

Ch. Reaction Kinetics

Course

KGP003

High Temperature Materials

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Ch. Reaction Kinetics

Kinetics is important as thermodynamics

Thermodynamics predicts the feasibility of a reaction and the energetic of a process

Kinetics has direct influence on engineering

Productivity

Factors affected on its increase

Both thermodynamics and kinetics are necessary for proper understanding of metallurgical processes

Ch. Reaction Kinetics

I. INTRODUCTION

Examples

1. Combustion of coal



A). Thermodynamically we can evaluate the heat generated by this reaction. However, if you would like to do this experience, coal will not burn if you don't heat it.

B). More air is blown on a piece of coal, the more it glows (red) and it will be consumed faster

Questions

Why coal, which gives off heat when it burns, has to be heated in order to make it burn?

2. Solubility of solid in a liquid

NaCl in H₂O

Why it has to be stirred to solubilize NaCl in water?

**Response of these questions as well as others
can be found in Kinetics study which is dealing with**

THE RATE OF CHEMICAL REACTIONS

Kinetics is of great economic and technical importance

Reactions are slow *Residence time in the process is long*

Plant : process is slow *Slow chemical reactions*

The productivity will be low and the rate of return on investment will also be low

Reactions are fast *Residence time in the process is short*

Plant : process is fast *Fast chemical reactions*

The productivity will be increase and the rate of return on investment will also increase

Questions

What are the factors can affect the rates of processes?

When the process is slow?

What we have to do to accelerate the process?

Kinetics is useful tool to investigate the mechanism reaction

Example: Iron dissolves readily in diluted acid, however, cooper is dissolved in presence of oxygen. It is found that cooper oxide dissolves slower than metal. This mechanism is incorrect then another mechanism must be found

Reactions always take place in steps. The slowest step determines the kinetics of whole process, which Is called rate-determining step to understand the mechanism reaction

REACTION RATE



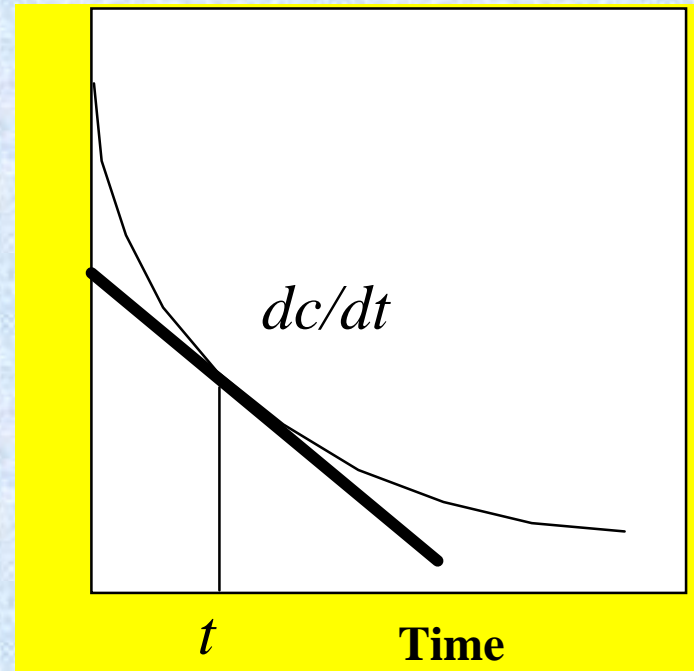
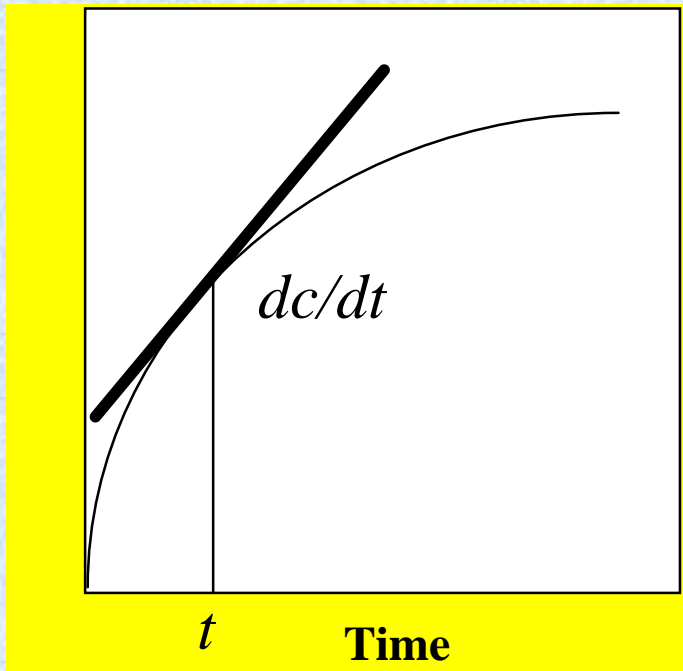
$$\text{Rate of reaction} = \frac{\text{Amount of substance transformed (or formed)}}{\text{Time of observation}}$$

C_1 — concentration of substance formed at t_1
 C_2 — its concentration at t_2

$$\text{Rate of reaction} = \frac{C_2 - C_1}{t_2 - t_1}$$

Limited case, when $C_2 - C_1$ became small

$$\text{Rate of reaction} = \frac{dC}{dt}$$

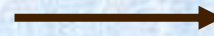


Rate of reactions vary from extremely slow to extremely fast

1. Concentration
2. Temperature
3. Mixing the phases
4. Particles size

Effect of concentration of reactions

Increasing [] reactant

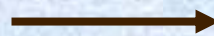


Reaction rates increase

uneconomical

Effect of temperature

Increasing T°C



Reaction rates increase

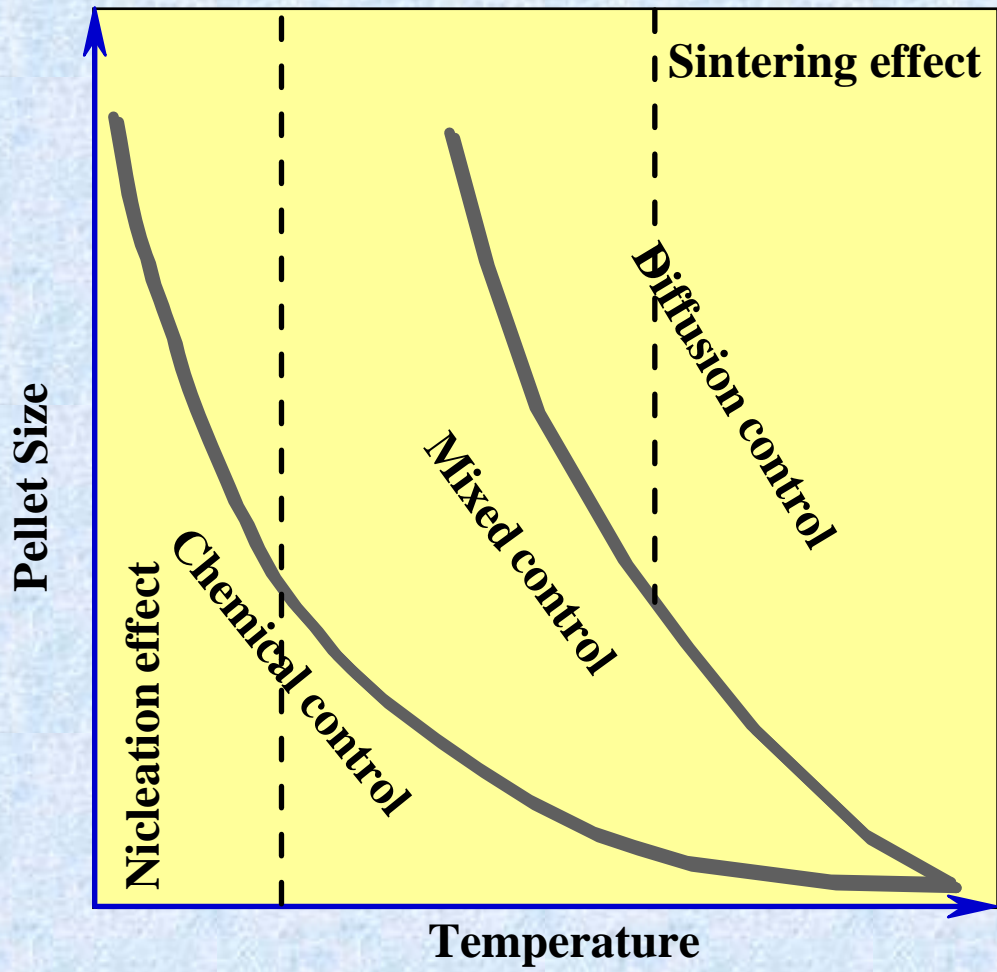
Effect of mixing the phases

Stirring of solid in liquid

Stirring of solid in liquid Changing gas flow in gas-solid reaction

Effect of particle size

Usually very fine grinding is necessary for slow reactions



Homogeneous and Heterogeneous Reactions

Homogeneous Reactions

One phase

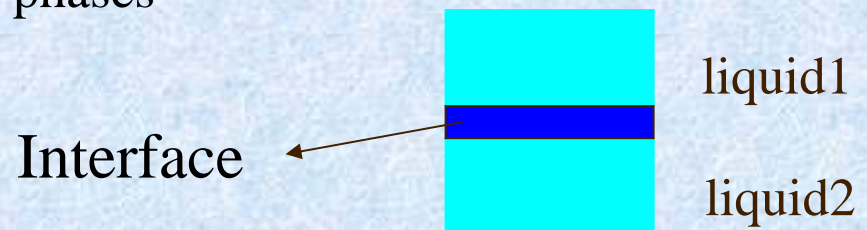
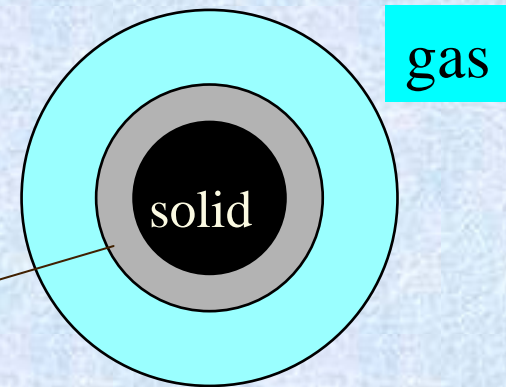
Reactants and products of reaction
Are either in the gas or in the liquid phase

Heterogeneous Reactions

Between more phases

Interface is the surface
that can separate these phases

Boundary between two phases



All heterogeneous reactions fall into 5 groups,
based on the nature of the interface

Solid-Gas

Solid-Solid

Liquid-Liquid

Solid-Liquid

Liquid-Gas

Interface	Type	Examples
Solid-gas		Physical
		Adsorption
		Chemical
	$S_1 + G \longrightarrow S_2$	Oxidation of metals
	$S_1 \longrightarrow S_2 + G$	Decomposition of carbonates or sulfates
	$S_1 + G_1 \longrightarrow S_2 + G_2$	Oxidation of sulfides or gaseous reduction of oxides

Interface

Type**Examples**

Solid-liquid**Physical:**

Melting

Dissolution-crystallization

Chemical:

Leaching

Cementation

Solid-Solid**Physical:**

Sintering, phase transformation

Chemical:

Reduction of oxides by carbon

Reduction of oxides or halides by metals

Liquid-liquid**Physical:**

Distillation-condensation

Absorption

Chemical:

Steelmaking by pneumatic processes

Absorption of gases in water

Interface

Type

Examples

Liquid-liquid

L_1



L_2

Solvent extraction

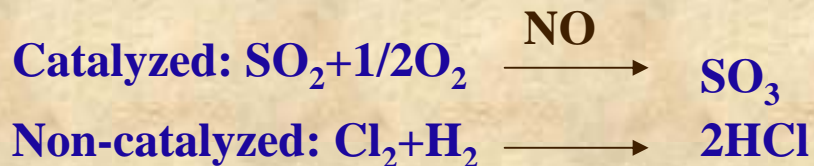
Slag-metal reactions

Liquid metal-liquid metal extraction

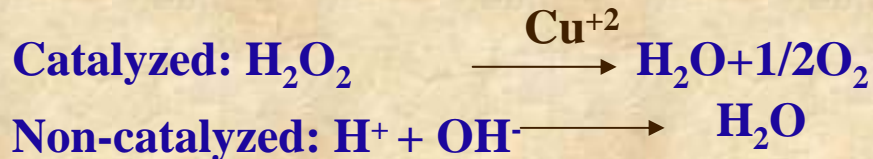
Catalysis

Homogeneous

Gas phase

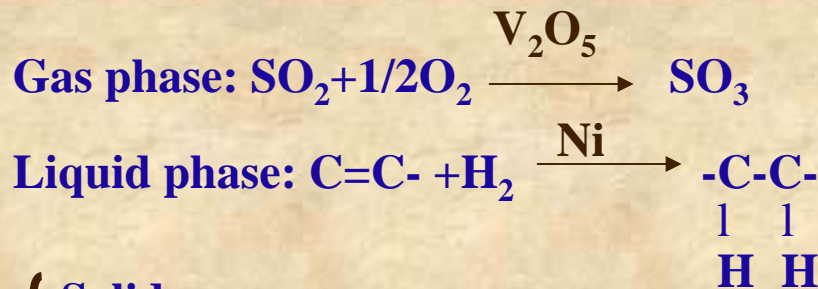


Liquid phase



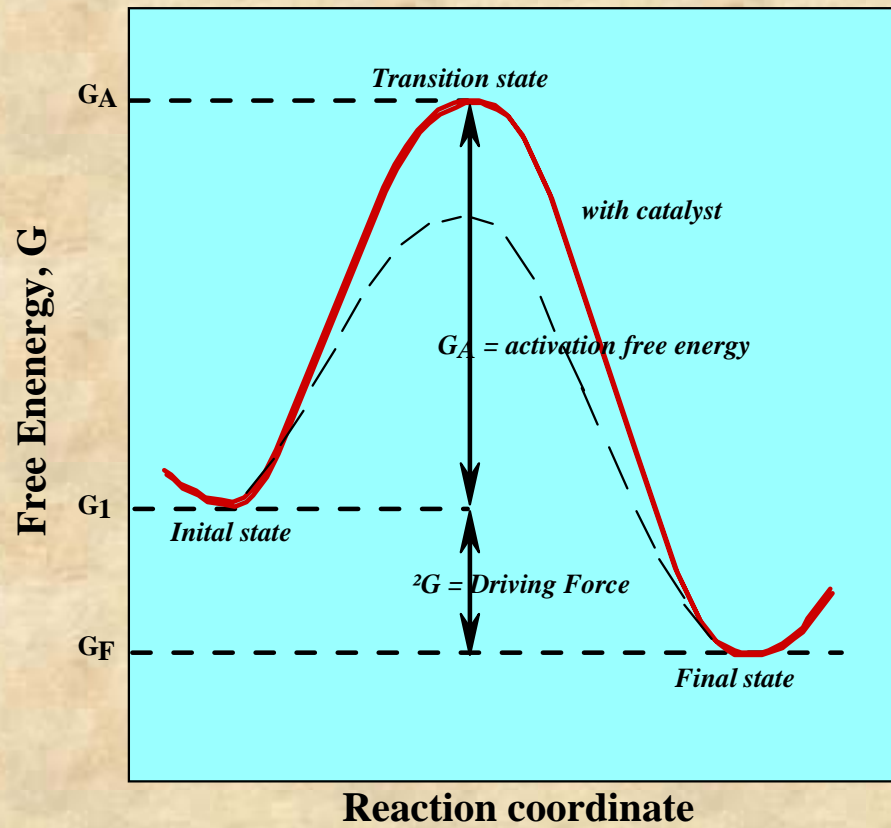
Heterogeneous

Catalyzed
(contact catalysis)



Non-catalyzed

- Solid-gas Gas-liquid
- Solid-liquid Liquid-liquid
- Solid-solid Metallurgical processes



Examples for heterogeneous reactions

Type	Application	Examples
Catalyzed	Chemical industry	NH ₃ synthesis (Fe), NH ₃ oxidation (Pt), H ₂ SO ₄ manufacture (V ₂ O ₅), hydrogenation of oils (Ni), etc.
Non-catalyzed	Nature	Formation and disintegration of rock
	Engineering	Corrosion of metals, combustion of coal
	Metallurgy	Leaching, roasting, and smelting of ores, Refining of metals
	Chemical industry	Cement, calcium carbide, calcium cyanamide, Fertilizers, burning sulfur for sulfuric acid Manufacture, ceramics, Nitration and sulfonation of organic compounds, refining of petroleum fractions by solvent extraction

Homogenous Reactions

Here, we will discuss on the factors controlling the rate of a homogeneous reactions

Ions in solution or molecules in gas are in constant movement



They collide with each other



They may separate unchanged

They may react in a different ways

Electrostatic Attraction

Transfer of proton or electron

The frequency of collisions depends on

**Concentration of the ions in solution or
the gas molecules in the gas phase**

Temperature

Homogenous Reactions

Effect of concentration or Pressure

The rate constant $A+B \longrightarrow C+D$

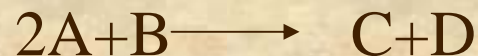
[A] ML	[B] ML	Rate ML.s	k
2.1×10^{-6}	2.1×10^{-6}	2.1×10^{-5}	0.36×10^7
4.2	2.1	3.2	0.36
6.3	2.1	4.8	0.36
6.3	2.1	9.5	0.36
6.3	2.1	14.3	0.36

$$\text{Rate} = k[A][B]$$

Homogenous Reactions

Effect of concentration or Pressure

The rate constant



[A] ML	[B] ML	Rate ML.s	<i>k</i>
1.6×10^{-4}	2.1×10^{-6}	2.6×10^{-6}	1.02×10^2
3.2	3.1	10.0	0.98
6.4	3.1	41.0	1.00
1.6	4.7	2.6	1.02
1.6	6.2	2.6	1.02

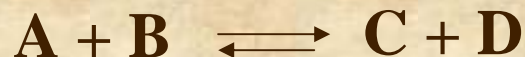
$$Rate = k'[A]^2$$

Homogenous Reactions

The equilibrium constant

The rate of a reaction increases with increased concentration of reactants

The equilibrium constant of the reaction is not influenced

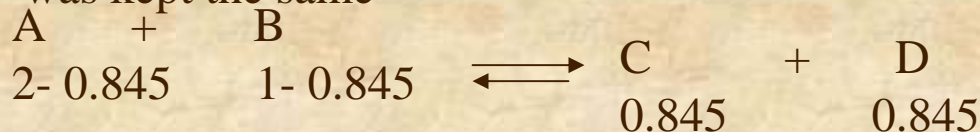


- 1** When [A] and [B] were used 66.7% were converted to C + D



$$K = \frac{0.667 \times 0.667}{(1 - 0.667) \times (1 - 0.667)} = 4$$

- 2** When twice [A] was used and [B] was kept the same 84.5% product formation



$$K = \frac{0.845 \times 0.845}{(2 - 0.845) \times (1 - 0.845)} = 4$$

Homogenous Reactions

Order of Reaction

First order, second order

Higher orders are rare, but fractional orders are common

The order of a reaction does not necessarily coincide with either its molecularity or correspond to the stoichiometric equation

