

### ❖ Eutectic Systems (Calculation of Eutectic Point)

In order to understand the eutectic systems in a comprehensive manner, we need to recall the general phase diagram for eutectic systems i.e.

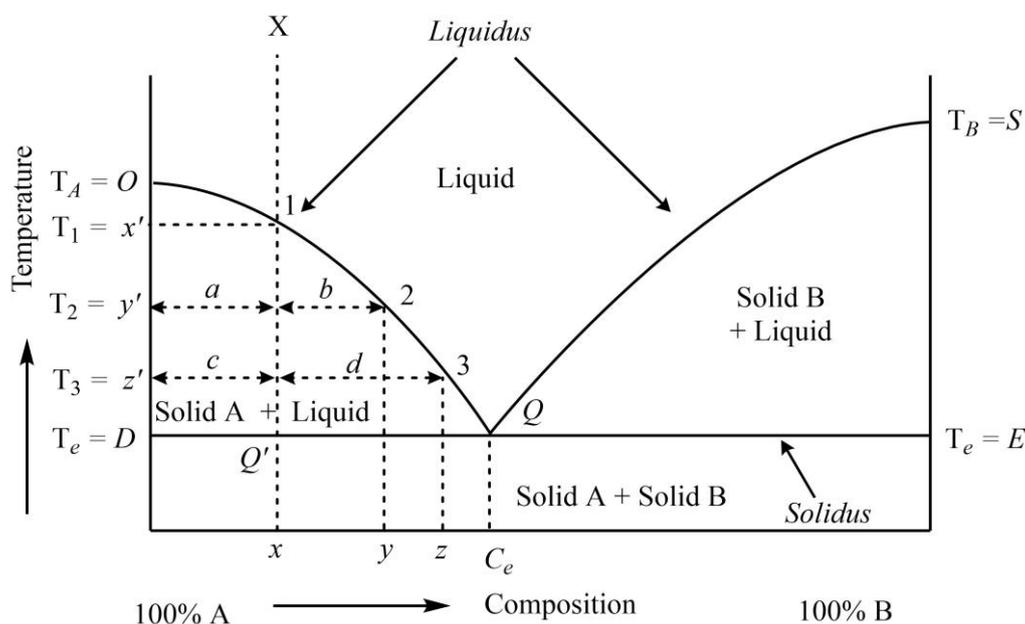


Figure 12. The general phase diagram of eutectic systems.

It is obvious from the phase diagram given above that the diagram has two curves  $OQ$  and  $QS$  enclosing the area  $ODQ$  and  $SQE$ , respectively. The significance of different parts of the above-depicted diagram is discussed below.

**1. The  $OQ$  and  $SQ$  curves:** The point  $O$  and point  $S$  represent the freezing point the pure compound  $A$  and compound  $B$ , respectively. When component  $B$  is added to component  $A$ , its freezing point of decreases regularly along  $OQ$ . Likewise, when component  $A$  is added to component  $B$ , its freezing point decreases regularly along  $SQ$ . In conclusion, we can say that the curve  $OQ$  and  $SQ$  represent the temperature-conditions at which solid  $A$  and solid  $B$  are in equilibrium with the liquid mixture. Since there are only two phases involved, and both are condensed in nature (solid and liquid), we need to use condensed or reduced phase rule here i.e. after putting  $C = 2$  and  $P = 2$  in equation (114), we get

$$F' = 2 - 2 + 1 = 1 \quad (117)$$

Which means that the system is univariate. In other words, only one condition is needed to be defined to define the whole system; for instance, if we define a particular composition of  $A$  and  $B$ , the freezing point of the mixture is completely fixed. The curve  $OQ$  and  $SQ$  also called as “liquidus” because they separate the field of all liquid from that of liquid + solid crystals.

**2. Point  $Q$  or the eutectic point:** At point ' $Q$ ', all the three phases (solid A + solid B + liquid) are in equilibrium with each other; and therefore, zero degrees of freedom exists at this point i.e.

$$F' = 2 - 3 + 1 = 0 \quad (118)$$

This means that we can neither change temperature nor composition without disturbing the mutual equilibrium of solid A, solid B and liquid. Moreover, below this temperature, the mixture freezes as a whole. This temperature is called as “eutectic point” and the composition corresponding to this point is called as eutectic composition.

**3. Area  $ODQ$  and  $SQE$ :** In addition to the enclosed area  $ODQ$  and  $SQE$ , there are also areas above  $OQS$  line and below  $DQE$  line as well.

