react with potassium iodide or with iodine have been shown to have sensitizing effects.

7. An emulsion having no excess of silver nitrate or potassium iodide has been prepared and found to be sensitive.

8. Washing to remove the excess of potassium iodide does not make the regular iodide emulsion sensitive.

9. The amount of moisture present in the emulsion has been shown to have considerable effect on the sensitiveness.

10. In general, sensitization has been effected by treatment with a chemical which would react with potassium iodide to remove it, or remain in the emulsion to combine with any iodine liberated.

11. The "non-sensitive" emulsions have been found to be sensitive when a strongly alkaline developer was employed.

12. It is concluded that the apparent non-sensitiveness of silver iodide emulsions is due primarily to adsorbed potassium iodide, secondarily to the absence of a sensitizer, gelatin not playing that role; and that ordinary, apparently non-sensitive, silver iodide emulsions are truly sensitive when a sufficiently strongly alkaline developer is used.

BOULDER, COLORADO

[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY FERRIC SALTS. II

BY VAN L. BOHNSON AND A. C. ROBERTSON

RECEIVED MAY 21, 1923

It has been known for some time that the decomposition of hydrogen peroxide is accelerated by the presence of iron salts in solution. The most recent quantitative investigations are those which were made by von Bertalan,[1] by Duclaux,[2] by Mummery,[3] and by one of the writers of this paper.[4] The purpose of the present paper is to present the results of subsequent experiments which necessitate certain modifications in the conclusions reached by these investigators. The work already reported was done with very dilute solutions of the catalyzing salts (up to 5 millimoles per liter). More concentrated solutions than this could not conveniently be used by the two first-named writers, owing to the difficulty of following the more rapid reactions by the cumbersome method of titrating samples with permanganate. On the other hand, the gasometric method offers an accurate means of measuring the rate of a reaction so rapid as to be entirely completed in 5 minutes.

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[1] von Bertalan, *Z. physik. Chem.*, **95**, 328 (1920).

[2] Duclaux, *Bull. soc. chim.*, **31**, 961 (1922).

[3] Mummery, *J. Soc. Chem. Ind.*, **32**, 889 (1913).

[4] Bohnson, *J. Phys. Chem.*, **25**, 19 (1921).

Optical Evidence of an Intermediate Compound

Somewhat indirect evidence led to the suggestion in the previous paper[4] that ferric acid (H_2FeO_4) is formed by the reaction between hydrogen peroxide and the iron salt, the ferric acid being subsequently reduced with the evolution of oxygen.

This hypothesis has been tested by photographing the absorption spectra of solutions of (1) ferric chloride alone, (2) barium ferrate dissolved in acetic acid, (3) potassium ferrate, and (4) mixtures of hydrogen peroxide and ferric chloride.[5] The source of illumination and reference was the iron arc; a quartz spectrometer was used, the solutions being contained in a quartz absorption cell. Instead of varying the concentration or thickness of the solution, the times of exposure were increased logarithmically and a number of photographs taken on the same plate in the usual manner. The reaction mixtures were chilled in order to avoid too rapid disappearance of the supposed intermediate compound.

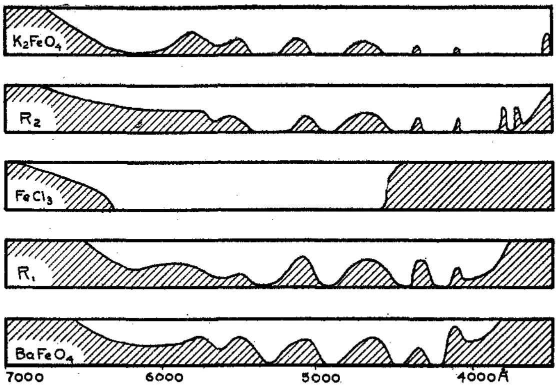

Fig. 1

Some of the results are shown graphically in Fig. 1, the shaded portion of which represents the absorption bands, plotted on a uniform scale of wave lengths in Ångstrom units. A striking similarity between the bands for the two ferrates and for the reaction mixtures (R_1 and R_2) is obvious. On the other hand, a solution of ferric chloride of much greater than equivalent concentration shows no such characteristic bands in the yellow and green and is totally opaque to the violet. When hydrogen peroxide is added to the ferric chloride, transmission of violet lines takes place and absorption bands appear in the yellow and green. These results lead to the conclusion that the original hypothesis was correct; namely, that FeO_4 ions are present in the reaction mixture. The difference between R_1 and R_2 in the extreme violet suggests that the former reaction was

