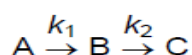


9. The kinetics of Complex reactions

In kinetics, a 'complex reaction' simply means a reaction whose mechanism comprises more than one elementary step. In the previous sections we have looked at experimental methods for measuring reaction rates to provide kinetic data that may be compared with the predictions of theory.

9-1 Consecutive reactions

The simplest complex reaction consists of two consecutive, irreversible elementary steps e.g.



An example of such a process is radioactive decay. This is one of the few kinetic schemes in which it is fairly straightforward to solve the rate equations analytically, so we will look at this example in some detail. We can see immediately that the following initial conditions hold.

$$\begin{aligned} \text{at } t = 0, \quad [A] &= [A]_0 \\ [B] &= 0 \\ [C] &= 0 \end{aligned}$$

$$\text{with at all times} \quad [A] + [B] + [C] = [A]_0.$$

Using this information, we can set up the rate equations for the process and solve them to determine the concentrations of [A], [B], and [C] as a function of time. The rate equations for the concentrations of A, B, and C are:

$$(1) \quad \frac{d[A]}{dt} = -k_1[A]$$

$$(2) \quad \frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$(3) \quad \frac{d[C]}{dt} = k_2[B]$$

Integrating (1) gives

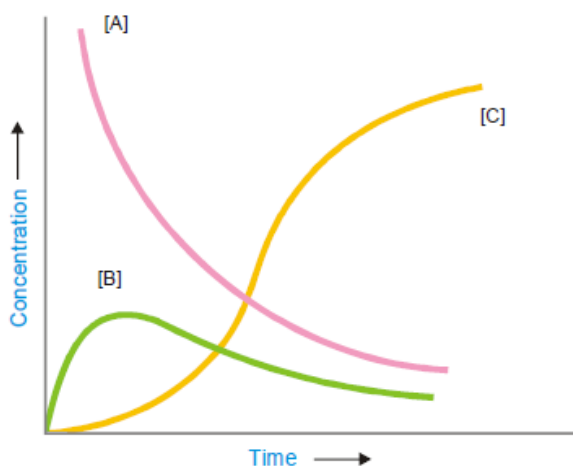
$$[A] = [A]_0 \exp(-k_1 t).$$

Substituting this into (2) gives $\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 \exp(-k_1 t)$, a differential equation with the solution

$$[B] = \frac{k_1}{k_2 - k_1} \{ \exp(-k_1 t) - \exp(-k_2 t) \} [A]_0$$

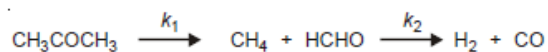
Finally, since $[C] = [A]_0 - [B] - [A]$, we find

$$[C] = \left(1 + \frac{k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)}{k_2 - k_1} \right) [A]_0$$

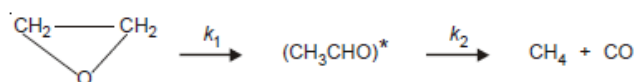


Examples of First Order Consecutive Reactions

(a) Decomposition of dimethyl ether in gaseous phase

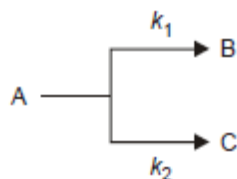


(b) Decomposition of Ethylene oxide



9-2 Parallel or Side Reactions:

In these reactions the reacting substance follows two or more paths to give two or more products. The preferential rate of such may be changed by varying the conditions like pressure, temperature or catalyst. The reaction in which the maximum yield of the products is obtained is called the main or major reaction while the other reaction (or reactions) are called side or parallel reactions. For example,



$$r_1 = \frac{-d[\text{A}]}{dT} = k_1[\text{A}] \quad \dots(i)$$

and
$$r_2 = \frac{-d[\text{A}]}{dT} = k_2[\text{A}] \quad \dots(ii)$$

The total rate of disappearance of A is given by

$$\begin{aligned} \frac{-d[\text{A}]}{dT} &= r_1 + r_2 = k_1[\text{A}] + k_2[\text{A}] \\ &= (k_1 + k_2)[\text{A}] \end{aligned}$$

$$= k' [A] \quad \dots (iii)$$

where k' is the first order rate constant. It is equal to the sum of the two constants k_1 and k_2 of two side reactions.

