CBE 40445
9/2/20

REVIEW FOR TEST #1

LECTURES: 8/10 – 8/31

BOOK: CHAPT 1 – 3

WITH EMPHASIS ON LECTURE TOPICS + HW.

- CHEMICAL EQUILIBRIUM
- REACTION KINETICS
- BATCH, CSTR, PFR REACTORS

- TRY REALLY HARD TO NAVIGATE AROUND LINGO:
  - FRACTIONAL CONVERSION
  - EXTENT OF REACTION ...

ANY "COVID QUESTION" WILL BE DIRECTLY RELATED TO THESE MAIN COURSE TOPICS

NOTE THAT COURSE TOPICS HAVE RELIED HEAVILY ON

- MASS BALANCES
- (CHEMICAL) THERMODYNAMICS

EXPECT

1 BIG MULTIPART QUESTION

1 MEDIUM QUESTION

1 SHORT QUESTION

~ 50% REALLY BASIC

~ 40% FROM TOTAL SCOPE OF COURSE MATERIAL

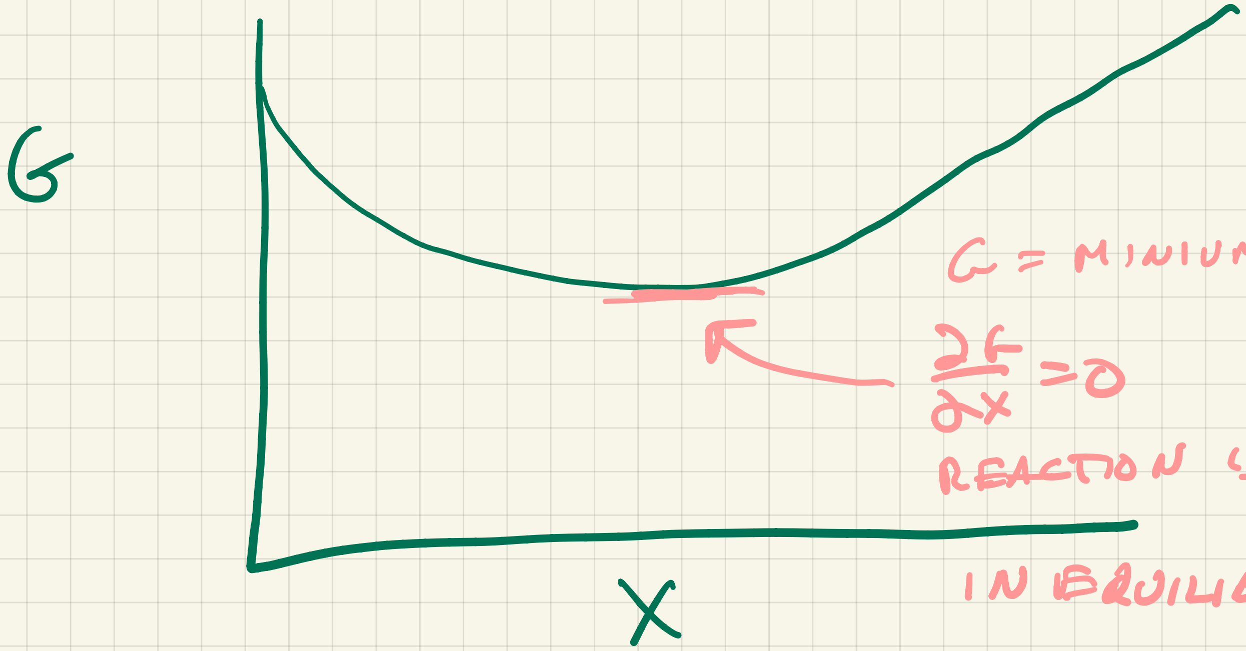
~ 10% MY CHOICE..

CHEMICAL REACTIONS

- IDENTIFY REACTANTS + PRODUCTS
- SPECIFY STOICHIOMETRY
- USE THERMODYNAMICS TO DETERMINE IF REACTION GOES TO COMPLETION OR ONLY PART OF THE WAY
- USE CONCEPTUAL MODELS, ARRHENIUS
  - DATA

  TO PREDICT/ DESCRIBE RATE

$$A + B \rightleftharpoons M + N$$



G = MINIUMUM

$$\frac{\partial G}{\partial X} = 0$$

REACTION IS IN EQUILIBRIUM

FOR REACTION

$$\Delta G = \sum_i \overset{\swarrow \text{ STOICHIOMETRIC COEFFICIENT}}{\nu_i} \underset{\uparrow \text{ CHEMICAL POTENTIAL}}{\mu_i}$$

