CBE 40445

9/21/20

CHAPTER 6

TRANSPORT LIMITATIONS

(MOSTLY MASS)

- EXTERNAL TO CATALYST PARTICLE
- INTERNAL WITH PARTICLE

→ A KEY TOPIC THAT IS ALMOST SOLELY THE DOMAIN OF CHEMICAL ENGINEERS . . .

AS WITH OTHER CHAPTERS,

A LOT OF INTERESTING

INFORMATION IN PROSE

→ FOR A PRACTICAL, EFFICIENT PROCESS,

MASS TRANSFER RATES AND

KINETIC RATES NEED TO BE

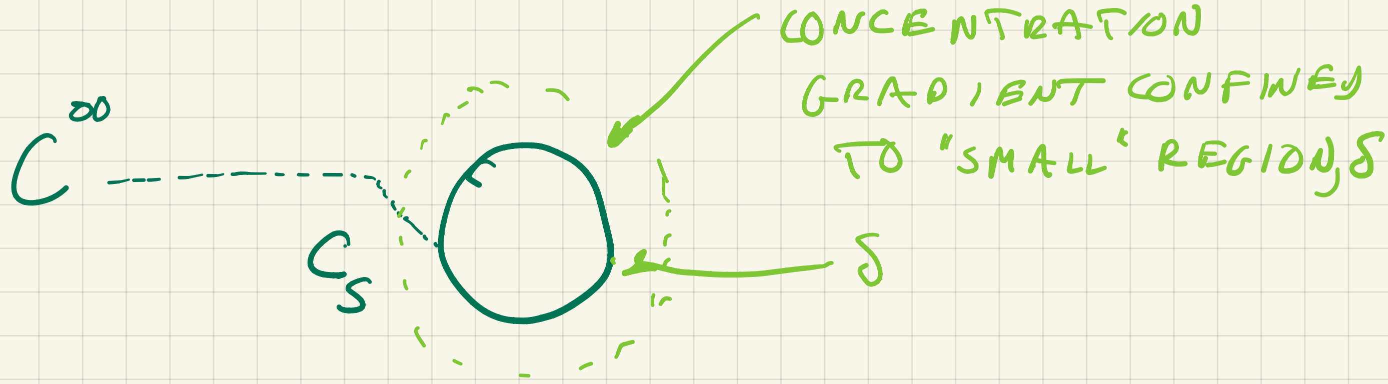
ABOUT THE SAME.

WEISZ REF: (1982) $1 \frac{\mu MOL}{cm^3\text{-}S}$

TURNOVER FREQUENCY: 1/S

$$V = \frac{10^6 \frac{MOLES}{HR}}{1 \frac{\mu MOL}{cm^3\text{-}S}} \rightarrow 300\ m^3$$

EXTERNAL MASS TRANSFER RESISTANCE



REACTANT IS BEING CONSUMED, CAUSING GRADIENT, IDEALLY FLUID MECHANICS CAN BE ADJUSTED SUCH THAT δ IS SMALL ENOUGH FOR MASS TRANSFER TO NOT LIMIT REACTION

PARTICLE COULD BE

- ~100 μm CRACKING CATALYST

  ~HIGH VELOCITY GAS FLOW

- COULD BE ~ 1 mm

  LIQUID PHASE HYDROTREATING

  HYDROGENATION ...

  (STIRRED TANK)

