

PHASE EQUILIBRIA

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Gibbs Phase Rule

A proper understanding of certain systems and processes in pharmaceutical practice necessitates knowledge of the principles that govern the equilibria between solid, liquid and gaseous phases.

The Phase Rule

Gibbs created the phase rule, which relates: the effect of the least number of independent variables (temperature, pressure and concentration) *upon* the various phases (solid, liquid and gaseous) that exist in an equilibrium system containing a given number of components.

Gibbs Phase Rule

- $P+F=C+2$
- P =Phase
- C = Components
- F = Degree of freedom

Phase

Phase

A phase is defined as any **homogeneous** and **physically distinct** part of a system that is separated from other parts of the system by **definite boundaries**.

- For example, **ice, water, and water vapour** are three separate phases; each is physically distinct and there are definite boundaries between them.
- **Pure liquids or solutions** constitute homogeneous phases, but two immiscible liquids (or solutions) constitute two phases since there is a definite boundary between them.
- A **mixture of gases** always constitutes one phase because the mixture is homogeneous and there are no bounding surfaces between the different gases in the mixture.

Number of Components

Number of components

The number of components of a system is the number of constituents expressed in the form of a chemical formula.

For example in the 3-phase system ice, water, water vapour, the no of components is 1, since each phase is expressed as H_2O .

A mixture of **salt and water is a 2 component system** since both chemical species are independent.

Degrees of Freedom

Degrees of freedom

The number of degrees of freedom is the number of variable conditions (e.g. temperature, pressure, and concentration) that may affect the phase equilibrium.

The relationship between:

- the number of phases P ,
- components C ,
- degrees of freedom F

for equilibria that are influenced only by temperature, pressure, and concentration is given by equation

Gibbs phase rule:

$$F = C - P + 2$$

Types of Equilibria



- **True Equilibrium**



- **Metastable Equilibrium**

True Equilibrium

- In Any system when the same state is obtained approach from either direction, a state of true equilibrium is obtained.

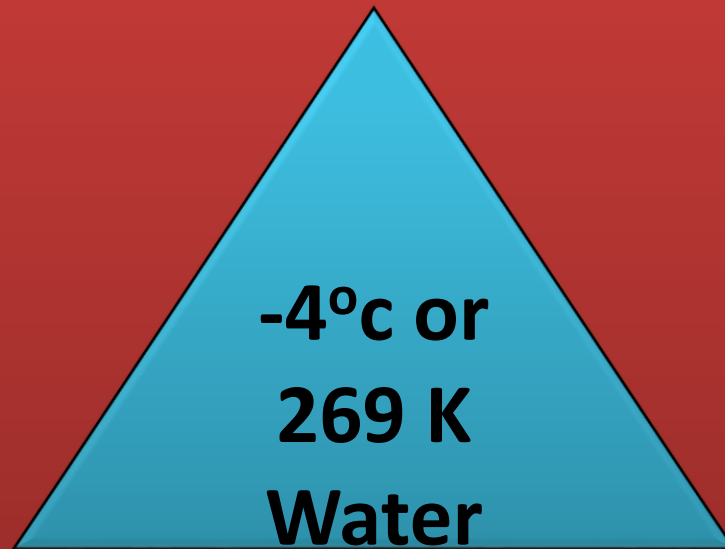


ICE (s)

**Water
(l)**

Metastable Equilibrium

A state of metastable equilibrium can be obtained only by careful approach from one direction.



