

Decomposition of Hydrogen Peroxide by Potassium Ferro- and Ferricyanides.

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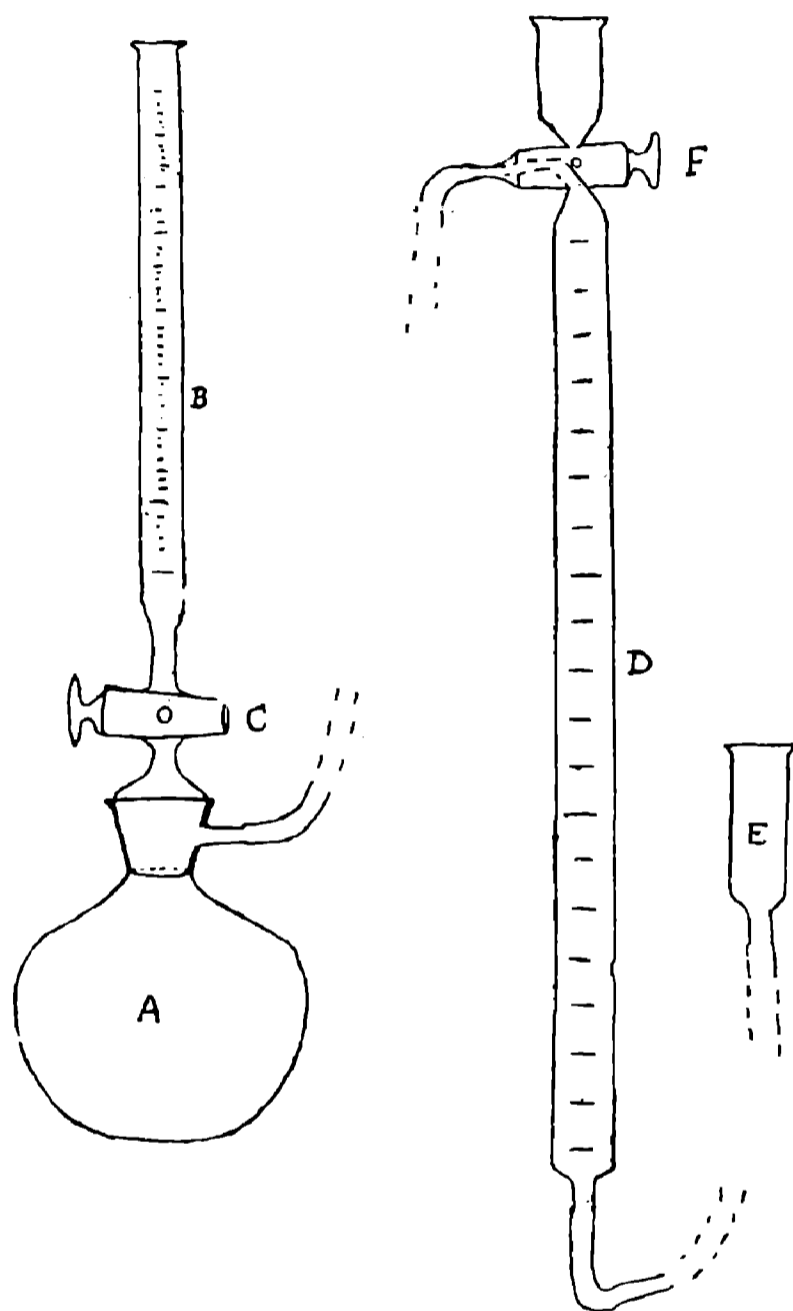
Kistiakowsky (*Z. physikal. Chem.*, 1900, 35, 431), finds that the decomposition of hydrogen peroxide in the presence of a few drops of a mixture of solutions of yellow and red prussiate of potash is greatly accelerated by previously exposing the mixture to light. The exposure, however short it might be, had a pronounced effect in that the activity continued long after the illumination had ceased. The activity is attributed to the formation of a new catalyst by the action of light and not to any photochemical after-effect. This presents a peculiar and an interesting reaction in that the time of exposure of the mixture, however short it might be, of yellow and red prussiate to light, does not seem to have any appreciable difference in the final effect. Hence a systematic examination of the decomposition of hydrogen peroxide by yellow and red prussiate of potash in dark and in light, seemed to us desirable.

EXPERIMENTAL.

