❖ Systems Forming Solid Compounds A_xB_y with Congruent and Incongruent Melting Points

In some two-component systems, the participants react together to form solid compounds A_xB_y. On the basis of the melting point of the compounds formed, these systems can be further divided.

➢ *Systems Forming Solid Compounds A_xB_y with Congruent Melting Points*

In these systems, the solid compound melts sharply at temperature T with the same composition as in the initial solid. These compound are said to possess a congruent melting point with the phase diagram as

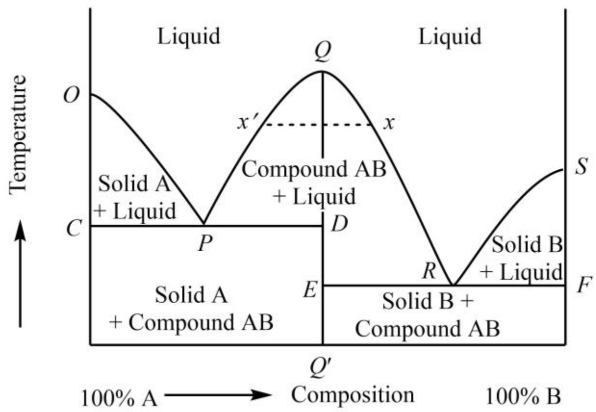

Figure 19. The general phase diagram of systems forming compounds with congruent melting points.

Consider two components *A* and *B* which also form a chemical compound AB by reacting with each other. Therefore, in the complete solid-state, there will be three phases named solid A, solid B and solid AB. Accordingly, there should also be three different freezing point curves i.e. *OP*, *PQR* and *RS*. In addition to this liquidus, there will be two solidus *CE* and *DE* as well. The significance of different parts of the above-depicted diagram is discussed below.

1. Curve *OP* and *RS*: The point *O* and point *S* represent the freezing point the pure compound A and compound B, respectively. When compound AB is added to component A, its freezing point decreases regularly along *OP*. Likewise, when component AB is added to component B, its freezing point decreases regularly along *SR*. In conclusion, we can say that the curve *OP* and *SR* 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

$$F' = 2 - 2 + 1 = 1 \tag{136}$$

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 AB (or B and AB), the freezing point of the mixture is completely fixed.

2. Curve *PQR*: When compound A is increased in compound AB, its freezing point of decreases regularly along *QP*. Likewise, when component B is added to compound AB, its freezing point decreases regularly along *QR*. In conclusion, we can say that the curve *PQR* represents the temperature-conditions at which compound AB is 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

$$F' = 2 - 2 + 1 = 1 \tag{137}$$

However, it is also worthy to mention that at the point Q also represents the congruent melting point of compound AB because liquid and solid phases have the same compositions. Consequently, we can also conclude that the system becomes one-component system at this point because the solid as well liquid phases contain only the compound AB alone. Furthermore, the congruent melting point of compound AB may lie above or below the congruent melting points of component A and component B.

3. Eutectic points *P* and *R*: In order to explain that the liquid phase can have two different compositions in equilibrium with the solid phase i.e. *x* and *x*', the curve *PQR* is divided into two parts by the vertical line *QQ'*. This makes the concept very simple as the left and right parts can be treated as simple eutectic systems separately. The right half of the diagram is a eutectic system with components B and AB (solidus *CD*); whereas left hand side is a eutectic system with components A and AB (solidus is *EF*). The eutectic temperature and eutectic composition for the left-hand side portion are given by point *P*. Similarly, the eutectic temperature and eutectic composition for the right-hand side portion are given by point *R*.

➢ ***Some Typical Examples of Systems Forming Compounds with Congruent Melting Points***

Some of the typical examples of two-components systems forming compounds with congruent melting points are given below for a more comprehensive analysis.

1. Magnesium-zinc system (Mg-Zn):

The Mg-Zn is a typical case of solid-liquid equilibria in a two-component system that form compounds with congruent melting points. The phases involved in this case are solid Mg, solid Zn, solid $MgZn_2$, liquid mixture of three ($Mg + Zn + MgZn_2$) and vapor phase too. 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.

$$F' = C - P + 1 \tag{138}$$

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 Mg and Zn 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 Mg and Zn). 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

