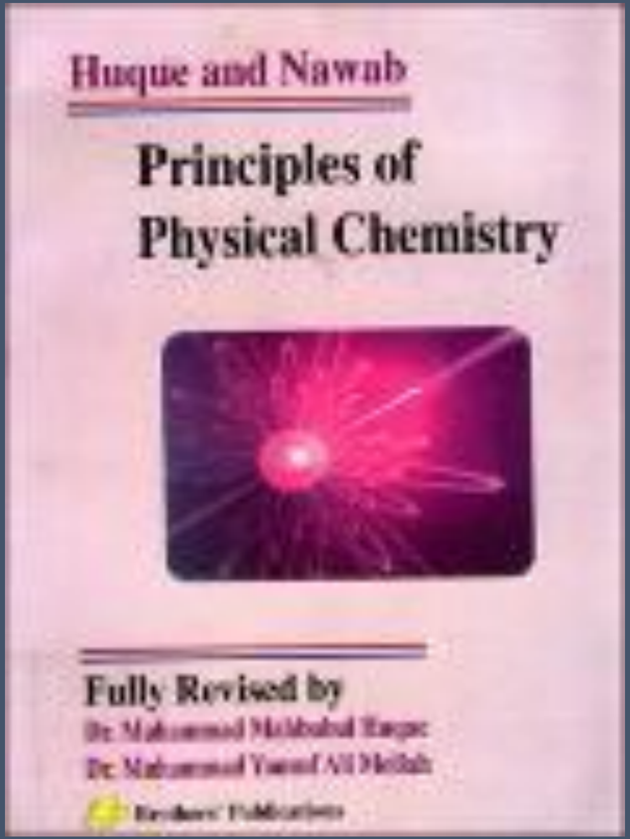
Phase Rule and Phase Diagram



Outlines

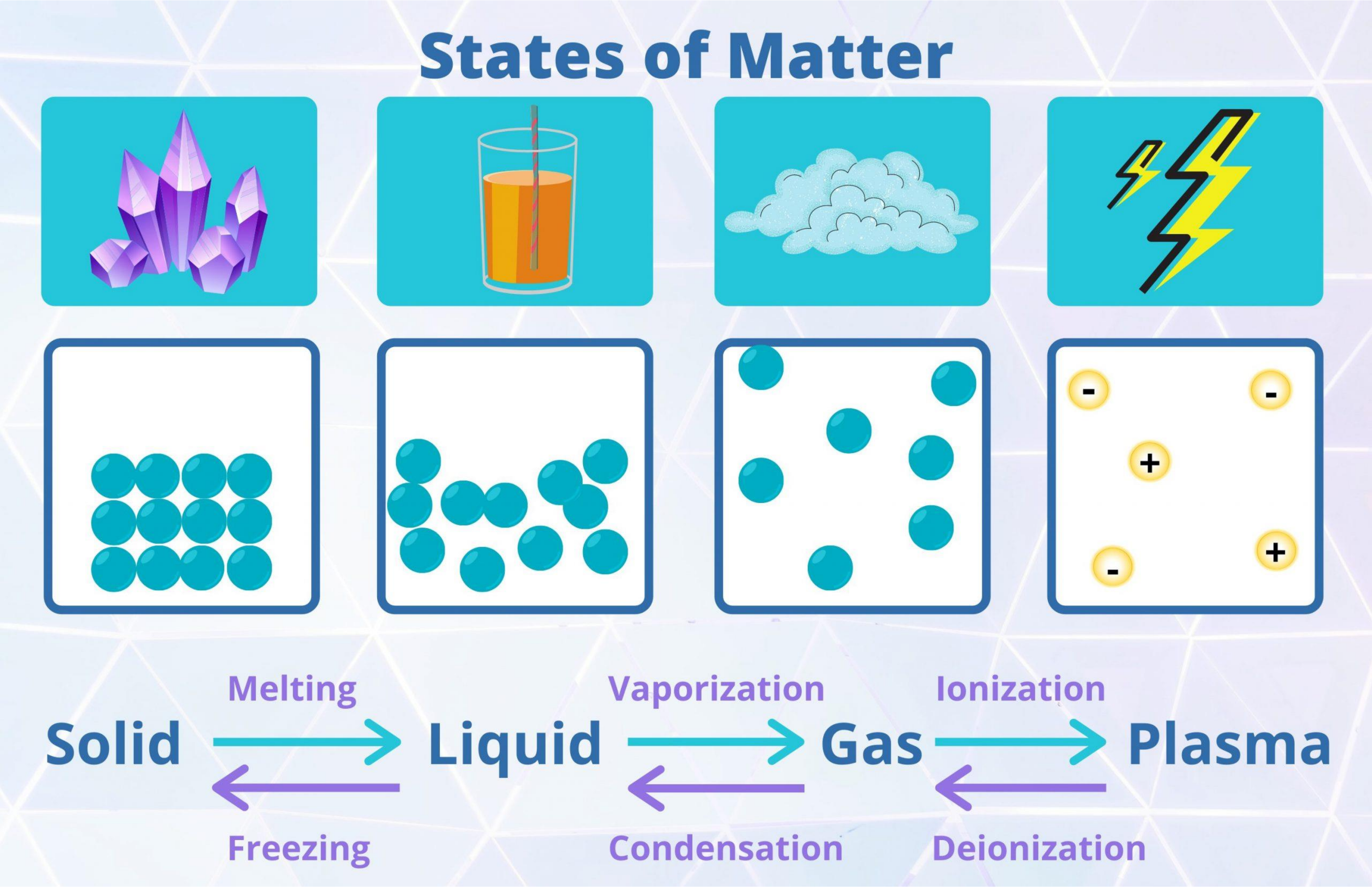
Phase equilibria

Phase rule

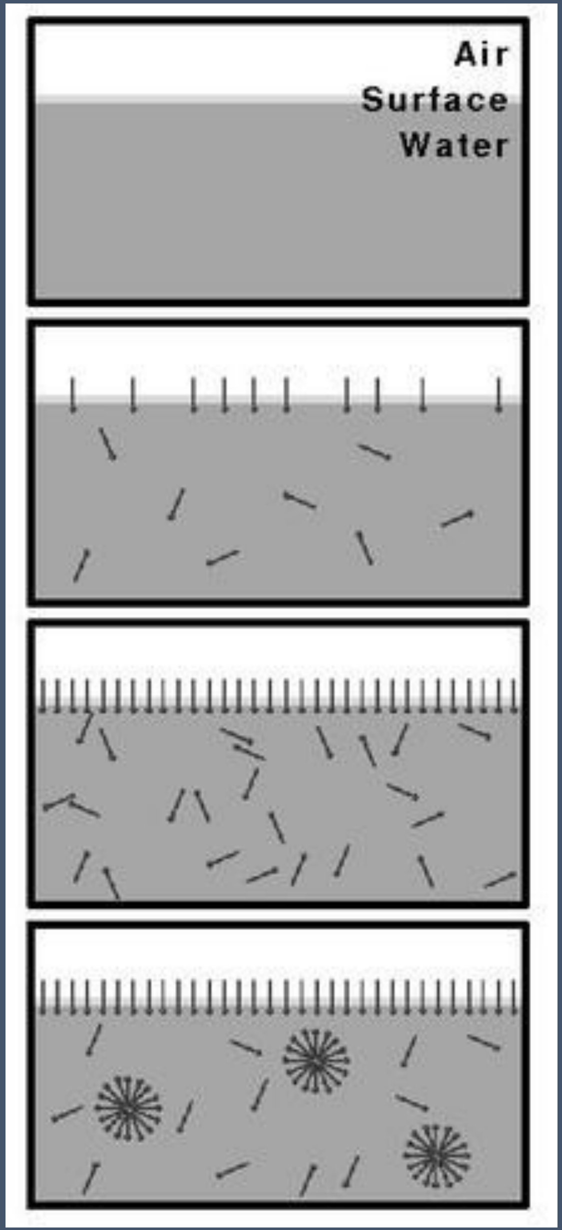
Component

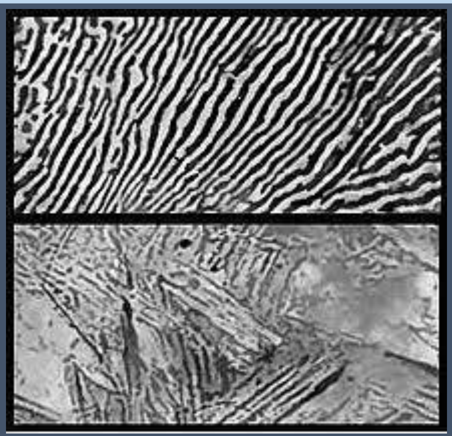
Degree of freedom

Phase diagrams


States of Matter
Melting
Vaporization
Ionization
Solid
Liquid
Gas
Plasma
Freezing
Condensation
Deionization