$$\Delta G - \Delta G^\circ = RT \sum_i \nu_i \ln a_i$$

$$= RT \ln\left(\prod_i a_i^{\nu_i}\right)$$

$$K = \prod_i \underset{\uparrow}{a_i}^{\nu_i}$$

E.G. FOR A GAS

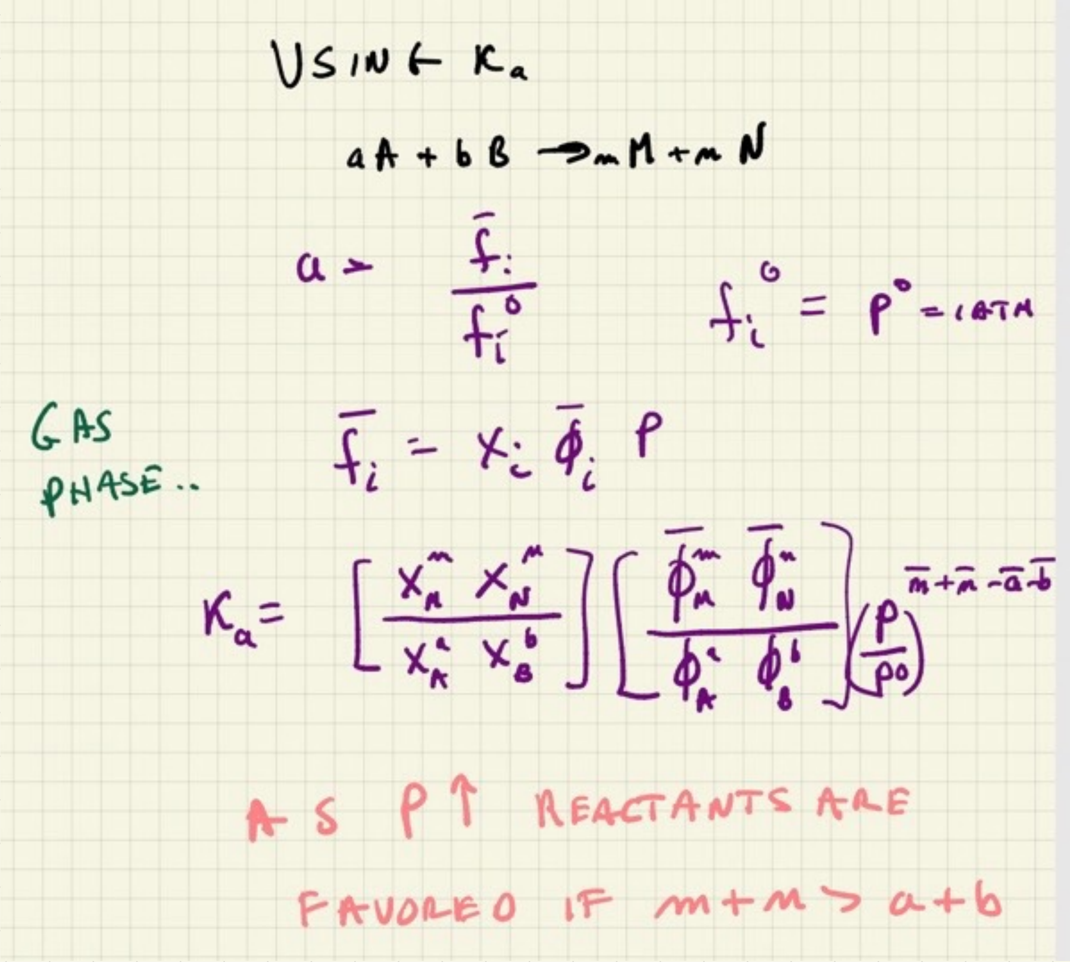
$$x_i \phi_i P$$

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

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

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

EXOTHERMIC
FAVORS
REACTANTS



USING K_a

$$aA + bB \rightarrow mM + nN$$

$$a \rightarrow \frac{\bar{f}_i}{f_i^\circ} \qquad f_i^\circ = P^\circ = 1\,\mathrm{ATM}$$

GAS
PHASE..

$$\bar{f}_i = x_i \bar{\phi}_i P$$

$$K_a = \left[\frac{x_M^m x_N^n}{x_A^a x_B^b}\right]\left[\frac{\bar{\phi}_M^m \bar{\phi}_N^n}{\phi_A^a \phi_B^b}\right]\left(\frac{P}{P^0}\right)^{\bar{m}+\bar{n}-\bar{a}-\bar{b}}$$

AS $P\uparrow$ REACTANTS ARE
FAVORED IF $m+n > a+b$

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

$$K_a = 6.6\times10^{-3}$$

$\boxed{\text{REACTANTS FAVORED!!}}$

$$K_a = \frac{X_{NH_3}}{X_{N_2}^{1/2}\, X_{H_2}^{3/2}} \; \frac{\phi_{NH_3}}{\phi_{N_2}^{1/2}\, \phi_{H_2}^{3/2}} \left[\frac{1}{P}\right] \left[1\,ATM\right]$$

