

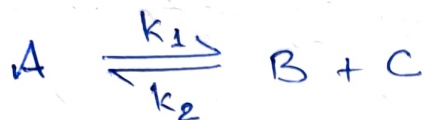
Paper : Physical Chemistry

Topic : Chemical Kinetics

Dr. Om Prakash Singh
 Department of Chemistry,
 Maharaja College, Ara.

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Case II :- Consider the next case when the first-order reaction is opposed by the reaction of the second order, viz.



where A is the reactant, B and C are products, k_1 is the rate constant for the forward reaction and k_2 is the second order rate constant for the backward reaction.

Suppose 'a' is the initial concentration of A, i.e. the concentration of B and C being initially zero. Let 'x' of A decomposes in time 't' to form 'x' of B and C. Then

$$\text{Rate of the forward reaction} = k_1 (a-x)$$

where $(a-x)$ is the concentration of A at time t.

$$\text{Rate of the backward reaction} = k_2 x^2$$

At equilibrium,

$$\text{Rate of forward reaction} = \text{Rate of backward reaction.}$$

$$\text{i.e. } k_1 (a-x_e) = k_2 x_e^2 \quad \text{--- (8)}$$

where x_e is the concentration of B and C at equilibrium, i.e. $x = x_e$.

From equation (8) we have

$$k_2 = k_1 \frac{(a-x_e)}{x_e^2} \quad \text{--- (9)}$$

But the net rate of forward reaction is given by

$$\frac{dx}{dt} = k_1(a-x) - k_2x^2 \quad \text{--- (10)}$$

On putting the value of k_2 from equation (9), we get-

$$\frac{dx}{dt} = k_1(a-x) - k_1 \cdot \frac{(a-x_e)}{x_e^2} \cdot x^2 \quad \text{--- (11)}$$

On separating the variables and integrating the equation, we get-

$$k_1 = \frac{x_e}{t(2a-x_e)} \ln \left[\frac{ax_e + x(a-x_e)}{a(x_e+x)} \right] \quad \text{--- (12)}$$

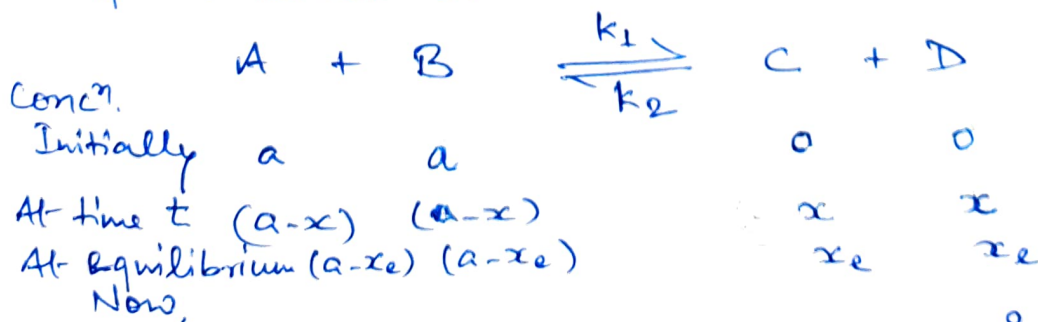
Thus, the value of k_1 can be calculated by using this equation if x_e , x and t are known. By substituting the value of k_1 in equation (9) we can calculate the value of k_2 .

Examples :-

(a) Hydrolysis of ethyl acetate.

(b) Decomposition of alkyl ammonium halide in a tertiary amine and an alkyl halide in solution.

Case III :- Let us consider the case when the second order reaction is opposed by the reaction of the same order.



Now,

$$\text{Rate of forward reaction} = k_1(a-x)^2$$

$$\text{Rate of backward reaction} = k_2x^2$$

Net rate of forward reaction =

Rate of forward reaction - Rate of backward reaction.

$$\text{i.e.} \quad \frac{dx}{dt} = k_1(a-x)^2 - k_2x^2 \quad \text{--- (13)}$$

At equilibrium, $\frac{dx}{dt} = 0$ and $x = x_e$

$$\text{So, } k_1(a-x_e)^2 = k_2 x_e^2 \quad \text{--- (14)}$$

$$\text{or, } k_2 = k_1 \frac{(a-x_e)^2}{x_e^2} \quad \text{--- (15)}$$

On putting the value of k_2 in equation (13) we get

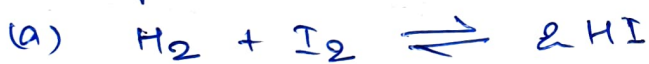
$$\frac{dx}{dt} = k_1(a-x)^2 - k_1 \left(\frac{a-x_e}{x_e}\right)^2 \cdot x^2 \quad \text{--- (16)}$$

On separating the variables and integrating the equation (16) under the condition that at $t=0$, $x=0$ we get—

$$k_1 = \frac{x_e}{2at(a-x_e)} \ln \left[\frac{x(a-2x_e) + ax_e}{a(x_e-x)} \right] \quad \text{--- (17)}$$

This equation gives the value of k_1 in terms of easily measurable quantities. Knowing k_1 , the value of k_2 can be calculated with the help of equation (15).

Examples :—



(b) Saponification of ester by an alkali.

Case IV :— Consider the case when the second order forward reaction is opposed by the first order backward reaction.



Initial concⁿ a a 0

Concⁿ at time t (a-x) (a-x) x

Equilibrium concⁿ (a-x_e) (a-x_e) x_e

Now,

Rate of forward reaction = $k_1(a-x)^2$

Rate of backward reaction = $k_2 x$

The net rate of forward reaction =

(21)

= Rate of forward reaction - Rate of backward reaction

i.e. $\frac{dx}{dt} = k_1(a-x)^2 - k_2x$ — (18)

At equilibrium, $\frac{dx}{dt} = 0$, and $x = x_e$, so that

$k_1(a-x_e)^2 = k_2x_e$ — (19)

or, $k_2 = k_1 \frac{(a-x_e)^2}{x_e}$ — (20)

From equations (18) and (20), we get-

$\frac{dx}{dt} = k_1(a-x)^2 - k_1 \frac{(a-x_e)^2}{x_e} \cdot x$

or, $\frac{dx}{dt} = \frac{k_1}{x_e} [(a-x)^2 \cdot x_e - (a-x_e)^2 \cdot x]$ — (21)

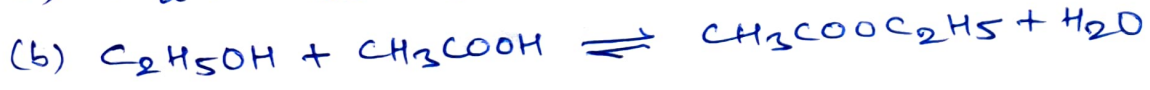
By separating the variables and integrating equation (21) under the condition that at $t = 0, x = 0$, we get-

$k_1 = \frac{x_e}{t(a^2-x_e^2)} \ln \left[\frac{x_e(a^2-x_e \cdot x)}{a^2(x_e-x)} \right]$ — (22)

Therefore, the value of k_1 can be calculated by using this equation if x, t and x_e are known.

On substituting the value of k_1 in equation (20) we can obtain the value of k_2 .

Examples :-



..... to be continued