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Homogeneous reactor

Chapter 5: Study of homogeneous isothermal chemical reactors with several reactions

Chapter 1: General

- Stoichiometry: Concept of conversion rate; Concept of advancement; Case of a single reaction; Case of several reactions.

Chapter 2: Classification of chemical reactors

- Perfectly stirred batch reactor;
- Perfectly stirred stationary continuous reactor;
- Stationary tubular continuous plug flow reactor.

Chapter 3: Material balances in ideal reactors

-Single reaction:
-Perfectly agitated closed reactor;
-Continuous perfectly stirred reactor in steady state;
-Piston reactor in steady state.

Chapter4: Study of homogeneous isothermal chemical reactors with one reaction

-R.D.P.A; R.C.P.A; R.C.P;
-Chemical Reactor Association:
    => Association of stationary continuous reactors in plug flow (series/parallel);
    => Association of perfectly stirred stationary continuous reactors (series/parallel);
-Comparative performances of ideal reactors.

Chapter 5: Study of homogeneous isothermal chemical reactors with several reactions

- Consecutive irreversible reactions;
-Competitive reactions;
-Selectivity and yield;

Chapter 6: Ideal non-isothermal reactors

-Notions of thermal balances in ideal non-isothermal reactors.

Chapter 5: Study of homogeneous isothermal chemical reactors with several reactions

- Consecutive irreversible reactions;
-Competitive reactions;
-Selectivity and yield;

……

V.1. Introduction

For a single stoichiometry reaction, knowledge of the conversion rate or progress chemical is sufficient to determine the distribution in relation to all the constituents involved in this reaction. However, in the case of a reaction with multiple stoichiometry, the simple Knowledge of these parameters is not sufficient to obtain the distribution. To do this, it is necessary to add other quantities, mainly selectivity (S) and yield (Y)

V.2. Definition

Consider a reaction with multiple stoichiometry:

$$\begin{tikzcd} & \nu_c C + \nu_D D \\ \nu_A A + \nu_B B \arrow[ur] \arrow[dr] & \\ & \nu_E E + \nu_G G \end{tikzcd}$$

- ***Selectivity:***

For a closed system, the overall selectivity for a product X compared to a reagent A ($S_{X/A}$) is defined by:

$$S_{X/A} = \frac{\Delta n_X}{\Delta n_A}\frac{\nu_A}{\nu_X}$$

Δn_X : Quantity of X formed
Δn_A : Quantity of A reacted

For an open system, the $S_{X/A}$ selectivity is defined by:

$$S_{X/A} = \frac{\Delta F_X}{\Delta F_A}\frac{\nu_A}{\nu_X}$$

ΔF_X : Flow of X formed
ΔF_A :Flow of reacted A

Remark:

For two very close instants t_1 and t_2, the instantaneous selectivity is defined as follows:

$$S_{X/A} = \frac{dn_X}{dn_A}\frac{\nu_A}{\nu_X} \rightarrow \text{Closed system}$$

$$S_{X/A} = \frac{dF_X}{dF_A}\frac{\nu_A}{\nu_X} \rightarrow \text{Open system}$$

If the closed system is isochoric (constant volume):

r_X: X formation speed

$-r_A$: speed of disappearance of A

$$S_{X/A} = \frac{1/V.dn_X/dt}{1/V dn_A/dt}\frac{\nu_A}{\nu_X} = \frac{(r_X)}{(-r_A)}\frac{|\nu_A|}{\nu_X}$$

- ***Yield:***

For a closed system, the overall yield for the production of product X relative to reactant A ($S_{X/A}$) is defined by:

$$Y_{X/A} = \frac{\Delta n_X}{n_{A0}}\frac{|\nu_A|}{\nu_X}$$

Δn_X : Quantity of X formed

n_{A0} : Initial quantity of A

For an open system, the overall yield is defined by:

$$Y_{X/A} = \frac{\Delta F_X}{F_{Ae}}\frac{|\nu_A|}{\nu_X}$$

ΔF_X : flow of X formed

F_{Ae} : flow of A at entrance

The instantaneous yield is obtained by substituting Δ by d

- ***Relationship between selectivity and yield***

$$Y_{X/A} = \frac{\Delta n_X}{n_{A0}}\frac{|\nu_A|}{\nu_X}\frac{\Delta n_A}{\Delta n_A} = \frac{\Delta n_A}{n_{A0}}\frac{\Delta n_X}{\Delta n_A}\frac{|\nu_A|}{\nu_X} = X_A \times S_{X/A}$$