WOULD BE 1'S FOR EXAM

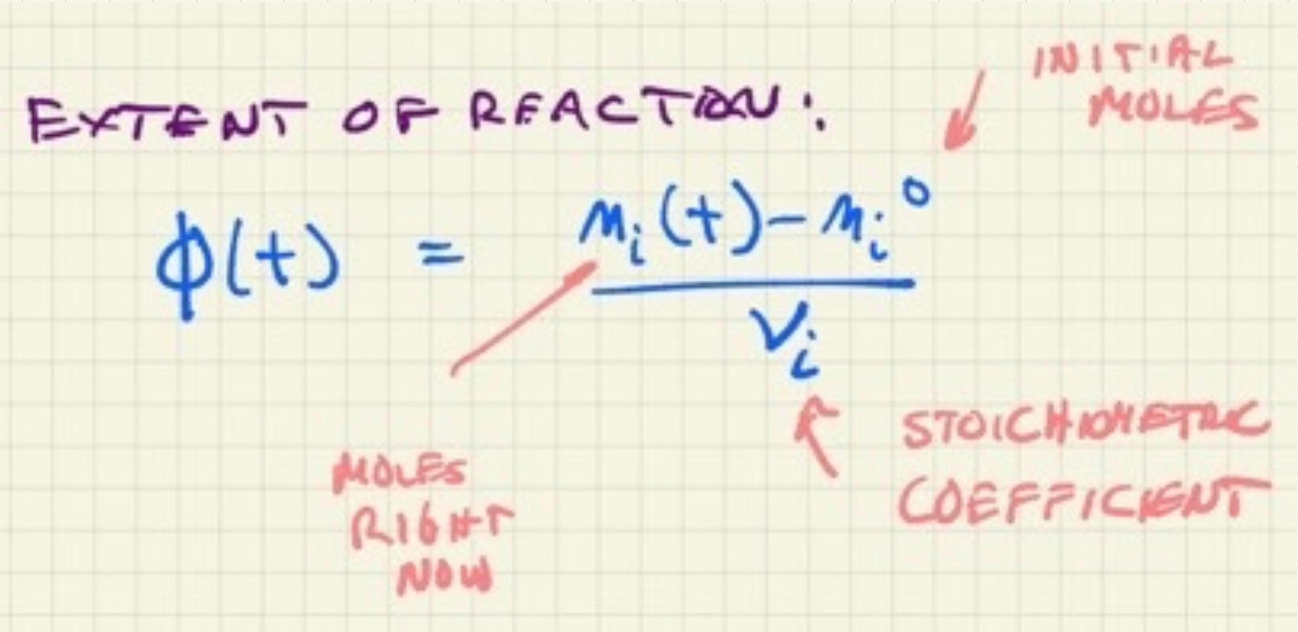
$$\frac{X_{NH_3}}{X_{N_2}^{1/2}\, X_{H_2}^{3/2}} = \frac{(1.14)^{1/2}(1.09)^{3/2}}{(.91)} \underbrace{(6.6\times10^{-3})}_{F(T)} \underbrace{(300\,ATM)}_{P} \left(\frac{1}{1\,ATM}\right)$$

$$= 2.64$$

MOST IMPT

STOICHOMETRIC TABLE

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



EXTENT OF REACTION:

INITIAL MOLES

$$\phi(t) = \frac{n_i(t) - n_i^{0}}{\nu_i}$$

MOLES RIGHT NOW

STOICHIOMETRIC COEFFICIENT

IF I USE THIS "LINGO" I'LL TELL YOU WHAT IT MEANS...

REACTION RATES

FOR NOW WE HAVE BEEN USING

$$\frac{\text{REACTION RATES}}{\text{VOLUME}}$$

$$r = \frac{1}{V}\frac{d\phi}{dt}$$

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

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

COULD BE:

$$r = kC_A, \quad kC_AC_B \ldots\ldots$$

ELEMENTARY REACTIONS

$$H_2 + Br_2 \rightarrow 2HBr$$

INITIATION $Br_2 + \text{"LIGHT"} \rightarrow 2Br^{\cdot}$

PROPAGATION $Br^{\cdot} + H_2 \rightarrow HBr + H^{\cdot}$

PROPAGATION $H^{\cdot} + Br_2 \rightarrow HBr + Br^{\cdot}$

TERMINATION $2Br^{\cdot} \rightarrow Br$

"MIGHT" TELL US MORE ABOUT REACTION RATE EXPRESSION

WE DIDN'T USE THESE TO DERIVE ANYTHING SO FAR.. – BUT JUST KNOW THIS COULD BE WHY..

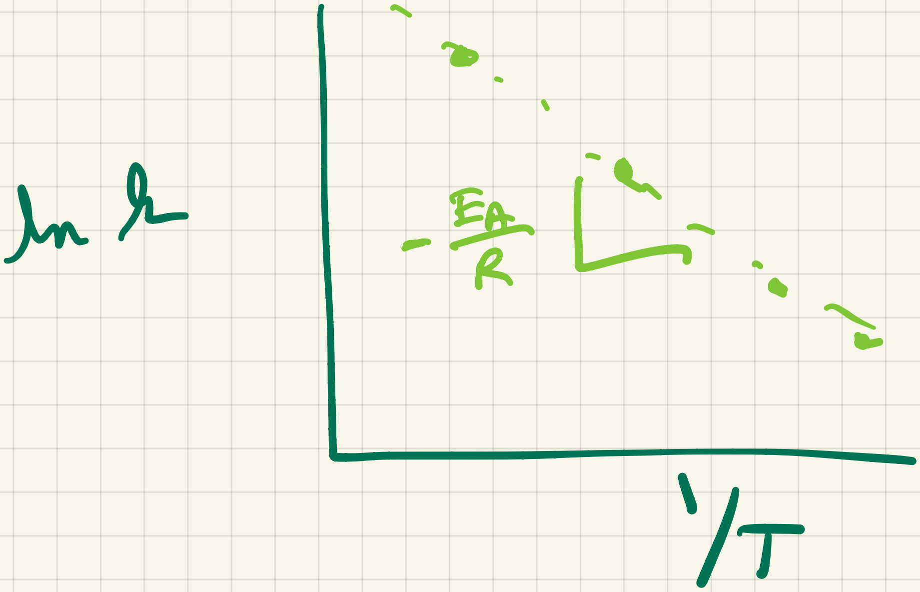
$$r = \frac{k_1 C_{H_2} C_{Br}^{1/2}}{k_2 + \frac{C_{HBr}}{C_{Br_2}}}$$

