

Phase Rule

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The various conditions of eqm^m between phases, such as the no. of phases (P), the no. of components (C) and degrees of freedom (F) can be correlated with one another with the help of phase rule.

Phase :-

A phase is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces.

For gaseous system, one phase is possible since gases are miscible with each other at any proportion.

For liquid, no. of phase is equal to no. of layers present.
For miscible liquids $\rightarrow 1$.

For solid, single phase for each solid except when a solid solution is formed.
Each polymorphic form and allotropic modification constitute a separate phase.

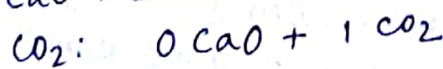
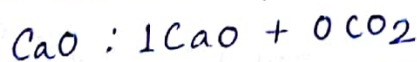
Number of components :-

It is the smallest no. of independent chemical constituents by means of which the composition of each and every phase can be expressed.

One-component system: water system
solid water (ice) \rightleftharpoons liquid water

Two component system: Dissociation of CaCO_3
 $\text{CaCO}_3 (\text{s}) \rightleftharpoons \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$.

No. of component of the system is two since two species are sufficient to express all three phases composition.



Dissociation of NH_4Cl i.e. $\text{NH}_4\text{Cl} (\text{s}) \rightleftharpoons \text{NH}_3 (\text{g}) + \text{HCl} (\text{g})$.

In vacuum component of the system one.
In presence of any gas, the component will be two.

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Degrees of Freedom :-

DOF or variance of the system is the minimum no. of independent variables such as temperature, pressure and concentration, that must be ascertained so that a given system in eqm^m is completely defined.

Triple point: Temperature and pressure fixed so that 3 phases co-exist in eqm^m

In case of H₂O 0.0098°C and 4.58 mm of Hg.

Derivation of Phase rule

Non reactive system, where it is assumed that all components are present in all phases.

$$\text{variance} = \frac{\text{Total no. of variables}}{\text{variables}} - \frac{\text{Total no. of eqm}^m \text{ that are available}}{\text{Number}}$$

Temperature of the system	1
pressure "	1

For each phase concentration 'c' have to be specified. So for 'P' no. of phases PC

So, total no. of variables needed to be specified $\Rightarrow (PC + 2)$

Types of eqm^m which are available

- i) Conditions of sum of the amount fractions in any phase is unity
- $$\begin{aligned} x_1(1) + x_2(1) + x_3(1) + \dots &= 1 \\ x_1(2) + x_2(2) + x_3(2) + \dots &= 1 \\ x_1(P) + x_2(P) + \dots + x_c(P) &= 1 \end{aligned}$$

So, there will be 'P' no. of eqm^m

- ii) Thermodynamic condition for equilibria
Chemical potential of any component will have the same value in all the P phases

$$\begin{aligned} \mu_1(1) = \mu_1(2) = \dots = \mu_1(P) \\ \mu_2(1) = \mu_2(2) = \dots = \mu_2(P) \\ \mu_c(1) = \mu_c(2) = \dots = \mu_c(P) \end{aligned}$$

For each component we will have $(P-1)$ eqn:
 for C " " " " " "
 " " " " " "
 \therefore Total no. of equations. $\frac{C(P-1) \text{ eqn.}}{P + C(P-1)}$

Hence. $F = (PC + 2) - \{P + C(P-1)\}$

$F = C - P + 2$

The mineralogical phase rule follows from Gibb's phase rule, which defines the number of DOF of the system consisting of different components C in different phases P that is, $F = C - P + 2$. Of the total number of independent intensive parameters (T, P, μ) the parameter that can assume arbitrary values within certain limits without disrupting the phase of the system have DOF (F) . Rocks form at arbitrary values of T and P , and the number of DOF in their formation can't be less than 2.