*i) Area above  $OQS$ :* It is obvious from the phase diagram that the area lying above the line  $OQS$  only has a liquid phase, which means

$$F' = 2 - 1 + 1 = 2 \quad (119)$$

Two degrees of freedom means that we can change temperature well as composition without disturbing completely melt state as long as the temperature-composition coordinates lie above the line  $OQS$ . In other words, we need to define both, temperature as well as composition, to define the system completely in this area.

*ii) Area below  $DQE$ :* It is also obvious from the phase diagram that the area lying below the line  $DQE$  has two solid phase, which means

$$F' = 2 - 2 + 1 = 1 \quad (120)$$

The only one degree of freedom means that we can change temperature only without disturbing the state of the system. In other words, we only need to define the temperature to define the system completely in this area. The curve  $DQE$  is also called as “solidus” because they separate the field of all solids from that of liquid + solid crystals.

*iii) Area enclosed by  $ODQ$ :* It is also obvious from the phase diagram that the area enclosed by  $ODQ$  line has solid A + liquid phases, which means

$$F' = 2 - 2 + 1 = 1 \quad (121)$$

The only one degree of freedom means that we can change temperature only without disturbing the state of the system. In other words, we only need to define the temperature to define the system completely in this area.

*iv) Area enclosed by  $SQE$ :* It is also obvious from the phase diagram that the area enclosed by  $SQE$  line has solid B + liquid phases, which means

$$F' = 2 - 2 + 1 = 1 \quad (122)$$

The only one degree of freedom means that we can change temperature only without disturbing the state of the system. In other words, we only need to define the temperature to define the system completely in this area.

It is also worthy to note that we can find out the equilibrium phase-composition at any temperature by simply plotting a horizontal line that cuts the line  $OQ$  or  $SQ$ . For instance, let such a line  $1x'$  that cuts  $OQ$  at  $x'$ , or  $2y'$  that cuts  $OQ$  at  $y'$ . The importance of this line will be discussed later in this section.

➤ **Cooling of a Liquid Mixture and the Calculation of Eutectic Point**

In order to understand the cooling profile of a liquid mixture and eutectic point, we must state the following rule first.

*During equilibrium melting or crystallization in a closed system, the initial composition of the system will be identical to the final composition of the system.*

Now consider the composition of the liquid mixture in which compound A is 80% while compound B is 20% (represented by the vertical line X). Therefore, it follows from the above-mentioned rule that after crystallization we must get the same composition i.e. 80% (solid A) + 20% (solid B).

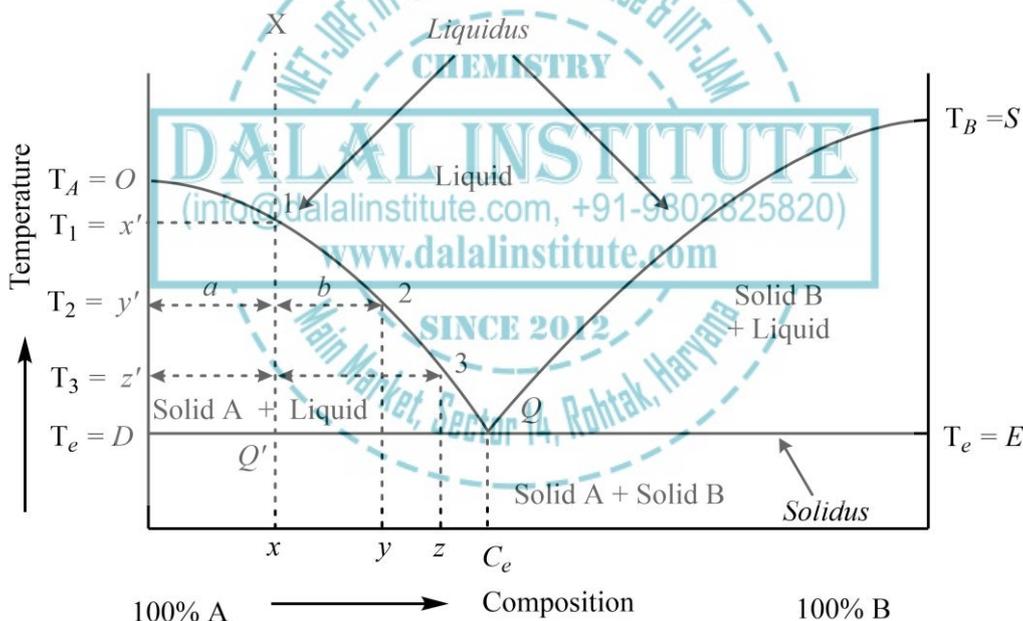


Figure 13. The cooling of a liquid mixture.

