3. The partial molal free energy of mercury in some mercurides has been calculated from the measured values of the electromotive force of amalgam concentration cells.
4. The values for the partial molal free energy of mercury in sodium and lead mercurides were found to be —61 and —12 calories, respectively.
5. The free energies of formation of sodium and lead mercurides are —18,351 and —280 calories, respectively.
6. The partial molal free energies of the constituents of mixed crystals of zinc-mercury, cadmium-mercury and thallium-mercury crystals have been tabulated.
7. With the exception of thallium, it has been found in the case of the mercurides and the mixed crystals studied, that the change in free energy has been greater for the electropositive metals than for mercury.

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

PROMOTER ACTION IN HOMOGENEOUS CATALYSIS. I. COPPER SALTS AS PROMOTERS IN THE IRON SALT CATALYSIS OF HYDROGEN PEROXIDE

BY VAN L. BOHNSON AND A. C. ROBERTSON

RECEIVED JUNE 11, 1923

The investigation described in this paper was an outgrowth of an earlier study[1,2] of the catalytic decomposition of hydrogen peroxide, during which it was noted that the rate of evolution of oxygen in the presence of a mixture of iron and copper salts is much more rapid than the rate which may be calculated on the assumption that each salt acts independently. This phenomenon is analogous to what has been known in cases of heterogeneous catalysis as "promoter action." The latter designation, first used in the patents of the Badische Anilin und Soda Fabrik, might well include, according to Pease and Taylor,[3] all those cases in which a mixture of two or more substances is capable of producing a greater catalytic effect than can be accounted for on the assumption that each substance in the mixture acts independently. So defined, the term is applicable not only to cases of heterogeneous catalysis, to which it was first applied, but also to homogeneous catalysis, and in this sense it is used in this paper; such a use is no intimation that the mechanism of reaction in the two different systems is the same.

The known examples of promoter action have been reviewed and classified by Pease and Taylor,[3] and therefore will not be described here. Ex-

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

[2] Bohnson and Robertson, THIS JOURNAL, **45**, 2493 (1923).

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

amples in the field of homogeneous catalysis are relatively few in number, the one best known being the effect of neutral salts in accelerating the acid-catalyzed hydrolysis of esters. Two reactions which are of interest in connection with the present study are the oxidation of potassium iodide by potassium persulfate,[4] and the reaction between hydrogen peroxide and hydriodic acid;[5] in both of these cases the reaction was "promoted" by the action of copper salts in the presence of iron salts.

Purpose and Method

In an attempt to outline in a preliminary way the mechanism of promotion, this paper will be devoted to a discussion of the factors involved in the accelerating effect of copper salts upon the iron-salt catalysis of hydrogen peroxide in acid solution. Further papers will deal with promoter action in other homogeneous reactions, such as the activation of chromic acid and its salts (catalyzing the decomposition of hydrogen peroxide) by certain cations, a reaction which is now being studied in this Laboratory.

It has been suggested by Pease and Taylor[3] that a distinction be made between simple "activation" of one catalyst by another substance not itself a catalyst for the reaction in question, and "co-activation," in which the catalytic effect of each active substance is increased by their joint presence. From this point of view, it is possible with the reaction in question that (1) the copper salt may be activated by the iron salt, (2) the iron may be activated by the copper, or (3) the two may activate each other. It is not always easy to decide among such hypotheses, but a determination of the promotion effect in the presence of various amounts of iron or copper may enable us to exclude certain of them, on the reasonable expectation that in any activation of one substance by another there is a limit to the accelerating effect of the primary catalyst when all the catalytic material has been "activated."

The method used for measuring the rate of reaction has been previously described.[2] The results obtained are merely summarized as in the previous paper, and are supported by numerous duplicates and intermediate values. In the tables the following abbreviations are used: T, temperature; N, normality of free acid present; C_{Fe}, concentration of iron salt in milligram-atoms of iron per liter; C_{Cu}, concentration of copper salt in milligram-atoms of copper per liter; K_R, the relative rate of reaction (see p. 2497 of preceding paper). In all experiments, unless otherwise noted, the concentration of free acid was 0.076 N, that of the hydrogen peroxide 130 millimoles per liter, and the temperature 30°. All experiments were performed in the diffused light of the laboratory, after it was

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[4] Price, *Z. phys. Chem.*, **27,** 499 (1893).

