

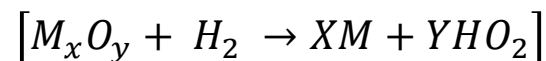
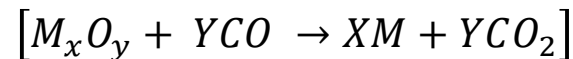
# LECTURE-25

## TOPOCHEMICAL REACTION

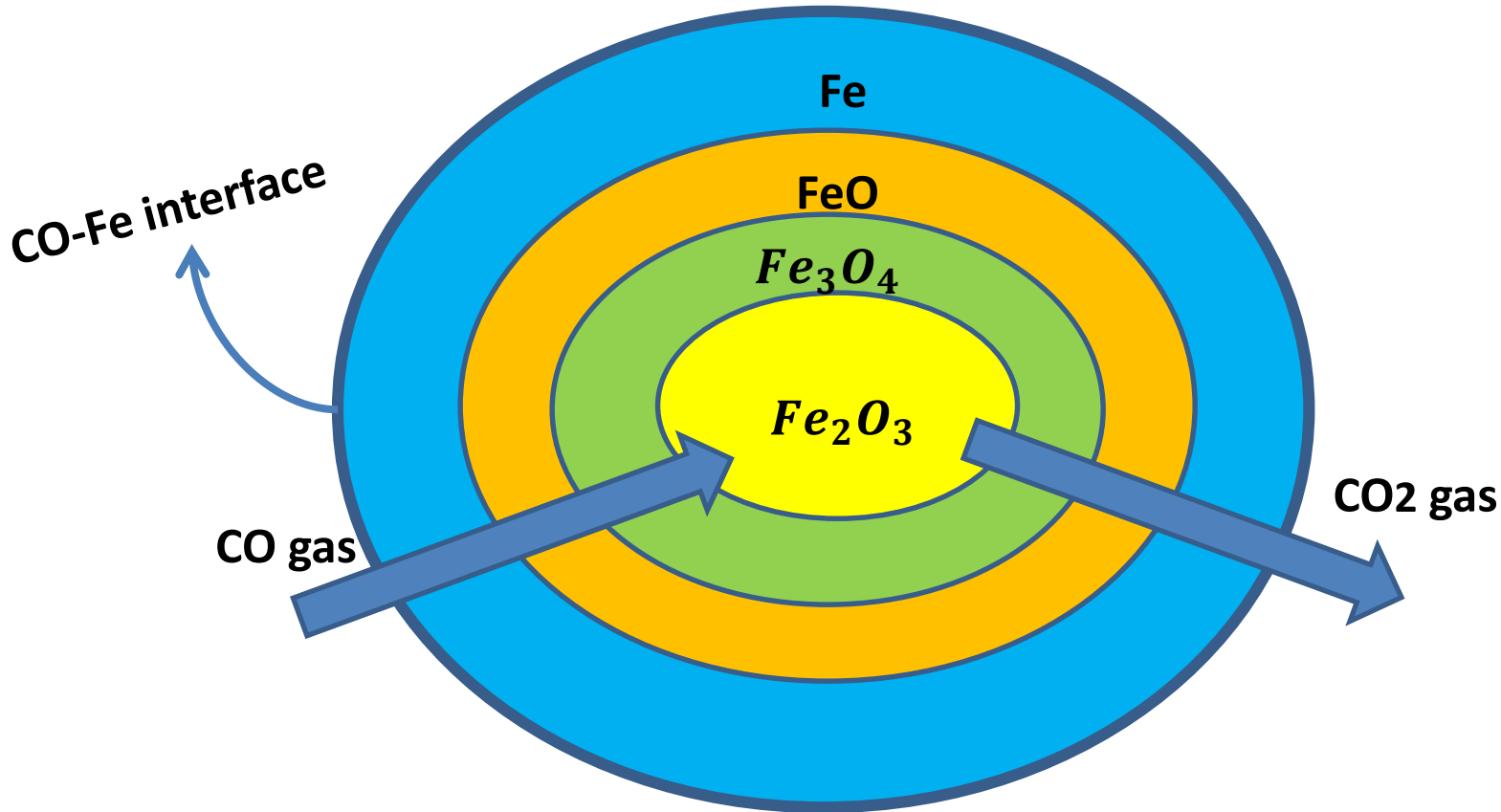
It is defined as the solid-gas reaction or phase boundary controlled reactions that occur by the movement of well-defined interface.

