

Irreversible Trimolecular-Type Third-Order Reactions. For the reaction



let the rate equation be

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B C_D \quad (20b)$$

or in terms of X_A

$$C_{A0} \frac{dX_A}{dt} = kC_{A0}^3 (1 - X_A) \left(\frac{C_{B0}}{C_{A0}} - X_A \right) \left(\frac{C_{D0}}{C_{A0}} - X_A \right)$$

On separation of variables, breakdown into partial fractions, and integration, we obtain after manipulation

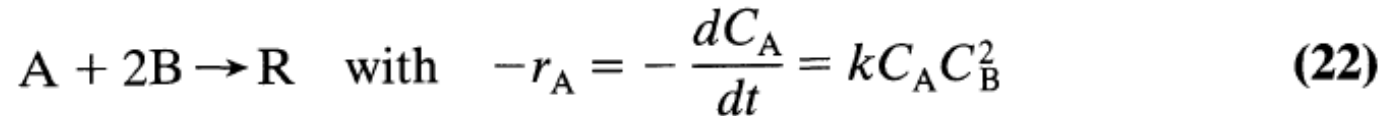
$$\begin{aligned} \frac{1}{(C_{A0} - C_{B0})(C_{A0} - C_{D0})} \ln \frac{C_{A0}}{C_A} + \frac{1}{(C_{B0} - C_{D0})(C_{B0} - C_{A0})} \ln \frac{C_{B0}}{C_B} \\ + \frac{1}{(C_{D0} - C_{A0})(C_{D0} - C_{B0})} \ln \frac{C_{D0}}{C_D} = kt \end{aligned} \quad (21)$$

Now if C_{D0} is much larger than both C_{A0} and C_{B0} , the reaction becomes second order and Eq. 21 reduces to Eq. 14.

$$\begin{aligned} \ln \frac{1 - X_B}{1 - X_A} &= \ln \frac{M - X_A}{M(1 - X_A)} = \ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{C_B}{M C_A} \\ &= C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt, \quad M \neq 1 \end{aligned}$$

(14)

Trimolecular Reactions



In terms of conversions the rate of reaction becomes

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

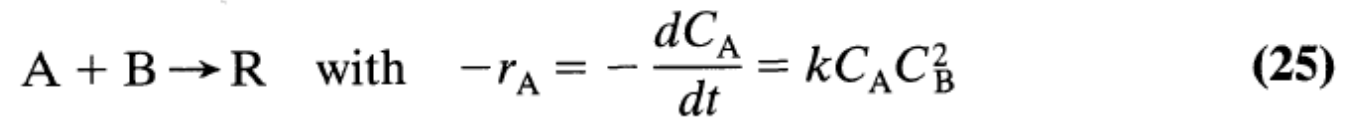
where $M = C_{B0}/C_{A0}$. On integration this gives

$$\boxed{\frac{(2C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln \frac{C_{A0}C_B}{C_A C_{B0}} = (2C_{A0} - C_{B0})^2 kt, \quad M \neq 2} \quad (23)$$

or

$$\boxed{\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 8kt, \quad M = 2} \quad (24)$$

Similarly, for the reaction



integration gives

$$\boxed{\frac{(C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln \frac{C_{A0}C_B}{C_{B0}C_A} = (C_{A0} - C_{B0})^2 kt, \quad M \neq 1} \quad (26)$$

or

$$\boxed{\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 2kt, \quad M = 1} \quad (27)$$

Empirical Rate Equations of n th Order. When the mechanism of reaction is not known, we often attempt to fit the data with an n th-order rate equation of the form

$$-r_A = -\frac{dC_A}{dt} = kC_A^n \quad (28)$$

which on separation and integration yields

$$\boxed{C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt, \quad n \neq 1} \quad (29)$$

Trial-and-error solution:

- Select a value for n and calculate k
- The value of n which minimizes the variation in k is the desired value of n

One curious feature of this rate form is that reactions with order $n > 1$ can never go to completion in finite time. On the other hand, for orders $n < 1$ this rate form predicts that the reactant concentration will fall to zero and then become negative at some finite time, found from Eq. 29, so

$$C_A = 0 \quad \text{at} \quad t \geq \frac{C_{A0}^{1-n}}{(1-n)k}$$

Since the real concentration cannot fall below zero we should not carry out the integration beyond this time for $n < 1$. Also, as a consequence of this feature, in real systems the observed fractional order will shift upward to unity as reactant is depleted.

