

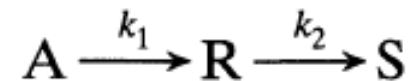
BT209

Bioreaction Engineering

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Irreversible reaction in series

Irreversible Reactions in Series. We first consider consecutive unimolecular-type first-order reactions such as



whose rate equations for the three components are

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

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

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

Let us start with a concentration C_{A0} of A, no R or S present,

Cont.

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

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

$$\frac{dy}{dx} + Py = Q$$

By multiplying through with the integrating factor $e^{\int P dx}$ the solution is

$$ye^{\int P dx} = \int Qe^{\int P dx} dx + \text{constant}$$

Cont.

Applying this general procedure to the integration of Eq. we find that the integrating factor is $e^{k_2 t}$. The constant of integration is found to be $-k_1 C_{A0}/(k_2 - k_1)$ from the initial conditions $C_{R0} = 0$ at $t = 0$, and the final expression for the changing concentration of R is

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

$$C_{A0} = C_A + C_R + C_S$$

$$C_S = C_{A0} \left(1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right)$$

Cont.

Thus, we have found how the concentrations of components A, R, and S vary with time.

Now if k_2 is much larger than k_1 , Eq. 50 reduces to

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

In other words, the rate is determined by k_1 or the first step of the two-step reaction.

If k_1 is much larger than k_2 , then

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

which is a first-order reaction governed by k_2 , the slower step in the two-step reaction. Thus, in general, for any number of reactions in series it is the slowest step that has the greatest influence on the overall reaction rate.

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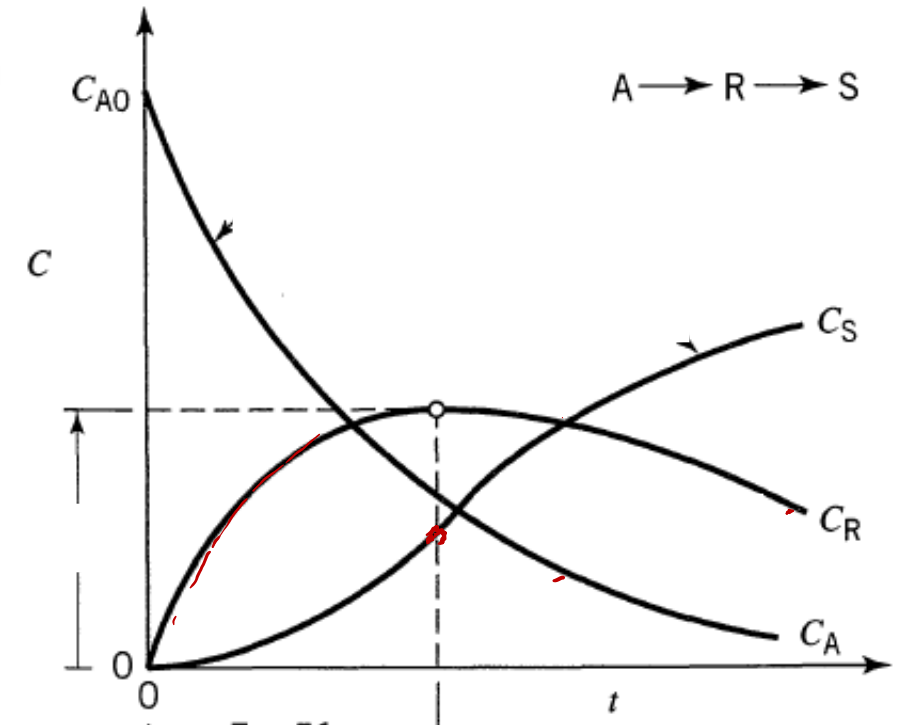
As may be expected, the values of k_1 and k_2 also govern the location and maximum concentration of R.

$$dC_R/dt = 0.$$

$$t_{\max} = \frac{1}{k_{\log \text{ mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

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

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

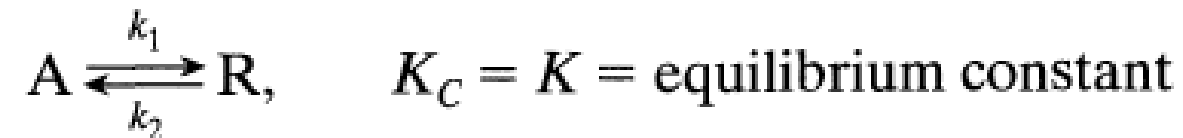


➤ A decreases exponentially, R rises to a maximum and then falls, and S rises continuously, the greatest rate of increase of S occurring where R is a maximum.

➤ In particular, this figure shows that one can evaluate k_1 and k_2 by noting the maximum concentration of intermediate and the time when this maximum is reached.

First order reversible reaction

First-Order Reversible Reactions. Though no reaction ever goes to completion, we can consider many reactions to be essentially irreversible because of the large value of the equilibrium constant. These are the situations we have examined up to this point. Let us now consider reactions for which complete conversion cannot be assumed. The simplest case is the opposed unimolecular-type reaction



Starting with a concentration ratio $M = C_{R0}/C_{A0}$ the rate equation is

$$\begin{aligned} \frac{dC_R}{dt} &= -\frac{dC_A}{dt} = C_{A0} \frac{dX_A}{dt} = k_1 C_A - k_2 C_R \\ &= k_1 (C_{A0} - C_{A0} X_A) - k_2 (M C_{A0} + C_{A0} X_A) \end{aligned}$$

Cont.

Now at equilibrium $dC_A/dt = 0$. Hence from Eq. 53 we find the fractional conversion of A at equilibrium conditions to be

$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{M + X_{Ae}}{1 - X_{Ae}}$$

and the equilibrium constant to be

$$K_C = \frac{k_1}{k_2}$$

$$\frac{dX_A}{dt} = k_1(1 - X_A) - k_2(M + X_A)$$

At equl. $\frac{dX_A}{dt} = 0$

$$X_A = X_{Ae}$$

Cont.

Combining the above three equations we obtain, in terms of the equilibrium conversion,

$$\frac{dX_A}{dt} = \frac{k_1 (M + 1)}{M + X_{Ae}} (X_{Ae} - X_A)$$

With conversions measured in terms of X_{Ae} , this may be looked on as a pseudo first-order irreversible reaction which on integration gives

$$\boxed{-\ln \left(1 - \frac{X_A}{X_{Ae}} \right) = -\ln \frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{M + 1}{M + X_{Ae}} k_1 t}$$

A plot of $-\ln (1 - X_A/X_{Ae})$ vs. t , as shown in Fig. gives a straight line.

