Thus

$$N_{Az} = \frac{-c\mathcal{D}_{AB}}{1-\frac{x_A}{2}} \frac{dx_A}{dz} = C_2$$

$$\therefore \ln\left(\frac{1-\frac{x_A}{2}}{1-\frac{x_{A0}}{2}}\right) = \frac{C_2 z}{2c\mathcal{D}_{AB}}$$ for $c, \mathcal{D}_{AB} = cst$

application of B.C. at $z=0$

To obtain C_2, must apply B.C. at $z=\delta$.

If instanteneous rxn, have $x_A|_\delta = 0$

$$\therefore \left(\frac{1-\frac{x_A}{2}}{1-\frac{x_{A0}}{2}}\right) = \left(1-\frac{x_{A0}}{2}\right)^{z/\delta}$$

and $$N_{Az} = \frac{2c\mathcal{D}_{AB}}{\delta} \ln\left(\frac{1}{1-\frac{x_{A0}}{2}}\right)$$

If rate of rxn is $k_1 C_A$ at surface, then at S.S.,

$$N_{Az}\Big|_\delta = k_1 C_A\Big|_\delta = k_1 c\, x_A\Big|_\delta$$

and obtain transcendental eq'n for N_{Az}:

$$N_{Az} = \frac{2c\mathcal{D}_{AB}}{\delta} \ln\left[\frac{1-\frac{N_{Az}}{2ck_1}}{1-\frac{x_{A0}}{2}}\right]$$

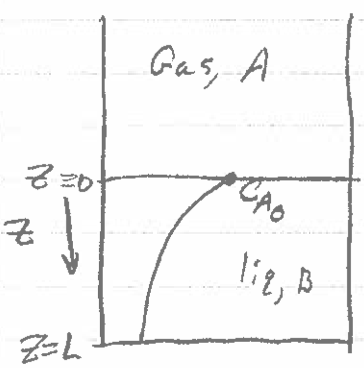
if k_1 is large,

$$N_{Az} \approx \frac{2c\mathcal{D}_{AB}/\delta}{1 + \frac{\mathcal{D}_{AB}}{k_1 \delta}} \ln\left(\frac{1}{1 - \frac{x_{A0}}{2}}\right)$$

ratio of diffusion to rxn

Now look at diffusion w/ homogeneous chem. rxn:

$A + B \rightarrow AB$ in liquid phase



Rather than dealing w/ 3-comp. system, assume $C_B \gg C_A, C_{AB}$

pseudo first order:

$$R_A = -k_1 C_A \quad \left(\text{moles}/\text{unit vol}\right)$$

C_{A0} det. by solubility (may be questioned in presence of rxn, but usually pretty good agreement w/ exp't.)

$$\underbrace{\frac{\partial C_A}{\partial t}}_{0} + \frac{\partial N_{Az}}{\partial z} = R_A = -k_1 C_A$$

or $\dfrac{dN_{Az}}{dz} + k_1 C_A = 0$

non-linear

Now $N_{Az} = \cancel{x_A}(N_{Az} + \cancel{N_{Bz}}) - c\,\mathcal{D}_{AB}\frac{dx_A}{dz}$

small, so neglect   stationary

Assume $c = cst$

$\therefore\ N_{Az} = -\mathcal{D}_{AB}\frac{dc_A}{dz}$

↳ assume AB doesn't affect diff. of A in B ⇒ binary diffusion

Thus $-\mathcal{D}_{AB}\frac{d^2c_A}{dz^2} + k_1 c_A = 0$

Obtain $\frac{c_A}{c_{A_0}} = \frac{\cosh\{b_1(1-z/L)\}}{\cosh b_1}$

$b_1 = \sqrt{k_1L^2/\mathcal{D}_{AB}}$ = Hatta No. : importance of rxn vs. diffusion.

$$\frac{\langle c_A\rangle}{c_{A_0}} = \int_0^1 \frac{\cosh\{b_1(1-x)\}}{\cosh b_1}\,dx = \frac{1}{b_1}\tanh(b_1)$$

Rate of absorption: $N_{Az}\big|_{z=0} = \left(\frac{\mathcal{D}_{AB}\,c_{A_0}}{L}\right) b_1 \tanh(b_1)$

Note: at S.S., if no rxn, $b_1 = 0$ & $N_{Az}\big|_{z=0} = 0$ ⇒ no absorpt

Review last problem

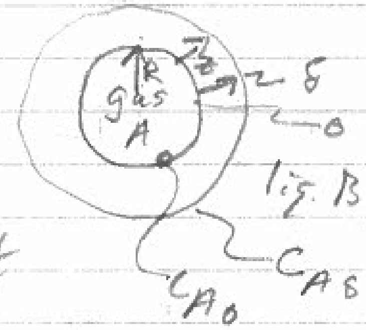
Very similar problem given in BS&L 17.4.1: gas abs. w/ rxn w/ B in liquid

Assumptions: same stagnant film thickness δ, gas A sparingly soluble in B, conc. outside film changes slowly, i.e., pseudo-ss at $C_{A\delta}$

slow reaction

what is efficiency? how does it depend on bubble size?

Look at isolated bubble:



if $\delta << R$, neglect curvature:

$$\frac{C_A}{C_{A0}} = \frac{\frac{C_{A\delta}}{C_{A0}} \sinh\left(b_1 \frac{z}{\delta}\right) + \sinh\left(b_1\left(1 - \frac{z}{\delta}\right)\right)}{\sinh b_1}$$

look thru sol'n yourselves

$$b_1 = \left(k_1 \delta^2 / \mathcal{D}_{AB}\right)^{1/2}$$

w/ no rxn, simply linear profile:

$$\frac{C_A}{C_{A0}} = \frac{C_{A\delta}}{C_{A0}} \left(\frac{z}{\delta}\right) + \left(1 - \frac{z}{\delta}\right)$$

End Lec-33

w/ fluxes:

$$N_{Az}\Big|_{z=0} = \frac{D_{AB} C_{A0}}{\delta} \; \frac{b_1 \cosh b_1 - b_1 \frac{C_{A\delta}}{C_{A0}}}{\sinh b_1}$$

w/ rxn

$$N_{Az}\Big|_{z=0} = \frac{D_{AB} C_{A0}}{\delta} \left(1 - \frac{C_{A\delta}}{C_{A0}}\right)$$

opposite

Also, need to determine $C_{A\delta}$: may do from balance on bulk of tank.