One component System

For one component system, the maximum number of degrees of freedom is two as,

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

and minimum number of degrees of freedom is zero as,

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Water System

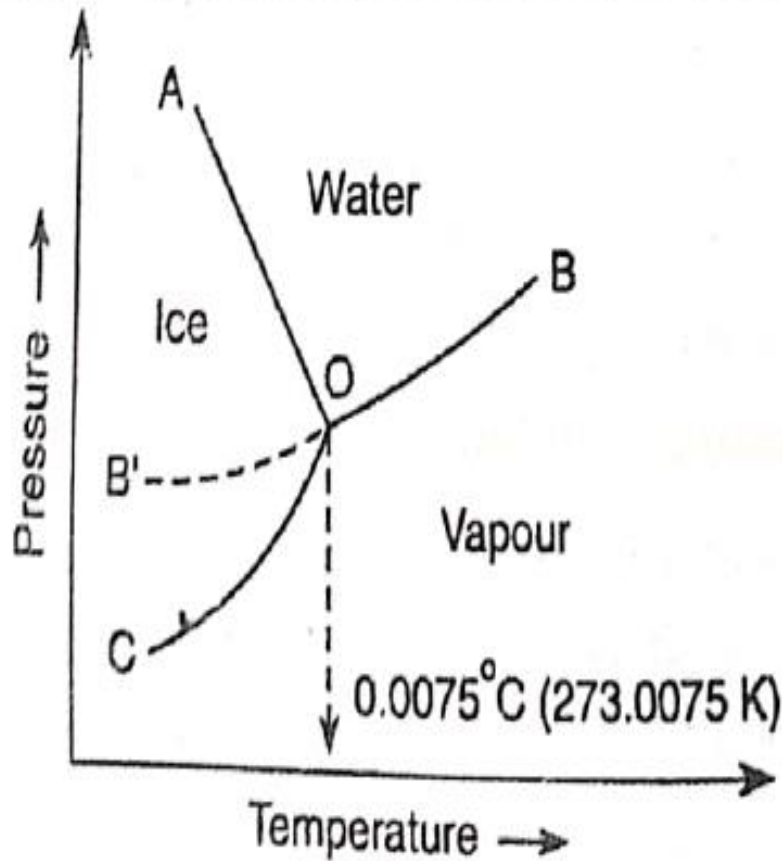


Fig. 1.1 : Phase diagram of water system

Areas: Bivariant

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

Curves: Univariant

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

Point O :- Invariant

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Sulphur System

❖ Polymorphism

❖ Allotropy

❖ Transition temperature

❖ Enantiotropic forms

Sulphur System

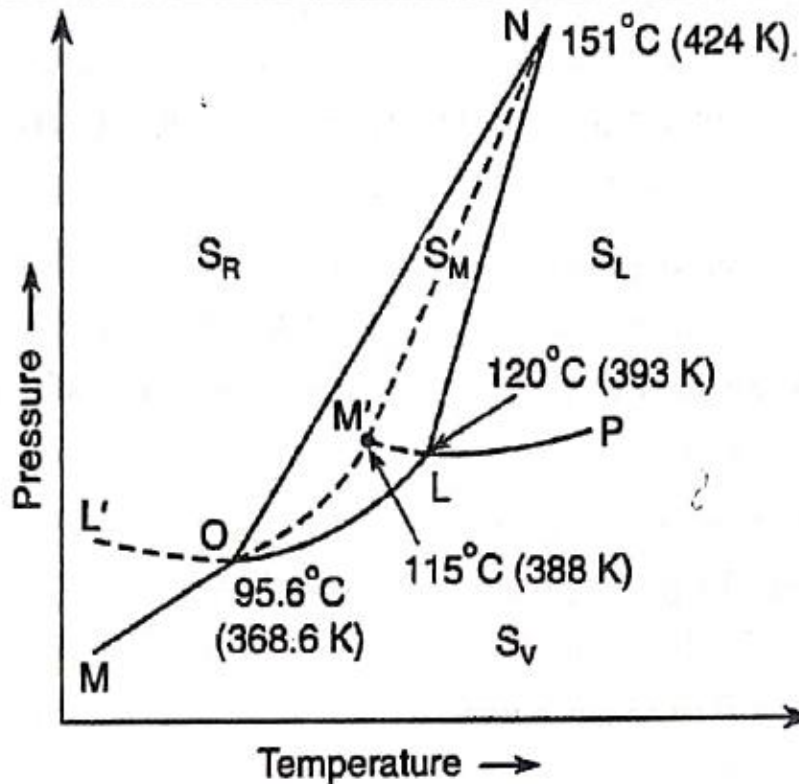


Fig. 1.2 : Phase diagram of sulphur system

Triple point: Invariant

- (i) Point - O : phases - S_R , S_M and S_V .
- (ii) Point - L : phases - S_M , S_L and S_V .
- (iii) Point - N : phases - S_R , S_M and S_L .
- (iv) Point - M' : phases - S_R , S_L and S_V (all metastable).

Areas: Bivariant

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

Curves: Univariant

Curve MO :

Curve OL :

Curve LP :

Curve ON :

Curve NM' :

