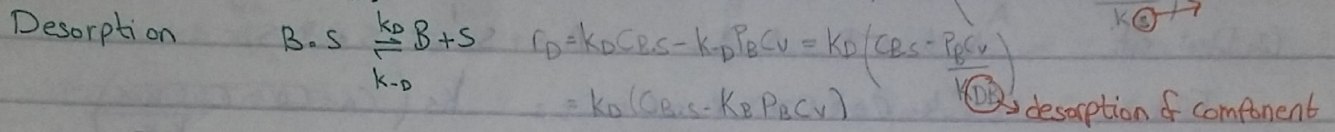
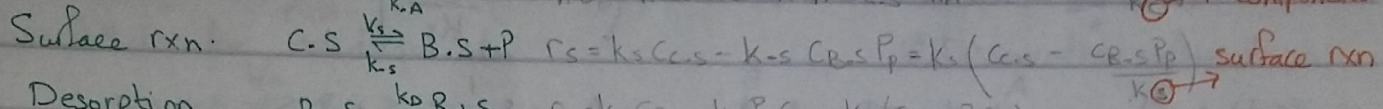
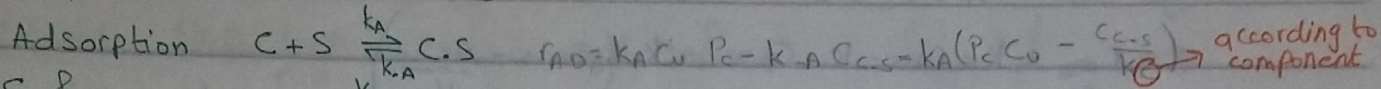


Studying chapter #10 - Fogler - From Page 701 To 713

→ Decomposition of cumene $C \rightarrow B + P$



units of $k_A: s^{-1} \cdot kPa^{-1}$ $k_A: s^{-1}$ $K_C: kPa^{-1}$
 $k_s: s^{-1}$ $k_s: (s \cdot kPa)^{-1}$ $K_S: kPa$
 $k_D: s^{-1}$ $k_D: (s \cdot kPa)^{-1}$ $K_D: kPa$ But $K_B = 1/K_D$

① Is adsorption is rate limiting step? $k_A \ll k_s, k_D$

* speaking strictly we must compare $k_A P_C$ with k_s & k_D in order to be consistent in units

overall rate of rxn expression $-r_C = r_{AD} = k_A (P_C C_V - \frac{C_{C \cdot S}}{K_C})$ is rate limiting step

• This means that

1. $\frac{r_C}{k_s} \approx 0 = \frac{C_{C \cdot S} + C_{B \cdot S} P_P}{K_S} - \frac{C_{C \cdot S}}{K_C} = \frac{C_{C \cdot S} - C_{B \cdot S} P_P}{K_S}$ (1)

2. $\frac{r_D}{k_D} \approx 0 = C_{B \cdot S} - K_B P_B C_V$ $C_{B \cdot S} = K_B P_B C_V$ substitute in (1)

$\Rightarrow C_{C \cdot S} = \frac{K_B P_B P_P C_V}{K_S}$

• $-r_C = r_{AD} = k_A (P_C C_V - \frac{K_B P_B P_P C_V}{K_S K_C})$ But Overall Partial Pressure eq. constant

$K_P = \frac{K_S K_C}{K_B}$

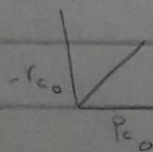
• Site balance $C_T = C_V + C_{C \cdot S} + C_{B \cdot S} = C_V + \frac{K_B P_B P_P C_V}{K_S} + K_B P_B C_V$

$C_V = \frac{C_T}{(1 + K_B P_B (\frac{P_P}{K_S} + 1))}$

$\Rightarrow -r_C = k_A (P_C C_V - \frac{P_B P_P C_V}{K_P}) = k_A C_V (P_C - \frac{P_B P_P}{K_P}) = \frac{k_A C_T (P_C - P_B P_P / K_P)}{(1 + K_B P_B P_P / K_S + K_B P_B)}$ ✓

- initial rate behaviour with respect to P_C

$-r_{C_0} = k_A C_T P_{C_0}$



linear relation

usually we first assume

② Is the surface-rxn rate limiting? $k_s \ll k_A P_C$

$$r_{AD} \approx 0 = k_A (P_C C_v - \frac{C_{C,s}}{K_C}) \quad K_C P_C C_v = C_{C,s}$$

$$r_D \approx 0 = k_D (C_{B,s} - \frac{P_B C_v}{K_{DB}}) \quad C_{B,s} = \frac{P_B C_v}{K_{DB}} = \frac{K_B P_B C_v}{K_{DB}}$$

$$-r'_C = r_s = k_s (C_{C,s} - \frac{C_{B,s} P_P}{K_s}) = k_s (K_C P_C C_v - \frac{K_B P_B C_v P_P}{K_s}) = k_s C_v (P_C - \frac{P_B P_P K_B}{K_s})$$

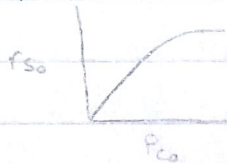
$$\text{site balance } C_T = C_v + C_{B,s} + C_{C,s} \rightarrow C_v = C_T - C_{B,s} - C_{C,s}$$

$$C_T = C_v + \frac{P_B C_v}{K_{DB}} + K_C P_C C_v \quad C_v = \frac{C_T}{(1 + P_B/K_{DB} + K_C P_C)}$$

$$\Rightarrow r_s = \frac{k_s C_T (P_C - P_B P_P K_B / K_s)}{1 + P_B K_B + K_C P_C} \quad P_C - \frac{P_B P_P K_B}{K_s} = \frac{K_P = K_s K_C}{K_B} \rightarrow K_C (P_C - \frac{P_B P_P}{K_P})$$

- initial rate behaviour wrt P_C

$$-r'_{C_0} = r_{s_0} = \frac{k_s C_T P_{C_0}}{1 + K_C P_{C_0}}$$



low $P_{C_0} \rightarrow k_s C_T P_{C_0}$
high $P_{C_0} \rightarrow k_s / K_C$

③ Is desorption of benzene rate limiting? $k_D \ll k_A P_C \& k_s$

$$r_{AD} \approx 0 \quad C_{C,s} = K_C P_C C_v$$

$$r_s \approx 0 \quad C_{C,s} = \frac{C_{B,s} P_P}{K_s} \quad C_{B,s} = \frac{K_s C_{C,s}}{P_P} = \frac{K_C K_s P_C C_v}{P_P}$$

$$r_D = k_D (C_{B,s} - K_B P_B C_v)$$

$$\text{site balance } C_T = C_v + C_{B,s} + C_{C,s} = C_v + K_C P_C C_v + \frac{K_C K_s P_C C_v}{P_P}$$

$$C_v = \frac{C_T}{1 + K_C P_C + K_C K_s P_C / P_P}$$

$$\rightarrow r_D = k_D \left(\frac{K_C K_s P_C C_v}{P_P} - K_B P_B C_v \right) = k_D C_v \left(\frac{K_s K_C P_C}{P_P} - K_B P_B \right) = \frac{K_D C_T (K_s K_C P_C / P_P - K_B P_B)}{1 + K_C P_C + K_C K_s P_C / P_P}$$

$$\frac{K_D C_T K_s K_C (P_C - P_B P_P / K_P)}{P_P + K_C P_C P_P + K_C K_s P_C} = \frac{K (P_C - P_B P_P / K_P)}{P_P + K_C P_C P_P + K_C K_s P_C} \quad \checkmark$$

- initial rate behaviour wrt P_C (to determine the dependence of initial rate on P_C)

$$-r_{C_0} = \frac{K P_{C_0}}{K_C K_s P_{C_0}} = \frac{K}{K_C K_s} = K_D C_T$$

iP inert was added in feed in ②

$$C_T = C_V + C_B \cdot S + C_C \cdot S + C_I \cdot S$$

$$\underline{C_{I \cdot S}} \quad C_{I \cdot S} = K_I P_I C_V$$

$$C_V = \frac{C_T}{1 + P_B K_B + K_C P_C + K_I P_I}$$

$$\rightarrow r_s = \frac{K_S C_T (P_C - P_B P_P K_B / K_S)}{1 + P_B K_B + K_C P_C + K_I P_I}$$

rxn of catalyst



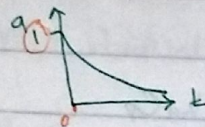
$$r_I = k_I P_I C_V - k_{-I} C_{I \cdot S} = k_I (P_I C_V - \frac{C_{I \cdot S}}{K_I})$$

$$r_I = 0 \rightarrow C_{I \cdot S} = P_I C_V K_I$$

10.7 Catalyst deactivation

- Mechanisms of deactivation are proposed by Butt and Petersen.
- analyzing rxn. over decaying catalyst $\rightarrow$ separable kinetics $-r_A' = a(-r_A')$ past history Fresh Catalyst
non separable kinetics $-r_A' = -r_A'(\text{Past, Fresh})$
existence of non ideal surface OR several element steps mechanism
- we will study only separable kinetics

$$a(t) = \frac{-r_A'(t)}{-r_A'(0)}$$



$$\rightarrow -r_A' = a(t) k_c(T) f_n(C_A, C_B, \dots, C_P)$$

$$\rightarrow r_d = \frac{-da}{dt} = P(a(t)) k_d h(C_A, C_B, \dots)$$

10.7.1 Types of catalyst deactivation

① Sintering or aging

- By $\rightarrow$ crystal agglomeration and growth of the metals deposited on support narrowing or closing of the pores inside the catalyst pellet.