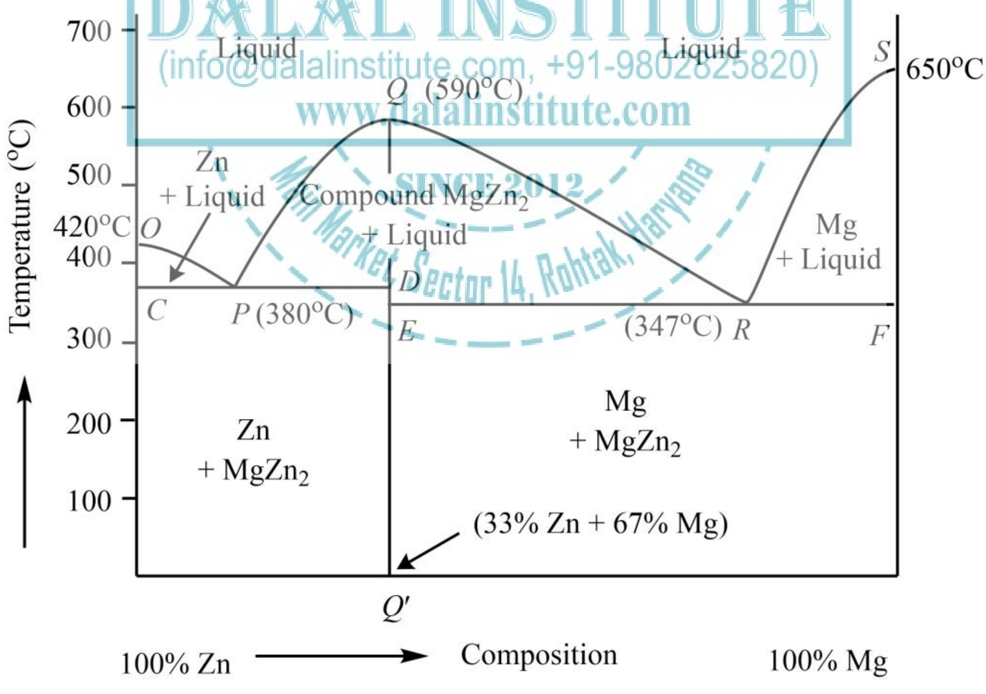

Figure 20. The phase diagram of Mg-Zn system.

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 OP and point P: The point *O* represents the freezing point of the pure Zn (420°C). When Mg is added to zinc, its freezing point of decreases regularly along *OP* and Zn separates out simultaneously. Since there are only two phases involved, i.e. after putting $C = 2$ and $P = 2$ in equation (138), we get

$$F' = 2 - 2 + 1 = 1 \tag{139}$$

Which means that the system is univariate. However, after the point P is reached, the compound $MgZn_2$ is formed and also starts separating out as solid. We can say that there are three phases that coexist at point P i.e. solid Zn, solid $MgZn_2$ and melt which makes the system invariant (for $P = 3$, $F' = 0$).

ii) Curve PQ and point Q: The point *Q* represents the freezing point of the compound $MgZn_2$ (590°C). When Mg is added to zinc after point P, it combines with zinc to form MgZn2 which keeps on separating and its freezing point increases regularly until point Q is reached (33% magnesium). Since there are only two phases involved, i.e. after putting $C = 2$ and $P = 2$ in equation (138), we get

$$F' = 2 - 2 + 1 = 1 \tag{140}$$

Which means that the system is univariate. Now since the liquid and solid phases have the same composition at point Q, the corresponding temperature can be called a congruent melting point of compound $MgZn_2$. Furthermore, as the number of components becomes one at point Q i.e. solid $MgZn_2$ and melt $MgZn_2$, the system becomes invariant at Q (for $P = 3$, $F' = 0$).

iii) Curve QR and point R: When Mg is further added to zinc after point Q, it goes into melt $MgZn_2$ separating out as solid, and therefore, the freezing point of $MgZn_2$ decreases regularly until point R is reached. Since there are only two phases involved along curve *QR*, i.e. after putting $C = 2$ and $P = 2$ in equation (138), we get the following

$$F' = 2 - 2 + 1 = 1 \tag{141}$$

Which means that the system is univariant. Moreover, we can also conclude here that there are three phases that coexist at point R i.e. solid Mg solid $MgZn_2$ and melt which makes the system invariant (for $P = 3$, $F' = 0$).

iv) Curve SR: When Mg is further added to zinc after point R, it starts separating out as solid, and therefore, the freezing point of Mg increases regularly until point S is reached. Since there are only two phases involved along curve *SR*, i.e. after putting $C = 2$ and $P = 2$ in equation (138), we get

$$F' = 2 - 2 + 1 = 1 \tag{142}$$

Which means that the system remains univariant along curve *SR*. in reverse we can also say that the freezing point of Mg decreases regularly along curve *SR* until point *R* is reached i.e. solid Mg solid $MgZn_2$ and melt which makes the system invariant (for $P = 3$, $F' = 0$).

