Summary

To summarize, we find (a) that although presence of oxygen and mercury are both essential, mercurous chloride plays an important part in the reaction leading to the formation of calomel and loss of hydrochloric acid and (b) that the observed e. m. f. corresponds within the limits of experimental error, to the actual concentration of the acid in the electrode vessel.

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HYDROGEN DISULFIDE

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Received October 5, 1929 Published June 6, 1930

Although hydrogen persulfide was discovered in 1777 by Scheele,[1] it has not proved an attractive subject for investigation and advances in the knowledge of the substance have been made slowly. Sabatier[2] succeeded in distilling the liquid in vacuo. This line of attack was followed by Block and Höhn,[3] who showed that crude hydrogen persulfide gave on fractionation two compounds, H_2S_2 and H_2S_3. Walton and Parsons[4] repeated and extended this work, using quartz apparatus in part.

In the present work the optimum conditions for the preparation of hydrogen disulfide were investigated, a method of purification was developed and the physical properties of the pure substance were determined.

Preliminary Experiments.—Preliminary experiments, which followed closely the final procedure, dealt with the effect of varying composition of the sodium polysulfide on the yields of the products. The results are given in Table I.

Table I

Effect of Composition of Reactants on Yield of Products

Polysulfide	Dilution[a]	Crude oil, g. per 100 g. total S	H_2S_3	H_2S_2
			G. per 100 g. crude oil	
Na_2S_2	750	47	29.0	7.8
$Na_2S_{2.25}$	700	60	21.9	9.3
$Na_2S_{2.50}$	700	59	23.6	13.5
Na_2S_3	650	81	28.6	5.6
Na_2S_4	600	80	25.5	5.6

[a] Dilution indicates weight of solution per gram mole of sodium polysulfide.

The crude oils obtained from the different solutions varied considerably in appearance and properties. The crude persulfide from Na_2S_2 was a

[1] "Chemische Abhandlung von der Luft und dem Feuer," p. 162.

[2] Sabatier, *Bull. soc. chim.*, [2] **44,** 169 (1885).

[3] Block and Höhn, *Ber.*, **41,** 1961 (1908).

[4] Walton and Parsons, This Journal, **43,** 2539 (1921).

rather mobile liquid, light yellow in color, and sensitive to impurities. It had a very sharp odor and the vapor was highly irritating to the nose and eyes. On fractionation it distilled very readily at 120°.

As the amount of sulfur in the sodium polysulfide solution increased, there was a gradual change in the properties of the resulting persulfide. That obtained from Na_2S_4 was a dark yellow viscous liquid with only a slight odor. It was comparatively stable. The oil distilled very slowly at 120°.

Preparation of Sodium Polysulfide.—These preliminary experiments showed that $Na_2S_{2.50}$ was the most satisfactory polysulfide. It was used in all later preparations of hydrogen disulfide. The solution used was made by heating on a water-bath a mixture containing 150 g. of flowers of sulfur, 725 g. of sodium sulfide crystals and 500 cc. of distilled water. A tared 2-liter flask was used and the mouth closed by a rubber stopper bearing a Bunsen valve. After solution of the solids was complete, distilled water was added to make the total weight of the solution 2650 g. and the flask was tightly stoppered.

Preparation of Crude Hydrogen Persulfide.—The preparation of hydrogen persulfide was carried out in a 3-liter pyrex beaker supported on rubber stoppers within an insulated battery jar used as a cooling bath. A suitable quantity of acetone was introduced into the battery jar and cooled to −40° by the addition of solid carbon dioxide. The pyrex beaker containing 1500 cc. of C. P. hydrochloric acid (sp. gr. 1.19) was put into position and stirring commenced. When the acid had cooled to −15° the sodium polysulfide solution was added from a dropping funnel, the tip of which was immersed in the acid to a depth of 2 cm. During the remainder of the operation the acetone bath was kept below −25° and the flow of the polysulfide solution regulated to keep the acid temperature between −10 and −15°.

After a liter of the solution had been added, the hydrogen persulfide began to rise to the surface as a scum and decompose with evolution of hydrogen sulfide. The addition of sodium polysulfide was then stopped, the beaker replaced by one containing a fresh portion of hydrochloric acid, and the operation completed with the remaining half of the polysulfide solution.

This preparation resulted in an emulsion of crude hydrogen persulfide with suspended sulfur, in an acid solution of sodium chloride. The mixture was allowed to stand for two to three hours with occasional stirring, the yellow crude oil settling mainly to the bottom of the beaker and the finely divided sulfur forming a thick layer just above this. The upper layer of liquid was decanted, the mixture diluted with cold water to one liter, transferred to a separating funnel and the persulfide layer drawn off into a tared Erlenmeyer flask. After the weight of the persulfide had been determined, a few grams of phosphorus pentoxide was added cautiously and the flask allowed to stand overnight. The phosphorus pentoxide was removed by filtering through asbestos and the filtered oil was fractionated. All apparatus used in this preparation was of pyrex and the surface was carefully acidified immediately before use by treatment with concentrated hydrochloric acid.

Fractionation of Hydrogen Persulfide.—The apparatus used in fractionation is shown in Fig. 1. It was built from pyrex glass: A, a 100-cc. flask; B, a special flask made from a 50-cc. distilling flask; C, made from a 100-cc. flask; G, a capillary contraction in the connecting tube. The inner tube of the condenser was constructed of tubing of 9 mm. outside diameter; all other tubing was 5 mm. outside diameter.

