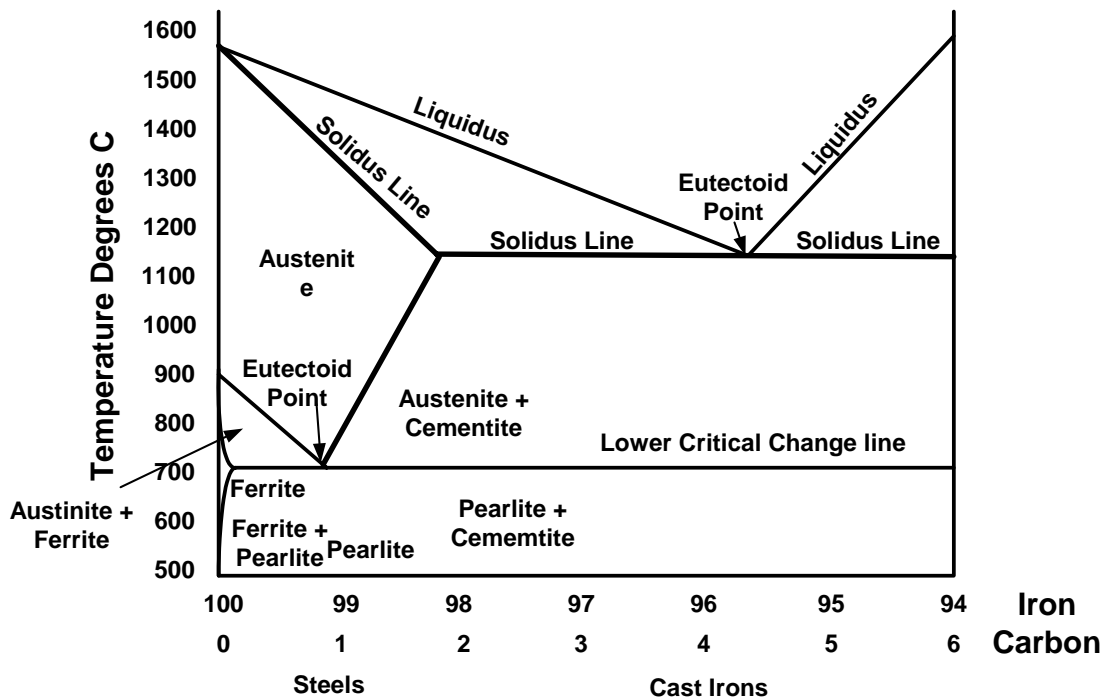
The ALLOTROPY of iron

Allotropy is the ability of some elements to exist in different physical forms (differing in color, hardness, melting point etc.). Iron is allotropic; at room temperature pure iron exists in the Body Centered Cubic crystal form but on heating transforms to a Face Centered Cubic crystal. The temperature that this first transformation takes place is known as a *critical point* and it occurs at 910 degrees Celsius. This change in crystal structure is accompanied by shrinkage in volume, since the atoms in the face centered crystal are more densely packed together than in the body centered cubic crystal. At the second critical point the F.C.C crystal changes back to a B.C.C crystal and this change occurs at 1390 degrees Celsius.

- Iron above 1390 degrees is known as *delta iron* ( $\delta$ ) BCC
- Iron between 1390 and 910 degrees is known as *gamma iron* ( $\gamma$ ) FCC
- Iron below 910 degrees is known as *alpha iron* ( $\alpha$ ). BCC

#### 4. The Iron Carbon Phase Equilibrium Diagram

Pure iron is a relatively soft, ductile low strength metal with few practical engineering applications. The addition of Carbon to pure iron increases strength and hardenability to useful levels. However it decreases ductility. The addition of Carbon influences the allotropic changes discussed above. Since mechanical behavior is directly related to the phases present it is important to study these phases and how they are influenced by temperature. A study of the Iron- Carbon phase diagram is used for this purpose. An Iron/Carbon phase diagram showing the phases present in any alloy containing up to 6% Carbon is shown in Figure 12.