2. Ferric chloride-water system ($FeCl_3$-H_2O):

The $FeCl_3$-H_2O is another typical case of solid-liquid equilibria in a two-component system that forms stable compounds with congruent melting point. The phases involved in this case are solid $FeCl_3$, ice, solid $Fe_2Cl_6.12H_2O$, $Fe_2Cl_6.7H_2O$, $Fe_2Cl_6.5H_2O$, $Fe_2Cl_6.4H_2O$, liquid mixture and vapor phase too. 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), the reduced phase rule can be used i.e.

$$F' = C - P + 1 \tag{143}$$

The complete phase diagram can be drawn on two dimensional paper with vertical and horizontal sides representing temperature and composition, respectively. The cooling of all the mixtures is carried out in open vessels so that the pressure remains constant (atmospheric pressure). After that, the plot of freezing points vs the composition is obtained.

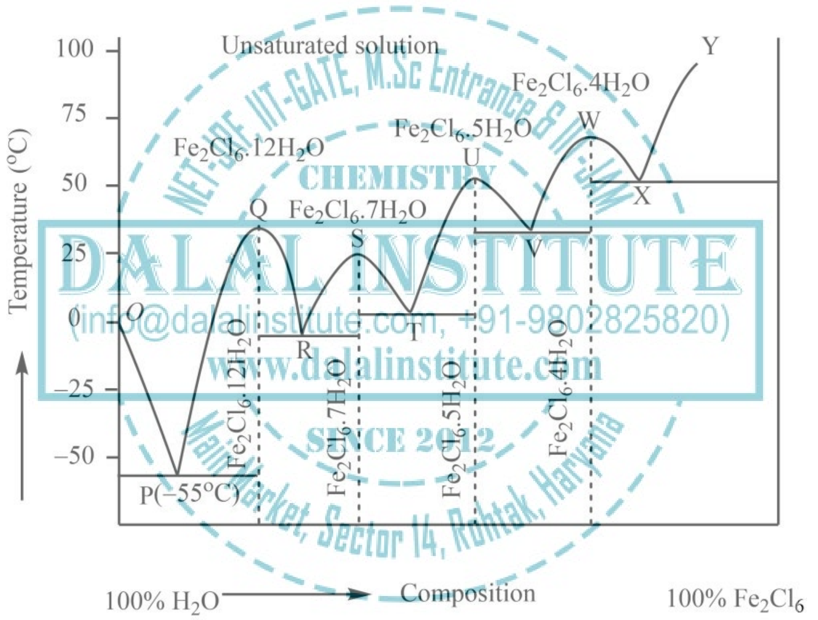

Figure 21. The phase diagram of $FeCl_3$-H_2O system.

i) Curve OP and point P: The point *O* represents the freezing point of the pure water (0°C). When $FeCl_3$ is added to water, the freezing point of water decreases regularly along *OP* and ice separates out simultaneously. Since there are only two phases involved along curve *OP* ($C = 2$ and $P = 2$), the equation (143) gives

$$F' = 2 - 2 + 1 = 1 \tag{144}$$

Which means that the system is univariant along curve *OP*. However, after reaching the point P, the liquid phase becomes saturated with compound $Fe_2Cl_6.12H_2O$ which also starts separating out as solid afterward. We can say that there are three phases that coexist at point *P* i.e. solid ice, solid $Fe_2Cl_6.12H_2O$ and solution which makes the system invariant (for $P = 3$, $F' = 0$). In other words, the point P is the "eutectic point for water and $Fe_2Cl_6.12H_2O$.

ii) Curve PQ and point Q: The point *Q* represents the congruent melting point of the compound $Fe_2Cl_6.12H_2O$ (37°C). When $FeCl_3$ is added to the water after point P, it combines with water to form $Fe_2Cl_6.12H_2O$ which keeps on separating and its freezing point increases regularly until point Q is reached. Since there are only two phases involved along curve *PQ*, i.e. after putting $C = 2$ and $P = 2$ in equation (143), we get

$$F' = 2 - 2 + 1 = 1 \tag{145}$$

Which means that the system is univariant. Furthermore, as the number of components becomes one at point Q i.e. solid $Fe_2Cl_6.12H_2O$ and solution, the system becomes invariant at Q (for $P = 2$, $F' = 0$).

