CE407 SEPARATIONS

Lecture 19

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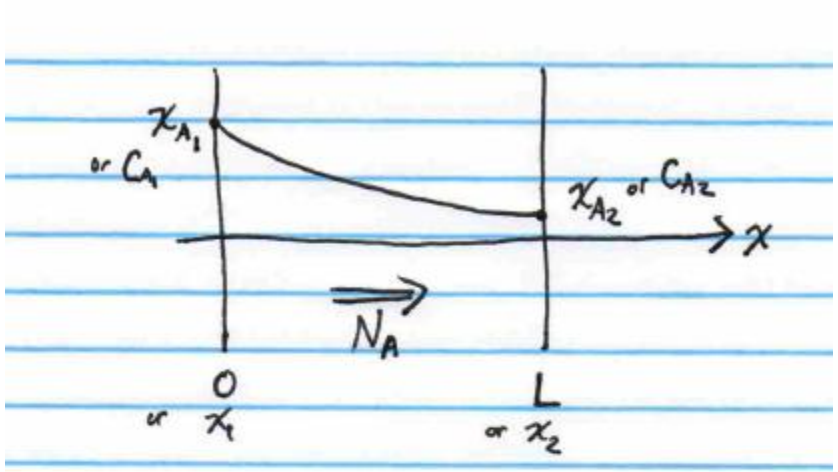
Diffusion



- There exists a concentration gradient across a membrane/liquid layer and we want to determine the flux of solute A, N_A, from the left to the right...

$$N_A = (N_A + N_B)x_A - D_{AB}\, c\, \frac{dx_A}{dx}$$

Convective Diffusive

- Unfortunately, N_A appears on both sides of the equation

Equimolar Counter Diffusion (Equimolal Diffusion)

- (This assumption is similar to constant molal flow in a rectification column, where the rate that the light component passes from liquid to vapor is equal to the rate that the heavy component passes from vapor to liquid)

$$\boldsymbol{N_A + N_B = 0}$$

- The fluxes are equal and opposite
  - In this case we are talking about A moving to the right and B moving to the left within the same phase
- Then… $\boldsymbol{N_A = (N_A + N_B)x_A - D_{AB}\, c\, \frac{dx_A}{dx}}$ becomes

$$\boldsymbol{N_A = -D\, c\, \frac{dx_A}{dx}}$$

Because $\boldsymbol{D_{AB} = D_{BA}}$ we can use $\boldsymbol{D}$

- This can be rearranged to be:

$$\boldsymbol{N_A\, dx = -D\, c\, dx_A}$$

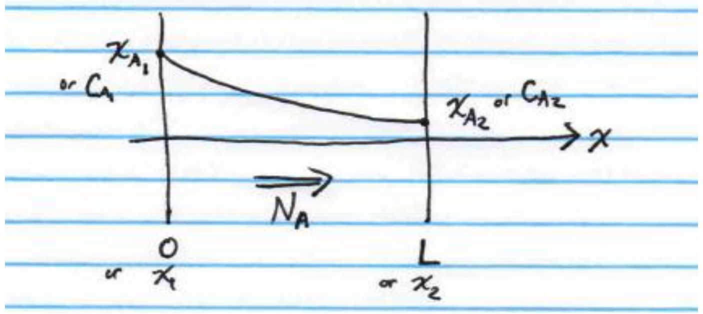
Equimolar Counter Diffusion

$$N_A\, dx = -D\, c\, dx_A$$

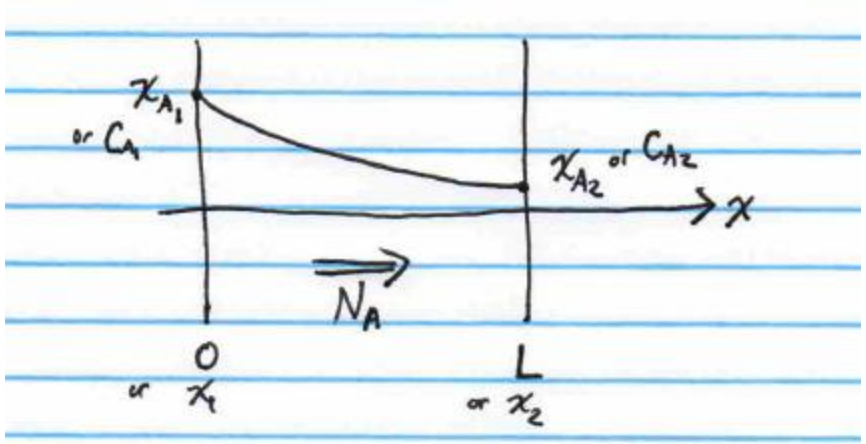
$$\int N_A\, dx = \int -D\, c\, dx_A$$

- Remember that for a given temperature and pressure, D is a constant and that we are considering c to be a constant, as well
- When we are at steady state N_A is constant across our system
  - Otherwise there would be an accumulation of solute A somewhere in the system
- We can pull all of the constant values out of the integral
- At x = x_1 = 0, the mole fraction is $x_{A,1}$ and at x = x_2 = L, the mole fraction is $x_{A,2}$

$$N_A \int_0^L dx = -D\, c \int_{x_{A,1}}^{x_{A,2}} dx_A$$



Equimolar Counter Diffusion



$$N_A \int_0^L dx = -D\,c \int_{x_{A,1}}^{x_{A,2}} dx_A$$

$$N_A(L-0) = -D\,c\left(x_{A,2}-x_{A,1}\right)$$

$$N_A = -\frac{D\,c}{L}\left(x_{A,2}-x_{A,1}\right)$$

- or $N_A = -\frac{D\,c}{x_2-x_1}\left(x_{A,2}-x_{A,1}\right) = -D\left(\frac{c_{A,2}-c_{A,1}}{x_2-x_1}\right) = -D\frac{\Delta C_A}{\Delta x}$ **Fick's Law**

$$\boxed{N_A = \frac{D\,c}{L}\left(x_{A,1}-x_{A,2}\right)}$$

- Flux in $\frac{moles}{area * time}$ for equimolar counter diffusion

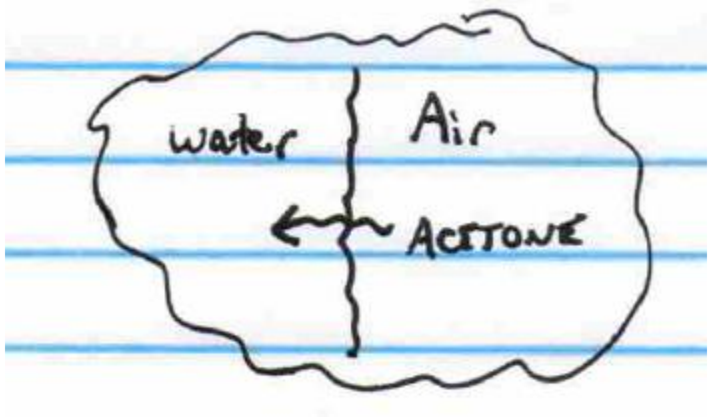
One Component Mass Transfer

- A diffusing through non-diffusing B
  - Book calls if “One-Way Diffusion”
- Remember the “Usual Assumptions” in gas absorption
  - Air did not diffuse into the water
  - Water did not evaporate into the air
- Call Acetone: A and Air: B
- For non-diffusing B: $N_B = 0$

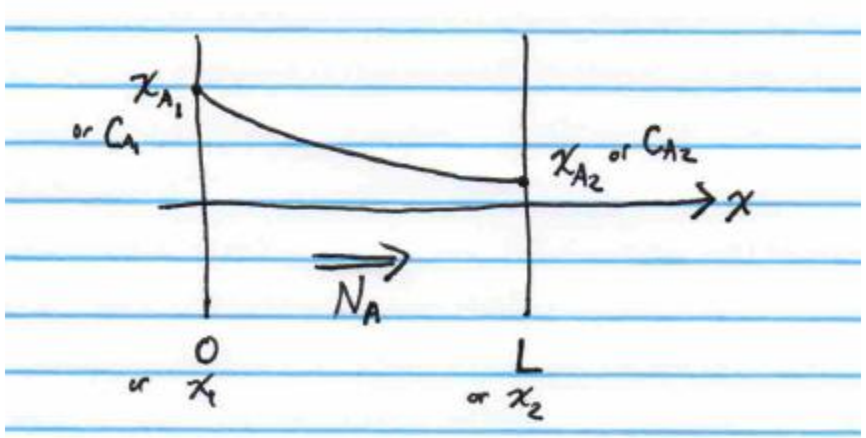
$$N_A = (N_A + N_B)x_A - D_{AB}\, c\, \frac{dx_A}{dx}$$

