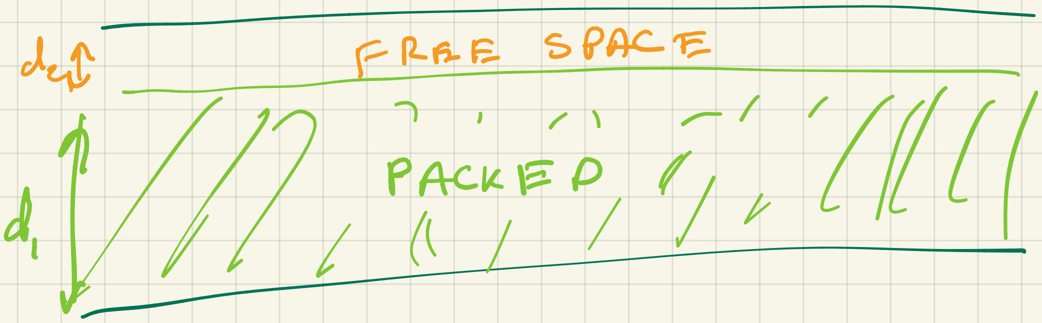
CBE 40445
FALL 2020
REVIEW 11/11/20

BIG IDEAS

1) MASS BALANCES TO ANALYZE REACTORS OF DIFFERENT CONFIGURATIONS
2) DETAILED QUANTITATIVE ANALYSIS OF KINETIC DATA
3) USE & LIMITATIONS OF SOLID CATALYSTS FOR REACTIONS
4) INCLUSION OF ENERGY BALANCE TO ANALYZE REACTORS THAT REQUIRE COOLING OR ARE NOT ISOTHERMAL
5) SOME CONSIDERATION OF FLOW LIMITATIONS OR MIXING IMPERFECTIONS

CHAPTER 10

THIS LAST ONE IS A BIT OF A CURIOSITY BUT CONSIDER



I COULD NOT ASK ON LAST EXAMINE THE FRACTION OF FLUID BYPASSING PACKING BUT.

$$f_f \equiv \frac{d_p \frac{\Delta P}{L}}{\rho_f u^2}, \quad Re \equiv \frac{d_p u \rho_f}{\mu_f}$$

$$f_f = \frac{1-\bar{\varepsilon}_B}{\bar{\varepsilon}_B^2}\left[1.75 + 150\,\frac{(1-\bar{\varepsilon}_B)}{Re}\right]$$

d_p ≡ DIAMETER OF CATALYST PELLET

$\bar{\varepsilon}_B$ ≡ VOID FRACTION ≈ 0.37 FOR IDENTICAL SPHERES

μ_f ≡ VISCOSITY OF LIQUID OR GAS

ρ_f ≡ DENSITY OF LIQUID OR GAS

u = "SUPERFICIAL VELOCITY = $\dfrac{\text{VOLUMETRIC FLOW}}{\text{CROSS-SECTION AREA}}$

