

Chemical reaction engineering

Chapter 8 : Multiple reactions

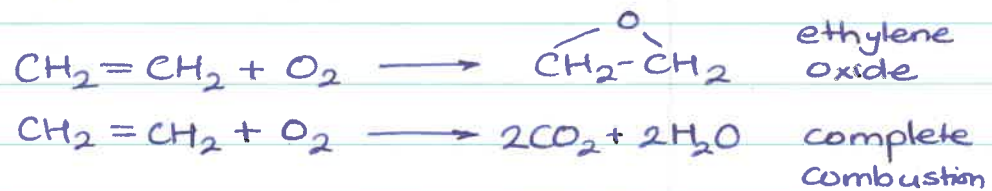
Parallel reactions

- competing reactions
- reactant is consumed by two different pathways to form different products

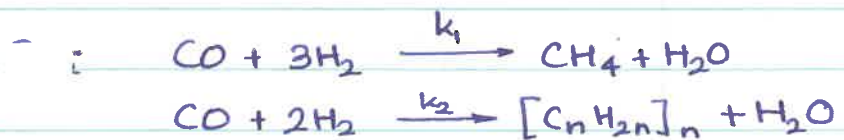


examples :

- Ethylene oxidation

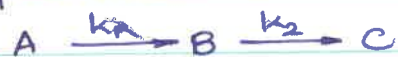


- Fischer - Tropsch



Series reactions

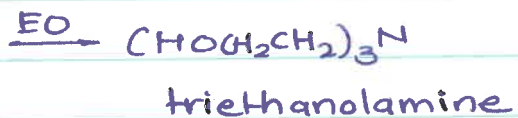
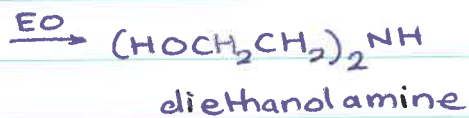
- consecutive reactions
- reactions where reactant forms an intermediate product, which reacts further to form another product.



example: ethylene oxide (EO) + ammonia



desired product →



Independent reactions

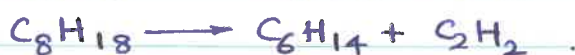
- reactions that occur at the same time but neither the products nor the reactants react with themselves or one another



example: cracking of crude oil.

↳ hundreds of reactions

e.g.



Complex reactions

- multiple reactions involving combination of series and parallel reactions



example: Formation of butadiene from ethanol

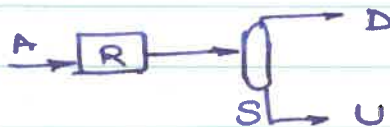


Desired and undesired reactions



⇒ Minimize formation of U and maximize formation of D

Greater the amount of U, ~~greater~~ greater is the cost of separation



Selectivity (S)

- How one product is favored over the other.

instantaneous
selectivity

The instantaneous selectivity of D with respect to U is the ratio of the rate of formation of D to the rate of formation of U

$$S_{D/U} = \frac{r_D}{r_U} = \frac{\text{rate of formation of D}}{\text{rate of formation of U}}$$

- Evaluating $S_{D/U}$ will guide in the design and selection of reactor system to maximize selectivity.

overall
selectivity

$$\bar{S}_{D/U} = \frac{F_D}{F_U} = \frac{\text{Exit molar flow rate of D}}{\text{Exit molar flow rate of U}}$$

overall
selectivity

For a CSTR $S_{D/U} = \bar{S}_{D/U}$

For batch reactor: $\bar{S}_{D/U} = \frac{N_D}{N_U}$

N_D : No. of moles of D at the end of reaction

For CSTR

$$F_D = r_D V$$
$$F_U = r_U V$$
$$\therefore \frac{F_D}{F_U} = \frac{r_D}{r_U} = \bar{S}$$

Yield (Y)

instantaneous yield

- ratio of the reaction rate of a given

$$Y_D = \frac{r_D}{-r_A}$$

product to the reaction rate of key reactant A.