### Diffusion steps:

- I. Diffusion of reducing gas ( $\text{CO}$ ,  $\text{H}_2$ ) from gas phase to the ore-pellet through surface film.
- II. Diffusion of reducing gas from ore-pellet to reductant layers.
- III. Chemical reaction carry out as



# Continued...



**Fig- Reduction of iron ore presence of CO gas**

- IV. Diffusion of product gas ( $CO_2$ ,  $H_2O$ ) from reductant layer to ore-pellet
- V. Diffusion of product gas from ore-pellet to surface film.

## **Factors affecting the reaction rate kinetics:**

- ☐ The physical state of both reactants and products.
- ☐ The concentrations of the reactants and products.
- ☐ The pressure or temperature at which the chemical reaction takes place.
- ☐ Presence of catalyst in the reaction.

## **Rate Controlling Step:**

- ☐ The slowest step of a multi-step reaction is the rate determining step.
- ☐ The rate of the whole reaction = the rate of the rate determining step.
- ☐ The rate law corresponds to the components of the rate determining step.
- ☐ The chemical reaction included the process of diffusion of gaseous species and that in intrinsic chemical reaction.
- ☐ If the effects of gas phase mass transfer being negligible and then the reaction rate being controlled by intrinsic interfacial chemical reaction and the diffusion of reactant and product gas species through solid product layer.

# Continued...

**Derivation:** Let us assume the particle which is participating in reduction reaction are spherical in nature for which the reaction is phase boundary type, then the presence or absence of product layer the rate of reaction depends on the interface area.

$$-\frac{dw}{dt} \propto A.C \Rightarrow -\frac{dw}{dt} = KAC \quad (277)$$

N.B.: Negative sign indicates that with increase in time the wt. decreases

[Where,  $K \rightarrow$  Reaction constant,  $A \rightarrow$  Interface area for reaction  
 $C \rightarrow$  Concentration of the reagent fluid.]

If “r” be the radius of the spherical molecules, participating in the equation (277) can be re-written as

$$-\frac{d}{dt} \left[ \frac{4}{3} \pi r^3 \cdot \rho \right] = K \cdot 4\pi r^2 \cdot 1 \quad (278)$$

[Where,  $A = 4\pi r^2$ ,  $C=1$ ]

# Continued...

Reaction not started so,  $C = 1$ , for unreacted core sphere.

$$\Rightarrow -\frac{dr}{dt} = \frac{3K}{\rho} \quad (279)$$

$$\Rightarrow -\frac{dr}{dt} = \frac{K'}{\rho} \quad (280)$$

$$\Rightarrow -\int_{r_0}^r dr = \frac{K'}{\rho} \int_0^t dt \quad (281)$$

$$\Rightarrow -(r - r_0) = \frac{K'}{\rho} t \quad (282)$$

$$\Rightarrow (r_0 - r) = \frac{K'}{\rho} t \quad (283)$$

Again,

$$\alpha = [\text{degree of reaction at } (t = t_0)] = \frac{W_0 - W}{W_0} = \frac{\text{Change in wt.}}{\text{Initial wt.}} \quad (284)$$

# Continued...

Since, the weight decreases with time. So, degree of reduction ( $\alpha$ ) expressed as

$$\text{Degree of reduction } (\alpha) = \frac{\text{Initial wt.} - \text{Final wt.}}{\text{Initial wt.}} \quad (285)$$

$$\alpha = \frac{W_0 - W}{W_0} = 1 - \frac{W}{W_0} = 1 - \left( \frac{\frac{4}{3}\pi r^3 \rho}{\frac{4}{3}\pi r_0^3 \rho} \right) = 1 - (r/r_0)^3 \quad (286)$$