$$P \leq C; F \geq 2.$$

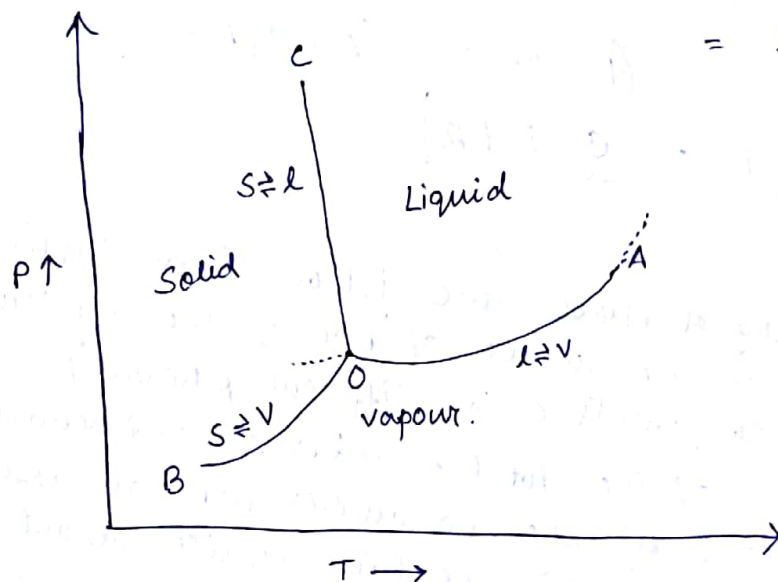
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Phase diagram of one component system :-

$$P = C + 2 - F \\ = 1 + 2 - 2 \\ = 1$$



Let, ice is placed in a vessel fitted with piston at a temp $< 0^\circ\text{C}$. The behaviour of the system is depicted in the phase diagram of water. The system attains eqm and it is found that the pressure within the vessel attains constant value. This pressure is the vapour pressure of solid water at -20°C . The point B represents ice in eqm with its vapour. The temp of the system raised slowly at const. volume. It is found that vapour pressure of the solid increases. The curve BO is the sublimation curve.

Thus, it may be concluded that the effect of isothermal increase and decrease of pressure on the solid-vapour equilibrium is to convert the two-phase eqm to that of one phase comprising of solid and vapour, respectively. Hence, the regions above and below the curve BO represent solid vapour phases, respectively.

If the temp of the system at point B is slowly increased at const. volume, eventually a temperature is reached where the vapour pressure of solid water becomes equal to that of liquid water, maintained at the same temp. At this stage the system contains three phases viz, solid, liquid and vapour in equilibrium with one another. This point

T_3 represents triple point. For water, this lies at 0.0075°C and 4.6 mm of Hg.

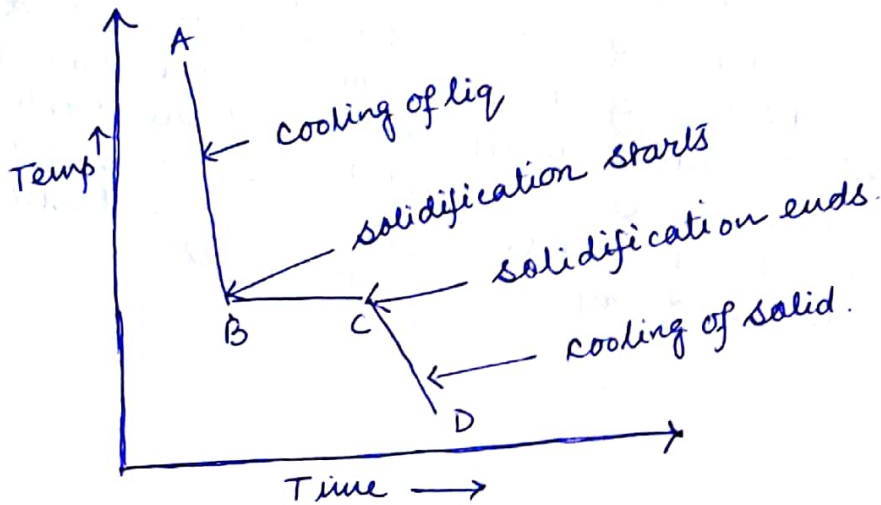
If the system on the line AO is rapidly cooled, it may happen that ice fails to appear at the triple point and the vapour pressure of liquid continues to move along OA' which now represents metastable equm involving liquid and vapour phases. Similarly, if the system on the line BO is rapidly heated, liquid may not appear at the triple point and the vapour pressure of solid continues along the continuation of the curve BO where metastable equm between solid and vapour phases exist.

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Phase diagram of two-component system

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cooling curve of a pure component:



The rate of cooling of liquid is smooth till solidification starts. System contains two phases in eqm^m. Hence

$$F = C - P + 1$$

$$F = 1 - 2 + 1$$

$$F = 0.$$

[reduced phase rule, at const external pressure.]