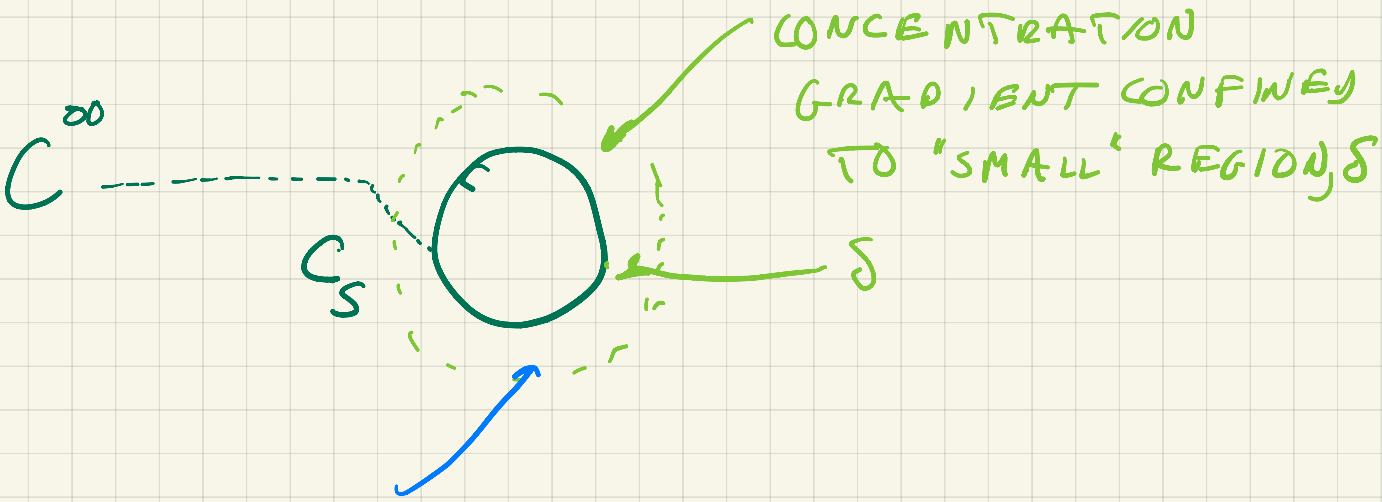
- 3-5 mm <u>PACKED BED</u>

  GAS FLOW

  LIQUID FLOW

IN MOST CASES, PELLET IS POROUS AND MOST OF ACTIVE CATALYST IS INSIDE

→ SO THERE ALSO CAN BE INTERNAL RESISTANCE



THE BOUNDARY LAYER IS NOT USUALLY STAGNANT.

BUT IT IS INSTRUCTIVE TO REVIEW DIFFUSION

STEFAN-MAXWELL EQ.

$$\nabla x_i = \sum_{\substack{j=1 \\ j \neq i}}^{m} \frac{1}{C D_{ij}} \left(x_i N_j - x_j N_i \right)$$

IF JUST 2 COMPONENTS

$$\nabla C_A = \frac{1}{D_{AB}} \left(x_A N_B - x_B N_A \right)$$

BUT $x_B = 1 - x_A$

$$\nabla C_A = \frac{1}{D_{AB}} \left[x_A (N_A + N_B) - N_A \right]$$

IF REACTANTS ⇄ PRODUCTS

$N_A = -N_B$ (EQUIMOLAR COUNTER DIFFUSION)

$$\nabla C_A = -\frac{N_A}{D_{AB}}$$

"FICK'S FIRST LAW"

$N_A = -D_{AB} \nabla C_A$ (ALSO REPRESENTS VERY DILUTE A, $x_A \approx 0$)

SMALL MOLECULE GASES

$D_{AB} = \sim 10^{-1}\ cm^2/s$

$D \sim T^{1.5},\ P^{-1}$

"CHAPMAN-ENSKOG"

SMALL SOLUTES IN LOW VISCOSITY LIQUIDS

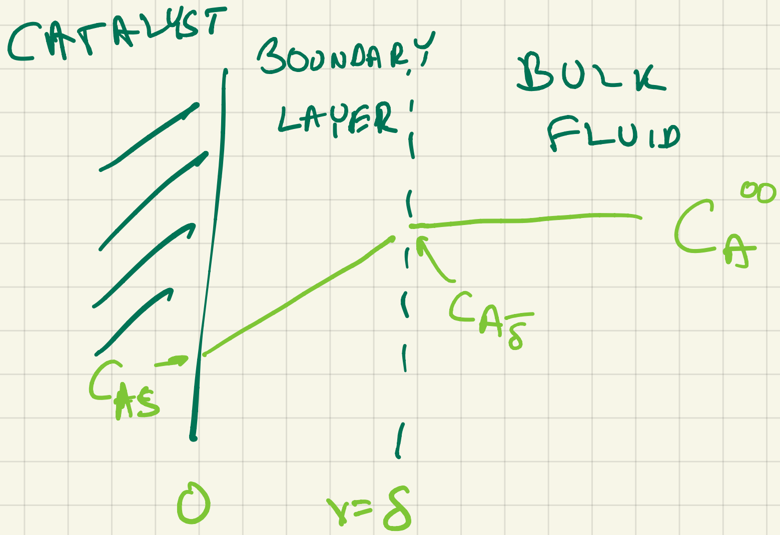
$D_{AB} = \sim 10^{-5}\ cm^2/s$

STOKES-EINSTEIN

$$D = \frac{kT}{6\pi \mu R}$$

$\mu(T) \sim A\exp(B/T)$

FIND FLUX TO A REACTION SURFACE



FICK'S LAW

$$N_{Ax} = -D_{AB}\frac{dC_A}{dx}$$

INSIDE BOUNDARY LAYER: NO REACTION SO FLUX = CONST.