iii) Curve QR and point R: When $FeCl_3$ is further added to the water after point Q, the freezing point of $Fe_2Cl_6.12H_2O$ decreases regularly until point R is reached. Since there are only two phases involved along curve *QR*, i.e. after putting $C = 2$ and $P = 2$ in equation (143), we get

$$F' = 2 - 2 + 1 = 1 \tag{146}$$

Which means that the system is univariant. After point R, the compound $Fe_2Cl_6.7H_2O$ is formed and also starts separating out as solid. However, we can say that there are three phases that coexist at point R i.e. solid $Fe_2Cl_6.12H_2O$, solid $Fe_2Cl_6.7H_2O$ and solution which makes the system invariant (for $P = 3$, $F' = 0$).

iv) Curve RS and point S: The point *S* represents the congruent melting point of the compound $Fe_2Cl_6.7H_2O$ (37°C). When $FeCl_3$ is added to the water after point R, it combines with water to form $Fe_2Cl_6.7H_2O$ which keeps on separating and its freezing point increases regularly until point S is reached. Since there are only two phases involved, i.e. after putting $C = 2$ and $P = 2$ in equation (143), we get

$$F' = 2 - 2 + 1 = 1 \tag{147}$$

Which means that the system is univariant. Furthermore, as the number of components becomes one at point S i.e. solid $Fe_2Cl_6.7H_2O$ and solution, the system becomes invariant at S (for $P = 2$, $F' = 0$).

v) Curve ST and point T: When $FeCl_3$ is further added to the water after point S, the freezing point of $Fe_2Cl_6.7H_2O$ decreases regularly until point T is reached. Since there are only two phases involved along curve *ST*, i.e. after putting $C = 2$ and $P = 2$ in equation (143), we get

$$F' = 2 - 2 + 1 = 1 \tag{148}$$

Which means that the system is univariant. After point T, the compound $Fe_2Cl_6.5H_2O$ is formed and also starts separating out as solid. However, we can say that there are three phases that coexist at point T i.e. solid $Fe_2Cl_6.7H_2O$, solid $Fe_2Cl_6.5H_2O$ and solution which makes the system invariant (for $P = 3$, $F' = 0$).

vi) Curve TU and point U: The point *U* represents the congruent melting point of the compound $Fe_2Cl_6.5H_2O$ (37°C). When $FeCl_3$ is added to the water after point T, it combines with water to form $Fe_2Cl_6.5H_2O$ which keeps on separating and its freezing point increases regularly until point U is reached. Since there are only two phases involved, i.e. after putting $C = 2$ and $P = 2$ in equation (138), we get

$$F' = 2 - 2 + 1 = 1 \quad (149)$$

Which means that the system is univariant. Furthermore, as the number of components becomes one at point U i.e. solid $Fe_2Cl_6.5H_2O$ and solution, the system becomes invariant at U (for $P = 2$, $F' = 0$).

vii) Curve UV and point V: When $FeCl_3$ is further added to the water after point U, the freezing point of $Fe_2Cl_6.5H_2O$ decreases regularly until point V is reached. Since there are only two phases involved along curve *UV*, i.e. after putting $C = 2$ and $P = 2$ in equation (143), we get

$$F' = 2 - 2 + 1 = 1 \quad (150)$$

Which means that the system is univariant. After point V, the compound $Fe_2Cl_6.4H_2O$ is formed and also starts separating out as solid. However, we can say that there are three phases that coexist at point V i.e. solid $Fe_2Cl_6.5H_2O$, solid $Fe_2Cl_6.4H_2O$ and solution which makes the system invariant (for $P = 3$, $F' = 0$).

viii) Curve VW and point W: The point *W* represents the congruent melting point of the compound $Fe_2Cl_6.4H_2O$ (37°C). When $FeCl_3$ is added to the water after point V, it combines with water to form $Fe_2Cl_6.4H_2O$ which keeps on separating and its freezing point increases regularly until point W is reached. Since there are only two phases involved, i.e. after putting $C = 2$ and $P = 2$ in equation (143), we get

$$F' = 2 - 2 + 1 = 1 \quad (151)$$

Which means that the system is univariant. Furthermore, as the number of components becomes one at point W i.e. solid $Fe_2Cl_6.4H_2O$ and solution, the system becomes invariant at Q (for $P = 2$, $F' = 0$).

