the extreme high–pressure modification, melts to form water at about 100°C under a pressure of 20,000 atm. It is interesting to see *the melting ice to be so hot* ! The existence of ice–IV has not been confirmed.
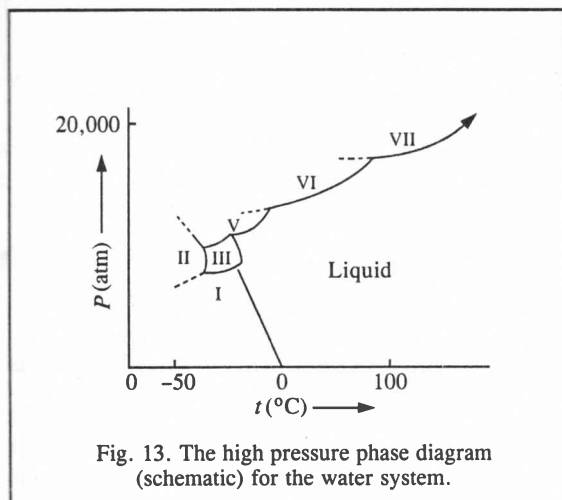

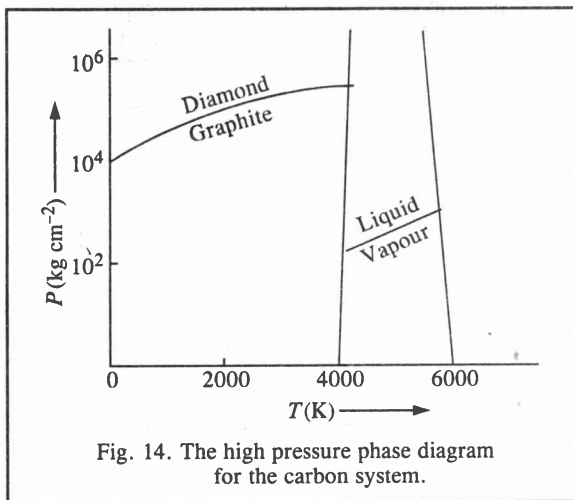Fig. 13. The high pressure phase diagram (schematic) for the water system.

Fig. 14. The high pressure phase diagram for the carbon system.

2. The Carbon System. Fig. 14 shows the phase diagram for the carbon system at high pressures. We see from this diagram that it is possible to convert graphite into diamond by compressing it at high temperature. It has been estimated that this conversion can take place at 4,000°C under a pressure of 2×10^6 (*i.e.,* two million) atm. Unfortunately, however, no containers can withstand these extremes of temperature and pressure. In the presence of a catalyst, such as cobalt or tantalum, the transformation can be affected at 2,000°C and 70,000 atm pressure.

THE TWO–COMPONENT SYSTEMS

For a two–component system, the phase rule becomes $F = 4 - P$

Since the minimum number of phases, P, in any system is 1, the maximum number of degrees of freedom, F, is 3. Thus, three variables would be necessary to describe a system. Since three variables are difficult to graph, it is customary to hold one of them say, the pressure, constant on a diagram of temperature plotted versus concentration. This reduces the degree of freedom of the system by one and the phase rule equation is then written as $F' = 3 - P$.

This is known as the **reduced phase rule equation.**

For the two–component solid–liquid equilibria, we come across the following cases : 1. The two components are miscible in the liquid state. 2. The two components are only partially miscible in the liquid state. We shall restrict ourselves to the former case. Under this category, we shall discuss the following cases :

A. The two components are not miscible in the solid state and form a eutectic mixture.

B. The two components form a stable compound with congruent melting point.

C. The two components form a compound with incongruent melting point.

We shall discuss some of these systems in the following pages.

TYPE A. SIMPLE EUTECTIC SYSTEMS

The general phase diagram of such a system is presented in Fig. 15.

