Isothermal Batch Reactor

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Zero-order reaction

- The zero-order kinetics is written as

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = k \qquad\qquad (34)$$

It may be written as $-\frac{dC_A}{dt} = k$ for constant volume batch reactor

On integration from $t = 0$, $C_A = C_{A0}$ to $t = t$, $C_A = C_A$, it results

$C_A = C_{A0} - kt$, which is a straight line

At t→ ∞ , C_A approaches to a negative value, which is never be possible as concentration cannot be negative.

Hence, the equation is valid up to $t = C_{A0}/k$ at which $C_A = 0$.

Zero-order reaction

- The equation $C_A = C_{A0} - kt$ thus valid within the range $t \le C_{A0}/k$ and at $t \ge C_{A0}/k$, $C_A = 0$. This is shown in the Fig.8
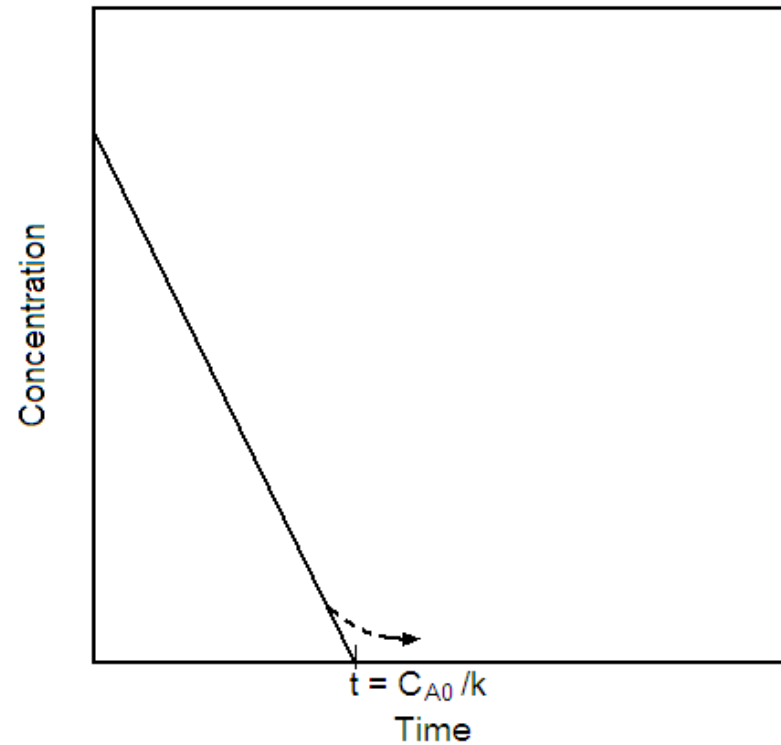

Fig. 8 Zero order reaction

First order reaction

- Let us consider a first order the rate equation as, $-r_A = kC_A$. The mole balance can be given as.

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = kC_A \qquad (35)$$

$$-r_A = -\frac{dC_A}{dt} = kC_A$$

- On integration from $t = 0$, $C_A = C_{A0}$ to $t = t$, $C_A = C_A$, it results

$$-\int_{C_{A0}}^{C_A}\frac{dC_A}{C_A} = k\int_0^t dt \qquad (36)$$

$$-ln\frac{C_A}{C_{A0}} = kt \qquad (37)$$

First order reaction in terms of conversion

$-ln(C_A/C_{A0})$ is calculated for different 't' and plotted against t.

From the slope rate constant k is obtained.

The first-order rate equation in terms of conversion X_A is

$$-r_A = -\frac{d[C_{A0}(1 - X_A)]}{dt} = kC_{A0}(1 - X_A) \qquad (38)$$

$$\frac{dX_A}{dt} = kC_{A0}(1 - X_A) \qquad (39)$$

- On integration of eq.(39) from $t = 0, C_A = C_{A0}$ to $t = t, C_A = C_A$ we have
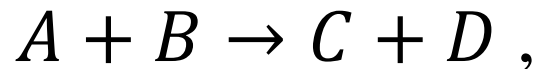$$-\ln(1 - X_A) = kt \qquad (40)$$

This equation may be used for finding k, if the batch reactor data are available as X_A versus t.