- sintering usually negligible at $T < 40\%$ melting T of solid.

most common decay rate $r_d = k_d a^2 = \frac{da}{dt}$

$$\int_1^a \frac{da}{a^2} = k_d \int_0^t dt \quad \left. \frac{-1}{a} \right|_1^a = k_d t \quad \boxed{\frac{1}{a} = k_d t + 1}$$

$$-1 + \frac{1}{a} = k_d t \quad \frac{1}{a} = k_d t + 1$$

$$a(t) = \frac{1}{k_d t + 1} \quad S_a = \frac{S_{a0}}{k_d t + 1}$$

apply Arrhenius law $k = k_0 \exp\left(\frac{-E_a}{R\left(\frac{1}{T} - \frac{1}{T_0}\right)}\right)$

Example 10.5 Conversion as a function of time

$$A \rightarrow B \quad a(t) = \frac{1}{k_d t + 1} \quad -r_A = a(t) k C_A$$

$$\frac{dN_A}{dt} = -r_A V \quad N_{A0} \frac{dx}{dt} = \frac{W k C_A}{k_d t + 1} = \frac{W k' C_{A0} (1-x)}{k_d t + 1} = \frac{W k' N_{A0} (1-x)}{V(k_d t + 1)} \quad \text{let } k = \frac{k' W}{V}$$

$$\int_0^x \frac{dx}{1-x} = k \int_0^t \frac{dt}{k_d t + 1} \quad \ln(1-x) = \frac{k}{k_d} \ln(k_d t + 1)$$

$$\ln(1-x) = \frac{k}{k_d} \ln(k_d t + 1) \quad \ln(1-x) = \ln(k_d t + 1)^{k/k_d} \quad (1-x) = (k_d t + 1)^{k/k_d}$$

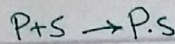
$$\boxed{x = 1 - (k_d t + 1)^{k/k_d}}$$

② Coking or Fouling

- $C_c = At^n$ Concentration of carbon on the surface
- Coking can be reduced by running at elevated pressure (2000-3000 kPa)
- Regeneration by burning ^{off} carbon "shrinking core model"

③ Poisoning

↳ Poison in feed



$$r_a = -\frac{da}{dt} = k_d C_p^m a^q = a(t) k_d C_p$$

$$-\frac{dC_t}{dt} = \frac{dC_{p.s}}{dt} = k_d (C_{t0} - C_{p.s}) C_p = r_{p.s}$$

Fraction of total number
F: of sites have been poisoned

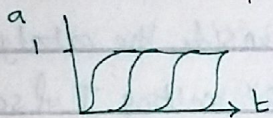
$$F = C_{p.s} / C_{t0}$$

Divide by C_{t0} $\frac{dF}{dt} = k_d (1-F) C_p$

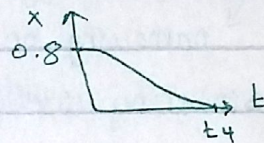
The activity

$$-dF = da$$

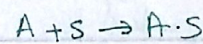
• Packed bed reactor poisoning



$$t_1 < t_2 < t_3 < t_4$$



↳ Poisoning by reactants or products



• if constant C_p and no spatial variation

$$r_a = -\frac{da}{dt} = k_d C_p^n a^n = k_d a^n$$

if first order $r_a = k_d a = -\frac{da}{dt}$ $\int_0^t k_d dt = \int_1^a \frac{-da}{a}$

$$k_d t = -\ln a$$

$$a = \exp(-k_d t)$$

⇒ Empirical decay laws

• $-\frac{da}{dt} = \beta_0$ $\int_1^a -da = \int_0^t \beta_0 dt$ $1-a = t\beta_0$ $a = 1-\beta_0 t$

• $-\frac{da}{dt} = \beta_1 a$ $\int_1^a \frac{da}{a} = -\int_0^t \beta_1 dt$ $\ln a = -\beta_1 t$ $a = \exp(-\beta_1 t)$

• $-\frac{da}{dt} = \beta_2 a^2$ $\int_1^a \frac{da}{a^2} = -\int_0^t \beta_2 dt$ $1 - \frac{1}{a} = -\beta_2 t$ $\frac{1}{a} = 1 + \beta_2 t$

$$\bullet \frac{-da}{dt} = \beta_3 a^n A_0^{1/5} \quad n = \frac{\beta_3 + 1}{\beta_3} \quad \int_1^a \frac{da}{a^n} = -\beta_3 A_0^{1/5} t \int_0^t dt \quad -n(a^{-n-1} - 1) = -\beta_3 A_0^{1/5} t$$

$$-n-1 = \frac{-\beta_3 - 1}{\beta_3} - 1 = \frac{-2\beta_3 - 1}{\beta_3}$$

$$n-1 = \frac{\beta_3 + 1}{\beta_3} - 1 = \frac{\beta_3 + 1 - \beta_3}{\beta_3} = \frac{1}{\beta_3} \quad \frac{1}{n-1} = \beta_3 \quad a^{-n} \quad (-n) a^{-n-1} \Big|_1^a \quad \frac{a^{-n-1}}{a^{-n-1} - 1}$$

→ In order to offset the decline chemical activity in decaying catalyst in Continuous Flow reactor

① Slow decay → Temperature time trajectories 10.7.2

Poisoning, used for hydrocracking

$$t = \frac{1 - \exp\left(\frac{EA - nEA + Ed}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)}{k_{d0} (1 - n + Ed/EA)}$$

n : decay order

EA : activation energy for main rxn

Ed : activation energy for catalyst decay

② Moderate decaying → Moving bed reactor

Catalytic cracking (coking)

$$\frac{dx}{dw} = \frac{a (1 - R'_A(t=0))}{F_{A0}}$$

$$\text{But } dt = \frac{dw}{U_s}$$

if first order decaying

$$-\frac{da}{dt} = k_d a^n \Rightarrow -\frac{da}{dw} = \frac{k_d a^n}{U_s}$$

assuming
steady state
Feed & catalyst at
the same speed.
diluted
with inert
constant
volume
assumed

• Example 10.7

$$-R'_A = 0.6 CA^2$$

$A \xrightarrow{k_d} \text{Products}$ First order decay rate, independent gas-phase

$$k_d = 0.72 \text{ min}^{-1} \text{ constant volume}$$

$$W = 22 \text{ kg} \quad U_s = 10 \text{ kg/min} = 10^4 \text{ g/min}$$

$$F_{A0} = \frac{30 \text{ mol}}{\text{min}} \quad C_{A0} = 0.07 \frac{\text{mol}}{\text{dm}^3} \quad X?$$

Design Equation

$$\frac{dx}{dt} = \frac{a (1 - R'_{A0})}{F_{A0}}$$

$$\frac{dx}{dt} = \frac{e^{-0.72t}}{30} \cdot \frac{2.94 \times 10^{-4} (1-x)^2}{30}$$

$$\frac{dx}{dw} = \frac{dS_B A_c dz}{S_B A_c dz} = S_B A_c dz$$

$$r_A = S_B r_A'$$

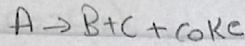
③ Fast decaying $\rightarrow$ Straight through transport reactor (STTR) OR circulating Fluidized bed (CFB) usually coking

$$\frac{dx}{dz} = \frac{S_B a(z/U_p) - r_A'}{F_{A0}} = \frac{S_B a(z/U_p) - r_A'}{C_{A0} U_g}$$

$$z = L = \frac{z}{U_p}$$

$$F_{A0} = C_{A0} U_g A_c$$

Example 10.8



$$C_{A0} = \frac{P_{A0}}{RT_0} = 0.2 \frac{\text{kmol}}{\text{m}^3}$$

$$Z = 10 \text{ m}$$

$$D = 1.6 \text{ m}$$

$$P_{A0} = 12$$

$$T_0 = 400$$

$$S_B = 80$$

$$U_g = 2.5$$

$$-r_A' = \frac{k' P_A}{1 + K_A P_A + K_B P_B + K_C P_C}$$

$$k' = 0.0014$$

$$K_A = 0.05$$

$$K_B = 0.15$$

$$K_C = 0.1$$

$$a = \frac{1}{1 + AE^{1/2}} \quad A = 7.6$$

activity & Conversion?

