than for sodium salts. The free energy differences of the reaction when potassium is substituted for sodium, or chloride for nitrate, are sensibly linear functions of the concentration of added neutral salt for 1, 2 and 3 molar additions.

3. Although all the ions involved are of negative sign, the shift in equilibrium does not follow the principle of specific interaction at these high concentrations.

4. For solutions of constant thermodynamic environment, K_c^∞ (tri-iodide formation neglected) is not constant when I^- is varied, whereas K'_c (tri-iodide considered) is constant. This furnishes additional evidence for the existence of tri-iodides in solution.

5. The shift in equilibrium on changing the cation from potassium to sodium is in qualitative agreement with the measurements of the greater velocity of the forward reaction in the presence of potassium ions.

NEW YORK CITY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MARYLAND]

A STUDY OF THE REACTION BETWEEN HYDROGEN SULFIDE AND SILVER

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RECEIVED AUGUST 16, 1929 PUBLISHED MARCH 6, 1930

In many of the elementary textbooks in inorganic chemistry the reaction between silver and hydrogen sulfide under normal conditions is said to give silver sulfide and hydrogen. Since the electro-potential of silver is greater than that of hydrogen, it seems rather peculiar that silver should so readily replace the hydrogen from this weak acid at ordinary temperatures. A difference in electro-potentials is, however, no criterion that the reaction would not take place, because the order of the electromotive series may be reversed in a great many different ways; but the textbooks indicate that the reaction takes place normally under room conditions.

We find several articles in the literature bearing on this subject and different views are expressed. Inasmuch as there is a difference of opinion in the literature, and many textbooks still hold to the simple replacement reaction, it was thought well to investigate the action of hydrogen sulfide on silver under room conditions, while controlling all variables as far as possible.

Historical Review

One of the earliest of the investigators to inquire into the conditions of the reaction between silver and hydrogen sulfide was J. M. Cabell,[1] who found that silver and hydrogen sulfide dried by phosphorus pentoxide

[1] Cabell, *Chem. News*, **50**, 208 (1884).

did not react appreciably even after a period of four months of summer weather. F. L. Hahn[2] bubbled hydrogen sulfide through de-aerated water in which silver had been placed. He found no reaction taking place. However, on addition of some hydrogen peroxide, or on bubbling oxygen through the solution of hydrogen sulfide, the silver instantly blackened. He also could not detect any hydrogen even after boiling. He therefore expressed the opinion that oxygen enters into the reaction in the following manner

$$2Ag + H_2S + {}^1/_2O_2 \longrightarrow Ag_2S + H_2O$$

Hahn, however, quotes W. Ostwald as stating that the affinity of silver (also copper) for sulfur is so great that this metal is able to liberate hydrogen from hydrogen sulfide. J. Percy[3] is also of the opinion that the reaction is of simple replacement. Treadwell[4] on the other hand is of the same opinion as F. L. Hahn.

F. G. Keyes and W. A. Felsing[5] investigated the equilibrium existing in the reaction between silver sulfide and hydrogen at several different temperatures between 749.15–889.63°K. With the data available, they calculated the heat of reaction at those temperatures by means of the van't Hoff reaction isochore. The thermochemical equation at those temperatures was found to be

$$Ag_2S + (H_2) \rightleftharpoons 2Ag + (H_2S) + 2410 \text{ cal.}$$

thus showing that the reaction between silver and hydrogen sulfide is endothermal. This would indicate that the reaction should proceed with great difficulty at the much lower room temperature.

Experimental

Materials Used

Silver.—The silver was purified by electrolysis of the nitrate and analysis indicated that samples obtained by this method were never less than 99.84% silver.

Hydrogen Sulfide.—Hydrogen sulfide was prepared by the reaction of water on aluminum sulfide.

De-aerated Water.—De-aerated water was prepared by boiling distilled water slowly for a period of four and a half hours.