ΔP = PRESSURE CHANGE

L = DISTANCE IN FLOW DIRECTION

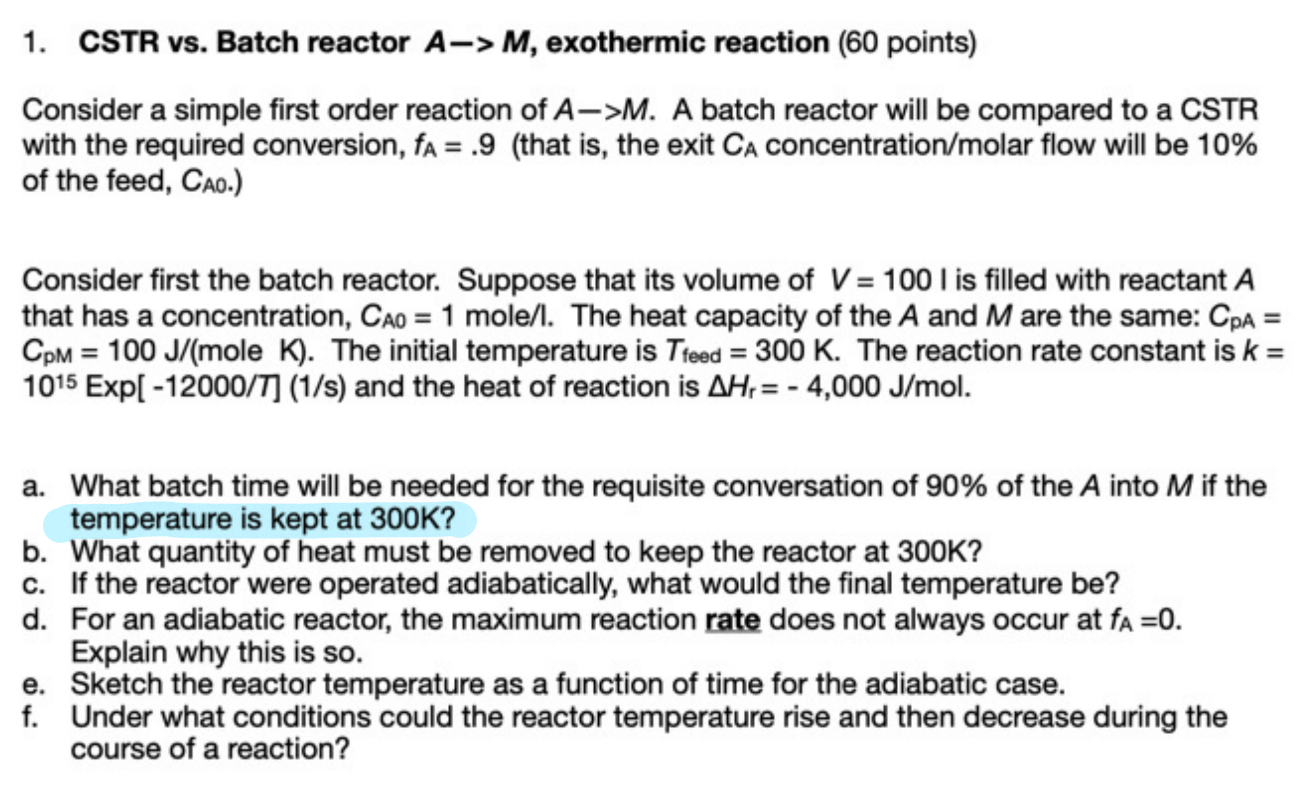
USE MY NUMBERS IF THIS COMES UP.

OTHERWISE FROM CHAPTER 10...

I WOULD KEEP A PDE SOLVER HANDY...

— I SUPPOSE I COULD ASK YOU TO INTERPRET RESULTS

– MASS BALANCES FOR REACTORS OF VARIOUS CONFIGURATIONS



1. **CSTR vs. Batch reactor *A—> M*, exothermic reaction** (60 points)

Consider a simple first order reaction of *A—>M*. A batch reactor will be compared to a CSTR with the required conversion, $f_A = .9$ (that is, the exit C_A concentration/molar flow will be 10% of the feed, C_{A0}.)

Consider first the batch reactor. Suppose that its volume of $V = 100$ l is filled with reactant *A* that has a concentration, $C_{A0} = 1$ mole/l. The heat capacity of the *A* and *M* are the same: $C_{pA} = C_{pM} = 100$ J/(mole K). The initial temperature is $T_{feed} = 300$ K. The reaction rate constant is $k = 10^{15}\,\mathrm{Exp}[-12000/T]$ (1/s) and the heat of reaction is $\Delta H_r = -4{,}000$ J/mol.

a. What batch time will be needed for the requisite conversation of 90% of the *A* into *M* if the temperature is kept at 300K?
b. What quantity of heat must be removed to keep the reactor at 300K?
c. If the reactor were operated adiabatically, what would the final temperature be?
d. For an adiabatic reactor, the maximum reaction **rate** does not always occur at $f_A = 0$. Explain why this is so.
e. Sketch the reactor temperature as a function of time for the adiabatic case.
f. Under what conditions could the reactor temperature rise and then decrease during the course of a reaction?

A ISOTHERMAL BATCH REACTOR

$$\frac{d(VC_A)}{dt} = \underset{\sim}{\text{NO FLOW}} - kC_AV$$

V=CONST

$k = .0042/s$

$$\frac{dC_A}{dt} = -kC_A$$

$$\int \frac{dC_A}{C_A} = -k\int dt$$

$$\ln\left(\frac{C_A}{C_A^0}\right) = -kt$$

$$C_A = C_A^0\exp(-kt)$$

$$t = \frac{-\ln\left(\frac{.1}{1}\right)}{k}$$

$$\boxed{t = 542\,s}$$

HEAT REMOVED TO KEEP T=300 $= \Delta H_r \, m \, f$

$= -4000 \frac{J}{MOLE} \times 100 \text{ MOLES} \times .9$

$Q = -360{,}000 \text{ J}$

<u>SUPPOSE ADIABATIC</u>

ALL HEAT GOES TO RAISING T OF FLUID

$\left(\text{HEAT REMOVED}\right)$

$0 = \Delta H \, m \, f + m \, C_p \left(T - T^{\text{INITIAL}}\right)$

$\Delta T = \frac{\Delta H \, f}{C_p} = \frac{\left(4000 \text{ J/MOLE}\right)\left(.9\right)}{100 \text{ J/MOLE} \cdot K}$

