and $$\Pi' = \frac{1}{\frac{1}{3}\left(\frac{3!}{1.328\Lambda}\right)^{1/3}\Gamma\left(\frac{1}{3}\right)}$$

$$\approx 0.6774\,\Lambda^{1/3}$$

Pollhausen gave $\Pi'(\zeta=0, \Lambda, K=0) \doteq 0.664\Lambda$

↳ curve fit for lge Λ

leads to

$$\frac{\tau_w}{\rho V_\infty^2} = \frac{q_w}{\rho \hat{C}_p V_\infty (T_0 - T_\infty)} Pr^{2/3} = \frac{J_{Aw}^{*}\; Sc^{2/3}}{c V_\infty\, (x_{A0} - x_{A\infty})}$$

$$= 0.332\, Re^{-1/2}, \quad Re = \frac{V_\infty x}{\nu}$$

Convenient analogies.

End lec 37

Multicomponent Systems

Thus far, just 2-components, now look at multicomponent systems:

Continuity: $\rho \dfrac{Dw_i}{Dt} = -\nabla \cdot j_i + r_i$

↑ for ρ cst so that $\nabla \cdot V =$

Motion: $\rho \dfrac{DV}{Dt} = +(\nabla \cdot \Pi) + \sum_{i=1}^{n} \rho_i g_i$

stress tensor $\Pi = \tau + p\,\delta$

Energy: $\rho \dfrac{D}{Dt}\left\{\hat{u} + \frac{1}{2}V^2\right\} = -\nabla \cdot q - \nabla \cdot \Pi \cdot V + \sum n_i \cdot g$

Note: $\hat{u}$ contains ht. of rxn, mixing terms as well.

To solve, need: $p = p(\rho, T, x_i)$

$\hat{u} = \hat{u}(\rho, T, x_i)$

$r_i \Rightarrow$ Kinetics eq'n

flux expressions $\underset{\sim}{j}_i$, $\underset{\approx}{\Pi}$, $\underset{\sim}{q}$ in terms of gradients.

Can derive equivalent forms of eq'ns:

$$\frac{\partial \rho_i}{\partial t} = -\underset{\sim}{\nabla} \cdot \{\rho_i \underset{\sim}{v} + \underset{\sim}{j}_i\} + r_i$$

$$\frac{\partial (\rho \underset{\sim}{v})}{\partial t} = -\underset{\sim}{\nabla} \cdot (\rho \underset{\sim}{v} \cdot \underset{\sim}{v} + \underset{\approx}{\Pi}) + \sum \rho_i \underset{\sim}{g}_i$$

$$\frac{\partial}{\partial t}\rho\left(\hat{u} + \tfrac{1}{2}\underset{\sim}{v}^2\right) = -\underset{\sim}{\nabla} \cdot \left\{\rho\left(\hat{u} + \tfrac{1}{2}v^2\right)\underset{\sim}{v} + \underset{\sim}{q} + \underset{\approx}{\Pi} \cdot \underset{\sim}{v}\right\} + \sum \underset{\sim}{n}_i \cdot \underset{\sim}{g}_i$$

Define $\underset{\approx}{\phi} = \rho \underset{\sim}{v}\underset{\sim}{v} + \underset{\approx}{\Pi}$ mom. flux w.r.t. stationary coordinates

$\underset{\sim}{e} = \rho\left[\left(\hat{u} + \frac{v^2}{2}\right)\underset{\sim}{v} + \underset{\sim}{q} + \underset{\approx}{\Pi} \cdot \underset{\sim}{v}\right]$ energy flux

& $\underset{\sim}{n}_i = \rho_i \underset{\sim}{v} + \underset{\sim}{j}_i$

$$\therefore \quad \frac{\partial \rho_i}{\partial t} = -\underset{\sim}{\nabla} \cdot \underset{\sim}{n}_i + r_i$$

$$\frac{\partial(\rho \underset{\sim}{V})}{\partial t} = -\underset{\sim}{\nabla} \cdot \underset{\approx}{\phi} + \sum \rho_i \underset{\sim}{g}_i$$

$$\frac{\partial\left[\rho\left(\hat{u} + \frac{V^2}{2}\right)\right]}{\partial t} = -\underset{\sim}{\nabla} \cdot \underset{\sim}{e} + \sum \underset{\sim}{n}_i \underset{\sim}{g}_i$$

In systems w/ temp. inequalities and conc. inequalities (double diffusive free convection):

Free convection arising from ∇x_A & ∇T

$$\rho \frac{D\underset{\sim}{V}}{Dt} = -\underset{\sim}{\nabla} p - \underset{\sim}{\nabla} \cdot \underset{\approx}{\tau} + \left(\rho \underset{\sim}{g} - \bar{\rho} \underset{\sim}{g}\right)$$

Now $\rho = \bar{\rho} + \left.\frac{\partial \rho}{\partial T}\right|_{\bar{T}, \bar{x}_A, \ldots} (T - \bar{T}) + \left.\frac{\partial \rho_A}{\partial x_A}\right|_{\bar{T}, \bar{x}_A} (x_A - \bar{x}_A) + \ldots$

$\ldots$ (just consider 2-component)

$$\therefore \rho = \bar{\rho} - \bar{\rho}\bar{\beta}(T - \bar{T}) + \bar{\rho}\bar{\xi}(x_A - \bar{x}_A) + \ldots$$

with $\bar{\xi} = \frac{-1}{\rho}\left(\frac{\partial \rho}{\partial x_A}\right)_T$

$$\therefore \rho \frac{D\underset{\sim}{V}}{Dt} = -\underset{\sim}{\nabla} p - \underset{\sim}{\nabla} \cdot \underset{\approx}{\tau} - \bar{\rho}\bar{\beta}\underset{\sim}{g}(T - \bar{T}) - \bar{\rho}\bar{\xi}\underset{\sim}{g}(x_A - \bar{x}_A)$$

Fluxes in Multicomponent systems

a) momentum flux: depends only on velocity gradient

b) energy flux: → temp gradients
→ also on mechanical driving force (conc., pressure, external forces, Dufour effect

c) mass flux: → mechanical driving forces
→ temp. gradients (Soret effect)

2 cross mech: not indep.: Onsager reciprocal relations (thermo of irrev. processes) tells us that same coeff. D_A^T (soret coeff.) can describe both Soret & Dufour effects.

Mom. flux: (newtonian)

$$\tau = -\mu\left[\nabla \underset{\sim}{v} + (\nabla \underset{\sim}{v})^T\right] + \left(\tfrac{2}{3}\mu - \kappa\right)(\nabla\cdot \underset{\sim}{v})\,\underset{\approx}{\delta}$$

local viscosity — local bulk viscosity

instantaneous

Note: $\kappa = 0$ for low density monatomic gases, not very important in dense gases and liquids.

