

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, IOWA STATE COLLEGE]

## A STUDY OF REACTIONS IN LIQUID HYDROGEN SULFIDE<sup>1</sup>

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The chemistry of liquid hydrogen sulfide was made the subject of investigation in this Laboratory in the effort to extend the work of several investigators<sup>2</sup> who have shown that a limited number of compounds are soluble in liquid hydrogen sulfide and that in a few cases the solutions conduct the electric current. The study of the solvent action of liquid hydrogen sulfide has been limited almost wholly to organic solutes and these did not include any of the sulfur derivatives such as the sulfides and mercaptans. In the inorganic field little has been done aside from a study of a few metallic elements, the halogens, several salts and a few oxidizing agents. In general, the investigators have come to the conclusion that in its properties liquid hydrogen sulfide is much like an organic solvent. The chief criticism is that the periods of observation were very short and the experiments were conducted at temperatures below the boiling point of liquid hydrogen sulfide. It is reasonable to suppose that in most cases equilibrium conditions were not observed.

### Preparation of Liquid Hydrogen Sulfide

The method of preparing and liquefying hydrogen sulfide in this Laboratory was a modification of that used by Antony and Magri.<sup>2c</sup>

The apparatus, Fig. 1, was constructed of soft lime glass and designed in such a way that all parts could be made and sealed together in the laboratory. The generator, consisting of Bottles G and B and Flask A, was filled with iron sulfide and hydrochloric acid. In K the acid spray was held back by a saturated solution of potassium sulfide; the gas was then dried by aluminum sulfide in L, with subsequent evolution of more hydrogen sulfide, and passed over iodine in M to remove possible traces of arsine. Any hydrogen iodide set free was held back in the potassium sulfide solution in K'. Again the gas was dried by passing over layers of aluminum sulfide in L'. The final drying was accomplished by allowing the gas to pass over phosphoric acid anhydride in N, N' and N".

Before the refrigerating process was started the gas was allowed to flow through the system until all the air had been swept out and the inner surfaces were dry. The water condensers O and O' were started and the liquefaction was completed by allowing the pure dry hydrogen sulfide to flow through the coils, in R and R', which were kept immersed in a bath of ether and solid carbon dioxide. The liquid hydrogen sulfide was collected in the reservoir T in a third Dewar vacuum tube containing the same refrigerat-

<sup>1</sup> This paper is constructed from a portion of a thesis submitted to the graduate school of Iowa State College by G. N. Quam in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>2</sup> (a) McIntosh and Steele, *Proc. Roy. Soc.*, **73**, 450 (1904). (b) Walker, McIntosh and Archibald, *J. Chem. Soc.*, **85**, 1098 (1904). (c) Antony and Magri, *Gazz. chim. ital.*, **35**, 206 (1905). (d) Magri, *Atti. accad. Lincei* [5] **16**, 171 (1907). (e) Archibald and McIntosh, *Proc. Roy. Soc.*, **73**, 454 (1904). (f) Skilling, *Am. Chem. J.*, **26**, 383 (1901).

ing mixture. The free gas was allowed to flow out by way of  $Q''$  over calcium chloride in  $W$  and into the back pressure column  $X$ . The water level in  $X$  was raised as high as the action of the generator would permit. The liquid hydrogen sulfide was removed from Reservoir  $T$  by closing Stopcock  $Q''$  and opening  $Q'$ , allowing it to flow out at  $V$ .

