# Yr 3: Advanced Reaction Systems - Exam Crib Sheet

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# 1 Complex Reactions

## 1.1 Reaction Types

Series:
$\mathrm{A + B \longrightarrow C}$
Parallel:
$\mathrm{A \longrightarrow B}$
$\mathrm{A \longrightarrow C}$
Series-parallel:
$\mathrm{A + B \longrightarrow C}$
$\mathrm{A + C \longrightarrow D}$

## 1.2 Parallel Reactions

$\mathrm{A \xrightarrow{k1} V}$ is considered desired
$\mathrm{A \xrightarrow{k2} W}$ is considered undesired

$$r_V = \frac{\mathrm{d}C_V}{\mathrm{d}t} = k_1 C_A^{\alpha_1} \tag{1.1}$$
$$r_W = \frac{\mathrm{d}C_W}{\mathrm{d}t} = k_2 C_A^{\alpha_2} \tag{1.2}$$
$$\frac{r_V}{r_W} = \frac{\mathrm{d}C_V}{\mathrm{d}C_W} = \frac{k_1}{k_2} C_A^{(\alpha_1 - \alpha_2)} \tag{1.3}$$

| Case: | Do: |
|---|---|
| $\alpha_1 > \alpha_2$ | Use a high concentration of A to promote instantaneous selectivity |
| $\alpha_1 < \alpha_2$ | Use a low concentration of A to promote instantaneous selectivity |
| $\alpha_1 = \alpha_2$ | Adjusting the concentration of A does not affect the instantaneous selectivity |

If instantaneous yield *increases* with increasing reactant concentration, use plug flow or batch reactors. If instantaneous yield *decreases* with increasing reactant concentration, use CSTRs. If at a maxima or minima of instantaneous yield, use a combination of CSTRs and PFRs.

## 1.3 Batch Reactions

| Case: | Do: |
|---|---|
| $C_A, C_B$ both high | Add A and B all at one time |
| $C_A, C_B$ both low | Add A and B slowly, level rises |
| $C_A$ high, $C_B$ low | Start with A, add B slowly |

## 1.4 Yield

$$y = \frac{v_A}{v_V} \frac{\mathrm{d}C_V}{\mathrm{d}C_A} \tag{1.4}$$

For a reaction scheme $\mathrm{aA \longrightarrow vV}$, $v_A = -a$, $v_V = v$ and assuming recycle of A:

$$Y = \frac{v_A}{v_V} \left( \frac{C_{VF} - C_{V0}}{C_{AF} - C_{A0}} \right) \tag{1.5}$$

With no recycle:

$$Y = \frac{v_A}{v_V} \left( \frac{C_{VF}}{-C_{A0}} \right) \tag{1.6}$$

### 1.4.1 CSTR Yield

$$Y_{CSTR} = y_{CSTR} = \frac{v_A r_{VF}}{v_V r_{AF}} \tag{1.7}$$

### 1.4.2 PFR or Batch Reactor Yield

$$C_{VF} - C_{V0} = \int_{C_{A0}}^{C_{AF}} \frac{v_V y}{v_A} \, \mathrm{d}C_A \tag{1.8}$$
$$Y = \frac{1}{C_{AF} - C_{A0}} \int_{C_{A0}}^{C_{AF}} y \, \mathrm{d}C_A \tag{1.9}$$

### 1.4.3 CSTRs in Series Yield

$$Y = \frac{\sum_{i=1}^{n} [y_i (\Delta C_A)_i]}{C_{An} - C_{A0}} \tag{1.10}$$

## 1.5 Series-Parallel Reactions

$\mathrm{A + B \xrightarrow{k1} V}$ series w.r.t. A
$\mathrm{A + C \xrightarrow{k2} W}$ parallel w.r.t. B

### 1.5.1 Quantitative Solution

Assuming the reaction above takes place in a plug flow or batch reactor and the reactions are first order with respect to each reactant (i.e. second order overall):

$$-\frac{\mathrm{d}C_A}{\mathrm{d}t} = k_1 C_A C_B \tag{1.11}$$
$$\frac{\mathrm{d}C_V}{\mathrm{d}t} = k_1 C_A C_B - k_2 C_V C_B \tag{1.12}$$
$$y = \frac{v_A}{v_V} \frac{\mathrm{d}C_V}{\mathrm{d}C_A} = \frac{k_1 C_A C_B - k_2 C_V C_B}{k_1 C_A C_B} \tag{1.13}$$
$$\frac{\mathrm{d}C_V}{\mathrm{d}C_A} = \frac{k_2}{k_1} \frac{C_V}{C_A} - 1 \tag{1.14}$$

For $k_2 \neq k_1$:

$$\frac{C_V}{C_{A0}} = \frac{1}{1-\frac{k_2}{k_1}}\left[\left(\frac{C_A}{C_{A0}}\right)^{\frac{k_2}{k_1}} - \frac{C_A}{C_{A0}}\right] + \frac{C_{V0}}{C_{A0}}\left(\frac{C_A}{C_{A0}}\right)^{\frac{k_2}{k_1}} \tag{1.15}$$