[5] Brode, *ibid.*, **37,** 257 (1908).

found that those performed in darkness were not retarded either in the presence of iron alone or of iron and copper together.

Preliminary Experiments

Ferric chloride in solution exerts an energetic decomposing effect on hydrogen peroxide even in the presence of hydrochloric acid, which retards the catalysis materially. Ferric sulfate in sulfuric acid solution has a marked effect, less than that of the chloride. On the other hand, much larger quantities of cupric chloride, either in acid or in neutral solution, have very little noticeable effect. In fact, the salts of few other metals act as vigorously as the iron salts. When, however, small amounts of copper salt are mixed with the iron salt, the rate of reaction is very markedly increased. This effect seems to be peculiar to copper compounds; nickel, cadmium, mercury, barium, lead, cobalt, zinc, tin, and magnesium salts appear to retard rather than accelerate the reaction. In sulfate systems silver appears to have a very slight accelerating effect.

Effect of a Fixed Concentration of Copper in the Presence of Variable Iron Concentration

Fig. 1 shows graphically the relation between the rates of reaction caused by each salt alone and by mixtures containing various fixed concentrations of copper salt and varying concentrations of iron salt; the data for the curves are given in Tables I and II. In all these experiments the chlorides were used; the effect in sulfate systems will be considered later.

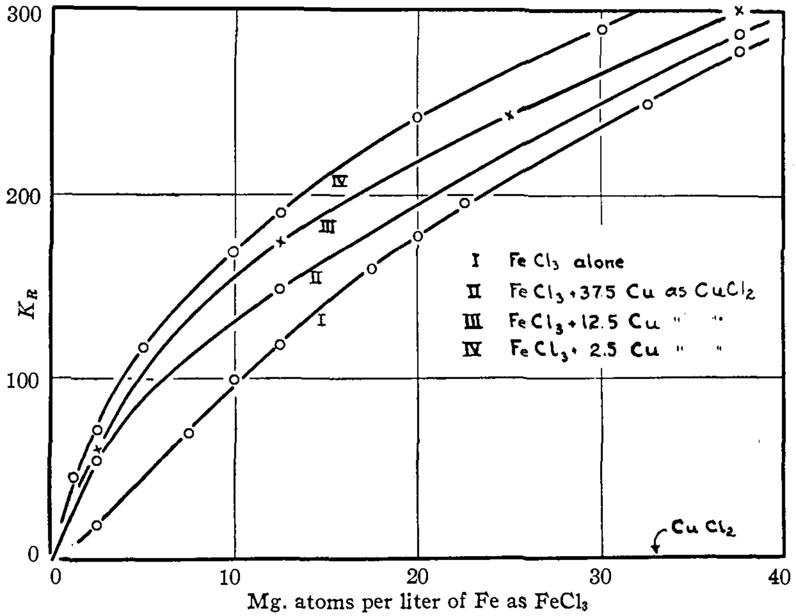

Fig. 1.—Effect on reaction rate of fixed copper with varying iron concentration

TABLE I

COMPARISON OF CATALYTIC EFFECT OF FERRIC AND COPPER CHLORIDES

$T = 30°$ $N = 0.076$

C_{Fe}	C_{Cu}	K_R	C_{Fe}	C_{Cu}	K_R	C_{Fe}	C_{Cu}	K_R
0	32.5	0.63	7.5	0	69	20	0	177
0	37.5	1.16	10	0	100	22.5	0	195
0	50	1.8	12.5	0	118	32.5	0	248
2.5	0	19.5	17.5	0	160	37.5	0	276

TABLE II

EFFECT ON THE RATE OF REACTION OF VARYING THE FERRIC CHLORIDE CONCENTRATION ONLY

$T = 30°$ $N = 0.076$ Chlorides

$C_{Cu} = 2.5$		$C_{Cu} = 2.5$		$C_{Cu} = 12.5$		$C_{Cu} = 37.5$	
C_{Fe}	K_R	C_{Fe}	K_R	C_{Fe}	K_R	C_{Fe}	K_R
1.25	46	15	207	2.5	61	2.5	55
2.5	71	20	241	12.5	174	12.5	148
5	117	30	289	20	224	37.5	286
10	169	35	317	25	241	..	..
12.5	190	..	...	37.5	300	..	...

