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[Contribution from the Laboratory of General Chemistry of the University of Wisconsin]

PROMOTER ACTION IN REACTIONS OF OXIDATION CONCOMITANT WITH THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE.[1,2]

I. THE OXIDATION OF HYDRAZINE

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Introduction

The catalytic decomposition of hydrogen peroxide by iron and copper salts has been studied in this Laboratory by Bohnson and Robertson,[3] who observed that when a slight amount of a copper salt was added to the iron salt used as the catalyst, a marked promoter effect was observed. This was explained by Robertson as being due to the fact that cupric acid reacts with hydrogen peroxide much faster than does ferric acid.

Walton and Christensen[4] showed that the oxidation of ethyl alcohol by hydrogen peroxide catalyzed by ferric salts was dependent on the same mechanism as that shown by Bohnson and Robertson to effect the catalytic decomposition of hydrogen peroxide. They were, however, unable to extend the parallel into the study of promoter action because the catalytic activity of the copper salts was inhibited by the presence of the ethyl alcohol. The purpose of this investigation is to extend these studies into fields that permit the investigation of the phenomenon of promoted oxidation concomitant with the catalytic decomposition of hydrogen peroxide by iron and copper salts. The oxidation of hydrazine is particularly well adapted to mechanistic studies of this nature as it does not interfere markedly with the action of the catalysts used.

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[1] This work is from a thesis presented by the author in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin, conducted under the personal direction of Professor James H. Walton.

[2] This research was made possible by a grant from the Research Committee of the University of Wisconsin, Dean C. S. Slichter, Chairman.

[3] Bohnson, *J. Phys. Chem.*, **25**, 19–54 (1921); Bohnson and Robertson, This Journal, **45**, 2493 (1923); Robertson, *ibid.*, **47**, 1299 (1925).

[4] Walton and Christensen, *ibid.*, **48**, 2083 (1926).

Browne and Shetterly[5] and others have pointed out that when hydrazine is oxidized by concentrated solutions of hydrogen peroxide, appreciable side reactions occur which result in the formation of considerable ammonia and some hydrazoic acid. However, preliminary experiments by the author showed that in the presence of the catalysts used the oxidation of hydrazine gave a yield of 98–100% nitrogen, justifying the equations

$$2H_2O_2 = 2H_2O + O_2$$
$$N_2H_4 + O_2 = 2H_2O + N_2$$

Experimental Part

Materials.—The hydrogen peroxide was obtained as Merck's Superoxol (30% H_2O_2) and was twice distilled at diminished pressure to remove all preservatives. It was stored in quartz.

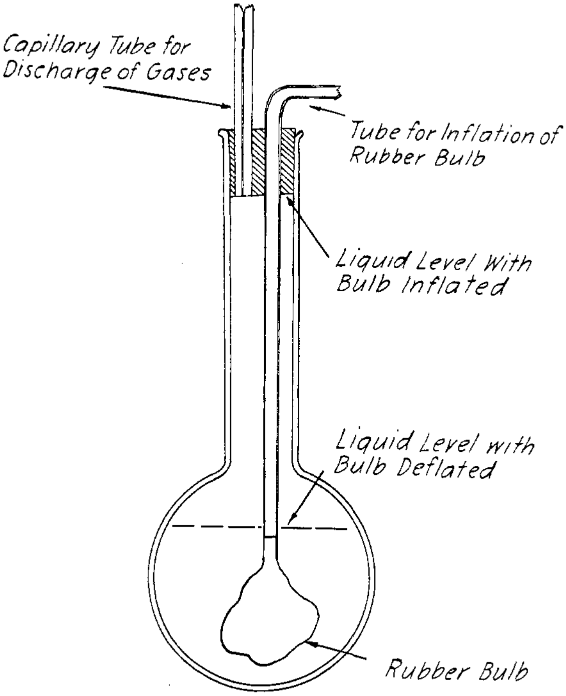

Fig. 1.—Reaction flask.

