Iron Making and Steel Making
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Module – 02
Lecture – 10
Kinetics of gas solid reaction: iron oxide reduction Part 02

Welcome.This is module 2,lecture number 10. Kinetics of gassolidreduction:Iron oxide reduction Part 2.In the last lecture, we have discussed the concept of shrinking core model and derived the time evolution of fractional reaction of solid reductant for chemically controlled process and gas film mass transport controlled process, using shrinking core model.

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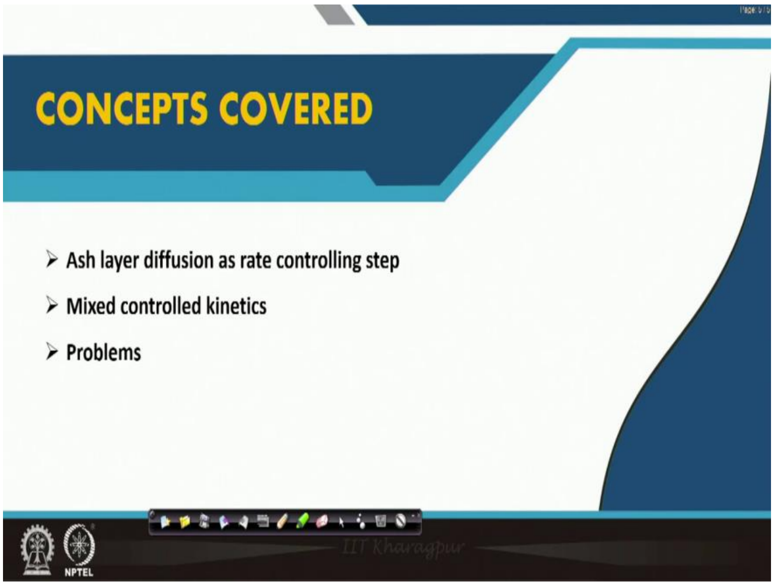

CONCEPTS COVERED

- Ash layer diffusion as rate controlling step
- Mixed controlled kinetics
- Problems

In this lecture, we will derive similar correlation for gas diffusion through the ash layer asthe rate controlling step.We also discuss the mixed controlled situation, followed by numerical problems.

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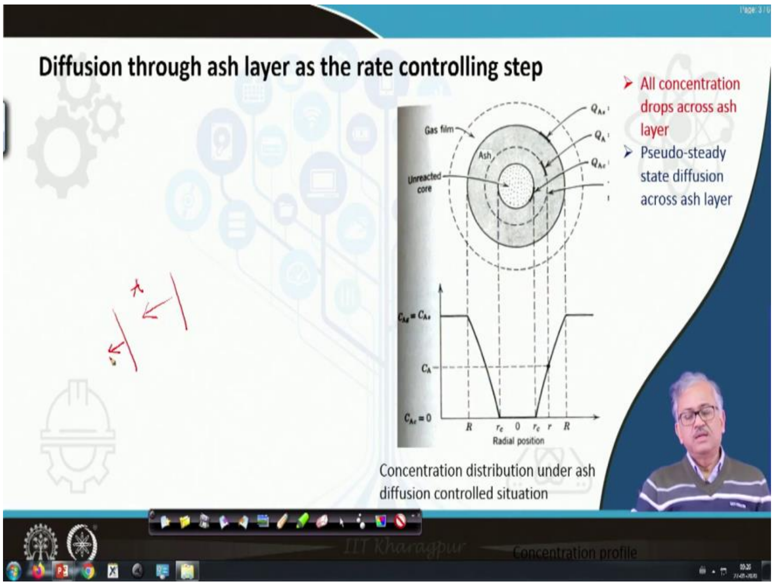

Diffusion through ash layer as the rate controlling step

- All concentration drops across ash layer
- Pseudo-steady state diffusion across ash layer

Concentration distribution under ash diffusion controlled situation

First, diffusion through the ash layer may be assumed at steady state. This is logical because when a gaseous species crosses two fixed boundaries, the process comes to a steady state after some time from the onset of the process. Frankly speaking, the boundary at the unreacted core-ash layer interface is not stationary and it is shrinking with time. But it is reasonable to that the time scale of this boundary shrinking is much smaller compared to the time scale of diffusion of gas through the ash layer, considering large difference of density between solid and gas by around 1000 times. In other words it will not be illogical to assume the reaction interface to be stationary during te diffusion of the gas through ash layer and therefore, this situation may be called pseudo-steady state.