Solidification occurs at const. temperature. As rate of liberation of heat during solidification becomes equal to that of transfer of heat from the system to surroundings.

cooling curve of mixture X and Y

We start with a mixture of two liquids of known composition. The system is heated. ~~to~~ to get it in the liquid phase. Here.

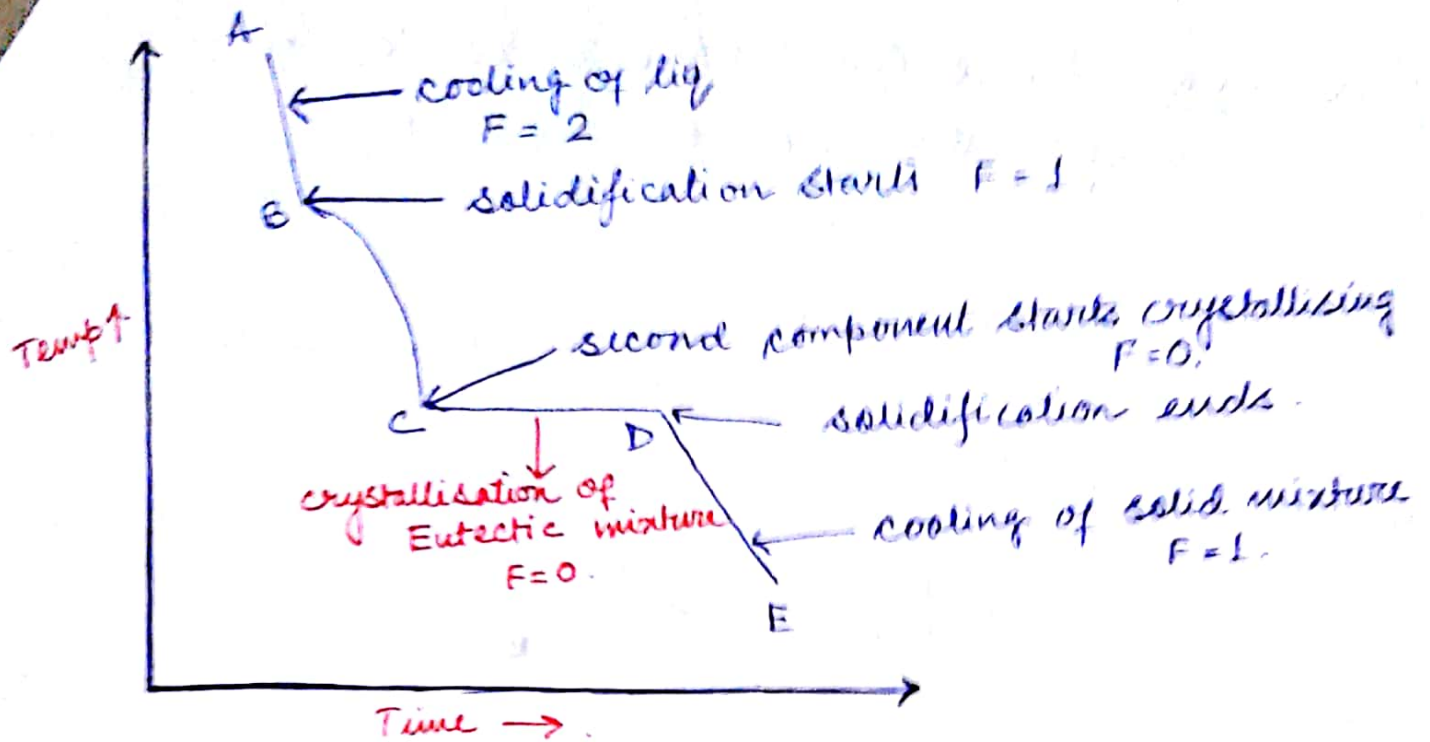
$$F = C - P + 1$$

$$= 2 - 1 + 1$$

$$= 2.$$

Solidification of X : Univariant i.e. $F = 1$.

