

### ❖ 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

$$F = C - P + 2 \quad (110)$$

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

$$F = 2 - P + 2 = 4 - P \quad (111)$$

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

$$F = 4 - 1 = 3 \quad (112)$$

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.

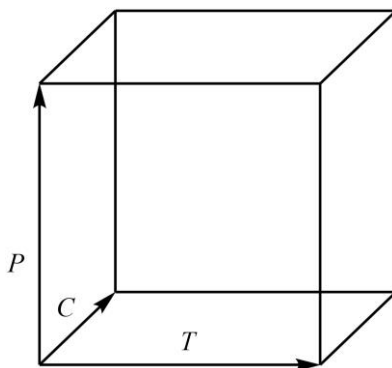


Figure 3. The graphical representation of a one-phase, two-component system.

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.

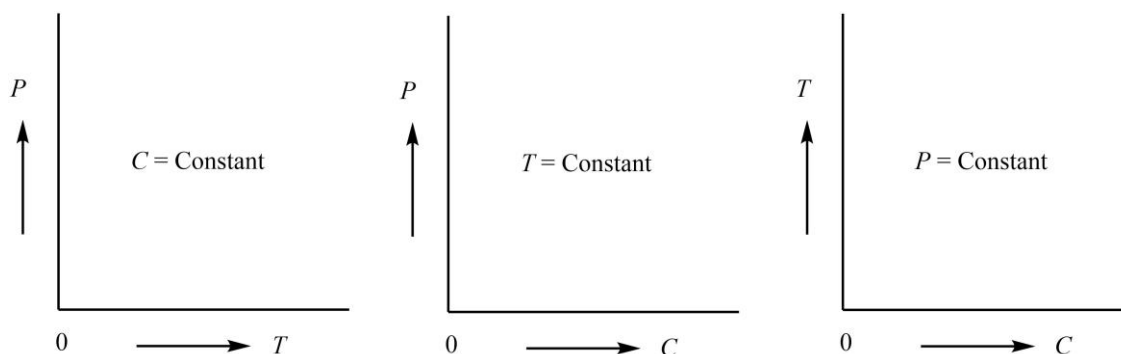


Figure 4. The two-dimensional variants of the one-phase-two-component system.

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

$$F = 4 - 2 = 2 \quad (113)$$

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

$$F = 4 - 3 = 1 \quad (114)$$

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.

$$F' = C - P + 1 \quad (115)$$

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  $Na_2SO_4 \cdot 10H_2O$ ). 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.

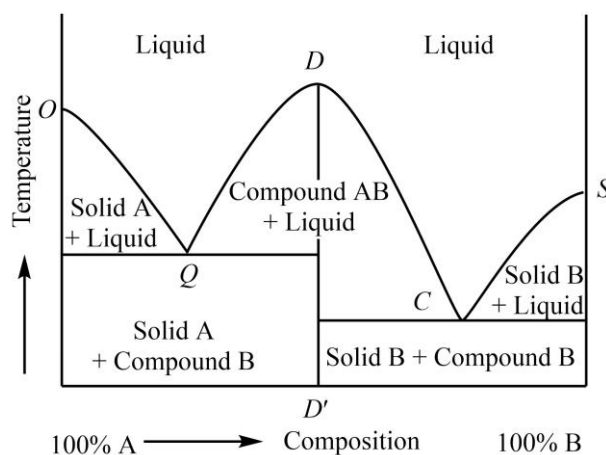


Figure 6. General phase diagram for systems forming solid compounds with congruent melting points.

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  $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$  and  $\text{NaCl-H}_2\text{O}$  systems. A typical transition can be represented as



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.