Overall yield

- ratio of moles of product formed at the end of the reaction to the number of moles of the key reactant A, that have been consumed.

$$\text{For batch } \bar{Y}_D = \frac{N_D}{N_{A0} - N_A}$$

$$\text{For CSTR } \bar{Y}_D = \frac{F_D}{F_{A0} - F_A}$$

- For CSTR, $Y_D = \bar{Y}_D$

- Overall selectivities \bar{S} , and yields \bar{Y} are important in determining profits
- Instantaneous selectivities give insights in choosing reactors, operating conditions, and reaction schemes that will maximize profit.

Conversion (X)

- gives insight into problem
- often conflicts with selectivity

Ideal world \rightarrow make as much D as possible simultaneously minimizing U

practical experience \rightarrow Greater the conversion more the undesired product U.

- not used in solving multiple reaction problems but calculated later for analysis.

For species A

Flow System	$X_A = \frac{F_{A0} - F_A}{F_{A0}}$
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Batch system	$X_A = \frac{N_{A0} - N_A}{N_{A0}}$
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For species B

Flow	$X_B = \frac{F_{B0} - F_B}{F_{B0}}$
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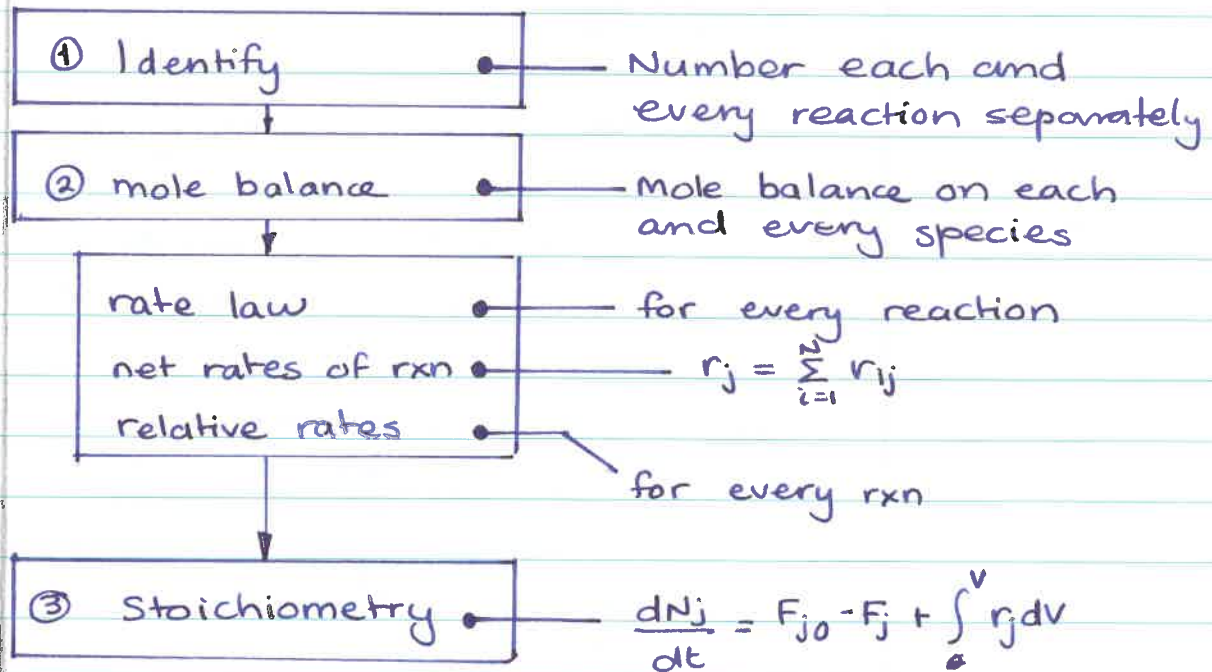
Batch	$X_B = \frac{N_{B0} - N_B}{N_{B0}}$
-------	-------------------------------------

For semibatch reactor where B is fed to A

$$X_A = \frac{C_{A0} V_0 - C_A V}{C_{A0} V_0}$$

$$X_B = \frac{F_{B0} t - C_B V}{F_{B0} t} \quad \text{for e.g. } t > 0.001 \text{ s}$$

Algorithm for multiple reactions



- Can be applied to parallel, series, independent, and complex reactions
- results in a system of ODEs
 - ↳ solve numerically
- for liquid systems conc. is usually the preferred variable for mole balance.