Integrating equation (iii), we get

$$\int \frac{-d[A]}{d T} = \int k' [A]$$

applying the limits $[A]_0$ & $[A]_t$ and 0 & t , we have

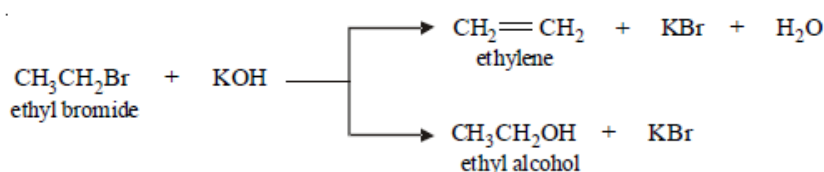
$$\int_{[A]_0}^{[A]_t} \frac{-d[A]}{d t} = k' \int_0^t d t$$

$$\ln \frac{[A]_0}{[A]_t} = k' t + (k_1 + k_2) t \quad \dots (iv)$$

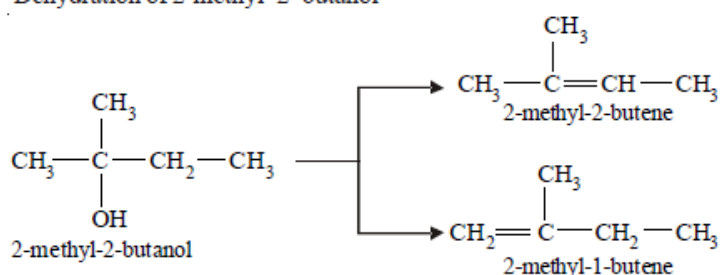
where $[A]_0$ is the initial concentration of the reactant A and $[A]_t$ is concentration of A at time t .

Examples of Parallel or Side Reactions

(a) Reaction of ethyl bromide with potassium hydroxide

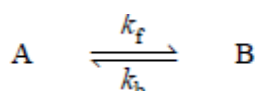


(b) Dehydration of 2-methyl-2-butanol



9-3 Reversible or Opposing Reactions

In reversible or opposing reactions the products formed also react to give back the reactants. Initially, we suggest that by the rate of forward reaction and the rate of backward or reverse reaction is first-order. A reaction of this type may be represented as



$$\frac{d[A]}{dt} = -k_f[A] + k_b[B]$$

$[A]_0$ = initial con. of A substance at $t=0$, at this time the conc. Of B =0, So

$[A]_0 = [A] + [B]$ at t time

$$\begin{aligned} \frac{d[A]}{dt} &= -K_f[A] + K_b([A]_0 - [A]) \\ &= -(K_f + K_b)[A] + K_f[A]_0 \end{aligned}$$

Integration of the expression gives:

$$[A] = [A]_0 \left(\frac{K_b + K_f \exp(-(K_f + K_b)t)}{K_f + K_b} \right)$$

If the reaction is irreversible $K_b=0$ and the conc. Of a will be

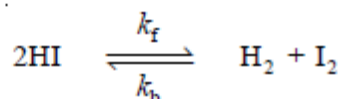
$$[A] = [A]_0 e^{-Kt}$$

As $t \rightarrow \infty$, the concentrations reach their equilibrium values, It follows that the equilibrium constant of the reaction is

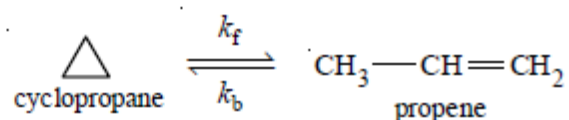
$$K = \left(\frac{[B]}{[A]} \right)_{eq} = \frac{[B]_{\infty}}{[A]_{\infty}} = \frac{K_f}{K_b}$$

Examples of Opposing Reactions

(a) Dissociation of hydrogen iodides



(b) Isomerisation of cyclopropane into propene



10- Reaction mechanism

The rate equations for virtually all complex reaction mechanisms generally comprise a complicated system of coupled differential equations that cannot be solved analytically. Very good approximate solutions may often be obtained by making simple assumptions about the nature of reactive intermediates.