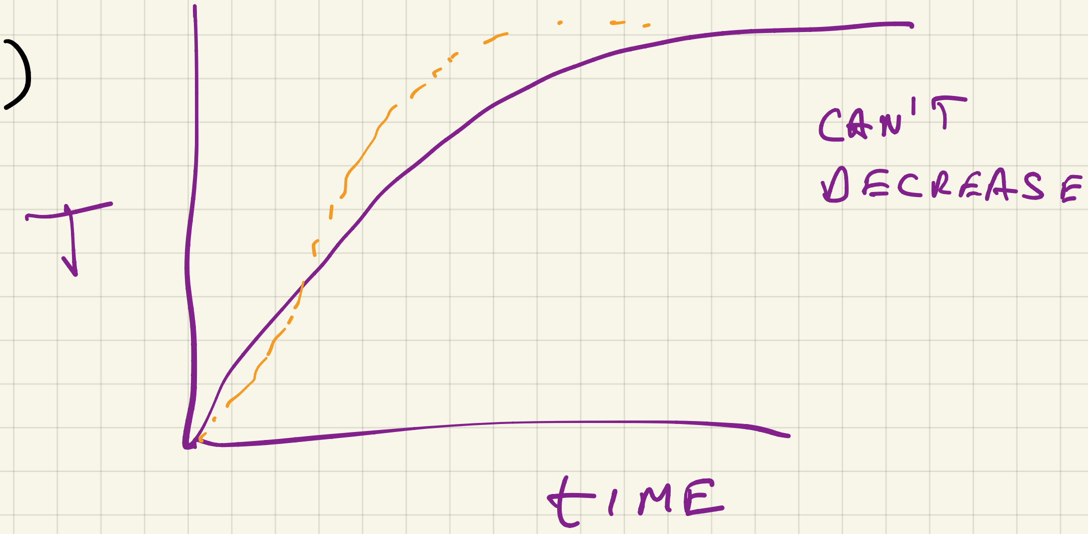
ADIABATIC TEMP RISE!

$\Delta T = 36 \text{ K}$

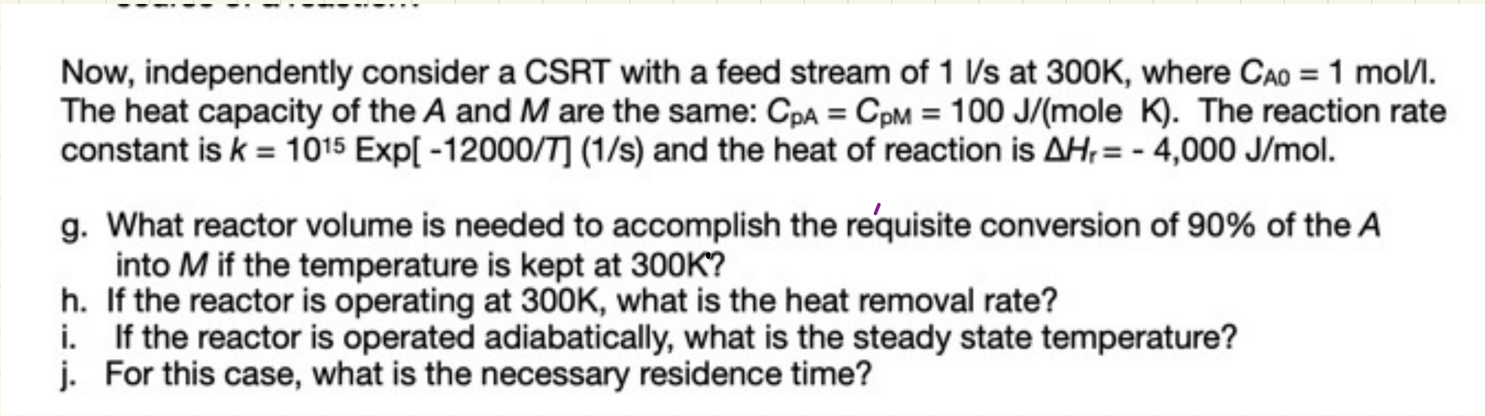
d) $r = k C_A$

IF T ↑ k ↑ FASTER THAN C_A ↓.