Aluminum Trioxide.—Aluminum hydroxide was precipitated from an aluminum chloride solution by the addition of ammonium hydroxide. It was then thoroughly washed free from chlorides by decantation and filtering by suction. It was then dried for two days at 80–85°. The resulting hard mass was pulverized and completely dehydrated during a period of one week at about 180°. The aluminum trioxide made in this way was found to be a very satisfactory dehydrating agent.[6]

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[2] Hahn, *Z. anorg. Chem.*, **99,** 118 (1917).

[3] Percy's "Metallurgy, Silver and Gold," Part I, **1880.**

[4] Treadwell, "Analytical Chemistry," Vol. I, 5th ed., p. 358.

[5] Keys and Felsing, THIS JOURNAL, **42,** 246 (1920).

[6] J. W. Marden and V. Elliott, *J. Ind. Eng. Chem.*, **7,** 320 (1915); F. M. G. Johnson, THIS JOURNAL, **34,** 911 (1912).

Silica Gel.—A good grade of commercial gel was strongly heated for about an hour so as to be completely dry.

Analysis of Material

Silver.—The silver analysis in these experiments was carried out by dissolving the silver in nitric acid, converting it to the chloride and weighing as such.

Hydrogen Sulfide.—Hydrogen sulfide prepared by the reaction of water on aluminum sulfide was found to be completely absorbed by a 50% solution of sodium hydroxide, giving no indication of the presence of hydrogen.

Phosphorus Pentoxide as a Drying Agent.—Many investigators have used phosphorus pentoxide as a drying agent for hydrogen sulfide. The following test was run on this material and it was found unfit for use.

A stream of hydrogen sulfide was passed through a drying tube containing phosphorus pentoxide for ten minutes. The gas coming from the drying tube was led into a sodium hydroxide solution. The phosphorus pentoxide was then washed out with water and extracted with carbon disulfide. When the carbon disulfide was allowed to evaporate from an evaporating dish, yellow crystals of sulfur appeared.

The sodium hydroxide solution was treated with dilute hydrochloric acid until neutral. The sulfide ions were precipitated with an excess of cadmium nitrate. It was filtered, the filtrate being tested with sodium nitroprusside to see if all sulfide ions were precipitated out. The filtrate was found to decolorize malachite green solution (0.025 g. in 300 cc. of water), and when barium nitrate was added, a white precipitate formed. This precipitate dissolved in hydrochloric acid; the resulting solution decolorized iodine solution. These tests indicate the presence of a sulfite. Phosphorus pentoxide is therefore unfit to use as a dryer of hydrogen sulfide, as it oxidizes this gas to sulfur dioxide.

Aluminum Trioxide and Silica Gel as Drying Agents.—Two drying tubes filled with silica gel were connected to another drying tube containing aluminum trioxide. The aluminum trioxide tube was connected to a weighed phosphorus pentoxide tube; this in turn was connected to another phosphorus pentoxide tube which was connected to a suction pump. Air saturated with moisture was then drawn through the system by means of the suction pump. The weighed phosphorus pentoxide tube showed no gain in weight. This indicates the efficiency of the system. The function of the silica gel is to dehydrate the gas from most of its moisture. The aluminum trioxide removes the least traces.[6]

Analysis of the Sulfides.—The amount of combined sulfur formed was found by the increase in weight in the silver sample. As a check, the sulfide was oxidized by fuming nitric acid to the sulfate and the silver was precipitated as the chloride. It was filtered, washed, dried and weighed, to serve as a check on the silver originally used. Barium sulfate was then precipitated out from the solution. It was filtered through a weighed Gooch crucible, washed, dried and weighed. The amount of combined sulfur was calculated from the amount of barium sulfate present.

Apparatus

Reaction Chamber.—The reaction chamber consisted of an eight-ounce bottle with a two-hole stopper covering it, containing an outlet tube. Both tubes (inlet and outlet) had a piece of gray vulcanized rubber tubing fitting snugly and overlapping each end. Pieces of solid tubing which fitted snugly into the rubber tubing were placed into the overlapping parts of the rubber tubing so that the edges of each piece of solid tubing were against the ends of both the inlet and outlet tubes. Paraffin was smeared into the edges, crevices and on all the rubber tubing so that the receptacle was air-tight. A reaction chamber of this type was found to hold hydrogen satisfactorily for a period longer than that required by the experiment.

Absorption Apparatus and Eudiometer.—Experiment showed that with the eudiometer used as little as 0.2 cc. of hydrogen could be detected. Since in preliminary tests it was found that enough sulfide was formed for the liberation of several cc. of hydrogen, it was thought that this was accurate enough for the work.

Carbon dioxide was used in the driving out of the gases in the reaction chamber. An absorption buret was used for the absorption of carbon dioxide and hydrogen sulfide, a 50% solution of sodium hydroxide being used as the absorption medium.

The apparatus was tested by mixing a definite quantity of hydrogen with hydrogen sulfide in the reaction chamber and then analyzing the mixture. The following table gives the results of the analysis.

Amount of hydrogen originally used, cc.	4.2	3.1	6.2	2.8
Amount of hydrogen by analysis, cc.	4.0	3.0	5.9	2.7

Method of Procedure and Data

The System Air–Moisture–Hydrogen Sulfide–Silver.—Three weighing bottles with a weighed amount of silver were placed in a reaction bottle. It was closed with a rubber stopper containing an inlet and outlet tube. One of the tubes was then closed by means of a piece of solid tubing. The reaction chamber was partially exhausted, after which it was connected to a hydrogen sulfide generator until equilibrium was established between the two. The reaction chamber was clamped shut and disconnected from the hydrogen sulfide generator. The remaining end was then completely closed with another piece of sealed glass tubing. All crevices, edges, ends and rubber tubing were completely covered with paraffin. Nine such reaction chambers were prepared.

The reaction was allowed to proceed for 500 hours, after which time the contents were analyzed as described. The results found are shown in Table I. It can be seen that no hydrogen was found after the reaction had taken place.

Table I

Reaction of Hydrogen Sulfide with Ag in the Presence of Air and Moisture at Room Temperature and Pressure

Silver, g.	Silver on analysis, g.	Combined sulfur		Yield of hydrogen	
		By direct wt., g	By analysis, g.	Calcd., cc.	Actual, cc.
1.0723	1.071	0.0051	0.0050	3.57	0
0.9760	0.9754	.0046	.0047	3.22	0
.8976	.8971	.0032	.0032	2.24	0
.9132	.9125	.0028	.0030	1.96	0
1.0534	1.0530	.0046	.0048	3.22	0
1.2142	1.2134	.0069	.0067	4.83	0
1.0053	1.0041	.0041	.0043	2.87	0
0.9241	...	.0036	...	2.52	0
1.1723	...	.0054	...	3.78	0

The System Water–Hydrogen Sulfide–Silver (No Air).—A weighing bottle with a weighed amount of silver was placed in a reaction chamber.

Water which had been boiled for four and a half hours was placed in the reaction chamber while still boiling, until the reaction chamber was nearly full. The water was boiled again for half an hour in order to rid it of any air which may have dissolved in the water during the process of transferring. The chamber was stoppered. While the water was still boiling hot, hydrogen sulfide was bubbled through the water to drive off any air which may have been present above the water. The chamber was then closed and the water allowed to cool. When cold, more hydrogen sulfide was bubbled through. The reaction chamber was then sealed up as usual. After 750 hours the hydrogen sulfide was boiled out and the silver was analyzed for sulfide. Five such reaction chambers were prepared, out of which only one showed a slight blackening of the silver. This was assumed to be an error. The results are given in Table II.

TABLE II

REACTION OF HYDROGEN SULFIDE WITH SILVER IN WATER FREE FROM AIR AT ROOM TEMPERATURE AND PRESSURE

Silver sample, g.	0.2934	0.3006	0.3249	0.2763	0.2891
Silver by anal., g.	.2929	.3002	.3249	.2754	.2884
Comb. sulfur by anal., g.	0	0	.0006 Sl. blackening	0	0

The System Hydrogen Sulfide–Silver–Air (No Moisture).—A weighing bottle with a weighed amount of silver which had been dried at 180° for several days was placed in a reaction chamber. The reaction chamber was then closed with a stopper containing the usual inlet and outlet tubes. One of the tubes was sealed in the usual way and the other was connected to an aluminum trioxide drying tube, which in turn was connected to two silica gel drying tubes. The reaction chamber was then partially evacuated several times, so as to make certain that the air in it was absolutely dry. The whole system was again partially evacuated and then connected to a hydrogen sulfide generator. The system was allowed to come to equilibrium with the generator and the reaction chamber was then sealed up as usual. After 600 hours the silver was weighed again and analyzed. Five such chambers were prepared, of which only one had a very slight coloration. This was assumed to be an error. The results are shown in Table III.

TABLE III

REACTION OF HYDROGEN SULFIDE ON SILVER IN THE PRESENCE OF DRY AIR AT ROOM TEMPERATURE AND PRESSURE

Silver sample, g.	0.4163	0.2993	0.3167	0.2834	0.3260
Ag after reaction, g.	.4164	.2993	.3168	.2836	.3260
Silver by analysis, g.	.4153	.2987	.3160	.2833	.3261
Comb. sulfur by anal., g.	0	0	0	.0001 Sl. coloration	0

The System Moisture–Air–Silver–Hydrogen Sulfide at 210°.—The open ends of four test-tubes were drawn out so as to make them easier to seal up. Silver was then placed in each test-tube. They were evacuated partially and allowed to come to equilibrium with a hydrogen sulfide generator. The tubes were then sealed off, placed in an oil-bath and heated up to 210°. They were kept at that temperature for one hour. The sealed tubes were then allowed to cool. One end of each tube was broken under a eudiometer tube containing a 50% solution of sodium hydroxide. The unabsorbed gas was tested for hydrogen and in no case was hydrogen shown to be present. The silver samples were analyzed for combined sulfur. The results are given in Table IV.

TABLE IV

REACTION OF HYDROGEN SULFIDE ON SILVER IN MOIST AIR AT 210°

Combined sulfur by analysis, g.	0.0092	0.0053	0.0051	0.0058
Calcd. yield of hydrogen, cc.	6.44	3.71	3.57	4.06
Actual yield of hydrogen, cc.	0	0	0	0

The System Hydrogen Sulfide–Silver (No Air, No Moisture).—Several test-tubes whose ends were drawn out and open were made and silver was placed in them. Dry hydrogen sulfide was then passed through to drive out the air. The tubes were sealed off at both ends and heated in an oil-bath for an hour and a half at 190°. The tubes were cooled. One end of each tube was broken under a eudiometer tube containing a 50% solution of sodium hydroxide. The tubes were found to contain 2.1 cc. and 1.3 cc. of hydrogen. No attempt was made to obtain an equilibrium reaction.

A test-tube containing silver and sulfur was sealed up and kept at room temperature. In one day the silver was found to have blackened. In a week's time practically all of the silver was converted to the sulfide.

Discussion of Results

The results of J. M. Cabell and F. L. Hahn have been fully confirmed in the present investigation. Furthermore, it has been shown conclusively that no hydrogen is formed under conditions where both moisture and air are present. The one experiment in which hydrogen was formed is what one would expect from the thermochemical equation $2Ag + H_2S + \Delta \rightleftarrows Ag_2S + H_2$, the reaction being endothermal in nature.

The results of this investigation would indicate almost conclusively that oxygen plays a part in the reaction, either in atomic, molecular or combined form.

F. G. Donnan and T. W. A. Shaw[7] have demonstrated that the oxygen dissolved in molten silver exists as atomic oxygen dissolved in a purely physical way, or it exists as ionic oxygen in the form of silver oxide.

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[7] Donnan and Shaw, *J. Soc. Chem. Ind.*, **29**, 987 (1917).

B. Brauner[8] has demonstrated that 152.2133 g. of silver gave off 0.844 cc. of oxygen between 450° and red heat. J. Percy[3] states that when silver is melted in the air some of it is oxidized to silver oxide. This substance on cooling tends to separate out from the silver since it is only sparingly soluble in solid silver. On further cooling the silver oxide breaks up into silver and gaseous oxygen. However, it is conceivable that a trace of silver oxide remains in solution in the solid silver. It is also reasonable to suppose that some silver oxide is left at the lower temperatures, since the decomposition of silver oxide is an equilibrium reaction. J. Percy also states that silver retains 0.545 of its volume of oxygen when cold.

I. Langmuir[9] has demonstrated that oxygen is adsorbed onto the surfaces of many metals in the form of stable films of atoms. These oxygen atoms are attached to the metallic atoms by primary valences. He has also shown that hydrogen molecules are adsorbed by platinum, tungsten and probably by other metallic surfaces in the form of atoms. The hydrogen so adsorbed by the metal is therefore able to react with the oxygen ions, if an oxide is present, or with the oxygen atoms if oxygen is adsorbed as atoms.

With the above facts in mind, one might formulate several theories to account for the reaction between silver and hydrogen sulfide. The following explanation seems quite feasible.

Hydrogen sulfide in contact with a limited supply of oxygen tends to be oxidized to water and sulfur: $H_2S + {}^1/_2O_2 \longrightarrow H_2O + S$, this occurring usually in solution. It is therefore conceivable that hydrogen sulfide gas in the presence of moisture may be oxidized by contact with the oxygen atoms or molecules attached to the silver surface, to water and sulfur. The sulfur atoms thus formed combine instantaneously with the silver atoms to form the sulfide.

Since the supply of oxygen atoms, molecules or ions on the silver surface is very small, it is evident that air or any other easily accessible source of oxygen must be in contact with the silver for the reaction to proceed to any extent. F. L. Hahn[2] reports that polysulfides react with silver to form the sulfide without the presence of oxygen. The reaction here as in the case of monosulfides is probably not that of a simple replacement, but is more likely to be due to the loose linkage of a sulfur-to-sulfur bond, which in contact with silver is easily broken with the consequent formation of the sulfide of silver.

Conclusions

1. Hydrogen is not formed as the result of the reaction between hydrogen sulfide and silver in the presence of air and moisture.

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[8] Brauner, *J. Chem. Soc.*, **55**, 400 (1889).

[9] Langmuir, *Trans. Faraday Soc.*, **17**, 607 (1922).

2. The results of J. M. Cabell and F. L. Hahn have been fully confirmed: the presence of both oxygen and moisture is required for the reaction between hydrogen sulfide and silver to take place at ordinary temperatures and pressures.

3. A theory has been advanced which takes into consideration the need for both oxygen and moisture.

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HYDROGENATION OVER METALLIC CESIUM

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Received August 16, 1929 Published March 6, 1930

If hydrogenations can be induced by alkali metals as catalysts, one would look to the intermediate compound theory for explanation, as the hydrides of these metals are readily formed and decomposed at moderate temperatures. Experiments on one such reaction over metallic cesium seem to indicate, however, that although hydrogenation occurs the hydride is not the catalyst and even hinders the reaction.

Experiment showed that ethylene and hydrogen reacted when admitted to distilled cesium even at room temperature. The rate as measured by pressure drop gave evidence of poisoning of the catalyst, for the decrease upward of ten millimeters per hour at the start, diminished steadily, and the total pressure only approached that consistent with ethane formation after a long period of time. At 200° the process was much more rapid, but a similar diminution in rate was observed.

Reaction was also found between carbon monoxide and hydrogen, commencing very rapidly at room temperature, and as rapidly diminishing, becoming zero at a pressure not susceptible of ready interpretation. Thus poisoning was again evident, though the experimental difficulties in analyzing the gases were such that the quantitative measurements were performed on the more easily handled ethylene and hydrogen.

Analysis showed that the reaction produced ethane, and also that (unaccounted for) hydrogen had disappeared from the gas phase. This is ascribed to the formation of cesium hydride, for the once silvery metal was covered with a white layer. Confirmation of this hypothesis was sought by heating the pure metal in an atmosphere of hydrogen, in which case the pressure decreased, and a similar white coating was obtained. When ethylene was admitted to this supposed hydride at room temperature no pressure change was observed, but analysis of the gas after some hours showed the presence of small quantities of ethane. Moissan[1] failed to find any reaction between ethylene and cesium hydride, a discrepancy

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[1] Moissan, *Bull. soc. chim.*, **31**, 556 (1904), *et al.*