Before setting up, all parts of the apparatus were carefully cleaned and dried. The rubber stoppers were soaked in hot beeswax. After setting up, the apparatus was warmed in a current of dry air. Dry hydrogen chloride was then passed through for ten minutes, care being taken to fill the funnel F by displacement. The apparatus was then pumped out using an efficient water pump which reduced the pressure to 10 mm. or less. The flask B was immersed in a bath of glycoline held at 120°. The test-tube D was immersed in acetone at −40°.

To start the distillation, stopcock S was closed, S_2 being open, and the crude hydrogen persulfide was allowed to drop slowly from F. After twenty minutes the flow of persulfide was cut off, though the distillation was allowed to continue for five minutes. The flask B was then one-third filled with a dark reddish-yellow viscous fluid. This was removed by opening stopcock S_2 and closing S, thus drawing the residue into A, where it solidified to a lemon-yellow, semi-crystalline mass. The distillation was then continued as before.

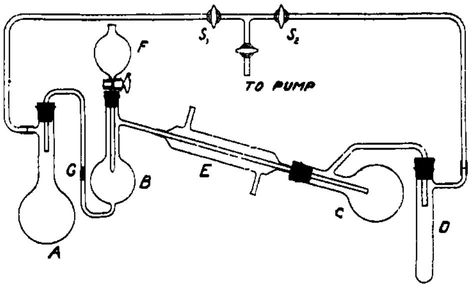

Fig. 1.

Two fractions were condensed. The first, collected in C, was approximately H_2S_3 by analysis and was considered to be hydrogen trisulfide. The second, condensed in D, was H_2S_2. hydrogen disulfide. The two liquids were removed, weighed and placed in quartz bulbs for storage at −78°.

Series of experiments were carried out to determine the effect of temperature and pressure of distillation on the yields of the two products. These results are shown in Table II.

Table II

Effect of Temperature and Pressure of Distillation on Yields of Disulfide

Sodium polysulfide	Press., mm.	Temp., °C.	G. per 100 g. of crude persulfide Trisulfide	Disulfide
Na_2S_2	10	102	30.2	10.3
Na_2S_2	10	118	29.0	7.8
$Na_2S_{2.50}$	10	112	26.6	15.2
$Na_2S_{2.50}$	10	122	36.5	11.2
$Na_2S_{2.50}$	10	135	14.6	8.3
$Na_2S_{2.50}$	30	120	9.5	10.4
$Na_2S_{2.50}$	18	120	30.3	12.5
$Na_2S_{2.50}$	10	120	36.5	11.3

It is evident that decrease in temperature of distillation leads to increased yields of hydrogen disulfide. The rate of distillation is, however, much slower. The most suitable temperature for the persulfide from $Na_2S_{2.50}$ is 122°. Increase in pressure leads to greatly decreased yields of hydrogen trisulfide.

Cracking of Trisulfide.—Observations were made by Block and Höhn and by Walton and Parsons to the effect that distillation of hydrogen trisulfide gave considerable amounts of hydrogen disulfide as a by-product. This appeared to offer a second method of obtaining the disulfide.

A 100-cc. flask was provided with a 50-cm. reflux condenser and two receivers in series, as in the fractionation apparatus. In one experiment 38 g. of trisulfide was placed in the flask, which was heated to 75° at the start and to 125° at the end. Seventeen g. of hydrogen disulfide was obtained.

Attempts to purify the trisulfide by distillation in vacuo met with slight success. The distillation must be carried out at very low pressures and below room temperature to avoid decomposition.

Purification of Disulfide.—The hydrogen disulfide prepared by the methods outlined above was purified by a distillation *in vacuo* from phosphorus pentoxide.

A pyrex still was used at first and the liquid was transferred by pouring. This type of still gave satisfactory results but the distilled liquid was hygroscopic and owing to moisture picked up in transfer it became turbid on cooling. Trouble was also caused by decomposition when the glass was not thoroughly acidified by the hydrogen chloride passed into the still.

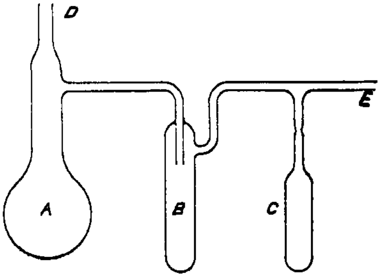

Fig. 2.

A quartz still was developed in which the hydrogen disulfide was distilled directly into apparatus in which measurements were made and sealed off. This is shown in Fig. 2. A is a 100-cc. distilling flask; the neck and side arm were drawn down and 7-mm. tubing sealed on. B is a receiver made from 16-mm. tubing. The tube at E is joined to the vacuum line by a de Khotinsky joint. After setting up and drying, phosphorus pentoxide was distilled into A. The air was displaced by dry carbon dioxide and the impure hydrogen disulfide introduced. The tube D was sealed off; the atmosphere of carbon dioxide prevented ignition of the disulfide vapor even at the high temperature needed to work quartz.

The distillation was carried out at 10 mm., A being at room temperature and B at −78°. When the receiver was filled, A was also cooled and the connecting tube sealed. The pressure was then reduced to less than 1 mm. by a Toepler pump and the stopcock to the vacuum line closed. The disulfide was distilled from B to the piece of apparatus attached at C. This was then sealed off.