The curve for cupric chloride alone may scarcely be distinguished from the horizontal axis; therefore, on the assumption that the joint effect of iron and copper salts is purely additive, the curve for this joint effect should coincide with the curve for ferric chloride alone. It will be noted, however, that the presence of only a small amount of copper salt causes a marked acceleration. A large concentration of copper, as shown by Curves II and III, has a smaller effect; it is therefore evident that some concentration of copper in the vicinity of 2.5 milligram-atoms per liter is more effective than any other. From these results we may exclude the hypothesis that the copper salt is activated by the iron.

Effect of a Varying Concentration of Copper with a Fixed Concentration of Iron

That there is a maximum effective concentration of copper salt is better illustrated by the results shown in Figs. 2 and 3 (Tables III and IV). The curves represent the variation in the rate of reaction caused by varying concentration of copper salt in the presence of different fixed concentrations of iron salt. A relatively minute amount of copper has a marked effect, but in each case a maximum rate of reaction is obtained with a concentration of only 1 milligram-atom per liter. Beyond this point, the rate continually decreases with the addition of more copper, an effect which is quite analogous to that caused by the addition of sodium chloride. The maximum effective concentration of copper appears to be independent of the concentration of iron salt.

TABLE III

EFFECT OF A VARYING CONCENTRATION OF COPPER CHLORIDE ON THE RATE OF REACTION

$T = 30°$ $N = 0.076$

$C_{Fe} = 2.5$		$C_{Fe} = 10$		$C_{Fe} = 20$	
C_{Cu}	K_R	C_{Cu}	K_R	C_{Cu}	K_R
0	19.5	0	100	0	177
0.05	44	0.05	135	0.1	224
0.2	63	0.1	146	0.2	233
0.375	66	0.2	159	0.3	238
0.5	68	0.25	165	0.5	243
1.0	68	0.75	174	0.875	244
2.5	71	1.0	174	1.5	244
12.5	61	1.25	173	2.5	241
37.5	55	2.0	173	5.0	240
...	..	2.5	169	30	191
...	..	4.0	166	...	...
...	..	40	133	...	...

TABLE IV

EFFECT OF A VARYING CONCENTRATION OF COPPER SULFATE ON THE RATE OF REACTION

$T = 30°$

$N = 0.076$ $C_{Fe} = 7.6$		$N = 0.076$ $C_{Fe} = 30.4$		$N = 0.038$ $C_{Fe} = 7.6$	
C_{Cu}	K_R	C_{Cu}	K_R	C_{Cu}	K_R
0	21	0	81	0	35
0.1	76	0.1	210	0.1	126
0.3	98	0.2	255	0.3	166
0.4	107	0.3	282	0.5	184
0.6	113	0.5	301	1.0	197
1.0	122	1.0	316	1.5	202
2.0	120	2.0	317	2.0	202
4.0	118	3.0	314	...	...
...	....	5.0	291	...	...

That the effect is common to both chloride and sulfate systems is evident; the maximum concentration of copper in each case is of the same order of magnitude, although ferric sulfate is a much less active catalyst than ferric chloride. It is also evident (Curve II, Fig. 3, and last column, Table IV) that the maximum effective concentration of copper is not altered by a large decrease in the concentration of the free acid present. These results lead to the conclusion that the iron salt is activated by the presence of a copper salt.

Conditions Affecting the Extent of Promotion

Promotion Factors.—It has been shown that for any given concentration of iron, a maximum rate of reaction is obtained with approximately the same absolute concentration of copper in all cases. By dividing the maximum rate by the normal rate for the given concentration of iron, a ratio is obtained which may conveniently be termed the "promotion factor;" this factor represents the extent of promotion under given conditions.

