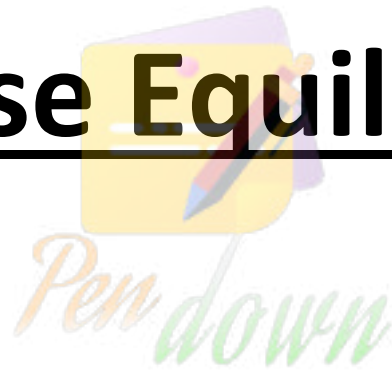# Phase Equilibria

Phase:

A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state.

Examples of Phase:

Example 1:

Two completely miscible liquids generate one phase system

As example, when water and ethanol (EtOH) are mixed in any proportion, one phase is generated (name of phase formed: H_2O-EtOH solution phase).

Similarly, mixing water and methanol (MeOH), one phase is generated.

Similar observation is obtained with water and acetone.

Example 2:

Two immiscible liquids generate two phase system.

As example, when water and chloroform ($CHCl_3$) are mixed in a test tube/beaker, two phases are generated. Lower phase is named as $CHCl_3$ phase (contains $CHCl_3$) and upper phase is named as aqueous or H_2O phase (contains H_2O).

[Similarly, mixing water and dichloromethane (CH_2Cl_2), two phases are formed. Lower phase is CH_2Cl_2 phase and upper phase is H_2O phase.]

Examples of Phase:

Example 3:
A solute completely dissolved in a solvent to produce unsaturated solution generate one phase system.
As example, small quantity of glucose is dissolved in large volume of water to produce an unsaturated glucose solution. Only one phase exists here which is glucose solution phase.

Example 4:
A solute completely dissolved in a solvent to produce saturated solution generate two phase system.
As example, glucose is dissolved in water to produce a saturated glucose solution. Two phases are existing here which are glucose solution phase and glucose solid phase.

Example 5:
Any gas mixture (being thoroughly miscible) produces one phase (name of the phase: gas phase)
As example, mixture of $H_2(g)$ and $O_2(g)$ gives one phase which is gas phase.

Phase Transition:

Change of phase without change of chemical composition.

1) $H_2O(S)$ stable phase below 0°C, but H_2O (L) is stable phase above 0°C.
2) Similarly, $H_2O(L)$ stable phase below 100°C, but H_2O (V) stable phase above 100°C.

Above phase transitions are observed at 0°C (for 1) and 100°C (for 2) under normal pressure (1 atm) condition. Both phases are existing at the corresponding transition temperature for 1 and 2.

However, there are examples of phase transition which occur at high temperature and high pressure condition.

Example is: Graphite ⇌ diamond phase transition.

Phase transition depends on the variables pressure and temperature which are correlated to Gibbs free energy function.

For phase transition to take place, following condition must be fulfilled:

Phase having lower Gibbs free energy (G) at a pressure (P) and Temperature (T) will be existing (most thermodynamically stable phase).

Few Important Definitions:

Phase diagram:
A diagram that shows the conditions of pressure and temperature at which various phases of a substance are thermodynamically stable is known as phase diagram.

Phase boundary:
The boundaries between regions on the phase diagram which show the values of pressure and temperature at which two phases are in equilibrium are known as phase boundaries.

Boiling point:
Temperature at which the vapour pressure of a liquid becomes equal to the <u>external pressure or applied pressure</u>.
When external pressure is 1 atm, it is called normal boiling point (T_b).

Melting point:

Temperature at which liquid and solid phase of a substance co-exist in equilibrium at a specified __external pressure__.

When external pressure is 1 atm, it is called normal melting point (T_f).

Triple point:

A point on the phase diagram where __three phases of a substance simultaneously co-exist in equilibrium.__

It is represented by a point where three phase boundaries are meeting. It is a characteristic physical property of a pure substance.

For pure water, triple point pressure is 0.006 atm,

and triple point temperature (T_3) is 0.01^{o}C (273.16 K)

