# MULTIPLE REACTIONS

* A key challenge in chemical reaction engineering is to use engineering acumen to control the product spectrum in multiple reactions.

① e.g.

$$\begin{tikzcd} & B \\ A \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\ & C \end{tikzcd}$$

Parallel reactions

Isomerization rxns. ≡ petroleum industry
(oxidation of ethylene)

② $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ Series reactions

e.g. oxidation of alcohols

③ Complex reactions:

$$A + B \longrightarrow C + D$$
$$A + C \longrightarrow E$$

e.g. cellular metabolism

④ **Independent reactions:**

$$A \rightarrow B + C$$
$$D \rightarrow E + F$$

e.g. thermal decomposition of chemicals (cracking)

Typically, when one has multiple reactions in a system, one is a desired rxn., the other may be undesired.

Recollect:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$ (batch reactor)

$$\frac{dC_A}{dt} = -k_1 C_A$$ ..... elementary rxn.

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

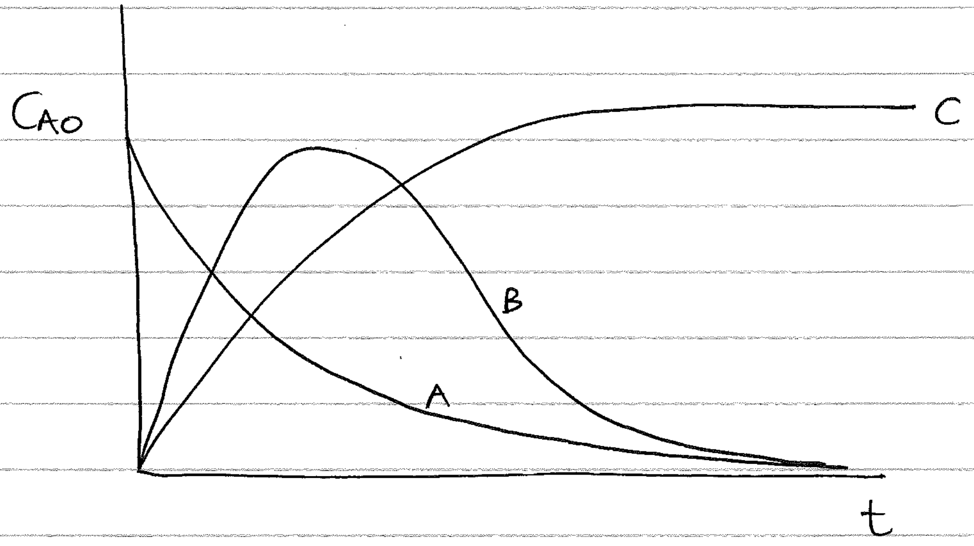
$$\frac{dC_C}{dt} = k_2 C_B$$ {& At $t=0$, $C_{A0}$ only}

Solving these ODEs we get:

$$C_A = C_{A0} \exp(-k_1 t)$$

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

$$C_C = C_{A0} + \left(\frac{C_{A0}}{k_1 - k_2}\right)\left[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)\right]$$



In this system, if B is the desired product, we want to cut off the rxn. when as much $C_B$ exists.

$$\therefore \frac{dC_B}{dt} = 0 \quad @ \, t_{opt}.$$

Find $t_{opt}$: $\qquad \dfrac{dC_B}{dt} = 0$

$$\therefore \; k_1 C_A = k_2 C_B$$

$$\therefore \; k_1 C_{A_0} \exp(-k_1 t_{opt}) = \frac{k_1 k_2 C_{A0}}{(k_1 - k_2)} \left[\exp(-k_2 t_{opt}) - \exp(-k_1 t_{opt})\right]$$

$$\therefore \; \left[\frac{k_1 - k_2}{k_2}\right] \exp(-k_1 t_{opt}) = \exp(-k_2 t_{opt}) - \exp(-k_1 t_{opt})$$

$$\therefore \; \exp(-k_1 t_{opt}) \left[\frac{k_1 - k_2}{k_2} + 1\right] = \exp(-k_2 t_{opt})$$

$$\therefore \; k_1 \exp(-k_1 t_{opt}) = k_2 \exp(-k_2 t_{opt})$$

$$\therefore \; \ln k_1 - k_1 t_{opt} = \ln k_2 - k_2 t_{opt}$$

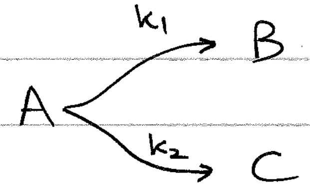
$$\therefore \; \ln\left(\frac{k_1}{k_2}\right) = t_{opt}(k_1 - k_2)$$

$$\boxed{\therefore \; t_{opt} = \left(\frac{1}{k_1 - k_2}\right) \ln\left(\frac{k_1}{k_2}\right)}$$