The points A and B represent the melting points of the components A and B. As increasing quantities of B are added to A, the freezing point of A falls along the curve AC. Similarly, as increasing

quantities of A are added to B, the freezing point of B falls along the curve BC. Thus, along the curve AC, the solid A is in equilibrium with the solution (liquid) of the component B in A. This is called the freezing point curve of the component A. Similarly, along the curve BC, the solid B is in equilibrium with the solution (liquid) of the component A in B. This represents the freezing point curve of the component B. The number of phases along AC, as well as along BC, is two. Since measurements are made at atmospheric pressure (*i.e.*, at constant pressure), we may apply the reduced phase rule equation. Thus, we have $F' = C-P+1 = 2-2+1 = 1$. Hence, the system is monovariant. The composition varies with temperature along AC or BC, as the case may be. The two curves intersect at some point C where both the solids A and B must be
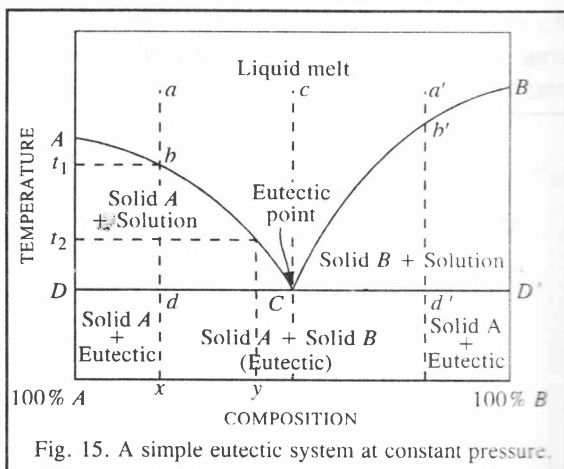

Fig. 15. A simple eutectic system at constant pressure.

in equilibrium with the liquid phase (*i.e.*, the liquid solution of the two components). The number of phases is 3. Applying the reduced phase rule equation, $F' = 0$. Thus, the system at C has no degree of freedom. It is invariant. This means that under a given pressure, the system consisting of two solids and their liquid solution, *i.e.*, $A-B-L$, can exist only at a definite temperature and that the composition of the liquid (solution) phase also is definite. The point C, as can be seen, is the lowest temperature at which liquid can exist in equilibrium with the solids A and B. Since the mixture of A and B of composition corresponding to point C, has the lowest melting point, the point C is known as the **eutectic point** (*eutectic* means *easy melting*).

In the area above the lines AC and BC, the two components are present only as a homogeneous liquid solution. As the system consists of only one phase in this area, it is bivariant. Therefore, in order to define any point in this area, it is necessary to specify the temperature as well as the composition. It is understood that the pressure has been kept constant.

Suppose, a liquid mixture of composition represented by a point a is cooled at a constant pressure. The temperature will fall without any change of composition until the point b on the freezing point curve AC is reached. At this temperature, which corresponds to t_1, the solid A separates out. The system now consists of two phases and is, therefore, monovariant (assuming pressure to be constant). The temperature will fall only with change in composition of the liquid phase. Therefore, as cooling continues, the component A keeps on separating out and the solution becomes relatively richer in B. The temperature and the solution composition both change along the curve bC. Thus, at temperature t_1, solid A is in equilibrium with solution of composition x and at temperature t_2 it is in equilibrium with solution of composition y. It is evident, therefore, that in area ACD, solid A is in equilibrium with solutions of varying composition given by the curve AC depending upon the temperature.

When the eutectic temperature is reached at d, the second solid B also begins to crystallise out. The system now has 3 phases and, therefore, at constant pressure, it becomes invariant. On further cooling the system, solid A and solid B separate out together in a fixed ratio so that the composition of the solution remains constant as indicated by the point C. The temperature also remains constant. When the solution phase has been completely solidified and the system consists only of a mixture of solid A and solid B, it becomes monovariant and continued cooling results in fall of temperature below the line DD' into the area within which only the two solids coexist, as shown.

Similarly, if the composition of the original liquid is on the right side of the eutectic point, as represented, say, by the point a', similar series of changes will be observed on cooling. In this case, however, on reaching the point b' on the freezing point curve BC, the solid B will separate out. As cooling continues, B keeps on separating and the solution becomes now richer and richer in A. The temperature and the composition both change along the curve $b'C$. Thus, in the area BCD', solid B is in

equilibrium with solutions of varying composition. Again, when the eutectic temperature is reached at the point d', A also begins to separate out. The system now becomes invariant. On withdrawing heat further from the system, the temperature remains constant and solid A and solid B continue to separate in the same ratio so that the solution composition also remains constant. Ultimately, the solution phase solidifies completely as before and thereafter the temperature of the system can fall below the line DD' into the area of coexistence of two solids A and B.