Commonly observed states of substances





Pressure
Temperature
Composition

Phase

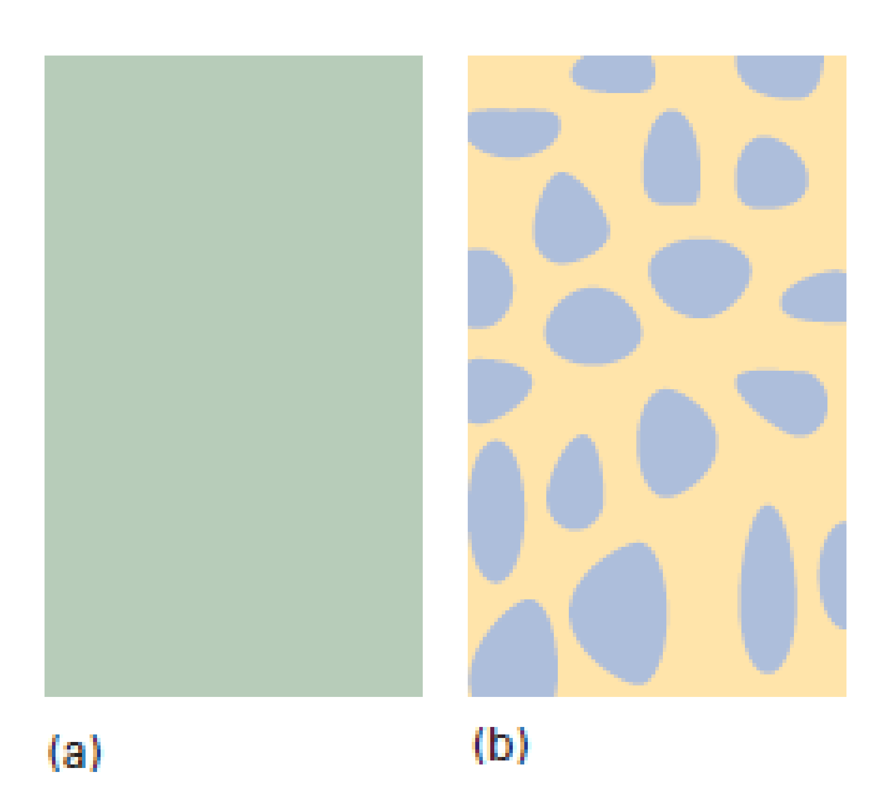


Fig. 4.1 The difference between (a) a single-phase solution, in which the composition is uniform on a microscopic scale, and (b) a dispersion, in which regions of one component are embedded in a matrix of a second component.

An allotrope is a particular form of an element (such as O_2 and O_3) and may be solid, liquid, or gas.

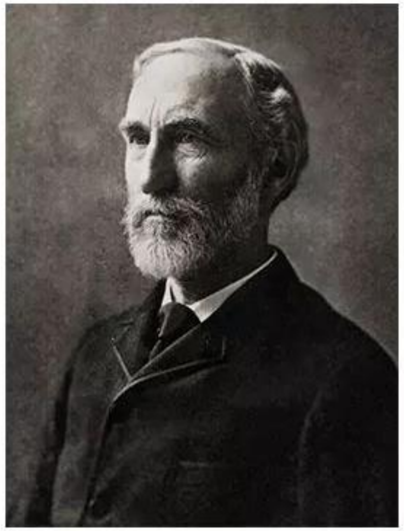
A polymorph is one of a number of solid phases of an element or compound.

Isotropic??? Anisotropic

Surface: Interface

Phase Rule: Josiah Williard Gibbs

In 1875, *Josiah Williard Gibbs* published a general principle governing systems in thermodynamic equillibrium called the **Phase Rule** in a paper titled *On the Equillibrium of Hetrogeneous Substances*.