Effect of Concentration of Catalyst.—The promotion factors for different concentrations of iron salt can be calculated from the values obtained by interpolation from the curves of Fig. 1 and Fig. 4. The latter, for which the data are shown in Table V, represents the promotion process when sulfates of iron and copper are used (in the presence of free sulfuric acid).

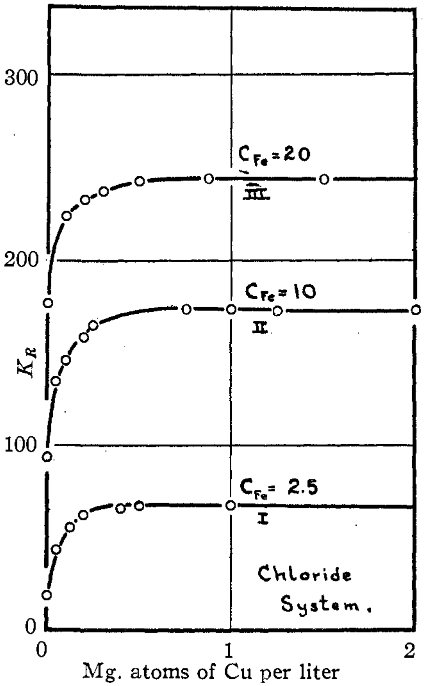

Fig. 2.—Effect on reaction rate of fixed iron with varying copper concentration

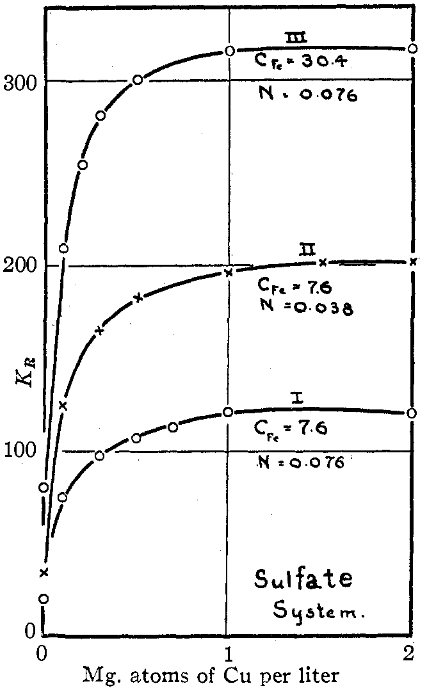

Fig. 3.—Effect on reaction rate of fixed iron with varying copper concentration

Table V

Effect of a Varying Concentration of Ferric Sulfate

C_{Fe}	3.8	7.6	15.2	22.8	30.4	38.0	60.8
K_R: no Cu	..	21	43	60	81	...	156
K_R: C_{Cu} = 1.0	72.5	..	200	263	320	366	...

Table VI

Variation of Promotion Factors with Concentration of Iron Salt

	Promotion factors			Promotion factors	
C_{Fe}	Chlorides	Sulfates	C_{Fe}	Chlorides	Sulfates
1	5.0	8.0	15	1.5	4.9
2	3.6	7.0	20	1.3	4.6
4	2.7	6.7	25	1.2	4.2
7	2.1	6.0	30	1.2	4.0
10	1.7	5.6	40	1.17	..

In this case, as is shown also in the last column of Table VI, the promotion factor is much larger than in the chloride system, although the normal rate is less.

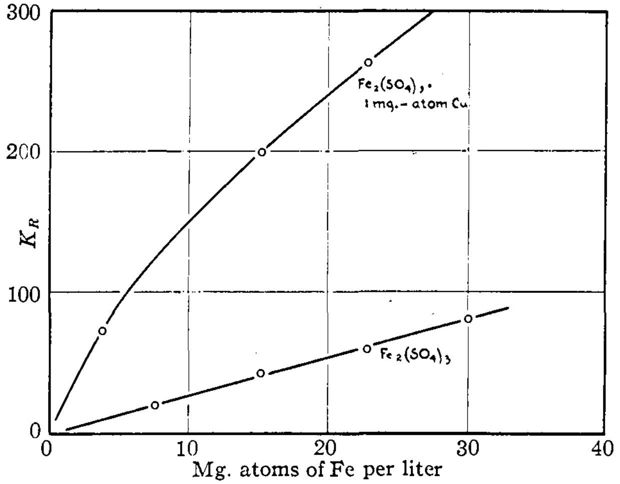

Fig. 4.—Effect on reaction rate of fixed copper with varying iron concentration

In both systems the promotion factor decreases as the concentration of iron salt increases, probably approaching 1 as a limiting value. This is shown graphically in Fig. 5; it appears that the promotion factors for the two systems approach each other in magnitude as the concentration

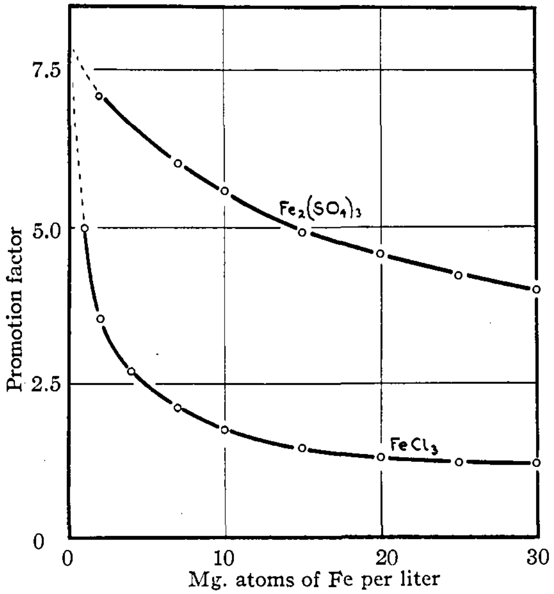

Fig. 5—Effect on the promotion factor of varying the concentration of primary catalyst

of catalyst is decreased, thus indicating that in very dilute solutions of the catalyst the mechanism of promotion is independent of the nature of the anion.

It may be noted here that the promotion factor is the same when ferrous sulfate is the catalyst as when ferric sulfate is used, in dilute solution. This fact is in accord with the initial rapid oxidation of ferrous sulfate, discussed in the previous paper.

Effect of Concentration of Free Acid.—The effect of acid on the promoter action has already been partly shown in Curve II, Fig. 3, where it is seen that in the sulfate system the maximum effective concentration of copper is not changed by a decrease in the acid concentration; it can be shown that the promotion factor for C_{Fe} = 7.6 is 5.8 whether the acid concentration is 0.038 N or 0.076 N. Similarly, for the chloride system, the promotion factor also remains unaltered when the concentration of free acid is changed from 0.076 N to 0.038 N. This is shown by the data of Tables VII and VIII, and in the curves of Fig. 6. The promotion factors obtained by interpolation from the latter are compared in Table VIII with those obtained from Fig. 1. The fact that free acid has the same effect on the accelerated reaction that it has in the presence of iron salt alone, further confirms the hypothesis that the iron salt is the primary catalyst and the copper salt the promoter.

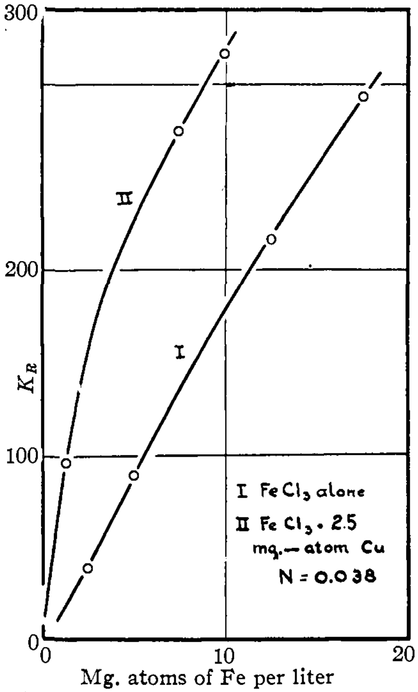

Fig. 6.—Promoter effect in the presence of decreased acid concentration

TABLE VII

EFFECT OF DECREASED ACID CONCENTRATION ON THE FERRIC CHLORIDE-COPPER CHLORIDE CATALYSIS

$T = 30 \quad N = 0.038$

C_{Fe}	2.5	5	12.5	17.5	1.25	7.5	10
C_{Cu}	0	0	0	0	2.5	2.5	2.5
K_R	39.5	89	216	293	96	275	317

TABLE VIII

EFFECT OF DECREASED ACID CONCENTRATION ON PROMOTION FACTORS

C_{Fe}	Promotion factors $N = 0.076$	Promotion factors $N = 0.038$	C_{Fe}	Promotion factors $N = 0.076$	Promotion factors $N = 0.038$
2	3.6	3.5	7	2.1	2.1
4	2.7	2.7	10	1.7	1.8

Effect of Temperature.—The effect of temperature on the extent of promotion is also negligible. It is shown in Table IX that the promotion factor in the chloride system remains constant, even though the reaction rate is greatly increased by raising the temperature. That the temperature coefficient is unchanged by the presence of copper is shown by Table X; this is again evidence for the hypothesis that the copper salt present activates the iron salt.

Table IX

Effect of Temperature on Promotion Factors

R_n = normal rate, with ferric chloride; R_p = rate when copper is present; P = promotion factor

	$T = 40°$			$T = 30°$			$T = 20°$		
C_{Fe}	R_n	R_p	P	R_n	R_p	P	R_n	R_p	P
2.5	75	275	3.7	19.5	71	3.6	4.1	15.1	3.7
5	171	417	2.4	46	118	2.6	10.6	25.5	2.4
10	326	587	1.8	98	173	1.8	...	..	...

Table X

Effect of Promoter on Temperature Coefficients

	Temperature coefficients			
	Fe alone		Fe = Cu	
C_{Fe}	40/30	30/2	40/30	30/20
2.5	3.85	4.75	3.87	4.70
5	3.72	4.34	3.54	4.63
10	3.47	..	3.40	..

Effect of the Anion.—The effect on the reaction rate of the addition of various potassium salts to the reaction mixture when iron salts alone are

Table XI

Effect of Neutral Salts on the Promoter Action

$T = 30°$ $N = 0.076$ C_{Fe}(as $FeCl_3$) = 10.0 $C_{Cu} = 1.1$

C_s = concn. of neutral salt in millimoles per liter

	Maximum rate, K_R			
C_s	KCl	KNO	K_2SO_4	K_3PO_4
0	176	176	176	176
1	...	...	...	150
5	...	...	145	76
10	159	176	132	33
15	...	...	114	..
16	...	...	...	1.2
18	...	...	...	0.8
20	...	175	105	0.6
25	153	...	...	...
30	...	...	84	...
50	142	171	62	...
75	138	...	44	...
100	132	165	...	...
150	124	...	32	...
400	86	157	25	...
1880	...	136	...	...

the catalysts, has been shown in a previous paper. The effect of such salts when copper is present as a promoter is shown in Fig. 7, the data being given in Table XI. A comparison of these results, plotted logarithmically, with those presented in the previous paper shows that the rate due to molecular salt is accelerated, as well as the rate due to iron ions.

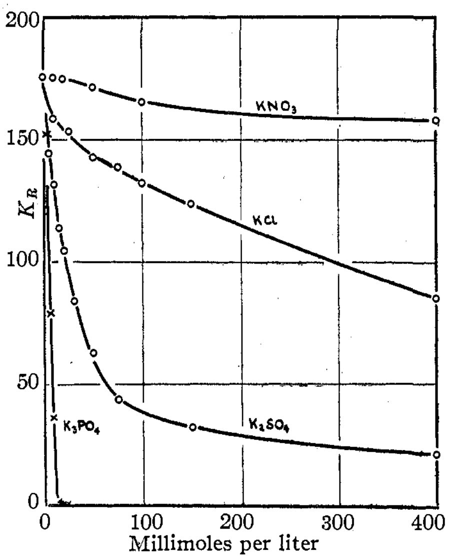

Fig. 7.—Effect of neutral salts on the promoter action

The Mechanism of Activation

It was shown in the previous paper[2] that the decomposition of hydrogen peroxide by iron salts alone is due to the formation and subsequent reduction by hydrogen peroxide of an intermediate compound, probably H_2FeO_4. The rate of evolution of oxygen from a given concentration of hydrogen peroxide is proportional to the concentration of the intermediate compound, which is in turn dependent upon the concentration of iron salt and of acid, and differs notably, depending upon whether the chloride, sulfate or nitrate of iron is used. In other words, the rate of reaction measured by the gasometric method can be no faster than the slower of the intermediate reactions, whether this be the formation of ferric acid, or its reduction by hydrogen peroxide, or some step in these processes. It is conceivable that the promoter, which is thus a secondary catalyst, might accelerate either one or both of the intermediate processes.

Two equal portions of a solution of barium ferrate in acetic acid were allowed to react with equal quantities of hydrogen peroxide. To one of the samples a very little copper acetate was added; measurements of the oxygen evolved showed that this one reacted much faster than the one to which no copper salt was added. This is an indication that the copper accelerates the reduction of the intermediate compound.

This experiment is not sufficient to explain the noticeable fact (compare Fig. 1 with Fig. 4) that although the rate for a given iron concentration is much lower when the sulfate is used, the maximum "promoted" rate is very close to that obtained when the chloride is used. If, however, we assume that the copper salt also accelerates the *formation* of the intermediate compound, the facts are more easily understood. It is probable, therefore, that the copper acts as a secondary catalyst, accelerating both the intermediate reactions. The exact mechanism of this secondary catalysis is not yet clear.

Summary

1. A small amount of copper salt greatly accelerates the decomposition of hydrogen peroxide by iron salts in acid solution. Other metallic salts do not appear to have this "promoter effect."

2. For a given concentration of iron salt, either sulfate or chloride, there is a maximum rate of reaction with about 1 millimole per liter of added copper salt. This maximum effective concentration of copper appears to be independent of the concentration of iron salt.

3. The extent of promotion (measured by the "promotion factor," which is the ratio of the maximum rate to the normal rate for the iron alone) is independent of the acid concentration and temperature.

4. The extent of promotion is much greater for ferric sulfate than for ferric chloride, although the maximum rate obtained in each case is the same. The promotion factors for the two systems approach each other as the concentration of iron approaches zero.

5. The facts are best explained by the following assumptions regarding the mechanism of promotion. (a) The iron salt is the primary catalyst, by virtue of its ability to form an intermediate compound. (b) The copper salt is a secondary catalyst, accelerating both the formation and subsequent decomposition of the intermediate product. The effect of the secondary catalyst is dependent upon its concentration only for very small quantities, a maximum effective concentration being noticeable. The mechanism of this secondary catalysis has not yet been completely explained.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, COLUMBIA UNIVERSITY, No. 420]

FERRIC SALT AS THE "SOLUTION LINK" IN THE STABILITY OF FERRIC OXIDE HYDROSOL[1]

BY ARTHUR W. THOMAS AND ALEXANDER FRIEDEN

RECEIVED JUNE 13, 1923

Ferric oxide hydrosol was first prepared by Arnold Maus.[2] It was regarded as a chemical compound[3] until the introduction of the process of dialysis. Péan de St. Gilles[4] and Thomas Graham[5] looked upon it as

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[1] This work was completed in February, 1922, and is adapted from the dissertation submitted by Alexander Frieden in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1922.

[2] Maus, *Ann. Phys. Chem.*, **11,** 75 (1827).

[3] Souberain, *Ann. chim. phys.*, **44,** 325 (1830). Rose, *Ann. Phys. Chem.*, **24,** 301 (1832). Schönbein, *ibid.*, **39,** 141 (1836). Scherer, *ibid.*, **44,** 453 (1838). Berzelius, "Lehrbuch der Chemie," **1845,** vol. III, p. 555.

[4] Péan de St. Gilles, *J. prakt. Chem.*, [1] **66,** 137 (1855).

[5] Graham, *Phil. Trans.*, **161,** 183 (1861).