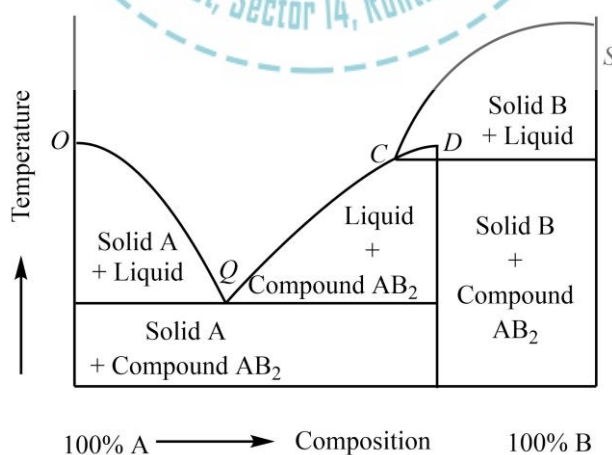


Figure 7. General phase diagram for systems forming solid compounds with incongruent melting points.

**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.

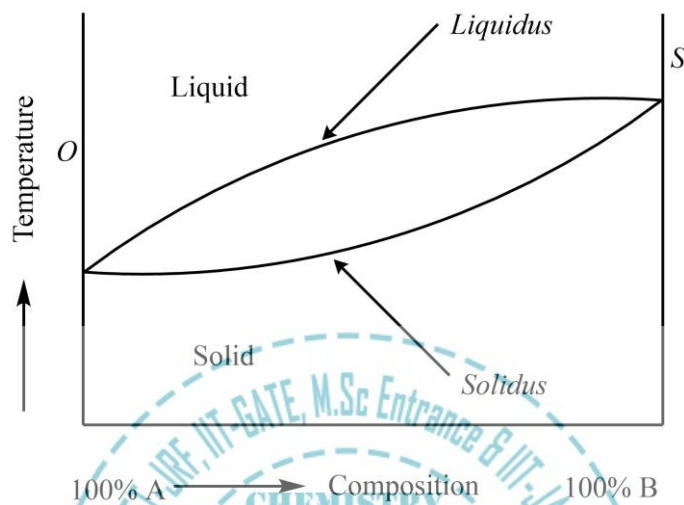


Figure 8. The general phase diagram of systems forming solid solutions.

➤ **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.

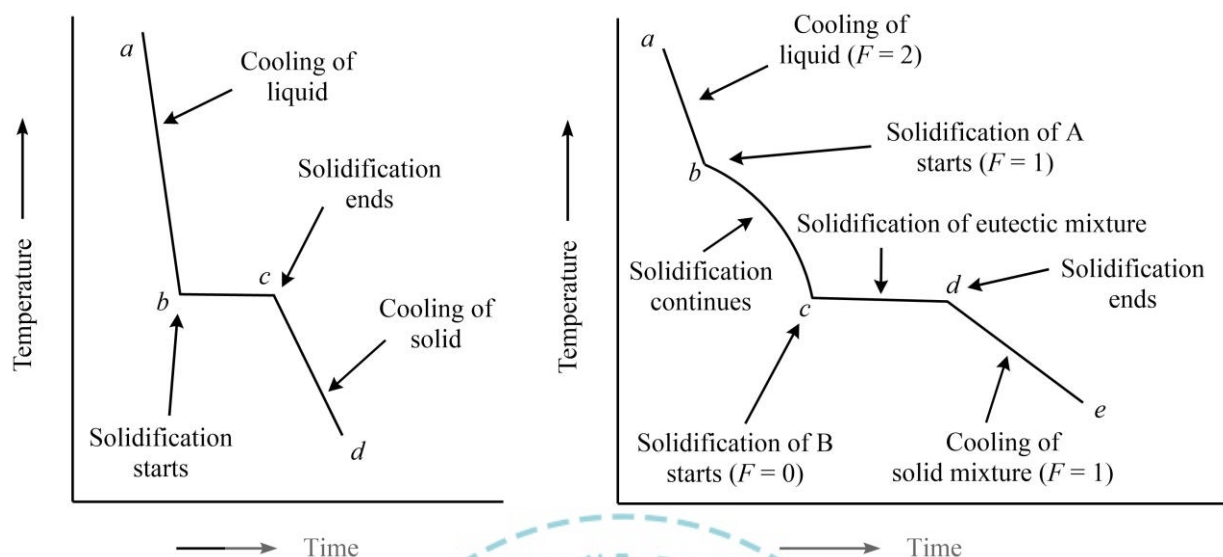


Figure 9. The typical cooling curves for pure a pure liquid (left) and a liquid mixture (right).

