

Yr 3: Advanced Reaction Systems - Exam Crib Sheet

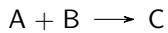
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Semester 3, Week 2

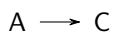
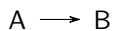
1 Complex Reactions

1.1 Reaction Types

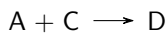
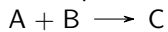
Series:



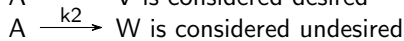
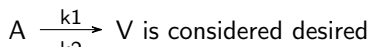
Parallel:



Series-parallel:



1.2 Parallel Reactions



$$r_V = \frac{dC_V}{dt} = k_1 C_A^{\alpha_1} \quad (1.1)$$

$$r_W = \frac{dC_W}{dt} = k_2 C_A^{\alpha_2} \quad (1.2)$$

$$\frac{r_V}{r_W} = \frac{dC_V}{dC_W} = \frac{k_1}{k_2} C_A^{(\alpha_1 - \alpha_2)} \quad (1.3)$$

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

$$y = \frac{v_A}{v_V} \frac{dC_V}{dC_A} \quad (1.4)$$

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

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

With no recycle:

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

1.4.1 CSTR Yield

$$Y_{CSTR} = y_{CSTR} = \frac{v_A r_{VF}}{v_V r_{AF}} \quad (1.7)$$

1.4.2 PFR or Batch Reactor Yield

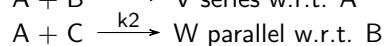
$$C_{VF} - C_{V0} = \int_{C_{A0}}^{C_{AF}} \frac{v_V y}{v_A} dC_A \quad (1.8)$$

$$Y = \frac{1}{C_{AF} - C_{A0}} \int_{C_{A0}}^{C_{AF}} y dC_A \quad (1.9)$$

1.4.3 CSTRs in Series Yield

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

1.5 Series-Parallel Reactions



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):

$$-\frac{dC_A}{dt} = k_1 C_A C_B \quad (1.11)$$

$$\frac{dC_V}{dt} = k_1 C_A C_B - k_2 C_V C_B \quad (1.12)$$

$$y = \frac{v_A}{v_V} \frac{dC_V}{dC_A} = \frac{k_1 C_A C_B - k_2 C_V C_B}{k_1 C_A C_B} \quad (1.13)$$

$$\frac{dC_V}{dC_A} = \frac{k_2}{k_1} \frac{C_V}{C_A} - 1 \quad (1.14)$$

For $k_2 \neq k_1$:

$$\frac{C_V}{C_{A0}} = \frac{1}{1 - \frac{k_2}{k_1}} \left[\left(\frac{C_A}{C_{A0}} \right)^{\frac{k_2}{k_1}} - \frac{C_A}{C_{A0}} \right] + \frac{C_{V0}}{C_{A0}} \left(\frac{C_A}{C_{A0}} \right)^{\frac{k_2}{k_1}} \quad (1.15) \quad C_{A0} - C_A = k\tau \quad (2.8)$$

For $k_1 = k_2$:

$$\frac{C_V}{C_{A0}} = \frac{C_A}{C_{A0}} \left(\frac{C_{V0}}{C_{A0}} - \ln \frac{C_A}{C_{A0}} \right) \quad (1.16) \quad \left(\frac{C_A}{C_{A0}} \right)_{\text{elem}} = e^{-k\tau} \quad (2.9)$$

Material balance on Species A yields:

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

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.

2.3.2 0th Order Reactions

2.3.3 1st Order Reactions

2.3.4 2nd Order Reactions

2.3.5 Variance

2.3.6 Recycle Ratio

2 Non-Ideal Flow

2.1 Pulse input

$$\int_0^\infty C(t) dt \approx \sum_i C_i \Delta t_i = \frac{m}{v} \quad (2.1)$$

$$E(t) = \frac{C_{\text{pulse}} v}{m} \quad (2.2)$$

$$(2.3)$$

2.2 General Residence Time Distribution Formulae

$$\tau = \frac{\int_0^\infty t C(t) dt}{\int_0^\infty C(t) dt} \quad (2.4)$$

$$\tau = \int_0^\infty t E(t) dt \approx \sum_i t_i E_i \Delta t_i \quad (2.5)$$

2.3 Kinetics

2.3.1 General

$$\frac{\bar{C}_A}{C_{A0}} = \int_0^\infty \left(\frac{C_A}{C_{A0}} \right)_{\text{elem}} E(t) dt \quad (2.6)$$

$$\approx \sum_i \left(\frac{C_A}{C_{A0}} \right)_{\text{elem}, i} E(t_i) \Delta t_i \quad (2.7)$$

2.4 Ideal Reactors

2.4.1 PFR Design Equation

Assume first order kinetics

$$\begin{aligned} \frac{dC_A}{dt} &= r_A = -kC_A \\ \int_{C_{A1}}^{C_{A2}} \frac{1}{C_A} dC_A &= -k \int_0^\tau dt \\ C_{A2} &= C_{A1} e^{-k\tau} \end{aligned}$$

2.4.2 CSTR Design Equation

In = Out + Disappearance

$$vC_{A0} = vC_{A1} + (-r_A)V_r$$

Assume first order kinetics

$$vC_{A0} = vC_{A1} + kC_{A1}V_r$$

$$C_{A0} = C_{A1} + kC_{A1}\tau$$

$$\frac{C_{A1}}{C_{A0}} = \frac{1}{1 + k\tau}$$

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 .

$$\theta_i = \frac{t}{\tau_i} \quad (2.16)$$

$$\theta = \frac{t}{\tau} \quad (2.17)$$

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