Assume A = surface area of bubbles, V = vol. liquid in tank, $A\delta \ll V$ (not bad), then:

$\boxed{C_{A\delta} V \xi \gg C_{A0} A\delta}$

$$-A D_{AB} \frac{dc_A}{dz}\Big|_{z=\delta} = V \cdot k_1 C_{A\delta}$$

flux of A into bulk   rxn in bulk

Assumes rxn pred. occurs in bulk

No!

Thus:

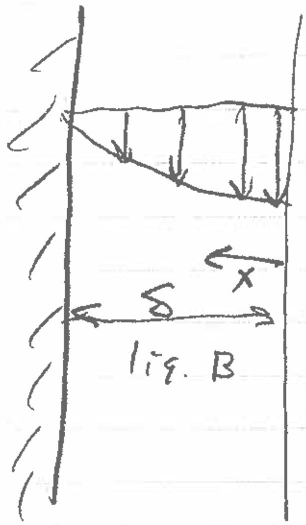
$$\frac{1 - \frac{C_{A\delta}}{C_{A0}} \cosh b_1}{\sinh b_1} = \left(\frac{V}{A\delta}\right)\left(\frac{C_{A\delta}}{C_{A0}} b_1\right)$$

or

$$C_{A\delta} = \frac{C_{A0}}{\cosh b_1 + b_1 \left(V/A\delta\right) \sinh b_1}$$

2 Dim. problems:

Absorption into falling laminar film



gas A

z

Assume diffusion does not affect velocity profile of B, no rxn, ~~small penetration depth of A.~~

$$V_z = V_{max}\left(1 - \left(\frac{x}{\delta}\right)^2\right)$$

$$\underbrace{\cancel{\frac{\partial C_A}{\partial t}}}_{0} + \frac{\partial N_{Az}}{\partial z} + \frac{\partial N_{Ax}}{\partial x} = \overbrace{\cancel{R_A}}^{0}$$

$$\therefore \quad \frac{\partial N_{Az}}{\partial z} + \frac{\partial N_{Ax}}{\partial x} = 0$$

Now $N_{Az} = x_A(N_{Az} + N_{Bz}) - c\,\mathcal{D}_{AB}\dfrac{\partial x_A}{\partial z}$

Assume const. c $(x_A \ll 1)$

$$\therefore N_{Az} = C_A\Big(\underbrace{\cancel{x_A}}_{\text{small}} V_{Az} + \underbrace{\cancel{x_B}}_{\approx 1}\,\underbrace{\cancel{V_{Bz}}}_{\approx V_z}\Big) - \underbrace{\cancel{\mathcal{D}_{AB}\frac{\partial C_A}{\partial z}}}_{\text{small relative to convection}}$$

$$\therefore \quad N_{Az} \approx C_A V_z$$

Now $N_{Ax} = x_A(N_{Ax} + N_{Bx}) - c\,\mathcal{D}_{AB} \frac{\partial x_A}{\partial x}$

$= \underbrace{c_A\,(x_A V_{Ax} + x_B V_{Bx})}_{\text{small rel. to}} - \mathcal{D}_{AB} \frac{\partial c_A}{\partial x}$

$\approx -\mathcal{D}_{AB} \frac{\partial c_A}{\partial x}$

$\therefore \quad v_z \frac{\partial c_A}{\partial z} = \mathcal{D}_{AB} \frac{\partial^2 c_A}{\partial x^2}$] convective Diffusion eq'n

B.C.'s : $z = 0, \quad c_A = 0$

$x = 0, \quad c_A = c_{A_0}$ (equilibrium)

$x = \delta, \quad \frac{\partial c_A}{\partial x} = 0$

Very similar to ht. transf. probs, just diff. velocity profile, B.C.'s

$\therefore \quad \left(1 - \frac{x^2}{\delta^2}\right) \frac{\partial c_A}{\partial z} = \frac{\mathcal{D}_{AB}}{v_{max}} \frac{\partial^2 c_A}{\partial x^2}$

should be able to solve in sleep!

Non-dimensionalize:

$x^* = x/\delta, \quad z^* = \frac{\mathcal{D}_{AB}\, z}{v_{max}\, \delta^2}, \quad c_A^* = \frac{c_{A_0} - c_A}{c_{A_0}}$

as $c_A \to c_{A_0}$ at large z.

$\therefore$ obtain equation:

$$(1-x^{*2})\frac{\partial C_A^*}{\partial z^*} = \frac{\partial^2 C_A^*}{\partial x^{*2}}, \qquad \begin{array}{l} z^*=0, \; C_A^*=1 \\ x^*=0, \; C_A^*=0 \\ x^*=1, \; \dfrac{\partial C_A^*}{\partial x^*}=0 \end{array}$$

Use separation of variables:

$$C_A^* = f(x^*)\,g(z^*)$$

$$\therefore \quad \frac{g'}{g} = \frac{f''}{f(1-x^{*2})} = -\sigma^2,$$

$$g = e^{-\sigma^2 z}, \quad \left.\begin{array}{l} f'' - \sigma^2(1-x^{*2})f = 0 \\ f(0) = f'(1) = 0 \end{array}\right\} \text{Sturm-Liouville prob,}$$

σ are real

Could solve for f using series expansion.

i.e. let $f = \sum_{n=0}^{\infty} a_n x^n$

$$\therefore \sum_{n=0}^{\infty}\left[n(n-1)\,a_n x^{n-2} - \sigma^2(1-x^2)\,a_n x^n\right] = 0$$

Work out rest of solution for yourselves.

Review 2 HW problems on radiant transport
linearization of wire / ht loss thru window

Review problem to this pt

What happens if penetration depth of A is small w.r.t. δ??