So, under steady state, the mass balance statement may be given as:

$$-\frac{1}{b}\frac{dN_B}{dt} = -\frac{dN_A}{dt} = 4\pi R^2 Q_{AS} = 4\pi r_c^{\,2} Q_{Ac} = 4\pi r^2 Q_A = 4\pi r^2 D\frac{dC_A}{dr} \tag{1}$$

Now integrating over ash layer yields:

$$\left(-\frac{1}{b}\frac{dN_B}{dt}\right)\int_R^{r_c}\frac{dr}{r^2} == 4\pi D\int_{C_{AS}=C_{Ag}}^{C_{Ac}} dC_A$$

$$-\frac{dN_A}{dt}\left(\frac{1}{r_c}-\frac{1}{R}\right)=-\frac{1}{b}\frac{dN_B}{dt}\left(\frac{1}{r_c}-\frac{1}{R}\right)=4\pi D_e\left(C_{Ag}-C_{Ae}\right)$$

(2)

Now, integrating with respect to time:

$$-\int_R^{r_c}\left(r_c-\frac{r_c^2}{R}\right)dr_c=\frac{D\left(C_{Ag}-C_{Ac}\right)}{\rho_B}\int_0^t dt$$

$$t=\frac{\rho_B R^2}{6bDC_{Ag}}\left(1-3\left(\frac{r_c}{R}\right)^2+2\left(\frac{r_c}{R}\right)^3\right)$$

(3)

The time for complete reaction may be given as:

$$\tau=\frac{\rho_B R^2}{6bD\left(C_{Ag}-C_{Ae}\right)}$$

(4)

Finally the relationship between fractional reaction and time may be given as:

$$\frac{t}{\tau}=1-3\left(1-X_B\right)^{\frac{2}{3}}+2\left(1-X_B\right)$$

(5)

Interesting, unlike in chemically controlled process and gas film mass transfer controlled process, it is observed that time for complete reaction is directly proportional to R2; while it was proportional to R in other two cases.

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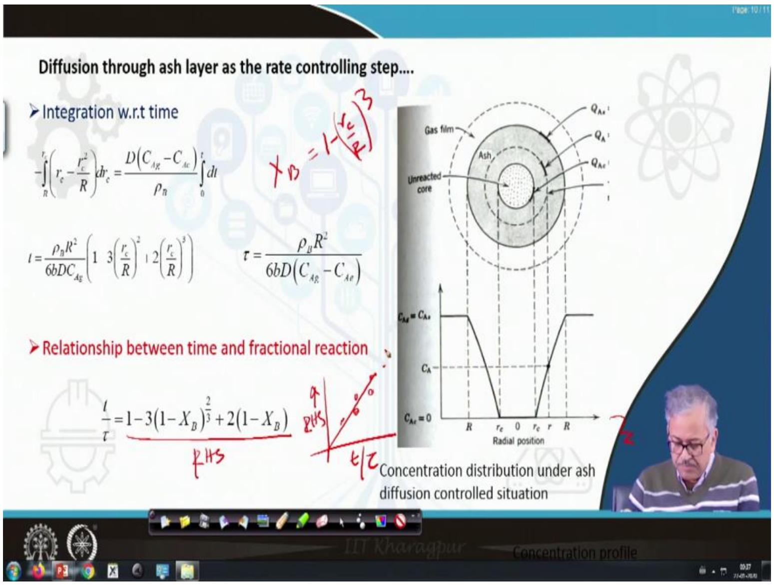

Diffusion through ash layer as the rate controlling step….

- Integration w.r.t time

$$-\int_R^{r_c}\left(r_c-\frac{r_c^2}{R}\right)dr_c=\frac{D\left(C_{Ag}-C_{Ac}\right)}{\rho_B}\int_0^t dt$$

$$t=\frac{\rho_B R^2}{6bDC_{Ag}}\left(1-3\left(\frac{r_c}{R}\right)^2+2\left(\frac{r_c}{R}\right)^3\right)\qquad \tau=\frac{\rho_B R^2}{6bD\left(C_{Ag}-C_{Ac}\right)}$$

$$X_B=1-\left(\frac{r_c}{R}\right)^3$$

- Relationship between time and fractional reaction

$$\frac{t}{\tau}=\underbrace{1-3\left(1-X_B\right)^{\frac{2}{3}}+2\left(1-X_B\right)}_{RHS}$$

Concentration distribution under ash diffusion controlled situation

So, if experimental data in terms of fractional conversional term, $1-3(1-X_B)^{\frac{2}{3}}+2(1-X_B)$ is plotted on y axis and dimensionless time t/τ on x-axis and if it follows a straight line passing through origin, the reaction may be considered as ash layer diffusion controlled.

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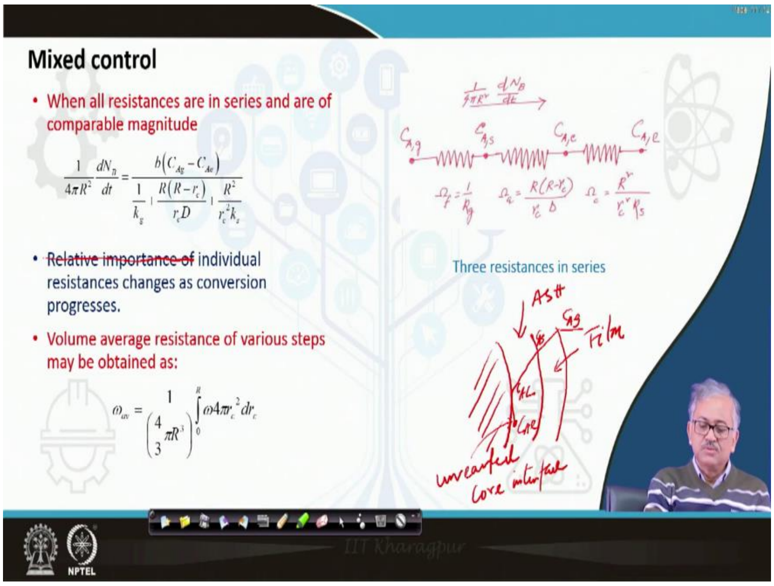


