BT209

Bioreaction Engineering

30/01/2023

Irreversible reaction in parallel

Irreversible Reactions in Parallel. Consider the simplest case, A decomposing by two competing paths, both elementary reactions:

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

The rates of change of the three components are given by

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

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

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

- Thus, in this system following C_A or C_R, or C_S alone will not give both k_1 and k_2,. At least two components must be followed.

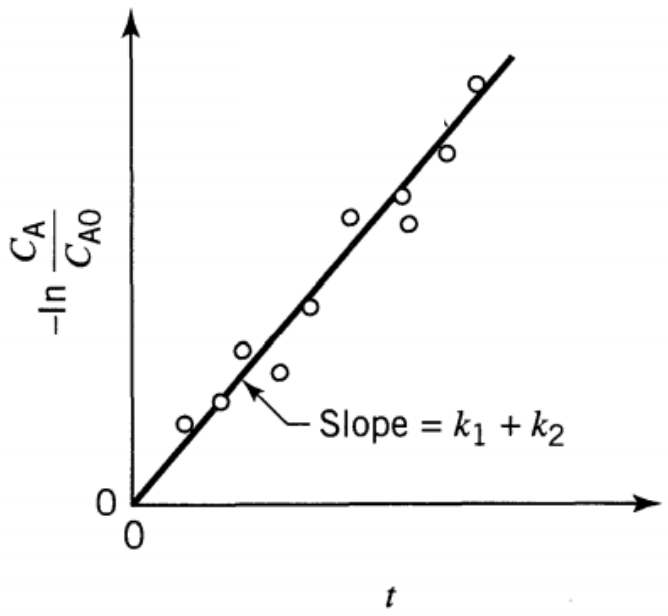
- Then, from the stoichiometry, noting that $C_A + C_R + C_s$ is constant, we can find the concentration of the third component

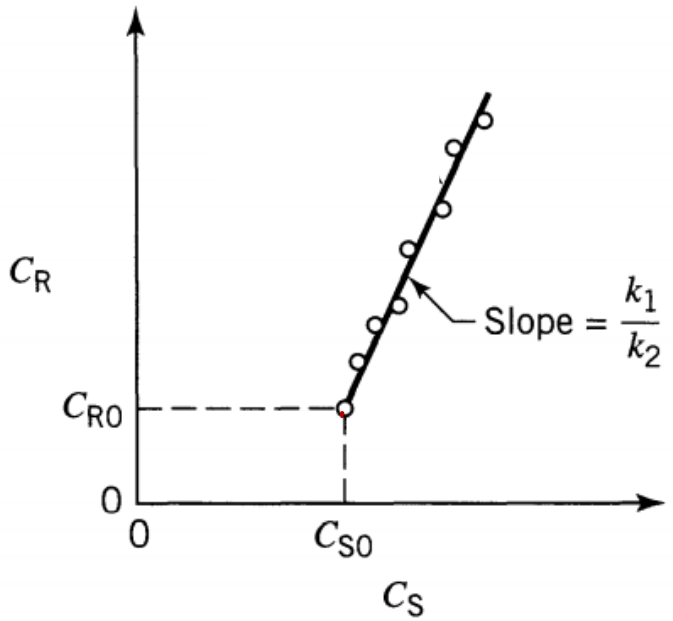
Cont.

$$-\ln \frac{C_A}{C_{A0}} = (k_1 + k_2)t$$

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$

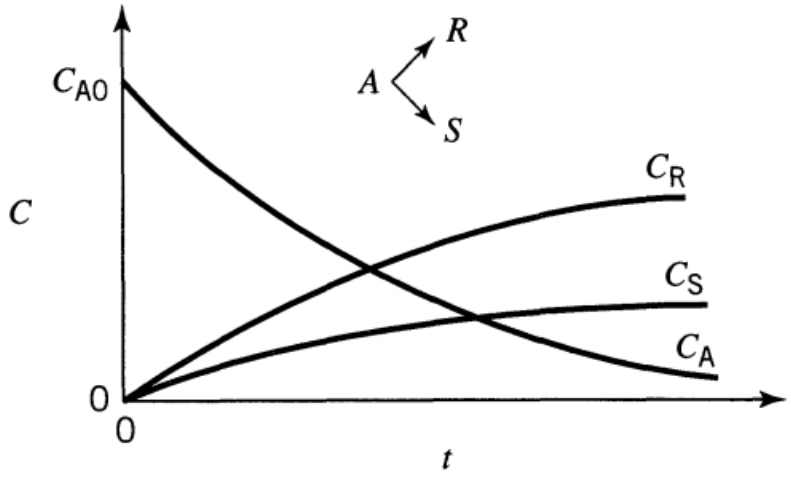
$$\boxed{\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{k_1}{k_2}}$$





Knowing k_1/k_2 as well as $k_1 + k_2$ gives k_1 and k_2.