**Figure 12 Iron Carbon**

This phase diagram tells us the various phases a particular alloy of Iron and Carbon will go through when allowed cooling down to room temp. In general iron carbon alloys up to 2% are known as steels while from 2% upwards the alloys are identified as cast iron. Our study mainly deals with the alloys up to 2% carbon i.e the steels part of the diagram so we will move on to look at this section of the diagram. To see the next page click on this diagram anywhere up to 2% Carbon content.

#### The Steel Section of the Iron - Carbon Diagram.

Shown here is the steel part of the iron carbon diagram containing up to 2% Carbon. At the eutectoid point 0.83% Carbon, Austenite which is in a solid solution changes directly into a solid

known as Pearlite which is a layered structure consisting of layers of Ferrite and Cementite. In order to fully understand the changes that occur in these different alloys of steels we will look at individual microstructures of common steel alloys. Here we see the various microstructures that exist in phases up to 2% Carbon content.

Notes added:

Liquidus line - This is the line at which all the alloys begin to solidify.

Solidus line - This is the line at which all the alloys complete their solidification. Anywhere below the solidus is solid.

Solvus line - separates two different solid phases in the material

### Sample exam type questions

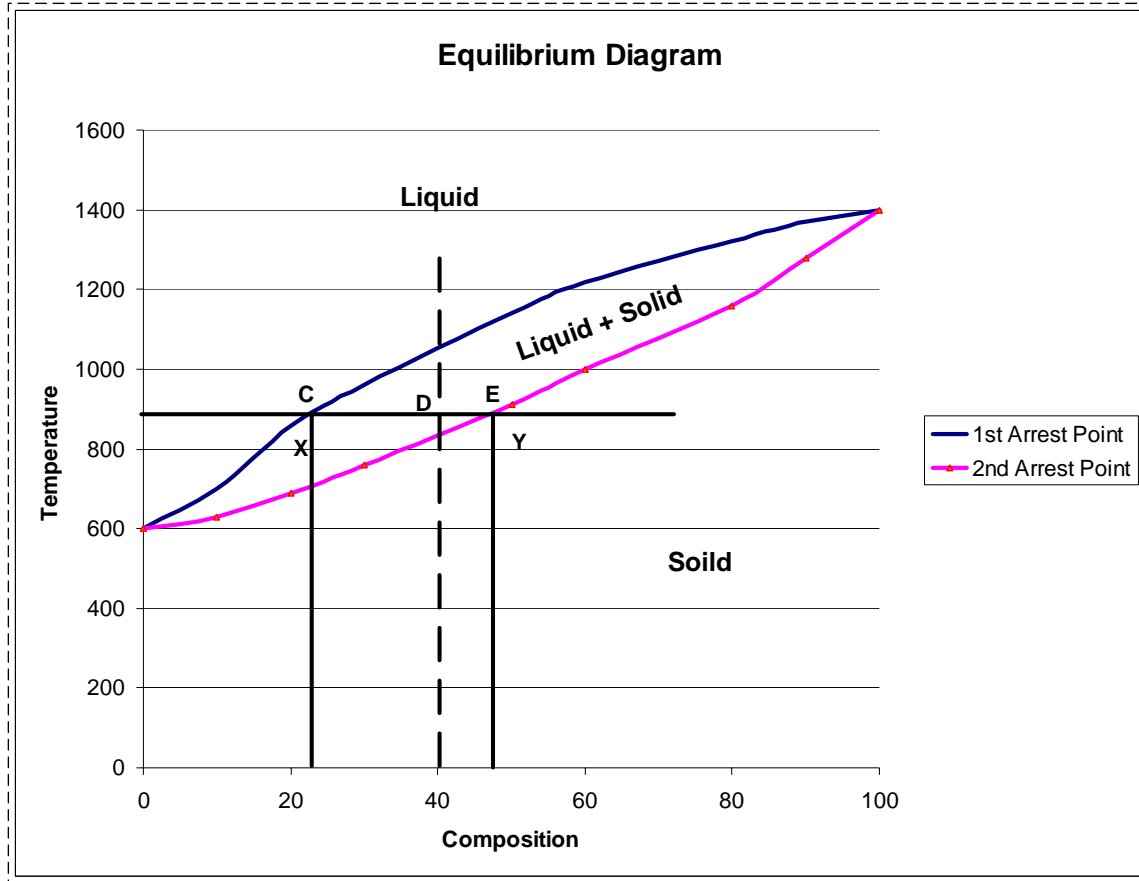
1. Metal A melts at 1400°C, Metal B melts at 600°C. Thermal arrest data is obtained from cooling curves for the alloy of AB and is shown below.

