## Experiment

## Catalytic decomposition of hydrogen peroxide $\left(\mathbf{H}_{2} \mathrm{O}_{2}\right)$

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Date: $\qquad$ Room Temperature: $28{ }^{\circ} \mathrm{C}$

## Objective

To study the catalytic decomposition of hydrogen peroxide ( $\mathbf{H}_{2} \mathrm{O}_{2}$ ).

## Requirements

(a) Glassware: Conical flask, Burette, Burette stand, Pipette, Measuring cylinder, Volumetric flask, Test tube, Watch glass, Beaker, Funnel, Stopwatch, Water bath.
(b) Chemicals:

- $0.02 \mathrm{M} \mathrm{KMnO}_{4}$
- $0.05 \mathrm{M} \mathrm{FeCl}_{3}+0.04 \mathrm{M} \mathrm{HCl}$
- $1 \%(\mathrm{v} / \mathrm{v}) \mathrm{H}_{2} \mathrm{O}_{2}$ of Concentrated $\mathrm{H}_{2} \mathrm{O}_{2}[30 \% \mathrm{w} / \mathrm{v}$ (or 100 volume) $]$
- Dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$ (Approx. 5 N )


## 1. Principle

The rate of the chemical reaction depends on a number of factors, e.g. concentrations of the reactants, temperature, catalysts, etc. A catalyst may markedly increase the velocity of the process, especially in the presence of accelerators and promoters.

Hydrogen peroxide $\left(\mathrm{H}_{2} \mathrm{O}_{2}\right)$ undergoes decomposition according to the equation:

$$
2 \mathrm{H}_{2} \mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{O}_{2}
$$

The rate is greatly accelerated by various catalysts, e.g. manganese dioxide, ferric chloride, or a mixture of ferric chloride and cupric chloride, latter compound acting as a catalytic promoter. The course of the reaction may be followed by titrating aliquots of the mixture with standard solution of potassium permanganate at various intervals of time.

## 2. Solution Preparation

## 2.1. $\quad 0.02 \mathrm{M} \mathrm{KMnO}_{4}$ in 250 mL

$$
\begin{aligned}
& w=\frac{\text { Molarity } \times \text { Mol. Wt. } \times \text { Volume }}{1000} \\
& w=\frac{0.02 \times 158.03 \times 250}{1000}=0.79 \mathrm{~g}
\end{aligned}
$$

Dissolve 0.79 g of $\mathrm{KMnO}_{4}$ in 250 mL volumetric flask with distilled water and
make upto the mark with distilled water.

## 2.2. $0.05 \mathrm{M} \mathrm{FeCl}_{3}+\mathbf{0 . 0 4} \mathbf{M ~ H C l}$ in 100 mL

$$
\begin{aligned}
w & =\frac{0.05 \times 162.2 \times 100}{1000} \\
& =0.811 \mathrm{~g} \mathrm{FeCl}_{3}
\end{aligned}
$$

and

$$
\begin{gathered}
\mathrm{N}_{1} \mathrm{~V}_{1}=\mathrm{N}_{2} \mathrm{~V}_{2} \\
11.6 \mathrm{~V}_{1}=0.04 \times 100 \\
\mathrm{~V}_{1}=0.34 \mathrm{~mL} \mathrm{HCl}
\end{gathered}
$$

Take 0.8110 g of $\mathrm{FeCl}_{3}$ and 0.34 mL of concentrated HCl in 100 mL volumetric flask and dissolve in distilled water and make upto the mark with distilled water.
2.3. $1 \%(v / v)(0.3 \mathrm{w} / \mathrm{v} \%) \mathrm{H}_{2} \mathrm{O}_{2}$ in 250 mL

Dissolve 2.5 mL concentrated $\mathrm{H}_{2} \mathrm{O}_{2}$ [ $30 \% \mathrm{w} / \mathrm{v}$ (or 100 volume)] in 250 mL volumetric flask in distilled water and make upto the mark with distilled water.

### 2.4. Dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$ (Appro. 5 N )

Dilute approximate 69.44 mL of concentrated $\mathrm{H}_{2} \mathrm{SO}_{4}$ to 500 mL with distilled water.

## 3. Procedure

Place the various solutions in the bath at room temperature for 30 minutes.
Exp. (A) Introduce 100 mL of $\mathrm{H}_{2} \mathrm{O}_{2} 1 \%$ solution into a flask, add 5 mL of distilled water and place the flask in the bath. Withdraw immediately $5-\mathrm{mL}$ of the solution, run it into dilute $\mathrm{H}_{2} \mathrm{SO}_{4}$ and titrate it with standard permanganate solution. Withdraw $5-\mathrm{mL}$ portions after $5,10,15,20,25,30,35,40,45,50,55$ minutes and repeat the above titrations in order to find the amounts of the peroxide left at these intervals of time.

Exp. (B) Carry out a similar experiment using a mixture of 100 mL of $1 \% \mathrm{H}_{2} \mathrm{O}_{2}$ and 5 mL of the $\mathrm{FeCl}_{3}$ solution. Withdraw $5-\mathrm{mL}$ portions after $0,5,10,15,20,25,30$, $35,40,45,50,55$ minutes and titrate as before.

## 4. Observation Table

Exp. (A)

| Reaction Mixture |  |
| :--- | :---: |
| $\mathbf{1 0 0} \mathbf{~ m L}, \mathbf{1} \% \mathbf{H}_{2} \mathbf{O}_{2}$ Solution | $\mathbf{5} \mathbf{~ L L ~ H} \mathbf{2}$ |

Aliquot : $5 \mathbf{m L}$ Reaction Mixture
Quenching Solution : Half test tube dilute $\mathbf{H}_{2} \mathrm{SO}_{4}$

| $\begin{gathered} \text { S. } \\ \text { No. } \end{gathered}$ | Time HH:MM | Time Interval ( $t$ ) (min) | Burette Reading |  | $\begin{gathered} B-A \\ (a-x) \\ (\mathrm{mL}) \end{gathered}$ | $\log (a-x)$ | $\frac{a}{(a-x)}$ | $\log \frac{a}{(a-x)}$ | $\begin{gathered} k_{\mathrm{A}}=\frac{2.303}{t} \log \frac{a}{(a-x)} \\ \left(\min ^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $\begin{gathered} \text { Initial } \\ A(\mathrm{~mL}) \end{gathered}$ | $\begin{gathered} \text { Final } \\ B(\mathrm{~mL}) \end{gathered}$ |  |  |  |  |  |
| 1 | 15:05 | 0 | 0 | 10.5 | 10.5 | 1.021 | 1.000 | 0.000 | - |
| 2 | 15:10 | 5 | 0 | 10.3 | 10.3 | 1.013 | 1.019 | 0.008 | $3.847 \times 10^{-3}$ |
| 3 | 15:15 | 10 | 0 | 10.3 | 10.3 | 1.013 | 1.019 | 0.008 | $1.923 \times 10^{-3}$ |
| 4 | 15:20 | 15 | 0 | 10.2 | 10.2 | 1.009 | 1.029 | 0.013 | $1.933 \times 10^{-3}$ |
| 5 | 15:25 | 20 | 0 | 10.2 | 10.2 | 1.009 | 1.029 | 0.013 | $1.450 \times 10^{-3}$ |
| 6 | 15:30 | 25 | 0 | 10.1 | 10.1 | 1.004 | 1.040 | 0.017 | $1.554 \times 10^{-3}$ |
| 7 | 15:35 | 30 | 0 | 9.9 | 9.9 | 0.996 | 1.061 | 0.026 | $1.962 \times 10^{-3}$ |
| 8 | 15:40 | 35 | 0 | 9.9 | 9.9 | 0.996 | 1.061 | 0.026 | $1.681 \times 10^{-3}$ |
| 9 | 15:45 | 40 | 0 | 9.8 | 9.8 | 0.991 | 1.071 | 0.030 | $1.725 \times 10^{-3}$ |
| 10 | 15:50 | 45 | 0 | 9.8 | 9.8 | 0.991 | 1.071 | 0.030 | $1.533 \times 10^{-3}$ |
| 11 | 15:55 | 50 | 0 | 9.7 | 9.7 | 0.987 | 1.082 | 0.034 | $1.585 \times 10^{-3}$ |
|  |  |  |  |  |  |  | Ave | ge $\boldsymbol{k}_{\text {A }}$ | $1.919 \times 10^{-3}$ |