Pure copper sulfate, ferric sulfate and hydrazine sulfate were available and were used without further purification.

The water used for the dilution of samples was obtained from the laboratory distilled water supply and redistilled in glass over barium hydroxide.

Apparatus and Method.—The hydrogen peroxide with hydrazine sulfate and catalysts was placed in a flask which was shaken with a shaking machine[6] which permitted

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[5] Browne and Shetterly, This Journal, **31**, 783–99 (1909).

[6] Walton, *Z. physik. Chem.*, **47**, 185 (1904).

the gases $N_2 + O_2$ to be evolved as soon as they were formed. The speed of the reaction was determined by measuring the rate at which these gases were evolved. The nitrogen contained in the gas evolved is a measure of the extent of the oxidation of the hydrazine and the estimation of this nitrogen necessitated the complete removal of the gas mixture from the reaction flask. This was effected by means of the rubber bag as shown in Fig. 1. By inflating the immersed rubber bag, it was possible to raise the liquid level to the top of the reaction flask and drive all the gas in the system into a gas buret. This gas mixture was then run repeatedly into alkaline pyrogallol until all the oxygen was absorbed. The remaining nitrogen was then measured in a gas buret, affording a measure of the extent of the oxidation of the hydrazine at the time when the gas was driven from the reaction flask. This time was carefully noted, making it possible to study the extent of the oxidation as a function of time. Since the nitrogen evolved is equal in volume to the oxygen consumed in the oxidation, the total volume of the gas evolved in the reaction is a true measure of the extent of the decomposition of the hydrogen peroxide.

Results

In this study the decomposition of the hydrogen peroxide and the concomitant oxidation of the hydrazine were studied as functions of time. In each run a volume of 120 cc. of solution was used, containing one millimole of hydrazine sulfate, hydrogen peroxide sufficient to give on decomposition 125 cc. of oxygen referred to standard conditions and the catalyst in quantities as noted. All runs were carried out at a temperature of 25.0°. The results obtained were checked by duplication. The decomposition of hydrogen peroxide was followed with an accuracy of about 3%, while the measurement of the rate of evolution of nitrogen was accurate to about 5%. These accuracies were sufficient to establish the relationships sought.

It was found that neither the first- nor second-order type of reaction was completely fulfilled in these reactions but it was observed that toward the middle of the reaction, a first-order constant was closely approached. This is shown in Table I and was found true in the oxidation of the hydra-

TABLE I

THE OXIDATION OF HYDRAZINE BY HYDROGEN PEROXIDE CATALYZED BY 0.200 MILLIMOLE OF COPPER SULFATE. DATA FOR THE DECOMPOSITION OF HYDROGEN PEROXIDE REFERRED TO STANDARD TEMPERATURE AND PRESSURE

Time in minutes	Cc. of gas mixture evolved	(a)	$(a - x)$	10^4K
00	00	125.0	125.0	..
16	35.3	125.0	89.7	3.46
25	50.5	89.7	74.5	3.44
30	57.5	74.5	67.5	3.32
36	65.0	67.5	60.0	3.26
40	69.0	60.0	56.0	2.83
46	74.5	56.0	50.5	2.90
60	85.5	50.5	39.5	2.90
75	94.5	39.5	30.5	2.88
End	125.0			

K as mean of last four values, 2.88.

zine and also the decomposition of the hydrogen peroxide. Because of the space required the original data are not given in detail, but are summarized in tables and graphs thoughout the text. For both reactions it was found that when the extent of reaction was plotted against time the graphs obtained were of the same type for various catalyst concentrations, so it was quite feasible to employ the constants as obtained above as measures of the reaction velocity. These computations were made using the second as the unit of time.

Copper Sulfate as a Catalyst.—The reactions under consideration were studied with various concentrations of copper sulfate and the results obtained are summarized in Table II. They are also given graphically in Fig. 2.