Solidification of both X and Y: If cooling is continued the sol^m may become saturated w.r.t. Y. Hence Y starts



solidifying along with X. At this stage

$$F = C - P + 1$$

$$F = 2 - 3 + 1$$

$$F = 0$$

Thus solidification from a solution of fixed composition takes place at constant temperature. At this temp the solubility of Y and X has to be maintained, it follows that the composition of solid phase will have the same composition of the liquid phase. The temp of the system will remain constant until the entire liquid has solidified.

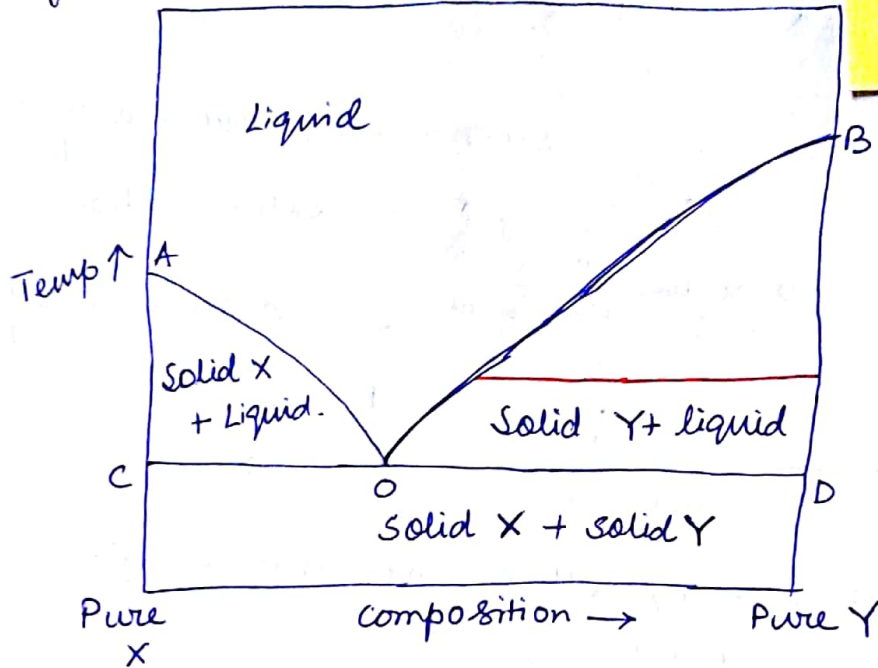
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Simple Eutectic Phase Diagram

crystallisation of pure component.

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A, B represent freezing point of Pure X and Pure Y.

<u>Location of the system</u>	<u>States of the system</u>	<u>Degrees of freedom</u>	<u>Kind</u>
		<u>No.</u>	
A	Freezing point of X	0	fixed T
B	Freezing point of Y	0	fixed T
AO	start of crystallisation of X	1	T or composition
BO	start of crystallisation of Y	1	T or composition
O	Eutectic point	0	fixed T and fixed composition.
Area above AOB	Liquid phase	2	T and composition
Area below COD	Solid mixture	1	T
Area ACOA	Solid A in eqm ^m with liquid phase whose composition lies on the curve BO.	1	T or composition
Area BDOB.	Solid B in eqm ^m with liquid phase whose composition lies on the curve BO.	1	T or composition
COD	system where both A and B crystallize together from liquid phase O.	0	fixed T and composition (Eutectic).

A point within the area BODB represents a system of solid Y in equm^m with liquid phase. The composition is given by the intersection point of the tie line drawn from the given point with the curve BO.

Similarly the area ACOA represents a system of solid X in equm^m with a liquid solution whose composition lies on curve AO.

A point on the line CD represents invariant system ($F=0$). The point 'O' has lowest temperature at which any liquid X or Y will freeze out. 'O' is known as eutectic point.

Line AOB is the liquidus curve as it gives composition of the liquid phase in equm^m with the solid phase.

The line ACODB is the solidus curve.