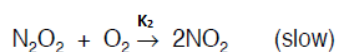
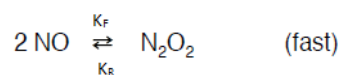
1- rate-determining step:

In multiple-step reactions

- A- The reaction mechanism include one or more reversible(fast) steps
- B- one of the elementary reactions in the sequence is often slower than the rest , It therefore determines the rate of reaction.

Example/ the overall reaction $2 \text{NO} + \text{O}_2 \longrightarrow 2 \text{NO}_2$

The mechanism



$[\text{N}_2\text{O}_2]$: intermediate substance

Rate= Rate of slow step

$$r = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

Note: the intermediate should not be included in the rate law

From the reversible step:

$$K_{eq} = \frac{K_F}{K_R} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2}$$

$$[\text{N}_2\text{O}_2] = (k_f/k_r)[\text{NO}]^2$$

So the rate :

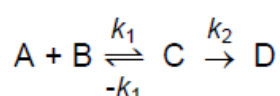
$$\begin{aligned} \text{rate} &= k_2 [\text{N}_2\text{O}_2][\text{O}_2] = k_2 (k_f / k_r) [\text{NO}]^2 [\text{O}_2] \\ &= k_2 K_{eq} [\text{NO}]^2 [\text{O}_2] \end{aligned}$$

2- Steady state approximation:

The steady-state approximation assumes that, after an initial induction period, an interval during which the concentrations of intermediates, R, rise from zero, and during the major part of the reaction, the rates of change of concentrations of all reaction intermediates are negligibly small.

If a reactive intermediate R is present at low and constant concentration throughout (most of) the course of the reaction, then we can set

$$d[\text{R}]/dt = 0$$



We can apply the steady state approximation (SSA) to C, to obtain

$$\frac{d[\text{C}]}{dt} = 0 = k_1[\text{A}][\text{B}] - k_{-1}[\text{C}] - k_2[\text{C}]$$

This may be solved to give [C] in terms of the reactant concentrations [A] and [B].

$$[\text{C}] = \frac{k_1}{k_{-1} + k_2} [\text{A}][\text{B}]$$

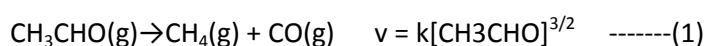
The overall rate is the rate of formation of the product, D, giving

$$v = \frac{d[\text{D}]}{dt} = k_2[\text{C}] = \frac{k_1 k_2}{k_{-1} + k_2} [\text{A}][\text{B}]$$

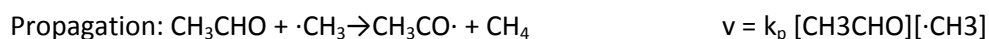
11-Chain reactions:

In a chain reaction, a reaction intermediate produced in one step generates an intermediate in a subsequent step, then that intermediate generates another intermediate, and so on. The intermediates in a chain reaction are called chain carriers. In a radical chain reaction the chain carriers are radicals.

A chain reaction can have a simple rate law. As a first example, consider the pyrolysis, or thermal decomposition in the absence of air, of acetaldehyde (ethanal, CH_3CHO), which is found to be three-halves order in CH_3CHO :



Some ethane is also detected. The mechanism for this reaction is as follows



The chain carriers $\cdot\text{CH}_3$ and $\cdot\text{CHO}$ are formed initially in the **initiation step**. To simplify the treatment, we shall ignore the subsequent reactions of $\cdot\text{CHO}$. The chain carrier $\cdot\text{CH}_3$ attacks other reactant molecules in the **propagation steps**, and each attack gives rise to a new carrier. Radicals combine and end the chain in the **termination step**. To test the proposed mechanism we need to show that it leads to the observed rate law. According to the steady-state approximation, the net rate of change of the intermediates ($\cdot\text{CH}_3$ and $\text{CH}_3\text{CO}\cdot$) may be set equal to zero:

$$\frac{d[\cdot\text{CH}_3]}{dt} = k_i[\text{CH}_3\text{CHO}] - k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] + k'_p[\text{CH}_3\text{CO}\cdot] - 2k_t[\cdot\text{CH}_3]^2 = 0$$

$$\frac{d[\text{CH}_3\text{CO}\cdot]}{dt} = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] - k'_p[\text{CH}_3\text{CO}\cdot] = 0$$