Mixed control

- When all resistances are in series and are of comparable magnitude

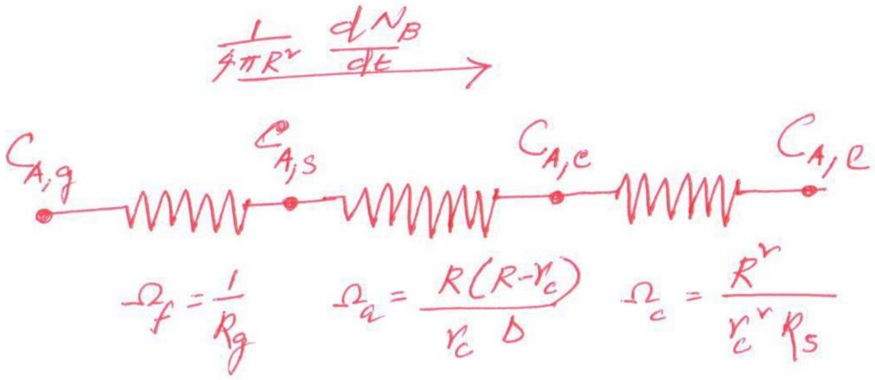
$$\frac{1}{4\pi R^2}\frac{dN_B}{dt}=\frac{b\left(C_{Ag}-C_{Ac}\right)}{\frac{1}{k_g}+\frac{R\left(R-r_c\right)}{r_cD}+\frac{R^2}{r_c^2k_s}}$$

- ~~Relative importance of~~ individual resistances changes as conversion progresses.
- Volume average resistance of various steps may be obtained as:

$$\omega_{av}=\frac{1}{\left(\frac{4}{3}\pi R^3\right)}\int_0^R \omega 4\pi r_c^2\,dr_c$$

Three resistances in series

So, let us analyze the mixed control situation.As I have said when the resistance of two or more steps are comparable and resistance are in series, then the overall resistance could be obtained by adding the resistances in series and the rate of the process will be mixed controlled. The electrical analogy for rate of reaction for a gas solid reaction involving three resistances in series is shown below:



Individual resistances for gas film mass transport, ash layer diffusion, and chemical reaction are also shown, which could be derived from the mass balance equations for individual rate controlled steps as described above and in previous lecture. Finally the rate expression for the mixed controlled step may be given as:

$$-\frac{1}{4\pi R^2}\frac{dN_B}{dt} = \frac{b\left(C_{Ag} - C_{Ae}\right)}{\frac{1}{k_g} + \frac{R\left(R - r_c\right)}{r_c D} + \frac{R^2}{r_c^{\,2} k_s}} \tag{6}$$

It could be observed that individual resistances (except gas film mass transfer resistance) depends on r_c and subsequently those will change significantly during the progress of reaction. Volume average resistance could be obtained by following integration:

$$\omega_{av} = \frac{1}{\left(\frac{4}{3}\pi R^3\right)} \int_0^R \omega 4\pi r_c^{\,2} dr_c$$

Finally it yields the rate expression in terms of average resistance during the course of reduction as follows:

$$-\frac{1}{4\pi R^2}\left\langle \frac{dN_A}{dt} \right\rangle = \frac{\left(C_{Ag} - C_{Ae}\right)}{\frac{1}{k_g} + \frac{R}{2D} + \frac{3}{k_s}}$$

Or, in terms of solid reductant, B:

$$-\langle \frac{dN_B}{dt} \rangle = 4\pi R^2 \times b \times \frac{\left(C_{A,g} - C_{A,e}\right)}{\left(\frac{1}{k_g} + \frac{R}{2D} + \frac{3}{k_s}\right)}$$