Energy flux:

molal enthalpy of species i at location

$$\underset{\sim}{q} = \underbrace{-k\underset{\sim}{\nabla}T}_{\text{conduction}} + \sum_{i=1}^{n} \bar{H}_i \underset{\sim}{J}_i + \text{Dufour effect}$$

Diffusion of species i

Dufour effect: quite complex, usually small

or

$$\underset{\sim}{e} = -k\underset{\sim}{\nabla}T + \sum \bar{H}_i J_i + \underbrace{\text{Dufour}}_{\text{neglect}} + (\underset{\approx}{\Pi}\cdot\underset{\sim}{v})$$

$$+ \rho\left\{\hat{u} + \underbrace{\frac{v^2}{2}}_{\text{neglect}}\right\}\underset{\sim}{v}$$

neglect $\underset{\approx}{\tau}\cdot\underset{\sim}{v}$

$$\approx -k\underset{\sim}{\nabla}T + \sum \bar{H}_i \underset{\sim}{J}_i + \underbrace{p\underset{\sim}{v} + \rho\hat{u}\underset{\sim}{v}}_{\rho\hat{H}\underset{\sim}{v}}.$$

$$= -k\underset{\sim}{\nabla}T + \sum \bar{H}_i \underset{\sim}{J}_i + \sum c_i \bar{H}_i \underset{\sim}{v}$$

$$= -k\underset{\sim}{\nabla}T + \sum \underset{\sim}{N}_i \bar{H}_i$$ } use for study of ht. transf. w/ mass transf.

Mass flux

$$\underset{\sim}{j}_i = \underbrace{\underset{\sim}{j}_i^{(x)}}_{\text{conc. gradient diffusion}} + \underbrace{\underset{\sim}{j}_i^{(p)}}_{\text{pressure diff}^n} + \underbrace{\underset{\sim}{j}_i^{(g)}}_{\text{forced diffusion}} + \underbrace{\underset{\sim}{j}_i^{(T)}}_{\text{diff}^n \text{ due to a } \Delta T}$$

pressure diff^n (centrifugal separation)

diff^n due to a ΔT (soret effect)

conc. gradient diffusion

forced diffusion
ex: important in ionic systems $\Rightarrow$ each species has different force acting on it

Clusius-Dickel column, used for separating isotopes or similar organic compounds.

Assign $\boxed{18.F}$, 18.N

multicomponent diffusivity $\neq \mathcal{D}_{ij}$

Gibb's free energy

$$= \frac{c^2}{\rho RT} \sum_{j=1}^{n} M_i M_j D_{ij} \left[x_i \sum_{k \neq j} \left(\frac{\partial \bar{G}_j}{\partial x_k} \right)_{\substack{T,P,x_s \\ s \neq j,k}} \nabla x_k \right]$$

$$+ \frac{c^2}{\rho RT} \sum_{j=1}^{n} M_i M_j D_{ij} \left[x_j M_j \left(\frac{\bar{V}_j}{M_j} - \frac{1}{\rho} \right) \nabla p \right]$$

$$- \frac{c^2}{\rho RT} \sum_{j=1}^{n} M_i M_j D_{ij} \left[x_j M_j \left(\underset{\sim}{g}_j - \sum_{k=1}^{n} \frac{\rho_k}{\rho} \underset{\sim}{g}_k \right) \right.$$

ext force on species i

if $g_i \equiv g$, term vanishes

multicomponent thermal diffusion coef.

$$- D_i^T \nabla \ln T$$

with $D_{ii} = 0$, $\sum_{i=1}^{n} \left[M_i M_k D_{ik} - M_i M_h D_{ih} \right] = 0$

$\sum D_i^T = 0$

for $n > 2$, $D_{ij} \neq D_{ji}$ in general

Look at 2 limiting cases: first, binary mixture: $D_{AB} = D_{BA}$, thus

$$\underset{\sim}{j}_A = -\underset{\sim}{j}_B = -\left(\frac{c^2}{\rho RT} \right) M_A^2 M_B D_{AB} x_A$$

$$\cdot \left[\left(\frac{\partial}{\partial x_A} \frac{\bar{G}_A}{M_A} \right)_{T,P} \nabla x_A - \frac{\rho_B}{\rho} \left(\underset{\sim}{g}_A - \underset{\sim}{g}_B \right) + \left(\frac{\bar{V}_A}{M_A} - \frac{1}{\rho} \right) \nabla p \right.$$

$$- D_A^T \nabla \ln T$$

Equation may be simplified using
$(d\bar{G}_A)_{T,P} = RT\, d\ln a_A$ & defining
thermal diffusion ratio $k_T = \frac{\rho}{c^2 M_A M_B} \frac{D_A^T}{D_{AB}}$

$$\underset{\sim}{j}_A = -\underset{\sim}{j}_B = -\frac{c^2}{\rho} M_A M_B D_{AB} \left[\left(\frac{\partial \ln a_A}{\partial \ln x_A}\right)_{T,P} \underset{\sim}{\nabla} x_A - \frac{M_A \rho_B x_A}{\rho RT}\left(\underset{\sim}{g}_A - \underset{\sim}{g}_B\right) + \frac{M_A x_A}{RT}\left(\frac{\bar{V}_A}{M_A} - \frac{1}{\rho}\right)\underset{\sim}{\nabla} P + k_T \underset{\sim}{\nabla} \ln T \right]$$

which is starting pt. for study ordinary, forced, pressure, & thermal diff$^{\underline{n}}$ for binary non-ideal mixtures.

Note: if $\underset{\sim}{g}_A = \underset{\sim}{g}_B$, $\underset{\sim}{\nabla} P$ negligible, k_T small, have

$$\underset{\sim}{j}_A = -\underset{\sim}{j}_B = -\frac{c^2}{\rho} M_A M_B \left[D_{AB} \left.\frac{\partial \ln a_A}{\partial \ln x_A}\right|_{T,P} \right] \underset{\sim}{\nabla} x_A$$

vs. $\underset{\sim}{j}_A = -\frac{c^2}{\rho} M_A M_B \left[\mathcal{D}_{AB} \right] \underset{\sim}{\nabla} x_A$ used before

for an ideal sol'n, $\left.\frac{\partial \ln a_A}{\partial \ln x_A}\right|_{T,P} = 1$

D_{AB} less conc. dep. than $\mathcal{D}_{AB}$, but $\mathcal{D}_{AB}$ reported more often
(in liquids)

2) Ordinary diff^n of multicomponent gases at low density

<u>ideal</u> mixture:

$$\underset{\sim}{j}_i = \frac{c^2}{\rho}\sum_{j=1}^{n} M_i M_j D_{ij} \underset{\sim}{\nabla} x_j$$

can relate D_{ij} to $\mathcal{D}_{ij}$ for binary mixture. $\mathcal{D}_{ij}$ <u>indep</u> of conc., ∴ more convenient to use.

$$D_{12} = \mathcal{D}_{12}\left[1 + \frac{x_3\left[\frac{M_3}{M_2}\mathcal{D}_{13} - \mathcal{D}_{12}\right]}{x_1\mathcal{D}_{23} + x_2\mathcal{D}_{13} + x_3 \ldots}\right]$$

for <u>ideal gases</u> (3 comp.)