Parallel reactions

Selectivity

Consider two competing reactions



The rate laws are

$$r_D = k_D C_A^{\alpha_1} \quad \text{--- (1)}$$

$$r_U = k_U C_A^{\alpha_2} \quad \text{--- (2)}$$

Net rate of disappearance of A

$$-r_A = r_D + r_U$$

$$-r_A = k_D C_A^{\alpha_1} + k_U C_A^{\alpha_2}$$

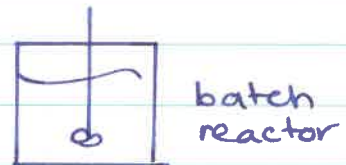
$$\boxed{S_{D/U} = \frac{r_D}{r_U} = \frac{k_D}{k_U} C_A^{\alpha_1 - \alpha_2}} \quad \text{--- (3)}$$

α_1, α_2 are positive orders

Case 1: $\alpha_1 > \alpha_2$

$$\alpha_1 - \alpha_2 = a$$

$$S_{D/U} = \frac{k_D}{k_U} C_A^a$$



⇒ To maximize selectivity, we want to carry out the reaction in a manner that will keep C_A as high as possible during the reaction

⇒ Use PFR or batch reactor

Gas phase reaction : • Use high pressure

• run without inerts

Liquid phase reaction : minimize diluent.

- Proper choice of solvent can enhance selectivity for a number of reactions
- In gas phase heterogeneous reactions, selectivity is important parameter of any particular catalyst.

Case 2 : $\alpha_2 > \alpha_1$

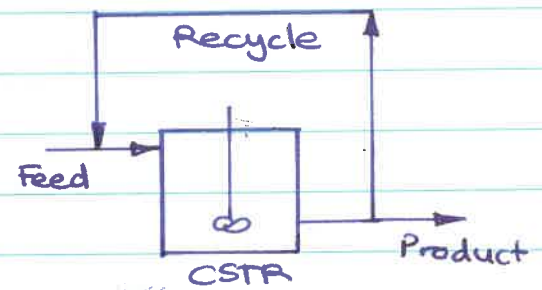
$$b = \alpha_2 - \alpha_1$$

$$S_{D/U} = \frac{k_D}{k_U} \frac{1}{C_A^b}$$

⇒ concentration of A should be as low as possible

⇒ Use CSTR, dilute feed stream

A recycle reactor can be used as well
→ product stream acts as diluent



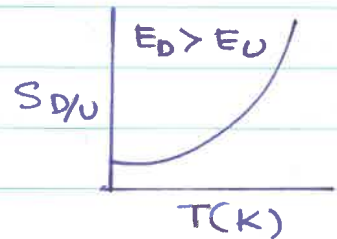
Effect of temperature : Need information on activation energy.

sensitivity to temp:

$$S_{D/U} \sim \frac{k_D}{k_U} = \frac{A_D}{A_U} e^{-[(E_D - E_U)/RT]}$$

Case 3 : $E_D > E_U$

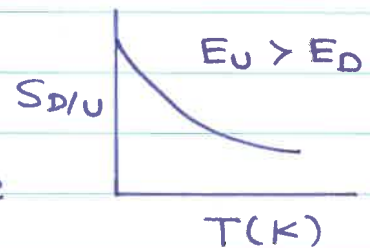
→ k_D increases more rapidly than $\frac{k_U}{k_D}$ with increase in temperature



⇒ Perform the reaction at highest possible temperature.

Case 4 : $E_U > E_D$

⇒ reaction should be carried out at lower temperature to maximize S_D/U .

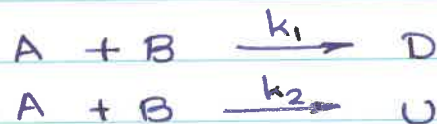


↳ The temperature should not be very low as it might affect reaction extent. Reaction may not proceed at low temperatures to any significant extent.