Josiah Williard Gibbs

It can be mathematically represented as

$$\boxed{P + F = C + 2}$$

Where,
P = the number of phases of a material
F = the number of degrees of freedom
C= the number of component of a system
2 represents the two variables (pressure and temperature)

Phase = a region of material that is chemically uniform, physically distinct and mechanically separable

Component = minimum number of independent species necessary to define the composition of all phases of the system.

Degree of Freedom = the number of intensive variables that are independent of each other, or in other words, the number of thermodynamic variables which can be specified independently without changing the phases in the equillibrium.

For a condensed system

$$\boxed{P + F = C + 1}$$

F = C – P + 2

F = C – P + 1

Terminology involved

Phase (P): A phase is defined as the part of the system which is physically and chemically uniform

OR

Any homogeneous and physically distinct part of the system which is bounded by a surface and is mechanically separable from the other part of the system is called a phase.

Component (C): It is defined as the minimum number of independent chemical species/constituents necessary to describe the composition of each and every phase of the system in equilibrium.

Degree of Freedom or Variance (F): The degree of freedom of a system is defined as the minimum number of independent variable such as temperature, pressure and concentration which must be specified in order to define the system completely.

OR

It is the minimum number of intensive variable that must be specified to know the values of all remaining intensive variables.

Phase (P)

Examples:

1. $NaCl + H_2O$ forms homogeneous solution and hence it is one phase system. (Liquid phase)
2. Gaseous mixture is a one phase system. (Gas phase)
3. Water + alcohol forms one phase system. (Liquid phase)
4. $CCl_4 + H_2O$ are immiscible and forms two phase system. (Two different liquid phases)
5. Mixture of graphite and diamond is a two phase system. (Two solid phases)

Phase (P)

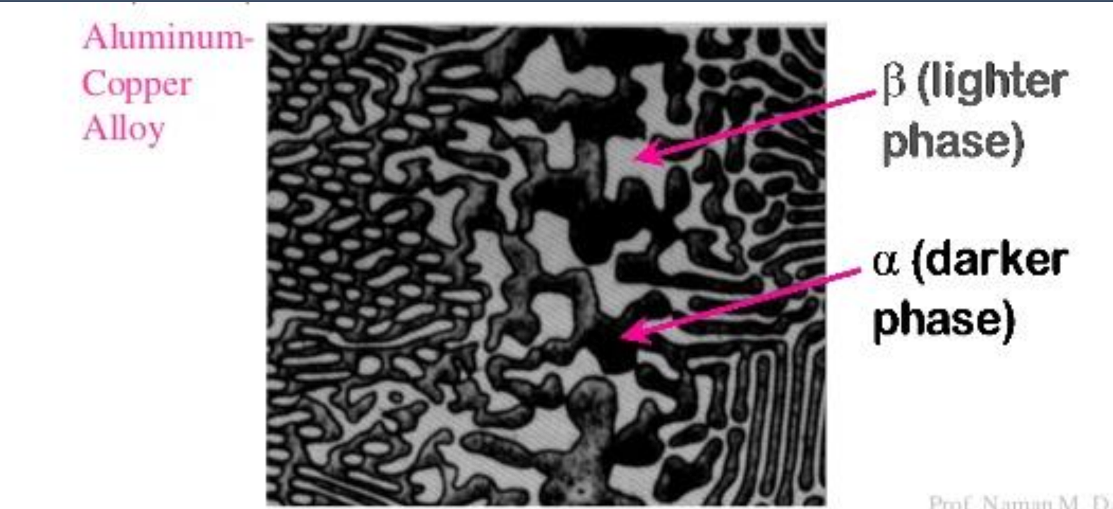
EXAMPLES :

WATER VAPOUR (GAS) ⟷ ICE (SOLID)

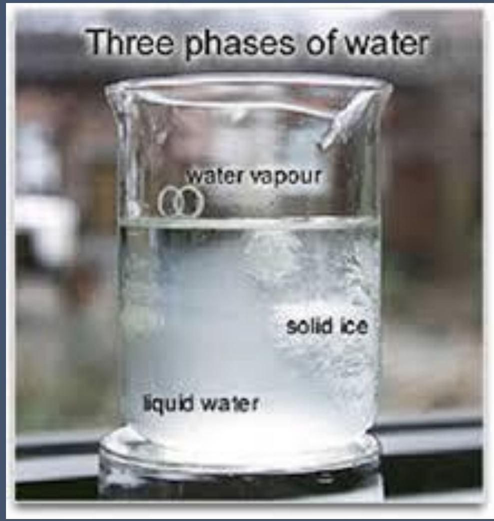
WATER (LIQUID)

As all these three phases contain only one chemical species that is H_2O so it is a one component three phase system.

