ponents, condensation would take place on the surface, and a solution would be formed. The amount of reaction would be dependent on several factors such as temperature, surface, rate of flow of chlorine, rates of diffusion, etc.

In Table III the observed vapor pressures of a solution saturated with potassium bromide and potassium chloride averaged 11.8 and 22.3 mm. at 20° and 30°, respectively. The close correspondence between the minimum effective concentrations and the vapor pressures of the saturated solutions cannot be entirely accidental.

In the case of potassium iodide and chlorine the point of minimum effective concentration is not so clearly marked. A study of Table I suggests that such a point does exist. The fact that there was no temperature control partly accounts for the obscuring of the result. The iodine replaced has, moreover, a much greater solubility than the bromine, and mention has been made of the adhesive nature of the reaction products. The vapor pressure of the saturated solution of potassium iodide and chloride was shown to be only 6 mm. at 21.5°. The vapor pressure of the saturated solution containing the reactants would no doubt be considerably below this value.

Summary

There is a minimum partial pressure of water vapor, for each temperature, which must be attained before any considerable reaction takes place between chlorine and potassium iodide or potassium bromide. This minimum effective partial pressure is approximately the vapor pressure of a saturated solution of the components present during the reaction.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE INFLUENCE OF WATER ON CERTAIN CHEMICAL REACTIONS. II. THE REACTION BETWEEN HYDROGEN SULFIDE AND IODINE IN ETHER SOLUTION[1,2]

BY L. B. PARSONS

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Although an enormous amount of research has been done on the influence of water on the rate of chemical reactions, most of the work has been qualitative in nature; very little attention has been given to the effect of changing the concentration of water. The object of this investigation

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[1] The author wishes to acknowledge a grant from the Research Committee of the University of Wisconsin, Dean C. S. Slichter, Chairman, which made it possible to carry out this investigation.

[2] The work in this paper is from the thesis presented by L. B. Parsons in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction.

was to study the effect of different amounts of water on a reaction taking place in a homogeneous system. The reaction between hydrogen sulfide and iodine in ether solution seemed well suited for this purpose.

According to Noyes and Sammet,[3] this reaction proceeds very slowly in anhydrous ether and rapidly in the presence of water. Since water is soluble in ether to the extent of 1% by volume, this solvent affords an opportunity for a considerable variation in water concentration. Ether has the added advantage that it is easily purified and at ordinary temperatures does not react with iodine to an appreciable extent.

Preparation of Reagents

Commercial ether was purified by distilling it from fused calcium chloride and allowing the product to stand over bright sodium wire until no further reaction took place. This reagent was then distilled from a dry apparatus into dried 250cc. containers which were then sealed. This method of storage was most satisfactory and insured a supply of pure, dry ether free from objectionable peroxides.

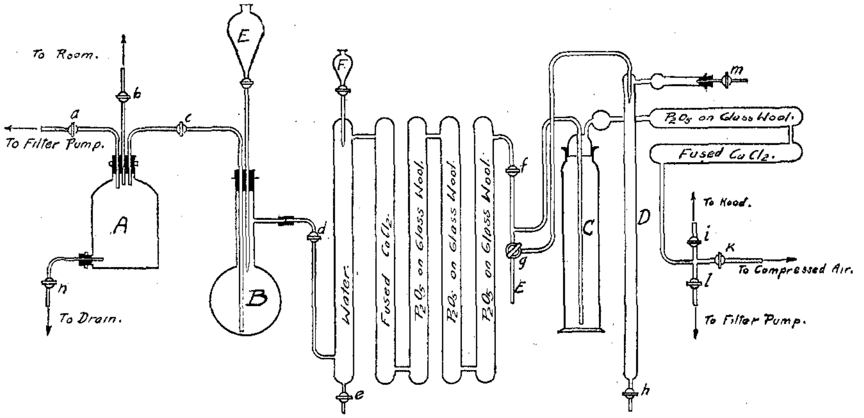

Fig. 1.—Apparatus for the preparation, storage and analysis of hydrogen sulfide-ether solutions.