Assign test as HW + analysis of problem II

What is penetration depth:

suppose some length L, fluid exposed to gas for char. time ($\to$ z direction)

$$t_D \sim L/V_{max}$$

During time t_D, diffuses $l \sim \left(\mathcal{D}_{AB} \frac{L}{V_{max}}\right)^{1/2}$

if $l/\delta \ll 1$, have only small penetration.

Expect similarity sol'n as eliminate length scale.

Now: $V_z \doteq V_{z\,max}\left(1 - \left(\frac{x}{\delta}\right)^2\right) \approx V_{z\,max}$

Small as $x \sim l$

$$\therefore \quad \frac{\partial C_A}{\partial z} \cong \frac{\mathcal{D}_{AB}}{V_{z\,max}} \frac{\partial^2 C_A}{\partial x^2}$$

w/ B.C.'s $\quad C_A = C_{A_0}, \; x = 0$

$C_A = 0, \; z = 0$

$C_A \to 0, \; x \to \infty$

mathematically identical to heating of semi-inf. slab

Non - Dim:

$$z^* = z/L \quad , \quad x^* = \frac{x}{\left(\mathcal{D}_{AB}\, L/V_{max}\right)^{1/2}} \quad , \quad C_A^* = C_A/C_{A_0}$$

$$\therefore \quad \frac{\partial C_A^*}{\partial z^*} = \frac{\partial^2 C_A^*}{\partial x^{*2}} \quad , \quad \begin{array}{l} C_A^* = 1, \; x^* = 0 \\ C_A = 0, \; z^* = 0, \; x^* \to \infty \end{array}$$

one dim. energy eqn if $z \equiv t$

Apply stretching:

$$\bar{C}_A = A C_A^* \;,\; \bar{x} = B x^* \;,\; \bar{z} = C z^*$$

$$\therefore \quad \frac{C}{B^2} = 1 \quad \text{or} \quad B/C^{1/2} = 1$$

$$\therefore \quad \text{let } \eta = \frac{x^*}{z^{*1/2}}$$

$$\frac{\partial C_A^*}{\partial z^*} = \frac{d C_A^*}{d \eta} \frac{\partial \eta}{\partial z^*} = \frac{d C_A^*}{d \eta}\left(-\frac{1}{2z^*}\eta\right)$$

$$\frac{\partial^2 C_A^*}{\partial x^{*2}} = \frac{\partial}{\partial x^*}\left(\frac{d C_A^*}{d\eta}\frac{\partial \eta}{\partial x^*}\right) = \frac{1}{z^*}\frac{d^2 C_A^*}{d\eta^2}$$

$$\therefore \quad \frac{d^2 C_A^*}{d\eta^2} = -\frac{\eta}{2}\frac{d C_A}{d\eta}$$

$$\therefore \quad \frac{d C_A^*}{d\eta} = c_1 e^{-\frac{\eta^2}{4}}$$

$$\text{and} \quad C_A/C_{A_0} = \operatorname{erfc} \frac{x}{\sqrt{4 \mathcal{D}_{AB} z / V_{max}}}$$

With a flux at the surface:

$$N_{Ax}\Big|_{x=0} = c_{A_0}\sqrt{\frac{\mathcal{D}_{AB} V_{max}}{\pi z}}$$

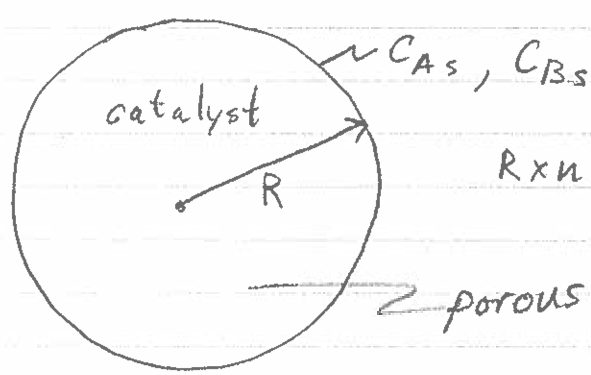
If film is of length L & width W, may integrate to obtain total rate of absorption:

$$\dot{Q}_A = \int_0^W \int_0^L N_{Ax}\Big|_{x=0} \, dz\,dy = (WL)\, c_{A_0}\sqrt{\frac{4\mathcal{D}_{AB} V_{max}}{\pi L}}$$

$$= WL\, c_{A_0}\sqrt{\frac{4\mathcal{D}_{AB}}{\pi t_D}}$$

$\uparrow$ contact time

Diffusion + Rxn in Porous Spherical Catalyst Pellet (BS&L 17.6)



Rxn $A \rightarrow B$

neglect external (film) diffusion resistances

A diffuses in, converts to B & diffuses out

Look at macroscopic picture:

R_A = rate of prod. of A per unit vol.

$\therefore$ $R_A \cdot 4\pi r^2 dr$ = <u>moles A prod</u> in spherical shell

$$\frac{\partial c_A}{\partial t} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{Ar}\right) = R_A$$

over catalyst & pores

define <u>effective</u> diffusivity $\mathcal{D}_A$ s.t.

$$N_{Ar} = -\mathcal{D}_A \frac{\partial c_A}{\partial r}$$ ← exp't f^{n} of T, P & pore structure

equimolar counter diff^{n} ($N_A = -N_B$)

$$\therefore -\mathcal{D}_A \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dc_A}{dr}\right) = R_A = -K_1 a C_A$$

rate on cat. surface

$$a \equiv \frac{\text{available catalyst surf. area}}{\text{total vol. solids \& void}}$$

B.C. $r = R$, $C_A = C_{As}$

$r = 0$, C_A = finite

let $C_A^* = C_A/C_{As}$, $r^* = r/R$

$$\therefore \frac{1}{r^{*2}}\frac{d}{dr}\left(r^{*2}\frac{dC_A^*}{dr}\right) = \frac{K_1 a R^2}{\mathcal{D}_A} C_A^*$$

let $C_A^* = f/r^*$ (convenient w/ operator)

$\therefore$ obtain $\frac{d^2 f}{dr^{*2}} = \left(\frac{k_1 a R^2}{\mathcal{D}_A}\right) f$