May invert eq^n:

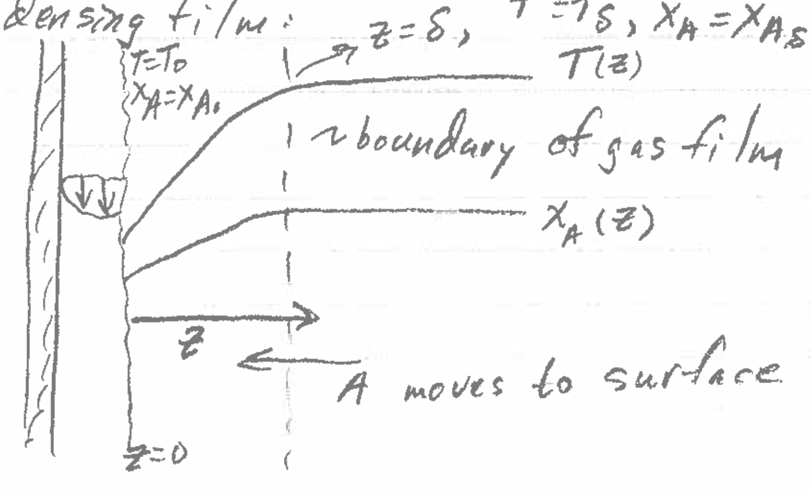
$$\underset{\sim}{\nabla} x_i = \sum_{j=1}^{n} \frac{1}{c\mathcal{D}_{ij}}\left(x_i \underset{\sim}{N}_j - x_j \underset{\sim}{N}_i\right)$$

Stefan-Maxwell eq^{n}s

End lec. 38 Used to study <u>ordinary</u> diffusion of multicomp. systems.

Examples: Simultaneous ht. & mass transfer

condensing film:



useful in psychometric calculations (wet/dry bulb)

B stagnant, binary system so:

$$N_{Az} = -\frac{c\mathcal{D}_{AB}}{1-x_A}\frac{dx_A}{dz}$$ ← assumes ideality, etc.

$$\frac{dN_{Az}}{dz} = 0, \quad \frac{de_z}{dz} = 0$$ ← steady-state, no body force

$$\underset{\sim}{e} = -k\underset{\sim}{\nabla}T + \sum \underset{\sim}{N}_i \tilde{H}_i + \underset{\approx}{\tau}\cdot\underset{\sim}{v} + \tfrac{1}{2}\rho v^2$$

$$\therefore \left(\frac{1-x_A}{1-x_{A_0}}\right) = \left(\frac{1-x_{A\delta}}{1-x_{A_0}}\right)^{z/\delta}$$

and $$N_{Az} = \frac{c\mathcal{D}_{AB}}{\delta}\ln\frac{1-x_{A\delta}}{1-x_{A_0}}$$

Now for energy:

$$e_z = -k\frac{dT}{dz} + (\tilde{H}_A N_{Az} + \tilde{H}_B \overset{0}{N_{Bz}})$$

$$= -k\frac{dT}{dz} + N_{Az}\tilde{C}_{pA}(T-T_0) \quad z < \delta$$

$$\therefore \frac{T-T_0}{T_\delta - T_0} = \frac{1-\exp[(N_{Az}\tilde{C}_{pA}/k)z]}{1-\exp[(N_{Az}\tilde{C}_{pA}/k)\delta]}$$

Non-linear due to flux of N_{Az}. Note: if $\frac{N_{Az}\tilde{C}_{pA}\delta}{k} \ll 1$, $\frac{T-T_0}{T_\delta - T_0} \cong \frac{z}{\delta}$

ice will melt faster in glass in moist rather than dry air

Energy flux:

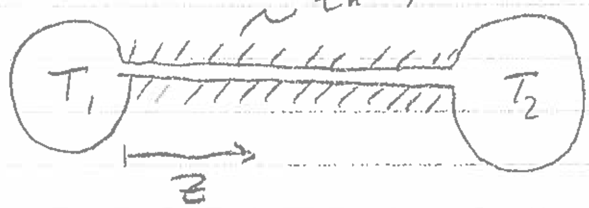
$$\frac{-k\left.\frac{\partial T}{\partial x}\right|_{z=0}}{-k\left.\frac{\partial T}{\partial x}\right|_{z=0} \text{ (no mass transfer) } N_{Az}=0} = \frac{\overbrace{-\delta N_{Az}\tilde{C}_{pA}/k}^{\text{negative}}}{1-\exp\left(\delta N_{Az}\tilde{C}_{pA}/k\right)}$$

$$= \frac{\text{rate conductive ht transf. w/ mass transf.}}{\text{rate w/out mass}}$$

Even more energy transport by enthalpy of vapor
~~Why energy transfer faster in moist air~~
for many applications $\delta N_{Az}\tilde{C}_{pA}/k \ll 1$ $\therefore$ nearly unity. Excess transport due primarily to convection

Thermal Diffusion:

thin, insulated tube (no convection)



Filled w/ A + B, obtain S.S. compositions.
neglect convection in tube

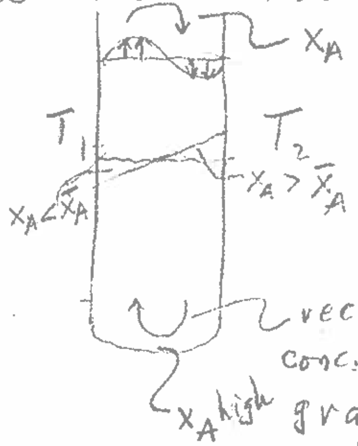
$$j_{Az} = -\frac{c^2}{\rho} M_A M_B \mathcal{D}_{AB}\left[\frac{\partial x_A}{\partial z} + \frac{k_T}{T}\frac{\partial T}{\partial z}\right]$$

$$\text{At SS} \quad \cancelto{0}{\frac{\partial \rho_A}{\partial t}} = -\frac{\partial}{\partial z}\left(\rho_i \cancelto{0}{v_z} + j_{Az}\right) + \cancelto{0}{r_A}$$

$$\therefore \frac{\partial j_{Az}}{\partial z} = 0 \qquad j_{Az} = cst = 0$$

$$\therefore \frac{\partial x_A}{\partial z} = -\frac{k_T}{T}\frac{\partial T}{\partial z} \qquad x_{A2} - x_{A1} = -\underbrace{k_T}_{\text{if indep. of concentration.}} \ln\frac{T_2}{T_1}$$