Reactor selection and operating conditions

Two simultaneous reactions and two reactants

consider two competing reactions with two reactants



$$r_D = k_1 C_A^{\alpha_1} C_B^{\beta_1}$$

$$r_U = k_2 C_A^{\alpha_2} C_B^{\beta_2}$$

Instantaneous selectivity

$$S_{D/U} = \frac{r_D}{r_U} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2}$$

- selectivity depends on the orders $\alpha_1, \alpha_2, \beta_1,$ and β_2 .
- Several reactor combinations exist.
- Reactor selection criteria
 - Safety
 - selectivity
 - yield
 - cost
 - temperature control

maximizing selectivity

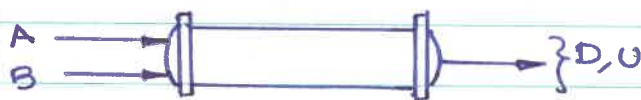
case 1 $\alpha_1 > \alpha_2, \beta_1 > \beta_2$

$$\alpha_1 - \alpha_2 = a \quad ; \quad \beta_1 - \beta_2 = b \quad a, b > 0$$

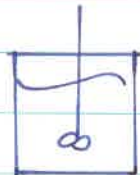
$$S_{D/U} = \frac{k_1}{k_2} C_A^a C_B^b$$

To maximize selectivity

- maintain the concentrations of both A, and B as high as possible.
- Use • tubular reactor
 - batch reactor
 - high pressure (gas phase),
reduce inerts.



Tubular reactor



batch reactor

Case 2 : $\alpha_1 > \alpha_2$, $\beta_2 > \beta_1$ ~~看~~

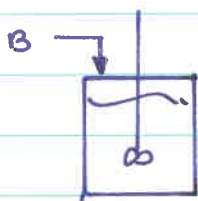
$$\text{Let } \alpha_1 - \alpha_2 = a \quad a, b > 0$$
$$\beta_2 - \beta_1 = b$$

$$S_{D/U} = \frac{k_1 C_A^a}{k_2 C_B^b}$$

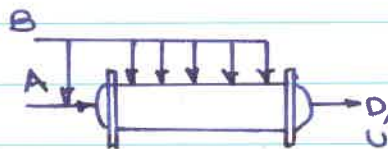
To maximize selectivity

- make conc. of A as high as possible
- make conc. of B low

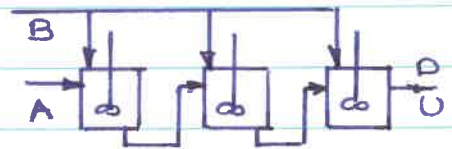
- Reactors :
- semibatch reactor with B is fed slowly into large amt. of A
 - membrane reactor / tubular reactor with side stream of B continually fed into the reactor
 - series of small CSTRs
 - ↳ A fed only to first reactor
 - ↳ small amt of B fed to each reactor



semibatch



membrane reactor,
tubular reactor
with side stream



series of small
CSTRs.

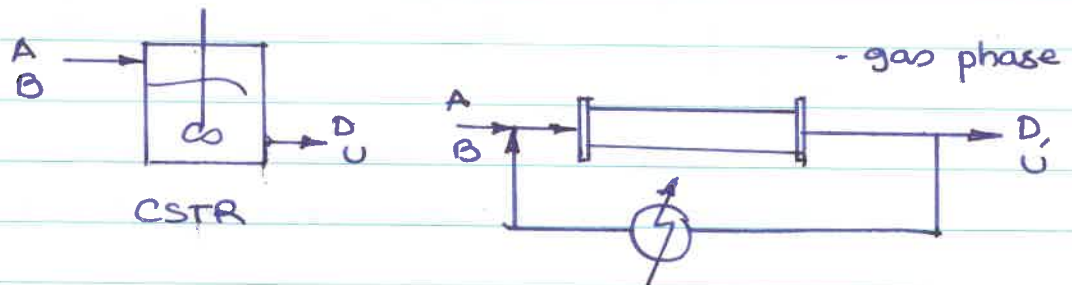
Case 3 : $\alpha_1 < \alpha_2$, $\beta_1 < \beta_2$

$$\text{Let } a = \alpha_2 - \alpha_1 \quad a, b > 0$$
$$b = \beta_2 - \beta_1$$

$$S_{D/U} = \frac{k_1}{k_2} \frac{1}{C_A^a C_B^b}$$

To make $S_{D/U}$ as large as possible
↳ low conc. of A, and B.

