ANALYSIS OF SOME IMPORTANT FIRST-ORDER REACTIONS Section - 3

Analysis of some important first-order reactions :

1. Decomposition of Hydrogen peroxide (H_2O_2)

$$2\,H_2O_2(\ell) \longrightarrow 2\,H_2O(\ell) + O_2(g)$$

The rate of this first order reaction is measured by titrating a fixed volume of H_2O_2 (undecomposed) against a standard solution of $KMnO_4$. Here $KMnO_4$ acts as *oxidising agent* and H_2O_2 as *reducing agent*. The volumes of $KMnO_4$ used for H_2O_2after regular intervals of time are as follows.

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_5
Vol. of $KMnO_4$	V_0	V_1	V_2	V_3	V_4	V_5

Volume of $KMnO_4$ at $t = 0$ corresponds to volume of H_2O_2 initially present $\Rightarrow$ $C_0 \propto V_0$

Volume of $KMnO_4$ at time instants $t_1, t_2, t_3, \ldots$ corresponds to volume of H_2O_2 remaining after $t_1, t_2, t_3, \ldots$ $\Rightarrow$ $C_t \propto V_t$

Now it being a first order reaction, follows first order kinetics : $kt = 2.303 \log_{10} \dfrac{V_0}{V_t}$

Now using the above expression, if we calculate the values of k for different time intervals $t_1, t_2, \ldots$ (for actual numerical data), the values of k should be same if the reaction follows first order kinetics.

2. Decomposition of ammonium nitrite (NH_4NO_2) and benzene diazonium chloride ($C_6H_5N{=}NCl$)

$$NH_4NO_2(s) \longrightarrow 2\,H_2O(\ell) + N_2(g)$$

$$C_6H_5-N=N-Cl(\ell) \longrightarrow C_6H_5-Cl(\ell) + N_2(g)$$

The rate of both the reaction is studied (measured) in similar manner. The volume of nitrogen (N_2) is collected after a regular interval of time as follows :

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t
Vol. of N_2	0	V_1	V_2	V_3	V_4	V_t

At $t = 0$, clearly the volume of $N_2 = 0$

Time instant $t = \infty$ means the end of a reaction i.e., when whole of NH_4NO_2 or $C_6H_5-N=N-Cl$ is decomposed.

$\Rightarrow$ At $t = \infty$, V_∞ corresponds to the initial volume of NH_4NO_2 or $C_6H_5-N=N-Cl$.

(Note that the ratio of stoichiometric coefficient for both $N_2 : NH_4NO_2$ or $N_2 : C_6H_5N=NCl$ is 1 : 1).

$\Rightarrow$ $C_0 \propto V_\infty$

At $t = t_1, t_2, t_3, \ldots\ldots$, the volume of N_2 corresponds to concentration of product formed i.e., equal to x.

$\Rightarrow$ $x \propto V_t$ $\Rightarrow$ $C_0 - x \propto V_\infty - V_t$

$$\Rightarrow \quad kt = 2.303 \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

3. Hydrolysis of esters ($CH_3COOC_2H_5$)

$$CH_3COOC_2H_5\,(\text{ester}) + H_2O + HCl\,(H^+) \longrightarrow CH_3COOH + C_2H_5OH$$

The reaction rate is measured by titrating the acid (CH_3COOH) produced against a standard alkali solution. Note that when a test sample is prepared from the reacting mixture, there are two acids : one is mineral acid H^+ (HCl or any other) and second is CH_3COOH produced. So volume of alkali used gives titration value for both acids. The data is collected in the following manner.

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_∞
Vol. of NaOH	V_0	V_1	V_2	V_3	V_4	V_∞

At $t = 0$, V_0 is the volume NaOH used to neutralise the mineral acid present (H^+) being used as catalyst. (At $t = 0$, *no* CH_3COOH *is yet produced*)

At $t = \infty$ (i.e. at the end of hydrolysis), V_∞ is the volume of NaOH used to neutralise whole of CH_3COOH *plus* vol. of HCl present. At $t = \infty$, volume of CH_3COOH corresponds to volume of ester taken initially.

$$\Rightarrow \quad C_0 \propto V_\infty - V_0 \qquad (\text{as } V_0 \equiv \text{vol. of HCl})$$

At $t = t_1, t_2, t_3, \ldots, V_1, V_2, V_3, \ldots$ corresponds to vol. of HCl *plus* vol. of CH_3COOH being produced.

$$\Rightarrow \quad x \propto V_t - V_0$$

$$\Rightarrow \quad C_0 - x \propto (V_\infty - V_0) - (V_t - V_0) \qquad \Rightarrow \qquad C_0 - x \propto V_\infty - V_t$$

$$\Rightarrow \quad kt = 2.303 \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$$

4. Kinetics of some reactions can be studied by measuring optical rotation of reaction mixture at different interval of time.