End lec. 34

and $\frac{C_A}{C_{As}} = \left(\frac{R}{r}\right) \frac{\sinh\left(\sqrt{k_1 a/\mathcal{D}_A}\; r\right)}{\sinh\left(\sqrt{k_1 a/\mathcal{D}_A}\; R\right)}$ } elim cosh as must be finite as $r \to 0$

$\dot{Q}_{A\,\text{surface}} = 4\pi R^2 N_{A_r}\Big|_{r=R}$

$= 4\pi R \mathcal{D}_A C_{As}\left[1 - \left(\frac{k_1 a R^2}{\mathcal{D}_A}\right)^{1/2} \coth\left(\frac{k_1 a R^2}{\mathcal{D}_A}\right)^{1/2}\right]$

If entire surface were exposed to C_{As},

$\dot{Q}_{A\,ref} = \frac{4}{3}\pi R^3 a (k_1 C_{As})$

$\therefore$ Thiele's effectiveness factor

$\eta = \frac{3}{K^2}(K \coth K - 1) = \frac{\dot{Q}_A}{\dot{Q}_{A\,ref}}$

where $K = \left(\frac{k_1 a}{\mathcal{D}_A} R^2\right)^{1/2} \equiv$ Thiele modulus

(similar to ~~Ha~~ Hatta # used earlier)

look at 2 limits:

$K \to 0$, $\eta = 1$ (no diffusion resistance) for large K, $\coth K \sim 1 + 2e^{-2K}$

$\therefore \eta \approx \frac{3}{K}$

Having small pores will decrease $\mathcal{D}_A$ & increase diff$^{\underline{n}}$ limitation <u>but</u> will increase area, $\therefore$ will increase total rate of reaction.

Obtain similar results for other shapes as well (slabs, cylinders, etc. ⇒ Aris)

defined Thiele modulus

$$\phi_m \equiv \frac{V_{particle}}{S_{external}} \sqrt{\frac{K_1 a}{\mathcal{D}_A}} \Bigg\} \text{ for general shape}$$

(surface area)

→ $\sim \frac{R}{3}$ for spheres, $\eta \sim \frac{1}{\phi_m}$ as $\phi_m \to \infty$

Now look at more complex problems (Ch. 19)

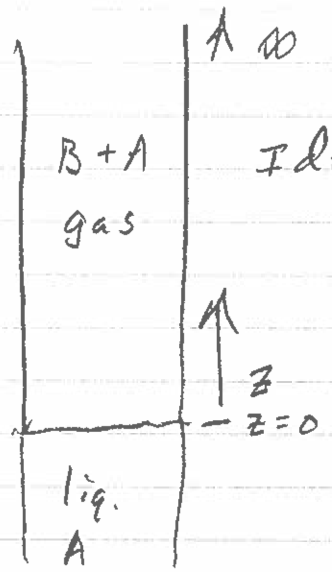
For many problems, have const. ρ, $\mathcal{D}_{AB}$, thus:

$$\frac{Dc_A}{Dt} = \frac{\partial c_A}{\partial t} + \underset{\sim}{v} \cdot \underset{\sim}{\nabla} c_A = \mathcal{D}_{AB} \nabla^2 c_A + R_A$$

(dilute sol$^{\text{n}}$s at const T, P)

→ same as energy transport! so may <u>solve by</u> analogy w/ ht. transfer

Let's look at unsteady problem:



Ideal gas, $\therefore$ c = const in gas phase

As before B ins. in A but no rxn!

No rxn, so $\frac{\partial c_A}{\partial t} + \frac{\partial N_{Az}}{\partial z} = 0$, $\frac{\partial c_B}{\partial t} + \frac{\partial N_{Bz}}{\partial z} = 0$

$$\therefore \frac{\partial c}{\partial t} = \frac{\partial c_A}{\partial t} + \frac{\partial c_B}{\partial t} = -\frac{\partial}{\partial z}\left(N_{Az} + N_{Bz}\right) = 0$$

$\therefore$ $N_{Az} + N_{Bz} = f^{n}(t)$ only } total molar flux

Note: this will be non-zero!

At $z = 0$, $N_{Bz} = 0$ (no flux)

Since $N_{Az} = x_A (N_{Az} + N_{Bz}) - c\mathcal{D}_{AB} \frac{\partial x_A}{\partial z}$

At $z = 0$ $N_{Az} = N_{A0} = -\frac{c\mathcal{D}_{AB}}{1 - x_{A0}} \left.\frac{\partial x_A}{\partial z}\right|_{z=0}$

Thus since $(N_{Az}+N_{Bz})\Big|_{z=0} = N_{A_0}$, obtain

$= (N_{A}+N_{B})$ anywhere

$\neq f(z)$

$$N_{Az} = x_A \left[-\frac{c\mathcal{D}_{AB}}{1-x_{A_0}} \frac{\partial x_A}{\partial z}\Big|_{z=0} \right] - c\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$$

$$\frac{\partial c_A}{\partial t} = c\frac{\partial x_A}{\partial t} = -\frac{\partial N_{Az}}{\partial z},$$

obtain equation:

$$\frac{\partial x_A}{\partial t} = \underbrace{\mathcal{D}_{AB}\frac{\partial^2 x_A}{\partial z^2}}_{\text{Fickian diffusion}} + \underbrace{\frac{\mathcal{D}_{AB}}{1-x_{A_0}}\frac{\partial x_A}{\partial z}\Big|_{z=0} \cdot \frac{\partial x_A}{\partial z}}_{\text{extra convection}}$$

B.C. $z=0$ $x_A = x_{A_0}$, $z=\infty$, $x_A = 0$

I.C. $x_A = 0$ at $t=0$

Now must determine solution: use similarity transform approach.