$$\frac{\partial N_A}{\partial x} = 0$$

$$\therefore \quad \frac{d^2 C_A}{dx^2} = 0$$

$$C_A(\delta) = C_{A\delta}$$

$$C_A(0) = C_{AS}$$

$$C_A = C_{As} + (C_{A\delta} - C_{As}) \frac{x}{\delta}$$

$$N_A = -D_{AB} \frac{dC_A}{dy}$$

$$= \frac{-D_{AB}}{\delta} (C_{A\delta} - C_{As})$$

⟹ GREATEST OF ALL EQUATIONS!

$$N_A = \bar{k}_c (C_{A\delta} - C_{As})$$

↑ MASS TRANSFER COEFFICIENT

OBTAIN FROM EXPERIMENTS CORRELATIONS OR NUMERICAL SIMULATION

$$N_A = \bar{k}_c (C_A^{\infty} - C_{As})$$

FOR OUR REACTION EXAMPLE, AT STEDY STATE REACTION MATCH MATCHES FLUX:

$$r = N_A = k_s C_{As} = \bar{k}_c (C_A^\infty - C_{As})$$

$$C_{As} = \frac{\bar{k}_c C_A^\infty}{k_s + \bar{k}_c}$$

$$r = k_s C_{As} = \frac{k_s \bar{k}_c C_A^\infty}{k_s + \bar{k}_c}$$

$$= \frac{C_A^\infty}{\frac{1}{k_s} + \frac{1}{\bar{k}_c}}$$

← SUM OF RESISTANCES

IF $k_s \gg \bar{k}_c$

$$r = \bar{k}_c C_A^\infty$$

NO EFFECT OF REACTION

WHERE DO "k_c's" COME FROM?

CORRELATIONS FROM R.E. TREYBAL "MASS TRANSFER OPERATIONS"

5.	Perpendicular to single cylinders	Re = 400–25 000 Sc = 0.6–2.6	$\frac{k_G p_t}{G_M} Sc^{0.56} = 0.281\, Re'^{0.4}$	5
		Re′ = 0.1–10^5 Pr = 0.7–1500	$Nu = (0.35 + 0.34\, Re'^{0.5} + 0.15\, Re'^{0.58})\, Pr^{0.3}$	16, 21, 42
6.	Past single spheres	Sc = 0.6–3200 $Re'' Sc^{0.5}$ = 1.8–600 000	$Sh = Sh_0 + 0.347(Re'' Sc^{0.5})^{0.62}$ $Sh_0 = \begin{cases} 2.0 + 0.569(Gr_D Sc)^{0.250} & Gr_D Sc < 10^8 \\ 2.0 + 0.0254(Gr_D Sc)^{0.333} Sc^{0.244} & Gr_D Sc > 10^8 \end{cases}$	55
7.	Through fixed beds of pellets§	Re″ = 90–4000 Sc = 0.6	$j_D = j_H = \frac{2.06}{\varepsilon} Re''^{-0.575}$	4, 23, 64
		Re″ = 5000–10 300 Sc = 0.6	$j_D = 0.95 j_H = \frac{20.4}{\varepsilon} Re''^{-0.815}$	
		Re″ = 0.0016–55 Sc = 168–70 600	$j_D = \frac{1.09}{\varepsilon} Re''^{-2/3}$	
		Re″ = 5–1500 Sc = 168–70 600	$j_D = \frac{0.250}{\varepsilon} Re''^{-0.31}$	

† Average mass-transfer coefficients throughout, for constant solute concentrations at the phase surface. Generally, fluid properties are evaluated at the average conditions between the phase surface and the bulk fluid. The heat-mass-transfer analogy is valid throughout.