Above temperature  $T_1$ , the composition X lies in the field of “all liquid”, and therefore, will exist as liquid completely. However, when the temperature is reduced to  $T_1$  (corresponding to point 1) the crystal formation of A will be initiated. The further lowering of the temperature will make more crystals of A to form. All this will result in a continuous change of composition of the liquid mixture which is becoming more and more enriched in B. Therefore, as the temperature is lowered from  $T_1$  to  $T_2$ , the composition of the liquid will change

from point  $x$  to point  $y$  (corresponding to point 2). Likewise, the further lowering of temperature from  $T_2$  to  $T_3$  and then to eutectic temperature ( $T_E$ ) will change the composition from  $y$  to  $z$  (corresponding to point 3) and then to  $C_e$  (corresponding to point Q), respectively.

As near point Q, the liquid will be rich in compound B relative to the initial composition, and the crystallization of compound B will also start at point Q; it is better to imagine the composition in solid mixture afterward. By recalling the fact that all the three phases coexist at point Q (solid A + solid B + liquid mixture), even an infinitesimal decrease in temperature will disturb the “eutectic point” and liquid B will also start converting into a solid phase. This will make the system move from point Q to Q', getting exactly the same composition  $x$  i.e. 80% solid A + 20% solid B (represented by the vertical line X). A further lowering of temperature will make the system to move downward from point Q' along the vertical line X again.

### 1. Determination of phase composition:

Now, it is clear from the phase diagram that above point 1 along line X, a 80% A and 20 % B will exist in the liquid state; whereas, below point Q', a 80% A and 20 % B will exist in solid-state. However, between point 1 and Q' (i.e. at temperatures between  $T_1$  and  $T_e$ ) two phases (liquid mixture of A and B + crystals of A) will be present in the system. If the crystallization process is at any point, the relative phase proportion can be obtained by simple lever rule. For this, left-hand side and right-hand side of line X are noted. For instance, at  $T_2$  temperature, the amount of crystals of A and liquid could be found by just measuring the distances  $a$  and  $b$  i.e.

$$\% \text{ of crystals of A} = \frac{b}{a+b} \times 100 \quad (123)$$

$$\% \text{ of liquid mixture} = \frac{a}{a+b} \times 100 \quad (124)$$

Similarly, at  $T_3$  temperature, the amount of crystals of A and liquid could be found by just measuring the distances  $c$  and  $d$  i.e.

$$\% \text{ of crystals of A} = \frac{d}{c+d} \times 100 \quad (125)$$

$$\% \text{ of liquid mixture} = \frac{c}{c+d} \times 100 \quad (126)$$

It is also worthy to note that the percentage composition of liquid at  $T_3$  65% compound A + 35% compound B. Now if  $c = 2$  and  $d = 3$  then putting in equation (125, 126), we get 60% of crystal A and 40% of the liquid mixture. This 60% solid is pure crystalline A while 40% liquid mixture is actually composed of 65% compound A (26) + 35% compound B (14).

At this point, three possibilities of calculating the eutectic point arise when the cooling curve under three different conditions. Now we need to study cooling curves at composition X, Y, pure A, and eutectic (let eutectic be 60% compound A and 40% compound B).

## 2. Calculation of eutectic point:

If the composition of the liquid mixture in which compound A is 80% while compound B is 20% (represented by the vertical line X). Therefore, it follows from the above-mentioned rule that after crystallization we must get the same composition i.e. 80% (solid A) + 20% (solid B). Now, if the system allowed to cool down and then the temperatures are plotted against time, we will get the cooling curves for the same systems. Since above point 1 the system is completely liquid, it will cool down very rapidly in going from point X to point 1. However, point 1, the crystalline of compound A will also start releasing a large amount of heat, and therefore, the rate of cooling will be slow until point Q is reached. Now since the system is getting solidified at eutectic temperature i.e. it is moving from Q to Q'; the temperature of the system will remain constant during this conversion.



Figure 14. The cooling of a liquid mixture (compound A and compound B) when composition exists left to the eutectic composition.