[5] It was suggested by von Bertalan (Ref. 1) that an optical method might indicate the nature of the iron compound present.

nearer completion, there being more ferric chloride present, decreasing the transmission in that region. None of the solutions transmitted wave lengths shorter than 3500.

The Mechanism of the Reaction

It was suggested by von Bertalan that the reaction takes place in the following stages,

$$H_2O_2 + 2\,Fe^{+++} \longrightarrow 2\,Fe^{++} + 2\,H^+ + O_2 \qquad (1)$$

$$H_2O_2 + 2\,Fe^{++} + 2\,H^+ \longrightarrow 2\,H_2O + 2\,Fe^{+++} \qquad (2)$$

the sum of the two yielding the equation for the decomposition of hydrogen peroxide. It is possible to test the probability of these reactions taking place by means of the criterion suggested by Bray,[6] that each of such a cycle of changes should be accompanied by a diminution of free energy. The standard free energy changes for Reactions 1 and 2 can be calculated, using the following values for the free energy of formation at 25°, in calories, given by Lewis and Randall:[7] H_2O_2 (aq.), —31,470; Fe^{+++}, —3120; Fe^{++}, —20,350; H_2O (l), —56,560; H^+, 0; O_2 (g), 0.

From these data, ΔF°_{298} for Reaction 1 can be shown to be —2990 cals., while for Reaction 2 it is —47,190 cals. The difference in these values indicates that while ferrous ion may be oxidized to ferric ion by hydrogen peroxide in acid solution, it is not so probable that subsequent reduction will take place.

We have shown experimentally that ferrate ion is formed by the action of hydrogen peroxide on ferric salts. The following must therefore take place,

$$3\,H_2O_2 + 2\,Fe^{+++} + 2\,H_2O \longrightarrow 2\,FeO_4^{--} + 10\,H^+ \qquad (3)$$

with subsequent reduction of the ferrate ion according to one or both of the following,

$$2\,FeO_4^{--} + 3\,H_2O_2 + 10\,H^+ \longrightarrow 2\,Fe^{+++} + 3\,O_2 + 8\,H_2O \qquad (4)$$

or

$$2\,FeO_4^{--} + 2\,H_2O_2 + 8\,H^+ \longrightarrow 2\,Fe^{++} + 3\,O_2 + 6\,H_2O \qquad (5)$$

with subsequent oxidation of the ferrous ion, or perhaps only decomposition of the ferrate ion by acid,

$$2\,FeO_4^{--} + 10\,H^+ \longrightarrow 2\,Fe^{+++} + 1^1/_2\,O_2 + 5\,H_2O \qquad (6)$$

or

$$2\,FeO_4^{--} + 8\,H^+ \longrightarrow 2\,Fe^{++} + 2\,O_2 + 4\,H_2O \qquad (7)$$

Unfortunately no data are available for the free energy of formation of such substances as chromate, permanganate and ferrate ion. The only unknown value for calculating ΔF°_{298} for Reactions 3, 4, 5, 6 and 7 is that for FeO_4^{--}. By an application of the known data to Equations 3 and 4 we are led to the conclusion that F°_{298} must have a large negative

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[6] Bray, THIS JOURNAL, **43,** 1262 (1921); **45,** 1251 (1923).

[7] **Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 607.**

value, probably between —106,885 cals. and —182,155 cals. Whatever its value,[8] since it is the same in all the reactions, it can be readily shown that the diminution in free energy is greater in Reactions 4 and 5 than in 6 and 7. This is in accord with the experimental result reported in the previous paper that the reduction of the ferrate ion takes place extremely readily in the presence of hydrogen peroxide. It can also be shown that ΔF°_{298} is greater in Reaction 4 than in Reaction 5, and greater in 6 than in 7, which leads to the conclusion that ferrous ion is less likely to be formed. We have shown experimentally that it is not present after the reaction is completed. It is also true that during the reaction the addition of a little potassium ferricyanide yields a blue precipitate, but this, in the presence of hydrogen peroxide, is at best very questionable evidence of the presence of ferrous salt (as pointed out by Mummery[3]) since the ferricyanide may be changed to ferrocyanide and react with the ferric salt.

Experimental Study of the Rate of Reaction

This opportunity is taken of very briefly describing the method of determining the rate of reaction under various conditions. This method, which was used also in obtaining some data on promoter action to be discussed in a subsequent paper, was fundamentally the same as that used in earlier studies,[4,9] with some modifications and improvements. The materials used were the same as in the earlier studies. The reaction was allowed to take place in a specially designed flask supported in a thermostat by a shaking device, and the gas evolved was measured in a buret kept at the same temperature as the thermostat. The catalyst solution in the flask having been allowed to attain the temperature of the bath, a known amount of Perhydrol (30% hydrogen peroxide) was dropped into it, the shaking begun, and the volume of gas evolved was measured at known time intervals. In order to avoid difficulties due to hydrolysis of the catalysts, concentrated acidified solutions of the latter were prepared; these were diluted just before using, in such a manner that a known excess of free acid was present in the reaction mixture.

Calculations—Explanations of Tables

As previously noted,[4] the reaction, due to disturbing effects, is not strictly monomolecular, the values obtained for "velocity constants" varying

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[8] Making the following arbitrary assumptions regarding F°_{299} for FeO_4^{--}, ΔF°_{298} for the several reactions is as follows.

	CALORIES				
F°_{298}	Reaction 3	4	5	6	7
−110,000	− 6,230	−144,310	−97,120	−69,040	−43,060
−140,000	− 66,230	− 84,310	−37,120	− 9,040	+13,060
−170,000	−126,230	− 24,310	+22,280	+50,960	+73,060

The largest value estimated is thus shown to be too large, as FeO_4^{--} is rapidly reduced in acid solution, even when hydrogen peroxide is not present.

[9] Bohnson, *J. Phys. Chem.*, **24,** 677 (1920).

slightly as the reaction proceeds. For the purpose, therefore, of comparing the rates of decomposition under different conditions, a velocity constant was calculated only over the second quarter of each reaction. A typical experiment, data for which are given in Table I, will serve to illustrate this method of calculation. In this table, as in all subsequent ones, the following abbreviations are used:

t = Time in minutes; T = temperature; N = normality of free acid present; C_{Fe} = concentration of iron salt in milligram-atoms of iron per liter; $C_{H_2O_2}$ = concentration of hydrogen peroxide in millimoles per liter.

Table I

Data for Typical Experiment

$T = 30°$ $N = 0.076$ $C_{Fe} = 10.0$ $C_{H_2O_2} = 130$

Total volume of gas evolved, 46.4 cc.; in second quarter of reaction, 11.6 to 23.2 cc.; time for second quarter of reaction, 18.7 min.; $K_R = 94$

t		0	4	10	18	24	28	
Cc. of O_2 evolved	0	4.9	8.2	12.7	18.0	21.5	23.6	46.4

The volume of oxygen evolved was carefully plotted against the time in minutes, and by interpolation from this curve the time was determined in which the second 25% of gas was evolved. The total volume of gas evolved was determined by a simultaneous experiment using the same concentration of hydrogen peroxide but a much larger concentration of catalyst, which caused the reaction in this experiment to reach completion in a very short time.

The usual expression for the monomolecular velocity constant, $0.4343\ K = (1/t) \log (a/(a - x))$, now becomes greatly simplified (since a is always 75%, and $a - x$ always 50% of the total gas evolution) to $K_1 = (1/t) \log (^3/_2)$, or $K_1 = 0.1761/t$. To avoid decimals, this constant is multiplied by 10^4, and the value so obtained called K_R. This method of expressing the rate of the reaction proved to have several advantages: (1) a shorter time was required to complete a set of experiments; (2) routine calculation was reduced to a minimum; (3) much closer duplication of results was secured than by averaging values obtained by the usual method, and (4) the figures obtained represent comparable conditions. It will be noted that the results obtained are in effect a comparison of the times necessary for the completion of equal fractions of the reaction under various conditions, and that K_R is a measure of the relative rate of the reaction.

In order to save space, complete data for the remaining experiments are omitted, only summaries being given. The values reported for the velocity constants are supported by numerous other determinations, not given, of duplicate and intermediate values. There was no difficulty in checking within 3%.

Conditions of Experiment.—Unless otherwise noted, the concentration of free acid was uniformly 0.076 *N*, that of the hydrogen peroxide 130 millimoles per liter, and the temperature 30°. All of von Bertalan's experiments were performed in complete darkness. This precaution having been found to be unnecessary, all of our experiments were performed in the diffused light of the laboratory.

The Effect of Ferrous Sulfate

It has already been shown[1] that the sulfates of both ferrous and ferric iron accelerate the decomposition of hydrogen peroxide, although less effectively than equivalent concentrations of either ferric chloride or nitrate.[4,10] It might be expected that equivalent concentrations of ferrous and ferric sulfates would have an identical effect; although von Bertalan worked with both these salts, his results do not shed much light on this particular problem. A more direct comparison of the effect of these two salts is possible by an examination of the data in Table II, which are shown graphically in Fig. 2.

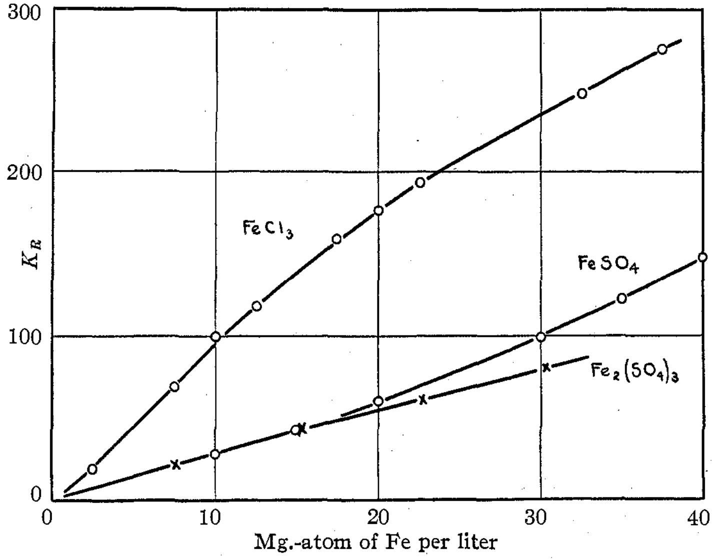

Fig. 2

Table II

Comparative Effects of Ferrous and Ferric Sulfates

$T = 30°$ $N = 0.076$ $C_{H_2O_2} = 130$

Ferrous sulfate				Ferric sulfate			
C_{Fe}	K_R	C_{Fe}	K_R	C_{Fe}	K_R	C_{Fe}	K_R
10	28	30	99	7.6	21	30.4	81
15	43	35	123	15.2	43	60.8	156
20	60	40	148	22.8	60	...	...

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[10] See also Fig. 2.

It will be noted that the curves for ferrous and ferric salts are coincident for concentrations of less than about 20 milligram-atoms of iron per liter, at which point the effect of the ferrous salt appears to become relatively and progressively greater. The reason for this divergence clearly lies in the fact that the ferrous sulfate is oxidized to ferric sulfate by the hydrogen peroxide, according to the equation, $2FeSO_4 + H_2O_2 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2H_2O$, with a necessary decrease in the concentration of free sulfuric acid in the solution. The original concentration of acid being 0.076 N, it is evident that the oxidation of 20 millimoles or more of ferrous sulfate removes a relatively large proportion of the acid; since, as has been shown in other papers, free acid has a marked retarding effect on this catalysis, a decrease in its concentration causes an accelerated reaction. To this phenomenon is probably due the apparently greater catalytic effect of ferrous salt noted by Mummery.[3]

Von Bertalan claims to have found ferrous salt present after the completion of the reaction. This we did not find to be the case; on the contrary, when either ferrous or ferric salt is used as the catalyst, qualitative tests show it to be in the more highly oxidized form after the reaction is completed. During the progress of the reaction, the iron is present partly at least in a still higher state of oxidation. Quantitative measurements showed that in all cases in which ferrous sulfate was used as a catalyst, the volume of oxygen evolved was not equivalent to the amount of hydrogen peroxide used, a portion of the latter having been utilized in the oxidation of the iron. It is possible that a rapid method for the quantitative estimation of ferrous and ferric salts in the presence of each other might be based upon a measurement of the oxygen evolved from a given quantity of hydrogen peroxide.

It is incorrect, therefore, to speak of the catalytic effect of ferrous ion, which is oxidized instantaneously to ferric ion, and appears as such after the completion of the reaction; whatever accelerating effect it may have is due to the formation of the ferric salt. There seems to be need of further investigation of the action of hydrogen peroxide on certain alcohols and organic acids in the presence of ferric salts, which are reported to have no catalytic influence,[11] while ferrous salts are said to have such an effect. Our preliminary experiments on this problem have led us to believe that ferric chloride at least is effective.

The Catalytic Effect of Non-ionized Salt

All previous work, as has been noted, was done with very dilute solutions of the iron salts. Von Bertalan, using only the sulfates, concluded that the rate of reaction was proportional to the concentration of iron ions.

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[11] Fenton, *J. Chem. Soc.*, **65**, 899 (1894). Fenton, *Proc. Chem. Soc.*, **14**, 119 (1898). Doroschevski and Bardt, *J. Russ. Phys. Chem. Soc.*, **46**, 754, 1669 (1914).

Duclaux, from an examination of our own previous work, concurred in this conclusion, even suggesting that this reaction is the best means of measuring the ionization and hydrolysis of iron salts, on the supposition that non-ionized salt is ineffective. This conclusion is supported by the facts that: (1) the effects of ferric chloride and nitrate in dilute solution are identical; (2) the suppression of ionization by added sodium or potassium salts is accompanied by a retardation of the reaction; (3) the addition of such a non-ionized salt as mercuric chloride had little or no effect, and (4) the products of hydrolysis had no effect.

On the other hand, the marked difference between the catalytic activities of ferric chloride and ferric sulfate is greater than might be expected from the different ionization of the two salts. This difference is more readily explained by assuming that the molecular salt has an activity independent of that of the ions. Such an assumption would be in accord with a well-known hypothesis (the "dual theory" of catalysis) regarding catalytic processes, which has been discussed by a number of investigators.[12]

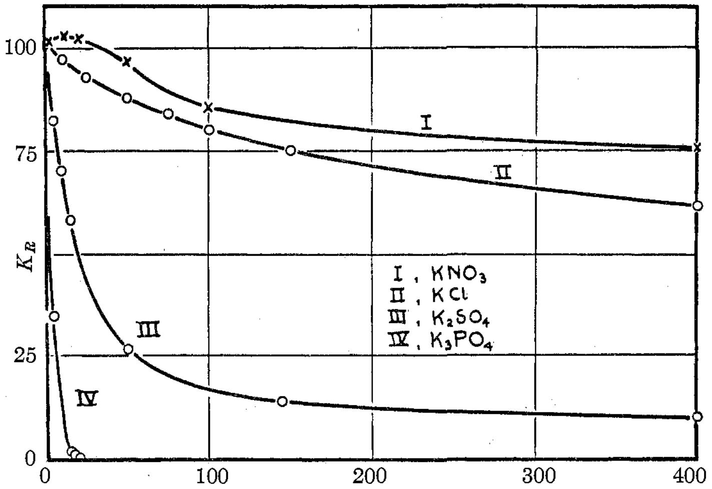

Fig. 3

The curves shown in Fig. 3 (plotted from the data of Table III) represent the change in the catalytic activity of a constant concentration of ferric chloride (10 millimoles per liter) in the presence of increasing quantities of various neutral salts. One result of the addition of these salts is obviously the formation by metathesis of another ferric salt existing at least partly in the molecular state. In this connection a comparison of

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[12] See, among others, Acree, *Am. Chem. J.*, **37**, 410 (1907); **38**, 258 (1907); **49**, 353 (1913). Snethlage, *Z. physik. Chem.*, **85**, 255 (1913). Senter, *J. Chem. Soc.*, **91**, 467 (1907).

the curves indicates that the several molecular species vary in activity, the nitrate being most active. Another effect of the inhibiting salt would be the suppression of the ionization of the iron salt; however, the addition of a quantity of neutral salt 40 times as great as that of the ferric chloride present is insufficient to inhibit the reaction completely. In the case of potassium nitrate, the addition of 188 times as much decreased the velocity constant only to 60, which represents a greater rate than would be expected on the supposition that iron ions alone are active. The rapid decrease in activity when potassium phosphate is added may be due to the removal of iron as a complex ferric-phosphate ion.[13]

Table III

Effect of Neutral Salts on Ferric Chloride Catalysis

$C_{Fe} = 10.0$

KCl		KNO_3		K_2SO_4		K_3PO_4	
C	K_R	*C*	K_R	*C*	K_R	*C*	K_R
0	100	0	100	0	100	0	100
10	98	2	101	5	82	1	82
25	93	5	103	10	70	5	35
50	88	10	103	15	58	10	6
75	83	20	102	20	47	16	2.2
100	79	50	96	50	26	18	1.1
150	75	100	86	150	14	20	0.8
400	62	400	75	400	10	..	...
...	...	1880	60	...	...	..	...

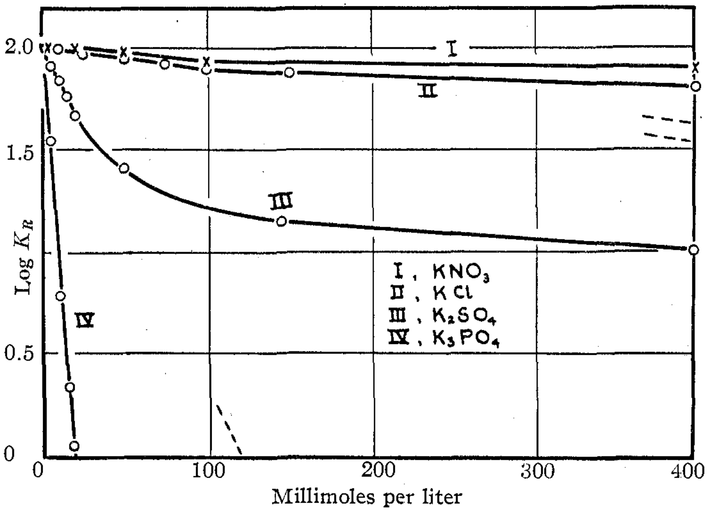

Fig. 4

It may be concluded, therefore, that in this reaction both the ions and the molecules are catalytically active.

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[13] Weinland and Ensgraber, *Z. anorg. Chem.*, **84**, 340 (1913).

In Fig. 4 the same data are plotted with the logarithms of K_R as ordinates. An examination of the curves thus obtained shows that they begin as straight lines, indicating that the first result of the addition of neutral salt is an exponential function of the concentration. The curve changes direction and proceeds again as a straight line with a different slope than formerly.[14] A second effect is thus indicated, of smaller magnitude than the first one. These facts admit of two interpretations.

1. The first segment in the curve for all salts but potassium chloride may represent the metathetical reaction, while the second represents the suppression of the ionization of the newly formed salt. This hypothesis fails to explain the marked break[15] in the potassium chloride curve. The single effect of the potassium phosphate curve is explained by the formation of a complex ion.
2. The two segments may represent two molecular forms of somewhat differing activity. The reason for such a difference is not clear, but the suggestion, which proves useful in a study of the accelerating effect of copper salts, will be discussed in a subsequent paper.

The Temperature Coefficient

In Table IV are shown the results of a number of experiments to determine the temperature coefficient of the reaction in the presence of different concentrations of catalyst and of acid. The results seem to be somewhat in accord with the assumption of the radiation hypothesis that "any agency which increases the reaction velocity diminishes the temperature coefficient,"[16] although the decrease in values with increasing con-

TABLE IV

EFFECT OF CATALYST AND ACID ON THE TEMPERATURE COEFFICIENT

C_{Fe}	$K_{40°}$	$K_{30°}$	$K_{20°}$	K_{40}/K_{30}	E_1	K_{30}/K_{20}	E_2
(a) Ferric Chloride $N = 0.076$							
2.5	75	19.5	4.1	3.85	25,300	4.75	27,400
5	171	46	10.6	3.72	24,650	4.34	25,800
10	326	94	..	3.47	23,350	..	....
20	607	177	43.5	3.43	23,140	4.07	24,670
50	1107	320	..	3.46	23,280	..	....
(b) Ferric Chloride $N = 0.038$							
2.5	145	39.5	..	3.67	24,410	..	....
5	321	89.3	..	3.60	24,010	..	....
(c) Ferric Sulfate $N = 0.076$							
7.6	75	21	5.6	3.57	23,880	3.75	23,230
60.8	486	156	48.5	3.12	21,820	3.22	20,530

Mean value for E = 23,960 cals.

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[14] These facts are more marked when all of our data are plotted on a large scale.

[15] When copper salts are present in addition (markedly increasing the reaction rate), there is no break in the potassium chloride curve.

[16] Lewis, *J. Chem. Soc.*, **109**, 796 (1916).

centration of catalyst is not particularly marked. It may be noted that the change of coefficient with temperature is not so great with sulfate as with chloride, the results for the former agreeing substantially with those of von Bertalan, who found $K_{40}/K_{30} = 3.2$ and $K_{30}/K_{20} = 3.3$.

In the columns E_1 and E_2 are shown the "critical increments" of the reaction according to the radiation hypothesis, calculated[17] from the expression $\frac{d \log K}{dT} = \frac{E}{RT^2}$. The mean value of the critical increment is 23,960 cals. per mole of hydrogen peroxide decomposed; this, when substituted in the expression $E = Nh\nu$ gives 2.5×10^{14} for the frequency of the active radiation, the wave length of which would therefore be 1.2×10^{-4} cm. = 1.2μ.

Summary

1. This paper is a continuation of a former study of the catalytic decomposition of hydrogen peroxide by ferric salts. The existence of an intermediate compound, H_2FeO_4, previously suggested, has been confirmed by a spectroscopic examination of the reaction mixture.

2. The free energy of formation of ferrate ion, FeO_4^{--}, is shown to be in the neighborhood of —140,000 cals. Free-energy relationships show that the ferrous-ferric ion intermediate reactions postulated by von Bertalan are improbable.

3. The catalytic effect of ferrous salts is shown to be due solely to the fact that they are oxidized first to ferric salts.

4. The molecules of ferric salt, as well as the ions, appear to exert catalytic activity. It is possible that there are two molecular forms of differing activity.

5. The temperature coefficient of the reaction shows the "critical increment" of the reaction to be 23,960 cals., the frequency of the active radiation 2.5×10^{14}, and its wave length 1.2μ.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

A WATER-JACKETED HYDROGEN ELECTRODE

BY HENRY S. SIMMS

RECEIVED MAY 21, 1923

A hydrogen electrode cell has been designed to give rapid and accurate results and at the same time offer greater convenience in manipulation when working with certain fluids, than other types of cells. The results have been sufficiently satisfactory to warrant publication of a description of the cell.

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[17] For the methods of these calculations, see among others, Daniels and Johnston, THIS JOURNAL, **43,** 53, 72 (1921).