Two component System

For one component system, the maximum number of degrees of freedom is two as,

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

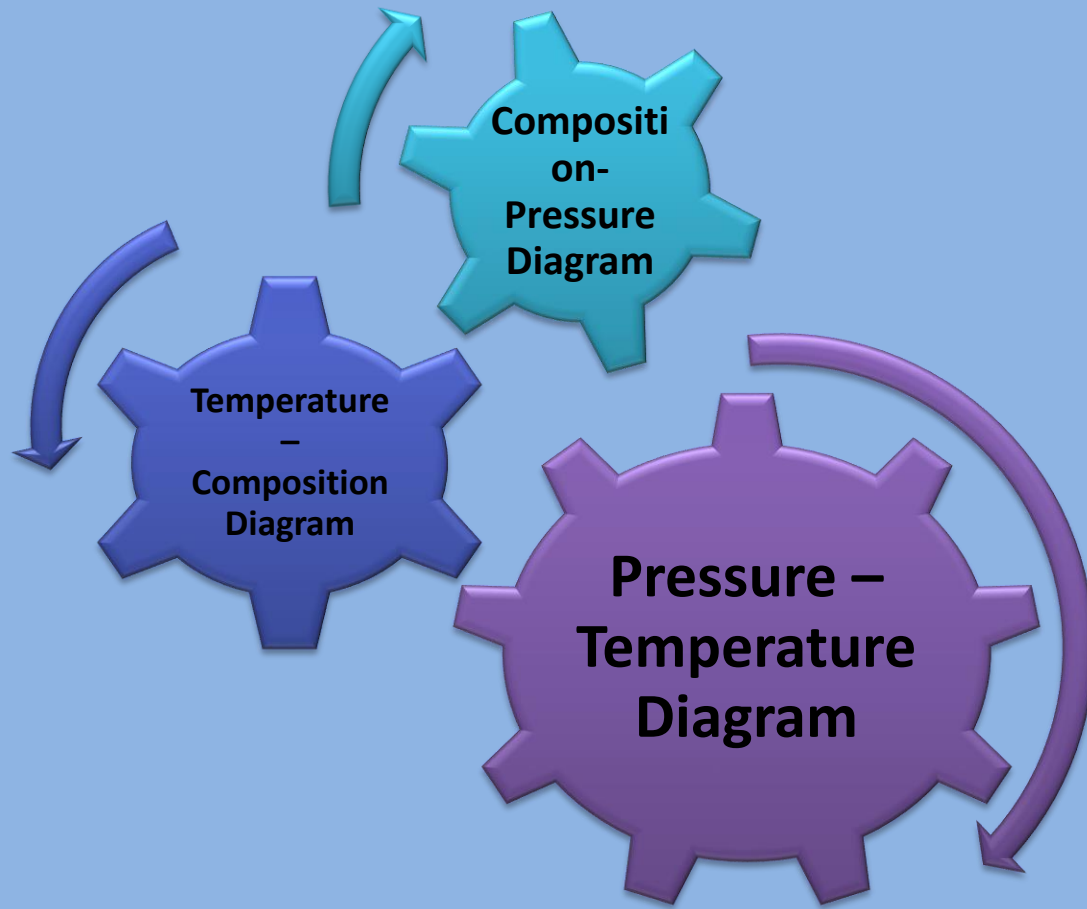
and minimum number of degrees of freedom is zero as,

