CHAPTER 6

Thermodynamics – II

❖ Clausius-Clapeyron Equation

The Clausius-Clapeyron equation was initially proposed by a German physics Rudolf Clausius in 1834 and then further developed by French physicist Benoît Clapeyron in 1850. This equation is extremely useful in characterizing a discontinuous phase transition between two phases of a single constituent.

➢ *Derivation of Clausius-Clapeyron Equation*

In order to derive the Clausius-Clapeyron equation, consider a system at equilibrium i.e. the free energy change for the ongoing process is zero ($\Delta G = 0$). However, we know from the principles of thermodynamics that the variation of free energy with temperature and pressure can be formulated by the following differential equation.

$$dG = VdP - SdT \tag{1}$$

For typical single-constituent equilibria, we have

$$Phase\ I \rightleftharpoons Phase\ II \tag{2}$$

Where phase I can be solid, liquid, or gas; whereas phase II can be liquid or vapor depending upon the nature of the transition whether it is melting, vaporization or sublimation, respectively.

Now consider a system at pressure P and temperature T; and the free energies of phase I and phase II of the same system are G_1 and G_2, respectively. Moreover, if we change the temperature from T to $T+dT$ and pressure from P to $P+dP$; the free energy changes in phase I and phase II will be dG_1 and dG_2, respectively. Mathematically, we can formulate the situation as given below.

$$dG_1 = V_1dP - S_1dT \tag{3}$$

$$dG_2 = V_2dP - S_2dT \tag{4}$$

Where V_1 and S_1 represent the molar volume and entropy of phase I, while V_2 and S_2 represent the molar volume and entropy of phase II. However, if the phase I and phase II are in equilibrium with each other, we have

$$\Delta G = 0 \tag{5}$$

$$G_2 - G_1 = 0 \tag{6}$$

Now recalling the fact that G_1 and G_2 are simply the free energies of the phase I and phase II at temperature T and pressure P; we can say the same must also be true at temperature $T+dT$ and pressure $P+dP$ i.e.

$$(G_2 + dG_2) - (G_1 + dG_1) = 0 \tag{7}$$

$$(G_2 - G_1) + (dG_2 - dG_1) = 0 \tag{8}$$

Since $G_2 - G_1 = 0$ from equation (6), the above equation takes the form

$$dG_2 - dG_1 = 0 \tag{9}$$

$$dG_2 = dG_1 \tag{10}$$

After putting the values of dG_1 and dG_2 from equation (3, 4) in equation (10), we get

$$V_2dP - S_2dT = V_1dP - S_1dT \tag{11}$$

or

$$V_2dP - V_1dP = S_2dT - S_1dT \tag{12}$$

$$(V_2 - V_1)dP = (S_2 - S_1)dT \tag{13}$$

$$\Delta V.dP = \Delta S.dT \tag{14}$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} \tag{15}$$

Now if the ΔH is the latent heat of phase transformation occurring at temperature, the entropy change is or

$$\Delta S = \frac{\Delta H}{T} \tag{16}$$

After using the value of ΔS from equation (16) into equation (15), we get

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \tag{17}$$

The equation was first developed by Calpeyron in 1834 and therefore is named after him Calpeyron equation. Now if phase I is solid while phase II is vapor i.e. solid ⇌ melt equilibria, the equation (17) takes the form

$$\frac{dP}{dT} = \frac{\Delta_{fus}H}{T_f\Delta V} \tag{18}$$

Where $\Delta_{fus}H$ is the latent heat of fusion and T_f is the melting point. The term $\Delta V = V_l - V_s$ i.e. the difference in the volume of melt and solid phase. Therefore, equation (18) can also be written as

$$\frac{dP}{dT} = \frac{\Delta_{fus}H}{T_f(V_l - V_s)} \tag{19}$$

For vaporisation equilibrium i.e. liquid ⇌ vapour,

$$\frac{dP}{dT}=\frac{\Delta_{vap}H}{T_b(V_v-V_l)} \tag{20}$$

Where $\Delta_{vap}H$ is the latent heat of vaporization and T_b is the boiling point. The term $\Delta V = V_v - V_l$ i.e. the difference in the volume of vapor and liquid phases. Now since the volume of the liquid is very small in comparison to the gaseous phase, the term V_l in equation (20) can simply be neglected for simplicity i.e.

$$\frac{dP}{dT}=\frac{\Delta_{vap}H}{TV_v} \tag{21}$$

If the vapor act as an ideal gas i.e. $PV_v = RT$ or $V_v = RT/P$, the above equation can be written as

$$\frac{dP}{dT}=\frac{\Delta_{vap}H}{RT^2}.P \tag{22}$$

or

$$\frac{1}{P}.\frac{dP}{dT}=\frac{\Delta_{vap}H}{RT^2} \tag{23}$$

or

$$\frac{d\,ln\,P}{dT}=\frac{\Delta_{vap}H}{RT^2} \tag{24}$$

The above equation is popularly known as the Clausius-Clapeyron equation.

One more popular form of Clausius-Clapeyron Equation is the integrated one which can easily be derived by using the rearranged form of equation (24) as given below.

$$d\,ln\,P=\frac{\Delta_{vap}H}{RT^2}dT \tag{25}$$

If the temperature changes from T_1 to T_2 and pressure is varied from P_1 to P_2, then we can say that

$$\int_{P_1}^{P_2} d\,ln\,P=\int_{T_1}^{T_2}\frac{\Delta_{vap}H}{RT^2}dT \tag{26}$$

or

$$ln\frac{P_2}{P_1}=\frac{\Delta_{vap}H}{R}\int_{T_1}^{T_2}\frac{1}{T^2}dT \tag{27}$$

$$ln\frac{P_2}{P_1}=\frac{\Delta_{vap}H}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right] \tag{28}$$

After converting to the common logarithm, we get

$$2.303\, log\frac{P_2}{P_1} = \frac{\Delta_{vap}H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{29}$$

or

$$log\frac{P_2}{P_1} = \frac{\Delta_{vap}H}{2.303\, R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{30}$$

Which is the integrated form of Clausius-Clapeyron equation.

➢ ***Applications of Clausius-Clapeyron Equation***

There are many applications of Clausius-Clapeyron equation ranging from chemistry to meteorology and climatology as well. Some of the most important applications in chemistry are given below.

i) For transitions between a gas and a condensed phase (liquid or solid), the Clausius-Clapeyron equation can be given as

$$ln\, P = -\frac{L}{R}\left(\frac{1}{T}\right) + C \tag{31}$$

Where C represents a constant. The symbol L represents the specific latent heat for a liquid-gas transition whereas specific latent heat of sublimation for a solid-gas transition. If the latent heat is known, then knowledge of one point on the coexistence curve determines the rest of the curve. Conversely, as the plot lnP vs 1/T is linear with the zero intercept, the simple linear fitting is used to estimate the latent heat of phase change. The latent heat of vaporization of any liquid can also be determined if the vapor pressures of the same are known at two different temperatures.

ii) The boiling point of a liquid at any temperature can be determined if the boiling point at a particular temperature and latent heat of vaporization of the same are known.

iii) If the latent heat of vaporization and the vapor pressure of a liquid at a particular temperature are known, the vapor pressure of the same liquid at any other temperature can be known.

iv) One more application of this equation is to check if a phase transition will occur via compression or expansion in solid ⇌ melt equilibria. To understand this, recall the

$$\frac{dP}{dT} = \frac{\Delta_{fus}H}{T_f\Delta V} \tag{32}$$

The sign for dP/dT can be positive or negative for expansion and compression, respectively.

❖ Law of Mass Action and Its Thermodynamic Derivation

According to the law of mass action, the rate of a chemical reaction is directly proportional to the product of the activities or simply the active masses of the reactants each term raised to its stoichiometric coefficients.

To understand the law of mass action in mathematical language, consider a reaction in which two reactants *A* and *B* react to form the product *C* and *D* i.e.

$$aA + bB \rightarrow cC + dD \tag{33}$$

Then the law of mass action says the rate of the above conversion should be

$$Rate \propto [A]^a[B]^b \tag{34}$$

$$Rate = k[A]^a[B]^b \tag{35}$$

Where *k* is the constant of proportionality and is typically labeled as rate constant of the reaction.

However, the actual rate of the reaction may or may not be equal to what is suggested by the "law of mass action" because the actual rate law may have powers raised to the active masses different from their stoichiometric coefficients. Mathematically, the actual rate law for the reaction given by equation (33) is

$$Rate \propto [A]^\alpha[B]^\beta \tag{36}$$

$$Rate = k[A]^\alpha[B]^\beta \tag{37}$$

Now comparing equation (35) and equation (37); the law of mass action and actual rate law will give same results when $a = \alpha$ and $b = \beta$; whereas different results will be observed when $a \neq \alpha$ and $b \neq \beta$.

➢ *Modern Definition of the Law of Mass Action*

The law of mass action can be used to study the composition of a mixture in a reversible reaction under equilibrium conditions. To do so, consider a typical reversible reaction i.e.

$$aA + bB \rightleftharpoons cC + dD \tag{38}$$

Now, from the law of mass action, we know that the rate of forward reaction (R_f) and rate backward reaction (R_b) will be

$$R_f = k_f[A]^a[B]^b \tag{39}$$

$$R_b = k_b[C]^c[D]^d \tag{40}$$

Where k_f and k_b are the rate constants for the forward and backward reactions, respectively. After equilibrium is reached, we have

$$R_f = R_b \tag{41}$$

$$k_f[A]^a[B]^b = k_b[C]^c[D]^d \tag{42}$$

or

$$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{43}$$

Since the k_f and k_b are also constant at equilibrium, the ratio of the two is also a constant and is typically labeled as K or the equilibrium constant. Therefore, equation (43) is modified as

$$K = \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{44}$$

All this leads to the modern definition of "law of mass action" that the ratio of the multiplication of molar concentrations of products raised to the power of their stoichiometric coefficients to the multiplication of the molar concentrations of the reactants raised to the power of their stoichiometric coefficients is constant at constant temperature and is called as "equilibrium constant". It is also worthy to mention that equation (44) is also known as the "law of chemical equilibrium".

- ***Thermodynamic Derivation of the Law of Mass Action***

In order to derive the law of mass action thermodynamically, recall the general form of a typical reversible reaction under equilibrium conditions in which reactants and products are ideal gases i.e.

$$aA + bB \rightleftharpoons cC + dD \tag{45}$$

Now, as we know that the total free energy of the reactant (G_R) can be formulated as

$$G_R = a\mu_A + b\mu_B \tag{46}$$

Where μ_A and μ_B are the chemical potentials of reactant A and B, respectively. Similarly, the total free energy of the products (G_P) can also be formulated i.e.

$$G_P = c\mu_C + d\mu_D \tag{47}$$

It is also important to mention that the temperature and pressure are kept constant. Moreover, the free energy change of the whole reaction can be obtained by subtracting equation (46) from equation (47) i.e.

$$\Delta G_{reaction} = G_P - G_R \tag{48}$$

$$\Delta G_{reaction} = (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) \tag{49}$$

Recalling the fact that the free energy change at equilibrium is zero, equation (49) is reduced to

$$(c\mu_C + d\mu_D) - (a\mu_A + b\mu_B) = 0 \tag{51}$$

Now recall the expression of the chemical potential of the ith species in gas phase i.e.

$$\mu_i = \mu_i^0 + RT\ln p_i \qquad (52)$$

Where p_i and μ_i^0 are the partial pressure and standard chemical potential of *i*th species, respectively. Now using equation (52) in equation (51), we get

$$[c(\mu_C^0 + RT\ln p_C) + d(\mu_D^0 + RT\ln p_D)] - [a(\mu_A^0 + RT\ln p_A) + b(\mu_B^0 + RT\ln p_B)] = 0 \qquad (53)$$

or

$$c\mu_C^0 + cRT\ln p_C + d\mu_D^0 + dRT\ln p_D - a\mu_A^0 - aRT\ln p_A - b\mu_B^0 - bRT\ln p_B = 0 \qquad (54)$$

$$c\mu_C^0 + RT\ln p_C^c + d\mu_D^0 + RT\ln p_D^d - a\mu_A^0 - RT\ln p_A^a - b\mu_B^0 - RT\ln p_B^b = 0 \qquad (55)$$

$$RT\ln p_C^c + RT\ln p_D^d - RT\ln p_A^a - RT\ln p_B^b = -c\mu_C^0 - d\mu_D^0 + a\mu_A^0 + b\mu_B^0$$

or

$$RT\ln\left(p_C^c p_D^d\right) - RT\ln\left(p_A^a p_B^b\right) = -[c\mu_C^0 + d\mu_D^0 - a\mu_A^0 - b\mu_B^0] \qquad (56)$$

$$RT\ln\frac{\left(p_C^c p_D^d\right)}{\left(p_A^a p_B^b\right)} = -[G_P^o - G_R^o] \qquad (57)$$

$$RT\ln\frac{\left(p_C^c p_D^d\right)}{\left(p_A^a p_B^b\right)} = -\Delta G_{reaction}^o \qquad (58)$$

Where $\Delta G_{reaction}^o$ is the standard free energy change of the reaction can be simply abbreviated as ΔG^o only. Therefore, the equation (58) can be rearranged as given below.

$$\ln\frac{\left(p_C^c p_D^d\right)}{\left(p_A^a p_B^b\right)} = -\frac{\Delta G^o}{RT} \qquad (59)$$

$$\frac{p_C^c p_D^d}{p_A^a p_B^b} = e^{-\frac{\Delta G^o}{RT}} \qquad (61)$$

Now because ΔG^o is a function of temperature only and R is a constant quantity, the right-hand side can be put equal to another constant, say 'K_p'.

$$e^{-\frac{\Delta G^o}{RT}} = K_p \qquad (62)$$

From equation (61) and equation (62), we have

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \qquad (63)$$

Which is again the modern statement of "law of mass action" but in terms of partial pressures.