Consider a special case when the liquid has the same composition as that of the eutectic. This is represented by the point c. On cooling, no solid will separate out until the eutectic temperature is reached. At this temperature, both the solids A and B crystallise out simultaneously. The temperature and composition of the solution remain constant until the system gets completely solidified.

Thermal Analysis. Cooling Curves

It can be seen on reference to Fig. 15 that when a liquid mixture (or melt) consisting of A and B is allowed to cool, solid A (or solid B) begins to separate out as soon as the temperature falls to a point on the line AC (or BC), as the case may be. The number of phases is now two, viz., the liquid mixture and the solid A or B. If cooling is continued thereafter, the given solid continues to deposit with the corresponding fall in temperature till the eutectic temperature (point C) is reached. At this point both the solids separate out and the number of phases rises from two to three. The system now becomes invariant and, therefore, the temperature remains constant.

One important point to be remembered in this connection is that the separation of the solid A (or B) from the liquid solution is an exothermic process. The heat evolved in the process is similar to the heat given out when the same substance changes from liquid to solid state at its freezing point. As a result of this, the rate of cooling is diminished as soon as the separation of solid A or B commences to take place. The rate of cooling is, therefore, slower than that before till the eutectic point is reached. After this, temperature remains unchanged.

The above facts can be represented by plotting fall of temperature with time as in Fig. 16. Such a graph is called a **cooling curve.** In the figure, the rate of cooling along ab is quite rapid. This is when separation of a solid has not yet commenced. At b one of the solids begins to separate. The rate of cooling along bd, therefore, slows down. The cooling curve thus shows a distinct break at the point b. At d, the eutectic point is reached. The temperature, therefore, remains constant along dd' until the solidification has taken place completely. With the disappearance of the liquid phase, the system now consisting only of solid phase, becomes univariant and further cooling results in fall of temperature along de. Thus, there are three breaks in the cooling curve. The first one occurs at the freezing point of the mixture where the solid first commences to form. The second break occurs at the eutectic point and the third one occurs when the mixture gets completely solidified.
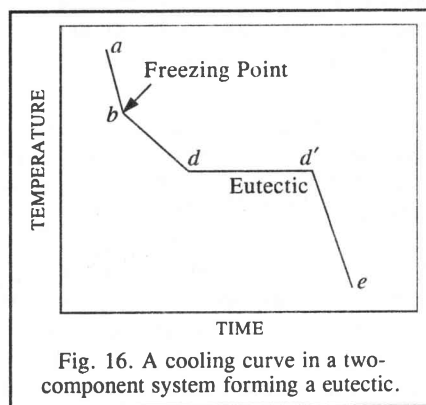

Fig. 16. A cooling curve in a two-component system forming a eutectic.

The above discussion provides a basis for the principle on which the method of **thermal analysis** used in the study of solid–liquid phase equilibria involving metals, is based. In actual practice, a number of mixtures of metals A and B of different compositions lying between 100% A and 100% B are prepared. These are heated above their respective melting points so that there is only one phase (i.e., liquid phase) in every case. Each liquid is then allowed to cool slowly and the temperature is recorded after small intervals of time. In this way several cooling curves are obtained, as shown in Fig. 17. The first break in each curve occurs at the freezing point, that is, at the commencement of the freezing of the mixture of that particular composition. As the mixtures differ in the compositions, their freezing will commence at different temperatures. The second break occurs at the point at which the temperature remains constant. This gives the eutectic temperature which will be the same in all the mixtures irrespective of their initial