## Optimisation metrics

parlance ⇒ "I am improving...." $\begin{cases} \rightarrow \text{selectivity} \\ \rightarrow \text{yield} \end{cases}$

## What is selectivity?



$$\boxed{\text{selectivity of B w.r.t. C} \equiv S_{B/C} = \frac{r_B}{r_C}}$$

It is a ratio of the rates of reactions forming a particular pair of products!

$$\boxed{\therefore \quad S_{B/C} = \frac{r_B}{r_C} \quad \left.\begin{matrix} \\ \\ \end{matrix}\right\} \text{also called "instantaneous" selectivity}}$$

Why? Because $r_B$ & $r_C$ are functions of time in batch reactors.

**overall selectivity** $$\boxed{\tilde{S}_{B/C} = \frac{N_B}{N_C}}$$

moles formed

For a CSTR, instantaneous & overall selectivity are equal.

What about a PFR? Yes!

$$\text{Similarly, yield} \begin{cases} \to \text{instantaneous} \\ \to \text{overall} \end{cases}$$

$$Y_B = \frac{r_B}{-r_A} \quad \& \quad \tilde{Y}_B = \frac{N_B}{N_{A_0} - N_A}$$

(instantaneous) (overall)

$$\boxed{\text{yield} \equiv \frac{\text{formation of product moles}}{\text{reactant moles consumed}}}$$

$$\therefore \boxed{\begin{array}{l} \text{Selectivity} \equiv \text{compares products} \\ \quad \& \\ \text{yield} \equiv \dfrac{\text{product formed}}{\text{reactant consumed}} \end{array}}$$

* selectivity engineering is a significant area of interest in the industry

Consider a simple system:

$$A \xrightarrow{k_1} B \quad \text{(desired)}$$

$$A \xrightarrow{k_2} C \quad \text{(undesired)}$$

$$\left.\begin{aligned} r_B &= k_1 C_A^{\alpha_1} \\ r_C &= k_2 C_A^{\alpha_2} \end{aligned}\right\} \text{we are assuming a very simple system}$$

$$\therefore \quad -r_A = k_1 C_A^{\alpha_1} + k_2 C_A^{\alpha_2}$$

$$\boxed{\therefore \quad -r_A = r_B + r_C} \longrightarrow ①$$

$$S_{B/C} = \frac{r_B}{r_C} = \frac{k_1 C_A^{\alpha_1}}{k_2 C_A^{\alpha_2}}$$

$$\therefore \quad S_{B/C} = \left(\frac{k_1}{k_2}\right) C_A^{\alpha_1 - \alpha_2}$$

If $\alpha_1 > \alpha_2$ , i.e. $\alpha_1 - \alpha_2 > 0$

$$\therefore \quad S_{B/C} = \left(\frac{k_1}{k_2}\right) C_A^{\alpha_1 - \alpha_2}$$

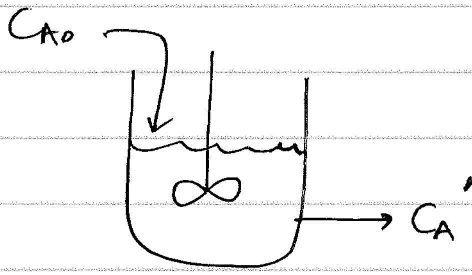
If B is desired, you want $S_{B/C}$ high.

$$\therefore \quad S_{B/C} = \left(\frac{k_1}{k_2}\right) \underbrace{C_A^{\alpha_1 - \alpha_2}}_{\substack{\text{make}\\ \text{as high}\\ \text{as possible}}}$$

How does one achieve high $C_A$?

