Fluid - Particle Reactions: Kinetics

The heterogeneous reactions in which a gas or liquid contacts a solid, reacts with it, and transforms it into product.

Such reactions may be represented by

A (fluid) + b B (solid) → fluid products —①

→ solid products —②

→ fluid & solid products —③

Solid particles remain unchanged in size during reaction when they contain large amounts of impurities which remain as a nonflaking ash. or

if they form a firm product material by the reactions of equ② or ③

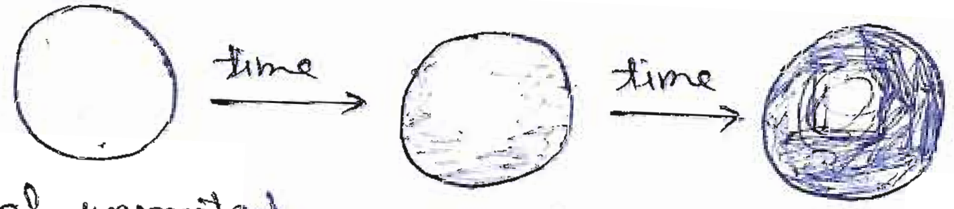


fig ⑨

Particles shrink in size during reaction when a flaking ash or product material is formed or when pure B is used in the reaction of equ①.

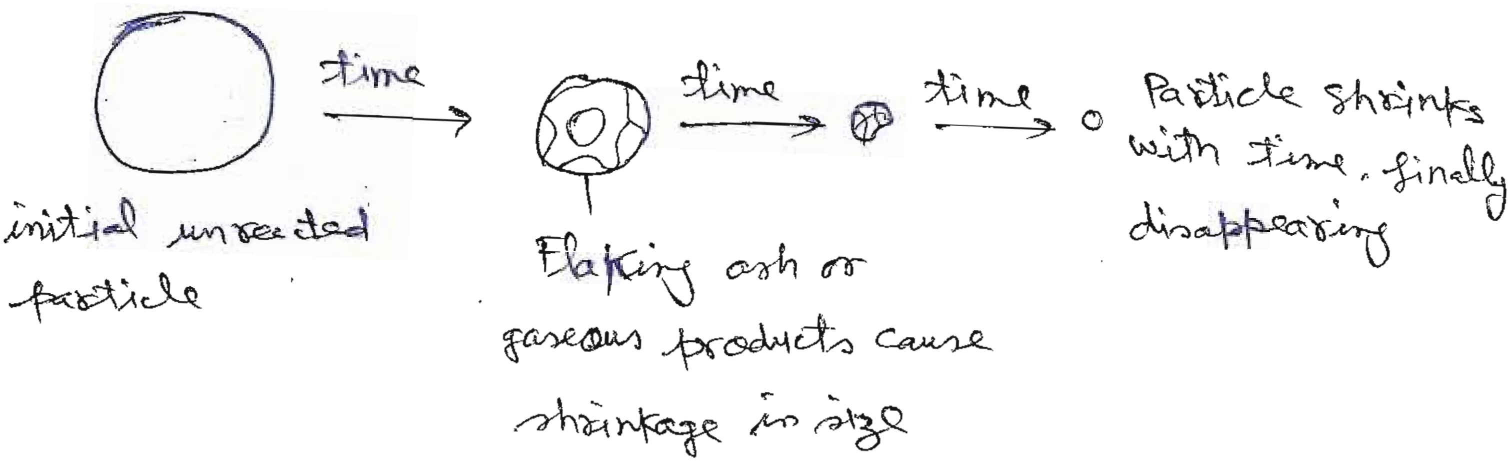


fig ⓑ

fig ⓐ & ⓑ - Different sorts of behavior of reacting solid particles.

Selection of a Model -

For the noncatalytic reaction of particles with surrounding fluid, we consider two simple idealized models.

(1) Progressive - Conversion Model (PCM)

(2) Shrinking - Core Model (SCM)

(1) Progressive - Conversion Model (PCM)

Here we visualize that reactant gas enters and reacts throughout the particle at all times, most likely at different rates at different locations within the particle.

Thus, solid reactant is converted continuously & progressively throughout the particle.