TABLE II

COPPER SULFATE AS A CATALYST

Concn. of $CuSO_4$, millimoles	0.05	0.100	0.150	0.20	0.30	0.50	0.70	1.00
10^4K	.443	.865	1.59	2.88	5.60	14.2	25.6	43.6
$10^4K'$	.320	.71	...	1.96	4.05	...	...	...

K, Reaction rate for decomposition of hydrogen peroxide.

K', Reaction rate for oxidation of hydrazine.

These results indicate that the mechanism of the oxidation of hydrazine is closely related to that of the decomposition of hydrogen peroxide since variations in catalyst concentration effect the same trends in both reactions.

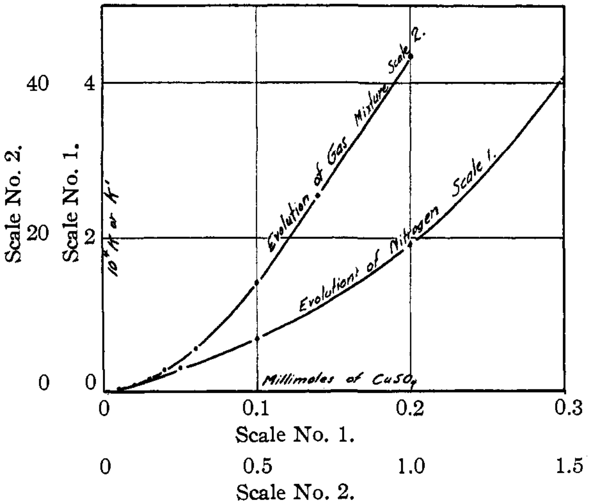

Fig. 2.—The oxidation of hydrazine by hydrogen peroxide catalyzed by cupric ions.

The accompanying graph shows that at concentrations of copper sulfate below 0.50 millimole an increase in catalyst concentration produces an increase in the rate of decomposition of the hydrogen peroxide, the slope of the curve increasing with increasing concentrations of copper sulfate. However, at higher concentrations the relationship is linear. This effect may be explained by the possibility that a compound may be formed between the hydrazine sulfate and the copper salt, there being exactly 1.00 millimole of the hydrazine salt present. It was not found practicable to carry the study of this effect into the oxidation of the hydrazine as the reaction velocity was so high at these catalyst concentrations that accurate readings were impossible.

Ferric Sulfate as a Catalyst.—Ferric sulfate was studied as a catalyst in a manner similar to that employed with copper sulfate. In this work, the milliatom, abbreviated as ma. and equal to one-half a millimole, was used as the unit of concentration. This was due to the fact that the active catalyst is assumed to be the ferric ion and not the ferric sulfate molecule. The results are summarized in Table III and Fig. 3.

TABLE III

FERRIC SULFATE AS A CATALYST

Concn. of $Fe_2(SO_4)_3$, milliatoms	0.20	0.40	0.50	0.70	1.00	1.50	2.00
10^4K	.39	.61	.74	.90	1.19	1.62	2.4
$10^4K'$	.20	..	.35	..	0.52	0.78	..

As in the case of copper sulfate, the reaction of oxidation follows closely that of the decomposition of the hydrogen peroxide, indicating that in this reaction, as in the one previously treated, the oxidation of the hydrazine is effected through the decomposition of the hydrogen peroxide and must be explained by the same mechanism established for this decomposition. The relationship is shown clearly in Fig. 3. There are also indications of compound formation as were observed with copper sulfate except that the first part of the curve showed a constantly decreasing slope indicating that the effect tends to accelerate the reaction. This effect was observed for the decomposition of the hydrogen peroxide and for the oxidation of the hydrazine as well, offering excellent confirmation of the suggested parallelism between these two reactions.

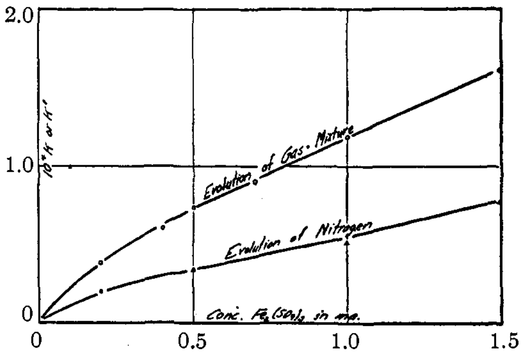

Fig. 3.—The oxidation of hydrazine by hydrogen peroxide catalyzed by ferric ions.