NaCl + water forms completely miscible solution but contains two chemical species viz. H_2O and NaCl so it is a two component one phase system.



Component (C)



$$H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(g)$$

Consider thermal decomposition of $CaCO_3$ in <u>a sealed tube</u>

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

What are the number of components?

Component (C)

Component, $C = N - R$

N = Constituents
R = Relation/Event

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

$N = 3$ $R = 1$

Component, $C = N - R = 3 - 1 = 2$

$$H_2O\,(s) \rightleftharpoons H_2O\,(l) \rightleftharpoons H_2O\,(g)$$

Component, $C = N - R = 3 - ? = ?$

Component (C)

$$NH_4Cl\,(s) \rightleftharpoons NH_3\,(g) + HCl\,(g)$$

$N = 3 \qquad R = 1$

$p_{NH3} \neq p_{HCl}$ Then $C = 3 - 1 = 2$

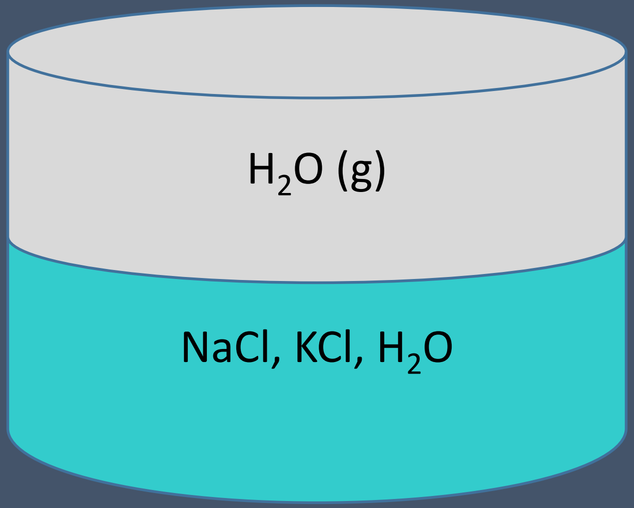
$p_{NH3} = p_{HCl}$ Then $C = 3 - 2 = \mathbf{1}$

Component, $\mathbf{C} = N - R = 7 - 4 = \mathbf{3}$

$NaCl + KCl + H_2O$- system

HOW?

1. $NaCl\,(s) \quad \leftrightarrow \quad Na^+\,(aq) \quad Cl^-\,(aq)$
2. $KCl\,(s) \quad \leftrightarrow \quad K^+\,(aq) \quad Cl^-\,(aq)$
3. $H_2O\,(l) \quad \leftrightarrow \quad H_2O\,(g)$
4. Electro-neutrality between cation-anion



Degree of freedom (F)

Variance, **F** = C – P + 2 (or 1)

F = 0, system is nonvarient
= 1, system is univarient
= 2, system is univerient

Temperature
Pressure
Concentration

Degree of Freedom or Variance (F) : The degree of freedom of a system is defined as the minimum number of independent variable such as temperature, pressure and concentration which must be specified in order to define the system completely.

OR

It is the minimum number of intensive variable that must be specified to know the values of all remaining intensive variables.

Deduce phase rule : **F = C – P + 2**

Degree of Freedom or Variance (F) : The degree of freedom of a system is defined as the minimum number of **independent variable** such as ***temperature, pressure and concentration***, which must be specified in order to define the system completely.