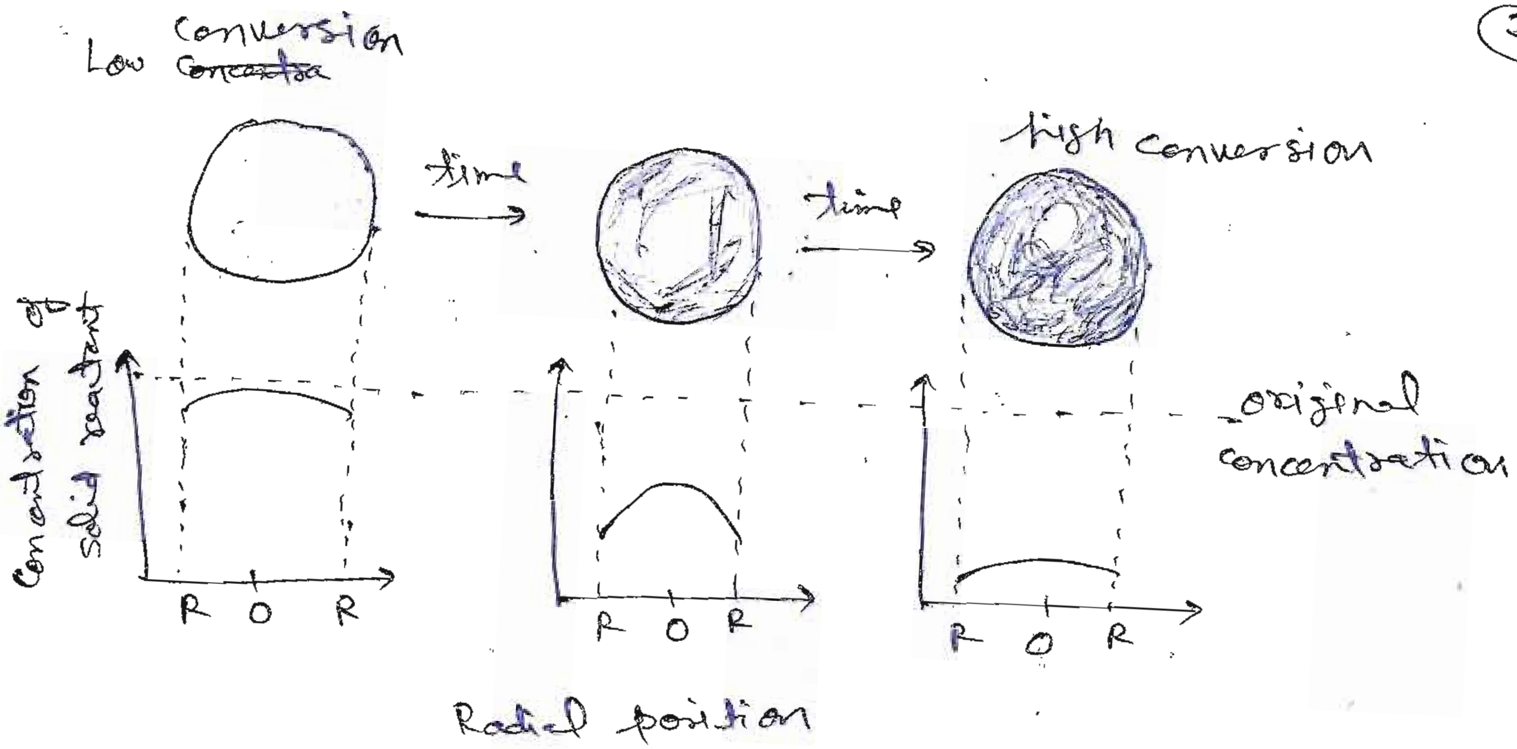


fig. - According to the ~~PC~~ PCM, reaction proceeds continuously throughout the solid particle.

(2) Shrinking - Core Model (SCM)

Here we visualize that reaction occurs first at the outer skin of the particle. The zone of reaction then moves into the solid, leaving behind completely converted material and inert solid.

We refer to these as 'ash'.

Thus, at any time there exists an unreacted core of material which shrinks in size during reaction.