$$N_A = N_A\, x_A - D\, c\, \frac{dx_A}{dx}$$

$$N_A(1 - x_A) = -D\, c\, \frac{dx_A}{dx}$$



One Component Mass Transfer



$$N_A(1 - x_A) = -D\,c\,\frac{dx_A}{dx}$$

$$N_A\,dx = -D\,c\,\frac{dx_A}{1 - x_A}$$

$$N_A\int_0^L dx = -D\,c\int_{x_{A,1}}^{x_{A,2}}\frac{dx_A}{1 - x_A}$$

$$\int\frac{dx_A}{1-x_A} = -ln(1 - x_A) + constant$$

$$ln(\alpha) - ln(\beta) = ln\left(\frac{\alpha}{\beta}\right)$$

$$N_A(L - 0) = D\,c\left[ln(1 - x_{A,2}) - ln(1 - x_{A,1})\right]$$

$$\boxed{N_A = \frac{D\,c}{L}\,ln\left(\frac{1 - x_{A,2}}{1 - x_{A,1}}\right)}$$

Dilute Solutions

$$\ln(1+\alpha) = \alpha + \text{higher order terms that drop off for small } \alpha$$

- For dilute solutions ($x_{A,1}$ and $x_{A,2}$ are both small)

$$\ln(1-x_{A,1}) \approx -x_{A,1} \text{ and } \ln(1-x_{A,2}) \approx -x_{A,2}$$

- Then $N_A \approx \frac{D\,c}{L}\left[-x_{A,2}-(-x_{A,1})\right] = \frac{D\,c}{L}(x_{A,1}-x_{A,2})$ which is approximately the same as the equimolar case

Recap

- Equimolar Diffusion

$$\boxed{N_A = \frac{D\,c}{L}\left(x_{A,1} - x_{A,2}\right)}$$

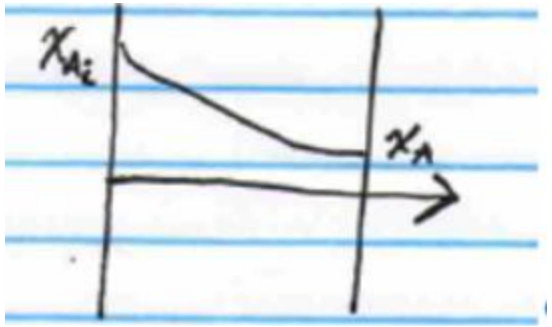
eq 17.19

- One-Component

$$\boxed{N_A = \frac{D\,c}{L}\ ln\left(\frac{1-x_{A,2}}{1-x_{A,1}}\right)}$$

eq 17.24

- The book uses the following notation $\frac{D\,c}{L} = \frac{D_V \rho_M}{B_T}$
- The book also uses terminology shown in this diagram
  - x_{Ai} is interface concentration
  - x_A is bulk concentration
- Book also shows this analysis using y for vapor phase
- Formulas are the same either way, just use consistent terms throughout



"One-Way Correction" term

- The one-component equation $N_A = \frac{D\,c}{L}\,ln\left(\frac{1-x_{A,2}}{1-x_{A,1}}\right)$ can be worked algebraically to the following:

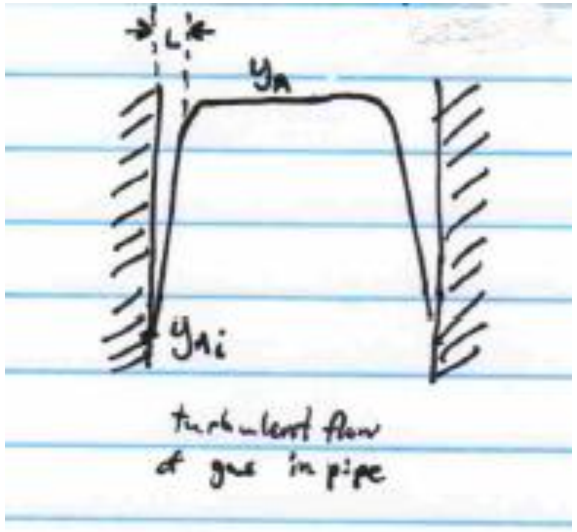
$$N_A = \frac{D\,c}{L}\frac{\left(x_{A,1} - x_{A,2}\right)}{\overline{(1 - x_A)_L}}$$