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.

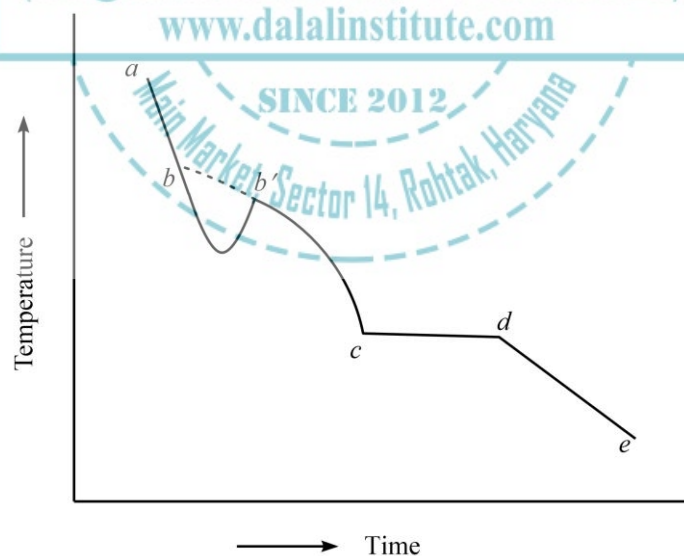


Figure 10. The typical cooling curves for a liquid mixture with supercooling.

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 curve 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.

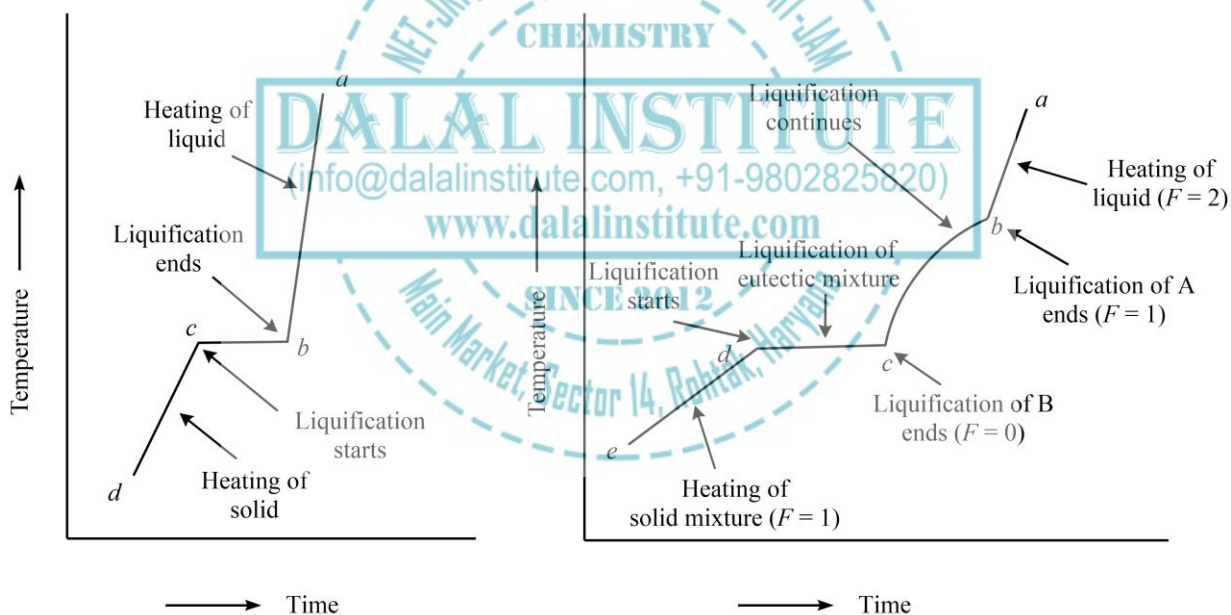


Figure 11. The typical Thaw-melting heating curves (temperature vs time) for a pure liquid (left) and a liquid mixture (right).