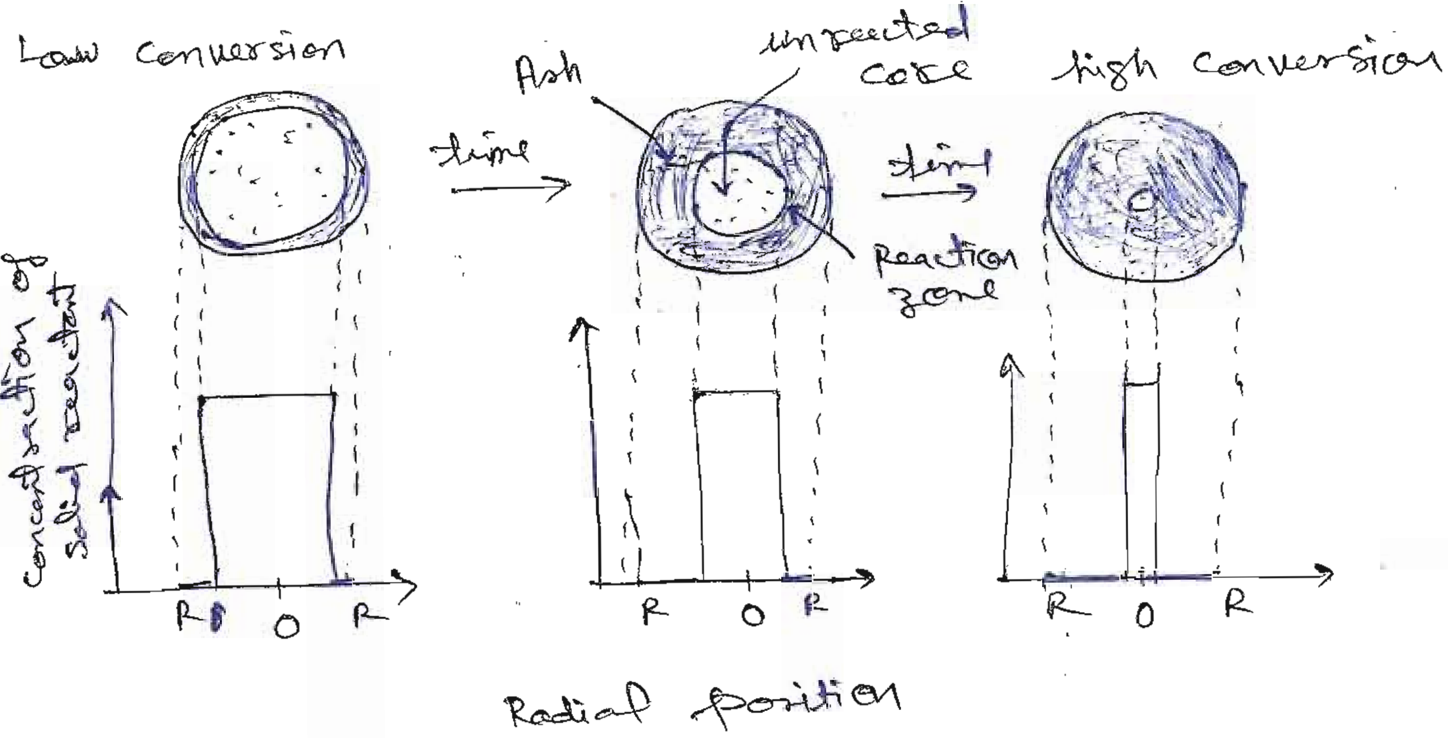


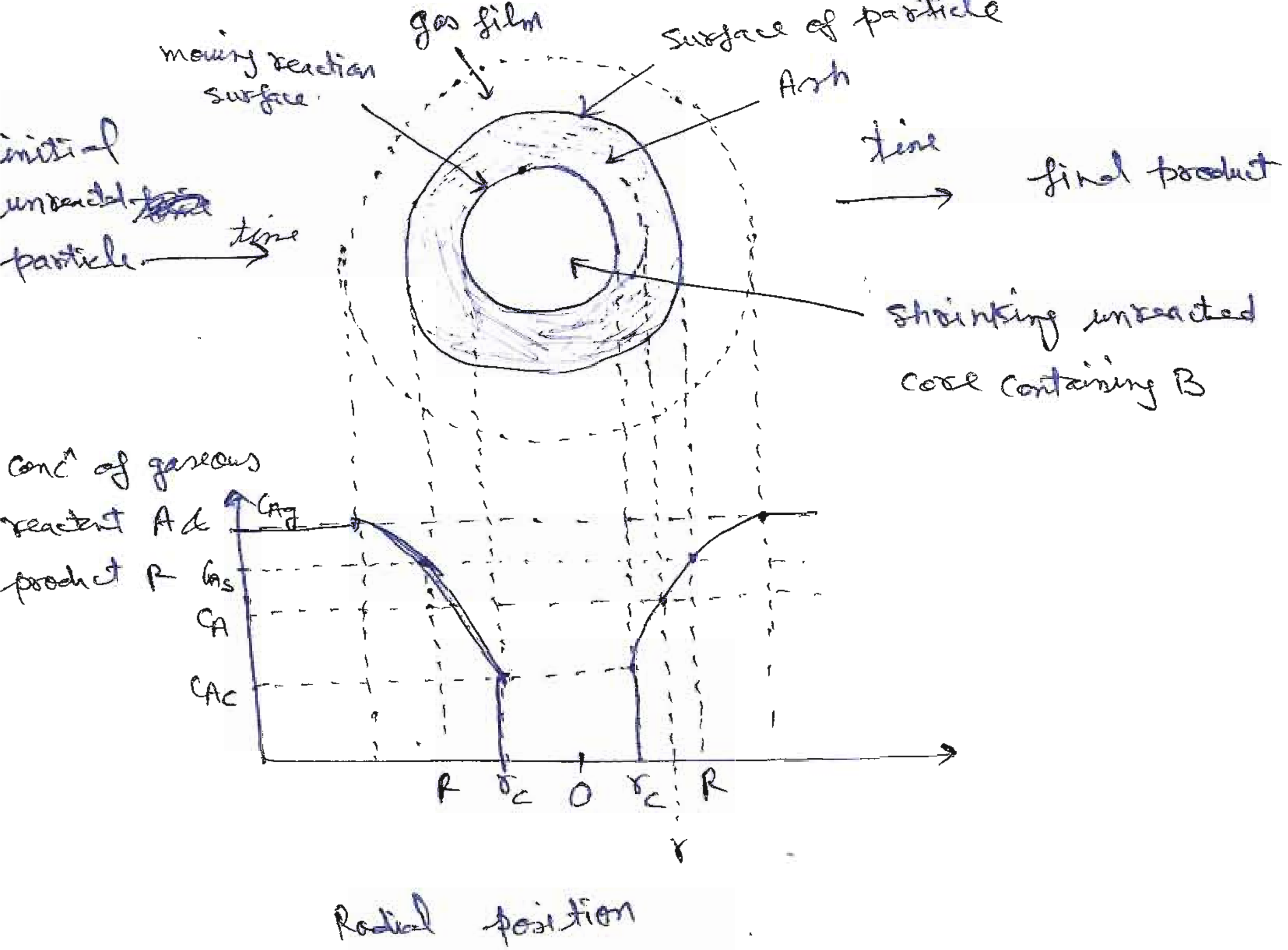
fig- According to SCM, reaction proceeds at a narrow front which moves into the solid particle. Reactant is completely converted as the front passes by.

In the most cases SCM approximates real particles more closely than does the PCM.

observations with burning coal, wood & tightly wrapped newspapers also favor the SCM model.

Shrinking-Core Model for spherical Particles of unchanging size.

$A(g) + bB(s) \rightarrow$ solid product



there are five steps occurring in succession during reaction

Step 1 – Diffusion of gaseous reactant A through the film surrounding the particle to the surface of the solid.

Step 2 – Penetration and diffusion of A through the blanket of ash to the surface of the unreacted core.

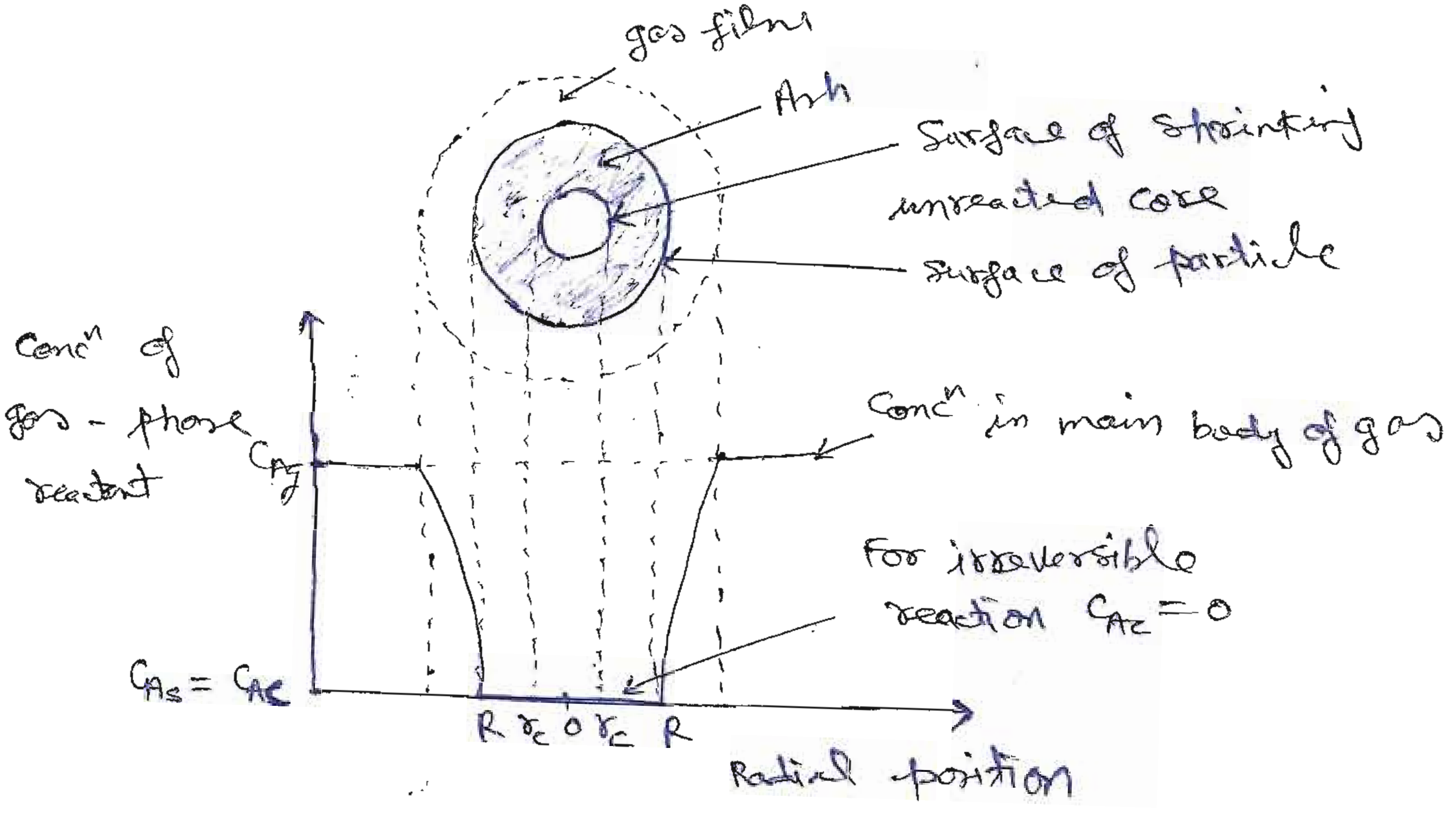
Step 3 - Reaction of gaseous A with solid at this reaction surface.

