

b) ANALYSIS OF A SERIES REACTION



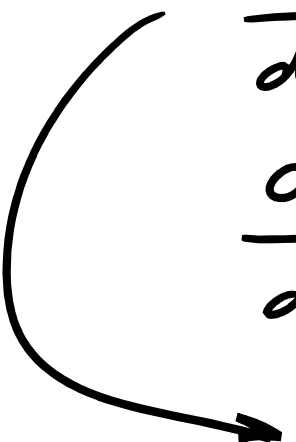
ALL FIRST
ORDER

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$C_A = C_{A0} @ t=0$$

$$\frac{dC_B}{dt} = k C_A - k_2 C_B$$

$$C_B = C_{B0} @ t=0$$



$$C_A = C_{A0} e^{-k_1 t}$$

$$\frac{dc_B}{dt} = k_1 \underbrace{c_{A0} e^{-k_1 t}} - k_2 c_B$$

$$\underbrace{\frac{dc_B}{dt} + k_2 c_B}_{C_B} = \underbrace{k_1 c_{A0} e^{-k_1 t}}_t$$

THIS DIFFERENTIAL EQN IS SOLVED BY A
 PROCEDURE INVOLVING A HOMOGENEOUS SOLUTION
 & A PARTICULAR SOLUTION $C_B = C_B^H + C_B^P$

HOMOGENEOUS SOLN

$$\frac{dc_B^H}{dt} + k_2 c_B^H = 0$$

$$c_B^H = A_0 e^{-k_2 t}$$

DO NOT
INSERT
INITIAL CONDITIONS
YET!

PARTICULAR SOLN

$$\frac{dc_B^P}{dt} + k_2 c_B^P = k_1 c_{A0} e^{-k_1 t}$$

TRY $c_B^P = A_1 e^{-k_1 t}$

$$\frac{dc_B^P}{dt} = -A_1 k_1 e^{-k_1 t}$$

$$-A_1 k_1 \cancel{e^{-k_1 t}} + k_2 A_1 \cancel{e^{-k_1 t}} = k_1 C_{A0} \cancel{e^{-k_1 t}}$$

$$-A_1 k_1 + k_2 A_1 = k_1 C_{A0}$$

$$A_1 (k_2 - k_1) = k_1 C_{A0}$$

$$A_1 = \frac{k_1 C_{A0}}{k_2 - k_1}$$

AS LONG
AS $k_2 \neq k_1$

SO THE SOLUTION IS

$$C_B = C_B^H + C_B^P$$

$$C_B = A_0 e^{-k_2 t} + \frac{k_1 C_{A0}}{k_2 - k_1} e^{-k_1 t} \quad k_1 \neq k_2$$

APPLY INITIAL CONDITION TO FIND A_0 $C_B = C_{B0}$ @ $t = 0$

$$C_{B0} = A_0 (1) + \frac{k_1 C_{A0}}{k_2 - k_1} (1)$$

$$A_0 = C_{B0} - \frac{k_1 C_{A0}}{k_2 - k_1}$$

$$\frac{dc_B}{dt} = k_1 c_A - k_3 c_B - k_4 c_B$$

$$c_{Bi+1} = \left(k_1 c_{Ai} - (k_3 + k_4) c_{Bi} \right) \Delta t + c_{Bi}$$

PROGRAM....

$$k_1 = 0.15 \text{ min}^{-1}$$

$$k_2 = 0.14 \text{ min}^{-1}$$

$$k_3 = 0.11 \text{ min}^{-1}$$

$$k_4 = 0.12 \text{ min}^{-1}$$

$$k_5 = 0.08 \text{ min}^{-1}$$

$$c_{A0} = 100 \text{ mM}$$

$$c_{B0} = 0$$

$$c_{C0} = 0$$

$$c_{D0} = 0$$

$$c_{E0} = 0$$

$$C_B = C_{B0} e^{-k_2 t} + \frac{k_1 C_{A0}}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right] \quad k_1 \neq k_2$$

IF $C_{B0} = 0$

THEN

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[e^{-k_1 t} - e^{-k_2 t} \right] \quad k_1 \neq k_2$$

IF $C_{B_0}=0$ FIND $t_{\max}$, THE TIME AT WHICH B CONCENTRATION REACHES A MAXIMUM.

$$0 = \frac{dC_B}{dt} = \frac{k_1 C_{A_0}}{k_2 - k_1} \left[\underbrace{-k_1 e^{-k_1 t_{\max}} + k_2 e^{-k_2 t_{\max}}}_{=0?} \right]$$

$$k_1 e^{-k_1 t_{\max}} = k_2 e^{-k_2 t_{\max}}$$

$$\frac{k_1}{k_2} = e^{t_{\max}(k_1 - k_2)}$$

$$\ln \left(\frac{k_1}{k_2} \right) = t_{\max} (k_1 - k_2)$$

$$t_{\max} = \frac{\ln(k_1/k_2)}{k_1 - k_2}$$

$$k_1 \neq k_2$$

NOTE: BECAUSE OF STOICHIOMETRY

$$C_A + C_B + C_C = \text{CONSTANT} = C_{A0} + C_{B0} + C_{C0}$$

$$C_C = C_{A0} + C_{B0} + C_{C0} - C_B - C_A$$

EXAMPLE 7

let $C_{A0} = 100$
 $C_{B0} = 0$
 $C_{C0} = 0$

3 CASES

A)	$k_1 = 0.025$	$k_2 = 0.10$	$k_2 > k_1$
B)	$k_1 = 0.049$	$k_2 = 0.051$	$k_1 \approx k_2$
C)	$k_1 = 0.10$	$k_2 = 0.025$	$k_1 > k_2$