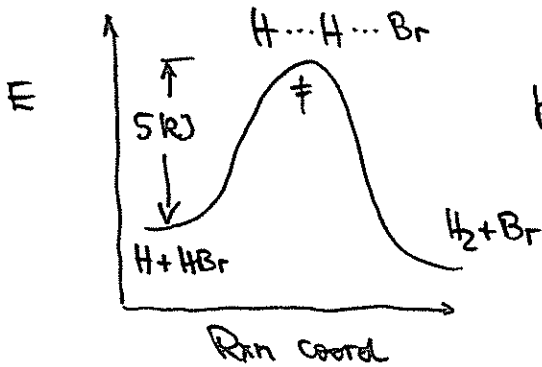


In homogeneous rxns, can analyze kinetics by using thermo
 ⇒ 'guesstimate' rate constants

e.g., $k_{rxn} = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT}\right)$

quantum chemistry/
 statistical thermo
 (partition functions,
 geometry of transition
 state, ...)

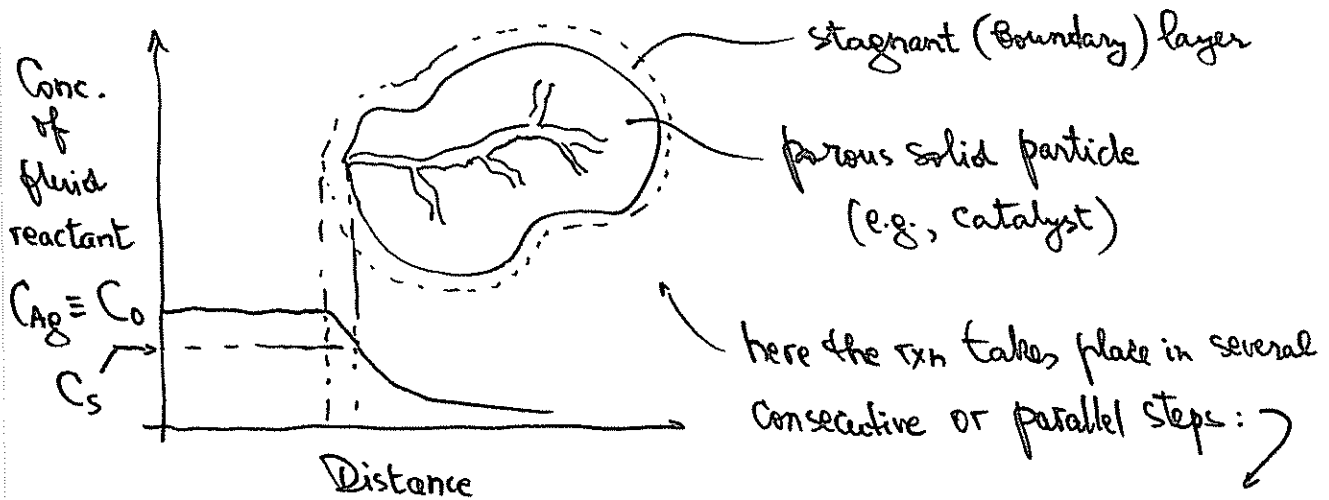
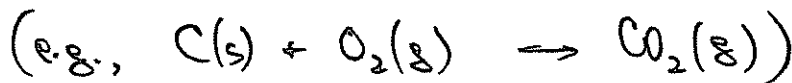
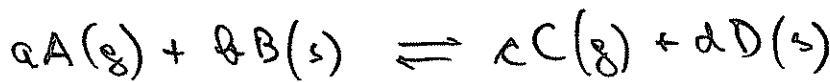


$k_{rxn} = \frac{k_B T}{h} \frac{q^\ddagger}{q_H q_{HBr}} \exp\left(-\frac{\Delta H^\ddagger}{RT}\right)$
 etc.

still

In heterogeneous rxns, we are far away from being able to do this, because of inability to treat the surface of a solid (or a liquid) using first principles.

⇓ a "phenomenological" approach



1. Diffusion of reactant fluid(s) from the bulk to external particle surface
2. - - - - - through the pores of B

- p. 8, 1-H (p. 11) *
3. Chemisorption of reactant fluid(s) on surface of B
 4. Rxn on the surface
 5. Desorption of product(s) from the surface of B
 6. Diffusion of product(s) through pores of B
 7. + ... - from external surface to bulk of fluid

- Steps 1, 2, 6, 7 are mass transfer processes (conc. gradient, diff. coeff., etc.)