Other forms of equation (63) can also be written depending upon the reactants and products involved. If the chemical potentials of the reactants and products are in mole fractions (x_i) i.e.

$$\mu_i = \mu_i^0 + RT \ln x_i \tag{64}$$

Then equation (63) takes the form

$$K_x = \frac{x_C^c\, x_D^d}{x_A^a\, x_B^b} \tag{65}$$

Similarly, If the chemical potentials of the reactants and products are in molar concentrations (c_i) i.e.

$$\mu_i = \mu_i^0 + RT \ln c_i \tag{66}$$

Then equation (63) takes the form

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{67}$$

Which is the popular form of "law of mass action".

❖ Third Law of Thermodynamics (Nernst Heat Theorem, Determination of Absolute Entropy, Unattainability of Absolute Zero) And Its Limitation

The third law of thermodynamics states that the entropy of a system approaches a constant value as its temperature approaches absolute zero.

In order to understand the abovementioned statement fully, we need to discuss some very important concepts and consequences of third law thermodynamics first such as "Nernst heat theorem" or "absolute entropies" etc.

➢ *Nernst Heat Theorem*

In 1906, Walther Nernst, a German chemist, studied the variation of enthalpy change and free energy change as a function of temperature. His results gained very much popularity as "Nernst heat theorem" in chemistry and built the foundation of many other discoveries. For detailed picture, recall the Gibbs-Helmholtz equation i.e.

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P \tag{68}$$

It is obvious from the above equation that the free energy change will become equal to the enthalpy change when the temperature is reduced to absolute zero i.e. $\Delta G = \Delta H$ at $T = 0$. Besides, Nernst also noted that the magnitude of $\partial(\Delta G)/\partial T$ declines gradually and approaches the zero with the decrease of temperature.

In other words, W. Nernst observed that as the temperature is decreased continuously, the Gibbs free energy change was decreasing while the enthalpy change was increasing gradually with the same magnitude. Therefore, the change in slope in both curves must become zero near absolute zero i.e.

$$\lim_{T \to 0} \frac{\partial(\Delta G)}{\partial T} = \lim_{T \to 0} \frac{\partial(\Delta H)}{\partial T} = 0 \tag{69}$$

Which is the mathematical form of Nernst heat theorem. The pictorial representation of these observations is also given below for a more clear perspective.

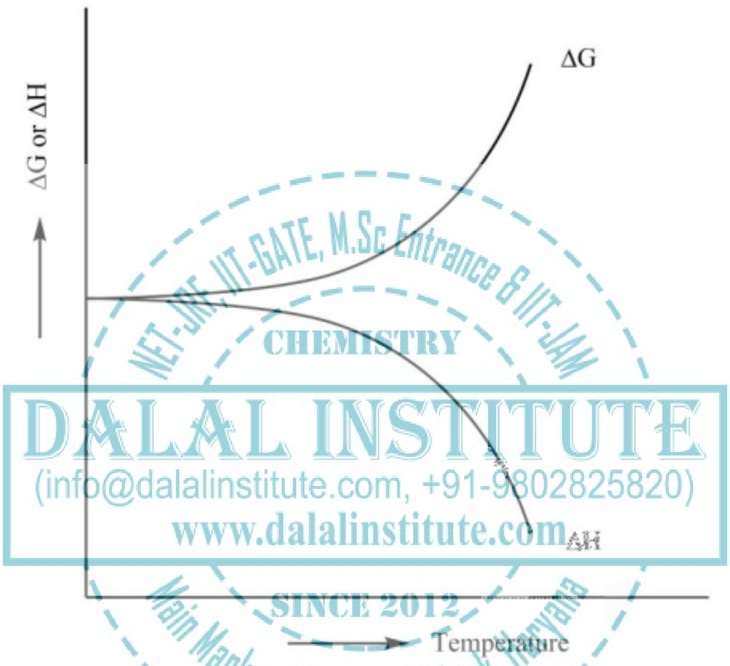

Figure 1. The graphical representation of Nernst heat theorem.

It is also worthy to mention that though we have shown ΔG greater than ΔH when the temperature is set greater than zero, the reverse may also be possible because $\partial(\Delta G)/\partial T$ can have positive as well as negative values.

Furthermore, we also know that variation of free energy change with the temperature at constant pressure is equal to the negative of entropy change i.e.

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = -\Delta S \tag{70}$$

Also, from the definition of change in the heat capacity, we have

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_P = \Delta C_P \tag{71}$$

After putting the values of equation (70, 71) in equation (69), we get

$$\lim_{T \to 0} (\Delta S) = 0 \qquad and \qquad \lim_{T \to 0} \Delta C_P = 0 \tag{72}$$

Now because, no gas or liquid at or in the vicinity of absolute zero, we can apply the Nernst heat theorem to solids only.

The right-hand side result given in equation (72) is extremely important as far as the third law of thermodynamics is concerned. Actually, we can say that the "third law of thermodynamics" follows from the results obtained by the Nernst heat theorem. In order to understand it more clearly, recall one of two results of Nernst heat theorem i.e.

$$\lim_{T \to 0} \Delta C_P = 0 \tag{73}$$

This means that as we approach absolute zero, the heat capacity of reactants becomes equal to the heat capacity of the product. In other words, we can say that the heat capacities of all substances are equal at absolute zero. Mathematically, it can be formulated as

$$\lim_{T \to 0} C_P(product) = \lim_{T \to 0} C_P(reactant) \tag{74}$$

Since the results of the quantum mechanics say that the heat capacity of tends to zero as the temperature approaches absolute zero, the above equation takes the form

$$\lim_{T \to 0} C_P = 0 \tag{75}$$

Similarly recalling the second result of Nernst heat theorem i.e.

$$\lim_{T \to 0} (\Delta S) = 0 \tag{76}$$

Which means that as we approach absolute zero, the entropy of reactants becomes equal to the entropy of the product. In other words, we can say that the entropy of all substances are equal at absolute zero. Mathematically, it can be formulated as

$$\lim_{T \to 0} S_{product} = \lim_{T \to 0} S_{reactant} \tag{77}$$

Using the same argument as in case of heat capacity, the above equation takes the form

$$\lim_{T \to 0} S = 0 \tag{78}$$

Therefore, the entropy of all crystalline substances can be taken as zero at absolute zero, which is the general statement of the third law of thermodynamics.

➢ *Determination of Absolute Entropy*

One of the most interesting and important applications of the third law of thermodynamics (or the Nernst heat theorem) is that it can be used to determine the absolute entropies of different substances at any temperature. The procedure employs the fact that we can calculate the entropy change easily and if the entropy of the initial state is zero then this difference will simply be equal to the absolute entropy i.e.

$$\Delta S = S_T - S_0 \tag{79}$$

Where S_T and S_0 are the entropies at temperatures T and 0K, respectively. Since we know from the third law of thermodynamics that $S_0 = 0$, the equation (79) takes the form

$$\Delta S = S_T - 0 = S_T \tag{80}$$

Before we proceed further, we must remember that a substance may change phase when it supplied with heat. Therefore, we need to discuss the absolute entropies in solid, liquid and gases separately.

1. Absolute entropies in case of solids: To calculate the absolute entropy of a solid at any temperature, we just need to find the total entropy change in shifting the absolute zero state to that temperature. The very small entropy change is given by

$$dS = \frac{\delta q}{T} \tag{81}$$

However, the general expression for heat capacity is

$$C_P = \frac{\delta q}{dT} \tag{82}$$

$$\delta q = C_P\, dT \tag{83}$$

After putting the value of δq from equation (83) into equation (81), we have

$$dS = \frac{C_P\, dT}{T} \tag{84}$$

In order to find the total entropy change in the same phase (solid in this case) when the temperature is raised from 0 to T, we need to integrate the above equation over the range of interest i.e.

$$\int_0^T dS = \int_0^T \frac{C_P\, dT}{T} \tag{85}$$

$$S_T - S_0 = \int_0^T C_P\, d\ln T \tag{86}$$

Since $S_0 = 0$, the above equation becomes

$$S_T = \int_0^T C_P \, d \ln T \tag{87}$$

Thus, the entropy of any solid at temperature T can be obtained by heat capacity at many temperature points between $0K$ to T. The total integral of equation (87) can be obtained by measuring the area under the plot of C_P vs ln T.

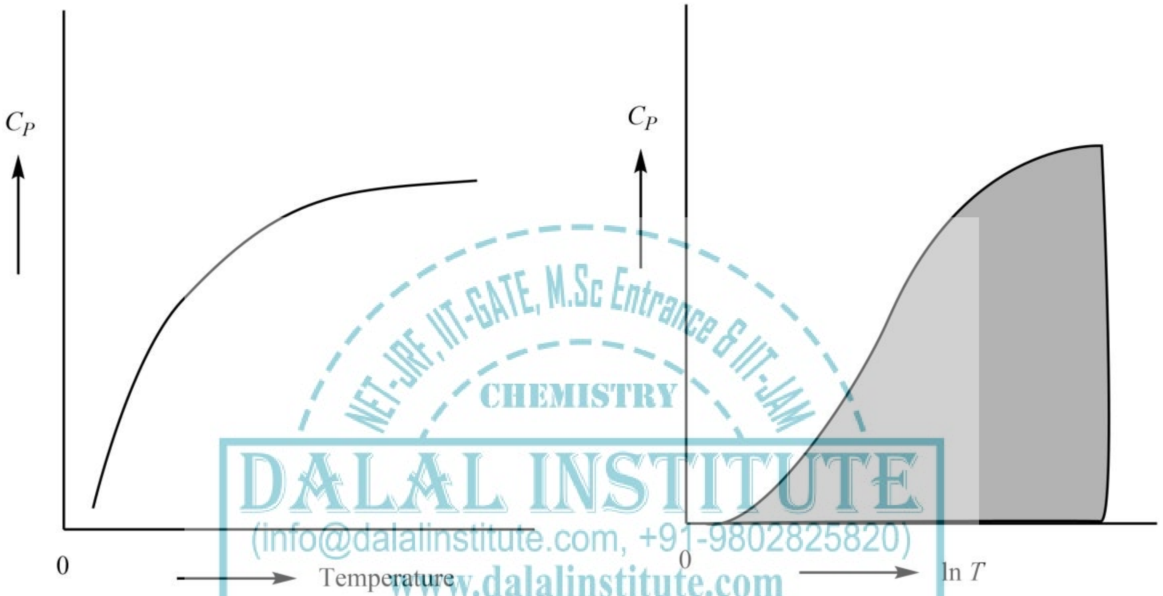

Figure 2. The plot of heat capacity vs T and ln T.

2. Absolute entropies in case of liquids: To calculate the absolute entropy of a liquid at any temperature, we just need to find the total entropy change in shifting the absolute zero state to that temperature. The whole process can be divided into three steps; one in heating up the solid phase form $0K$ to it melting or the fusion point, then phase change from solid to liquid at fusion temperature, and the last step in which liquid is heated up to temperature T.

i) Entropy change from 0K to T_f:

$$\Delta S_1 = \int_0^{T_f} C_P(s) \, d \ln T \tag{88}$$

ii) Entropy change of fusion at T_f:

$$\Delta S_2 = \frac{\Delta H_f}{T_f} \tag{89}$$

iii) Entropy change from T_f to T :

$$\Delta S_3 = \int_{T_f}^{T} C_P(l)\, d \ln T \tag{90}$$

The total entropy change for the process can be obtained by simply adding equations (88–90) i.e.

$$S_T - S_0 = \Delta S_1 + \Delta S_2 + \Delta S_3 \tag{91}$$

$$S_T = \int_0^{T_f} C_P(s) d \ln T + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T} C_P(l)\, d \ln T \tag{92}$$

Where $C_P(s)$ and $C_P(l)$ are the heat capacities for solid and liquid phases, respectively. The symbol ΔH_f represents the latent heat of fusion.

3. Absolute entropy in case of gases: To calculate the absolute entropy of a gas at any temperature, we just need to find the total entropy change in shifting the absolute zero state to that temperature. The whole process can be divided into five steps; one in heating up the solid phase form $0K$ to it melting or the fusion point, then phase change from solid to liquid at fusion temperature, followed by the raising the temperature from T_f to T_b. The fourth step includes the vaporization of liquid phase to gaseous phase at boiling point followed by the last step in which the temperature must be raised from T_b to the required temperature T.

i) Entropy change from $0K$ to T_f :

$$\Delta S_1 = \int_0^{T_f} C_P(s)\, d \ln T \tag{93}$$

ii) Entropy change of fusion at T_f :

$$\Delta S_2 = \frac{\Delta H_f}{T_f} \tag{94}$$

iii) Entropy change from T_f to T_b :

$$\Delta S_3 = \int_{T_f}^{T_b} C_P(l)\, d \ln T \tag{95}$$

iv) Entropy change of vaporization at T_b :

$$\Delta S_4 = \frac{\Delta H_{vap}}{T_b} \tag{96}$$

v) Entropy change from T_b to T:

$$\Delta S_5 = \int_{T_b}^{T} C_P(g)\, d\ln T \tag{97}$$

The total entropy change for the process can be obtained by simply adding equations (88–90) i.e.

$$S_T - S_0 = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 \tag{98}$$

$$S_T = \int_{0}^{T_f} C_P(s) d\ln T + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} C_P(l)\, d\ln T + \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T} C_P(g)\, d\ln T \tag{99}$$

Where $C_P(s)$, $C_P(l)$ and $C_P(g)$ are the heat capacities for solid, liquid and gas phases, respectively. The symbol ΔH_{vap} represents the latent heat of vaporization.