First-order reactions



$$\frac{d[A]}{dt} = k[A]$$

Wilhelmy's Law

1850

If a is the initial concentration of A, x is the amount reacted after the lapse of time t , then the amount remaining in the given volume is

$$a - x = [A] \text{ at any } t$$

$$\frac{d(a-x)}{dt} = k(a-x)$$

Since a is const

$$-\frac{d(a-x)}{dt} = \frac{d(x)}{dt}$$

$$\frac{d(x)}{dt} = k(a-x)$$

Homogenous Reactions

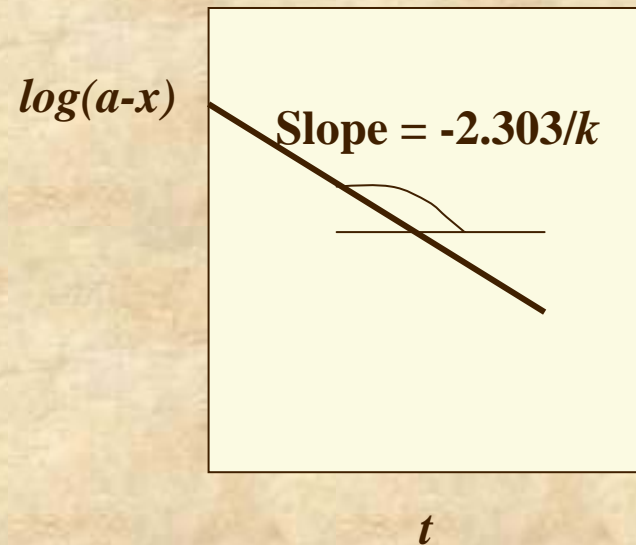
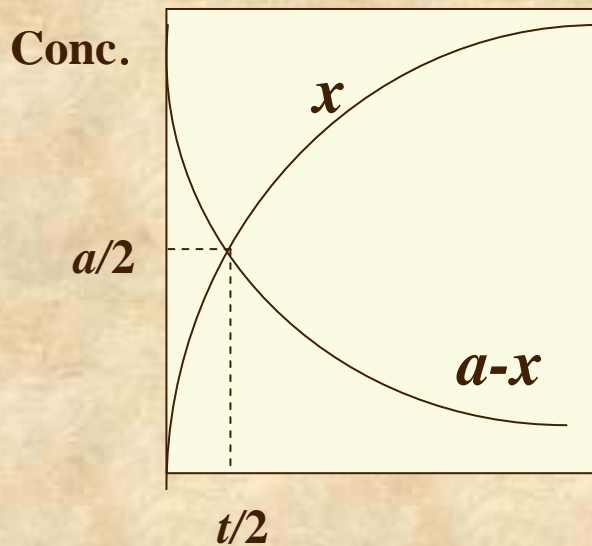
Order of Reaction

$$t = \frac{1}{k} \ln \frac{a}{(a-x)}$$

$$\int_0^t dt = \frac{1}{k} \int_0^x \frac{d(x)}{(a-x)}$$

$$2.303/k \log a - 2.303/k \log(a-x)$$

Plot of t versus $\log(a-x)$ gives a straight line with a slope equal to $-2.303/k$



Homogenous Reactions

Characteristics

$$x = t_{1/2} = \frac{2.303}{k} \log 2 = \frac{0.693}{k} = \text{const}$$

The time required to reduce the concentration or pressure of reacting substance to half its initial value is a constant quantity for a given first-order reaction $t_{1/2}$ is called the half-life of the reaction

The velocity of reaction is constantly decreasing and in theory the reaction should come to an end only after an infinite period of time, when:

$$x \longrightarrow a \quad \ln a / (a-x) \quad \text{becomes very large}$$

$$t \longrightarrow \infty \quad t = \frac{1}{k} \ln \frac{a}{a-x}$$

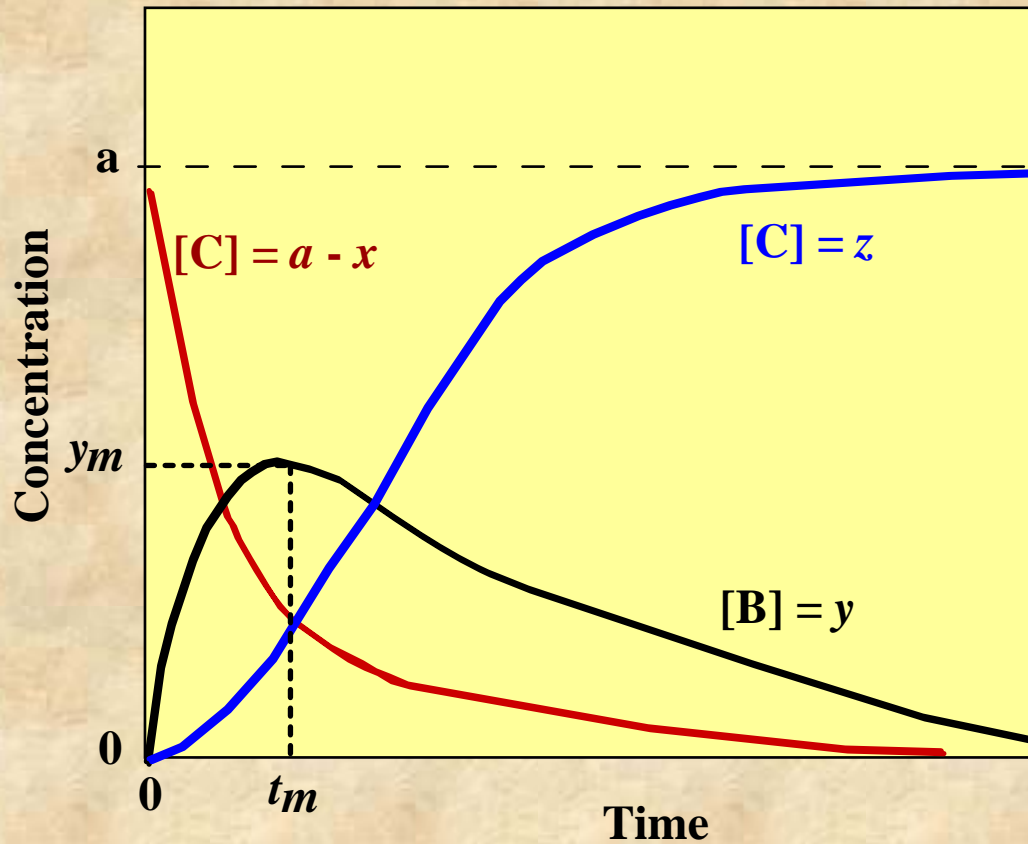
$$\frac{a}{a-x} = e^{kt}$$

$$a-x = ae^{-kt}$$

Consecutive reactions



a = initial concentration of A
 x = the amount of A transformed at t
 y = amount of B, z amount of C produced at t



Initial concentrations of B and C started at zero

$$x = y + z$$

1. Rate of transformation of A: $a-x = a x e^{-k_1 t}$ $x = a(1 - e^{-k_1 t})$ (1)

2. Rate of transformation of C is proportional to concentration of B

$$dz/dt = k_2[B] = k_2 y = k_2(x-y) \quad \text{therefore}$$

$$dz/dt + k_2 z = k_2 x \quad \text{Substituting } x \text{ from (1) we get:}$$

$$dz/dt + k_2 z = k_2 a(1 - e^{-k_1 t})$$

$$z = a \left[1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2} \right]$$

$$y = x - z$$

$$y = a(1 - e^{-k_1 t}) - a \left[1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2} \right]$$

$$y = \frac{a k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t})$$

$$y_m = a \left[\frac{k_2}{k_1} \right] \frac{k_2}{k_1 - k_2} \quad t_m = \frac{\ln \frac{k_1}{k_2}}{k_1 - k_2}$$

Second-order Reactions



If the reaction is to be second -order, when the rate depends on two concentration terms

$$-\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt}$$

$$\text{Rate} = k[\text{A}][\text{B}]$$

A and b are int. concent. of A and B respectively, and x is the amount of each that reacted after time t , then

$$\frac{dx}{dt} = k(a-x)(b-x)$$
$$\int_0^1 dt = \frac{1}{k} \int_0^x \frac{dx}{(a-x)(b-x)}$$

$$t = \frac{1}{k(a-b)} \ln \frac{b(a-x)}{a(b-x)} = \frac{2.303}{k(a-b)} \log \frac{b}{a} - \frac{2.303}{k(a-b)} \log \frac{a-x}{b-x}$$

If B is present in excess, then $a - b = -b$, and $b - x = b$

$$t = \frac{2.303}{k(b)} \log \frac{a}{a-x}$$

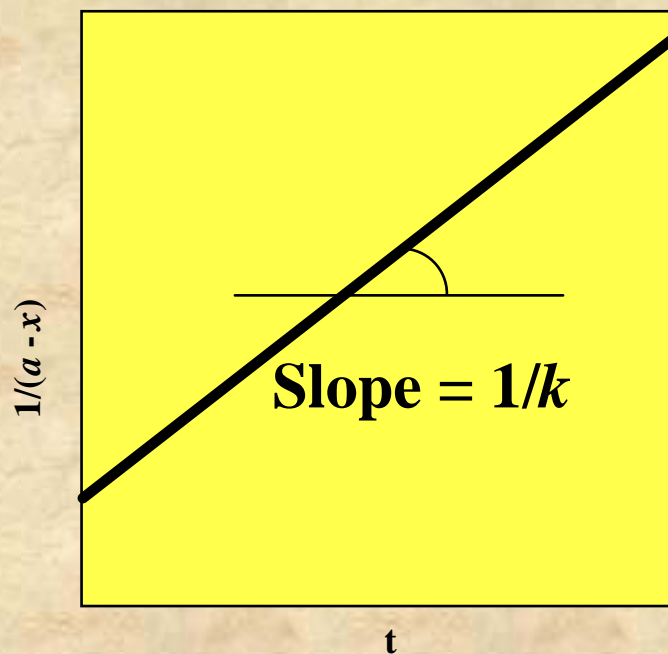
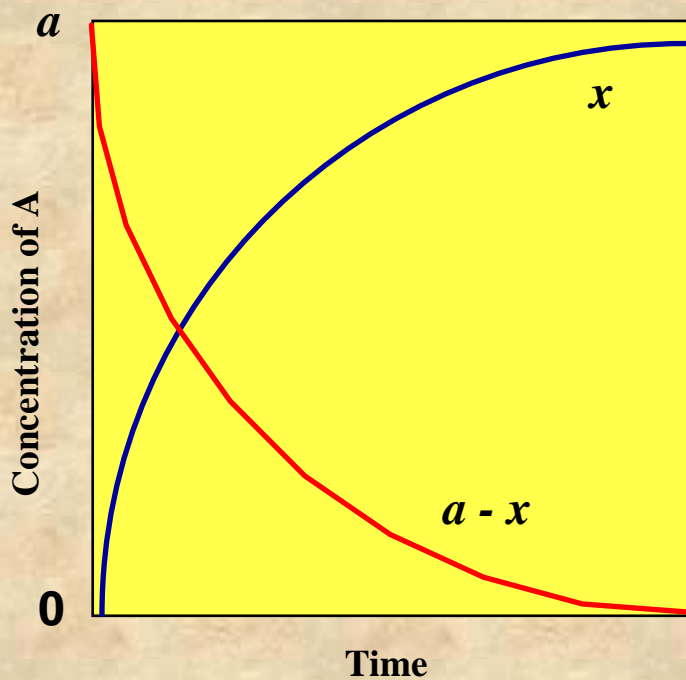
Reaction rate becomes first order, with respect to A and is independent to B, or zero eith respect to B.

If a and b are equal, then $\frac{dx}{dt} = k(a - x)^2$

$$T = 1/k \left[\frac{1}{(a - x)} - \frac{1}{a} \right]$$

$$x = 1/2a$$

$$t = 1/ka$$



Flow in a viscous medium

$$F/A = \eta dv/dr$$

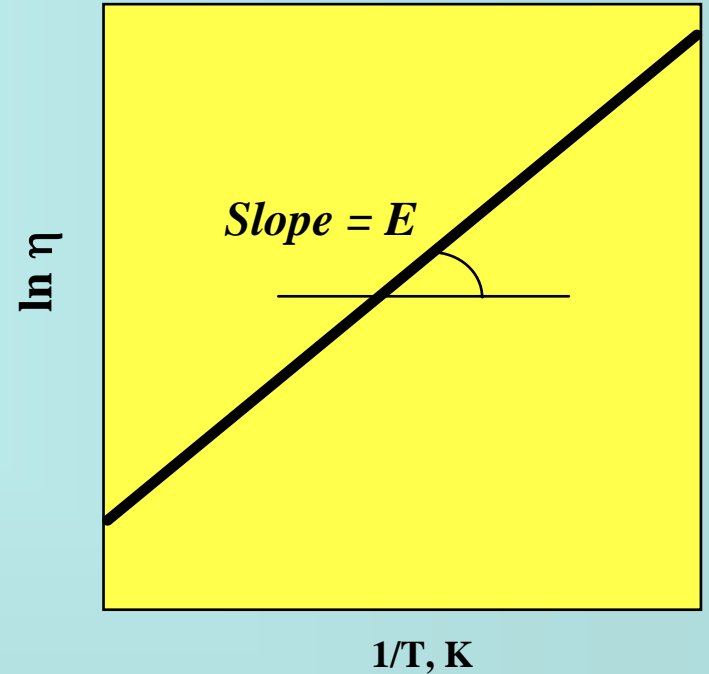
$$\eta = (\text{dynes}\cdot\text{sec})/\text{cm}^2$$

$$= \text{g}/\text{cm}\cdot\text{sec}$$

1. Liquid



$$\eta = Ae^{E/RT}$$



2. Gas

$$\eta = \frac{1}{\pi^{3/2} \sigma^2} \sqrt{mkT}$$

Contrary to liquids, the η of gases increases with increased T

Diffusion

Diffusion in gases, liquids, and solids

Fick's law

$$dn/dt = -D.A dC/dx$$

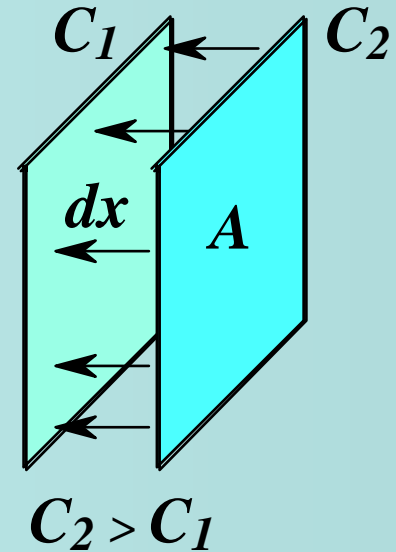
$$D = D_0 e^{-E/RT}$$

E, Kcal/mole

Solids 60 - 200

Slag (molten) 12 - 90

Aqueous solutions 1 - 6



When $E = RT$, D_0 does not become a strong function of T

Case : Liquid

$$D = RT / (6 \pi r \eta N)$$

Gases

The rate of gas diffusion is a function of its density

Graham's law

$$V_1/V_2 = d_2/d_1 \quad V_1/V_2 = M_2/M_1$$

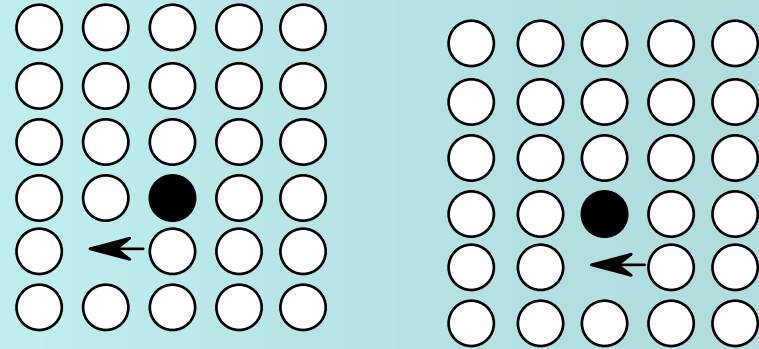
Knudsen law

Pores of solid are less than 0.1μ

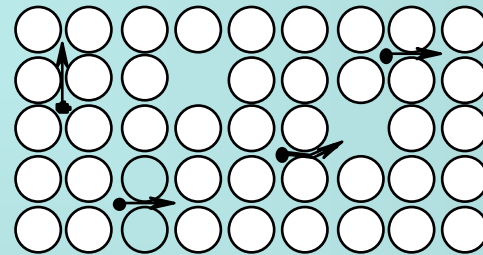
$$D_k = 9700 r \sqrt{\frac{T}{M}} \quad \text{cm}^2/\text{sec}$$

Diffusion in solids

By jumping mechanism



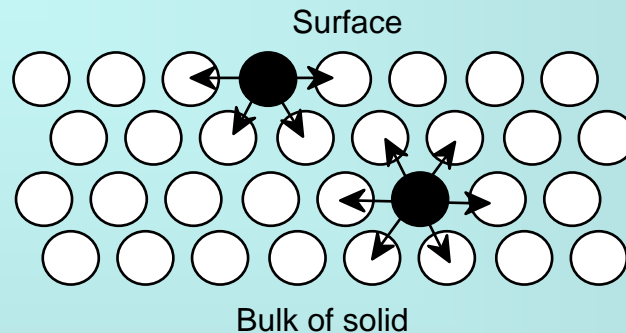
By squeezing mechanism



ADSORPTION

Adsorption. Is the accumulation of a gas, a liquid, or a dissolved substance on the surface of a solid

Desorption is the reverse process, the elimination of the absorbed substance from a surface

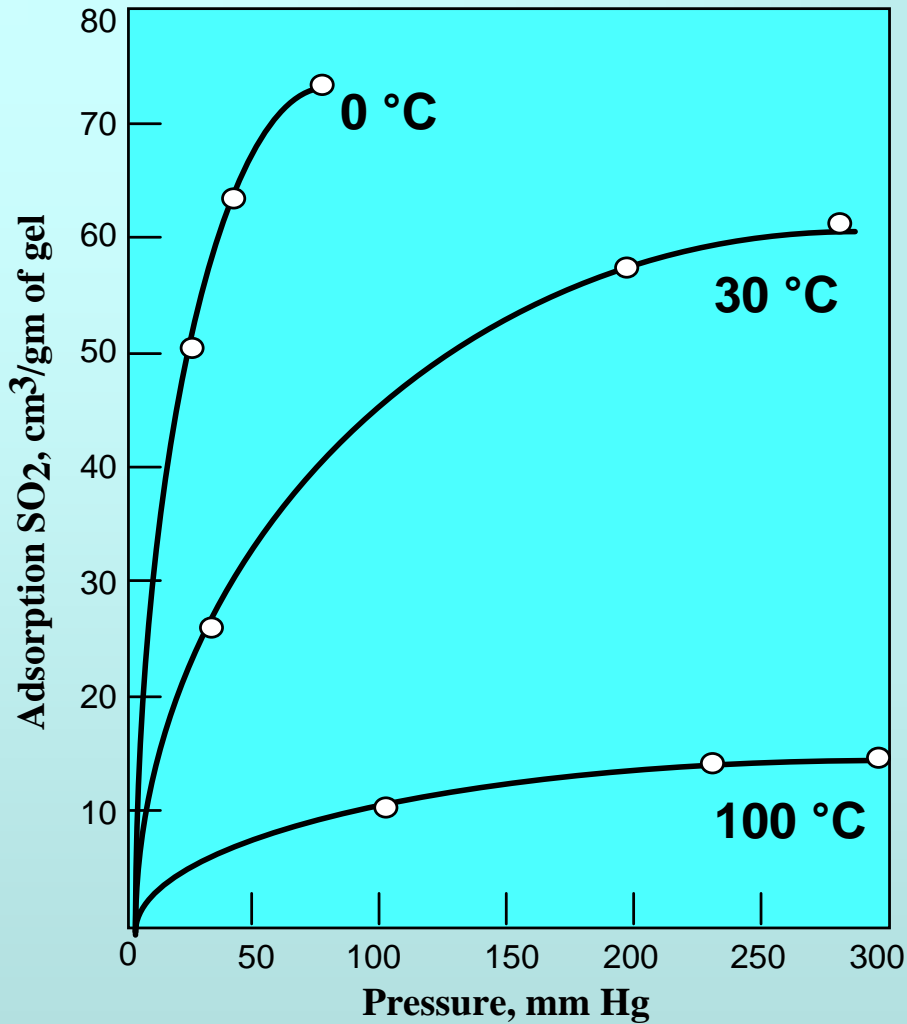


Interatomic forces acting on surface atoms as compared to those in the bulk of the solid

Adsorption Process depends on:

The properties of the solid surface

The nature of adsorbate: ionic species, a polar or a nonpolar molecule.