$\rightarrow$ Activity

$$a = \frac{1}{1 + 0.76 E^{1/2}}$$

$$E = \frac{z}{U_p}$$

$$a = \frac{1}{1 + 0.76 \sqrt{z} U_p^{-1/2}}$$

$$= \frac{1}{1 + 2.4 U_p^{-1/2}}$$

$$\rightarrow \frac{dx}{dz} = \frac{80 \times \frac{1}{1 + 2.4 U_p^{-1/2}} \times \frac{0.0014 P_A}{1 + 0.05 P_A + 0.15 P_B + 0.1 P_C}}{0.2 \times 2.5}$$

assuming $U = U_g = U_p$

$$U = \frac{V}{A_c} = \frac{V_0 (1 + \epsilon X)}{A_c}$$

$$\epsilon = Y_{A0} \delta$$

$$\delta = 1, Y_{A0} = 1$$

$$U = U_0 (1 + \epsilon X)$$

$$P_A = P_{A0} \frac{(1 - X)}{(1 + \epsilon X)}$$

$$P_B = P_C = \frac{P_{A0} X}{(1 + \epsilon X)}$$

CHAPTER #13

Distributions of residence times for chemical reactors

PART 1 Characterization and diagnostics

→ Major uses for residence time distribution → diagnose problems
predict conversion exiting for new reaction

• Examples of non ideality

1. ESTR bubble residence time gas-liquid stirred tank reactor

2. PBR channeling

3. CSTR bypass & dead zones

→ Three concepts in characterization

residence time distribution / quality of mixing / model used to describe the system

⇒ Thinking about non ideal reactor

step 1 considering either CSTR or PBR PFR → Plug Flow reactor

step 2 macromixing information (RTD)

step 3 micromixing information (To take prediction about conversion)

13.1.1 RTD Function

* not all RTD are unique to a particular reactor type, it depends also on the type of mixing occurring within it.

13.2 Measurement of the RTD "Tracer"

• Tracer properties

1. non reactive species that is easily detectable

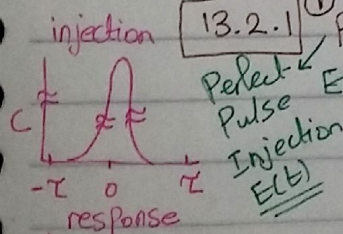
2. similar properties to that in the mixture and completely soluble in the mixture

3. not be adsorb on the wall or other surface in the reactor

→ colored and radioactive materials along with inert gases are the most common

13.2.1 Pulse input experiment

single input single output with flow (no dispersion)



$$E(t) = \frac{\Delta N}{N_0} = \frac{C(t) \dot{V} \Delta t}{\int_0^\infty C(t) \dot{V} dt}$$

$$E(t) \Delta t = \frac{N}{N_0} \Rightarrow E(t) = \frac{1}{\Delta t} \frac{N}{N_0}$$

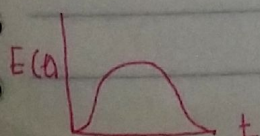
residence time distribution Function

$$E(t) = \frac{C(t)}{\int_0^\infty C(t) dt}$$

• Alternative way

Fraction of material leaving has resided from t_1 to t_2

$$\int_0^\infty E(t) dt = 1$$

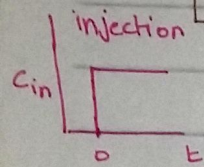


Drawbacks (Disadvantages)

1. pulse time must be short relative to residence time in various segments
2. no dispersion (must be negligible) between the tracer injection and entrance
3. long C curve tail $\Rightarrow$ approximate by exponential decay (for integration).

Example 13.1

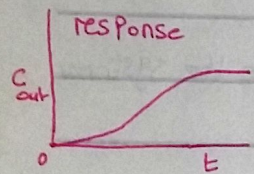
13.2.2 (2) Positive step tracer experiment (imperfect pulse injection) $\underline{F(t)}$



$$C_0(t) = \begin{cases} 0 & t < 0 \\ C_0 & t \geq 0 \end{cases} \quad \text{"Dirac delta function"}$$

$$C_{out}(t) = \int_0^t C_{in}(t-t') E(t') dt'$$

$\underbrace{E(t') \text{ as function}}$



* The concentration of tracer in the feed is kept until the effluent concentration in the effluent is indistinguishable from that in the feed.

Since C_{in} is constant

$$\left[\frac{C_{out}(t)}{C_{in}} \right]_{\text{step}} = \int_0^t (t-t') E(t') dt' = F(t) \quad \text{accumulative function}$$

$$E(t) = \frac{d [C_{out}(t)/C_{in}]_{\text{step}}}{dt} = \frac{d F(t)}{dt}$$

Advantages

* Experimentally, step is easier than pulse.

* The total amount concentration (amount) of tracer not have to be known.

Disadvantages

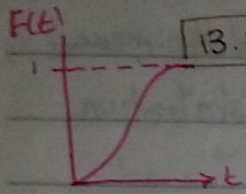
1. requires big amount of tracer.
2. difficulty in maintaining constant concentration.
3. large errors may appear when differentiation.

(3) Other methods other than ⁺ve step and pulse

- ve step (elution), frequency-response methods
- They are usually more difficult to be carried on.

13.3 Characteristic of the RTD

$E(t)$ is called "exit-age distribution Function"



13.3.1 Integral relationship

$$F(t) = \int_0^t E(t) dt \quad t \text{ time or less (effluent)}$$

$$1 - F(t) = \int_t^{\infty} E(t) dt \quad \text{longer than time } t \text{ (effluent)}$$

$F(t)$ sometimes is used in the same manner as RTD in reactor modeling

13.3.2 Mean residence time

$$\tau = t_m = \int_0^{\infty} t E(t) dt$$

- Assuming constant volume and [no dispersion] (closed systems)
- For gas phase, $\varepsilon = 0 \Rightarrow V$ is constant, no P drop, isothermal

$$\text{if } \varepsilon \neq 0 \quad \tau = \frac{t_m}{1 + \varepsilon x} \quad t_m = \frac{\tau}{1 + \varepsilon x}$$

Proof maize filling reactor, at $t=0 \quad V=V$

Definition maize leaving at $t > 0 \Rightarrow dV = v dt (1 - F(t))$

$$V = \int_0^{\infty} v (1 - F(t)) dt \quad \text{Since } v \text{ is constant}$$

$$\tau = \frac{V}{v} = \int_0^{\infty} (1 - F(t)) dt \quad \text{Integration by parts}$$

$$\tau = t(1 - F(t)) \Big|_0^{\infty} - \int_0^{\infty} t(dF(t)) = t(1 - F(t)) \Big|_0^{\infty} + \int_0^{\infty} t E(t) dt$$

$$\tau = \int_0^{\infty} t E(t) dt \quad (1)$$

Definition

First moment, mean value

$$t_m = \frac{\int_0^{\infty} t E(t) dt}{\int_0^{\infty} E(t) dt} = \int_0^{\infty} t E(t) dt \quad (2)$$

(1) & (2) are equal #

13.3.3 Other moments of RTD

$\int_0^\infty (t^2 - 2t t_m + t_m^2) E(t) dt$ Second moment variance, squared of standard deviation, σ^2

$$\int_0^\infty t^2 E(t) dt - 2t_m \int_0^\infty t E(t) dt + t_m^2 \int_0^\infty E(t) dt$$

$$\sigma^2 = \int_0^\infty (t - t_m)^2 E(t) dt$$

distribution around the mean spread around distribution

Third moment skewness

$$S^3 = \frac{1}{\sigma^{3/2}} \int_0^\infty (t - t_m)^3 E(t) dt$$

extent the distribution is skewed in one direction or another in mean reference

Example 13.2

13.3.4 Normalized RTD Function $E(\theta)$

- dealing with θ instead of t $\theta = \frac{t}{\tau}$ $E(\theta) = \tau E(t)$ $\int_0^\infty E(\theta) d\theta = 1$
- θ represents the number of reactor volumes of fluid based on entrance conditions that has flowed through the reactor at time t
- Purpose: Flow performance inside reactor at different sizes can be compared directly
- For CSTR $E(t) = \frac{1}{\tau} e^{-t/\tau}$ $E(\theta) = e^{-\theta}$

13.3.5 Internal age distribution not included

13.4 RTD in ideal reactors

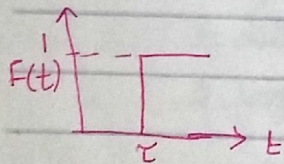
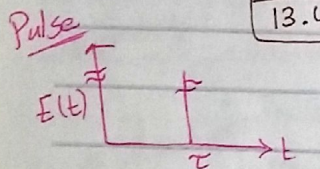
13.4.1 RTDs in batch and plug flow reactors

$$E(t) = \delta(t - \tau) \quad \int_0^\infty E(t) dt = 1$$

$$t_m = \int_0^\infty t \delta(t - \tau) dt = \tau$$

$$\sigma^2 = \int_0^\infty (t - \tau)^2 \delta(t - \tau) dt = 0$$

$$F(t) = \int_0^t E(t) dt = \int_0^t \delta(t - \tau) dt$$



13.4.2 Single CSTR RTD

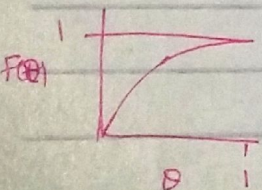
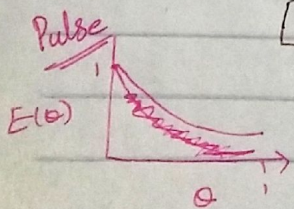
mass balance on tracer

in - out = accumulation

$$0 - V \frac{dc}{dt} = v c$$

$$\int_{-\tau}^0 dt = \int_{c_0}^c \frac{dc}{c}$$

$$\frac{t}{\tau} = \ln \frac{c_0}{c} \quad C = C_0 \exp^{-t/\tau}$$



$$E(t) = \frac{C(t)}{\int_0^\infty C(t) dt} = \frac{C_0 \exp^{-t/\tau}}{\int_0^\infty C_0 \exp^{-t/\tau} dt} = \frac{\exp(-t/\tau)}{-\tau \exp(-t/\tau)} = \frac{e^{-t/\tau}}{\tau}$$

