5. The actual concentrations of HCl in the two sets become 2(N) and 1(N) as 25 ml acid solution is mixed with 25 ml sucrose solution.

Thus, $\dfrac{K_{2(N)}HCl}{K_{1(N)}HCl} = \cdots$. The expected value is 2. If it is, we may conclude that in this reaction HCl acts as a homogeneous catalyst.

Experiment 3

Kinetic study of the decomposition of hydrogen peroxide in presence of ferric chloride solution and effect of catalyst on the rate constant.

Theory: Hydrogen peroxide undergoes decomposition in accordance with the equation

$H_2O_2 = H_2O + \frac{1}{2}O_2$ and the rate of decomposition is markedly accelerated by the presence of various catalysts. In this experiment we will study the above decomposition reaction in presence of $FeCl_3$ solution which acts as a positive catalyst and whose concentration remains unchanged during the course of the reaction. The course of the reaction may be followed by titrating the hydrogen peroxide with potassium permanganate in acid medium, the volume of permanganate solution required at any time being proportional to the concentration of hydrogen peroxide remaining at that time.

Let V_0 be the volume of potassium permanganate solution required corresponding to the initial concentration of hydrogen peroxide a at time $t = 0$, and V_t be the volume of potassium permanganate solution required corresponding to the concentration of hydrogen peroxide remaining $(a - x)$ at time t. Since the reaction follows first order kinetics, the expression of rate constant at laboratory temperature is given by

$$K = \frac{2.303}{t} \log \frac{a}{a-x} \qquad \text{or, i.e., } K = \frac{2.303}{t} \log \frac{V_0}{V_t}.$$

It is difficult to measure V_0 as the decomposition starts as soon the catalyst is mixed with hydrogen peroxide and it can be eliminated by taking the difference in time $\Delta t_n = t_n - t_1$ such that

$$K = \frac{2.303}{\Delta t_n} \log \frac{V_1}{V_n} \qquad [n = 2, 3, 4, \cdots]$$

or, $\quad \log \dfrac{V_1}{V_n} = \dfrac{K}{2.303} \Delta t_n$, $\hfill (1)$

where V_1 is the volume of permanganate solution required for a particular volume (say, 5 ml) of reaction mixture at time t_1 after the initiation of the reaction and V_n is that at time $t_2, t_3, \cdots$ after the initiation of the reaction. If $\log \dfrac{V_1}{V_n}$ is plotted against Δt_n, a straight line passing through the origin will be obtained from the slope of which K can be determined. The reaction is studied using two different concentrations of $FeCl_3$ solution, K_1 and K_2 are determined and the result is interpreted from ratio $\dfrac{K_1}{K_2}$.

Materials: (i) 2(V) hydrogen peroxide, (ii) 1.0% and 0.5% $FeCl_3$ solution, (iii) 1(N) H_2SO_4, (iv) $\frac{N}{50}$ $KMnO_4$ solution, (v) Ice, (vi) Pipettes, burettes, conical flasks, etc.

Procedure ·

1. In the laboratory, the hydrogen peroxide which is available is labelled as 30% (100 volumes). Prepare 250 ml 2(V) H_2O_2 from this concentrated H_2O_2 (5 ml is diluted to 250 ml with distilled water).

2. Prepare 100 ml 1% anhydrous $FeCl_3$ solution (1 gm is dissolved in 100 ml water) and then from this solution prepare 50 ml 0.5% $FeCl_3$ solution by exact dilution (25 ml $FeCl_3$ solution 1% + 25 distilled water).

3. Prepare 250 ml 1(N) H_2SO_4 from concentrated H_2SO_4 [36 (N)]. Dilute ≈ 7 ml concentrated H_2SO_4 to 250 ml carefully.

4. Prepare 500 ml $\dfrac{N}{50}$ $KMnO_4$ solution (dissolved ≈ 0.3 ml $KMnO_4$ in 500 ml water).

5. Take 50 ml of 2(V) H_2O_2 in a 250 ml stoppered bottle and add 10 ml of 1% $FeCl_3$ solution starting the stop-watch when the pipette is half-emptied. Shake the reaction mixture well and withdraw 5 ml portions of the reaction mixture at intervals of 3 minutes and then run it into 10 ml ice-cold (IN) H_2SO_4, noting the time of the half-discharge of the reaction mixture. Immediately titrate it against $\dfrac{N}{50}$ $KMnO_4$ solution. Note the burette readings when just pink colour appears in each case. Take at least seven readings.

