# BT209

# Bioreaction Engineering

**19/01/2023**

# Irreversible bimolecular type 2nd order reaction

Consider, $A + B \rightarrow \text{products}$ with $-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B$

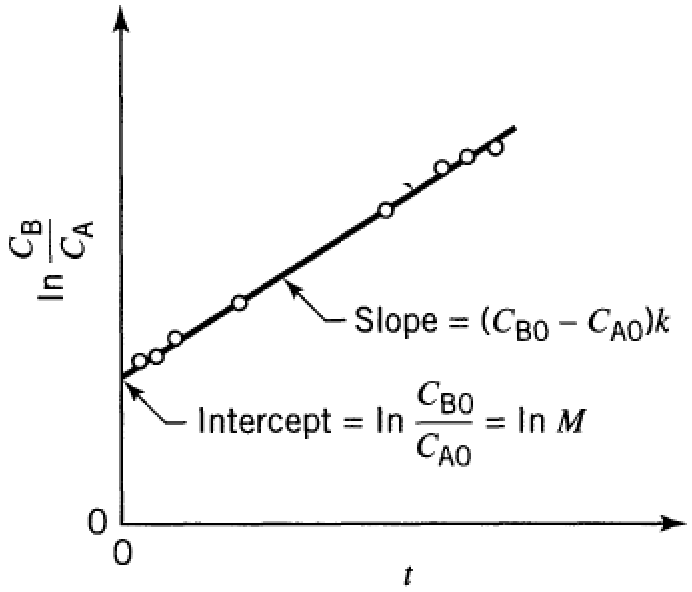
$$-r_A = C_{A0}\frac{dX_A}{dt} = k(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$

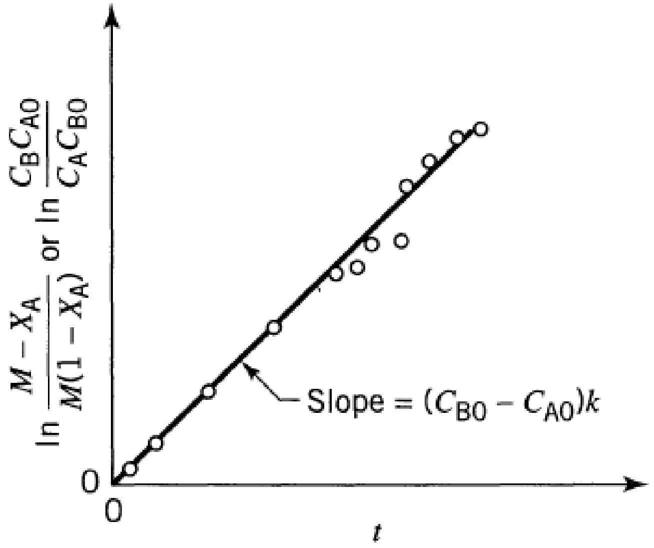
$$-r_A = C_{A0}\frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A) \qquad M = C_{B0}/C_{A0}.$$

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

$$\ln\frac{1 - X_B}{1 - X_A} = \ln\frac{M - X_A}{M(1 - X_A)} = \ln\frac{C_BC_{A0}}{C_{B0}C_A} = \ln\frac{C_B}{MC_A}$$

$$= C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt, \qquad M \neq 1$$



# Bimolecular type 2nd order reaction with equal initial concentration

***Caution 1.*** $\quad A + B \rightarrow \text{products}$

For 2nd order reaction with equal initial concentration $C_{A0} = C_{B0}$,

$$-r_A = C_{A0}\frac{dX_A}{dt} = k(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A)$$
$$= kC_{A0}^2(1 - X_A)^2$$
$$= kC_A^2$$