- reactors :
- CSTR
 - Feed diluted with inerts
 - low pressure (gas phase)
 - ~~PFR~~ ^{tubular reactor} with large recycle ratio.



Tubular reactor with recycle

- Can be used for highly exothermic reactions
 - recycle stream is cooled and returned to the reactor to dilute and cool inlet stream.
 - Avoid hot spots and runaway reactions.

case 4: $\alpha_1 < \alpha_2$, $\beta_1 > \beta_2$

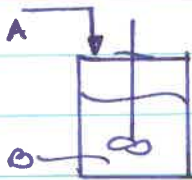
$$\text{Let } a = \alpha_2 - \alpha_1 \quad a, b > 0$$

$$b = \beta_1 - \beta_2$$

$$S_{D/U} = \frac{k_1 C_B^b}{k_2 C_A^a}$$

To maximize $S_{D/U}$

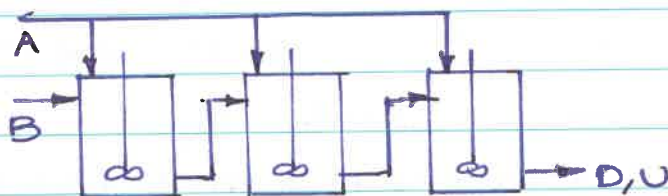
- Semibatch reactor with A slowly fed to large amount of B
- membrane reactor with side stream of A
- Series of small CSTRs with fresh A to each reactor.



semibatch reactor



membrane reactor or tubular reactor with side stream

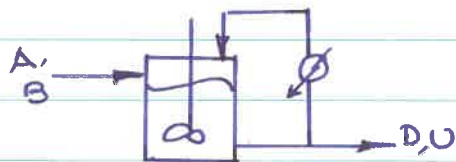


Series of small CSTRs with A fed to each reactor

- Instantaneous selectivity, $S_{D/U}$ can be used to guide initial selection of type of reactor and reactor system.
- Final selection should be made after calculating overall selectivity, $\bar{S}_{D/U}$ for the reactor and operating conditions chosen.

Other reactors

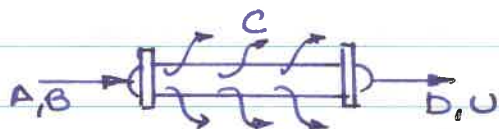
- Highly exothermic liquid phase reactions
 - CSTR with recycle
 - avoid hot spots, runaway reactions.
 - product as diluant



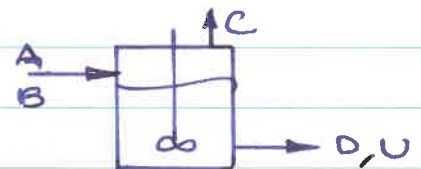
- Thermodynamically limited reactions where equilibrium lies far to the left



- membrane reactor gas phase

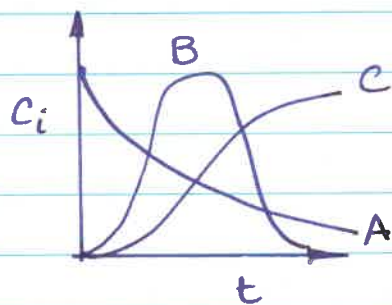
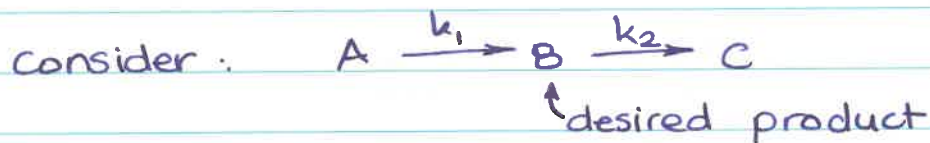


- reactive distillation liquid phase



Reactions in series (consecutive reactions)

- The most important variable is time
 - ↳ Batch time (real time)
 - ↳ Space time (continuous reactor)



- If $k_1 \ll k_2$ - first rxn is slow
 - ↳ extremely difficult to produce significant amt of B
- If $k_1 \gg k_2$ - first rxn is fast
 - ↳ large yield of B can be achieved.