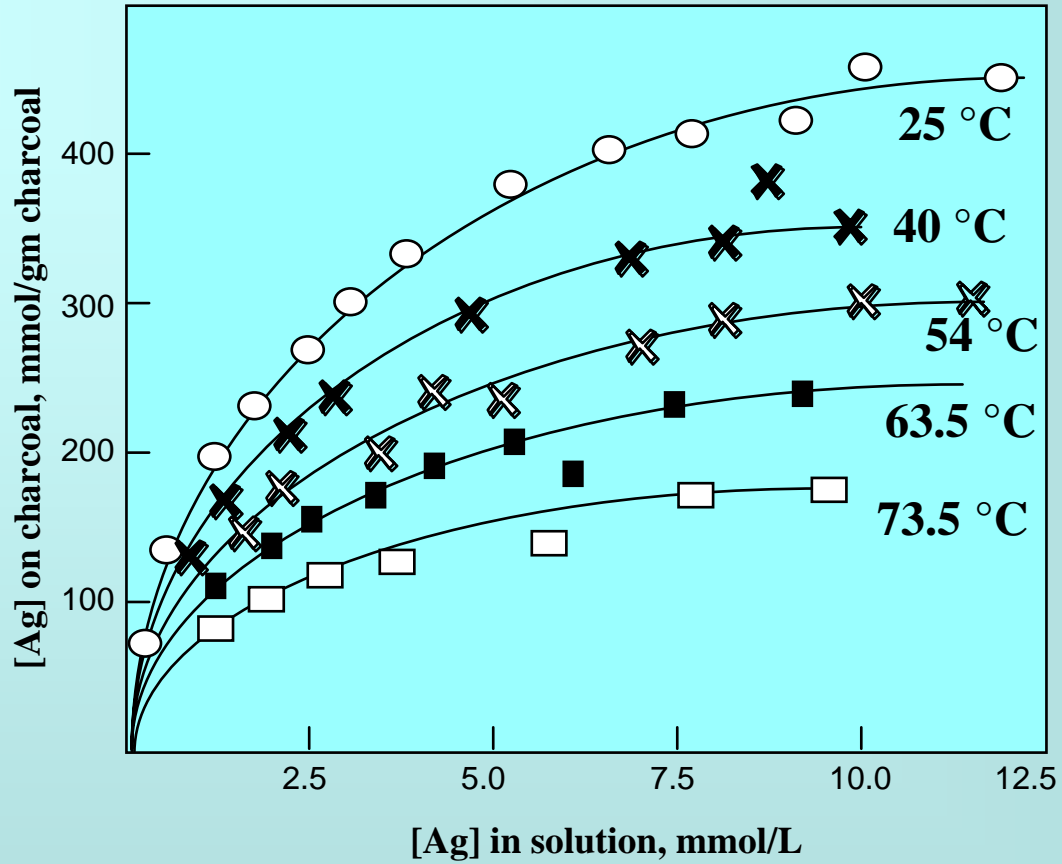


Adsorption amount of SO₂ is higher at 0°C than that 100 °C

Adsorption amount of SO₂ is higher at low pressure than at high pressure

Curves of this type are called *adsorption isotherms*

Adsorption of SO₂ on silica gel (E.B. Miller, 1920)

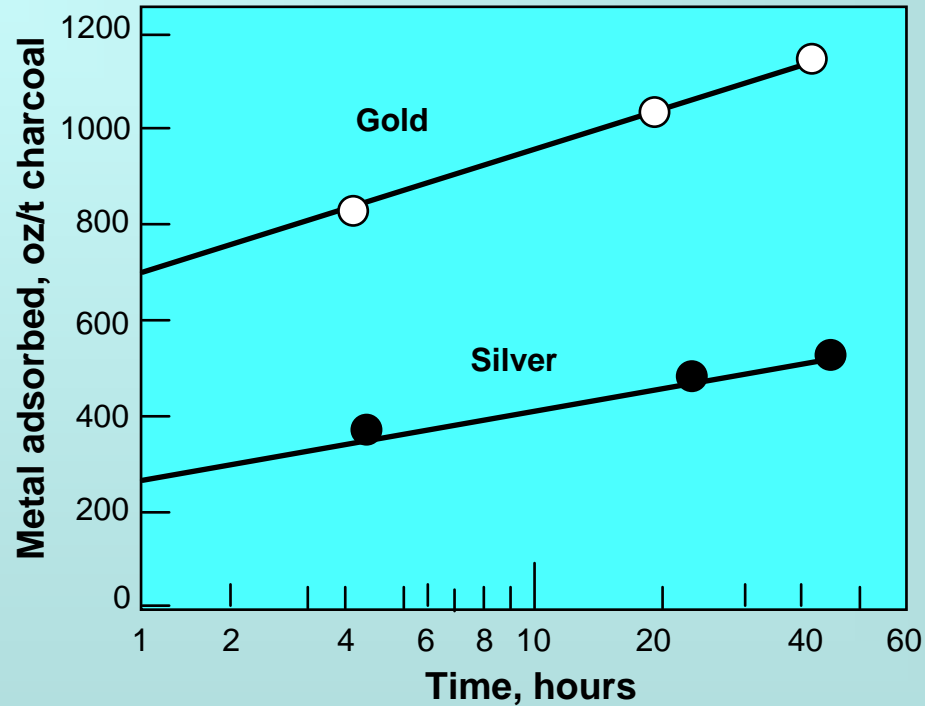


Adsorption isotherm for Ag cyanide on activated charcoal (Dixon et al. 1978)

Kinetics

The eq describing the kinetics of chemisorption is known as the Elovich eq.

$$w = k \log t$$



Adsorption of gold and silver on activated charcoal, by Gross and Scott, 1927)

Nucleation

The role of nucleation process is important in heterogeneous reactions in solids, liquids, and gases.

The formation of nuclei in the first stages of reaction may be the rate determining step.

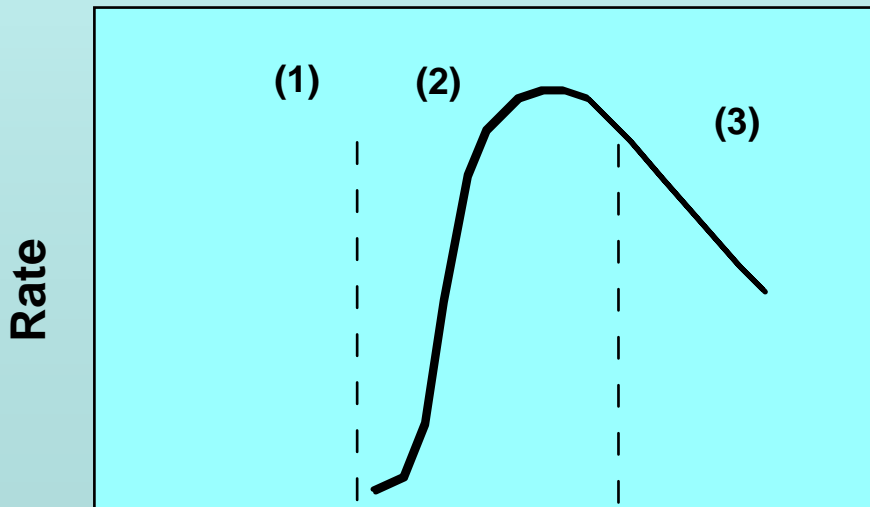
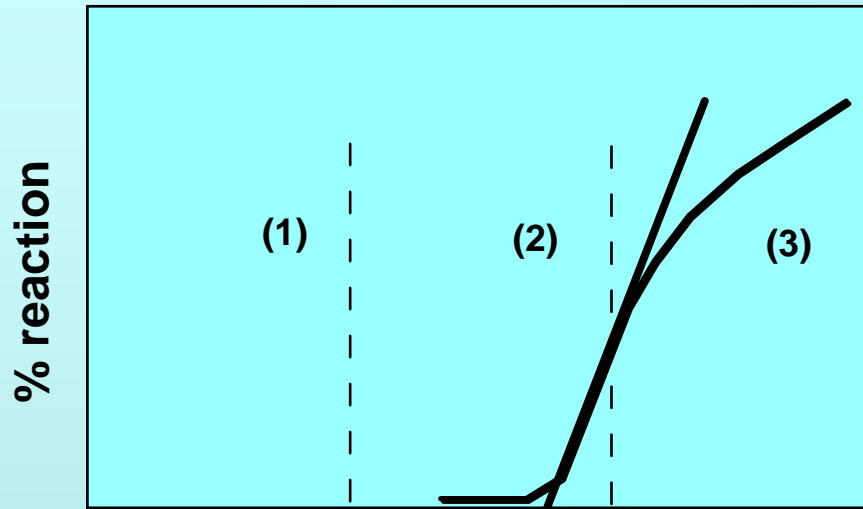
Solids: (1) Nucleation, (2) formation of the reaction interface and (3) propagation of the reaction interface

Liquids: nucleation may take place at the walls of the container.
Example: Many hydrometallurgical processes are accelerated by introducing nuclei in the solution

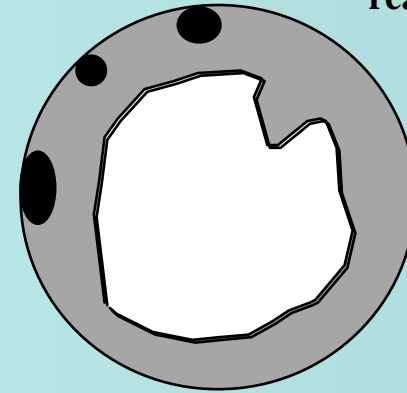
Gases: Production of metallic Ni is based on the decomposition of $\text{Ni(CO)}_4(\text{g})$ at high temperature.

Nucleation

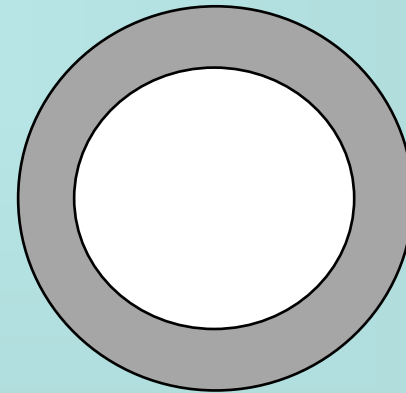
Process taking place during the decomposition of solids



(1) Nucleation
(2) Formation of reaction interface



(3) Propagation of reaction interface



Time

Ch. Reaction Kinetics

Phase transformations

Transformation of phases gives certain structural transformation

Ex: Solid - Liquid, Polymorf $\alpha\text{-Fe}_2\text{O}_3 \rightleftharpoons \beta\text{-Fe}_2\text{O}_3$

The transformation of phases depends on the changing of ΔG of the system

Point defect \longrightarrow ΔG change

When: $G_\alpha = G_\beta$, the phases are in equilibrium

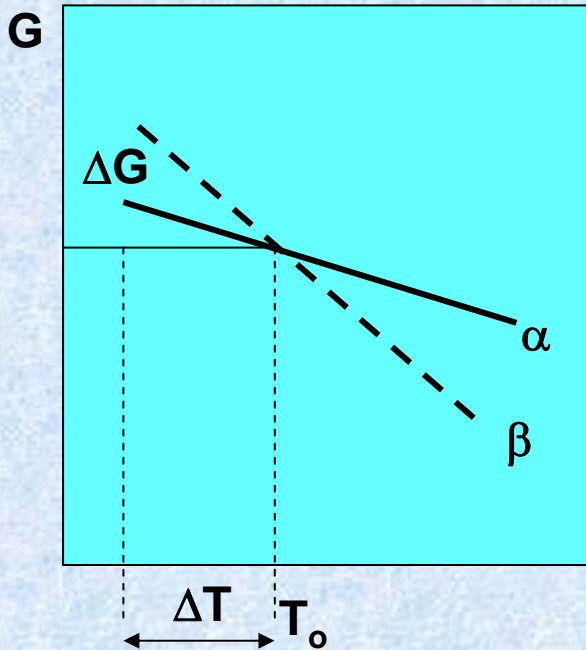
$T < T_0$ α - phase is stable

$T > T_0$ β - phase is stable

ΔT very high, it needs energy for the transformation

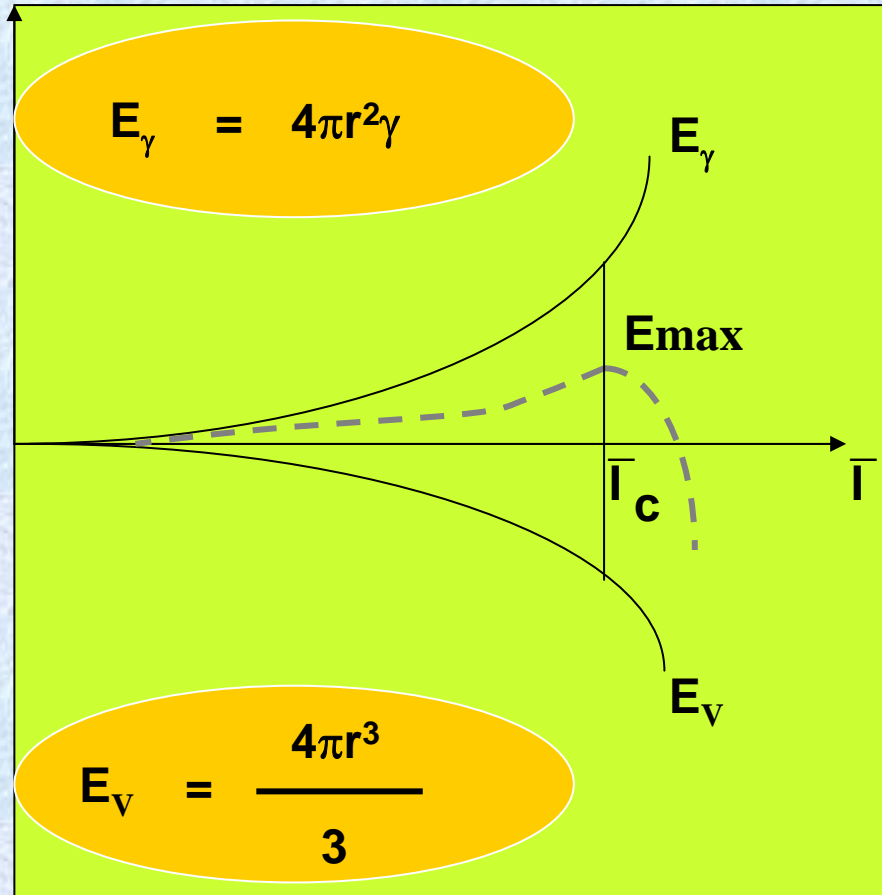
$$\Delta G = G_\alpha - G_\beta$$

$$\Delta G_0 = 0 \text{ at } T_0 = \text{transformation}$$



$$\Delta G = K \Delta T$$

Ch. Reaction Kinetics



$$E_\gamma = 4\pi r^2\gamma$$

$$E_V = \frac{4\pi r^3}{3} \cdot \Delta G \quad (\Delta G < 0)$$

$$E_{tot} = \frac{4\pi r^3}{3} \cdot \Delta G + 4\pi r^2\gamma$$

$$\frac{dE}{dr} = 0$$

$$4r_c^2 \cdot \Delta G = -8\pi r_c \gamma$$

$$\bar{r}_c = -\frac{2\gamma}{\Delta G} = -\frac{2\gamma}{K\Delta T}$$

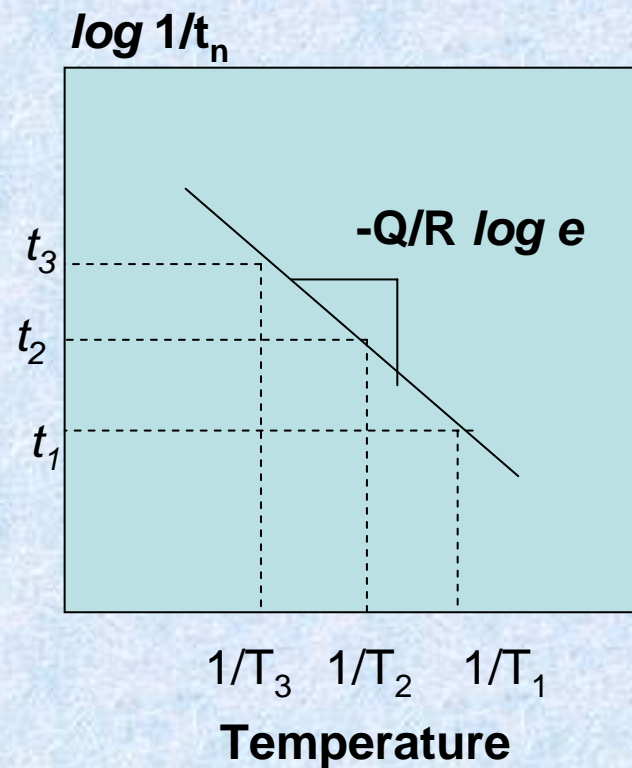
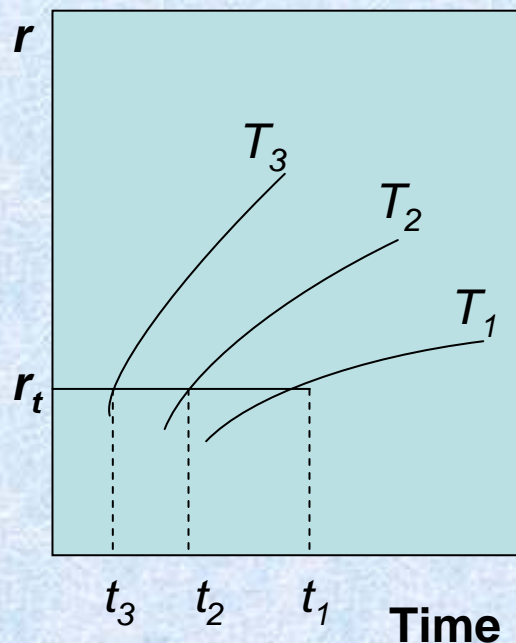
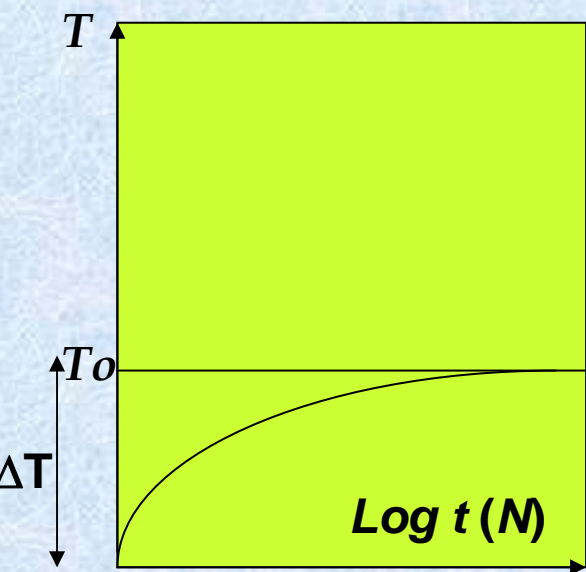
\bar{r}_c Critical radius

