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PROMOTER ACTION IN HOMOGENEOUS CATALYSIS. II MECHANISM OF THE PROMOTION BY COPPER SALTS IN THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY FERRIC SALTS[1]

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In a previous paper[2] the interpretation of the experimental data led to the conclusion that the function of the copper as the promoter in the ferric salt catalysis of hydrogen peroxide was that of a secondary catalyst, accelerating both the formation and subsequent decomposition of the intermediate product (ferric acid). The mechanism of that promotion was not made clear at that time.

The purpose of this paper is to present further data and by a critical examination of the data of the former paper, to show the probable mechanism of the promotion effect. In the previous paper the classification of Pease and Taylor[3] was used in order to facilitate a systematic interpretation of the results. Further work has shown that the result of using this terminology is to obscure the relationships rather than to render them more clear, hence it has been abandoned completely. Investigation of the phenomenon of promotion should go further than merely finding whether "A" activates "B" or the converse. In fact the term "activation" loses its significance, once it has been shown that it is highly probable that we have a certain definitely known mechanism—it does not matter whether we call it a catalytic effect or a chemical reaction—in these homogeneous reactions. To find the mechanism of the promotion is a highly important matter, since that knowledge will facilitate a thorough and searching study of other examples. On the other hand, because of the difficulties inherent in heterogeneous systems, the term "activation" will prove useful for some time in discussing the phenomenon of promotion in such systems.

It did not seem probable to the writer that a substance should act either alternately or simultaneously as a catalyst for the oxidation and reduction of the same compound. Therefore, the working hypothesis was developed that the ferric acid formed as the intermediate in the catalytic decomposition of hydrogen peroxide by ferric salts reacts chemically with the cupric salt used as the promoter, thereby producing a compound which is more active catalytically than either the cupric salt or the ferric salt.

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[1] The work discussed in this paper constitutes part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Bohnson and Robertson, THIS JOURNAL, **45**, 2521 (1923).

[3] Pease and Taylor, *J. Phys. Chem.*, **24**, 241 (1920).

The apparent effect of such a reaction would be an activation of the ferric salt serving as the catalyst, or a displacement of an equilibrium between active and inactive molecular species of the catalyst.

In considering this hypothesis, it is well first to state the properties of one of the higher oxides of copper. Copper peroxide, $CuO_2 \cdot H_2O$, is a dark brown powder, which readily decomposes upon standing, or by solution in acids. It also rapidly auto-reduces hydrogen peroxide by contact. This last property is much the same as that of ferric acid which indeed it resembles a great deal, except in the matter of solubility. Assuming that the substance is more rapidly auto-reduced by hydrogen peroxide than ferric acid itself, then we have a possible key to the phenomenon in the system that we are considering. Briefly it is this: the hydrogen peroxide oxidizes the ferric salt to ferric acid, and this ferric acid—a very unstable substance—oxidizes the cupric salt to cupric acid more rapidly than the hydrogen peroxide itself would be capable of doing. The cupric acid then displays its property of rapidly auto-reducing hydrogen peroxide (probably more rapidly than ferric acid would) and as a result there is an effect much greater than had either copper or iron been present alone in the same concentrations.

Existence of Cupric Acid in the Promoted Reactions

Copper forms at least two higher oxides, CuO_2 and Cu_2O_3. The first is best formed in alkaline solution at 0° by the action of hydrogen peroxide upon copper hydroxide,[4] but has also been made by adding concd. hydrogen peroxide to copper sulfate solution at 6°. This substance is the one that might well be expected to exist in the reaction being studied. Copper peroxide is itself insoluble, but dissolves in acids and then probably exists as the acid H_2CuO_3. It is interesting to note that Moser[5] has observed that copper peroxide acts catalytically in decomposing solutions of hydrogen peroxide, but did not attempt to distinguish this from auto-reduction.

A second, higher oxide of copper is said to be made in an analogous manner to that for ferric acid, namely, by bubbling a stream of chlorine through a suspension of copper hydroxide in a concentrated solution of potassium hydroxide. A dark red solution is reported to be formed, from which a barium salt may be precipitated. This barium salt seems to be a chemical individual, but the existence of the potassium and sodium salts is in question.[6] The writer's attempts to prepare this oxide for spectroscopic studies were fruitless. The evidence for the existence of $CuO_2 \cdot H_2O$, on the contrary, is quite definite and is substantiated by a large number of workers.

One of the earliest investigators, W. Schmid,[7] held the opinion that the

[4] Thenard, *Ann. chim. phys.*, [2] **9**, 51 (1818).

[5] Moser, *Z. anorg. Chem.*, **54**, 127 (1907).

[6] Aldridge and Applebey, *J. Chem. Soc.*, **121**, 238 (1922).

[7] Schmid, *J. prakt. Chem.*, **98**, 136 (1866).

oxide CuO_2 is not formed in the absence of ferrous salts. Krüss[8] denied this and proved that it might be made in the absence of iron, but admitted that the presence of a trace of ferric iron hastened its formation.