SOME GENERAL OBSERVATIONS ABOUT RATES OF REACTION:

$$r = k(T)\,\bar{F}(C_i, T)$$

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

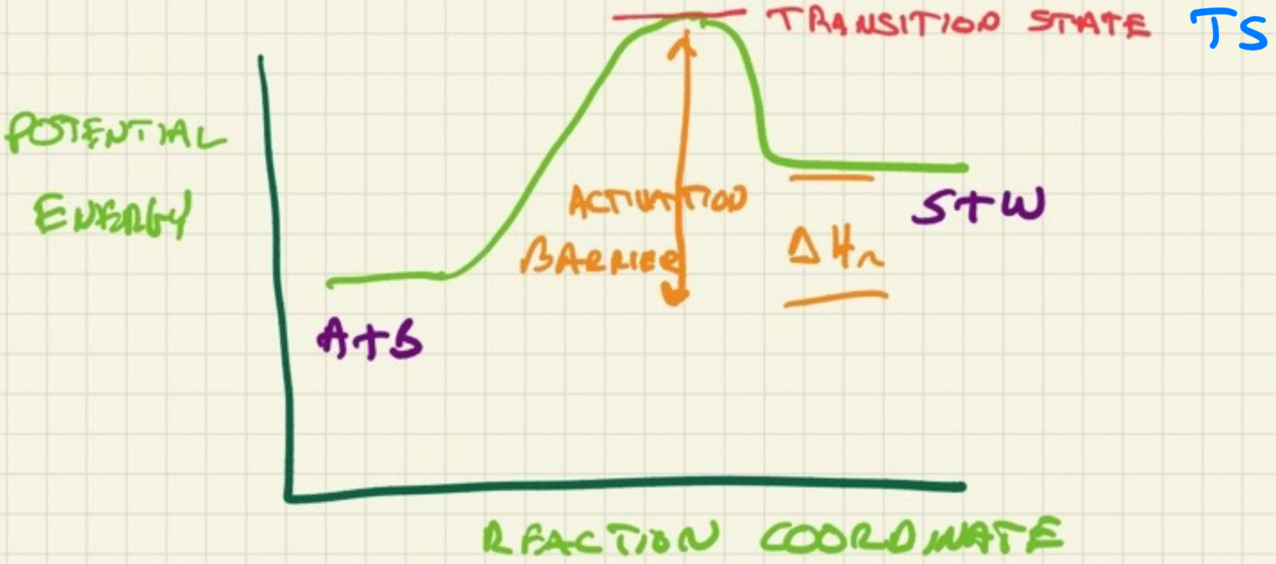
EXPECT SIGNIFICANT
CHANGE OF RATES
WITH T



AN EXPLANATION OF ARRHENIUS

"TRANSITION STATE THEORY"

$A + B \rightleftharpoons S + W$



$$A + B \rightleftharpoons S + W$$

$$A + B \rightleftharpoons TS$$

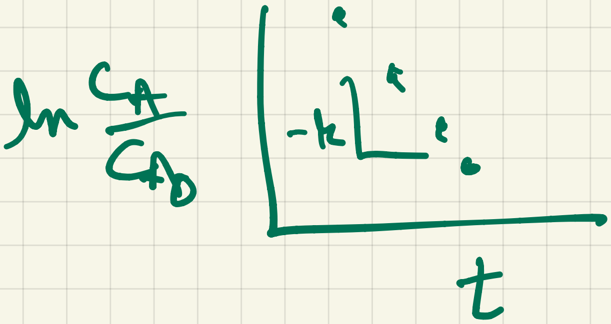
$$(\Delta G = \Delta H - T\Delta S)$$

$$\Rightarrow \quad r = \underbrace{\frac{\bar{k}T}{h}\exp\left[\frac{\Delta S_0^{\#}}{R}\right]}_{A}\underbrace{\exp\left[-\frac{\Delta H_0^{\#}}{RT}\right]}_{\exp\left(-\frac{E_A}{RT}\right)} c_A c_B$$

SOME RATE EXPRESSIONS

FIRST ORDER

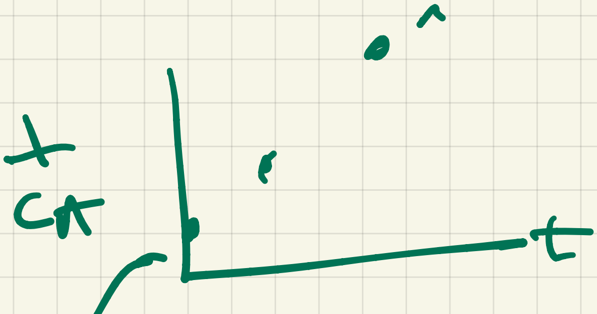
$r = kC_A$ $\qquad A \longrightarrow M$



$C_A = C_{A0}\exp(-kt)$

2ND ORDER

$r = kC_AC_B$ $\qquad A + B \longrightarrow 2M$



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

WITH A CATALYST, E THAT IS LIMITING

$A \rightarrow M,$

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

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

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

USE $\frac{dC_{AE}}{dt} = 0$ STEADY-STATE

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

FOR C_A SUFFICIENTLY SMALL..