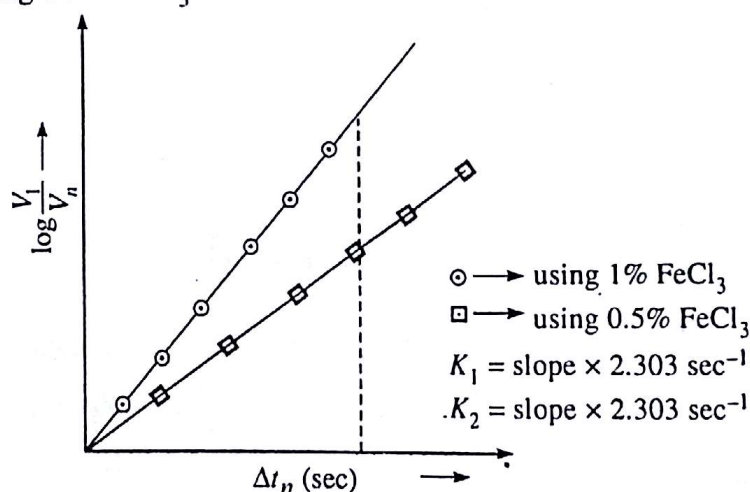6. Repeat the same using 0.5% $FeCl_3$ solution.

Fig. 8.5: Plot of $\log \dfrac{V_1}{V_n}$ vs. Δt_n

vii. Plot $\log \dfrac{V_1}{V_n}$ vs. Δt_n for the two sets a data on the same graph paper and determine K_1 and K_2 for two sets. The expected nature of graph will be as follows.

viii. Interpret the result.

N.B.:

a. Before starting the experiment a blank titration of H_2O_2 is necessary. For this purpose take 50 ml of 2(V) H_2O_2 (prepared) and add 10 ml of distilled water instead of $FeCl_3$ solution. Withdraw 5 ml of that H_2O_2 and then run into 10 ml of 1(N) H_2SO_4. Titrate it against $\dfrac{N}{50}$ thio and note the burette reading. If the burette reading lies in the range 20 ml to 30 ml, then start the experiment. Otherwise adjust the strength of H_2O_2 so that the burette reading lies approximately on the above range. The blank titration of H_2O_2 is necessary because the strength of H_2O_2, which is available in the laboratory, is not correctly known, some of it may decompose and its strength may change from 30% i.e., 100 volumes.

b. During performing the experiment there may always some bubbling at the time of pipetting. Minimize the rate of bubbling by adjusting the strength of $FeCl_3$ solution. Whatever may be the strength of $FeCl_3$ solution adjusted, the strength of one should be just half of the other.]

Results and Calculations

1. Recording of laboratory temperature

	Before experiment	After experiment	Mean
Temperature →	°C	°C	°C

2. Titration results of set 1 (using 1% $FeCl_3$ solution)

Time (sec)	Δt_n (sec)	Volume of $KMnO_4$ required (ml)	$\log \dfrac{V_1}{V_n}$ [$n = 2, 3, 4, \cdots$]
t_1	—	V_1	—
t_2	$t_2 - t_1$	V_2	...
t_3	$t_3 - t_1$	V_3	...
t_4	$t_4 - t_1$	V_4	...
t_5	$t_5 - t_1$	V_5	...
t_6	$t_6 - t_1$	V_6	...

3. Titration results for set 2 (using 0.5% $FeCl_3$ solution)

Time (sec)	Δt_n (sec)	Volume of $KMnO_4$ required (ml)	$\log \dfrac{V_1}{V_n}$ [$n = 2, 3, 4, ...$]
t_1	—	V_1	—
t_2	$t_2 - t_1$	V_2	...
t_3	$t_3 - t_1$	V_3	...
t_4	$t_4 - t_1$	V_4	...
t_5	$t_5 - t_1$	V_5	...
t_6	$t_6 - t_1$	V_6	...

4. Calculations and Conclusion

From the plot of $\log \dfrac{V_1}{V_n}$ vs. Δt_n.

For set 1 $K_1 = \text{slope} \times 2.303 \text{ sec}^{-1}$

For set 2 $K_2 = \text{slope} \times 2.303 \text{ sec}^{-1}$

$\therefore$ the ratio $\dfrac{K_1}{K_2} = \cdots$.

[It has been found that $\dfrac{K_1}{K_2} \neq 2$. The expected value of the ratio is nearly 1.5.

If it is, we can conclude that $FeCl_3$ does not act as a homogenous catalyst. In case of a homogeneous catalyst the expected value of the ratio is 2].

P.C.P.—15