❖ **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 ith constituent (μ_i) can be given by the following relation.

$$\mu_i = \mu_i^* + RT \ln x_i \qquad (164)$$

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

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

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

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

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

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

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.
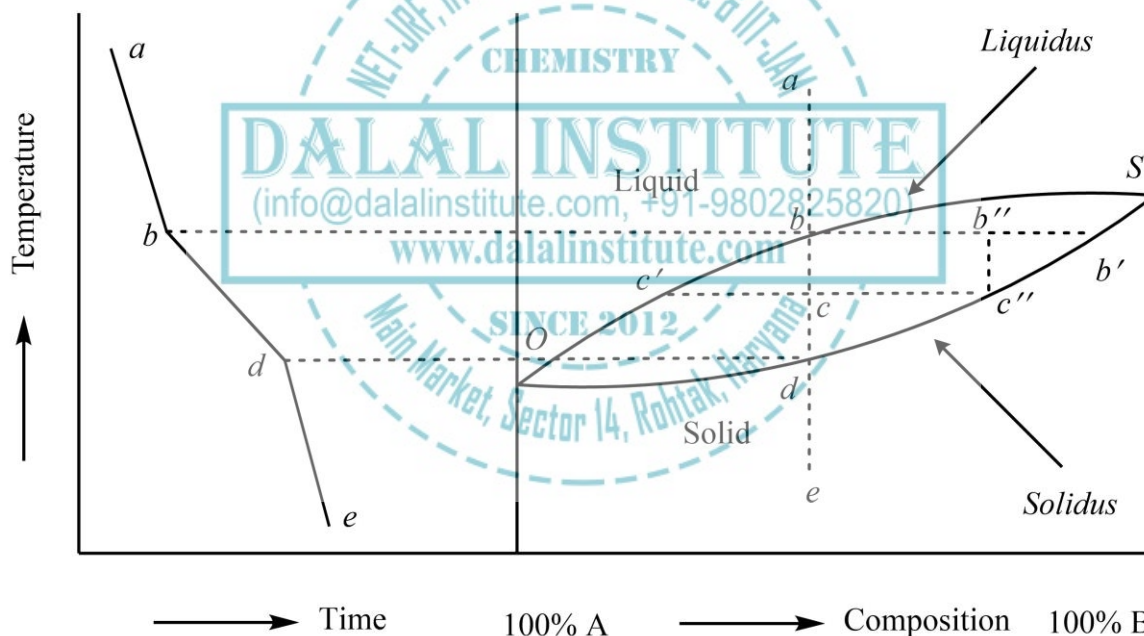
Figure 25. The phase diagram of ascending solid solutions.

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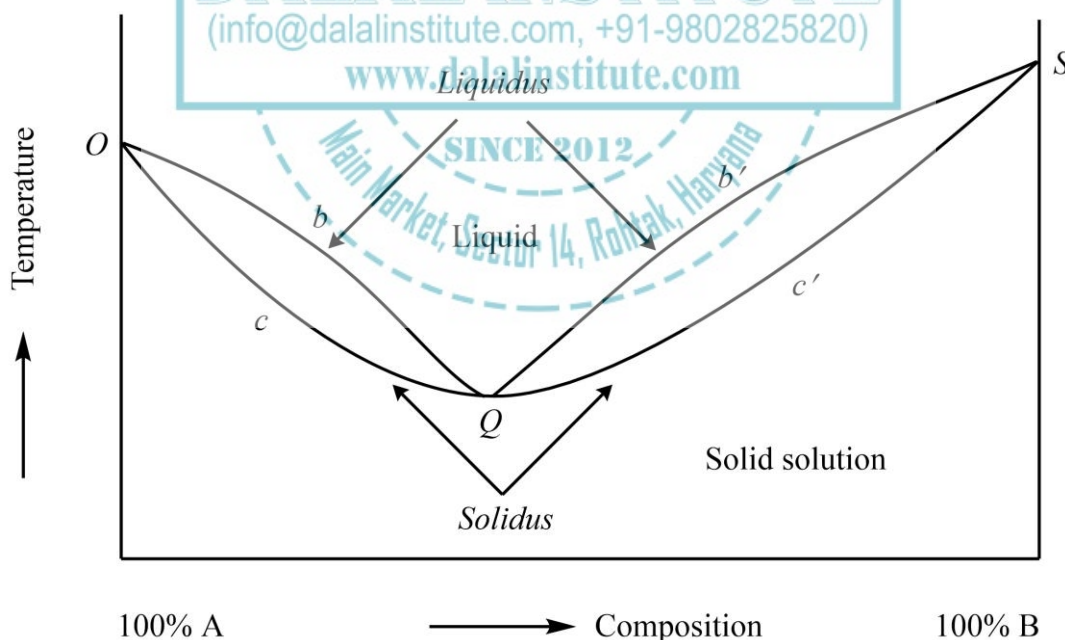
Figure 26. The phase diagram of minimum-type solid solutions.