C. P. iodine was ground with potassium iodide and sublimed. This sublimate was resublimed and placed on a large watch glass in a desiccator over phosphorus pentoxide for several days. It was then bottled and preserved in a desiccator over phosphorus pentoxide.

Hydrogen sulfide was prepared from a 25% solution of sodium sulfide by treatment with concentrated acid. The gas was washed with distilled water and dried by calcium chloride and phosphorus pentoxide.

Preparation of Solutions

Ether and Hydrogen Sulfide.—In order to prepare a solution of hydrogen sulfide in anhydrous ether and have it ready for analysis and use, the apparatus illustrated in Fig. 1 was devised. *B* is the hydrogen sulfide generator, *A* a device for removing exhausted solutions from *B* without the introduction of air into the system, *C* is the satura-

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[3] Noyes and Sammet, This Journal, 24, 498 (1902).

tor and storage chamber for the hydrogen sulfide-ether solution, while *D* is a 50cc. buret for measuring definite volumes of the solution for analysis and use. The actual manipulations involved in the operation of this apparatus will be obvious from a study of the diagram. It was found that solutions of hydrogen sulfide in ether prepared and stored in this apparatus underwent no appreciable change, even when kept for several days.

Ether and Iodine Solutions.—A solution of iodine in ether was prepared by quickly transferring the purified ether from a sealed flask to a clean, well-dried, glass-stoppered bottle. Approximately the desired amount of iodine was dissolved in the ether and the bottled solution kept in a large desiccator over phosphorus pentoxide for analysis and use. Solutions were usually made up on the same day that they were used in order to avoid the formation of ether peroxide which takes place when ether is exposed to air.

Reaction Mixtures.—The concentrations of the hydrogen sulfide and iodine were adjusted by adding definite volumes of iodine and hydrogen sulfide solutions of known concentrations to a volumetric flask and making up to volume with the pure dry ether. Since the concentration of hydrogen sulfide tends to change, an additional check was made by determining the excess of hydrogen sulfide in a known volume of the reaction mixture. This was done iodimetrically.

The water concentration was adjusted at low concentrations by adding a known amount of water to a known volume of ether and pipetting out aliquot portions to the reaction mixture. For higher concentrations, the water was added to the iodine solution or to the solution of hydrogen sulfide directly. It was found necessary to have all of the water in the solution before mixing the hydrogen sulfide and iodine solutions, since these substances react at once in the liquid water phase and give discordant results.

In handling the reaction mixtures and the solutions of hydrogen sulfide in ether, it was found necessary to arrange a device for forcing the solutions into the pipets. This procedure was adopted to avoid the loss of hydrogen sulfide which occurred when the pipets were filled in the usual manner.

Analytical Methods

Analysis of Hydrogen Sulfide-Ether Solutions.—For low concentrations of hydrogen sulfide in ether, the iodimetric method was most satisfactory. A 25cc. sample was run in below the surface of 300 cc. of 1% potassium iodide solution containing an excess of standard iodine solution. The excess of iodine was titrated with thiosulfate solution. This method is not applicable to high concentrations of hydrogen sulfide since the liberated sulfur particles tend to stick together and absorb iodine.

For high concentrations of hydrogen sulfide the neutral cadmium sulfate method was used. A known volume of the ether solution was placed in a suitable container and air was aspirated through the ether and two gas-washing bottles containing a 3% cadmium sulfate solution neutral to methyl orange. Finally, the ether container was warmed and the ether evaporated through the cadmium sulfate solution, insuring complete removal of the hydrogen sulfide. The precipitated cadmium sulfide in the wash bottles was filtered off, washed thoroughly and the acidity of the filtrate determined by titration with 0.1 *N* sodium hydroxide solution. The filter paper containing the cadmium sulfide was placed in a 2 liter beaker, an excess of 0.1 *N* iodine solution added and the whole diluted to 1.5 liters. The solution was then strongly acidified with hydrochloric acid, thoroughly stirred, the excess of iodine titrated with thiosulfate solution and the hydrogen sulfide content calculated from these data. The following analyses carried out on ether solutions of hydrogen sulfide saturated at 26° show the accuracy to be expected from this method.

