LECTURE-26

TYPES OF REACTION:

There are basically two types of reactions existing. The differences between two reactions are given below

Homogeneous Reaction	Heterogeneous Reaction
- It takes place entirely within one phase where reactants and products both are in one phase as well as reaction carry out in that phase.	- It involves more than one phase. Example: slag-metal reaction; molten slag is in one phase and molten metal in another phase, reaction takes place at interface.
- Reaction occurs in the bulk i.e. within the phase.	- Reaction occurs not in bulk but at the interface.
- Rate of chemical reaction is proportional to the volume of the phase.	- Rate of chemical reaction to the interfacial area between the two or more phases

Continued…

Homogeneous Reaction	**Heterogeneous Reaction**
- No adsorption and desorption are involved in homogeneous reaction	- Heterogeneous reaction involves following steps (a) Absorption of reactants into the interfacial layer (b) Chemical reaction between absorbed components (c) Desorption of products into the phase.
- Reaction mechanism is not complex **Example:** Reaction between gas molecules to produce gaseous products	- Reaction mechanism is complex. **Example:** Transfer of a element or ion from molten slag to molten metal in a refining process.

Continued…

Most of the metallurgical reactions are heterogeneous. The main types of heterogeneous reactions are discussed below:

<u>Gas – Solid :</u> Reaction of oxide with $\left({}^{CO}/_{H_2}\right)$ gas oxidation of metal

<u>Example:</u>

$$Fe_2O_2(s) + 3CO(g) \rightarrow 2Fe + 3CO_2$$

$$2Fe + O_2 \rightarrow 2FeO$$

<u>Gas –Liquid:</u> Gaseous reduction in hydro-metallurgy.

<u>Liquid – Liquid:</u> Metal – slag reaction

Continued…

Liquid – Solid: Leaching and corrosion reactions

Example: Leaching of sulphide with liberation of elemental of S

$$\mathrm{CuS^{+} + \ 2Fe^{3+}\ (ferric) \rightarrow \ Cu^{2+} + \ S + 2\ Fe^{2+}(ferrous)}$$

Cementation process:

$$\mathrm{Cu^{2+}\ (cupric) + \ Fe \ \rightarrow Cu\ (metallic\ copper) + \ Fe^{2+}(ferrous)}$$

Solid – Solid:

Example: Reduction of ZnO with C as

$$\mathrm{ZnO + C \ \rightarrow Zn + CO}$$

Metallothermic reaction

$$\mathrm{Cr_2O_3 + \ 2Al \ \rightarrow \ Cr_2 + \ Al_2O_3}$$

Continued…

In metallurgy,

- The reaction kinetics are principally employed to study the Solid-Gas reactions. Till yet, the major studies have been done on Gas interaction with solid porous pellets.
- The reduction of iron ore pellets by the reduct gas (CO, H_2) mainly depends on pellet size, composition of pellet and volume of pore spaces available for reaction.
- Moreover the interface thickness, rate of gas diffusion, temperature and pressure gradient plays very vital role during the reduction of pellets.

Continued…

Reaction of Flat Plate: Let us consider a small plate of material having area and thickness d. For the first instant let's assume that any one of the surface has been exposed to a reacting gas.

During the course of the reaction let's assume the thickness of the product produced is 'y' and with increase in time that thickness gets increased. If the diffusion of reacting gas through the product layer is the rate controlling step, then rate of the reaction is given by

$$Rate\ of\ reaction = \frac{dw}{dt} = \frac{D.A.C}{y} \qquad (293)$$

[Where, w – Weight of product after time t, D – Diffusion co-efficient

A – Area of the surface available for reaction

C – Concentration]

Continued…

Since , Weight (w) = volume × Density = (Area × Length) × Density

= A. y. ρ (294)

Put equation (294) in equation (293), we have

$$\frac{d(A.y.\rho)}{dt} = \frac{D.A.C}{y} \tag{295}$$

$$\Rightarrow \frac{dy}{dt} = \left(\frac{D.C}{\rho}\right) \times \frac{1}{y} \tag{296}$$

Since $\frac{DC}{\rho} = constant = K$ (suppose), then equation (296) becomes

$$\frac{dy}{dt} = \frac{K}{y} \tag{297}$$

$$\Rightarrow \int ydy = K \int dt \tag{298}$$

$$\Rightarrow y^2 = Kt \tag{299}$$

The above equation (299) is known as **Parabolic law**.