- ***The unattainability of Absolute Zero***

One more statement of the third law of thermodynamics is that the lowering of the temperature of a material body to the absolute zero is impossible in the finite number of steps. To understand this claim, recall the concept of Carnot refrigerator first. A Carnot refrigerator is basically just the reverse of the Carnot heat engine i.e. Carnot heat engine working in reverse cycle. Since a Carnot heat engine provides work through reversible isothermal-adiabatic compressions and expansions, a net amount of work must be done in Carnot refrigerator making it electricity consumer.

Let q_1 be the amount of heat absorbed by a Carnot refrigerator form a body at lower temperature T_1 and q_2 as the amount of heat rejected by the same refrigerator to a body at higher temperature T_2. The coefficient of performance (β) of the reversible Carnot refrigerator can be given by the following relation.

$$\beta = \frac{1}{q_2/q_1 - 1} \tag{100}$$

Since for a Carnot cycle, we know that

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} \tag{101}$$

or

$$\frac{q_2}{q_1} = \frac{T_2}{T_1} \tag{102}$$

After using the value of q_2/q_1 from equation (102) in equation (100), we get

$$\beta = \frac{1}{T_2/T_1 - 1} \tag{103}$$

Furthermore, we also know that the coefficient of performance of an ideal Carnot refrigerator is simply the ratio of the cooling effect to the work done i.e.

$$\beta = \frac{q_1}{w} \tag{104}$$

Which means that how much heat is removed from the body at lower temperature per unit of work done. Now from equation (103) and equation (104), we have

$$\frac{q_1}{w} = \frac{1}{T_2/T_1 - 1} \tag{105}$$

$$\frac{q_1}{w} = \frac{T_1}{T_2 - T_1} \tag{106}$$

Taking reciprocal of the above result, we get

$$\frac{w}{q_1} = \frac{T_2 - T_1}{T_1} \tag{107}$$

Thus, it is obvious from the above equation that as the lower temperature T_1 approaches zero, more and more work will be needed to remove the same amount of heat (w is inversely proportional to T_1), which is the unattainability of the absolute zero.

- ***Limitation of Third Law of Thermodynamics***

Although the third law of thermodynamics is very useful in determining various thermodynamic properties of various substances, there are some limitations of the same. The reason being is the fact that entropies obtained using the third law of thermodynamics are thermal entropies and are somewhat smaller than the entropy values obtained using statistical mechanics. This deviation is typically in range of 3–5 JK^{-1} mol^{-1}.

From this, we may conclude that there is some entropy present even at the 0K temperature. This entropy is called as "residual entropy" and can be obtained using the following relation.

$$S = k \ln W \tag{108}$$

Where k is Boltzmann constant and the W is the thermodynamic probability which represents the number of equally probable orientations of the molecule under consideration. For instance, consider a sample of N number of carbon monoxide molecules. Since each molecule can have two orientations that are equally probable (CO CO OC CO OC OC), the thermodynamic probability will be $W = 2^N$. The residual entropy is

$$S = k \ln W = k \ln 2^N = kN \ln 2 \tag{109}$$

For one mole of sample $kN = R$, the above equation takes the form

$$S = R \ln 2 = 2.303R \log 2 = 5.85 \text{ JK}^{-1}\text{mol}^{-1} \tag{110}$$

❖ Phase Diagram for Two Completely Miscible Components Systems

Before we discuss the phase diagram for two completely miscible components systems, it is better to recall the Gibbs phase rule which states that

$$F = C - P + 2 \tag{110}$$

Where *F* is the number of degrees of freedom, *C* represents the number of components and *P* simply gives the total number of phases. For a two components system, the equation (110) reduces to

$$F = 2 - P + 2 = 4 - P \tag{111}$$

At this point, there are three major possibilities depending upon the number of phases involved which will be discussed one by one.

➢ *Types of Two-Component Systems Based on Number of Phases*

i) When we use $P = 1$ in equation (111), we get

$$F = 4 - 1 = 3 \tag{112}$$

This means that for a one-phase and two-component system, there are three degrees of freedom. This single-phase can be gaseous, solid solution, or two completely miscible liquids. Moreover, since the number of degrees of freedom is three, there are three conditions that can be varied without disturbing the total number of phases at equilibrium state.

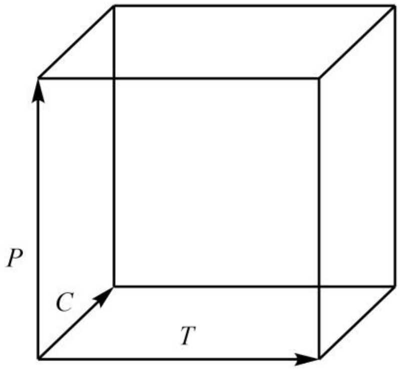

Figure 3. The graphical representation of a one-phase, two-component system.

Hence, the three degrees of freedom can be depicted along the three axes of a cube. However, it is more common to vary only two variables while keeping the third one as constant. For instance, in case of pressure-temperature diagrams, composition is kept constant; while in case of pressure-composition curves, the temperature is kept fixed at a particular value. Furthermore, in case of temperature-composition curves, the pressure of the system is always kept constant. Now although all the possibilities are there, it is more convenient to fix the pressure of the system at atmospheric pressure and vary the temperature and composition.

Therefore, we can say that instead of using three variables, it is more popular to keep one constant and vary the other two. This will also simplify the graphical representation of a simple two-component system.

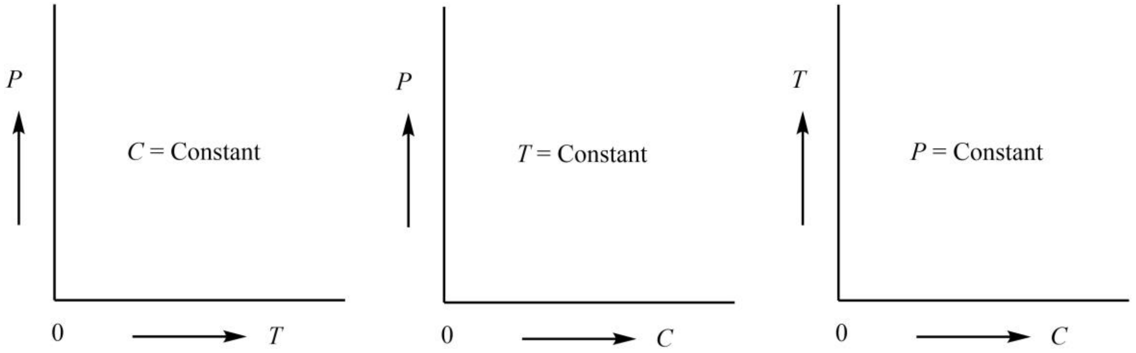

Figure 4. The two-dimensional variants of the one-phase-two-component system.

ii) When we use $P = 2$ in equation (111), we get

$$F = 4 - 2 = 2 \tag{113}$$

This means that for a two-phase and two-component system, there are two degrees of freedom. These phases can be liquid-vapour, liquid-liquid, or solid-liquid. Moreover, since the number of degrees of freedom is two, there are two variables that can be varied without disturbing total number of phases at equilibrium state.

iii) When we use $P = 3$ in equation (111), we get

$$F = 4 - 3 = 1 \tag{114}$$

Which means that for a three-phase and two-component system, there is only one degree of freedom. These phases can be liquid-liquid-vapour, solid-liquid-liquid, or solid-solid-liquid. Moreover, since the number of degrees of freedom is one, there is only one variable that can be varied without disturbing the total number of phases at equilibrium state.

Now although a complete phase diagram for two-component systems must be able to show the different phases up to number three, the situation is slightly simple for "condensed systems". More specifically, if all the phases in two-component systems are either solid or liquids only (solid-liquid equilibria), a minor pressure disturbance will have little to no effect on the system. Therefore, we can conclude that the number of degree of freedom in such "condensed systems" is actually reduced by one i.e.

$$F' = C - P + 1 \tag{115}$$

Which is the reduced or condensed phase rule where F' is the total number of degrees of freedom excluding pressure. Now because the total number of phases that can exist simultaneously are reduced to 2 (system become univariant at P =2), The complete phase diagram can be drawn on two dimensional paper with vertical and horizontal sides representing temperature and pressure, respectively.

➢ *Types of Completely Miscible Two-Component Systems in Solid-Liquid Equilibria*

We know that in a solid-liquid equilibrium, the solid can be one of the constituents or solid solution which are completely miscible in the liquid phase.

Consider a liquid mixture of two components *A* and *B* 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. At this point, assume that we have a number of such mixtures with the same components *A* and *B* but with different compositions (i.e. with different ratios of *A* and *B*). The cooling of all the mixtures is carried out in open vessels so that the pressure remains constant (atmospheric pressure). After that, the only thing we need to do is to plot these freezing point vs the composition. These completely miscible two-component systems can primarily be classified into three categories.

1. Eutectic systems: In these types of systems, the components do not react with each other but only the simple mixing takes place in the solution or in the molten state. The common examples of such systems are lead-silver system, bismuth-cadmium system, potassium iodide-water system.

Figure 5. General phase diagram of eutectic systems.

2. Systems forming solid compounds A_xB_y with congruent and incongruent melting points: In these types of systems, the components do react with each other and the formation of a compound takes place. The common example of such systems are the Mn-Zn system (forming $MgZn_2$) and Na_2SO_4-H_2O system (forming $Na_2SO_4.10H_2O$). These types of systems can further be classified.

i) Systems forming solid compounds with congruent melting point: In these types of systems, the two components react to give a compound which is quite stable until its melting point is reached. When melted, the composition remains the same as that of the solid, and such compounds are said to have a congruent melting point. Some of the common examples of such systems are Mg-Zn and $FeCl_3$-H_2O systems.

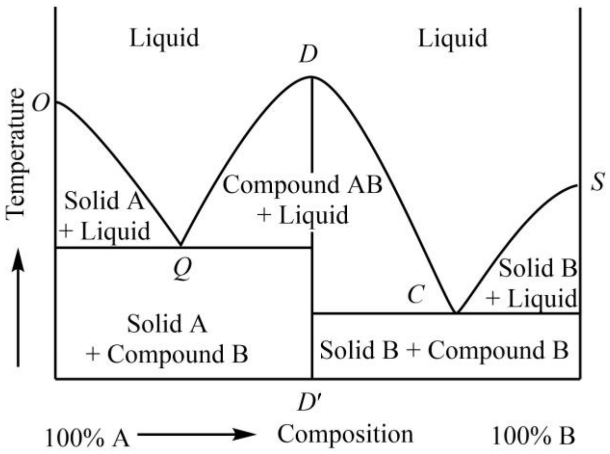

Figure 6. General phase diagram for systems forming solid compounds with congruent melting points.

ii) Systems forming solid compounds with incongruent melting point: 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 a congruent melting point. Some of the common examples of such systems are Na_2SO_4-H_2O and NaCl-H_2O systems. A typical transition can be represented as

$$C_1 \rightleftharpoons C_2 + \text{melt or solution} \tag{116}$$

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.

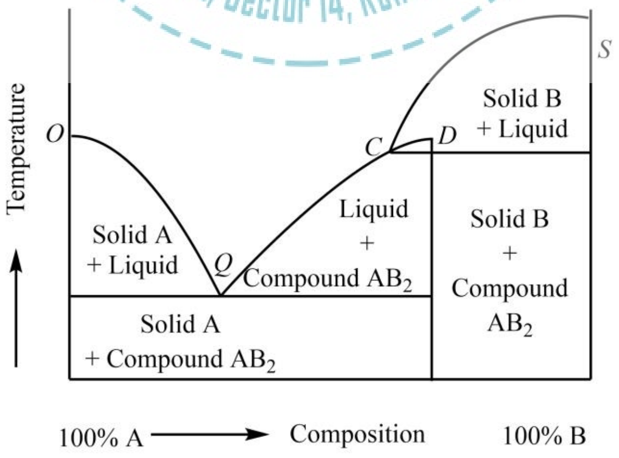

Figure 7. General phase diagram for systems forming solid compounds with incongruent melting points.

3. Systems forming solid solutions: In these types of systems, the components are completely miscible with each other in solid phase and completely homogeneous solid solutions are produced. The X-ray diffraction studies are typically employed to check that single crystalline phase is obtained rather than a mixture of two solid phases. The common example of such systems are Co-Ni system, Au-Ag system and AgCl-NaCl system.

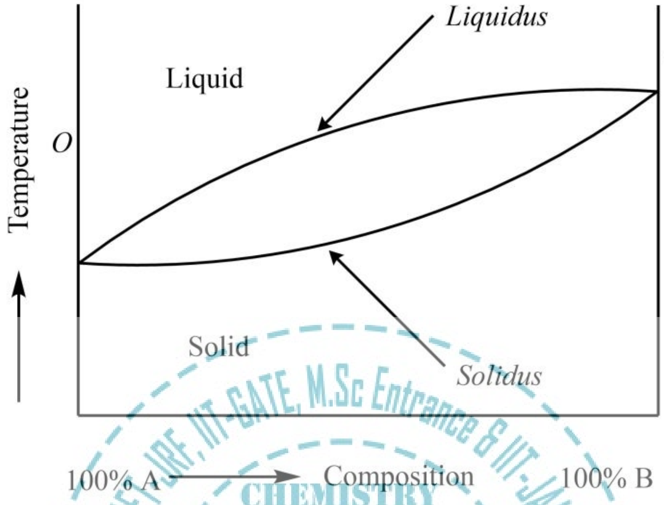

Figure 8. The general phase diagram of systems forming solid solutions.