Method of Analysis.—All analyses were made by the method of Walton and Parsons.[4] A sample of about 1 cc. was transferred to a quartz weighing tube and weighed. The sample was poured into a porcelain evaporating dish and the tube washed with 10 cc. of carbon disulfide. Ten cc. of acetone was added, causing a quiet decomposition of the hydrogen persulfide. The solvents were allowed to evaporate overnight and the sulfur was weighed.

Owing to the small quantities of material available, analyses were made only to check improvements in procedure. The mean results are

	H_2S, %
Crude persulfide from Na_2S_2	17.7
Disulfide from fractionation	47.0
Disulfide from cracking	48.0
Redistilled disulfide	51.3
Theoretical value for disulfide	51.2
Trisulfide from fractionation	32.4
Trisulfide from cracking	32.4
Theoretical value for trisulfide	34.7

Containers for Persulfides.—The problem of keeping hydrogen disulfide and trisulfide presented a number of difficulties. The products from the initial fractionation decomposed rapidly at room temperature, even in all-quartz containers. Long-necked quartz bulbs immersed in solid carbon dioxide were satisfactory for short periods. It was possible to keep the carefully purified disulfide in sealed bulbs for indefinite periods without decomposition.

Cleaning of Apparatus.—The necessity for most rigorous care in cleaning and acidification of all apparatus cannot be too greatly emphasized. Aqua regia proved very useful in cleaning, as an unusually rapid evolution of chlorine indicated the presence of surface impurities. Acidification of apparatus with dry hydrogen chloride was found to be necessary in all cases.

Melting Point.—Two determinations were made of the melting point of hydrogen disulfide. The sample was enclosed in a sealed tube which was immersed in an ether-bath cooled by liquid air.[5] The temperature was determined by a platinum resistance thermometer. The first sample had stood in pyrex glass for eight days at −78°; its melting point was −88.6°. The second sample was condensed in quartz; its melting point was −89.8°.

Freezing Point Curve with Sulfur.—The freezing points of solutions of sulfur in hydrogen disulfide were determined in the following way. A quantity of hydrogen disulfide was placed in a small quartz tube and weighed. A suitable quantity of sulfur was added and the tube immersed in a bath of ether cooled by liquid air. The bath temperature was lowered until a solid was precipitated from the solution on stirring vigorously. The temperature was measured by a thermometer in contact with the freezing point tube. This freezing point was then checked, the temperature being varied more slowly. The tube was then removed from the bath, another portion of sulfur added and the mixture stirred until solution was complete. The next point was then obtained. Solution of the solid, which appeared to be sulfur, was very slow unless

TABLE III

FREEZING POINTS OF SOLUTION OF SULFUR IN HYDROGEN DISULFIDE

Run 1, weight of H_2S_2, 1.831 g.			Run 2. weight of H_2S_2, 1.7035 g.		
Sulfur added, g.	S (added) H_2S_x	Freezing point, °C.	Sulfur added, g.	S (added) H_2S_x	Freezing point, °C.
0.020	0.011	−91	0.126	0.069	−46
.108	.055	−55	.271	.137	−13.6
.156	.079	−41	.450	.209	− 0.9
.240	.116	−23	.562	.248	6.3
.300	.141	−17	.744	.303	15.6
.356	.163	−10	.771	.312	17.6
.504	.216	− 1	.811	.323	19.4
.596	.246	4	.897	.345	22.7
.689	.271	7.5			
.786	.300	11.7			
.885	.326	13.5			
1.003	.354	20.1			
1.045	.363	21.0			
1.115	.378	22.7			

A pentane thermometer was used up to 4° and stem corrections were estimated within 2°.

A pentane thermometer was used for the first point, and a mercury thermometer for the others.

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[5] Maass and McIntosh, THIS JOURNAL, **36**, 738 (1914).

the tube was warmed nearly to room temperature. The results are tabulated and are shown in Fig. 3.

The results obtained by Walton and Whitford are also shown in the figure. These investigators determined the solubility of sulfur in the hydrogen persulfide. They added an excess of sulfur to a sample of the persulfide kept in a constant temperature bath. The mixture was stirred until the equilibrium was reached and a sample of the liquid phase analyzed. They claimed that the disulfide and the trisulfide gave solutions of the same composition when saturated at 0°. Hydrogen trisulfide was used for all points except that at −34.72°, where hydrogen disulfide was substituted. Their results were recalculated to the basis used in the present work.

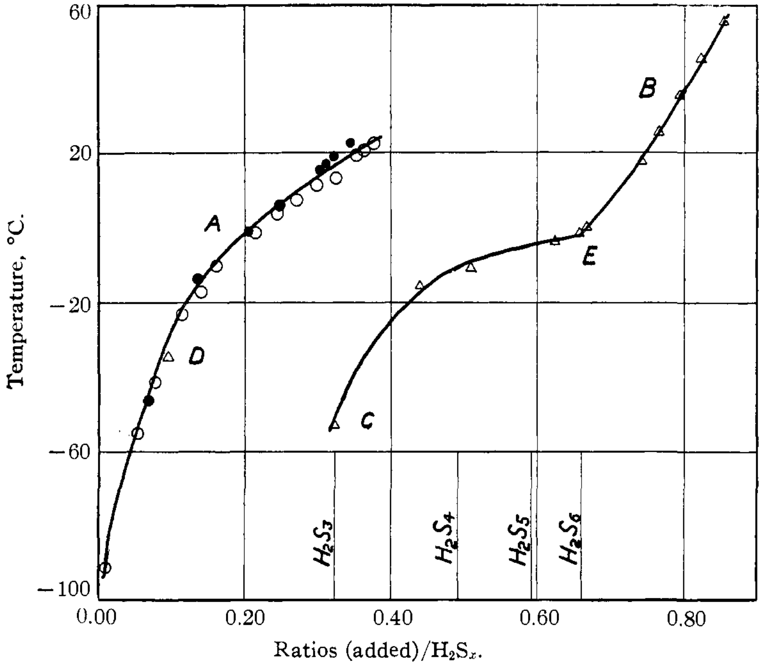

Fig. 3.