For $k_1 \gg k_2$:

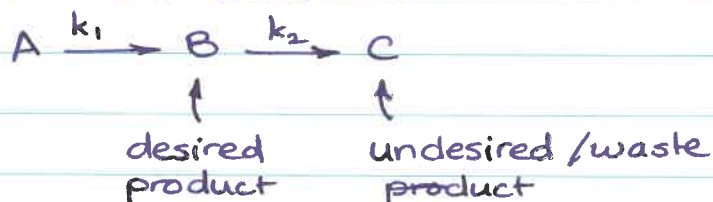
- If reaction is allowed to proceed for a long time in batch reactor, or in a very long tubular reactor, desired product B will be converted to undesired product C.

→ Accuracy of time needed to carry out the reaction is vital.

↑ prediction for

Series reactions in a batch reactor

consider the reaction

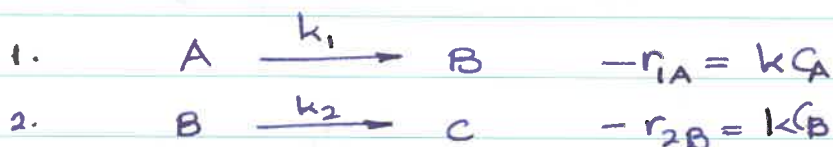


We are interested in

- conc. vs time profile
- max conc. of B
- quench time (time to stop when C_B is $_{\max}$)
- Overall selectivity and yield.

Number of reactions :

The series reaction can be written as two reactions



Mole balances :

Next we write mole balances for all three species.

Mole balance on A

$$\frac{dN_A}{dt} = r_A V$$

$$\Rightarrow \frac{dC_A}{dt} = r_A \quad \text{for } V = V_0$$

$$r_A = r_{1A} = -k_1 C_A$$

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

Integrate: $\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = \int_0^t -k_1 dt$

$$\ln \frac{C_A}{C_{A0}} = -k_1 t$$

solving for C_A :

$$C_A = C_{A0} e^{-k_1 t} \quad \text{--- ①}$$

Mole balance on B

$$\frac{dC_B}{dt} = r_B$$

r_B :

→ a. Elementary reaction: $r_{2B} = -k_2 C_B$

→ relative rates: rate of formation of B in rxn 1
 $r_{1B} = -r_{1A} = k_1 C_A$ = rate of disappearance of A in rxn 1

net rates :

$$r_B = r_{1B} + r_{2B}$$

$$r_B = k_1 C_A - k_2 C_B$$

$$\therefore \frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

substituting for C_A (eq ①)

$$\frac{dC_B}{dt} = k_1 C_{A0} e^{-k_1 t} - k_2 C_B$$

$$\therefore \frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t} \quad \text{--- ②}$$

This equation is of the form

$$\frac{dy}{dx} + f(x)y = g(x)$$

$$f(x) = k_2$$

$$g(x) = k_1 C_{A0} e^{-k_1 t}$$

we can treat it as a linear equation and use integrating factor (IF)

$$IF = e^{\int f(x) dx}$$

$$\therefore IF = e^{k_2 t}$$

multiplying both sides of ② with IF

$$\frac{d}{dt} C_B e^{k_2 t} = k_1 C_{A0} e^{(k_2 - k_1) t}$$

integrating both sides

$$C_B e^{k_2 t} = \frac{k_1 C_{A0}}{(k_2 - k_1)} e^{(k_2 - k_1)t} + C$$

$$\text{@ } t=0 \quad C_B = 0$$

$$\therefore C = -\frac{k_1 C_{A0}}{(k_2 - k_1)}$$

$$\therefore C_B = \frac{k_1 C_{A0}}{(k_2 - k_1)} \left[\frac{e^{(k_2 - k_1)t}}{e^{k_2 t}} - \frac{1}{e^{k_2 t}} \right]$$

$$\therefore \boxed{C_B = \frac{k_1 C_{A0}}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}]} \quad \text{--- ③}$$