➢ ***Experimental Methods for The Determination of Phase Diagram of Two-Component Systems***

The most common approaches for the determination of phase diagram of two-component systems are "cooling curve" and "thaw melt" methods. These methods are quite popular due to their easiness and practicability to many systems.

1. Cooling curve method: In this approach, a liquid mixture of two components *A* and *B* at temperature *T* is allowed to cool down below the freezing point of the mixture, the solid will start to separate out. A number of such mixtures with the same components *A* and *B* but with different compositions (i.e. with different ratios of *A* and *B*) are then allowed to cool down in open vessels so that the pressure remains constant (atmospheric pressure). The temperature of the system is regularly recorded at different times to obtain temperature vs time plots. After that, from the breaks and arrests in those plots, important information such as freezing point or solidification time are obtained for different compositions.

Now in order to understand the concept more clearly, a variation of temperature with time for pure and a liquid mixture must be discussed. In the case of a liquid mixture, above point *b*, the system is completely liquid and it will cool down very rapidly in going from point *a* to point *b*. Now because at point *b*, the crystallization of the compound A will start releasing a large amount of heat, and therefore, the rate of cooling will be slightly slower until point *c* is reached. Now since the system is getting solidified at eutectic temperature i.e. it is moving from *c* (solidification of B starts) to *d* the temperature of the system will remain constant during this conversion. After point *d*, the system will cool down as a solid mixture with two degrees of freedom.

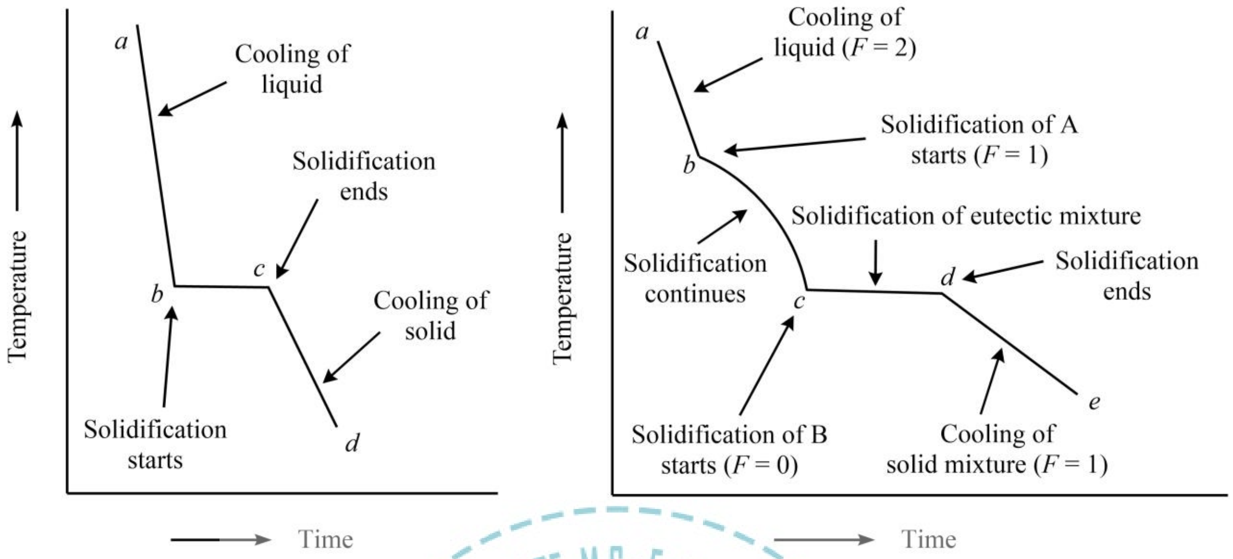

Figure 9. The typical cooling curves for pure a pure liquid (left) and a liquid mixture (right).

It is also worthy to mention that in some cases a phenomenon called "supercooling" is observed in which the break at point '*b*' is absent and cooling of liquid continues along *a*-*b* with sudden rise after some time giving an abnormal break at *b′* instead of *b*. The correct break is found by extrapolating from point *b′* backward.

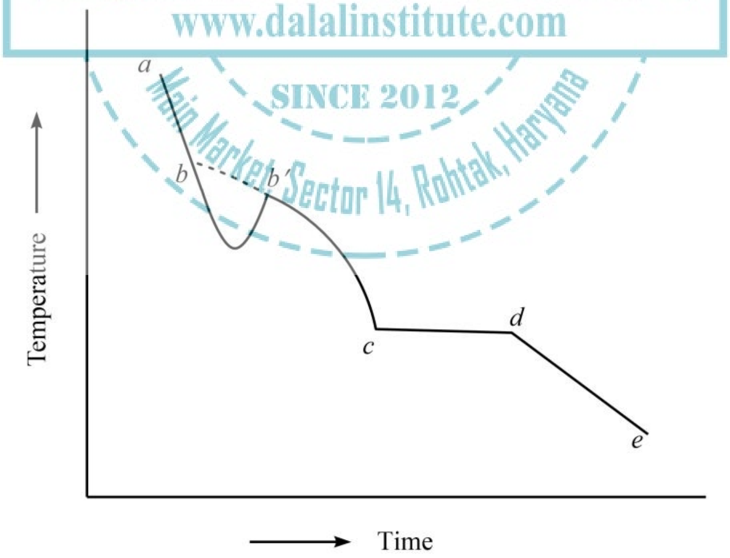

Figure 10. The typical cooling curves for a liquid mixture with supercooling.

Now although the supercooling phenomenon does not create a major problem in most of the cases, it can be a real mess in some systems. Therefore, another method that can overcome these limitations must be discussed.

2. Thaw-melt method: This method is free from the limitation of the “supercooling phenomenon” posed by the cooling carve method. In this approach, a solid mixture of two components *A* and *B* at temperature *T* is heated continuously. This is exactly opposite of what we follow in cooling curve method and we will note down melting points for different compositions. A number of such solid mixtures with same components *A* and *B* but with different compositions (i.e. with different ratios of *A* and *B*) are then heated up in open vessels so that the pressure remains constant (atmospheric pressure). The temperature of system is regularly recorded at different times to obtain temperature vs time plots. After that, from the breaks and arrests in those plots, important information such as melting point or liquefaction time are obtained for different compositions.

Now in order to understand the concept more clearly, a variation of temperature with time for pure and a liquid mixture must be discussed. In the case of a solid mixture, below point *e*, the system is completely solid and it will heat up slowly in going from point *e* to point *d*. Now since the system is getting liquefied at eutectic temperature i.e. it is moving from *d* to *c*; the temperature of the system will remain constant during this conversion. Now because at point *c*, the melting of A compound will continue requiring a large amount of heat, and therefore, the rate of heating will be slightly slower until point *b* is reached. After point *b*, the system will heat up as liquid mixture with two degrees of freedom very rapidly.

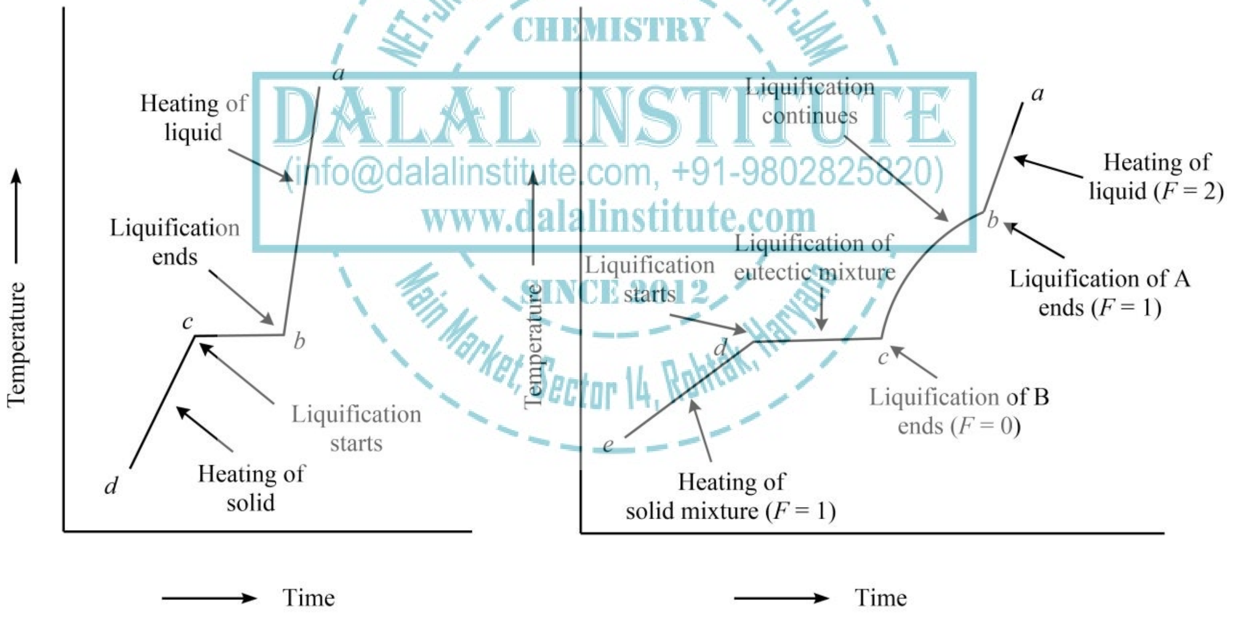

Figure 11. The typical Thaw-melting heating curves (temperature vs time) for a pure liquid (left) and a liquid mixture (right).

It is also worthy to mention that the temperature at which the melting of the solid mixture starts is typically called as “thaw point” and the temperate at which liquefaction ends is called as “melting point”.

❖ 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.

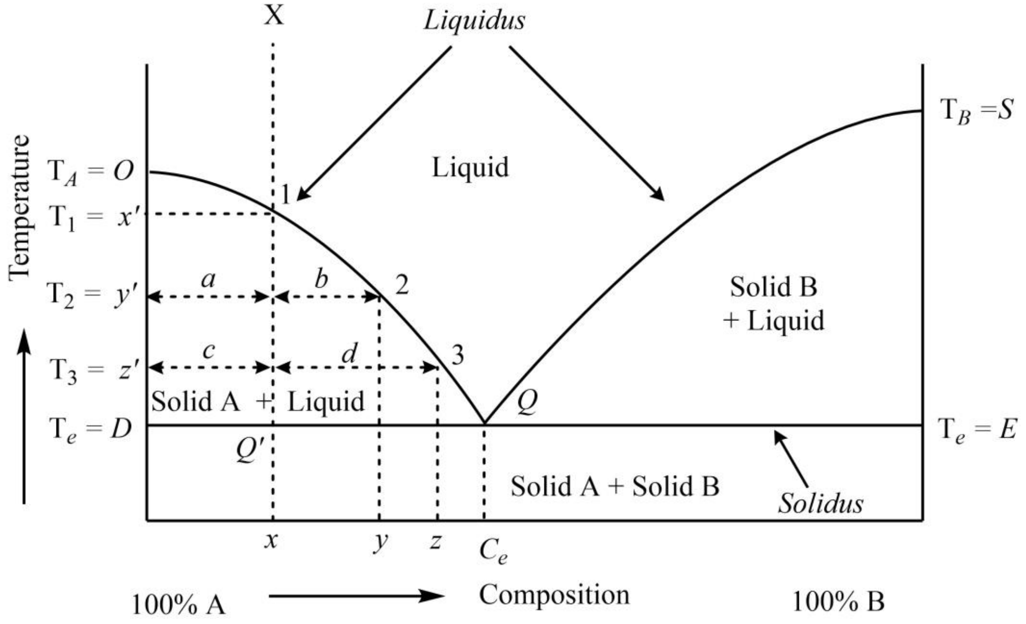

Figure 12. The general phase diagram of eutectic systems.

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

$$F' = 2 - 2 + 1 = 1 \tag{117}$$

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.

$$F' = 2 - 3 + 1 = 0 \tag{118}$$

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

$$F' = 2 - 1 + 1 = 2 \tag{119}$$

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

$$F' = 2 - 2 + 1 = 1 \tag{120}$$

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

$$F' = 2 - 2 + 1 = 1 \tag{121}$$

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

$$F' = 2 - 2 + 1 = 1 \tag{122}$$

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 1*x'* that cuts *OQ* at *x'*, or 2*y'* that cuts *OQ* at *y'*. The importance of this line will be disused 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).

