



CE407 SEPARATIONS

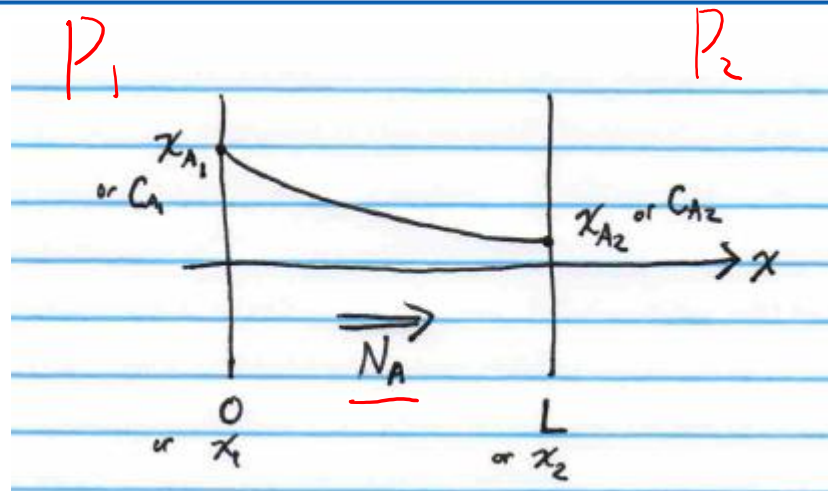
Lecture 19

Instructor: Miao Yu



*Lecture material is provided by courtesy of Prof. David Courtemanche.

Diffusion

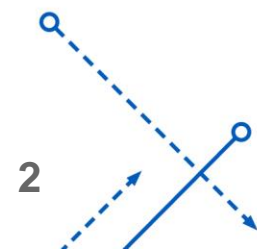


- There exists a concentration gradient across a membrane/liquid layer and we want to determine the flux of solute A, N_A , from the left to the right...

$$N_A = \underbrace{(N_A + N_B)}_{\text{Convective}} x_A - \underbrace{D_{AB} C}_{\text{Diffusive}} \frac{dx_A}{dx}$$

$C \cdot x_{A1} = C_{A1}$

- Unfortunately, N_A appears on both sides of the equation



Equimolar Counter Diffusion (Equimolar 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)

$$N_A + N_B = 0$$

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

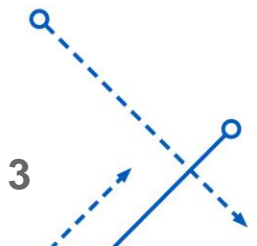
$$N_A = -D c \frac{dx_A}{dx}$$

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

- This can be rearranged to be:

$$N_A dx = -D c dx_A$$

direction



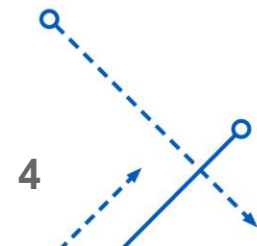
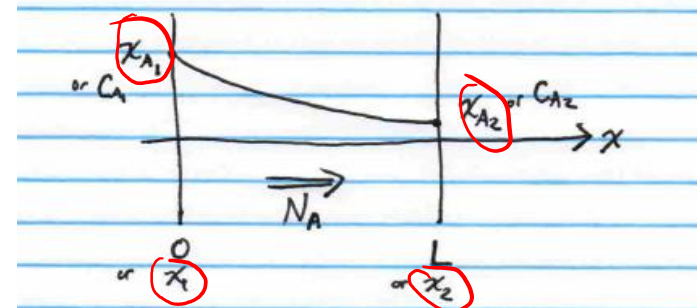
Equimolar Counter Diffusion