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

Reduced Phase Rule

$$P + F' = C + 1 \quad \text{or} \quad F' = C - P + 1$$

Two component System



Simple Eutectic System

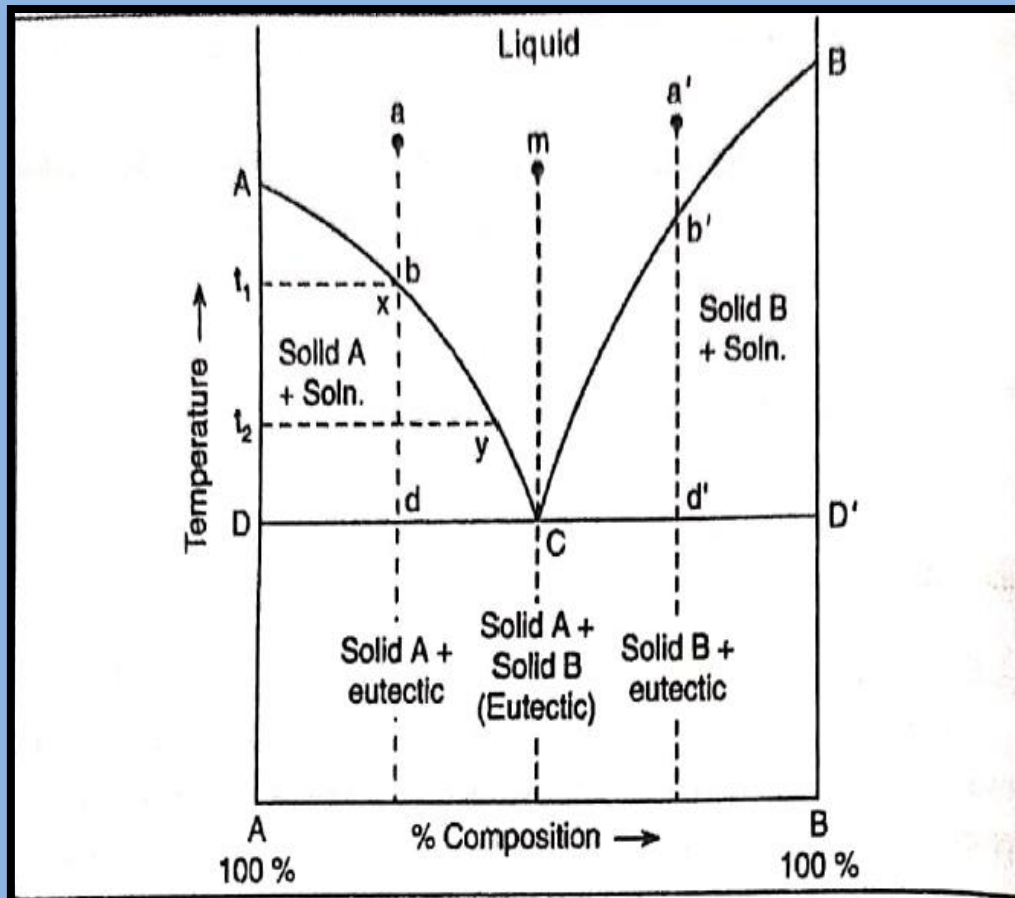


Fig. 1.3 : Simple eutectic diagram

Curves: Univariant

$$F' = C - P + 1 = 2 - 2 + 1 = 1,$$

Point C: Invariant

$$F' = C - P + 1 = 2 - 3 + 1 = 0,$$

Point C: Eutectic Point

Area above line AC and BC

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

AC and BC: - Liquidus

DD', AD and BD':- Solidus

Lead – Silver (Pb-Hg) System

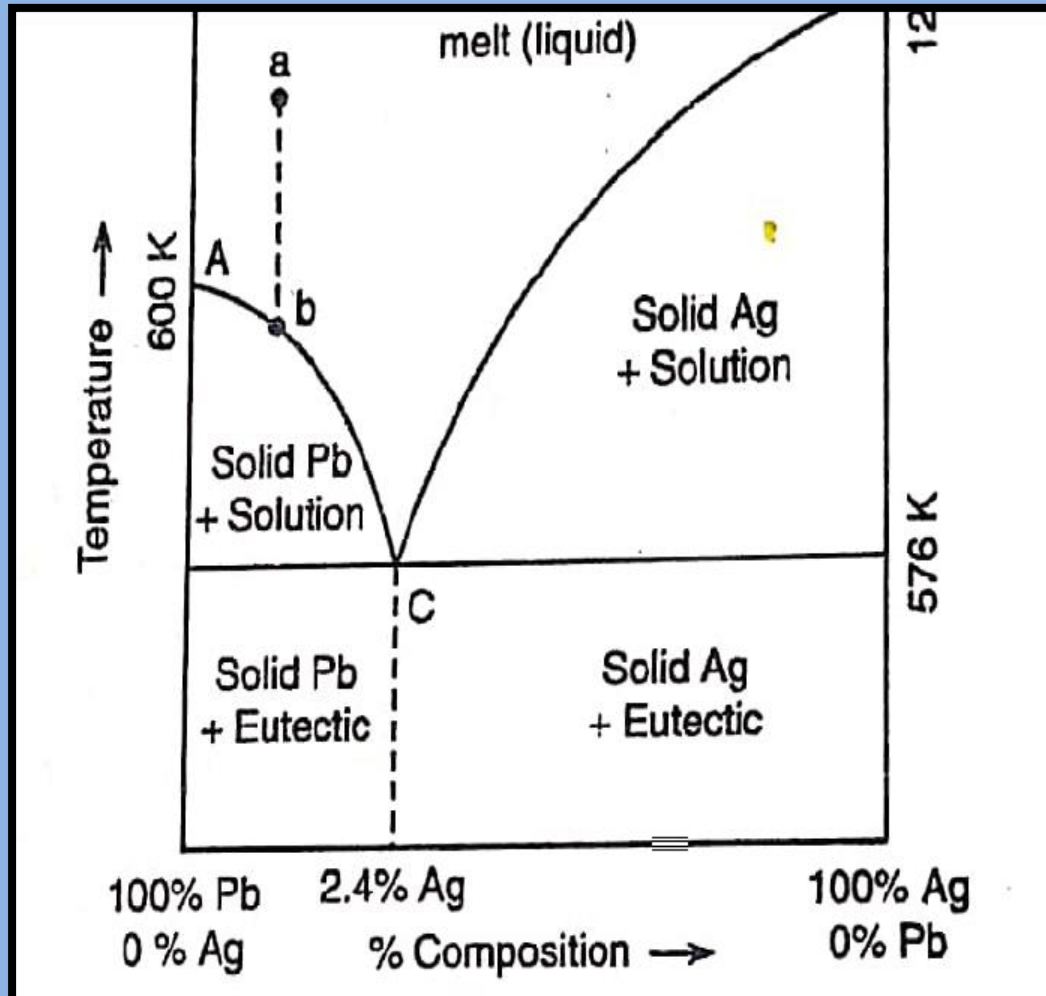


Fig. 1.4 : Phase diagram of Pb-Ag system

Curve AC :

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

Curve BC :

Point C :

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

Pattinson's Process of Desilverisation of Lead

Alloy	M. P. in K respectively	Composition of eutectic mixture
Pb-Ag	600, 1234, 576	2.4% Ag
Zn-Cd	692, 594, 538	18% Zn
Cu-Ag	1394, 1234, 1051	60% Ag