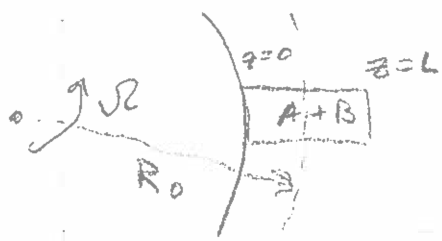
Not much separation: Clusius Dickel column uses nat. convection to amplify:



$T_1 > T_2$

recirculation means that at equilibrium, conc. is dep on vert position ⇒ amplifies gradients: interesting problem to analyze) solve for HW in '87

Pressure diffusion: centrifuge



$$\frac{dp}{dz} = -\rho\,\Omega^2 R_0$$

$$j_{Az} = 0 = -\frac{c^2}{\rho} M_A M_B D_{AB}\left[\frac{\partial \ln a_A}{\partial \ln x_A}\frac{dx_A}{dz} - \frac{M_A \rho_B x_A}{\rho R T}\left(\cancel{g_{Az} - g_{Bz}}\right)^{\to 0} + \frac{M_A x_A}{RT}\left(\frac{\bar{V}_A}{M_A} - \frac{1}{\rho}\right)\frac{dp}{dz}\right]$$

Assume ideal solution: $\dfrac{\partial \ln a_A}{\partial \ln x_A} = 1$

$$\therefore \frac{1}{x_A}\frac{dx_A}{dz} = \frac{-M_A}{RT}\left[\frac{\bar{V}_A}{M_A} - \frac{1}{\rho}\right]\frac{dp}{dz} = \frac{M_A}{RT}\left[\frac{\bar{V}_A}{M_A} - \frac{1}{\rho}\right]\rho$$

neglect changes w/ comp & position $\rho\,\Omega_0^2$

Thus

mult by $\bar{V}_B$

$$\bar{V}_B \frac{\partial(\ln x_A)}{\partial z} = -\left(\frac{\Omega^2 R_0}{RT}\right)\left[-\rho \bar{V}_A \bar{V}_B + M_A \bar{V}_B\right]$$

Similarly:

$$\bar{V}_A \frac{\partial(\ln x_B)}{\partial z} = -\left(\frac{\Omega^2 R_0}{RT}\right)\left[-\rho \bar{V}_A \bar{V}_B + M_B \bar{V}_A\right]$$

subtract to get:

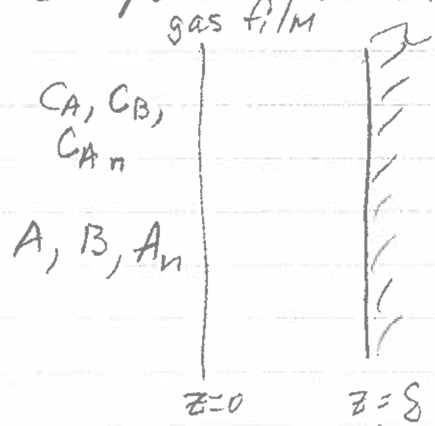
$$\therefore \frac{\partial}{\partial z} \ln\left[x_A^{\bar{V}_B}\, x_B^{-\bar{V}_A}\right] = \frac{\Omega^2 R_0}{RT}\left(M_B \bar{V}_A - M_A \bar{V}_B\right)$$

$$\therefore \left(\frac{x_A}{x_{A_0}}\right)^{\bar{V}_B} \left(\frac{x_{B_0}}{x_B}\right)^{\bar{V}_A} = \exp\left\{\left(\bar{V}_A M_B - \bar{V}_B M_A\right)\frac{\Omega^2 R_0}{RT} z\right\}$$

at S.S.

---

3 component diffusion w/ heterogeneous Rxn



$nA \rightarrow A_n$ at surface

$B \equiv$ stagnant film

$$N_{Az} = k_n x_A^n = -n N_{A_n z} \Big|_{\text{at surface}}$$

but Rxn = 0 in gas, so

$$\frac{\partial N_{Az}}{\partial z} = \frac{\partial N_{A_n z}}{\partial z} = 0$$

Stefan-Maxwell eq'ns for A, B:

$$\frac{dx_A}{dz} = \frac{1}{c\mathcal{D}_{AA}}\cancelto{0}{\left(x_A N_{Az} - x_A N_{Az}\right)} + \frac{1}{c\mathcal{D}_{AB}}\left(x_A N_{Bz} - x_B N_{Az}\right) + \frac{1}{c\mathcal{D}_{AA_n}}\left(x_A N_{A_n z} - x_{A_n} N_{Az}\right)$$

$$\frac{dx_B}{dz} = \frac{1}{c\mathcal{D}_{BA}}\left(x_B N_{Az} - x_A \cancelto{0}{N_{Bz}}\right) + \frac{1}{c\mathcal{D}_{BA_n}}\left(x_B N_{A_n} - x_{A_n}\cancelto{0}{N_{Bz}}\right)$$

$$= \frac{1}{c\mathcal{D}_{BA}} x_B N_{Az} + \frac{1}{c\mathcal{D}_{BA_n}} x_B N_{A_n}$$ ← related to N_{Az}

$$= \frac{x_B}{c\mathcal{D}_{BA_n}} N_{Az}\left[\frac{\mathcal{D}_{BA_n}}{\mathcal{D}_{BA}} - \frac{1}{n}\right]$$

Using $N_{Bz} = 0$, $N_{Az} = -n N_{A_n z}$, $\Sigma x_i = 1$

can obtain ~~simplified~~ dimensionless equations:

$$\frac{1}{\nu_{A_nB}}\frac{dx_A}{dz^*} = r_{A_n}\left(1 - \frac{1}{n}\right)x_A + \left(r_{A_n} - r_B\right)x_B - r_{A_n}$$

uncoupled ⇒ solve x_B first

$$\frac{1}{\nu_{A_nB}}\frac{dx_B}{dz^*} = \left(r_B - \frac{1}{n}\right)x_B$$

Dimensionless reaction rate

where $z^* = z/\delta$, $\nu_{A_nB} = \dfrac{N_{Az}\,\delta}{c\,\mathcal{D}_{A_nB}}$