V. 3. Series reaction

$$\nu_A A \xrightarrow{k_1} \nu_B B \xrightarrow{k_2} \nu_C C$$

V. 3.1. Closed reactor

We consider that $|\upsilon_A| = |\upsilon_B| = |\upsilon_C| = 1$ and that the reactions are elementary (partial order equal to 1). The aim is to obtain, as a function of time, the concentration profiles of the species as well as the selectivity and yield of B and C based on material balances.

Constituent A

$$Disp + Acc = 0$$

$$(-r_A)V + dn_A/dt = 0$$

$$k_1C_AV + dn_A/dt = 0$$

$$k_1C_A + dC_A/dt = 0$$

$$dC_A/C_A = -k_1dt \rightarrow C_A = \alpha e^{-k1t}$$

At t = 0, $C_A = C_{A0}$ → $\alpha = C_{A0}$ → $C_A = C_{A0}e^{-k1t}$ ...(1)

Constituent B

App = Disp + Acc

$(r_B)V = (-r_B)V + dn_B/dt = 0$ /

$k_1C_AV = k_2C_BV + dn_B/dt = 0$

knowing that $(r_B) = (-r_A)$

$$\mathbf{dC_B/dt + k_2C_B = k_1C_A = k_1C_{A0}e^{-k1t}} \ldots\mathbf{(2)}$$

➔ Solution :

$dC_B/dt + k_2C_B = 0 \rightarrow \boldsymbol{C_B = \beta e^{-k2t}}$ ***…(3)***

$dC_B/dt = \beta' e^{-k2t} - k_2\beta\, e^{-k2t}$ ***…(4)***

We replace (3) and (4) in (2) we obtain:

$\beta' = k_1C_{A0}e^{(k2-k1)t} \rightarrow \beta = [k_1C_{A0}/(k_2-k_1)]e^{(k2-k1)t} + \gamma$ (γ : constant of integration)

$$C_B = [[k_1C_{A0}/(k_2-k_1)]e^{(k2-k1)t} + \gamma]e^{-k2t} \qquad \mathbf{(5)}$$

At t = 0, $C_B = 0 \rightarrow \gamma = -kC_{A0}/(k_2-k_1)$

$$\frac{C_B}{C_{A0}} = \frac{k_1}{k_2-k_1}\left(e^{-k_1t} - e^{-k_2t}\right)[k_1C_{A0}/(k_2-k_1)]e^{(k2-k1)t} + \gamma$$

Substituting γ by its expression, equation (3) is written:

$$\frac{C_B}{C_{A0}} = \frac{k_1}{k_2-k_1}\left(-e^{-k_1t} - e^{-k_2t}\right) \qquad (6)$$

Constituent C

$$App = Acc$$
$$(r_c)V = dn_c/dt$$
$$k_2C_BV = dn_c/dt$$
$$dC_c/dt = k_2C_B$$

knowing that $(r_C) = (-r_B)$

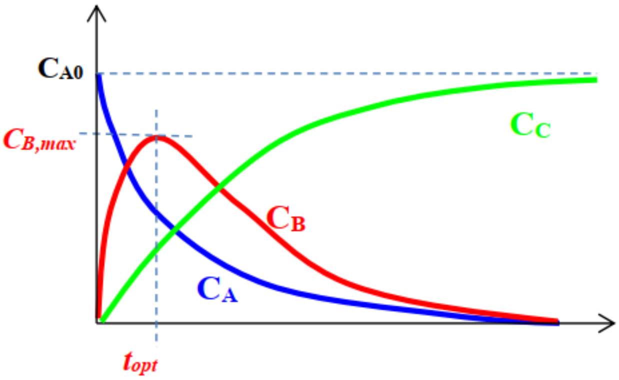
$$\frac{C_C}{C_{A0}} = \frac{k_1k_2}{k_2-k_1}\left(\frac{-e^{-k_1t}}{k_1} + \frac{e^{-k_2t}}{k_2}\right) \qquad (7)$$

This last equation can be obtained directly from the equation:

$$\boldsymbol{C_{A0} = C_A + C_B + C_C}$$
$$\boldsymbol{C_C = C_{A0} - C_A - C_B}$$

- Concentration profile and optimal conditions for “B”

The concentration profiles of A, B and C are shown in the figure below. An optimum by relation to constituent B is observed. If B is the desired compound, the reaction should be stopped at t_{opt}, moment when the concentration of B is maximum ($C_{B,max}$).