After point Q' both compounds will exist as solids, and therefore, the system will cool down below point Q' along the vertical line X. The same type of curve will be obtained if we start from a composition left to the "eutectic composition". The only difference will be that the compound B will separate out first up to point Q, and then the solidification of compound A will start.

## 3. Some additional points:

Besides the features we already discussed, there are also some additional remarks which are based on the experimental results and can also be justified theoretically are given below.

- Although the temperature corresponding to point '1' depends upon the initial composition, the temperature corresponding to Q to Q' always remains the same for compositions.
- If the composition of the mixture is more close to the eutectic composition, the portion 1-Q will be small whereas the portion Q-Q'. The reason for this type of behavior lies in the diagram itself. Assume a composition Y which is closer to the eutectic composition than composition X.

Now, if the system allowed to cool down and then the temperatures are plotted against time, we will get the cooling curves for the same systems. Since above point 2, the system is completely liquid, it will cool down very rapidly in going from point Y to point 2. After point 2, the crystallization of compound A will also start releasing a large amount of heat, and therefore, the rate of cooling will be slow until point Q is reached. Now, since the composition X has less A and more B than composition Y, the solidification of A (up to point Q) will take less time but solidification of B will take more time. This will make portion 2–Q smaller than 1–Q but will make portion Q–Q' larger.

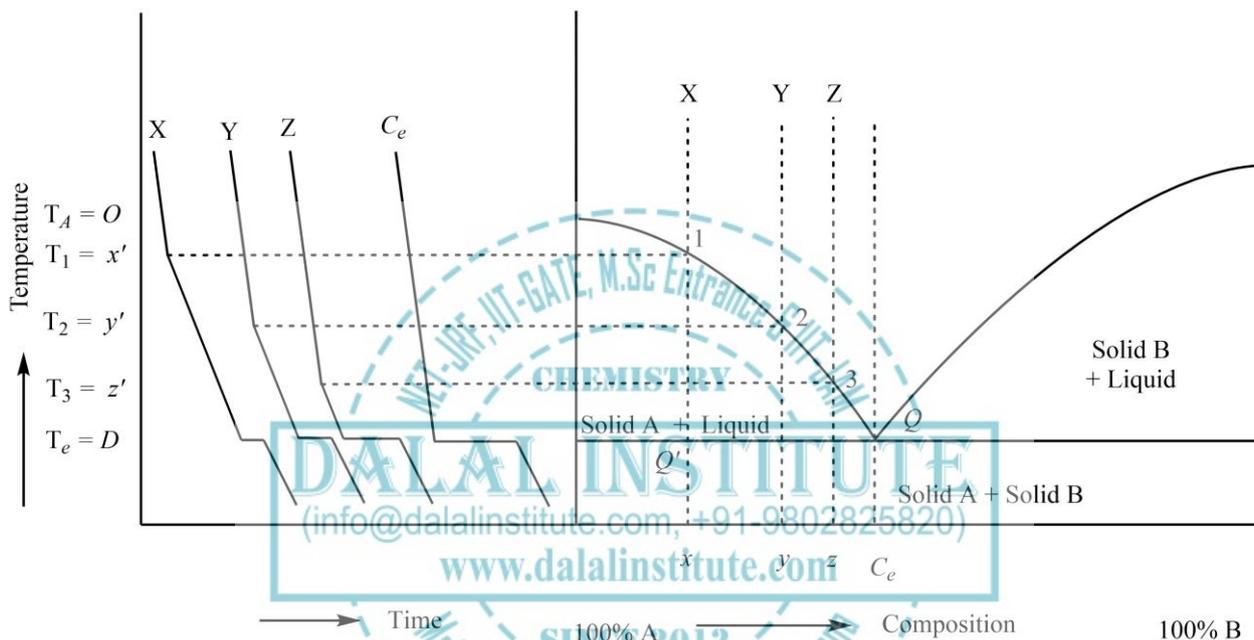


Figure 15. The cooling of a liquid mixture (compound A and Compound B) when compositions exist at eutectic point or left to the eutectic composition.

Now since the system is getting solidified at eutectic temperature i.e. it is moving from Q to Q'; the temperature of the system will remain constant during this conversion.

iii) When the liquid mixture composition is the same as that of “eutectic composition” (shown by line Z), then the cooling will take place in all-liquid phase up to point Q first, which means that there will be no break from point Z to Q.

However, after reaching point Q, the solidification of both compounds (A as well as B) will start to take place. Now since point Q is at eutectic temperature, there will be no change in temperature until this process completes. This will create a long halt (Q–Q') in the cooling curve since the whole liquid needs more time to solidify than some fraction left in solid-liquid equilibria.