Cupric Sulfate Used in Various Concentrations with 0.200 Ma. of Ferric Sulfate as Catalyst.—For the purpose of detecting and studying the phenomenon of promoter action, the study of the catalytic properties of mixtures of ferric and cupric sulfates was undertaken next. In these studies, the concentration of one of the catalysts was fixed while that of the other was varied. For the first group of runs it was found convenient to fix the ferric sulfate concentration at 0.200 ma. and to vary the copper sulfate concentration. The results obtained are given in Table IV and are graphed in Fig. 4.

TABLE IV

CUPRIC SULFATE USED IN VARIOUS CONCENTRATIONS WITH 0.200 MILLIATOM OF FERRIC SULFATE AS CATALYST

Concentration of $CuSO_4$, millimoles	0.00	0.05	0.10	0.15	0.20
10^4K	.39	1.47	2.84	5.4	10.1
$10^4K'$	.20	0.78	1.6	2.8	4.3

It was found that the mixtures of catalysts studied showed a total effect much greater than additive. The quantitative expression of this promotion will be considered in a later portion of this paper. It is, however, immediately apparent that these results differ from those of Robertson, who found that the greatest effect relative to the copper concentration was obtained with the smaller quantities of the copper salt while these results show that in the presence of hydrazine sulfate the promoter effect continues with increased concentrations of the copper salt. These relationships are made more apparent in the quantitative discussion of the promoter action. The effect was observed both for the decomposition of the hydrogen peroxide and for the oxidation of the hydrazine.

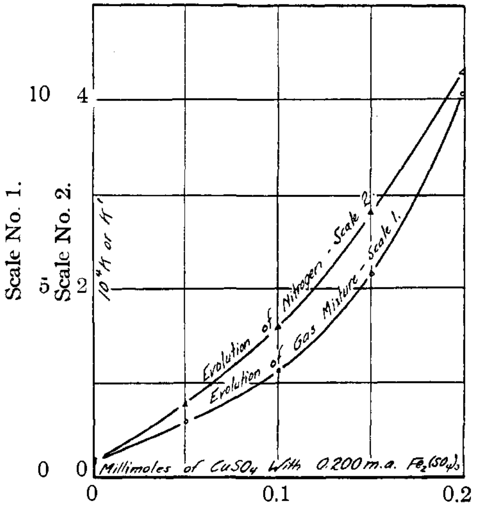

Fig. 4.—The oxidation of hydrazine by hydrogen peroxide catalyzed by 0.200 ma. of ferric sulfate with various quantities of cupric sulfate.

Ferric Sulfate Used in Various Concentrations with 0.100 Millimole of Cupric Sulfate as Catalyst.—Continuing the study of the catalytic activity of mixtures of ferric and cupric sulfates, the reaction velocities were determined for a group of runs in which the concentration of cupric sulfate was fixed and that of the ferric sulfate varied. The results are summarized in Table V and in Fig. 5.

As before, in this group of runs, a marked promotion was observed. However, as can be seen by comparison of Fig. 5 with Fig. 4, the effect of

TABLE V

FERRIC SULFATE USED IN VARIOUS CONCENTRATIONS WITH 0.100 MILLIMOLE OF CUPRIC SULFATE AS CATALYST

Concn. of $Fe_2(SO_4)_3$ in milliatoms	0.00	0.200	0.400	0.700	1.00	1.50
10^4K	.87	2.8	5.0	6.3	7.7	9.2
$10^4K'$	.71	1.63	2.1	2.4	..	..

increasing the concentration of cupric sulfate was quite different from that observed when the concentration of ferric sulfate was the variable studied. In general it was observed in the study of mixtures of the two catalysts that when the concentration of one was varied, the reaction rate for both the decomposition of the hydrogen peroxide and for the oxidation of the hydrazine followed the general trends observed when that catalyst was used alone in varying concentrations.