E_γ = energy consumption for making new surface

E_V = gain energy

$E_{tot} = E_\gamma + E_V$

Ch. Reaction Kinetics

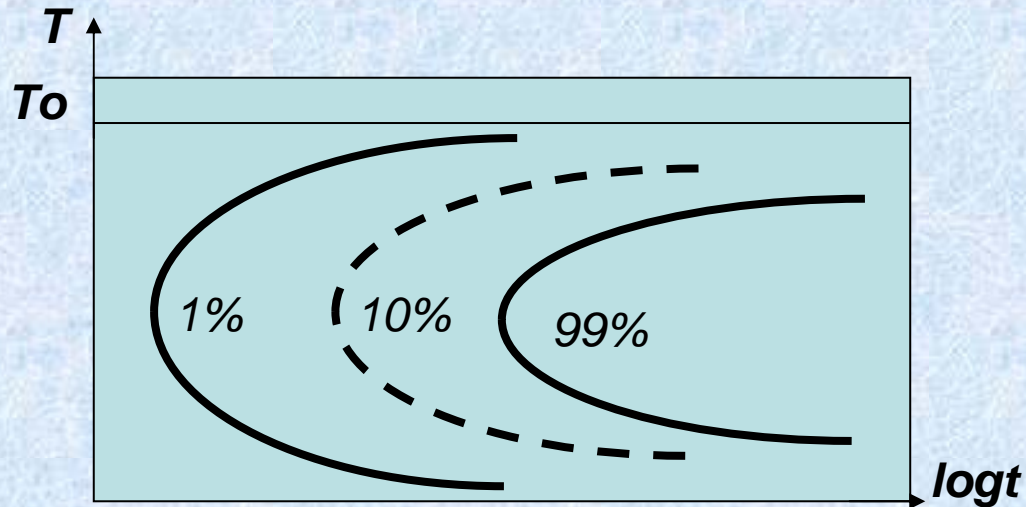
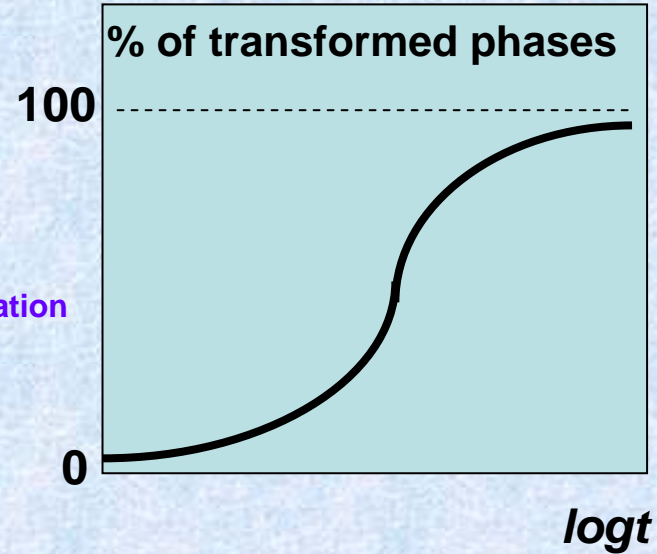
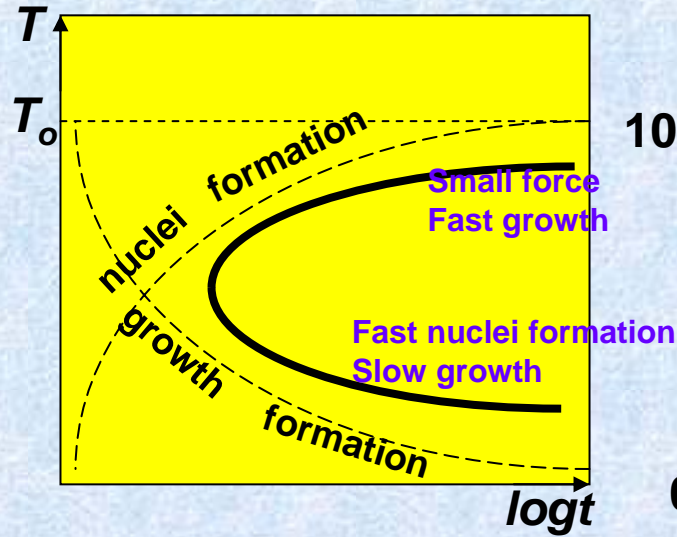
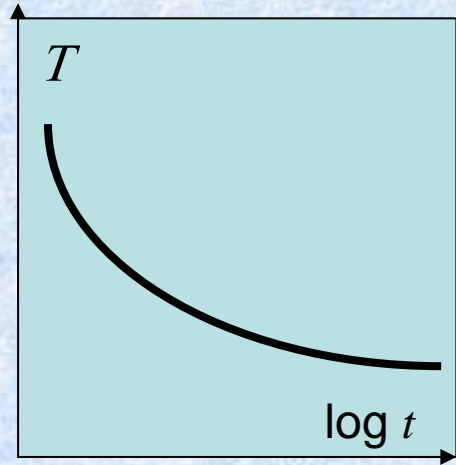


$$\dot{X} = A \cdot e^{-Q/RT}$$

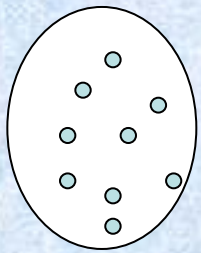
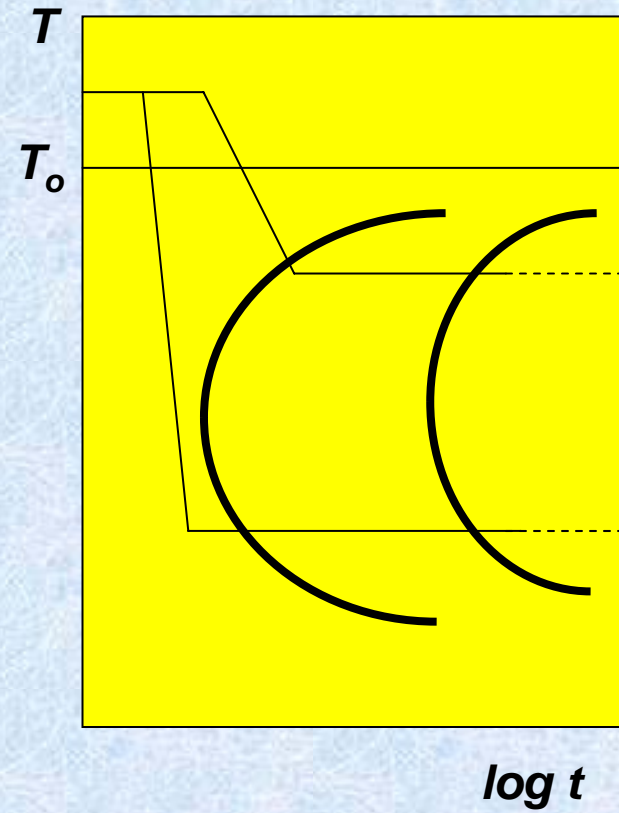
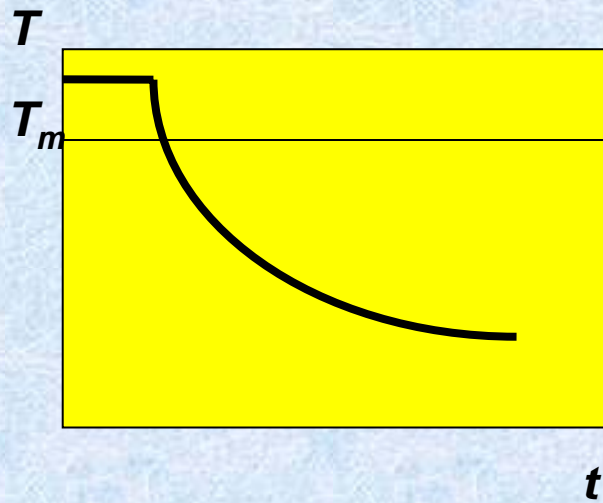
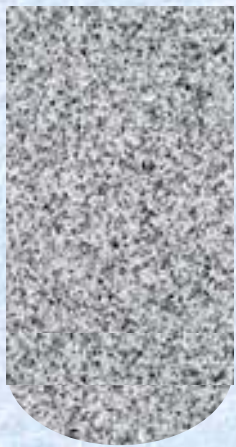
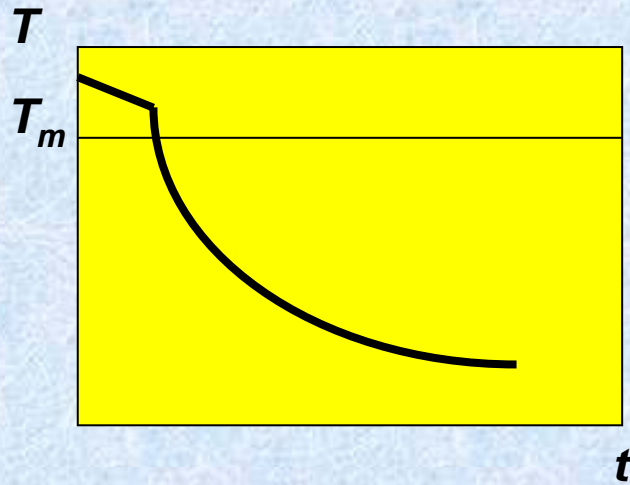
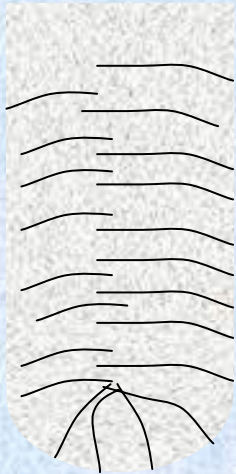
$$\dot{X} \text{ is prop } 1/t_x \quad \frac{1}{t_x} = B \cdot e^{-Q/RT}$$

$$\log \frac{1}{t_x} = \log B - Q/RT$$

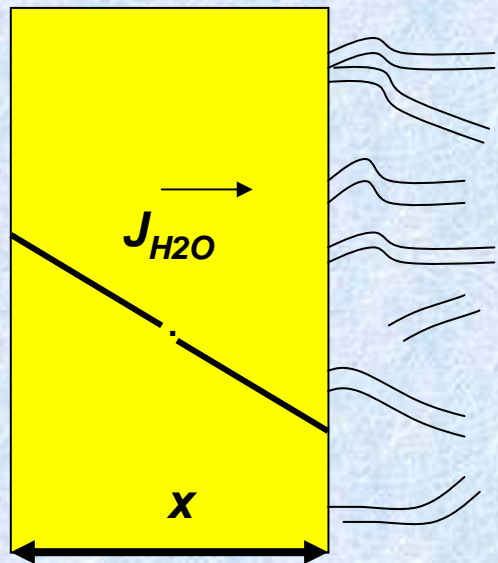
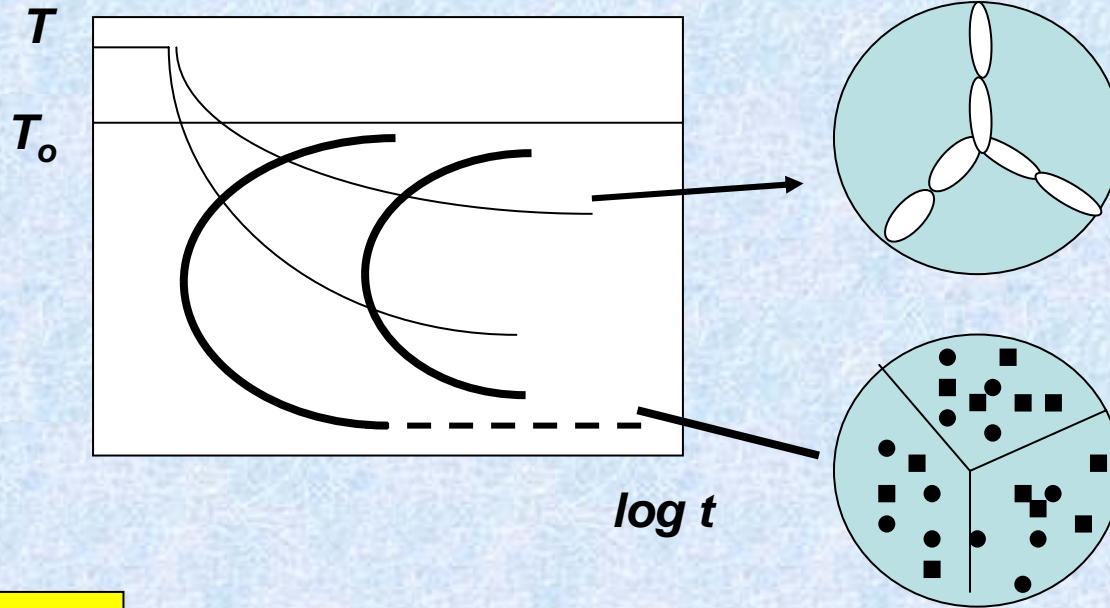
Ch. Reaction Kinetics



Ch. Reaction Kinetics



Ch. Reaction Kinetics

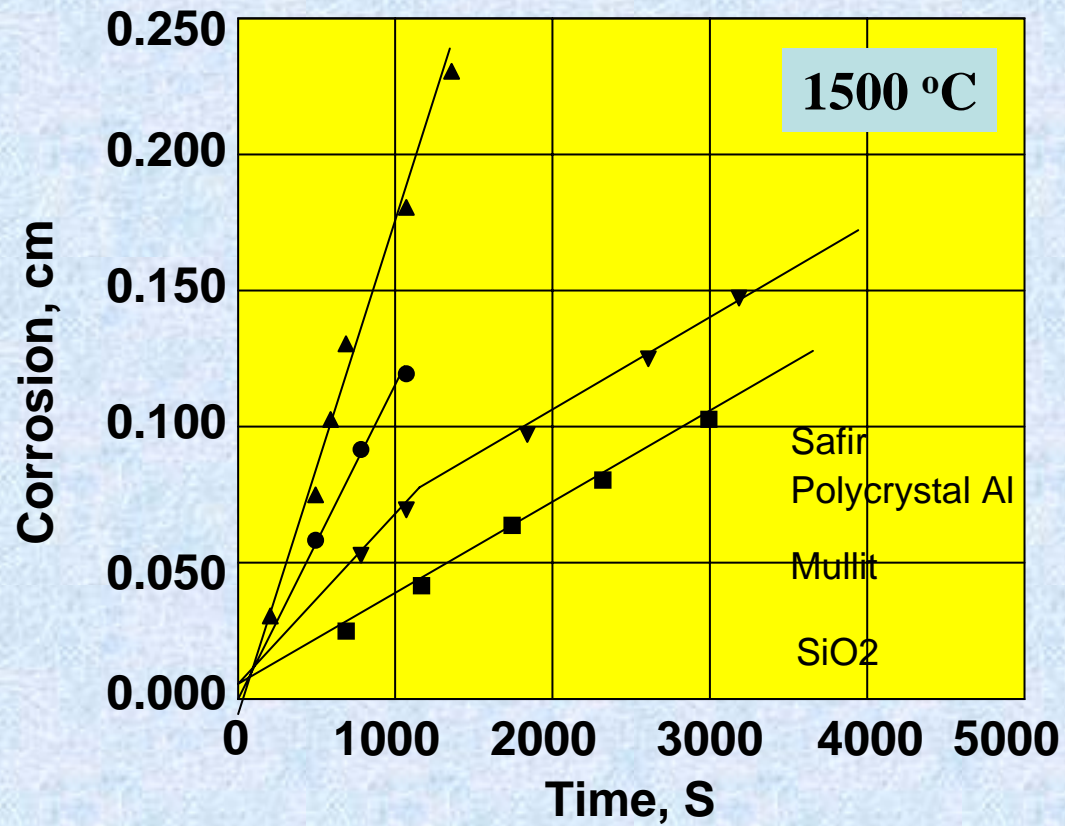


$$J = K \frac{dP}{dx}$$

$\Delta P = P_s - P_m$ is about $2\gamma/r$

$$J = (1/K\rho) dx/dt = -K dP/dx = -K \Delta P/rx = 2\gamma/rx$$

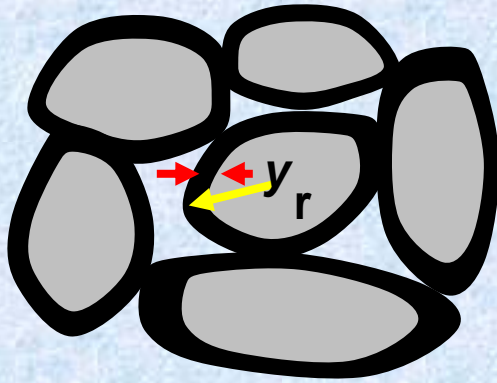
Ch. Reaction Kinetics



40% Ca – 20%Al₂O₃ – 40%SiO₂

Ch. Reaction Kinetics

Powder reaction



$$y = r \left[1 - \sqrt[3]{1 - \alpha} \right]$$

$$\left[1 - \sqrt[3]{1 - \alpha} \right]^2 = \left[\frac{KD}{r^2} \right] t$$

In many ceramic processes, Solid-solid reactions of fine powders, the close contacts between particles take place.

