Paper : Physical Chemistry
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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.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B + C$$

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

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

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

Rate of the backward reaction $= k_2 x^2$

At equilibrium,

Rate of forward reaction = Rate of backward reaction.

i.e. $k_1 (a-x_e) = k_2 x_e^2$ ——— (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

$$\frac{dx}{dt} = k_1(a-x) - k_2 x^2 \quad \text{——— (10)}$$

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

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

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.

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D$$

Concn.	A	B	C	D
Initially	a	a	0	0
At time t	$(a-x)$	$(a-x)$	x	x
At Equilibrium	$(a-x_e)$	$(a-x_e)$	x_e	x_e

Now,

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

Rate of backward reaction $= k_2 x^2$

Net rate of forward reaction = Rate of forward reaction − Rate of backward reaction.

i.e.
$$\frac{dx}{dt} = k_1(a-x)^2 - k_2 x^2 \quad \text{——— (13)}$$

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

So, $k_1(a-x_e)^2 = k_2 x_e^2$ — (14)

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

(a) $H_2 + I_2 \rightleftharpoons 2HI$

(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.

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$$

	A	B	C
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 =

= Rate of forward reaction − Rate of backward reaction

i.e. $\frac{dx}{dt} = k_1 (a-x)^2 - k_2 x$ —— (18)

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

$$k_1 (a - x_e)^2 = k_2 x_e \quad \text{—— (19)}$$

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

—— (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 :-

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(b) $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

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