Note: non-lin term

let $x_A = a\bar{X}_A$, $z = b\bar{z}$, $t = c\bar{t}$

$$\therefore \frac{a}{c}\frac{\partial \bar{X}_A}{\partial \bar{t}} = \mathcal{D}_{AB}\frac{a}{b^2}\frac{\partial^2 \bar{X}_A}{\partial \bar{z}^2} + \frac{\mathcal{D}_{AB}}{1-x_{A_0}}\frac{a^2}{b^2}\frac{\partial \bar{X}_A}{\partial \bar{z}}\left.\frac{\partial \bar{X}_A}{\partial \bar{z}}\right|_{\bar{z}=0}$$

thus $\frac{c}{b^2} = 1$, $\frac{ac}{b^2} = 1$ $\therefore$ $\frac{c}{b^2} = 1$, $a = 1$

from B.C., $a\bar{X}_A = X_{A_0}$ at $\bar{z} = 0$ $\therefore$ $a = 1$

Will admit transform: just happenned to work → non-linear term produced same restriction as B.C. & diffusion.

Will not work in general ⇒ time dep. analog to prob. 5. will not.

$$\eta = \frac{z}{(\mathcal{D}_{AB}t)^{1/2}}, \quad X = x_A / x_{A_0}$$

$$\therefore -\frac{1}{2}\eta X' = X'' + \frac{x_{A_0}}{1-x_{A_0}} X'(0)\, X'$$

$$\text{or } X'' = -X'\left(\frac{1}{2}\eta + \frac{x_{A_0}}{1-x_{A_0}}X'(0)\right)$$

$$X' = c_1 e^{-\left(\frac{1}{2}\eta + \frac{x_{A_0}}{1-x_{A_0}}X'(0)\right)^2}$$

$$X = c_2 + c_1 \operatorname{erf}\left(\frac{1}{2}\eta + \frac{x_{A_0}}{1-x_{A_0}}X'(0)\right)$$

Applying B.C. at $\zeta = 0$ and $\zeta = \infty$ gives

$$\frac{x_A}{x_{A_0}} = \frac{1 - \mathrm{erf}\left(\frac{1}{2}\zeta + \frac{x_{A_0}}{1-x_{A_0}} X'(0)\right)}{1 - \mathrm{erf}\left(\frac{x_{A_0}}{1-x_{A_0}} X'(0)\right)}$$

with

$$X'(0) = \frac{e^{-\left(\frac{x_{A_0}}{1-x_{A_0}} X'(0)\right)}}{1 - \mathrm{erf}\left(\frac{x_{A_0}}{1-x_{A_0}} X'(0)\right)}$$

as implicit equation for $X'(0)$

Useful for measuring diffusivities of volatile materials. If neglect non-linear term, obtain Fick's second law:

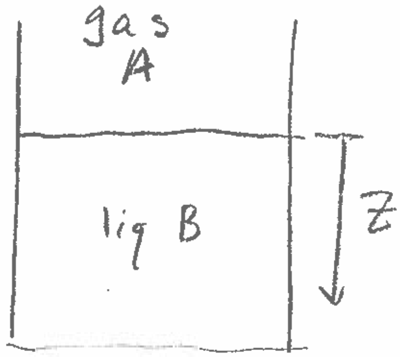
$$\frac{\partial x_A}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 x_A}{\partial z^2}$$

End lec. 35

w/ sol'n: $\frac{x_A}{x_{A_0}} = 1 - \mathrm{erf}\left(\frac{1}{2}\zeta\right)$

Unsteady Diff$^{\underline{n}}$ & Chem. Rxn (general solution)

$A + B \rightarrow C$ in liquid phase



Have D.E.:

$$\frac{\partial c_A}{\partial t} + \frac{\partial N_{Az}}{\partial z} = +k_1 c_A$$

$k_1 < 0$

with $N_{Az} = -c\mathcal{D}_{AB}\frac{\partial x_A}{\partial z} \cong -\mathcal{D}_{AB}\frac{\partial c_A}{\partial z}$

for $x_A \approx 0$ (dilute)

Thus $\frac{\partial C_A}{\partial t} = \mathcal{D}_{AB}\nabla^2 C_A + K_1 C_A \quad (K_1 < 0)$

Typical I.C.: $t=0,\ C_A = 0$

B.C. at surfaces $C_A = C_{A_s}$, such as drop of liquid surrounded by gas

where C_{A_s} may be $f^{\underline{n}}$ position, but independent of time

let f be sol'n w/out rxn:

i.e. let $\frac{\partial f}{\partial t} = \mathcal{D}_{AB}\nabla^2 f$,

at $t=0$, $f=0$; at surf, $f = C_{A_s}$

~~Taking Laplace transform w.r.t. t, obtain~~

won't discuss technique

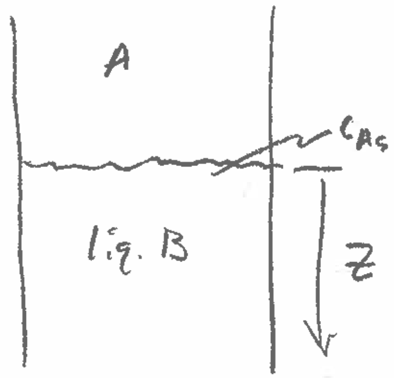
Making use of Laplace transform, can show that

$$C_A = -K_1\int_0^t f e^{K_1 t'}\,dt' + f e^{K_1 t},$$

thus may obtain rxn sol'n from simple diffusion

~~Unsteady~~

Apply this to one D conduction:



have $\frac{\partial c_A}{\partial t} = \mathcal{D}_{AB} \nabla^2 C_A + k_1 c_A$

and $\frac{\partial f}{\partial t} = \mathcal{D}_{AB} \nabla^2 f$

Know that $f = C_{A_s}\, \mathrm{erfc}\left(\frac{z}{2(\mathcal{D}_{AB} t)^{1/2}}\right)$

$$\therefore \frac{C_A}{C_{A_s}} = -k_1 \int_0^t \left(1 - \mathrm{erfc}\left(\frac{z}{2(\mathcal{D}_{AB} t')^{1/2}}\right)\right) e^{k_1 t'}\, dt'$$

integrate by parts once, then integrate remainder

$$+ e^{-k_1 t}\, \mathrm{erfc}\left(\frac{z}{2(\mathcal{D}_{AB} t')^{1/2}}\right)$$

$$= \frac{1}{2} \exp\left(-z\sqrt{\frac{-k_1}{\mathcal{D}_{AB}}}\right) \mathrm{erfc}\left[\frac{z}{\sqrt{4\mathcal{D}_{AB} t}} - \sqrt{-k_1 t}\right]$$