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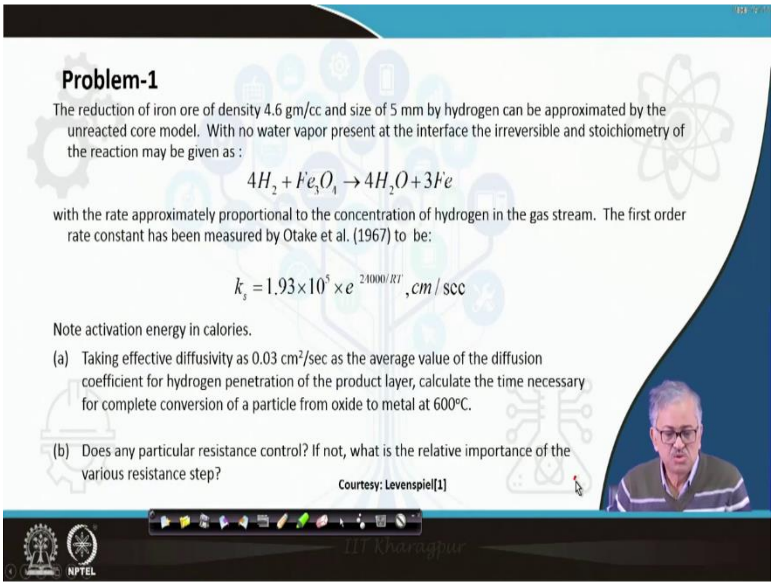

Problem-1

The reduction of iron ore of density 4.6 gm/cc and size of 5 mm by hydrogen can be approximated by the unreacted core model. With no water vapor present at the interface the irreversible and stoichiometry of the reaction may be given as :

$$4H_2 + Fe_3O_4 \rightarrow 4H_2O + 3Fe$$

with the rate approximately proportional to the concentration of hydrogen in the gas stream. The first order rate constant has been measured by Otake et al. (1967) to be:

$$k_s = 1.93 \times 10^5 \times e^{24000/RT}, cm/sec$$

Note activation energy in calories.

(a) Taking effective diffusivity as 0.03 cm^2/sec as the average value of the diffusion coefficient for hydrogen penetration of the product layer, calculate the time necessary for complete conversion of a particle from oxide to metal at 600°C.

(b) Does any particular resistance control? If not, what is the relative importance of the various resistance step?

Courtesy: Levenspiel[1]

Now, we will discuss two problems. Problem number 1: Let us consider the reduction of iron ore (magnetite, Fe_3O_4) of density 4.6 g/cc and size of 5 mm by hydrogen. Unreacted core model is asked to apply. Magnetite reduction by hydrogen may be safely considered irreversible because of very low requirement of equilibrium hydrogen at the interface.

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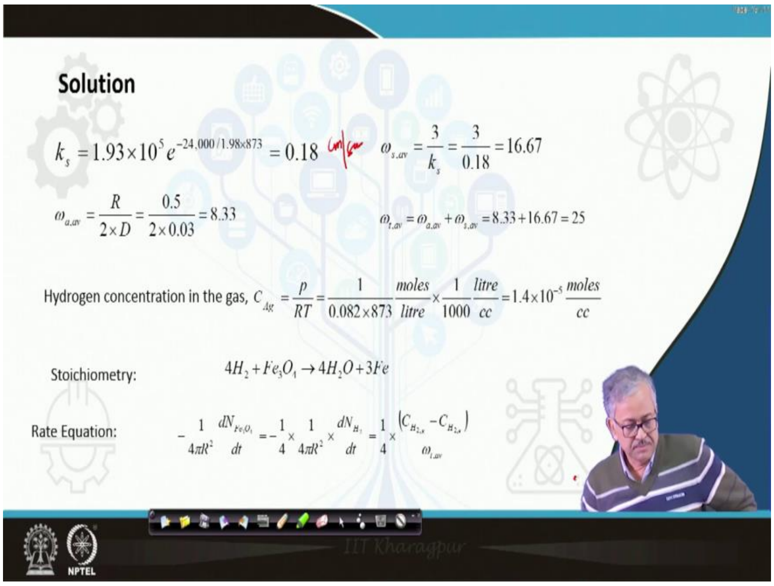

Solution

$k_s = 1.93\times10^5 e^{-24,000/1.98\times873} = 0.18$ cm/sec $\omega_{s,av} = \frac{3}{k_s} = \frac{3}{0.18} = 16.67$

$\omega_{a,av} = \frac{R}{2\times D} = \frac{0.5}{2\times0.03} = 8.33$ $\omega_{t,av} = \omega_{a,av} + \omega_{s,av} = 8.33 + 16.67 = 25$

Hydrogen concentration in the gas, $C_{Ag} = \frac{p}{RT} = \frac{1}{0.082\times873}\frac{moles}{litre}\times\frac{1}{1000}\frac{litre}{cc} = 1.4\times10^{-5}\frac{moles}{cc}$

Stoichiometry: $4H_2 + Fe_3O_4 \rightarrow 4H_2O + 3Fe$

Rate Equation: $-\frac{1}{4\pi R^2}\frac{dN_{Fe_3O_4}}{dt} = -\frac{1}{4}\times\frac{1}{4\pi R^2}\times\frac{dN_{H_2}}{dt} = \frac{1}{4}\times\frac{(C_{H_2,g} - C_{H_2,s})}{\omega_{t,av}}$

Solution:

$$k_s = 1.93\times10^5 e^{-24,000/1.98\times873} = 0.18$$

The average resistance of chemical reaction.