TABLE I

SOLUBILITY OF HYDROGEN SULFIDE IN ETHER AT 26° AND 740 MM.

Soln. used, Cc.	0.1 *N* iodine used, Cc.	H_2S *N*	0.1 *N* alkali used, cc.	H_2S *N*
9.48	47.96	0.506	47.80	0.505
6.60	34.40	.520	33.80	.515

The solubility of hydrogen sulfide in ether at ordinary temperatures and pressures is therefore about 8.8 g. per liter or 5.7 volumes per volume of ether.

Determination of Hydrogen Sulfide in Reaction Mixtures.—Although the method of making up solutions of known concentrations gave approximately the calculated results, there was always a slight loss of hydrogen sulfide. It was consequently necessary to determine the hydrogen sulfide content of the system after the reaction mixture had been made up. When the mixture was sealed in tubes of 10 cc. each, the mean of the analyses of the first and last tube was taken as the concentration of hydrogen sulfide in the system. The mixture was run into an excess of iodine solution in aqueous potassium iodide and titrated back with standard thiosulfate solution. Since the concentration of iodine in the ether solution was known and the amount of standard iodine used up by the excess of hydrogen sulfide was determined, the concentration of hydrogen sulfide was easily calculated.

Determination of Iodine in Ether-Iodine Solutions.—The iodine concentration in ether solution was determined by direct titration with thiosulfate solution of a known volume of solution dissolved in aqueous potassium iodide. A colorimetric method was also used to determine the iodine concentration in ether solution. A sample compared in the colorimeter at three widely different settings of the standard gave ratios of 0.71, 0.72 and 0.72. The corresponding concentration of iodine was 0.00269 g. per cc. The result obtained by titration was 0.00266 g. per cc.

Determination of Iodine in the Reaction Mixtures.—The iodine was estimated colorimetrically, using iodine in ether as a standard solution. At low concentrations of iodine in the reaction mixtures, a tint slightly different from the standard was noted. To obtain a match, comparisons were made with as deep a column of liquid as was practicable. The results obtained were probably accurate to within 10%. A direct comparison method was later adopted. It consisted in sealing a series of standards varying by 0.5 millimole from concentrations of 0.5 to 10 millimoles of iodine per liter. These standards were all sealed in test-tubes of a uniform size and were preserved in the dark; however, it was found that even six months' standing in the diffused daylight of the laboratory did not appreciably change the concentration. The reaction mixtures were then sealed in clean, carefully dried test-tubes of the same size as those used for the standards and the concentrations of iodine in the mixtures determined from time to time by direct comparison. Operating in this way, the concentration of iodine could be determined to ±0.2–0.5 millimole per liter, depending upon the concentration.

Results

The Effect of Atmospheric Oxygen on the Reaction.—It was soon found that whenever moisture was present the oxygen from the air had a great effect on the reaction between hydrogen sulfide and iodine in the ether solutions. The following experiments show the magnitude of the effect.

Several sets of reaction mixtures containing the same concentrations of hydrogen sulfide and iodine, but with various concentrations of water, were placed in 100cc. glass-stoppered flasks. As a precaution against evaporation, the runs were made at 0°. The concentrations of iodine in the reaction mixture at any given time were determined by comparing a sample in the colorimeter with a standard solution. Table II shows the results obtained.