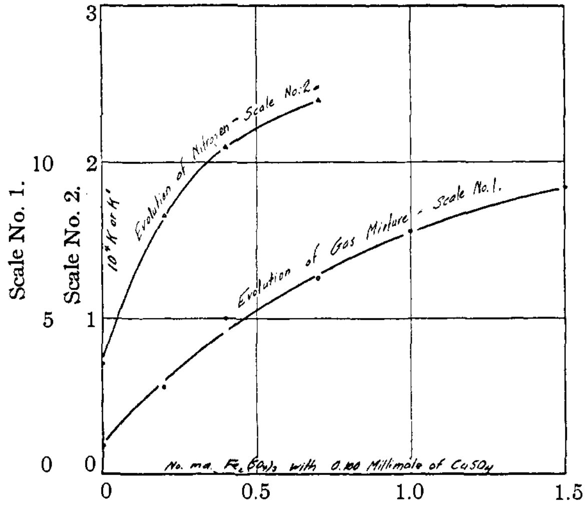

Fig. 5.—The oxidation of hydrazine by hydrogen peroxide catalyzed by 0.100 millimole of copper sulfate with various quantities of ferric sulfate as noted.

The Effect of Acidity.—The effect of the addition of various quantities of sulfuric acid to the reaction system was studied with copper sulfate and ferric sulfate used individually and in combination as catalysts for the oxidation of hydrazine by hydrogen peroxide. The results obtained showed the effect on the reaction to parallel closely that on the decomposition of the peroxide, offering still further evidence that these two reactions are dependent upon the formation of the same catalytic intermediates. An increase in acidity resulted in an inhibition of the two concomitant reactions quite similar to that observed in the earlier studies of the catalytic decomposition of hydrogen peroxide by iron and copper salts.

A Quantitative Measure of Promoter Action.—Attention has been called in an earlier part of this paper to the fact what when the two catalysts ferric sulfate and cupric sulfate are used together, the resulting rate is greater than the sum of the rates obtained when the same catalysts are used separately. In order to obtain a mathematical evaluation of promotion, the following conventions are employed

K_t = reaction rate for mixture of catalysts
K_{fe} = reaction rate for ferric sulfate at concentration noted
K_{cu} = reaction rate for copper sulfate at concentration noted

$$A = \frac{(K_t - K_{fe})\ (0.200)}{(K_{cu})\ (\text{Concn. ferric sulfate})} = \text{Promotion factor for cupric sulfate}$$

$$B = \frac{(K_t - K_{cu})\ (0.100)}{(K_{fe})\ (\text{Concn. cupric sulfate})} = \text{Promotion factor for ferric sulfate}$$

For the reaction of the decomposition of hydrogen peroxide, the symbols are used as above but for the oxidation of hydrazine, the letters are primed, as A' and B'.

The promotion factor for cupric sulfate as defined by the above formula is the ratio of the increase in the rate of reaction effected by its addition to a reaction system already containing 0.200 milliatom of ferric sulfate, to the reaction velocity effected by its use as a catalyst in the absence of the ferric sulfate. Likewise, the promotion factor for ferric sulfate is the ratio of the increase in reaction velocity resulting from its addition to a reaction system already containing 0.100 millimole of copper sulfate, to the reaction velocity obtained by its use alone as a catalyst. Since the promotion factor of each catalyst is referred to a certain definite concentration of the other, this factor will change with variation in catalyst concentration. The last term in the numerator together with the last term in the denominator form an approximating correction term for the concentration of the reference catalyst. Since this correction term is only approximate, assuming a linear relationship, the true values for A and A' are reached only from the data obtained with the ferric sulfate concentration fixed at 0.200 milliatom, when the correction term becomes unity and drops out of the computation. Likewise, the true values of B and B' are obtained only from the data obtained with the cupric sulfate concentration fixed at 0.100 millimole.