(KI-H₂O) System

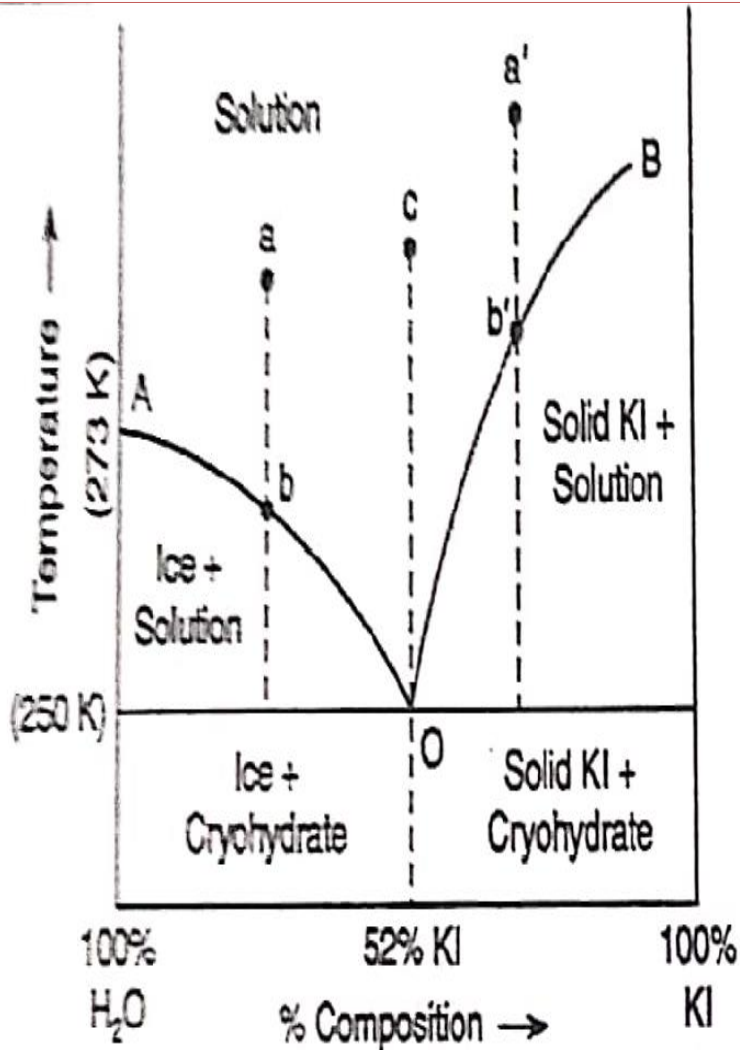


Fig. 1.5 : Phase diagram of KI-H₂O system

Curve AO :

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

Curve BO :

Point 'O' :

$$F' = C - P + 1 = 2 - 3 + 1 = 0$$

cryohydric point or quadrupole point.

Effect of cooling KI solution :