TABLE II

THE EFFECT OF ATMOSPHERIC OXYGEN ON THE REACTION AT 0°

	Concn. of reactants Millimoles per liter			Concn. of iodine after elapsed time				
Sample	H_2S	I_2	H_2O	0	18.5	22.5	47	90 hrs.
1	10.4	5.2	0	5.2	5.2	5.1	5.2	5.2
2	10.4	5.2	111	5.2	3.6	3.2	3.7	4.2
3	10.4	5.2	278	5.2	3.2	2.8	3.5	4.0
4	10.4	5.2	556	5.2	1.8	1.7	4.2	5.2

These above are very discordant. With Sample 1, in which the concentration of water was zero, the concentration of iodine remained unchanged. With Samples 2, 3 and 4, the iodine was at first used up and then after a time was regenerated, the concentration gradually increasing to the point where it was nearly equal to the original concentration. It seemed that this peculiar behavior might be connected with the fact that atmospheric oxygen was unavoidably admitted to the reaction mixture when the samples were pipetted out for analysis. An experiment was made to determine whether the various reaction mixtures at the end of 90 hours still contained sufficient hydrogen sulfide to react completely with the free iodine present. Samples of the various mixtures were shaken with an excess of water. It was found that Sample 1 was completely decolorized, proving that there was still enough hydrogen sulfide present to react with the iodine. Samples 2, 3 and 4, however, showed no appreciable change in color; evidently all of the hydrogen sulfide had disappeared from the mixtures. These observations might be interpreted in two ways—either the oxygen of the air oxidized the hydrogen sulfide to sulfur and water, or the oxygen oxidized the hydriodic acid formed in the reaction to water and iodine. The former view does not seem tenable, since the hydrogen sulfide was not oxidized to a very great extent in the dry sample. The possibility that water may catalyze either or both of these reactions should not be overlooked. From the preceding reasoning, it seemed evident that the results obtained in the presence of oxygen would not indicate the true course of the reaction between hydrogen sulfide and iodine, so a method of procedure to exclude atmospheric oxygen had to be devised. It seemed that the procedure least open to objection would be to seal small samples of the reaction mixture and at the desired time to open them and analyze them at once.

A large number of ordinary 20cm. test-tubes were thoroughly cleaned and dried. They were then drawn out, heated and while still hot placed in a large desiccator over phosphorus pentoxide. The reaction mixtures were made up and placed in these clean, dry tubes which were immediately sealed. A series of runs, using this method of procedure, showed that there were no irregular variations in the iodine content with time. Reaction mixtures containing water quickly reached an equilibrium value, while dry reaction mixtures proceeded gradually to completion. For data showing this behavior see Table III.

The Effect of Light on the Reaction.—It was thought essential to determine whether the reaction velocity was influenced by the diffused daylight of the laboratory. A set of experiments designed to test this point revealed no differences in the rates of reaction between the contents of tubes kept in the light and in the dark.

Table III

Comparison of Wet and Dry Reactions

Concn. of iodine = 8.9 millimoles per liter
Concn. of hydrogen sulfide = 34 millimoles per liter. Temp. = 30°

Elapsed time Hours	Concn. of iodine in millimoles per liter		
	Concn. of water = 0	135 mm. per liter	277 mm. per liter
0	8.9	8.9	8.9
24	8.3	6.2	4.8
48	5.7	6.2	4.5
72	4.1	6.1	4.4
96	2.7	...	...
168	1.7	...	...
192	1.2	6.0	4.5

The Effect of Varying the Concentration of the Reactants.—Further studies were carried out on the effect of the concentration of water on the reaction between the hydrogen sulfide and iodine. The results were obtained by sealing samples of the reaction mixture in test-tubes, and determining the iodine colorimetrically from time to time. Table III shows the results obtained when the concentration of water was varied, the hydrogen sulfide and iodine concentrations remaining constant.