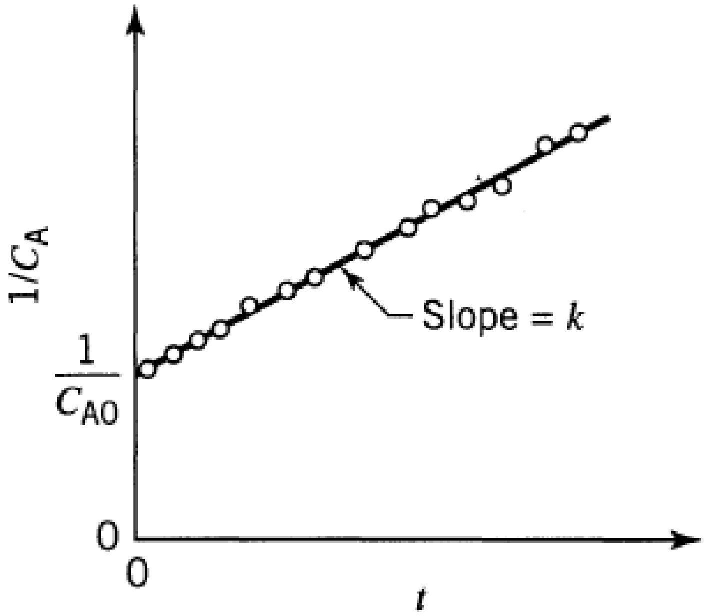
Change of A=$C_{A0}X_A$
Change of B=$C_{B0}X_B$
From stoichiometry ,
$C_{A0}X_A$=$C_{B0}X_B$

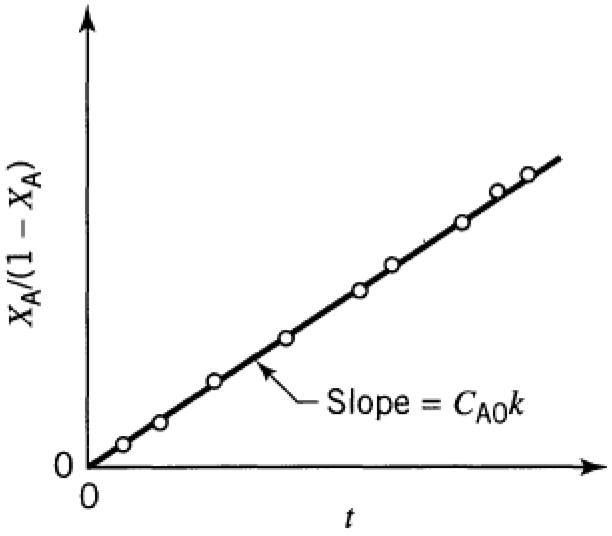
**2ND ORDER** **SAME EXPRESSON**

$2A \rightarrow \text{products}$

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1 - X_A)^2$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}}\frac{X_A}{1 - X_A} = kt$$



# CONT..

***Caution 2.*** The integrated expression depends on the stoichiometry as well as the kinetics. To illustrate, if the reaction

$$A + 2B \rightarrow \text{products}$$

is first order with respect to both A and B, hence second order overall, or

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B = kC_{A0}^2 (1 - X_A)(M - 2X_A)$$

$$\ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{M - 2X_A}{M(1 - X_A)} = C_{A0}(M - 2)kt, \qquad M \neq 2$$

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = 2kt, \qquad M = 2$$

These two cautions apply to all reaction types. Thus, special forms for the integrated expressions appear whenever reactants are used in stoichiometric ratios, or when the reaction is not elementary.