Mole balance on C

$$\frac{dC_C}{dt} = r_C$$

$$r_C = -r_B = k_2 C_B$$

$$\therefore \frac{dC_C}{dt} = k_2 C_B$$

$$\text{Substituting } \textcircled{2} \quad \frac{dC_C}{dt} = \frac{k_1 k_2 C_{A0}}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \quad \text{--- ④}$$

Integrating (4)

$$C_c = \frac{k_1 k_2 C_{A0}}{(k_2 - k_1)} \left[\frac{-1}{k_1} e^{-k_1 t} + \frac{1}{k_2} e^{-k_2 t} \right] + c$$

$$\text{@ } t = 0 \quad C_c = 0$$

$$\therefore c = \frac{k_1 k_2 C_{A0}}{(k_2 - k_1)} \left[\frac{1}{k_1} - \frac{1}{k_2} \right]$$

$$\therefore C_c = \frac{k_1 k_2 C_{A0}}{(k_2 - k_1)} \left[\frac{-1}{k_1} e^{-k_1 t} + \frac{1}{k_2} e^{-k_2 t} \right] + \frac{k_1 k_2 C_{A0}}{(k_2 - k_1)} \left[\frac{1}{k_1} - \frac{1}{k_2} \right]$$

$$\therefore C_c = \frac{C_{A0}}{(k_2 - k_1)} \left[k_2 (1 - e^{-k_1 t}) - k_1 (1 - e^{-k_2 t}) \right] \quad \text{--- (5)}$$

$$\text{As } t \rightarrow \infty \quad C_c \rightarrow C_{A0}$$

$\Rightarrow C_c$ could have been obtained more easily from overall balance

$$C_c = C_{A0} - C_A - C_B \quad \text{--- (6)}$$

Concentration and time at maximum

To find maximum let's set $\frac{dC_B}{dt} = 0$

$$\frac{dC_B}{dt} = \frac{k_1 C_{A0}}{(k_2 - k_1)} \left[-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \right]$$

$$\text{@ } t = t_{\max} \quad dC_B/dt = 0$$

solving for t_{\max}

$$-k_1 e^{-k_1 t_{\max}} + k_2 e^{-k_2 t_{\max}} = 0$$

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

taking log

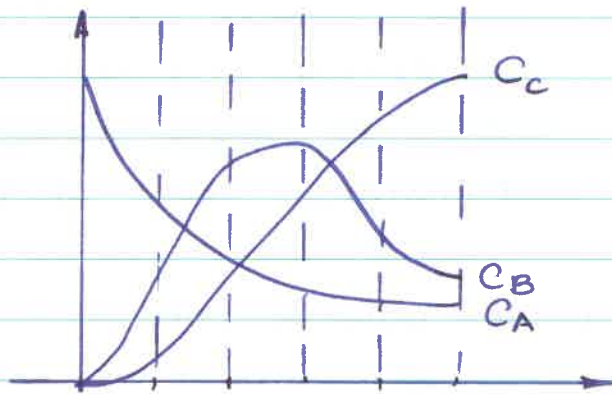
$$t_{\max} = \frac{1}{(k_2 - k_1)} \ln \left(\frac{k_2}{k_1} \right) \quad \text{--- (7)}$$

conc. @ max:

$$C_A = C_{A0} \left[\frac{k_1}{k_2} \right]^{k_1/(k_2 - k_1)}$$

$$C_B = \frac{k_1 C_{A0}}{k_2 - k_1} \left[\left(\frac{k_1}{k_2} \right)^{\frac{k_1}{k_2 - k_1}} - \left(\frac{k_1}{k_2} \right)^{\frac{k_2}{k_2 - k_1}} \right]$$

Concentration profile



Another approach is to solve following differential equations simultaneously.

$$\textcircled{1} \quad \frac{dC_A}{dt} = -k_1 C_A$$

$$\textcircled{2} \quad \frac{dC_B}{dt} = k_1 C_A - k_2 C_B$$

$$\textcircled{3} \quad \frac{dC_C}{dt} = k_2 C_B$$

\Rightarrow can be done using appropriate numerical method.