e)



f) WOULD REQUIRE COOLING



Now, independently consider a CSRT with a feed stream of 1 l/s at 300K, where C_{A0} = 1 mol/l. The heat capacity of the *A* and *M* are the same: $C_{pA} = C_{pM}$ = 100 J/(mole K). The reaction rate constant is $k = 10^{15}$ Exp[-12000/*T*] (1/s) and the heat of reaction is ΔH_r = - 4,000 J/mol.

g. What reactor volume is needed to accomplish the requisite conversion of 90% of the *A* into *M* if the temperature is kept at 300K?
h. If the reactor is operating at 300K, what is the heat removal rate?
i. If the reactor is operated adiabatically, what is the steady state temperature?
j. For this case, what is the necessary residence time?

ISOTHERMAL CSTR

$$\overset{\rightarrow 0}{\frac{d\, VC_A}{dt}} = q\, C_{Af} - q\, C_A - k C_A V$$

$$\frac{C_A}{C_{Af}} = \frac{1}{1 + k\tau} \qquad \tau = \frac{V}{q}$$

$$\tau = \frac{C_{Af} - C_A}{C_A\, k}$$

$$\tau = 2120 \text{ s} \qquad q = 1\ \text{l/s}$$

$$\boxed{V = 2120 \text{ L}}$$

HEAT REMOVAL THROUGH WALL/COILS = RATE OF GENERATION

$$\left(\frac{1}{\text{TIME}}\right) \qquad \dot{Q} = (\Delta H_r)\left(\begin{array}{c}\text{RATE OF}\\ \text{REACTION}\end{array}\right)$$

$$\left(\frac{1}{\text{MOLE}}\right)\left(\frac{\text{MOLES}}{\text{TIME}}\right)$$

$$= \Delta H_r \, k C_A \, V \quad (= \Delta H \, F_A f)$$

$$= -4000 \, J/\text{mol} \left(\frac{.0042}{s}\right)\left(0.1 \frac{M}{L}\right)(21202)$$

$$\dot{Q} = -3600 \, J/s$$

ADIABATIC, BUT SOMEHOW STILL GET SAME f.

$$0 = \Delta H_r F_A f + F_A\left[(1-f)C_{p_A} + f C_{p_M}\right]\Delta T$$

$$-\Delta T = \frac{-3600 \, J/s}{(1 \, \text{mole}/s)\left(.1 \, \frac{100 J}{\text{mole K}} + .9 \, \frac{100 J}{\text{mole K}}\right)}$$

$$\Delta T = 36 \, K$$

I AGAIN PICKED THE CONCEPT OF 90% CONVERSION + T_{FINAL}

$= 336$

$k_2(336) = .31/s$

$\tau = 30s$

COMPARE BATCH + CSTR

FOR BOTH $\Delta T = \frac{\Delta H f}{C_{p\,FINAL\,MIX}}$

AS LONG AS NO DILUENTS

OR AT LEAST IF

$\frac{\text{MOLES A}}{\text{MOLES INERT}} =$ SAME FOR BOTH

NO MATTER WHAT . . .