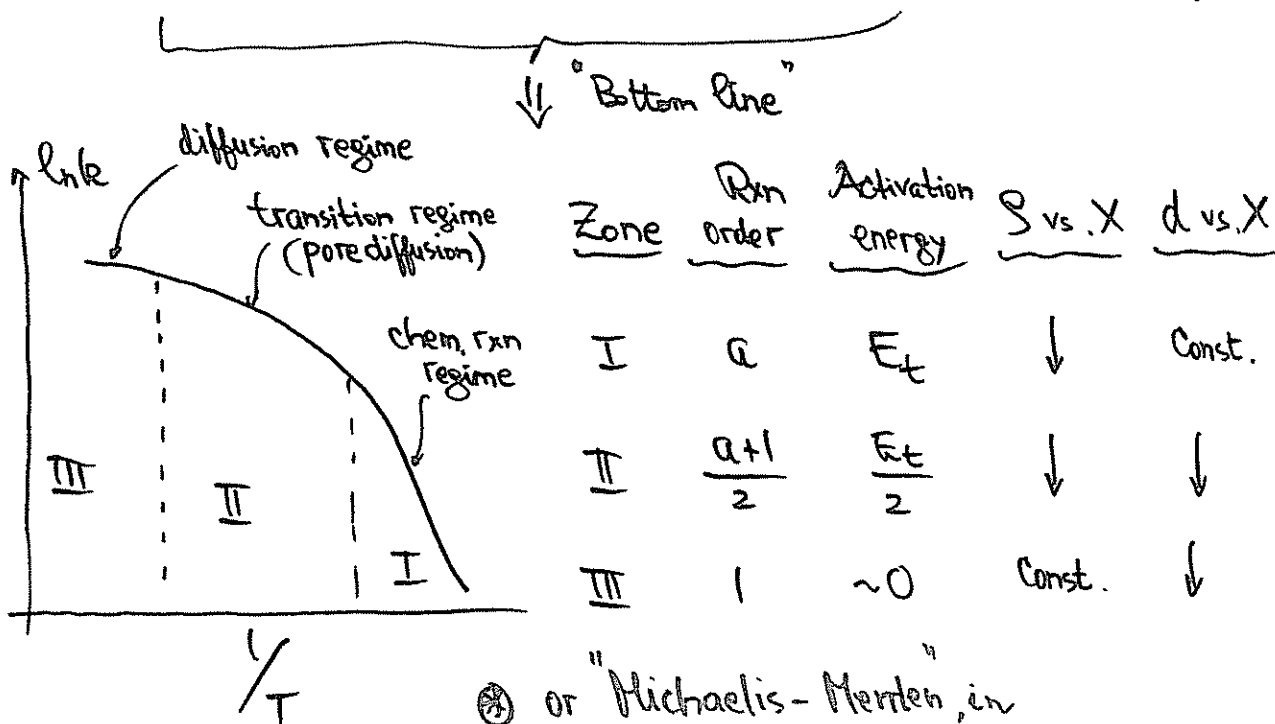
- Here we shall analyze mostly the chem. kinetic steps (3-5)

$$- \frac{dC_B}{dt} = k C_A^a C_B^b$$

Problem 1
How to determine and normalize?

Problem 2
Possible concentration gradients between bulk and interior (see cartoon)...

Problem 3
How to characterize the solid surface? (TSA, ASA...)



* or "Michaelis-Menten" in enzyme catalysis

- typical situation (porous solid, Catalyst particle):

See Ch. 28 (Atkins)



TSA: Physisorption of a suitable adsorbate (e.g., N_2 , CO_2 , Ar)

ASA: Chemisorption of a suitable adsorbate (e.g., H_2 , O_2), TEM, etc.

(e.g., "catalyst dispersion")

e.g., Langmuir eqn.

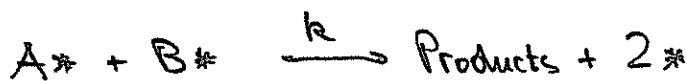
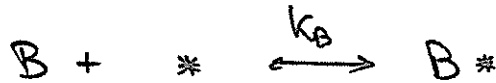
How does one determine and use this number?

[Ch. 28, Atkins]

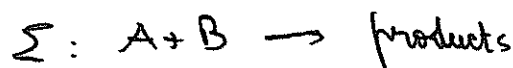
Rate = Rate of adsorption of reactants = Rate of surf. rxn. =
= Rate of desorption of products

(steady state, consecutive scheme!)

$$\Rightarrow \text{Rate}_{\text{ads}} = R_{\text{ads}} = [\text{Reactant}] [\text{Active sites}]$$



Want to maximize this (for maximum rate...)

