2. A set of curves has been given to show the relation between the increase in density of an isotopic mixture and the cut. These curves exhibit one curvature when the amount of the heavier isotope is less than 50%, the opposite curvature when the amount is greater, and a point of inflection at this percentage. When several isotopes are present there may be several points of inflection.

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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

HYDROGEN HEXASULFIDE AND THE SOLUBILITY OF SULFUR IN THE PERSULFIDES OF HYDROGEN

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Introduction

Since the time of Scheele, who first prepared the oily liquid usually known as hydrogen persulfide, much work has been done on the composition of this material. The results of analyses of various investigators gave empirical formulas varying from H_2S_5 to H_2S_9. Bloch and Höhn[1] have shown that the distillation of this oil yields two compounds of the composition H_2S_2 and H_2S_3. Their results were later confirmed by Walton and Parsons[2] who perfected a method for preparing the yellow oil in quantity, improved the method for distilling it and obtained the di- and trisulfides of hydrogen in a state of great purity. A new and extremely accurate method for the analysis of the persulfides was devised and their behavior towards a number of catalysts was investigated qualitatively.

Hydrogen disulfide and hydrogen trisulfide dissolve sulfur copiously, a fact that may be explained as a purely physical solution of the sulfur, a combination of the sulfur to form higher sulfides, or by these two effects operating simultaneously.

It is probable that the yellow oily liquid that separates when an excess of hydrochloric acid is added to a solution of a polysulfide of an alkali is a complex mixture of sulfides of hydrogen with dissolved sulfur. That sulfides higher than the hydrogen trisulfide do exist is evidenced by the existence of addition compounds. Among these are the strychnine compound, $(C_{21}H_{22}N_2O_2).H_2S_6$, prepared by Hoffman[3] and the brucine compound, $(C_{23}H_{26}N_2O_4)_3(H_2S_6)_2$, prepared by Schmidt.[4] Both of these were obtained by treating an alcoholic solution of strychnine or brucine with an alcoholic solution of ammonium polysulfide.

[1] Bloch and Höhn, *Ber.*, **41**, 1961 (1908).

[2] Walton and Parsons, THIS JOURNAL, **43**, 2539 (1921).

[3] Hoffman, *Ber.*, **10**, 1087 (1877).

[4] Schmidt, *Ann.*, **180**, 287 (1876); *Ber.*, **10**, 1289 (1877).

Brunner and Vuilleumier[5] prepared persulfides and used them to react with various aldehydic and ketonic substances. The method employed was to dissolve the aldehyde or ketone in carbon disulfide, chloroform or some other suitable solvent and then add the persulfides directly. Following this procedure, they were able to obtain and characterize the following addition compounds: $(C_6H_5CHO).H_2S_3$, from benzaldehyde; $(C_6H_4OCH_3CHO)_2.H_2S_3$, from anisic aldehyde; $C_9H_8O.H_2S_4$, from cinnamic aldehyde; and $(C_6H_4O_2)_4H_2S_5$, a violet powder from benzoquinone. The object of this investigation was to determine at various temperatures the composition of the liquid phase in the system in which solid sulfur exists in equilibrium with the hydrogen sulfides. It was hoped that in this way information concerning the existence of higher sulfides of hydrogen might be obtained.

Experimental

Materials.—The carbon disulfide used in the following experiments was purified by allowing it to stand over metallic copper and later over metallic mercury and mercuric chloride. It was then distilled. The acetone was dried over fused calcium chloride and then fractionated, the middle fraction being the only one used. As a check on the purity of these two reagents, about 25 cc. of each was evaporated in a crystallizing dish. No visible residue could be detected.

In preparing pure rhombic sulfur, a saturated solution of sulfur in pure carbon disulfide was prepared at 25° and then chilled in an ice-bath. The sulfur which separated was filtered off, recrystallized several times and finally dried at 90°.

The method of obtaining hydrogen trisulfide and hydrogen disulfide was essentially that of Bloch and Höhn as modified by Walton and Parsons. A solution of sodium polysulfide was run slowly into chilled hydrochloric acid with constant stirring. The yellow oil which formed was washed in a separatory funnel with distilled water, dried in a quartz flask (glass decomposes the persulfides) over phosphorus pentoxide and filtered through asbestos. It was then distilled at about 6 cm. pressure, the fractions showing upon analysis the approximate compositions, H_2S_3 and H_2S_2, respectively.

Temperature Control.—The problem of controlling the temperature during the following determinations was a comparatively simple one. At 0° a bath of ice and water was used. For temperatures from +25° to +55.3° an ordinary thermostat heated by an electric lamp was used. Below room temperature the bath was cooled by water running through a metal coil. The temperatures within the above temperature ranges could be kept constant with a variation of not more than ±0.02°.

Greater difficulties were encountered when freezing mixtures were used, but in most instances satisfactory temperature control was obtained. A large Dewar flask with a small, rapidly revolving stirrer was used as a container for the freezing mixtures.

These mixtures suggested by Guthrie[6] are listed below.

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[5] Brunner and Vuilleumier, *Schweiz. Wochschr.*, **46**, 436 (1908); *C. A.*, **2**, 3347 (1908).

