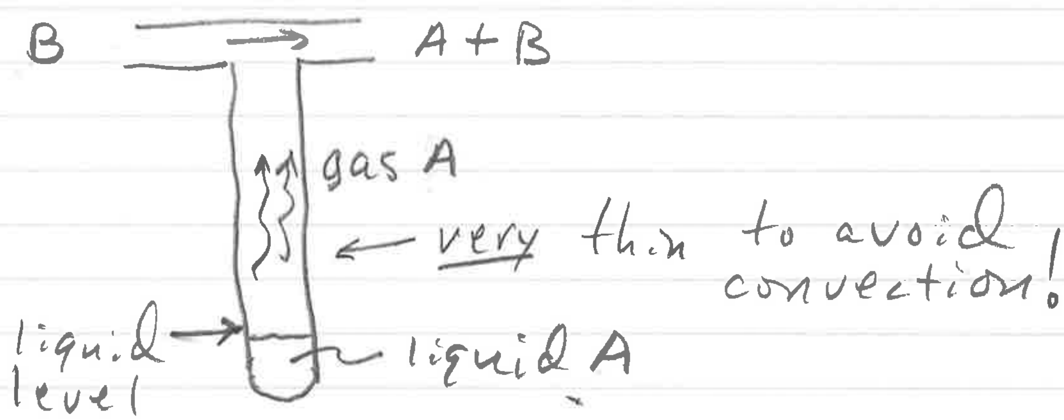
Now we use this to solve mass transfer problems!

Classic example: the <u>Stefan Tube</u>



Developed in 1874 to measure gas phase diffusivities

Key idea: at $z=0$ the evaporating liquid is at equilibrium w/ molar concentration x_{A_1}. It diffuses out the tube & is swept away by gas B. As it evaporates the liquid level drops very slowly! You would measure this change and use it to calculate $\mathcal{D}_{AB}$!

we have the equation for $\underset{\sim}{N}_A$:

$$\underset{\sim}{N}_A = x_A(\underset{\sim}{N}_A + \underset{\sim}{N}_B) - c\mathcal{D}_{AB}\underset{\sim}{\nabla} x_A$$

$$\frac{\partial c_A}{\partial t} + \underset{\sim}{\nabla}\cdot\underset{\sim}{N}_A = R_A$$

w/ similar eq'n for B.

We only need to worry about flux in z-direction. We have no rxn ($R_A = 0$). We assume pseudo-steady state! The molar conc. in the liquid is 10^3 higher than the gas, so this is good!

This yields:

$$\frac{\partial N_{Az}}{\partial z} = 0 \quad ; \quad \frac{\partial N_{Bz}}{\partial z} = 0$$

$$\therefore N_{Az} = cst \, ; \; N_{Bz} = cst \, !$$

We further assume B doesn't dissolve in liquid A!

$$\therefore N_{Bz}\Big|_{z=0} = 0 \quad \text{so} \quad N_{Bz} = 0 \text{ everywhere!}$$

So:
$$N_{Az} = x_A\left(N_{Az} + \cancel{N_{Bz}}^{\,0}\right) - c\,\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$$

<u>and</u> $N_{Az} = N_{A_0}$ (constant)

Thus $-c\,\mathcal{D}_{AB}\dfrac{\partial x_A}{\partial z} = (1 - x_A)\,N_{A0}$

with B.C.'s $x_A\big|_{z=0} = x_{A_0}$, $x_A\big|_{z=h} = x_{A_1} = 0$

(usually take $x_{A_1} = 0$ for "clean" B)

Let's render <u>dimensionless</u>

$$x_A^* = \frac{x_A}{x_{A_0}} \qquad z^* = \frac{z}{h} \qquad N_{A_0}^* = \frac{N_{A_0}}{N_{A_c}}$$

$$\therefore\ -c\,\mathcal{D}_{AB}\frac{x_{A_0}}{h}\frac{\partial x_A^*}{\partial z^*} = \left(1 - x_{A_0}x_A^*\right)N_{A_0}^*N_{A_c}$$

