

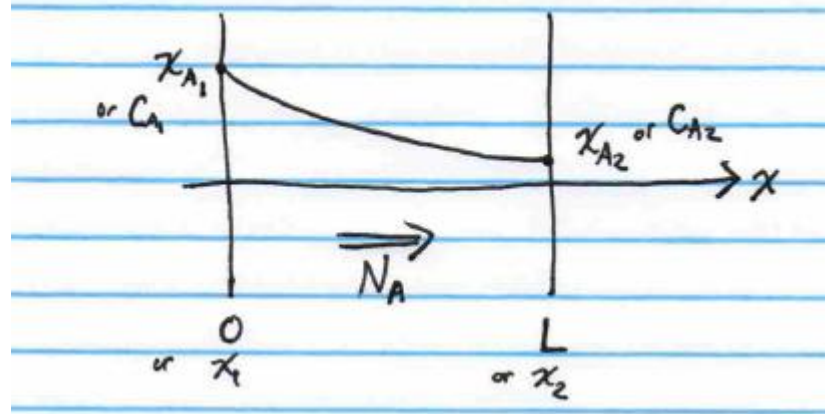


# CE407 SEPARATIONS

Lecture 19

Instructor: 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...

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

Convective      Diffusive

- Unfortunately,  $N_A$  appears on both sides of the equation

# Equimolar Counter Diffusion (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

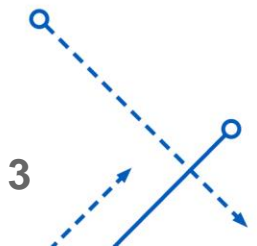
- Then...  $N_A = (N_A + N_B)x_A - D_{AB} c \frac{dx_A}{dx}$  becomes

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

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

- This can be rearranged to be:

$$N_A dx = -D c dx_A$$



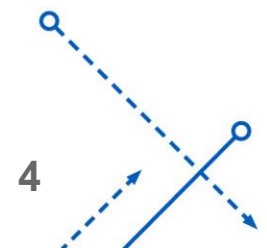
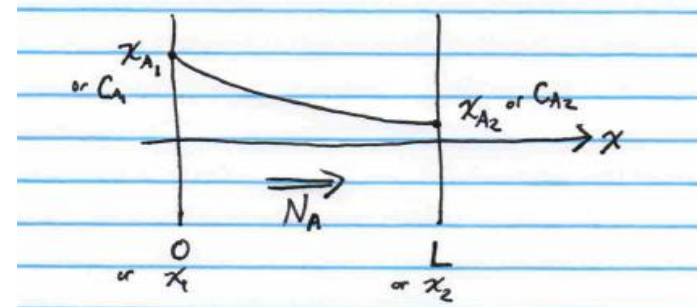
# Equimolar Counter Diffusion

$$N_A dx = -D c dx_A$$

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

- 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  $x_{A,2}$

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



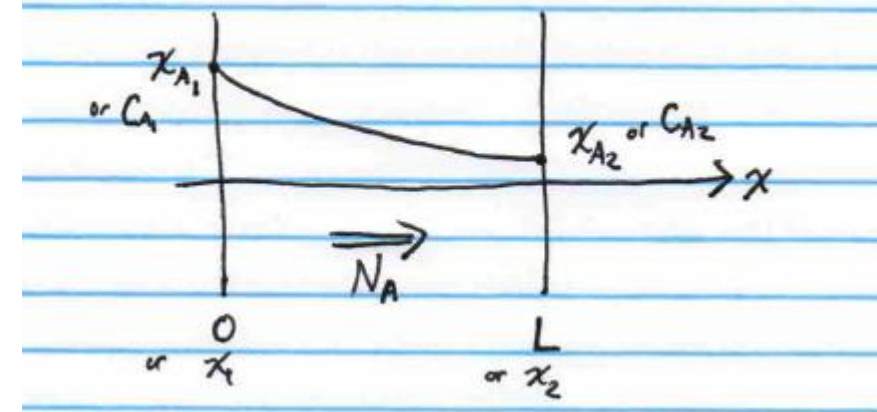
# Equimolar Counter Diffusion

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

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

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

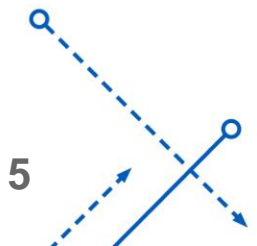
- or 
$$N_A = -\frac{D c}{x_2 - x_1} (x_{A,2} - x_{A,1}) = -D \left( \frac{c_{A,2} - c_{A,1}}{x_2 - x_1} \right) = -D \frac{\Delta C_A}{\Delta x}$$