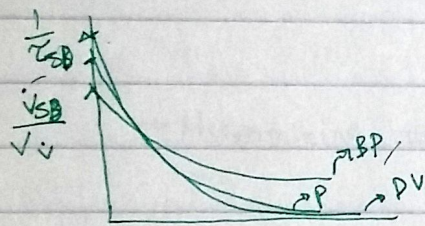
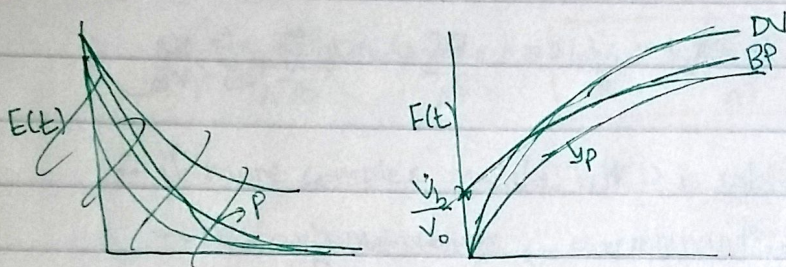
$$E(0) = \frac{1}{\tau} E(t) = \frac{1}{\tau} e^{-t/\tau} = e^{-0} = 1$$

$$t_m = \int_0^\infty t E(t) dt = \int_0^\infty \frac{t}{\tau} e^{-t/\tau} dt = \left[-t e^{-t/\tau} \right]_0^\infty = \tau$$

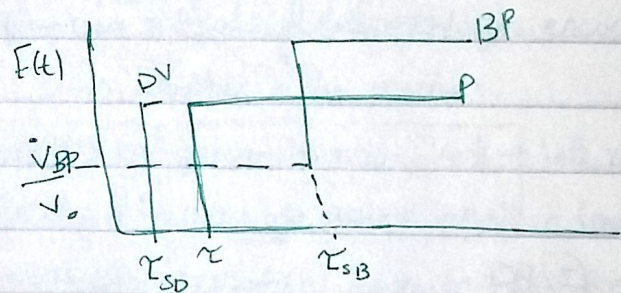
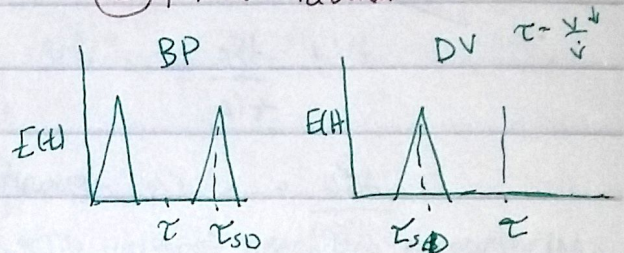
$$\sigma^2 = \int_0^\infty (t-\tau)^2 E(t) dt = \int_0^\infty \frac{(t-\tau)^2}{\tau} e^{-t/\tau} dt = \tau^2$$

13.5 Diagnostics and Troubleshooting

① CSTR



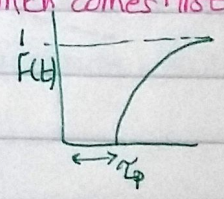
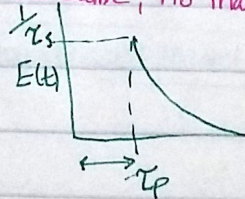
② PFR Tubular



③ PFR / CSTR in series

(I) CSTR Then PFR delayed by τ_p $E(t)$ is the same, no matter which comes first

$$E(t) = \begin{cases} t < \tau_p & E(t) = 0 \\ t \geq \tau_p & E(t) = \frac{1}{\tau_s} e^{-(t-\tau_p)/\tau_s} \end{cases}$$



* The RTD is not a complete description of structure for a particular reactor or system of reactors

* RTD is unique for system / reactors, But, reactors not unique for a particular RTD.

Part 2 Predicting conversion and exit concentration

13.6 Reactor modeling using the RTD

RTD + Model + kinetics $\Rightarrow$ exit $\begin{cases} \text{conversion} \\ \text{concentration} \end{cases}$

• models for predicting conversion from RTD Data

1. Zero adjustable parameters: a. segregation model
b. maximum mixedness model

2. One adjustable parameters: a. Tanks in series model
b. Dispersion model

3. Two adjustable parameters: real reactors modeled as a combination of ideal reactors

$\therefore$ if First order rxn. the RTD is enough, reaction rate must be known

Batch reactor $\frac{dN}{dt} = r_A V$ $\frac{N_{A0} dx}{dt} = -r_A V = +k C_A V = k \frac{N_A V}{x}$

$$N_{A0} \frac{dx}{dt} = k N_{A0} (1-x)$$

$$\frac{dx}{dt} = k(1-x)$$

$\therefore$ if more complex models, RTD is not enough,

$\rightarrow$ two extreme models
information

$\rightarrow$ macromixing $\rightarrow$ RTD without specifying encountering
specifying
 $\rightarrow$ micromixing $\rightarrow$ how molecules of different ages encounter
on another in the reactor.

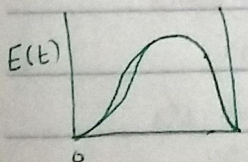
$\rightarrow$ Micromixing, two extremes

$\rightarrow$ Complete segregation $\rightarrow$ macrofluid $\rightarrow$ late mixing
all molecules of the same age remain together (not mixed)
Maximum mixedness point $\rightarrow$ microfluid $\rightarrow$ early mix.
molecules of different age groups are completely mixed

* For rxn orders $\rightarrow < 0$ or $> 1 \rightarrow$ highest conversion by complete segregation
between 0 and 1 $\rightarrow$ highest conversion by maximum mix.

13.7 Zero-parameter model

$\Rightarrow$ 13.7.1 segregation model



• globules behave as a batch reactors operated for different times.

• lumping (mixing) all the molecules that have exactly the first same residence time in the reactor into the same globule.

• the molecule globe which exit as it enters is physically channels rapidly (Small residence time).

$\rightarrow$ First order rxn. $-r_A = k C_A$

even though working on CSTR, $\frac{dx}{dt} = k(1-x)$
since are like batch reactor

$$\bar{X} = \int_0^t x(t) E(t) dt$$

$$\bar{X} = \int_0^{\infty} x(t) E(t) dt$$

$$\int_0^{\infty} \frac{dx}{1-x} = \int_0^t k dt$$

$$-\ln(1-x) + \ln 1 = kt$$

$$\ln(1-x) = -kt$$

$$x(t) = 1 - e^{-kt}$$

$$\bar{X} = \int_0^{\infty} (1 - e^{-kt}) E(t) dt = \int_0^{\infty} E(t) dt - \int_0^{\infty} e^{-kt} E(t) dt$$

segregation model

$$\bar{X} = 1 - \int_0^{\infty} e^{-kt} E(t) dt$$

Example 13.4

First order, $\bar{X}$? (a) ideal PFR (b) ideal CSTR (c) laminar flow

$$-r = k N_{A0} (1-x) \rightarrow \frac{dx}{dt} = k(1-x) \quad \int_0^x \frac{dx}{1-x} = \int_0^t k dt \quad \ln 1 - \ln(1-x) = kt$$

Zero

Ideal $\ln(1-x) = -kt$ $e^{-kt} = 1-x$ $x(t) = 1 - e^{-kt}$

(a) PFR $\rightarrow E(t) = \delta(t-\tau)$

$$\bar{X} = \int_0^{\infty} x(t) E(t) dt = \int_0^{\infty} (1 - e^{-kt}) (\delta(t-\tau)) dt =$$

Ideal $\int_0^{\infty} \delta(t-\tau) dt = \int_0^{\infty} e^{-kt} \delta(t-\tau) dt = 1 - e^{-k\tau} = 1 - e^{-Da}$

(b) CSTR $\rightarrow E(t) = \frac{1}{\tau} e^{-t/\tau}$

$$\bar{X} = \int_0^{\infty} \frac{1}{\tau} e^{-t/\tau} (1 - e^{-kt}) dt = \int_0^{\infty} \frac{1}{\tau} e^{-t/\tau} dt - \int_0^{\infty} \frac{1}{\tau} e^{-t(\frac{1}{\tau} + k)} dt$$

$$= \left(\frac{1}{\tau} \cdot \tau \right) - \left(\frac{1}{\tau} \cdot \frac{1}{\frac{1}{\tau} + k} \right) = 1 - \frac{1}{1 + k\tau} = \frac{1 + 1}{1 + Da} =$$

$$\frac{1 + Da \bar{X}}{1 + Da} = \frac{Da}{1 + Da}$$

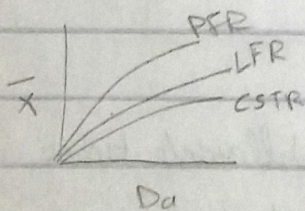
* it is the same expression from mole balance Because it is first order rxn