ix) Curve WX and point X: When $FeCl_3$ is further added to the water after point W, the freezing point of $Fe_2Cl_6.4H_2O$ decreases regularly until point *X* is reached. Since there are only two phases involved along curve *WX*, i.e. after putting $C = 2$ and $P = 2$ in equation (143), we get

$$F' = 2 - 2 + 1 = 1 \quad (152)$$

Which means that the system is univariant. After point X, anhydrous Fe_2Cl_6 is formed and also starts separating out as solid. However, we can say that there are three phases that coexist at point R i.e. solid $Fe_2Cl_6.4H_2O$, anhydrous Fe_2Cl_6 and solution which makes the system invariant (for $P = 3$, $F' = 0$).

x) Curve XY: The point *Y* represents the freezing point of the compound Fe_2Cl_6. When $FeCl_3$ is added to the water after point X, it combines with water to yield anhydrous Fe_2Cl_6 which keeps on separating and its freezing point increases regularly along XY is reached. Since there are only two phases involved along curve *XY*, i.e. after putting $C = 2$ and $P = 2$ in equation (143), we get

$$F' = 2 - 2 + 1 = 1 \quad (153)$$

Which means that the system is univariant.

➢ ***Systems Forming Solid Compounds A_xB_y with Incongruent Melting Points***

In these types of systems, the two components react to give a compound which is not stable up to its melting point. When heated, the decomposition starts before the melting point is reached; and a new solid phase and a solution or melt with a different composition from the original solid are formed. Such compounds are said to undergo peritectic or transition reaction are labeled to have congruent melting point. A typical transition can be represented as

$$C_1 \rightleftharpoons C_2 + \text{melt or solution} \tag{154}$$

Where C_1 is the compound formed by the reaction between participating components whereas C_2 represents the compound formed as a result of decomposition of C_1 below its fusion temperature.

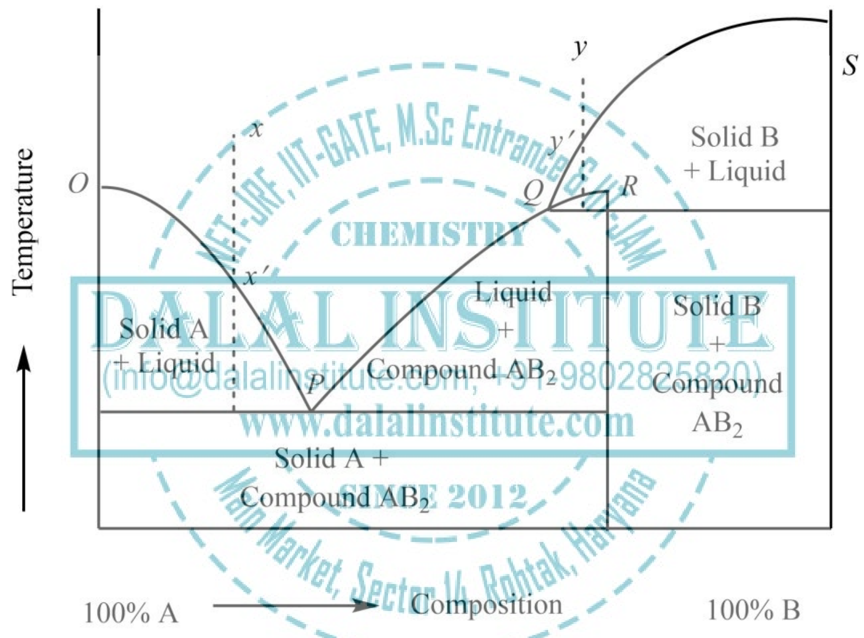

Figure 22. The general phase diagram of systems forming compounds with incongruent melting points.

Consider two components *A* and *B* which also form a chemical compound AB_2 by reacting with each other. The cooling of all the mixture-compositions is carried out in open vessels so that the pressure remains constant (atmospheric pressure). After that, the plot of freezing points vs the composition is obtained. The significance of different parts of the above-depicted diagram is discussed below.

1. Point *O, S, Q* and *R*: The point *O* and point *S* represent the freezing point the pure compound A and compound B, respectively. The point *Q*, however, is quite strange because it represents the transition temperature (incongruent melting point of AB_2) where compound AB_2 decomposes into compound B. If does not decompose at this temperature, its congruent melting point would be *R*. In other words, we can say that the point *R* represents the hypothetical congruent melting point of compound AB_2.