This series of runs brought out the rather astonishing fact that, while the reaction in the anhydrous solvent was apparently a very slow one, it eventually went to completion. On the other hand, the reaction in the presence of water was an incomplete reaction which reached equilibrium fairly rapidly. In order to establish definitely whether the reaction in the anhydrous solvent was complete, and whether the reaction in the presence of water reached a state of equilibrium, a set of reaction mixtures was sealed in tubes and allowed to stand for a period of three months. At the end of this time the samples were opened and the iodine contents determined colorimetrically. Table IV gives the results of this series of experiments.

TABLE IV

EFFECT OF VARYING THE CONCENTRATIONS OF THE REACTANTS

Series	Sample	Concn., millimoles per liter H_2O	H_2S	I_2	Concn. of iodine Millimoles per liter after three months
A	1	0	40	6.4	0.0
	2	278	40	6.4	1.2
	3	410	40	6.4	0.4
	4	556	40	6.4	.2
B	1	0	38	12.5	.0
	2	111	38	12.5	6.0
	3	222	38	12.5	4.0
	4	333	38	12.5	2.5
	5	444	38	12.5	1.5
C	1	0	60	8.5	0.0
	2	222	60	8.5	2.0
	3	444	60	8.5	0.5

From a consideration of Table IV it is evident that in the absence of water the reaction is complete, while in the presence of water the reaction is incomplete. Furthermore, the point of equilibrium is dependent upon the concentration of water in the system. It seemed worth while to attempt to find the limiting concentration of water which would give an equilibrium mixture, and also to determine the manner in which the point of equilibrium varied with the concentration of water. To secure comparable results, it was necessary to keep the concentrations of the hydrogen sulfide and iodine constant and to vary the concentration of water gradually from zero to a relatively large value.

In order to follow the course of the reaction, without sealing an excessive number of samples, the analysis was carried out by direct comparison of the colors with a series of standard ether—iodine solutions sealed in test-tubes of an exactly uniform size. To secure a sufficient color variation to insure an accuracy of ±0.2–0.5 millimole, it was necessary to work at concentrations below 6 millimoles per liter. Four samples at each concentration of water were sealed and preserved as checks upon one another. From time to time these samples were compared with one another and with a series of standard solutions of iodine in ether, the concentrations of which varied by steps of 0.5 millimole, from 0 to 6 millimoles per liter. Between the readings the samples were kept at the laboratory temperature in a laboratory locker. Table V shows the results obtained with this series of samples.

TABLE V

EFFECT OF VARYING THE CONCENTRATION OF WATER

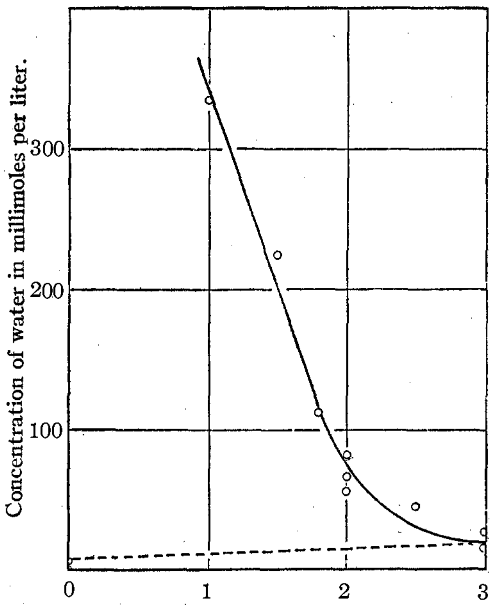
Concn. of hydrogen sulfide = 18 millimoles per liter. Concn. of iodine = 5.5 millimoles per liter.