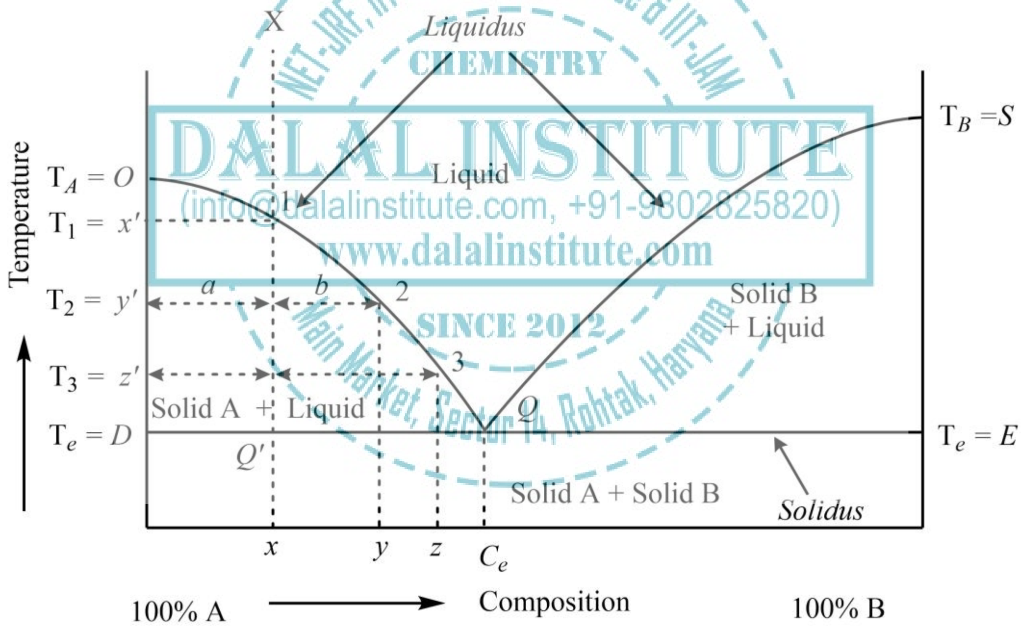

Figure 13. The cooling of a liquid mixture.

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.

$$\% \ of \ crystals \ of \ A = \frac{b}{a+b} \times 100 \tag{123}$$

$$\% \ of \ liquid \ mixture = \frac{a}{a+b} \times 100 \tag{124}$$

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.

$$\% \ of \ crystals \ of \ A = \frac{d}{c+d} \times 100 \tag{125}$$

$$\% \ of \ liquid \ mixture = \frac{c}{c+d} \times 100 \tag{126}$$

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.

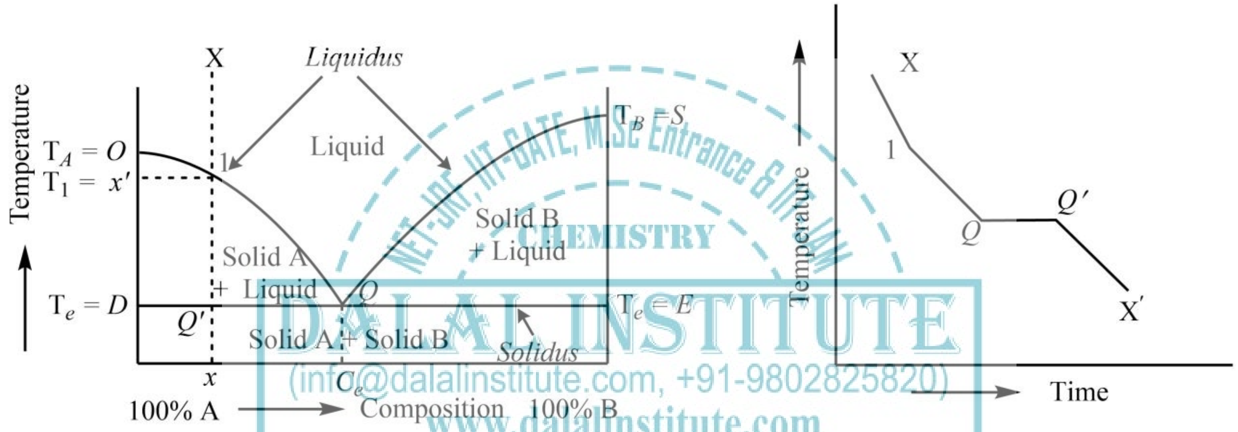

Figure 14. The cooling of a liquid mixture (compound A and compound B) when composition exists left to the eutectic composition.

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.

i) 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.

ii) 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.

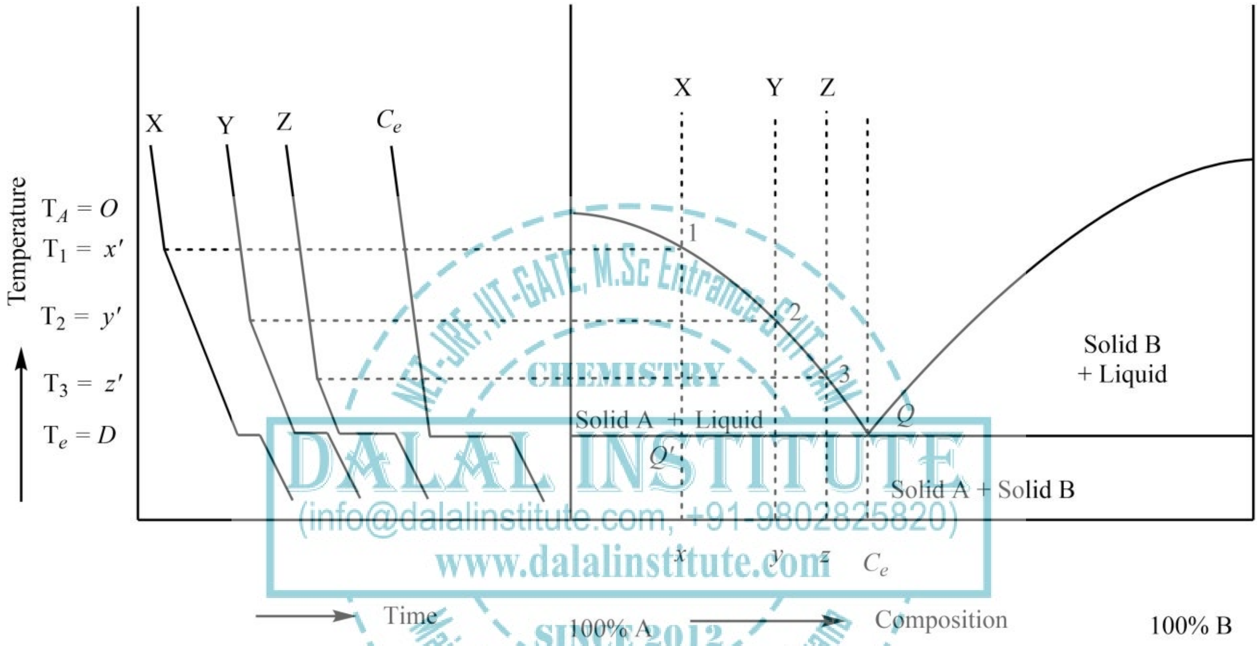

Figure 15. The cooling of a liquid mixture (compound A and Compound B) when compositions exist at eutectic point or left to the eutectic composition.

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.

$$F' = C - P + 1 \tag{127}$$

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

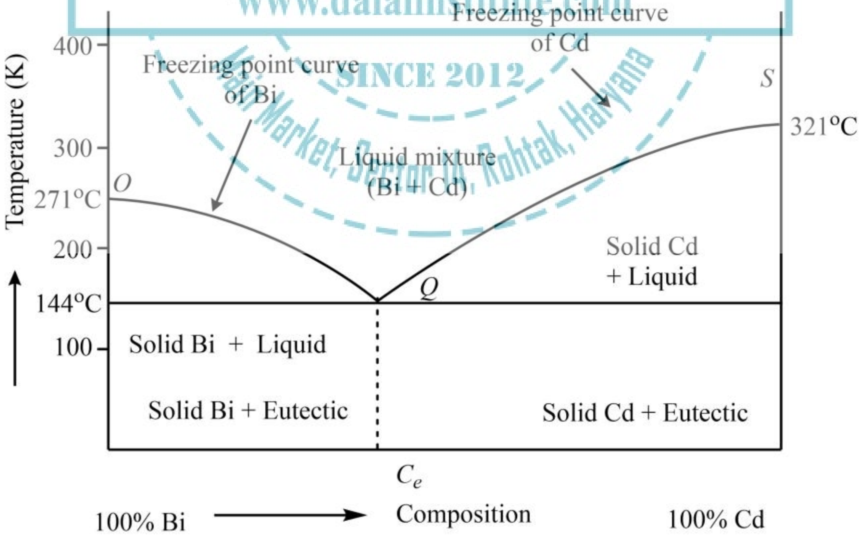

Figure 16. The phase diagram of Bi-Cd system.

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

$$F' = 2 - 2 + 1 = 1 \tag{128}$$

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.

$$F' = 2 - 3 + 1 = 0 \tag{129}$$

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.

$$F' = C - P + 1 \tag{130}$$

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

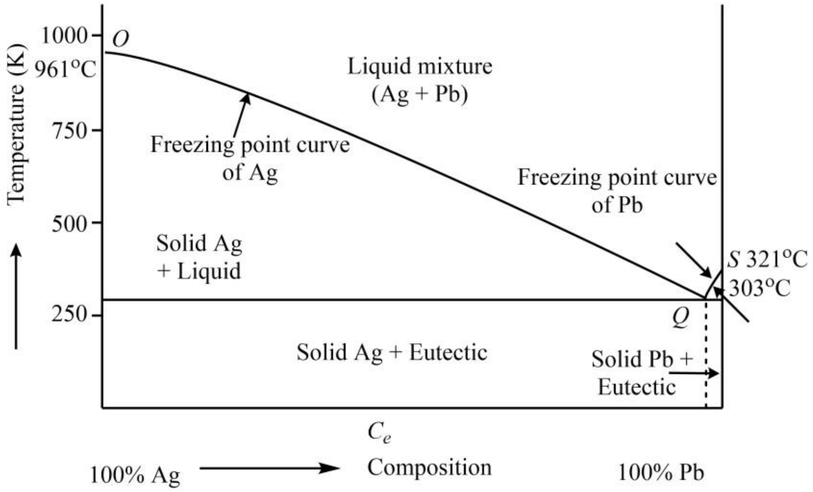

Figure 17. The phase diagram of Pb-Ag system.

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°C) and pure Pb (327°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

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

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.

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

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°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_2O):

The KI-H_2O 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_2O) 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.

$$F' = C - P + 1 \tag{133}$$

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_2O 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_2O). 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

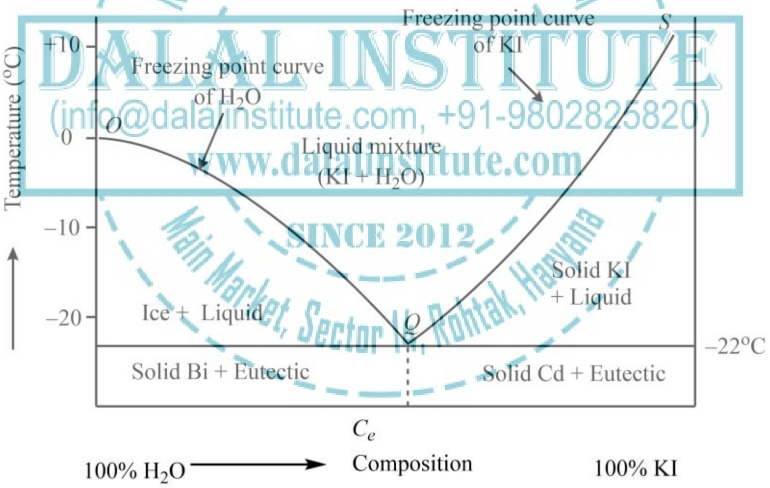

Figure 18. The phase diagram of KI-H_2O system.

The discussion on different parts (curve OQ, Curve SQ and the eutectic point) of phase diagram of KI-H_2O 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_2O 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

$$F' = 2 - 2 + 1 = 1 \tag{134}$$

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_2O and ice in molten KI, respectively.

ii) Eutectic point (Q): At point '*Q*', all the three phases (solid KI + solid H_2O + liquid) are in equilibrium with each other; and therefore, zero degree of freedom exists at this point i.e.

$$F' = 2 - 3 + 1 = 0 \tag{135}$$

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°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_2O).

❖ 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

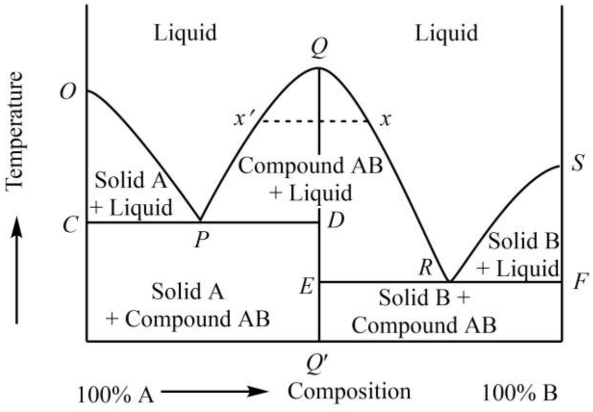

Figure 19. The general phase diagram of systems forming compounds with congruent melting points.