2. Curve *OP*, *SQ* and *QP*: When compound B is added to component A, its freezing point decreases regularly along *OP*. In other words, *OP* is the fusion curve of compound A along which solid A is in equilibrium with melt or solution. The line *SQ* is the fusion curve of compound B along which solid B is in equilibrium with melt or solution. Similarly, *QP* is the fusion curve of compound AB_2 along which solid AB_2 is in equilibrium with melt or solution.

When a liquid mixture with composition X is allowed to cool down, it will do so by keeping its composition the same until point 1 is reached where the compound A will just start to separate out as solid. Further cooling will lead to a change in composition along the line 1*P*. When point *P* is attained, the formation of compound AB will be started; and since three phases coexist at this point (solid A, solid AB and liquid), the reduced phase rule gives

$$F' = C - P + 1 \tag{155}$$

$$F' = 2 - 3 + 1 = 0 \tag{156}$$

Which means that there will be no degree of freedom at point *P* (*P* is non-variant). On the other hand, if liquid mixture with composition Y is allowed to cool down, it will do so by keeping its composition the same until point 2 is reached where the compound B will just start to separate out as solid. Further cooling will lead to a change in composition along the line 2*Q*. When point *Q* is attained, the following meritectic reaction will take place

$$Solid\ B + Solution \rightleftharpoons Solid\ AB_2 \tag{157}$$

Therefore, the formation of compound AB_2 will be started; and since three phases coexist at this point (solid B, solid AB and liquid), the point Q also become invariant. Furthermore, it is also worthy to mention that the transformation of compound B to compound AB_2 occurs at a constant temperature, and therefore, the point Q is also called a peritectic point.

➢ ***Some Typical Examples of Systems Forming Compounds with Incongruent Melting Points***

Some of the typical examples of two-components systems forming compounds with incongruent melting points are given below for a more comprehensive analysis.

1. Sodium chloride-water system (NaCl-H_2O):

The NaCl-H_2O is a typical case of solid-liquid equilibria in a two-component system that forms compounds with an incongruent melting point. The phases involved in this case are solid NaCl, solid NaCl.2H_2O, ice, liquid mixture, and vapour phase too. 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.

$$F' = C - P + 1 \tag{158}$$

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 water and NaCl 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 H_2O and NaCl). 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

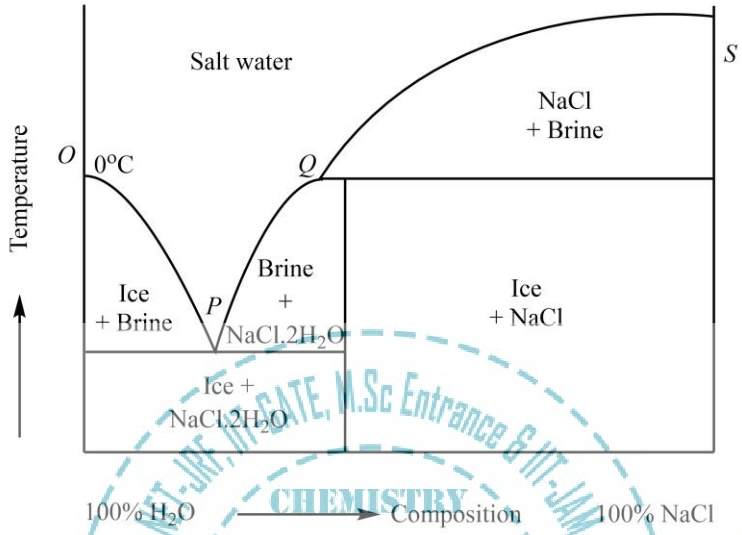

Figure 23. The phase diagram of NaCl-H_2O system.

i) Point O, S and Q: The point O and point S represent the freezing point the pure water and pure NaCl, respectively. The point Q, however, is quite strange because it represents the transition temperature (incongruent melting point of $NaCl.2H_2O$) where compound $NaCl.2H_2O$ decomposes into pure NaCl.

ii) Curve OP, SQ and QP: When NaCl is added to water, its freezing point decreases regularly along OP. In other words, OP is the fusion curve of water along which the ice is in equilibrium with the solution. The line SQ is the fusion curve of pure NaCl along which solid NaCl is in equilibrium with the brine solution. Similarly, QP is the fusion curve of compound $NaCl.2H_2O$ along which solid $NaCl.2H_2O$ is in equilibrium with solution.