First order reaction

- $X_A = 1 - e^{-kt}$ $or, \ C_A = C_{A0}e^{-kt}$ if k is the rate constant
- $so, \ at \ t = \frac{1}{k}, \ \ C_A = \frac{C_{A0}}{e}, \ \ \ t = \frac{2}{k}, \ \ C_A = \frac{C_{A0}}{e^2}$

Second order reaction

The same procedure may be followed for an elementary second order reaction of type,

$A + B \rightarrow C + D$,

$$-r_A = -\frac{dC_A}{dt} = kC_A \, C_B$$ (41)

Second order reaction

- Let the A and B are added with a molar ratio of $= C_{B0}/C_{A0}$,
$C_A = C_{A0}(1 - X_A)$ and $C_B = C_{B0}(1 - X_B) = C_{A0}(M - X_A)$
as, $C_{A0}X_A = C_{B0}X_B$,
Eqn. (41) is written as a function of X_A ,

$$-r_A = C_{A0}\frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A) \qquad (42)$$

Integrating eq. (42) from $t = 0$, $X_A = 0$ to $t = t$, $X_A = X_A$,

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M - X_A)} = \int_0^t kC_{A0}\, dt$$

$$ln[(M - X_A)/(M - 1)] = C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt \qquad (43)$$

Second order reaction

- In the above equation $M > 1$ value should be used to get finite solution.
- A straight line is obtained when $ln[(M - X_A)/(M - 1)]$ is plotted against t . The slope of the straight line gives the value of rate constant.
- If the reactants are fed to the reactor in equal molar ratio, then $= 1$. Equation (42) is written as

$$-r_A = -\frac{dC_A}{dt} = kC_A^2$$

- The integrated form of equation is

$$\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 2kt \qquad\qquad\qquad (33)$$

- The eq(33) can be used for kinetic analysis. Again, if C_A is replaced by X_A we have the rate as a function of conversion

Second order reaction

Or, $$-r_A = C_{A0}\frac{dX_A}{dt} = C_{A0}^2(1 - X_A)^2 \qquad (41)$$

- On integration, one can obtain

$$\frac{X_A}{1 - X_A} = C_{A0}kt \qquad (42)$$

- In case of conversion-time data, $X_A/(1-X_A)$ versus t plot will be straight line.

- The rate constant k will be obtained again from the slope of this straight line plot.

Negative order or fractional order reaction

For n^{th} order reaction $-r_A = kC_A^n$

$$\frac{dC_A}{dt} = -kC_A^n$$

$$\int_{C_{A0}}^{C_A} C_A^{-n} dC_A = -\int_0^t k dt$$

$$\frac{1}{-n+1}(C_A^{-n+1} - C_{A0}^{-n+1}) = -kt$$

$$C_A = C_{A0}\left[1 + (n-1)kC_{A0}^{n-1}t\right]^{1/(1-n)} \qquad (43)$$

In the equation if 'n' is fraction or negative, second term is negative. Then as t→∞, $C_A \to -ve$ and for $C_A = 0$, $t \geq \dfrac{1}{(1-n)kC_{A0}^{n-1}}$