PFR mole balance: $N_{A0} \frac{dx}{dV} = -r_A$ $N_{A0} \frac{dx}{dV} = k C_{A0} (1-x)$ $N_{A0} \frac{dx}{dV} = k \frac{N_{A0}}{V_0} (1-x)$

$$\frac{dx}{dDa} = (1-x) \quad \int \frac{dx}{1-x} = \int dDa \quad -\ln(1-x) = Da$$

$$1-x = e^{-Da} \quad x = 1 - e^{-Da} \quad \#$$

CSTR mole balance: $V = \frac{F_{A0} X}{k C_{A0} (1-x)} = \frac{V_0 C_{A0} X}{k C_{A0} (1-x)}$ $\tau V = \frac{X}{1-x}$ $Da = \frac{X}{1-x}$ $X = \frac{Da}{1+Da}$

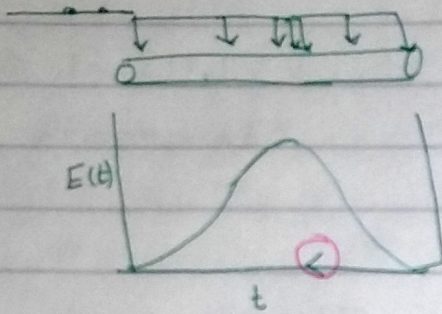


First order rxn, only $E(t)$ is required to determine the conversion. independent on micromixing or pattern of the reactor flow.

⇒ 13.7.2 Maximum mixedness model

- Fluid entered the reactor and completely mixed radially
- RTD of PFR with side entrance is identical to the RTD of the real reactor

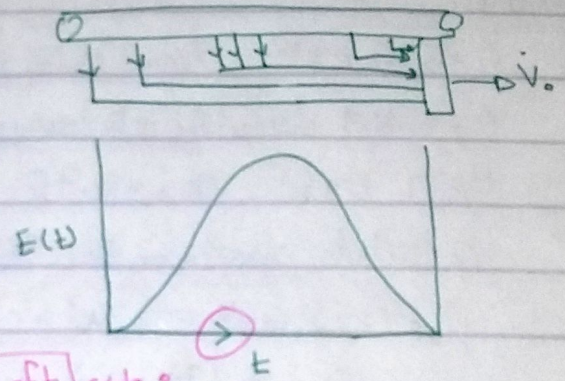
model: maximum mixedness



Left side:

globules correspond to molecules that spend long time, while at far right correspond to "channeling"

segregation model



Left side:

molecules near the entrance of the reactor correspond to molecules having short residence time "channeling"

⇒ 13.9.1 Segregation model RTD and multiple rxns.

- we consider each of the globules in the reactor to have different concentrations of reactants (C_A) and products (C_P).

$$\bar{C}_A = \int_0^\infty C_A(t) E(t) dt \quad dC_A/dt = r_A = \sum_{i=1}^n r_{Ai}$$

$$\bar{C}_B = \int_0^\infty C_B(t) E(t) dt \quad dC_B/dt = r_B = \sum_{i=1}^n r_{Bi}$$

$$\frac{d\bar{C}_A}{dt} = C_A(t) E(t)$$

$$\frac{d\bar{C}_B}{dt} = C_B(t) E(t)$$

* There is an example on segregation model on cleaning slides.

CHAPTER #7 : Reaction mechanisms, Pathway, bioreactions

7.1 Active intermediates and non elementary rate law

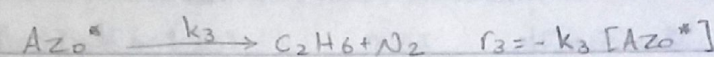
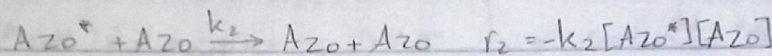
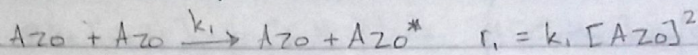
• Active intermediate : a highly-energy molecule that reacts virtually as it is formed. presented in small conc. , results from collision between or interaction with other molecules :

• Types of active intermediate : 1. Free radical 2. ionic intermediate 3. enzyme substrate complex
 ~ Lindermann & Ahmed Zewail

7.1.2 PSSH, Pseudo Steady State Hypothesis

• gas-phase decomposition of isomethane example

reaction constants are defined w.r.t AzO^*



• Be careful the reaction constants are defined to what species.

• To check the overall rxn put as reversible in 1 rxn.

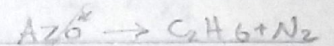
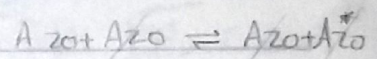
$$r_3 = k_3 [AzO^*]$$

$$PSSH : \sum_{i=1}^n r_i AzO^* = 0 \quad k_1 [AzO]^2 - k_2 [AzO^*][AzO] - k_3 [AzO^*] = 0$$

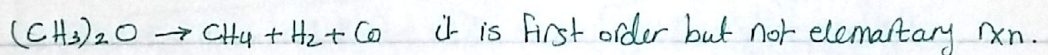
$$[AzO^*] = \frac{k_1 [AzO]^2}{k_2 [AzO] + k_3}$$

$$r_3 = \frac{k_3 k_1 [AzO]^2}{k_2 [AzO] + k_3} = \frac{k_1 [AzO]^2}{\frac{k_2}{k_3} [AzO] + 1}$$

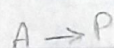
To check the overall :-



• PSSH can explain why one observes so many first order rxns. such as



this rxn includes inert in the steps.



$$r = +k_3 [A^*]$$

$$r_p = \frac{k_3 k_1 [A][M]}{k_2 [M] + k_3}$$

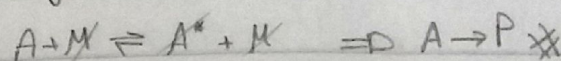
since [M] is constant

$$\sum_{i=1}^n r_i A^* = 0 \quad k_1 [A][M] - k_2 [A^*][M] - k_3 [A^*] = 0$$

$$[A^*] = \frac{k_1 [A][M]}{k_2 [M] + k_3}$$

$$\text{let } k = \frac{k_3 k_1 [M]}{k_2 [M] + k_3} \Rightarrow r_p = k [A] \quad \text{OR} \quad r_p = \frac{k_1 [M][A]}{\frac{k_2}{k_3} [M] + 1} = \frac{k' [A]}{k'' + 1}$$

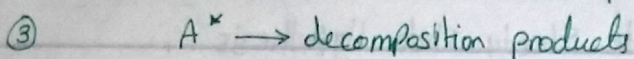
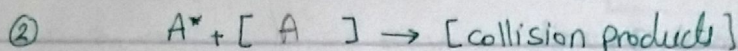
* checking the overall



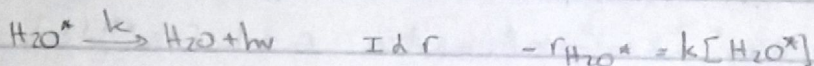
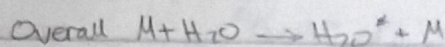
⇒ 7.1.2 Searching For a mechanism

* General considerations

- $\frac{\text{numerator}}{\text{denominator}} \rightarrow \text{species conc.} \rightarrow$
 - ① active intermediate from this species.
 - ② collision with active intermediate
 - ③ decomposition of active intermediate
- $\text{constant} \rightarrow$ decomposition of active intermediate

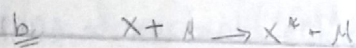
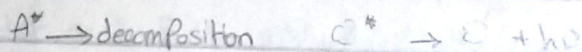


Repeat Example 7.1

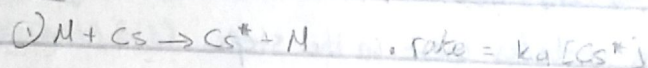


Stern-Volmer plots

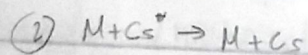
$$\frac{I_0}{I} = \frac{a[x] + b}{a + b[x]} \quad \frac{I}{I_0} = \frac{1}{1 + b[x]}$$



Mechanism



$$0 = k_1[M][CS] - k_2[X][CS^*] - k_3[X][CS^*] - k_4[CS^*]$$



$$[CS^*] = \frac{k_1[M][CS]}{k_2[M] + k_3[X] + k_4}$$

with I rate = $\frac{k_1 k_1 [M][CS]}{k_2 [M] + k_3 [X] + k_4} = \frac{k' [CS]}{k'' + k_3 [X]}$

without I rate = $k_4 [CS^*] = \frac{k_1 k_4 [M][CS]}{k_2 [M] + k_4} = \frac{k'}{k''}$

$$\frac{I_0}{I} = \frac{k'}{k''} \times \frac{k'' + k_3 [X]}{k' [CS]} = \frac{k' + k_3 [X]}{k''} = 1 + \frac{k_3 [X]}{k''} \quad a=1 \quad b = \frac{k_3}{k_2 [M] + k_4}$$

✗

⇒ 7.2 : Enzymatic reaction Fundamentals

- Enzyme : high molecular weight protein or protein like substance that acts on substrate (reactant molecule) to transform it chemically at a greatly accelerated rate, $10^3 - 10^7$ faster than the catalyzed rate.
- active intermediate called enzyme-substrate complex.
- enzymes are specific, working at ambient conditions.
- naming enzymatic rxns. : suffix use to the substrate, or rxn they catalyze, there are some exceptions.

