



# ENGINEERING CHEMISTRY

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Department of Science and Humanities

# ENGINEERING CHEMISTRY

## Module 2- Phase equilibria

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### *Module content:*

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

# ENGINEERING CHEMISTRY

## Module 2- Phase equilibria

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### *Class content:*

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

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## Module 2- Phase equilibria



### 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
- Gibbs energy is an **extensive property**

### Chemical potential

- Chemical potential is defined as the **partial molar Gibbs energy** for a component  $i$  in a mixture, and is denoted by  $\mu$

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

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## Module 2- Phase equilibria



### 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



**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

# ENGINEERING CHEMISTRY

## Module 2- Phase equilibria

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### 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

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### Counting the number of phases

1) **Solid  $\rightleftharpoons$  liquid  $\rightleftharpoons$  vapour** ;  $P = 3$

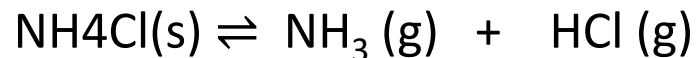
- Ice in the system is a single phase even if it is present as a number of pieces.

2) **Calcium carbonate undergoes thermal decomposition**



- $P = 3$ ; 2 solid phases,  $\text{CaCO}_3$  and  $\text{CaO}$  and one gaseous phase, that of  $\text{CO}_2$

3) **Ammonium chloride undergoes thermal decomposition**



- $P = 2$ ; one solid,  $\text{NH}_4\text{Cl}$  and one gaseous, a mixture of  $\text{NH}_3$  and  $\text{HCl}$

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## Module 2- Phase equilibria

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### 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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## Module 2- Phase equilibria

### Counting the number of components:

- **1-component system**

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

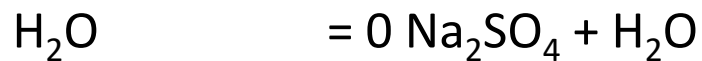
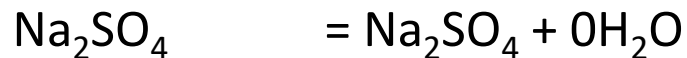
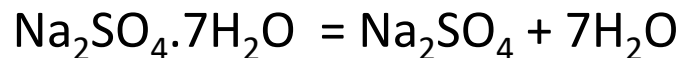
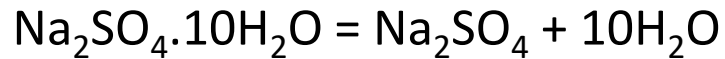
solid water  $\rightleftharpoons$  liquid water

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

- **2-component system**

- **Salt hydrate system**

e.g.  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  ; **C=2**



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

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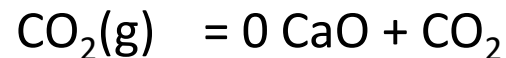
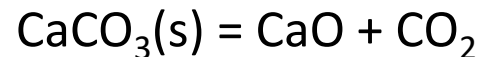
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- Thermal decomposition of solid  $\text{CaCO}_3$  in a closed container ;  $C = 2$

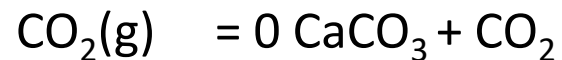


- Though there are 3 species present, the number of components is only two
- Phases are :  $\text{CaCO}_3(s)$ ,  $\text{CaO}(s)$  and  $\text{CO}_2(g)$
- Any two of the three constituents may be chosen as the components

- If  $\text{CaO}$  and  $\text{CO}_2$  are chosen,



- If  $\text{CaCO}_3$  and  $\text{CO}_2$  are chosen,

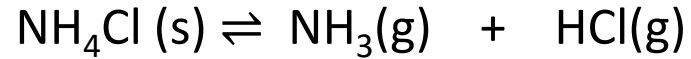


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- Thermal decomposition of ammonium chloride in a closed system ; **C = 1**



- Phases are : solid phase of  $\text{NH}_4\text{Cl(s)}$  and gaseous phase of  $\text{NH}_3\text{(g)}$  and  $\text{HCl(g)}$

**solid :  $\text{NH}_4\text{Cl (s)} = \text{NH}_4\text{Cl}$**

**gas :  $\text{NH}_3\text{(g)} + \text{HCl(g)} = \text{NH}_4\text{Cl}$**

- The composition of both the solid and gaseous phase can be expressed in terms of  $\text{NH}_4\text{Cl}$ . Hence the number of components is one;  $C=1$
- If additional  $\text{HCl}$  (or  $\text{NH}_3$ ) were added to the system, then **C = 2**
- The decomposition of  $\text{NH}_4\text{Cl}$  would not give the correct composition of the gas phase
- A second component,  $\text{HCl}$  (or  $\text{NH}_3$ ) would be needed to describe the gas phase, therefore  $C=2$

# ENGINEERING CHEMISTRY

## Module 2- Phase equilibria

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### 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;  **$F = 2$**

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## Module 2- Phase equilibria



- **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  $\rightleftharpoons$  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  $\rightleftharpoons$  liquid water  $\rightleftharpoons$  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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