Typical concentration-time curves of the three components in a batch reactor for the case where $C_{Ro} = C_{so} = 0$ and k1 > k2 are shown in Fig



Autocatalytic reaction

Autocatalytic Reactions. A reaction in which one of the products of reaction acts as a catalyst is called an autocatalytic reaction. The simplest such reaction is

$A + R \rightarrow R + R$ for which the rate equation is $-r_A = -\frac{dC_A}{dt} = kC_AC_R$

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

Thus, the rate equation becomes

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

Rearranging and breaking into partial fractions, we obtain

$$-\frac{dC_A}{C_A(C_0 - C_A)} = -\frac{1}{C_0}\left(\frac{dC_A}{C_A} + \frac{dC_A}{C_0 - C_A}\right) = k\,dt$$

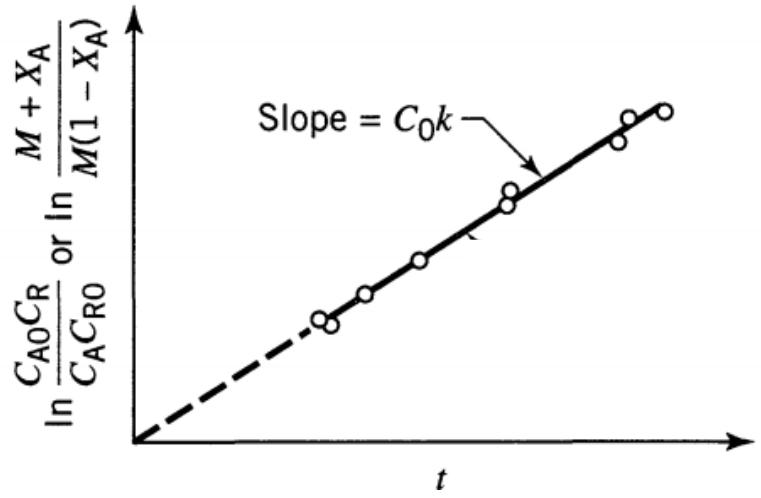
which on integration gives

$$\ln\frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = \ln\frac{C_R/C_{R0}}{C_A/C_{A0}} = C_0kt = (C_{A0} + C_{R0})\,kt$$

Cont.

In terms of the initial reactant ratio $M = C_{R0}/C_{A0}$ and fractional conversion of A, this can be written as

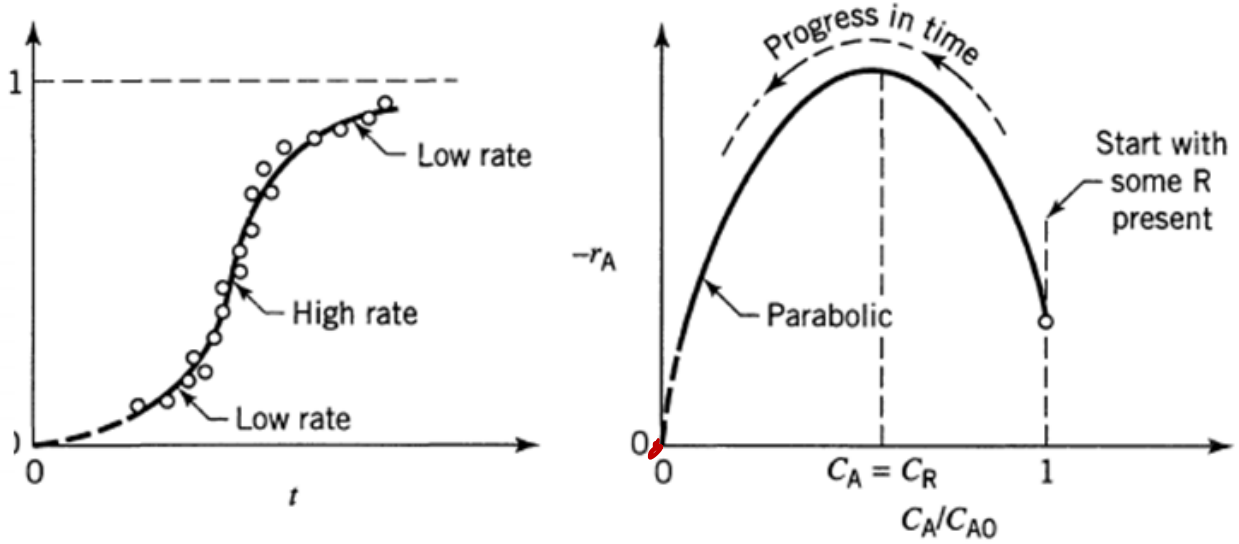
$$\ln \frac{M + X_A}{M(1 - X_A)} = C_{A0}(M + 1)kt = (C_{A0} + C_{R0})kt$$