‡ Mass-transfer data for this case scatter badly but are reasonably well represented by setting $j_D = j_H$.

§ For fixed beds, the relation between ε and d_p is $a = 6(1 - \varepsilon)/d_p$, where a is the specific solid surface, surface per

Fluid motion		Range of conditions	Equation	R
1.	Inside circular pipes	Re = 4000–60 000 Sc = 0.6–3000	$j_D = 0.023\, Re^{-0.17}$ $Sh = 0.023\, Re^{0.83} Sc^{1/3}$	41 52
		Re = 10 000 – 400 000 Sc > 100	$j_D = 0.0149\, Re^{-0.12}$ $Sh = 0.0149\, Re^{0.88} Sc^{1/3}$	44
2.	Unconfined flow parallel to flat plates‡	Transfer begins at leading edge Re_x < 50 000	$j_D = 0.664\, Re_x^{-0.5}$	32
		$Re_x = 5 \times 10^5$–3×10^7 Pr = 0.7–380	$Nu = 0.037\, Re_x^{0.8} Pr_0^{0.43} \left(\frac{Pr_0}{Pr_i}\right)^{0.25}$	65
		$Re_x = 2 \times 10^4$–5×10^5 Pr = 0.7–380	Between above and $Nu = 0.0027\, Re_x Pr_0^{0.43} \left(\frac{Pr_0}{Pr_i}\right)^{0.25}$	
3.	Confined gas flow parallel to a flat plate in a duct	Re_e = 2600–22 000	$j_D = 0.11\, Re_e^{-0.29}$	46
4.	Liquid film in wetted-wall tower, transfer between liquid and gas	$\frac{4\Gamma}{\mu}$ = 0–1200, ripples suppressed	Eqs. (3.18)–(3.22)	20, 37
		$\frac{4\Gamma}{\mu}$ = 1300–8300	$Sh = (1.76 \times 10^{-5}) \left(\frac{4\Gamma}{\mu}\right)^{1.506} Sc^{0.5}$	

SO, AS EXPECTED WE WILL USE DIMENSIONLESS GROUPS...

$$Sh = \frac{\bar{k}_c (2R_p)}{D_{AB}}$$

SHERWOOD NUMBER

ENHANCEMENT OF MASS TRANSFER BY FLUID FLOW

$$Sh = 2 + 0.6\, Re^{1/2} Sc^{1/3}$$

↑ PURE DIFFUSION (the 2)

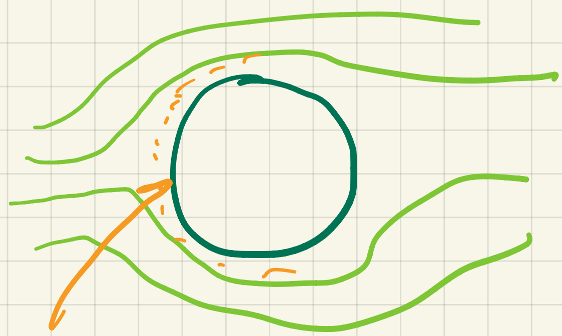
↑ INCREASE CAUSED BY FLUID FLOW (the $0.6\, Re^{1/2} Sc^{1/3}$ term)

POWERS ON Re + Sc COME FROM SCALING ANALYSIS

IF $Sc \gg 1$,

BALANCE OF CONVECTION + DIFFUSION REQUIRES:

$$Sh \sim Re^{1/2} Sc^{1/3}$$



STAGNATION POINT HERE, BUT OTHERWISE, THINNING OF BOUNDARY-LAYER IN FRONT OF SPHERE

$$u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2}$$

IF $Sc \gg 1$ (USUAL CASE FOR LIQUIDS)

INSIDE BOUNDARY LAYER

$u_x = \alpha y$, $u_y = \beta y^2$ (FROM CONTINUITY)

$$\alpha \delta \frac{\Delta c}{L} \sim \beta \delta^2 \frac{\Delta c}{\delta} = \frac{1}{D} \frac{\Delta c}{\delta^2}$$

$$Sc \equiv \frac{\mu}{\rho D_{AB}} = \frac{\nu}{D_{AB}} \quad \frac{\text{MOMENTUM DIFFUSIVITY}}{\text{MASS DIFFUSIVITY}}$$

$$Re \equiv \frac{u \rho (2R_p)}{\mu} \quad \frac{\text{INERTIA FORCES}}{\text{VISCOUS FORCES}}$$

D + D WRITE ABOUT "J" FACTORS

$$J \equiv \frac{Sh}{Sc^{1/3} Re} \sim \frac{f}{2}$$

← FRICTION FACTOR

SO FOR TURBULENT FLOW, IF YOU KNOW f, YOU KNOW J.