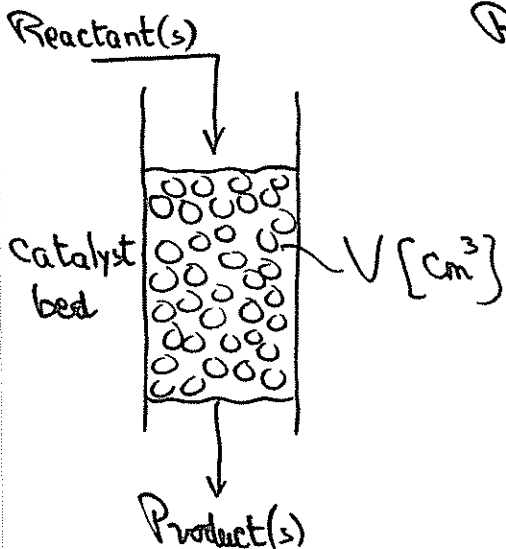


site balance: $[L] = [*] + [A^*] + [B^*]$

$$\theta_A \equiv \frac{[A^*]}{[L]} ; \theta_B \equiv \frac{[B^*]}{[L]} \text{ etc.}$$

$[L] \equiv 10^{15} \text{ cm}^{-2}$
Show!

In heterogeneous rxns, it is of interest to express ("normalize") the rate w/ to ASA:



$$\text{Rate, } \frac{\text{mol}}{\text{cm}^3 \cdot \text{s}} = \frac{\text{mol}}{\text{active site} \cdot \text{s}} \times \frac{\text{number of active sites}}{\text{cm}^3}$$

this is of practical interest
(and a link to homog. rxns)

TURNOVER
FREQUENCY

(this is of fundamental interest)

How do we measure this?

$$\frac{\# \text{ of active sites}}{\text{cm}^3 \text{ bed}} = \frac{\text{g catalyst}}{\text{cm}^3 \text{ particle}} \left(\frac{1 - \text{bed porosity}}{\frac{\text{cm}^3 \text{ particle}}{\text{cm}^3 \text{ bed}}} \right) \times \frac{\left\{ \begin{array}{l} \text{catalyst} \\ \# \text{ of surface sites} \end{array} \right\}}{\left\{ \begin{array}{l} \text{total \# of catalyst} \\ \text{sites} \end{array} \right\}}$$

$$= \frac{\# \text{ of active sites}}{\# \text{ of surface sites}} \times \frac{N_A, \frac{\text{sites}}{\text{mol}}}{M_{\text{cat}}, \frac{\text{g cat}}{\text{mol}}}$$

DISPERSION
(fraction exposed)
[D]

e.g., $40 \frac{\mu\text{mol adsorbate}}{\text{g cat}}$ (typical for highly dispersed Pt, H₂ adsorption e.g., 2% Pt on C support)

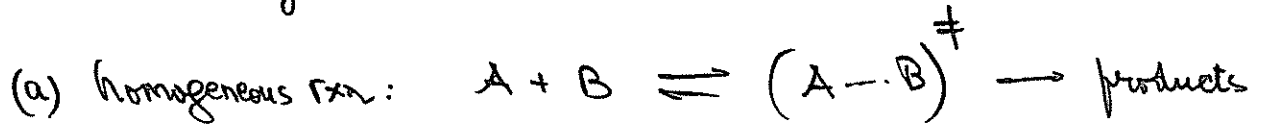
$$D = 40 \times 10^{-6} \frac{\text{mol H}_2}{\text{g cat}} \frac{2 \text{ atoms H}}{1 \text{ mol H}_2} \dots$$

↓ Show!

$$= 0.78 \text{ (78\% of all Pt atoms are on the surface, or exposed to the adsorbate, and therefore to the reactants as well)}$$

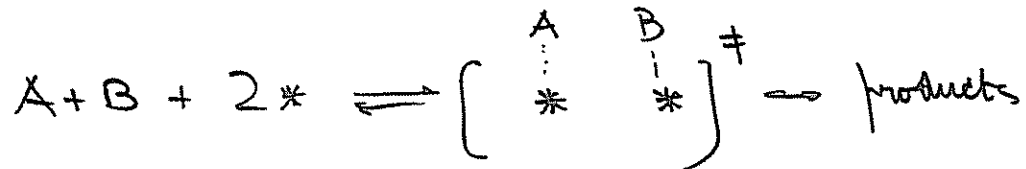
!?

