

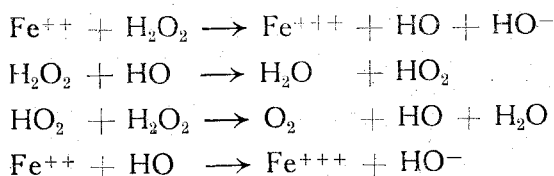
# The Catalytic Decomposition of Hydrogen Peroxide by Ferrous Ions

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## INTRODUCTION

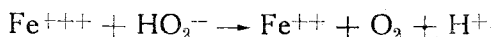
Recent work on the decomposition of  $\text{H}_2\text{O}_2$  by  $\text{Fe}^{++}$  salts was done by HABER and WEISS (1). They propose the reaction scheme which goes over the following steps:



This reaction scheme has been accepted by a number of investigators i.e. BAXENDALE, EVANS and PARK (2) while ABEL (3) and ANDERSEN (4) are opposed to it.

The HABER and WEISS scheme does not show any influence of hydrogen ions on the velocity of the reaction and the kinetic chain length - the ratio of decomposed hydrogen peroxide molecules to the oxidized iron ions - should be independent of the pH of the solutions. The influence of hydrogen ions, however, is present and HABER and WEISS explain it by assuming that additional reactions to the above mentioned scheme must be considered. These additional reactions, however, are of importance at the end of the reaction when about 99 % of the original iron (II) has reacted. The calculations supporting this view are based on unsound assumption (WEISS, Discussions of the Faraday Society 2 — 213 (1947)).

The catalytic decomposition of  $\text{H}_2\text{O}_2$  by  $\text{Fe}^{+++}$  salts has also been investigated by HABER and WEISS (1) (there is also older literature given) to explain the kinetics of this reaction an additional reaction



and the equilibrium reaction



is assumed.

Strong objections to this scheme are presented by ABEL (3). Quite recently ANDERSEN (4) reexamined the kinetics of iron (III) catalysis of the  $\text{H}_2\text{O}_2$  solutions. He found that the previously proposed kinetic equations require a corrections and proposed a mechanism which does not agree with the HABER-WEISS or other schemes. I think that the scheme proposed by ANDERSEN is open to some objections. For this reason it was thought very interesting to investigate the whole reaction again.

The reaction was conducted in very dilute solutions at different pH with different ratios of hydrogen peroxide and iron, at temperatures between  $0^\circ\text{C}$  and  $25^\circ\text{C}$ .

Herewith I express my thanks to the Director of the Institute, Prof. Dr. Parts, for suggesting the field of study and continued help during the progress of the investigation.

## I. SUBSTANCES USED

Ammonium Thiocyanate — Reagent, Baker & Adamson.

A 20 per cent solution used as a reagent.

$\alpha, \alpha'$  — Dipyridyl — Hopkin & Williams Ltd.

100 mg substance dissolved in 100 ml and used as a reagent.

Iron sulphate (ferrous) —  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  — Merck Darmstadt, pure crystals.

Iron — Ammonium Sulphate (ferrous) —  $\text{FeSO}_4 (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  — Merck Darmstadt, extra pure crystals.

Iron — Ammonium Sulphate (ferric) —  $\text{Fe}_2 (\text{NH}_4)_2 (\text{SO}_4)_4 \cdot 24\text{H}_2\text{O}$  — Schering-Kahlbaum A. G. Crystals.

Hydrazine Hydrate — Schering - Kahlbaum A. G. Pour analyse

Sulphuric acid — Judex Chemicals, pure,  $d = 1.840$ .

Sodium Hyposulfite —  $\text{Na}_2\text{S}_2\text{O}_4 \cdot 24\text{H}_2\text{O}$  — Ordinary laboratory reagent purified for the work. The method for purification from iron (II) ions was taken from «The Colorimetric Methods of Analysis, Snell I.311. (1945)».

Hydrogen Peroxide — The hydrogen peroxide used in the reactions was obtained always by diluting perhydrol. It was prepared by three different methods.

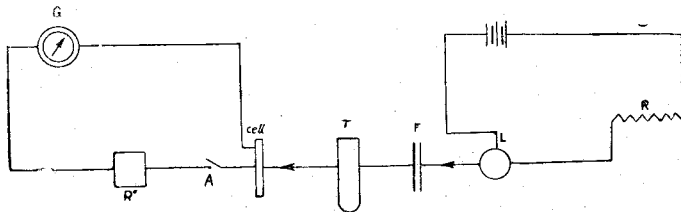
- i — By direct dilution of perhydrol.
- ii — 250 ml of 10 per cent hydrogen peroxide, obtained from perhydrol, was distilled (ordinary distillation) with 0.05 g sodium hydroxide.
- iii — By vacuum distillation of 250 ml of 10 % hydrogen peroxide with 0.10 g sodium hydroxide. The portions that passed over between 20—30 mmHg pressure and 32.0—52.0°C temperature were taken from vacuum distillation. For every reaction the vacuum distillation was repeated. The obtained solution contained about 0.5 molar hydrogen peroxide. For titration of the hydrogen peroxide  $M/20$  potassium permanganate was used. The calibration of potassium permanganate was done by sodium oxalate.

## II. APPARATUS

For the determination of iron a photoelectric colorimeter, the details of which are described below, was built.

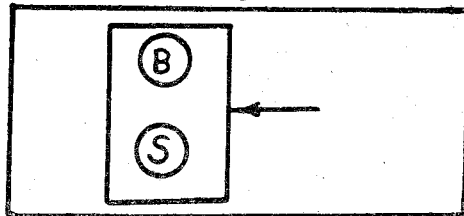
The apparatus, the scheme of which is given in Schemata 1 and 2, consisted of a lamp (L), a filter, chosen according to the region of the maximum absorption of the coloured liquid, tubes for solution through which the light was directed (T), photocell,

spot galvanometer (G) with mirror, a scale for the reading of the image given by the mirror, and resistances. As the current from the town's network was fluctuating, the current for the lamp L was taken from a 6 volt accumulator of 80 amper-hours capacity. The intensity of the light given by lamp L was regulated by a sliding resistance R' (2.7 ohms, 12.3 amps.). Right in front of the lamp was placed a filter F that allowed light of wavelengths between 487 and 565  $m\mu$  to pass. The light that passed the filter went through the middle of the tube B containing water (Schema 1). The tubes used for water and solutions were



Schema 1

specially made of pyrex glass and were of equal length and cross section, 15 cm long and 17.5 mm diameter. As B or S were brought in front of the light beam it went through water or solution and fell on the photocell (Schema 2). It was possible to



Schema 2

measure the light intensity as different illumination of the photocell gives different currents through the galvanometer that was in series with the cell. A resistance box R' is in the galvanometer circuit. The galvanometer gives a deflection of 50 mm for one microampere on a scale one meter distant.

When the apparatus does not work and we illuminate the galvanometer mirror from some source, then at the focal length

of the mirror (120 cm) we get a thin line. When there is no current through the galvanometer then the spot is on the left at 25.00. This point is taken as the origin O of the deflections. In this case the resistance of the resistance box  $R''$  is zero, and no light falls on the photocell. Tube S is for coloured solutions. By moving tube-carrier C, tube B is brought into the field of the light beam coming through the filter. The tubes are filled in such a way that all light falling on the photocell must pass through liquid. The test tubes were always carefully cleaned. From the resistance box  $R''$  9000 and 900 ohms resistances are connected into the circuit and by pressing the button A the cell galvanometer circuit is closed. First 9000 ohms are taken out of the circuit. The spot, owing to the deflection of the mirror, moves to the right. Then 900 ohms are taken out of the circuit. In this case the deflection increases. By the help of the resistance  $R'$  the deflection in the case of pure water is brought to the end of the scale. During this the test tube is covered with a box to prevent the effect of light that enters through the top of the tube. When the pressure on the button A is released then the spot will return to its original position at 25.00 on the left. By moving the carrier C the tube S is brought in front of the light. In the tube S there is again pure water. With both test tubes the deflection must be the same. As the test tubes might be a little different from one another then by changing the surface on which the light is falling the calibration is secured. If the deflections are the same when both tubes contain pure water then the apparatus is ready for use. For every independent experiment the calibration must be made. Coloured solution is put in the tube S and the galvanometer deflection noted. Depending on the density of the colour the deflection is less than when the tube B was in place. The deflections, however, do not change proportionally. For this reason a comparison chart is prepared in the following way :

a = the deflection from 25.00 when the tube B is in front of the light,

b = the deflection from the same zero point but with tube S in front of the light.

In the standard comparison chart  $(a - b) / a$  is plotted against the concentration of iron ions.

As the light intensity of the lamp L is slowly but continuously decreasing then all the calculations must be made according to the preceding proportion.

At 0°C, in order to remove the effect of condensed vapour on the tubes used to measure the concentration of iron ions, two crucibles containing dry phosphorous pentoxide were put at either side of the tubes.

#### Thermostat :

The reactions were carried out in a cylindrical copper thermostat of 45 cm height and 40 cm diameter. The thermostat was filled with water. Around it was felt to prevent the loss of heat. In the thermostat was a helical lead tubing that touched its sides. When the room temperature was higher than that necessary for the reaction then by circulating tap water in the lead tubing the temperature of the thermostat was lowered. 0°C was obtained by mixing ice and water in the thermostat. During all the reactions the water in the thermostat was strongly stirred by a stirrer. The temperature was kept constant to within  $\pm 0.01^\circ\text{C}$  by a mercury filled regulator.

#### Measurement of pH:

A Beckman type apparatus with glass electrode was used for all pH measurements. The other electrode was calomel. The measurements were made with an error of  $\pm 0.01$ . In the course of the measurements the electrodes were always washed with the solution and sufficient time was allowed to elapse.

### III. METHODS OF DETERMINATION

For the investigation of  $\text{Fe}^{++} - \text{H}_2\text{O}_2$  reaction it is necessary to determine  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{H}_2\text{O}_2$  in  $10^{-5} - 10^{-6}$  molar concentrations. There have been developed many methods for the determination of iron in the mentioned concentrations. The greater part of these methods depend on colorimetric analysis. In Table A some properties of reagent, used for colorimetric determination of iron, are given. Polarographic method, that gives much more dependable results than the classic volumetric and gravimetric methods, can only in some special cases be used for the deter-

mination of iron in  $10^{-4}$  molar concentrations (11, 12). The results in the table are mostly taken from the work of WOODS and MELLON (13).

More detailed information about the different methods of determination can be obtained from: F. D. SNELL and C. T. SNELL—Colorimetric Methods of Analysis, D. van Nostrand Co. New York and E. B. SANDELL—Colorimetric Determinations of Traces of Metals, Interscience Publishers, Inc. New York.

#### The determination of iron with thiocyanate:

For the determination of iron (III) the thiocyanate method was selected, because the reagent is comparatively cheap, and can be used in determinations in strongly acid solutions (13). The structure of the complex between iron and thiocyanate is not known. The reaction takes place by the formation of complexes, the formulas of which depend on the conditions at the time of the experiment. The colour is caused by complexes of different composition that are not dissociated. It was thought that the complex causing the colour was  $Fe(CNS)_6^{---}$  in water solutions and  $FeFe(CNS)_6$  in non polar solutions, but more recent investigations show the formation of complexes like  $Fe(CNS)^{++}$  and  $Fe(CNS)_2^+$  in this colour reaction (14, 15, 16, 17).

As the intensity of the colour is dependent on many factors, the reaction is very sensitive to disturbing influences. The change in the intensity is dependent upon the concentration of the reagent, on the kind and concentration of the acid in solution, the time during which the reaction was allowed to continue. The thiocyanate used as reagent, was added in comparatively great quantities. In this case the sensitivity of the colour towards time and light lessens and the intensity remains approximately constant when pH changes. As a small change in the concentration of thiocyanate causes a relatively great change in the intensity of the colour care must be taken to insure that equal amounts are added to the sample and standard solutions.

The acidity of the solution, if it is such that it prevents the hydrolysis of iron (III) ions, does not affect much the intensity of the colour. But if the acid is inclined to form complexes, then

the intensity is reduced. Nitric and hydrochloric acids are suitable. Sulfuric acid, on the other hand, reduces the intensity as it is inclined to form complexes.

Iron (III) — thiocyanate system does not agree with Beer's Law, that is the intensity of the colour does not change linearly with the concentration of added iron ions. The best agreement with Beer's Law is at pH 1.5 — 2 with sulfuric acid (13). It has been established that iron determination in nitric acid solution of pH 1.50 — 1.65 agree with Beer's Law (18).

In case of quantitative measurements another error comes from the fading with time of the colour. Iron (III) ions are reduced by thiocyanate or by the products of its decomposition. At the beginning the fading of the colour takes place proportionally to the time. In 0.5 M solution of nitric acid fading takes place very quickly in the first minutes and about fifteen minutes later starts to increase. Because of this we preferred not to use nitric acid for acidifying. The fading with time of the colour in the iron (III) — thiocyanate solution can be reduced greatly by adding some oxidising agent to the solution. It is known that hydrogen peroxide is a suitable oxidising agent (19).

It is a condition that the thiocyanate used as a reagent be free from iron ions. It is known that many reagents contain iron (20). Thiocyanic acid can be used in preference to thiocyanates as the former is easily cleaned from iron. But in order to be able to work in the pH=4 zone with the same reagent, we chose ammonium thiocyanate.

Iron (III) — thiocyanate complex can be extracted from water solutions by amyl alcohol or better still, a mixture of 5 volumes of amyl alcohol and 2 volumes of ether (21) or by a mixture of monobutyl ether, ethylene glycol, and ethyl ether (22) or by ethyl acetate (23). As the colour in these solutions is more intense, this method can be used for the determination of traces of iron. On top of this it is possible to determine iron more exactly by adding 50 — 60 % acetone. However, we did not prefer this method, because of loss of time during the extraction in the experiments on the velocity of reaction, and because of the necessity of making certain that foreign matter and organic radicals do not influence the reaction.



**Experiments for the standard comparison chart of  $\text{Fe}^{+++}$ :**

As the maximum absorption of iron - thiocyanate is at  $480 \text{ m}\mu$  the light falling on the solution was made to pass through a filter, that lets light between  $487 - 565 \text{ m}\mu$  pass. In order to scrutinize the fading of the colour with time, experiments shown in Table 1 were made.

**Determination of iron (II) with  $\alpha, \alpha'$  - dipyridyl:**

It has been long known that  $\alpha, \alpha'$  - dipyridyl gives a red colour with iron (II) ions. Maximum absorption of the colour is in the  $522 \text{ m}\mu$  region (24). The filter we used let light between  $487-565 \text{ m}\mu$  to pass. The colour is attributed to the complex  $\text{Fe} [\text{C}_{10}\text{H}_8\text{N}_2]_3\text{X}_2$  composed of iron (II) ion and three  $\alpha, \alpha'$ -dipyridyl molecules (25). In this complex the six coordination positions of the iron ion are occupied by nitrogen atoms. When the pH changes between 3 and 9 there is no change in the intensity of the colour that is formed. The working range of the reagent has been determined more exactly as pH 3.5-8.5 (26). If pH is smaller than 2.5 the formation of the colour takes place very slowly. If pH is smaller than 2 or greater than 9.5 the colour that is formed, fades. In order that the iron ions would stay in solution as iron (II) ions some reducing agent is added. Titan (II) chloride, ascorbic acid, sulfurous acid, sodium dithionate, sodium sulfite, hydrazine sulfate and hydrazine hydrate are recommended (24, 27).

The colour that is formed is very stable. It will keep for more than a year in a glass stoppered pyrex bottle (26). Foreign ions can disturb the reaction if they are present in comparatively great amount as compared to iron (II) ions. This effect depends on the pH of the solution, the time waited and the kind of the foreign ions (27). The effect of iron (III) ions is not greater than that of others.

The above mentioned complex can be used as a reduction-oxidation indicator. For this reason it is very convenient to form the perchlorate salt of the complex (28). If there are in the solution iron (II) ions and hydrogen peroxide molecules, iron (III) ions will be formed. If we add  $\alpha, \alpha'$ -dipyridyl then the iron (II) ions that are left over will give the complex that will not

react with hydrogen peroxide. But the iron (III) ions by reacting with hydrogen peroxide are reduced to iron (II). As these ions again form a complex with  $\alpha, \alpha'$ -dipyridyl the intensity of the colour will increase with time. This effect seen in our experiments has previously been qualitatively described (29).

#### IV. EXPERIMENTAL RESULTS

For the investigation of the reaction between iron (II) and hydrogen peroxide, the concentrations of iron (II) ions, iron (III) ions and decomposed molecules of hydrogen peroxide were determined.

In Table 1 and 2 are given the results of comparison experiments for the determination of iron (III) with ammonium thiocyanate. In Table 1 are presented the results of the experiments made for the determination of the fading of the colour with time. For all iron (III) determinations with ammonium thiocyanate later on the required correction was made by taking into account the time from the formation of the colour to the end of the measurement. In order to be able to do this a stop watch was started the moment the reagent was added to the solution of iron (II) and hydrogen peroxide. Three measurements were taken for water and for the coloured solution. By extrapolating the value  $(a - b) / a$  for these measurements the value of  $(a - b) / a$  at the time of formation of the colour was found. In Table 2 the values of  $(a - b) / a$  at different pH of the solution and at different concentrations of iron (III) ions are presented. The measurements representing the change of iron (III) ion concentration between  $10^{-5}$  and  $10^{-6}$  M are presented in Fig. 1. The measurements representing the change of iron (III) ion concentration between  $1 \cdot 10^{-5}$  and  $3 \cdot 10^{-5}$  are presented in the Fig. 1a.