When NaCl is added to pure water, ice will just start to separate out as solid along path OP. This will lead to a change in composition along the line OP. When point P is attained, the formation of compound $NaCl.2H_2O$ will start; and since three phases coexist at P (ice, $NaCl.2H_2O$ and liquid), the reduced phase rule

$$F' = 2 - 3 + 1 = 0 \tag{159}$$

Which means that there will be no degree of freedom at point P (P is non-variant). On the other hand, the curve SQ is the fusion curve of NaCl. The further cooling will lead to a change in composition along the line SQ. When point Q is attained, the following meritectic reaction will take place

$$Solid\ NaCl + Solution \rightleftharpoons Solid\ NaCl.2H_2O \tag{160}$$

Therefore, the formation of compound $NaCl.2H_2O$ will be started; and since three phases coexist at this point (solid NaCl, solid $NaCl.2H_2O$ and liquid), the point *Q* also become invariant. Furthermore, it is also worthy to mention that the transformation of compound NaCl to compound $NaCl.2H_2O$ occurs at a constant temperature, and therefore, the point *Q* is also called as peritectic point.

2. Sodium sulphate-water system (Na_2SO_4-H_2O):

The Na_2SO_4-H_2O is another typical case of solid-liquid equilibria in a two-component system that forms compounds with an incongruent melting point. The phases involved in this case are solid Na_2SO_4, solid $Na_2SO_4.10H_2O$, ice, liquid mixture, and vapor phase too. 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.

$$F' = C - P + 1 \quad (161)$$

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 water and Na_2SO_4 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 H_2O and Na_2SO_4). 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

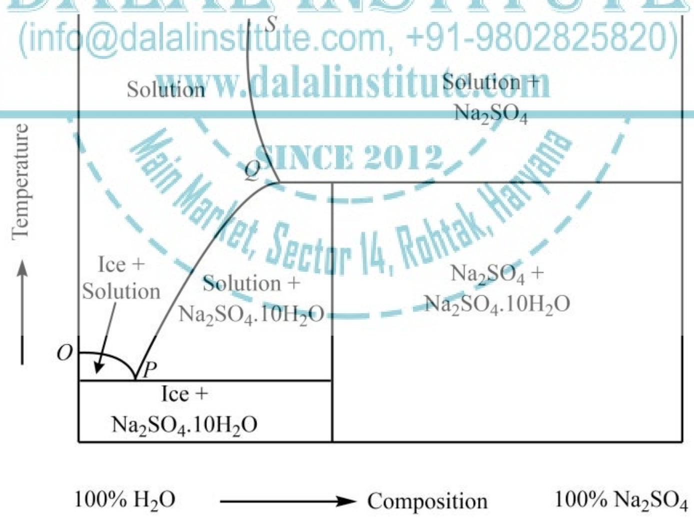

Figure 24. The phase diagram of Na_2SO_4-H_2O system.

i) Point O and Q: The point *O* represents the freezing point the pure water. The point *Q*, however, is quite strange because it represents the transition temperature (incongruent melting point of $Na_2SO_4.10H_2O$) where compound $Na_2SO_4.10H_2O$ decomposes into pure Na_2SO_4.

ii) Curve OP, SQ and QP: When Na_2SO_4 is added to water, its freezing point decreases regularly along *OP*. In other words, *OP* is the fusion curve of compound water along which ice is in equilibrium with the solution. The line *SQ* is the fusion curve of pure Na_2SO_4 along which Na_2SO_4 is in equilibrium with the solution. Similarly, *QP* is the fusion curve of compound $Na_2SO_4.10H_2O$ along which solid $Na_2SO_4.10H_2O$ is in equilibrium with the solution.

When Na_2SO_4 is added to water, ice will start to separate out along *OP*. This will lead to a change in composition along the line *OP*. When point *P* is attained, the formation of compound $Na_2SO_4.10H_2O$ will be started; and since three phases coexist at *P* (ice, Na_2SO_4-H_2O and solution), the reduced phase rule gives

$$F' = 2 - 3 + 1 = 0 \tag{162}$$

Which means that there will be no degree of freedom at point *P* (*P* is non-variant). On the other hand, the curve *SQ* is fusion curve of Na_2SO_4. The further cooling will lead to a change in composition along the line S*Q*. When point *Q* is attained, the following meritectic reaction will take place

$$Solid\ Na_2SO_4 + Solution \rightleftharpoons Solid\ Na_2SO_4.10H_2O \tag{163}$$

Therefore, the formation of compound $Na_2SO_4.10H_2O$ will be started; and since three phases coexist at this point (solid Na_2SO_4, solid $Na_2SO_4.10H_2O$ and liquid), the point Q also become invariant. Furthermore, it is also worthy to mention that the transformation of compound Na_2SO_4 to compound $Na_2SO_4.10H_2O$ occurs at a constant temperature, and therefore, the point Q is also called a peritectic point.