$$k_1 C_A << k_2 \text{ or } k_r$$

$$\frac{dC_A}{dt} \cong - \frac{k_2 k_2 C_E^0}{(k_2 + k_r)} C_A$$

FIRST ORDER

$$= -K \, C_A$$

FOR C_A SUFFICIANTLY LARGE

$$k_1 C_A >> k_2 + k_r$$

ZERO ORDER

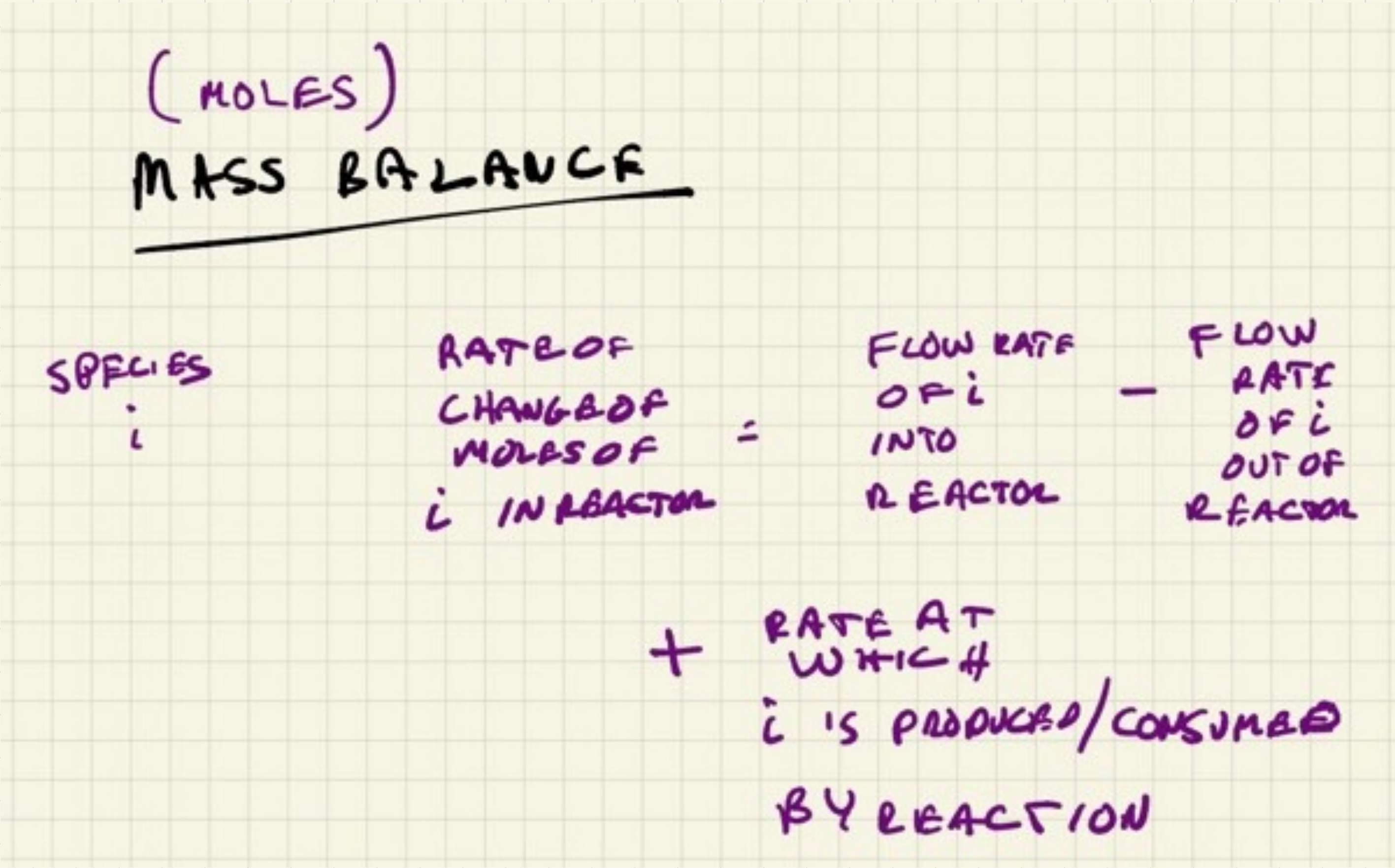
$$\frac{dC_A}{dt} = - k_2 C_{E_0} = -K$$

FIRST ORDER IN E_0

CHAPTER 3

ANALYSIS OF SIMPLE REACTORS

- BATCH
- CSTR
- PFR



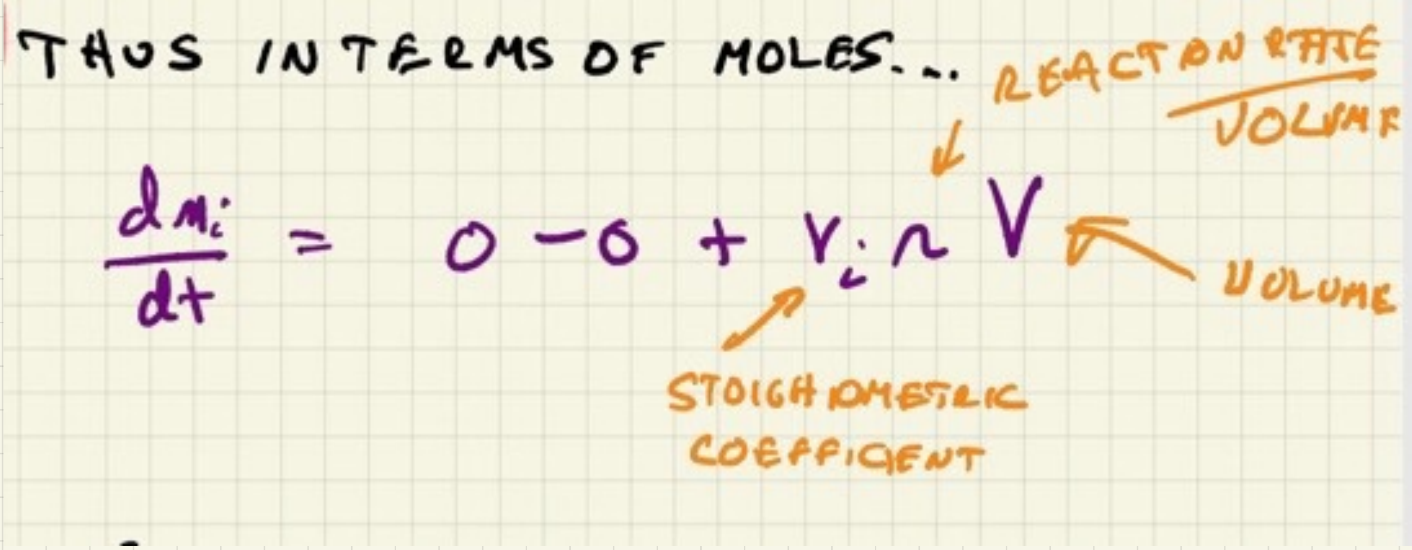
(MOLES)