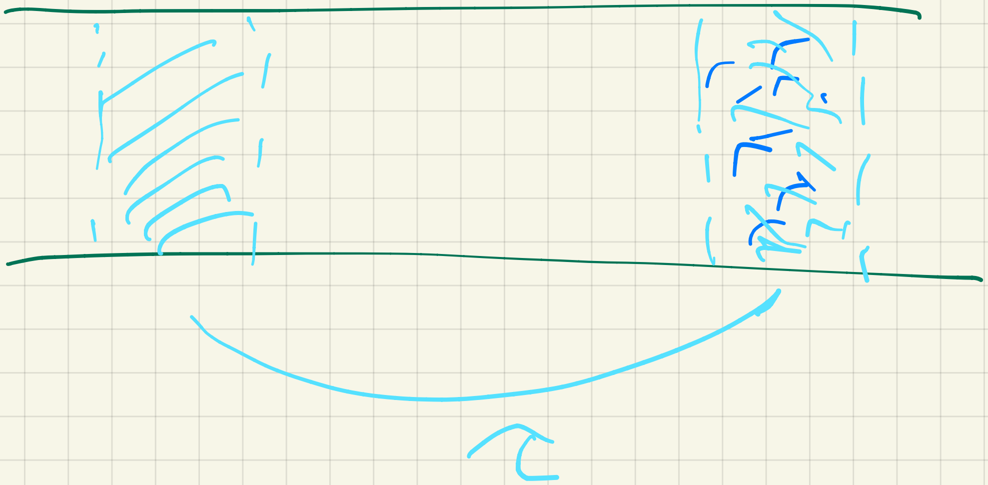
IF A MOLE OF M IS PRODUCED

$\Delta H = -4000\ J$

IF FLUIDS ARE TO STAY ISOTHERMAL

THIS MUCH HEAT HAS TO BE REMOVED

PLUG FLOW/TUBULAR REACTOR



$$\frac{dF_A}{dV_r} = \nu_A r, \quad F_A^\circ \frac{df_A}{dV_r} = -\nu_A r$$

$$\tau = \frac{V_r}{q}, \quad C_A^\circ = \frac{F_A^\circ}{q}$$

$$r = k C_A$$
$$= k C_A C_B \ldots$$

$$\frac{dC_A}{d\tau} = \nu_A r$$

REACTION EQUILIBRIUM

$\Delta G = 0$ AT EQUILIBRIUM

$$\Delta G - \Delta G^{0} = RT \sum_{i} \nu_i \ln a_i$$

$$= RT \prod_{i} a_i^{\nu_i}$$

$$K \equiv \prod_{i} a_i^{\nu_i}$$

GAS

$$a_i = \frac{x_i \phi_i P}{P^0}$$

$$\ln K = -\frac{\Delta G^0}{RT}$$

$$\Delta G^0 = \sum_{i} \Delta G_{i\,\text{FORMATION}}$$

$$\frac{\partial \ln K}{\partial\, 1/T} = \frac{\Delta H_r}{RT^2}$$

$$\ln K \sim \frac{\Delta H}{RT}$$

EXOTHERMIC

→ REACTANTS

$$aA + bB \rightleftharpoons mM + nN$$

$$K_a = \frac{x_M^m \, x_N^n}{x_A^a \, x_B^b}\left[\frac{\phi_M^m \, \phi_N^n}{\phi_A^a \, \phi_B^b}\right]\left(\frac{P}{P^\circ}\right)^{m+n-a-b}$$

FILL IN x'S FROM A MASS BALANCE

$$\tfrac{1}{2} N_2 + \tfrac{3}{2} H_2 \rightleftharpoons NH_3$$

	INITIAL	EQUILIBRIUM
N_2	25	$25 - \xi$
H_2	75	$75 - 3\xi$
NH_3	0	2ξ
	100	$100 - 2\xi$