Promotion factors computed by the method just discussed from the data obtained in the studies of the catalytic effects of the mixed catalysts are given in Tables VI and VII.

It is evident that the approximating factor introduced gives satisfactory results in the computation of B and B' but gives values deviating markedly from the true values in the computation of A and A' in Table VII. Although the true values of the promotion factors show slight trends, it is entirely practicable within the concentration limits studied to express these relationships as constant. The averages of these values are $A = 3.0$; $A' = 1.8$; $B = 5.5$; $B' = 4.5$.

Table VI

Promotion Factors Obtained with 0.200 Milliatom of Ferric Sulfate with Various Quantities of Cupric Sulfate as Noted

	Concn. of $CuSO_4$ in millimoles			
	0.05	0.10	0.15	0.20
A	2.5	2.8	3.1	3.4
A'	1.8	2.0	1.6+	2.1
B	5.3	5.1	6.5	9.4
B'	4.6	4.6	4.0	5.7

Table VII

Promotion Factors Obtained with 0.100 Millimole of Cupric Sulfate with Various Quantities of Ferric Sulfate as Noted

	Concn. of $Fe_2(SO_4)_3$ in milliatoms				
	0.20	0.40	0.70	1.00	1.50
A	2.8	2.5	1.8	1.5	1.2
A'	2.0	1.3	0.8	...	...
B	4.9	6.7	5.9	5.6	5.2
B'	4.7	4.8	4.1	...	...

The Mechanism of the Oxidation.—It has been shown that hydrazine is oxidized by hydrogen peroxide in the presence of ferric sulfate or copper sulfate or mixtures of the two, and that all factors tending to affect the rate of decomposition of the hydrogen peroxide have a similar influence on the rate of oxidation of the hydrazine. This inter-relationship is so complete that there is no doubt that the oxidation is facilitated through the formation and decomposition of the same intermediates that have previously been shown to effect the decomposition of the hydrogen peroxide, namely, ferric and cupric acids. The qualitative facts cited above, however, do not give definite evidence as to whether the oxidation is due to reaction of the hydrazine directly with these catalytic intermediates or with the oxygen released in the reaction of the hydrogen peroxide with the ferric and cupric acids. The hydrogen peroxide is in too dilute a solution to effect alone a measurable portion of the observed oxidation in the period of time involved. It seems probable that the oxidation is effected by both of the suggested possible means. Of the two catalytic intermediates, the ferric acid must be considered the stronger oxidizing agent because it will react with a cupric ion to form cupric acid. This is not conclusive evidence, however, that the oxidation velocity would be the greater, although it is hoped by means of the promotion factors to show that this is the case. The phenomenon of promotion alone is strong evidence that the oxygen released in the reaction of the ferric or cupric acid with hydrogen peroxide plays a very marked role in the oxidation of the hydrazine, because a mixture of oxidizing agents such as ferric and cupric acids, except as they might react with each other, would not show more than additive effects. The hydrogen peroxide is present in such a relatively high concentration as would make reaction of a molecule of ferric acid with a molecule of cupric acid quite infrequent. Even if they did react, the oxygen liberated would probably be less potent than that liberated by the reaction of either cupric or ferric acid with hydrogen peroxide because, as has been previously cited, hydrogen peroxide is capable of forming either cupric or ferric acid from a lower state of oxidation. The fact that the promotion factors for the decomposition of hydrogen peroxide are much larger is some indication that the oxidation is not entirely due to the oxygen evolved in the reaction of the hydrogen peroxide with the ferric or cupric acids but that these catalytic intermediates may act directly as oxidizing agents, an increase in the rate of their decomposition rate resulting in a decrease in their oxidizing efficiency. It was observed that the ratio of A to A' was much greater than the corresponding ratio of B to B'. ($A/A' = 1.65$ and $B/B' = 1.22$.) This is quite definite indication that the oxidizing power of ferric acid is greater than that of cupric acid. This relationship may perhaps be clarified by saying that the addition of ferric sulfate to a reaction system already containing a certain mixture of both catalysts produces a certain increase in the rate of decomposition of the hydrogen peroxide and also a definite increase in the rate of oxidation of the hydrazine, and that the addition to the same original reaction system of enough cupric sulfate to effect the same increase in the rate of the decomposition of the hydrogen peroxide will result in a smaller increase in the rate of oxidation of the hydrazine than did the ferric sulfate. This may seem at variance with the fact that when the catalysts are used separately, the ratio of $K'_{\mathrm{cu}}/K_{\mathrm{cu}} = 0.73$ from Table II, and from Table III the ratio $K'_{\mathrm{fe}}/K_{\mathrm{fe}} = 0.48$. (These are average values.) However, this fact does not necessarily condition the behavior of these two catalysts when used together because, as has been suggested by Robertson, the ferric acid acts on the cupric ion to form cupric acid more rapidly than does hydrogen peroxide alone.