➤ **Some Typical Eutectic Systems**

Some of the typical examples of two-components systems forming eutectic mixtures are given below for a more comprehensive analysis.

**1. Bismuth-cadmium system (Bi-Cd):**

The Bi-Cd is a typical case of solid-liquid equilibria in a two-component system that form a eutectic mixture. The phases involved in this case are solid Bi, solid Cd, liquid mixture of two (Cd + Bi) and gas-phase also. Now since a minor pressure disturbance will have little to no effect on the system and all the phases in two-component systems are either solid or liquids only (solid-liquid equilibria), Which is the reduced or condensed phase rule i.e.

$$F' = C - P + 1 \quad (127)$$

Now because the total number of phases that can exist simultaneously are reduced to 3 (system becomes non-variant at  $P = 3$ ).

The complete phase diagram can be drawn on two dimensional paper with vertical and horizontal sides representing temperature and composition, respectively. Consider a liquid mixture of Bi and Cd at temperature  $T$ . Now if this liquid mixture is allowed to cool down below the freezing point of the mixture, the solid will start to separate out. Prepare a number of such mixtures but with different compositions (i.e. with different ratios of Bi and Cd). The cooling of all the mixtures is carried out in open vessels so that the pressure remains constant (atmospheric pressure). After that, the plot freezing points vs the composition is

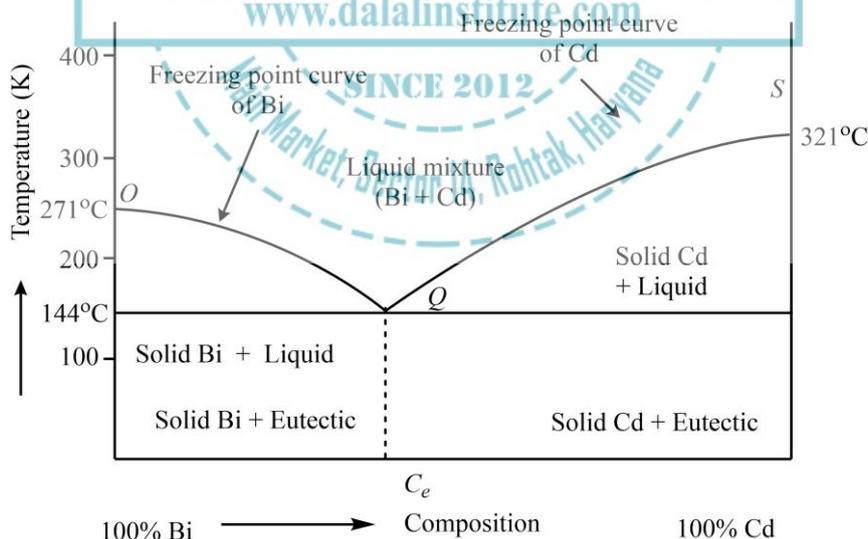


Figure 16. The phase diagram of Bi-Cd system.

The discussion on different parts (curve OQ, Curve SQ and the eutectic point) of the phase diagram of Bi-Cd system is given below.

*i) Curve OQ and SQ:* The point *O* and point *S* represent the freezing point the pure Bi (271°C) and pure Cd (321°C), respectively. When cadmium is added to bismuth, its freezing point of decreases regularly along *OQ*. Likewise, bismuth is added to cadmium, its freezing point of decreases regularly along *OQ*. In conclusion, we can say that the curve *OQ* and *SQ* represent the temperature-conditions at which solid Bi and solid Cd are in equilibrium with the liquid mixture. Since there are only two phases involved, i.e. after putting  $C = 2$  and  $P = 2$  in equation (127), we get

$$F' = 2 - 2 + 1 = 1 \quad (128)$$

Which means that the system is univariate. In other words, only one condition is needed to be defined to define the whole system; for instance, if we define a particular composition of Bi and Cd, the freezing point of the mixture is completely fixed. Since the points on *OQ* and *SQ* represent the initial freezing temperature whereas the points on solidus *DE* represent final freezing temperature; *OQ* and *SQ* can also be considered as the solubility curves of Bi in molten Cd and Cd in molten Bi, respectively.