$$\Rightarrow \left( \frac{r}{r_0} \right)^3 = 1 - \alpha \quad (287)$$

$$\Rightarrow r/r_0 = (1 - \alpha)^{1/3} \quad (288)$$

$$\Rightarrow r = r_0 (1 - \alpha)^{1/3} \quad (289)$$

Replacing the in equation (289) in equation (283), the equation becomes

$$\Rightarrow [r_0 - r_0(1 - \alpha)^{1/3}] = \frac{K' t}{\rho} \quad (290)$$

# Continued...

$$\Rightarrow r_0[1 - (1 - \alpha)^{1/3}] = \frac{K't}{\rho} \quad (291)$$

$$\Rightarrow r_0[1 - (1 - \alpha)^{1/3}] = \frac{K't}{\rho} \quad (292)$$

The above equation (292) is known as **Mckewan relation or model**.

If we will take the experimental data and plot  $[1 - (1 - \alpha)^{1/3}]$  vs  $t$  and getting a straight line, then we can say reduction reaction obeys Mckewan relation.

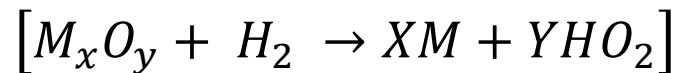
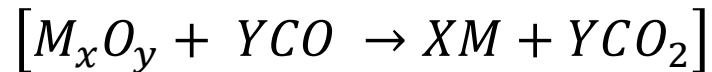
## **Factors affecting the reaction rate kinetics:**

- The physical state of the reactants and products.
- The concentrations of the reactants and products.
- The temperature or pressure at which the reaction occurs.
- Whether or not any catalysts are present in the reaction.

# Continued...

**REACTION IN LUMPS:** Steps followed during reaction in lump are given by

1. Diffusion of reductant gas CO/H<sub>2</sub> through boundary surface.
2. Diffusion of reductant gas CO/H<sub>2</sub> through macro pore.
3. Diffusion of reductant gas CO/H<sub>2</sub> through micro pore.
4. Diffusion of reductant gas CO/H<sub>2</sub> through product layer.
5. Reaction between CO/H<sub>2</sub> gas & Metal Oxide



**Example:**  $Fe_2O_3 + 3CO/H_2 = 2Fe + 3CO_2/H_2O(\uparrow)$

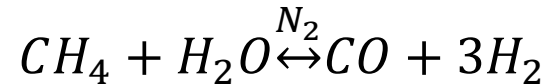
6. Diffusion of product gas CO<sub>2</sub>/H<sub>2</sub>O through product layer.
7. Diffusion of product gas CO<sub>2</sub>/H<sub>2</sub>O through micro pore.
8. Diffusion of product gas CO<sub>2</sub>/H<sub>2</sub>O through macro pore.
9. Diffusion of product gas CO<sub>2</sub>/H<sub>2</sub>O through boundary layer/surface.



# Continued...

## IMPORTANT NOTES:

- ❑ Reformed Natural Gas: It is defined as the gas that produces due to reaction between  $CH_4$  with  $H_2O$  using  $N_2$  catalyst.



- ❑ Degree of Reduction: It is defined as the ratio of amount of  $O_2$  removed at any time (t) to that of total possible amount of removal oxygen.

$$\text{Degree of reduction}(\alpha) = \frac{\text{Amount of } O_2 \text{ removed at time t}}{\text{Total possible } O_2 \text{ removal}}$$

- ❑ Metallization: It is defined as the ratio of metal Fe to that of total Fe present in Fe and its oxides.

$$\text{Metallization} = \frac{\text{Metal Fe}}{\text{Total Fe}}$$

$$\text{Degree of Metallization} = \text{Metallization} \times 100$$

# **Assignment – 4(a)**

Q.1 –Explain the positive and negative deviation of real solutions from ideal behavior with the help of suitable examples.

Q.2 –State the principal application of Gibbs-Duhem equation during phase transformation.

Q.3 –Why most of the Gibbs free energy-composition curves are followed “U” shape?

Q.4–State and explain the major techniques, that is mostly employed for solvus curve determination.

Q.5 –How the rate-controlling step is determined and state its importance.