Exp. (B)

| Reaction Mixture |  |
| :---: | :---: |
| $\mathbf{1 0 0} \mathbf{~ m L}, \mathbf{1} \% \mathbf{H}_{\mathbf{2}} \mathrm{O}_{\mathbf{2}}$ Solution | $\mathbf{5} \mathbf{~ m L}, \mathbf{0 . 0 5} \mathbf{M ~ F e C l}_{3}$ Solution |

## Aliquot : $\mathbf{5} \mathbf{m L}$ Reaction Mixture

Quenching Solution : Half test tube dilute $\mathbf{H}_{2} \mathrm{SO}_{4}$

| $\begin{gathered} \text { S. } \\ \text { No. } \end{gathered}$ | TimeHH:MM | Time Interval <br> ( $t$ ) (min) | Burette Reading |  | $\begin{gathered} B-A \\ (a-x) \\ (\mathrm{mL}) \end{gathered}$ | $\log (a-x)$ | $\frac{a}{(a-x)}$ | $\log \frac{a}{(a-x)}$ | $\begin{gathered} k_{\mathrm{B}}=\frac{2.303}{t} \log \frac{a}{(a-x)} \\ \left(\min ^{-1}\right) \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | Initial $A(\mathrm{~mL})$ | $\begin{gathered} \text { Final } \\ B(\mathrm{~mL}) \end{gathered}$ |  |  |  |  |  |
| 1 | 15:05 | 0 | 0 | 9.5 | 9.5 | 0.978 | 1.000 | 0.000 | - |
| 2 | 15:10 | 5 | 0 | 7.6 | 7.6 | 0.881 | 1.250 | 0.097 | $4.464 \times 10^{-2}$ |
| 3 | 15:15 | 10 | 0 | 6.3 | 6.3 | 0.799 | 1.508 | 0.178 | $4.108 \times 10^{-2}$ |
| 4 | 15:20 | 15 | 0 | 5.2 | 5.2 | 0.716 | 1.827 | 0.262 | $4.018 \times 10^{-2}$ |
| 5 | 15:25 | 20 | 0 | 4.2 | 4.2 | 0.623 | 2.262 | 0.354 | $4.082 \times 10^{-2}$ |
| 6 | 15:30 | 25 | 0 | 3.8 | 3.8 | 0.580 | 2.500 | 0.398 | $3.666 \times 10^{-2}$ |
| 7 | 15:35 | 30 | 0 | 3.2 | 3.2 | 0.505 | 2.969 | 0.473 | $3.628 \times 10^{-2}$ |
| 8 | 15:40 | 35 | 0 | 2.6 | 2.6 | 0.415 | 3.654 | 0.563 | $3.703 \times 10^{-2}$ |
| 9 | 15:45 | 40 | 0 | 2.2 | 2.2 | 0.342 | 4.318 | 0.635 | $3.658 \times 10^{-2}$ |
| 10 | 15:50 | 45 | 0 | 1.9 | 1.9 | 0.279 | 5.000 | 0.699 | $3.577 \times 10^{-2}$ |
| 11 | 15:55 | 50 | 0 | 1.5 | 1.5 | 0.176 | 6.333 | 0.802 | $3.692 \times 10^{-2}$ |
|  |  |  |  |  |  |  | Average $\boldsymbol{k}_{\mathrm{B}}$ |  | $3.860 \times 10^{-2}$ |

## 5. Calculation

The values of $(a-x)$, i.e. the titration figures, are proportional to the concentrations of the peroxide remaining at time $t$. Plot $\log (a-x)$ versus $t$ and draw the best straight lines through the point obtained for Exp. (A) and (B) (Fig. 1).