MASS BALANCE

SPECIES i

RATE OF CHANGE OF MOLES OF i IN REACTOR = FLOW RATE OF i INTO REACTOR − FLOW RATE OF i OUT OF REACTOR

+ RATE AT WHICH i IS PRODUCED/CONSUMED BY REACTION



THUS IN TERMS OF MOLES...

REACTION RATE / VOLUME

$$\frac{dn_i}{dt} = 0 - 0 + \nu_i r V$$

VOLUME

STOICHIOMETRIC COEFFICIENT

WE CAN WRITE!

$$\frac{d\,c_i V}{dt} = \nu_i r V \qquad V = \text{CONST}$$

$$A \to M, \quad r = kC_A$$

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

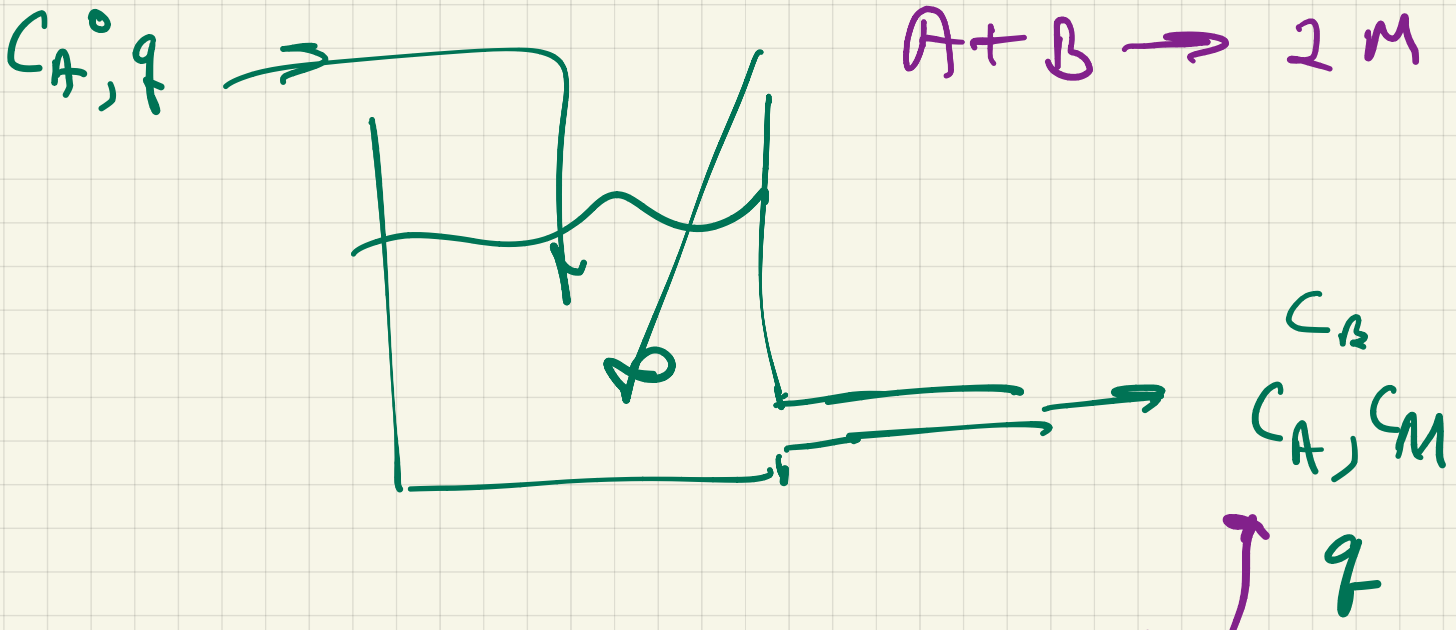
$$\ln\frac{C_A}{C_{A0}} = -kt$$

$$C_A = C_{A0}\exp(-kt)$$

OR 2ND ORDER $\sim \left(\frac{1}{C_A} - \frac{1}{C_A^0}\right) = kt$

CSTR

$A + B \rightarrow 2M$



OPERATES AT EXIT COMPOSISTION

$$r = kC_AC_B$$

SO IF YOU WANT HIGH CONVERSION, $C_A \ll C_A^0$

RATE WILL BE LOW ...

NEED A LARGE REACTOR!!