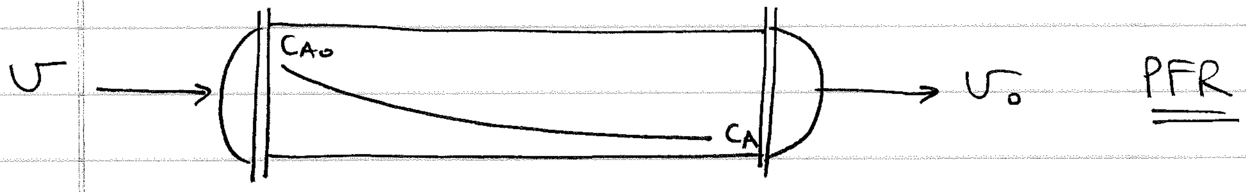
→ no inert streams or diluents

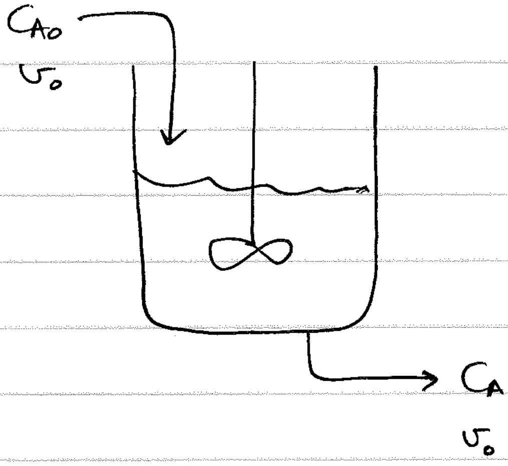
→ batch / PFR only. why?

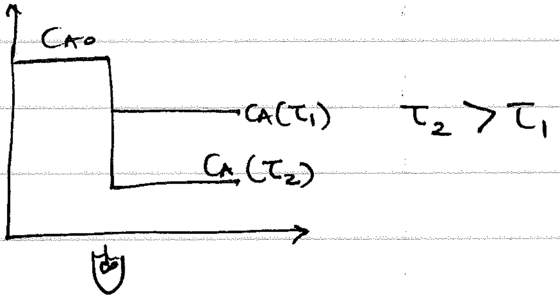


this value is the lowest it can get in the system.

CSTR is undesirable.







If you want to keep $C_A$ as low as possible, which reactor do you use?

$$F_{A0} - F_A = (-r_A)\, V_{CSTR}$$

$$F_A = F_{A0} - (-r_A)\, V_{CSTR}$$

$$\therefore \; C_A = C_{A0} - (-r_A)\,\tau$$

'Abrupt' change $\equiv$ <u>hard to control</u> ($\Rightarrow$ CSTR)

If $\alpha_1 < \alpha_2$ i.e. $\alpha_1 - \alpha_2 < 0$

$$S_{B/C} = \frac{k_1}{k_2} \underbrace{C_A^{\alpha_1 - \alpha_2}}_{\text{you want this as low as possible}}$$

→ CSTRs are good in this case

→ use diluents or inerts

$$S_{B/C} = \frac{k_1}{k_2} \underbrace{C_A^{\alpha_1 - \alpha_2}}_{\Downarrow \text{ we looked at this term}}$$

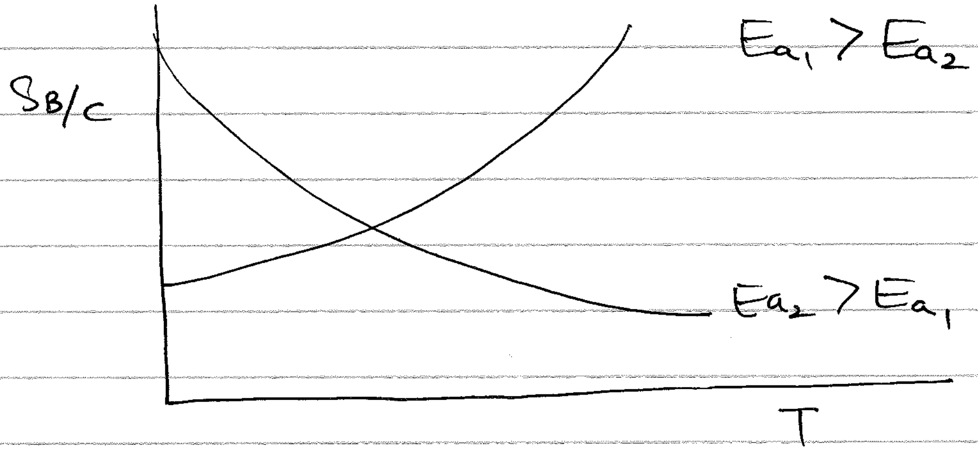
what about the rate constants?