"t_{opt}" as well as "C_{Bmax}" can be determined analytically by equating the derivative of C_B by relative to time to zero, as follows:

$$\frac{C_{B,\max}}{C_{A0}} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1 t_{opt}} - e^{-k_2 t_{opt}}\right)$$

$$\frac{dC_B}{dt} = 0 \Longrightarrow t_{opt} = \frac{\ln(\frac{k_2}{k_1})}{k_2 - k_1}$$

Similarly, the concentrations of A and C at t_{opt} can be determined as follows:

$$C_A / C_{A0} = e^{-k1 t_{opt}}$$

$$\frac{C_C}{C_{A0}} = \frac{k_1 k_2}{k_2 - k_1}\left(\frac{-e^{-k_1 t_{opt}}}{k_1} + \frac{e^{-k_2 t_{opt}}}{k_2}\right)$$

- Selectivity $S_{B/A}$ and Yield $Y_{B/A}$

$$S_{B/A}=\frac{dn_B}{dn_A}\frac{\nu_A}{\nu_X}=\frac{dC_B}{dC_A}\frac{\nu_A}{\nu_X}\frac{C_B-0}{C_A-C_{A0}}\frac{-1}{1}=\frac{C_B}{C_{A0}-C_A}=\frac{\frac{C_B}{C_{A0}}}{1-\frac{C_A}{C_{A0}}}=\frac{k_1}{k_2-k_1}\frac{\left(e^{-k_1t}-e^{-k_2t}\right)}{1-e^{-k_1t}}$$

$$(S_{B/A})_{\max}=\frac{k_1}{k_2-k_1}\frac{\left(e^{-k_1t_{opt}}-e^{-k_2t_{opt}}\right)}{1-e^{-k_1t_{opt}}}$$

$$R_{B/A}=\frac{dn_B}{n_{A0}}\frac{|\nu_A|}{\nu_X}=\frac{dC_B}{C_{A0}}\frac{|\nu_A|}{\nu_X}\frac{C_B-0}{C_{A0}}\frac{1}{1}=\frac{C_B}{C_{A0}}=\frac{k_1}{k_2-k_1}\left(e^{-k_1t}-e^{-k_2t}\right)$$

$$(R_{B/A})_{\max}=\left(\frac{C_B}{C_{A0}}\right)_{\max}=\frac{k_1}{k_2-k_1}\left(e^{-k_1t_{opt}}-e^{-k_2t_{opt}}\right)$$

V. 3.2. Piston reactor

$$A\xrightarrow{k_1}B\xrightarrow{k_2}C$$

Constituent A

In = out + disp

$$F_A = F_A + dF_A + (-r_A)dV$$

$$-dF_A = (-r_A)\,dV$$

$$F_A = QC_A \rightarrow dF_A = QdC_A,\ \text{and } dV= Qd\tau \qquad (\tau\ \text{passage time})$$

$$-QdC_A = (-r_A)Qd\tau$$

$$-dC_A = (-r_A)\,d\tau\ \text{or}\ dC_A/d\tau = (-r_A)$$

V. 3.3. Open reactor

Constituent A

$$\mathrm{E} = S + Disp$$

$$F_{Ae} = F_{As} + (-r_A)V$$

Or: $F_A = QC_A$ et $V= Q\tau$ (τ est le temps de passage)

$$QC_{Ae} = QC_{As} + (-r_A)Q\tau = QC_{As} + k_1C_{As}Q\tau = QC_{As}\,(1 + k\tau)$$