$$N_A dx = -D c dx_A$$

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

- 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 $x_{A,2}$

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



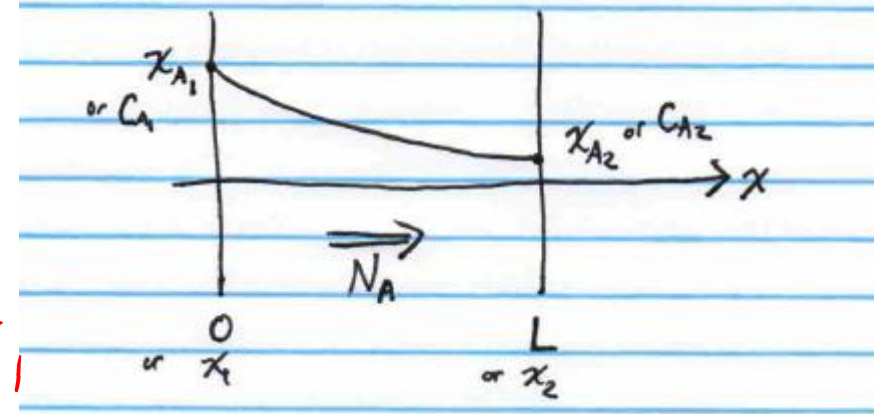
Equimolar Counter Diffusion

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

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

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

$L = x_2 - x_1$



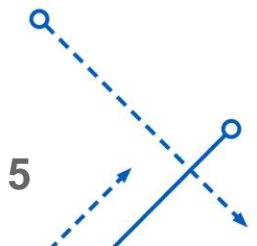
- or

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

Fick's Law

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

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



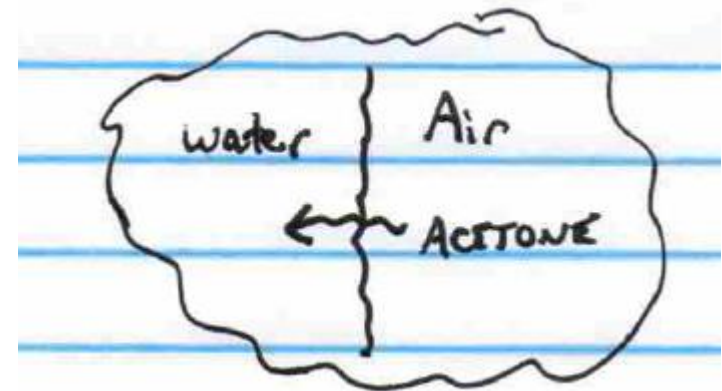
One Component Mass Transfer

- A diffusing through non-diffusing B
 - Book calls it “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: $N_B = 0$

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

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

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



One Component Mass Transfer

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

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

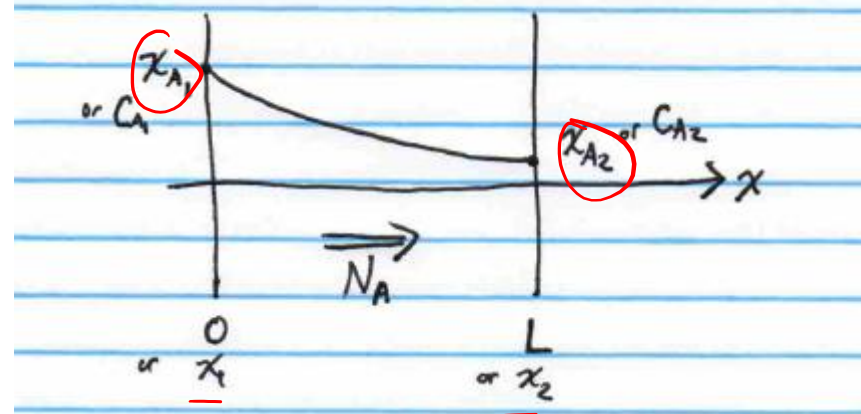
$$\int_0^L N_A dx = -D c \int_{x_{A,1}}^{x_{A,2}} \frac{dx_A}{1 - x_A}$$