Step 4 - Diffusion of gaseous products through the ash back to the exterior surface of the solid.

Step 5 - Diffusion of gaseous products through the gas film back into the main body of fluid.

In some situations some of these steps do not exist. For example, if no gaseous products are ~~product~~ formed, step 4 & 5 do not contribute directly to the resistance to reaction.

Diffusion through Gas film Controls -



whenever the resistance of the gas film controls,

no gaseous reactant is present at the particle surface,

hence, the concentration driving force $C_{Ag} - C_{As}$ becomes C_{Ag} & is constant at all times during reaction of the particle.

the unchanging exterior surface of a particle = S_{ex}

$$A(g) + bB(s) \longrightarrow \text{solid product for a particle of unchanging size}$$

$$dN_B = b\,dN_A$$

rate of reaction based on surface

$$-r''_B = -\frac{1}{S_{ex}}\frac{dN_B}{dt} = -\frac{1}{4\pi R^2}\frac{dN_B}{dt} = -\frac{b}{4\pi R^2}\frac{dN_A}{dt}$$

$$= bk_g(C_{Ag} - C_{As}) = bk_g C_{Ag} = \text{constant} \longrightarrow ①$$

where k_g - mass transfer coefficient b/w fluid & particles.

let ρ_B - molar density of B in the solid, $\left(\frac{\text{moles B}}{m^3\ \text{solid}}\right)$

V - Volume of particle, (m^3 solid)

the amount of B present in a particle

$$N_B = \rho_B V$$

$$dN_B = \rho_B\,dV$$

$$dN_B = \rho_B \, d\left(\frac{4}{3}\pi r_c^3\right) \qquad \left[V = \frac{4}{3}\pi r_c^3\right]$$

$$dN_B = 4\pi \rho_B r_c^2 \, dr_c \quad — ②$$

from equ ①

$$-\frac{1}{4\pi R^2}\frac{dN_B}{dt} = b k_g C_{Ag}$$

$$-\frac{1}{\cancel{4\pi} R^2} \times \cancel{4\pi} \rho_B r_c^2 \frac{dr_c}{dt} = b k_g C_{Ag}$$

$$-\frac{\rho_B}{R^2} r_c^2 \, dr_c = b k_g C_{Ag} \, dt \quad — ③$$

~~taking integ~~ By integrating & find how the unreacted core shrinks with time

$$-\frac{\rho_B}{R^2}\int_R^{r_c} r_c^2 \, dr_c = b k_g C_{Ag}\int_0^t dt$$

$$-\frac{\rho_B}{R^2}\left[\frac{r_c^3}{3}\right]_R^{r_c} = b k_g C_{Ag} t$$

$$t = \frac{-\rho_B}{3 b k_g C_{Ag} R^2}\left[r_c^3 - R^3\right]$$

⑤

$$t = \frac{\rho_B R}{3 b K_g C_{Ag}} \left[1 - \left(\frac{r_c}{R} \right)^3 \right] \quad \text{---} ④$$

let the time for complete conversion of a particle be τ i.e taking $r_c = 0$

$$\boxed{\tau = \frac{\rho_B R}{3 b K_g C_{Ag}}} \quad \text{---} ⑤$$

the radius of unreacted core in terms of fractional time for complete conversion is obtained by eqn ④ & ⑤

$$\frac{t}{\tau} = 1 - \left(\frac{r_c}{R} \right)^3 \quad \text{---} ⑥$$

fractional conversion

$$1 - X_B = \left(\frac{\text{Volume of unreacted core}}{\text{total Volume of particle}} \right) = \frac{\frac{4}{3} \pi r_c^3}{\frac{4}{3} \pi R^3} = \left(\frac{r_c}{R} \right)^3 \quad \text{---} ⑦$$

from ⑥ & ⑦

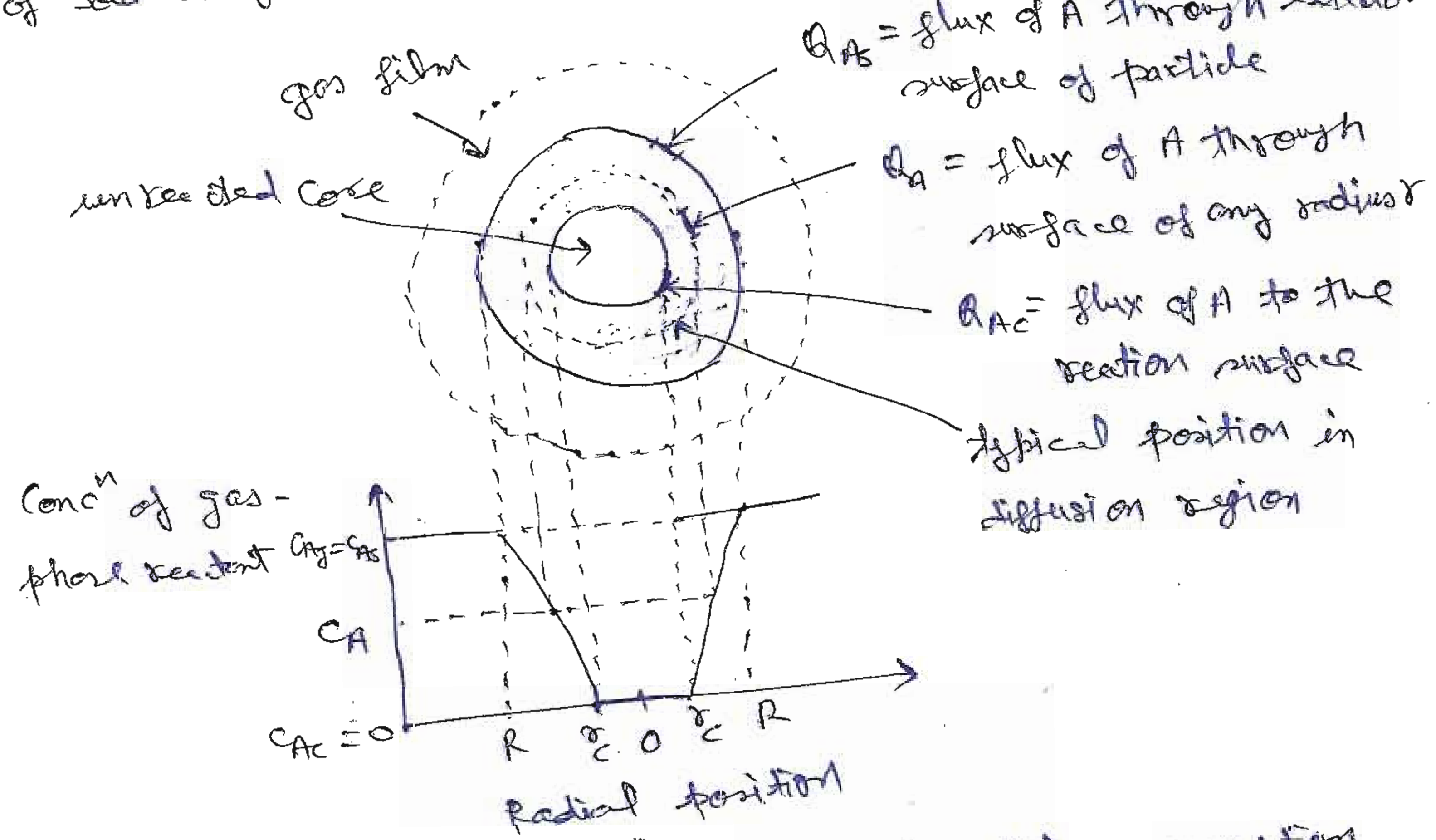
$$\boxed{\frac{t}{\tau} = 1 - \left(\frac{r_c}{R} \right)^3 = X_B} \quad \text{---} ⑧$$