How does a catalyst increase the rxn rate, w/r to a homogeneous or uncatalyzed rxn?



$$R_{\text{hom}} = k[A][B] = \frac{RT}{h} \frac{f^\ddagger}{f_A' f_B'} \exp\left(-\frac{E_{\text{hom}}}{RT}\right) [A][B]$$

(b) heterogeneous (catalytic) rxn:



$$R_{\text{cat}} = [L]_{\text{cat}} \frac{RT}{h} \frac{f''^\ddagger}{f_A' f_B' f_L''} \exp\left(-\frac{E_{\text{het}}}{RT}\right) [A][B]$$

$$\therefore \frac{R_{\text{cat}}}{R_{\text{hom}}} \approx \frac{[L]_{\text{cat}} f''^\ddagger}{f_A' f_L''} \exp\left[\frac{E_{\text{hom}} - E_{\text{het}}}{RT}\right]$$

?! 15⁻² < 10²⁷ cm⁻³

of the order of 10²⁷ cm⁻³ (use [L]_{uncat} for het. uncatal. rxns)

$$[L] \approx 10^{15} \text{ cm}^{-2} = \left(10^{15} \frac{1}{\text{cm}^2}\right) \left(\dots \frac{\text{cm}^2}{g}\right) \left(\dots \frac{g}{\text{cm}^3}\right) \approx \dots \text{cm}^{-3}$$

Obviously, if $E_{\text{hom}} \approx E_{\text{het}}$, $R_{\text{het}} \approx R_{\text{cat}}$ would be much less than R_{hom} !?

$\Rightarrow E_{\text{cat}} < E_{\text{hom}}$ (By how much?)
!!

let's now analyze in more detail the rxn rate expression for heterogeneous rxn, having in mind the need to integrate it and obtain the rxn time.

$$\text{Rate} = k C_A^a C_B^b$$

$\left[\frac{\text{mol A}}{\text{cm}^3 \cdot \text{s}} \right]$ $\left[\frac{\text{mol A}}{\text{cm}^3} \right]$ $\left[\frac{\text{mol A}}{\text{cm}^3} \right]$

$b = 1$ (assume!) TSA? \downarrow \downarrow S

natural units: $\frac{\text{cm}^2}{\text{cm}^3} = \frac{\text{cm}^2}{S} \frac{g}{\text{cm}^3}$

$= R_s = k_s C_A$ (assume 1st order for simplicity and illustration)

$\frac{\text{mol A}}{\text{cm}^2 \cdot \text{s}}$ $\frac{\text{cm}}{s}$ vs. $k_v (=) \frac{1}{s}$ (1st order homogeneous rxn)

(i.e., $\text{Rate} = -\frac{1}{S_v} \frac{dC_A}{dt} = -\frac{1}{S_v} \frac{a}{b} \frac{dC_B}{dt}$)

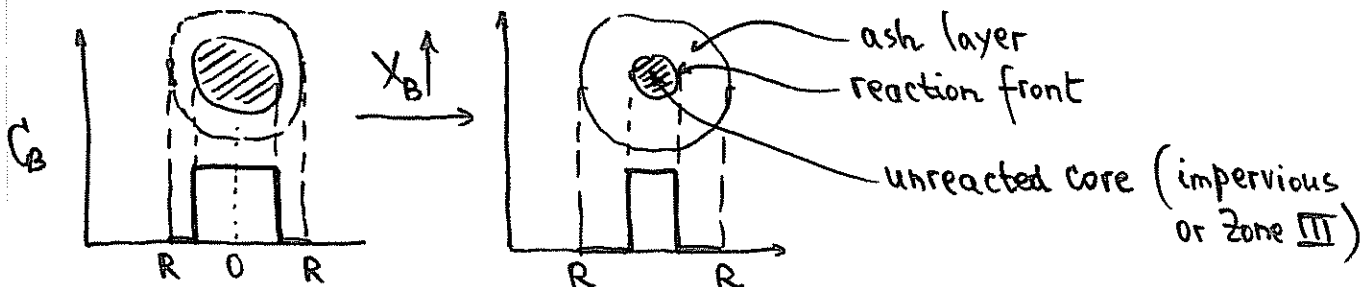
\Downarrow How to \int ?

