ENGINEERING CHEMISTRY

Department of Science and Humanities

Module content:

- ***Phase equilibria***
- ***Gibb's phase rule***
- ***Phase diagram of 1-component system***
- ***Phase diagram of 2-component system***

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Class content:

- ***Free energy in Phase equilibria***
- ***Chemical potential***
- ***Phase equilibria***
  - ***Phase***
  - ***Component***
  - ***Degree of freedom***

Free energy in Phase equilibria

- All substances have tendency to **minimize their Gibbs energy** at constant temperature and pressure to attain stable state
- **Phase transformations** from one phase to another occur to reduce free energy of the system
- Gibb's energy is an **extensive property**

Chemical potential

- Chemical potential is defined as the **partial molar Gibb's energy** for a component *i* in a mixture , and is denoted by **μ**

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j \neq i}$$

Phase equilibria

- Phase equilibria between phases exist when **chemical potential of a component is equal in all the phases** in equilibrium

  e.g. for water at triple point

  Solid $\rightleftharpoons$ liquid $\rightleftharpoons$ vapour

The chemical potential of water will be equal in all the three phases

- For systems not at equilibrium, the chemical potential will point to the **direction in which the system can move** in order to achieve equilibrium viz. , the system moves from higher chemical potential to lower chemical potential
- When various phases are in equilibrium with one another in a heterogeneous system, there can be **no transfer of energy or mass** from one phase to another.
- For a system at equilibrium, the various phases must have the **same temperature and pressure and their respective compositions must remain constant** all along

Phase

A phase is defined as any **homogeneous and physically distinct part of a system** bounded by a surface and is mechanically separable from other parts of the system. It is denoted by P

- **Gaseous state :** P =1 gases are completely miscible

- **Liquid state :** P = No. of layers when liquids are immiscible
  P = 1 when liquids are completely miscible

- **Solid state :** Each solid constitutes a separate phase
  Each polymorphic form constitutes a separate phase
  P = 1 for solid solution

Counting the number of phases

1) **Solid ⇌ liquid ⇌ vapour** ; P = 3

- Ice in the system is a single phase even if it is present as a number of pieces.

2) **Calcium carbonate undergoes thermal decomposition**

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

- P= 3; 2 solid phases, $CaCO_3$ and CaO and one gaseous phase, that of CO_2

3) **Ammonium chloride undergoes thermal decomposition**

$$NH4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

- P = 2; one solid, NH_4Cl and one gaseous, a mixture of NH_3 and HCl

Components

- A component is defined as the **smallest number of independently varying chemical constituents** using which the composition of **each and every phase** in the system can be expressed

- When no reaction is taking place in a system, the number of components is the same as the number of constituents

- While expressing in terms of constituents **zero and negative values** are allowed

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Counting the number of components:

- **1-component system**

e.g. **Pure water** ; **C = 1**

solid water ⇌ liquid water

All the different phases can be expressed in terms of the single constituent water

- **2-component system**
  - **Salt hydrate system**

e.g. $Na_2SO_4.10H_2O$; **C=2**

$Na_2SO_4.10H_2O = Na_2SO_4 + 10H_2O$

$Na_2SO_4.7H_2O = Na_2SO_4 + 7H_2O$

$Na_2SO_4 = Na_2SO_4 + 0H_2O$

$H_2O = 0\,Na_2SO_4 + H_2O$

The composition of all the phases can be expressed in terms of 2 components

- **Thermal decomposition of solid $CaCO_3$ in a closed container** ; **C = 2**

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

  - Though there are 3 species present, the number of components is only two
  - Phases are : $CaCO_3(s)$, $CaO(s)$ and $CO_2(g)$
  - Any two of the three constituents may be chosen as the components
  - **If CaO and CO_2 are chosen**,

    $CaCO_3(s) = CaO + CO_2$

    $CaO(s) = CaO + 0\ CO_2$

    $CO_2(g) = 0\ CaO + CO_2$
  - **If $CaCO_3$ and CO_2 are chosen**,

    $CaCO_3(s) = CaCO_3 + 0\ CO_2$

    $CaO(s) = CaCO_3 - CO_2$

    $CO_2(g) = 0\ CaCO_3 + CO_2$

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Module 2- Phase equilibria

- **Thermal decomposition of ammonium chloride in a closed system ;C = 1**

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

- Phases are : solid phase of $NH_4Cl(s)$and gaseous phase of $NH_3(g)$ and $HCl(g)$

  solid : $NH_4Cl\,(s) = NH_4Cl$

  gas : $NH_3(g) + HCl(g) = NH_4Cl$

- The composition of both the solid and gaseous phase can be expressed in terms of NH_4Cl. Hence the number of components is one**;** C=1
- If additional HCl (or NH_3) were added to the system, then **C = 2**
- The decomposition of NH_4Cl would not give the correct composition of the gas phase
- A second component, HCl (or NH_3) would be needed to describe the gas phase, therefore C=2

Degrees of freedom (or variance)

The degrees of freedom or variance of a system is defined as the **minimum number of intensive variables** such as temperature, pressure, concentration, which must be fixed in order to define the system completely; it is denoted by F

OR

The degree of freedom of a system may also be defined as the number of variables, such as temperature, pressure and concentration that can be **varied independently** without altering the number of phases.

Example : water system

- **Only 1 phase** (solid , liquid or gas)
    - Both temperature and pressure need to be mentioned in order to define the system; **F = 2**

- **2 phases in equilibrium**,
  - Only one variable, either temperature or pressure need to be specified in order to define the system; **F =1**
  - solid water ⇌ liquid water
  - If the pressure on the system is maintained at 1 atm, then the temperature of the system gets automatically fixed at 0°C, the normal melting point of ice

- **3 phases in equilibrium**,
  - No variable can be changed
  - temperature and pressure are fixed, **F = 0**
  - solid water ⇌ liquid water ⇌ water vapour
  - Three phases, ice, water, vapour can coexist in equilibrium at triple point of water at 0.0098°C and 4.58mm of Hg pressure only

THANK YOU

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