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Volume I

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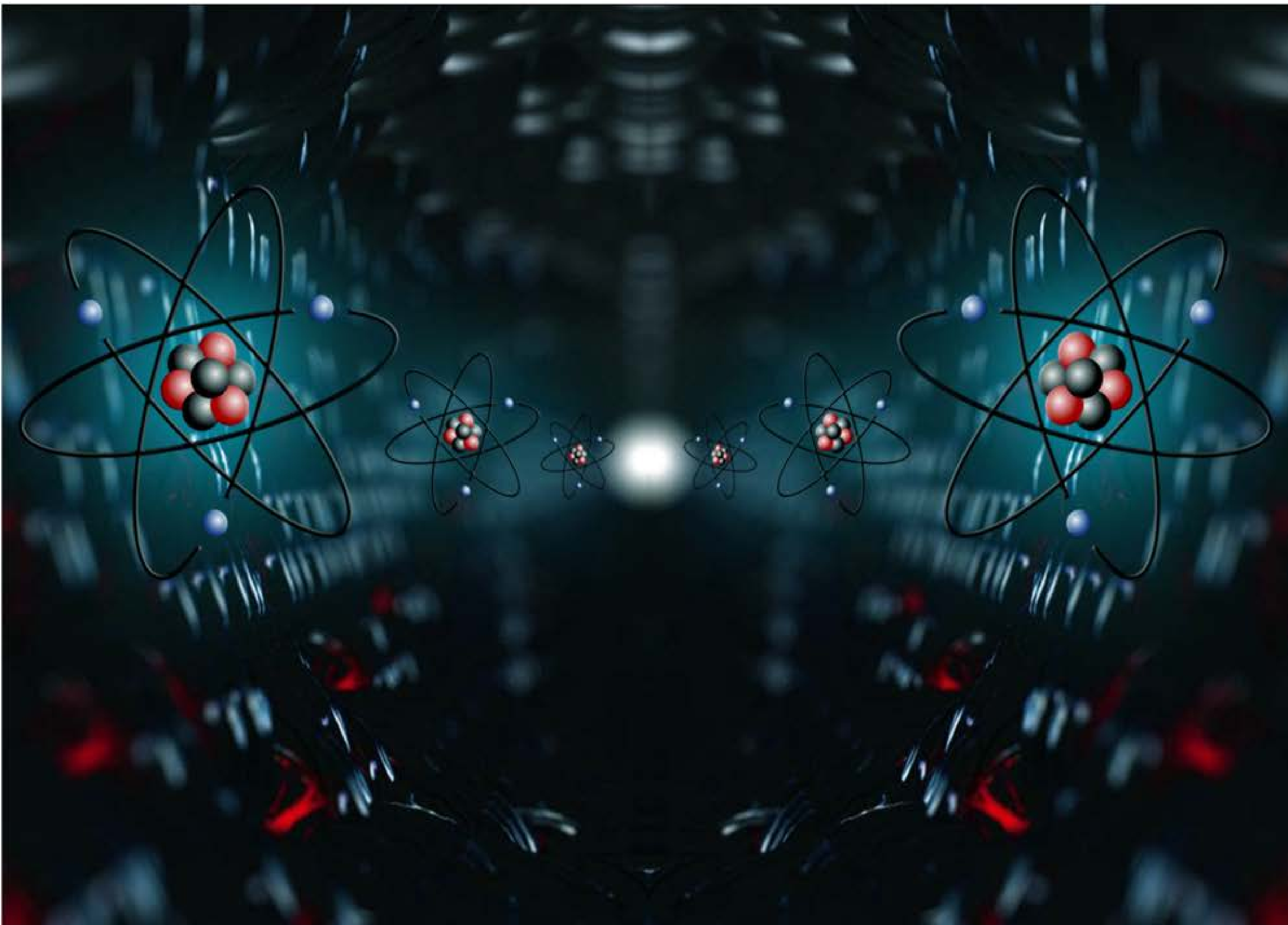

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