➢**To test for an autocatalytic reaction, plot the .time and concentration coordinates of Eq. as shown in Fig. and see whether a straight line passing through zero is obtained.**

Cont.

- For an autocatalytic reaction in a batch reactor some product R must be present if the reaction is to proceed at all.
- Starting with a very small concentration of R, we see qualitatively that the rate will rise as R is formed.
- At the other extreme, when A is just about used up the rate must drop to zero.
- This result is given in Fig which shows that the rate follows a parabola, with a maximum where the concentrations of A and R are equal.



Reactions of shifting order

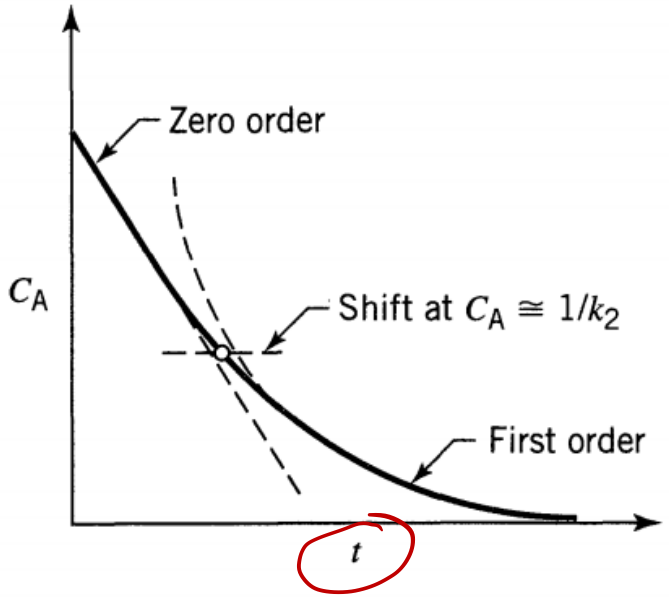
In searching for a kinetic equation it may be found that the data are well fitted by one reaction order at high concentrations but by another order at low concentrations. Consider the reaction

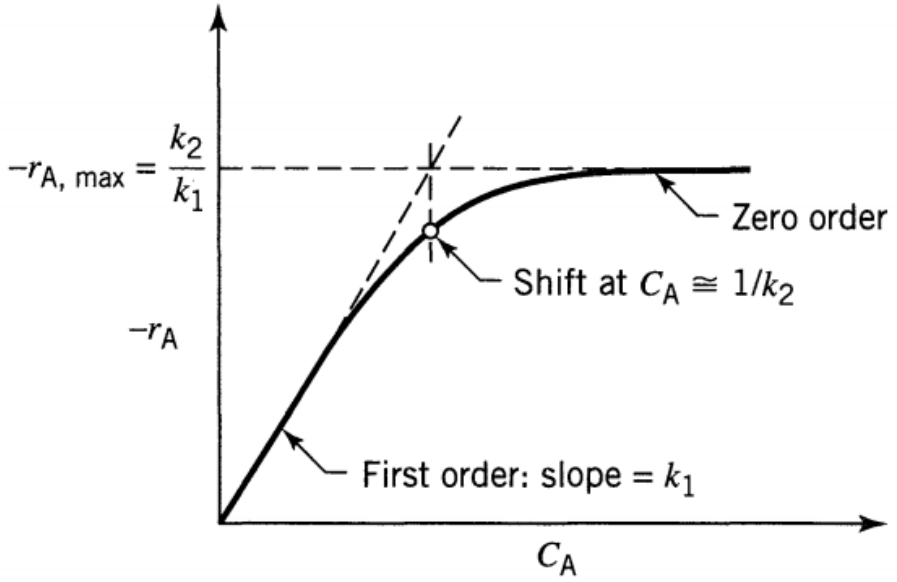
$$A \rightarrow R \quad \text{with} \quad -r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A}$$