| %A               | 0   | 10  | 20  | 30  | 50   | 60   | 80   | 90   | 100  |
|------------------|-----|-----|-----|-----|------|------|------|------|------|
| 1st Arrest Point | 600 | 700 | 860 | 960 | 1140 | 1220 | 1320 | 1370 | 1400 |
| 2nd Arrest Point | 0   | 630 | 690 | 760 | 910  | 1000 | 1160 | 1280 | 0    |

- (i) plot and label the equilibrium diagram
- (ii) for an alloy containing 40% of A and 60% B state
  - (a) solidification commencing temperature
  - (b) solidification ending temperature
  - (c) composition of phases at 900°C
  - (d) the ratio of phases

### **Solution**

- (i)

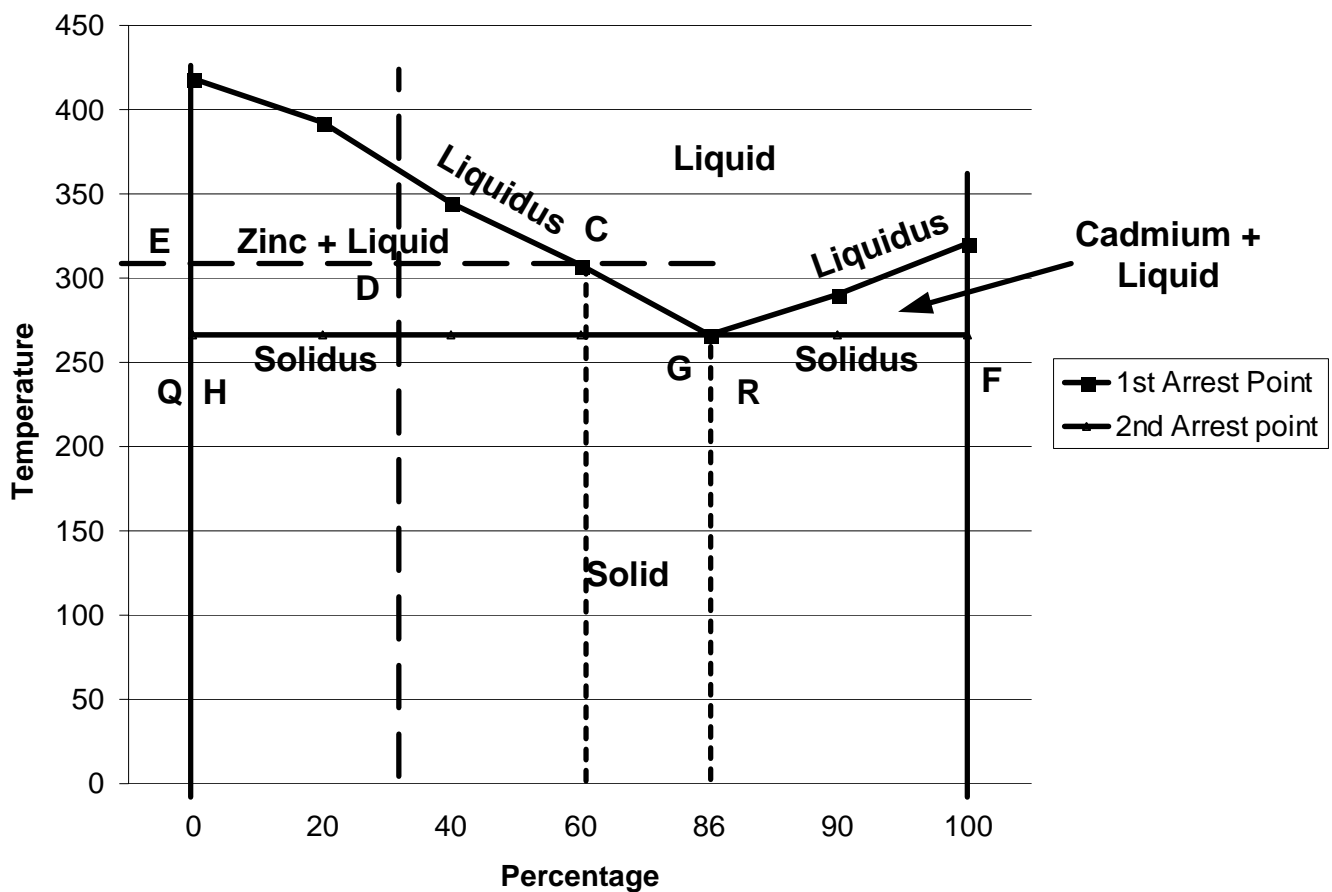


- (ii) (a) Solidification commencing at 1060°C  
 (b) Solidification ending at 840°C  
 (c) Composition of phases at 900°C = Liquid Point C = 25% A 75% B  
 Solid point E = 45% A and 65% B  
 (d) Ratio is Law of Lever rule. Moments about D.  
 $X \cdot CD = Y \cdot DE$   
 $X \cdot (40 - 25) = Y \cdot (48 - 40)$   
 $X \cdot 15 = Y \cdot 8$   
 $Y/X = 15/8 = 1.875$

2. From the cooling curves of the various alloys of Zinc and Cadmium the following data were obtained,

| % Cadmium        | 0   | 20  | 40  | 60  | 86  | 90  | 100 |
|------------------|-----|-----|-----|-----|-----|-----|-----|
| 1st Arrest Point | 419 | 392 | 345 | 308 | 266 | 290 | 321 |
| 2nd Arrest point |     | 266 | 266 | 266 |     | 266 |     |

- (i) Draw and label the equilibrium diagram
- (ii) With reference to the cooling curve, describe the cooling of an alloy containing 30% cadmium:
  - (a) composition of the alloy at 320°C
  - (b) Ratio of liquid to solid phase at 320°C
  - (c) The proportion of eutectic in the final structure

**Solution****Equilibrium Diagram**

- (iii) (a) at 320°C there will be dendrites of pure Zinc in a liquid, whose composition is given by point C
- (b) Ratio of solid phase is lever rule.  
 Moments about d =  $Y(ED) = X(CD)$   
 $Y(100-70) = X(70-47)$   
 $Y/X = 22/30$

(d) At the solidus, the ratio of solid zinc is again given by the lever rule.

Moments about G. Q= solid zinc and R= Eutectic