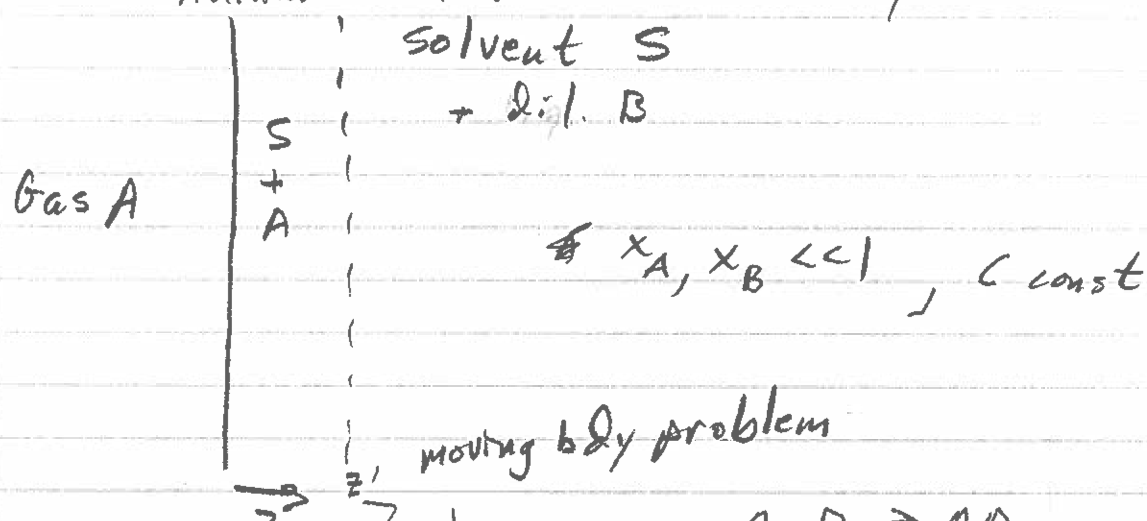
$$+ \frac{1}{2} \exp\left(z\sqrt{\frac{-k_1}{\mathcal{D}_{AB}}}\right) \mathrm{erfc}\left[\frac{z}{\sqrt{4\mathcal{D}_{AB} t}} + \sqrt{-k_1 t}\right]$$

Note that this solution was <u>not</u> obtainable via simple stretching similarity transform.

Another problem:

Gas absorption w/ rapid Chem. Rxn:

A diffuses to bdy , B diffuses to bdy



z' where rxn $A + B \to AB$ occurs instantaneously ~~(similar to melting~~

$$\frac{\partial c_A}{\partial t} + \frac{\partial N_{Az}}{\partial z} = 0 \qquad \frac{\partial c_B}{\partial t} + \frac{\partial N_{Bz}}{\partial z} = 0$$

$$N_{Az} \cong -\mathcal{D}_{AS} \frac{\partial c_A}{\partial z}$$

$$\therefore \frac{\partial c_A}{\partial t} = \mathcal{D}_{AS} \frac{\partial^2 c_A}{\partial z^2} \quad , \quad \frac{\partial c_B}{\partial t} = \mathcal{D}_{BS} \frac{\partial^2 c_B}{\partial z^2}$$

w/ B.C. $c_A\big|_{z=0} = c_{A0}$ $\qquad$ w/ B.C. $c_B\big|_{z\to\infty} = c_{B0}$

$c_A\big|_{z=z'(t)} = 0$ $\qquad$ $c_B\big|_{z=z'} = 0$

$c_A = 0$ at $t=0$ $\qquad$ $c_B = c_{B0}$ at $t=0$

similar (but not identical) to melting bdy prob.

obtain similarity transform:

stretching $c_A = A\bar{c}_A$, $z = B\bar{z}$, $z' = C\bar{z}'$, $t = D\bar{t}$

$\therefore$ from D.E. obtain $\frac{B^2}{D} = 1$

from B.C.'s obtain $A = 1$

and loc. of interface $B\bar{z} = Cz'$

$\therefore \frac{B}{C} = 1$

Thus $\eta = \frac{z}{2(\mathcal{D}_{AS}t)^{1/2}}$, $z' \sim (4\,\mathcal{D}_{AS}t)^{1/2}$!

have solved for growth of region of A already!

To obtain full sol'n, have

$$\frac{c_A}{c_{A_0}} = c_A^* = a_1 + a_2 \operatorname{erf} \frac{z}{\sqrt{4\mathcal{D}_{AS}t}}$$

at $z = 0$, $c_A^* = 1 \therefore a_1 = 1$

$$\frac{c_B}{c_{B_0}} = c_B^* = b_1 + b_2 \operatorname{erf} \frac{z}{\sqrt{4\mathcal{D}_{AS}t}}$$

at $z = \infty$, $c_A^* = 1 \therefore b_1 + b_2 = 1$

At $z = z'(t)$, $c_A^* = c_B^* = 0$

<u>and</u> $$-\mathcal{D}_{AS}\frac{\partial c_A}{\partial z} = +\mathcal{D}_{BS}\frac{\partial c_B}{\partial z}$$

$$\frac{z'}{\sqrt{4\mathcal{D}_{As}t}} = \left(\frac{\alpha}{\mathcal{D}_{As}}\right)^{1/2}$$

$$z' = \alpha^{1/2}\, 2\sqrt{t}$$

$$\alpha = \frac{z'^2}{4t}$$

Let $\eta = \frac{z}{(4\mathcal{D}_{As}t)^{1/2}}$; $\eta' = \frac{z'}{(4\mathcal{D}_{As}t)^{1/2}} = \frac{\sqrt{\alpha}}{(\mathcal{D}_{As})^{1/2}}$

$$\therefore \frac{c_A}{c_{A0}} = 1 - \frac{\operatorname{erf}(\eta)}{\operatorname{erf}(\eta')}$$