the relationship of time with radius & with conversion.

Diffusion through Ash layer controls

Consider a partially reacted particles. Both reactant A and the boundary of the unreacted core move inward toward the center of the particle.

But for G/s systems the shrinkage of the unreacted core is slower than the flow rate of A toward the unreacted core by a factor of about 1000, which is roughly the ratio of densities of solid to gas.



For G/s systems the use of the steady-state assumption, the rate of reaction of A at any instant is given by its rate of diffusion to the reaction surface.

$$-\frac{dN_A}{dt} = 4\pi r^2 Q_A = 4\pi R^2 Q_{As} = 4\pi r_c^2 Q_{Ac} = \text{constant} \quad \text{— ⑨}$$

let the flux of A within the ash layer be expressed by Fick's law for equimolar counterdiffusion.

$$Q_A = D_e \frac{dC_A}{dr} \quad \text{— ⑩}$$

D_e - effective diffusion coefficient of gaseous reactant in the ash layer

from ① & ②

$$-\frac{dN_A}{dt} = 4\pi r^2 D_e \frac{dC_A}{dr} \quad \text{— ⑪}$$

integrating across the ash layer from R to r_c

$$-\frac{dN_A}{dt}\int_{R}^{r_c} \frac{dr}{r^2} = 4\pi D_e \int_{C_{Ag}}^{0} dC_A$$

$$-\frac{dN_A}{dt}\left(\frac{1}{r_c} - \frac{1}{R}\right) = 4\pi D_e C_{Ag} \quad \text{— ⑫}$$

This expression represents the conditions of a reacting particle at any time.

we know from equ ②

$$dN_B = \rho_B \, dV$$

$$b \, dN_A = \rho_B \, d\left(\frac{4}{3}\pi r_c^3\right)$$

$$dN_A = \frac{4\pi \rho_B r_c^2 \, dr_c}{b}$$ put in ⑫

$$-\frac{\cancel{4\pi}\rho_B r_c^2}{b}\left(\frac{1}{r_c}-\frac{1}{R}\right)\frac{dr_c}{dt} = \cancel{4\pi} D_e C_{Ag}$$

By integration

$$-\rho_B \int_R^{r_c}\left(\frac{1}{r_c}-\frac{1}{R}\right) r_c^2 \, dr_c = b D_e C_{Ag}\int_0^t dt$$

$$-\rho_B \left[\frac{r_c^2}{2} - \frac{r_c^3}{3R}\right]_R^{r_c} = b D_e C_{Ag} \, t$$

~~$t = \frac{\rho_B}{b D_e C_{Ag}}\Big[$~~

$$-\rho_B \left[\frac{r_c^2}{2} - \frac{r_c^3}{3R} - \frac{R^2}{2} + \frac{R^2}{3}\right] = b D_e C_{Ag} \, t$$

$$t = \frac{\rho_B R^2}{6 b D_e C_{Ag}}\left[1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3\right] \quad \text{—} \; ⑬$$

for the complete conversion of particle, $r_c = 0$

$$\boxed{\tau = \frac{\rho_B R^2}{6 b D_e C_{Ag}}}$$ — ⑭

fractional time

$$\boxed{\frac{t}{\tau} = 1 - 3\left(\frac{r_c}{R}\right)^2 + 2\left(\frac{r_c}{R}\right)^3}$$ — ~~⑧~~ ⑮