If the reaction is isotherm, the reaction rate in the reaction zone will depend on diffusion. In the beginning of the reaction, the growth of boundary Layer can be described by the parabolic eq.

$$X = (K't)^{1/2}.$$

X and growth is proportional to \sqrt{Dt}

The volume of un-reacted material V:

$$V = 4/3 \pi (r-y)^3$$

$$\text{Or } V = 4/3 \pi r^3 (1-\alpha)$$

α is % conversion or % volume reacted

$$\frac{KD}{r^2}$$

characterises the reaction.

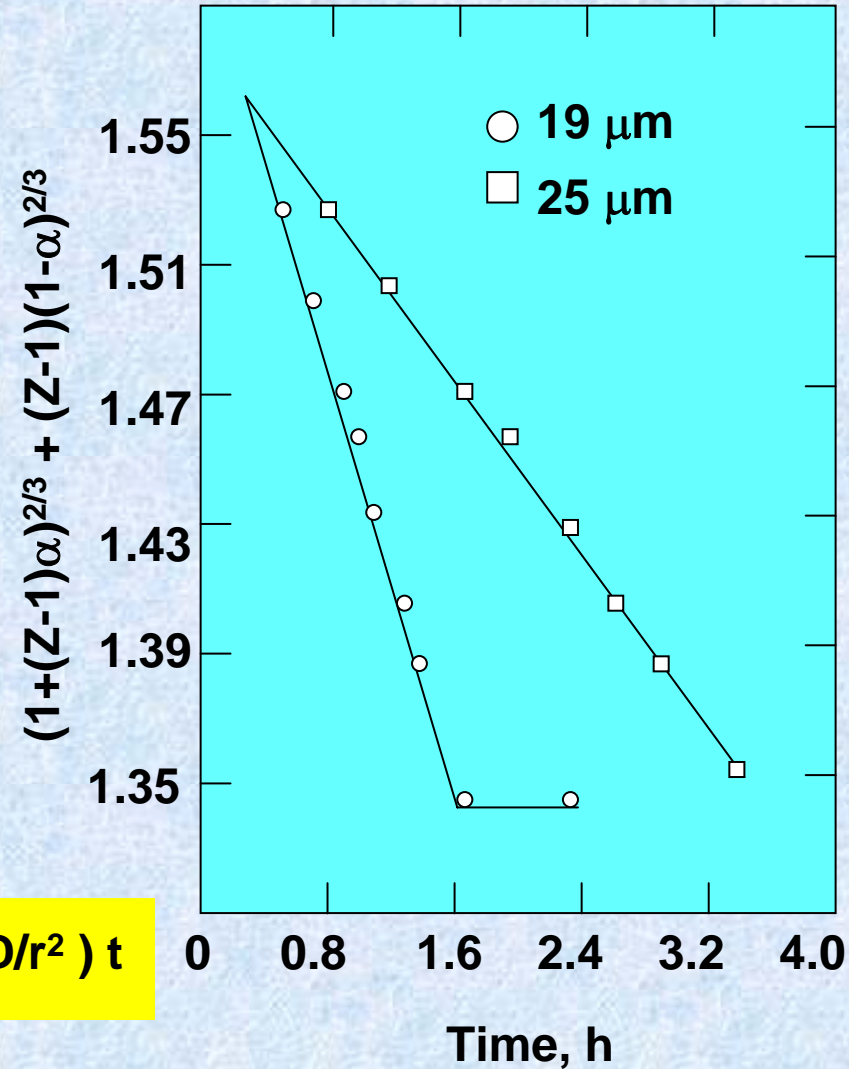
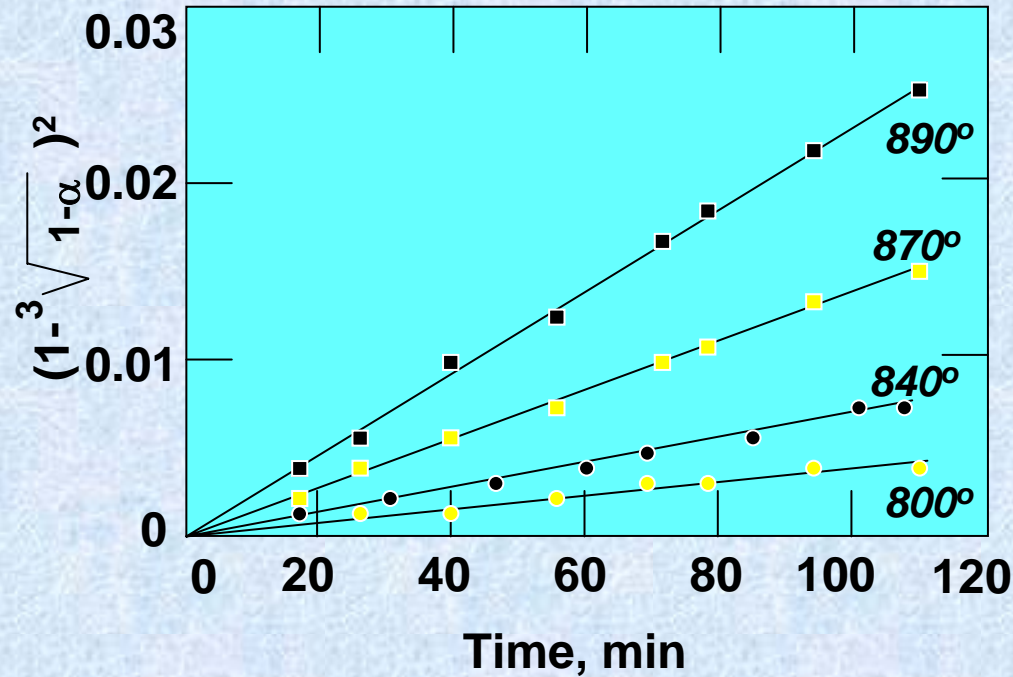
This eq. Can be used for different solid-solid reactions. Ex. silicate system.

$X = (K't)^{1/2}$ can be used if the surfaces are flat

K depends on different chemical potential between the specieses which are diffused in boundary layer and also depends on the geometry of powder particles.

Ch. Reaction Kinetics

BaCO₃ with SiO₂

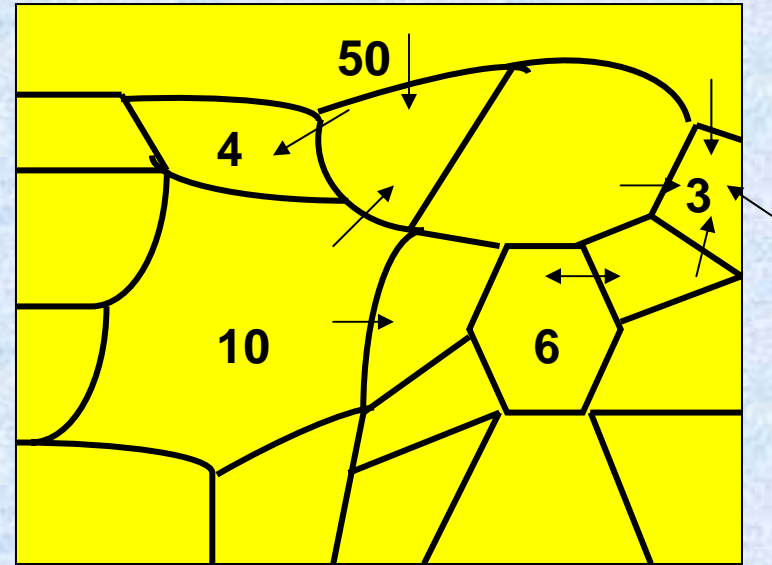


$$(1 + (Z - 1)\alpha)^{2/3} + (Z - 1)(1 - \alpha)^{2/3} = Z + 2(1 - Z) \left(\frac{KD}{r^2} \right) t$$

Ch. Reaction Kinetics

The process of growth of nuclei depends on temperature. When some nuclei become big in size, some other nuclei become small and disappeared. In this case the energy is different between small and big nuclei which result in decreasing of the total surface and thereby the surface energy.

At high temperature, the mention of atoms is very high and the growth is fast.

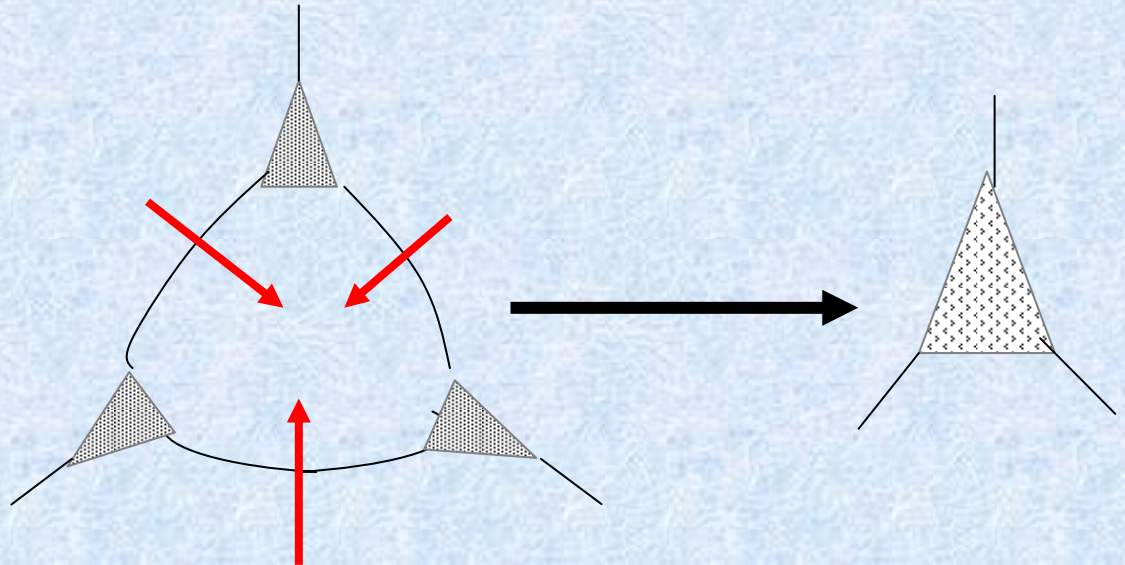


$$d^n - d_0^n = kt$$

d^n Middle size of nuclei at t

d_0^n Middle size of nuclei at t_0

$n = 2$ is ideal case



Radioactive Decay

Why is it important to investigate the rates of this reaction for metallurgical engineering?

Disposal problems of radioactive wastes generated from treatment of uranium and thorium ores.

Traces of uranium and thorium in other ores. Example: the slag resulted from the production of ferro-niobium is radioactive.

Phosphate treatment (wet or thermal treatment), the residues obtained contain traces of uranium.

Plutonium needs special attention because of its toxicity.

Types of Decay

Naturally occurring radioactive elements start $Z_a = 84$.

The radioactive elements have many protons in the nucleus

Repulsion forces between protons

α particles are emitted in stages in a complex way

α ray

β ray

Radioactive series

Naturally occurring radioactive elements form three series,

Uranium series

Actinium series

Thorium series

β^- . emission results in an increase in atomic number, and atomic weight is const.

α^- . emission results in an decrease in atomic number by 2, and atomic weight is decreased by 4.

Ch. Reaction Kinetics

Radon and its isotopes

Radioactive inert gases formed from the decay of their parent nuclide

Series	Gas	Symbol	Mass number	Half-life
Uranium	Radon	Rn	222	3.8 days
Thorium	Thoron	Tn	220	54.5 sec
Actinium	Actinon	An	219	3.9 sec

Radioactivity and Avogadro's number

Toxicity of decay products

α particles

Human beings

Max amount of radium that safely be allowed to accumulated in the human body is 1×10^{-7} grams.

Ch. Reaction Kinetics

THE DECAY LAW

Homogeneous reactions

$$\frac{dN}{dt} = -\lambda N \quad N = N_0 e^{-\lambda t}$$

$$t_{1/2} = \frac{1}{\lambda} \ln 2 = 0.693 / \lambda$$

Since one gram atom of any element contains 6.025×10^{23} atoms

$$N_1/N_2 = \frac{\frac{W_1}{\text{at. Wt.}} \times \text{Avogadro's number}}{\frac{W_2}{\text{at. Wt.}} \times \text{Avogadro's number}} = \frac{W_1/\text{at.wt.}}{W_2/\text{at.wt.}}$$

For the same nuclide

$$N_1/N_2 = W_1/W_2$$

Average life or life expectancy of a radioactive nucleus

$$= \int_{N_0}^{N_0} t dN$$

Ch. Reaction Kinetics

$$\text{Av. life} = \int_0^{\infty} \lambda t e^{-\lambda t} dt = 1/\lambda$$

The decay constant is the reciprocal of the average life

Example: λ of thorium is $4.2 \times 10^{11}/\text{years}$, therefore $1/\lambda = 2.4 \times 10^{10}$

The rate of decay is not influenced by temperature or pressure since it is a nuclear and not a chemical process

Activity

Physical methods, and the most successful method is:

Ionization of gaseous atoms when bombarded by the radiations

Ex. A single α particle having an energy of a few MeV generates 100 000 to 200 000 ions pairs when it runs its full course in air. Then the number of particles can be counted

Ch. Reaction Kinetics

The rate of decay

The rate of radioactive substance is called the activity A , of that substance

$$-dN/dt = \lambda N = A$$

Units of activity

$$\text{Curie} = C_i$$

Becquerel: is one disintegration per second, (Henri Becquerel), Bq

Nature of Interface

Defects in the solid state

Non-stoichiometric compounds

The role of impurities

Effect of Crystalline Form

Area of Interface

Geometry of Interface

Flat surface

Sphere

Cube

Pellet

Rate equations expressed in terms of fraction reacted

Ch. Reaction Kinetics

Nature of Interface

The rates of chemical reactions can be affected by:

Lattice defects
Non-stoichiometry
Impurities

} At interface

Defects in the solid state

Ideal crystal Type AB, N_a of A = N_a B

At $T^\circ\text{C}$ above absolute 0, thermal vibrations of the atoms make possible defection of lattice

Schottky defect

Frenkel defect

Ch. Reaction Kinetics

Non-stoichiometric compounds

The NSTC is a group of compounds, in which some sites in the lattice can be unoccupied and the atoms of A do not exactly = N_a of B

Ex: Oxides heated in oxygen atm. Some oxides lose (O) thus becoming metal high grade . Others gain (O), thus becoming metal low grade

Iron sulfide, is usually written as FeS, now you have several compounds over composition range Fe_{1.00}S to Fe_{0.88}S

Ch. Reaction Kinetics

The Role of impurities

Impurities have a substantial influence on the kinetics of heterogeneous reactions

In metals: electrical conductivity increases or decreases as a result of the presence of impurities.

Ch. Reaction Kinetics

Effect of crystalline form

For different crystalline forms of the same solid, solubility and rates reactions are different

Ex: with liquids or with gases

HgS in nature:	A. Red cinnabar.	D= 8.1
	B. Black meta-cinnabar	D= 7.7

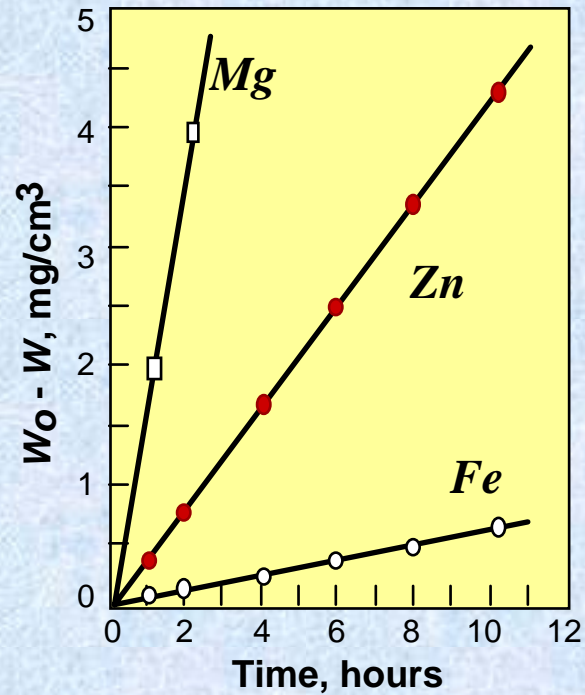
A: Red cinnabar crystallizes in the hexagonal system

B: Black meta- cinnabar crystallizes in the tetrahedron system

A is soluble in Na_2S

B: is not soluble in Na_2S

Flat surface



Dissolution of metallic flat surface in 0.1 N H₂SO₄

Ch. Reaction Kinetics

Sphere

The surface area A will decrease with time

$$\text{Rate} = -dW/dt = kAC \quad (1)$$

$$A = 4\pi r^2 \quad (2)$$

$$\rho = W/V, \text{ then } W = V \rho \quad (3)$$

$$W = 4/3\pi r^3 \rho, \text{ then } r = (3W/4\pi\rho)^{1/3} \quad (4)$$

$$\text{From (2), we have, } A = 4\pi(3/4\pi\rho)^{2/3} W^{2/3} \quad (5)$$

$$\text{From (1), we have, } -dW/dt = k4\pi(3/4\pi\rho)^{2/3} W^{2/3}C \quad (6)$$

$$-dW/dt = k'W^{2/3} \quad (7)$$

$$-\int_{W_0}^W dW/W^{2/3} = k' \int_0^t dt \quad 3(W_0^{1/3} - W^{1/3})k't$$

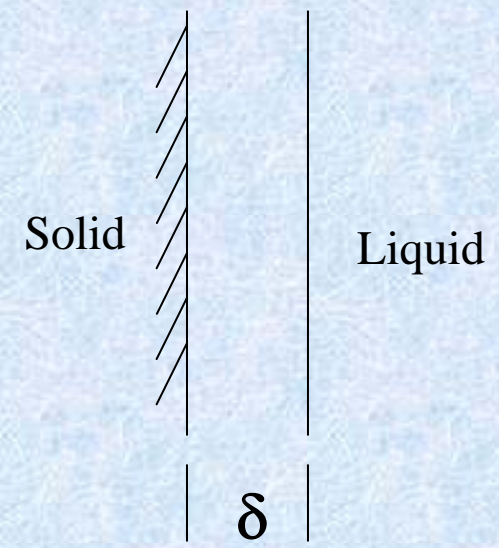
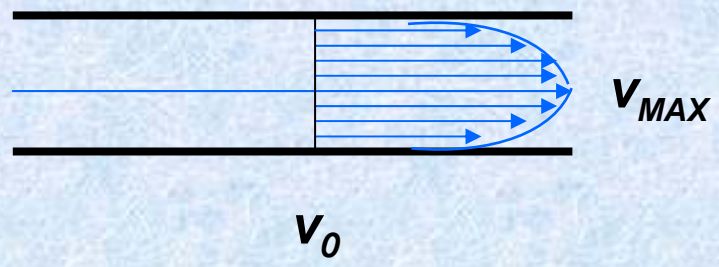
Introduction