LECTURE-27

JOHNSON – MEHL'S EQUATION:

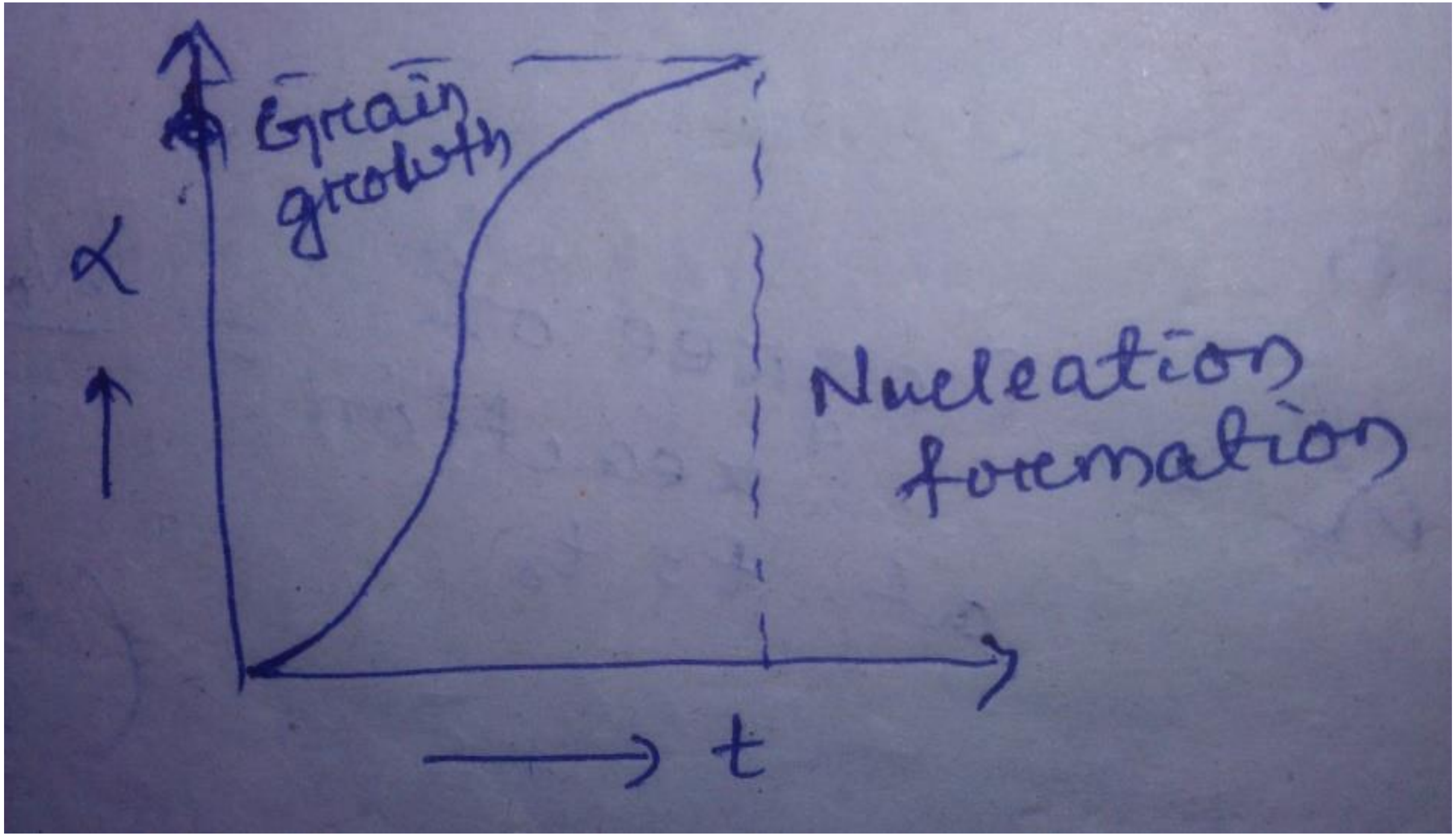

Fig- Graph of α vs t

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JOHNSON – MEHL'S EQUATION:

- ☐ It is based on α vs t graph.
- ☐ Initially, rate of reaction(α) increase with time to a fixed extent with a faster rate. But, after maximum point the rate of reaction (α) increase with time with a slower rate.
- ☐ It is used to find out the dimension & order of reaction.