Table 3 contains the necessary comparison values for the determination of iron (II) with  $\alpha, \alpha'$ -dipyridyl in solutions more dilute than  $10^{-5}$  M.  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{NH}_2 \cdot \text{NH}_2 - \text{H}_2\text{O}$  was used during the experiments to prevent the iron (II) in solution from being oxidized. Fig. 2 is drawn by taking the mean of three experiments.

In Tables 4-15 are given the results of the investigation of the reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$  by determining iron (II)

ions with  $\alpha, \alpha'$ -dipyridyl. In the experiments pH was changed from 3.20 to 4.73 and the temperature from 15.20 to 25.00°C. Every experiment was repeated at least once and the results in the tables were drawn into graphs. In going from tables to the graphs the calculations were made in the following manner: Let the original concentration of hydrogen peroxide be  $a$  and the original concentration of iron (II) ions be  $b$ , then if the concentration of iron (III) ions, formed during time  $t$  taken from the beginning of the reaction is  $x$ , and supposing the reaction to be bimolecular, we have:

$$\begin{aligned} (\text{H}_2\text{O}_2) &= (a - x/2), & (\text{Fe}^{++}) &= (b - x) \\ kt &= \ln \frac{b(a - x/2)}{a(b - x)} : (2a - b) \end{aligned} \quad (1)$$

If we plot  $\ln \frac{b(a - x/2)}{a(b - x)}$  against  $t$  we should have a straight line, the slope of which will give the reaction rate constant.

In Table 12 are presented the results obtained when iron (II) ions and hydrogen peroxide molecules are taken in nearly equivalent concentrations. If the concentration at the beginning of hydrogen peroxide is  $a$  and that of iron (II) ions is  $b$ , and if after time  $t$ ,  $x$  moles of iron (III) are formed, then:

$$\begin{aligned} \frac{dx}{dt} &= k(a - x)(b - 2x) \\ z &= (b - 2x) \\ \beta &= (2a - b) \\ kt &= \left( \frac{1}{z} - \frac{1}{z_0} \right) - \frac{\beta}{2} \left( \frac{1}{z^2} - \frac{1}{z_0^2} \right) \end{aligned}$$

The results of the same experiments, calculated as explained above for non-equivalent concentrations, are to be found in Table 13.

The results of experiments for the determination of whether the reaction velocity depends on the way the hydrogen peroxide was prepared, are given in Table 4. In the first two experiments where the concentrations of hydrogen peroxide and iron (II) were the same and pH was kept the same, the solutions

were prepared by dilution of ordinary hydrogen peroxide. Hydrogen peroxide, used in the third experiment, was prepared by distilling ordinary hydrogen peroxide with the addition of a little caustic.

If the values of  $k$ , the reaction rate constant, calculated in the manner shown below, are compared, it is seen that they agree well. In addition to be certain in all the reactions which were followed by the determination with  $\alpha, \alpha'$ -dipyridyl were made with hydrogen peroxide, distilled in vacuum.

In the experiments presented in Table 4 the pH was 3.25, in those experiments presented in Tables 5 and 6 it was 4.02 and 4.20 respectively. In the last columns of the tables the calculated reaction velocity constants are given. The periods of time that passed from the beginning of the reaction to the end of the measurement were substituted in equation (1) for time  $t$ . The variation of  $k$  with every experiment shows that the reaction does not follow equation (1). It is seen from the fact that in different experiments where pH is different the reaction rate constant has different values, that  $H_3O^+$  ions have an effect on the oxidation of iron (II).

The results in Tables 7. and 8 show the reaction at different temperatures with different concentrations of hydrogen peroxide.

In Tables 8, 9, 10, 11 results of the experiments conducted at 25.00°C are given. The values of pH are greater than 4.20 and the concentration of hydrogen peroxide is always greater than the equivalent amount. In Fig. 3 we see these results compared. The difference that is seen in the repetition of experiments in Table 10, are attributed to the decomposition of  $10^{-5}$  molar hydrogen peroxide because of the time waited before the experiment. For the verification of this the experiments shown in Tables 14 and 15 were made. After the first reaction  $10^{-5}$  molar hydrogen peroxide was put aside for two hours and then the experiment repeated. The curves in Fig. 4 show these deviations clearly. In experiments after this the decomposition with time of hydrogen peroxide was taken into account, and immediately after the preparation of the solutions the experiments were begun.

Tables 16 to 27 contain measurements for the  $Fe^{++} - H_2O_2$  reaction at 0.00, 15.00 and 25.00°C and pH 0.10, 1.80 and 3.50.

At the same temperature and pH three different experiments were made. The results of the repeated experiments are noted in the table after leaving a little free room. The ratio of  $\text{H}_2\text{O}_2$ :  $\text{Fe}^{++} = a:b$  was taken as 1:1, 1:1.5, 1.5:1. Because of the increase in the reaction rate, a greater surplus of hydrogen peroxide or of iron (II) was not found practical. As the reaction is bimolecular the values of  $\ln(a-x/2)/(b-x)$  opposite the time  $t$ , from the beginning of the reaction, were given the proper signs and the necessary curves drawn. When we investigate the results of the experiments at the three different temperatures, we see that in approximately normal and centinormal acid solutions the reaction is bimolecular. The reaction rate constant  $k$  for the experiments in acid solutions was calculated from the slope of the straight lines. In Fig. 14 and 15 we see two examples of the iron (II)-hydrogen peroxide reaction that follows the course of bimolecular reactions in acid solution. In Table 28 all the reaction rate constants  $k$  were found in this way from graphs. The deviations towards the end of the experiment seen in the graphs can be explained by the increase in the relative error during the determination of the colour intensity. If we plot  $\ln(a-x/2)/(b-x)$  against  $t$  for pH greater than 3 we see that they are not on a straight line.

Table 28 shows the collected results of the bimolecular reaction. By scrutinising this table we see that the reaction rate constants at the three different temperatures are dependent on the pH. The values for the reaction rate constant obtained at  $\text{pH} \sim 0$  are smaller than those obtained at  $\text{pH} \sim 2$ . In the first case the mean values of the reaction rate constant are 19.1, 49.7 and 78.9, in the second case they are 23.2, 54.8, 82.5. Again by the inspection of Table 28 we find that the reaction rate constant is not dependent upon the original ratio of hydrogen peroxide and iron (II) concentrations.

From Fig. 5 to 13 we can easily see that when the pH changes between 3 and 4.5 the reaction is not bimolecular, and that the reaction rate constants are continuously varying. As the determinations with  $\alpha, \alpha'$ -dipyridyl can be made in the same region of pH, we see that the determinations with both of the two methods show that the reaction is not bimolecular. As the pH increases the deviation from the straight line becomes more

prominent. Looking at the Fig. 6 and 14 that contain the results of Table 18 we see that at pH 3.20 the deviation is comparatively small. But in the other experiments this deviation, corresponding to the increase of pH becomes more noticeable. The comparison of Fig. 17 and 15 that contain the results of the Table 19 show this clearly. In Fig. 17 the pH was 4.18. It is found that the graphs were the pH is greater than 4 the curves go through a maximum. The same situation was met with in the determination of iron (II).

After having established by two different methods that at pH greater than 3 the reaction is not bimolecular, we can ask whether the two different methods give the same results. With this in view special experiments were not performed. But, if we compare the results of the determinations with  $\alpha, \alpha'$ -dipyridyl, presented in Tables 4 and 15 with experiments at approximately the same pH and at the same temperature, presented in Tables 20 and 25 then we see that they agree quite well.

In order to get a better insight into the reaction that can be followed by two different methods that give agreeing results, the following method was used:

It is noted that when the pH is greater than 4 all of the iron (II) ions are not oxidised. Is the reason for this that the reaction stops? In order to be able to give an answer to this problem it is necessary to determine the decreasing amount of hydrogen peroxide. For this two different ways were used:

- 1). The reactions were conducted at pH about 2 and the beginning concentrations of hydrogen peroxide (a) and iron (II) (b) equal to  $10^{-5}$ . The results are given in Tables 29 to 32. After making the determinations with solution taken from the reaction vessel and after the reaction had continued for 15min 00 sec or for 26 min 30 sec 0.10 ml of M/2.5 iron (II) solution was added to 100 ml reaction solution in the thermostat, and stirred strongly with a glass agitator. As the concentration of iron (II) ions in the solution was about  $10^{-3}$  molar, it reacted with all the hydrogen peroxide, and a corresponding amount of iron (III) ions was formed. The concentration of these iron (III) ions was determined. Experiments made in exactly the same way were started in solutions with pH 4-4.20 and the determi-

nations made. In these cases again after the reaction had continued for 15 min 00 sec and 26 min 30 sec the same amount iron (II) ions were added in addition to 0.035 ml sulphuric acid. The result was that the determined pH of the solutions was around 1.70, as is seen from the tables. Also in this case the iron (II) ions enter into the reaction with the hydrogen peroxide present and a corresponding amount of iron (III) is formed. Is there any difference in the amount of iron (III) ions when the reaction was started in solutions where the pH was about 2 or about 4? From Tables 29 to 32, where the corresponding experiments are given, we see that at higher pH the amount of iron (III) is smaller. That is, in solutions with pH about 4 more hydrogen peroxide is decomposed during 15 min 00 sec or 26 min 30 sec than in solutions with pH about 2. The differences calculated from the results given in the tables can be lined up as follows:

time $t = 15.00$ min	time $t = 26$ min 30 sec
$\text{Fe}^{+++}$ difference	$\text{Fe}^{+++}$ difference
$0.390 \times 10^{-5}$	$0.680 \times 10^{-5}$
$0.390 \times 10^{-5}$	$0.510 \times 10^{-5}$
$0.310 \times 10^{-5}$	$0.500 \times 10^{-5}$
$0.380 \times 10^{-5}$	$0.480 \times 10^{-5}$

From the beginning of the reaction, and in comparison with the solution of pH about 2 we see that after 15.00 min an average of  $0.367/2 \times 10^{-5}$  mole more of hydrogen peroxide was decomposed, after 26 min 30 sec an average of  $0.542/2 \times 10^{-5}$  mole more of hydrogen peroxide is decomposed.

2). In order to find out how much the concentration of hydrogen peroxide changes in spite of the fact that no change takes place in the concentration of iron (II) ions, a second series of experiment were made in the following way:

First the reaction was let to continue for half an hour in a solution with pH of about 5. The concentrations of  $\text{H}_2\text{O}_2$  (a) and  $\text{Fe}$  (II) ions (b) were  $\approx bx$ . After the reaction had continued for 30.00 min at this high pH 0.035 ml. concentrated sulphuric acid was added to 100 ml. of the reaction solution. The result was that the pH of the solution fell to 1.70. Table 33 contains the results of three different experiments. The results of reactions that were started with  $\text{pH} = 1.75$  but with the same concentrations are

given in Table 34. The results in Table 34 are plotted in Fig. 16 (III) and  $k = 53.4$  is found from the slope of the straight line. The first reactions in Table 33 for  $\text{pH} = 5.20$  are represented in Fig. 16 (I) by the lowest points. It is seen that iron (II) ions show almost no change. After the reaction had continued for 30.00 min it was made bimolecular again by the addition of acid. The concentration of hydrogen peroxide was taken to be  $1.086 \times 10^{-5}$  and  $k$  was found to be 29.6 from the slope of the straight line in Fig. 16 (II). That is after the reaction had continued for 30.00 min the amount (a) of hydrogen peroxide had decreased. To find the decomposed amount of hydrogen peroxide a smaller value than  $1.086 \times 10^{-5}$  was substituted in equation (1). This calculation was repeated for three different concentrations. The results of calculations are shown in Table 35. In order to adjust the value 53.4 for  $k$  found from the Fig. 16 (III) a must be taken to be  $0.680 \times 10^{-5}$ . That is, the amount of hydrogen peroxide has decreased within half an hour by  $1.086 - 0.680 = 0.406 \times 10^{-5}$  mole. As a conclusion we see that in the reaction between iron (II) and hydrogen peroxide, when the pH is about 4 and the concentration of iron (II) ions does not change, the amount of decomposed hydrogen peroxide is far greater than in reactions that are bimolecular ( $\text{pH} \sim 2$ ).

#### Activation energy:

Fig. 17 is drawn for the calculation of activation energy and activation constant from the results presented in Table 28, of experiments conducted at three different temperatures in normal and centinormal acid solutions.

In normal acidic solutions:

$$k = 7.06 \times 10^8 e^{-\frac{8.99 \times 10^3}{RT}} \text{ mol}^{-1} \text{ liter sec}^{-1}$$

In centinormal acidic solutions:

$$k = 6.61 \times 10^8 e^{-\frac{8.54 \times 10^3}{RT}} \text{ mol}^{-1} \text{ liter sec}^{-1}$$

Values calculated earlier: HABER & WEISS (1)

$$k = 4.0 \times 10^7 e^{-\frac{9.5 \times 10^3}{RT}} \text{ mol}^{-1} \text{ liter sec}^{-1}$$

and BAXENDALE, EVANS, PARK (2)

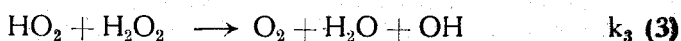
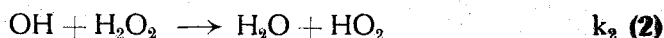
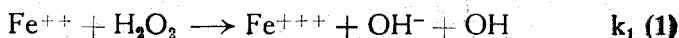


$$k = 1.78 \times 10^9 e^{-\frac{10.1 \times 10^3}{RT}} \text{ mol}^{-1} \text{ liter sec}^{-1}$$

The comparison of experimental results with those given earlier in literature is made above.

## V. DISCUSSION

The catalytic decomposition of hydrogen peroxide by iron (II) and iron (III) was examined by HABER and WEISS (1). According to these investigators, there were in the reaction steps  $\text{OH}$ ,  $\text{HO}_2$  radicals and  $\text{HO}_2^-$  anions and the reaction was a chain or radical one. By small changes in the reaction conditions one type of reaction can be changed into another with ease. They write that they tried to explain these reactions independently of one another. For the explanation of the catalytic action of iron (II) they assumed the following steps:



The equations (1) till (4) express the main course of the reaction and only for extremely great  $\text{H}_2\text{O}_2$  to  $\text{Fe}^{++}$  ratios additional complications are encountered.

In stationary cases we can write for the kinetics of the reaction:

$$\frac{d(\text{OH})}{dt} = \frac{d(\text{HO}_2)}{dt} = 0$$

$$(\text{OH}) = \frac{k_1}{k_2} (\text{H}_2\text{O}_2)$$

$$(\text{HO}_2) = \frac{k_1 k_2}{k_3 k_4} (\text{H}_2\text{O}_2)$$

$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = k_1 (\text{Fe}^{++}) (\text{H}_2\text{O}_2) + 2 \frac{k_1 k_2}{k_4} (\text{H}_2\text{O}_2)^2 \quad (5)$$

$$\frac{d(\text{O}_2)}{dt} = \frac{k_1 k_2}{k_4} (\text{H}_2\text{O}_2)^2$$

$$-\frac{d(\text{Fe}^{++})}{dt} = 2 k_1 (\text{Fe}^{++}) (\text{H}_2\text{O}_2) \quad (6)$$

The average decomposition ratio of hydrogen peroxide,  $\Delta\text{H}_2\text{O}_2/\Delta\text{Fe}^{++}$  gives us the length of the chains if the concentrations of the radicals are taken to be stationary. The investigators have tried to determine this ratio under different conditions. The decomposition ratio is

$$n = \frac{d(\text{H}_2\text{O}_2)}{d(\text{Fe}^{++})} = 0.5 + \frac{k_2(\text{H}_2\text{O}_2)_m}{k_4(\text{Fe}^{++})_m} \quad (A)$$

but is possible to determine the average ratio only. For the average decomposition ratio  $\bar{n}$ , WEISS (5) has given later the following right expression:

$$\bar{n} = \frac{-\Delta\text{H}_2\text{O}_2}{-\Delta\text{Fe}^{++}} = \frac{\int_0^t -\frac{d(\text{H}_2\text{O}_2)}{dt} dt}{\int_0^t -\frac{d(\text{Fe}^{++})}{dt} dt} = 0.5 + \frac{k_2 \int_0^t (\text{H}_2\text{O}_2)^2 dt}{k_4 \int_0^t (\text{H}_2\text{O}_2) (\text{Fe}^{++}) dt} \quad (B)$$

In this work HABER and WEISS determined the concentration of iron (II) and of hydrogen peroxide at the beginning and after the reaction had continued for a certain time. In the same work according to Table VI the ratio of  $(\text{H}_2\text{O}_2)_0 : (\text{Fe}^{++})_0$  was changed from 262 to 9. The ratio  $n = \Delta\text{H}_2\text{O}_2 : \Delta\text{Fe}^{++}$  was determined. The results varied between 23.5 and 3.5. The ratio of the concentration of iron (II) after the time  $t$  to that at the beginning was defined as  $f = \text{Fe}_t^{++}/\text{Fe}_0^{++}$  and by using equation (7) from the same work  $f = e^{-2 k_1(\text{H}_2\text{O}_2)t}$  was found. By substituting in the equation defining  $\bar{n}$  the values of  $f$  were calculated. For  $f \sim 10^{-2}$  was found in this way and by changing the original concentration ratio 30 times until 1% of iron (II) was left it was decided that  $f$  remains constant. By putting the results of HABER and WEISS, given in their Table VI into the by WEISS (5) corrected expression (B), I determined the values of  $f$ . I used the following way:

$$-\frac{d(\text{Fe}^{++})}{dt} = 2 k_1 (\text{Fe}^{++}) (\text{H}_2\text{O}_2)$$

$$\int -\frac{d(\text{Fe}^{++})}{\text{Fe}^{++}} = \int 2k_1 (\text{H}_2\text{O}_2) dt,$$

$$\ln \frac{(\text{Fe}^{++})_t}{(\text{Fe}^{++})_0} = -2k_1 (\text{H}_2\text{O}_2)t$$

$$f = \frac{(\text{Fe}^{++})_t}{(\text{Fe}^{++})_0} = e^{-2k_1 (\text{H}_2\text{O}_2)t}$$

$$(\text{Fe}^{++})_t = f \times (\text{Fe}^{++})_0$$

As hydrogen peroxide was taken in excess, we suppose it to be constant and have:

$$\int_0^t (\text{H}_2\text{O}_2)_m^2 dt = (\text{H}_2\text{O}_2)_m^2 t$$

$$\int_0^t (\text{H}_2\text{O}_2)_m (\text{Fe}^{++})_0 e^{-2k_1 (\text{H}_2\text{O}_2)_m t} dt = -\left( \frac{(\text{Fe}^{++})_0}{2k_1} e^{-2k_1 (\text{H}_2\text{O}_2)_m t} - 1 \right)$$

By substituting these expressions in (B) in place of the integrals we obtain the following expression:

$$\frac{\Delta (\text{H}_2\text{O}_2)}{\Delta (\text{Fe}^{++})} = 0.5 + \frac{k_2}{k_4} \frac{(\text{H}_2\text{O}_2)_m^2 t}{\frac{(\text{Fe}^{++})_0}{2k_1} (e^{-2k_1 (\text{H}_2\text{O}_2)_m t} - 1)}$$

$$= 0.5 - \frac{k_2}{k_4} 2k_1 \frac{(\text{H}_2\text{O}_2)_m^2 t}{(\text{Fe}^{++})_0 (e^{-2k_1 (\text{H}_2\text{O}_2)_m t} - 1)}$$

$$\text{If } \Delta = 0.5 - 2 \frac{k_1 k_2}{k_4} \frac{(\text{H}_2\text{O}_2)_m^2 t}{(\text{Fe}^{++})_0 (e^{-2k_1 (\text{H}_2\text{O}_2)_m t} - 1)}$$

$$t = \frac{\ln f}{-2k_1 (\text{H}_2\text{O}_2)_m}$$

are substituted in the previous expression, we obtain the following relation:

$$\frac{\ln f}{f - 1} = (\Delta - 0.5) \frac{k_4}{k_2} \times \frac{(\text{Fe}^{++})_0}{(\text{H}_2\text{O}_2)_m}$$

If we take from the investigation of HABER and WEISS the value  $2.8 \times 10^{-2}$  for  $k_2/k_4$  and by taking into consideration the value of  $v_0$  and the corresponding value  $\bar{n}$  from the same work then the value of  $f$  can be expressed in the following table:

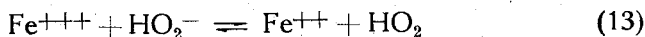
**Table 36**

$v_j = \frac{(H_2O_2)_0}{(Fe^{+++})_0}$	$n = \frac{H_2O_2}{Fe^{++}}$	f
262	23.5	$4.4 \times 10^{-2}$
208	17.0	$5.9 \times 10^{-2}$
203	16.3	$6.2 \times 10^{-2}$
45	15.7	$5.8 \times 10^{-6}$
28	14.7	$1.4 \times 10^{-8}$
25	11.1	$2.6 \times 10^{-7}$
21	6.8	$2.2 \times 10^{-5}$
13	6.2	$1.4 \times 10^{-7}$
15	5.7	$6.0 \times 10^{-7}$
11	4.9	$6.4 \times 10^{-7}$
10	4.3	$1.3 \times 10^{-6}$
9	3.5	$6.8 \times 10^{-6}$

In the work of HABER and WEISS in Table VI the value of f is given as  $\sim 10^{-2}$ .

This means that the reactions 1, 2, 3, 4 do not explain the actual course of the reaction.

To through light on the catalytic reaction of iron (III) ions, HABER and WEISS, in the second part of their work, take into consideration the following reaction:



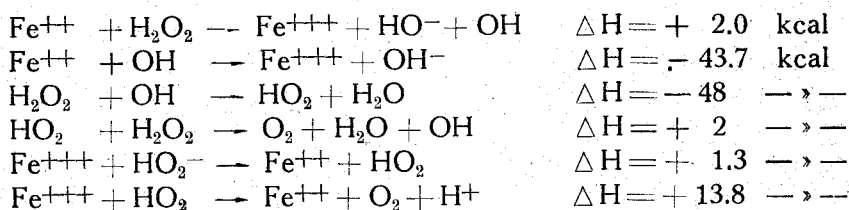
They write that they have determined that there is no difference in principle between the reactions started with iron (II) or iron (III) ions, but they have investigated the reaction of iron (III) according to the equation (13) given above. By using this reaction they obtained the following expression:

$$-\frac{d(H_2O_2)}{dt} = k \frac{Fe^{+++}}{H^+} (H_2O_2) \quad (C)$$

$k_{13} = 6.0 \times 10^7$  (mol<sup>-1</sup> liter sec<sup>-1</sup>, 20.00°C). So that the chain reaction could turn into a radical one they took into consideration the following reaction:



If we make a thermodynamic investigation of the reactions proposed by HABER and WEISS and summarised above, we obtain :



The results above are obtained on the assumption that the reactions take place in aqueous solutions. The formation enthalpy of  $-13$  kcal for the reaction  $1/2 \text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2(\text{g})$  is calculated from the most probable value given by WALSH (6). The change in enthalpy in the reaction  $\text{HO}_2(\text{g}) \rightarrow \text{HO}_2(\text{aqueous solution})$  was taken to be  $-12$  kcal on the supposition that it is the same as for  $\text{H}_2\text{O}_2$ . The value for the formation enthalpy of  $\text{HO}_2^-$  ion in aqueous solutions was taken from the work of EVANS and URI (7). For most of the reactions the change in enthalpy is negative but for some it is around zero. It is seen from these results that the reactions given above are possible at ordinary temperatures from the thermodynamic point of view. The enthalpy of the reaction does certainly not determine the progress of the reaction. For most of these reactions the change in entropy is not known. But  $\Delta H$  can give some idea whether the reaction will take place at relatively low (ordinary) temperatures.

When I investigated the iron-hydrogen peroxide reaction I saw that in solutions with pH smaller than 2 the reaction took place according to the reaction mechanism proposed earlier. This result is shown clearly in Fig. 14, 15 and 16 (III) that are drawn according to the tables which contain the results of the experiments where pH was 0 and 2, the temperature 0.50, 15.00, 25.00°C and the ratio  $\text{Fe}^{++} : \text{H}_2\text{O}_2$  varying. In addition to this at low pH we notice a small difference by investigating Table 28, namely that the reaction rate depends on pH but changes very little. It is found that the reaction rate of the bimolecular reaction is a little greater in the case when the pH is 2 than when  $\text{pH} = 0$ .

In solutions with pH about 3, 4, 5 the given mechanism does not explain the experimental results. The investigation of tables and graphs given shows that the points lie on a curve. The deviation from a straight line at pH=3 is comparatively small but at pH greater than four the curves go through a maximum, Fig. 5 & 6. From Fig. 16 (I) we see that when pH is greater than 5 the concentration of iron (II) ions does not change. The oxidation of iron (II) has decrease or like in Fig. 16 (I) stopped completely, on the other hand, however, the decomposition of hydrogen peroxide has increased. The concentration of hydrogen peroxide, decomposing faster in solutions of pH about 4 or 5 than in acid solutions, were determined by two different methods that are explained in detail under 'Experimental Results'. It is possible to combine these results with the following thoughts: When giving the mechanism of iron-hydrogen peroxide it is not right to talk about the action of iron (II) and iron (III) separately. When the reaction is started with iron (II) there are also formed in solution iron (III) ions. In solutions with pH greater than 3 it is probable that the decomposition of hydrogen peroxide is continued by iron (III) ions. It is seen from the fact that the graphs for pH greater than 4 go through a maximum and from the fact that in solutions where pH greater than 5 the iron (II) concentration is practically constant, and the decomposition of hydrogen peroxide is greater than at smaller pH, that the mechanism is dependent on other factors in addition to those given.

If we think of the catalysis of iron (III) ions by taking into consideration the equation

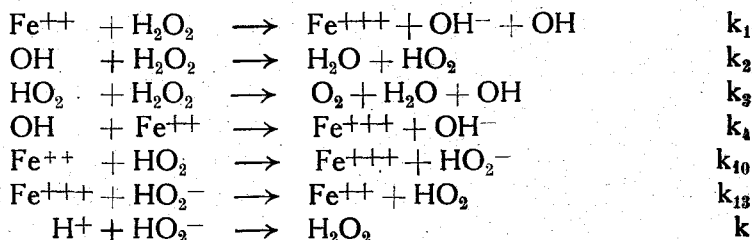
$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = k \frac{\text{Fe}^{+++}}{\text{H}^+} (\text{H}_2\text{O}_2)$$

given in literature, then it is not possible to explain the decomposition rate that I observed. For example if we apply to this equation the results of experiments given in Table 25, taking the average  $\text{Fe}^{+++} = 0.366 \times 10^{-5}$ , average  $(a - x/2) = 0.909 \times 10^{-5}$  and pH = 3.73 then

$$\begin{aligned} -d(\text{H}_2\text{O}_2)/dt &= (k \times 0.366 \times 10^{-5} / 10^{-3.73}) 0.909 \times 10^{-5} \\ &= k \times 1.42 \times 10^{-7}, \quad k = 1.16 \times 10^{-4} \text{ (HABER-WEISS)} \\ &= 1.16 \times 10^{-4} \times 1.42 \times 10^{-7} \\ &= 1.65 \times 10^{-11}. \end{aligned}$$

As the amount of decomposed hydrogen peroxide is of the order  $10^{-5}$ , it is seen that this amount is about  $10^6$  times greater than that calculated with the help of this equation. This means that the equation does not define the reaction's kinetics. It is necessary to take into consideration other reactions.

By taking into consideration at the same time the following equations:



for the catalysis by iron (II) and iron (III) ions, let us investigate the reaction kinetics:

$$-\frac{d(Fe^{++})}{dt} = k_1(Fe^{++})(H_2O_2) + k_4(OH)(Fe^{++}) + k_{10}(Fe^{++})(HO_2) - k_{13}(Fe^{+++})(HO_2^-) \quad (a)$$

$$\frac{d(HO_2)}{dt} = k_2(OH)(H_2O_2) - k_3(HO_2)(H_2O_2) + k_{13}(Fe^{+++})(HO_2^-) - k_{10}(Fe^{++})(HO_2) = 0 \quad (b)$$

$$\frac{d(OH)}{dt} = k_1(Fe^{++})(H_2O_2) - k_2(OH)(H_2O_2) + k_3(HO_2)(H_2O_2) - k_4(OH)(Fe^{++}) = 0 \quad (c)$$

If we suppose that in stationary cases the concentration of the radicals is constant and add the three equations, we get:

$$-\frac{d(Fe^{++})}{dt} = 2k_1(Fe^{++})(H_2O_2) \quad (d)$$

On the other hand

$$-\frac{d(O_2)}{dt} = k_3(HO_2)(H_2O_2) \quad (e)$$

$$-\frac{d(H_2O_2)}{dt} = 2k_3(HO_2)(H_2O_2) + k_1(Fe^{++})(H_2O_2) \quad (f)$$

From (b) and (c) we can solve for  $HO_2$ .

If we substitute

$$(\text{HO}_2) = \frac{k_1(\text{Fe}^{++})(\text{H}_2\text{O}_2) + k_{13}k \frac{\text{Fe}^{+++}}{\text{H}^+}(\text{H}_2\text{O}_2) + \frac{k k_{13} k_4}{k_2} \frac{\text{Fe}^{+++}}{\text{H}^+}(\text{Fe}^{++})}{k_{10}(\text{Fe}^{++}) + \frac{k_3 k_4}{k_2}(\text{Fe}^{++}) + \frac{k_{10} k_4}{k_2} \frac{(\text{Fe}^{++})^2}{\text{H}_2\text{O}_2}}$$

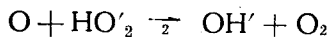
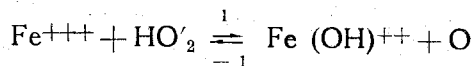
in (f) then we obtain:

$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = k_1(\text{Fe}^{++})(\text{H}_2\text{O}_2)$$

$$+ 2k_3(\text{H}_2\text{O}_2) \frac{k_1(\text{Fe}^{++})(\text{H}_2\text{O}_2) + k_{13}k \frac{\text{Fe}^{+++}}{\text{H}^+}(\text{H}_2\text{O}_2) + \frac{k k_{13} k_4}{k_2} \frac{\text{Fe}^{+++}}{\text{H}^+}(\text{Fe}^{++})}{k_{10}(\text{Fe}^{++}) + \frac{k_3 k_4}{k_2}(\text{Fe}^{++}) + \frac{k_{10} k_4}{k_2} \frac{(\text{Fe}^{++})^2}{(\text{H}_2\text{O}_2)}}$$

In the expression obtained for the decomposition of hydrogen peroxide the concentration of iron (II) is found in the denominator. As the concentration of iron (II) decreases then the decomposition of hydrogen peroxide must increase gradually and when the concentration of iron (II) is very small the decomposition of hydrogen peroxide must be infinite. As this is not possible we understand that from purely kinetical standpoint the 7 reactions above are insufficient to describe the  $\text{H}_2\text{O}_2$  decomposition by Fe (II) and Fe (III) ions.

As this work was being done there was made an investigation of the catalytic decomposition of hydrogen peroxide by iron (III) ions by ANDERSEN (4). According to the experiments made in that work the following reaction mechanism was proposed:



The decomposition according to ANDERSEN is not bimolecular but follows the empirical formula:

$$Bt + \tau = \log \frac{a}{x} + A \left( \frac{1}{x} - \frac{1}{a} \right)$$

$a$  = the concentration of hydrogen peroxide at the beginning

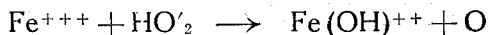


$x$  = the concentration of hydrogen peroxide after time  $t$

$A$  and  $B$  are constants to be determined experimentally

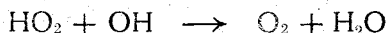
$\tau$  = a small constant that makes it possible to reckon time from the actual beginning of the experiment.

In the equation above  $A$  and  $B$  are proportional to the concentration of iron (III) ions.  $A$  is not dependent on the concentration of hydrogen ions whereas  $B$  is more or less inversely proportional to it. If the heat effect for the reaction



is calculated then  $\Delta H$  is found to be  $+40$  Kcals. I cannot see how a reaction that shows such a great change of enthalpy at ordinary temperatures can possibly occur. This means that the reaction proposed by ANDERSEN presents some impossibilities from the point of view of thermodynamics.

At the time of writing of this work, WEISS and HUMPHREY published a summary in *Nature* 163.691 (1949) containing corrections to the previous scheme of the decomposition of hydrogen peroxide by iron (II) and iron (III) ions. They retained the scheme given by HABER and WEISS, adding only a chain breaking reaction



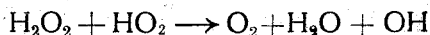
At the same time they substituted the following reaction



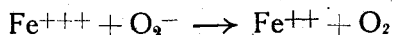
in place of reaction (14).

It is not certain whether with this new reaction scheme the dependence on pH of the decomposition of hydrogen peroxide by iron (II) ions can be explained, because in the published summary this problem was not considered quantitatively.

In the same number of *Nature*, on the page following the mentioned work, BARB, BAXENDALE, GEORGE and HARGRAVE propose a different scheme to that proposed by WEISS and HUMPHREY. According to their scheme the third reaction



was left out and



reaction was not considered.

To determine how far this represents the real state of affairs it is necessary to investigate the quantitative results.

In both of these works, as I found according to my investigations, it is insistently defined that the manner of the reaction is efficiently determined by the pH of the solution

## VI. SUMMARY

I. In the presented work I investigated the time dependence of the reaction between  $\text{Fe}^{++}$  ions and  $\text{H}_2\text{O}_2$ . The reaction has been followed in the concentration range between  $1.5 - 1 \times 10^{-5}$   $\text{Fe}^{++}$  and  $\text{H}_2\text{O}_2$ . The ratios of  $\text{Fe}^{++} : \text{H}_2\text{O}_2$  used in different experiments were 1.5:1, 1:1, 1:1.5.

II. pH was changed from 0 to 5 and the measurements were conducted at three different temperatures of 0,00, 15.00 and 25.00°C.

III. The course of the reaction was followed determining  $\text{Fe}^{++}$  with  $\alpha, \alpha'$ -dipyridyl and (or)  $\text{Fe}^{+++}$  with ammonium rodanide colorimetrically. The sensitivity of the method at this concentration was  $0.5 \times 10^{-7}$   $\text{Fe}^{++}$  or  $\text{Fe}^{+++}$ .

IV. The determination of  $\text{Fe}^{++}$  or  $\text{Fe}^{+++}$  give the same value for the velocity constant of the reaction.

V. At pH up to about three the reaction is of second order, being of first order in  $\text{Fe}^{++}$  and first order in  $\text{H}_2\text{O}_2$ . The moles of  $\text{H}_2\text{O}_2$  used up is half the moles of  $\text{Fe}^{++}$  oxidized to  $\text{Fe}^{+++}$ .

VI. At pH higher than three more  $\text{H}_2\text{O}_2$  is used up and the course of the reaction cannot be represented by the equation used at low pH of the solution.

VII. The surplus of  $\text{H}_2\text{O}_2$  decomposed at pH 3 cannot be ascribed to pure  $\text{Fe}^{+++}$  catalysis because it exceeds the amount calculated by a factor of  $10^3$ .

VIII. The mechanisms proposed for this reaction do not agree quantitatively with the experimental results, especially concerning the dependence of reaction on pH of the solution.

IX The qualitative picture of the reaction does not change with temperature in the investigated range.

X. The activation energy and collision factor were found to be:

$E = 8.99 \times 10^3$  cal/mol,  $A = 7.06 \times 10^8$  in the normal acid solutions

$E = 8.54 \times 10^3$  cal/mol,  $A = 6.61 \times 10^8$  in the n/100 acid solutions.

## VII. LITERATURE

- (1) — HABER, WEISS — Proc. Roy. Soc. A. 147.332-51. (1939)
- (2) — BAXENDALE, EVANS, PARK — Trans. Far. Soc. 42.155. (1946)
- (3) — ABEL — Öster. Chem. Zeitung. 49.79. (1948)
- (4) — ANDERSEN — Act. Chem. Scandi. 2.1. (1948)
- (5) — WEISS — Disc. Far. Soc. 2.213. (1947)
- (6) — WALSH — J. Chem. Soc. 331. (1948)
- (7) — WEISS, HUMPHREY — Nature 163.691. (1949)
- (8) — BARB, BAXENDALE, GEORGE, HANGRAVE — Nature 163.692 (1949)
- (9) — FOWLER, BRIGHT — J. Research Nat. Bur. Standards 15.493. (1935)
- (10) — HUCKABA, KEYES — J. Am. Chem. Soc. 70.1640. (1948)
- (11) — MERTES — Anal. Chemistry 20.895. (1948)
- (12) — LINGANE — Anal. Chemistry 21.45. (1949)
- (13) — WOODS, MELLON — Ind. Eng. Chem. Anal. Ed. 13.554. (1941)
- (14) — SCHLESINGER, VALDENBURGH — J. Am. Chem. Soc. 53.1212 (1931)
- (15) — BENT, FRENCH — J. Am. Chem. Soc. 63.568. (1941)
- (16) — M. MOLLER — Chem. Abst. 23.9179. (1939)
- (17) — MOLLER — Kem. Maanedstid. 18.138. (1937)
- (18) — SANDELL — Colorimetric Determination of Traces of Metals Interscience Publishers, Inc. New York (1944)
- (19) — PETERS, MASTERS, FRENCH — Ind. Eng. Chem. Anal. Ed. 11.502. (1939)
- (20) — SMITH, COOKE — Analyst 51.503. (1927)
- (21) — STOKES, CAIN — J. Am. Chem. Soc. 29.409. (1907)
- (22) — BERNHARD, DEKTER — Science 75.517. (1932)
- (23) — VANOSSI — Anales. Soc. Quim. Argentina 29.48. (1941)
- (24) — MOSS, MELLON — Ind. Eng. Chem. Anal. Ed. 14.862. (1942)
- (25) — BLAU — Ber. 21.1077. (1888); Monatsb. 19.647. (1898)
- (26) — HILL — Proc. Roy. Soc. B. 407.205. (1930)
- (27) — SNELL — Colorimetric Method of Analysis. D. Van Nostrand Co. N.Y.
- (28) — CAGLE, SMITH — Anal. Chemistry. 19.384. (1947)
- (29) — KUHN, WASSERMANN — Ann. Chemie. 503.203. (1933)

Table A  
Properties of Some Reagents for the Colorimetric Determination of Iron

Reagent	Sensitivity	Stability of colour	pH range	Effect of excess reagent	Beer's Law
$\alpha$ , $\alpha'$ -Dipyridyl	0.007 (522 m $\mu$ )	1 year	3—9	None	Obeded
2, 2', 2''-Terpyridyl	0.005 (522 m $\mu$ )	1 year	3—10	None	Obeded
Ferron	0.015 (610 m $\mu$ )	1—2 weeks	2.7—3.1	Change in hul	Not obeded
o-Phenanthroline	0.005 (508 m $\mu$ )	6 months or more	2—9	None	Obeded
Salicylic Acid	0.03 (520 m $\mu$ )	2—3 days	2.5—2.7	Increases intensity	Obeded
Thiocyanate	0.008 (480 m $\mu$ )	Fades rapidly	0.05—1 N	Increases intensity	Slight deviation
Thiocyanate and Acetone	0.004 (480 m $\mu$ )	Fades	0.05—1 N	Increases intensity	Slight deviation
Mercaptoacetic acid	0.014 (540 m $\mu$ )	Several hours	7—12	None	Obeded

**Table 1**

$$\text{Fe}^{+++} \text{ mol/litre} \times 10^{-5} = 1.0013$$

$$\text{pH} = 0.32 (\text{H}_2\text{SO}_4)$$

$$t = 25.00^\circ\text{C}$$

25.00 ml  $\text{Fe}^{+++}$  + 5.00 ml Ammonium Thiocyanat

t Time passed from the beginning of the reaction, in minutes

t	$\frac{a-b}{a}$	t	$\frac{a-b}{a}$	t	$\frac{a-b}{a}$
1.5	0.2022	1.5	0.2020	2.0	0.2000
3.5	0.2004	3.5	0.2014	3.5	0.1986
6.5	0.1991	7.0	0.1995	5.0	0.1971
9.5	0.1984	8.0	0.1982	7.5	0.1952

Table 2

Fe<sup>+++</sup> (Iron-Ammonium sulphate)(H<sub>2</sub>SO<sub>4</sub>), (NH<sub>4</sub>CNS %20)25.00 ml Fe<sup>+++</sup> + 5.00 ml Ammonium Thiocyanate

$10^5 \times \text{Fe}^{+++}$ mol/litre	pH	$\frac{a-b}{a}$
1.001	0.40	0.188 , 0.186
0.800	0.40	0.153 , 0.154
0.601	0.40	0.118 , 0.118
0.401	0.40	0.079 , 0.080
0.200	0.40	0.044 , 0.042
1.004	3.20	0.197 , 0.196 , 0.198
0.801	3.20	0.163 , 0.161 , 0.162
0.600	3.20	0.123 , 0.123 , 0.123
0.400	3.20	0.077 , 0.075 , 0.076
0.200	3.20	0.040 , 0.038 , 0.039
1.000	1.80	0.190 ; 0.190
0.801	1.80	0.155 , 0.157
0.600	1.80	0.121 , 0.122
0.401	1.80	0.080 , 0.080
0.200	1.80	0.043 , 0.043
1.000	1.75	0.190
1.500	1.75	0.286
2.000	1.75	0.362
2.500	1.75	0.423
3.000	1.75	0.487

**Table 3** $Fe^{++}$  (Iron-Ammonium Sulphate) $\alpha, \alpha'$  - Dipyridyl25.00 ml  $Fe^{++}$  + 2.00 ml DipyridylIn the first two series  $Na_2S_2O_4$  and in the third  $NH_2-NH_2 \cdot H_2O$  was used as reducing agent

$10^5 \times Fe^{++}$ mol/litre	pH	$\frac{a-b}{a}$
1.003	5.74	0.186 , 0.187 , 0.187
0.8022	5.75	0.150 , 0.150 , 0.150
0.5002	5.77	0.100 , 0.099 , 0.098
0.3021	5.76	0.063 , 0.061 , 0.059
0.1996	5.80	0.037 , 0.040 , 0.041
1.005	5.70	0.183 , 0.185 , 0.186
0.8030	5.66	0.150 , 0.150
0.5016	5.68	0.100 , 0.094 , 0.101
0.3003	5.63	0.058 , 0.062 , 0.063
0.2010	5.68	0.033 , 0.032 , 0.032
1.003	4.74	0.183 , 0.185 , 0.185
0.8022	4.83	0.149 , 0.150
0.5002	5.19	0.095 , 0.095
0.3011	5.39	0.058 , 0.060
0.2001	5.59	0.038 , 0.037

Table 4

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$ 1.  $a=0.888 \cdot 10^{-5}$  mol/lit,  $\text{H}_2\text{O}_2$  ordinary,  $b=1.015 \cdot 10^{-5}$   $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ 2.  $a=0.888 \cdot$  » » »  $b=1.022$  » » »3.  $a=0.938 \cdot$  » ordinary distilled  $b=1.000$  » » »

pH=3.28

3.26 ( $\text{H}_2\text{SO}_4$ )  $t=15.20^\circ\text{C}$ 

3.20

Time in minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$(a-x/2) 10^5$	$(a-x) 10^5$	$k$ $\text{mol}^{-1} \times$ $\text{sec}^{-1} \times \text{lt.}$
1. 15 00	0.315	0.731	0.700	25.7
21 56	0.395	0.691	0.620	26.1
30 02	0.450	0.663	0.565	21.1
40 15	0.540	0.618	0.475	19.9
60 45	0.625	0.576	0.390	18.6
89 00	0.645	0.566	0.370	16.4
99 45	0.695	0.541	0.320	14.1
2. 7 28	0.177	0.800	0.845	24.5
15 15	0.315	0.731	0.707	24.3
25 06	0.432	0.672	0.590	22.3
41 56	0.542	0.617	0.480	19.1
65 59	0.607	0.585	0.415	18.7
86 10	0.672	0.552	0.350	15.8
120 45	0.712	0.532	0.310	13.5
3. 6 13	0.132	0.872	0.868	21.1
17 02	0.308	0.784	0.692	20.7
26 27	0.400	0.738	0.600	19.4
43 31	0.525	0.676	0.475	18.4
81 14	0.613	0.632	0.387	13.0
101 36	0.684	0.596	0.316	12.9
116 29	0.710	0.583	0.290	13.1



Table 5

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$   
 $a = 0.794 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$  Vacuum distilled,  
 $b = 1.040 \times 10^{-5}$  mol/lit  $\text{FeSO}_4$   
 $\text{pH} = 4.02$  ( $\text{H}_2\text{SO}_4$ ),  
 $t = 16.30^\circ\text{C}$

Time in minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$(a-x/2) 10^5$	$(b-x) 10^5$	$k$ $\text{mol}^{-1} \times \text{sec}^{-1} \times \text{lit}$
5 05	0.007	0.790	1.033	1.01
25 35	0.141	0.724	0.899	6.35
47 40	0.315	0.636	0.725	9.25
58 25	0.375	0.604	0.665	9.04
7 15	0.020	0.784	1.020	2.83
20 35	0.115	0.736	0.915	7.71
38 20	0.235	0.677	0.805	7.67
65 04	0.345	0.622	0.695	7.43
90 31	0.368	0.610	0.672	5.82
117 45	0.385	0.601	0.655	4.73

Table 6

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$   
 $a = 0.794 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$  V. Dist.,  
 $b = 1.263 \times 10^{-5}$ ,  $1.293 \times 10^{-5}$  mol/lit  $\text{FeSO}_4$   
 $\text{pH} = 4.20$  ( $\text{H}_2\text{SO}_4$ ),  
 $t = 16.30^\circ\text{C}$

Time in minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$(a-x/2) 10^5$	$(b-x) 10^5$	$k$ $\text{mol}^{-1} \times \text{sec}^{-1} \times \text{lit}$
5 27	0.023	0.782	1.240	2.97
26 30	0.186	0.701	1.077	6.72
41 32	0.331	0.632	0.932	9.35
62 22	0.410	0.589	0.853	7.72
87 05	0.468	0.560	0.795	6.66
110 19	0.505	0.541	0.758	6.43
6 49	0.033	0.777	1.260	3.49
24 25	0.133	0.727	1.160	4.72
43 57	0.233	0.677	1.060	5.06
67 35	0.338	0.625	0.955	5.33
96 41	0.393	0.597	0.900	4.51

Table 7

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$   
 $a = 3.920 \times 10^{-5}$  mol/lt  $\text{H}_2\text{O}_2$  Vacuum distilled,  
 $b = 1.010 \times 10^{-5}$ ,  $1.018 \times 10^{-5}$  mol/lt  $\text{FeSO}_4$ ,  
 pH = 4.40 ( $\text{H}_2\text{SO}_4$ ),  
 $t = 20.00^\circ\text{C}$

Time in minute	$10^5 \times \text{Fe}^{+++}$ mol/lt	$(a-x/2) 10^5$	$(b-x) 10^5$	$k$ $\text{mol}^{-1} \times \text{sec}^{-1} \times \text{lt}$
2 17	0.215	3.812	0.795	22.60
8 39	0.520	3.660	0.490	18.5
15 48	0.675	3.582	0.335	14.1
22 02	0.730	3.555	0.280	13.1
1 26	0.148	3.846	0.870	23.5
6 33	0.478	3.681	0.540	21.3
13 13	0.658	3.591	0.360	17.6
18 42	0.743	3.548	0.275	15.8
25 25	0.780	3.530	0.238	12.6
30 40	0.813	3.514	0.205	11.9

Table 8

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$   
 $a = 2.115 \times 10^{-5}$  mol/lt  $\text{H}_2\text{O}_2$  Vacuum distilled,  
 $b = 1.020 \times 10^{-5}$  mol/lt  $\text{FeSO}_4$ ,  
 pH = 4.31 ( $\text{H}_2\text{SO}_4$ ),  
 $t = 25.00^\circ\text{C}$

Time in minute	$10^5 \times \text{Fe}^{+++}$ mol/lt	$(a-x/2) 10^5$	$(b-x) 10^5$	$k$ $\text{mol}^{-1} \times \text{sec}^{-1} \times \text{lt}$
3 25	0.225	2.003	0.795	30.3
9 19	0.435	1.898	0.585	25.0
16 17	0.553	1.839	0.467	20.5
25 45	0.640	1.795	0.380	16.6
37 33	0.690	1.770	0.330	13.3
50 21	0.715	1.758	0.305	10.6
7 15	0.380	1.925	0.640	27.0
15 11	0.560	1.835	0.460	20.5
29 43	0.702	1.764	0.318	17.2
42 05	0.740	1.745	0.280	13.6
66 13	0.780	1.725	0.240	9.75

Table 9

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$   
 $a = 4.794 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$  Vacuum distilled,  
 $b = 0.990 \times 10^{-5}$  mol/lit  $\text{FeSO}_4$   
\text{H}\_2\text{SO}\_4),  
 $t = 25.00^\circ\text{C}$

Time in minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$(a-x/2) 10^5$	$(b-x) 10^5$	$k$ mol $^{-1} \times \text{sec}^{-1} \times \text{lt}$
2 55	0.242	4.673	0.748	17.0
8 19	0.610	4.499	0.880	21.4
13 15	0.705	4.441	0.285	17.1
21 32	0.797	4.395	0.193	13.9
2 00	0.260	4.664	0.745	26.4
7 17	0.580	4.504	0.425	21.3
14 27	0.735	4.426	0.270	16.6
22 27	0.787	4.400	0.218	12.5

Table 10

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$   
 $a = 2.866 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$  Vacuum distilled,  
 $b = 1.000 \times 10^{-5}$  mol/lit  $\text{FeSO}_4$   
\text{H}\_2\text{SO}\_4),  
 $t = 25.00^\circ\text{C}$

Time in minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$(a-x/2) 10^5$	$(b-x) 10^5$	$k$ mol $^{-1} \times \text{sec}^{-1} \times \text{lt}$
2 26	0.275	2.728	0.725	39.4
8 05	0.555	2.593	0.445	30.9
13 50	0.670	2.531	0.330	17.3
22 20	0.770	2.481	0.230	20.5
30 40	0.792	2.470	0.208	16.3
2 37	0.383	2.674	0.617	55.7
10 15	0.678	2.527	0.322	35.9
19 42	0.794	2.469	0.206	25.6
27 13	0.845	2.443	0.155	22.1

Table 11

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$   
 $a = 1.335 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$  Vacuum distilled,  
 $b = 1.010 \times 10^{-5}$ ,  $0.990 \times 10^{-5}$  mol/lit  $\text{FeSO}_4$   
 $\text{pH} = 4.30$  ( $\text{H}_2\text{SO}_4$ ),  
 $t = 25.00^\circ\text{C}$

Time in minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$(a-x/2) 10^5$	$(b-x) 10^5$	k $\text{mol}^{-1} \times \text{sec}^{-1} \times \text{lt}$
3 21	0.145	1.262	0.865	29.6
11 40	0.392	1.139	0.618	28.6
30 24	0.610	1.030	0.400	22.0
40 18	0.690	0.990	0.320	21.2
52 01	0.743	0.958	0.267	19.3
66 21	0.806	0.932	0.204	18.8
3 58	0.169	1.295	0.821	39.42
8 51	0.320	1.175	0.670	29.5
15 09	0.435	1.117	0.555	26.2
24 56	0.535	1.067	0.455	22.0
36 00	0.605	1.032	0.385	18.9
50 33	0.668	1.001	0.322	16.0
60 46	0.705	0.982	0.285	13.4

Table 12

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$   
 $a = 1.208 \times 10^{-5}$ ,  $1.093 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$  Vacuum distilled,  
 $b = 2.000 \times 10^{-5}$  mol/lit  $\text{FeSO}_4$   
 $\text{pH} = 3.30$  ( $\text{H}_2\text{SO}_4$ ),  
 $t = 25.00^\circ\text{C}$

Time in minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$(a-x/2) 10^5$	$(b-x) 10^5$	k $\text{mol}^{-1} \times \text{sec}^{-1} \times \text{lt}$
1 49	0.085	1.165	1.915	15.9
12 00	0.630	0.893	1.370	25.4
21 18	0.800	0.808	1.200	20.4
34 58	0.978	0.719	1.022	17.5
48 35	1.015	0.700	0.985	13.5
58 54	1.090	0.663	0.910	12.8
69 59	1.135	0.640	0.865	11.6
2 59	0.142	1.002	1.858	19.7
9 31	0.438	0.874	1.562	22.2
24 19	0.715	0.735	1.285	16.8
37 44	0.810	0.688	1.190	13.4

Table 13

$a = 1.208 \times 10^{-5}$ ,  $1.093 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$  Vacuum Distilled  
 $b = 2.000 \times 10^{-5}$   $\text{FeSO}_4$   
 pH = 3.30 ( $\text{H}_2\text{SO}_4$ )  
 $t = 25.00^\circ\text{C}$

Time in minute	$1/z \times 10^5$	$1/z^2 \times \beta/2 \times 10^5$	k $\text{mol}^{-1} \times \text{sec}^{-1} \times \text{lt}$
1 49	0.522	0.057	16.0
12 00	0.730	0.111	23.8
21 18	0.833	0.144	18.9
34 58	0.979	0.199	16.8
48 35	1.015	0.214	12.1
58 54	1.099	0.251	11.3
69 59	1.156	0.278	10.2
2 59	0.538	0.027	19.6
9 31	0.640	0.038	21.6
24 19	0.778	0.056	16.9
37 44	0.840	0.066	13.2

Table 14

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$ 

$a = 3.238 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$  Vacuum distilled,  $b = 1.000 \times 10^{-5}$  mol/lit  $\text{FeSO}_4$ , pH = 4.31 ( $\text{H}_2\text{SO}_4$ ),  $t = 25.00^\circ\text{C}$

First reaction, 10 minutes after preparing the solutions

Second reaction, 135 minutes after preparing the solutions

Time in Minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$(a-x/2) 10^5$	$(b-x) 10^5$	$k$ mol <sup>-1</sup> × sec <sup>-1</sup> × lit
3 08	0.328	3.074	0.672	35.6
19 19	0.720	2.878	0.280	18.6
27 30	0.768	2.854	0.232	15.0
35 52	0.774	2.851	0.226	11.7
3 11	0.274	3.101	0.726	28.7
20 46	0.658	2.909	0.342	14.5
30 12	0.705	2.885	0.295	11.1
39 20	0.763	2.856	0.237	10.4

Table 15

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$ 

$a = 1.102 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$  Vacuum distilled,  $b = 1.000 \times 10^{-5}$  mol/lit  $\text{FeSO}_4$ , pH = 4.30 ( $\text{H}_2\text{SO}_4$ ),  $t = 25.00^\circ\text{C}$

First reaction, 20 minutes after preparing the solutions

Second reaction, 135 minutes after preparing the solutions

Time in Minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$(a-x/2) 10^5$	$(b-x) 10^5$	$k$ mol <sup>-1</sup> × sec <sup>-1</sup> × lit
2 46	0.098	1.053	0.902	28.6
11 16	0.330	0.937	0.670	29.3
27 48	0.505	0.849	0.495	22.0
54 44	0.624	0.790	0.376	16.3
65 30	0.665	0.769	0.335	15.5
2 57	0.090	1.057	0.910	25.5
24 35	0.392	0.906	0.608	17.0
31 32	0.428	0.888	0.572	14.9
58 42	0.494	0.855	0.506	10.1
70 12	0.530	0.837	0.470	9.5

**Table 16**  
Reaction between H<sub>2</sub>O<sub>2</sub> and Fe<sup>++</sup>

a = 1.046 × 10 <sup>-5</sup> mol/lit b = 1.033 × 10 <sup>-5</sup> » pH = 0.15 (H <sub>2</sub> SO <sub>4</sub> ) t = 0.00°C k = 18.2			a = 1.019 × 10 <sup>-5</sup> mol/lit b = 0.991 × 10 <sup>-5</sup> » pH = 1.75 (H <sub>2</sub> SO <sub>4</sub> ) t = 0.00°C k = 22.4			a = 1.041 × 10 <sup>-5</sup> mol/lit b = 1.033 × 10 <sup>-5</sup> » pH = 3.98 (H <sub>2</sub> SO <sub>4</sub> ) t = 0.00°C		
t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x}{b-x}$	t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x}{b-x}$	t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x}{b-x}$
0 00	—	0.012	0 00	—	0.028	0 00	—	0.008
4 50	0.150	0.095	5 01	0.140	0.112	4 38	0.076	0.047
10 45	0.239	0.154	12 10	0.268	0.202	9 37	0.138	0.083
17 25	0.321	0.216	22 29	0.434	0.365	21 14	0.250	0.180
26 52	0.472	0.367	37 33	0.550	0.523	33 59	0.348	0.236
34 21	0.482	0.379	48 02	0.634	0.676	48 22	0.408	0.292
41 54	0.585	0.521				63 48	0.482	0.373
6 06	0.135	0.086	5 57	0.150	0.116	9 03	0.130	0.078
15 11	0.262	0.171	16 45	0.330	0.256	14 03	0.179	0.108
20 54	0.385	0.276	32 12	0.503	0.454	27 50	0.300	0.195
36 47	0.532	0.443	43 57	0.620	0.647	41 22	0.395	0.280
29 48	0.470	0.357	57 41	0.723	0.898	50 45	0.428	0.313
						61 38	0.472	0.361

**Table 17**  
Reaction between  $H_2O_2$  and  $Fe^{++}$

$a = 1.376 \times 10^{-5}$ mol/lit $b = 1.013$ » $pH = 0.10$ ( $H_2SO_4$ ) $t = 0.00^\circ C$ $k = 17.7$		$a = 1.387 \times 10^{-5}$ mol/lit $b = 0.991$ » $pH = 1.73$ ( $H_2SO_4$ ) $t = 0.00^\circ C$ $k = 22.8$		$a = 1.405 \times 10^{-5}$ mol/lit $H_2O_2$ $b = 1.013$ » $pH = 3.50$ ( $H_2SO_4$ ) $t = 0.00^\circ C$				
t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$
0 00		0.306	0 00		0.337	0 00		0.327
3 58	0.120	0.328	5 05	0.145	0.441	4 42	0.082	0.382
11 06	0.268	0.511	14 33	0.402	0.700	16 40	0.193	0.472
18 24	0.363	0.609	20 56	0.485	0.817	25 49	0.337	0.604
29 25	0.500	0.884	28 50	0.570	0.962	33 22	0.384	0.657
37 30	0.635	1.030	38 40	0.603	1.030	51 50	0.514	0.833
43 27	0.665	1.099	49 55	0.750	1.483	62 03	0.557	0.882
6 20	0.140	0.403	10 13	0.255	0.522	4 16	0.072	0.375
12 20	0.286	0.528	20 18	0.443	0.745	9 53	0.192	0.466
21 07	0.380	0.628	29 49	0.560	0.943	20 05	0.280	0.505
28 53	0.490	0.771	38 17	0.659	1.160	30 01	0.394	0.668
34 35	0.600	0.958	44 31	0.775	1.383	39 33	0.473	0.772
40 30	0.665	1.099	67 09	0.846	1.895	49 50	0.506	0.821



Table 18  
Reaction between H<sub>2</sub>O<sub>2</sub> and Fe<sup>++</sup>

$a = -1.035 + 10^{-5}$ mol/lit $b = 1.487 \times 10^{-5}$ » pH = 0.15 (H <sub>2</sub> SO <sub>4</sub> ) $t = 0.00^\circ\text{C}$ $k = 21.3$			$a = 1.035 \times 10^{-5}$ mol/lit $b = 1.487$ » pH = 1.88 (H <sub>2</sub> SO <sub>4</sub> ) $t = 0.00^\circ\text{C}$ $k = 24.4$			$a = 1.035 \times 10^{-5}$ mol/lit $b = 1.487$ » pH = 3.20 $t = 0.00^\circ\text{C}$		
t, minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$
0 00		-0.363	0 00		-0.363	0 00		-0.363
4 42	0.152	-0.332	5 03	0.215	-0.315	55 13	0.174	-0.326
9 39	0.296	-0.295	11 55	0.389	-0.267	13 35	0.335	-0.283
17 53	0.485	-0.235	17 49	0.505	-0.226	24 58	0.560	-0.205
23 15	0.585	-0.194	24 45	0.615	-0.181	36 13	0.640	-0.170
34 30	0.713	-0.131	35 35	0.810	-0.072	47 46	0.721	-0.125
43 27	0.852	-0.042	52 43	1.007	0.103	60 33	0.870	-0.028
5 30	0.192	-0.321	6 27	0.250	-0.307	11 06	0.307	-0.291
13 37	0.377	-0.270	17 13	0.477	-0.237	16 21	0.404	-0.263
23 34	0.612	-0.183	24 33	0.620	-0.179	27 43	0.545	-0.211
33 22	0.795	-0.081	36 23	0.800	-0.079	33 26	0.609	-0.183
43 30	0.990	0.172	50 38	0.982	0.074	51 27	0.760	-0.097
			61 37	1.130	0.275	63 35	0.865	-0.031

**Table 19**  
Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$

$a=1.545 \times 10^{-5}$ mol/lit $b=1.004$ » » pH=4.18 ( $\text{H}_2\text{SO}_4$ ) $t=15.00^\circ\text{C}$			$a=1.498 \times 10^{-5}$ mol/lit $b=1.009$ » » pH=1.70 ( $\text{H}_2\text{SO}_4$ ) $t=15.00^\circ\text{C}$ $k=58.7$			$a=1.545 \times 10^{-5}$ mol/lit $b=1.004$ » » pH=0.10 ( $\text{H}_2\text{SO}_4$ ) $t=15.00^\circ\text{C}$ $k=54.1, 48.7$		
t minute	$10^5 \times \text{Fe}^{++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$	t minute	$10^5 \times \text{Fe}^{++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$	t minute	$10^5 \times \text{Fe}^{++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$
0 00		0.431	0 00		0.396	0 00		0.431
2 27	0.170	0.560	3 27	0.265	0.608	2 30	0.245	0.629
7 32	0.355	0.745	7 49	0.438	0.807	7 55	0.480	0.912
18 35	0.398	0.798	17 25	0.723	1.380	15 52	0.715	1.414
24 00	0.385	0.782	23 38	0.840	1.853	22 46	0.855	2.015
28 02	0.435	0.848	28 16	0.938	2.674	27 47	0.900	2.353
			33 41	0.995	4 280			
2 48	0.195	0.582				3 12	0.255	0.638
8 03	0.230	0.614	6 43	0.395	0.751	8 46	0.560	1.049
18 19	0.382	0.778	11 54	0.552	0.984	14 09	0.665	1.275
23 21	0.381	0.777	15 43	0.652	1.190	23 59	0.855	2.015
28 59	0.387	0.784	20 50	0.775	1.560	30 47	0.967	2.750
			24 44	0.840	1.853			
0 00		0.431				0 00		0.431
2 45	0.090	0.495				1 58	0.233	0.617
7 10	0.247	0.631				6 46	0.441	0.858
19 00	0.402	0.803				16 43	0.781	1.645
27 40	0.417	0.823				21 35	0.843	1.944
34 56	0.391	0.789				26 37	0.903	2.383
39 43	0.347	0.736				31 53	0.947	5.239
45 57	0.330	0.671						
4 32	0.217	0.602				3 25	0.285	0.794
12 35	0.350	0.740				8 45	0.485	0.920
20 13	0.393	0.793				13 32	0.515	1.158
25 50	0.345	0.734				18 55	0.749	1.525
31 58	0.306	0.690				24 04	0.852	1.996
41 19	0.266	0.649						
47 45	0.190	0.578						

Table 20  
Reaction between H<sub>2</sub>O<sub>2</sub> and Fe<sup>++</sup>

a = 1.056 × 10 <sup>-5</sup> mol/lit b = 1.014 » » pH = 0.10 (H <sub>2</sub> SO <sub>4</sub> ) t = 15.00°C k = 47.3			a = 0.999 × 10 <sup>-5</sup> mol/lit b = 1.009 » » pH = 1.80 (H <sub>2</sub> SO <sub>4</sub> ) t = 15.00°C k = 52.7			a = 1.034 × 10 <sup>-5</sup> mol/lit b = 0.999 » » pH = 3.90 (H <sub>2</sub> SO <sub>4</sub> ) t = 15.00°C		
t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x}{b-x}$	t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x}{b-x}$	t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x}{b-x}$
0 00		0.041	0 00		-0.009	0 00		0.034
2 35	0.208	0.166	3 23	0.193	0.101	5 13	0.150	0.122
9 25	0.412	0.345	8 02	0.373	0.270	11 00	0.245	0.190
14 23	0.495	0.444	12 50	0.507	0.396	22 17	0.405	0.337
22 10	0.687	0.780	21 42	0.670	0.672	31 31	0.467	0.409
30 48	0.748	0.942	28 34	0.762	0.917	42 55	0.513	0.471
37 00	0.860	1.416	34 40	0.817	1.125	57 02	0.565	0.550
			42 35	0.895	1.580	90 00	0.503	0.457
3 44	0.245	0.194						
11 29	0.470	0.412	7 03	0.288	0.171	5 53	0.175	0.139
16 29	0.567	0.548	11 03	0.412	0.284	16 42	0.370	0.300
24 07	0.690	0.787	22 03	0.640	0.610	26 40	0.460	0.400
29 27	0.748	0.942	31 37	0.775	0.962	39 05	0.518	0.477
35 15	0.880	1.527	45 18	0.870	1.400	50 54	0.552	0.528
39 54	0.899	1.693	58 38	0.982	2.936	62 30	0.560	0.542
			64 28	0.995	3.580	71 05	0.538	0.507

Table 21  
Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$

$a = 1.020 \times 10^{-5}$ mol/lit $b = 1.478$ » $\text{pH} = 0.15$ ( $\text{H}_2\text{SO}_4$ ) $t = 15.00^\circ\text{C}$ $k = 49.0$			$a = 1.042 \times 10^{-5}$ mol/lit $b = 1.513$ » $\text{pH} = 1.75$ ( $\text{H}_2\text{SO}_4$ ) $t = 15.00^\circ\text{C}$ $k = 53.0$			$a = 1.044 \times 10^{-5}$ mol/lit $b = 1.513$ » $\text{pH} = 3.75$ ( $\text{H}_2\text{SO}_4$ ) $t = 15.00^\circ\text{C}$		
t	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$
minute			minute			minute		
0 00		-0.371	0 00		-0.365	0 00		-0.371
2 04	0.222	-0.323	2 53	0 268	-0.315	3 40	0.195	-0.331
6 34	0.445	-0.258	8 02	0.518	-0.240	11 02	0.435	-0.265
16 32	0.760	-0.115	14 31	0.763	-0.126	22 13	0.594	-0.207
22 13	0.896	-0.010	21 57	0.992	0.047	32 13	0.687	-0.164
30 46	1.050	0.120	28 43	1.165	0.279	42 56	0.755	-0.128
35 34	1.099	0.217	36 16	1.250	0.461	52 13	0.782	-0.113
7 08	0.480	-0.246	5 33	0.390	-0.282	7 18	0.318	-0.300
11 58	0.675	-0.162	11 50	0.646	-0.210	18 12	0.536	-0.230
17 37	0.835	-0.064	18 33	0.855	-0.068	27 51	0.640	-0.187
			26 58	1.087	0.169	38 31	0.755	-0.128
			33 02	1.172	0.280	46 40	0.803	-0.099
			39 46	1.268	0.510	54 10	0.875	-0.052

Table 22  
Reaction between  $H_2O_2$  and  $Fe^{++}$

$a = 1.375 \times 10^{-5}$ mol/lit $b = 1.430$ » $pH = 0.10$ ( $H_2SO_4$ ) $t = 15.00^\circ C$ $k = 47.0$			$a = 1.392 \times 10^{-5}$ mol/lit $b = 1.014$ » $pH = 0.07$ ( $H_2SO_4$ ) $t = 15.00^\circ C$ $k = 49.7$			$a = 2.087 \times 10^{-5}$ mol/lit $b = 1.014$ » $pH = 0.10$ ( $H_2SO_4$ ) $t = 15.00^\circ C$ $k = 54.2$		
t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$
0 00		-0.039	0 00		0.317	0 00		0.722
2 06	0.258	0.061	3 01	0.255	0.511	2 33	0.347	1.054
8 06	0.586	0.249	6 04	0.500	0.798	7 26	0.612	1.489
14 10	0.823	0.464	14 33	0.665	1.110	12 53	0.801	2.024
21 00	1.025	0.757	21 40	0.785	1.474	19 41	0.900	2.665
28 08	1.120	0.967	31 10	0.878	1.947	1 52	0.286	0.983
33 16	1.207	1.242	36 55	0.944	2.578	7 27	0.583	1.427
3 38	0.372	0.117	2 02	0.195	0.458	13 20	0.808	2.101
10 15	0.685	0.327	9 35	0.505	0.814	19 27	0.919	2.842
16 05	0.908	0.568	15 44	0.677	1.140	24 25	0.955	3.307
22 05	1.045	0.795	21 22	0.785	1.474	28 41	0.995	4.429
27 35	1.130	0.994	25 30	0.848	1.764			
33 55	1.215	1.274						

**Table 23**  
Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$

$a = 1.718 \times 10^{-5}$ mol/lit $b = 1.430$ >      > pH = 0.10 ( $\text{H}_2\text{SO}_4$ ) $t = 15.00^\circ\text{C}$		
t minute	$10^5 \times \text{Fe}^{+++}$ mol/t	$\ln \frac{a-x/2}{b-x}$
0 00		0.184
2 15	0.315	0.270
7 06	0.627	0.559
11 53	0.885	0.851
17 11	1.045	1.215
24 24	1.195	1.566
3 14	0.419	0.400
8 20	0.768	0.701
13 25	0.902	0.876
18 57	1.087	1.231
25 42	1.220	1.663
Solutions are of the same concentrations pH = 2.30		
5 20	0.448	0.420
10 25	0.742	0.671
22 01	1.052	1.149
31 22	1.140	1.376

Table 24  
Reaction between  $H_2O_2$  and  $Fe^{++}$

$a = 1.123 \times 10^{-5}$ mol/lit $b = 1.013$ pH = 0.05 ( $H_2SO_4$ ) $t = 25.00^\circ C$ $k = 75.0$			$a = 1.204 \times 10^{-5}$ mol/lit $b = 1.003$ pH = 0.25 ( $H_2SO_4$ ) $t = 25.00^\circ C$ $k = 84.2$			$a = 0.901 \times 10^{-5}$ mol/lit $b = 1.003$ pH = 0.20 ( $H_2SO_4$ ) $t = 25.00^\circ C$ $k = 82.1$		
t	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$
minute			minute			minute		
0 00		0.103	0 00		0.182	0 00		-0.207
2 27	0.298	0.295	1 55	0.225	0.338	2 35	0.249	0.029
9 31	0.657	0.804	6 47	0.494	0.632	7 30	0.425	0.170
13 42	0.726	0.974	11 49	0.692	1.015	14 09	0.576	0.362
18 37	0.752	1.052	19 06	0.880	1.821	20 20	0.702	0.603
23 58	0.848	1.444	25 06	0.920	2.193	26 35	0.810	0.944
29 29	0.896	1.753	31 00	0.922	2.216	32 32	0.861	1.199
4 08	0.352	0.360	37 26	0.995	4.482	39 40	0.912	1.587
17 50	0.737	1.005	3 01	0.303	0.408	3 36	0.275	0.048
22 35	0.800	1.223	8 03	0.520	0.670	8 45	0.467	0.219
27 43	0.840	1.402	14 32	0.710	1.064	16 33	0.636	0.463
			21 51	0.898	1.973	22 55	0.723	0.657
			28 03	0.920	2.193	29 16	0.808	0.936
			33 54	0.962	2.870	34 33	0.852	1.146
						40 24	0.914	1.607

Table 25  
Reaction between  $H_2O_2$  and  $Fe^{++}$

$a = 1.082 \times 10^{-5}$ mol/lit $b = 1.000$ > $pH = 0.15$ ( $H_2SO_4$ ) $t = 25.00^\circ C$ $k = 86.4$			$a = 1.058 \times 10^{-5}$ mol/lit $b = 0.997$ > $pH = 1.94$ ( $H_2SO_4$ ) $t = 25.00^\circ C$ $k = 76.0$			$a = 1.092 \times 10^{-5}$ mol/lit $b = 0.990$ > $pH = 3.73$ ( $H_2SO_4$ ) $t = 25.00^\circ C$		
t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$	t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x}{b-x}$
0 00		0.079	0 00		0.059	0 00		0.094
2 28	0.449	0.243	4 01	0.340	0.308	4 13	0.155	0.195
7 03	0.467	0.466	8 40	0.510	0.500	5 39	0.212	0.237
15 07	0.728	0.971	13 50	0.657	0.764	13 37	0.302	0.313
21 41	0.787	1.174	17 30	0.730	0.954	26 17	0.414	0.430
27 43	0.918	2.028	20 00	0.741	0.989	33 45	0.453	0.478
32 41	0.957	2.644	25 41	0.830	1.350	45 56	0.508	0.553
38 46	0.999	—	35 13	0.940	2.335	66 31	0.518	0.568
3 45	0.334	0.318	6 06	0.410	0.374	8 01	0.251	0.269
10 39	0.619	0.688	15 30	0.690	0.843	18 36	0.357	0.367
17 46	0.689	0.864	20 22	0.770	1.087	28 00	0.413	0.429
25 57	0.892	1.773	26 32	0.875	1.628	41 35	0.468	0.497
31 02	0.944	2.388	31 21	0.908	1.915	53 22	0.473	0.504
						61 48	0.448	0.471
						77 08	0.348	0.358



Table 26  
Reaction between H<sub>2</sub>O<sub>2</sub> and Fe<sup>++</sup>

a = 1.416 × 10 <sup>-5</sup> mol/lit b = 0.978 pH = 0.20 (H <sub>2</sub> SO <sub>4</sub> ) t = 25.00°C k = 69.7		a = 1.357 × 10 <sup>-5</sup> mol/lit b = 0.997 pH = 1.80 (H <sub>2</sub> SO <sub>4</sub> ) t = 25.00°C k = 82.0		a = 1.325 × 10 <sup>-5</sup> mol/lit b = 0.997 pH = 4.08 (H <sub>2</sub> SO <sub>4</sub> ) t = 25.00°C	
t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x}{b-x}$	t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x}{b-x}$
0 00		0.370	0 00		0.308
2 45	0.357	0.690	2 45	0.320	0.570
9 16	0.575	1.030	7 05	0.580	0.940
17 29	0.840	1.742	12 13	0.767	1.437
22 25	0.893	2.434	21 30	0.960	3.164
2 03	0.282	0.606	26 09	0.980	3.933
7 44	0.455	0.821	3 45	0.365	0.621
12 31	0.690	1.314	8 13	0.575	0.931
18 45	0.828	1.900	12 50	0.728	1.307
25 53	0.887	2.370	17 15	0.828	1.720
			20 35	0.880	2.060
			0 00		0.274
			4 27	0.345	0.570
			11 13	0.425	0.666
			22 20	0.200	0.430
			31 15	0.125	0.371
			51 25	0.075	0.335
			66 52	0.065	0.327
			6 38	0.355	0.581
			16 08	0.298	0.520
			25 42	0.155	0.393
			35 26	0.135	0.378
			47 20	0.093	0.347
			74 42	0.050	0.324

**Table 27**  
Reaction between  $H_2O_2$  and  $Fe^{+++}$

$a = 1.034 \times 10^{-5}$ mol/lit $b = 1.560 \times 10^{-5}$ » pH = 0.10 ( $H_2SO_4$ ) $t = 25.00^\circ C$ $k = 76.0$		$a = 1.023 \times 10^{-5}$ mol/lit $b = 1.560$ » pH = 1.70 ( $H_2SO_4$ ) $t = 25.00^\circ C$ $k = 89.4$		$a = 1.092 \times 10^{-5}$ mol/lit $b = 1.485$ » pH = 3.53 ( $H_2SO_4$ ) $t = 25.00^\circ C$				
t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$	t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$	t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$
0 00		-0.411	0 00		-0.422	0 00		-0.308
2 41	0.293	-0.356	3 34	0.463	-0.326	4 05	0.382	-0.202
7 27	0.615	-0.262	7 42	0.768	-0.216	8 40	0.585	-0.118
13 48	0.928	-0.096	13 19	1.052	-0.024	21 46	0.861	0.059
23 24	1.165	0.135	19 10	1.258	0.266	31 20	0.975	0.171
32 35	1.333	0.483	27 49	1.391	0.663	44 48	1.080	0.309
4 12	0.423	-0.323	32 50	1.440	0.926	55 55	1.115	0.369
9 58	0.791	-0.185	2 38	0.348	-0.356	93 31	1.097	0.338
15 10	0.976	-0.067	7 02	0.685	-0.251	3 30	0.350	-0.213
23 15	1.130	0.087	11 35	0.895	-0.144	12 27	0.672	-0.073
26 15	1.263	0.305	16 03	1.097	0.026	26 20	0.895	0.089
29 47	1.298	0.385	30 08	1.310	0.387	36 04	1.033	0.242
23 24	1.165	0.135				46 52	1.097	0.338
						84 50	1.185	0.511
						107 03	1.140	0.414

Table 28

The Velocity Constants of  $\text{Fe}^{++}$ - $\text{H}_2\text{O}_2$  Reactions at Different Temperatures

$\text{H}_2\text{O}_2 \times 10^5$ mol/lit	$\text{Fe}^{++} \times 10^5$ mol/lit	pH	Temperature °C	$\text{k mol}^{-1}$ liter $\text{second}^{-1}$
1.046	1.033	0.15	0.00	18.2
1.019	0.991	1.75	0.00	22.4
1.376	1.013	0.10	0.00	17.7
1.378	0.991	1.73	0.00	22.8
1.035	1.487	0.15	0.00	21.3
1.035	1.487	1.88	0.00	24.4
1.545	1.004	0.10	15.00	54.1
1.545	1.004	0.10	15.00	48.7
1.498	1.009	1.70	15.00	58.7
1.056	1.014	0.10	15.00	47.3
0.999	1.009	1.80	15.00	52.7
1.020	1.478	0.15	15.00	49.0
1.042	1.513	1.75	15.00	53.0
1.375	1.430	0.10	15.00	47.0
1.392	1.014	0.07	15.00	49.5
2.087	1.014	0.10	15.00	54.2
1.718	1.430	0.10	15.00	47.5
1.123	1.023	0.05	25.00	75.0
1.204	1.003	0.25	25.00	84.2
0.901	1.003	0.20	25.00	82.1
1.082	1.000	0.15	25.00	86.4
1.058	0.997	1.94	25.00	76.0
1.416	0.978	0.20	25.00	69.7
1.357	0.997	1.80	25.00	82.0
1.034	1.560	0.10	25.00	76.0
1.023	1.560	1.70	25.00	89.4

Table 29

$$a = 1.122 \times 10^{-5} \text{ mol/l}$$

$$b = 0.996 \times 10^{-5}$$

$$t = 15.00^\circ\text{C}$$

First Reaction pH = 1.85 (H <sub>2</sub> SO <sub>4</sub> )			Second Reaction pH = 4.00 At the beginning pH = 1.80 At the end		
t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/l	ln $\frac{a-x/2}{b-x}$	t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/l	ln $\frac{a-x/2}{b-x}$
4 44	0.350	0.383	5 18	0.214	0.261
9 14	0.515	0.587	9 40	0.260	0.299
42 00	2.830		29 50	2.440	
49 35	2.830		44 10	2.440	
At t = 15' 00" to 100 ml. reacting solution 0.10 ml. M/2.5 Fe <sup>++</sup> was added.			At t = 15' 00" to 100 ml. reacting solution 0.10 ml. M/2.5 Fe <sup>++</sup> and 0.035 ml. H <sub>2</sub> SO <sub>4</sub> was added.		
Third Reaction pH = 1.82 (H <sub>2</sub> SO <sub>4</sub> )			Forth Reaction pH = 3.20 At the beginning pH = 1.60 At the end		
t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/l	ln $\frac{a-x/2}{b-x}$	t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/l	ln $\frac{a-x/2}{b-x}$
6 20	0.420	0.460	5 31	0.155	0.217
10 45	0.555	0.651	12 30	0.185	0.239
18 38	0.745	1.095	19 05	0.150	0.213
66 25	2.830		45 30	2.150	
80 15	2.830		55 00	2.150	
At t = 26' 30" to 100 ml. reacting solution 0.10 ml. M/2.5 Fe <sup>++</sup> was added.			At t = 26' .30' to 100 ml. reacting solution 0.10 ml. M/2.5 Fe <sup>++</sup> and 0.035 ml. H <sub>2</sub> SO <sub>4</sub> was added.		

Table 30

$$a = 1.122 \times 10^{-5} \text{ mol/lit}$$

$$b = 0.996 \times 10^{-5} \text{ } \rangle$$

$$t = 15.00^\circ C$$

First Reaction pH = 1.80 ( $H_2SO_4$ )			Second Reaction pH = 4.10 At the beginning pH = 1.80 At the end		
t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$	t minute	$10^5 \times Fe^{+++}$ mol/lit	
8 35	0.520	0.594	46 08	2.04	
16 50	0.740	1.077	52 23	2.040	
42 05	2.550		56 25	2.040	
54 50	2.550				
At t = 26' 30" to 100 ml. reacting solution 0.10 ml. M/2.5 $Fe^{++}$ was added.			At t = 26' 30" to 100 ml. reacting solution 0.10 ml. M/2.5 $Fe^{++}$ and 0.035 ml $H_2SO_4$ was added.		
$a = 1.110 \times 10^{-5} \text{ mol/lit}$ $b = 0.996 \times 10^{-5} \text{ } \rangle$ $t = 15.00^\circ C$					
pH = 4.20 At the beginning pH = 1.60 At the end					
t minute	$10^5 \times Fe^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$			
5 35	0.155	0.207			
9 55	0.200	0.238			
42 50	2.160				
55 37	2.160				
At t = 15' 00" to 100 ml. reacting solution 0.10 ml. M/2.5 $Fe^{++}$ and 0.035 ml. $H_2SO_4$ was added.					

Table 31

$$a = 1.113 \times 10^{-5} \text{ mol/lit}$$

$$b = 1.000 \times 10^{-5} \text{ ,}$$

$$t = 15.00^\circ\text{C}$$

First Reaction pH=1.64 (H <sub>2</sub> SO <sub>4</sub> )			Second Reaction pH=4.20 At the beginning pH=1.80 At the end		
t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x/2}{b-x}$	t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x/2}{b-x}$
6 05	0.393	0.413	15 00	0.212	0.245
12 14	0.595	0.701	18 52	0.155	0.204
35 45	2.490		46 55	1.990	
43 10	2.490		60 30	1.990	
At t = 15' 00" to 100 ml. reacting solution 0.10 ml. M/2.5 Fe <sup>++</sup> was added.			At t = 26' 30" to 100 ml. reacting solution 0.10 ml. M/2.5 Fe <sup>++</sup> and 0.035 ml. H <sub>2</sub> SO <sub>4</sub> was added.		
Third Reaction pH=1.80 (H <sub>2</sub> SO <sub>4</sub> )			Forth reaction pH=4.10 At the beginning pH=1.85 At the end		
t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit		t minute	10 <sup>5</sup> × Fe <sup>+++</sup> mol/lit	ln $\frac{a-x/2}{b-x}$
24 30	2.460		6 30	0.175	0.218
31 10	2.460		9 47	0.233	0.262
			38 22	2.150	
			42 50	2.150	
At t = 15' 00" to 100 ml. reacting solution 0.10 ml. M/2.5 Fe <sup>++</sup> was added.			At t = 15' 00" to 100 ml. reacting solution 0.10 ml. M/2.5 Fe <sup>++</sup> and 0.035 ml. H <sub>2</sub> SO <sub>4</sub> was added.		

Table 32

$$a = 1.088 \times 10^{-5} \text{ mol/lit}$$

$$b = 1.000 \times 10^{-5}$$

$$t = 15.00^\circ\text{C}$$

First Reaction pH = 1.92 ( $\text{H}_2\text{SO}_4$ )			Second Reaction pH = 4.25 At the beginning pH = 1.85 At the end		
t minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$	t minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	
16 55	0.687	0.868			
40 30	2.550		56 05	2.070	
45 30	2.550		61 20	2.070	
At t = 22' 00" to 100 ml. reacting solution 0.10 ml. M/2.5 $\text{Fe}^{++}$ was added.			At t = 26' 30" to 100 ml. reacting solution 0.10 ml. M/2.5 $\text{Fe}^{++}$ and 0.035 ml. $\text{H}_2\text{SO}_4$ was added.		
Third Reaction pH = 1.87 ( $\text{H}_2\text{SO}_4$ )			Forth Reaction pH = 4.23 At the beginning pH = 1.80 At the end		
t minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$	t minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$
14 55	0.650	0.779	4 40	0.131	0.181
43 00	2.450		10 10	0.240	0.242
49 00	2.450		37 28	2.070	
			42 13	2.070	
At t = 15' 00" to 100 ml. reacting solution 0.10 ml. M/2.5 $\text{Fe}^{++}$ was added.			At t = 15' 00" to 100 ml. reacting solution 0.10 ml. M/2.5 $\text{Fe}^{++}$ was added.		

Table 33

$$a = 1.085 \times 10^{-5} \text{ mol/lit}$$

$$b = 1.013 \times 10^{-5} \text{ ,}$$

$$t = 15.00^\circ\text{C}$$

pH = 5.20 At the beginning

pH = 1.70 At the end ( $\text{H}_2\text{SO}_4$ )

The time of the acid addition	t	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$
First Reaction	0 00	—	0.070
	6 45	0.070	0.108
	12 25	0.035	0.089
	23 22	0.035	0.089
t = 30' 00"	8 04	0.270	0.247
	14 56	0.378	0.345
	27 07	0.525	0.524
	Second Reaction	6 24	0.060
t = 30' 00"	17 35	0.035	0.095
	27 45	0.033	0.089
	5 25	0.253	0.240
	20 57	0.493	0.487
Third Reaction	35 40	0.728	0.938
	10 28	0.047	0.101
	20 10	0.032	0.093
t = 33' 00"	10 07	0.350	0.324
	23 46	0.510	0.509
	30 05	0.645	0.731



Table 34

$$a = 1.086 \times 10^{-5} \text{ mol/lit}$$

$$b = 1.013 \times 10^{-5} \text{ } >$$

$$t = 15.00^\circ\text{C}$$

$$\text{pH} = 1.75 (\text{H}_2\text{SO}_4)$$

	t minute	$10^5 \times \text{Fe}^{+++}$ mol/lit	$\ln \frac{a-x/2}{b-x}$
First Reaction	0 00		0.075
	16 47	0.610	0.670
	21 35	0.704	0.873
	30 50	0.818	1.254
	7 35	0.405	0.381
	13 43	0.553	0.573
	18 52	0.698	0.858
	23 22	0.768	1.061
	29 47	0.831	1.314
	36 13	0.878	1.577
41 14	0.918	1.963	
Second Reaction	9 15	0.400	0.375
	22 58	0.720	0.916
	38 37	0.895	1.700

Table 35

At the beginning  $a = 1.086 \times 10^{-5}$  mol/lit

$b = 1.013 \times 10^{-5}$  ,

$t = 15.00^\circ\text{C}$

$\text{pH} = 5.20$

After 30.00 minutes to 100 ml of the reacting mixture 0.035 ml  $\text{H}_2\text{SO}_4$  was added and the reaction measurements continued. In that case  $\text{pH} = 1.70$ .

t minute	$\ln \frac{a-x/2}{b-x}$	$\ln \frac{a-x/2}{b-x}$	$\ln \frac{a-x/2}{b-x}$
	$a = 0.800$	$a = 0.700$	$a = 0.650$
0 00	-0.236	-0.369	-0.443
8 04	-0.111	-0.274	-0.365
14 56	-0.038	-0.218	-0.320
27 07	0.096	-0.108	-0.229
5 25	-0.120	-0.281	-0.372
20 57	0.063	-0.136	-0.252
35 40	0.425	0.165	0.004
10 07	-0.059	-0.233	-0.334
23 46	0.080	-0.123	-0.242
30 05	0.262	0.024	-0.118

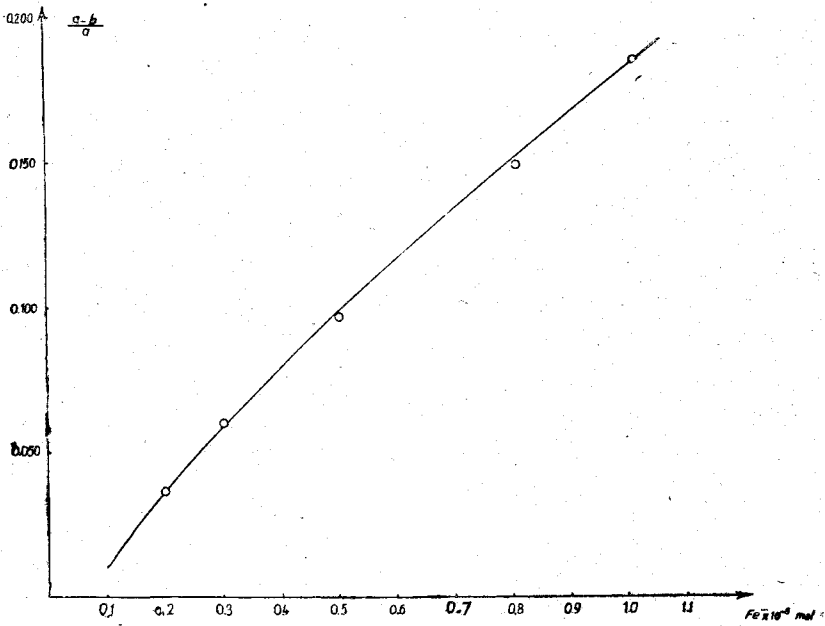


Fig. 1

Standard Comparison Graph of  $Fe^{++}$  Table 3, (Middle Values)

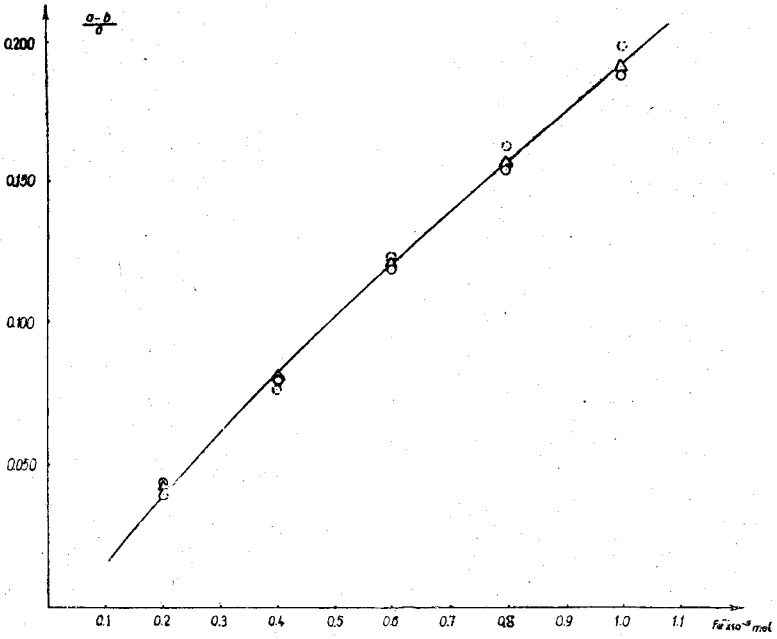


Fig.  
Standard Comparison Graph of  $Fe^{+++}$   
Table 2. (1), (2), (3)  
○...pH = 0.40  
□...pH = 3.20  
△...pH = 1.80

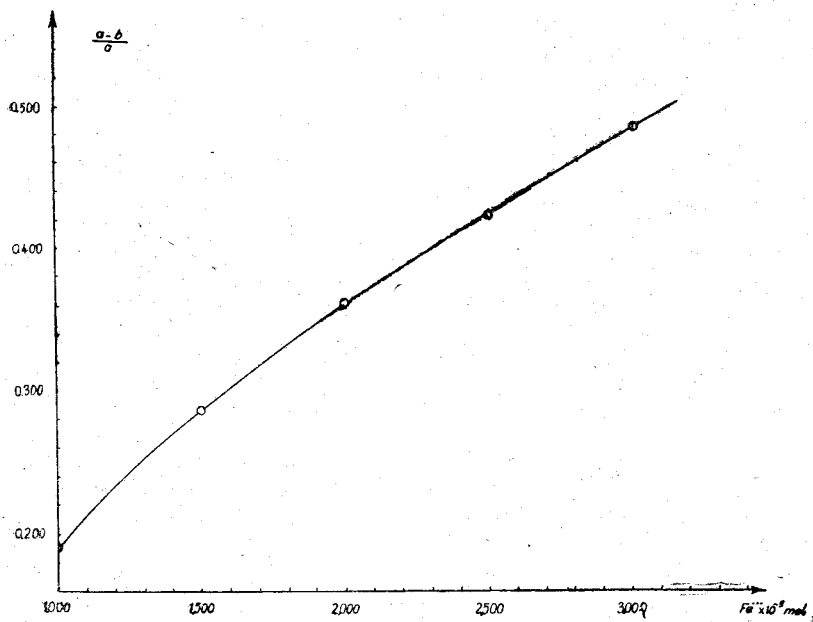


Fig. 2 a  
Standard Comparison Graph of  $Fe^{+++}$  Table 2. (4)

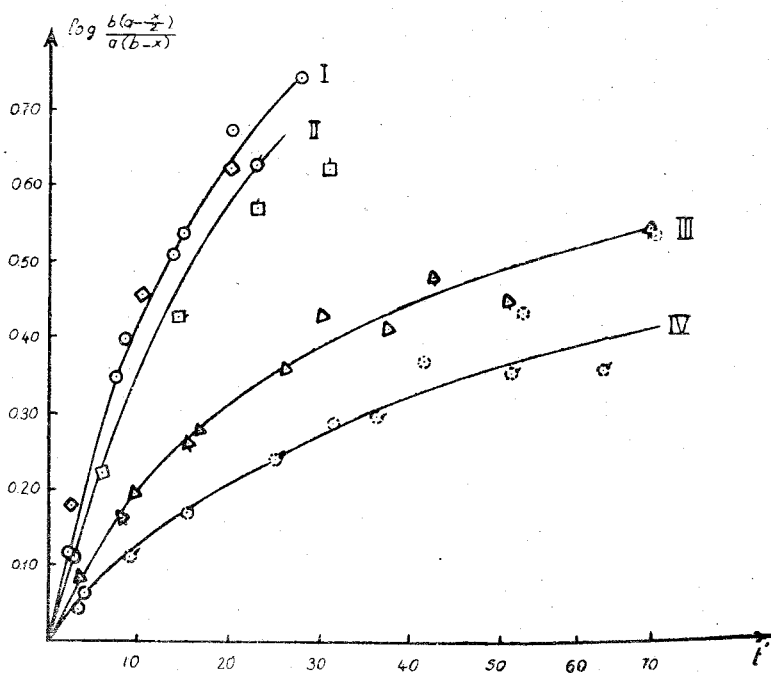


Fig. 3

Reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{++}$ 

- (I) —  $a=4.794 \times 10^{-5}$  mol/lt  $\text{H}_2\text{O}_2$ ,  $b=0.990 \times 10^{-5}$  mol/lt  $\text{Fe}^{++}$ ,  
pH=4.40 ( $\text{H}_2\text{SO}_4$ ) Table 9.
- (II) —  $a=2.866 \times 10^{-5}$  mol/lt  $\text{H}_2\text{O}_2$ ,  $b=1.000 \times 10^{-5}$  mol/lt  $\text{Fe}^{++}$ ,  
pH=4.73 ( $\text{H}_2\text{SO}_4$ ) Table 10.
- (III) —  $a=2.115 \times 10^{-5}$  mol/lt  $\text{H}_2\text{O}_2$ ,  $b=1.020 \times 10^{-5}$  mol/lt  $\text{Fe}^{++}$ ,  
pH=4.31 ( $\text{H}_2\text{SO}_4$ ) Table 11.
- (IV) —  $a=1.385 \times 10^{-5}$  mol/lt  $\text{H}_2\text{O}_2$ ,  $b=1.010 \times 10^{-5}$  mol/lt  $\text{Fe}^{++}$ ,  
pH=4.80 ( $\text{H}_2\text{SO}_4$ ) Table 12.

$t=25.00^\circ\text{C}$

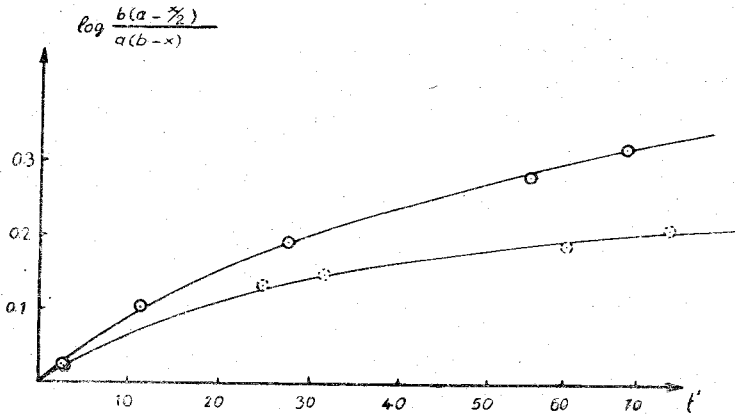


Fig. 4

$a = 1.102 \times 10^{-5}$  mol/lit  $H_2O_2$ ,  $b = 1.000 \times 10^{-5}$  mol/lit  $Fe^{++}$   
 Table 15.  $pH = 4.30(H_2SO_4)$ ,  $t = 25.00^\circ C$

- ...First reaction, 20 minutes after preparing the solutions
- ⊙...Second reaction, 135 minutes after preparing the solutions

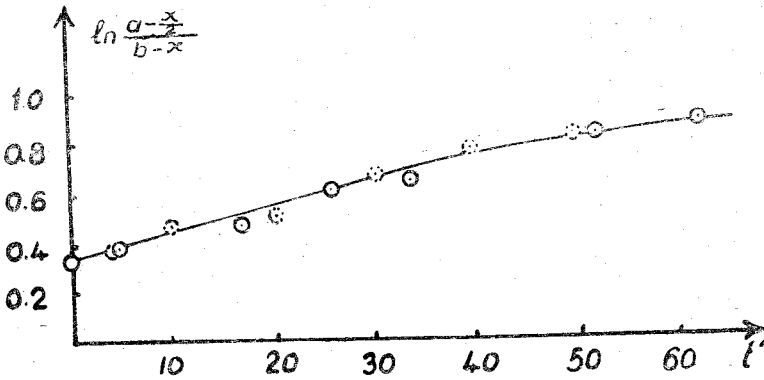


Fig. 5

$a = 1.405 \times 10^{-5}$  mol/lit  $H_2O_2$ ,  $b = 1.018 \times 10^{-5}$  mol/lit  $Fe^{++}$   
 Table 17.  $pH = 3.51(H_2SO_4)$ ,  $t = 0.00^\circ C$

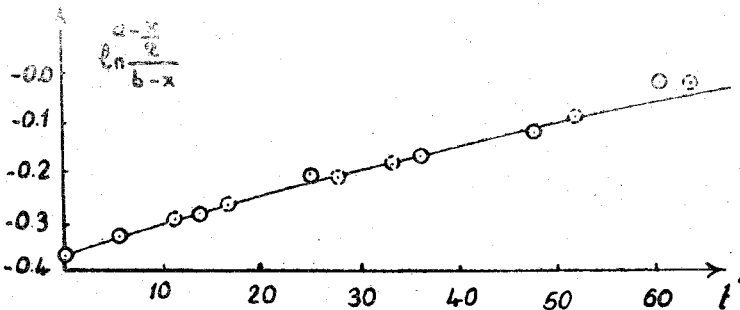


Fig. 6

$a = 1.035 \times 10^{-5}$  mol/lit  $H_2O_2$ ,  $b = 1.487 \times 10^{-5}$  mol/lit  $Fe^{++}$   
 Table 18.  $pH = 3.20(H_2SO_4)$ ,  $t = 0.00^\circ C$

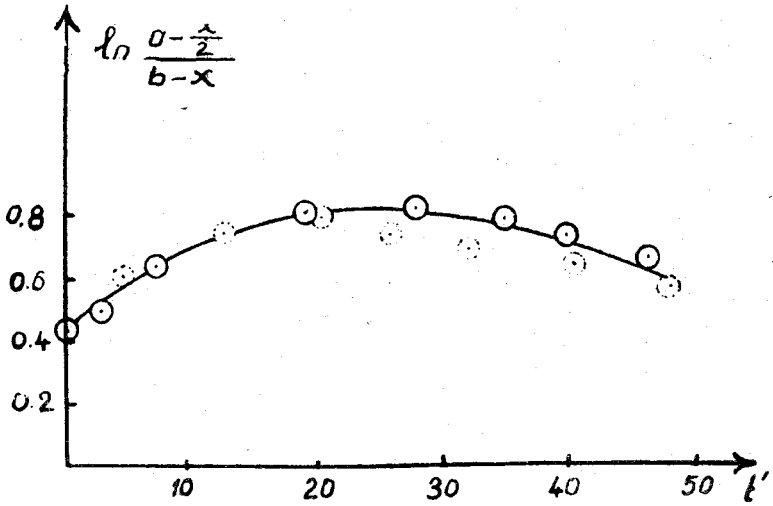


Fig. 7

$a = 1.545 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$ ,  $b = 1.004 \times 10^{-5}$  mol/lit  $\text{Fe}^{++}$   
Table 19. (2)  $\text{pH} = 4.18$  ( $\text{H}_2\text{SO}_4$ ),  $t = 15.00^\circ\text{C}$

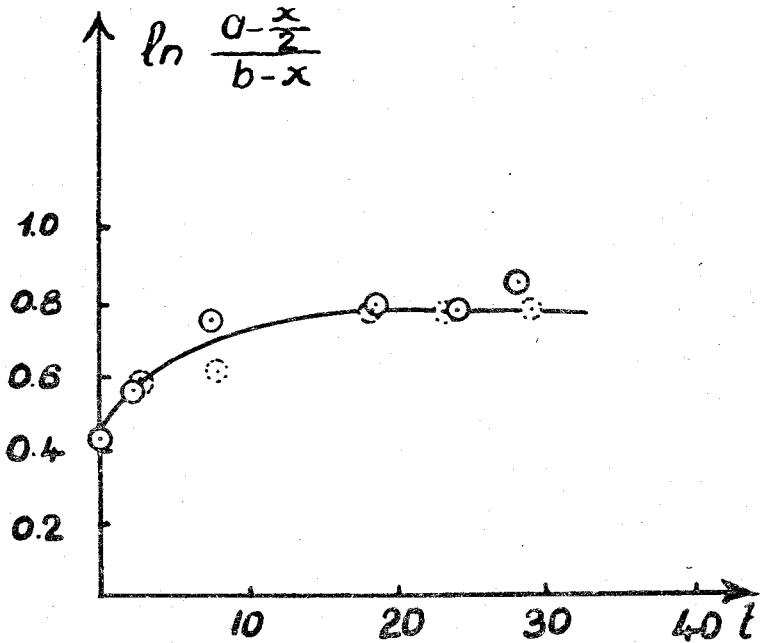


Fig. 8

$a = 1.545 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$ ,  $b = 1.004 \times 10^{-5}$  mol/lit  $\text{Fe}^{++}$   
Table 19 (1)  $\text{pH} = 4.18$  ( $\text{H}_2\text{SO}_4$ ),  $t = 15.00^\circ\text{C}$



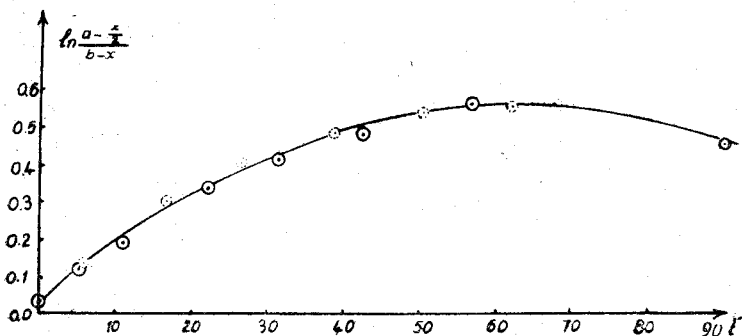


Fig. 9

$a = 1.034 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$ ,  $b = 0.960 \times 10^{-5}$  mol/lit  $\text{Fe}^{++}$ .  
 Table 20. pH = 3.90 ( $\text{H}_2\text{SO}_4$ ),  $t = 15.00^\circ\text{C}$

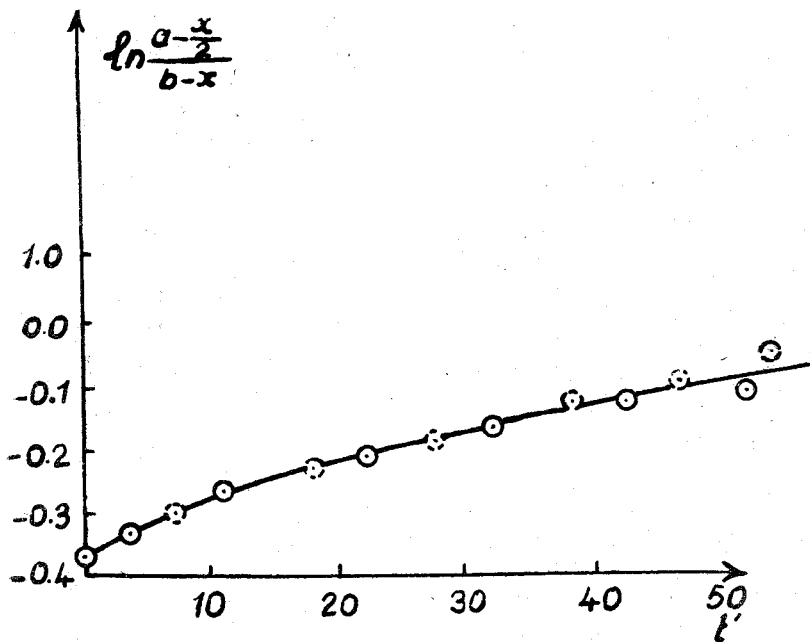


Fig. 10

$a = 1.044 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$ ,  $b = 1.513 \times 10^{-5}$  mol/lit  $\text{Fe}^{++}$ .  
 Table 21. pH = 3.75 ( $\text{H}_2\text{SO}_4$ ),  $t = 15.00^\circ\text{C}$

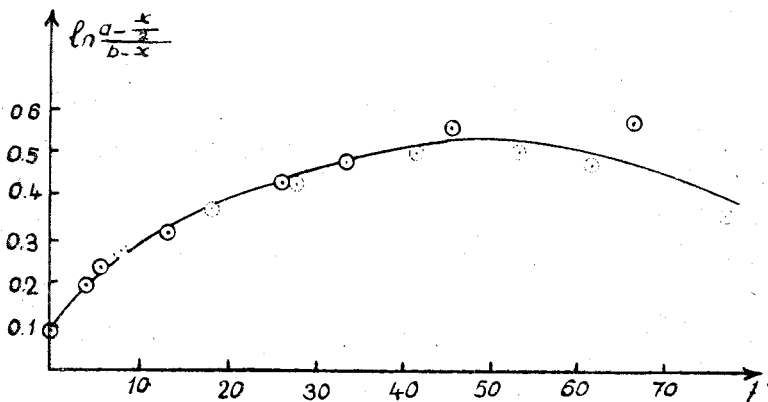


Fig. 11

$a = 1.092 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$ ,  $b = 0.990 \times 10^{-5}$  mol/lit  $\text{Fe}^{++}$   
 Table 25. pH = 3.73 ( $\text{H}_2\text{SO}_4$ ),  $t = 25.00^\circ\text{C}$

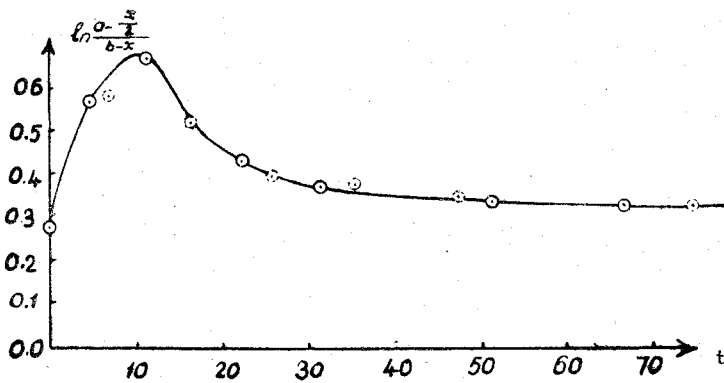


Fig. 12

$a = 1.325 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$ ,  $b = 0.997 \times 10^{-5}$  mol/lit  $\text{Fe}^{++}$   
 Table 25. pH = 4.08 ( $\text{H}_2\text{SO}_4$ ),  $t = 25.9^\circ\text{C}$

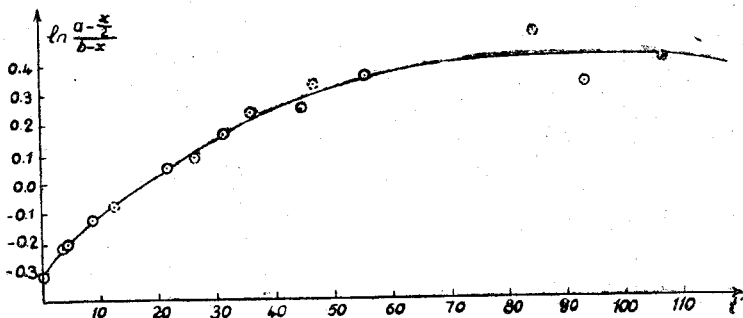


Fig. 13

$a = 1.092 \times 10^{-5}$  mol/lit  $H_2O_2$ ,  $b = 1.485 \times 10^{-5}$  mol/lit  $Fe^{++}$

Table 27. pH = 3.53 ( $H_2SO_4$ ),  $t = 25.00^\circ C$

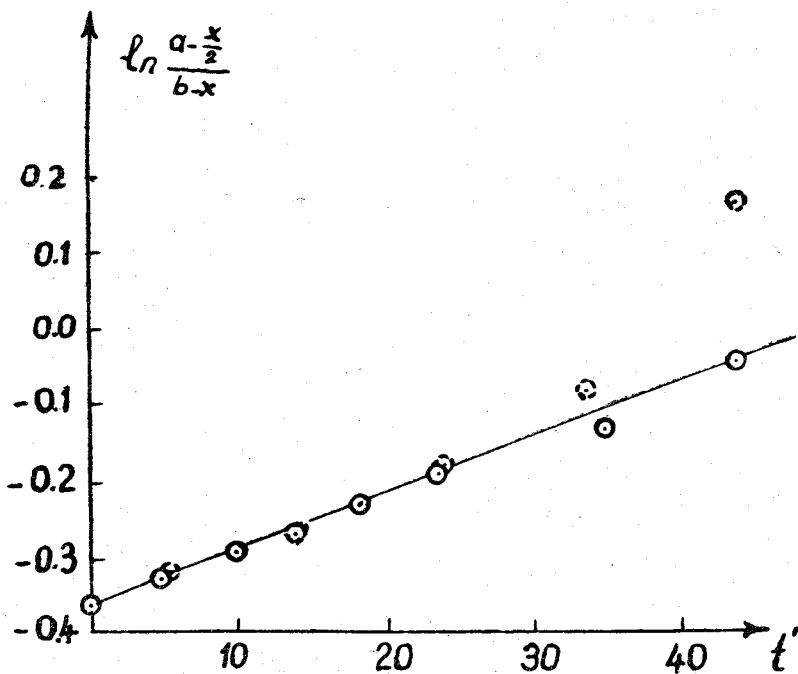


Fig. 14

$a = 1.035 \times 10^{-5}$  mol/lit  $H_2O_2$ ,  $b = 1.487 \times 10^{-5}$  mol/lit  $Fe^{++}$

Table 18. pH = 0.15 ( $H_2SO_4$ ),  $t = 0.00^\circ C$

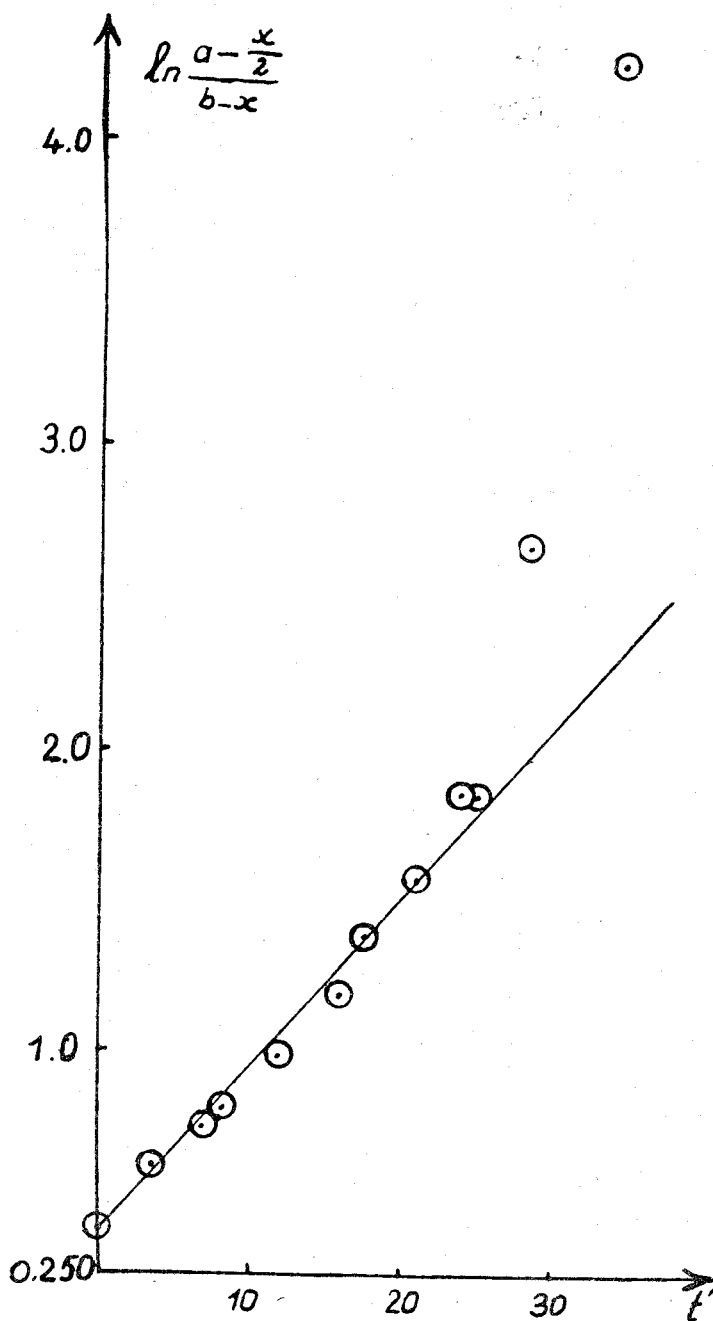


Fig. 15

$a = 1.498 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$ ,  $b = 1.009 \times 10^{-5}$  mol/lit  $\text{Fe}^{++}$   
 Table 19. pH = 1.70 ( $\text{H}_2\text{SO}_4$ ),  $t = 15.00^\circ\text{C}$

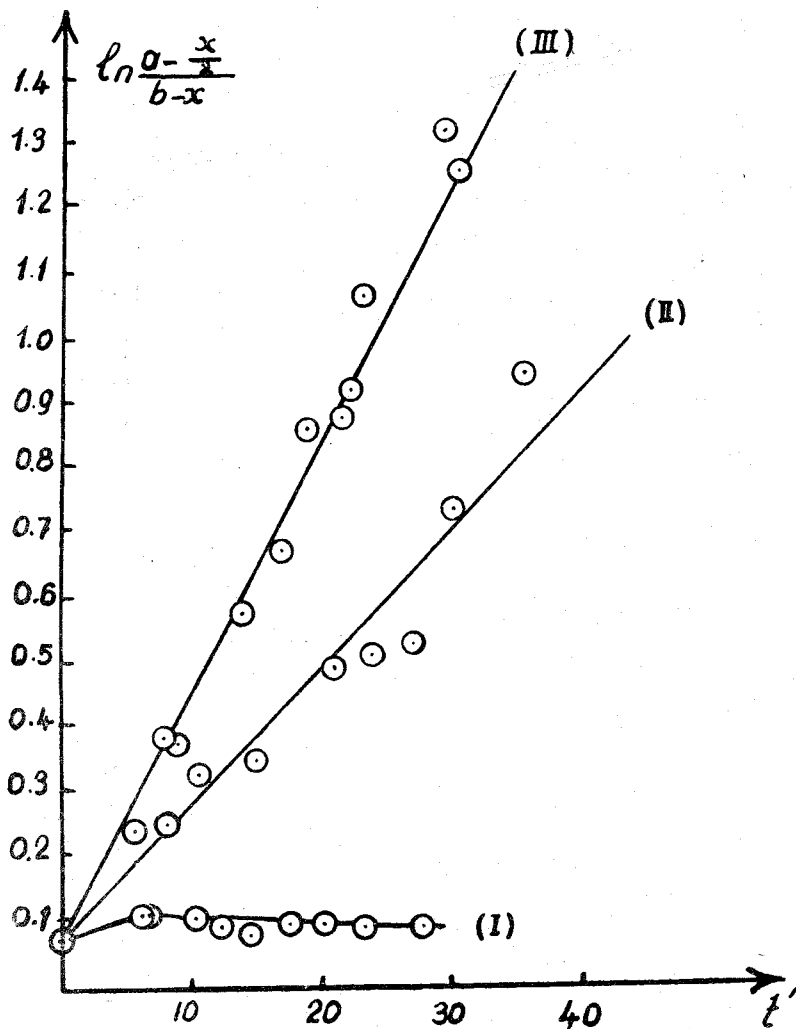


Fig. 16

$a = 1.086 \times 10^{-5}$  mol/lit  $\text{H}_2\text{O}_2$ ,  $b = 1.018 \times 10^{-5}$  mol/lit  $\text{Fe}^{++}$ ,  $t = 15.00^\circ\text{C}$

At the beginning pH = 5.20... (I), Table 33.

At the end pH = 1.70 ( $\text{H}_2\text{SO}_4$ )... (II), Table 33

(III)... Table 34.

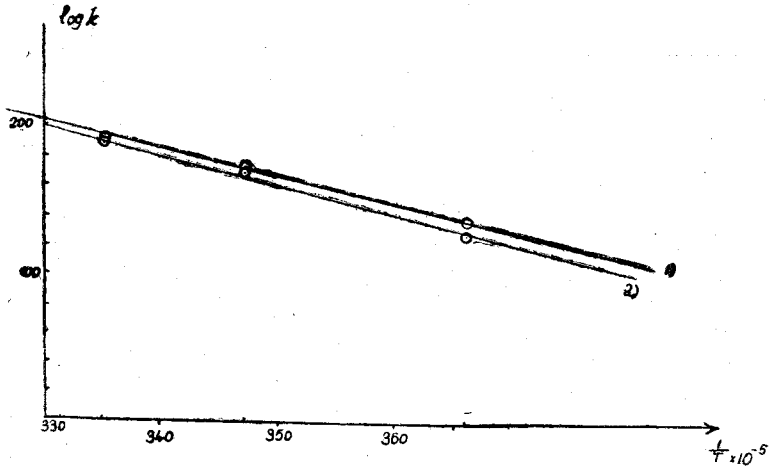


Fig. 17

(1) pH = 1,80

(2) pH = 0,10