$r_{A_n} = \dfrac{\mathcal{D}_{A_nB}}{\mathcal{D}_{AA_n}}$ $\qquad r_B = \dfrac{\mathcal{D}_{A_nB}}{\mathcal{D}_{AB}}$

May integrate eq'n for x_B to obtain

$x_B = x_{B_0} \exp\left(R\,\nu_{A_nB}\,z^*\right)$ where $R = r_B - \frac{1}{n}$

Now plug into equation for A to obtain:
(integ. 1st order lin. ODE)

$$x_A = \left(x_{A_0} - \frac{1}{N} + \frac{1}{M}x_{B_0}\right)\exp\left(N r_{A_n}\nu_{A_nB}\,z^*\right) + \frac{1}{N} - \frac{1}{M}x_{B_0}\exp\left(R\,\nu_{A_nB}\,z^*\right)$$

where $N = 1 + \frac{1}{n}$, $M = 1 - \frac{1}{n}\left[\dfrac{1 - r_{A_n}}{r_B - r_{A_n}}\right]$

Use $N_A = K_h x_A^h$ at $z = \delta$ to get

$\nu_{A_nB} = \dfrac{N_{Az}\,\delta}{c\,\mathcal{D}_{A_nB}}$ $\Rightarrow$ transcendental eq'n

Note: Do not use eq'n for N_{A_n} as may be obtained from stoichiometry

End lec. 39

8K Dimensional Analysis for Binary Isothermal fluid mixtures

Assume const. μ, $\mathcal{D}_{AB}$; ρ, c const except for free convection driving term

$$\nabla \cdot \underset{\sim}{v} = 0, \quad \frac{D x_A}{Dt} = \mathcal{D}_{AB} \nabla^2 x_A$$

$$\rho \frac{D\underset{\sim}{v}}{Dt} = \mu \nabla^2 \underset{\sim}{v} + \begin{cases} -\nabla p + \rho \underset{\sim}{g} & \text{forced} \\ -\rho \xi \underset{\sim}{g} (x_A - x_{A0}) & \text{free} \end{cases}$$

$\underset{\sim}{v}^* = \underset{\sim}{v} / V \leftarrow$ char. velocity

$p^* = (p - p_0) / \rho V^2$

$t^* = Vt / D \leftarrow$ char length scale

$$x_A^* = \frac{x_A - x_{A0}}{\underbrace{x_1 - x_{A0}}_{\text{char } \Delta x}}$$

∴ obtain dimensionless eq'ns:

Forced: $\nabla^* \cdot \underset{\sim}{v}^* = 0$

$$\frac{D x_A^*}{Dt^*} = \frac{1}{Re\,Sc} \nabla^{*2} x_A^*, \quad \frac{D\underset{\sim}{v}^*}{Dt^*} = -\nabla^* p^* + \frac{1}{Re} \nabla^{*2} \underset{\sim}{v}^* + \frac{1}{Fr} \frac{\underset{\sim}{g}}{g}$$

For free convection, $V \sim \nu/D$

$\therefore\ \underset{\sim}{V}^{**} = v\,\frac{D\rho}{\mu}, \quad t^{**} = \frac{t\mu}{\rho D^2}$

and obtain eq'ns:

$$\underset{\sim}{\nabla}^{*} \cdot \underset{\sim}{V}^{**} = 0$$

$$\frac{D x_A^{*}}{D t^{**}} = \frac{1}{Sc} \nabla^{*2} x_A^{*}$$

$$\frac{D \underset{\sim}{V}^{**}}{D t^{**}} = \nabla^{*2} V^{**} - x_A^{*} Gr_{AB} \frac{\underset{\sim}{g}}{g}$$

w/ $Gr = \dfrac{\rho^2 g \xi (x_{A_1} - x_{A_0})}{\mu^2}$

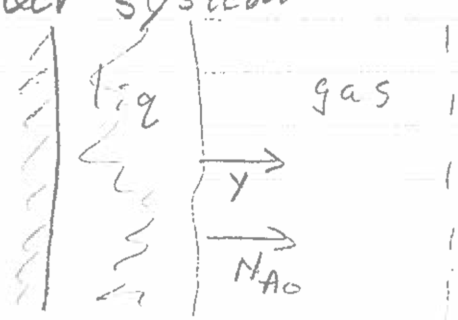
Skip

Note: above <u>identical</u> to that obtained for ht. transf: governing equations are the same

Further analogy to ht. transfer:

Mass transfer Coefficients. (at interface

Consider system:



liq. Diffuses into gas at interface

Flux <u>into</u> phase of interest (gas phase) is related to conc. gradient at interface, thus define:

$$J^*_{Ay}\Big|_{y=0} = -J^*_{By}\Big|_{y=0} \equiv k^{\bullet}_{x,loc}\,\Delta x_A$$

Thus $N_{A_0} - x_{A_0}(N_{A_0} + N_{B_0}) = k^{\bullet}_{x,loc}\,\Delta x_A$

if have add'l constraint on N_A or N_B (i.e. $N_B = 0$), then solve problem if know x_{A0} & $k^{\bullet}_{x,loc}$

The dot emphasizes that $k^{\bullet}_{x,loc}$ dep. on mass transfer rate: Mass transfer distorts conc. & velocity profiles due to flow of A & B. For small N_A & N_B, effect is small

$$N_{A_0} - x_{A_0}(N_{A_0} + N_{B_0}) = k_{x,loc}\,\Delta x_A$$

no dots, same as ht. tran

For area A, can talk of average (mean) values & write:

$$W_A^{(m)} - x_{A_0}\left[W_A^{(m)} + W_B^{(m)}\right] = k^{\bullet}_x A\,\Delta x_A$$

flux · Area

For small mass transfer rates:

$$W_A^{(m)} - x_{A_0}\left[W_A^{(m)} + W_B^{(m)}\right] = k_x A\,\Delta x_A$$

For closed channels (e.g., a pipe), use Δx_A as $x_{A0} - x_{Ab}$ ← bulk

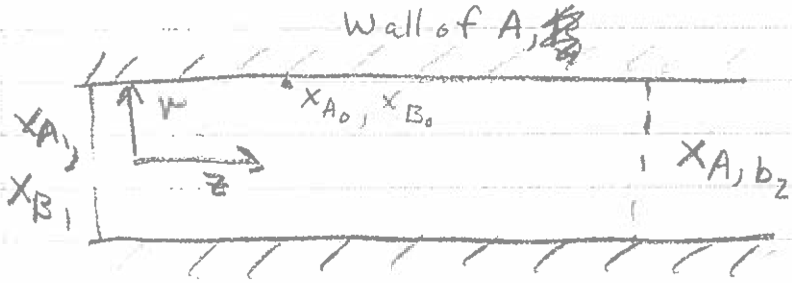
for submerged object, $\Delta x_A = x_{A0} - x_{A\infty}$, etc.
interface