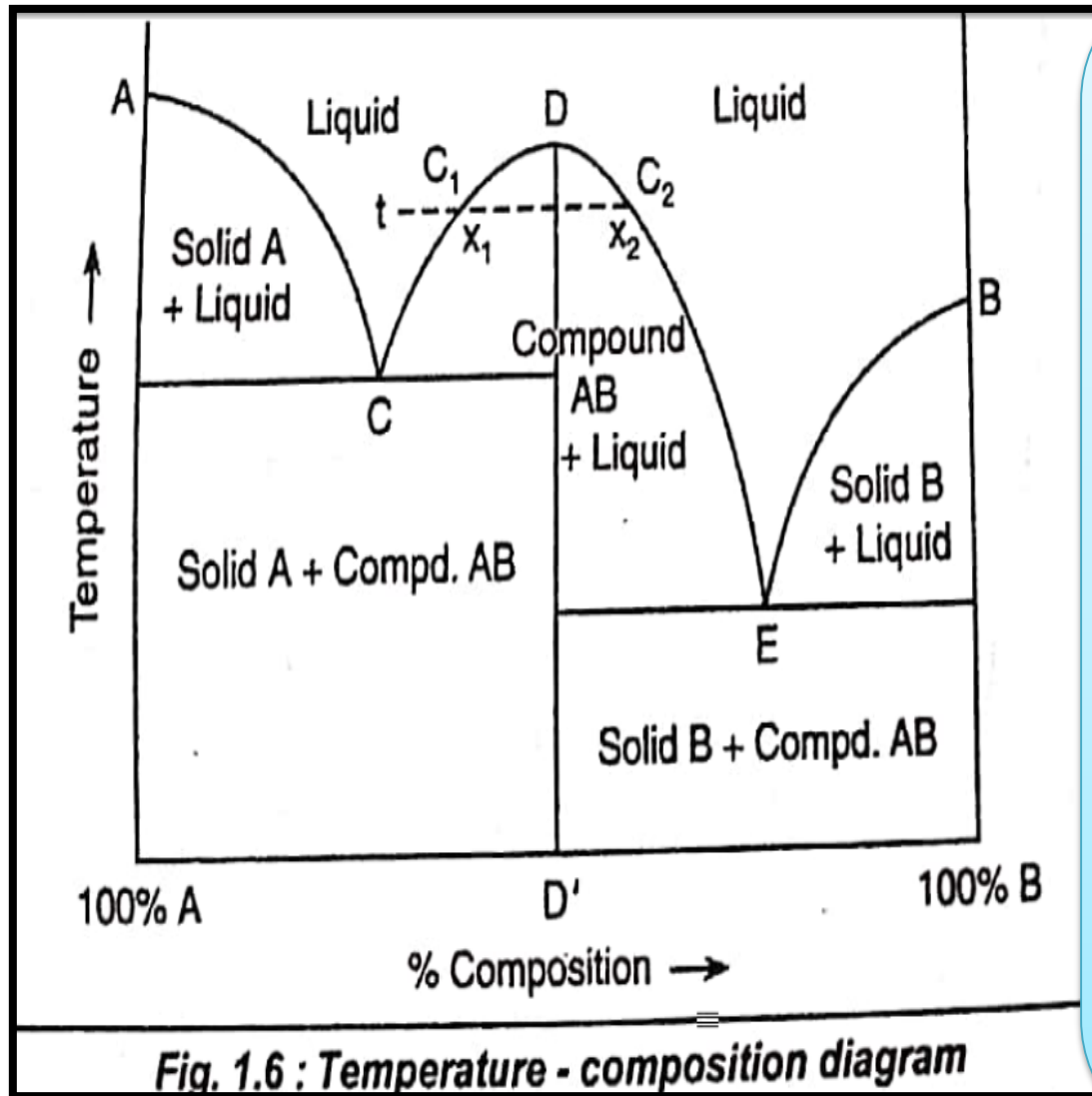
Theory of freezing mixture

System (Freezing mixture)	Composition (% of salt)	Cryohydric temperature
KI + Ice	52.0	250 K (-23°C)
NH_4Cl + Ice	20.1	257 K (-16°C)
NaCl + Ice	23.0	251 K (-22°C)
CaCl_2 + Ice	15.2	217.1 K (-55.9°C)

Formation of compound with Congruent Melting Point

The temperature at which a solid melts sharply into a liquid of the same composition as that of the solid is known as **Congruent Melting Point**”

Formation of compound with Congruent Melting Point



retroflex solubility.

'solidus'

Fig. 1.6 : Temperature - composition diagram

Ferric chloride and Water System ($\text{FeCl}_3\text{-H}_2\text{O}$ system)

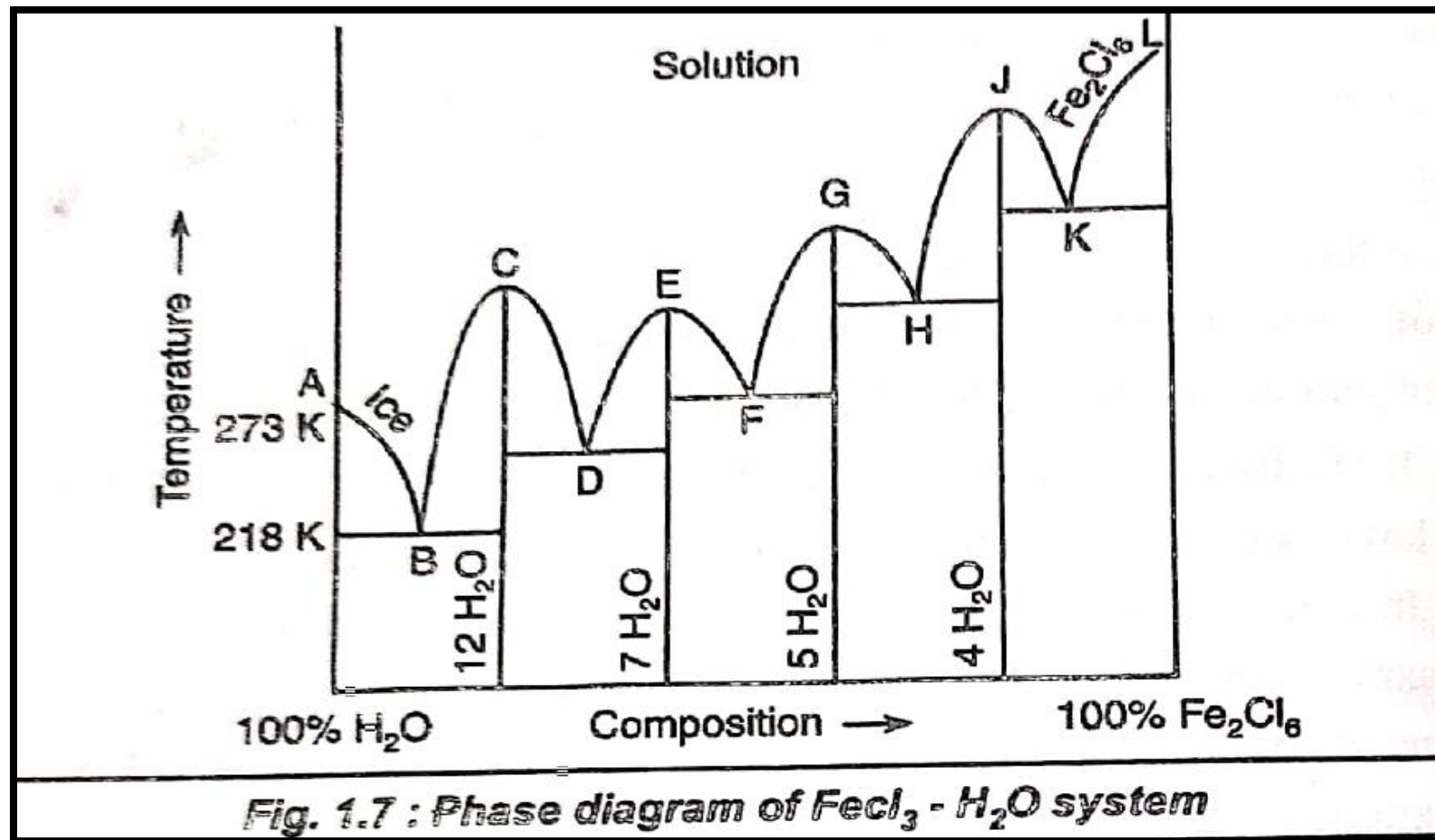


Fig. 1.7 : Phase diagram of $\text{FeCl}_3\text{-H}_2\text{O}$ system

Ferric chloride and Water System (FeCl₃-H₂O system)