D'où $\boldsymbol{C_{As}/C_{Ae} = 1/(1 + k_1\tau)}$

Constituent B

Bila de matière/B : $E + App = S + Disp$

$$F_{Be} + (r_B)V = F_{Bs} + (-r_B)V$$

Or: $F_B = QC_B$ et $V = Q\tau$ (τ est le temps de passage)

$$QC_{Be} + k_1 C_{As} Q\tau = QC_{Bs} + k_2 C_{Bs} Q\tau$$

Pour $C_{Be} = 0$:

$$\tau_{opt} = \frac{\ln\left(\frac{k_2}{k_1}\right)}{k_2 - k_1}$$

Constituent C

Bila de matière/C : $E + App = S$

$$F_{Ce} + (r_C)V = F_{Cs}$$

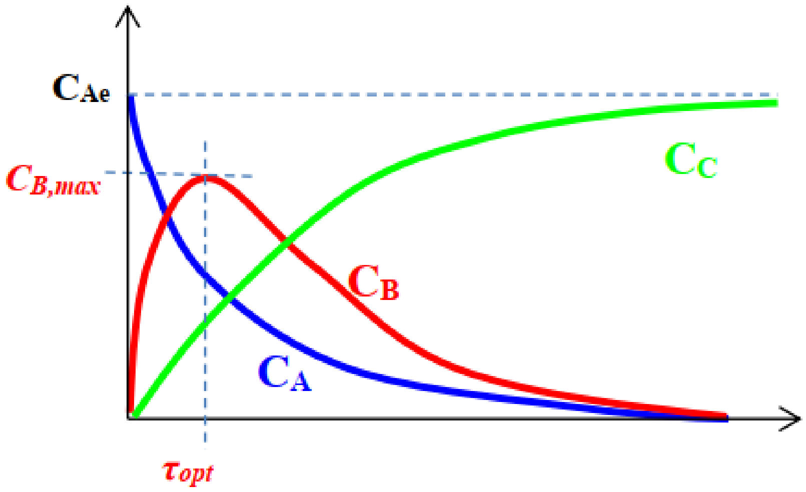
Or: $F_C = QC_C$ et $V = Q\tau$ (τ est le temps de passage)

$$QC_{Ce} + k_2 C_{Bs} Q\tau = QC_{Cs}$$

Pour $C_{Ce} = 0$:

$$\frac{C_{B,\max}}{C_{Ae}} = \frac{k_1}{k_2 - k_1}\left(e^{-k_1\tau_{opt}} - e^{-k_2\tau_{opt}}\right)$$

Concentration profile and optimal conditions compared to “B”



τ_{opt} as well as $C_{B,max}$ can be determined analytically in the same way as we did for the closed reactor, by equating the derivative of CB with respect to τ to zero. we get:

$$\tau_{opt} = \frac{1}{\sqrt{k_1 k_2}}$$

$$\frac{C_{B,\max}}{C_{Ae}} = \frac{k_1 \frac{1}{\sqrt{k_1 k_2}}}{(1 + k_1 \frac{1}{\sqrt{k_1 k_2}})(1 + k_2 \frac{1}{\sqrt{k_1 k_2}})}$$

- Si $k_1 = k_2 = k$:

$$\tau_{opt} = 1/k$$

$$C_{B,\max} = 1/4$$

- Selectivity $S_{B/A}$ and Yield $Y_{B/A}$

$$S_{B/A} = \frac{C_B}{C_{A0} - C_A} = \frac{\frac{k_1 \tau}{(1 + k_1 \tau)(1 + k_2 \tau)}}{1 - \frac{1}{(1 + k_1 \tau)}} = \frac{1}{(1 + k_2 \tau)}$$

$$(S_{B/A})_{\max} = \frac{1}{(1 + k_2 \tau)} = \frac{1}{(1 + k_2 \frac{1}{\sqrt{k_1 k_2}})} = \frac{1}{\left(1 + \sqrt{\frac{k_2}{k_1}}\right)}$$

$$Y_{B/A} = \frac{C_B}{C_{A0}} = \frac{k_1 \tau}{(1 + k_1 \tau)(1 + k_2 \tau)}$$

$$(Y_{B/A})_{\max} = \left(\frac{C_B}{C_{A0}}\right)_{\max} = \frac{k_1 \frac{1}{\sqrt{k_1 k_2}}}{(1 + k_1 \frac{1}{\sqrt{k_1 k_2}})(1 + k_2 \frac{1}{\sqrt{k_1 k_2}})}$$