Divide out:

$$-\underbrace{\left[\frac{c\,\mathcal{D}_{AB}\,x_{A_0}}{h\,N_{A_c}}\right]}_{=1}\frac{\partial x_A^*}{\partial z^*} = \left(1 - x_{A_0}x_A^*\right)N_{A_0}^*$$

$$\therefore\ N_{A_c} = \frac{c\,\mathcal{D}_{AB}\,x_{A_0}}{h}$$

This is the characteristic magnitude of the molar flux

So:
$$\frac{\partial x_A^*}{\partial z^*} = -\left(1 - x_{A_0} x_A^*\right) N_{A_0}^*$$

$$x_A^*\Big|_{z^*=0} = 1 \qquad x_A^*\Big|_{z^*=1} = 0$$

Let's look at the dilute limit $x_{A_0} << 1$

In this case,
$$\frac{\partial x_A^*}{\partial z^*} \cong -N_{A_0}^*$$

$$x_A^* = -N_{A_0}^* z^* + C_1$$

but $x_A^*\Big|_{z^*=0} = 1 \quad \therefore \quad C_1 = 1$

and since $x_A^*\Big|_{z^*=1} = 0, \quad N_{A_0}^* = 1$!

So $x_A^* = 1 - z^*$

Which is identical to SS cond. in a slab!

In this limit:

$$N_{Az} = N_{A_c} = \frac{c\mathcal{D}_{AB} x_{A_0}}{h}$$

So if you measure N_{Az} by looking at the liquid level and know x_{A_0}, you get $\mathcal{D}_{AB}$!

OK, what if x_{A_0} isn't small??

we have:

$$\frac{\partial x_A^*}{\partial z^*} = -\left(1 - x_{A_0} x_A^*\right) N_{A_0}^*$$

Divide:

$$\frac{1}{1 - x_{A_0} x_A^*} \frac{\partial x_A^*}{\partial z^*} = - N_{A_0}^*$$

$$\frac{1}{x_{A_0}} \frac{\partial \ln\left(1 - x_{A_0} x_A^*\right)}{\partial z^*} = N_{A_0}^*$$

$$\therefore \ \ln\left(1 - x_{A_0} x_A^*\right) = x_{A_0} N_{A_0}^* z^* + C_1$$

$$x_A^* \Big|_{z^*=0} = 1$$

$$\therefore \ \ln\left(1 - x_{A_0}\right) = C_1$$

so $\ln\left(\dfrac{1 - x_{A_0} x_A^*}{1 - x_{A_0}}\right) = x_{A_0} N_{A_0}^* z^*$

but at $z^* = 1$ $x_A^* = 0$

$\therefore$ $\ln\left(\dfrac{1}{1 - x_{A_0}}\right) = x_{A_0} N_{A_0}^*$

so $N_{A_0}^* = \dfrac{-\ln(1 - x_{A_0})}{x_{A_0}} \geq 1$

and the flux is increased by this factor due to the convection arising from diffusion!

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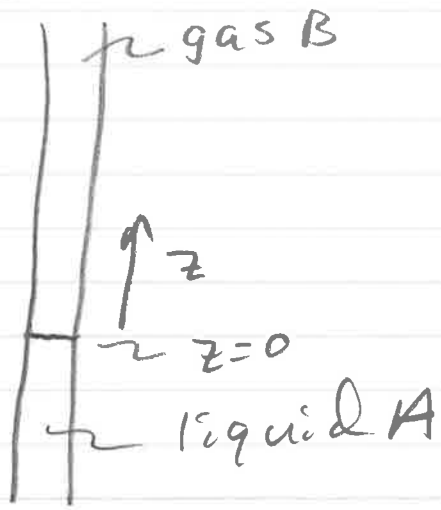
ok, what if we look at the transient problem?



We have a long tube filled w/ gas B & dip it into liquid A so that the liquid level is kept at $z = 0$

Again,

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

Let's add these!

$$\underbrace{\frac{\partial (c_A + c_B)}{\partial t}}_{''} + \frac{\partial}{\partial z}\left(N_{Az} + N_{Bz}\right) = 0$$

$\frac{\partial c}{\partial t} = 0$ because c is constant for our gas!

$N_{Bz}\big|_{z=0} = 0$

$\therefore N_{Az} + N_{Bz} = N_{A_0} \neq f^n(z)$!

but both N_{Az} & N_{Bz} will be $f^n(z,t)$ - just the sum is only a $f^n(t)$

$$\text{So} \quad N_{Az} = x_A\left(N_{Az} + N_{Bz}\right) - c\,\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$$

At $z = 0$ $N_{Bz} = 0$, $N_{Az} = N_{A_0}$ ($f^n(t)$)