F = No. of total variables – No. of dependent variables

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

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

$$F = C - P + 2$$

For details see in the book

$$F = C - P + 1$$

for condensed system where pressure shows an insignificant effect

Phase Diagram

Phase rule : $F = C - P + 2$

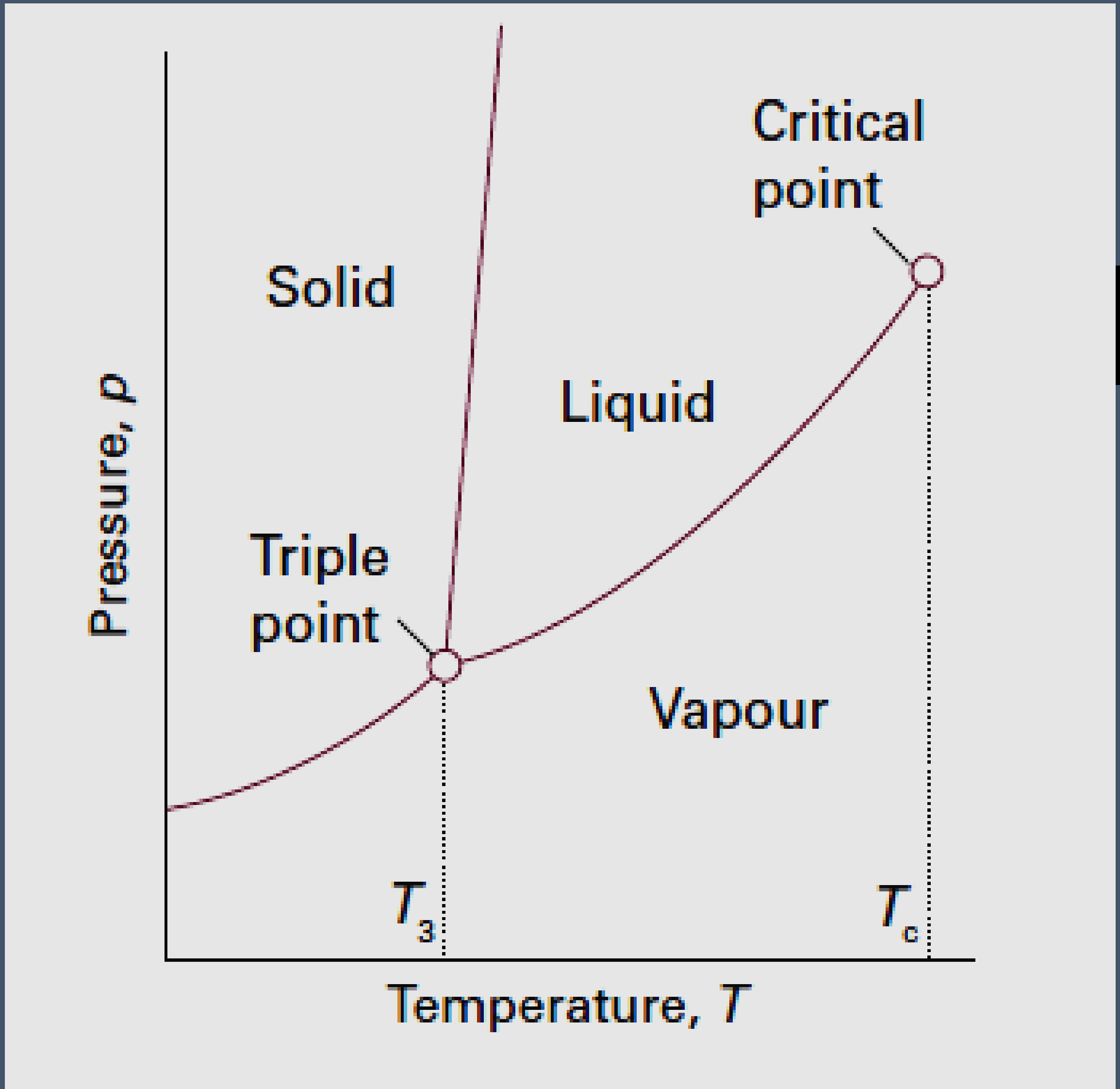
Vaporization, melting (fusion), and the conversion of graphite to diamond are all examples of changes of phase without change of chemical composition.

Phase diagram

The conditions of equilibria between/among various phases of a substance can be presented on a single diagram...

Graph summarizes various phases that are in equilibrium

A general phase diagram: One component system



M(*s*) $\rightleftharpoons$ M(*l*) $\rightleftharpoons$ M(*g*)

Make a list of characteristic features of this diagram …