$$\omega_{s,av} = \frac{3}{k_s} = \frac{3}{0.18} = 16.67$$

The average resistance of the ash layer

$$\omega_{a,av} = \frac{R}{2\times D} = \frac{0.5}{2\times0.03} = 8.33$$

Total average resistance due to chemical reaction and average resistance of the ash layer

$$\omega_{t,av} = \omega_{a,av} + \omega_{s,av} = 8.33 + 16.67 = 25$$

Bulk hydrogen concentration, C_{H_2}

$$= \frac{p}{RT} = \frac{1}{0.082\times873}\frac{moles}{litre}\times\frac{1}{1000}\frac{litre}{cc} = 1.4\times10^{-5}\frac{moles}{cc}$$

Reaction stoichiometry:

$$4H_2 + Fe_3O_4 \rightarrow 4H_2O + 3Fe$$

Rate expression:

$$-\frac{1}{4\pi R^2}\frac{dN_{Fe_3O_4}}{dt} = -\frac{1}{4}\times\frac{1}{4\pi R^2}\times\frac{dN_{H_2}}{dt} = \frac{1}{4}\times\frac{\left(C_{H_{2,g}} - C_{H_{2,e}}\right)}{\omega_{t,av}}$$

Integration over time

$$-\int_R^0 r_c{}^2 dr_c = \frac{1}{4}\times\frac{\left(C_{H_{2,g}} - C_{H_{2,e}}\right)}{\omega_{t,av}\times\rho_{Fe_3O_4}}\times R^2\int_0^\tau dt$$

Time for complete reaction

$$\tau = \frac{4\times\omega_{t,av}\times\rho_{Fe_2O_3}\times R}{3\times\left(C_{H_{2,g}} - C_{H\,2,e}\right)} = \frac{4\times 25\times\left(\frac{4.6}{168}\right)\times 0.5}{3\times\left(1.4\times 10^{-5} - 0\right)} = 32596\sec = 9hrs$$

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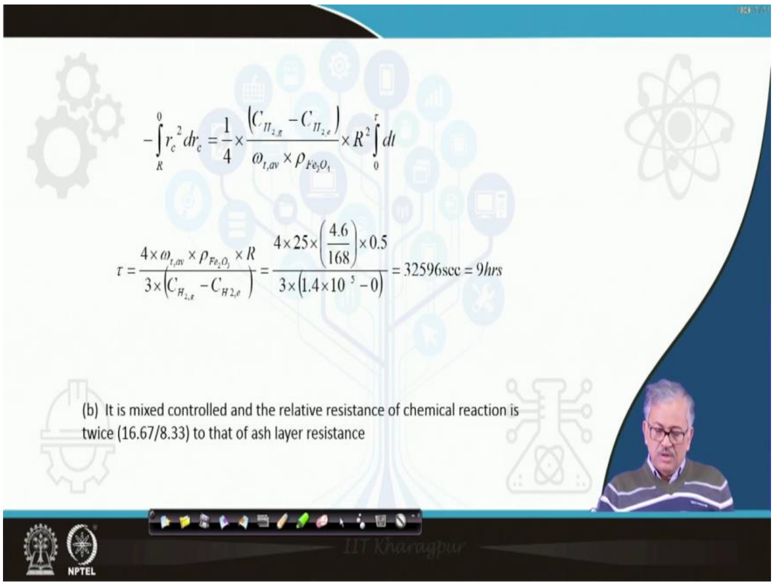

$$-\int_R^0 r_c{}^2 dr_c = \frac{1}{4}\times\frac{\left(C_{H_{2,g}} - C_{H_{2,e}}\right)}{\omega_{t,av}\times\rho_{Fe_3O_4}}\times R^2\int_0^\tau dt$$

$$\tau = \frac{4\times\omega_{t,av}\times\rho_{Fe_2O_3}\times R}{3\times\left(C_{H_{2,g}} - C_{H\,2,e}\right)} = \frac{4\times 25\times\left(\frac{4.6}{168}\right)\times 0.5}{3\times\left(1.4\times 10^{-5} - 0\right)} = 32596\sec = 9hrs$$

(b) It is mixed controlled and the relative resistance of chemical reaction is twice (16.67/8.33) to that of ash layer resistance

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Problem 2:

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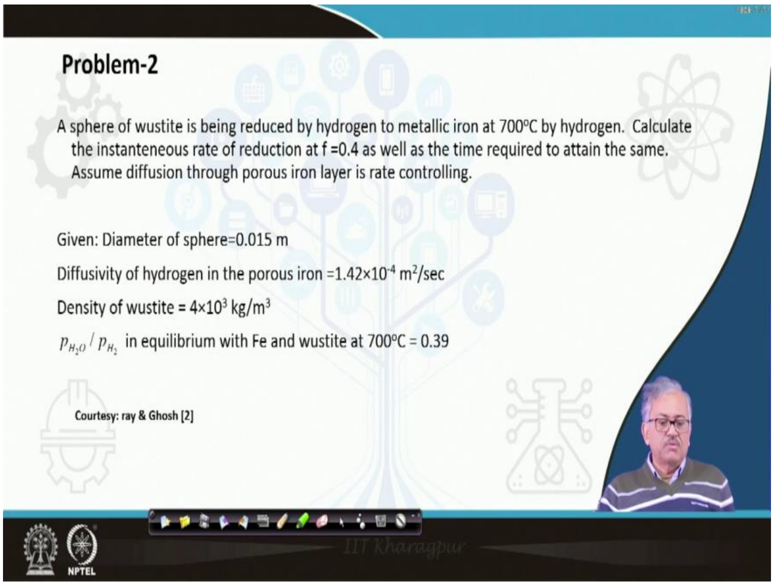