Sample	Concn. of water Millimoles per liter	Concentration of iodine at end of times below 0	74	122	146	242	410 hrs.
1	0	5.5	3.0	2.0	1.8	1.5	0.8
2	5	5.5	4.0	3.0	2.8	2.0	1.5
3	16	5.0	3.0	3.0	3.0	3.0	3.0
4	27	4.0	3.0	3.0	3.0	3.0	3.0
5	44	3.5	2.5	2.5	2.5	2.5	2.5
6	55	3.0	2.0	2.0	2.0	2.0	2.0
7	66	2.5	2.0	2.0	2.0	2.0	2.0
8	82	2.0	2.0	2.0	2.0	2.0	2.0
9	112	2.0	1.8	1.8	1.8	1.8	1.8
10	225	1.5	1.5	1.5	1.5	1.5	1.5
11	335	1.0	1.0	1.0	1.0	1.0	1.0

It can be seen from Table V that the iodine content in Samples 1 and 2 decreased gradually with time, and at about the same rate; in the other samples the iodine content soon reached a minimum equilibrium value and then remained constant. It was found that the first two had gone to completion at the end of six weeks, while even at the end of six months there was still approximately the same free iodine content in the other samples. In order to be sure that there was sufficient hydrogen sulfide present to react with the iodine, the various tubes were broken, the contents of each poured into a test-tube containing an excess of water, and shaken. In every case there was an immediate reaction, the iodine disappearing almost instantly. Fig. 2 shows graphically the data contained in Table V. It can be easily seen that below concentrations of 100 millimoles of water per liter small changes in the concentration of water produce marked changes in the point of equilibrium. Above this value, however, the change in the equilibrium values with changing concentrations is not so pronounced. This is evidently purely a mass effect. If the reaction under consideration were entirely an equilibrium one, there would be no apparent break in the curve, as indicated by the dotted line. It would be expected that at zero concentration the value of the iodine concentration would be 5.5 millimoles per liter.

Discussion of Results

The obvious conclusion to be drawn from the results just described is that the reaction of hydrogen sulfide with iodine in ether solution proceeds in two ways, depending upon whether or not water is present. In the absence of water the reaction is complete, while when the concentration of water is above a certain minimum value the reaction is incomplete.



Concentration of iodine at equilibrium in millimoles per liter.

Fig. 2.—The effect of various concentrations of water on the reaction between hydrogen sulfide and iodine in ether solution.

In the absence of water it seems probable that the reaction proceeded according to the equation, $H_2S + I_2 \longrightarrow 2HI + S$. This view was further confirmed by the fact that visible films of sulfur were deposited in many instances on the walls of these reaction tubes. In the presence of water a suitable mechanism of the reaction must account for the equilibrium reaction and also show that the theoretical shift of the point of equilibrium due to changing the concentration of the reactants is the same as that actually found. The following series of reactions has been formulated to explain the observed facts.

$$3H_2O + 3I_2 \rightleftharpoons 6HI + 3[O] \qquad (1)$$

$$3[O] + H_2S \rightleftharpoons H_2SO_3 \qquad (2)$$

$$H_2SO_3 + 6HI \rightleftharpoons 3H_2O + H_2S + 3I_2 \qquad (3)$$

Formulating the above in a single equation,

$$H_2S + 3H_2O + 3I_2 \rightleftharpoons H_2SO_3 + 6HI \qquad (4)$$

Attempts to isolate the products of the reaction were unsuccessful on account of the high dilution of the reaction mixtures and their complicated nature.