$$Q(HG)=R(GF)$$

$$Q(100-70)= R(70-15)$$

$$Q(30)= R(55)$$

$$Q/R = 55/30$$

The final proportion of the Eutectic in the final grain structure =  $30/55+30= 35.3\%$

### 2002 Higher Level

- (a) Explain **any two** of the following terms used in the heat treatment of steel.
- Recalescence;
  - Annealing;
  - Critical range;
  - Martensite.
- (b) Differentiate between **any two** of the following:
- Flame hardening and induction hardening;
  - Ferrite and pearlite;
  - Grey cast iron and white cast iron;
  - Eutectic and eutectoid.
- (c) The diagram represents a simplified equilibrium diagram for iron and carbon.
- Name the regions labelled;
  - Redraw the given diagram into your answer-book and highlight the temperature zones for hardening and stress relieving;
  - For a structure containing 0.6% carbon at 870°C, distinguish between the effects of rapid cooling and slow cooling.

### Solution

(a) (i) When a piece of high carbon steel is heated to its critical point at 720, the structure begins to change internally. There is little or no increase in temperature as this critical stage begins. The point at which it begins is referred to as the Decalesence point. If allowed to cool slowly the changes occur in reverse and the corresponding point is referred to as Recalesence.

(ii) Annealing: This is a heat treatment process to render a material as soft as is possible.

(iii) The Critical range starts at the point of Decalesence at 720 degrees. During this period the material glows less brightly, contracts dimensionally. A loss of magnetism is also experienced.

(iv) Martensite: A hard needle like structure that results from rapid cooling after the critical temperature. It is also very brittle. **8 + 8**

(b) (i) The component moves at a steady rate through the flames followed by water jets hardening the surface of the work. The component is placed inside a coil. The high frequency current in the coil induces eddy currents in the work. This in turn causes a rapid rise in the temperature in the outer layers. The component is cooled by water jets.