Problem-2

A sphere of wustite is being reduced by hydrogen to metallic iron at 700^oC by hydrogen. Calculate the instantaneous rate of reduction at f =0.4 as well as the time required to attain the same. Assume diffusion through porous iron layer is rate controlling.

Given: Diameter of sphere=0.015 m

Diffusivity of hydrogen in the porous iron =1.42×10^{-4} m^2/sec

Density of wustite = 4×10^3 kg/m^3

p_{H_2O}/p_{H_2} in equilibrium with Fe and wustite at 700^oC = 0.39

Courtesy: ray & Ghosh [2]

Now, we go to the problem number 2. Here we discuss a sphere of wustite is being reduced by hydrogen to metallic iron at 700^oC by hydrogen. We need to calculate the instantaneous rate of reduction at fractional reaction of 40 percent as well as the time required to attain the same. It is asked to solve the problem assuming ash layer diffusion as rate controlling step. So chemical reaction will attend equilibrium and equilibrium gas composition is given. Let us conceder the reaction is controlled by H_2O diffusion through the ash layer.

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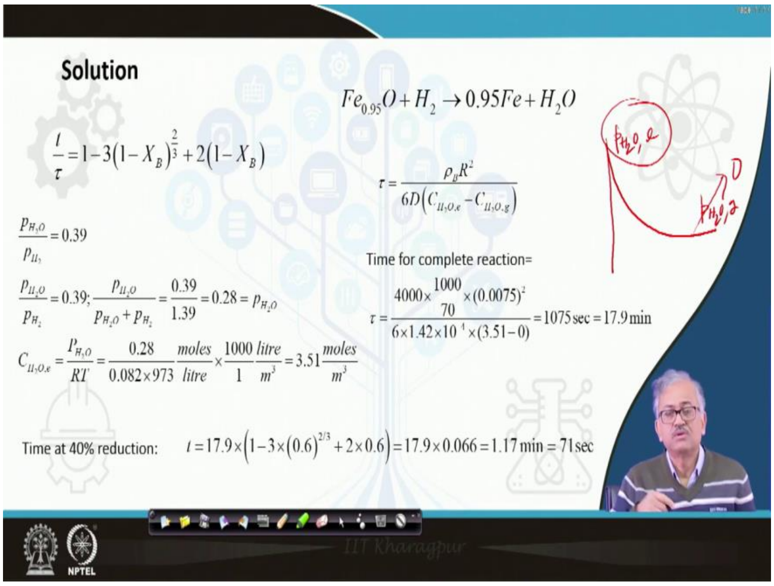

Solution

$$Fe_{0.95}O + H_2 \rightarrow 0.95Fe + H_2O$$

$$\frac{t}{\tau} = 1 - 3(1 - X_B)^{\frac{2}{3}} + 2(1 - X_B)$$

$$\tau = \frac{\rho_B R^2}{6D\left(C_{H_2O,e} - C_{H_2O,g}\right)}$$

$$\frac{p_{H_2O}}{p_{H_2}} = 0.39$$

$$\frac{p_{H_2O}}{p_{H_2}} = 0.39; \frac{p_{H_2O}}{p_{H_2O} + p_{H_2}} = \frac{0.39}{1.39} = 0.28 = p_{H_2O}$$

$$C_{H_2O,e} = \frac{P_{H_2O}}{RT} = \frac{0.28}{0.082\times973}\frac{moles}{litre}\times\frac{1000}{1}\frac{litre}{m^3} = 3.51\frac{moles}{m^3}$$

Time for complete reaction=

$$\tau = \frac{4000\times\frac{1000}{70}\times(0.0075)^2}{6\times1.42\times10^{-4}\times(3.51-0)} = 1075\,\text{sec} = 17.9\,\text{min}$$

Time at 40% reduction: $t = 17.9\times\left(1 - 3\times(0.6)^{2/3} + 2\times0.6\right) = 17.9\times0.066 = 1.17\,\text{min} = 71\,\text{sec}$

Solution:

Reaction stoichiometry:

$$Fe_{0.95}O + H_2 \rightarrow 0.95Fe + H_2O$$

$$\frac{t}{\tau} = 1 - 3\left(1 - X_B\right)^{\frac{2}{3}} + 2\left(1 - X_B\right)$$

$$\tau = \frac{\rho_B R^2}{6D\left(C_{H_2O,e} - C_{H_2O,g}\right)}$$

Unlike magnetite reduction, Wustite reduction may not be considered irreversible because of large amount of hydrogen is needed, or H_2O should be below a certain limit at the interface to maintain the equilibrium. Equilibrium volume ration of H_2O/H_2 is given as 0.39.