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

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

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

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



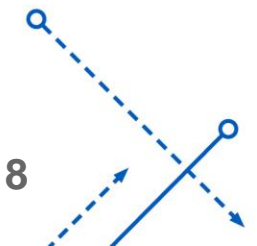
Dilute Solutions

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

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

$$\begin{array}{l}
 1 + (-)x_{A,1} \\
 \ln(1 - x_{A,1}) \approx -x_{A,1} \text{ and } \ln(1 - x_{A,2}) \approx -x_{A,2}
 \end{array}$$

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



Recap

- Equimolar Diffusion

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

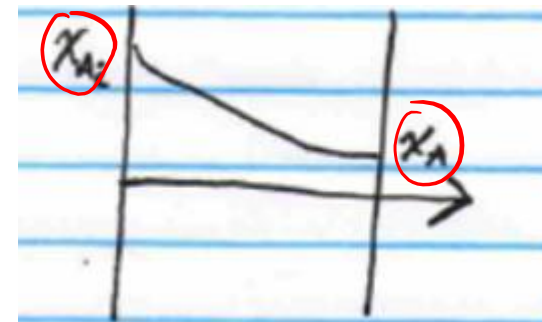
eq 17.19

- One-Component

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

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 $N_A = \frac{Dc}{L} \ln \left(\frac{1-x_{A,2}}{1-x_{A,1}} \right)$ can be worked algebraically to the following:

$$N_A = \frac{Dc(x_{A,1} - x_{A,2})}{L \overline{(1-x_A)}_L}$$

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

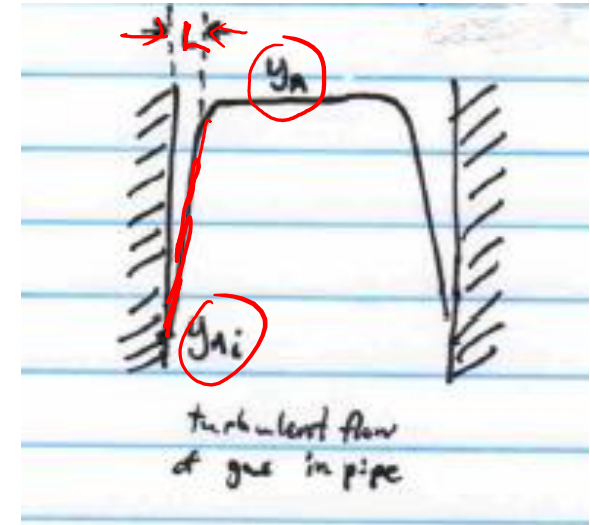
Film Theory

- A diffusing through non-diffusing B



gas phase $N_A = \frac{Dc}{L} \ln \left(\frac{1-y_A}{1-y_{Ai}} \right)$

liquid phase $N_A = \frac{Dc}{L} \ln \left(\frac{1-x_A}{1-x_{Ai}} \right)$



- 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"

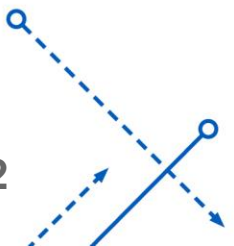
Film Theory

- We can express the flux in each phase as

$$\text{gas phase } N_A = k_y \ln \left(\frac{1-y_A}{1-y_{Ai}} \right)$$

$$\text{liquid phase } N_A = k_x \ln \left(\frac{1-x_A}{1-x_{Ai}} \right)$$

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



Film Theory

$$N_A = k_y \ln \left(\frac{1-y_A}{1-y_{Ai}} \right)$$

$$N_A = k_x \ln \left(\frac{1-x_A}{1-x_{Ai}} \right)$$

- These equations can be manipulated into:

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

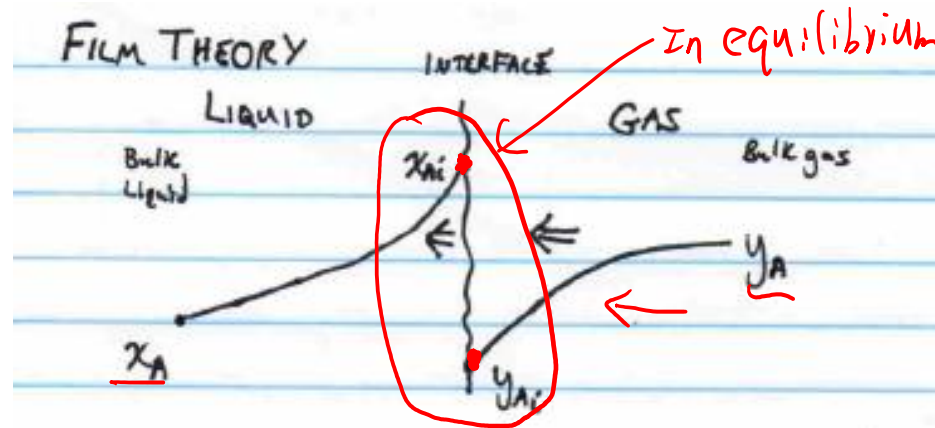
Where $(1-x_A)_L = \frac{(1-x_A) - (1-x_{Ai})}{\ln \left[\frac{(1-x_A)}{(1-x_{Ai})} \right]}$ is the log mean of $(1-x_A)$ and similar for y values

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

$$N_A = k'_y (y_{Ai} - y_A)$$

$$N_A = k'_x (x_{Ai} - x_A)$$

Film Theory – Gas Absorption Case



$$N_A = k_x \ln \left(\frac{1-x_A}{1-x_{Ai}} \right)$$

$$N_A = k_y \ln \left(\frac{1-y_{Ai}}{1-y_A} \right)$$

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...

$$N_A = \frac{k_x}{(1-x_A)_L} (x_{Ai} - x_A) = k'_x (x_{Ai} - x_A)$$

$$N_A = \frac{k_y}{(1-y_A)_L} (y_A - y_{Ai}) = k'_y (y_A - y_{Ai})$$

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

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

$$N_A = k_y (y_A - y_{Ai})$$

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

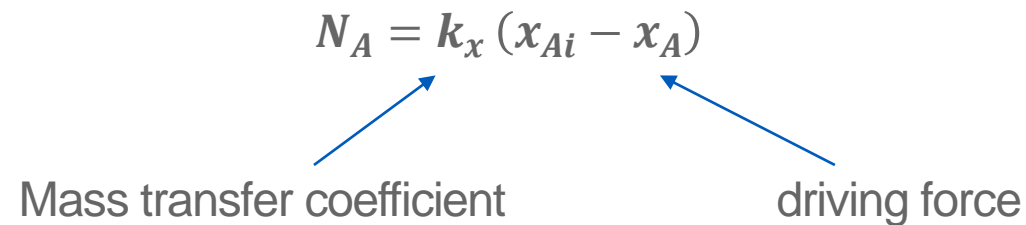


Mass Transfer Coefficient

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

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

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:

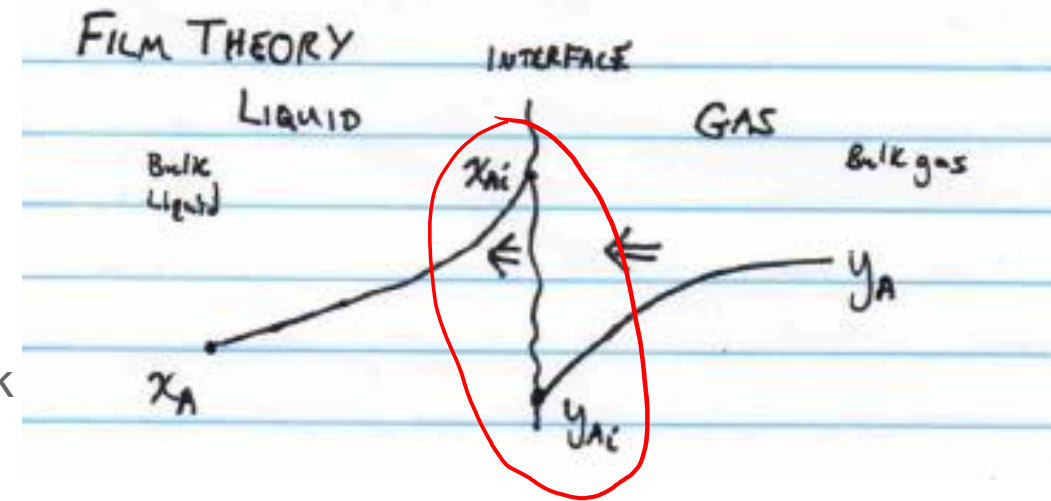
- Flux of solute A traveling from bulk gas to the interface MUST equal the flux of solute A traveling from the interface to the bulk liquid
 - Equality of Flux