TABLE IV

RESULTS OF WALTON AND WHITFORD

Temp., °C.	Sulfur not evolved as H_2S, %	$\frac{(X-2)S}{H_2S_x}$	Temp., °C.	Sulfur not evolved as H_2S, %	$\frac{(X-2)S}{H_2S_x}$
−34.72	53.56	0.099	17.92	86.77	0.743
−15.42	71.18	.441	25.4	87.98	.767
−10.6	75.16	.511	35.4	89.46	.795
− 3.75	80.71	.626	45.15	91.00	.825
− 1.45	82.50	.660	55.3	92.49	.854
0.05	82.97	.669			

The ratios corresponding to the various possible persulfides are shown by vertical lines in the figure.

Point C is the freezing point of hydrogen trisulfide as given by Walton and Parsons and by Bloch and Höhn. Point D was obtained by Walton and Whitford using hydrogen disulfide.

Curve A represents the solubility of sulfur in hydrogen disulfide. There is no evidence for a break corresponding to the composition $H_2S_2 + S$, and the freezing point of such a solution is far above the recorded freezing point of H_2S_3. It may be stated, therefore, that hydrogen trisulfide is not a molecular compound of hydrogen disulfide with sulfur.

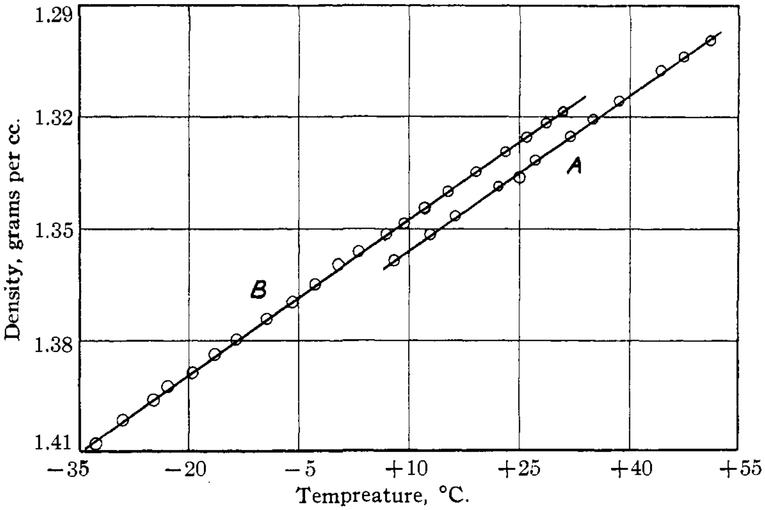

Fig. 4.

It is obvious that Curve B must be drawn to represent the results of Walton and Whitford, and that Point D does not fall on this curve. This curve represents the solubility of sulfur in hydrogen trisulfide; it has a break at E corresponding to the molecular compound $H_2S_3 \cdot 3S$.

The evidence is strongly in favor of the existence of two chemical compounds H_2S_2 and H_2S_3 and a molecular compound $H_2S_3 \cdot 3S$.

Density.—Two determinations were made of the density and coefficient of expansion of hydrogen disulfide. The first dilatometer had a bulb of 2.73 cc. A scale from a Beckmann thermometer was attached to the stem. Calibration was carried out with water.

The dilatometer was filled with hydrogen disulfide by using a pyrex capillary funnel. The material had been redistilled, but not from phosphorus pentoxide, and was slightly turbid at 0°. The density was determined from 8 to 51°. The values are tabulated below and are shown in Fig. 4, Curve A.

In the second determination a quartz dilatometer similar to the first was used. The volume of the bulb was 2.08 cc. and of the stem 0.0446 cc. per cm. A reference mark was scratched on the stem about 15 mm. above the top of the bulb. Readings were made by placing the dilatometer so that the stem was in a vertical position and measuring the distance from the reference mark to the bottom of the meniscus with a cathetometer.

Hydrogen disulfide was distilled into the dilatometer from a pyrex still and the apparatus sealed off. A bath of ether stirred by a stream of air was used. Temperatures were measured with a mercury thermometer correct to one-tenth degree. The densities were corrected for the buoyancy of the air. The results are tabulated, and are given in Curve B of Fig. 4. This curve was used for calculating surface tension, since much greater weight must be given to this second determination. A few points lying close to the curves are omitted from the figure.