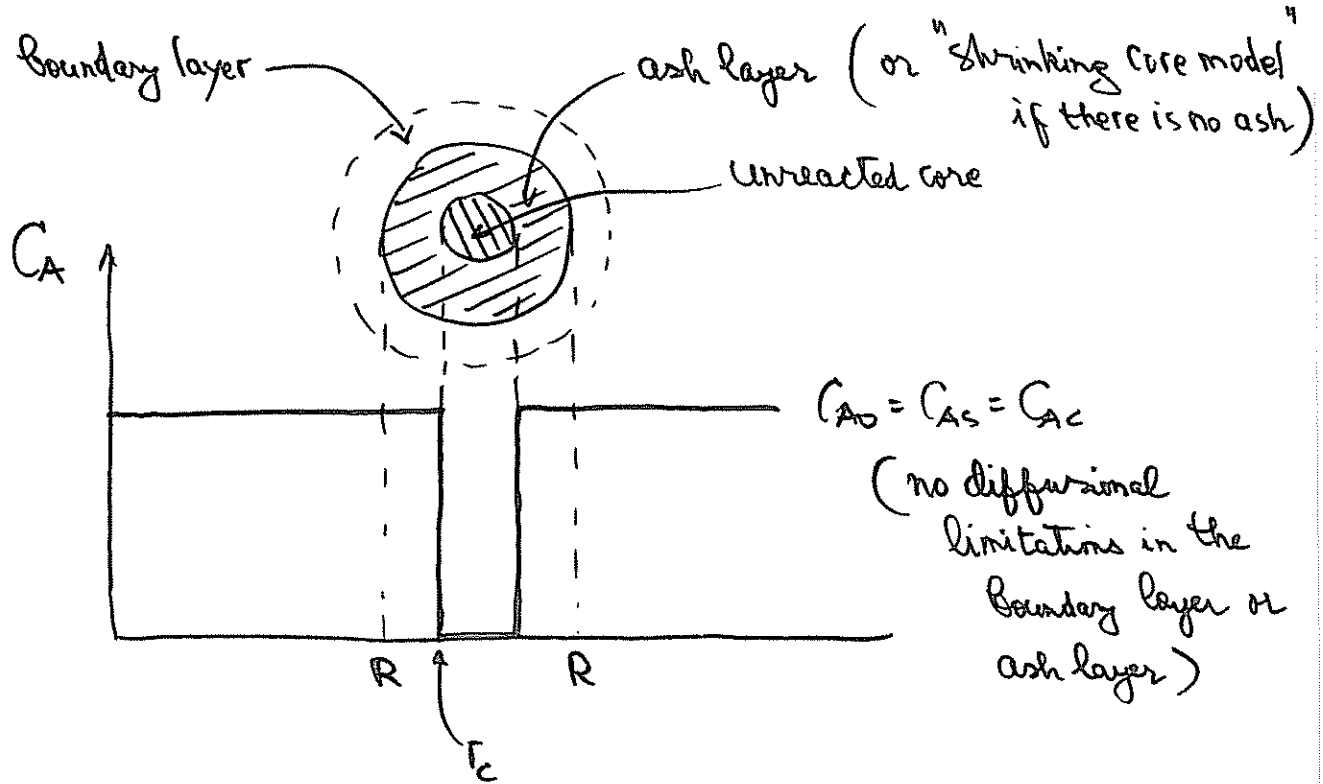
e.g., $-\int \frac{dC_A}{C_A} = -\frac{a}{b} \int \frac{dC_B}{C_B} = \int R S_v dt = k \int S_v dt$

e.g. $\therefore S_v \stackrel{?}{=} f(t)$

... this is the key issue in heterogeneous rxn kinetic studies

Unreacted core model (spherical particles, unchanging size)





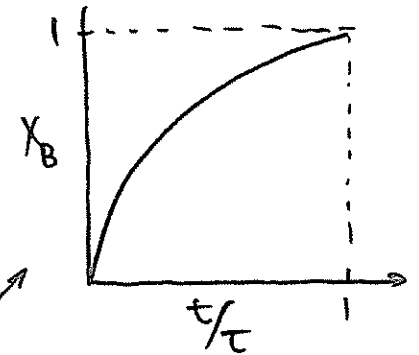
$$\Rightarrow \frac{1}{S_{exp}} \frac{dV_B}{dt} = \frac{1}{S_{ex}} \frac{dN_B}{dt} = k_s C_{A0}$$

$\frac{C_m^2}{C_m^3}$ $\frac{C_m^2}{C_m^3}$ $4\pi r_c^2$

$$\Rightarrow \frac{1}{4\pi r_c^2} \frac{d}{dt} \left(\frac{\rho_B V}{M_B} \right) = k_s C_{A0}$$

$C_{A0} \neq f(t)$
 $\rho_B \neq f(t)$ } assume!

$$\Rightarrow - \frac{\rho_B}{M_B} \frac{dr_c}{dt} = k_s C_{A0} \quad / \quad \int_0^t \quad \int_R^{r_c}$$



$$\therefore t = \frac{\rho_B}{M_B k_s C_{A0}} (R - r_c)$$

$$\tau = \frac{\rho_B R}{M_B k_s C_{A0}}$$

i.e., $\tau \in R$!