Kistiakowsky (*loc. cit.*) followed the reaction by titrating definite amounts of the reaction mixture from time to time with dilute permanganate and after making a small, but rough correction for the amount of ferrocyanide taken, took the titre value as a measure of hydrogen peroxide still undecomposed in solution. This difficulty is eliminated in the following paper by finding out the amount of hydrogen peroxide decomposed by measuring the volume of oxygen evolved from time to time. The reaction was allowed to go on to completion for more than 24 hours. The total amount of oxygen was noted as infinity reading and from this the original concentration of hydrogen peroxide known. A small volume of gas that is dissolved in the liquid is not taken into account. This does not make any great error in the velocity coefficients since under the conditions of the experiments described here, it does not amount to more than 0.3 c.c. on the whole.

Chemically pure ferro- and ferricyanides of potash were used; fresh solutions were always made before any set of experiments. The hydrogen peroxide used throughout was of Schering-Kahlbaum suitably diluted.

FIG. 1.



The apparatus consists a reaction vessel A, connected to a graduated 10 c.c. pipette B, and capable of communicating with a nitrometer burette D and levelling tube E through a side hole in the ground joint at the neck of the vessel. In most of the experiments 5 c.c. of suitably diluted hydrogen peroxide was placed in the reaction vessel and 10 c.c. of ferro- or ferricyanide of potash solution were taken in the pipette. The nitrometer burette was filled with water and the three way tap F was turned to be in connection with the vessel A and to the atmosphere. The reaction vessel with the hydrogen peroxide solution was placed in an electrically controlled thermostat (correct to $\pm 0.05^\circ$) so that it was immersed in water up to the neck. Time was allowed for the flask and its contents

to attain the temperature of the bath. Then 5 c.c. of the solution from the pipette was allowed to run into the flask along the sides of the vessel and thus allowed to mix without shaking and the tap F was turned quickly to connect the reaction vessel and the measuring burette. The time was noted and the volume of gas in the burette at atmospheric pressure was read off. The decomposition was followed by the amount of oxygen collected at atmospheric pressure, from time to time.

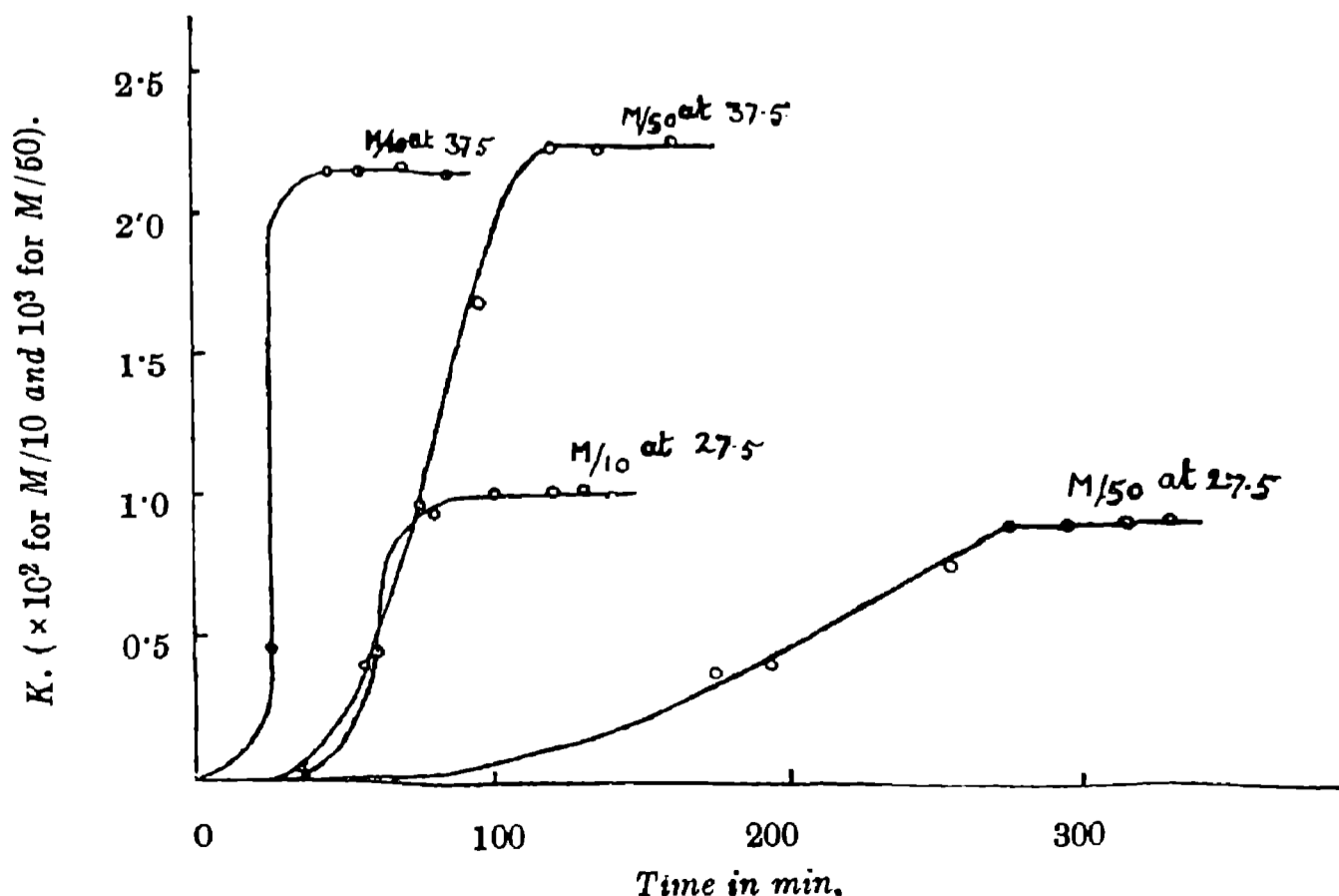
Care was taken not to expose the reaction mixture or the original solution to the action of light, except when it was so desired.

Experiments with Potassium Ferrocyanide.

Experiments were conducted with 5 c.c. of hydrogen peroxide solution and 5 c.c. of $M/10$ -potassium ferrocyanide solution at 25° . Reproducible data were obtained, but the results were too complicated to be represented by the ordinary velocity equations. It appears that the reaction is not one of simple decomposition of hydrogen peroxide by ferro-cyanide but is complicated by subsidiary ones taking place as well. The following possibilities suggest themselves.

- (1) Decomposition of H_2O_2 by ferrocyanide.
- (2) Oxidation of ferrous ion to ferric state by H_2O_2 .
- (3) Decomposition of H_2O_2 by ferri-cyanide formed.
- (4) Enhancement of reaction (1) by the inductive action of (2).

FIG. 2.



K —Instantaneous rates reactions with 5 c.c. of H_2O_2 and 5 c.c. of $K_3Fe(CN)_6$.

Hence experiments with ferrocyanide were abandoned and the decomposition of H_2O_2 by ferricyanide was studied in a detailed manner.

Experiments with Ferricyanide.

Reaction velocity and the period of induction.—The following tables and the graphs (Fig. 2) give the summary of their results on the kinetics of the decomposition of hydrogen peroxide by potassium ferricyanide solutions.

Since the speed of the reaction is measured by the rate of evolution of oxygen from the liquid, it would be incorrect to calculate the velocity constant from the beginning by the application of the usual formula. Hence the instantaneous rates and the velocity coefficients were calculated at each point in the course of the reaction. For a unimolecular reaction it is given by

$$dx/dt \times 1/C_m,$$

where dx is the amount of oxygen evolved or H_2O_2 decomposed in interval dt , and C_m is the mean concentration of H_2O_2 in that interval.

TABLE I.

$\text{H}_2\text{O}_2 = 5$ c.c. $M/10 - \text{K}_3\text{Fe}(\text{CN})_6 = 5$ c.c. Temp. = 27.5° .

Time min in.	0	5	10	30	60	80	100	120	130	140	∞
Burette reading in c.c.	0.5	0.5	0.5	0.5	2.8	5.4	7.9	9.9	10.7	11.4	18.6
Conc. of H_2O_2 in terms of c.c. of O_2	18.1	15.8	13.2	10.7	8.7	7.8	7.1	...
Instantaneous rates	0.0090	0.0104	0.0103	0.0109	0.0100	
										<u>0.0101</u>	mean 0.0101

TABLE II.

$\text{H}_2\text{O}_2 = 5$ c.c. $M/10 - \text{K}_3\text{Fe}(\text{CN})_6 = 7.5$ c.c. Temp. = 27.5° .

Time in min.	0	40	60	80	100	120	130	140	150	160	170	180	∞
Burette reading in c.c.	10.0	10.0	10.0	10.5	11.2	12.9	14.4	15.85	17.25	18.50	19.60	20.60	28.60
Conc. of H_2O_2 in terms of c.c. of O_2	18.6	18.1	17.4	15.4	14.2	12.75	11.35	10.1	9.0	8.0	...
Instantaneous rates	0.0108	0.0111	0.0115	0.0115	0.0117			
										<u>0.0117</u>			mean 0.0117

TABLE III.

$$\text{H}_2\text{O}_2 = 5 \text{ c.c. } M/10\text{-K}_3\text{Fe (CN)}_6 = 10 \text{ c.c. } \text{Temp.} = 27.5^\circ.$$

Time in min.	0	40	60	80	100	120	140	150	160	180	200	220	∞	
Burette reading in c.c.	2.0	2.0	2.0	2.0	4.1	6.0	8.6	9.65	10.60	12.20	13.35	14.40	18.5	
Conc. of H_2O_2 in terms of c.c. of O_2	16.5	14.4	12.5	9.9	8.85	7.9	6.3	5.15	4.1	
Instantaneous rates						0.0116	0.0112	0.0111	0.0112	0.0101	0.0114	...
													mean	0.0111

It appears that there is an initial disturbance after which the velocity coefficients are constant. The reaction is unimolecular and does not depend on the initial concentration of the hydrogen peroxide. The initial period consists of two definite portions; a short one where there is no evolution of gas followed by another period of gradually increasing rate of chemical transformation, till the regular velocity coefficients are obtained. The first one corresponds to a 'pseudo' period of induction as is usually observed in measurements of this type where the gas is retained by the liquid depending on its saturation capacity (*cf.* Veley, *Phil. Mag.*, 1903 (vi) 6, 271; Marchand, *Ann. chim. phys.*, 1873 (iv) 4, 30, 302). The regular period of induction corresponds to that when there is a slow and increasing rate of evolution of gas.

In order to verify this, experiments were performed with the same concentration of solutions but with different quantities so that the total volumes of the liquid were different. The results are described in Tables I, II and III. Other conditions being the same the total volume of the reaction mixture varies from 10 to 15 c.c. It is seen that the 'pseudo' period of induction depends on the volume of the liquid. Thus for a total volume of 10 c.c., the period is about 50 to 60 min., for 12.5 c.c. it is between 60 to 80 minutes and for 15 c.c. it is between 80 to 100 minutes.

Next experiments were performed with various concentrations of ferricyanide solution at 27.5° . and at 37.5° . The results are presented in Fig. 2 by means of graphs. The velocity coefficients at various times are plotted against the times. It is seen that the period of induction increases with dilution. With $M/100$, it was seen

that even after 6 hours working the period of induction was not passed. Experiments with $M/500$ at 37.5° . showed that the reaction was immeasurably slow even after 2 days. Table IV shows that the product of the period of induction and concentration is fairly constant. At 37.5° the constant is about $2/5$ its value at 27.5° corresponding to a temperature coefficient of the reaction velocity of about 2.5, described in the next section.

The data also shows the effect of dilution of potassium ferricyanide on the velocity coefficients.

TABLE IV.

Molar conc. of $K_3Fe(CN)_6$...	0.1	0.05	0.02
Period of induction θ_1 at 27.5°	61	122	275
„ „ „ θ_2 at 37.5°	2.5	...	110
$\theta_1 \times C$...	6.1	6.1	5.5
$\theta_2 \times C$...	2.5	...	2.2

N. B. The values for the period of induction have been obtained from the graphs.

Temperature coefficient.—Experiments were performed at 27.5° and at 37.5° with concentrations of $N/10$ and $N/50$ -potassium ferricyanide. The summary of the results are given in Table V. The velocity coefficients after the initial period were always taken for the velocity constants.

TABLE V.

Conc. of ferricyanide.	$K_{27.5}$.	$K_{37.5}$.	$K_{37.5}/K_{27.5}$.
$M/10$	0.0101	0.0217	2.2
$M/50$	0.00093	0.002225	2.5

Thus the temperature coefficient of the reaction velocity is about 2.3.

Effect of light.—Kistiakowsky (*loc. cit.*) mentions the extraordinary sensitivity of this reaction to light, which persists even after the exposure has long ceased. He believes that it is due to the formation of a new catalyst in the presence of light and which catalyst is of

a colloidal nature. Two samples $M/10$ solutions of ferricyanide were exposed to bright sun light at midday, one for 5 minutes and the other for 30 minutes. The solutions were well cooled to 27.5° and experiments were conducted with them. The results are given in Tables VI and VII. The reaction starts at once and proceeds rapidly. It is clear that the only effect of such a treatment is to eliminate the period of induction. The velocity coefficients in both the cases were the same and the value is actually lower (about a third) than that obtained before exposing the solution to light. However, Kistia-kowsky failed to notice the period of induction, described here. So it is obvious that he has been comparing these values with the reaction rates during the period of induction; At such concentrations as he worked with, it is likely that the period of induction persists for many hours.

TABLE VI.

$H_2O_2 = 5$ c.c.		$M/10-K_3Fe(CN)_6 = 5$ c.c.			Temp. = 27.5° .
Time of exposure = 5 min.					
Time in min.	0	60	92	123	∞
Burette reading (c.c.)	4.2	14.2	18.2	21.2	31.2
Instantaneous rates	...	0.00669	0.00695	0.00668	Mean 0.00674

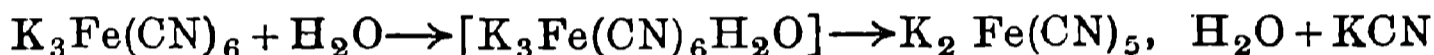
TABLE VII.

$H_2O_2 = 5$ c.c.		$M/10-K_3Fe(CN)_6 = 5$ c.c.			Temp. = 27.6° .
Time of exposure = 30 min.					
Time in min.	0	82	101	160	∞
Burette reading (c.c.)	4	16.6	18.7	23.4	33.9
Instantaneous rates	..	0.00689	0.00680	0.00650	Mean 0.00673

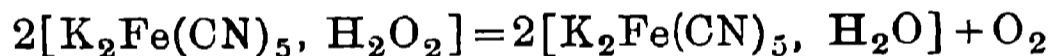
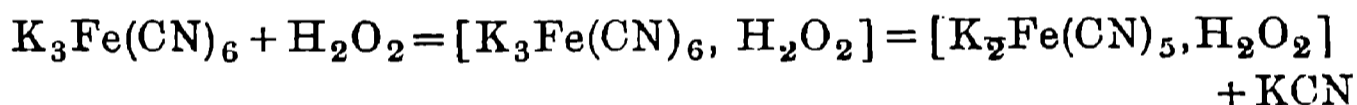
A solution of potassium ferricyanide, which is yellow, when exposed to light seems to undergo a gradual change. At first the solution becomes slightly greenish and in about half an hour it is dark blue. This appears to be colloidal in nature. On prolonged exposure prussian blue is precipitated, (cf. Friend, "Inorganic Chemistry" Vol. IX, Part II, p. 304; Vorländer, *Ber.*, 1913, 46, 181). Hence it appears that the elimination of the period of induction

after exposure to light is due to the formation of prussian blue (of a colloidal nature) which act as nuclei for the bringing together of H_2O_2 and $\text{K}_3\text{Fe}(\text{CN})_6$ by suitable adsorption.

The Mechanism of the reaction.—As there is a period of induction it is evident that the reaction proceeds through the formation of an intermediate complex. When a solution of H_2O_2 is added to a solution of potassium ferricyanide, it is noted qualitatively that gradually the colour of the solution deepens and after some time, depending on the concentration of ferricyanide, changes from yellow to deep red. When the colour does not deepen further there is a brisk evolution of gas. On the analogy of Briggs (*J. Chem. Soc.*, 1920, 117, 1026) who shows that ferricyanide reacts with water to a slight extent as giving aquopentacyanoferrate;



it is possible that H_2O_2 reacts more rapidly than water giving a hydrogen peroxide of pentacyanoferrate which decomposes giving aquopentacyanoferrate and oxygen as:



It is seen qualitatively that a solution of ferricyanide after treatment with hydrogen peroxide contains a greater quantity of potassium cyanide than the other for equal intervals of time. However in the absence of further evidence this is only a tentative explanation of the reaction.

SUMMARY AND CONCLUSIONS.

(1) The decomposition of hydrogen peroxide by potassium ferrocyanide appears to be of a complicated nature.

(2) The decomposition of hydrogen peroxide by potassium ferricyanide is unimolecular.

(3) The reaction is attended with a period of induction which has been shown to be partly 'pseudo' (due to the retaining of the gas in solution) and partly 'real.'

(4) The period of induction is inversely proportional to the concentration of ferricyanide and decreases with temperature

in the inverse ratio of the temperature coefficient of the reaction velocity.

(5) The temperature of the reaction velocity is about 2.3.

(6) Light does not accelerate the reaction as is supposed by Kistiakowsky (*loc. cit.*); light decomposes ferricyanide to prussian blue which acts as centres for the reaction to start, thus eliminating the period of induction.

(7) A mechanism of the reaction has been suggested on the basis of an intermediate complex formed between H_2O_2 and $\text{K}_3\text{Fe}(\text{CN})_6$.

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