(i) Inversion of Cane Sugar ($C_{12}H_{22}O_{11}$)

$$C_{12}H_{22}O_{11} + H_2O + H^+ \longrightarrow C_6H_{12}O_6\,(\text{glucose}) + C_6H_{12}O_6\,(\text{fructose})$$

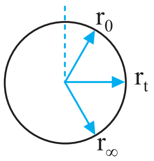
The rate is measured by measuring the change in the angle of rotation (optical activity) by a polarimeter. Sucrose is *dextro-rotatory*, glucose is *dextro-rotatory* and fructose is *leavo-rotatory*. The change produced in rotatory power in time *t* gives a measure of *x*, the quantity of sucrose decomposed in that time. The total change in the rotatory power produced at the end of the reaction gives the measure of C_0, the initial concentration of sucrose.

If r_0, r_t and r_∞ represent rotations at the start of reaction, after time t and at the end of reaction respectively, then

$$\Rightarrow \quad C_0 \propto r_0 - r_\infty \qquad \text{and} \qquad x \propto r_0 - r_t$$

$$\Rightarrow \quad C_0 - x \propto r_t - r_\infty$$

$$\Rightarrow \quad kt = 2.303 \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$



(ii) Consider the following first order reaction in which A, B and C are optically active compounds which rotate the plane polarized light in the clockwise or anticlockwise direction.

$$\text{A (soln.)} \longrightarrow \text{B (soln.)} + \text{C (soln.)}$$

Time	0	t	∞
Total rotation in degrees	r_0	r_t	r_∞

Let the specific optical rotations of A, B and C per unit concentration be, r_a, r_b and r_c (including +ve or –ve sign).

Let the initial concentration of A be C_0 and the decrease in concentration till time t be x.

	A (soln.) ⟶	B (soln.) +	C (soln.)
At time = 0	C_0	0	0
At time = t	$C_0 - x$	x	x
At time = ∞	0	C_0	C_0

Such that $$k = \frac{1}{t} \ln \frac{C_0}{C_0 - x}$$

Optical rotation at time = 0, $$r_a C_0 = r_0 \qquad \text{....(i)}$$

Optical rotation at time = t, $$r_a (C_0 - x) + x r_b + x r_c = r_t$$

$$r_a C_0 + x (r_b + r_c - r_a) = r_t$$

$$r_0 + x (r_b + r_c - r_a) = r_t \qquad \text{....(ii)}$$

Optical rotation at time = ∞, $$C_0 (r_b + r_c) = r_\infty \qquad \text{....(iii)}$$

From equation (ii)

$$x = \frac{r_t - r_0}{(r_b + r_c - r_a)} \qquad \text{....(iv)}$$

Since constant involved in x is $\frac{1}{(r_b + r_c - r_a)}$, the same constant must appear in the expression of C_0.

Thus, subtracting equation (i) from equation (iv), we get :

$$C_0 = \frac{r_\infty - r_0}{(r_b + r_c - r_a)} \qquad \text{....(v)}$$

Subtracting equation (iv) from equation (v)

$$C_0 - x = \frac{r_\infty - r_t}{(r_b + r_c - r_a)}$$

$$\therefore \qquad k = \frac{1}{t} \ln \frac{r_\infty - r_0}{r_\infty - r_t}$$

5. In first-order reactions involving gases, sometime measuring the pressure of the reaction mixture is very good method for measuring reaction rates.

For example consider decomposition of arsine gas (AsH_3).

$$AsH_3\,(g) \longrightarrow As\,(s) + \frac{3}{2} H_2\,(g)$$

The rate of reaction is measured as the *increase* in pressure of the reaction mixture. Note that there is an increase in number of moles of the gaseous products to the right, so as the reaction proceeds, there will be an increase in pressure of contents ($P \propto n$).

Let the initial pressure of $AsH_3(g)$ is P_0, if x is the decrease in pressure of $AsH_3(g)$ after time t.

	$AsH_3(g)$	$\longrightarrow$	$As\,(s)$	$+$	$\frac{3}{2} H_2(g)$
$C_0 \equiv$ initial pressure	P_0		0		0
$C_t \equiv$ partial pressure	$P_0 - x$		0		$\frac{3}{2} x$

Arsenic is solid, so $P(As) = 0$

After time t, let P_t be the total pressure, then

$$P_t = P(AsH_3) + P(H_2) = (P_0 - x) + \frac{3x}{2}$$

$$\Rightarrow \quad P_t = P_0 + \frac{x}{2} \qquad \Rightarrow \qquad x = 2\,(P_t - P_0)$$

Now $\quad C_0 \propto P_0$

and $\quad C_t \propto P_0 - x \equiv P_0 - 2\,(P_t - P_0) \equiv 3P_0 - 2P_t \qquad \Rightarrow \qquad kt = 2.303 \log_{10} \dfrac{P_0}{3P_0 - 2P_t}$

On similar pattern, please try to write the expression for Ist order rate law for following first-order reactions.(*in terms of* P_o *and* P_t)

1. $N_2O(g) \longrightarrow N_2(g) + \frac{1}{2} O_2(g)$

2. $(CH_3)_3C-O-O-C(CH_3)_3\,(g) \longrightarrow 2\,(CH_3)_2C=O(g) + C_2H_6(g)$