Eutectic points

B : 218 K (−55°C) - ice, Fe₂Cl₆·12H₂O

D : 299 K (26°C) - Fe₂Cl₆·12H₂O, Fe₂Cl₆·7H₂O

F : 303 K (30°C) - Fe₂Cl₆·7H₂O, Fe₂Cl₆·5H₂O

H : 328 K (55°C) - Fe₂Cl₆·5H₂O, Fe₂Cl₆·4H₂O

K : 339 K (66°C) - Fe₂Cl₆·4H₂O, Fe₂Cl₆

Congruent M. P.

C : 310 K (37°C) - Fe₂Cl₆·12H₂O

E : 305.5 K (32.5°C) - Fe₂Cl₆·7H₂O

G : 329 K (56°C) - Fe₂Cl₆·5H₂O

J : 346.5 K (73.5°C) - Fe₂Cl₆·4H₂O

Three component System

For three component system, number of components $C = 3$, hence phase rule equation becomes,

$$F = 3 + 2 - P \quad \text{i.e.} \quad F = 5 - P$$

$$F = 3 - P$$

Three component System

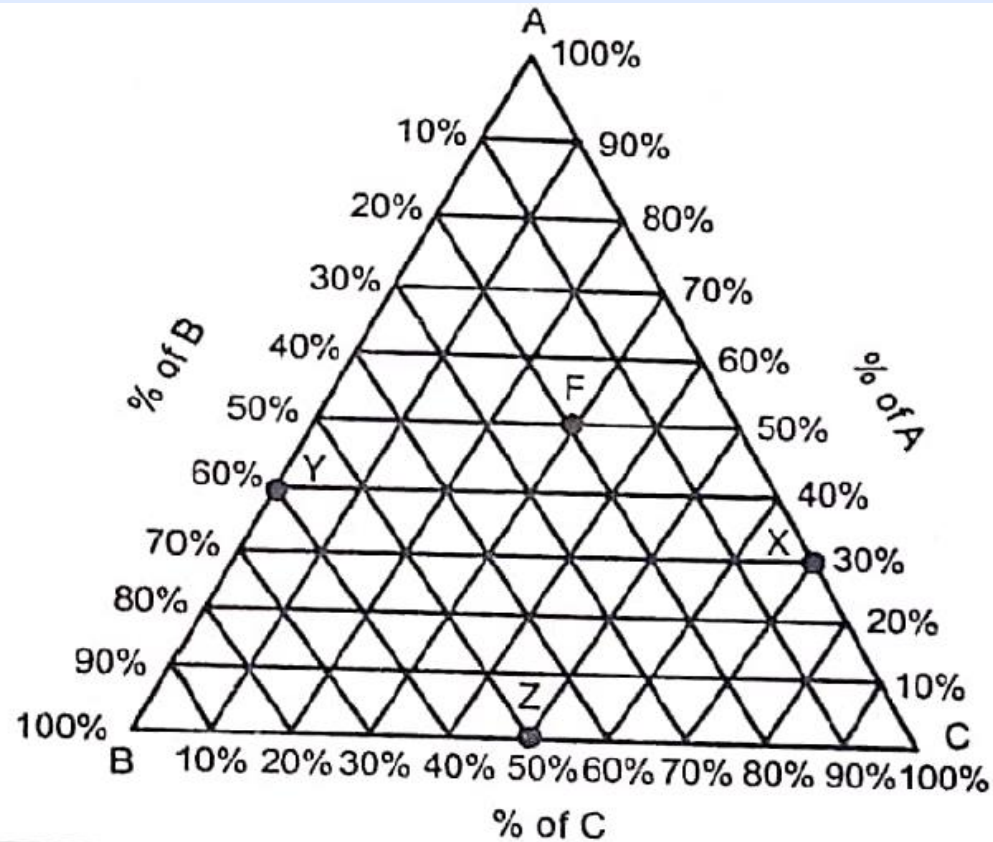
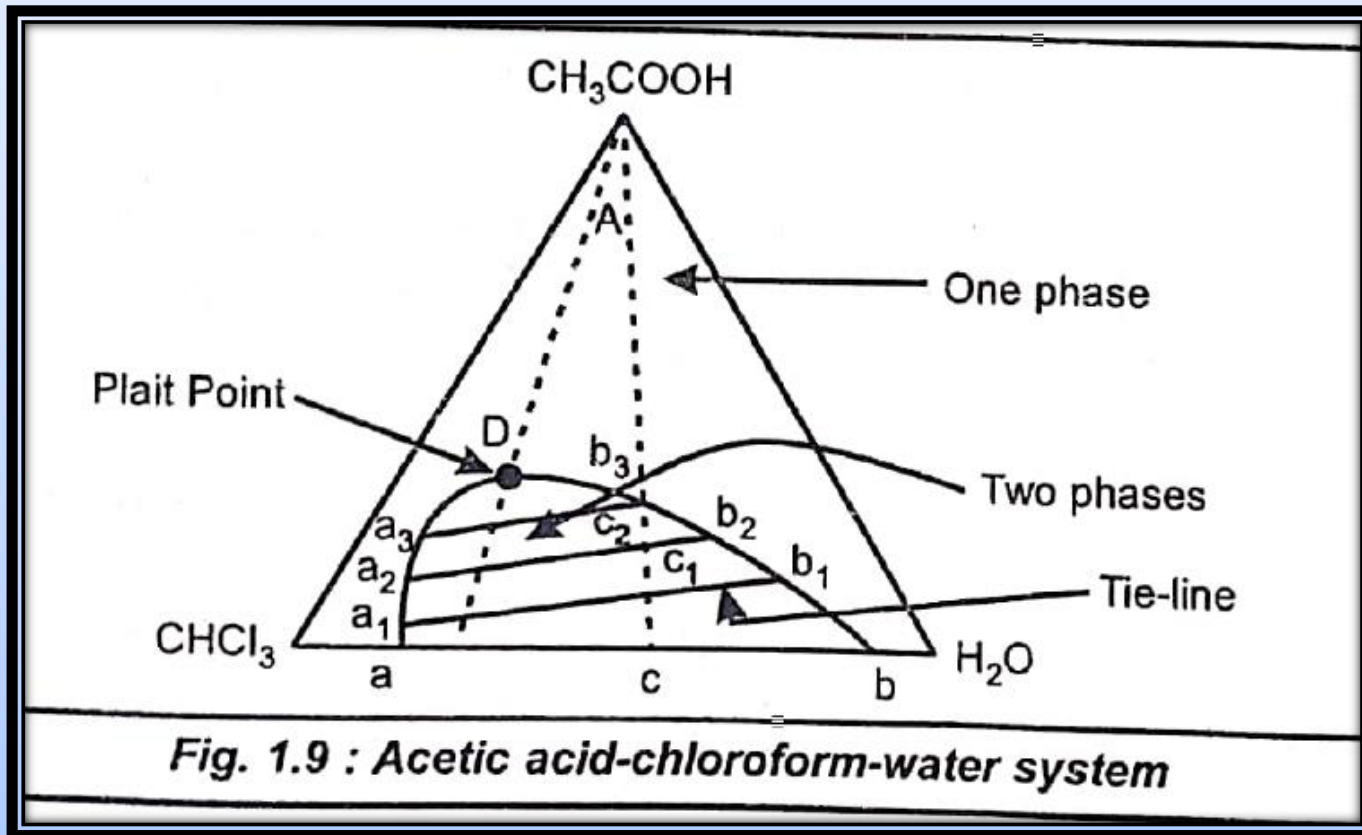