$t/r_c=0$

$$t/T = \frac{R - r_c}{R} = 1 - (1 - X_B)^{1/3}$$

Show that $1 - X_B = (r_c/R)^3$

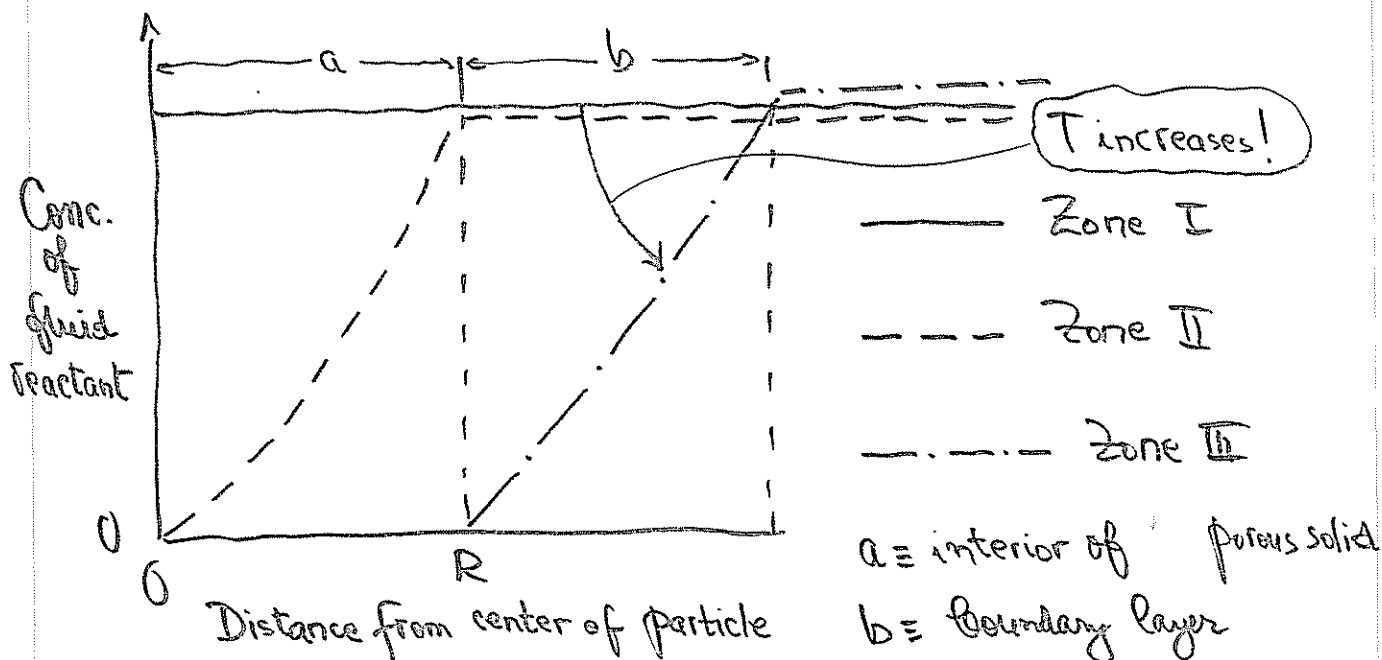
Example 1. Calculate the time needed for complete consumption of particles of graphite ($R = 5 \text{ mm}$, $\rho_B = 2.2 \text{ g/cm}^3$, $R_s = 20 \text{ cm/s}$) in air at 900°C and 1 atm.

$$\tau = \frac{?}{?} = \underline{\underline{0.58 \text{ h}}}$$

Example 2. If the rate constant for the same rxn is 40 cm/s at 900°C and the activation energy is ca. 30 kcal/mol , calculate the consumption time for $100 \mu\text{m}$ activated carbon particles ($\rho_B = 1.5 \text{ g/cm}^3$) at 1500°C and 1 atm air.

$$\tau = \frac{?}{?} = \underline{\underline{143 \text{ ms}}}$$

Now we need to analyze (briefly) the effect of diffusion:



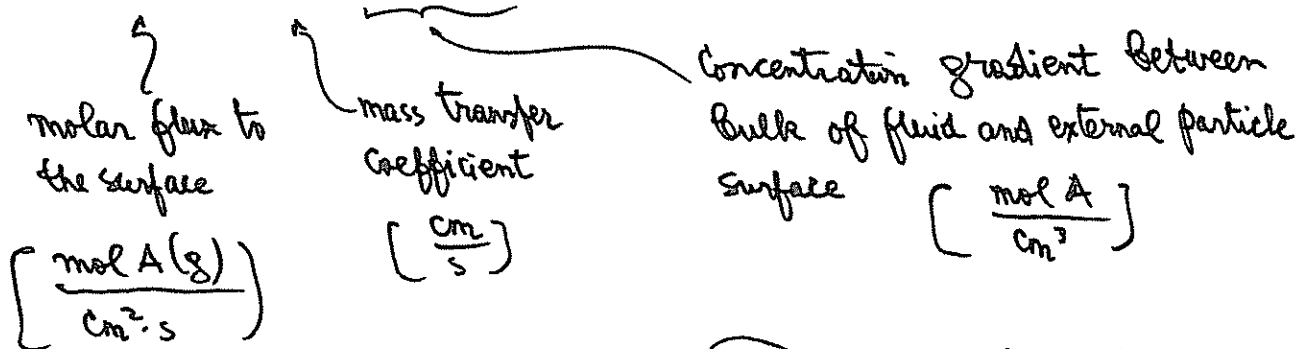
How do the molecules of a fluid reactant reach the external surface of the solid (reactant or catalyst)?

(Note: pore diffusion is beyond the scope of our discussion.)

⇒ boundary layer diffusion (zone III)

$$J_{As} = k_g (C_{Ao} - C_{As})$$

Fick's law



$$\Rightarrow R_{ext} = k_d (C_{Ao} - C_{As}) = \lambda J_{As}$$

stoichiometric ratio

$$\frac{\text{mol B(s)}}{\text{mol A(g)}}$$

rate of rxn per unit external surface area

$$\left[\frac{\text{mol B(s)}}{\text{cm}^2 \cdot \text{s}} \right]$$

diffusional rate constant

depends on fluid mechanics (momentum transport)

$$k_d = \lambda k_g$$

particle diameter

$$Sh \equiv \frac{k_g d_p}{D_{Ag}} = f(Re, Sc)$$

Sherwood #

mass diffusivity (cm²/s)

Reynolds #

$$\frac{d \bar{v} \rho}{\mu}$$

Schmidt #

$$\frac{\mu}{\rho D}$$

[mass transfer]

[fluid dynamics]

e.g., $Sh = 2 \left(1 + c Re^{0.5} Sc^{1/3} \right)$ [empirical correlations]

⇒ Derivation of the R^2 law of Carbon (coal) Combustion (or SCM):

- high T , $Sc = 1$; assume stagnant gas surrounding particles, $Re \gg 1$

$$\Rightarrow Sh \approx 2.0 = \frac{k_g dp}{D_A} \Rightarrow k_g = \frac{2D_A}{dp} \Rightarrow k_d = \frac{2\lambda D_A}{dp}$$

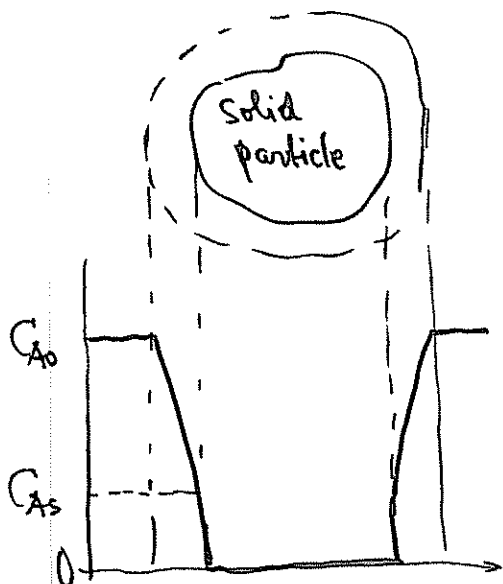
$$\Rightarrow R_{ext} = \frac{2\lambda D_A}{dp} (C_{A0} - C_{As}) = -\frac{1}{S_{ex}} \frac{dN_B}{dt}$$

$$\Rightarrow -\frac{\rho_B}{M_B} \frac{dR}{dt} = \frac{2\lambda D_A}{2R} (C_{A0} - C_{As})$$