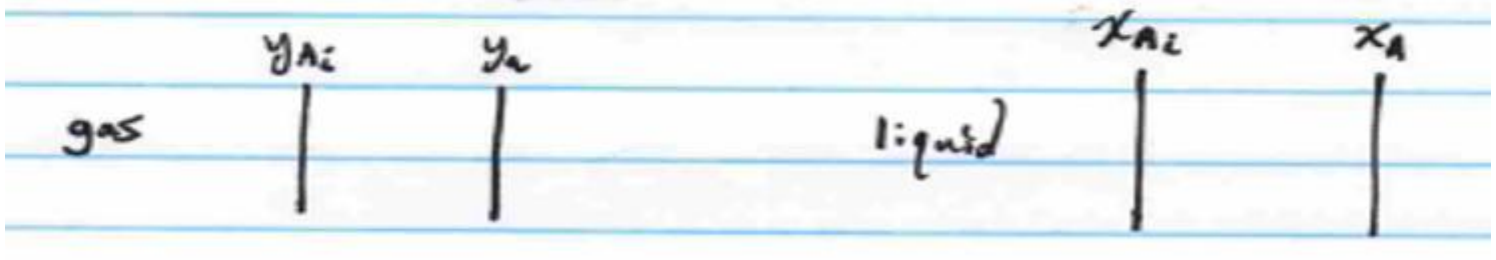
Where $\overline{(1 - x_A)_L} = \frac{(1-x_{A,2})-(1-x_{A,1})}{ln\left[{(1-x_{A,2})}/{(1-x_{A,1})}\right]}$ the log mean of $(1 - x_A)$

- $\overline{(1 - x_A)_L}$ is referred to as "One-Way Correction" as it converts equimolar equation to one-way equation

Film Theory

- A diffusing through non-diffusing B





gas phase $N_A = \frac{D\,c}{L}\,ln\left(\frac{1-y_A}{1-y_{Ai}}\right)$ liquid phase $N_A = \frac{D\,c}{L}\,ln\left(\frac{1-x_A}{1-x_{Ai}}\right)$

- These equations apply directly when all mass transfer occurs due to pure molecular diffusion
- Consider a case where there is turbulent flow… gas in a pipe (See figure in upper right corner)
  - This is a much more complicated case than pure molecular diffusion
  - Concentration = y_A in the bulk gas
  - Concentration at wall = y_{Ai} at wall
  - Concentration difference takes place across a zone of width “L”

Film Theory

- We can express the flux in each phase as

gas phase $N_A = k_y \, ln\left(\frac{1-y_A}{1-y_{Ai}}\right)$ liquid phase $N_A = k_x \, ln\left(\frac{1-x_A}{1-x_{Ai}}\right)$

- These expressions are dependent on the same bulk and surface mole fractions as before but now the constant is no longer $\frac{D\,c}{L}$, but is something different…
- k_x and k_y are MASS TRANSFER COEFFICIENTS
  - They are determined experimentally
  - They are ***NOT*** equal to $\frac{D\,c}{L}$
    - $\frac{D\,c}{L}$ is for pure molecular diffusion
    - The mass transfer coefficients are affected by bulk mixing, etc

Film Theory

$$N_A = k_y\, ln\left(\frac{1-y_A}{1-y_{Ai}}\right) \qquad N_A = k_x\, ln\left(\frac{1-x_A}{1-x_{Ai}}\right)$$

- These equations can be manipulated into:

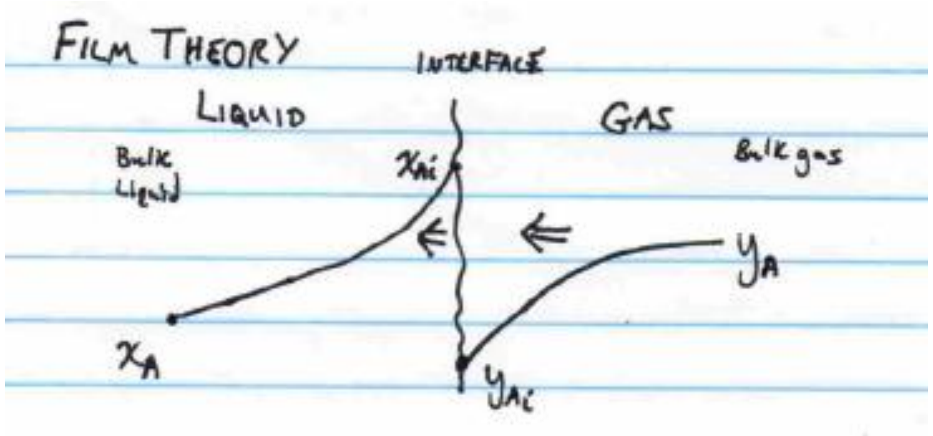
$$N_A = \frac{k_y}{\overline{(1-y_A)}_L}(y_{Ai} - y_A) \qquad N_A = \frac{k_x}{\overline{(1-x_A)}_L}(x_{Ai} - x_A)$$