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 temperature at which liquefaction ends is called as “melting point”.

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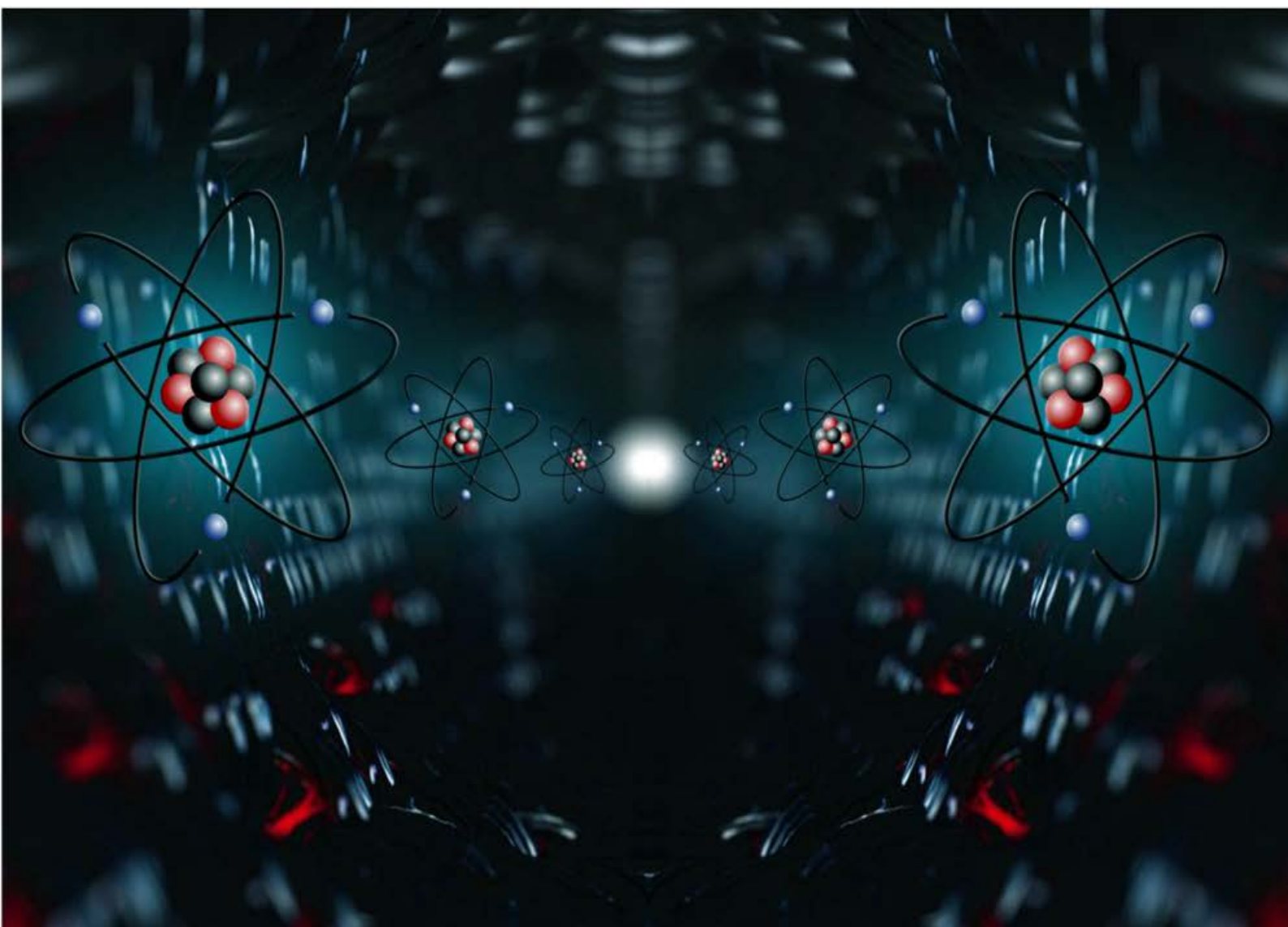
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