For $k_1 = k_2$:

$$\frac{C_V}{C_{A0}} = \frac{C_A}{C_{A0}}\left(\frac{C_{V0}}{C_{A0}} - \ln\frac{C_A}{C_{A0}}\right) \tag{1.16}$$

Material balance on Species A yields:

$$C_{A0} + C_{V0} + C_{W0} = C_A + C_V + C_W \tag{1.17}$$
$$C_{B0} - C_B = (C_V - C_{V0}) + 2\,(C_W - C_{W0}) \tag{1.18}$$
$$-r_A V = QC_{A0} - QC_{AF} \tag{1.19}$$
$$-r_V V = QC_{V0} - QC_{VF} \tag{1.20}$$
$$\tau = \frac{V}{Q} = \frac{C_{A0} - C_A}{-r_A} = \frac{C_{V0} - C_V}{-r_V} \tag{1.21}$$
$$\frac{C_{V0} - C_V}{C_{A0} - C_A} = -1 + \frac{k_2 C_V}{k_1 C_A} \tag{1.22}$$
$$\frac{C_V}{C_{A0}} = \frac{\frac{C_{V0}}{C_{A0}} + \left(1 - \frac{C_A}{C_{A0}}\right)}{1 + \frac{k_2}{k_1}\left(\frac{C_{A0}}{C_A} - 1\right)} \tag{1.23}$$

The graphical interpretation of this equation is given separately, one must calculate the amount of B consumed, then determine the ratio of rate constants and then parameters can be read off from the chart.

# 2 Non-Ideal Flow

## 2.1 Pulse input

$$\int_0^\infty C(t)\ \mathrm{d}t \approx \sum_i C_i \Delta t_i = \frac{m}{v} \tag{2.1}$$
$$E(t) = \frac{C_{\text{pulse}} v}{m} \tag{2.2}$$
$$\tag{2.3}$$

## 2.2 General Residence Time Distribution Formulae

$$\tau = \frac{\int_0^\infty t\ C(t)\ \mathrm{d}t}{\int_0^\infty C(t)\ \mathrm{d}t} \tag{2.4}$$
$$\tau = \int_0^\infty t\ E(t)\ \mathrm{d}t \approx \sum_i t_i E_i \Delta t_i \tag{2.5}$$

## 2.3 Kinetics

### 2.3.1 General

$$\frac{\bar{C}_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}}\right)_{\text{elem}} E(t)\ \mathrm{d}t \tag{2.6}$$
$$\approx \sum_i \left(\frac{C_A}{C_{A0}}\right)_{\text{elem, } i} E(t_i)\Delta t_i \tag{2.7}$$

### 2.3.2 0th Order Reactions

$$C_{A0} - C_A = k\tau \tag{2.8}$$

### 2.3.3 1st Order Reactions

$$\left(\frac{C_A}{C_{A0}}\right)_{\text{elem}} = \mathrm{e}^{-k\tau} \tag{2.9}$$

### 2.3.4 2nd Order Reactions

$$\left(\frac{C_A}{C_{A0}}\right)_{\text{elem}} = \frac{1}{1 + kC_{A0}t} \tag{2.10}$$

### 2.3.5 Variance

$$\sigma^2 = \int_0^\infty t^2\ E(t)\ \mathrm{d}t - \tau^2 \tag{2.11}$$
$$\sigma^2 \approx \frac{\sum_i (t_i - \tau)^2 C_i \Delta t_i}{\sum_i C_i \Delta t_i} - \tau^2 \tag{2.12}$$
$$\Delta\sigma^2 = \sigma_{out}^2 + \sigma_{in}^2 = \frac{\Delta\tau^2}{N} \tag{2.13}$$
$$\tag{2.14}$$

### 2.3.6 Recycle Ratio

$$R = \frac{\sigma^2}{\bar{\tau}^2 - \sigma^2} \tag{2.15}$$

## 2.4 Ideal Reactors

### 2.4.1 PFR Design Equation

$$\begin{gathered}
\text{Assume first order kinetics} \\
\frac{\mathrm{d}C_A}{\mathrm{d}t} = r_A = -kC_A \\
\int_{C_{A1}}^{C_{A2}} \frac{1}{C_A}\ \mathrm{d}C_A = -k\int_0^t \mathrm{d}t \\
C_{A2} = C_{A1}\mathrm{e}^{-kt}
\end{gathered}$$

### 2.4.2 CSTR Design Equation

$$\begin{gathered}
In = Out + Disappearance \\
vC_{A0} = vC_{A1} + (-r_A)V_r \\
\text{Assume first order kinetics} \\
vC_{A0} = vC_{A1} + kC_{A1}V_r \\
C_{A0} = C_{A1} + kC_{A1}\tau \\
\frac{C_{A1}}{C_{A0}} = \frac{1}{1 + k\tau}
\end{gathered}$$

## 2.5 Tanks in series

$N$ plug flow reactors in series with a total volume $V$ gives the same conversion as a single plug flow reactor of volume $V$.

$$\theta_i = \frac{t}{\tau_i} \tag{2.16}$$

$$\theta = \frac{t}{\tau} \tag{2.17}$$

$$\tau E(t) = \left(\frac{t}{\tau}\right)^{N-1} \frac{N^N}{(N-1)!} \mathrm{e}^{\frac{-tN}{\tau}} \tag{2.18}$$