Fig. 1. Plot of $\log (a-x)$ versus time interval $t$.
Graph shows that the decomposition of $\mathrm{H}_{2} \mathrm{O}_{2}$ is of the first order under the experimental conditions, i.e. it obeys the kinetic equation

$$
k=\frac{2.303}{t} \log \frac{a}{(a-x)}
$$

where $a$ is the initial concentration of the reactant, and $(a-x)$ is that at time $t$. Find the slope $(S)$ of the lines in each case and thus calculate the velocity constants.

Exp. (A): $S_{\mathrm{A}}=\frac{y_{2}-y_{1}}{x_{2}-x_{1}}=\frac{1.00-1.02}{50-20}=-0.000666=-6.7 \times 10^{-4}$

$$
\begin{aligned}
k_{\mathrm{A}} & =-S_{\mathrm{A}} \times 2.303 \\
& =6.7 \times 10^{-4} \times 2.303
\end{aligned}
$$

$$
=1.543 \times 10^{-3} \mathrm{~min}^{-1}
$$

$\operatorname{Exp}(B): S_{B}=\frac{y_{2}-y_{1}}{x_{2}-x_{1}}=\frac{0.41-0.57}{35-25}=-0.016$

$$
\begin{aligned}
k_{\mathrm{B}}=-S_{\mathrm{B}} \times 2.303 & =0.016 \times 2.303 \\
& =0.0368 \mathrm{~min}^{-1} \\
& =3.680 \times 10^{-2} \mathrm{~min}^{-1}
\end{aligned}
$$

## 6. Results and Discussion

The velocity constant, $k$, of the decomposition of $\mathrm{H}_{2} \mathrm{O}_{2}$ is found under the experimental conditions as following:

## By the graphical method:

Rate constant of the Exp. $\mathrm{A}=k_{\mathrm{A}}=1.543 \times 10^{-3} \mathrm{~min}^{-1}$

Rate constant of the Exp. $\mathrm{B}=k_{\mathrm{B}}=3.680 \times 10^{-2} \mathrm{~min}^{-1}$

## By the integration method:

Rate constant of the Exp. $\mathrm{A}=k_{\mathrm{A}}=1.919 \times 10^{-3} \mathrm{~min}^{-1}$

Rate constant of the Exp. $\mathrm{B}=k_{\mathrm{B}}=3.860 \times 10^{-2} \mathrm{~min}^{-1}$

The first-order decomposition of $\mathrm{H}_{2} \mathrm{O}_{2}$ reaction is probably proceed via an unstable intermediate compound, as in the case of a catalyst consisting of a mixture of a halogen and a halide ion.

## 7. Precautions

(i) $\mathrm{KMnO}_{4}$ should be added drop by drop for titration.
(ii) $\mathrm{H}_{2} \mathrm{O}_{2}$ should be carefully diluted.
(iii) Burette reading should be noted carefully in lower meniscus.

## 8. Further Reading

(i) Read up details of the first order kinetic.
(ii) Advanced Physico-Chemical Experiments, J Rose, Sir Isaac Pitman \& Sons Ltd, London.
(iii) Physical Chemistry, P. W. Atkins and J. D. Paula, Eds: $7^{\text {th }}$, Oxford University Press.
(iv) Principle of Physical Chemistry, B. R. Puri, L. R. Sharma, and Pathania, Vishal Publishing Co. Jalandhar.