In order to verify the work of the previous investigators as to the effect of ferric salt upon the formation of copper peroxide, the effect of cupric salts upon the catalytic decomposition of hydrogen peroxide was studied with and without the added ferric salt. The probable series of reactions for the copper alone is,

$$Cu^{++} + H_2O_2 \longrightarrow CuO_2 + 2H^+ \tag{1}$$
$$CuO_2 + H_2O_2 + 2H^+ \longrightarrow Cu^{++} + 2H_2O + O_2 \tag{2}$$

the sum of which is the reaction for the decomposition of hydrogen peroxide. It will be noticed that Equation 1 indicates that the presence of free acid decreases the amount of copper peroxide formed. Acids also dissolve the copper peroxide, forming the compound that will be referred to as cupric acid. This is easily shown experimentally. As stated before, solid copper peroxide may be formed by adding concd. hydrogen peroxide to a chilled solution of copper sulfate. Better yields are obtained when the solution is alkaline, but when acid is added to the copper sulfate, no *solid* copper peroxide is obtained.

Now, since the reaction rate of the catalytic decomposition of hydrogen peroxide is proportional to the amount of intermediate present, and since the intermediate is known to be copper peroxide, it is possible to follow its rate of formation under certain conditions. To test the effect of ferric salts upon its formation, a series of experiments was carried out. In one case the reaction velocity for the catalytic decomposition of hydrogen peroxide was determined when cupric salts alone were used, in a second when ferric salts alone were used, and in a third when a mixture of the two was used. It was found that the addition of a very small concentration of ferric salt did indeed have an effect upon the catalytic decomposition of hydrogen peroxide by cupric salts. The single effect of the ferric salt was

TABLE I

EFFECT OF LOW CONCENTRATION OF FERRIC SULFATE UPON RATE OF CUPRIC SULFATE CATALYSIS

Acid, 0.076 *N*

Concn. of Cu	Concn. of Fe	K_{total}	$K_{\text{corr.}} = (K_{\text{total}} - K_{\text{Fe}})$
100	0	1.4	1.4
	0.1	3.4	3.2
	1.0	21.0	18.8
	2.0	30.5	26.1
	5.0	42.0	32.8
	10.0	61.0	39.0
	30.0	143	66
0	5	11	11
0	30	77	77

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[8] Krüss, *Ber.*, **17**, 2594 (1884).

then subtracted from the total effect (K_{total}), and it was found that the corrected rate ($K_{\text{corr.}}$) was still much larger than that for the cupric salt alone. The data are shown in Table I and Fig. 1. Since the effect due to the iron is relatively small, and has been corrected for, the additional effect is most probably due to the formation of more cupric acid. Hence, this effect was taken as evidence to show that the presence of the ferric salt does catalyze the formation of copper peroxide, thus confirming the statements of earlier investigators whose experiments were not quantitative, nor so extensive. Indeed, the amount of copper peroxide formed seems to be proportional to the amount of added ferric salt below a concentration of about one millimole per liter for the iron. Above this region the relationships are, no doubt, involved and the data are, therefore, difficult to interpret. It is the region of lower iron concentration that is the more interesting, for it is here we are able to satisfy that most searching criterion of a catalyst, namely, that a minimal amount of the substance accelerates the reaction. Here we have such a condition, for the exceedingly slow reaction is caused to proceed at a tremendously increased rate. The increase in rate observed is about 2000%, while in the case where cop-

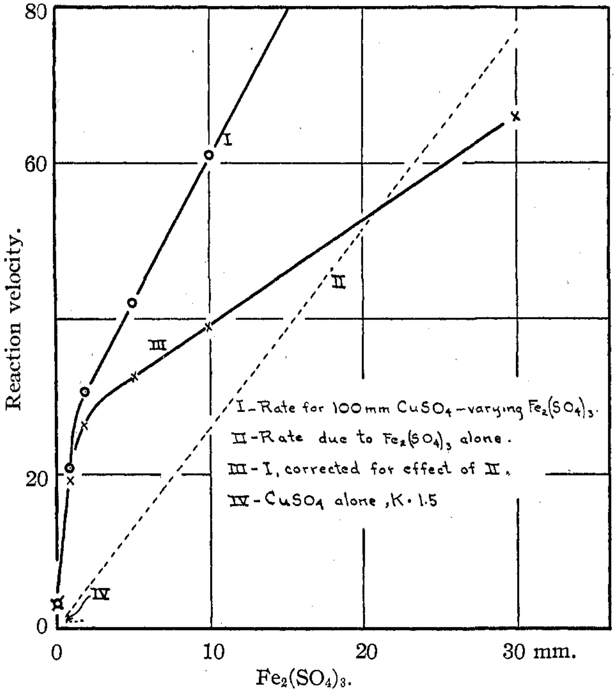

Fig. 1.—The effect of low concentrations of iron upon the cupric salt catalysis of hydrogen peroxide. (Mm. = millimoles.)

per is added to the iron, a reaction of appreciable speed is merely increased until the increase in rate for corresponding conditions would probably be somewhat less than 100%.

It is also possible to follow the catalytic formation of cupric acid by means of absorption spectra. This is made possible by the fact that copper peroxide is soluble in dil. acetic acid, giving a green solution that keeps for several days without a great deal of decomposition, a fact that does not seem to be stated in the literature.

Copper peroxide for this study was prepared by a modification of the method of Weltzien.[9] A solution of cupric sulfate was precipitated with ammonium hydroxide until the first faint color of the copper-ammonia complex was apparent; hydrogen peroxide was then added to the chilled solution while the mixture was shaken until the addition of more was attended by the decomposition of the reagent. The copper peroxide thus prepared is brown when freshly prepared and pure, but turns olive-green upon standing, or in the presence of an excess of the hydrogen peroxide. The supernatant liquid was decanted and the precipitate washed by decantation five or six times until the washings gave no test for ammonia or copper. The brown copper peroxide was dissolved in dil. acetic acid and the solution kept cool until needed. Difficulty was encountered ineffecting true solution, since the acetic acid tended to peptize the copper peroxide. However, by filtration through asbestos mats of increasing fineness, all the suspended matter was removed and a solution obtained which showed only the usual slight Tyndall effect.

Several absorption spectra of cupric acid prepared in this way were taken. They gave a characteristic absorption, as shown in the spectrograms. Upon treatment with a few drops of concd. sulfuric acid, these solutions faded from a green to a less intense blue, evolving gas at the same time. The solutions obviously were of practically the same copper concentration, but now contained copper sulfate and not cupric acid. Absorption spectra were taken as before. Inspection shows that the solution of cupric acid is opaque in the violet, 3400Å., while a solution of cupric sulfate of identical concentration transmits quite well in that region. Indeed, the difference is so great that in order to get the characteristic peaks of the solutions of cupric acid, a longer cell had to be used as it was impracticable to prepare a more concentrated solution of this reagent.

This difference showed that it was practical to follow the formation of cupric acid spectrographically. Accordingly, a number of experiments were devised with this in mind.

Spectrograms were taken of solutions of (1) cupric sulfate alone, 50 millimoles per liter; (2) cupric sulfate plus hydrogen peroxide; (3) cupric sulfate plus a small amount of ferric sulfate (0.2–0.8 millimole per liter) plus hydrogen peroxide; (4) ferric sulfate (0.8 millimole per liter) plus hydrogen peroxide.

In order that the results might be comparable, the same concentrations of hydrogen peroxide and salts were used in the various solutions. A definite time and order of mixing was also used so as to permit photography

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[9] Weltzien, *Ann.*, **140**, 207 (1866).

of the absorption during corresponding parts of the reaction. A quartz cell and spectrograph were used as in the previous article. The iron arc was used as a source of illumination, and as a standard of wave length.

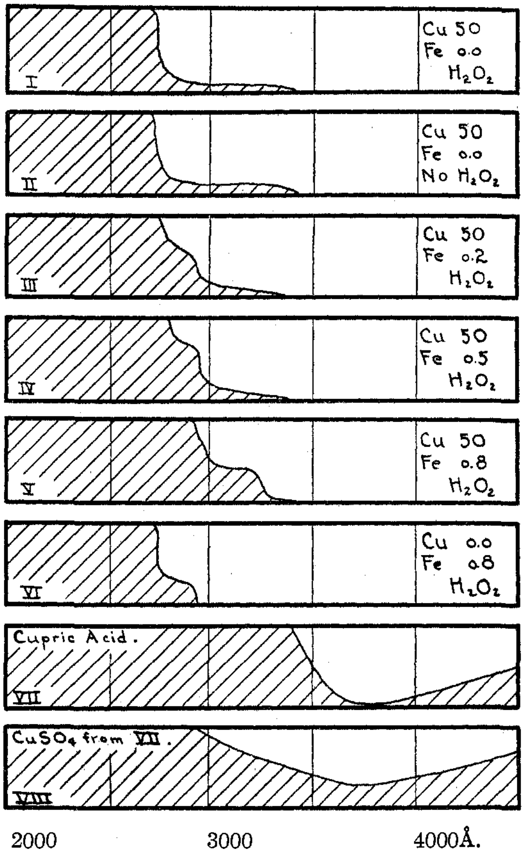

Fig. 2.

The results are shown in Fig. 2 where the logarithm of exposure is plotted against wave lengths in Ångström units as abscissa. Upon comparing Spectrogram I with Spectrogram II it will be noticed that the addition of hydrogen peroxide to a solution of copper sulfate changes the absorption very little, if at all. This means that little cupric acid—which absorbs in the region where copper sulfate is transmissive—had been formed. The absorption is practically identical, hence it may be concluded that hydrogen peroxide in acid solution forms little cupric acid, a conclusion in agreement with the kinetic experiments. However, the addition of a small amount of ferric sulfate to such a solution moves the region of transmission toward the red, from 2740Å. to 2920Å.

Since a solution of ferric sulfate and hydrogen peroxide which has the same concentration of iron as that added to the solution of cupric sulfate and hydrogen peroxide shows transmission in the region where absorption takes place, it would seem that the addition of ferric iron to a solution of cupric sulfate containing hydrogen peroxide increases the formation of cupric acid. The high transmissive powers of cupric salts and cupric acid make it impractical to obtain characteristic absorption "peaks;" consequently, this evidence, based upon the moving of the region of absorption, is not in itself definite proof of the formation of cupric acid. However, the possibility of a reaction between the ferric iron and the hydrogen peroxide has been considered and Spectrogram VI shows that this effect is so slight that it may be ignored. The remaining possibilities are that the iron and copper react with each other to form a complex molecule having new properties, or the iron (as ferric acid) oxidizes the copper to cupric acid. This first effect is highly improbable, since both iron and copper salts are about equally basic. The evidence seems to show that there is the formation of a compound whose solution is more transmissive in the green than is any of the components; cupric acid fits this description and consequently the formation of this compound appears very probable.

A Possible Relation between the Compounds of Iron and Copper in the Promotion

It is interesting to consider the relationship between the copper and the iron in connection with the extent of promotion. In order to do this, the

Table II

Variation of the Promotion Factor with Concentration and Composition

Ferric Chloride

Concn. of Fe mm./L.	Concn. of Cu mm./L.	Mol. % of Cu	K_r	P. Factor
20	0.0	0.0	177	1.00
	0.1	0.5	224	1.265
	0.2	1.0	233	1.315
	0.3	1.5	238	1.345
	0.5	2.5	243	1.37
	0.88	4.2	244	1.38
	1.5	7.0	244	1.38
	2.5	11.1	241	1.365
	5.0	20.0	240	1.355
	30.0	60.0	191	1.08
10	0.0	0.0	100	1.00
	0.05	0.5	133	1.33
	0.1	1.0	146	1.46
	0.2	2.0	159	1.59
	0.25	2.4	165	1.65
	0.75	7.0	174	1.74
	1.0	9.1	174	1.74
	1.25	11.1	173	1.73
	2.00	16.7	173	1.73
	2.5	20.0	169	1.69
	4.0	28.6	166	1.66
	40.0	80.0	133	1.33
2.5	0.0	0.0	19.5	1.00
	0.05	2.0	44	2.26
	0.20	7.4	63	3.23
	0.38	13.0	66	3.38
	0.50	16.7	68	3.49
	1.0	28.6	68	3.49
	2.5	50.0	71	3.64
	12.5	83.5	61	3.13
	37.5	93.6	55	2.82

TABLE II (*Concluded*)

FERRIC SULFATE

Concn. of Fe mm./L.	Concn. of Cu mm./L.	Mol % of Cu	K_r	P. Factor
30.4	0.0	0.0	81	1.00
	0.1	0.3	210	2.59
	0.2	0.6	255	3.14
	0.3	1.0	282	3.48
	0.5	1.4	301	3.71
	1.0	3.2	316	3.90
	2.0	6.2	317	3.91
	3.0	9.0	314	3.88
	5.0	14.1	291	3.59
30.0	30.0	50.0	180	2.34
	100.0	76.9	135	1.75
	0.0	0.0	77	1.00
7.6	0.0	0.0	21	1.00
	0.1	1.3	76	3.52
	0.3	3.8	98	4.66
	0.4	5.0	107	5.10
	0.6	7.3	113	5.38
	1.0	11.5	122	5.82
	2.0	20.9	120	5.71
	4.0	34.5	118	5.61

promotion factors were calculated both from previous results and from new experiments which had been performed for the purpose of giving sufficient values to cover the system properly. The promotion factor, which is defined as the quotient obtained by dividing the value for the "promoted" rate by that for the normal rate for that concentration of catalyst, is given in Table II for each concentration of iron and is plotted in Figs. 3 and 4 against the mole per cent. of copper, referred to total heavy metal present, as abscissas. Molar percentages were used in order that any stoichiometric relation between the iron and the copper used with it, might be apparent. Upon this promotion curve, which gives the ratio of promoted reaction velocities to those not promoted, for certain fixed concentrations of iron, a maximum will obviously present a region of greatest chemical effect between the compounds of the iron and copper.

An inspection of these curves shows that the region of maximum promotion moves toward the ordinate of 100% copper as the concentration of the iron decreases. The value of the promotion factor also increased as was shown in the previous paper. It was also shown in that connection that the promotion factor in the various systems increased as the iron decreased in concentration, and only reached the same value for the sulfate and chloride systems as the solution became infinitely dilute. It would seem that the true mechanism of promotion is evident in solutions so dilute that all disturbing effects are absent. For that reason it is desirable to find the region of maximum promotion in a solution of exceedingly small concentration. Since experimental difficulties made it nearly impossible to obtain checks in very dilute solution, it was necessary to determine this region by means of extrapolation. To do this the mole fraction corresponding to the region of maximum promotion was plotted against the concentration of iron corresponding to it, and the curve then prolonged to cut the axis of zero iron concentration. This gave the value for a solution infinitely dilute in ferric salt. Two curves were extrapolated, one from the sulfate system and one from the chloride system. The extrapolation is a rather difficult one and extends over some distance, which is necessitated by the fact that it is difficult to obtain checks in solutions as dilute as 2 to 5 millimoles per liter. The sulfate system is by far the worse in this respect and since the promotion factor is in the order of 6.5, the errors are multiplied very considerably. Hence, the determinations of the rates for the ferric sulfate system, 2 millimoles per liter, were not used here. In spite of these difficulties the extrapolation is felt to be justified by effects noted before, which show that the mechanism is probably the same in both systems in very dilute solution.

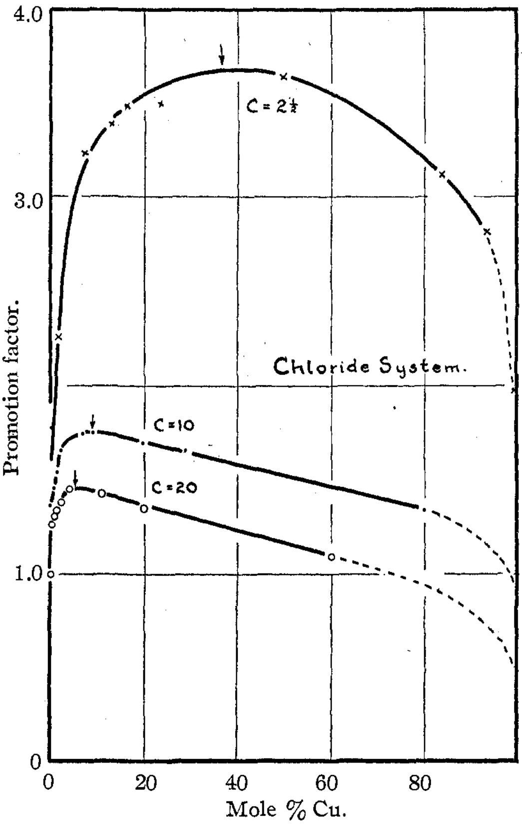

Fig. 3.—The variation of the region of maximum promotion with the concentration of ferric salt.

The results of extrapolation seem to indicate that the value is less than 65% and more than 50% copper, using the mole fraction of total heavy metal present. If there be a chemical reaction, one might well expect the true value to be one of the fractions 2/5, 1/2, 3/5, 2/3, or 3/5 from Dalton's law, but when one considers the properties of the substances, there are but two possibilities.

$$3CuO + 2FeO_3 \longrightarrow 3CuO_2 + Fe_2O_3 \qquad (3)$$

$$6CuO + 2FeO_3 \longrightarrow 3Cu_2O_3 + Fe_2O_3 \qquad (4)$$

Thus we have only to choose between the values of 60 and 75 mole per cent., which represent Reactions 3 and 4, respectively. The value is undoubtedly nearer 60% than 75%, showing that the relationship indicated in Reaction 3 is highly probable and that the oxide of copper is indeed CuO_2.

Free Energy Relationships

An examination of free energy relationships is very interesting in considering the reactions previously described. As Bray and Livingston[10] noted, the catalysts for hydrogen peroxide will be those whose oxidation potential lies within certain limits. Those with low oxidation potentials such as cupric salts, for instance, will obviously be those which have a slow "oxidation" reaction—one accompanied by a slight diminution of free energy. Since the total diminution in free energy is a fixed quantity, being the difference between the free energies of hydrogen peroxide and water, it follows that the diminution of free energy in the "reduction" reaction must, therefore, be relatively large. Ferric chloride, on the other hand, has a higher oxidation potential and, hence, the first reaction is more rapid than is the case in the cupric chloride catalysis.

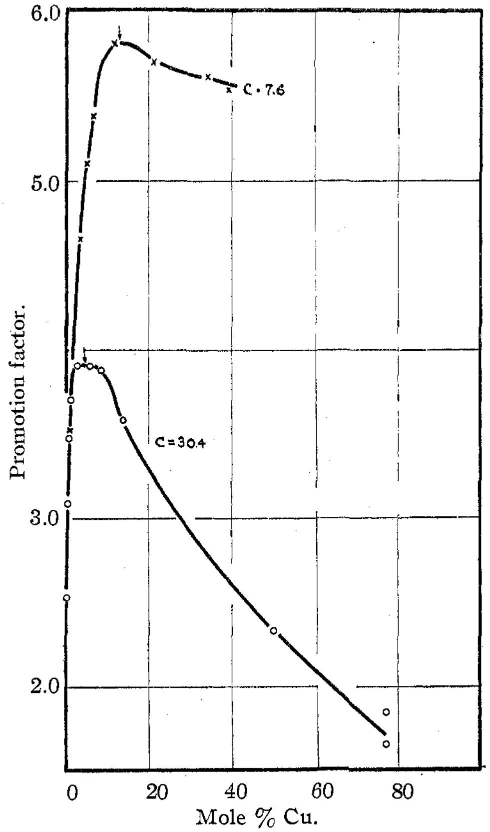

Fig. 4.—Sulfate system. The variation of the region of maximum promotion.

The equation for the catalytic decomposition of hydrogen peroxide by cupric salts may be written as in Reactions 1 and 2. These equations alone, however, do not enable one to draw any conclusion. To do that it is necessary to consider several other reactions in conjunction with these. They are the decomposition of copper peroxide in acid solution and the reaction between cupric salts and ferric acid.

$$CuO_2 + 2H^+ \longrightarrow Cu^{++} + H_2O + \frac{1}{2}O_2 \qquad (5)$$

$$3Cu^{++} + 2FeO_4^{--} + 4H^+ \longrightarrow 2Fe^{+++} + 3CuO_2 + 2H_2O \qquad (6)$$

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[10] Bray and Livingston, This Journal, **45**, 1255 (1923).

Assuming various free energies for copper peroxide, the diminution in free energy for the various reactions is as follows.

$\Delta F.^\circ_{298}$	Reaction (1)	(2)	(5)	(6)	(6a)
−15,000	+ 558	−50,738	−25,678	+67,904	+47,904
−25,000	− 9,442	−40,738	−15,678	+37,904	+17,904
−35,000	−19,442	−30,738	− 5,678	+ 7,904	−12,096
−45,000	−29,442	−20,738	+ 4,322	−22,096	−42,096

From these calculations, knowing that copper peroxide decomposes in acid solutions, we conclude that its free energy is more than —45,000 calories. This is true, since Reaction 5 takes place, and a larger negative value for the free energy of copper peroxide gives a positive diminution in free energy for this reaction. Such a condition is contrary to the hypotheses governing free-energy relationships; hence, Reaction 5 indicates that the value is above —45,000 calories. Reaction 6 is one that has been demonstrated to take place. Therefore, the value sought is less than —35,000 calories, this value giving a positive diminution of free energy. The value is now placed between —35,000 and —45,000 calories, but is dependent upon the value, obtained in a previous investigation, for the free energy of the ferrate ion. This value was —140,000, but could not have been more than —130,000 calories at the most.[11] This latter (and less probable) assumption places the value between —25,000 and —35,000 calories, while the first places it between —35,000 and —37,500 calories, and so the probable value will be assumed to be about —35,000 calories. This is a matter of no great importance in itself, but it may prove useful later in studying other reactions. However, the underlying purpose of these calculations is that of verifying the possibility of Reaction 6. While the main factor in this proof was Reaction 5, the values are shown for the other reactions also. It is evident that the results of this treatment agree with the conclusions drawn from spectrographic and kinetic studies.

Promoter Action and the Steady State

One explanation of promotion may be based upon the conception of the steady state in catalysis set forth by Bray and Livingston[12] in a recent article. In this article all the possible reactions for the systems, Br_2, Br^-, H^+, H_2O_2, were studied, and the catalysis of hydrogen peroxide by bromides in acid solution was completely accounted for by two reactions. They are,

$$H_2O_2 + 2Br^- + 2H^+ \longrightarrow Br_2 + 2H_2O \qquad (7)$$

$$H_2O_2 + Br_2 \longrightarrow O_2 + 2Br^- + 2H^+ \qquad (8)$$

the sum of which is the reaction for the decomposition of hydrogen peroxide. These reactions are irreversible and hence are assumed to take place together during the whole course of the reaction.

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[11] See footnote, p. 2496, Ref. 2.

[12] Ref. 10, p. 1251.

Considering Reaction 7, it will be seen that the amount of the intermediate, which in this case is bromine, steadily increases as the oxidation reaction proceeds. It will eventually reach a maximum dependent upon the several variables. In the case of Reaction 8, the rate of the reduction reaction and the amount of the intermediate formed decreases during the course of the reaction and approaches zero as the limit. When these reactions occur simultaneously there must be a time when the rate of formation is equal to the rate of its decomposition. This condition is known as the steady state of catalysis; after it is reached the concentration of intermediate remains constant and the reaction is (externally) purely catalytic. The amount of intermediate present at the steady state obviously is a measure of the rate of the catalytic reaction.

Never before has a catalytic reaction been studied so thoroughly and the path been demonstrated so rigorously. Such conclusive evidence has not been obtained for other reactions[13] and may possibly never be realized again. The bromine-bromide catalysis of hydrogen peroxide is unique in the opportunities that it offers for exact measurement. The intermediate may be prepared in a pure state for the study of the reduction reaction and the rates of reaction are not so fast that they may not be measured easily. On the contrary, however, the intermediates of both the cupric and ferric salt catalyses cannot be prepared in a state of high purity, and the reduction reaction is so rapid, for the copper at least, that accurate measurement is impracticable. Because of this, it has not been possible to prove that there is a steady state dependent only upon the oxidation-reduction cycle shown in Reactions 1 and 2. However, the mechanism postulated by Bray and Livingston is considered to be applicable to this system.

Spectrographic and kinetic measurements show that the rate of formation of cupric acid is slow under the conditions used. In addition, kinetic measurements show that the cupric acid is rapidly auto-reduced by hydrogen peroxide. Hence, the steady state for the oxidation-reduction reactions may be shown by Fig. 5.