Let $\lambda = \sqrt{\frac{\mathcal{D}_{As}}{\mathcal{D}_{Bs}}}$ $\quad \therefore \sqrt{\frac{\alpha}{\mathcal{D}_{Bs}}} = \lambda\eta'$

$$\frac{c_B}{c_{B0}} = 1 - \frac{1}{1-\operatorname{erf}(\lambda\eta')} + \frac{\operatorname{erf}(\lambda\eta)}{1-\operatorname{erf}(\lambda\eta')}$$

$$= \frac{\operatorname{erf}(\lambda\eta) - \operatorname{erf}(\lambda\eta')}{1-\operatorname{erf}(\lambda\eta')}$$

$$\operatorname{erf}\lambda\eta' = \frac{c_B}{c_{B_0}}\frac{1}{\lambda}\operatorname{erf}(\eta')\exp\left[\eta'^2(1-\lambda^2)\right]$$

flux balance ⇒ implicit eq'n for η'

Which yields solutions:

$$\frac{c_A}{c_{A_0}} = 1 - \frac{\operatorname{erf}\left(\frac{z}{\sqrt{4\mathcal{D}_{AS}t}}\right)}{\operatorname{erf}\left\{\left(\frac{\alpha}{\mathcal{D}_{AS}}\right)^{1/2}\right\}}$$

$$\frac{c_B}{c_{B_0}} = 1 - \frac{1}{1-\operatorname{erf}\sqrt{\frac{\alpha}{\mathcal{D}_{BS}}}} + \frac{\operatorname{erf}\left(\frac{z}{\sqrt{4\mathcal{D}_{BS}t}}\right)}{1-\operatorname{erf}\sqrt{\frac{\alpha}{\mathcal{D}_{BS}}}}$$

Where α is given implicitly by

$$1-\operatorname{erf}\sqrt{\frac{\alpha}{\mathcal{D}_{BS}}} = \frac{c_{B_0}}{c_{A_0}}\sqrt{\frac{\mathcal{D}_{BS}}{\mathcal{D}_{AS}}}\left(\operatorname{erf}\sqrt{\frac{\alpha}{\mathcal{D}_{AS}}}\right)\exp\left[\frac{\alpha}{\mathcal{D}_{AS}}-\frac{\alpha}{\mathcal{D}_{BS}}\right.$$

Boundary layer theory:

Simultaneous ht. mass & momentum

$(A+B) \longrightarrow$

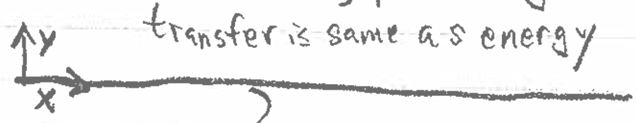
V_∞

$x_{A\infty}, x_{B\infty}$

T_∞

not nec.
$\underline{A\ \text{dilute}}$
if A dilute, transfer is same as energy

Applications:
combustion of solid fuel
heterogeneous catalysis



T_0, x_{A_0}

B insoluble in A, plate of A sublimes → ablative cooling.

$\rho, \mu, k, \hat{C}_p, c, \mathcal{D}_{AB} = \underline{cst}$

note: if both ρ & c are cst., then $M_A = M_B = M$ (or dilute) w/ these assumptions, have equations:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$$

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = \nu \frac{\partial^2 v_x}{\partial y^2}$$

$$v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2}$$

$$v_x \frac{\partial x_A}{\partial x} + v_y \frac{\partial x_A}{\partial y} = \mathcal{D}_{AB} \frac{\partial^2 x_A}{\partial y^2}$$

B.C. $x \leq 0$ or $y = \infty$:

$v_x = v_\infty$, $T = T_\infty$, $x_A = x_{A\infty}$

At $y = 0$ $v_x = 0$, $T = T_0$, $x_A = x_{A_0}$

but $v_y \neq 0$, rather $N_B = 0$

so different method of sol'n.

End 36 lec.

From CE, obtain $v_y = v_{y_0} - \int_{y=0}^{y} \frac{\partial v_x}{\partial x} dy$

where v_{y_0} = y-velocity at $y=0$ $= \frac{M_A N_{A_0}}{\rho}$

Now $N_{A_0} = x_{A_0}(N_{A_0} + \cancelto{0}{N_{B_0}}) - c\mathcal{D}_{AB} \left.\frac{\partial x_A}{\partial y}\right|_{y=0}$

$$\therefore N_{A_0} = \frac{-c\mathcal{D}_{AB}}{1 - x_{A_0}} \left.\frac{\partial x_A}{\partial y}\right|_{y=0}$$

$$\therefore\ V_y = \frac{-M_A\ c\,\mathcal{D}_{AB}}{(1-x_{A_o})\,\rho}\ \frac{\partial x_A}{\partial y}\bigg|_{y=0} - \int_0^y \frac{\partial v_x}{\partial x}\,dy$$

but since $M_A = M_B = M$, $\frac{Mc}{\rho} = 1$

and $$V_y = -\frac{\mathcal{D}_{AB}}{1-x_{A_o}}\ \frac{\partial x_A}{\partial y}\bigg|_{y=0} - \int_0^y \frac{\partial v_x}{\partial x}\,dy$$

Now define dimensionless variables & param:

$$\Pi_V = \frac{V_x - V_{x_o}}{V_{x_\infty} - V_{x_o}} = \frac{V_x}{V_\infty} \qquad \Lambda_V = \frac{\nu}{\nu} = 1$$

$$\Pi_T = \frac{T - T_o}{T_\infty - T_o} \qquad \Lambda_T = \frac{\nu}{\alpha} = Pr$$

$$\Pi_{AB} = \frac{x_A - x_{A_o}}{x_{A_\infty} - x_{A_o}} \qquad \Lambda_{AB} = \frac{\nu}{\mathcal{D}_{AB}} = Sc$$