REACTION RATES

MOLES NOW

INITIAL MOLES

$$\phi(t) \equiv \frac{m_i(t) - m_i^0}{\nu_i}$$

EXTENT OF REACTION

STOICHIOMETRIC COEFFICIENT

$$r = \frac{\text{MOLES/TIME}}{\text{VOLUME}} = \frac{1}{V}\frac{d\phi}{dt}$$

$$= \frac{1}{V\nu_i}\frac{dm_i}{dt}$$

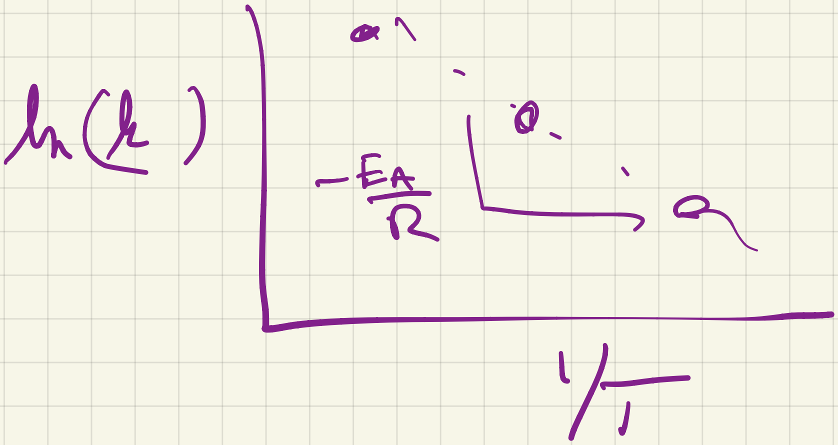
$$= \frac{1}{V\nu_i}\frac{dC_iV}{dt}$$

$$r = kC_A, \quad kC_AC_B, \quad \frac{kC_A}{B + KC_A}$$

WE EXPECT

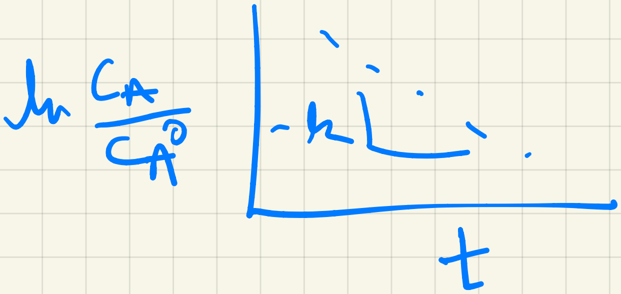
$$r = k(T)\,F(C_i, T)$$

$$k = \bar{A}\exp\left[-\frac{E_A}{RT}\right]$$ ARRHENIUS

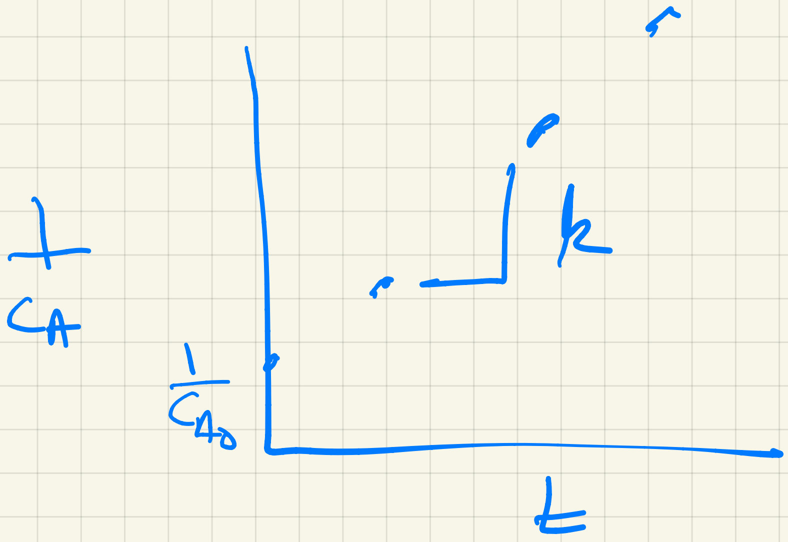


FOR RATE EXPRESSION

$$r = k\,C_A$$



2ND ORDER



$$\left(\frac{1}{C_A} - \frac{1}{C_{A0}}\right) = kt$$

$$A \xrightarrow{(E)} M$$

$$A + E \underset{k_r}{\overset{k_1}{\rightleftharpoons}} AE \xrightarrow{k_2} M + E$$