Since the rate of decomposition is a function of the concentration of the intermediate, it follows that any increase in the amount of intermediate

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[13] Abel [*Z. physik. Chem.*, **96**, 1 (1920)] has studied the iodide-iodine catalysis of hydrogen peroxide and considered the steady state in this reaction. It was found possible to do this only in solutions from 10^{-6} to 10^{-7} *N* in hydrogen ion, and buffer solutions of acetic acid and sodium acetate were used to achieve this condition. This investigation lacks the elements of simplicity requisite for a rigorous proof. In this connection, see Willstätter [*Ber.*, **36**, 1828 (1903)] who has found that sodium acetate forms a crystalline compound with hydrogen peroxide. Unpublished work in this Laboratory has shown that an equilibrium reaction exists between sodium acetate and hydrogen peroxide in solution. The introduction of this large, variable factor may be responsible for the complexities noted in Abel's studies. For this reason the work of Bray and Livingston is given first consideration.

will also result in an increase in the rate of reaction. An examination of Fig. 5 shows that this is possible, for it is evident that an increase in the rate of formation of the intermediate will increase the amount of intermediate if the rate of reduction remains the same. Now the rate for formation of the intermediate is a function of acidity and concentration, and when these are fixed, it also is fixed. The rate of reduction is fixed in a somewhat similar manner. However, it has been shown that there is an increase in the rate of formation of cupric acid when a minimal amount of ferric salt is added to the solution. This may be represented by increasing the slope of the curve O_1, represented by the curve O_2, and will result in the steady state being achieved at a higher concentration, S_2, of intermediate. This means that the addition of a very small amount of ferric salt to a cupric salt solution displaces the region of the steady state and increases the apparent rate of reaction, and therefore gives us the condition that we have defined as "promoter action."

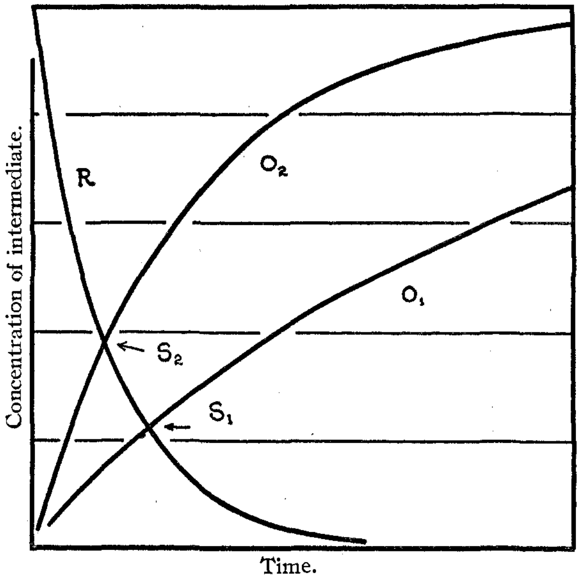

Fig. 5.—The shift of Steady State with increased rate of the oxidation reaction.

Discussion of Old and New Data

The experiment wherein the addition of a small amount of copper salt to a solution of ferric acid increased its rate of auto-reduction with hydrogen peroxide may now be logically explained. The explanation offered at the time was that the copper hastened the reduction of the intermediate compound. It is now postulated that a new compound is formed which is more rapidly auto-reduced than the ferric acid, a situation that gives the same external effect. This compound is cupric acid. However, it is not now possible to explain the fact that the slower reaction rates with ferric sulfate are promoted to nearly the same rate as the ferric chloride systems, except by the conception that the formation of cupric acid requires the reduction of ferric acid derived from ferric sulfate and displaces any possible equilibrium between ferric sulfate, sulfuric acid and possible complex anions containing ferric sulfate.[14] It is to be noted that this discrepancy disappears in more dilute solutions where dissociation would minimize this effect.

It would have been more consistent to have called the case where the iron catalyzes the formation of cupric acid a case of promoter action in the copper-rich portion of the system, but that would have obscured the actual chemical relationship, a change in the path of the reaction with a concomitant displacement of the region of the steady state.

Not only may promotion be considered as a displacement of the steady state in the manner we have discussed, but it may also be regarded as a condition where a change occurs in the course of the reactions constituting together the catalytic reaction. The oxidation of cupric salts by hydrogen peroxide is a slow reaction, Reaction 1. The oxidation of cupric salts by ferric acid is a much faster reaction, probably instantaneous. Hence, in a system containing both cupric and ferric salts and hydrogen peroxide, the course of the reaction, instead of passing only through ferric acid as an intermediate, very probably passes through cupric acid. The ferric acid oxidizes the cupric salt to cupric acid more rapidly than would hydrogen peroxide, the cupric peroxide then is auto-reduced more rapidly by hydrogen peroxide than the ferric acid would have been. The reaction, confronted as it were by two paths, the first part of one and the last part of the other being difficult, chooses to pursue the easy one until it becomes difficult, and then changes to the second path, which is easier to pursue from that point onward.

With this as a basis, it is formulated as a working hypothesis that we probably will have promotion in the catalytic decomposition of hydrogen peroxide when there is the possibility of the formation of a second intermediate more unstable, that is, more rapidly auto-reduced by hydrogen peroxide than the first intermediate. A more theoretical discussion of this will be considered later. It is possible that cases of negative catalysis can

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[14] Ferric sulfate forms with sulfuric acid two ferri-sulfuric acids wherein the iron is in the anion. The formulas are $H[Fe(SO_4)_2]$ and $H_3[Fe(SO_4)_3]$. Ferri-disulfuric acid has been prepared in the pure state and salts of both acids are known. See among others, Weinland and Ensgraber [*Z. anorg. Chem.*, **84**, 340 (1913)], Skrabal [*ibid.*, **38**, 319 (1904)] and Komar [*Chem.-Ztg.*, **30**, 15 (1906)]. This effect was noted in a previous paper [THIS JOURNAL, **45**, 2501 (1923)] in an investigation of the neutral salt effect. The action due to sulfates is similar to the effect caused by phosphates, although not nearly of the same magnitude.

also be explained by this conception of the change in the path of the catalytic reactions.

In a former paper it was shown that nickel, cadmium, mercury, barium, lead, cobalt, zinc, tin or magnesium salts did not promote the ferric salt catalysis of hydrogen peroxide. Using the conception of the stability of the higher oxides of the metals (toward auto-reduction by hydrogen peroxide) as an index of their power of promotion it would seem that these metals form higher oxides that are more stable than that of copper. Conversely, one would expect that salts of these metals would be promoted by cupric salts, if they acted as catalysts. Barium, zinc and magnesium salts are not good possibilities as catalysts, since it is probable that their oxides are peroxidates and, hence, would not have any tendency to decompose hydrogen peroxide.

Of the metals that form polyoxides, to use the terminology of Mendeléeff, we have among others, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, molybdenum, ruthenium, tantalum, tungsten, osmium, iridium, platinum, mercury, thallium, lead, bismuth and uranium. Salts of nearly all of these metals catalyze the decomposition of hydrogen peroxide, some more strongly than others. It is known that the polyoxide of copper is more unstable than those enumerated in the first list, and so it would be expected upon this basis that copper would promote their catalysis of hydrogen peroxide. This has been tried in a qualitative manner, and it has been found that copper does promote the catalytic action of lead and manganous salts and dichromates. Other promoters have also been found for the dichromate system. The results obtained are so satisfactory that the work will be extended, using the other metals mentioned.

In conclusion the writer desires to express his thanks to Professor J. H. Walton, with whom this research was carried out, for his kindly interest and help during its progress.

Summary

1. Cupric acid has been shown to be present in cases where the catalytic decomposition of hydrogen peroxide by ferric salts is promoted by copper.
2. The formation of cupric acid is catalyzed by the presence of minimal amounts of ferric salt.
3. The region of the maximum promotion varies with the concentration of the iron and approaches the value 2Fe–3Cu as the concentration of the iron is indefinitely reduced. This points toward the possibility of the reaction, $2FeO_3 + 3CuO \longrightarrow Fe_2O_3 + 3CuO_2$, as a possible mechanism of promotion.
4. It is suggested as a working hypothesis that promotion will occur when there is the possibility of the formation, as a second intermediate, of

a compound more rapidly auto-reduced by hydrogen peroxide than the first intermediate. Several new cases of promotion have been discovered by means of this hypothesis.

5. Promotion may be provisionally defined as a change in the path of reaction with a concomitant displacement of the steady state.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF BRITISH COLUMBIA]

THE SOLUBILITIES IN WATER OF RUBIDIUM AND CESIUM CHLOROPLATINATES

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Potassium, rubidium and cesium form a group of elements very closely related and with very interesting characteristics. Any relationship among the properties of their compounds is of corresponding interest, and not the least interesting of the properties that must be considered in this connection is the solubility of their salts in water. One of the first of the salts of rubidium and cesium to be tested as to its solubility in water was the chloroplatinate. Bunsen[1] published certain results dealing with the solubilities of these two compounds as early as 1861. But as the methods of separating potassium from rubidium and cesium material now available are better than those known at the time Bunsen made his determinations, and as a knowledge of the correct values for the solubilities of the three chloroplatinates seemed desirable, it was thought worth while to make some further measurements in the case of the rubidium and cesium compounds.

Preparation of Materials

Cesium Chloroplatinate.—A good sample of pollucite (an aluminum silicate of cesium) was used as a source of cesium. The mineral had been finely ground, and 167 g. of it was digested for 40 hours in hot, concd. hydrochloric acid. The residue was filtered off, the filtrate was mixed with water and the iron and aluminum were precipitated as hydroxides by the addition of ammonium hydroxide. After the precipitates had been removed and the liquid evaporated to expel any excess of ammonia, hydrochloric acid was added and the solution was evaporated almost to dryness. This left cesium chloride mixed with some ammonium, sodium, potassium and perhaps rubidium chlorides.

For the purpose of purifying the cesium chloride, the residue last obtained was dissolved in water, the solution diluted to 200 cc. and 30 g. of iodine added. The mixture was then heated nearly to boiling and a stream

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[1] Bunsen, *Pogg. Ann.*, **113**, 337 (1861); *Chem. News*, **4**, 44 (1861).