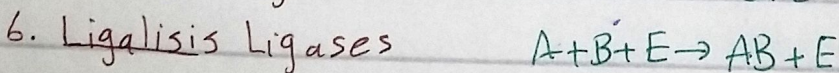
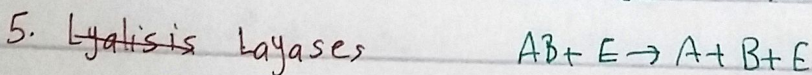
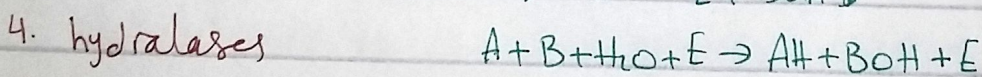
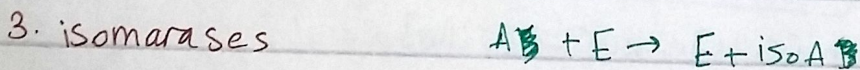
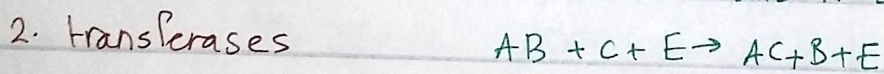
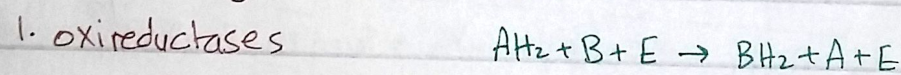
⇒ 7.2.1 Enzyme-Substrate Complex.

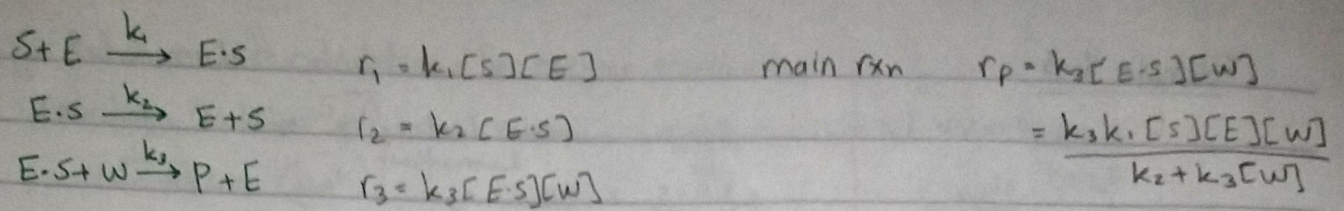
- Key factor (this rxn is unique) in having enzyme-substrate complex.
- In many cases, the enzyme's active sites are found where various folds or loops interact.
- Much of the catalyst power is attributed to the binding energy of substrate to enzyme.
- "denatured enzyme" : enzyme unfold, losing the active sites, due to exposure to extreme temperature and pH environment.

* Two models for substrate-enzyme interactions :-

1. lock and the key model → was ~~prepe~~ preferred
2. induced fit model → is preferred, due to the weakening of the bonds

* 6 classes of enzyme and ONLY six :-





• PSSH on E·S

$$\sum_{i=1}^3 r_i = 0 \quad k_1 [S][E] - k_2 [E \cdot S] - k_3 [E \cdot S][W] = 0$$

$$[E \cdot S] = \frac{k_1 [S][E]}{k_2 + k_3 [W]}$$

• Enzyme balance

$$[E_t] = [E \cdot S] + [E] = [E] + [E] \frac{k_1 [S]}{k_2 + k_3 [W]} \quad [E] = \frac{[E_t]}{1 + \frac{k_1 [S]}{k_2 + k_3 [W]}}$$

$$\rightarrow r_p = \frac{k_1 k_3 [S][W][E_t]}{k_2 + k_3 [W] + k_1 [S]} = \frac{k_3 [W]}{k_2 + k_3 [W] + k_1 [S]} \cdot \frac{k_1 [S][E_t]}{1 + \frac{k_1 [S]}{k_2 + k_3 [W]}} = \frac{V_{\max} [S]}{K_M + [S]}$$

7.2.3. Michaelis-Menten Equation

1/time unit

$$\begin{aligned}
 k_{\text{cat}} &= k_3 W \\
 K_M &= \frac{k_2 + k_3}{k_1} \\
 V_{\max} &= k_{\text{cat}} E_t
 \end{aligned}$$

"Turnover constant" when $S \gg K_M$

"Michaelis-Menten constant" "affinity constant"

$$r_p = \frac{V_{\max} S}{K_M + S}$$

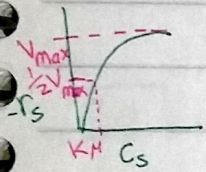
$S \gg K_M \rightarrow r_p = -r_s \approx V_{\max}$ Zero order

$K_M \gg S \rightarrow r_p = -r_s \approx \frac{V_{\max} S}{K_M}$ First order

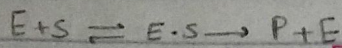
$$\therefore \text{if } r_p = \frac{1}{2} V_{\max} \rightarrow \frac{1}{2} V_{\max} = \frac{V_{\max} S_{1/2}}{K_M + S_{1/2}}$$

$$1 = \frac{2 S_{1/2}}{K_M + S_{1/2}} \quad K_M + S_{1/2} = 2 S_{1/2} \quad \boxed{K_M = S_{1/2}} \text{ concentration unit.}$$

• One way to compare catalytic efficiency of different enzymes is to compare the ratio k_{cat}/K_M , if approaches 10^8 to $10^9 \text{ dm}^3/(\text{mol} \cdot \text{s})$ the diffusion limited rxn.



• Example 7-3



$$-r_s = \frac{V_{max} S}{K_M + S}$$

$$\frac{1}{-r_s} = \frac{K_M + S}{V_{max} S} = \frac{K_M}{V_{max} S} + \frac{1}{V_{max}}$$

K_M mol/dm³ K_M mol/dm³

V_{max} mol/(dm³·s)

Plot $1/s$ against $\frac{1}{-r_s}$

slope = $\frac{K_M}{V_{max}}$

intercept $\frac{1}{V_{max}}$

"Lineweaver-Burk" plot

$$-r_s = V_{max} - K_M \left(\frac{-r_s}{S} \right)$$

"Eadie-Hofstee"

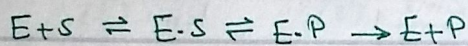
not good for low substrate conc.

$$\frac{S}{-r_s} = \frac{K_M}{V_{max}} + \frac{1}{V_{max}} (S)$$

"Hanes-Woolf"

good (accurate for V_{max})

* The product enzyme complex "Briggs-Haldane Rate law"



$$-r_s = \frac{V_{max} (C_s - C_p/K_c)}{C_s + K_{max} + K_p C_p}$$

above

7.2.4 Batch reactor calculations for enzyme reactions

$$-\frac{dN_s}{dt} = -r_s V \quad \text{constant volume isothermal} \quad -\frac{dS}{dt} = -r_s \quad \& \quad -r_s = \frac{V_{max} S}{K_M + S}$$

$$-\frac{dS}{dt} = \frac{V_{max} S}{K_M + S} \quad \int_0^t dt = \int_S^{S_0} \frac{K_M + S}{V_{max} S} dS \quad t = \int_S^{S_0} \frac{K_M}{V_{max} S} dS + \int_S^{S_0} \frac{1}{V_{max}} dS =$$

$$t = \frac{K_M}{V_{max}} \ln \frac{S_0}{S} + \frac{(S_0 - S)}{V_{max}} = \frac{K_M}{V_{max}} \ln \frac{1}{1-X} + \frac{S_0 X}{V_{max}}$$

$$\frac{V_{max}}{E K_M} = \frac{1}{t} \ln \frac{S_0}{S} + \frac{(S_0 - S)}{E K_M}$$

$$\frac{1}{t} \ln \frac{S_0}{S} = \frac{V_{max}}{K_M} - \frac{1}{t} \frac{(S_0 - S)}{K_M} \quad \text{linearized form}$$

Example 7.4

$$X = 0.99 \quad V = 0.5 \quad S_0 = 0.1 \quad E_t = 0.001$$

$$t = \frac{0.0266 \ln \frac{1}{0.01}}{2.66 \times 10^{-4}} + \frac{0.1 \times 0.99}{2.66 \times 10^{-4}}$$

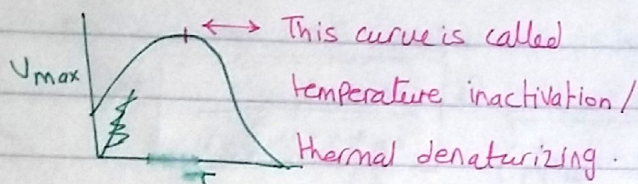
$$= 832 \text{ s} = 13.9 \text{ min.}$$

$$V_{max} = 1.33 \text{ when } E_t = 5 \quad V_{max} = k_{cat} E_t$$

$$k_{cat} = 0.266 \quad V_{max} = 2.66 \times 10^{-4} \text{ mol/(dm}^3 \cdot \text{s)}$$

careful!