TABLE V

VARIATION OF DENSITY OF HYDROGEN DISULFIDE WITH TEMPERATURE

Run No. 1		Run No. 2		Run No. 2	
Temp., °C.	Density	Temp., °C.	Density	Temp., °C.	Density
7.9	1.3583	−32.5	1.4074	− 5.8	1.3697
9.6	1.3557	−31.4	1.4054	− 3.9	1.3669
11.0	1.3535	−28.8	1.4012	− 2.5	1.3649
12.5	1.3517	−26.9	1.3986	− 1.1	1.3635
12.9	1.3515	−24.7	1.3959	0.6	1.3596
14.7	1.3490	−22.6	1.3921	1.7	1.3594
16.3	1.3467	−22.1	1.3918	3.5	1.3563
22.2	1.3386	−21.1	1.3906	5.6	1.3535
25.0	1.3360	−19.3	1.3883	7.2	1.3513
27.3	1.3314	−17.0	1.3853	8.0	1.3503
32.1	1.3250	−16.1	1.3836	9.7	1.3485
35.1	1.3203	−15.5	1.3826	10.8	1.3463
38.7	1.3152	−14.7	1.3816	12.4	1.3442
44.3	1.3072	−13.3	1.3797	14.0	1.3419
45.0	1.3065	−11.8	1.3776	15.4	1.3401
47.4	1.3037	−10.7	1.3761	19.5	1.3347
48.7	1.3015	− 9.1	1.3741	23.4	1.3294
51.0	1.2992	− 7.8	1.3726	26.3	1.3253
		− 6.9	1.3711	29.0	1.3217
				31.2	1.3185

The two values for the density at 15° are 1.341 and 1.348 as compared with Bloch and Höhn's value of 1.376. The purer sample has the lower density and hence it is probable that the disulfide used by Bloch and Höhn contained an excess of sulfur. The density at 0° is 1.3615 and at 25°, 1.3270; the coefficient of expansion is 0.00104.

Vapor Pressures.—For measuring the vapor pressure of hydrogen disulfide a special type of apparatus was needed, since the vapor was decomposed by mercury and the liberated hydrogen sulfide attacked the mercury surface. The apparatus shown in Fig. 5 used a buffer column of air and a soda lime tube in series to protect the mercury surface. A is a 100-cc. flask; B, C and D are bulbs made from pyrex test-tubes. B is provided with a stirrer consisting of a piece of iron wire enclosed in pyrex tubing. C and D are designed so that any liquid distilling from B will collect in the bottom without blocking the connecting tube. E is a pyrex to soft glass ground joint. The manometer was constructed of tubing 1 cm. in diameter. One arm was open to the air. The paper scale was calibrated against a standard steel scale.

Two determinations were carried out with hydrogen disulfide. The disulfide was distilled from A over phosphorus pentoxide into B and a seal made at F. B, C and D were then immersed in a four-liter beaker of water; the stirrer was put in motion and the temperature brought to a suitable point.

A rough guess was made of the vapor pressure and the manometer set to this point by manipulation of the taps K and L. The apparatus was evacuated by opening H until practically all the air had been driven from C and D by the vapor from the boiling liquid. Tap H was closed and G opened, thus connecting the manometer to the system. Equilibrium was reached within a minute and readings were made of both sides of the manometer and the temperature of the bath. This procedure was repeated until several readings were obtained.

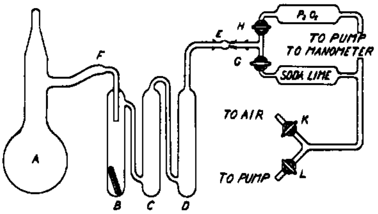

Fig. 5.—Vapor pressure apparatus.

TABLE VI

VARIATION OF VAPOR PRESSURE OF HYDROGEN DISULFIDE WITH TEMPERATURE

First Series

Temperature °C.	Temperature °K.	Pressure, mm. of Hg at 0°	Log P	$I/T \times 10^4$
0.2	273.3	33.3	1.522	36.59
6.8	279.9	44.2	1.645	35.73
10.6	283.7	55.5	1.744	35.25
14.7	287.8	67.1	1.827	34.75
20.1	293.2	87.8	1.944	34.11
24.3	297.4	108.6	2.036	33.62
29.1	302.2	142	2.155	33.09
34.1	307.2	204	2.310	32.55
38.5	311.6	291	2.464	32.09
41.9	315.0	427	2.630	31.75

Second Series

Temperature °C.	Temperature °K.	Pressure, mm. of Hg at 0°	Log P	$I/T \times 10^4$
0.1	273.2	23.9	1.378	36.60
12.6	285.7	54.1	1.733	35.01
24.1	297.2	91.2	1.960	33.65
30.0	303.1	143.6	2.163	32.99
34.0	307.1	187	2.274	32.56
37.2	310.3	202	2.305	32.23
39.8	312.9	277	2.442	31.96
42.5	315.6	273	2.438	31.68
44.6	317.7	315	2.498	31.47

Greater weight was given to the first determination since the stirring was more efficient. Although the observations were carried up to 44°, those above 30° are of little value, due to decomposition of the material in B. When the bath was heated above room temperature, there was considerable difficulty in obtaining correct values, since the liquid distilled into the connecting tubing and decomposed.

The temperature of the bath was taken with a standard mercury thermometer. The readings of the manometer were corrected to 0°. The results are tabulated and shown in Fig. 6. The pressure–temperature curve is merely a smooth curve through the observed points. The log P–$1/T$ curve is a straight line drawn through the observed points. This line passes through the observed value for the boiling point.

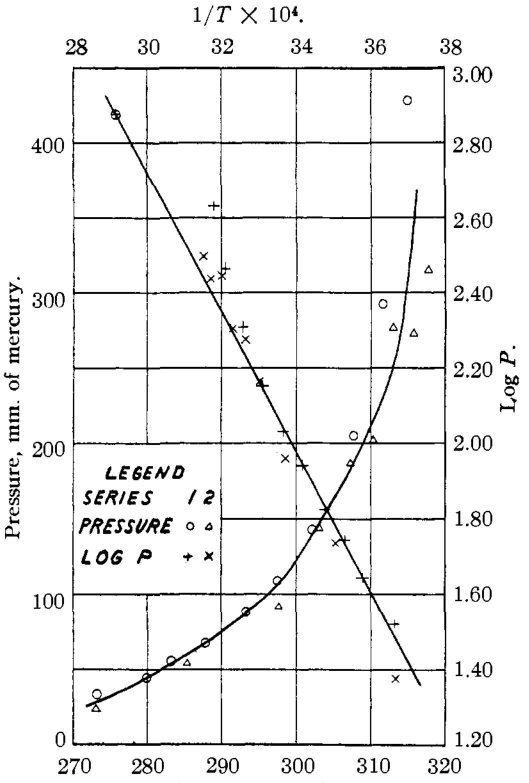

Fig. 6.

The value of the latent heat of evaporation is calculated from the slope of the vapor pressure curve by the formula

$$M\lambda = \frac{2.303 \log (P_1/P_2)}{1/T_1 - 1/T_2}$$

It is found that the molecular heat of evaporation, $M\lambda$, is 8544 cal. and the latent heat per gram, λ, is 129.2 cal.

Boiling Point.—The boiling point of hydrogen disulfide was determined by Bloch and Höhn, and by Walton and Parsons. Since their materials may have been impure and since the vapor came in contact with glass, their values were probably in error by several degrees. It was decided, therefore, to determine the boiling point in an apparatus so designed that the vapor could come in contact only with quartz. The platinum in quartz resistance thermometer (Heraeus type) was placed so that the rubber connection could not come in contact with the vapor.

A sample of hydrogen disulfide was prepared by distillation in a pyrex still from phosphorus pentoxide and transferred into the apparatus. The liquid was heated by a micro flame and boiled quietly for five minutes, the temperature remaining constant. Superheating was prevented by fragments of quartz tubing. Decomposition then started and was detected by a sudden drop in temperature and by a change in the size of bubbles within the liquid.

Owing to a hysteresis effect for the type of thermometer used, the calibration cannot be trusted above room temperature. The platinum thermometer was, therefore, transferred directly from the boiling liquid to a bath of water at approximately the same temperature and compared with a standard mercury thermometer.

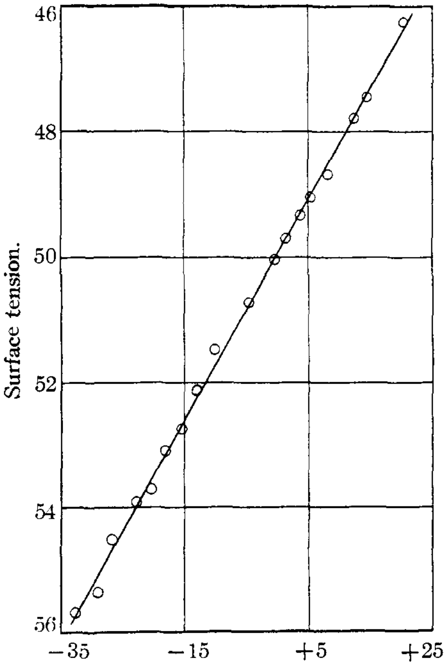

Fig. 7.

The value obtained for the boiling point was 69.9° at 749 mm. A second determination gave 70.6° at 748 mm. The boiling point at 760 mm. may be given as 70.7 ± 0.5°.

From the boiling point and the calculated value for the heat of evaporation the value 24.9 is obtained for Trouton's constant. This value indicates association of the liquid.

Surface Tension.—The surface tension of hydrogen disulfide was determined by measuring the rise in a capillary tube. The liquid was distilled directly into the capillarimeter from a pyrex still and sealed off *in vacuo*. The instrument, built entirely of quartz, is essentially that of Richards.[6] The capillary had an internal diameter of about 1.4 mm. and the wide tube about 13 mm. The constant for the instrument was obtained by a calibration with benzene over a range of temperature.

The capillarimeter was completely immersed in an ether-bath cooled by addition of solid carbon dioxide and stirred by a current of air. The difference in level of the menisci was measured by a cathetometer. Temperatures were measured by a mercury thermometer. The values of the surface tension are tabulated and are given in Fig. 7.

From the smooth curve for the surface tension one may obtain values for

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[6] Richards, THIS JOURNAL, **37**, 1656 (1915).

TABLE VII

VARIATION OF SURFACE TENSION OF HYDROGEN DISULFIDE WITH TEMPERATURE

Temp., °C.	Rise, mm.	d	γ	Temp., °C.	Rise, mm.	d	γ
−32.7	11.35	1.406	55.6	− 4.5	10.60	1.367	50.7
−29.0	11.30	1.401	55.3	− 0.3	10.50	1.361	50.0
−26.8	11.15	1.398	54.5	1.5	10.45	1.359	49.7
−22.8	11.10	1.392	53.9	3.8	10.40	1.355	49.3
−20.5	11.05	1.389	53.7	5.4	10.35	1.354	49.0
−18.2	10.95	1.386	53.1	8.3	10.30	1.350	48.7
−15.9	10.90	1.383	52.7	12.4	10.15	1.344	47.8
−12.9	10.80	1.379	52.1	14.6	10.10	1.341	47.4
−10.1	10.70	1.375	51.5	20.5	9.90	1.333	46.2

calculation of the molecular surface energy, the total surface energy and the Ramsay and Shields constant. The variation of molecular surface energy with temperature is shown in Table VIII.

TABLE VIII

VARIATION OF SURFACE ENERGY OF HYDROGEN DISULFIDE WITH TEMPERATURE

t	γ	d	$\gamma(M/d)^{2/3}$
−30	55.10	1.4028	719.1
−20	53.41	1.3890	701.7
−10	51.71	1.3752	683.9
0	50.02	1.3615	666.0
10	48.32	1.3477	647.7
20	46.63	1.3339	630.4

This gives for the Ramsay and Shields constant the value of −1.78. This is lower than the normal value, −2.12, indicating that the liquid is associated. $d\gamma/dt = -0.1695$ and hence the total surface energy, $\gamma + T(d\gamma/dT)$, is 96.3 ergs. The critical temperature may be calculated from the surface tension data; the value found is 278°, which is in good agreement with that calculated from the boiling point. These values cannot be considered as exact, since the liquid is associated.

Heat Capacity.—Measurements were made of the total heats of hydrogen disulfide from various initial temperatures to 25° in an adiabatic calorimeter.

TABLE IX

TOTAL HEATS OF HYDROGEN DISULFIDE BETWEEN 25° AND LOWER TEMPERATURE

Expt.	Initial temp., °C.	Heat capacity to +25.00° (cal. per g.)	Expt.	Initial temp., °C.	Heat capacity to +25.00° (cal. per g.)
1	0.0	7.62	8	−113.5	63.85
2	− 32.2	18.90	9	−113.5	68.91
3	− 34.2	19.11	10	−115.0	64.80
4	− 78.5	34.09	11	−115.0	69.49
5	− 78.5	34.59	12	−140.0	73.29
6	− 78.5	34.77	13	−184.8	79.71
7	−113.5	63.84	14	−186.8	79.66

A sample of hydrogen disulfide was purified by distillation from phosphorus pentoxide in a quartz still. This sample, contained in a quartz bulb, showed no evidence of decomposition over a period of ten weeks. The apparatus and method of procedure was similar to that of Maass and Barnes.[7] The variation in the temperature of the thermostat in which the disulfide was cooled was less than one degree. The total heat of the quartz bulb from the initial temperature to +25° was obtained from a mean specific heat curve given by Sosman.[8] The results of the determinations are tabulated and are shown in Fig. 8.

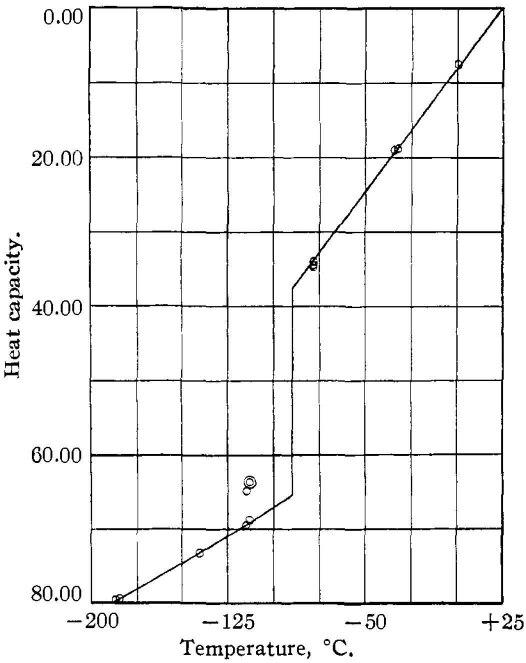

Fig. 8.

The deviation of Expts. 7, 8 and 10 is much too large to be caused by the container not reaching the temperature of the thermostat. It is practically certain that these anomalous results indicate the existence of a metastable crystalline form of hydrogen disulfide. It was impossible to freeze the liquid without supercooling to about −105° and owing to this supercooling the metastable form can exist. These results permit calculation of the specific heats of the liquid and solid and of the latent heat of fusion.

Specific heat of liquid hydrogen disulfide	0.333
Specific heat of solid hydrogen disulfide	0.142
Latent heat of fusion of hydrogen disulfide	27.3 cal. per g.

Refractive Index.—The refractive index of hydrogen disulfide was measured by an Abbé refractometer. The prisms were carefully washed, using successively benzene, alcohol, hydrochloric acid, water, alcohol and ether. Observations were made over five minutes and the curve extrapolated to zero time. A typical series was

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[7] Maass and Barnes, *Proc. Roy. Soc.* (London), A111, 224 (1926).

[8] Sosman, "Properties of Silica," The Chemical Catalog Co., Inc., New York, 1927, p. 315.

Time, minutes	0:30	1:00	2:00	2:30	3:00	4:00	5:00
Refractive index	1.6326	1.6340	1.639	1.643	1.651	1.659	1.675

The value of the refractive index was found to be $n_D = 1.6322$ at 22°. The molecular refractive power, $R = (n^2 - 1)/(n^2 + 2) \times M/d$ may be calculated and has the value 17.730.

Conclusions

The present investigation allows a number of comparisons to be made between H_2S, H_2S_2, H_2O and H_2O_2.