A $\quad 0 = q_A C_{A0} - q C_A - k C_A C_B V$

B $\quad 0 = q_B C_{B0} - q C_B - k C_A C_B V$

M $\quad = 0 - q C_M + 2 k C_A C_B V$

$$q = q_A + q_B$$

CAN ALWAYS SOLVE FOR C_B

(SUBTRACT FIRST 2 EQ'S)

$$C_B = \frac{1}{q}\left(q_B C_{B0} - q_A C_{A0}\right) + C_A$$

REACTOR TIME SCALE

$$\tau = \frac{V}{q}$$

SPACE TIME
RESIDENCE TIME

REACTION TIME SCALE

$$\frac{1}{k}, \qquad \frac{1}{k C_{A0}}$$

FIRST ORDER

2ND ORDER

FIRST ORDER CSTR

$$0 = q C_{A0} - q C_A - k C_A V$$

$$\frac{C_A}{C_{A0}} = \frac{1}{1 + k\tau} \qquad \tau = \frac{V}{q}$$

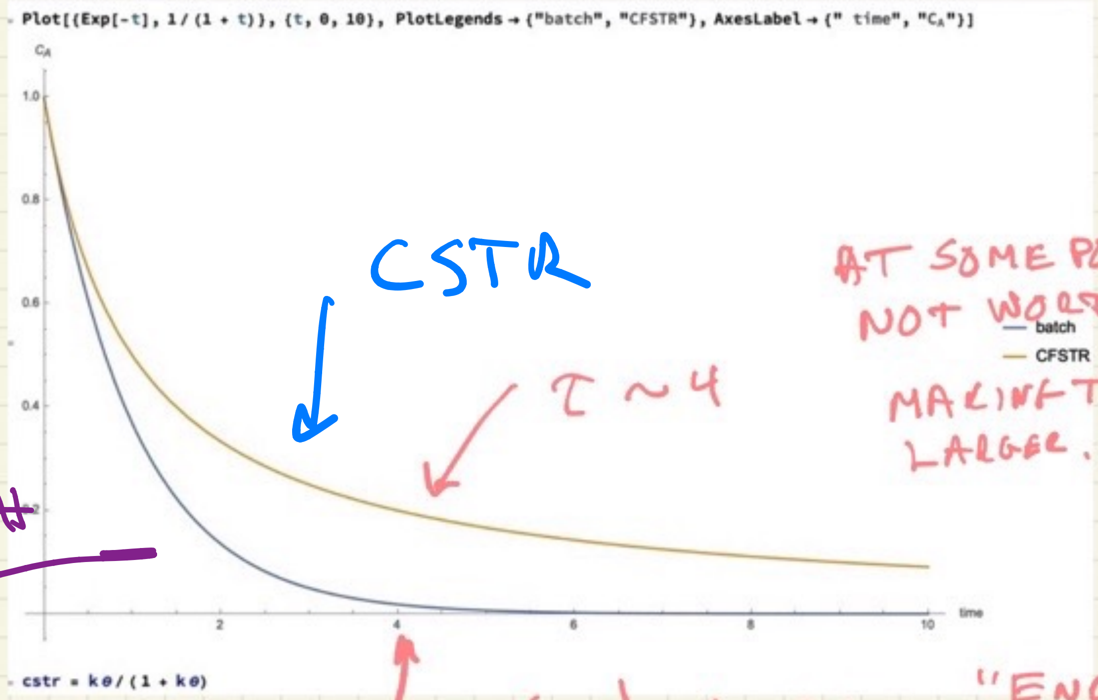
For M $\quad 0 = -q\,C_M + k\,C_A\,V$

$$C_M = k\,\tau\,C_A$$

$$\frac{C_M}{C_{A_0}} = \frac{k\,\tau}{1 + k\,\tau}$$

COMPARE TO BATCH!

$$\frac{C_A}{C_{A_0}} = \exp(-kt)$$



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Plot[{Exp[-t], 1/(1 + t)}, {t, 0, 10}, PlotLegends → {"batch", "CFSTR"}, AxesLabel → {" time", "CA"}]
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```
cstr = kθ/(1 + kθ)
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CSTR

BATCH

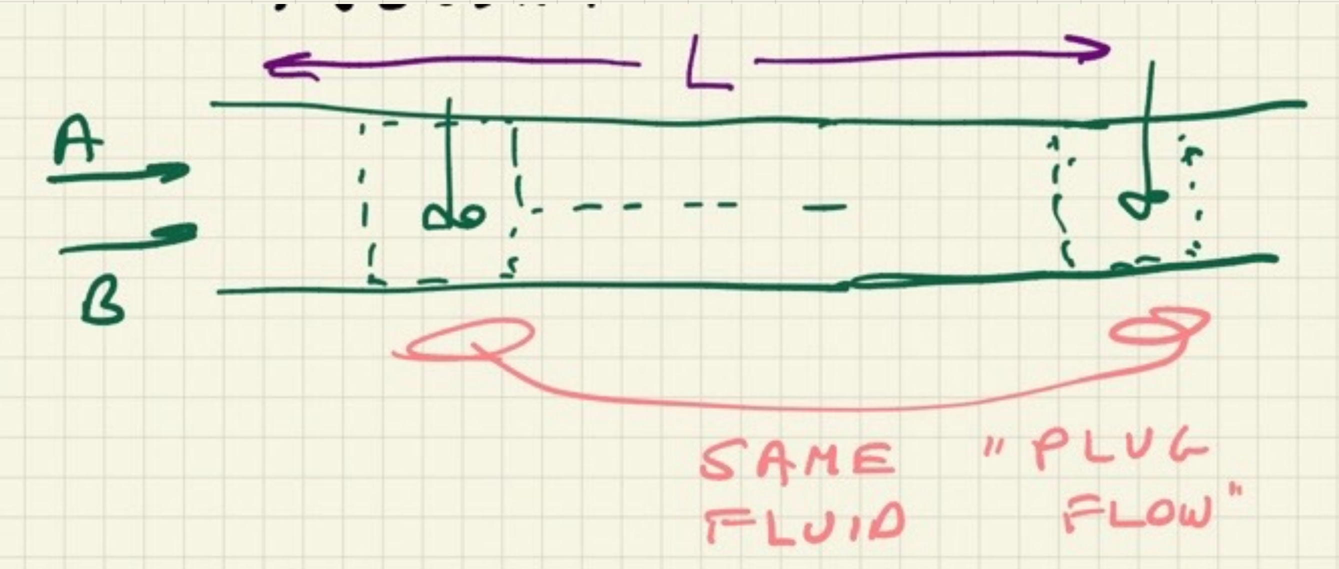
$\tau \sim 4$

AT SOME POINT NOT WORTH MAKING THIS LARGER...