fractional conversion

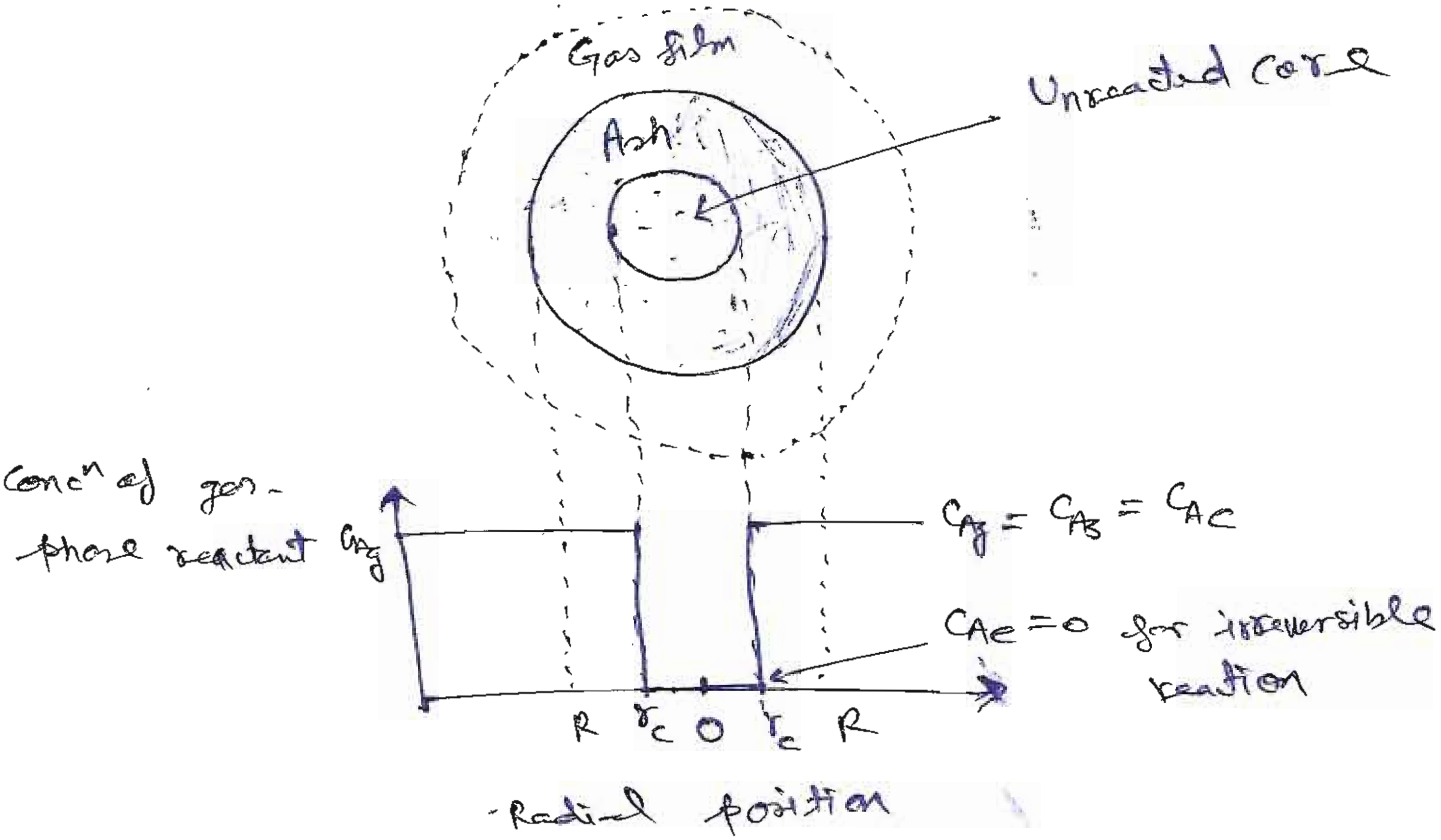
$$1 - X_B = \left(\frac{r_c}{R}\right)^3$$ — ~~⑧~~ ⑯

from ~~⑧ & ⑨~~ ⑮ & ⑯

$$\boxed{\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)}$$ — ~~⑩~~ ⑰

Chemical Reaction Controls

Concentration gradients within a particle when chemical reaction controls.



Since the progress of the reaction is unaffected by the presence of any ash layer, the rate is proportional to the available surface of unreacted core.

Thus, based on unit surface of unreacted core, r_c, the rate of reaction $A(g) + bB(s) \rightarrow$ Products

$$-\frac{1}{4\pi r_c^2}\frac{dN_B}{dt} = -\frac{b}{4\pi r_c^2}\frac{dN_A}{dt} = bK'' C_{Ag} \quad (18)$$

K'' – Ist order rate constant for the surface reaction.

we know from ②

$dN_B = 4\pi \rho_B r_c^2 \, dr_c$ put in ⑧

$$-\frac{1}{\cancel{4\pi r_c^2}} \rho_B \cancel{4\pi r_c^2} \frac{dr_c}{dt} = bK'' C_{Ag}$$

$-\rho_B \dfrac{dr_c}{dt} = bK'' C_{Ag}$ —— ⑲

By integration

$$-\rho_B \int_R^{r_c} dr_c = bK'' C_{Ag} \int_0^t dt$$

$$\rho_B (R - r_c) = bK'' C_{Ag} \, t$$

$t = \dfrac{\rho_B}{bK'' C_{Ag}} (R - r_c)$ —— ⑳

from complete conversion, $r_c = 0$

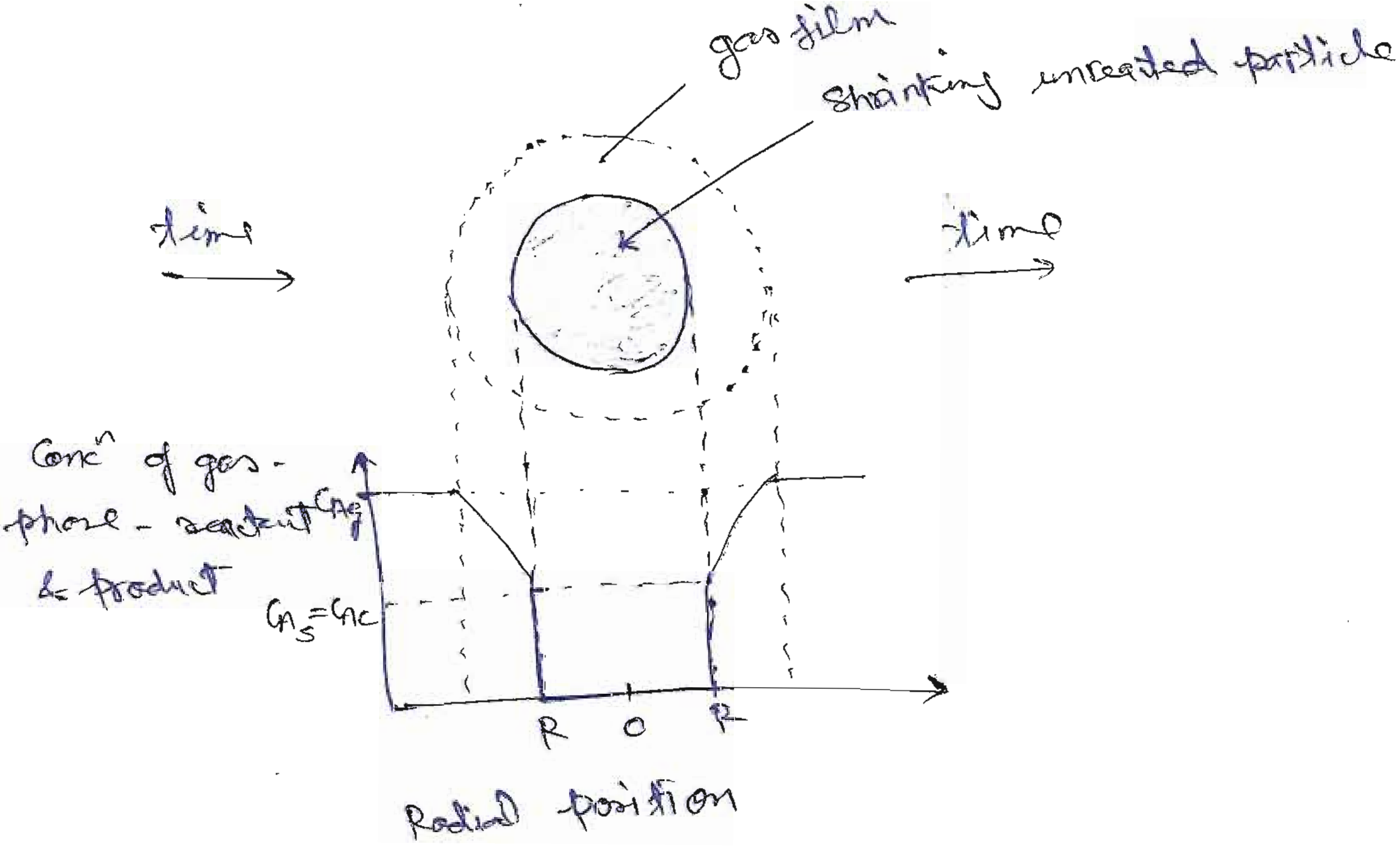
$\boxed{\tau = \dfrac{\rho_B R}{bK'' C_{Ag}}}$ —— ㉑