Walther Nernst (1864 – 1941) and his collaborators have started to investigate the kinetics of dissolution processes (heterogeneous non-catalyzed reactions), and in 1904 they formulated the concept of the boundary layer

ORIGINS OF CONCEPT

Contact of solid with liquid \longrightarrow Stagnant film (0,03 mm in thickness)

Nernst boundary layer



Stagnant layer

$$\frac{d[C]}{dt} = k ([C]_s - [C]) \quad (1)$$

$[C]$ is the concentration of the solute at time t .
 $[C]_s$ is its solubility in H_2O at T_{ex} .
 i.e its concentration at saturation,
 k is the velocity constant,

From this eq.

$$\int_0^t \frac{d[C]}{[C]_s - [C]} = k \int_0^t dt \quad (2)$$

$$\int_0^t d \ln [C]_s - [C] = k \int_0^t dt \quad (3)$$

$$2.303 \log \frac{[C]_s}{[C]_s - [C]} = kt \quad (4)$$

3

4

Ch. Reaction Kinetics

$[C]_s / ([C]_s - [C])$ versus t gives a straight line

Fick's law of diffusion to this process : at constant volume:

$$dn / dt = -\mathcal{D}A dC/dX$$

$$dn/dt = \mathcal{D}A / \delta ([C]_s - [C])$$

$$[C] = n/V$$

$$d[C]/dt = \mathcal{D}A / \delta V ([C]_s - [C])$$

n is the number of species diffusing in unit time

$$k = \mathcal{D}A / \delta V$$

V is the volume of solution

- The dissolution rate of a solid in water increased with increased agitation because δ of the boundary layer decreased.
- The temperature has no influence on the dissolution rate, an $E_a < 5$ kcal/mole was usually observed. This is in agreement with a diffusion

Types of Heterogeneous Reactions

Physical process are diffusion-controlled

Chemical and electrochemical reactions may be diffusion-controlled, chemically controlled, or intermediate-controlled reactions.

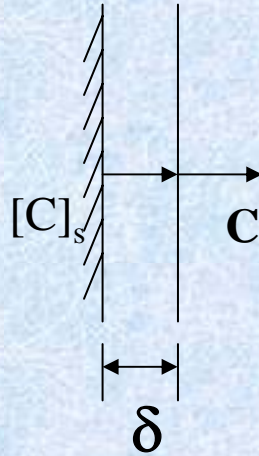
Physical process

Ex: dissolution of NaCl in certain volume of water, the crystal salt will be immediately covered by thin layer of saturated solution of NaCl. The ion will diffuse in water following Fick's law until the water becomes saturated.

$$Rate = \bar{D}A / \delta V ([C]_s - [C])$$

Chemical processes

An ionic or covalent solid has a plate form of surface area A .
This solid is in contact with an aqueous solution
This solution contains reagent R that reacts with the species C
dissolving from the solid.



At interface, the concentration of the solute will be that of a saturated solution, $[C]_s$, and the bulk of solution will equal $[C]$

1. When the rate of reaction of R with the dissolving species in the bulk of the solution is very fast, then $[C]$ equal to zero, the process will be controlled by the rate of diffusion of C through the boundary layer

$$Rate = \mathcal{D}A / \delta ([C]_s - [C]) = k_1 A [C]_s = \text{const} \quad k_1 = \mathcal{D} / \delta$$

2. When the rate of reaction of R with the dissolving species in the bulk of the solution is very low, then the diffusion does not play any role, and there will be accumulation of C in solution, i.e. $[C] = [C]_s$. Rate of reaction will depend on $[R]$ since $[C]_s$ is const., the process is **chemically controlled**

$$Rate = k_2 A [R]$$

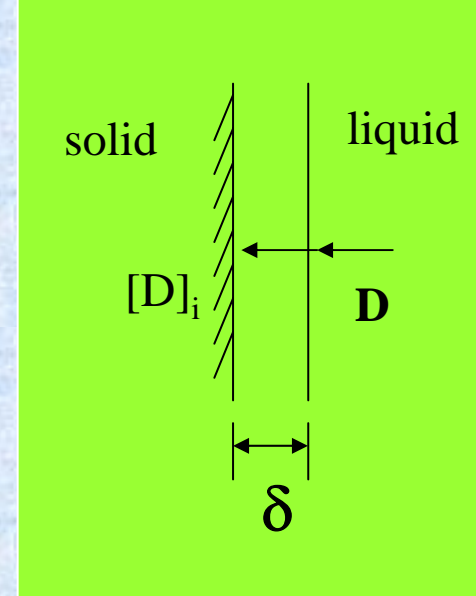
3. When the rate of reaction of R with dissolving species in the bulk of the solution equals that of the rate of diffusion, the process is known as **intermediate control**.

Electrochemical processes

Metal or semi-conducting solid reacts through an oxidation-reduction process (transfer of electrons).

[D]. Concentration of reagent in the solution, which diffuses through the boundary layer to pick up e⁻ from the interface

3 cases may be considered



1. When the rate of chemical reaction at the interface is much faster than the rate of diffusion of reactants to the interface, in this case, $[D]_i = 0$. These reactions are therefore called **diffusion-controlled reactions**

$$\text{Rate} = \mathcal{D}/\delta A ([D] - [D]_i) = k_1 A [D] \longrightarrow k_1 \mathcal{D}/\delta$$

1

2. When rate of chemical reaction at the interface is much slower than the rate of diffusion, $[D]_i > 0$. These reactions called chemically-controlled.

$$\text{Rate} = k_2 A [D]_i$$

2

3. When both rate are equal, then the process is intermediate control. In this case a concentration gradient is formed across the boundary layer. $[D]_i > 0$

From 1 and 2

$$\text{Rate} = k_1 A ([D] - [D]_i) = k_2 A [D]_i$$

3

$$[D]_i = \frac{k_1}{k_1 + k_2} [D]$$

$$\text{Rate} = \frac{k_1 k_2}{k_1 + k_2} A [D] = k A [D]$$

$$k = \frac{k_1 k_2}{k_1 + k_2}$$

- If $k_1 (< \text{ or } =) k_2$, then $k = k_1 = \mathcal{D}/\delta$ **The process is diffusion-controlled**
- If $k_2 (< \text{ or } =) k_1$, then $k = k_2$. **The process is chemically controlled**

Characteristics of Heterogeneous Reactions

Diffusion-controlled reactions can be characterized from chemically controlled reactions by two factors:

1. Effect of fluid velocity

2. Effect of temperature

1. Effect of fluid velocity

With increasing the rate of stirring in a S-L reactions, the rate of dissolution increases, when the process is diffusion –controlled. See fig. 6.4

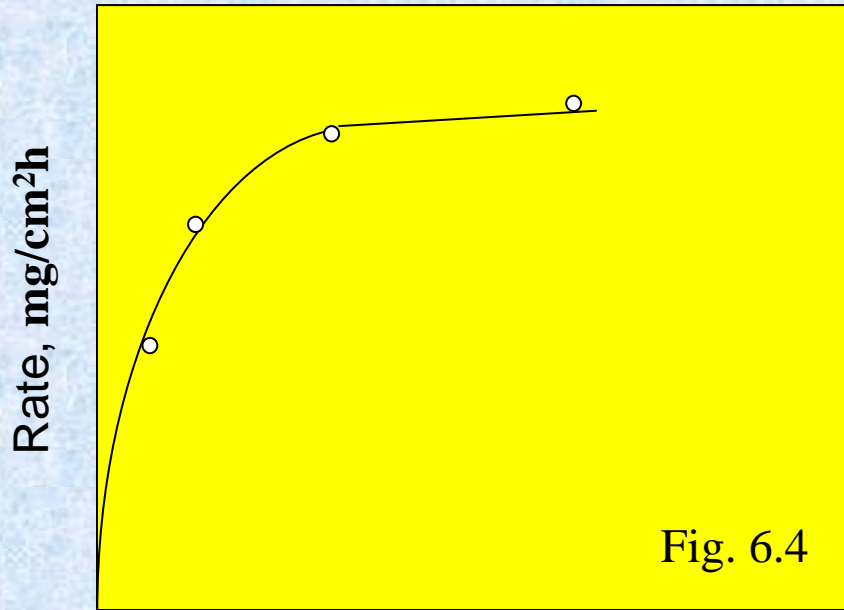
This process follows the rate law:

$$\text{Rate} = \mathcal{D}/\delta A[C]$$

Since δ decreases with increased velocity of stirring, also the speed of dissolution increases. The rate of dissolution can be usually expressed as a function of speed of stirring:

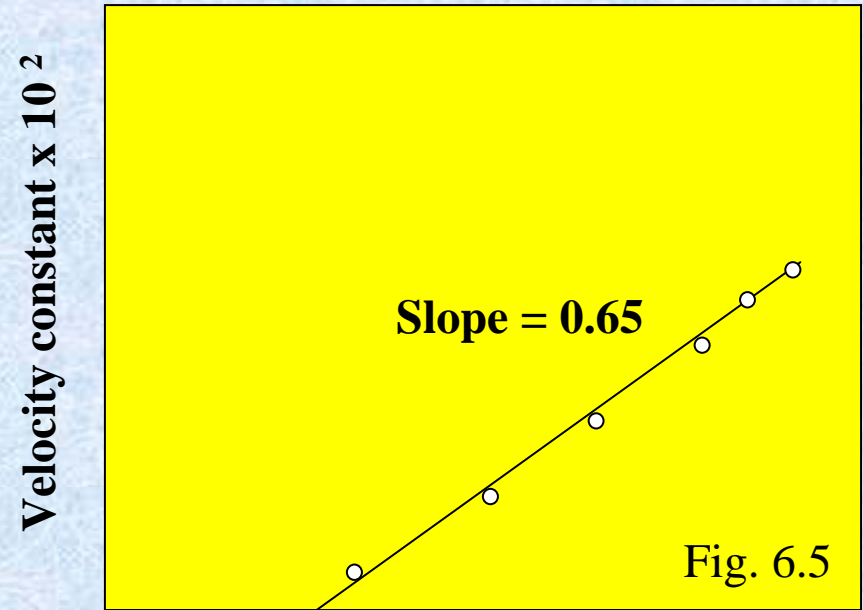
$$\text{Rate of dissolution} \propto \text{Rpm}^a$$

$a < 1$. This value can be obtained from Fig. 6.5



Speed of stirring x 10² rpm

Effect of speed of stirring on the dissolution of zinc in acid (Skerka and Akimov, 1960)

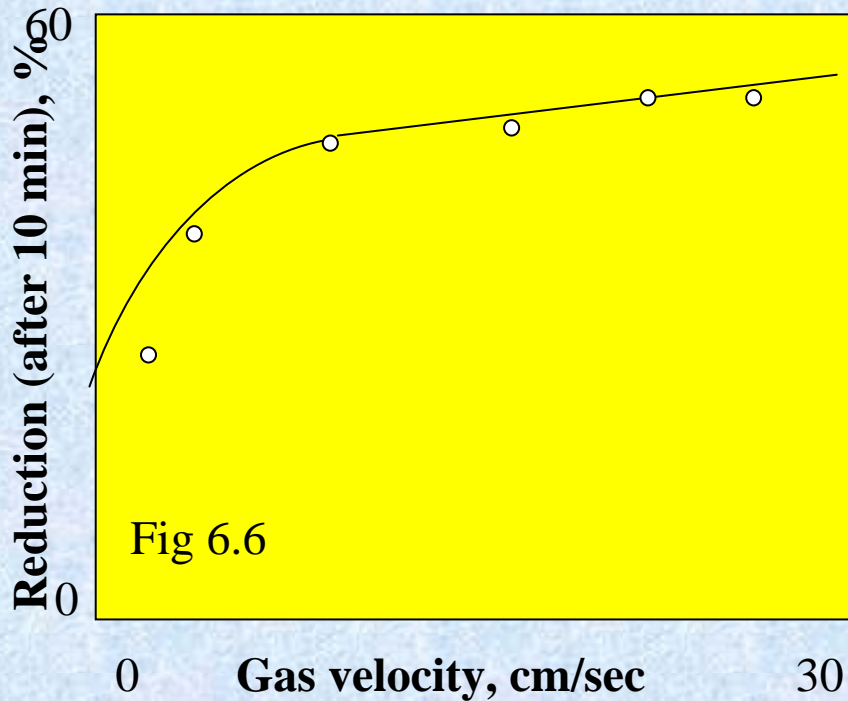


rpm x 10²

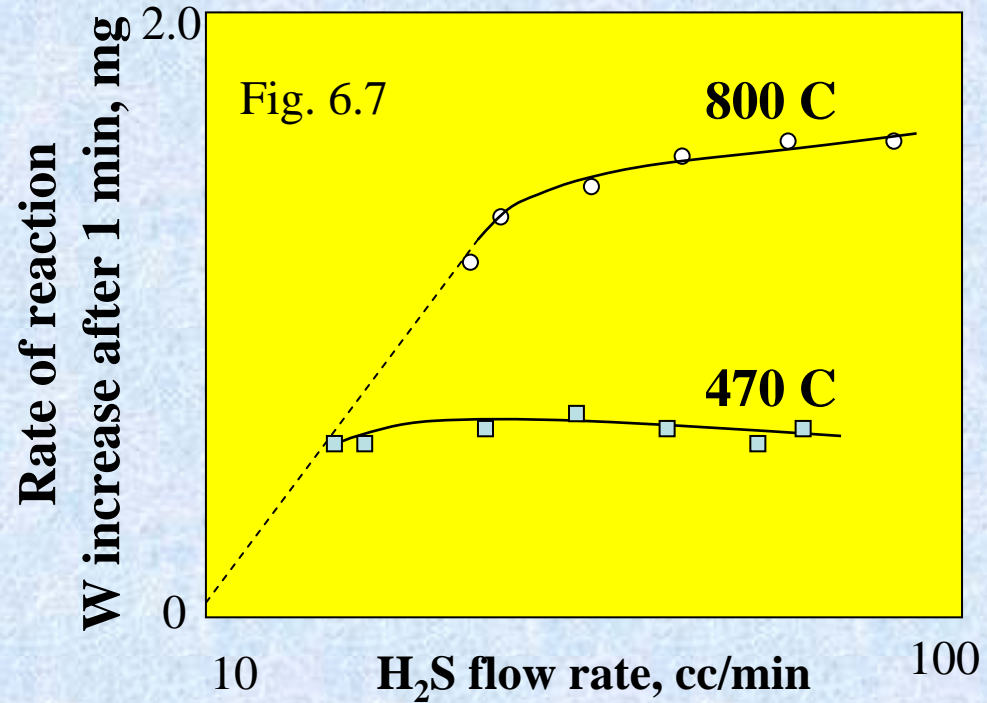
Effect of speed of stirring on the dissolution of copper in aqueous ammonia (Lu and Graydon, 1955)

In solid-gas reactions, a diffusion controlled process depends on the rate of flow of gas, while a chemically controlled process does not. As can be seen from fig 6.6, at low T C, the process is usually **diffusion-controlled**

The region in which the gas flow rate influences the rate of reaction is a function of temperature, see Fig. 6.7



Effect of gas velocity on rate of reduction of Fe_2O_3 with CO at 1000 C



Effect of temperature and gas rate on rate of reaction of H_2S with CaO (Habashi and Mikhaill, 1976)

2. Effect of temperature

A diffusion-controlled process is slightly dependent on temperature

A chemically controlled process is strongly dependent on temperature.

This because the diffusion coefficients are linearly dependent on temperature

$$\mathcal{D} = \frac{RT}{N} \frac{1}{2 \pi r n}$$

$$k = A e^{-E/RT}$$

E_a		Process
1 - 3 kcal/mole	→	Diffusion-controlled
5 - 8 kcal/mole	→	Intermediate-controlled
> 10 kcal /mole	→	Chemically-controlled

Solid - solid reactions, the situation is different since \mathcal{D} change exponentially

$$\mathcal{D} = \mathcal{D}_0 e^{-E/RT}$$

In this case, E_a (200 – 400 kcal/mole)

Change of Mechanism in a heterogeneous Reaction

The mechanism of a reaction may change from diffusion-control to chemical control or vice versa.

Because: Change of concentration of reagent

Gas pressure

Temperature

B

e

c

Change of concentration of reagent

a

u

Solid-liquid reactions

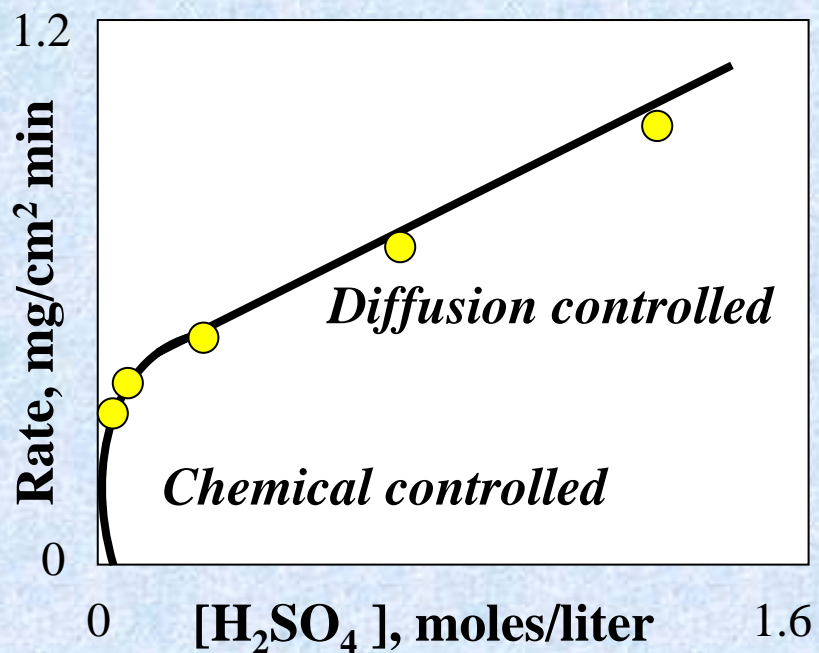
Chemical control mechanism at low reagent concentration

e

The rate is low and controls the whole process

Increasing $[R]$, the rate of reaction increases and the slowest step becomes the diffusion

Effect of concentration or gas pressure



Effect of acid concentration on the
dissolution of CuO
(Wadsworth and Wadia, 1955)

The rate is not linear as function of reagent concentration

Effect of concentration or gas pressure

Solid-liquid reactions

Electrochemical mechanism. At low [R], the reaction is diffusion-controlled.