Where $\overline{(1-x_A)_L}$ = $\frac{(1-x_A)-(1-x_{Ai})}{ln\left[{(1-x_A)}/{(1-x_{Ai})}\right]}$ is the log mean of $(1-x_A)$ and similar for y values

- Remember the log mean is the “one way correction” factor
- Now we can also express as:

$$N_A = k'_y(y_{Ai} - y_A) \qquad N_A = k'_x(x_{Ai} - x_A)$$

Film Theory – Gas Absorption Case



$$N_A = k_x \, ln\left(\frac{1-x_A}{1-x_{Ai}}\right) \qquad N_A = k_y \, ln\left(\frac{1-y_{Ai}}{1-y_A}\right)$$

Note that expressions are for flow from right to left

- In these processes the concentrations are often dilute and the error introduced by the following approximation is less than the uncertainty in the values of the mass transfer coefficients…

$$N_A = \frac{k_x}{(1-x_A)_L}(x_{Ai} - x_A) = k'_x(x_{Ai} - x_A) \qquad N_A = \frac{k_y}{(1-y_A)_L}(y_A - y_{Ai}) = k'_y(y_A - y_{Ai})$$

- In these dilute cases $k_x \approx k'_x$ and $k_y \approx k'_y$, so…

$$N_A = k_x(x_{Ai} - x_A) \qquad N_A = k_y(y_A - y_{Ai})$$

- This expression is not strictly true, but in dilute cases the difference between One-Component and Equimolar mass transfer is not that large

Mass Transfer Coefficient

- Flux is a mass transfer coefficient multiplied by a driving force

$$\boldsymbol{N_A = k_x\,(x_{Ai} - x_A)}$$

Mass transfer coefficient driving force

- The mass transfer coefficient contains (via experimental data and, perhaps, correlations) all of the complicated physics of mixing, etc)

Two Film Theory

- A molecule travels from bulk gas phase to bulk liquid phase

At steady state:

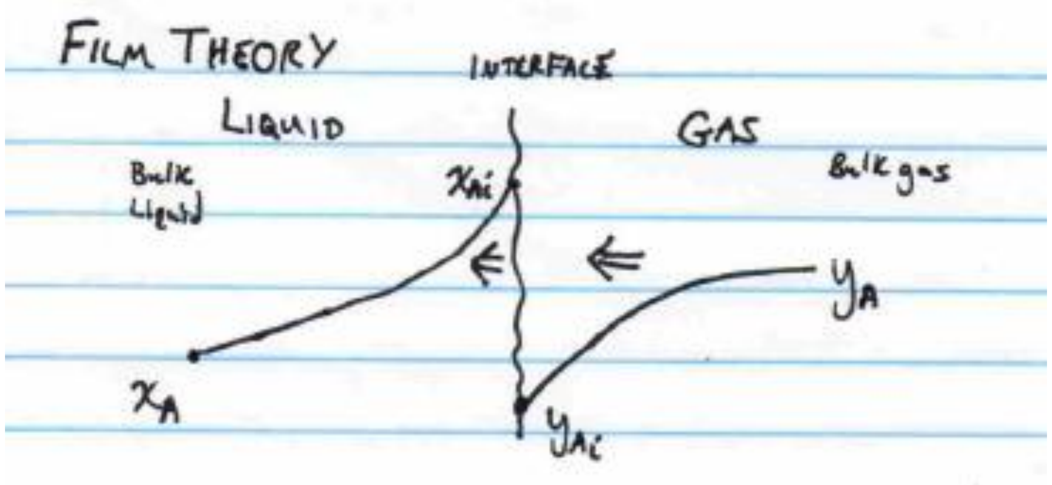
- Flux of solute A traveling from bulk gas to the interface MUST equal the flux of solute A traveling from the interface to the bulk liquid
  - Equality of Flux

$$k_y\,(y_A - y_{Ai}) = k_x\,(x_{Ai} - x_A)$$

- The concentration of y_{Ai} and x_{Ai} are in equilibrium with one another

$$y_{Ai} = y^*(x_{Ai})$$

  - Might be Raoult's or Henry's Law or some other relationship…



Two Film Theory

- Measuring bulk concentrations, x_A and y_A, is challenging enough – measuring interfacial concentrations, x_{Ai} and y_{Ai}, is much more difficult.
  - What to do?