Zero-Order Reactions. A reaction is of zero order when the rate of reaction is independent of the concentration of materials; thus

$$-r_A = -\frac{dC_A}{dt} = k \quad (30)$$

Integrating and noting that C_A can never become negative, we obtain directly

$$\boxed{\begin{aligned} C_{A0} - C_A = C_{A0}X_A = kt \quad &\text{for } t < \frac{C_{A0}}{k} \\ C_A = 0 \quad &\text{for } t \geq \frac{C_{A0}}{k} \end{aligned}} \quad (31)$$

which means that the conversion is proportional to time, as shown in Fig. 3.4.

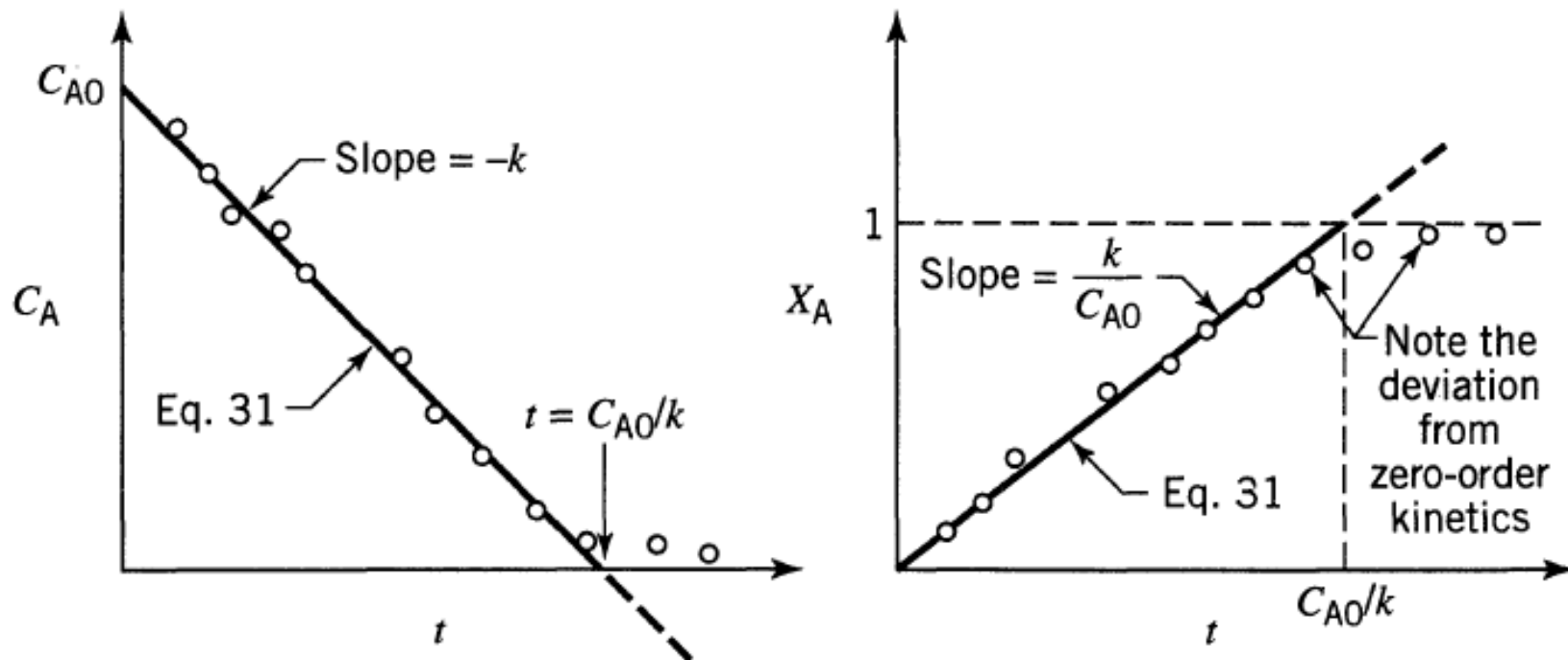
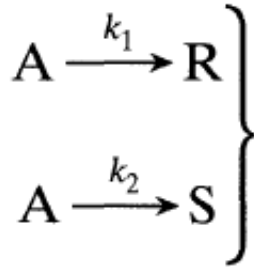