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

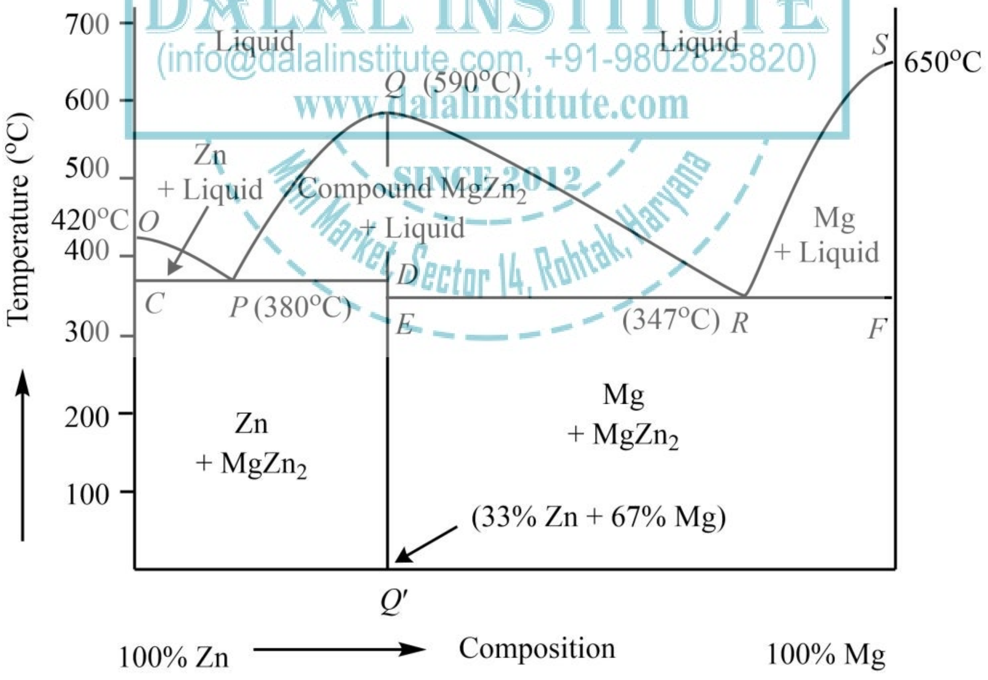

Figure 20. The phase diagram of Mg-Zn system.

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.

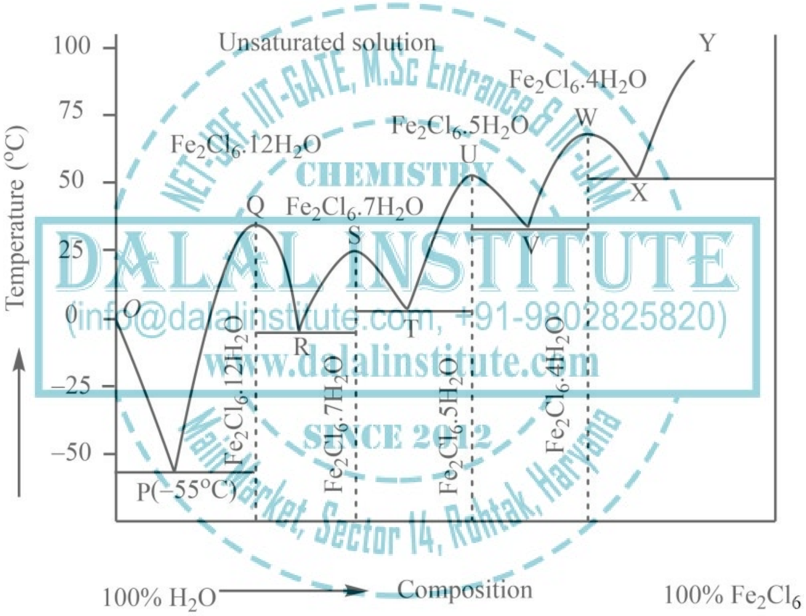

Figure 21. The phase diagram of $FeCl_3$-H_2O system.

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

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

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

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

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

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

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

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

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

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

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.

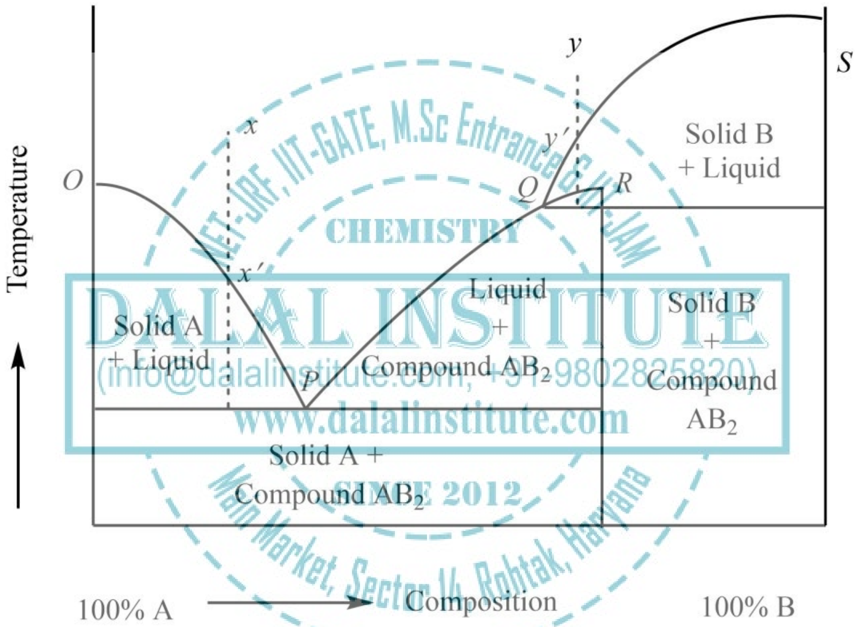

Figure 22. The general phase diagram of systems forming compounds with incongruent melting points.

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

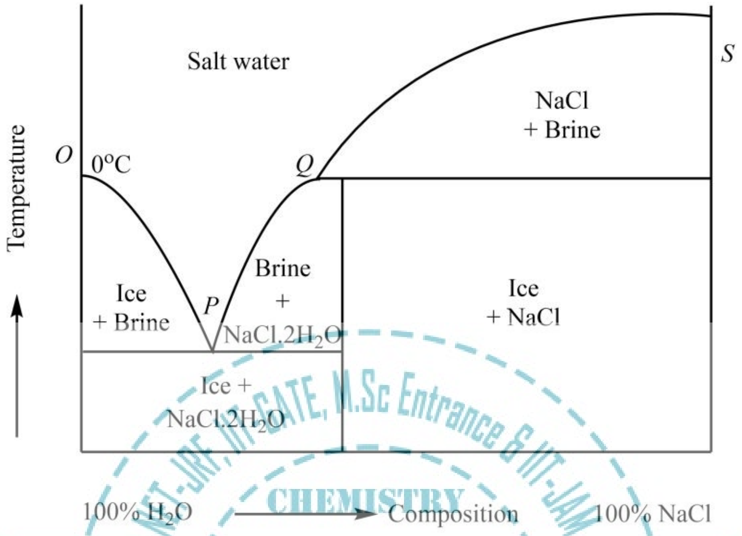

Figure 23. The phase diagram of NaCl-H_2O system.

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 S*Q*. 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.

$$F' = C - P + 1 \tag{161}$$

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

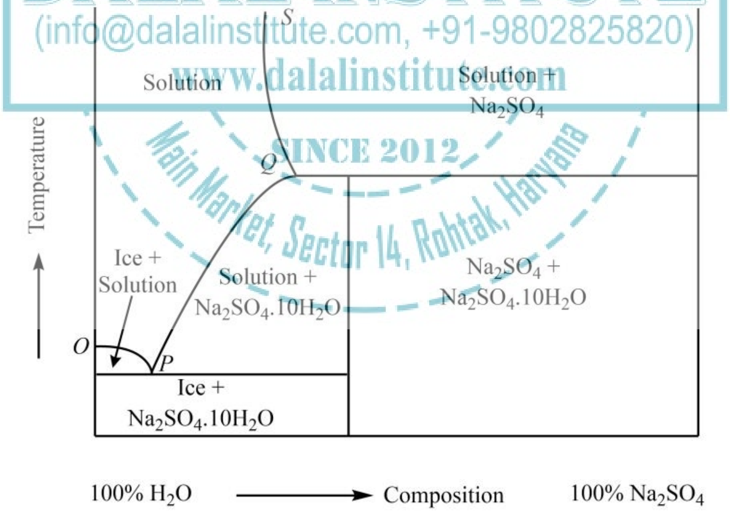

Figure 24. The phase diagram of Na_2SO_4-H_2O system.

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.

❖ Phase Diagram and Thermodynamic Treatment of Solid Solutions

In these types of systems, the components are completely miscible with each other in solid phase and completely homogeneous solid solutions are produced. The X-ray diffraction studies are typically employed to check that single crystalline phase is obtained rather than a mixture of two solid phases. In order to draw and understand the phase diagrams of solid solutions, we need to discuss the same in a comprehensive thermodynamic framework first.

➢ *General Thermodynamic Treatment of Solid Solutions*

The general thermodynamic treatment of solid solutions includes the shift in the solvent's freezing point during the crystallization and the nature of the cooling curve as well. The necessary discussion on both concepts is given below.

1. The shifting of solvent's freezing point during crystallization: The thermodynamic expression for the shift of solvent's freezing point when the solid begins to solidify during cooling can be obtained by assuming the solid solution as an ideal solution. Therefore, the chemical potential for *i*th constituent (μ_i) can be given by the following relation.

$$\mu_i = \mu_i^* + RT \ln x_i \tag{164}$$

Where x_i represents the fractional composition of the constituent whereas μ_i^* is the chemical potential of the pure solid. After setting the primary condition for the phase equilibria between solid and liquid, we have

$$\mu_1(s) = \mu_1(l) \tag{165}$$

Considering both as ideal, we can write above equation using equation (164) as

$$\mu_1^*(s) + RT\ln x_1(s) = \mu_1^*(l) + RT\ln x_1(l) \tag{166}$$

After rearranging, we get

$$RT\ln x_1(s) - RT\ln x_1(l) = \mu_1^*(l) - \mu_1^*(s) \tag{167}$$

$$RT[\ln x_1(s) - \ln x_1(l)] = \mu_1^*(l) - \mu_1^*(s) \tag{168}$$

$$R\ln\frac{x_1(s)}{x_1(l)} = \frac{\mu_1^*(l) - \mu_1^*(s)}{T} \tag{169}$$

Now since $\mu_1^*(l) - \mu_1^*(s)$ represents the molar free energy of the fusion for the pure solvent at p pressure and T temperature, the equation can also be written as

$$R\ln\frac{x_1(s)}{x_1(l)} = \frac{\Delta_{fus}\,\mu_1^*}{T} \tag{170}$$

Now putting the value of molar free energy of fusion ($\Delta_{fus}\,\mu_1^* = \Delta_{fus}H_{1,m}^* - T\Delta_{fus}S_{1,m}^*$) in the above equation, we get

$$R\ln\frac{x_1(s)}{x_1(l)} = \frac{\Delta_{fus}H_{1,m}^* - T\Delta_{fus}S_{1,m}^*}{T} \tag{171}$$

$$R\ln\frac{x_1(s)}{x_1(l)} = \frac{\Delta_{fus}H_{1,m}^*}{T} - \Delta_{fus}S_{1,m}^* \tag{172}$$

Recalling the entropy of fusion at for the pure solvent at a temperature T_1^* (melting point) i.e.

$$\Delta_{fus}S_{1,m}^* = \frac{\Delta_{fus}H_{1,m}^*}{T_1^*} \tag{173}$$

Using the above result in equation (172), we get

$$R\ln\frac{x_1(s)}{x_1(l)} = \frac{\Delta_{fus}H_{1,m}^*}{T} - \frac{\Delta_{fus}H_{1,m}^*}{T_1^*} \tag{174}$$

$$R\ln\frac{x_1(s)}{x_1(l)} = \Delta_{fus}H_{1,m}^*\left[\frac{1}{T} - \frac{1}{T_1^*}\right] \tag{175}$$

or

$$R\ln\frac{x_1(s)}{x_1(l)}=\Delta_{fus}H_{1,m}^*\left[\frac{T_1^*-T}{TT_1^*}\right] \tag{176}$$

After putting $T-T_1^*=\Delta T_f$, the above equation takes the form

$$R\ln\frac{x_1(s)}{x_1(l)}=\Delta_{fus}H_{1,m}^*\left[\frac{-\Delta T_f}{TT_1^*}\right] \tag{177}$$

If the solution is very dilute, the melting point T_1^* will be quite close to temperature T; therefore, TT_1^* can be replaced by T_1^{*2}. Therefore, the equation (177) takes the form

$$R[\ln x_1(s)-\ln x_1(l)]=\Delta_{fus}H_{1,m}^*\left[\frac{-\Delta T_f}{T_1^{*2}}\right] \tag{178}$$

Furthermore, for very dilute solutions, we have

$$\ln x_1(s)=\ln[1-x_2(s)]\approx -x_2(s) \tag{179}$$

$$\ln x_1(l)=\ln[1-x_2(l)]\approx -x_2(l) \tag{180}$$

Using equation (179, 180) in equation (178), we get

$$R[-x_2(s)+x_2(l)]=\Delta_{fus}H_{1,m}^*\left[\frac{-\Delta T_f}{T_1^{*2}}\right] \tag{181}$$

or

$$-\Delta T_f=\frac{R\,T_1^{*2}}{\Delta_{fus}H_{1,m}^*}[x_2(l)-x_2(s)] \tag{182}$$

$$-\Delta T_f=\frac{R\,T_1^{*2}}{\Delta_{fus}H_{1,m}^*}x_2(l)\left[1-\frac{x_2(s)}{x_2(l)}\right] \tag{183}$$

Recalling the expression for molality i.e.

$$x_2(l)=\frac{n_2(l)}{n_1(l)+n_2(l)}\approx\frac{n_2(l)}{n_1(l)}=\frac{n_2(l)}{m_1(l)/M_1}=\left[\frac{n_2(l)}{m_1(l)}\right]M_1=mM_1 \tag{184}$$

Using the above result in equation (183), we have

$$-\Delta T_f=\frac{R\,T_1^{*2}M_1}{\Delta_{fus}H_{1,m}^*}m\left[1-\frac{x_2(s)}{x_2(l)}\right] \tag{185}$$

or

$$\Delta T_f = -K_f m[1 - K] \tag{186}$$

Where K is the distribution coefficient given by $x_2(s)/x_2(l)$. In other words, the distribution coefficient the ratio of the fractional amount of the solute in the solid phase to the fractional amount of the solute in the solution phase.