i.e

$\boxed{\dfrac{t}{\tau} = 1 - \dfrac{r_c}{R} = 1 - (1 - X_B)^{1/3}}$ —— ㉒ $\left[1 - X_B = \left(\dfrac{r_c}{R}\right)^3\right]$

* Rate of Reaction for shrinking spherical Particles

when no ash forms, as in the burning of pure carbon in air, the reacting particle shrinks during reaction, finally disappearing.



$$A(g) + bB(s) \longrightarrow rR(g)$$

there are three steps occuring

Step 1 - Diffusion of reactant A from the main body of gas through the gas film to the surface of solid.

Step 2 - Reaction on the surface b/w reactant A & solid.

Step 3 - Diffusion of reaction products from the surface of the Solid through the gas film back into the main body of gas.

Note that the ash layer is absent and does not contribute any resistance.

Chemical Reaction Controls -

When chemical reaction controls, the behavior is identical to that of particles of unchanging size:

equ ⑳ or ㉒

i.e

$$t = \frac{\rho_B}{b\, k'' C_{Ag}} (R - r_c) \quad — ⑳$$

$$\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3} \quad — ㉒$$

equ ⑳ ㉒ will represent the conversion - time behavior of single particles - both shrinking & of constant size.

Gas film Diffusion Controles

Film resistance at the surface of a particle is dependent on numerous factor,

such as - the relative velocity b/w particle & fluid,

- size of particle &
- fluid properties.

These have been Correlated for various ways of contacting fluid with solid, such as packed beds, fluidized beds, and ~~fraction~~ solid in free fall.

For example -

for mass transfer of a component of mole fraction y in a fluid to free-falling solids

$$\frac{k_g d_p y}{D} = 2 + 0.6\,(Sc)^{1/3}\,(Re)^{1/2} = 2 + 0.6\left(\frac{\mu}{\rho D}\right)^{1/3}\left(\frac{d_p u \rho}{\mu}\right)^{1/2} \quad ㉓$$

During reaction a particle changes in size, hence k_g also varies.

In general k_g rises for an increase in gas velocity & for small particles.

i.e $k_g \propto \frac{1}{d_p}$ for small d_p & u — ㉔

$k_g \propto \frac{u^{1/2}}{d_p^{1/2}}$ for large d_p & u — ㉕

equ ㉔ represents particles in the stokes law regime.

Let us develop conversion-time expressions for such particles.

Stokes Regime (small particles) -

At the time when a particle, originally of size R_o has shrunk to size R.

$$= 4\pi R^2 dR$$

$$dN_B = \rho_B dV = \cancel{4\pi \rho_B r^2 dr}$$ — ㉕

rate of ~~equation~~ reaction based on surface, from equ ①

$$-r_B'' = -\frac{1}{S_{ex}}\frac{dN_B}{dt} = -\frac{b}{S_{ex}}\frac{dN_A}{dt} = bK_g C_{Ag}$$ — ① ~~㉕~~

$$\left[\frac{N_B}{2} = N_A\right]$$

i.e. $$-\frac{1}{S_{ex}}\frac{dN_B}{dt} = bK_g C_{Ag}$$ — ㉖

from equ ㉕ & ㉖

$$-\frac{\cancel{4\pi}\rho_B \cancel{R^2} dR}{\cancel{4\pi} \cancel{R^2} dt} = bK_g C_{Ag}$$

in stokes regime equ ③

$$K_g = \frac{2D}{d_p}$$

$$K_g = \frac{D}{R}$$

$$-\rho_B \frac{dR}{dt} = \frac{bC_{Ag}D}{R}$$

$$-RdR = \frac{bC_{Ag}D}{\rho_B}dt$$

By integration $$-\int_{R_o}^{R} RdR = \frac{bC_{Ag}D}{\rho_B}\int_0^t dt$$

$$-\left[\frac{R^2}{2}-\frac{R_o^2}{2}\right] = \frac{b\,C_{Ag}\,D}{\rho_B}\,t$$

$$t = \frac{\rho_B R_o^2}{2b\,C_{Ag}\,D}\left[1-\left(\frac{R}{R_o}\right)^2\right] \quad — ㉗$$

from complete conversion, $R=0$

$$\boxed{\tau = \frac{\rho_B R_o^2}{2b\,C_{Ag}\,D}} \quad — ㉘$$

fractional conversion

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

i.e $$\boxed{\frac{t}{\tau} = 1-\left(\frac{R}{R_o}\right)^2 = 1-(1-X_B)^{2/3}} \quad — ㉙$$

This relationship of size versus time for shrinking particles in the stokes regime.

it well represents small burning solid particles and small burning liquid droplets.

Determination of the Rate-controlling step

The kinetics and rate-controlling steps of a fluid-solid reaction are deduced by noting how the progressive conversion of particles is influenced by particle size & operating temperature.

There are following observations:

(1) Temperature - The chemical step is usually much more temp-sensitive than physical steps.

hence, experiments at different temperatures should easily distinguish b/w ash or film diffusion on the one hand and chemical reaction on the other hand as the controlling step.

(2) Time - fig ⓐ & ⓑ show the progressive conversion of spherical solids when chemical reaction, film diffusion, & ash diffusion in turn control.