# Application to n=1/2

- $C_A = C_{A0}\left[1 + (n-1)kC_{A0}{}^{n-1}t\right]^{1/(1-n)}$

- $C_A = C_{A0}\left[1 + (1/2 - 1)kC_{A0}{}^{1/2-1}t\right]^{1/(1-1/2)}$

- $C_A = C_{A0}\left[1 - 1/2ktC_{A0}{}^{-1/2}\right]^2$

- If $1/2ktC_{A0}{}^{-1/2}$ is negative and as t→∞, $C_A\ will\ be\ -ve$

- C_A=0 for $1/2ktC_{A0}{}^{-1/2}$ equals to 1, $t = 2C_{A0}{}^{1/2}/k$

- Similarly for nth-order(fractional or negative) $t = 1/(n-1)kC_{A0}{}^{n-1}$

  $t \geq 1/(n-1)kC_{A0}{}^{n-1}$, C_A=0

Negative order or fractional order reaction
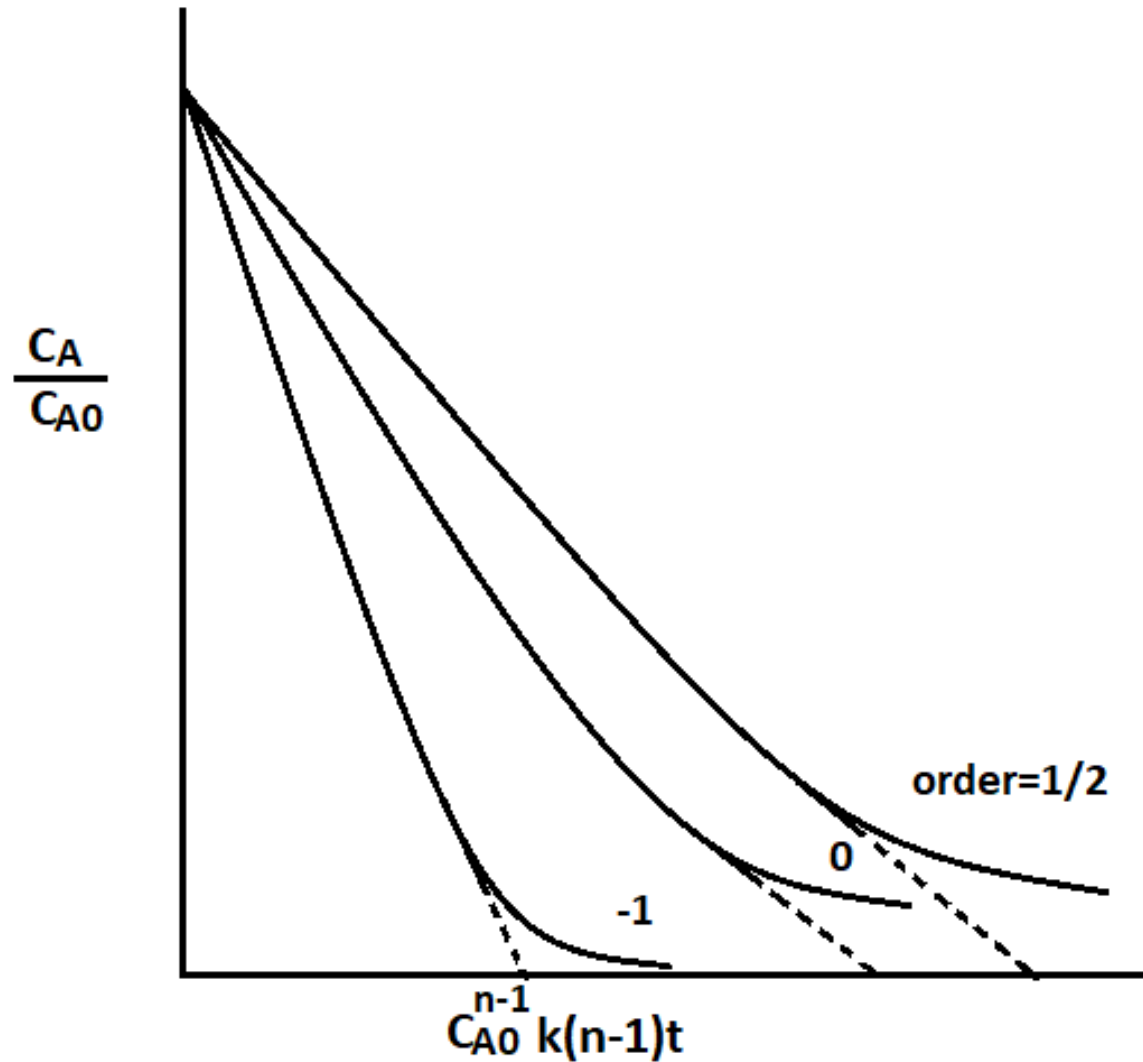
Overall Order of Irreversible Reaction by Half life period method

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

$$-r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b$$
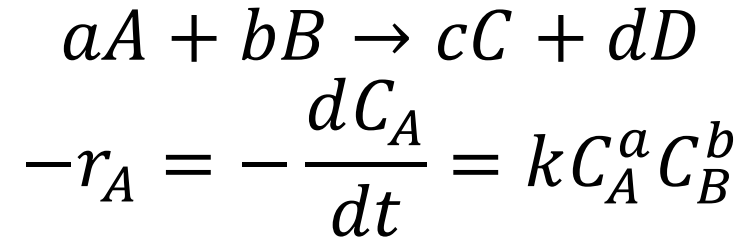
Reaction is performed with a stoichiometric ratios throughout the reaction period.