In enclosed systems where area not well characterized, use

$$dW_A^{(m)} = \left[(k_x a)_{loc}\, dV \right] (x_A - x_{Ab}) + x_{A0}\left[dW_A^{(m)} + dW_B^{(m)} \right]$$

can measure product experimentally

How does this work? example: (BS&L 21.2)



Low mass transfer rates

Total diffusive flux:

$$\int_0^L \left\{ c\, \mathcal{D}_{AB} \frac{\partial x_A}{\partial r}\bigg|_w \right\} 2\pi R\, dz \equiv \pi D L \cdot \overline{k_{x\,wall}}\,(\overline{x_A} - \overline{x_{Ab}})$$

mean values

$$= W_{A,w}^{(m)} - x_{A0}\left[W_{A,w}^{(m)} + W_{B,w}^{(m)} \right]$$

$$\equiv \pi D L\, k_{x_1} (x_{A0} - x_{A_1}), \text{etc}$$ ⇔ different mass transfer coeff.

If no viscous dissip & No rxn in bulk, energy transport same as mass transport

Thus dimensionless profiles & gradients are the same:

$$\frac{k_{x,1} D}{c \mathcal{D}_{AB}} = Nu_{AB,1} = \text{same } f^{\underline{n}} (Re, Sc, L/D)$$

as $Nu_1 \equiv \frac{h_1 D}{k} = f^{\underline{n}} (Re, Pr, L/D)$

Similarly, for free convection around submerged objects:

$$Nu_{mean} = f^{\underline{n}} (Gr, Pr)$$

$$Nu_{AB,mean} = \text{same } f^{\underline{n}} (Gr_{AB}, Sc)$$

i.e., for forced convection, obtained for around sphere ht. transf.:

$$\frac{h_m D}{k_f} = 2 + 0.6 \left(\frac{D V_\infty \rho_f}{\mu_f}\right)^{1/2} \left(\frac{\hat{C}_p \mu}{k}\right)_f^{1/3}$$

for const. surface temp.

$\therefore$ for mass transf (low rates only)

$$\frac{k_{x,m} D}{c_f \mathcal{D}_{AB_f}} = 2 + 0.6 \left(\frac{D V_\infty \rho_f}{\mu_f}\right)^{1/2} \left(\frac{\mu}{\rho \mathcal{D}_{AB}}\right)_f^{1/3}$$

will rate be higher or lower if we include effect of mass transport?
lower for diff^{n} outward, higher if inward

Table 21.2-1 gives corresponding quantities in ht. & mass transp.

Chilton-Colburn analogy:

$$j_H = j_D = f^n(Re, \text{geom.} \& B.C.'s)$$

$$j_H = \frac{h}{\rho \hat{C}_p V_\infty}\left(\frac{\hat{C}_p \mu}{k}\right)^{2/3}; \quad j_D = \frac{k_x}{c_f V_\infty}\left(\frac{\mu}{\rho \mathcal{D}_{AB}}\right)^{2/3}$$

Not exact, but useful for wide variety of flow problems.
i.e. forced convection around spheres at large Re, Pr.

Ex: evap of freely falling drop:

Drop of water, $d = 0.05$ cm, falling w/ terminal velocity $v_\infty = 215$ cm/sec thru still, dry air

obtain from sol'n of momentum eq'n

$T_s = 70°F$, $T_a = 140°F$

normally obtain from solution of energy eq'n

A = water, B = air

$x_B\Big|_{\text{liquid phase}} << 1$,

if evap. rate small,

$$W_A^{(m)} = K_{xm}\pi D^2 \frac{x_{A0} - x_{A\infty}}{1 - x_{A0}}$$

$$\frac{K_{xm} D}{c_f \mathcal{D}_{ABf}} = 2.0 + 0.60\left(\frac{D V_\infty \rho_f}{\mu_f}\right)^{1/2}\left(\frac{\mu}{\rho \mathcal{D}_{AB}}\right)_f^{1/3}$$

x_{Af} is small $\Rightarrow$ does not affect physical prop. of air.

SKIP

Thus may obtain: $Sc = 0.58$, $Re = 63$

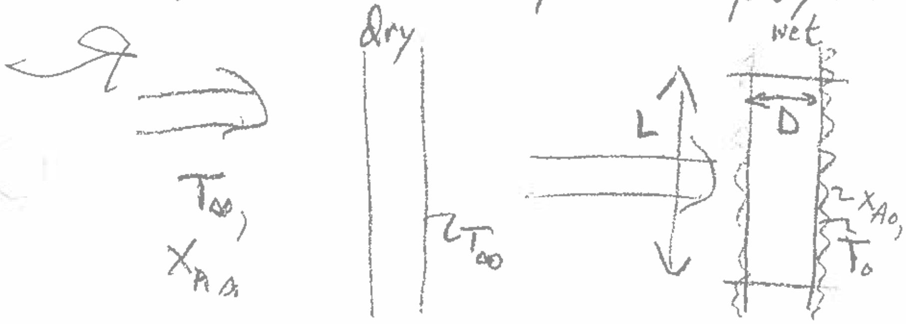
and $K_{xm} = 1.35 \times 10^{-3}$ gmole/sec cm²

$\therefore W_A^{(m)} = 2.70 \times 10^{-7}$ gmole/sec,

corresponds to $\frac{d(\text{dia})}{dt} = 1.23 \times 10^{-3}$ cm/sec

$\therefore$ goes a long way before it evaporates.

Ex: wet & dry bulb psychrometer



can use temp. depression to determine $x_{A\infty}$

let A be evap. liquid in inert B.