Thus:

mass $$v_x \frac{\partial \Pi_{AB}}{\partial x} - \left[\frac{\mathcal{D}_{AB}}{1-x_{A_o}}\ \frac{\partial x_A}{\partial y}\bigg|_{y=0} + \int_0^y \frac{\partial v_x}{\partial x}\,dy\right]\frac{\partial \Pi_{AB}}{\partial y} = \frac{\nu}{\Lambda_{AB}}\frac{\partial^2 \Pi}{\partial y}$$

energy $$v_x \frac{\partial \Pi_T}{\partial x} - \left[\quad\right]\frac{\partial \Pi_T}{\partial y} = \frac{\nu}{\Lambda_T}\ \frac{\partial^2 \Pi_T}{\partial y^2}$$

mom $$v_x \frac{\partial \Pi_v}{\partial x} - \left[\quad\right]\frac{\partial \Pi_v}{\partial y} = \frac{\nu}{\Lambda_v}\ \frac{\partial^2 \Pi_v}{\partial y^2}$$

w/ B.C.'s $x \leq 0$ or $y = \infty$ $\Pi = 1$ & $\Pi' = 0$

at $y = 0$, $\Pi = 0$

despite evap., will still admit sim. transform:

let $\eta = \frac{y}{2}\sqrt{\frac{V_\infty}{\nu x}}$: dimensionless

Obtain transformed O.D.E.'s:

$$\Lambda\left[\frac{1}{\Lambda_{AB}}\frac{x_{A_0} - x_{A_\infty}}{1 - x_{A_0}}\Pi_{AB}'(0) - \int_0^\eta 2\,\Pi_V\, d\eta\right]\Pi' = \Pi''$$

w/ B.C.'s $\eta = 0$ $\Pi = 0$, $\eta = \infty$, $\Pi = 1$

3 eq'ns:
no subscript on Π means may be any of 3

Rate of mass transfer at wall affects all 3 prof.

Define $f \equiv -K + \int_0^\eta 2\,\Pi_V\, d\eta$,

$$K = \frac{1}{\Lambda_{AB}}\frac{x_{A_0} - x_{A_\infty}}{1 - x_{A_0}}\Pi_{AB}'(0) = \text{cst},$$

obtain $-\Lambda f\,\Pi' = \Pi''$, at $\eta = 0$, $\Pi = 0$

at $\eta = \infty$, $\Pi = 1$

Note: still non-linear for Π_V

May integrate:

$$\Pi' = c_1 \exp\left(-\int_0^{\zeta} \Lambda f \, d\zeta'\right)$$

$$\Pi = c_1 \int_0^{\zeta} \exp\left[-\int_0^{\zeta'} \Lambda f \, d\zeta''\right] d\zeta' + \cancel{c_2}$$

$c_2 \to 0$ from B.C.

at $\zeta = \infty, \Pi = 1 \therefore$

$$\Pi = \frac{\int_0^{\zeta} \exp\left[-\Lambda \int_0^{\zeta'} f \, d\zeta''\right] d\zeta'}{\int_0^{\infty} \exp\left[-\Lambda \int_0^{\zeta} f \, d\zeta'\right] d\zeta}$$

How do we solve now? Numerically:

first do Π_v:

$$\Pi_v = \frac{\int_0^{\zeta} \exp\left[-\int_0^{\zeta'} f \, d\zeta''\right] d\zeta'}{\int_0^{\infty} \exp\left[-\int_0^{\zeta} f \, d\zeta'\right] d\zeta}$$

$$\text{w/} \quad f = -K + \int_0^{\zeta} 2\, \Pi_v \, d\zeta$$

pick some K, then find f which satisfies simultaneous eq'ns.

Once obtain f, simply have to integrate to get π_T, π_{AB}.

B. S & L gives results for variety Pr, Sc, K (fig. 19.3-2) ⇒ BL thickens for $K > 0$, thins for $K < 0$ as expect.

Has imp. application to ablative cooling: thickening of B.L. reduces visc. dissip. heating.

Interested in gradients (fluxes) at wall

$$\pi'\Big|_{\eta=0} = \frac{1}{\int_0^\infty \left[\exp\left(-\Lambda \int_0^\eta f \, d\eta'\right)\right] d\eta}$$

$$\pi_\nu'\Big|_{\eta=0} = \frac{2\,\tau_{yx}\big|_{wall}}{\rho\, V_\infty^2} \sqrt{\frac{V_\infty x}{\nu}}$$

$$\pi_T'\Big|_{\eta=0} = \frac{2\,\Lambda_T\, q_w}{\rho\, \hat{C}_p V_\infty (T_0 - T_\infty)} \sqrt{\frac{V_\infty x}{\nu}}$$

$$\pi_{AB}'\Big|_{\eta=0} = \frac{2\,\Lambda_{AB}\, J_{Ay}^*\big|_{y=0}}{c\, V_\infty (x_{A0} - x_{A\infty})} \sqrt{\frac{V_\infty x}{\nu}}$$

Look at special case : $|K| << 1$
(Diffusional B.L. << Mom. B.L.)

$\therefore\ \Pi_v \approx \frac{1.328}{2}\zeta$ ← linear velocity profile from slope at $\zeta = 0$

Similar to HW probem ⑤, if $\delta \sim x^{-1/2}$) one have solved before

and for $\Lambda >> 1$ (Pr, Sc $>> 1$) ← Integ. twice to get from linear prob

$$\Pi \approx \frac{\int_0^{\zeta} \exp\left[\Lambda K \zeta' - \frac{1.328\Lambda}{3!}\zeta'^3\right] d\zeta'}{\int_0^{\infty} \exp\left[\qquad\right] d\zeta}$$

$$\Pi' = \frac{1}{\int_0^{\infty} \exp\left[\Lambda K \zeta - \frac{1.328\Lambda}{3!}\zeta^3\right] d\zeta}$$

As $K \to 0$,

$$\Pi = \frac{\int_0^{\zeta} \exp\left(-\frac{1.328\Lambda}{3!}\zeta'^3\right) d\zeta'}{\int_0^{\infty} \exp\left(-\frac{1.328\Lambda}{3!}\zeta^3\right) d\zeta}$$

$$= \frac{\Gamma(\frac{1}{3}, u)}{\Gamma(\frac{1}{3}, \infty)}, \quad u = \frac{1.328\Lambda}{3!}\zeta^3$$