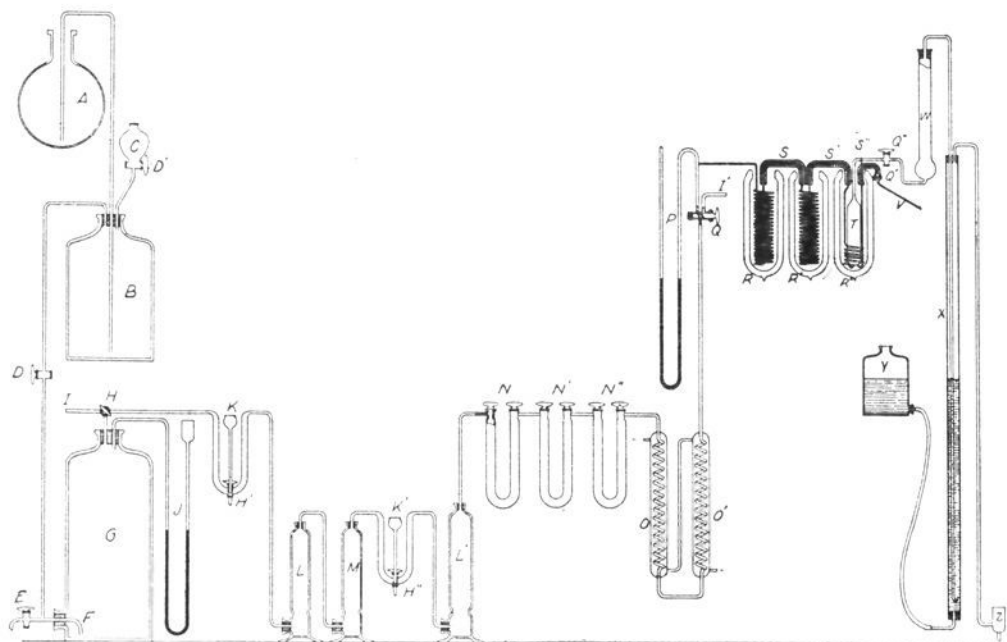


Fig. 1.—Apparatus for the liquefaction of hydrogen sulfide.

### Observations of Solubilities and Reactions

In order to make observations over an extended period of time, the liquid and the product were sealed in strong glass tubes which would withstand the vapor pressure of the solutions at room temperature. In preparing to store away reaction tubes for extended observation, thin-walled capsules that held the products to be placed in contact with liquid hydrogen sulfide, were lowered into the sturdy reaction tubes which were capped with drying tubes. The reaction tubes were charged with liquid hydrogen sulfide by slipping them over the outlet tube  $V$ , Fig. 1. The liquid that first came into Tube  $V$  was vaporized and this vapor displaced the air in the reaction tube with hydrogen sulfide gas. When the required amount of liquid was introduced the tube was sealed off and stored for repeated observations. In order to bring the product into contact with the liquid hydrogen sulfide the capsule was shaken in the reaction tube until the thin end was shattered. Observations were made from time to time over a period of several months. In some cases the temperature was lowered again in order to observe separations. The tubes were finally opened and the liquid and solid phases analyzed.

Table I lists the products studied and classifies in a general way the observations made. Many of the observations are in contradiction to those made in earlier investigations. Contrary to the report of Antony and Magri<sup>2c</sup> dry sulfur dioxide reacted vigorously with liquid hydrogen

TABLE I

## SUMMARY OF CHEMICAL ACTIVITY OF SUBSTANCES WITH LIQUID HYDROGEN SULFIDE

Soluble and non-reactive	Soluble and reactive	Apparently insoluble and reactive	Insoluble and non-reactive
Sulfur	Selenium	Sodium	Carbon
Iodine	Chlorine	Silver	Gold
Carbon dioxide	Bromine	Copper	Phosphorus (red)
Phosphorus pentasulfide	Phosphorus pentoxide	Mercury	Tellurium
Arsenic trisulfide	Sulfur dioxide	Arsenic	Lead sulfide
Antimony trisulfide	Pyrosulfuric acid	Antimony	Aluminum sulfide
Ammonium sulfohydrate	Stannous chloride	Sodium peroxide	Ferrous sulfide
Hydrogen chloride	Stannic chloride	Barium peroxide	Potassium sulfhydrate
Hydrogen bromide	Phosphorus trichloride	Arsenic trioxide	Phosphorous acid
Zinc chloride	Phosphorus pentachloride	Selenium dioxide	Metaboric acid
Gasoline	Arsenic trichloride	Water	Potassium chloride
Kerosene	Antimony trichloride	Lead chloride	Ammonium chloride
Vaseline	Bismuth trichloride	Cuprous chloride	Barium chloride
Benzene	Sulfur monochloride	Cobaltous chloride	Aluminum chloride
Toluene	Iodine trichloride	Mercuric chloride	Cadmium chloride
Diphenyl	Mercuric iodide	Selenium tetrachloride	Potassium iodide
Naphthalene	Mercuric bromide	Tellurium tetrachloride	Ammonium acetate
Anthracene	Phosphorus oxychloride	Silver nitrate	Ammonium thiocyanate
Chloroform	Thionyl chloride	Bismuth nitrate	Zinc sulfate
Bromoform	Selenium oxychloride	Ammonium nitrate	Disodium phosphate
Iodoform	Sulfuryl chloride	Potassium permanganate	Barium sulfate
Carbon tetrachloride	Thio-acetic acid	Potassium chromate	Boron nitride
<i>n</i> -Amyl bromide	Benzaldehyde	Potassium dichromate	Barium thiocarbonate
Ethyl disulfide	Nitrobenzaldehyde	Sodium bromate	Cystine
<i>n</i> -Butyl sulfide	Furfural	Ammonium persulfate	Thio-urea
<i>n</i> -Butyl mercaptan	Pyridine	Potassium ferricyanide	Thiobarbituric acid
Thiophenol	Piperidine	Potassium carbonate	Congo red
Thiocresol	Quinoline	Copper sulfate	Tartaric acid
Thiophene	Azobenzene	Sodium nitroprusside	Citric acid
Thiocarbamide	Dimethylamide-azobenzene	Ferric citrate	Raffinose
<i>n</i> -Butyl sulfonal	Dinitrobenzene	Methyl orange	Sucrose
isoButyl alcohol	Picric acid	Coal, bituminous	Glucose
Glycerol	Aniline	Litmus	Maltose
Phenol		Calcium carbide	Lactose
Resorcinol			Mannose
Pyrogallol			Arabinose
Ethyl ether			Amino-acetic acid
Acetone			Phenolphthalein
Trichloro-acetic acid			
Stearic acid			
Salicylic acid			
Cinnamic acid			
Phthalic acid			
Acetamide			
Phenylhydrazine hydrochloride			
Hydroxylamine hydrochloride			
Plantation rubber			
Para rubber			
Smoked rubber			
Vulcanized rubber			