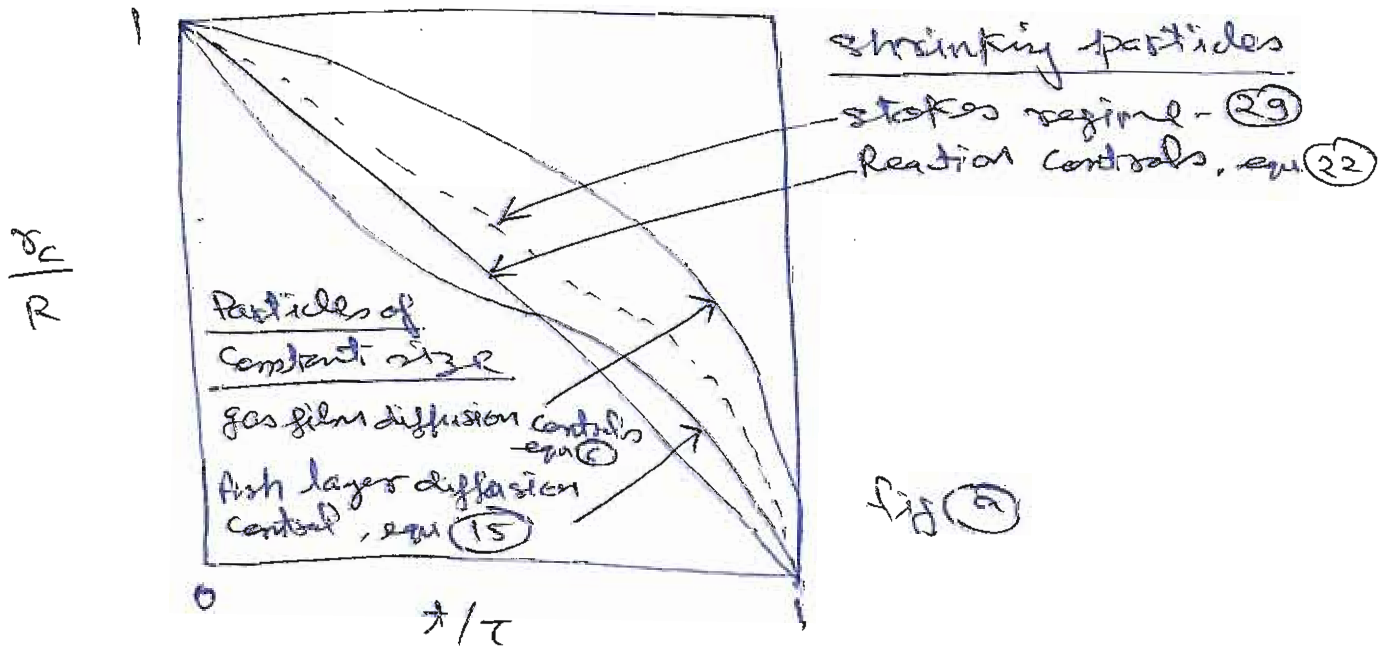


fig ⓐ

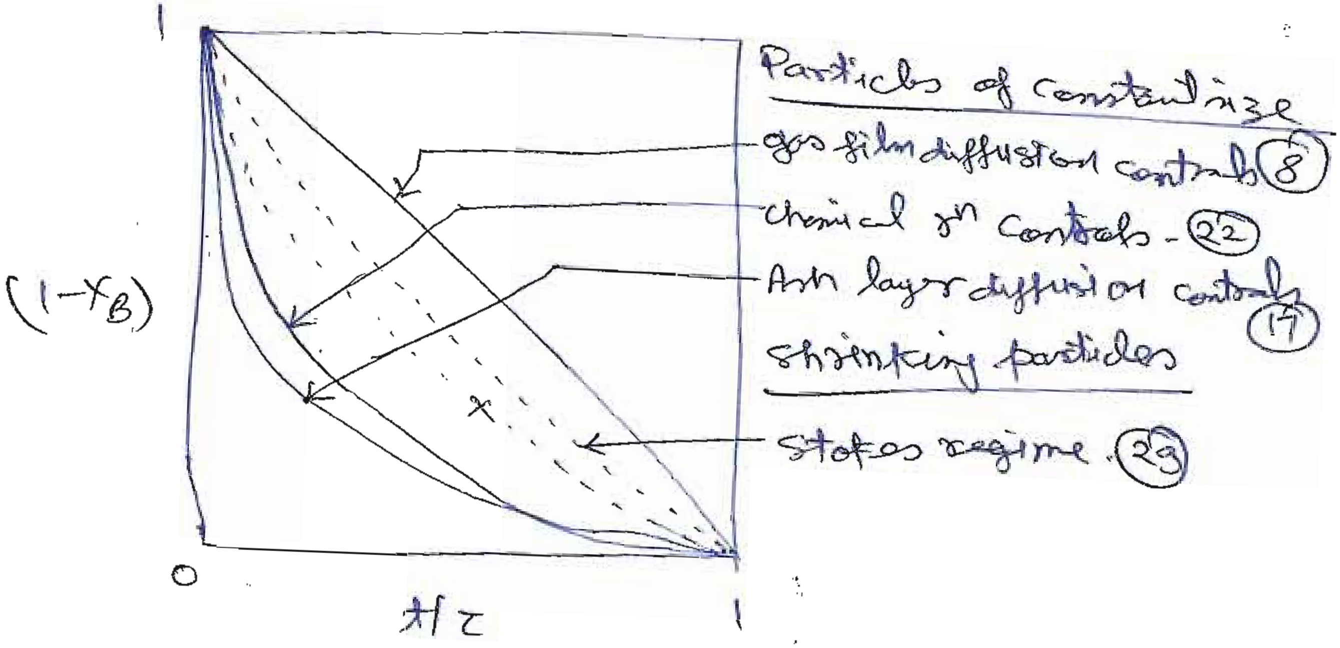


fig ⓑ

(3) Particle size – for small dp & u

i.e. $k_g \propto \frac{1}{d_p}$ or $k_g \propto \frac{1}{R}$ — (24)

for film diffusion controlling

from equ (4) & (24)

$t \propto R^{1.5 \text{ to } 2}$ — (30)

for ~~film~~ ash diffusion controlling, from equ ~~(4) & (24)~~ (13)

$t \propto R^2$ — (31)

for chemical reaction controlling, from equ (20)

$t \propto R$ — (32)

Ash Versus Film Resistance -

When a hard solid ash forms during reaction, the resistance of gas-phase reactant through this ash is usually much greater than through the gas film surrounding the particle.

Hence in the presence of a nonflaking ash layer, film resistance can safely by ignored.

i.e ash resistance is unaffected by changes in gas velocity.

Overall Versus Individual Resistance -

If a plot of individual rate coefficients is made as a function of temperature. the overall coefficient. cannot be higher than any of the ~~iti~~ individual coefficients.