[6] Guthrie, *Phil. Mag.*, **49**, 269 (1875).

TABLE I

FREEZING MIXTURES USED FOR CONSTANT TEMPERATURES

Salts used with cracked ice	Temperatures obtained ° C.	Salts used with cracked ice	Temperatures obtained ° C.
$CuSO_4.5H_2O$	− 1.45	NH_4Cl	−15.42
$MgSO_4.7H_2O$	− 3.47	$CaCl_2.6H_2O$	−34.72
KCl	−10.6		

Calcium chloride with 6 molecules of water of hydration held the temperature constant for about 4 hours; in no instance could the temperature be maintained for more than 8 or 10 hours.

Methods of Obtaining Equilibrium and Analysis of the Liquid Layer.—To saturate the persulfide, 15 cc. of the compound was placed in a quartz test-tube and brought to the temperature of the bath. An excess of powdered sulfur crystals was added and the mixture stirred by means of a quartz stirrer. To withdraw samples, the stirrer was removed and the sulfur allowed to settle. A sample of the clear, supernatant liquid was forced by air pressure through the quartz tube A into the quartz weighing tube B. The sampling apparatus is shown in Fig. 1. This operation was repeated at intervals of from 1/2 to 1 hour until 3 or 4 samples had been taken.

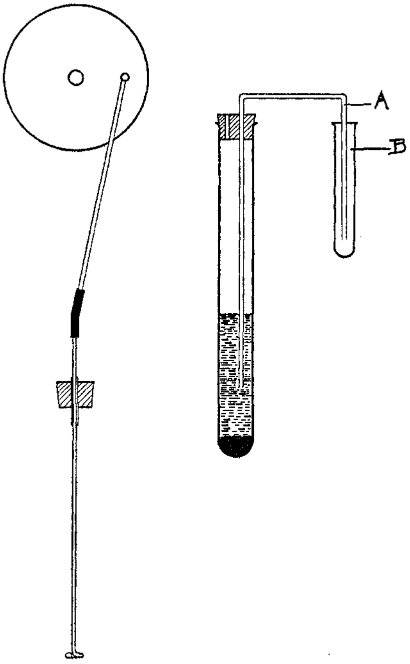

Fig. 1.

The method of analysis employed was that used by Walton and Parsons.[2]

> The weighed sample was washed into a crystallizing dish by means of pure carbon disulfide. About 10 cc. of acetone was then added to decompose the persulfide, and the solvents were allowed to evaporate spontaneously. The residual rhombic sulfur was then heated to constant weight at 90° and weighed as "sulfur not evolved as hydrogen sulfide." In practically every case the results checked to within 0.1% and in several instances varied but a few hundredths of a per cent.

It was first of all necessary to determine whether or not saturating hydrogen disulfide and hydrogen trisulfide with sulfur at the same temperatures results in the same system. To test this point, samples of the 2 persulfides were placed in quartz tubes, agitated at 0° with an excess of sulfur and the liquid phase was analyzed. As shown in Table II hydrogen disulfide and hydrogen trisulfide, when saturated with sulfur, give solutions of the same composition. Since the trisulfide is more easily prepared than the disulfide, this was used in the following determinations with the exception of that at —34.72°.

TABLE II

COMPOSITION OF LIQUID PHASES FORMED BY SATURATING H_2S_2 AND H_2S_3 WITH SULFUR AT 0°

Hydrogen persulfide used	% Sulfur not evolved as H_2S		
	I	II	III
Trisulfide	82.87	82.93	82.90
Disulfide	82.98	82.96	...

To obtain equilibrium between the liquid persulfide and sulfur at low temperatures, an experiment was made in which the persulfide was saturated with sulfur at a higher temperature and then cooled to a lower temperature with stirring in the presence of the solid phase. This method did not readily give a state of equilibrium as the following table illustrates.

TABLE III

COMPOSITION OF LIQUID PHASES OBTAINED BY SATURATING H_2S_3 WITH SULFUR AT ROOM TEMPERATURE AND COOLING

Temperature ° C.	% Sulfur not evolved as H_2S		
	I	II	III
− 2.85	84.50	84.69	84.66
−10.32	85.51	85.57	85.63
−15.4	82.08	81.97	82.10
−21.3	77.60	77.71	...

The original sample of trisulfide was used in each case and allowed to warm to room temperature between runs. It is to be noted that the amount of sulfur not evolved as hydrogen sulfide at —10.32° is approximately 1% higher than that at —2.85°. While the analyses from a given run agreed, no agreement was found between different runs. The results in Table III, when plotted as a solubility curve, are very irregular. The solution prepared in the manner described comes to equilibrium very slowly. A similar behavior has been noticed in the case of other viscous solutions. A supersaturated sugar solution, for instance, arrives at equilibrium very slowly even in the presence of crystals of the solid phase. Undoubtedly final equilibrium could be obtained by precipitating sulfur from supersaturated solutions of the solute in the persulfides by chilling. The process is so slow, however, that at low temperatures a constant temperature could not be maintained over the period necessary. For this reason, freshly prepared trisulfide or disulfide was used and equilibrium obtained by dissolving sulfur in it as previously described.