Figure 3.4 Test for a zero-order reaction, or rate equation, Eq. 30.

Reactions are of zero order only in certain concentration ranges (e.g. higher concentrations)

Parallel Reactions

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



The rates of change of the three components are given by

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A + k_2 C_A = (k_1 + k_2) C_A \quad (34)$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A \quad (35)$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A \quad (36)$$

The k values are found using all three differential rate equations. First of all, Eq. 34, which is of simple first order, is integrated to give

$$\boxed{-\ln \frac{C_A}{C_{A0}} = (k_1 + k_2)t} \quad (37)$$

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

which when integrated gives simply

$$\boxed{\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{k_1}{k_2}} \quad (38)$$

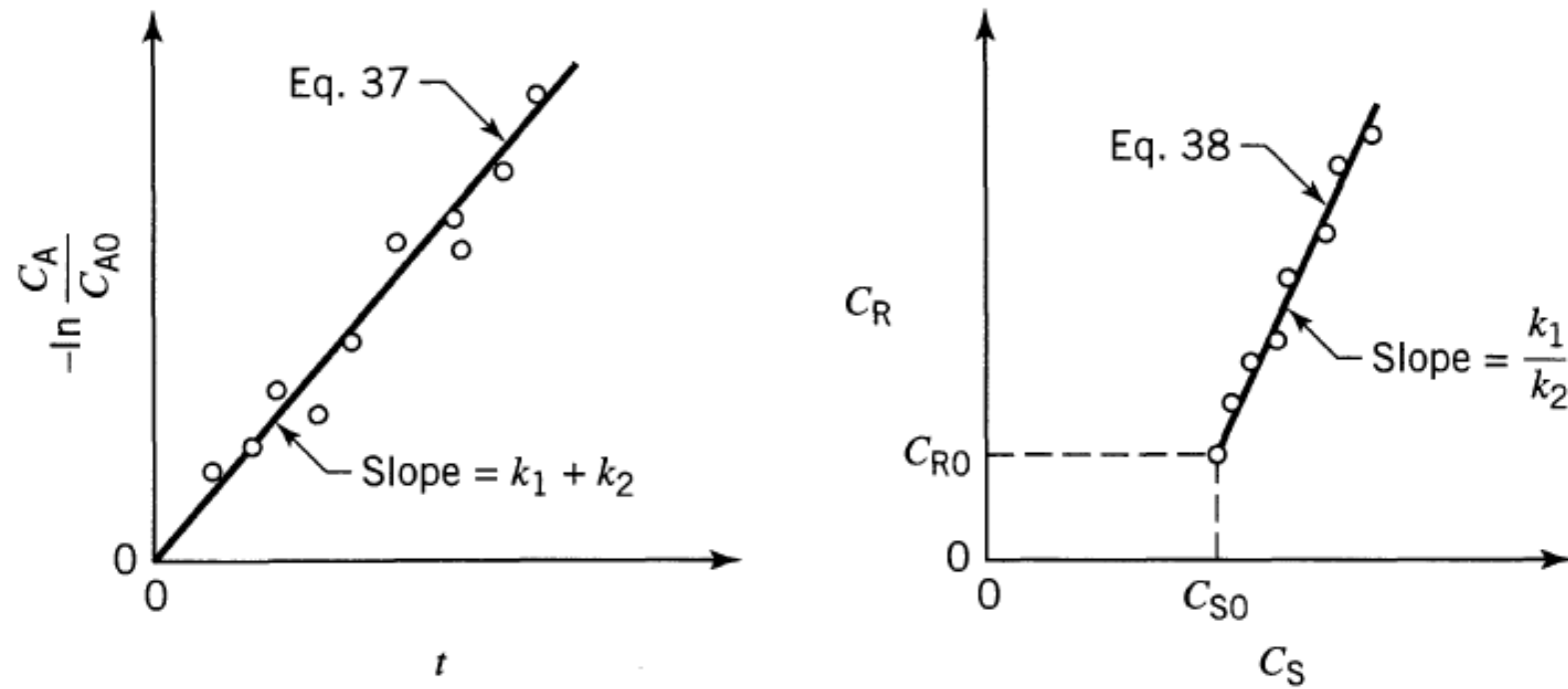


Figure 3.6 Evaluation of the rate constants for two competing elementary

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

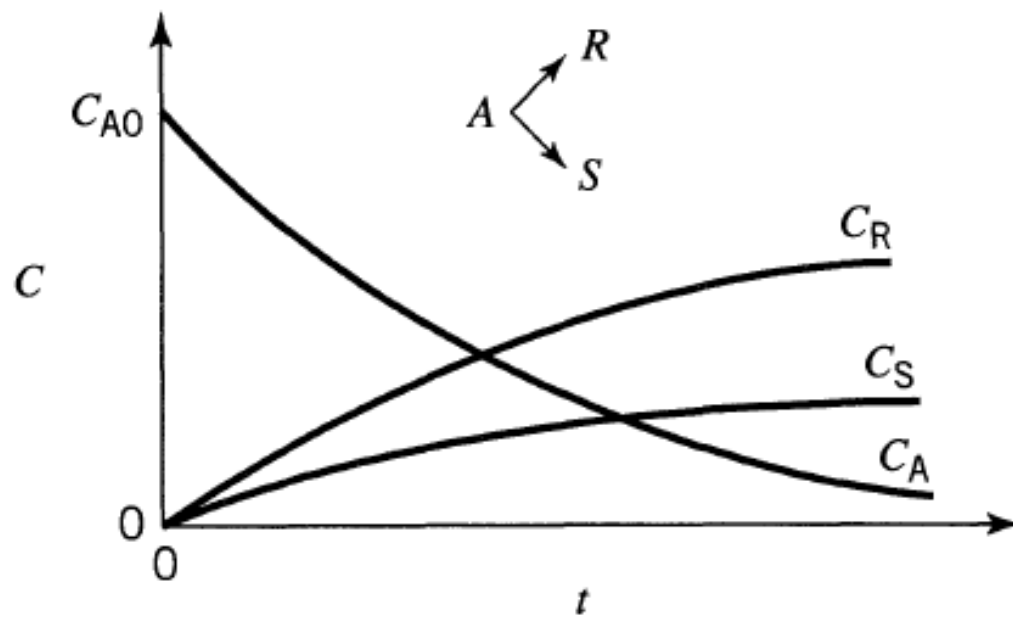


Figure 3.7 Typical concentration-time curves for competing reactions.

where $C_{R0} = C_{S0} = 0$ and $k_1 > k_2$

Additional examples of integrated rate equations are given in the course text, as noted below.

Irreversible reactions

series reactions p. 54
catalyzed reactions p. 51
autocatalytic reactions p. 52

Reversible reactions

unimolecular 1st order p. 56
bimolecular 2nd order p. 58

Reactions of changing order

unimolecular p. 59