(ii) Ferrite is almost pure iron, Pearlite is alternate layers of ferrite and cementite. Cementite is a compound of iron and carbon.



(iii) Grey cast iron has flakes of graphite and is weak in tension and is generally softer than white, it has self-lubricating properties White cast iron is hard and brittle, the carbon is present in the form of ferrite and cementite.

(iv) Eutectic is a liquid to solid rapid change point where as Eutectoid is a solid to solid change point. **8 + 8**

(c)

(i) A: Ferrite.

B: Austenite and Ferrite.

C: Austenite.

D: Austenite and Cementite.

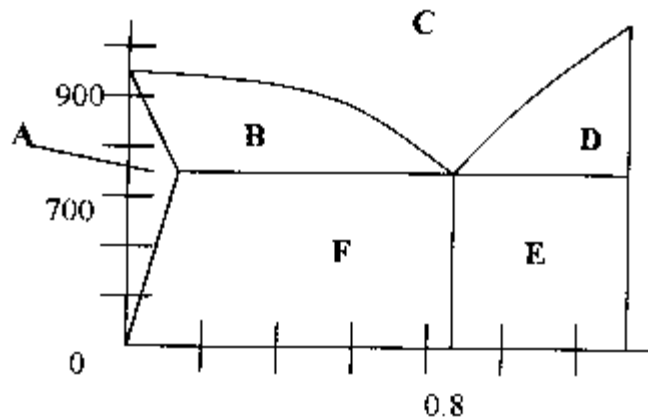
E: Pearlite and Cementite.

F: Ferrite and Pearlite.

(ii) Blue area: Stress relieving.

Red area: Hardening.

(iv) For a structure with 0.6% carbon when quenched rapidly the carbon in solution will have insufficient time to revert back and is essentially trapped in solution. The resulting structure is a hard needle like form referred to as Martensite. When cooled slowly all the critical changes occur in reverse and the reverts back to its original form. **18**



2005 HL

(a) Answer **any two** of the following:

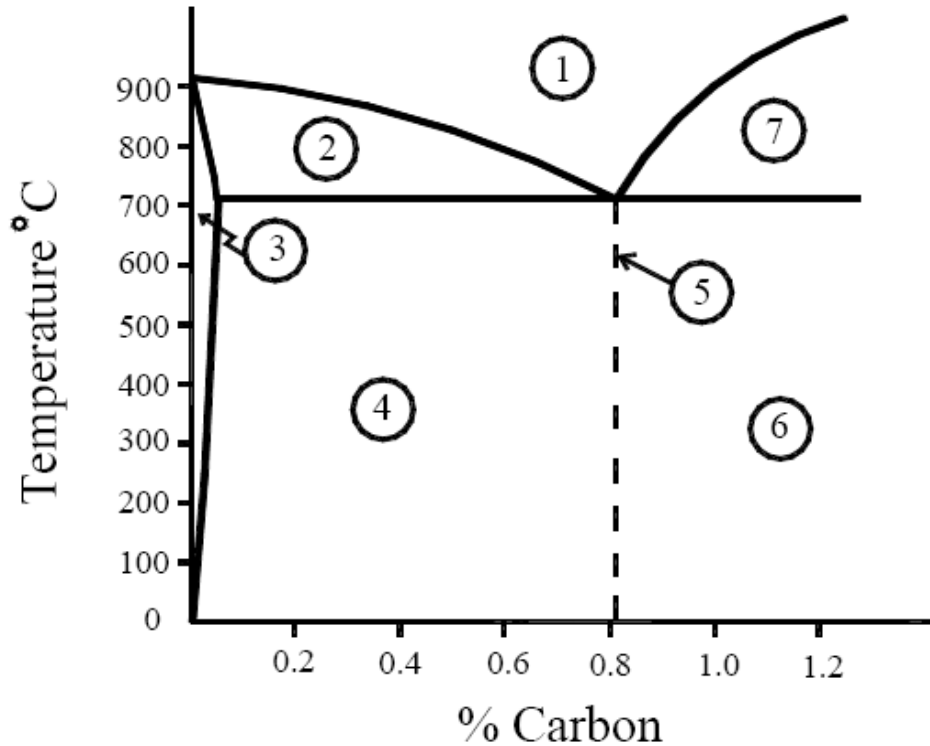
(i) Compare eutectic and eutectoid reactions, stating any temperature and structural changes;

(ii) Describe **one** method of measuring temperature in heat treatment furnaces;

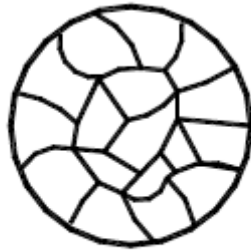
(iii) Differentiate between grey and white cast iron;

(iv) Explain the term recrystallisation in relation to heat treatment.

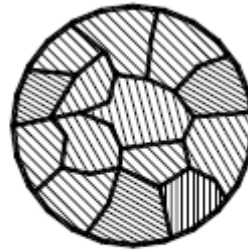
(b) A simplified portion of the iron-carbon equilibrium diagram is shown.



- (i) Name the regions 1, 2, 3, 4, 5, 6 and 7.  
 (ii) Identify the region most suited to each of the microstructures shown below.



A



B

(c) Describe **any two** of the following heat treatment processes:

- (i) Annealing;  
 (ii) Normalising;  
 (iii) Stress Relieving.

**Solution:**

(a) (i) **Eutectic:** This is a special change point where a liquid to solid change occurs. For steel this occurs at a temperature of 1140°C for the alloy with 4.3% carbon. Liquid changes directly to solid austenite and cementite.

**Eutectoid:** For steel, this reaction occurs during the solid state. Solid austenite changes to solid pearlite. This occurs at a temperature of 723°C for the alloy with 0.83% carbon.

(ii) Methods used to measure furnace temp:

**Optical pyrometer:** The optical pyrometer compares the intensity of the Light coming from the filament of a lamp. The current flowing in the lamp is adjusted to match the light from the furnace using a variable resistance. When a colour match is obtained the lamp filament disappears and a temperature scale reading is taken.

**Thermo-electric pyrometer:** If two dissimilar metals are joined together, with a Galvanometer placed in closed circuit at the open end, a rise in temperature of the joined end produces an electrical current which is recorded by the galvanometer. The galvanometer is calibrated to read in degrees of temperature instead of indicating electrical units.

• Seager cones is another method employed.

(iii) **Grey cast iron:** Forms due to slow cooling. Carbon is present as graphite flakes. Grey cast iron is soft, weak in tension, easy to machine. It has self lubricating and vibration dampening properties. It resists corrosion in many common engineering environments.

**White cast iron:** Forms under quick cooling conditions. The carbon is present in the form of ferrite and cementite. White cast iron is hard and brittle.

(iv) **Recrystallisation:** This is where new crystals begin to grow from the distorted or dislocated nuclei formed during cold working. The component is heated as for annealing and as the temperature is increased, the new crystals grow until they have completely replaced the original distorted structure Degrees of hardness, tensile strength and percentage elongation all improve during recrystallisation. **(Any two) 8 + 8**

(b) (i) **1** – Austenite

**2** – Austenite and ferrite

**3** – Ferrite

**4** – Ferrite and pearlite

**5** – Pearlite

**6** – Pearlite and cementite

**7** – Austenite and cementite **7 × 2**

(ii) Region **3** – Diagram **A**

Region **5** – Diagram **B 2 + 2**

(c) (i) **Annealing:** This process fully softens the steel. The steel is heated to above its upper critical temperature. It is then allowed to “soak” in the furnace at this temperature. Cooling is controlled by, reducing the temperature of the furnace gradually.

(ii) **Normalising:** Normalising removes internal stresses and refines abnormal grain structures which occur during hot or cold rolling and forging. The steel is heated to approximately 50°C above its upper critical temperature and allowed cool in air. This improves machinability.

(iii) **Stress Relieving:** An annealing process which is carried out below the lower critical temperature of carbon steel. The component is heated and held at a specified temperature for a long period of time. It is cooled slowly, the temperature and time dependent on the component. This is used to relieve the build-up of internal stresses caused during cold working, thus reducing brittleness. **(Any two) 8 + 8**