Evidence to show that sulfurous acid is capable of oxidizing hydriodic acid in ether solution was obtained as follows. A sample of ether containing some dissolved water was partially saturated with gaseous hydrogen iodide. A solution of sulfur dioxide in ether was also prepared. When portions of these two solutions were mixed an immediate liberation of iodine took place. When enough water was added to this mixture to form two layers, the excess of sulfur dioxide immediately reduced the iodine to hydriodic acid. This experiment is directly in line with the reaction represented in Equation 3. The fact that an excess of water causes the reaction to go to completion can be explained either on the assumption of the incomplete reaction being driven to completion by an infinite amount of water or that an entirely different reaction takes place in the water phase. While it is usually assumed that in the water phase the reaction between iodine and hydrogen sulfide proceeds according to the equation, $H_2S + I_2 \longrightarrow 2HI + S$, there can be no doubt that the reaction is more complex than this, with side reactions resulting in the formation of various thionic acids. The theory that has been proposed also accounts for the strange behavior of atmospheric oxygen. In Table II it was shown that in the presence of water the iodine content first decreased and then increased, while in the absence of water there was no change in the concentration of the iodine. Also, in the absence of water there was sufficient hydrogen sulfide at the end of the run to react completely with the iodine, while when water was present, it was found that there was not enough hydrogen sulfide to react with the iodine. This behavior is explained by the fact that atmospheric oxygen will oxidize ether to ether peroxide.[4] Ether peroxide is capable of oxidizing hydriodic acid to free iodine and water. The peroxide, at least in the absence of water does not oxidize hydrogen sulfide to sulfur and water. This is shown by the fact that Sample 1, Table II, had enough hydrogen sulfide to react completely with the iodine at the end of 90 hours. The fact that the iodine concentration of this sample did not change was probably due to the hydriodic acid being oxidized to iodine as fast as it was formed in the very slow complete reaction.

The behavior of Samples 2, 3 and 4 indicates that the observations are complicated by two reactions taking place simultaneously.

$$H_2S + 3H_2O + 3I_2 \rightleftharpoons H_2SO_3 + 6HI \qquad (5)$$

$$(C_2H_5)_2O_2 + 2HI \longrightarrow (C_2H_5)_2O + H_2O + I_2 \qquad (6)$$

Since the last reaction is irreversible, it would follow that the free iodine restored to the system would react with more hydrogen sulfide until a point was reached where all the hydrogen sulfide had been used up. Then the remaining hydriodic acid in the system would be oxidized by the ether peroxide and the final concentration of free iodine should be the same that

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[4] Clover, THIS JOURNAL, **44,** 1107 (1922).

it was originally. This result was obtained experimentally in Sample 4, while in the other cases there could be little doubt that the original concentration would eventually be reached, since the free iodine concentration was still increasing when the experiment was discontinued. It must be pointed out here that sulfurous acid should be left as a product of the reaction. It would seem that when the reaction mixture was shaken with an excess of water the iodine should be reduced by the sulfurous acid. Sulfurous acid, however, is very easily oxidized, so no doubt the ether peroxide or even the oxygen from the air had oxidized this completely to sulfuric acid. This possibility presents another complicating factor in predicting the equilibrium point of the reaction in the presence of atmospheric oxygen.

Summary

1. A study of the reaction between hydrogen sulfide and iodine in ether solution has been carried out.
2. The reaction takes place in two ways, depending upon whether or not water is present in the ether solution. In the presence of water the reaction is incomplete; in the absence of water it is complete.
3. The equilibrium point in the reaction depends upon the relative concentration of the water.
4. Diffused daylight has no appreciable effect on the reaction.
5. Atmospheric oxygen changes the nature of the reaction and suitable precautions must be taken to exclude air.
6. A satisfactory mechanism has been formulated for the reaction and the observations are explained upon this basis.

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[CONTRIBUTION FROM THE LABORATORY OF GENERAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE INFLUENCE OF WATER ON CERTAIN CHEMICAL REACTIONS. III. THE REACTIONS BETWEEN CERTAIN METALS AND IODINE[1]

BY L. B. PARSONS

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Although dry zinc and dry iodine do not react to form zinc iodide[2] in the absence of water, the addition of a few drops of water causes an immediate and violent reaction. Several other examples have been recorded in the literature in which the various well-dried halogens failed to react

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[1] The work in this paper is from the thesis presented by L. B. Parsons in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin. The subject of this research was suggested by Professor James H. Walton and the investigation was conducted under his direction.

[2] Noyes and Sammet, THIS JOURNAL, **24,** 498 (1902).