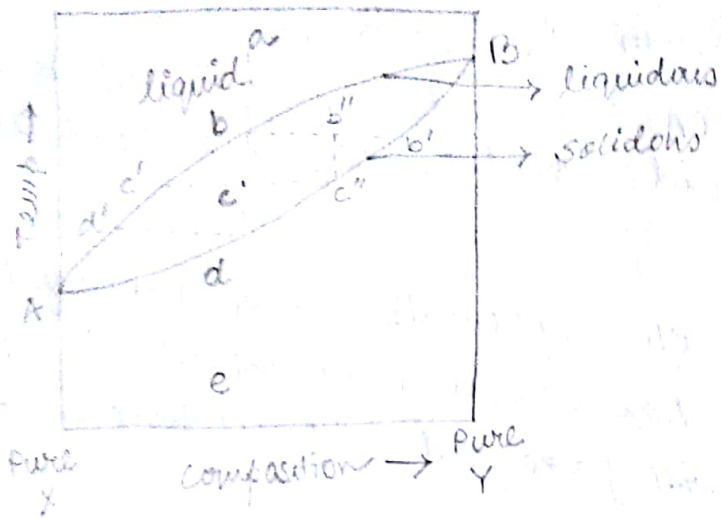
Lines AC, COD and DB represent respectively solid X, mixtures of solid X and Y in equm^m with liquid phase of composition 'O' and solid Y.

Cooling of a system on the line CD will result into the solidification of X and Y together from the liquid phase of eutectic composition O.

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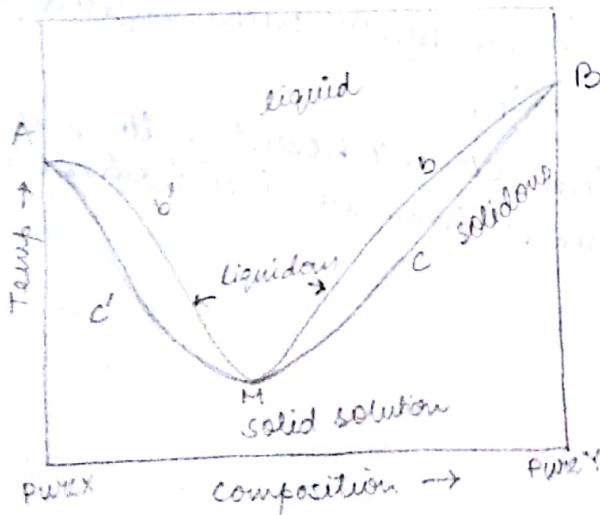
① phase diagram for a system exhibiting continuous series of solid solutions with no maximum/minimum



- A Freezing point of X
- B Freezing point of Y
- AB B Freezing point curve of solid solution
- ADB Fusion point curve of solid solution.

Area below ADB. Solid solution
Area above AB B. Liquid.

② phase diagram of a system exhibiting continuous series of solid solutions with a minimum freezing point.



- A Freezing point of X.
- B Freezing point of Y.
- M Minimum freezing point of the liquid solution.

Here the composition of solid & liquid solution is same. System is non variant. The freezing or fusion takes place at const T.

Area above AB'MBB liquid

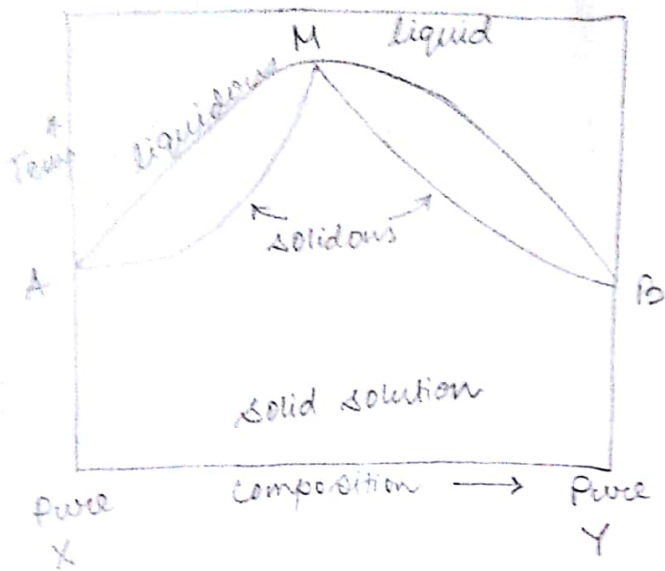
Area below AC'MCB solid solution.

Area AB'MC'A solid solnⁿ in eqm^m with lig. solnⁿ (AC'M)

Area Bb'MCB solid solnⁿ in eqm^m with liquid solnⁿ (Mbb)

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Phase diagram for a system exhibiting continuous series of solid solutions with a maximum.



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