As the concentration increases the process becomes chemical-controlled

Why?

Because at [R], the rate of diffusion is very low and therefore governs the whole process. With increasing [R], the rate of diffusion increases to such an extent that it supersedes the rate of chemical reaction.

Ex: dissolution of Zn in HCl see the following table:

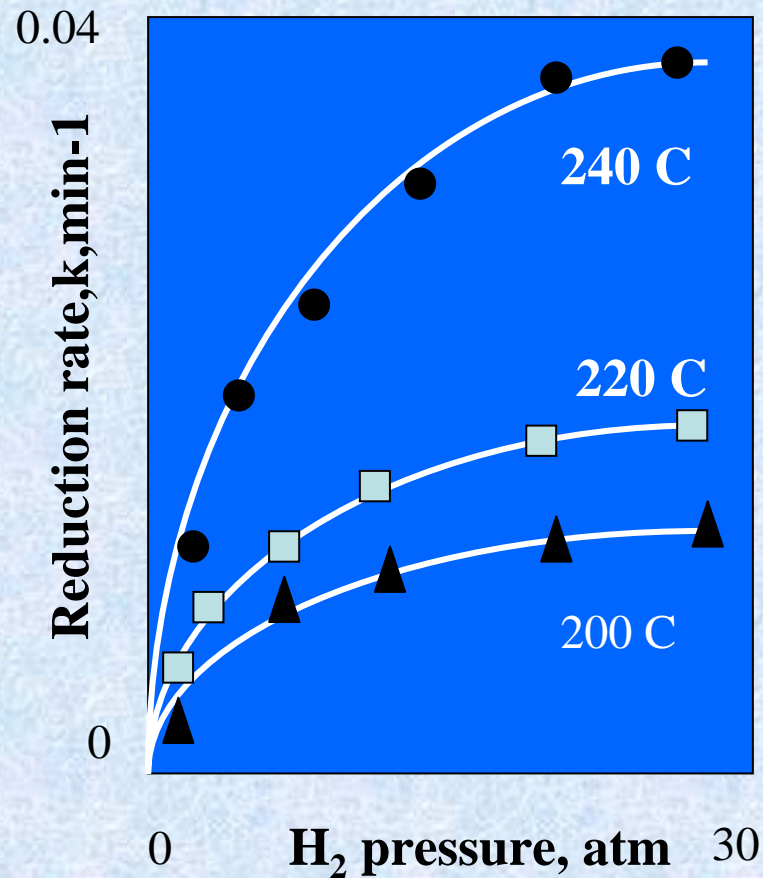
T : 20 – 80C

Metal	[HCl], N			
	0.05	0.10	0.50	1.0
Zn	1.2	4.9	25.7	28.5
Al	1.4	7.6	6.9	10.2

Ch. Reaction Kinetics

Effect of concentration or gas pressure

Solid-gas



Effect of gas pressure on the rate of reduction NiO by H₂
(Kurosawa et al. 1972)

Effect of temperature

The heterogeneous reactions are usually chemically controlled at low temperature, and become diffusion-controlled at high temperature

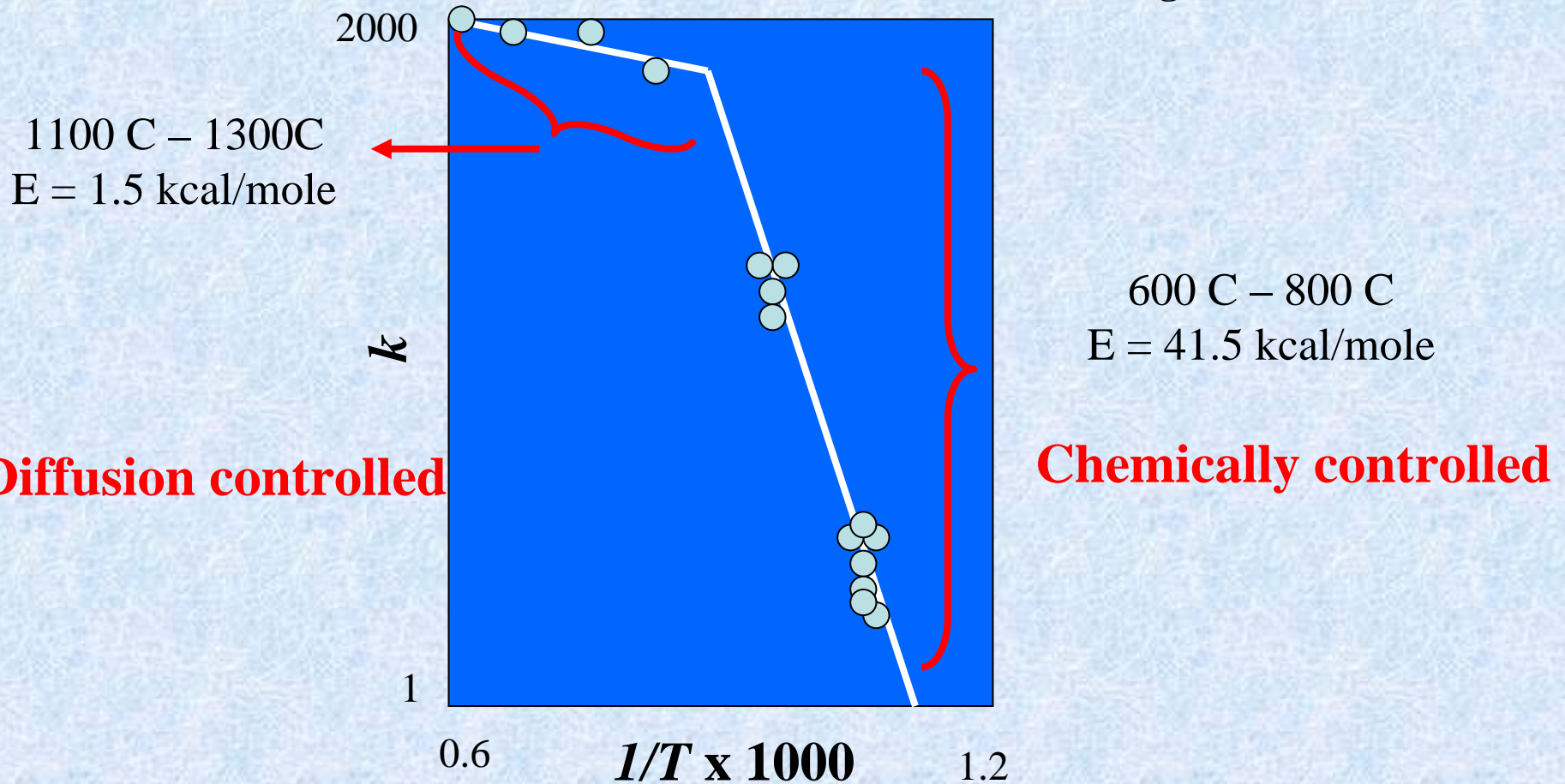
At low temperature

The rate of chemical reactions is so slow \lll the rate of diffusion. The process becomes diffusion-controlled

Ch. Reaction Kinetics

Effect of Temperature

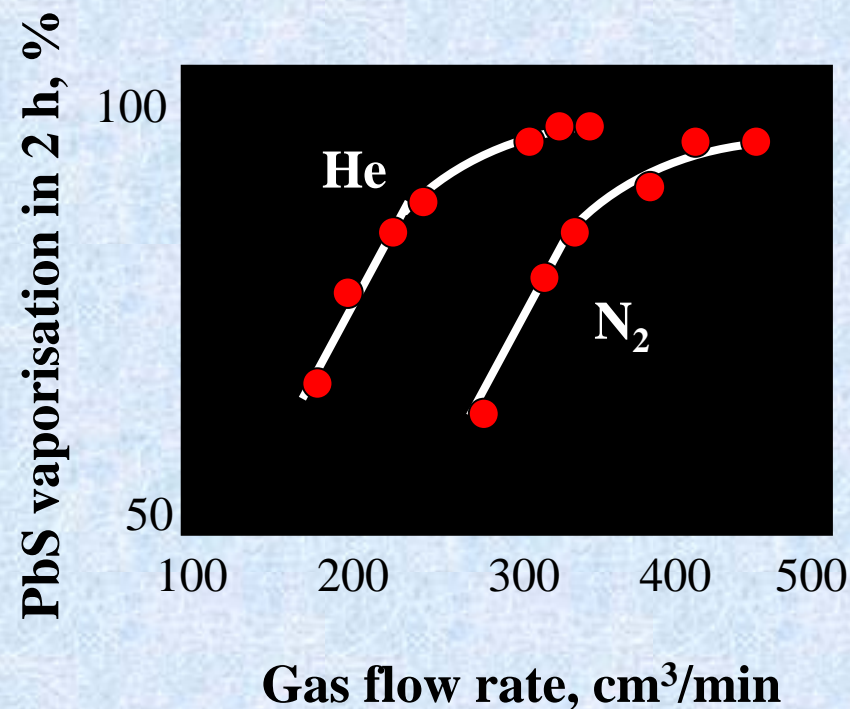
Fig. 6.10



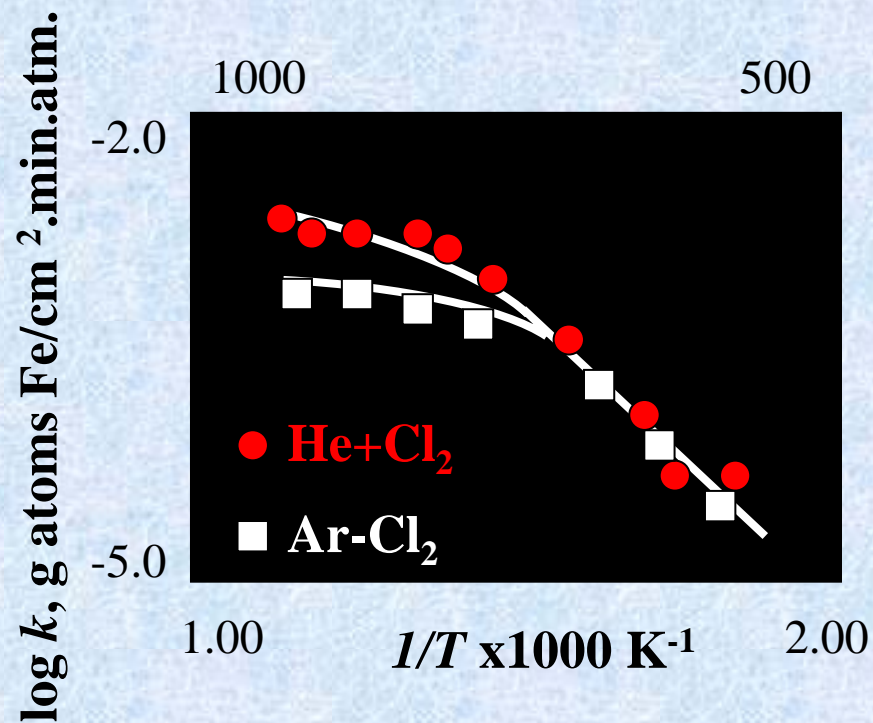
Effect of T C on the reaction $C + 1/2 O_2 = CO$

Blyholder and Eyring, 1957)

Effect of inert gas



Effect of the nature of gas on the rate of volatilization of PbS at 1000 C
(Cole et al. 1974)



Effect of diluent gas on the rate of reaction of chlorine with iron
(Fruehman, 1972)

- Heterogeneous non-catalyzed reactions may be a physical, chemical or electrochemical process

- Physical processes are diffusion-controlled, other may be diffusion-controlled, chemical controlled or intermediate control.

We can distinguish between these mechanism by:

- ★ Effect of speed of agitation in solid-liquid reaction
gas flow rate in solid-reaction
- ★ Low E_a for diffusion-controlled reactions
High E_a for chemically controlled

Mechanism of reactions can be change by changing $[R]$ in solid-liquid, (gas pressure in solid-gas), or change in temperature. The presence of inert gas also in solid-gas reactions causes a change

Nature of Solid Reaction Product

Porous and nonporous solids

Criteria for porosity

Formation of a Nonporous Product

Case of flat surface

Case of a spherical particle

Generalized Rate Equation

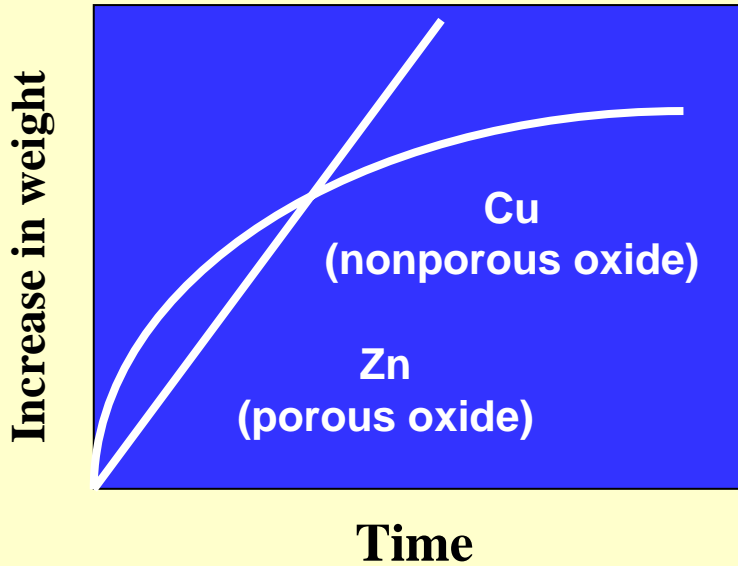
Porous and nonporous solids

Products of reaction is a porous layer

1. Non resistance to the reagents reaching the interface
2. The rate will not be affected

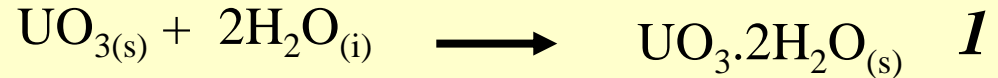
Products of reaction is nonporous layer

1. The reagents reaching the interface has to diffuse through this film
2. The kinetics differ markedly.



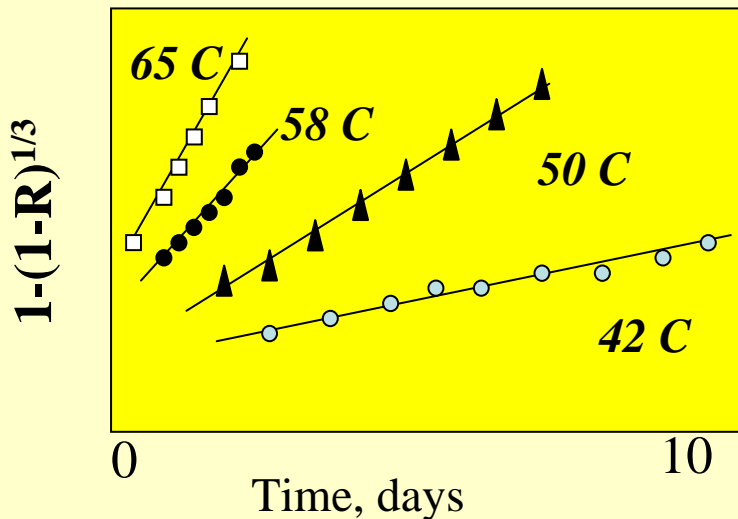
In the case of copper, a nonporous oxide is formed, the rate decreases gradually with time

Similar observations are found in solid-liquid reactions



Oxidation kinetics of flat surfaces of metals

The product of this reaction is porous, and does not affect the rate.



This process is not influenced by diffusion

Kinetics of reaction 1 (Dell and Wheeler, 1963)

Ch. Reaction Kinetics

$$Z = \frac{1}{\alpha} \left(\frac{M_p/\rho_p}{M_R/\rho_R} \right)$$

Criteria for porosity

M_p = molecular weight of solid product

M_R = molecular weight of solid reactant

ρ_p = density of solid product

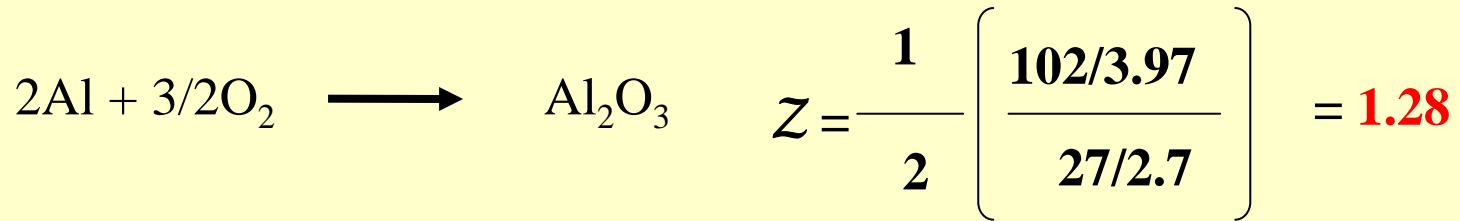
ρ_R = density of solid reactant

α = stoichiometry factor

- If $z < 1$ **The product will occupy less volume than the reactant**
Then the pores will be created within the solid
- If $z > 1$ **The product will occupy more volume than the reactant**
Then a dense nonporous layer will be formed

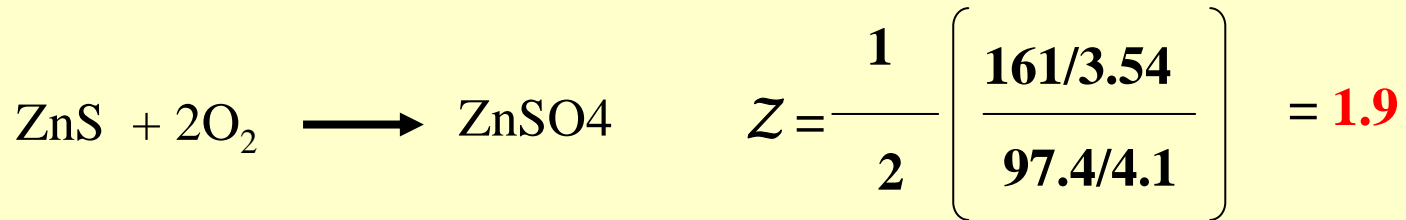
This was observed during oxidation metals see Table 7.2 page138

Other ex:



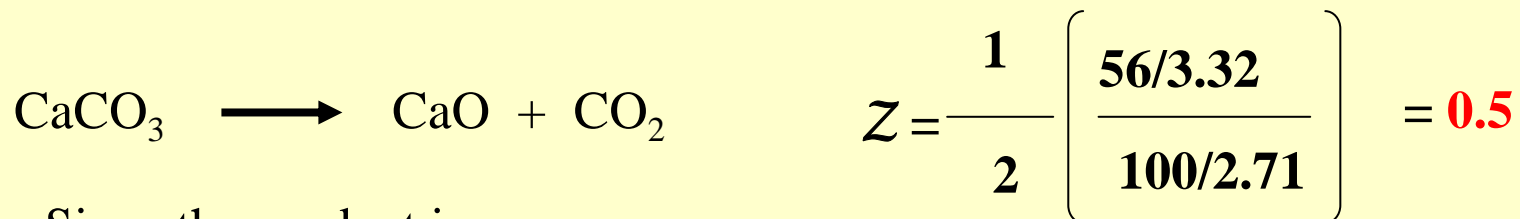
The rate of oxidation is retarded by the oxidation film, this is because $Z > 1$

Similar ex:



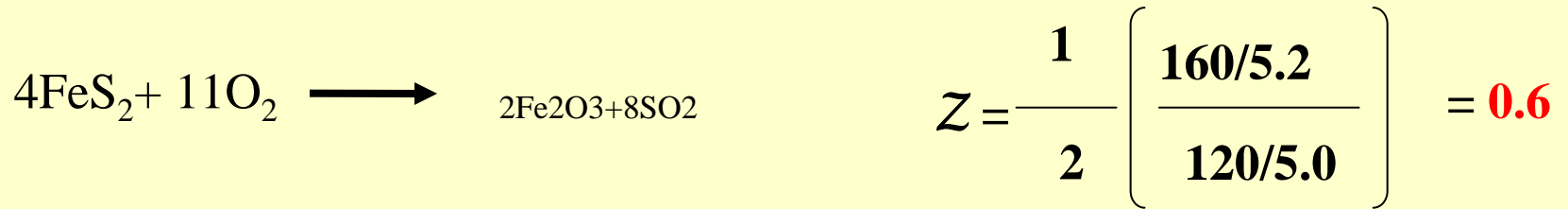
The rate will decrease as the reaction continues because of the dense film of product formed around the reacting solid.