$\exp(-4) < .02$

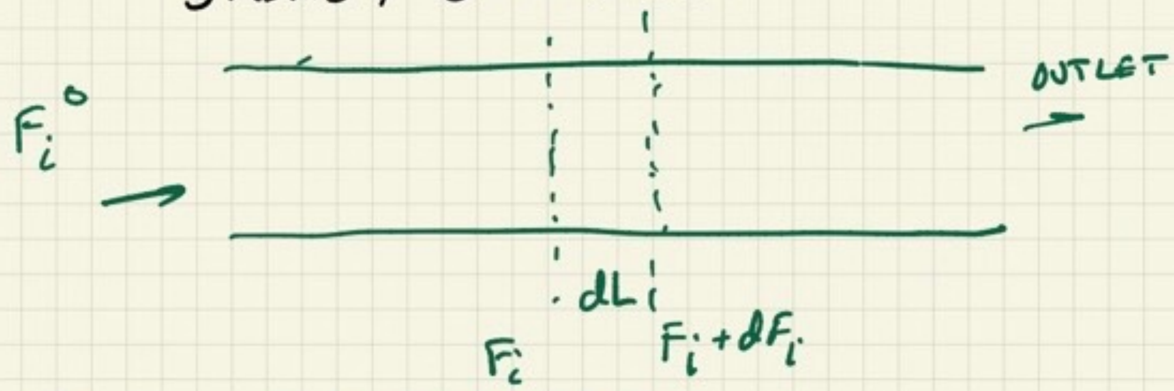
"END" FOR A 1ST ORDER CHANGE PROCESS.

PLUG FLOW REACTOR:



PFR ANALYSIS

STEADY OPERATION



FOR DIFFERENTIAL SLICE:

$$0 = \underbrace{F_i}_{\text{MOLAR FLOW IN}} - \underbrace{(F_i + dF_i)}_{\text{MOLAR FLOW OUT}} + \underbrace{\nu_i r A_c dL}_{\text{MOLES REACTED}}$$

$$\frac{1}{A_c}\frac{dF_i}{dL} = \nu_i r$$

[redacted]

$$F_i = q C_i \qquad \tau = \frac{V}{q}$$

$$\frac{q}{A_c}\frac{dC_i}{dL} = \frac{dC_i}{d\tau} = \nu_i r$$

SAME AS BATCH REACTOR

$$A \longrightarrow M$$

$$\frac{dC_A}{d\tau} = -kC_A$$

$$\frac{C_A}{C_{A0}} = \exp(-k\tau)$$

COULD ASK FOR C_A, OR

$\tau \Longrightarrow$ VOLUME OF REACTOR

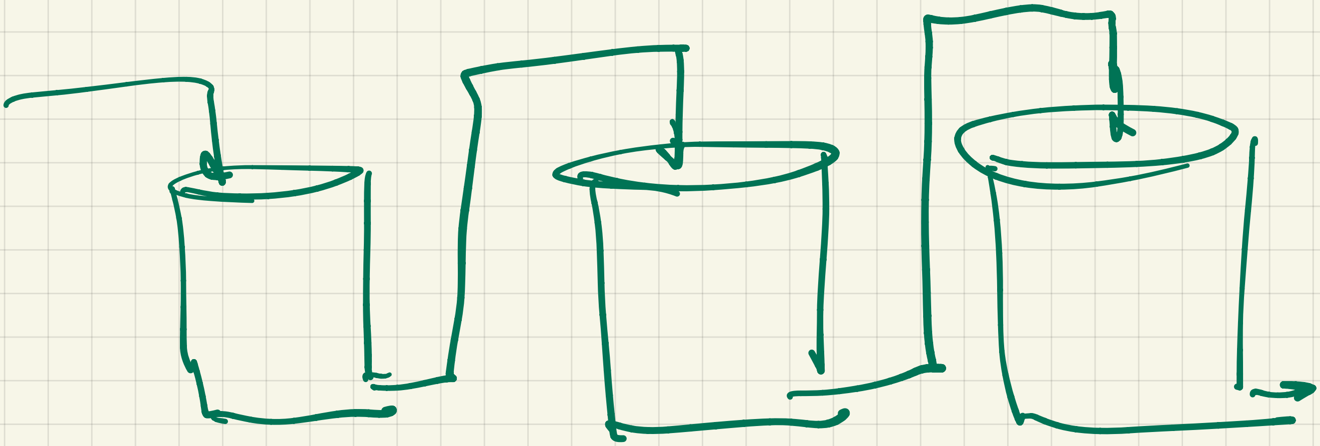
ALSO FROM MON:

"PRODUCTION" = $q C_M$

MOLES OF
PRODUCT/TIME

ONE LAST POINT:

IF YOU "LIKE" CSTR BUT
PERFORMANCE NOT QUITE
WHAT YOU NEED!



USE 2, 3, 4 ... IN SERIES.