Series reactions in CSTR



- determine exit conc. from CSTR
- value of space time τ that will maximize conc. of B.

Mole balance on A

$$\begin{aligned} \text{in} - \text{out} + \text{generation} &= 0 \\ F_{A0} - F_A + r_A V &= 0 \\ v_0 C_{A0} - v_0 C_A + r_A V &= 0 \end{aligned}$$

$$\tau = V/v_0$$

$$\therefore C_{A0} - C_A + r_A \tau = 0$$

$$r_A = -k_1 C_A$$

$$\therefore C_{A0} - C_A - k_1 C_A \tau = 0$$

$$\therefore \boxed{C_A = \frac{C_{A0}}{1 + k_1 \tau}} \quad \text{--- (1)}$$

we use the same procedure for B and C

mole balance on B

$$\text{in} - \text{out} + \text{generation} = 0$$

$$F_{B0} - F_B + r_B V = 0$$

$$-v_0 C_B + r_B V = 0$$

$$-C_B + r_B \tau = 0$$

$$r_B = k_1 C_A - k_2 C_B$$

$$\therefore -C_B + (k_1 C_A - k_2 C_B) \tau = 0$$

$$C_B = \frac{k_1 C_A \tau}{1 + k_2 \tau}$$

substitute for C_A

$$C_B = \frac{k_1 C_{A0} \tau}{(1 + k_1 \tau)(1 + k_2 \tau)} \quad \text{--- (2)}$$

mole balance on C

$$\text{in} - \text{out} + \text{generation} = 0$$

$$-F_C + r_C V = 0$$

$$-v_0 C_C + r_C V = 0$$

$$-C_C + r_C \tau = 0$$

$$r_c = k_2 C_B$$

$$\therefore C_c = r_c \tau = k_2 C_B \tau$$

substituting for C_c

$$\boxed{C_c = \frac{k_1 k_2 \tau_{A0} \tau^2}{(1+k_1 \tau)(1+k_2 \tau)}} \quad \text{--- (3)}$$

Optimum concentration of B

$$\text{For optimum concentration: } \frac{dC_B}{d\tau} = 0$$

$$0 = \frac{dC_B}{d\tau} = \frac{k_1 C_{A0} (1+k_1 \tau) (1+k_2 \tau) - k_1 C_{A0} \tau (k_1 + k_2 + 2k_1 k_2 \tau)}{[(1+k_1 \tau)(1+k_2 \tau)]^2}$$

solving for τ

$$\boxed{\tau_{\max} = \frac{1}{\sqrt{k_1 k_2}}} \quad \text{--- (4)}$$

The exiting concentration of B is max.
at $\tau = \tau_{\max}$.

substitute (4) in (2)

$$C_B = \frac{k_1 C_{A0} \tau_{max}}{(1 + k_1 \tau_{max})(1 + k_2 \tau_{max})}$$

$$= \frac{k_1 C_{A0} \tau_{max}}{1 + k_1 \tau_{max} + k_2 \tau_{max} + k_1 k_2 \tau_{max}^2}$$

$$C_B = \frac{C_{A0} \frac{k_1}{\sqrt{k_1 k_2}}}{1 + \frac{k_1}{\sqrt{k_1 k_2}} + \frac{k_2}{\sqrt{k_1 k_2}} + 1}$$

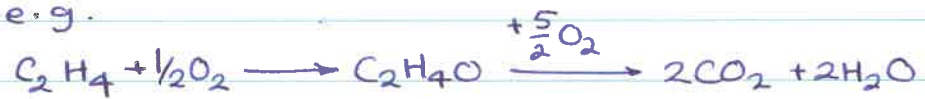
$$C_B = \frac{k_1 C_{A0}}{2\sqrt{k_1 k_2} + k_1 + k_2} \quad (5)$$

Membrane reactors to improve selectivity in multiple reactions

→ Selectivity can be increased by injecting one of the reactants along the length of the reactor

⇒ Partial oxidation of hydrocarbons, chlorination, ethoxylation, hydrogenation, nitration, sulfonation reactions.

e.g.



desired.