	H_2S	H_2S_2	H_2O	H_2O_2
Melting point, °C.	−82.9	−89.6	0.0	−0.89
Boiling point, °C.	−59.6	70.7	100.0	151.4
Heat of evaporation	5210	8544	9709	11610
Trouton's constant	24.4	24.9	26.2	27.3
Specific heat of liquid	....	0.333	1.00	0.579
Specific heat of solid	....	0.142	0.45	0.47
Heat of fusion	....	1800	1430	2500
Density at 20°	0.964 (−60°)	1.3339	0.9982	1.4418
dD/dt	0.00163	0.00138	0.00021	0.00107
Surface tension at b. p.	28.2	38.1	55.9	55.3
Total surface energy	82.2	96.3	113.1	121.0
Ramsay and Shields constant	1.91	1.78	1.08	0.92
Parachor (obs.)	82.9	130.0	52.8	69.6
Parachor (calcd.)	82.4	130.6	54.1	74.1
Refractive index, n_D^{22}	1.384	1.6322	1.3328	1.4139
Molecular refractive power (obs.)	9.64	17.730	3.715	5.900
Molecular refractive power (calcd.)	9.89	17.58	3.725	5.250

The melting point of hydrogen disulfide is a little lower than that of hydrogen sulfide. The melting point of hydrogen peroxide is slightly lower than that of water. The boiling point of hydrogen disulfide is considerably higher than that of hydrogen sulfide; the boiling point of hydrogen peroxide is considerably higher than that of water. The general conclusion is that the change in physical property due to the added sulfur atom in the sulfur compounds is followed in an analogous manner by the change in physical property due to the addition of an oxygen atom in the oxygen compounds. Thus a striking similarity is brought out in the physical properties, as well as the chemical, of hydrogen disulfide and hydrogen peroxide.

Association of the liquids increases in the order H_2S, H_2S_2, H_2O, H_2O_2, the latter two being much more highly associated, as is shown by the Ramsay and Shields constant and the melting point. The agreement of the observed values of the parachor and molecular refractive power with those calculated for the formula H–S–S–H proves that hydrogen disulfide does not contain a double bond or a coördinate bond. The deviation between the observed and calculated values for hydrogen peroxide indicates a possible coördinate bond in this compound.

Acknowledgment is made of a studentship and a fellowship granted to one of us by the Research Council of Canada.

Summary

The preparation and purification of hydrogen disulfide have been described and the conditions investigated for obtaining large yields. It was shown that the higher persulfides are not formed by the solution of sulfur in hydrogen disulfide. The solubility of sulfur in the hydrogen disulfide was measured. The melting point, vapor pressures, density of the liquid, surface tension, refractive index, specific heat and latent heat of fusion of hydrogen disulfide were determined, and related constants were calculated. A comparison of the physical properties of hydrogen sulfide, hydrogen disulfide, water and hydrogen peroxide brings out the relations existing between these compounds.

MONTREAL, CANADA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF STANFORD UNIVERSITY]

THE NATURE OF THE SORPTION BY CHARCOAL OF GASES AND VAPORS UNDER GREAT PRESSURE

BY JAMES W. MCBAIN AND GEORGE T. BRITTON

RECEIVED NOVEMBER 7, 1929 PUBLISHED JUNE 6, 1930

The McBain–Bakr sorption balance[1] has enabled regions of sorption previously inaccessible to be explored with comparative ease. Nearly all studies of sorption have been broken off below atmospheric pressure,[2]

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[1] The microbalance described by McBain and Tanner [*Proc. Roy. Soc.* (London), **A125**, 579 (1929)] has many points of superiority over the McBain–Bakr balance. It is of the beam type, of extreme sensitivity, robust and compact enough to be placed within a glass tube and subjected to great extremes of temperature and pressure while in use.

[2] The chief investigations in which higher pressures have been used are: J. Hunter [*J. Chem. Soc.*, **24**, 76 (1871)], charcoal with ammonia and cyanogen to 3.5 atmospheres and carbon monoxide to 5.3 atmospheres in a Fontana experiment; E. W. R. Pfeiffer ["Dissertation," Erlangen, **1882**, *cf. Beiblätter*, **8**, 630 (1884)], glass wool or charcoal with glass wool in Cailletet's compression apparatus with carbon dioxide or ammonia between 2 and 8 atmospheres, showing no saturation value; Sir James Dewar [*Proc. Roy. Inst.*, **18**, 437 (1906)], 1 g. of charcoal at −185° sorbed 9.3 cc. of hydrogen at 1 atmosphere pressure; this was raised to 13.81, 156.7, 149.3, 145.5 and 138.1 cc. at 5, 10, 15, 20 and 25 atmospheres, respectively; Dewar regarded this as constancy. J. I. Graham [*The Colliery Guardian*, **122**, 809 (1921)], carbon dioxide, methane and nitrogen by dry and moist coal up to about 30 atmospheres. The moist sorbed about one-third as much as the dry coal dust, 1 g. of which, together with a small amount of glass wool, at 30 atmospheres, sorbed about 10 cc. of nitrogen, the amount still apparently rising with increase in pressure. H. Briggs and W. Cooper [*Proc. Roy. Soc. Edinburgh*, **41**, 119 (1921)] tested the capacity of steel cylinders partly filled with moist or dry charcoal or silica, using nitrogen, oxygen and hydrogen in some cases up to 100 atmospheres. They found agreement between their results and the Williams–Henry formula, but in some cases the term $k_2 \times x/m$ of that formula was negligible. F. A. Henglein and M. Grzen-