Fig. 1.8 : Triangular Plot for Three Component System

Three component System



Systems Containing One Component

The phase diagram for the ice-water-water vapour system

(phase diagram = graphical representation which indicates the phase equilibrium)

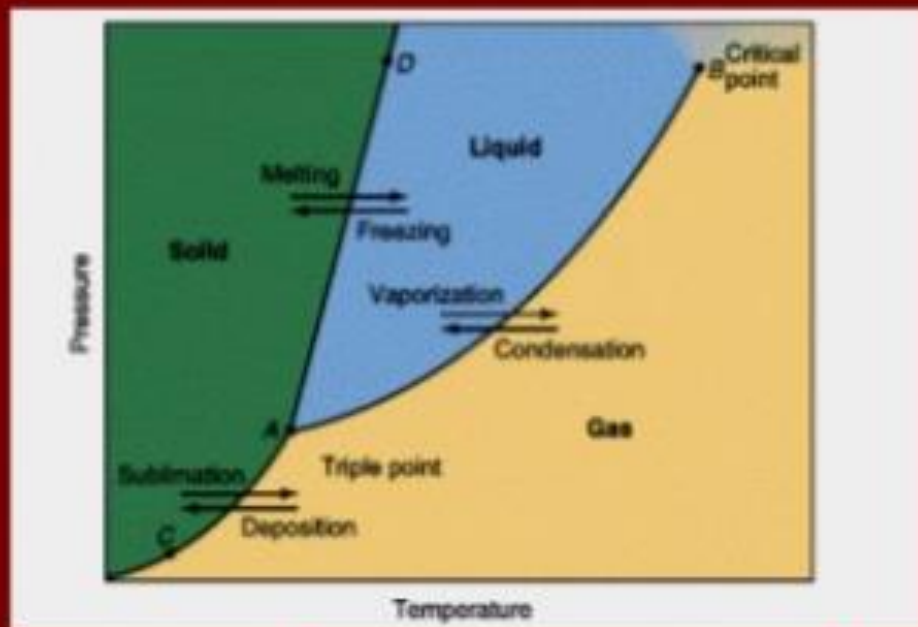
Each area correspond to a single phase.

The number of degrees of freedom in each area is :

$$F = C - P + 2$$

$$F = 1 - 1 + 2 = 2$$

This means that temperature and pressure can be varied independently within these areas without change in number of phases





THANK

YOU!