Data.—Following the methods outlined, the solubility of sulfur in the persulfides was determined at the temperatures listed in Table IV. At each temperature samples of the liquid phase were taken 1 or 2 hours apart. The analysis of these samples showed when equilibrium between sulfur and the liquid phase was established. The data in the second column are averaged from analyses of the samples taken after equilibrium had been reached.

TABLE IV

THE SOLUBILITY OF SULFUR IN THE PERSULFIDES OF HYDROGEN

Temperature ° C.	% Sulfur not evolved as H_2S	Temperature ° C.	% Sulfur not evolved as H_2S
55.3	92.49	− 1.45	82.50
45.15	91.00	− 3.75	80.71
35.4	89.46	−10.6	75.16
25.4	87.98	−15.42	71.18
17.92	86.77	−34.72	53.56
0.05	82.97	.....	...

From the figures given in this table, it is apparent that the solubility of sulfur in the persulfides increases rapidly with an increase in temperature until, at —1.45° and above, the temperature effect becomes less marked. An inspection of the solubility curve of Fig. 2 shows a break at —1.45°.

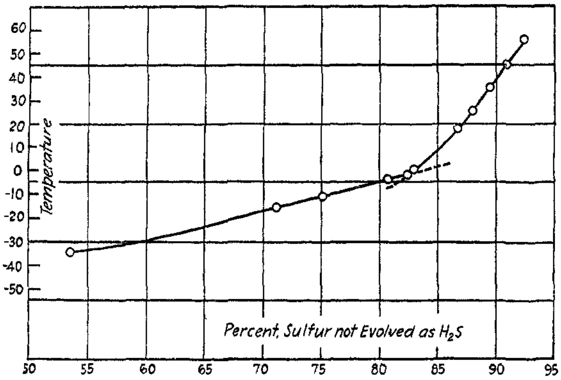

Fig. 2.

At this temperature the liquid has the composition very close to H_2S_6. Further evidence of the existence of a break at this point was obtained by saturating a solution of the trisulfide at —5° and allowing it to warm slowly in the presence of the solid phase, with constant stirring. This experiment was repeated several times. On plotting the temperature readings against times, the curves showed marked breaks between the temperatures of —1.5° and —0.8°. With the compound H_2S_6 the percentage of sulfur not evolved as hydrogen sulfide is 82.47%. Analysis of the saturated solution at —1.45° gave a result of 82.50% sulfur not evolved as hydrogen sulfide. These facts indicate that at —1.45° the liquid phase consists of the pure hexasulfide of hydrogen.

Above this temperature the hexasulfide seems to decompose very readily. This was strikingly shown in the following experiment. A solution of hydrogen disulfide was saturated with sulfur at about —70°. It was then stirred in the presence of excess of the solid phase and the temperature allowed to rise slowly. No change was apparent until the temperature —1.5° was reached, when the entire liquid layer began to decompose with the rapid evolution of hydrogen sulfide.

Within the temperature limits of this investigation, no other breaks were observed. It seems probable, therefore, that below and above —1.45° the liquid phases consist of equilibrium mixtures of various persulfides, always with the possibility of the presence of dissolved sulfur. The solubility curve readily explains the results obtained by Rebs[7] who poured alkali polysulfides corresponding to H_2S_2, H_2S_3 and H_2S_5, into cold conc. hydrochloric acid. He obtained a product that he considered to be H_2S_5, although the analysis varied from $H_2S_{4.7}$ to $H_2S_{5.7}$. In the light of the foregoing experiments it is evident that Rebs obtained equilibrium mixtures of sulfur and polysulfides, the composition varying with the temperature of the reaction mixture. The free sulfur necessary for equilibrium could easily have been provided by decomposition of some of the polysulfides, which always occurs when the yellow oil is prepared.

It is of further interest to point out that the instability of hydrogen hexasulfide above —1.45° explains the necessity of keeping the reaction mixture cold when preparing the yellow oil.

Summary

1. Hydrogen disulfide and hydrogen trisulfide dissolve sulfur copiously. When these two liquids are saturated with sulfur at a given temperature the two resulting liquid phases have the same composition.

2. A solubility curve has been established by saturating hydrogen trisulfide with sulfur at temperatures ranging from —34.71° to +55.3°.

3. The existence of a compound having the composition H_2S_6 has been established. This compound is stable below —1.45°.

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[Contribution from the Chemical Laboratory of the University of Illinois]

A STATISTICAL THEORY OF MONOMOLECULAR REACTIONS

By W. H. Rodebush

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The change of specific reaction rate with the temperature can be represented fairly well for many reactions by an equation of the form, $k = s\, e^{-E/RT}$ where s is presumably a constant characteristic of the reaction in question and E, R and T have their usual significance. If we assume that only those molecules react which have acquired, through a particularly violent collision or otherwise, a certain "critical" amount of energy greatly in excess of the average energy per molecule, then the kinetic theory offers us a physical basis for the derivation of the equation above. A

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[7] Rebs, *Ann.*, 246, 356 (1888).