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

- 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...



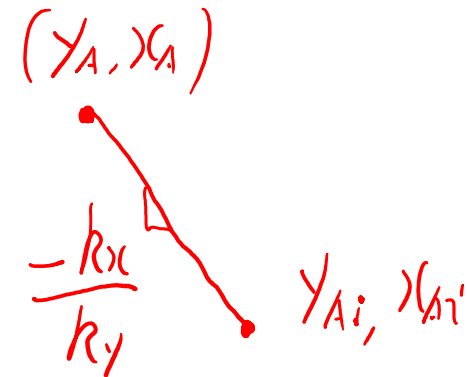
Two Film Theory

- 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:

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

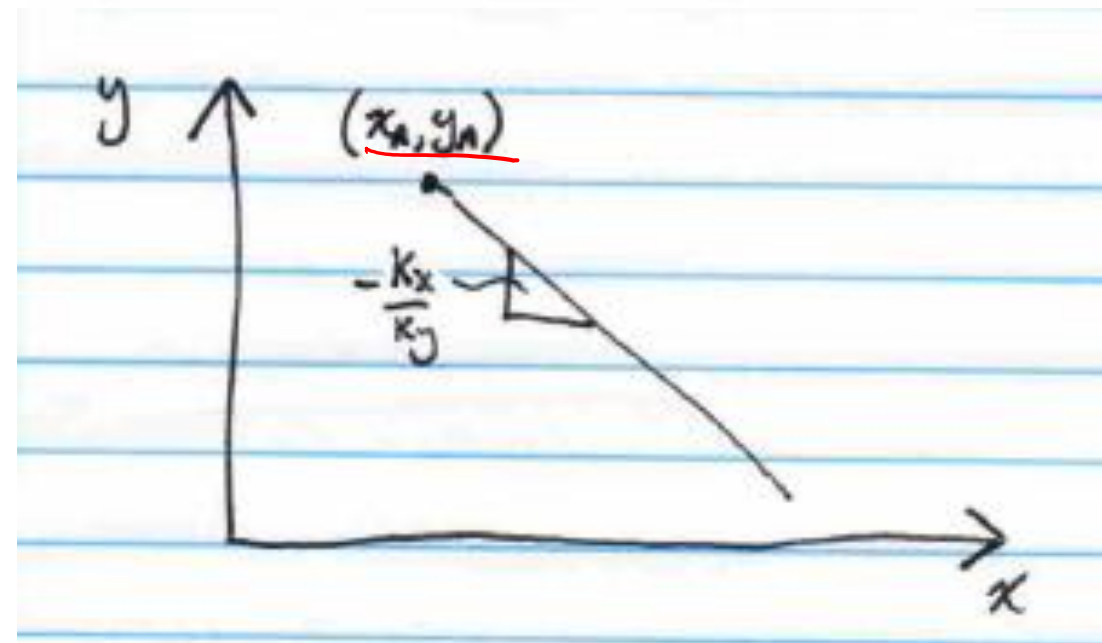
- From the previous slide:

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

- 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)