From this rate equation we see

At high C_A (or $k_2 C_A \gg 1$)—the reaction is of zero order with rate constant k_1/k_2

At low C_A (or $k_2 C_A \ll 1$)—the reaction is of first order with rate constant k_1





Cont.

To apply the integral method, separate variables and integrate Eq

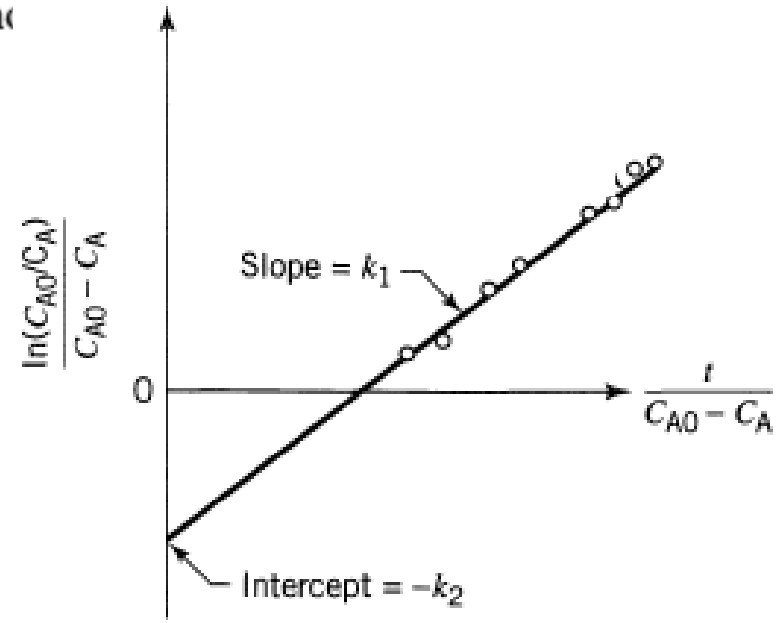
$$\ln\frac{C_{A0}}{C_A} + k_2\,(C_{A0} - C_A) = k_1 t$$

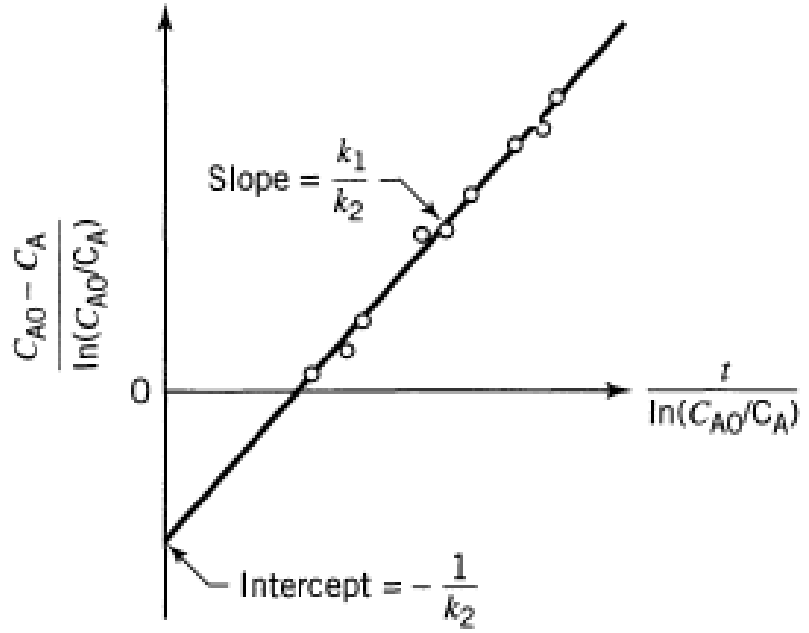
$$\frac{C_{A0} - C_A}{\ln\,(C_{A0}/C_A)} = -\frac{1}{k_2} + \frac{k_1}{k_2}\left(\frac{t}{\ln\,(C_{A0}/C_A)}\right)$$