$$\frac{C_B}{C_A} = \frac{b}{a} \text{ and } -\frac{dC_A}{dt} = kC_A^a \left(\frac{b}{a}C_A\right)^b = k\left(\frac{b}{a}\right)^b C_A^{a+b} = k'C_A^n$$
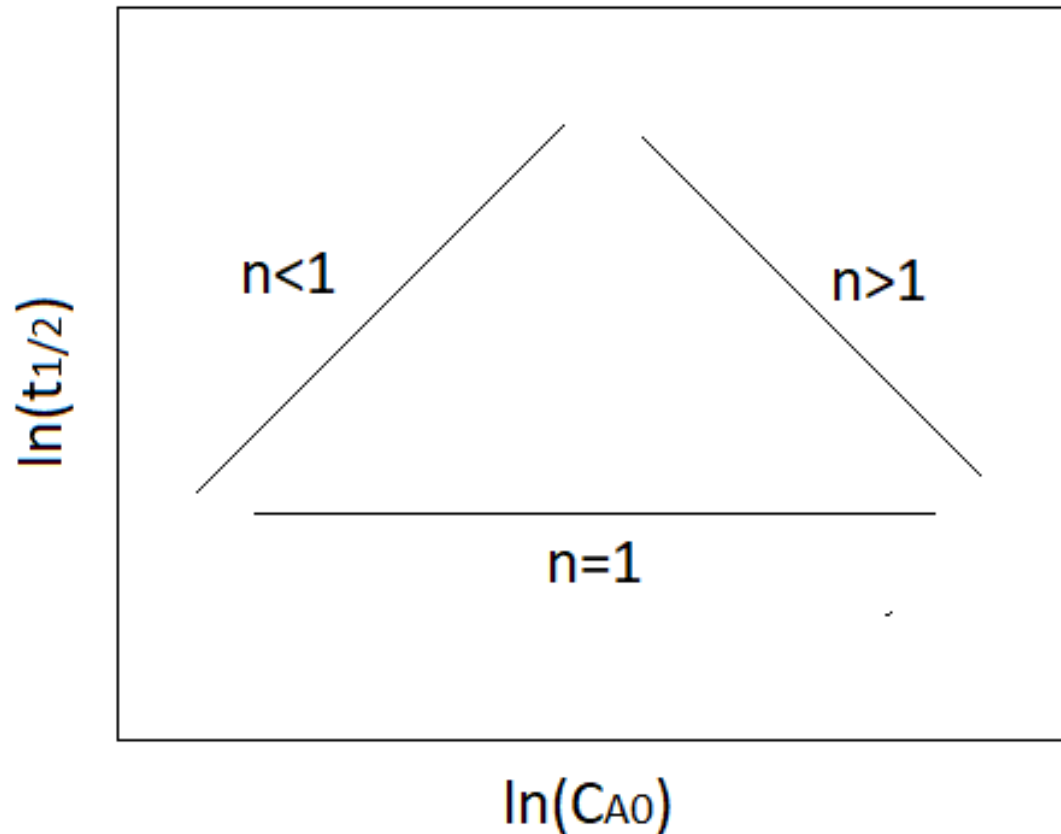
By integrating for n≠1 gives

$$(C_A^{1-n} - C_{A0}^{1-n}) = k(n-1)t$$

For half-life period: $t = \frac{1}{2}$, $C_A = \frac{C_{A0}}{2}$ and $t_{\frac{1}{2}} = \frac{0.5^{1-n}-1}{k(n-1)} C_{A0}^{1-n}$ (44)

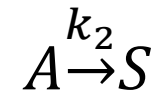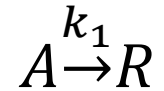$$t_{\frac{1}{2}} = \frac{0.5^{1-n}-1}{k(n-1)} C_{A0}^{1-n}$$

$\ln(t_{1/2})$ versus $\ln(C_{A0})$ plot gives a straight line with slope $= 1-n$

Seeing the slope this plot, we can decide about the order of the reaction

Irreversible parallel reaction

Let the reactions

$$A \xrightarrow{k_1} R$$

$$A \xrightarrow{k_2} S$$

$$-r_A = -\frac{dC_A}{dt} = (k_1 + k_2)C_A$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A$$

$$at\ t = 0, C_A = C_{A0}\ ; C_{R0} = C_{S0} = 0$$

$$-\ln\frac{C_A}{C_{A0}} = (k_1 + k_2)t = k't$$ where k' is obtained from the plot of $-\ln\frac{C_A}{C_{A0}}$