$$\frac{dC_A}{dt} = -k_1 C_A C_E + k_r C_{AE}$$

$$\frac{dC_{AE}}{dt} = k_1 C_A C_E - k_r C_{AE} - k_2 C_{AE}$$

$$\frac{dC_M}{dt} = k_2 C_{AE}$$

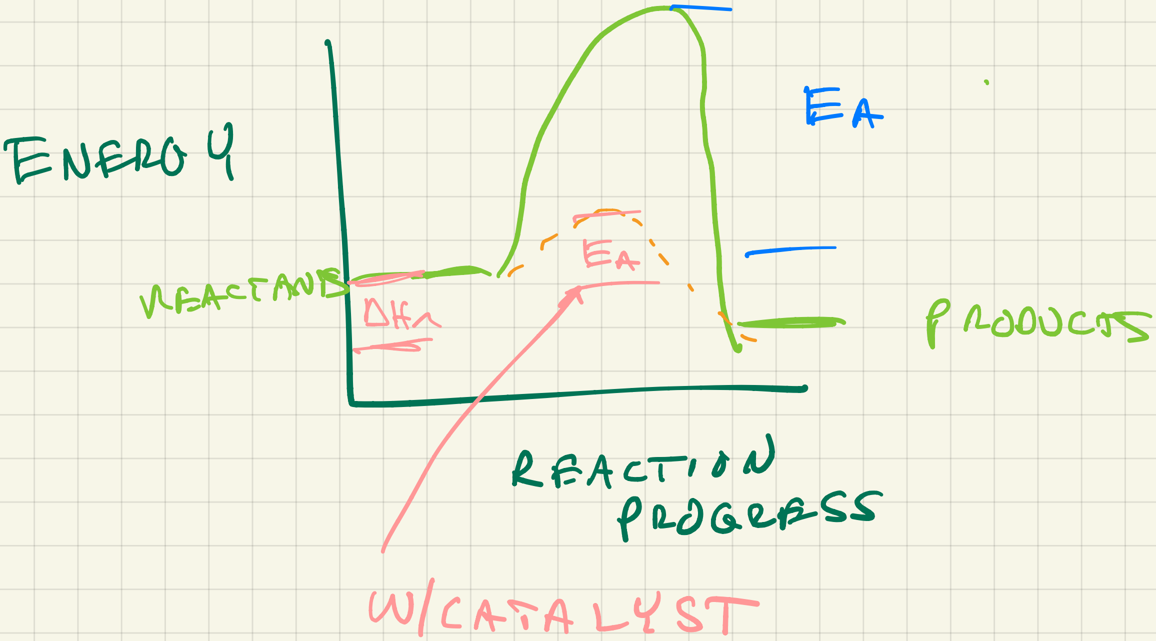
IF YOU WANT $\frac{dC_A}{dt}$, "ASSUME" $\frac{dC_{AE}}{dt} = 0$

$$C_{AE} = \frac{k_1 C_A C_E}{k_2 + k_r}$$

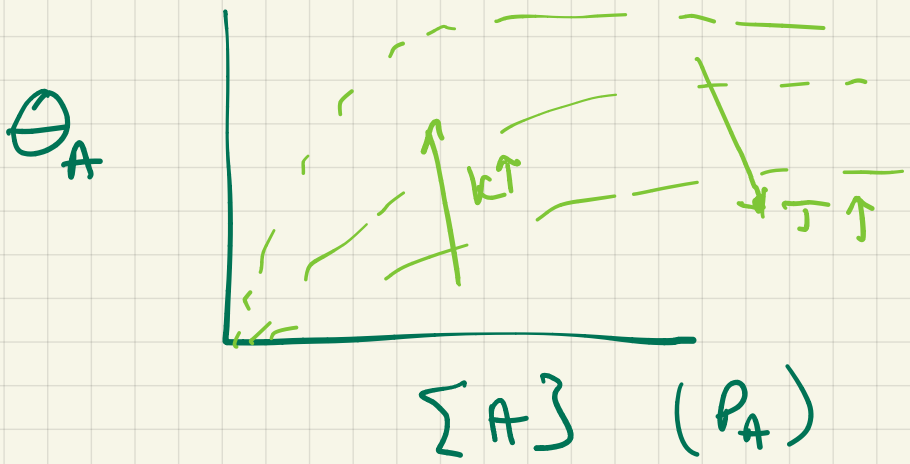
$$E^0 = E + AE$$

$$\frac{dC_A}{dt} = \frac{k_1 k_2 C_A C_E^{0}}{k_1 C_A + k_2 + k_r}$$

CATALYSTS


ENERGY
EA
REACTANTS
ΔH
EA
PRODUCTS
REACTION PROGRESS
W/CATALYST

LANGMUIR ADSORPTION



$$\theta_A = \frac{K_{ADS}[A]}{1 + K_{ADS}[A]}$$

$$\Delta G = \underset{\substack{\uparrow \\ \text{NEGATIVE}}}{\Delta H} - T\underset{\text{NEGATIVE}}{\Delta S}$$

(EQUILIBRIUM)

(SEE TEST 2 REVIEW)

$A \rightarrow M$, CATALYTIC SITES $\rightarrow$ *

$$r = \frac{k_2 K_{ADS}[A][*]_0}{1 + \frac{k_2}{k_{des}} + K_{ADS}[A]}$$

CATALYSTS!