The H_2O concentration at the interface may be calculated by applying the gas law:

$$\frac{p_{H_2O}}{p_{H_2}} = 0.39$$

$$\frac{p_{H_2O}}{p_{H_2}} = 0.39; \frac{p_{H_2O}}{p_{H_2O} + p_{H_2}} = \frac{0.39}{1.39} = 0.28 = p_{H_2O}$$

$$C_{H_2O,e} = \frac{P_{H_2O}}{RT} = \frac{0.28}{0.082 \times 973} \frac{moles}{litre} \times \frac{1000}{1} \frac{litre}{m^3} = 3.51 \frac{moles}{m^3}$$

The total time for conversion:

$$\tau = \frac{4000 \times \frac{1000}{70} \times (0.0075)^2}{6 \times 1.42 \times 10^{-4} \times (3.51 - 0)} = 1075 \sec = 17.9 \min$$

Time required for 40% conversion

$$t = 17.9 \times \left(1 - 3 \times \left(0.6\right)^{2/3} + 2 \times 0.6\right) = 17.9 \times 0.066 = 1.17 \min = 71 \sec$$

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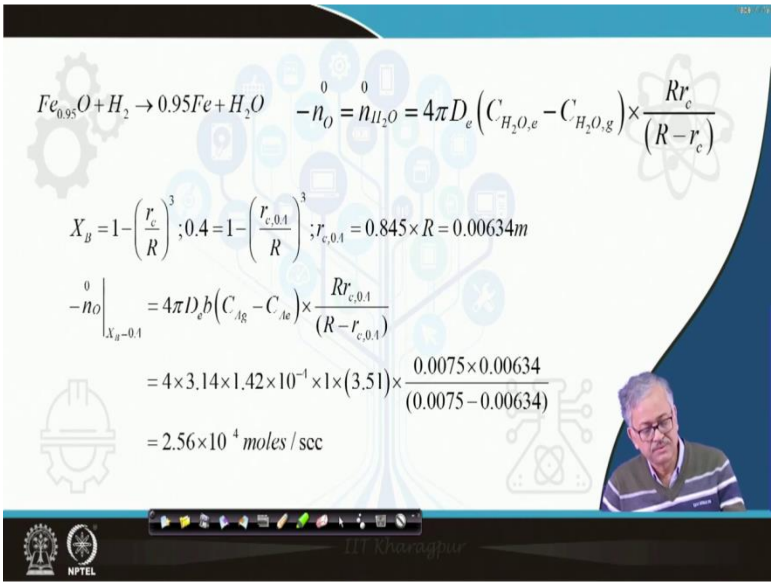

$Fe_{0.95}O+H_2 \rightarrow 0.95Fe+H_2O$ $\quad -\overset{0}{n}_O = \overset{0}{n}_{H_2O} = 4\pi D_e\left(C_{H_2O,e}-C_{H_2O,g}\right)\times\frac{Rr_c}{(R-r_c)}$

$X_B = 1-\left(\frac{r_c}{R}\right)^3; 0.4 = 1-\left(\frac{r_{c,0.4}}{R}\right)^3; r_{c,0.4} = 0.845\times R = 0.00634m$

$-\overset{0}{n}_O\Big|_{X_B=0.4} = 4\pi D_e b\left(C_{Ag}-C_{Ae}\right)\times\frac{Rr_{c,0.4}}{(R-r_{c,0.4})}$

$= 4\times 3.14\times 1.42\times 10^{-4}\times 1\times(3.51)\times\frac{0.0075\times 0.00634}{(0.0075-0.00634)}$

$= 2.56\times 10^{-4}$ moles / sec

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Reaction stoichiometry:

$$Fe_{0.95}O+H_2 \rightarrow 0.95Fe+H_2O$$

Instantaneous rate:

$$-\overset{0}{n}_O = \overset{0}{n}_{H_2O} = 4\pi D_e\left(C_{H_2O,e}-C_{H_2O,g}\right)\times\frac{Rr_c}{(R-r_c)}$$

Instantaneous rate at 40% conversion:

$$X_B = 1-\left(\frac{r_c}{R}\right)^3; 0.4 = 1-\left(\frac{r_{c,0.4}}{R}\right)^3; r_{c,0.4} = 0.845\times R = 0.00634m$$

$$\frac{t}{\tau} = 1-3\left(1-X_B\right)^{\frac{2}{3}}+2\left(1-X_B\right)$$

$$-\overset{0}{n}_O\Big|_{X_B=0.4} = 4\pi D_e b\left(C_{Ag}-C_{Ae}\right)\times\frac{Rr_{c,0.4}}{(R-r_{c,0.4})}$$

$$= 4\times 3.14\times 1.42\times 10^{-4}\times 1\times(3.51)\times\frac{0.0075\times 0.00634}{(0.0075-0.00634)}$$