*ii) Eutectic point (Q):* At point '*Q*', all the three phases (solid Bi + solid Cd + liquid) are in equilibrium with each other; and therefore, zero degrees of freedom exist at this point i.e.

$$F' = 2 - 3 + 1 = 0 \quad (129)$$

This means that we can neither change temperature nor composition without disturbing the mutual equilibrium of solid Bi, solid Cd and liquid. Moreover, below this temperature (144°C), the mixture freezes as a whole. This temperature is called as "eutectic point" and the composition corresponding to this point is called as eutectic composition (40% Cd + 60% Bi).

## 2. Lead-Silver system (Pb-Ag):

The Pb-Ag is a typical case of solid-liquid equilibria in a two-component system that form eutectic mixture. The phases involved in this case are solid Ag, solid Pb, liquid mixture of two (Ag + Pb) and gas-phase also. Now since a minor pressure disturbance will have little to no effect on the system and all the phases in two-component systems are either solid or liquids only (solid-liquid equilibria), Which is the reduced or condensed phase rule i.e.

$$F' = C - P + 1 \quad (130)$$

Now because the total number of phases that can exist simultaneously are reduced to 3 (system becomes non-variant at  $P = 3$ ).

The complete phase diagram can be drawn on two dimensional paper with vertical and horizontal sides representing temperature and composition, respectively. Consider a liquid mixture of Ag and Pb at temperature *T*. Now if this liquid mixture is allowed to cool down below the freezing point of the mixture, the solid will start to separate out. Prepare a number of such mixtures but with different compositions (i.e. with different ratios of Ag and Pb). The cooling of all the mixtures is carried out in open vessels so that the pressure remains constant (atmospheric pressure). After that, the plot freezing points vs the composition is

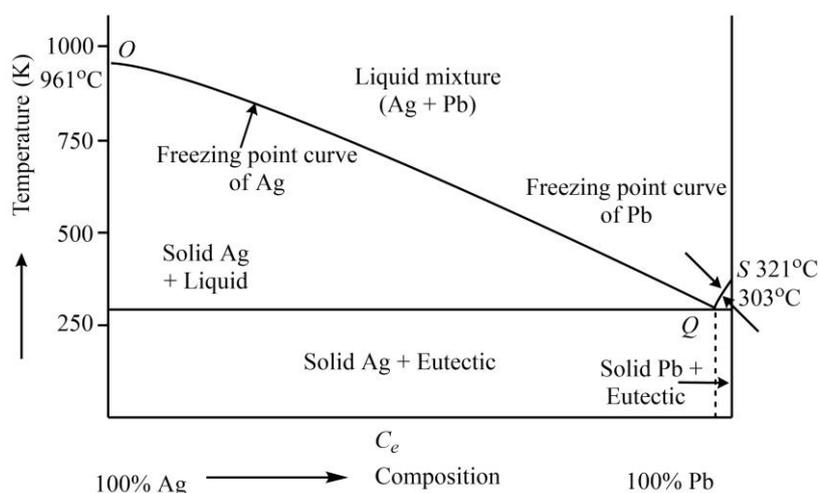


Figure 17. The phase diagram of Pb-Ag system.

The discussion on different parts (curve  $OQ$ , Curve  $SQ$  and the eutectic point) of the phase diagram of Pb-Ag system is given below.

*i) Curve  $OQ$  and  $SQ$ :* The point  $O$  and point  $S$  represent the freezing point the pure Ag ( $961^\circ\text{C}$ ) and pure Pb ( $327^\circ\text{C}$ ), respectively. When lead is added to silver, its freezing point of decreases regularly along  $OQ$ . Likewise, silver is added to lead, its freezing point of decreases regularly along  $OQ$ . In conclusion, we can say that the curve  $OQ$  and  $SQ$  represent the temperature-conditions at which solid Ag and solid Pb are in equilibrium with the liquid mixture. Since there are only two phases involved, i.e. after putting  $C = 2$  and  $P = 2$  in equation (130), we get

$$F' = 2 - 2 + 1 = 1 \quad (131)$$

Which means that the system is univariate. In other words, only one condition is needed to be defined to define the whole system; for instance, if we define a particular composition of Ag and Pb, the freezing point of the mixture is completely fixed. Since the points on  $OQ$  and  $SQ$  represent the initial freezing temperature whereas the points on solidus  $DE$  represent final freezing temperature;  $OQ$  and  $SQ$  can also be considered as the solubility curves of Ag in molten Pb and Pb in molten Ag, respectively.