$$\Rightarrow \int_{R_0}^R R dR = \frac{\lambda D_A C_{A0} M_B}{\rho_B M_B} \int_0^t dt \Rightarrow t = \frac{\rho_B R_0^2}{2\lambda C_{A0} D_A M_B} \left[1 - \left(\frac{R}{R_0}\right)^2 \right]$$

$$\therefore \tau = \frac{\rho_B}{2\lambda C_{A0} D_A M_B} R_0^2 \quad \text{i.e. } \tau \propto R_0^2$$

$$\frac{\frac{\rho_B}{\text{cm}^3} \text{cm}^2}{\frac{\text{mol B}}{\text{mol A}} \frac{\text{mol A}}{\text{cm}^3} \frac{\text{cm}^2}{\text{s}} \frac{\rho_B}{\text{mol B}}} (=) \text{ s (OK)}$$



Rate = $k_g(C_{A0} - C_{As}) = R_s C_{As}$ processes in series!

- eliminate C_{As} :

$$\text{Rate} = k_g C_{A0} - k_g C_{As} = k_g C_{A0} - k_g \frac{\text{Rate}}{R_s}$$

$$\Rightarrow \text{Rate} \left(1 + \frac{k_g}{R_s} \right) = k_g C_{A0}$$

$$\therefore \text{Rate} = \frac{1}{\frac{1}{k_g} + \frac{1}{R_s}} C_{A0}$$

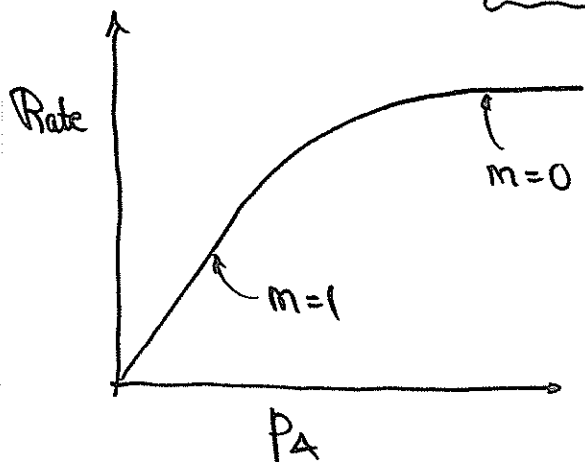
Zone III:
 $R_s \gg k_g$

// OK!

$$\left. \begin{aligned} R_{ads} &= k_{ads} P_A (1 - \theta_A) \\ R_{des} &= k_{des} \theta_A \end{aligned} \right\} \Rightarrow k_{ads} P_A (1 - \theta) = k_{des} \theta_A$$

$$\therefore \theta_A = \frac{k_{ads} P_A}{1 + k_{ads} P_A} \quad \leftarrow \text{Langmuir (isotherm)}$$

$$R_{rxn} = k_{des} \theta_A = k_{des} \frac{k_{ads} P_A}{1 + k_{ads} P_A} = \underbrace{k_{obs} P_A^m}_{\text{empirical, power law}}$$

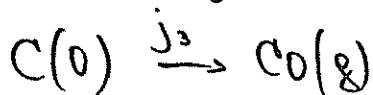
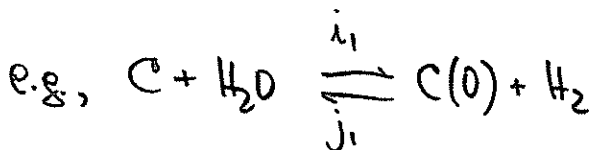


$$k_{ads} P_A \ll 1 \Rightarrow R_{rxn} = k_{ads} P_A \quad (\text{low } p)$$

Adsorption-controlled rxn

$$k_{ads} P_A \gg 1 \Rightarrow R_{rxn} = k_{des} \quad (\text{high } p)$$

desorption-controlled rxn



important in IGCC (21st century electricity!?)

⇓ Show!

$$\theta = \frac{i_1 [H_2O]}{i_1 [H_2O] + j_1 [H_2] + j_2}$$

$$\text{and Rate} = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2} + k_3 P_{H_2O}}$$

L-H. rate eqn.

For combustion of carbon (Esserhigh):

$$\theta = \frac{k_5 \left[\left(1 + \frac{4k_1 P_{O_2}}{k_5} \right)^{0.5} - 1 \right]^2}{4k_1 P_{O_2}}$$

← Show that this reduces to 1st order at low p and zero-order at high p !