$$= 2.56\times 10^{-4}\ moles/\sec$$

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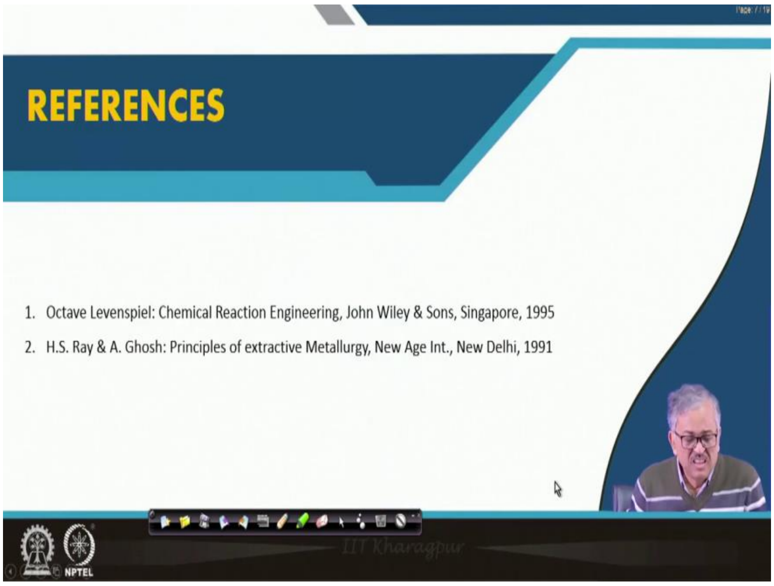

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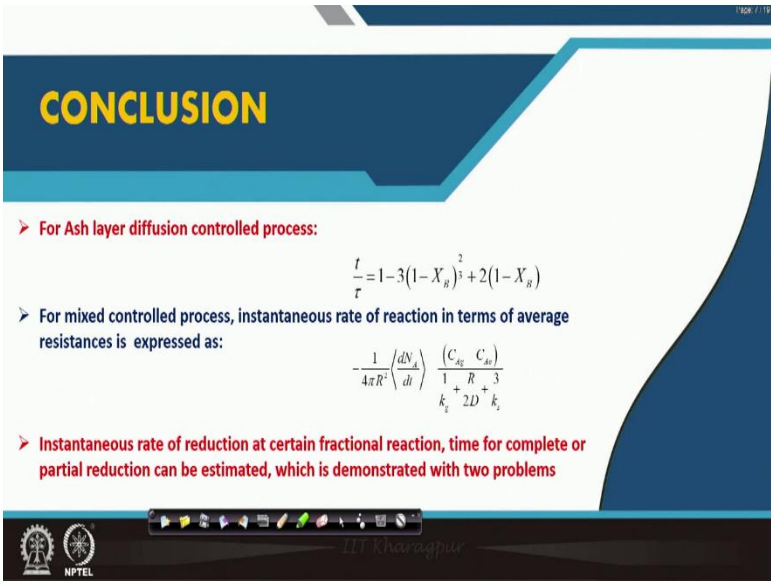
1. Octave Levenspiel: Chemical Reaction Engineering, John Wiley & Sons, Singapore, 1995
2. H.S. Ray & A. Ghosh: Principles of extractive Metallurgy, New Age Int., New Delhi, 1991

So, these are the two references.



CONCLUSION

- For Ash layer diffusion controlled process:

$$\frac{t}{\tau}=1-3\left(1-X_B\right)^{\frac{2}{3}}+2\left(1-X_B\right)$$

- For mixed controlled process, instantaneous rate of reaction in terms of average resistances is expressed as:

$$-\frac{1}{4\pi R^2}\left\langle\frac{dN_A}{dt}\right\rangle \quad \frac{\left(C_{Ag} \quad C_{Ae}\right)}{\frac{1}{k_g}+\frac{R}{2D}+\frac{3}{k_s}}$$

- Instantaneous rate of reduction at certain fractional reaction, time for complete or partial reduction can be estimated, which is demonstrated with two problems

In conclusion, following points may be noted:

1. The dimensionless correlation for fractional conversion for ash layer diffusion is:

$$\frac{t}{\tau}=1-3\left(1-X_B\right)^{\frac{2}{3}}+2\left(1-X_B\right)$$

Where,

$$\tau = \frac{\rho_B R^2}{6bD\left(C_{Ag} - C_{Ae}\right)}$$

2. For mixed controlled reaction, the rate may be expressed in terms of average resistances for film transport, ash layer diffux=sion and chemical reaction interface as follows:

$$-\langle\frac{dN_B}{dt}\rangle = 4\pi R^2 \times b \times \frac{\left(C_{A,g} - C_{A,e}\right)}{\left(\frac{1}{k_g} + \frac{R}{2D} + \frac{3}{k_s}\right)}$$

So, instantaneous rate of reduction at certain fractional reaction, time for complete or partial reduction can be estimated using these formula, which is demonstrated by these two problems.