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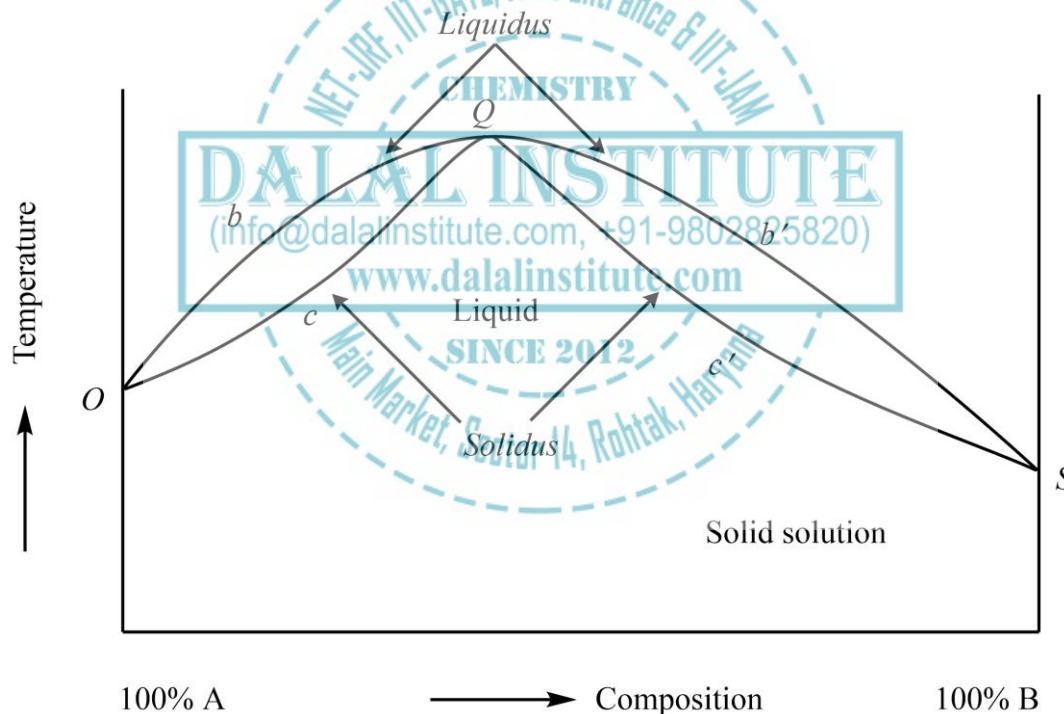
Figure 27. The phase diagram of maximum-type solid solutions.

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*).

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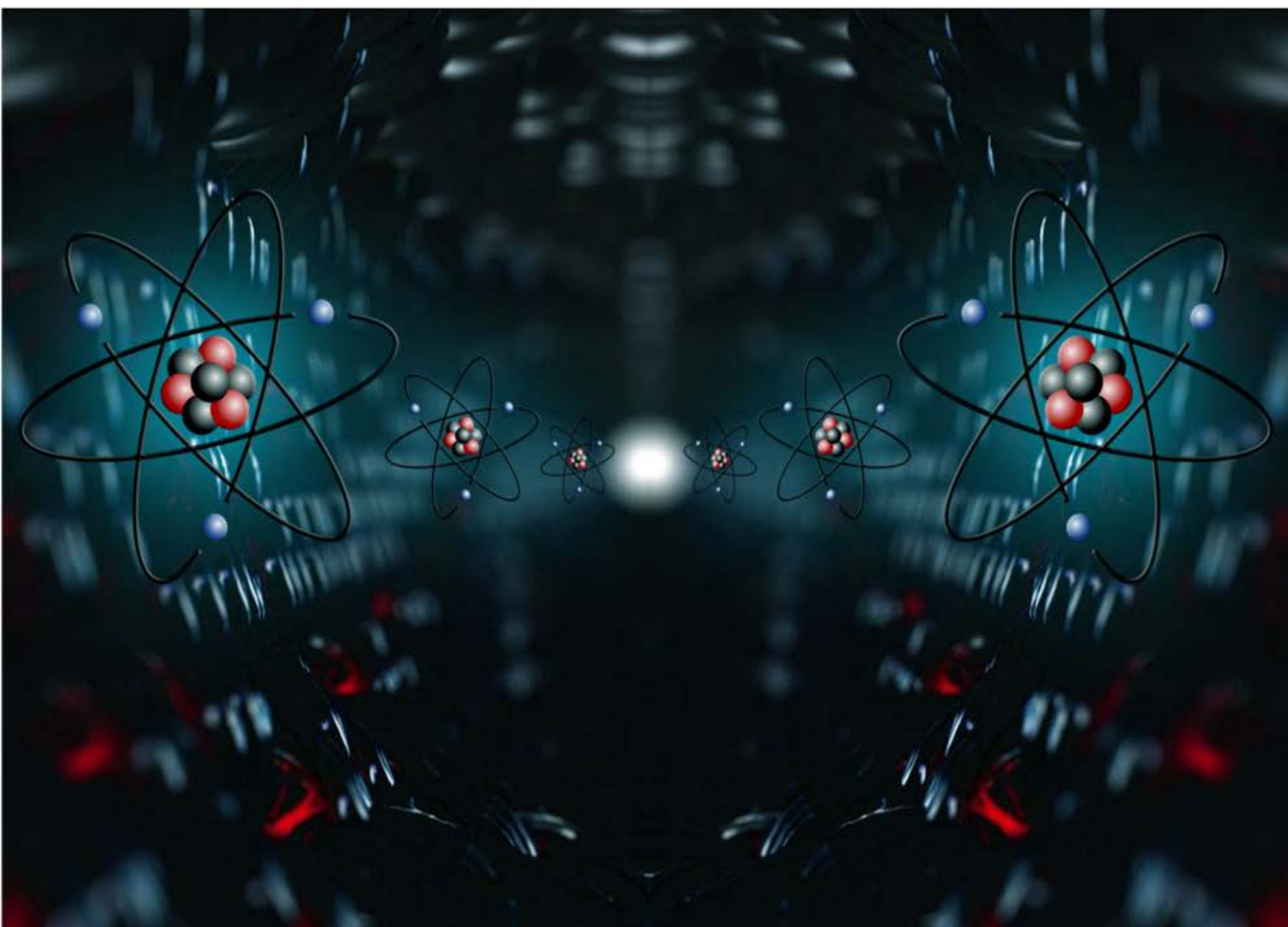
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