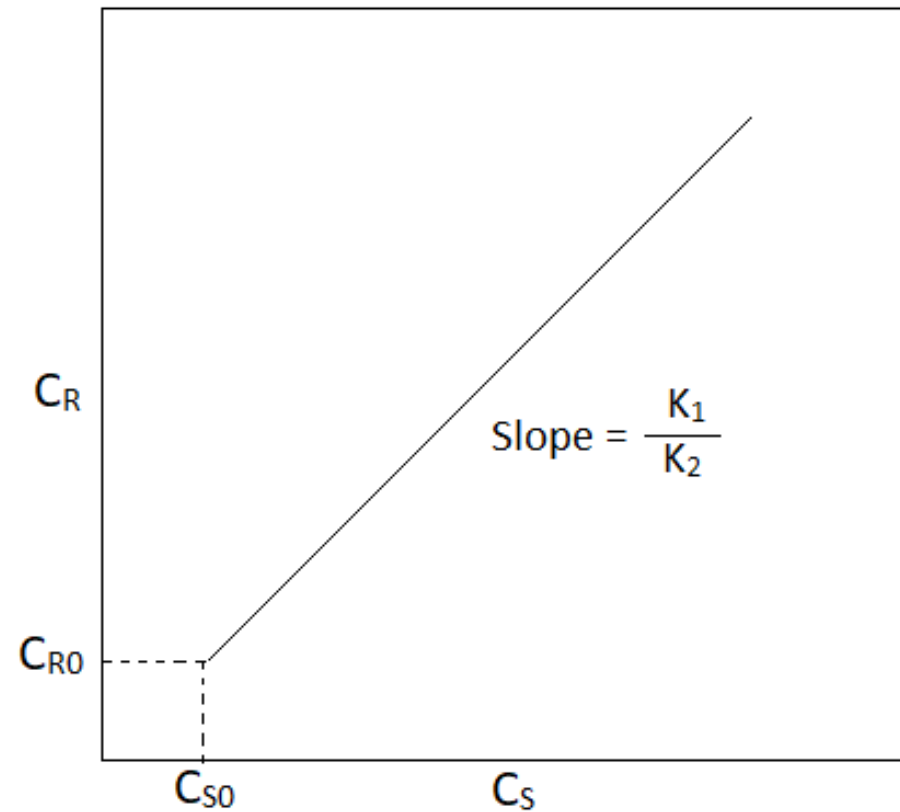vs. t. We know the sum of two constant $(k_1 + k_2)$.

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2} \Longrightarrow \frac{C_R - C_{R0}}{C_S - C_{S0}} = k''$$

If we know C_R and C_S at different time 't', C_R is to be plotted against C_S.

$$Slope = \frac{k_1}{k_2}, \qquad k_1 > k_2$$

Irreversible parallel reaction

From the slope $= \dfrac{k_1}{k_2}$ and $(k_1 + k_2) = k'$,rate constants are to be determined.

Series Reaction of type $A \xrightarrow{k_1} R \xrightarrow{k_2} S$

This is a multiple reaction of consecutive form

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

all steps are irreversible and elementary

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

or, $-\ln \frac{C_A}{C_{A0}} = k_1 t$ or, $C_A = C_{A0} e^{-k_1 t}$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} e^{-k_1 t}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R$$

$\frac{dy}{dx} + Py = Q$ type differential equation

$$Solution: \quad y e^{\int P dx} = \int Q e^{\int P dx} \, dx + Const$$

Series Reaction

- $C_R e^{\int k_2 dt} = \int \left(k_1 C_{A0} e^{-k_1 t} e^{\int k_2 dt} \right) dt + Const$

- $C_R e^{k_2 t} = C_{A0} k_1 \dfrac{e^{(k_2 - k_1)t}}{k_2 - k_1} + Const$

- $At \ \ t = 0, \ C_{R0} = 0, \ Const = -\dfrac{k_1 C_{A0}}{k_2 - k_1}$

- $C_R = C_{A0} k_1 \left[\dfrac{e^{-k_1 t}}{k_2 - k_1} + \dfrac{e^{-k_2 t}}{k_1 - k_2} \right]$

- $As, C_{A0} = C_A + C_R + C_S$

- $C_S = C_{A0} \left[1 + \dfrac{k_2}{k_1 - k_2} e^{-k_1 t} + \dfrac{k_1}{k_2 - k_1} e^{-k_2 t} \right]$