Relation between rate of reaction and time defined by the following equation

$$\frac{d\alpha}{dt} = K^n \, t^{n-1}(1-\alpha) \qquad (300)$$

$$\Rightarrow \int \frac{d\alpha}{1-\alpha} = K^n \int t^{n-1}dt \qquad (301)$$

$$\Rightarrow -\ln(1-\alpha) = \frac{K^n t^n}{n} \qquad (302)$$

Continued…

$$\Rightarrow \ln(1-\ \alpha)^{-1} = \ln\left(\frac{1}{1-\alpha}\right) = \frac{K^n t^n}{n} \tag{303}$$

$$\Rightarrow \frac{1}{(1-\alpha)} = \exp\left(\frac{K^n t^n}{n}\right) \tag{304}$$

$$\Rightarrow \alpha = 1 - \left[{}^{1}/_{\exp\left(\frac{K^n t^n}{n}\right)}\right] \tag{305}$$

<u>OR</u>

From equation (303), we can also write as

$$\Rightarrow \log({}^{1}/_{1-\alpha}) = \frac{1}{2.303}\ (K' t)^n \tag{306}$$

[Where $K' = {}^{K}/_{n^{1/n}}$]

Continued…

$$\Rightarrow \log\log\left({}^{1}/_{1-\alpha}\right) = n\log K' + \ n\log t - \log(2.303) \tag{307}$$

$$\Rightarrow \ \int \frac{d\alpha}{1-\ \alpha} = \ K^{n} \ \int t^{n-1}\, dt \tag{308}$$

$$\Rightarrow \ln\left(\frac{1}{1-\ \alpha}\right) = \ \left(\frac{K'}{n^{1/n}}\right)^{n} \ = \ (K')^{n}\ t^{n} \tag{309}$$

$$\Rightarrow \log\left(\frac{1}{1-\ \alpha}\right) = \ \frac{\left(K'\right)^{n}\ t^{n^{n}}}{2.303} \tag{310}$$

$$\Rightarrow \log\log\left(\frac{1}{1-\ \alpha}\right) = n\log K' + \ n\log t - \log 2.303 \tag{311}$$

Continued…

Boundary Layer Thickness (t):

- ❑ When a fluid past to the rigid interface of an immersed body or flows over a fixed impermeable wall, it is a necessary condition that the velocity is zero at any fixed point or surface.
- ❑ The extent of modification in flow character depends upon the viscosity magnitude.
- ❑ For the streamlined body along with fluid flow having very small viscosity value , the modification effect becomes confined within a very narrow region around the solid surfaces is known as boundary layer.
- ❑ Within the boundary layer the fluid velocity changes rapidly changes that's gives a steep gradient in shearing stress

Continued…

- A more precise criterion of well-defined laminar boundary layer thickness is the flow with high Reynolds number but within the laminar flow.

Controlling Factors to control the reductant gas diffusion

The different rate controlling factors which control the overall rate of reduction are given below:

1) Boundary Layer Control

- In boundary layer control is based on control of diffusion gas and heat through the boundary layer around each particle. The diffusion rate of the reduct gas through the boundary layer is usually proportional to the concentration gradient of the gas across the boundary layer and further the heat flow rate through the particles is proportional with the temperature gradient across the boundary layer.

Continued…

- In most direct reduction process contact among solids and gas is achieved by means of counter current movement of preheated gas and solids movement. The general application boundary control mechanism can be observed during blast furnace operation

2) Phase Boundary Reaction Control

- The chemical reaction at the FeO-Fe interface is the rate controlling factor. Since In this case the reduction rate per unit area of the rest iron oxides is remained constant with time and this mechanism is known as “Phase Boundary Reaction Control”.
- In this case, the counter diffusion of both reduct and product gas over the outer reduced layer is very fast in spite of same reduct gas concentration over both the reacting and particle surface.

Continued…

- In this case, the reaction rate at the Fe-FeO interface is controlled the overall reduction rate and this mechanism is preferably happen at the beginning of reduction known as phase boundary reaction.

3) Gaseous Diffusion Control

- The mass rate of inward reduct gas flow and outward product gas flow across the reduced Fe layer can control the reduction rate of iron oxides is called as “Gaseous Diffusion Control” which usually occurs in large sized particles.
- When rate controlling step is the gaseous diffusion, the inward diffusion rate of reduct gas and outward diffusion rate of product gas through the porous outer Fe layer is slower than the overall rate of reaction.
- In this case, the reduct gas concentration decreases with increase in product gas concentration at the interface. The variation in the gas composition is lower down the reduction rate till to produce a pseudo steady state.

Continued…

4) Mixed Control

- The combination of both Phase Boundary Reaction Control and Gaseous Diffusion Control mechanism in controlling the reduction rate is termed as “Mixed Control”.
- In mixed control, the gas boundary layer acts along with two other such as gaseous diffusion and phase boundary reaction to predict the overall rate of reaction.