or

$$\frac{\ln\,(C_{A0}/C_A)}{C_{A0} - C_A} = -k_2 + \frac{k_1 t}{C_{A0} - C_A}$$

Two ways to test this rate form are then sh





Overall Order of Irreversible Reactions from the Half-Life ($t_{1/2}$)

$$\alpha A + \beta B + \cdots \rightarrow \text{products}$$

we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b \cdots$$

If the reactants are present in their stoichiometric ratios, they will remain at that ratio throughout the reaction. Thus, for reactants A and B at any time $C_B/C_A = \beta/\alpha$, and we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a \left(\frac{\beta}{\alpha} C_A\right)^b \cdots = \underbrace{k\left(\frac{\beta}{\alpha}\right)^b \cdots}_{\tilde{k}} \underbrace{C_A^{a+b+\cdots}}_{C_A^n}$$

Cont.

or

$$-\frac{dC_A}{dt} = \tilde{k}C_A^n$$

Integrating for $n \neq 1$ gives

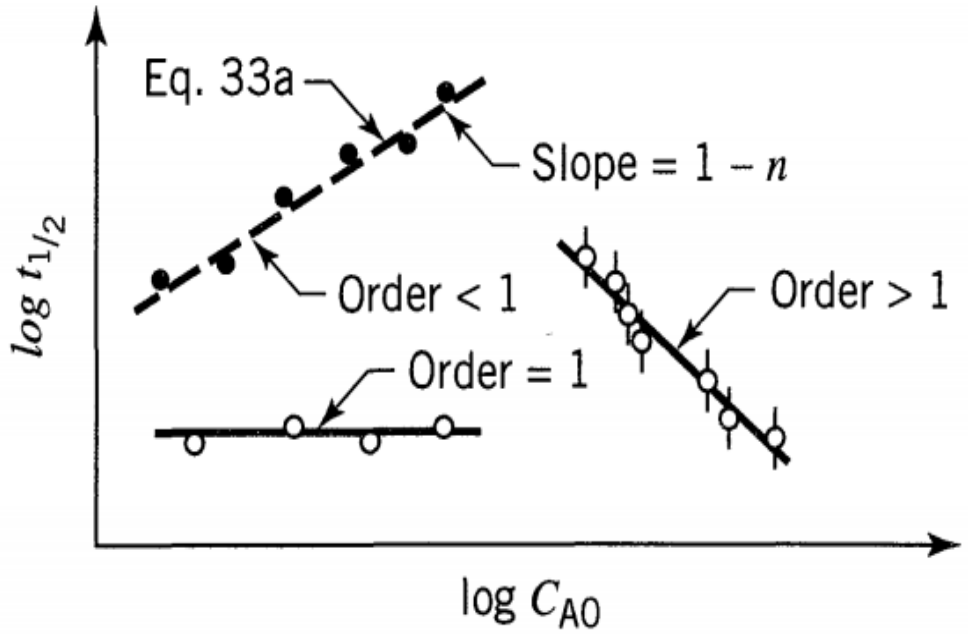
$$C_A^{1-n} - C_{A0}^{1-n} = \tilde{k}(n-1)t$$

Defining the half-life of the reaction, $t_{1/2}$, as the time needed for the concentration of reactants to drop to one-half the original value, we obtain

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

Cont.

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



The half-life method requires making a series of runs, each at a different initial concentration, and shows that the fractional conversion in a given time rises with increased concentration for orders greater than one, drops with increased

Fractional Life Method t_F

- The half-life method can be extended to any fractional life method in which the concentration of reactant drops to any fractional value $F = C_A/C_{A0}$ in time t_F.

- The derivation is a direct extension of the half-life method giving

$$t_F = \frac{F^{1-n} - 1}{k(n-1)} C_{A0}^{1-n}$$

Thus, a plot of log t_F versus log C_{A0}, will give the reaction order