- Neglecting, k_1 when $k_2 \gg k_1,$ $\quad C_S = C_{A0}\left(1 - e^{-k_1 t}\right)$

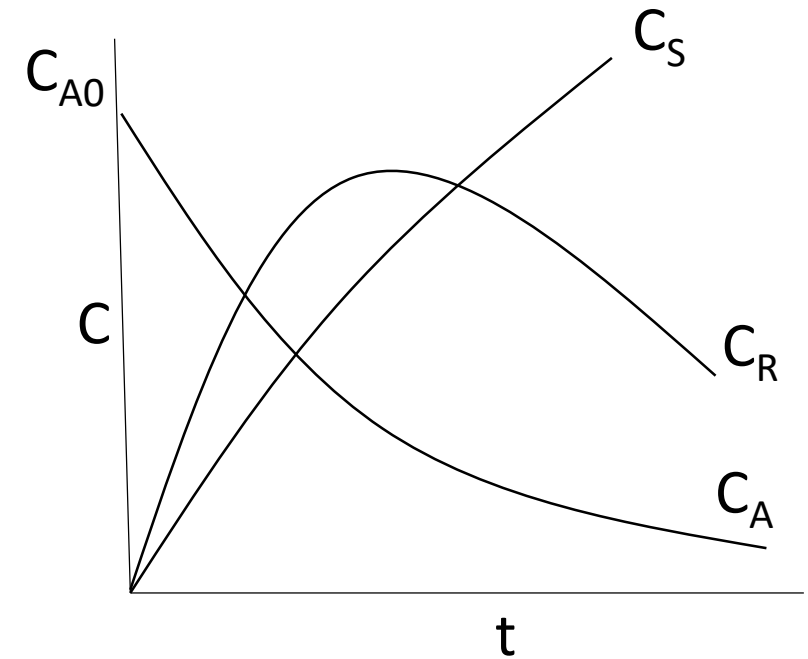- which is a first order , $first \ step \ is \ controlling$

Series Reaction

$k_1 \gg k_2, C_S = C_{A0}\left(1 - e^{-k_2 t}\right)$, the second step is the controlling one.

$$At, \frac{dC_R}{dt} = 0, \quad t_{max} = \frac{1}{k_{Log\ mean}} = \frac{\ln\frac{k_2}{k_1}}{k_2 - k_1}$$

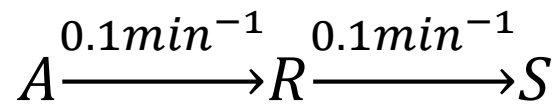and $\dfrac{C_{R,max}}{C_{A0}} = \left(\dfrac{k_1}{k_2}\right)^{k_2/(k_2 - k_1)}$

Concentration profile for $\quad A \xrightarrow{k_1} R \xrightarrow{k_2} S$

Example-1 For reactions $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, $\quad k_1 = k_2 = 0.1 min^{-1}$. $C_{A0} = 10 \frac{mols}{L}$. Derive the expression for C_R as a function of time. Find $C_{R,max}$ and t_{max} .

Solution:

$$A \xrightarrow{0.1min^{-1}} R \xrightarrow{0.1min^{-1}} S$$

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

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_1 C_R$$

$$C_R e^{\int k_1 dt}$$

$$= \int \left(k_1 C_{A0} e^{-k_1 t} e^{\int k_1 dt} \right) dt + I$$

$$C_R = k_1 C_{A0} e^{-k_1 t}$$

steps are elementary

or, $\quad -\ln \frac{C_A}{C_{A0}} = k_1 t$ or, $C_A = C_{A0} e^{-k_1 t}$

$$\frac{dC_R}{dt} + k_1 C_R = k_1 C_{A0} e^{-k_1 t}$$

$$C_R e^{k_1 t} = \int (k_1 C_{A0}) \, dt + I ,$$

$$at \; t = 0, C_R = 0 \; and \; I = 0$$

Example-1

$$\frac{dC_R}{dt} = -k_1^2 C_{A0} e^{-k_1 t} t + k_1 C_{A0} e^{-k_1 t} = 0$$

$$k_1 C_{A0} e^{-k_1 t} (1 - k_1 t) = 0 \; or \; t_{max} = 1/k_1$$

$$C_{R,max} = k_1 C_{A0} e \frac{1}{k_1} = 3.679 \; moles/L$$