A METHOD OF CORRELATING FORCED CONVECTION HEAT TRANSFER DATA AND A COMPARISON WITH FLUID FRICTION[1]

By ALLAN P. COLBURN

ABSTRACT

A general method for the correlation of forced convection heat transfer data is proposed, which consists in plotting, against the Reynolds number, a dimensionless group representing the experimentally measured data from which film heat transfer coefficients would be calculated, namely, $[(t_1 - t_2)/\Delta t_m](S/A)$, or its equivalent, h/cG, multiplied by the two-thirds power of the group, $(c\mu/k)$. Data are cited from the literature which show that the resulting plots of heat transfer data for flow parallel to plane surfaces and for fully turbulent flow inside tubes, coincide (when the properties are taken at the "film" temperature) with the best data on fluid friction plotted in the customary manner, as the friction factor,

$$\tfrac{1}{2}f = \frac{\Delta P g}{\rho u^2}\frac{S}{A} = \frac{R}{\rho u^2},$$

TRANS. AM. INST CHEM ENG 1933

IT IS INSTRUCTIVE TO DETERMINE HOW MASS TRANSFER COEFFICIENT VARIES

$$\bar{k}_c \sim \frac{(D_{AB})^{2/3}\, u^{1/2}\, \rho^{1/6}}{(R_p)^{1/2}\, (\bar{\mu})^{1/6}}$$

"STIR FASTER" ~ BUT SMALL PARTICLES FOLLOW STREAMLINES

(NEED A DENSITY DIFFERENCE)

HEAT TRANSFER IS ANALOGOUS

"GREATEST" EQUATION FOR HEAT TRANSFER

$$q = h_t(T^{\infty} - T_s)$$

CONDUCTION

NATURAL CONVECTION

FORCED CONVECTION

REACTION RATE WITH ΔH_{RXN} INCLUDED

ENDO THERMIC RXN

$$r_{obs}(\Delta H_r) = h_t(T^{\infty} - T_s)$$

$$k_c(C_A^{\infty} - C_{As})\Delta H_r = h_t(T^{\infty} - T_s)$$

ENERGY BALANCE AT STEADY STATE.

INTERNAL MASS TRANSFER RESISTANCE!