Therefore, we can conclude that the value of ΔT_f can be negative or positive depending upon the magnitude of K.

i) When ΔT_f is negative: The magnitude of ΔT_f will be negative if $K < 1$; which means that $T < T_1^*$. The physical significance is that depression in the freezing point of the solvent will be observed.

ii) When ΔT_f is positive: The magnitude of ΔT_f will be positive if $K > 1$; which means that $T > T_1^*$. The physical significance is that a less elevation in the freezing point of the solvent will be observed.

The two above-mentioned conditions can also be can be summarized in one statement that if the addition of a component induces a decline in the freezing point of the solvent, it fractional amount must be greater in liquid phase than in the solids phase, and vice-versa.

2. The nature of cooling curve of the solid solution: Now because the two components of a solid solution are completely miscible with each other, the maximum number of phases which can coexist is only two (solid solution + liquid). Therefore, recalling reduced phase

$$F' = C - P + 1 \tag{187}$$

After putting $C = 2$ and $P = 2$, we get

$$F' = 2 - 2 + 1 = 1 \tag{188}$$

Which means that there is only one degree of freedoms i.e. univariant system. In other words, only one variable is needed to be defined to define the system completely which can either be temperature or the composition. Therefore, we can conclude that the solid-liquid equilibria can exist at different conditions of temperatures. Also, the composition of the two solutions will be fixed at a given temperature.

Furthermore, there will be two breaks in the cooling curve; one at the start of the freezing of the solid solution, and another at the end of the freezing of solid solution. However, if the composition of the solid solution is exactly same to the solid solution, it will become a one-component system, and therefore, after putting $C = 1$ and $P = 2$ in equation (187), we get

$$F' = 1 - 2 + 1 = 0 \tag{189}$$

Which means that there is no degree of freedoms i.e. non-variant system. In other words, we will not be able to change temperature or composition without disturbing the state of equilibrium. Furthermore, the melting or freezing process at this point will occur at constant temperature, which in turn, would result in arrests in corresponding cooling curve.

➢ *General Discussion on the Phase Diagrams of Solid Solutions*

Depending upon the value of $K_{A\ in\ B}$ and $K_{B\ in\ A}$, the phase diagrams of very dilute solid solutions of component A in B or B in A can primary be classified into three categories. A general discussion on these three types of solid solutions is given below.

1. Ascending solid solutions:

In these types of solutions, $K_{B\ in\ A} > 1$ (B is solute and A is solvent i.e. $x_B(s)/x_B(l)$) and $K_{A\ in\ B} < 1$ (A is solute and B is solvent i.e. $x_A(s)/x_A(l)$). Furthermore, the solid solutions with $K_{B\ in\ A} < 1$ and $K_{A\ in\ B} > 1$ also fall into this category. The freezing points of such solutions exist in-between the freezing points of pure solvents. Now, in order to draw the phase diagram of such solid solutions, we need to understand nature of the solidus and liquidus in the thermodynamic framework first. To do so, rearrange equation (175).

$$R\ln\frac{x_1(l)}{x_1(s)} = -\Delta_{fus}H_{1,m}^*\left[\frac{1}{T}-\frac{1}{T_1^*}\right] \tag{190}$$

or

$$\frac{x_1(l)}{x_1(s)} = e^{-a} \tag{191}$$

Where the parameter *a* is defined as

$$a = \frac{\Delta_{fus}H_{1,m}^*}{R}\left[\frac{1}{T}-\frac{1}{T_1^*}\right] \tag{192}$$

Likewise, the second exponent can be written as

$$\frac{x_2(l)}{x_2(s)} = e^{-b} \tag{193}$$

with

$$b = \frac{\Delta_{fus}H_{1,m}^*}{R}\left[\frac{1}{T}-\frac{1}{T_2^*}\right] \tag{194}$$

For solid and liquid phases, we have

$$x_1(l) = 1 - x_2(l) \tag{195}$$

and

$$x_1(s) = 1 - x_2(s) \tag{196}$$

Now putting the value of equation (196) in equation (191), we get

$$\frac{x_1(l)}{1-x_2(s)}=e^{-a} \tag{197}$$

Now putting the value of $x_2(s)$ from equation (193), we get

$$\frac{x_1(l)}{1-x_2(l)/e^{-b}}=e^{-a} \tag{198}$$

After putting the value of $x_2(l)$ from equation (195), we get

$$\frac{x_1(l)}{1-[1-x_1(l)]/e^{-b}}=e^{-a} \tag{199}$$

The solution of the above equation for $x_1(l)$ gives

$$x_1(l)=\frac{e^{-a}\left(e^{-b}-1\right)}{e^{-b}-e^{-a}} \tag{200}$$

Using the above result in equation (191), we get

$$x_1(s)=\frac{e^{-b}-1}{e^{-b}-e^{-a}} \tag{201}$$

Similarly, we can solve for $x_2(l)$ and $x_2(l)$ as

$$x_2(l)=1-x_1(l)=\frac{e^{-b}\left(e^{-a}-1\right)}{e^{-a}-e^{-b}} \tag{202}$$

and

$$x_2(s)=1-x_1(s)=\frac{e^{-a}-1}{e^{-a}-e^{-b}} \tag{203}$$

It is obvious from the equation (200-203) that none of them is linear; and the expressions for $x_1(l)$ and $x_1(s)$ are different from each other excepting at T_1^* and T_2^* only. At any temperature T that lies in the range of T_1^* and T_2^*, a is negative ($e^{-a}>1$) and b is positive ($e^{-b}<1$). Therefore, at this point, we can conclude from equation (200) that

$$x_1(l)=\frac{e^{-a}\left(e^{-b}-1\right)}{e^{-b}-e^{-a}}=\frac{Negative}{Positive}=Positive\ value \tag{204}$$

Similarly, the equations (201-203) can also be proved to have positive values. The physical significance of these results can be summarized by the statement that the physically meaningful compositions are obtained if, and only if, the temperature of the system (T) lies in-between the T_1^* and T_2^*.

i) If $T_1^*\leq T\leq T_2^*$*:* The equations (191, 193) result in the following conclusions.

$$\frac{x_1(l)}{x_1(s)} > 1 \tag{205}$$

$$\frac{x_2(l)}{x_2(s)} < 1 \tag{206}$$

ii) If $T_2^* \leq T \leq T_1^*$*:* The equations (191, 193) result in the following conclusions.

$$\frac{x_1(l)}{x_1(s)} < 1 \tag{207}$$

$$\frac{x_2(l)}{x_2(s)} > 1 \tag{208}$$

Hence, we can conclude that if the liquid is richer that solid, a depression in the freezing point will be observed; whereas if solid is richer than liquid, an elevation in the freezing point will be observed. The general phase diagram is for such systems is given below.

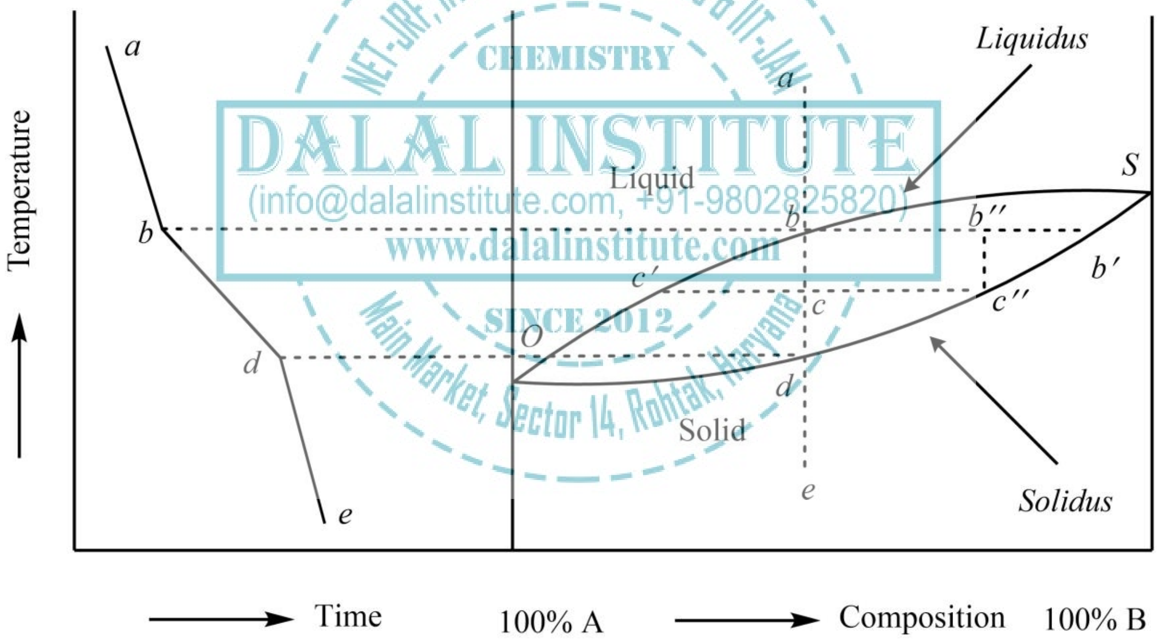

Figure 25. The phase diagram of ascending solid solutions.

The overall phase diagram can be easily understood by analyzing the cooling curve given in the left-hand side of the diagram. Consider a liquid composition represented by the vertical line *abcde* which is allowed to cool down. The system will maintain its liquid state until point *b* is attained where the crystals of the solid solution will start to form. The point corresponding to the crystal formation can be obtained by the tie line *b-b′′*. Now because the solid solution is richer in *B* while the liquid phase is less rich in B, the compositional point of the liquid phase will move towards left. Continuing the process of crystallization, the temperature of the system will decrease and the composition of the liquid phase will move along *bc'd'O*. When the overall system is at point *c*, we have a solid solution with composition c'' in equilibrium with the liquid solution with composition c'. These two points are obtained by the tie line through point *c* easily; while the relative amounts in solid and liquid phase can be calculated via lever rule. Furthermore, it is also very obvious from the phase diagram that as the system goes from point *b* to *d*, the left part of the tie lines is increasing whereas right hand side decreases continuously. This means that in going from point *b* to point *d*, the amount of solid solution increases continuously. When the temperature is lowered to point *d*, almost all of the liquid is transformed into solid which has the same composition as of the starting liquid solution.

The point O and S represent the freezing points of pure A and pure B, respectively. The curve *ObS* is the freezing point curve of the liquid solution whereas the curve *OdS* represents the fusion point curve of the solid solution. In the area above the curve *ObS*, the system is completely liquid; while it is completely solid below the curve *OdS*. In the area between the curve *ObS* and *OdS*, the liquid solution is in equilibrium with the solid solution.

2. Minimum-type solid solutions:

In these types of solutions, $K_{B\ in\ A} < 1$ (B is solute and A is solvent i.e. $x_B(s)/x_B(l)$) and $K_{A\ in\ B} < 1$ (A is solute and B is solvent i.e. $x_A(s)/x_A(l)$). The freezing points of such solutions exist below the freezing points of pure solvents. In other words, the freezing points are depressed in these cases.

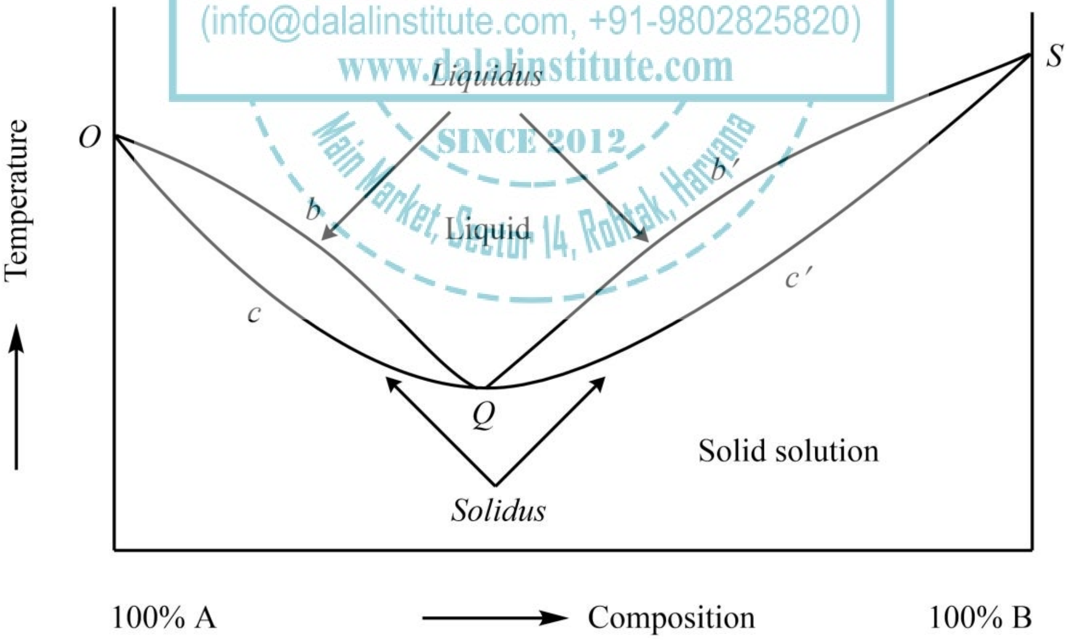

Figure 26. The phase diagram of minimum-type solid solutions.