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



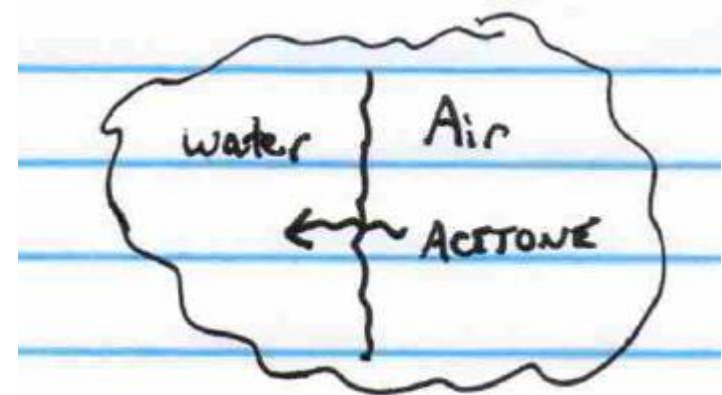
# One Component Mass Transfer

- 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:  $N_B = 0$

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

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

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



# One Component Mass Transfer

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

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

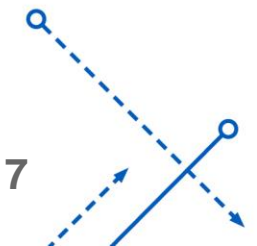
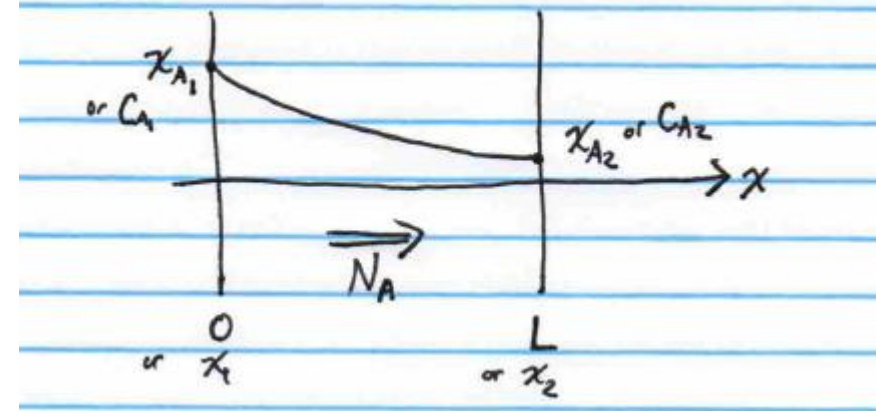
$$\int_0^L N_A dx = -D c \int_{x_{A,1}}^{x_{A,2}} \frac{dx_A}{1 - x_A}$$

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

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

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

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



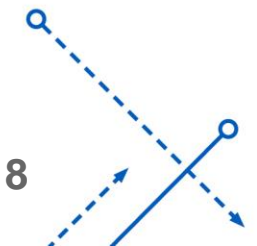
# Dilute Solutions

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

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

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

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





# Recap

- Equimolar Diffusion

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

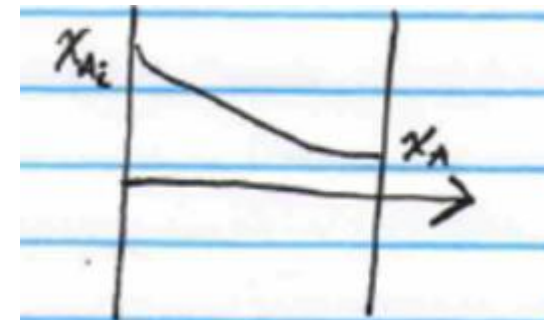
eq 17.19

- 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



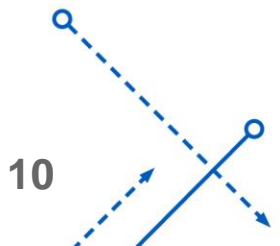
## “One-Way Correction” term

- 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:

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

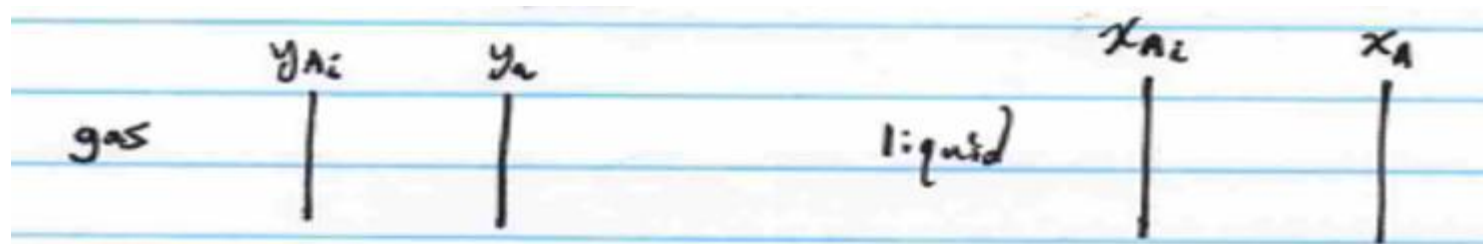
Where  $\overline{(1-x_A)}_L = \frac{(1-x_{A,2}) - (1-x_{A,1})}{\ln \left[ \frac{(1-x_{A,2})}{(1-x_{A,1})} \right]}$  the log mean of  $(1-x_A)$

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



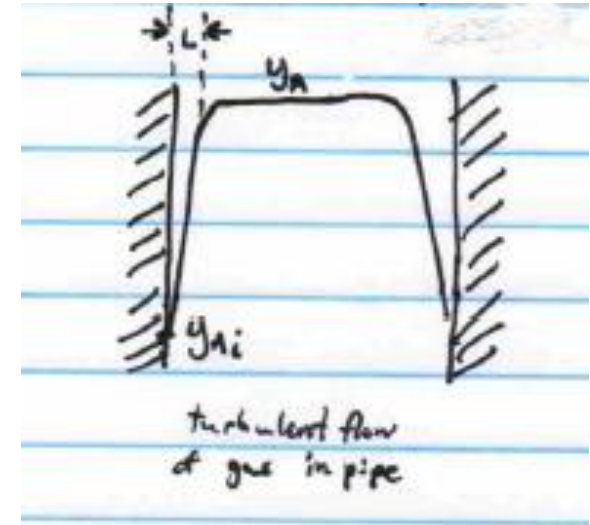
# Film Theory

- A diffusing through non-diffusing B



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

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



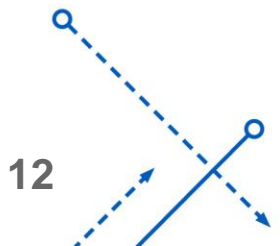
- These equations apply directly when all mass transfer occurs due to pure molecular diffusion
- Consider a case where there is turbulent flow... gas in a pipe (See figure in upper right corner)
  - This is a much more complicated case than pure molecular diffusion
  - Concentration =  $y_A$  in the 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

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

- These expressions are dependent on the same bulk and surface mole fractions as before but now the constant is no longer  $\frac{D c}{L}$ , 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:

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

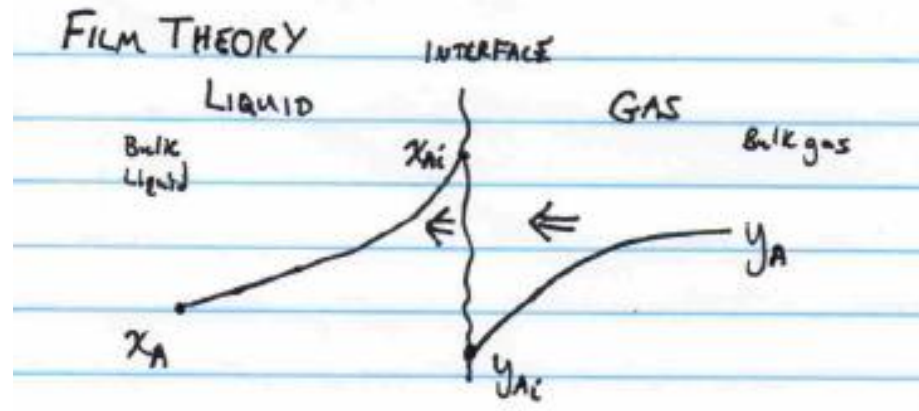
Where  $(1-x_A)_L = \frac{(1-x_A) - (1-x_{Ai})}{\ln \left[ \frac{(1-x_A)}{(1-x_{Ai})} \right]}$  is the log mean of  $(1-x_A)$  and similar for y values

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

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



# Film Theory – Gas Absorption Case



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

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

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

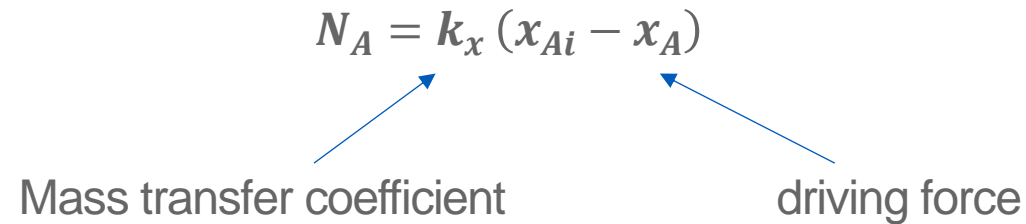


# Mass Transfer Coefficient

- 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:

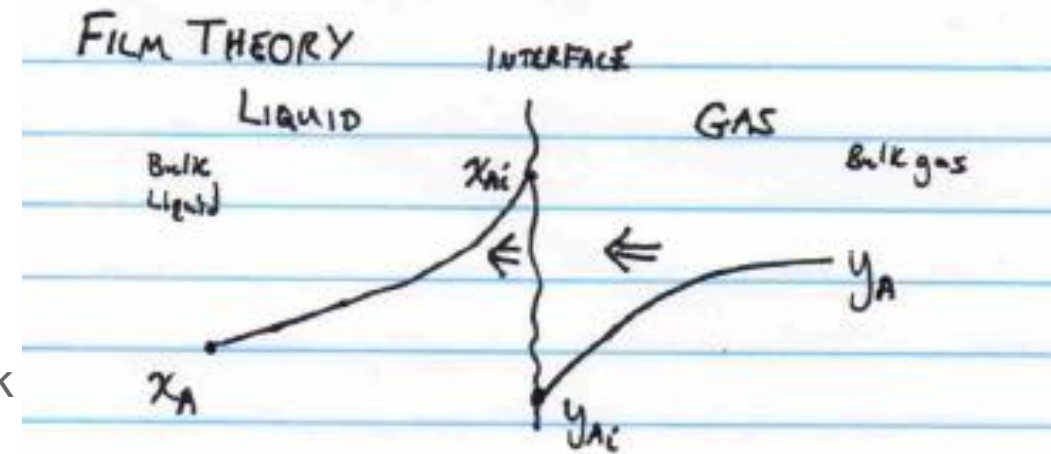
- Flux of solute A traveling from bulk gas to the interface MUST equal the flux of solute A traveling from the interface to the bulk liquid
  - Equality of Flux

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

- 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:

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

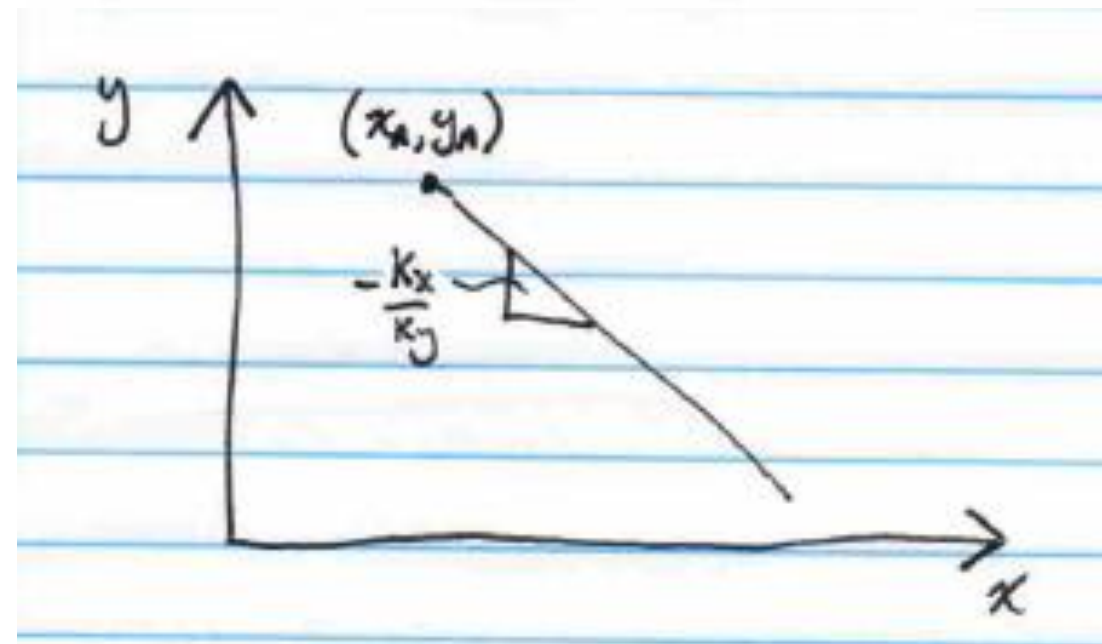
- From the previous slide:

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

- 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  $(x_A, y_A)$