sulfide. Selenium dioxide reacted more slowly to form free selenium, sulfur and water. Liquid hydrogen sulfide formed a hydrate with water, whose composition was found to be  $H_2S \cdot 5.7H_2O$  when using the method of de Forcrand.<sup>3</sup> This result is in fair agreement with the calculated re-

<sup>3</sup> De Forcrand, *Compt. rend.*, **135**, 959 (1902).

sults of Scheffer and Meijer.<sup>4</sup> The sulfides and sulfohydrates were only slightly soluble, when they were soluble at all. Of the inorganic acids pyrosulfuric acid reacted vigorously and hydrochloric acid showed marked solubility. The latter was soluble to the extent of 43.2 mole per cent. at the temperature of the ether-carbon dioxide bath. The inorganic halides showed a consistent gradation in reactivity. The chlorides of ammonium, potassium, barium and aluminum did not change when in contact with liquid hydrogen sulfide. Lead chloride slowly changed to the sulfide. Anhydrous cuprous chloride and cobalt chloride darkened at once and after several weeks all had changed to the sulfide and hydrogen chloride. Mercuric halides changed first to the black sulfide and then to the red sulfide in which form it remained stable in liquid hydrogen sulfide. The chlorides of tin and phosphorus were all soluble, and slow decomposition resulted in the formation of the respective sulfides. With both elements the chloride of the lower valence yielded sulfides most readily. With arsenic trichloride the formation of solution and decomposition were almost simultaneous. Antimony trichloride, on the other hand, was readily soluble and remained as a clear solution. Upon evaporation or cooling, however, a yellow solid separated from the solution containing antimony, sulfur and chlorine. The quantitative results indicated the possibility of a mixture of antimony sulfochloride,  $SbSCl$  and antimony trisulfide. Bismuth trichloride reacted in a similar manner but the separation of a reddish-orange solid took place readily. Analysis of this solid indicated that it had the formula  $BiSCl$ . Muir and Eagles<sup>5</sup> prepared a substance of this formula by passing hydrogen sulfide gas over bismuth trichloride at dull redness. The above four chlorides of the fifth group are consistent in gradation in the formation of sulfides and sulfochlorides. The action indicates some analogy to the chemistry of water. In the case of bismuth trichloride and liquid hydrogen sulfide we have a chemical change, analogous to that with water, which we may call thiohydrolysis. Sulfur monochloride formed a clear solution which became colloidal due to the partial separation of free sulfur. Selenium tetrachloride reacted vigorously with liquid hydrogen sulfide with the separation of free sulfur and selenium. Tellurium tetrachloride reacted in a similar manner. The halides of the fifth and sixth group elements studied all yielded hydrogen chloride when placed in contact with liquid hydrogen sulfide as described above. From a comparison of the halides studied we can conclude that as the basicity of the positive radical decreases, the solubility increases, and for any one group a given type of reaction has the greater tendency to go to completion, the lower the atomic weight. The oxychlorides of sulfur and selenium reacted vigorously with liquid hydrogen

<sup>4</sup> Scheffer and Meijer. *Verslag Akad. Wetenschappen Amsterdam*, **27**, 1104 (1919).