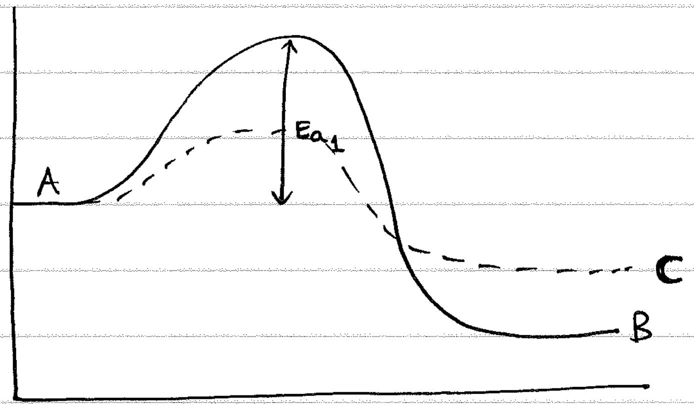
$$\frac{k_1}{k_2} = \frac{A_1 \exp\left(\frac{-E_{a1}}{RT}\right)}{A_2 \exp\left(-\frac{E_{a2}}{RT}\right)}$$

$$\therefore \frac{k_1}{k_2} = \underbrace{\left(\frac{A_1}{A_2}\right)}_{\substack{\text{generally}\\ \text{similar}\\ \text{order}\\ \text{of magnitude}}} \exp\left(\frac{E_{a_2} - E_{a_1}}{RT}\right)$$

$$\therefore \frac{k_1}{k_2} \approx \exp\left[\frac{E_{a_2} - E_{a_1}}{RT}\right]$$

we want $\frac{k_1}{k_2}$ to be as high as possible





Think of
this as
"motivation"/"energy"
to run
over a hill

once the energy/motivation goes beyond the treshold, running over the steep hill is not as bad!

The activation energy case is also important when $\alpha_1 = \alpha_2$

$$\boxed{\therefore \; S_{B/C} = \frac{k_1}{k_2}}$$

Let us consider a more complex case:

$$A \xrightarrow{k_1} X \quad \text{(undesired)}$$

$$A \xrightarrow{k_2} B \quad \text{(desired)}$$

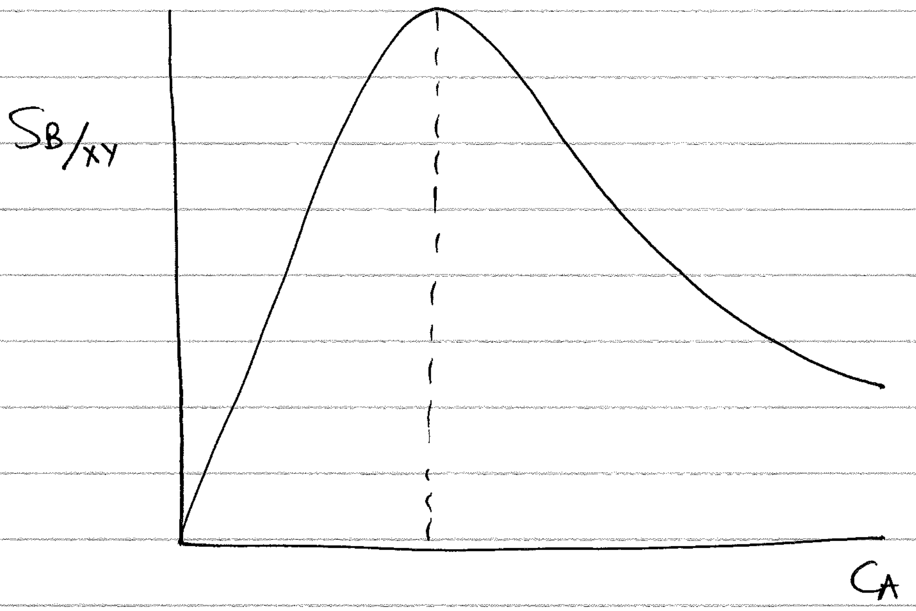
$$A \xrightarrow{k_3} Y \quad \text{(undesired)}$$

$r_X = k_1$ ..... 0th order

$r_B = k_2 C_A$ .... 1st order

$r_Y = k_3 C_A^2$ .... 2nd order

$$S_{B/XY} = \frac{r_B}{r_X + r_Y} = \frac{k_2 C_A}{k_1 + k_3 C_A^2}$$



Like in the series reactions case,

$S_{B/XY}$ has a maximum.