The point O and S represent the freezing points of pure A and pure B, respectively. The point *Q* is the minimum freezing point of the liquid solution where solid and liquid solutions have the same composition. The system becomes non-variant at point *Q* and freezing takes place at a constant temperature with an arrest in cooling curve.

The curve *ObQb'S* is the freezing point curve of the liquid solution whereas the curve *OcQc'S* represents the fusion point curve of the solid solution. In the area above the curve *ObQb'S*, the system is completely liquid; while it is completely solid below the curve *OcQc'S*. In the area *ObQcO*, the liquid solution (composition on *ObQ*) is in equilibrium with the solid solution (composition on *OcQ*). In the area *Sb'Qc'S*, the liquid solution (composition on *Sb'Q*) is in equilibrium with the solid solution (composition on *Sc'Q*).

3. Maximum-type solid solutions:

In these types of solutions, $K_{B\ in\ A} > 1$ (B is solute and A is solvent i.e. $x_B(s)/x_B(l)$) and $K_{A\ in\ B} > 1$ (A is solute and B is solvent i.e. $x_A(s)/x_A(l)$). The freezing points of such solutions exist above the freezing points of pure solvents. In other words, the freezing points are elevated in these cases.

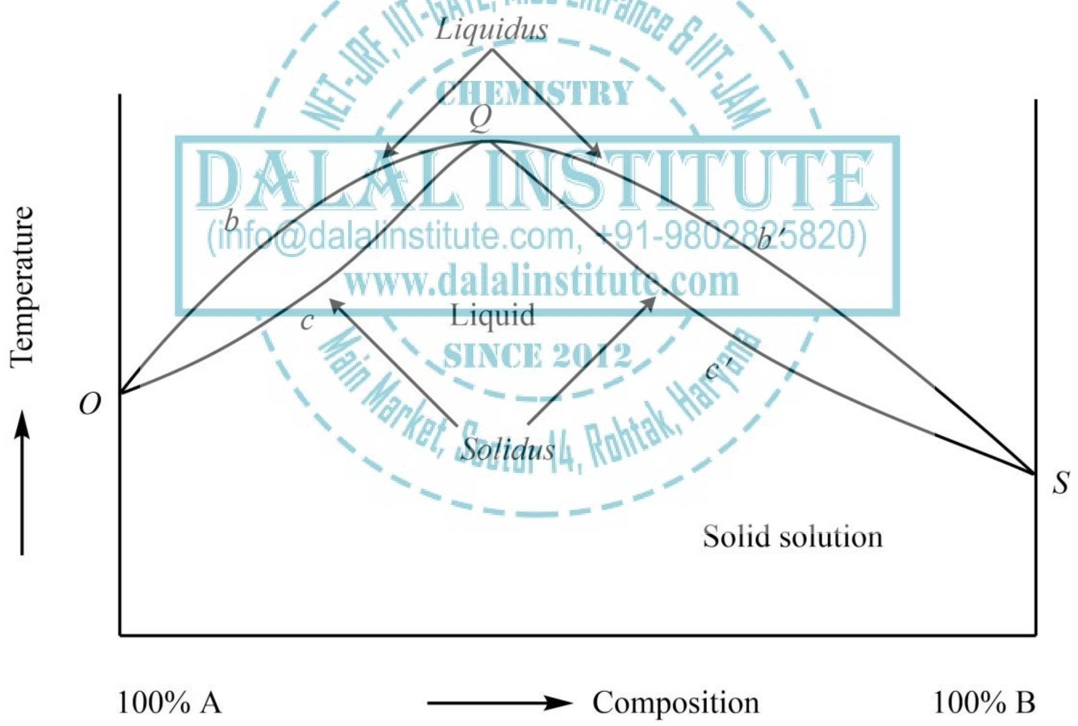

Figure 27. The phase diagram of maximum-type solid solutions.

The point *O* and *S* represent the freezing points of pure A and pure B, respectively. The point *Q* is the maximum freezing point of the liquid solution where solid and liquid solutions have the same composition. The system becomes non-variant at point *Q* and freezing takes place at a constant temperature with an arrest in cooling curve.

The curve *ObQb'S* is the freezing point curve of the liquid solution whereas the curve *OcQc'S* represents the fusion point curve of the solid solution. In the area above the curve *ObQb'S*, the system is completely liquid; while it is completely solid below the curve *OcQc'S*. In the area *ObQcO*, the liquid solution (composition on *ObQ*) is in equilibrium with the solid solution (composition on *OcQ*). In the area *Sb'Qc'S*, the liquid solution (composition on *Sb'Q*) is in equilibrium with the solid solution (composition on *Sc'Q*).

❖ Problems

Q 1. Derive and discuss the Clausius-Clapeyron equation.

Q 2. What is the law of mass actions? How is it different from actual rate law?

Q 3. Derive the law of mass action in the thermodynamic framework.

Q 4. State and discuss the Nernst heat theorem.

Q 5. What is the third law of thermodynamics? How it can be used to obtain the absolute entropies?

Q 6. What do you mean by reduced phase rule? Discuss the same for two-component systems.

Q 7. Draw and discuss the phase diagram of eutectic systems with reference to the cooling curve method.

Q 8. Define congruent and incongruent melting points.

Q 9. Draw and discuss the phase diagram of lead-silver system.

Q 10. Draw and discuss the phase diagram of NaCl-H_2O system.

Q 11. What are solid solutions? Discuss the thermodynamic treatment for the same with special reference to ascending-type solid solutions.

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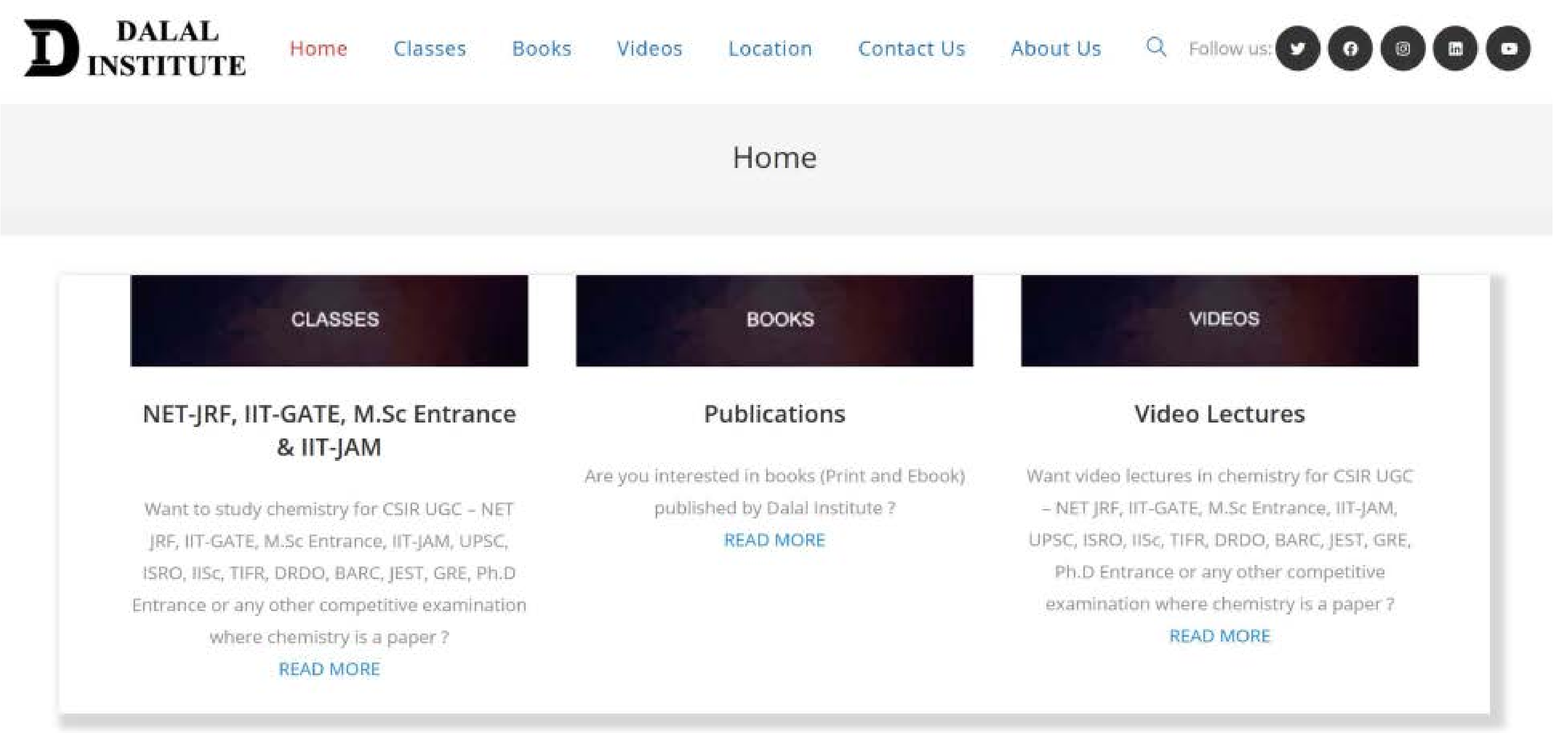

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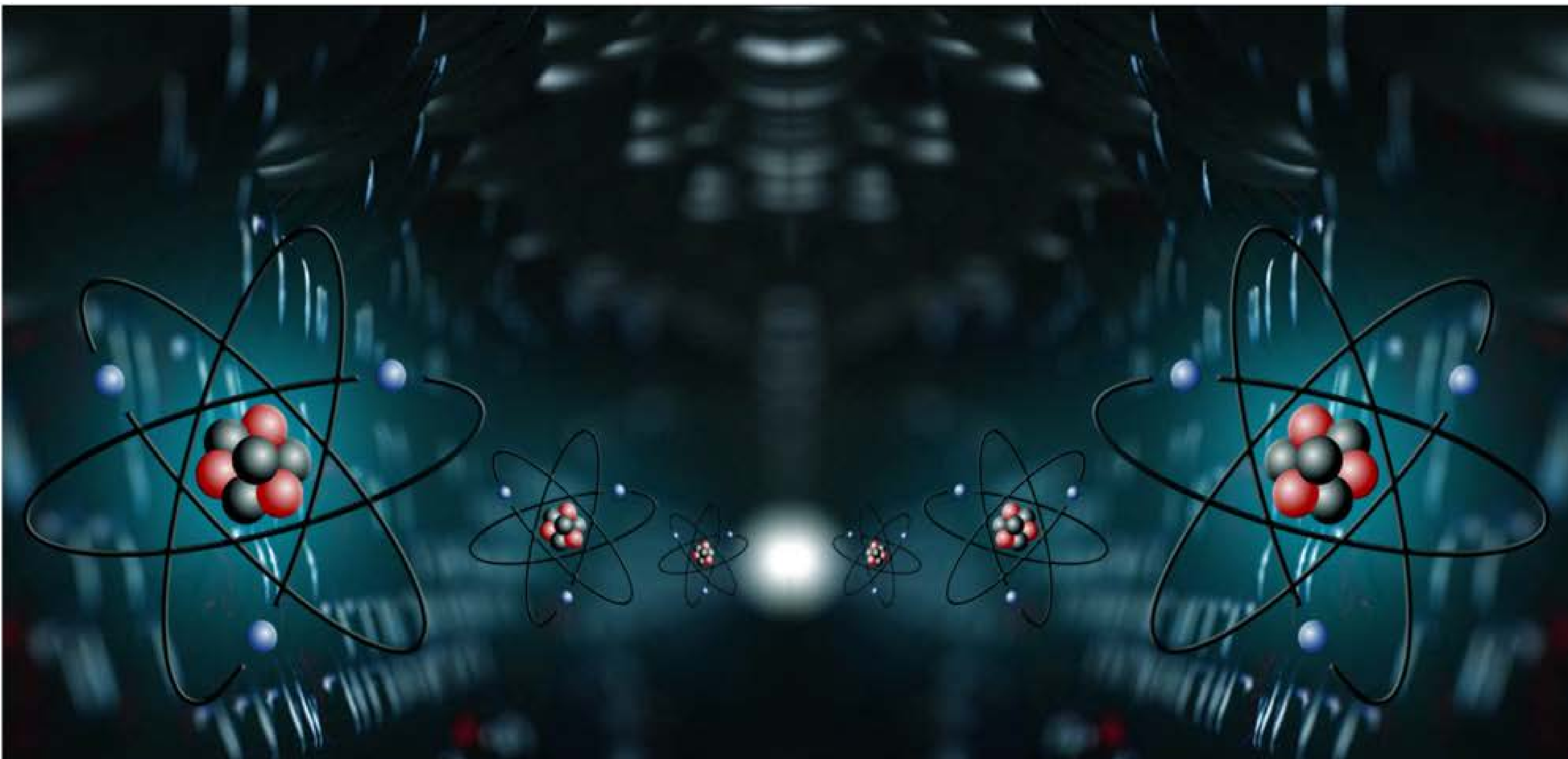

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