<sup>5</sup> Muir and Eagles, *J. Chem. Soc.*, **67**, 90 (1895).

sulfide with the formation of the corresponding chlorides, oxides and the free elements, selenium or sulfur or both. The salts studied, other than halides, were few in number. Of these the nitrates of silver, bismuth and ammonium reacted with the formation of sulfide and free sulfur. The distinctive oxidizing agents studied all-caused the separation of free sulfur. Potassium permanganate passed through the color changes violet-green  $\rightarrow$  dark brown  $\rightarrow$  reddish-brown, during a period of three months. Other products passing through color changes indicating reduction were potassium chromate, potassium dichromate, potassium ferricyanide and sodium nitroprusside.

All the reactions discussed above took place very slowly, the lengths of time required ranging from several hours to several weeks. Samples of the chlorides and iodides of mercury were dissolved in pyridine and added to liquid hydrogen sulfide with the result that the changes described above for these salts took place within 30 seconds. These observations are in harmony with those of Schroeder<sup>6</sup> who passed dry hydrogen sulfide gas into a solution of the mercuric salt in pyridine. If we grant that the speed of reaction is due to the hydrogen sulfide ionized, the conclusion regarding the reactions in pure liquid hydrogen sulfide is obvious. The analogy to the chemistry of water is quite evident but it is difficult with the data at hand to account for the observations with the sulfides and the sulfohydrates. Here the reactivity with inorganic substances is almost nil.

It is to be noted from Table I that most of the products soluble in liquid hydrogen sulfide are organic. All the hydrocarbons, halogen derivatives, sulfides, mercaptans, thio derivatives of aromatic hydroxy compounds, alcohols and aromatic hydroxy compounds studied were soluble and non-reactive in liquid hydrogen sulfide. Urea and thio-urea were insoluble but thiocarbanilide was soluble. Thio-acetic acid dissolved at once, and in the course of two weeks lemon-yellow crystals appeared. Analysis indicated a sulfur content sufficient to account for one molecule of hydrogen sulfide for each molecule of thio-acetic acid. Benzaldehyde and furfural were soluble, but decomposition was evident after a few days. The solution remaining after boiling the hydrogen sulfide from the former had a distinct odor of mercaptan. The precipitate formed in the furfural solution was a sticky, rubber-like mass and had the odor of an organic sulfide. Pyridine, piperidine and quinoline formed solutions in which precipitates appeared upon standing. The azo and nitro derivatives of benzene were all soluble and were reduced to lower forms. Acetamide was soluble, but amino-acetic acid did not appear to dissolve. Hydrazine hydrochloride was insoluble but phenylhydrazine hydrochloride and hydroxylamine hydrochloride were soluble. Liquid hydrogen sulfide extracts some of the hydrocarbon derivatives from bituminous coal. Calcium carbide appeared

<sup>6</sup> Schroeder, *Z. anorg. Chem.*, **44**, 16 (1905).

to be insoluble, but a color change took place. The residue did not yield acetylene with water and had a sharp odor of mercaptan, indicating the possibility of the formation of thio-acetaldehyde. The plantation rubber dissolved completely forming a thick, viscous, opalescent solution. Para and smoked rubber were less soluble and the solutions were not viscous. Vulcanized rubber was only slightly soluble.

With organic products liquid hydrogen sulfide acts much like an organic solvent. Reactions with the solute seemed to occur best when a double-bonded oxygen or a trivalent nitrogen was present in the solute molecule. This would lead one to believe that reactions result in addition products, which is apparently the case with thio-acetic acid. A review of all the individual observations made shows that results with nearly 50% of the organic products studied were cases of simple solubility while with inorganic products more than 50% showed indications of reactions. Reactions in liquid hydrogen sulfide, in general, take place very slowly, even at room temperature. Some of the earlier investigators observed neither solubility nor reaction in case of the oxidizing agents, and other products shown to be soluble or reactive, because they made all their observations at low temperature and for a relatively short period of time.

In conclusion the writer expresses his sincere appreciation to Dr. J. A. Wilkinson for timely suggestions and encouragement in the course of this work.

### Summary

A simple method of preparing liquid hydrogen sulfide and making a study of reactions in it over a wide range of temperature has been described.

The action of a number of organic and inorganic products in liquid hydrogen sulfide has been studied.

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