* Effect of temperature



As $\uparrow T \rightarrow$ before max, $\uparrow V_{max}$ Arrhenius
 $\downarrow V_{max}$ "denatured enzyme"

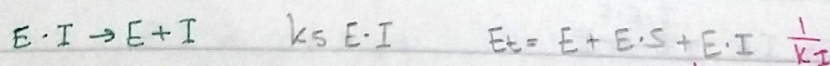
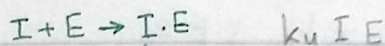
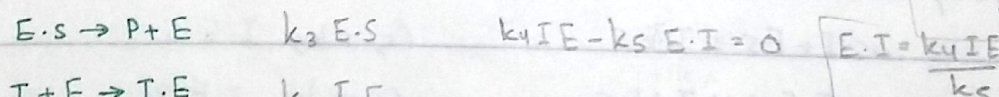
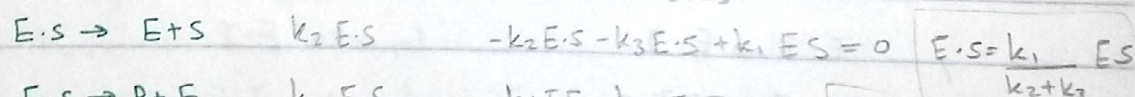
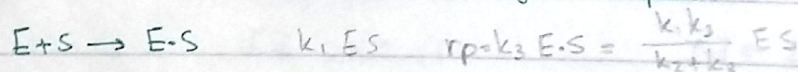
7.3 Inhibition of enzyme reactions

Enzyme

Inhibitor: species that interact with enzymes and render the enzyme ineffective to catalyze its specific rxn.

Three most common types of reversible inhibition &-

① Competitive inhibitor inhibitor-enzyme complex



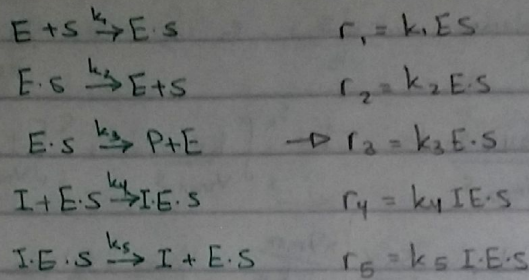
$$r_p = \frac{k_3 E_t S}{1 + \frac{k_1 S}{k_2 + k_3} + \frac{k_4 I}{k_5}} = \frac{S V_{max}}{K_M (1 + \frac{I}{K_I})} = \frac{S V_{max}}{S + K_M (1 + \frac{I}{K_I})}$$

$$\frac{1}{-r_s} = \frac{1}{V_{max}} + \frac{1}{S} \frac{K_M (1 + I/K_I)}{V_{max}}$$

$\uparrow I \rightarrow \uparrow \text{slope} \downarrow \text{rate}$

bigger amount of S is needed to achieve specific rate

② Uncompetitive inhibi-inhib inhibition. inhibitor-enzyme-substrate complex



• Σr_i :

$$(E \cdot S) \quad 0 = k_1 E S - k_2 E \cdot S - k_3 E \cdot S \rightarrow E \cdot S = k_1 E S / (k_2 + k_3) = E S / K_M$$

$$(I \cdot E \cdot S) \quad 0 = k_4 I E \cdot S - k_5 I \cdot E \cdot S \rightarrow I \cdot E \cdot S = \frac{k_4}{k_5} I E \cdot S = \frac{I}{K_I} E \cdot S$$

• Enzyme balance

$$E_t = E + E \cdot S + I \cdot E \cdot S = E + E \left(\frac{1}{K_M} S + \frac{I}{K_I} \frac{1}{K_M} S \right)$$

$$E = \frac{E_t}{1 + \frac{S}{K_M} + \frac{S}{K_M} \frac{I}{K_I}}$$

$$\Rightarrow r_p = k_3 E \cdot S = \frac{k_3 E_t S}{K_M (1 + \frac{S}{K_M} + \frac{S}{K_M} \frac{I}{K_I})} = \frac{V_{max} S}{K_M + S (1 + \frac{I}{K_I})} \quad \#$$

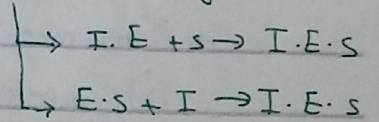
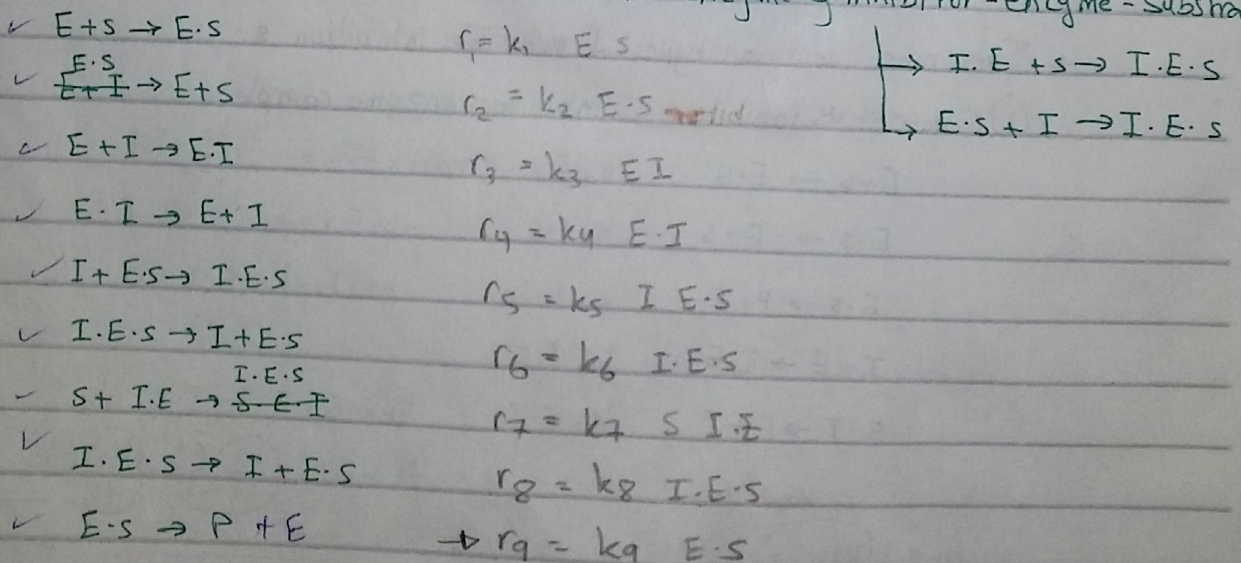
linearized form

$$\frac{1}{r_p} = \frac{1}{-r_6} = \frac{K_M}{V_{max}} \left(\frac{1}{S} \right) + \frac{1}{V_{max}} \left(1 + \frac{I}{K_I} \right)$$

$\uparrow I$ $\uparrow$ intercept $\downarrow$ rate
slope unchanged

e.g. heavy
metal ions
such as Pb^{2+} ,
 Ag^+ , Hg^{2+}

③ Non-competitive inhib inhibition inhibitor-enzyme & inhibitor-enzyme-substrate



$$-r_s = k_9 E \cdot S$$

• $\sum r_i$

$$(E \cdot S) \quad k_1 E S - k_2 E \cdot S - k_5 I E \cdot S + k_6 I E \cdot S + k_8 I \cdot E \cdot S - k_9 E \cdot S = 0 \rightarrow (1)$$

$$(E \cdot I) \quad k_3 E I - k_4 E \cdot I - k_7 S I E = 0 \rightarrow (2)$$

$$(I \cdot E \cdot S) \quad k_5 I E \cdot S - k_6 I E \cdot S + k_7 S I E - k_8 I \cdot E \cdot S = 0 \rightarrow (3)$$

$$(1) \& (3) \quad k_1 E S - k_2 E \cdot S + k_7 S I E - k_9 E \cdot S = 0$$

$$(2) \quad I \cdot E = \frac{k_3 E I}{k_4 + k_7}$$

$$E \cdot S = \frac{k_1 E S + k_7 S I \cdot E}{k_2 + k_9} = \frac{k_1 E S + k_7 k_3 E I}{(k_4 + k_7)(k_2 + k_9)}$$

$$-r_s = \frac{V_{max} S}{(S + K_M) \left(1 + \frac{I}{K_I}\right)}$$

$$\frac{1}{-r_s} = \left(1 + \frac{I}{K_I}\right) \frac{1}{V_{max}} + \left(\frac{1}{S}\right) \frac{K_M \left(1 + \frac{I}{K_I}\right)}{V_{max}}$$

$\uparrow I \quad \uparrow \text{slope} \quad \uparrow \text{intercept} \quad \downarrow \text{rate}$

$\Rightarrow$ 7.3.4 Substrate inhibition

the substrate it self can act as an inhibitor, in the case of uncompetitive inhibition, S-E-S inactive mole is formed $S + E \cdot S \rightarrow S \cdot E \cdot S$

$$-r_s = \frac{V_{max} S}{K_M + S + \frac{S^2}{K_I}}$$

if $\downarrow S$

$$-r_s \approx \frac{V_{max} S}{K_M}$$

$\uparrow S \quad \uparrow \text{rate}$

$\uparrow S$

$$-r_s \approx \frac{V_{max} K_I}{S}$$

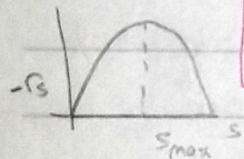
$\uparrow S \quad \downarrow \text{rate}$

Optimization is needed

differentiate the above relation and equal to zero

$$S_{max} = \sqrt{K_M K_I}$$

when substrate inhibition is possible, semibatch reactor called a fed batch is often used as a CSTR to maximize the reaction rate and conversion.