*ii) Eutectic point ( $Q$ ):* At point ' $Q$ ', all the three phases (solid Ag + solid Pb + liquid) are in equilibrium with each other; and therefore, zero degree of freedom exists at this point i.e.

$$F' = 2 - 3 + 1 = 0 \quad (132)$$

This means that we can neither change temperature nor composition without disturbing the mutual equilibrium of solid Ag, solid Pb, and liquid. Moreover, below this temperature ( $303^\circ\text{C}$ ), the mixture freezes as a whole. This temperature is called as "eutectic point" and the composition corresponding to this point is called as eutectic composition (2.6% Ag + 97.4% Bi).

### 3. Potassium iodide-water system (KI-H<sub>2</sub>O):

The KI-H<sub>2</sub>O is a typical case of solid-liquid equilibria in a two-component system that form eutectic mixture. The phases involved in this case are solid KI, ice, liquid mixture of two (KI + H<sub>2</sub>O) and gas-phase also. Now since a minor pressure disturbance will have little to no effect on the system and all the phases in two-component systems are either solid or liquids only (solid-liquid equilibria), Which is the reduced or condensed phase rule i.e.

$$F' = C - P + 1 \quad (133)$$

Now because the total number of phases that can exist simultaneously are reduced to 3 (system becomes non-variant at  $P = 3$ ).

The complete phase diagram can be drawn on two dimensional paper with vertical and horizontal sides representing temperature and composition, respectively. Consider a liquid mixture of KI and H<sub>2</sub>O at temperature  $T$ . Now if this liquid mixture is allowed to cool down below the freezing point of the mixture, the solid will start to separate out. Prepare a number of such mixtures but with different compositions (i.e. with different ratios of KI and H<sub>2</sub>O). The cooling of all the mixtures is carried out in open vessels so that the pressure remains constant (atmospheric pressure). After that, the plot freezing points vs the composition is

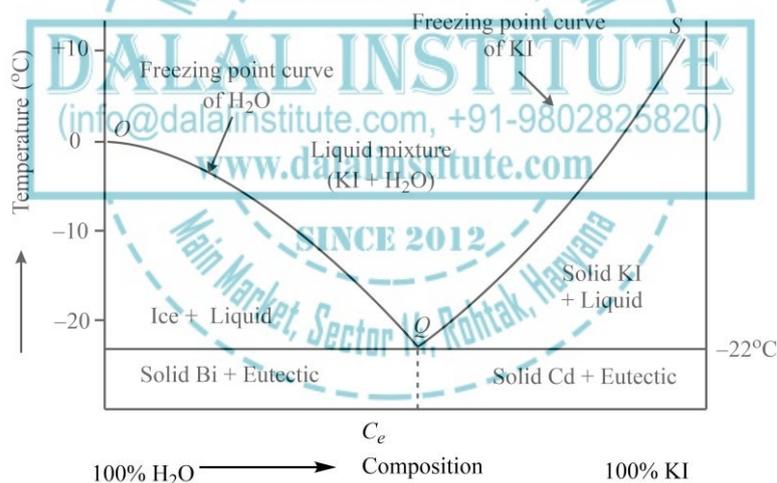


Figure 18. The phase diagram of KI-H<sub>2</sub>O system.

The discussion on different parts (curve OQ, Curve SQ and the eutectic point) of phase diagram of KI-H<sub>2</sub>O system is given below.

i) *Curve OQ and SQ:* The point  $O$  represents the freezing point pure water (0°C). However, the curve  $SQ$  is incomplete because it is impossible to reach the melting point of KI in the presence of water. When KI is added to water, its freezing point of decreases regularly along  $OQ$ . Likewise, when water is added to KI, its freezing point of decreases regularly along  $SQ$ . In conclusion, we can say that the curve  $OQ$  and  $SQ$  represent the

temperature-conditions at which solid KI and solid H<sub>2</sub>O are in equilibrium with the liquid mixture. Since there are only two phases involved, i.e. after putting  $C = 2$  and  $P = 2$  in equation (133), we get

$$F' = 2 - 2 + 1 = 1 \quad (134)$$

Which means that the system is univariate. Since the points on  $OQ$  and  $SQ$  represent the initial freezing temperature whereas the points on solidus  $DE$  represent final freezing temperature;  $OQ$  and  $SQ$  can also be considered as the solubility curves of KI in molten H<sub>2</sub>O and ice in molten KI, respectively.