$\therefore\ W_A^{(m)} \Delta \tilde{H}_{A,vap} = h_m \pi D L (T_\infty - T_0)$

(energy balance)

$W_A^{(m)} (1 - x_{A0}) = K_{xm} \pi D L (x_{A0} - x_{A\infty})$

$$\therefore\ \frac{x_{A0} - x_{A\infty}}{(T_\infty - T_0)(1 - x_{A0})} = \frac{h_m}{K_{xm} \Delta \tilde{H}_{A,vap}}$$

have for slow mass transf.:

$$j_H = j_D$$

$$\frac{h_m}{\rho \hat{C}_p V_\infty} Pr^{2/3} = \frac{K_{xm}}{c_f V_\infty} Sc^{2/3}$$

thus $\dfrac{h_m}{K_{xm}} = \tilde{C}_p \left(\dfrac{Sc}{Pr} \right)^{2/3}$

$$\therefore\ \frac{x_{A0} - x_{A\infty}}{(T_\infty - T_0)(1 - x_{A0})} = \frac{\tilde{C}_p}{\Delta \tilde{H}_{A,vap}} \left(\frac{Sc}{Pr} \right)^{2/3}$$

$x_{A0} \approx \dfrac{P_{A,vap}}{P}$, thus may use observed $T_\infty - T_0$ to get $x_{A\infty}$:

Let $T_\infty = 140°F$, $T_0 = 70°F$

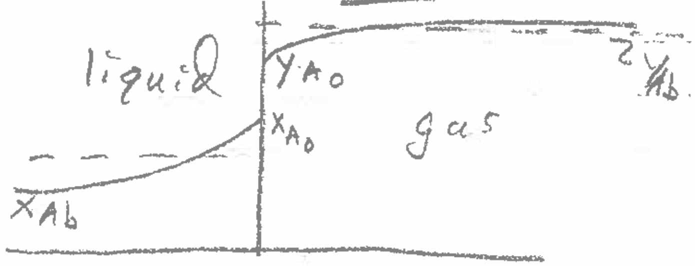
$x_{A0} = 0.0247$, $Sc = 0.58$, $Pr = 0.74$,

$$\frac{c_{pf}}{\Delta\tilde{H}_{A,vap}} = 3.69 \times 10^{-4}\ °F^{-1}$$

$$\therefore\ x_{A\infty} = 0.0033, \quad \frac{x_{A\infty}}{x_{A0}} \approx 13\%\ RH$$

Skip

Two phase Binary mass transf. coeff.: gradients on <u>both</u> sides of interface



let $y_{A0} = f(x_{A0}) \Rightarrow$ equilibrium condition.

For slow rates of mass transfer,

$$(1 - x_{A0})\, dW_{A,liq}^{(m)} = k_x (x_{A0} - x_{Ab})\, dA$$

$$(1 - y_{A0})\, dW_{A,gas}^{(m)} = k_y (y_{A0} - y_{Ab})\, dA$$

since $dW_{A,gas}^{(m)} = -dW_{A,liq}^{(m)}$, obtain:

$$\frac{y_{A0} - y_{Ab}}{x_{A0} - x_{Ab}} = \frac{-k_x / (1 - x_{A0})}{k_y / (1 - y_{A0})}$$

difficult to measure single phase coeff., may use over-all mass transfer coeff.

K_x or K_y:

$$\frac{1-x_{Ae}}{K_x}\frac{dW^{(m)}_{A,liq}}{dA} = x_{Ae} - x_{Ab}$$

in equilib. w/ y_{Ab}, i.e. $y_{Ab} = f(x_{Ae})$

and

$$\frac{1-y_{Ae}}{K_y}\frac{dW^{(m)}_{A,gas}}{dA} = y_{Ae} - y_{Ab}\,; \quad y_{Ae} = f(x_{Ab})$$

May relate K_x, K_y to k_x, k_y:

$$(y_{Ae} - y_{Ab}) = (y_{Ae} - y_{A0}) + (y_{A0} - y_{Ab})$$

$$= \left(\frac{y_{Ae} - y_{A0}}{x_{Ab} - x_{A0}}\right)(x_{Ab} - x_{A0}) + (y_{A0} - y_{Ab})$$

$$= m_y (x_{Ab} - x_{A0}) + (y_{A0} - y_{Ab})$$

slope of equilibrium curve (ave.); sim result for $x_{Ae} - x_{Ab}$

$$\frac{1-y_{Ae}}{K_y} = \frac{m_y(1-x_{A0})}{k_x} + \frac{1-y_{A0}}{k_y},$$

$$\frac{1-x_{Ae}}{K_x} = \frac{1-x_{A0}}{k_x} + \frac{1-y_{A0}}{m_x k_y}$$

if equilib. curve is a line, ($m_x = m_y = m$), obtain:

$$\frac{1-y_{Ae}}{K_y} = m \frac{1-x_{Ae}}{K_x},$$ relates K_x & K_y => both contain same information.

Look at different sort of problem:
diffusion of a trace quantity of dye

Ref: Stochastic D.E.'s: closely related to probability

One dim. unsteady case:

$$\frac{\partial c_A}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 c_A}{\partial x^2},$$ c_A is dilute

at $t=0$ $c_A = \delta(x)$; i.e. $\int_{-\varepsilon}^{+\varepsilon} c_A(x)\,dx = I$

total moles/Area injected

and $c_A \to 0$ as $x \to \infty$

How do we solve? Use sim. transforms

$c_A = A\bar{c}_A$, $x = B\bar{x}$, $t = C\bar{t}$

$\therefore$ from eq'n: $\frac{B}{C^{1/2}} = 1$

& from B.C.

$$\int_{-\varepsilon}^{\varepsilon} (AB)\, \bar{C}_A \, d\bar{x} = I$$

$-\varepsilon \leftarrow$ arbitrary

$\therefore \; AC^{1/2} = 1$

Thus $C_A = \dfrac{I}{\sqrt{4\mathcal{D}_{AB} t}} f(\eta) \; ; \; \eta = \dfrac{x}{\sqrt{4\mathcal{D}_{AB} t}}$

$$\frac{\partial C_A}{\partial t} = -\frac{1}{2}\frac{1}{t}\frac{I}{\sqrt{4\mathcal{D}_{AB} t}} f - \frac{1}{2}\frac{1}{t}\eta\frac{I}{\sqrt{4\mathcal{D}_{AB} t}} f'$$

$$\frac{\partial^2 C_A}{\partial x^2} = \frac{1}{4\mathcal{D}_{AB} t}\frac{I}{\sqrt{4\mathcal{D}_{AB} t}} f''$$

Thus obtain O.D.E. : $f'' + 2\eta f' + 2f = 0$

w/ B.C.'s $f = 0$ as $\eta \to \infty$,

$$\int_{-\varepsilon/\sqrt{4\mathcal{D}_{AB} t}\,\big|_{t=0}}^{\varepsilon/\sqrt{4\mathcal{D}_{AB} t}\,\big|_{t=0}} f(\eta)\, d\eta = \int_{-\infty}^{\infty} f(\eta)\, d\eta = 1$$