CHAPTER 14 (only 14.7.1 & 14.9)

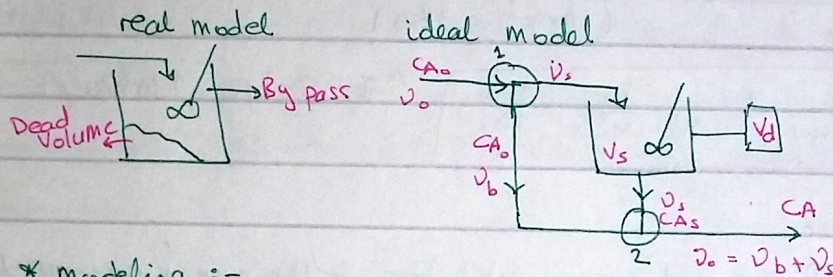
14.7 The Two Parameter models - modeling real reactors with combinations of ideal reactors

- it may not be necessary to calculate the RTD function ($E(t)$), the model parameters may be acquired directly from measurements of effluent concentration in the tracer test.

⇒ 14.7.1 Real CSTR modeled using by passing and dead space

- Tracer experiment to evaluate V_s, V_b (~~ideal CSTR parameters~~)

⇒ 14.7.1.A Solving the model system for CA and X $A \rightarrow B$



* modeling :-

1. mole balance at junction point #2

$$CA_s V_s + CA_0 V_b = CA V_0 \quad CA = CA_s V_s + CA_0 V_b$$

$$CA = (1-\beta) CA_s + \beta CA_0 \quad (1)$$

2. mole balance at CSTR, if first order rxn

$$CA_0 V_s - CA_s V_s - k CA_s V_s = 0 \quad CA_s = CA_0 V_s / (V_s + k V_s)$$

$$CA_s = \frac{CA_0 (1-\beta) V_0}{(1-\beta) V_0 + k d V} \quad (2) \quad \text{Now, substitute (2) in (1)}$$

$$CA = \frac{(1-\beta) CA_0 (1-\beta) V_0}{(1-\beta) V_0 + k d V} + \beta CA_0 \quad \frac{CA}{CA_0} = 1 - X = \beta + \frac{(1-\beta)^2}{(1-\beta) + k d \tau} \quad \text{✗}$$

$$\tau = \frac{V}{V_0}$$

$$\frac{CA}{CA_0} = 1 - X = \beta + \frac{(1-\beta)^2}{(1-\beta) + d \tau k}$$

Two Parameters :-

$$\text{Let } \alpha = \frac{V_s}{V_0} \quad \alpha = V_s / V_0$$

$$\beta = V_b / V_0$$

$$\frac{V_s}{V_0} = 1 - \beta \quad \frac{V_b}{V_0} = 1 - \alpha$$

→ 14.7.1.B Using a tracer to determine the model parameters in CSTR with dead space and by pass model.

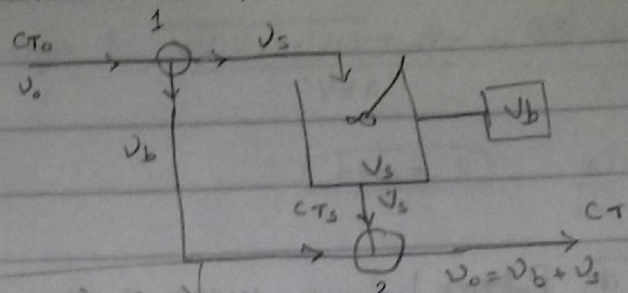
$$\alpha = V_s/V \quad 1 - \alpha = V_b/V$$

$$\beta = V_b/V_0 \quad 1 - \beta = V_s/V_0$$

1. Balance around junction 2

$$C_{T_0} V_b + C_{T_s} V_s = V_0 C_T$$

$$C_T = \frac{C_{T_0} V_b + C_{T_s} V_s}{V_0} \quad (1)$$



2. Unsteady state mole balance at the CSTR reactor

$$C_{T_0} V_b - C_{T_s} V_s = \frac{dN_{T_s}}{dt} = V_s \frac{dC_{T_s}}{dt} \quad (2)$$

Substitute (1) in (2), but after integrating

$$(1 - \beta) V_0 (C_{T_0} - C_{T_s}) = \alpha V \frac{dC_T}{dt} \quad \frac{dC_T}{C_{T_0} - C_{T_s}} = \frac{(1 - \beta)}{\alpha \tau} dt \quad -\ln(C_{T_0} - C_{T_s}) \Big|_{C_{T_0}}^{C_{T_s}} = \frac{(1 - \beta)}{\alpha \tau} t$$

$$\frac{C_{T_s} - C_{T_0}}{C_{T_0} - C_{T_s}} = \exp\left[-\frac{(1 - \beta)}{\alpha} \frac{t}{\tau}\right]$$

Now, substitute

$$\frac{C_T}{C_{T_0}} = \frac{V_b}{V_0} + \frac{C_{T_s}}{C_{T_0}} \frac{V_s}{V_0}$$

$$\frac{C_T}{C_{T_0}} = \beta + (1 - \beta) \left(1 - \exp\left[-\frac{(1 - \beta)}{\alpha} \frac{t}{\tau}\right]\right) = \beta + 1 - \exp\left[-\frac{(1 - \beta)}{\alpha} \frac{t}{\tau}\right] + \beta \exp\left[-\frac{(1 - \beta)}{\alpha} \frac{t}{\tau}\right]$$

$$\frac{C_T}{C_{T_0}} = 1 - (1 - \beta) \exp\left[-\frac{(1 - \beta)}{\alpha} \frac{t}{\tau}\right]$$

get it in the linearized form

$$\ln \frac{C_{T_0} - C_T}{C_{T_0} - C_{T_s}} = \ln(1 - \beta) + \frac{(1 - \beta)}{\alpha \tau} t$$

Example 14.4 $A + B \rightarrow C + D$

$$V_s + V_b = V = 1 \quad V_0 = 0.1 \quad k = 0.28 \quad C_A = C_B = 2$$

$$\tau = 10 \quad \text{First, find } \alpha \text{ \& } \beta$$

Plot the data

semi-log plot

$$\text{intercept} = 1.25 = \frac{1}{1 - \beta} \quad \beta = 0.2$$

$$\text{slope} = 0.115 = \frac{(1 - \beta)k}{\alpha \tau} \quad \alpha \tau = 7 \text{ min} \quad \alpha = 0.7$$

Then, find x \& C_A

$$(1) \quad C_A V_s + C_{A_0} V_b = C_A V_0 \quad C_A = \frac{C_A V_s + C_{A_0} V_b}{V_0}$$

$$(2) \quad V_s C_{A_0} - V_s C_A - k C_A C_B V_s = 0 \quad V_s C_{A_0} - V_0 C_A - k C_A C_B (1 - x)^2 V_s = 0$$

$$V_s C_{A_0} - V_0 C_A - k V_s C_A^2 = 0 \quad k V_s C_A^2 + V_0 C_A - V_s C_{A_0} = 0$$

$$C_A = \frac{-V_0 \pm \sqrt{V_0^2 + 4k V_s V_0 C_{A_0}}}{2k V_s}$$

$$V_s = (1 - \beta) V_0 = 0.08 \quad \tau_s = 8.75 \text{ min} \\ V_s = \alpha V = 0.7$$

$$C_A = 0.722$$

$$b = 1 \quad a = \tau_s k \quad c = -C_{A_0}$$

$$C_A = 0.978$$

$$1 - x = \frac{C_A}{C_{A_0}} \quad x = 0.511$$

$$\ln \frac{C_{T_0} - C_T}{C_{T_0} - C_{T_s}} = \ln \frac{1}{1 - \beta} + \frac{(1 - \beta)k}{\alpha \tau} t$$

slope intercept intercept slope

$$\ln 0 - \ln(C_{T_0} - C_{T_s}) = \frac{(1-\beta)}{\alpha} \frac{b}{\tau}$$

$$1 - \ln \frac{C_{T_0}}{C_{T_s}} = \frac{1-\beta}{\alpha} \frac{b}{\tau}$$

$$\ln \frac{C_{T_0}}{C_{T_s}} = 1 - \frac{1-\beta}{\alpha} \frac{b}{\tau}$$

$$+ \ln \frac{C_{T_s}}{C_{T_0}} = 1 + \frac{1-\beta}{\alpha} \frac{b}{\tau}$$

If ideal reactor

$$C_A = 0.685 = \frac{-V_0 \pm \sqrt{V_0^2 + 4k V_0 C_{A0}}}{2kV} \quad \text{1 equation (mole balance).}$$

$$1 - X = \frac{C_A}{C_{A0}}$$

$$X = 0.66$$

14.9 Return to book (15 page) Page # 47