- Rearrange the equality of flux expression:

$$k_y\,(y_A - y_{Ai}) = k_x\,(x_{Ai} - x_A)$$

$$\frac{y_A - y_{Ai}}{x_{Ai} - x_A} = \frac{k_x}{k_y}$$

$$\frac{y_{Ai} - y_A}{x_{Ai} - x_A} = \frac{y_A - y_{Ai}}{x_A - x_{Ai}} = -\frac{k_x}{k_y}$$

Two Film Theory

- Pick a location (height) in your tower and determine the values of the bulk concentrations, x_A and y_A
- Plot the point (x_A, y_A) on your graph
- Draw a line from that point with a slope of $-\frac{k_x}{k_y}$
- The equation of this line will be:

$$y - y_A = -\frac{k_x}{k_y}(x - x_A)$$

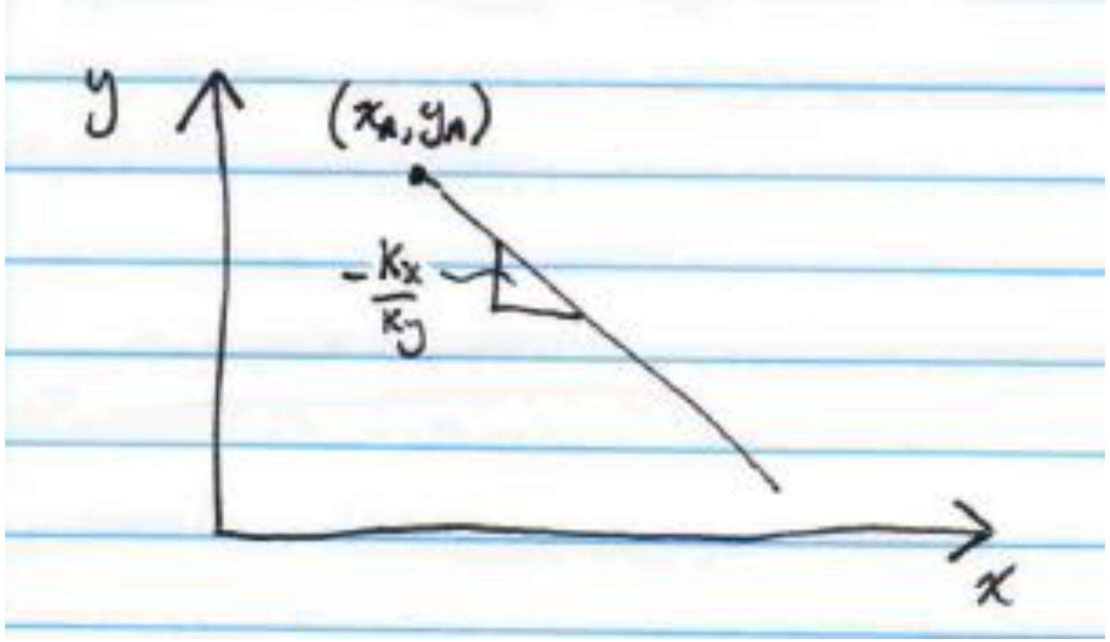
- From the previous slide:

$$\frac{y_{Ai} - y_A}{x_{Ai} - x_A} = -\frac{k_x}{k_y}$$

- Substitute that into the equation for this line

$$y - y_A = \frac{y_{Ai} - y_A}{x_{Ai} - x_A}(x - x_A)$$

- Note that when $x = x_{Ai}$ then $y = y_{Ai}$
- Therefore this line is a collection of all points (x_{Ai}, y_{Ai}) that satisfy the Equality of Flux Requirement



Two Film Theory

- Any point on that line will satisfy the Equality of Flux Requirement for bulk conditions (x_A, y_A)
- We know that the true interfacial mole fractions (x_{Ai}, y_{Ai}) must be in equilibrium with one another
- Add the equilibrium curve to the graph
- We know that all the combinations of mole fractions that are in equilibrium will be on the EQ curve
- The intersection of the line and the equilibrium curve is the actual pair of mole fractions (x_{Ai}, y_{Ai}) that satisfy both the Equality of Flux and the Equilibrium Requirement!
- This graphical method has allowed us to determine the interfacial mole fractions (x_{Ai}, y_{Ai}) based on the more easily measured bulk mole fractions (x_A, y_A)