*ii) Eutectic point (Q):* At point 'Q', all the three phases (solid KI + solid H<sub>2</sub>O + liquid) are in equilibrium with each other; and therefore, zero degree of freedom exists at this point i.e.

$$F' = 2 - 3 + 1 = 0 \quad (135)$$

This means that we can neither change temperature nor composition without disturbing the mutual equilibrium of solid KI, ice and liquid. Moreover, below this temperature ( $-22^{\circ}\text{C}$ ), the mixture freezes as a whole. This temperature is called as "eutectic point" and the composition corresponding to this point is called as eutectic composition (52% KI + 48% H<sub>2</sub>O).

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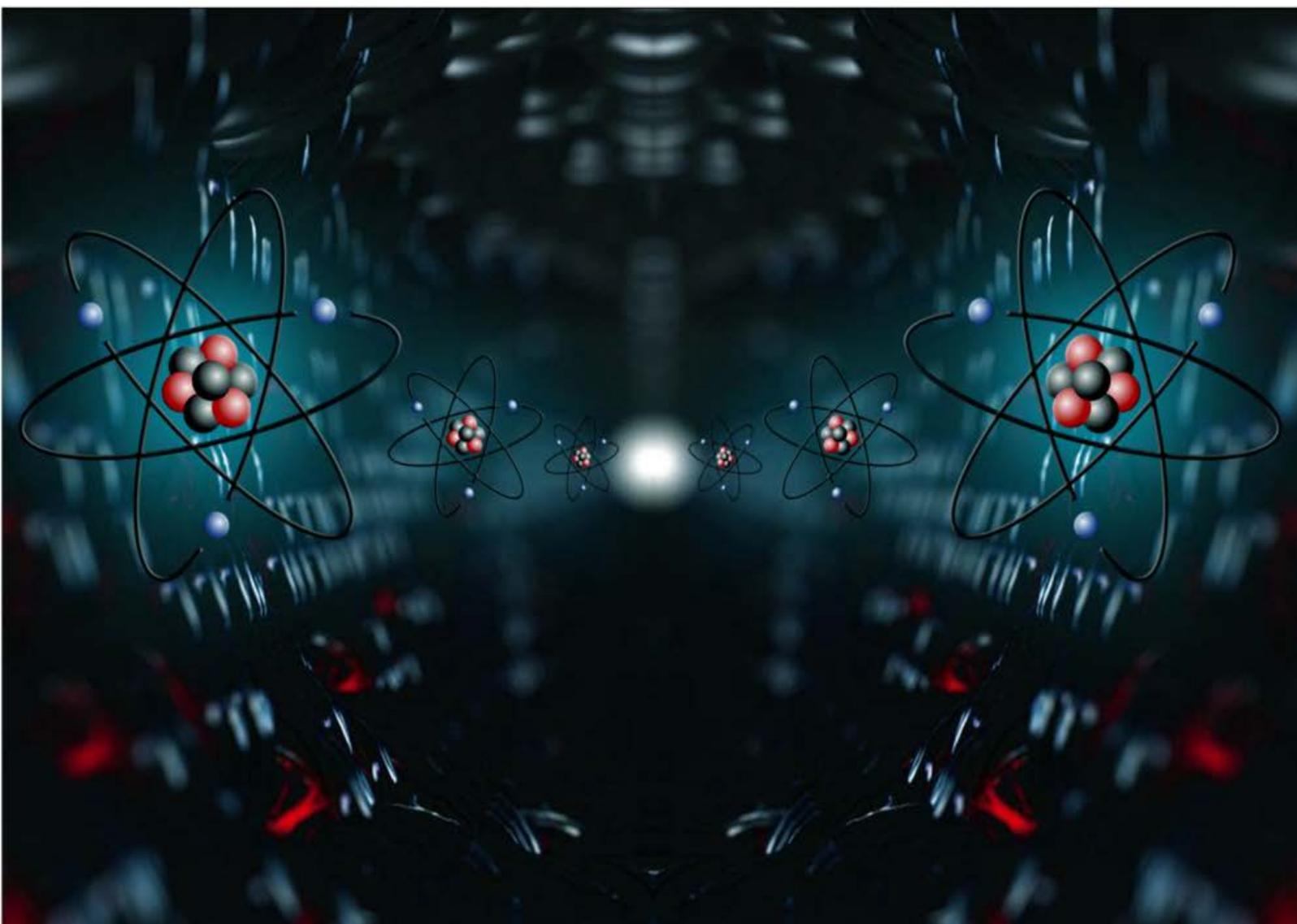
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