Solving O.D.E. :

$$(f' + 2\eta f)' = 0 \qquad \therefore \; f' + 2\eta f = C_1$$

and $$f = e^{-\eta^2}\left(c_2 + c_1 \int_0^{\eta} e^{\eta'^2}\, d\eta'\right)$$

B.C. at ∞ is $f = 0$ $\therefore$ $c_1 = 0$

Thus $$f = \frac{e^{-\eta^2}}{\int_{-\infty}^{\infty} e^{-\eta^2}\, d\eta} = \frac{1}{\sqrt{\pi}}\, e^{-\eta^2}$$

and $$c_A = \frac{I}{\sqrt{4\pi \mathcal{D}_{AB} t}}\, e^{-\frac{x^2}{4\mathcal{D}_{AB} t}}$$

Related to normal distrib. f^n (probability)

$$c_A = \frac{I}{\sqrt{2\pi}\,\sigma}\, e^{-\frac{x^2}{2\sigma^2}} \quad ; \quad \sigma^2 = 2\mathcal{D}_{AB} t = \text{varian}$$

This solution may be used to solve for arbitrar initial distrib. $g_0(x)$ $\Rightarrow$ problem linear, so made up of distribution of δ f^ns

$$\therefore\; C_A(x,t) = \int_{-\infty}^{\infty} g_0(x')\, \frac{1}{\sqrt{2\pi}\,\sigma}\, e^{-\frac{(x-x')^2}{2\sigma^2}}\, dx'$$

easy to verify that this satisfies D.E. & B.C.

Readily extend to two (or more) dim:

$$\frac{\partial c_A}{\partial t} = \mathcal{D}_{AB}\left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2}\right); \quad c_A\Big|_{t=0} = I\,\delta(x-x_0)\,\delta(y-y_0)$$

May solve in same manner: obtain

$$c_A = \frac{1}{4\pi \mathcal{D}_{AB} t} f(\eta, \xi) \; ; \; \eta = \frac{x}{\sqrt{4\mathcal{D}_{AB} t}} \; , \; \xi = \frac{y}{\sqrt{4\mathcal{D}_{AB} t}}$$

Solve $f(\eta, \xi)$ by separation of variables (or recognize that it is $f^{\underline{n}}(\eta^2 + \xi^2)$)

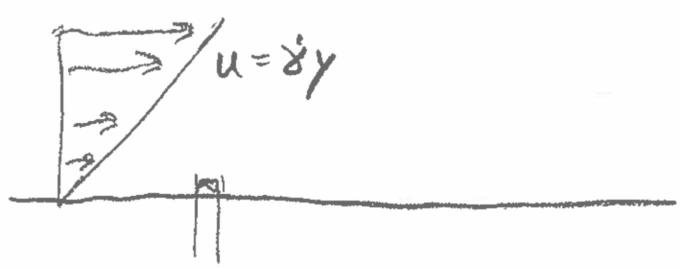
$$\therefore \; f(\eta, \xi) = e^{-\eta^2} e^{-\xi^2}$$

Thus for arb. init distrib. $g_0(x, y)$:

$$c_A(x, y, t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{g(x', y')}{4\pi \mathcal{D}_{AB} t} e^{-\frac{\left[(x-x')^2 + (y-y')^2\right]}{4\mathcal{D}_{AB} t}} dx' dy'$$

Now look at diff problem:

Suppose we have env. eng. problem: asked to det conc. distrib. of toxic waste. Comp. dumping conc. waste into river at bank:



Neglect diff. in x-dir.

What is conc. profile?

$$u \frac{\partial C_A}{\partial x} = \mathcal{D}_{AB} \frac{\partial^2 C_A}{\partial y^2}$$

$$B.C. \equiv \int_0^\infty u\, C_A\, dy = Q \quad \text{(rate of pollution)}$$

$$C_A \to 0 \text{ at } \infty$$

Solve using similarity sol'n:

$$C_A = A\bar{C}_A, \quad y = B\bar{y}, \quad x = C\bar{x}$$

verify

$$\therefore\ u = \dot{\gamma} y \ ; \quad \frac{y}{C^{1/3}} = 1; \quad AB^2 = AC^{2/3} = 1$$

$$\text{Thus} \quad C_A = \frac{Q}{\dot{\gamma}\left(\frac{\mathcal{D}_{AB}\, x}{\dot{\gamma}}\right)^{2/3}} f(\eta) \ ; \quad \eta = \frac{y}{\left(\frac{\mathcal{D}_{AB}\, x}{\dot{\gamma}}\right)^{1/3}}$$

$$\frac{\partial C_A}{\partial x} = \frac{Q}{\dot{\gamma}\left(\frac{\mathcal{D}_{AB}\, x}{\dot{\gamma}}\right)^{2/3}} \left[-\frac{2}{3}\frac{1}{x} f - \frac{1}{3}\frac{1}{x}\eta f' \right]$$

$$\frac{\partial^2 C_A}{\partial y^2} = \frac{Q}{\dot{\gamma}\left(\frac{\mathcal{D}_{AB}\, x}{\dot{\gamma}}\right)^{2/3}} \frac{1}{\left(\frac{\mathcal{D}_{AB}\, x}{\dot{\gamma}}\right)^{2/3}} f''$$

Thus $f'' + \frac{1}{3}\left[\eta^2 f' + 2\eta f\right] = 0$;

$\int_0^\infty f(\eta)\,d\eta = 1$; $f(\eta) = 0$ as $\eta \to \infty$

Now $\left[f' + \frac{1}{3}\eta^2 f\right]' = 0$

$\therefore\ f' + \frac{1}{3}\eta^2 f = \cancel{c_1} \nearrow 0$

$$f = \frac{e^{-\frac{1}{9}\eta^3}}{\int_0^\infty e^{-\frac{1}{9}\eta^3} d\eta} = \frac{e^{-\frac{1}{9}\eta^3}}{\left(\frac{1}{6}\right)^{1/3}\Gamma\left(\frac{1}{3}\right)}$$

$$c_A = \frac{Q}{\dot{\gamma}\left(\frac{\mathcal{D}_{AB} x}{\dot{\gamma}}\right)^{2/3}} \frac{e^{-\frac{1}{9}\frac{\dot{\gamma} y^3}{\mathcal{D}_{AB} x}}}{\left(\frac{1}{6}\right)^{1/3}\Gamma\left(\frac{1}{3}\right)}$$

c_A max at shore, only goes as $1/x^{2/3}$

we can use this solution to obtain sol'n for arbitrary flux distribution on bank:

let $q(x)$ be flux distrib:

$$c_A(x,y) = \int_0^\infty \frac{q(x')}{\dot{\gamma}\left(\frac{\mathcal{D}_{AB}(x-x')}{\dot{\gamma}}\right)^{2/3}} \frac{e^{-\frac{1}{9}\frac{\dot{\gamma} y^3}{\mathcal{D}_{AB}(x-x')}}}{\left(\frac{1}{6}\right)^{1/3}\Gamma\left(\frac{1}{3}\right)} dx'$$