In the case of decomposition of CaCO_3



Since the product is porous

Similar ex:



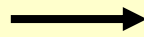
Because of the low value of Z , the oxidation of film will not affect the rate of reaction

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Formation of a Nonporous Product

Solid-gas

Formation of solid product on the surface



This product will vary with the geometry of the solid

Solid-liquid

Flat surface or spherical particle

● Flat surface

$$\frac{dW}{dt} = \alpha \frac{DAC}{y}$$

y = thickness of the film layer

W = weight at time t

$y = kW$, where k is const

When C is const, i.e., when there is a continuous supply of the reagent

$$\frac{dW}{dt} = \frac{\alpha}{k} \frac{DAC}{W}$$

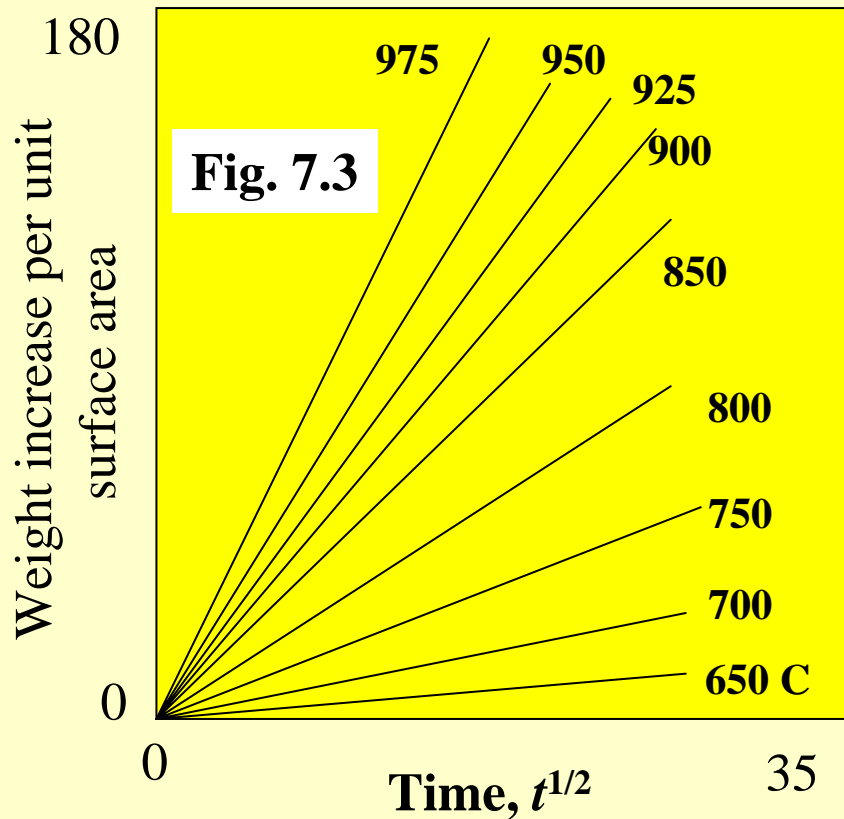
This eq. is a parabola

$$\int W dW = \frac{\alpha}{k} DAC \int dt$$

$$\frac{W^2}{2} = k't + \text{Constant}$$

Parabolic law

The plot of W against $t^{1/2}$ → A straight line



Oxidation of iron_ the parabolic law
(Davies et al., 1951)

At $t=0$, $W = W_0$

$$\frac{1}{2} (W_0^2 - W^2) = k't$$

In terms of fraction reacted

$$R = 1 - W/W_0$$

The parabolic eq. Can be transformed as:

$$W/W_0 = 1 - R$$

$$W^2 = (1 - R)^2 W_0^2$$

$$W_0^2 - (1 - R)^2 W_0^2 = 2k't$$

$$W_0^2 (1 - (1 - R)^2) = 2k't$$

$$(1 - (1 - R)^2) = 2k't / W_0^2$$

$$k'' = 2k't / W_0^2$$

Spherical particle

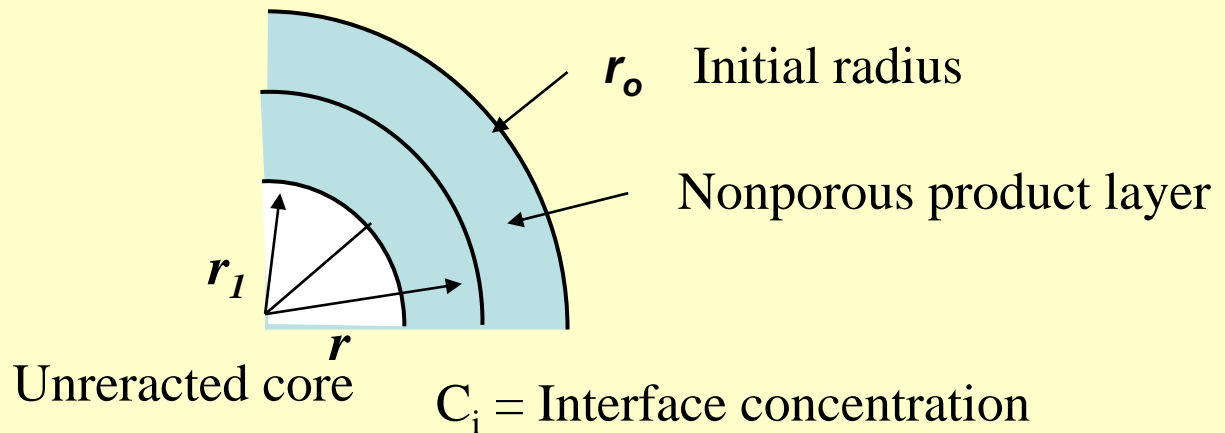
The parabolic law will not apply in this case, because A is continuously decreasing during the reaction

Several solutions

● *Jander's solution* $\left[1 - (1 - R)^{1/3} \right]^2 kt$

● *Simplified solution (Crank-Ginstling and Braunshtein)*

J is the number of moles of the reagent diffusing in t through the product layer



Then using Fick's law: $J = -A \mathcal{D} dC/dr = -4\pi r^2 \mathcal{D} dC/dr$

$$\int_{C_i}^C dC = -\frac{J}{4\pi \mathcal{D}} \int_{r_1}^{r_0} \frac{dr}{r^2}$$

$$C - C_i = -\frac{J}{4\pi \mathcal{D}} \frac{r_0 - r_1}{r_0 r_1}$$

For diffusion-controlled process, $C_i = 0$

$$J = -4\pi \mathcal{D} \frac{r_0 r_1}{r_0 - r_1} C$$

When C is constant, then fraction reacted

$$R = \frac{4/3\pi r_0^3 - 4/3\pi r_1^3}{4/3\pi r_0^3} = \left[\frac{r_1}{r_0} \right]^3$$

$$1 - R = \left[\frac{r_1}{r_0} \right]^3$$

$$r_1 = r_0 (1 - R)^{1/3}$$

The number of moles of unreacted solid at any time t :

$$N = \frac{4}{3}\pi r_1^3 \rho / M$$

$$dN/dt = dN/dr_1 \times dr_1/dt$$

$$dN/dt = \frac{4/3\pi\rho}{M} 3r_1^2 \times \frac{dr_1}{dt}$$

$$dN/dt = \frac{4\pi\rho r_1^2}{M} \times \frac{dr_1}{dt}$$

$$J = -4\pi D \frac{r_0 r_1}{r_0 - r_1} C = \alpha 4\pi \frac{\rho}{M} r_1^2 \frac{dr_1}{dt}$$

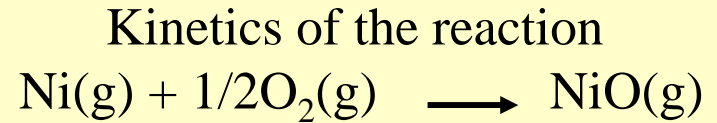
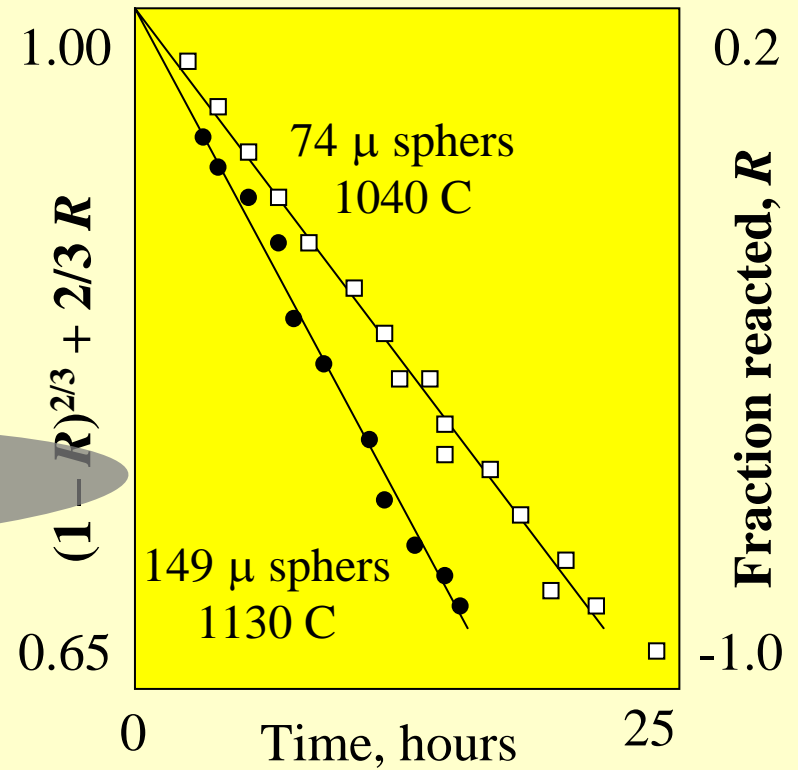
$$\frac{MDC}{\alpha \rho} t = \frac{1}{2}r_1^2 - \frac{1}{6}r_0^2 - \frac{1}{3}r_1^3/r_0$$

Substitute for r_1 in terms of R :

$$\frac{2MDC}{\alpha \rho r_0^2} t = 1 - 2/3R - (1 - R)^{2/3}$$

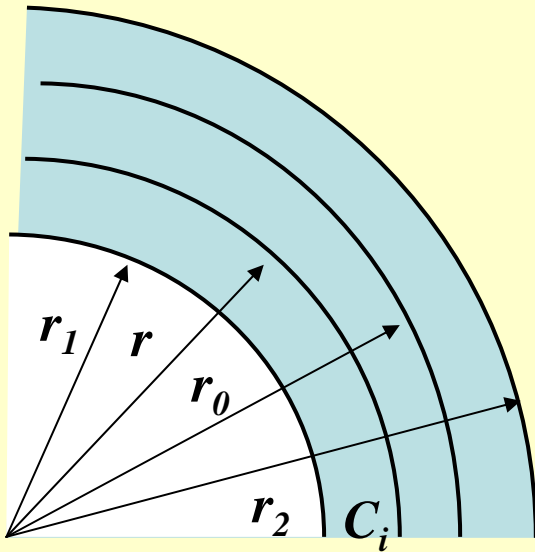
Ch. Reaction Kinetics

$$\frac{2MDC}{\alpha \rho r_0^2} t = 1 - \frac{2}{3}R - (1 - R)^{2/3}$$



(Carter, 1963)

From Fick's diffusion law



Un-reacted core Product layer

$$J = -4\pi\mathcal{D} \frac{r_1 r_2}{r_2 - r_1} (C - C_i)$$

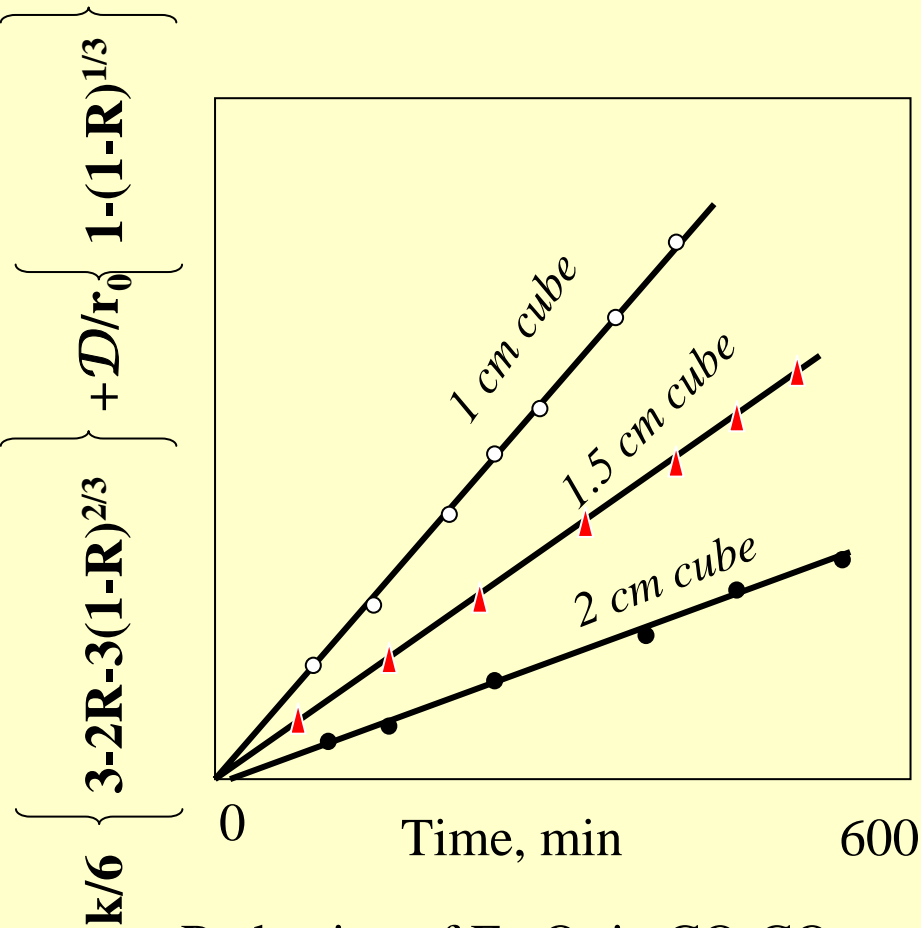
For diffusion-controlled process, $C_i = 0$

$$J = -4\pi\mathcal{D} \frac{r_1 r_2}{r_2 - r_1} C$$

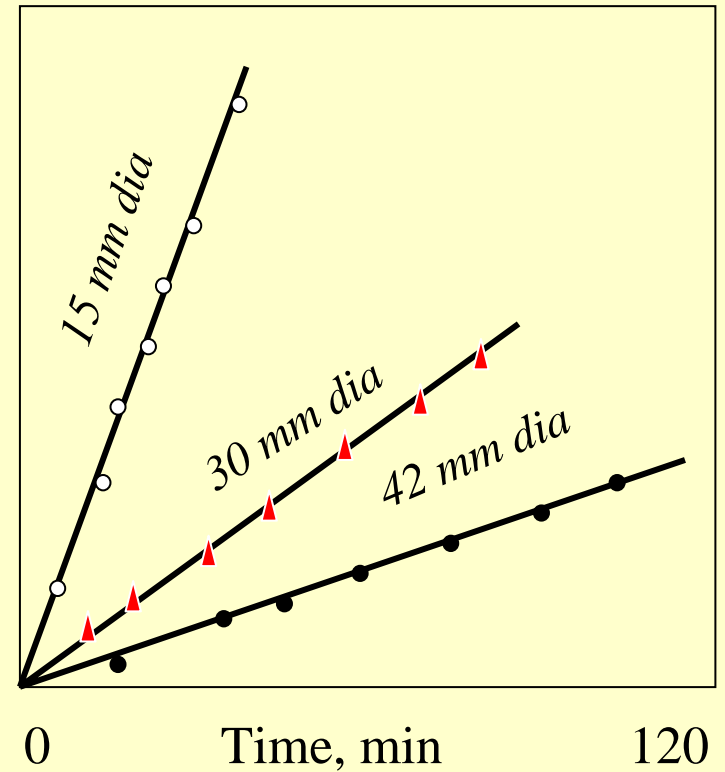
Formation of nonporous
reaction products

If the supply of the reagent is replenished continuously, $C = \text{const}$. The rate of change of W is proportional to J , and the number of moles of reagent diffusing through the spherical shell of thickness $r_2 - r_1$

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Reduction of Fe_3O_4 in CO-CO_2 at 850 C (Seth and Ross, 1966)



Reduction of Fe_2O_3 ore by H_2 at 800 C (Seth and Ross, 1966)