Summary

1. The oxidation of hydrazine by hydrogen peroxide catalyzed by ferric sulfate, cupric sulfate and various mixtures of the two has been studied and found to be comparatively free from side reactions.

2. The effects of the variation of catalyst concentrations were studied for the individual catalysts and for various mixtures of the two. Attention was given both to the reaction of the decomposition of the hydrogen peroxide and the oxidation of the hydrazine. When the catalysts were used separately, copper sulfate was found to be a much more effective catalyst than ferric sulfate for both reactions.

3. The phenomenon of promoter action was found to enter into both

the decomposition of the hydrogen peroxide and the oxidation of the hydrazine, and promotion factors were computed.

4. The effect of acidity was studied and observed to be quite analogous to the inhibition noted in studies of the decomposition of hydrogen peroxide in the absence of hydrazine.

5. The mechanism of the oxidation of the hydrazine is probably as follows. The hydrazine is oxidized both by the oxygen liberated in the reaction of the catalyst intermediate with the hydrogen peroxide and by that catalyst intermediate itself. When ferric and cupric sulfates are used together, producing both cupric and ferric acids, the ferric acid is more effective in the oxidation than is the cupric acid, the observed promotion in the oxidation reaction being almost wholly due to oxidation by the evolved oxygen which is liberated in an activated state.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

REACTIONS IN LIQUID HYDROGEN SULFIDE. VIII. SPECIFIC CONDUCTANCE OF LIQUID HYDROGEN SULFIDE

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Introduction

There is but little agreement in the published values for the specific conductance of liquid hydrogen sulfide. Steele, McIntosh and Archibald[2] reported it as being an extremely poor conductor and gave the value for the specific conductance as about 0.1×10^{-6} at $-81°$. Magri[3] found it "much less than 4×10^{-7} at $-60°$." Quam and Wilkinson[4] concluded from qualitative observations that it was much less than this, being less than 1×10^{-11} reciprocal ohms. Borgeson,[5] using a sensitive Wheatstone bridge set-up, obtained values varying from 10^{-6} to 10^{-8} at $-78.5°$.

In view of these varying results it was the purpose of this work to make a quantitative determination of the specific conductance of liquid hydrogen sulfide at $-77°$.

Experimental

The liquid hydrogen sulfide was prepared in the apparatus described by Quam.[6] The conductivity cell was made from a wide test-tube with a stopper through which passed the glass tubes making mercury connections

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[1] Assistant Professor of Physics at Iowa State College.

[2] Steele, McIntosh and Archibald, *Phil. Trans. Roy. Soc.*, **205A**, 99 (1906).

[3] Magri, *Atti Accad. Lincei*, [5] **16**, I, 510 (1907).

[4] Quam and Wilkinson, THIS JOURNAL, **47**, 989 (1925).

[5] Borgeson, unpublished data from this Laboratory.

[6] Quam, THIS JOURNAL, **47**, 103 (1925).