compositions. The freezing points of pure *A* and pure *B* (*i.e.,* 100% *A* and 100% *B*) are also determined in a similar manner. The equilibrium diagram for the system of two metals (*A* and *B*) under examination is thus determined. This is illustrated in Fig. 17.
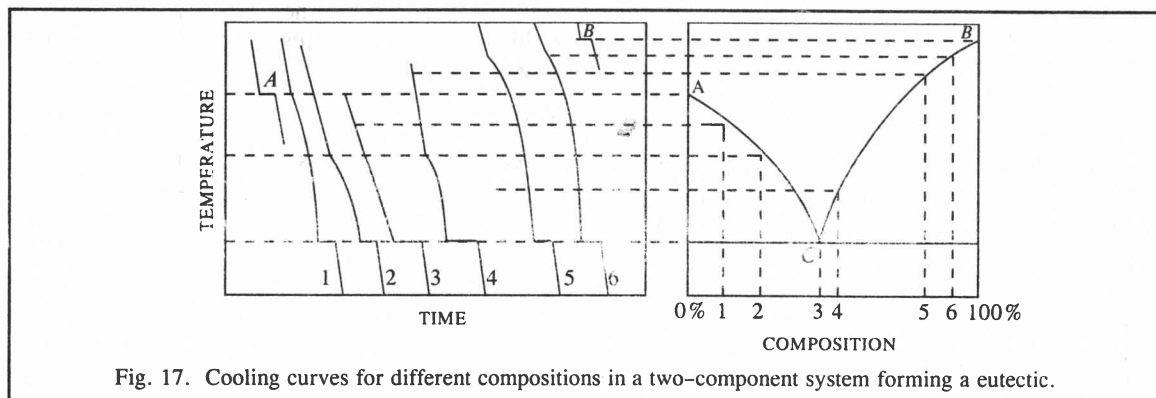

Fig. 17. Cooling curves for different compositions in a two-component system forming a eutectic.

There are many two–component systems which follow the general behaviour as depicted in Fig. 15. They include pairs of metals, metallic alloys, organic compounds and a number of salts and water. Two representative cases, one involving metals and the other involving a salt and water will be discussed here.

LEAD—SILVER SYSTEM

These metals are completely miscible in liquid state and do not give rise to any compound formation. The equilibrium diagram, therefore, is similar to that shown in Fig. 15. The various features are illustrated in Fig. 18.

Pure lead melts at 327°C and the addition of silver lowers its melting point along *AC*. Thus, *AC* is the freezing point curve of lead containing varying amounts of silver. Pure silver melts at 961°C and the addition of lead lowers its melting point along *BC*. Thus, *BC* is the freezing point curve of silver. Along *AC*, solid lead and solution (melt) coexist while along *BC*, solid silver and solution (melt) coexist. The system, at constant pressure, is monovariant along *AC* as well as along *BC*.

C is the **eutectic point** where the three phases, solid lead, solid silver and their

Fig. 18. The phase diagram for lead–silver caption system.

liquid solution (melt), coexist. It is an invariant point. The temperature of the eutectic is 303°C and the composition of the solution phase is 2·6 per cent silver, as shown in the figure. The phases coexisting in the various areas or regions are also shown in the figure.

The phase diagram of lead—silver system has a special significance in connection with the **desilverisation of lead.** The argentiferous lead consisting of a very small percentage of silver is first heated to a temperature well above its melting point so that the system consists only of the liquid phase represented, say, by the point *a*, in the figure. It is then allowed to cool. The temperature of the melt will fall along the line *ab*. As soon as the point *b* is reached, lead will begin to crystallise out and the
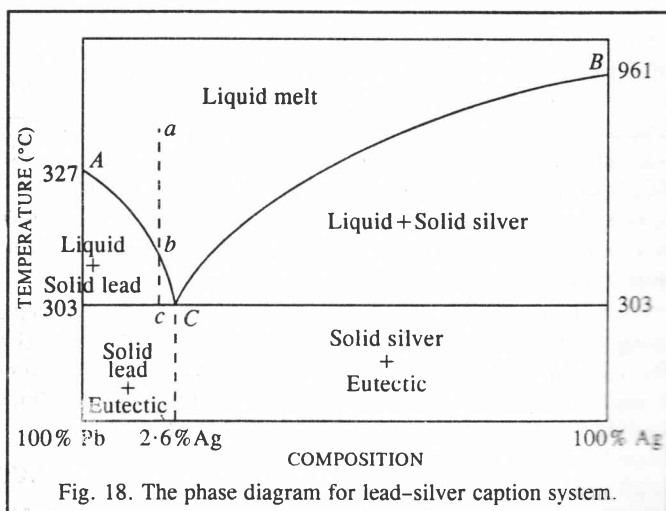
solution will contain relatively increasing amounts of silver. Further cooling will shift the system along the line bC. Lead continues to separate out and is constantly removed by means of ladels. The melt continues to be richer and richer in silver until the point C is reached where the percentage of silver rises to 2·6. Thus, the original argentiferous lead which might have contained 0·1 per cent (or even less) of silver, can now contain up to 2·6 per cent of this metal. The process of raising the relative proportion of silver in the alloy is known as **Pattinson's process.**