$$\therefore \frac{dS_{B/XY}}{dC_A} = 0 \quad @ \quad C_{A_{opt}}$$

Since we want to operate the process at a single conc., we use a CSTR

$$\therefore \frac{dS_{B/XY}}{dC_A} = \frac{(k_1 + k_3 C_A^2)(k_2) - (k_2 C_A)(2k_3 C_A)}{(k_1 + k_3 C_A^2)^2}$$

$$\therefore \frac{dS_{B/XY}}{dC_A} = \frac{k_1 k_2 + k_2 k_3 C_A^2 - 2 k_2 k_3 C_A^2}{(k_1 + k_3 C_A^2)^2}$$

$\hookrightarrow$ set $= 0$

$$\therefore k_1 k_2 - k_2 k_3 C_A^2 = 0$$

$$\therefore k_1 - k_3 C_A^2 = 0$$

$$\therefore C_A = \left(\frac{k_1}{k_3}\right)^{1/2}$$

$$\boxed{\therefore C_{A_{opt}} = \left(\frac{k_1}{k_3}\right)^{1/2}}$$

What $\underset{-r_A}{\underline{\text{was}}}$? $\underline{\underline{-r_A}} = \underset{k_1+}{k_2} C_A + k_3 C_A^2$ ! (Discuss this)

$$A \xrightarrow{k_1} B \qquad -r_{A_1} = k_1 C_A = r_B$$

$$A \xrightarrow{k_2} C \qquad -r_{A_2} = k_2 C_A = r_C$$

$$\therefore \quad r_B = k_1 C_A$$

$$r_C = k_2 C_A$$

$$-r_A = k_1 C_A + k_2 C_A = r_B + r_C$$

$$\therefore \quad -r_A = r_B + r_C$$

In general,

$$\boxed{r_j = \sum_{i=1}^{q} r_{ij}}$$

Also, $aA + bB \rightarrow cC + dD$

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{D}$$

What is $-r_A$ in the previous example?

$-r_A = k_2 C_A + k_3 C_A^2 + K_1$ !

Consider a system of parallel reactions with 2 species:

$$A + B \xrightarrow{k_1} D \quad \text{(desired)}$$

$$A + B \xrightarrow{k_2} U \quad \text{(undesired)}$$

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

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

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

$$\therefore S_{D/U} = \left(\frac{k_1}{k_2}\right) C_A^{\alpha_1 - \alpha_2} C_B^{\beta_1 - \beta_2}$$

Simple cases: ① $\alpha_1 > \alpha_2$, $\beta_1 > \beta_2$

⇒ PFR/batch, no inerts or diluents

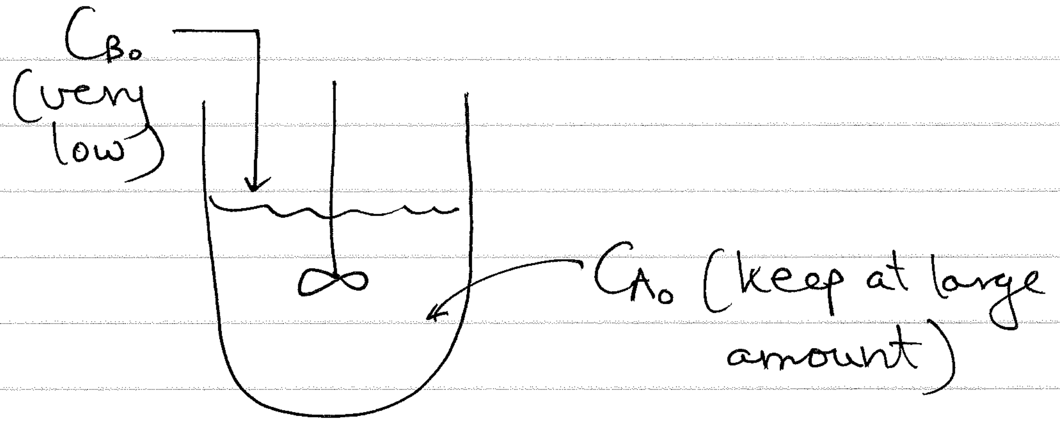
② $\alpha_1 < \alpha_2$, $\beta_1 < \beta_2$

⇒ CSTRs, use diluents

## 'Mixed' cases: $\alpha_1 > \alpha_2$ & $\beta_1 < \beta_2$

(or $\alpha_1 < \alpha_2$ & $\beta_1 > \beta_2$)

$$\boxed{\therefore\ S_{D/u} = \left(\frac{k_1}{k_2}\right) \underbrace{C_A^{\alpha_1-\alpha_2}}_{C_A \text{ as high as possible}} \ \underbrace{C_B^{\beta_1-\beta_2}}_{C_B \text{ as low as possible}}}$$



* we use the semi-batch system here

Also possible: