Fick’s Law for Binary Systems

SHR §3.1.1

Molar Fluxes in Binary Systems

$$N_A = c x_A v_A$$

$$N = N_A + N_B$$

$$v_M = \frac{N}{c} = \frac{N_A + N_B}{c} = x_A v_A + x_B v_B$$

Here we have assumed 1-D.
We could use vectors for
fluxes & velocities...

- A species "A" in mixture of A & B.
- N_A molar flux of A.
- v_A velocity of A.
- x_A mole fraction of A.
- c mixture molar concentration.
- N total molar flux.
- v_M mixture molar-averaged velocity.

$$\boxed{J_A} = N_A - \boxed{c x_A v_M}$$

molar diffusive flux of A (relative to v_M)

molar convective flux of A (carried by v_M)

- J_A - molar diffusive flux of A relative to a molar averaged velocity. (motion of A relative to the mixture motion)
- Diffusive fluxes are only defined relative to a convective and total flux!
- Diffusive and convective fluxes are NOT independent (they must sum to N_A).

Fick's "Law" $\mathbf{J}_A = -c D_{AB} \nabla x_A$

- Fick's law is a MODEL for J_A (has limitations!)
- $D_{AB} = D_{BA}$
- $J_A = -J_B$
- For $C > 2$ components, everything changes! (graduate school, anyone?)

$$J_A = -c D_{AB} \frac{\mathrm{d}x_A}{\mathrm{d}z}$$

$$N_A = c x_A v_M - c D_{AB} \frac{\mathrm{d}x_A}{\mathrm{d}z}$$

$$= x_A N - c D_{AB} \frac{\mathrm{d}x_A}{\mathrm{d}z}$$

$$N_B = x_B N - c D_{AB} \frac{\mathrm{d}x_B}{\mathrm{d}z}$$

Often we know something about $x_A(z)$ and v_M. Fick's law lets us get N_A.

“Mixture Velocities”

Motorcycle: $u_m = 50$

Dump Truck: $u_t = 30$

If there are n_m motorcycles and n_t trucks on the road, what is the average velocity?

Number averaged: $v_\# = \dfrac{n_m v_m + n_t u_t}{n_m + n_t}$

$$u_t = v_\# + v^\#_{t,\text{diff}}$$

$$u_m = v_\# + v^\#_{m,\text{diff}}$$

what if n_m=n_t?

Mass averaged: $v = \dfrac{n_m m_m v_m + n_t m_t u_t}{n_m m_m + n_t m_t}$

$$u_t = v + v_{t,\text{diff}}$$

$$u_m = v + v_{m,\text{diff}}$$

what if n_m=n_t and $m_t \gg m_m$?

Molar flux

(analogous to number flux)

$$\begin{aligned} N_A &= c_A v_M && + J_A \\ &= x_A c v_M && + J_A \\ &= x_A N && + J_A \end{aligned}$$

$$v_A = \frac{N_A}{c_A} = \frac{N_A}{c x_A}$$

$$v_{A,\text{diff}} = J_A / c_A$$

$$v_M = \frac{N}{c} = \frac{N_A + N_B}{c}$$

Fick’s Law gives us a relationship between J_A & x_A.

Steady-State Diffusion in Binary Systems

$$N_A = x_A \underbrace{(N_A + N_B)}_{N} + J_A$$

$$n_A = x_A \underbrace{(n_A + n_B)}_{n} + A J_A$$

Be careful with areas!
(flux vs. flow rate)

$$J_A = -cD_{AB}\frac{\mathrm{d}x_A}{\mathrm{d}z}$$

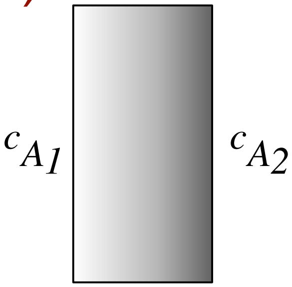
If there is no “bulk flow” ($N = 0$) then

$$N_A = -cD_{AB}\frac{\mathrm{d}x_A}{\mathrm{d}z}$$

$$= -D_{AB}\frac{\mathrm{d}c_A}{\mathrm{d}z} \quad \text{(if } c \text{ is constant)}$$

Planar system with constant N_A (or n_A):

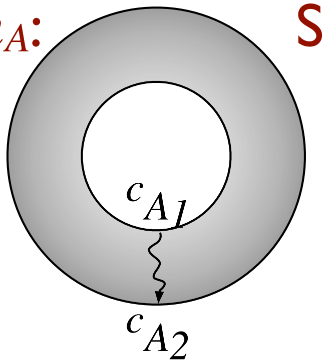
$$N_A = -D_{AB}\left(\frac{c_{A_2} - c_{A_1}}{z_2 - z_1}\right)$$



Note: in cylindrical & spherical coordinates, constant n_A does not imply constant N_A.

Concentric cylinders with constant n_A:

$$n_A = -2\pi L D_{AB}\left(\frac{c_{A_2} - c_{A_1}}{\ln\left({}^{r_2}/{}_{r_1}\right)}\right)$$



Spherical shell with constant n_A:

$$n_A = -4\pi r_1 r_2 D_{AB}\left(\frac{c_{A_2} - c_{A_1}}{r_2 - r_1}\right)$$

The Molar Balance Equations (Again)

$$\mathbf{N}_i = c_i \mathbf{v}_M + \mathbf{J}_i = x_i \mathbf{N} + \mathbf{J}_i$$

Integral Forms

In terms of "total" species fluxes:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathsf{V}} c_i \, \mathrm{dV} = -\int_{\mathsf{S}} \mathbf{N}_i \cdot \mathbf{a} \, \mathrm{dS} + \int_{\mathsf{V}} S_i \, \mathrm{dV}$$

In terms of "convective" and "diffusive" species fluxes:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathsf{V}} c_i \, \mathrm{dV} = -\int_{\mathsf{S}} x_i c \mathbf{v}_M \cdot \mathbf{a} \, \mathrm{dS} - \int_{\mathsf{S}} \mathbf{J}_i \cdot \mathbf{a} \, \mathrm{dS} + \int_{\mathsf{V}} S_i \, \mathrm{dV}$$

Differential Forms

In terms of "total" species fluxes:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + S_i$$

In terms of "convective" and "diffusive" species fluxes:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot (c_i \mathbf{v}_M) - \nabla \cdot \mathbf{J}_i + S_i$$

For a binary system of "A" and "B": $\mathbf{J}_A = -c D_{AB} \nabla x_A$

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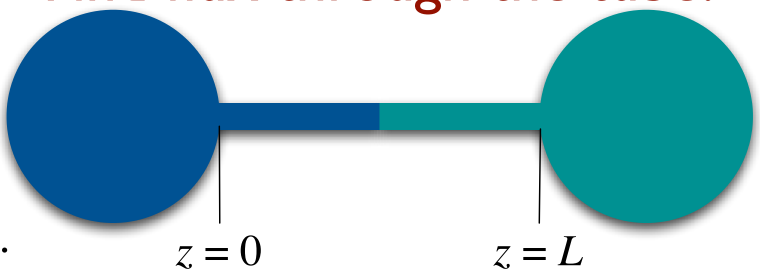
Fick's Law Example: Equimolar Counter-diffusion

<u>Assume</u>:

- T, p are constant
- No reaction
- 1-D domain $z=[0,L]$
- Compositions are known at domain boundaries $z=0$, $z=L$.

Find flux through the tube.



$$x_A = x_A^0 \qquad z=0$$
$$x_A = x_A^L \qquad z=L$$

<u>Equimolar counter-diffusion</u>: for every mole of A that moves to the left, a mole of B moves to the right.

Total flux must be zero (closed system, constant T, p).

Therefore, $N = cv_M = 0$ so $v_M = 0$.

pseudo-steady state $\quad v_M = 0 \quad$ no reaction

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \cancel{c_i}\,\mathrm{dV} = -\int_S x_i c\cancel{\mathbf{v}_M}\cdot\mathbf{a}\,\mathrm{dS} - \int_S \mathbf{J}_i\cdot\mathbf{a}\,\mathrm{dS} + \int_V \cancel{S_i}\,\mathrm{dV}$$

Break the surface integral into pieces:

Tube sides: $\int_S \mathbf{J}_A\cdot\mathbf{a}\,\mathrm{dS} = 0$

Tube face at z=0: $\mathbf{a} = -\hat{z} \quad \int_S \mathbf{J}_A\cdot\mathbf{a}\,\mathrm{dS} = -A_c J_A^0$

Tube face at z=L: $\mathbf{a} = \hat{z} \quad \int_S \mathbf{J}_A\cdot\mathbf{a}\,\mathrm{dS} = A_c J_A^L$

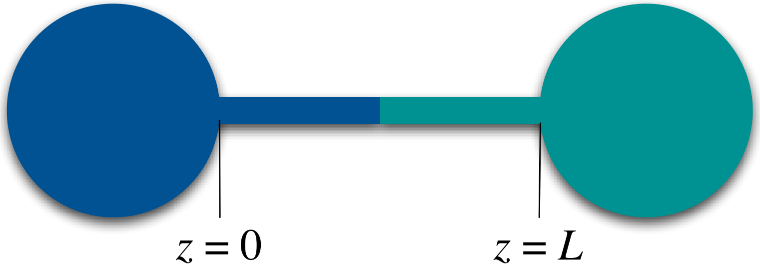
∴ Tube mole balance gives:

$$A_c J_A^L - A_c J_A^0 = 0$$
$$J_A^0 = J_A^L$$

<u>Note</u>: we could have done this integral balance on any segment of the tube and arrived at the same conclusion regarding J_A. Therefore, it must be constant! Since $J_A = N_A$, N_A is also constant!

$$N_A = x_A N + J_A$$
$$= J_A = -cD_{AB}\frac{\mathrm{d}x_A}{\mathrm{d}z}$$
$$N_A\mathrm{d}z = -cD_{AB}\mathrm{d}x_A$$
$$\int_0^L N_A\mathrm{d}z = -\int_{x_A^0}^{x_A^L} cD_{AB}\mathrm{d}x_A$$
$$N_A\int_0^L \mathrm{d}z = -cD_{AB}\int_{x_A^0}^{x_A^L}\mathrm{d}x_A$$

$$\boxed{N_A = \frac{-cD_{AB}}{L}\left(x_A^L - x_A^0\right)}$$



We previously showed:

- $N_A = J_A$ (no bulk flow/convection)
- N_A is constant (so J_A is constant)

What is the species mole fraction profile through the tube?

$$J_A = -cD_{AB}\frac{\mathrm{d}x_A}{\mathrm{d}z} = \alpha$$

$$dx_A = -\frac{\alpha}{cD_AB}dz$$

$$\int_{x_A^0}^{x_A} dx_A = -\frac{\alpha}{cD_AB}\int_0^z dZ$$

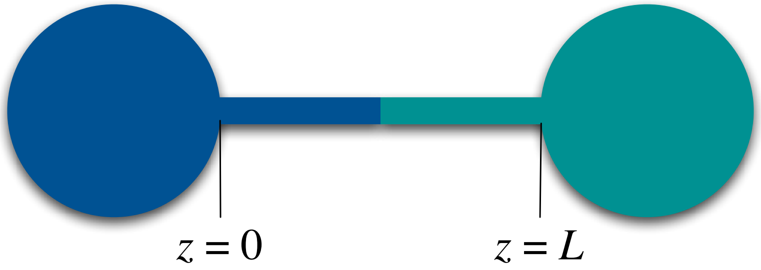
$$x_A - x_A^0 = -\frac{\alpha}{cD_AB}z$$

Note: to determine α, we can use $x_A(L) = x_A^L$

$$\boxed{x_A = x_A^0 + \left(x_A^L - x_A^0\right)\frac{z}{L}}$$

"Bulb" Balances

Find the composition in each bulb as a function of time.



$$N_A = \frac{-cD_{AB}}{L}\left(x_A^L - x_A^0\right)$$

Pseudo-steady state:
The tube is at steady state (adjusts to the slowly changing bulb compositions quickly).

$v_M = 0$ no reaction

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\mathsf{V}} c_i\,\mathrm{dV} = -\int_{\mathsf{S}} x_i c\,\cancel{\mathbf{v}_M}\cdot\mathbf{a}\,\mathrm{dS} - \int_{\mathsf{S}} \mathbf{J}_i\cdot\mathbf{a}\,\mathrm{dS} + \int_{\mathsf{V}} \cancel{S_i}\,\mathrm{dV}$$

For the "left" bulb:

$$cV_0\frac{\mathrm{d}x_A^0}{\mathrm{d}t} = -N_A^0 A_c \qquad V_0\frac{\mathrm{d}x_A^0}{\mathrm{d}t} = \frac{A_c D_{AB}}{L}\left(x_A^L - x_A^0\right)$$

We need to eliminate x_A^L

Mole balance on A relating to steady-state conditions:

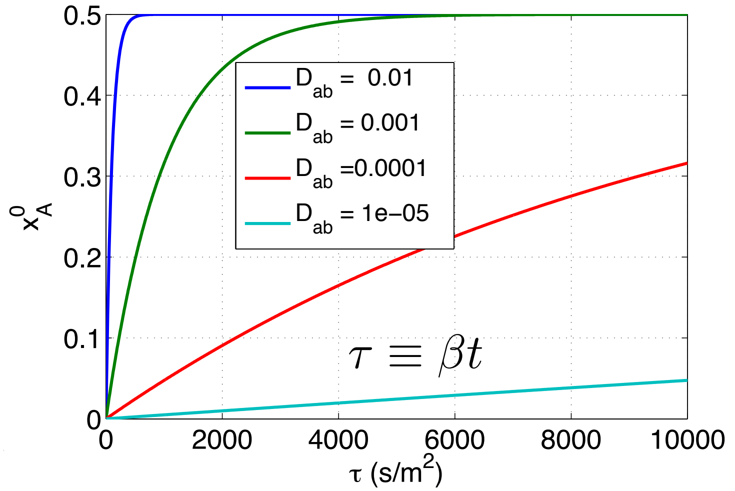
$$\underbrace{cx_A^0 V_0 + cx_A^L V_L}_{\text{at time t}} = \underbrace{cx_A^\infty (V_0 + V_L)}_{\text{at } t=\infty}$$

$$x_A^L = x_A^\infty\left(1 + {}^{V_0}\!/_{V_L}\right) - x_A^0\,{}^{V_0}\!/_{V_L}$$

$$\frac{\mathrm{d}x_A^0}{\mathrm{d}t} = \frac{A_c D_{AB}}{V_0 L}\left[\left(x_A^\infty - x_A^0\right)\left(1 + {}^{V_0}\!/_{V_L}\right)\right]$$

$$= \beta D_{AB}\left(x_A^\infty - x_A^0\right) \qquad \beta \equiv \frac{A_c}{V_0 L}\left(1 + \frac{V_0}{V_L}\right)$$

"Geometry factor"



Separate & solve...

$$x_A^0 = x_A^\infty + \left(x_{A,0}^0 - x_A^\infty\right)\exp(-\beta D_{AB} t)$$

A nice way to determine D_{AB} experimentally!

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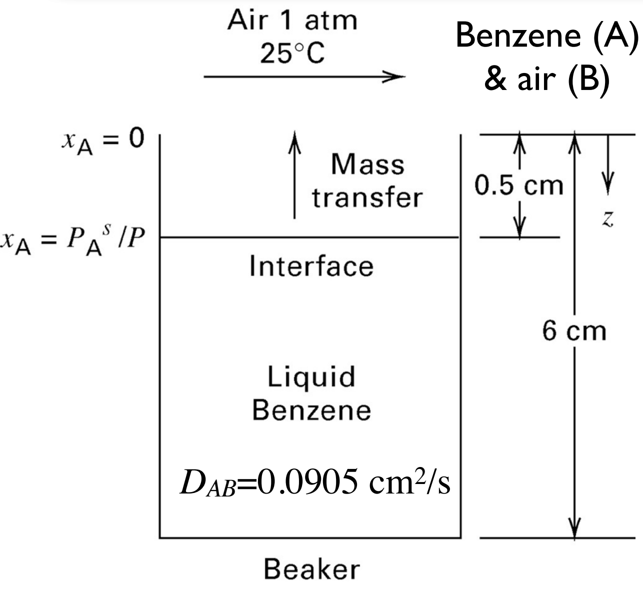
Example: Evaporation from a Beaker

(Unimolecular Diffusion)



Determine $x_A(z)$.

$$N_A = x_A N + J_A$$

What do we know about N_A & N_B?

$$N_A = x_A N_A + J_A$$
$$= \frac{J_A}{1 - x_A}$$
$$N_A = \frac{-cD_{AB}}{1 - x_A} \frac{\mathrm{d}x_A}{\mathrm{d}z}$$

$(1-x_A)$ accounts for "bulk flow."
In very dilute systems ($x_A \rightarrow 0$),
this effect is small relative to J_A.

$$\frac{-N_A}{cD_{AB}} \int_{z_0}^{z} dz = \int_{x_A^0}^{x_A} \frac{dx_A}{1 - x_A}$$

$$N_A = \frac{cD_{AB}}{z - z_0} \ln\left(\frac{1 - x_A}{1 - x_A^0}\right)$$

or

$$x_A = 1 - (1 - x_A^0) \exp\left[\frac{N_A(z - z_0)}{cD_{AB}}\right]$$

Note: from $x_A(z)$ and N_A you can determine anything else about the system (e.g. $J_A(z)$).

1. Estimate gas-phase composition of benzene at the vapor-liquid interface (from equilibrium thermo).
2. Determine N_A from x_A at z=0.
3. Determine $x_A(z)$.

The Log-Mean

$$N_A = \frac{cD_{AB}}{z - z_0} \ln\left(\frac{1 - x_A}{1 - x_A^0}\right)$$

$$(1 - x_A)_{\mathrm{LM}} = (x_B)_{\mathrm{LM}} = \frac{(1 - x_{A_2}) - (1 - x_{A_1})}{\ln\left[\frac{1 - x_{A_2}}{1 - x_{A_1}}\right]}$$

$$= \frac{x_{A_1} - x_{A_2}}{\ln\left[{(1 - x_{A_2})}/{(1 - x_{A_1})}\right]}$$

Log-mean of x_A at the two ends of the diffusion path.

$$N_A = \frac{cD_{AB}}{(1 - x_A)_{\mathrm{LM}}} \frac{-\Delta x_A}{\Delta z}$$

This makes things look a bit "cleaner" and allows us to express N_A in terms of Δx_A.

You will see this used more when we start dealing with Mass-Transfer Coefficients (soon)...

Comments on Fick's Law

- In this class, we typically assume that the total molar concentration, c, is constant.
  - This is usually reasonable for isothermal, isobaric systems or for liquid systems.
- We have only considered binary systems.
  - For multicomponent systems, things become considerably more complex.
- Other driving forces:
  - other species can cause strange diffusion (push a species against its gradient) for $C > 2$ components.
  - pressure gradients (centrifugation)
  - thermal gradients (Soret effect)
  - In general, the chemical potential is the correct driving force for diffusion.

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