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

$$\text{So} \quad N_{A_0} = \frac{-c\,\mathcal{D}_{AB}}{1 - x_{A_0}}\left.\frac{\partial x_A}{\partial z}\right|_{z=0}$$

$$\therefore N_{Az} = x_A \underbrace{\left(-\frac{c\mathcal{D}_{AB}}{1-x_{A_0}}\right)\frac{\partial x_A}{\partial z}\bigg|_{z=0}}_{\text{extra term due to convection}} - c\mathcal{D}_{AB}\frac{\partial x_A}{\partial z}$$

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

$$\therefore \underbrace{\frac{\partial x_A}{\partial t}}_{\text{accum}} = \underbrace{\mathcal{D}_{AB}\frac{\partial^2 x_A}{\partial z^2}}_{\text{dif}^{\underline{n}}} + \underbrace{\frac{\mathcal{D}_{AB}}{1-x_{A_0}}\frac{\partial x_A}{\partial z}\bigg|_{z=0}\frac{\partial x_A}{\partial z}}_{\text{convection from diffusion}}$$

BC's are $x_A\big|_{z=0} = x_{A_0}$, $x_A\big|_{t=0} = 0$, $x_A\big|_{z\to\infty} = 0$

Let's scale: $x_A^* = \dfrac{x_A}{x_{A_0}}$ (from BC)

$t^* = t/t_c \qquad z^* = z/z_c$

$$\therefore \frac{x_{A_0}}{t_c}\frac{\partial x_A^*}{\partial t^*} = \frac{\mathcal{D}_{AB}x_{A_0}}{z_c^2}\frac{\partial^2 x_A^*}{\partial z^{*2}} + \frac{\mathcal{D}_{AB}x_{A_0}}{z_c^2}\frac{x_{A_0}}{1-x_{A_0}}\frac{\partial x_A^*}{\partial z^*}\bigg|_{z^*=0}\frac{\partial x_A^*}{\partial z^*}$$

Divide out:

$$\left[\frac{z_c^2}{\mathcal{D}_{AB} t_c}\right] \frac{\partial x_A^*}{\partial t^*} = \frac{\partial^2 x_A^*}{\partial z^{*2}} + \frac{x_{A_0}}{1 - x_{A_0}} \left.\frac{\partial x_A^*}{\partial z^*}\right|_{z^*=0} \frac{\partial x_A^*}{\partial z^*}$$

$$= 1 \quad \therefore \frac{z_c}{(\mathcal{D}_{AB} t_c)^{1/2}} = 1 \quad \text{or } z_c = (\mathcal{D}_{AB} t_c)^{1/2}$$

B.C.'s $\left. x_A^* \right|_{z^*=0} = 1 \qquad \left. x_A^* \right|_{t^*=0} = \left. x_A^* \right|_{z^* \to \infty} = 0$

Note that t_c disappeared - but we never specified it! That means that our problem is self-similar!

$\therefore$ from scaling (or affine stretching!)

$$x_A^* = f(\eta) \quad ; \quad \eta = \frac{z^*}{t^{*1/2}}$$

Getting the transformed ODE isn't too bad:

$$\frac{\partial x_A^*}{\partial z^*} = t^{*-1/2} f' \qquad \frac{\partial^2 x_A^*}{\partial z^{*2}} = t^{*-1} f''$$

$$\frac{\partial x_A^*}{\partial t^*} = -\frac{1}{2}\frac{\zeta}{t^*} f'$$

$$\therefore\ -\frac{1}{2}\frac{\zeta}{t^*} f' = \frac{1}{t^*} f'' + \frac{x_{A_0}}{1-x_{A_0}} f'(0)\, f' \frac{1}{t^*}$$

so
$$f'' = -\frac{1}{2}\zeta f' - \frac{x_{A_0}}{1-x_{A_0}} f'(0) f'$$
$$= -\left(\frac{1}{2}\zeta + \frac{x_{A_0}}{1-x_{A_0}} f'(0)\right) f'$$

$$f(0) = 1,\quad f(\infty) = 0$$

It's probably easier to solve numerically, but the analytic solution is:

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

where
$$f'(0) = \frac{e^{-\left(\frac{x_{A_0}}{1-x_{A_0}} f'(0)\right)}}{1 - \operatorname{erf}\left(\frac{x_{A_0}}{1-x_{A_0}} f'(0)\right)}$$

which is an implicit expression for $f'(0)$

This is useful for measuring $\mathcal{D}_{AB}$ for volatile materials. Note that if $x_{A_0} << 1$ (dilute), then we get

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

and (from heat transfer problem!)

$$\frac{x_A}{x_{A_0}} = 1 - \text{erf}\left(\tfrac{1}{2}\zeta\right)$$