BISMUTH–CADMIUM SYSTEM

The fully labelled phase diagram for the bismuth–cadmium system is shown in Fig. 19. The characteristic features of this sytem are similar to those of lead–silver system described above.

Pure bismuth melts at 317°C and the addition of cadmium to molten bismuth lowers its freezing point along the curve AC which is the freezing point curve of bismuth containing varying amounts of cadmium. Similarly, addition of bismuth to molten cadmium lowers the freezing point of cadmium along the curve BC which is the freezing point curve of cadmium containing varying amounts of bismuth. In the region above the curves AC and CB, bismuth and cadmium are present in the form of a melt. Since in this region, $P=1$, $F=2$, i.e., the system is bivariant. The two degrees of freedom are the temperature and the composition. Thus in this region, temperature and composition can be varied

Fig. 19. The phase diagram for the bismuth–cadmium sytem

without changing the number of phases. Along the curve AC, bismuth freezes out and along the curve BC, cadmium freezes out. Thus, in the area below AC and down to the eutectic point there are two phases, viz., bismuth and liquid whose composition is determined by the temperature. Similarly, in the area below BC down to the eutectic, the two phases in equilibrium are cadmium and liquid. Since in these regions, $P=2$, $F=1$, i.e., the system is univariant.

At the eutectic point C, three phases coexist ; these are bismuth, cadmium and liquid. The composition of the eutectic is 40% cadmium. At C, $P=3$ so that $F=0$, i.e., the system is invariant. The eutectic temperature is 146°C. The area below the eutectic point is a two–phase region as labelled in the phase diagram. Since in this region $P=2$, $F=1$. Thus, only the temperature need be specified to describe the system completely.
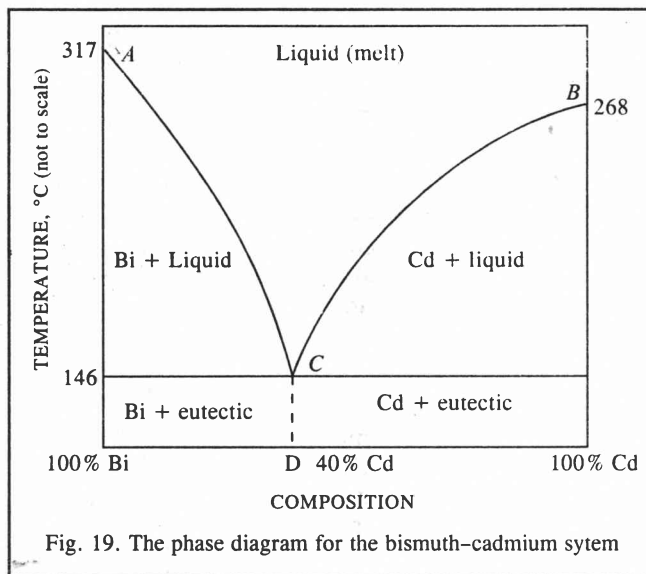
POTASSIUM IODIDE—WATER SYSTEM

The potassium iodide—water system is a typical example of a binary system involving a salt and water which form a eutectic mixture and will be discussed in some details.

One essential feature of a salt—water system is that the melting point of the salt is usually very high, even higher than the critical temperature of water. It is, therefore, not possible to represent melting points of both the components in the equilibrium diagram as has been done in the case of the binary systems involving metals.

The equilibrium diagram of potassium iodide—water system is shown in Fig. 19. Its resemblance with the general diagram for binary systems forming eutectics (Fig. 15) is quite evident. However, the melting point of potassium iodide, as expected, is not realised in practice, as explained above.

A is the melting point of ice (or freezing point of water). At a pressure of 1 atm and in the presence