# CONT..

$$A + 2B \rightarrow R \quad \text{with} \quad -r_A = -\frac{dC_A}{dt} = kC_A C_B^2$$

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

where $M = C_{B0}/C_{A0}$. On integration this gives

$$\boxed{\frac{(2C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln \frac{C_{A0}C_B}{C_A C_{B0}} = (2C_{A0} - C_{B0})^2 kt, \qquad M \neq 2}$$

or

$$\boxed{\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 8kt, \qquad M = 2}$$

# CONT..

Similarly, for the reaction

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{R} \quad \text{with} \quad -r_{\mathrm{A}} = -\frac{dC_{\mathrm{A}}}{dt} = kC_{\mathrm{A}}C_{\mathrm{B}}^2$$

integration gives

$$\boxed{\frac{(C_{\mathrm{A0}} - C_{\mathrm{B0}})(C_{\mathrm{B0}} - C_{\mathrm{B}})}{C_{\mathrm{B0}}C_{\mathrm{B}}} + \ln\frac{C_{\mathrm{A0}}C_{\mathrm{B}}}{C_{\mathrm{B0}}C_{\mathrm{A}}} = (C_{\mathrm{A0}} - C_{\mathrm{B0}})^2kt, \qquad M \neq 1}$$

or

$$\boxed{\frac{1}{C_{\mathrm{A}}^2} - \frac{1}{C_{\mathrm{A0}}^2} = 2kt, \qquad M = 1}$$

# Homogeneous catalyzed reaction

**Homogeneous Catalyzed Reactions.** Suppose the reaction rate for a homogeneous catalyzed system is the sum of rates of both the uncatalyzed and catalyzed reactions,

$$\left.\begin{aligned} A &\xrightarrow{k_1} R \\ A + C &\xrightarrow{k_2} R + C \end{aligned}\right\}$$

with corresponding reaction rates

$$-\left(\frac{dC_A}{dt}\right)_1 = k_1 C_A$$

$$-\left(\frac{dC_A}{dt}\right)_2 = k_2 C_A C_C$$

This means that the reaction would proceed even without a catalyst present and that the rate of the catalyzed reaction is directly proportional to the catalyst concentration. The overall rate of disappearance of reactant A is then

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

# Cont.

On integration, noting that the catalyst concentration remains unchanged, we have

$$-\ln \frac{C_A}{C_{A0}} = -\ln(1 - X_A) = (k_1 + k_2 C_C)t = k_{observed}\, t$$

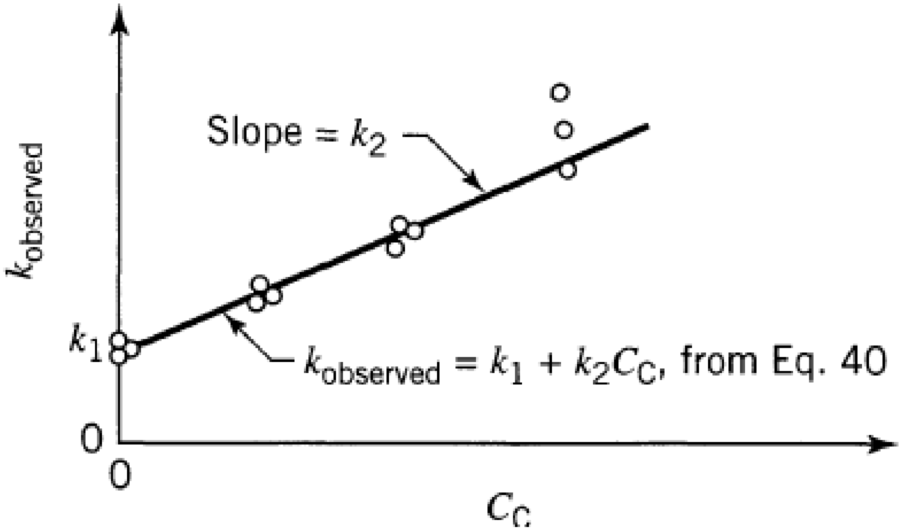



**Figure 3.8** Rate constants for a homogeneous catalyzed reaction from a series of runs with different catalyst concentrations.

Making a series of runs with different catalyst concentrations allows us to find $k_1$ and $k_2$. This is done by plotting the observed $k$ value against the catalyst concentrations as shown in Fig. 3.8. The slope of such a plot is $k_2$ and the intercept $k_1$.