INTERNAL DIFFUSION:

RATE CONST

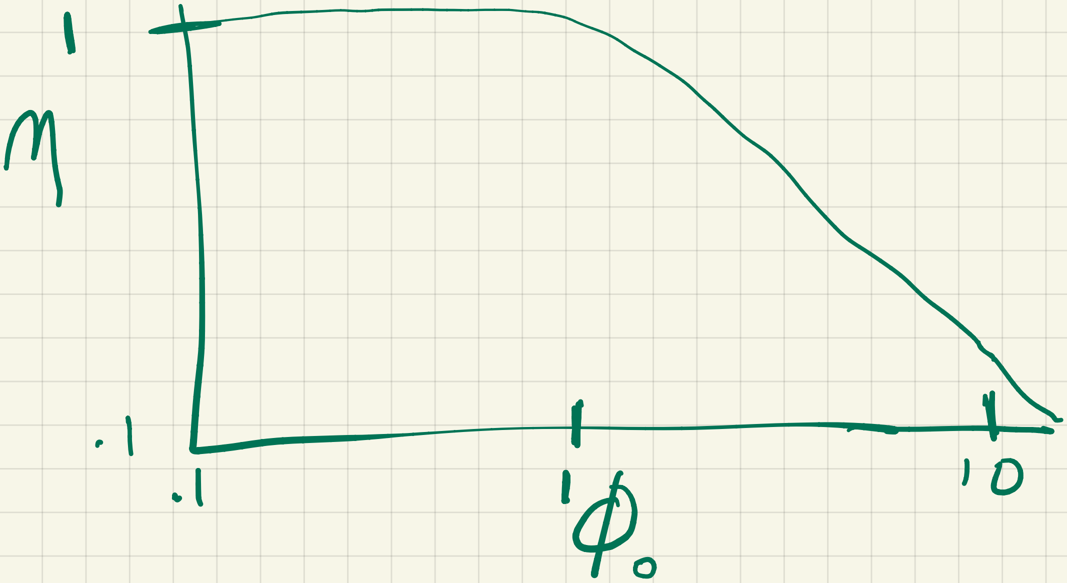
$$\frac{d^2 C_A}{dx^2} - \frac{k\, C_A}{D_{TA}} = 0$$

EFFECITIVE DIFFUSIVITY

$$\frac{d^2 \Theta}{dX^2} - \frac{k L^2}{D_{TA}} \Theta = 0$$

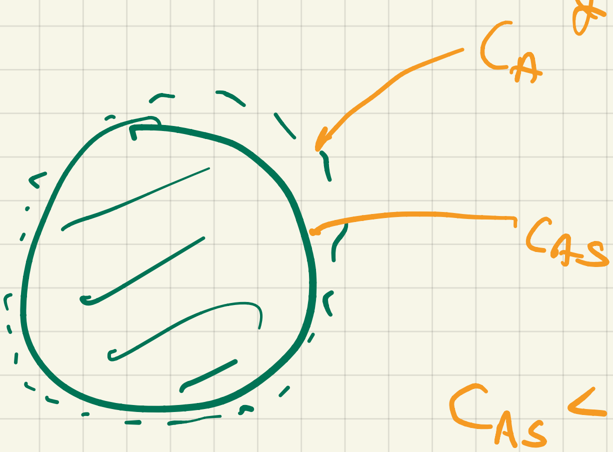
$$\phi^2 \equiv \frac{k L^2}{D_{TA}}$$ THIELE MODULUS

$$\eta \equiv \frac{\Lambda_{OBSERVED}}{\Lambda_{MAX}} =$$ EFFECTIVENESS FACTOR



$$\eta = \frac{\tan \phi_0}{\phi_0}$$

COULD HAVE EXTERNAL RESISTANCE



$C_{AS} < C_A^*$

$$Sh = \frac{\bar{k}_c L_p}{D_A}$$

$$Sh = 2 + .6\, Re_p^{1/2}\, Sc^{1/3}$$

$$Re_p = \frac{L_p U^{\infty} \rho}{\mu}$$

$$Sc = \frac{\mu/\rho}{D_A}$$

EXTERNAL COMPARED TO INTERNAL RESISTANCE

Biot #

$$Bi = \frac{L k_c}{D_{TA}} \qquad \frac{\text{EXTERNAL RESISTANCE}}{\text{INTERNAL RESISTANCE}}$$

FOR 1ST ORDER, CONST D_{TA} SOLUTION IS EASY TO GET!

$$0 = \frac{d^2\theta}{dx^2} - \phi^2 \theta$$

$$\left.\frac{d\theta}{dx}\right|_{x=1} = -Bi\left(\theta(1) - 1\right)$$

$$\theta(x) = \frac{Bi \cosh(x\phi)}{Bi \cosh(\phi) + \phi \sinh(\phi)}$$

BACK TO NON ISOTHERMAL