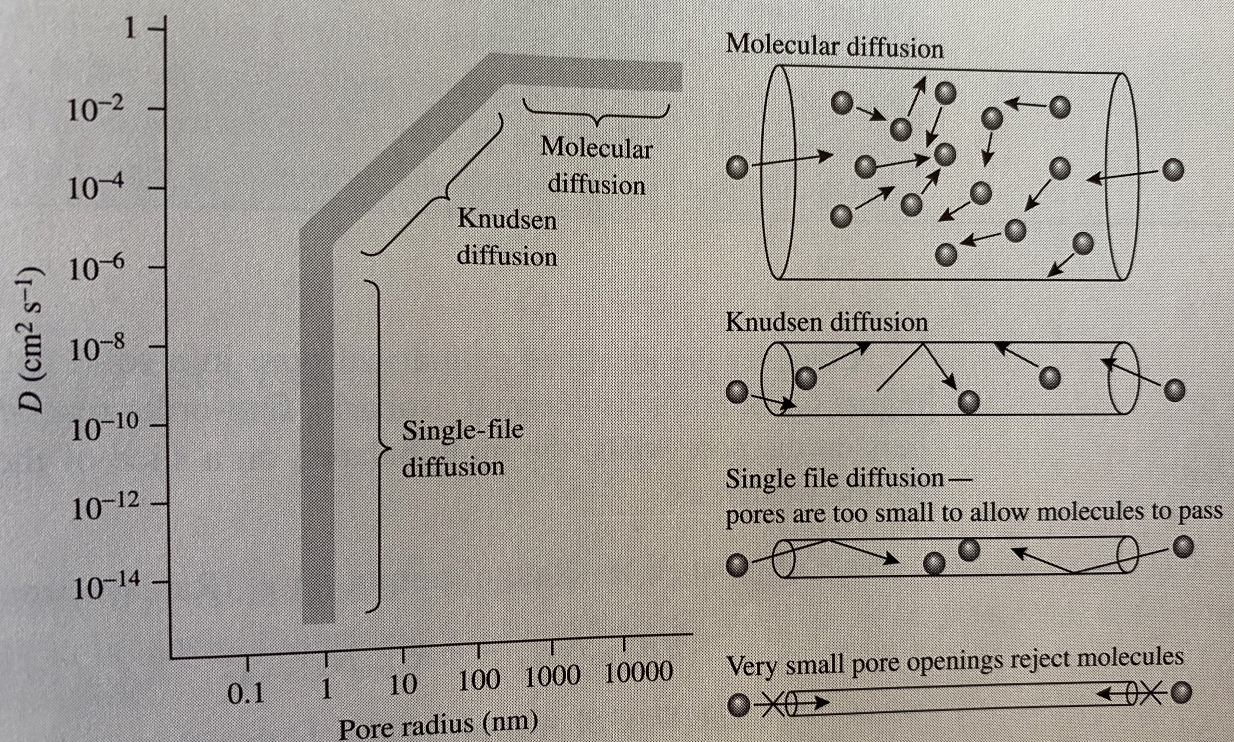


Figure 6.3.1 | Influence of pore size on diffusivity of gas-phase molecules.

a K_3P CO term in the denominator suggest?

7. For the reaction of *A* to form *B* over a solid catalyst, the reaction rate has the form:

$$r = \frac{kK_A P_A}{(1 + K_A P_A + K_B P_B)^2}$$

However, there is a large excess of inert in the reactant stream that is known to readily adsorb on the catalyst surface. How will this affect the reaction order with respect to *A*?

8. G. Thodor and C. F. Stutzman [*Ind. Eng. Chem.*, **50** (1958) 413] investigated the following reaction over a zirconium oxide-silica gel catalyst in the presence

$$A + D \rightarrow B$$

WITH INERT

EQ ADSORPTION $A + * \rightleftharpoons A^*$

EQ ADSORPTION $D + * \rightleftharpoons D^*$

$$A^* + D^* \xrightarrow{k_2} B^*$$

EQ ADSORPTION $B^* \rightleftharpoons B + *$

EQ ADSORPTION $I + * \rightleftharpoons I^*$

THUS: RATE $\rightarrow k_2 A^* D^*$

ULTIMATELY, D^* WILL BE IN EXCESS

RESTRICT TO CASE WHERE REACTION IS SLOW, ALL ADSORPTION IS IN EQUILIBRIUM

FIRST LOOK AT ADSORPTION:

$$[*]_0 = [*] + [A^*] + [D^*] + [B^*] + [I^*]$$

$$[*]_0 = [*] + K_A[A][*] + K_D[D][*] + K_B[B][*] + K_I[I][*]$$

$$[*] = \frac{[*_0]}{1 + K_A[A] + K_D[D] + K_B[B] + K_I[I]}$$

NOW WE CAN GO TO RATE

$$r = k[A^*][D^*]$$

$$= k K_A[A][*] K_D[D][*]$$

NOW SUB IN FOR *

$$r = \frac{k K_A K_D [A][D][*]_0^2}{(1 + K_A[A] + K_D[D] + K_B[B] + K_I[I])^2}$$

NOW FOR CONST VOLUME DEVICE

$$[A] = \frac{\text{MOLES}}{V} = \frac{n_A}{V} = \frac{P_A}{RT}$$

$$r = \frac{k K_A' K_D' [*]_0^2 P_A P_D}{(1 + K_A' P_A + K_D' P_D + K_B' P_B + K_I' P_I)^2}$$

NOW IF $P_D \gg P_A$, BUT $K_D' \ll K_A'$ ...

REACTION WILL BE PSEUDO FIRST ORDER

$$A \rightarrow B$$

$$r \cong \frac{k'' K_A P_A}{(1 + K_A' P_A + K_B' P_B + K_I' P_I)^2}$$

https://www.youtube.com/watch?v=3ULzdD_0GXA