Phase diagram of water (Simplified and Semi-quantitative):
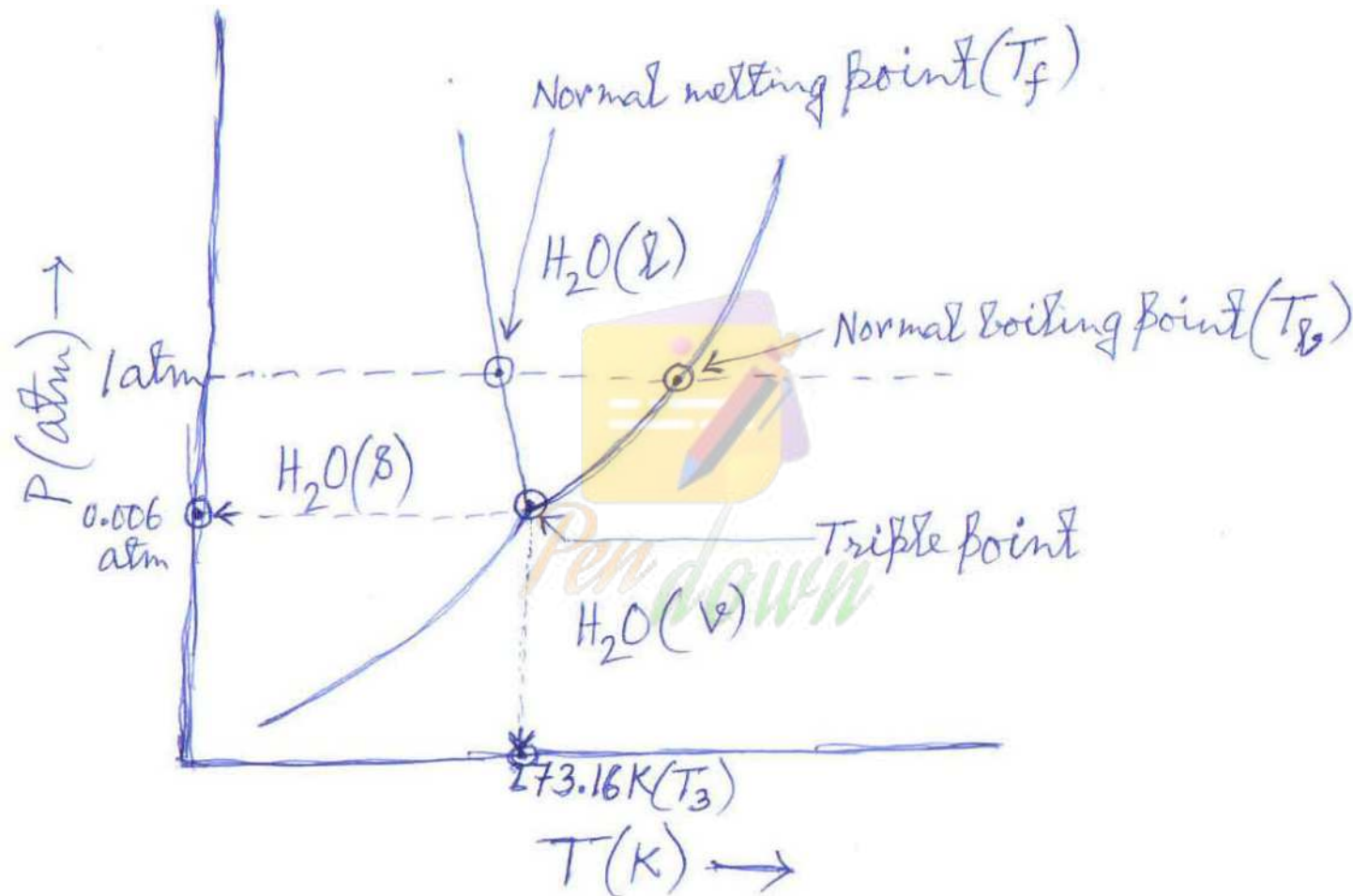
Normal boiling point (T_b): 100°C (373.15 K)
Normal melting point (T_f): 0°C (273.15 K)
Triple point pressure: 0.006 atm and Triple point temperature (T_3): 0.01°C (273.16 K)

Phase diagram of water (Simplified and Semi-quantitative):

S $\rightleftharpoons$ L phase boundary: very steep negative slope
i.e. melting point decreases as pressure increased.

This unique behavior is due to decrease in volume that occurs on melting of ice. So it is more favorable for ice (solid) to transform into water (liquid) as pressure is increased.

Water molecules held apart by extensive hydrogen-bonds between them in $H_2O(s)$, but this three-dimensional structure partially collapses on melting, and $H_2O(l)$ is having higher density than $H_2O(s)$.

Phase Rule:

When the equilibrium between any number of phases is influenced by only temperature, pressure and concentration, then,

Degrees of freedom, $F = C - P + 2$

where, C is number of components, P is number of phases.

Degrees of freedom of an equilibrium system is defined as the number of intensive variable needed to specify its intensive state.

['Intensive state' means specification of its thermodynamic state except for the sizes of the phases. Equilibrium intensive state is described by intensive variables: Pressure (P), Temperature (T) and mole fractions in each of the phases.

Components:

Number of components of a system are the smallest number of independent chemical constituent taking part in equilibrium by means of which the composition of each phase can be expressed either directly or in terms of chemical equations.

Procedure to calculate the number of components:

1) First, number of chemical constituent present in the given system has to be found out or calculated.

2) Second: number of equilibrium constant relation between the chemical constituent has to be found out.

3) Third: to find out number of any other constraints or any other correlation (like, charge neutrality or balance of molar quantities).

4) Number of components = (Number of chemical constituent) – (Number of equilibrium constant relation) – (Number of any other constraints)

Example of components:

A) To find the number of component in pure $H_2O(l)$.

In the above system, one equilibrium is existing: $H_2O\ (l) \rightleftharpoons H^+(aq.) + OH^-\ (aq.)$

Hence, there are three chemical constituents: H_2O, H^+ and OH^-
Only one equilibrium constant relation can be written as:

$$\text{Equilibrium constant, } K = \frac{a_{H^+}\ a_{OH^-}}{a_{H_2O}}$$

where, 'a' denotes the activity terms of H^+, OH^- and H_2O.

Pure $H_2O(l)$ is considered here and hence, charge neutrality must be holding here.
Mole fraction of H^+ ion must be equal to mole fraction of OH^- ion,
i.e., mole fraction of H^+ ion = mole fraction of OH^- ion.

Number of components = 3 – 1 – 1
$$= 1$$

Example of components:

B) To find the number of components for the reaction: $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

There are three chemical constituents: NH_3, N_2 and H_2
Only one equilibrium constant relation can be written as:

$$\text{Equilibrium constant, } K = \frac{a_{N_2}\, a_{H_2}^3}{a_{NH_3}^2}$$

where, 'a' denotes the activity terms of NH_3, N_2 and H_2.
Another correlation in terms of mole fraction is also there which is as follows:
(mole fraction of N_2) = 1/3 (mole fraction of H_2)

Number of components = 3 − 1 − 1
                              = 1

Important note: All chemical constituents in above example (A) and (B) are in same phase. [In example (A), chemical constituents are in liquid phase and in example (B), they all are in gas phase.] If chemical constituents are in different phases, calculation of components will be different and more complicated.