The sum of the two equations is

$$k_i[\text{CH}_3\text{CHO}] - 2k_t[\cdot\text{CH}_3]^2 = 0$$

which shows that the steady-state approximation also implies that the rate of chain initiation is equal to the rate of chain termination. The steady-state concentration of $\cdot\text{CH}_3$ radicals is

$$[\cdot\text{CH}_3] = \left(\frac{k_i}{2k_t}\right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2}$$

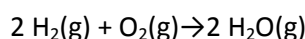
It follows that the rate of formation of CH_4 is

$$\frac{d[\text{CH}_4]}{dt} = k_p[\cdot\text{CH}_3][\text{CH}_3\text{CHO}] = k_p\left(\frac{k_i}{2k_t}\right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

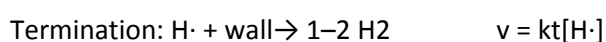
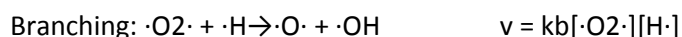
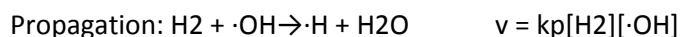
which is in agreement with the three-halves order observed experimentally in eq. (1).

11-1 Explosions

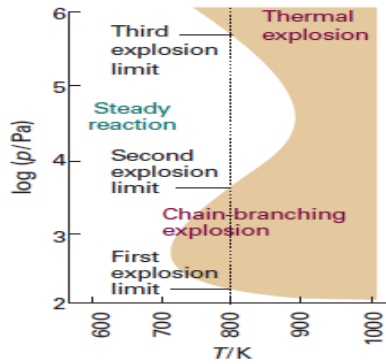
A thermal explosion is a very rapid reaction arising from a rapid increase of reaction rate with increasing temperature. The temperature of the system rises if the energy released by an exothermic reaction cannot escape, and the reaction goes faster. The acceleration of the rate results in an even faster rise of temperature, so the reaction becomes catastrophically fast. A chain-branching explosion occurs when the number of chain centres grows exponentially. An example of both types of explosion is the reaction between hydrogen and oxygen:



Although the net reaction is very simple, the mechanism is very complex and has not yet been fully elucidated. A chain reaction is involved, and the chain carriers include $\text{H}\cdot$, $\cdot\text{O}\cdot$, and $\cdot\text{OH}$. Some steps involving $\text{H}\cdot$ are:



A branching step is an elementary reaction that produces more than one chain carrier. The occurrence of an explosion depends on the temperature and pressure of the system, and the explosion regions for the reaction, the conditions under which explosion occurs, are shown in the Fig. below.



At very low pressures the system is outside the explosion region and the mixture reacts smoothly. At these pressures the chain carriers produced in the branching steps can reach the walls of the container where they combine. Increasing the pressure along a vertical line in the illustration takes the system through the first explosion limit (provided the temperature is greater than about 730 K). The chain carriers react before reaching the walls and the branching reactions are explosively efficient. The reaction is smooth when the pressure is above the second explosion limit. The concentration of third-body M molecules is then so high compared to the concentrations of chain carriers that the combination of H· atoms with O₂ molecules to form relatively unreactive HO₂· molecules becomes faster than the branching reaction between H· atoms and O₂ molecules. These long-lived HO₂· molecules then diffuse to the walls and are removed there, in what amounts to another termination step. When the pressure is increased to above the third explosion limit, diffusion of HO₂· molecules to the walls becomes so slow that they can react with H₂ molecules (now at very high concentrations) to regenerate H atoms and H₂O₂ molecules.