and 59.6° C. for 62.38 and 66.2% LiBr in water, respectively, in agreement with the present solubility study.

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Liquid Hydrogen Sulfide in Contact with Sulfur

J. J. SMITH, DAN JENSEN, and BEAT MEYER
Chemistry Department, University of Washington, Seattle, Wash. 98105

Sulfur in contact with liquid hydrogen sulfide at equilibrium pressure was studied between −81° and 120° C. The solubility of solid sulfur is 5 × 10^{-6} mole of S_8 per gram of H_2S at −80° C. and 5 × 10^{-5} at 80° C. Over this range, log solubility vs. $1/T$ gives a straight line. From a least squares analysis of the data, $\Delta H_S = 2.1 \pm 0.1$ kcal. per mole. From 80° to −80° C., the solubility can be represented by $\log S = \frac{-4.52 \times 10^2}{T} - 3.00$. In contact with liquid H_2S, sulfur melts at 98° C., below the critical point of H_2S. The melting point depression of sulfur is about 20° C., indicating that H_2S dissolves appreciably in solid sulfur. NMR spectra show that no detectable chemical reaction occurs up to 120° C. Photolysis yields a white, finely powdered precipitate, probably photosulfur, which redissolves or converts to orthorhombic sulfur within 4 weeks after irradiation; no sulfanes are formed. Slow reaction occurs between liquid sulfur and gaseous H_2S above 150° C.

THE MUTUAL SOLUBILITY of sulfur and hydrogen sulfide has been studied under three conditions: gaseous hydrogen sulfide and liquid sulfur; solid sulfur and gaseous hydrogen sulfide; and solid sulfur and liquid hydrogen sulfide. In the first system, Fanelli (*4*) observed that the solubility of hydrogen sulfide goes through a maximum between 150° and 200° C. In this range pure liquid sulfur undergoes a marked viscosity change and its color turns from yellow to red. The presence of hydrogen sulfide suppresses the viscosity increase.

In recent years, Hyne and coworkers (*5*) and Wiewiorowski and Turro (*15, 16*), using NMR and infrared spectra, established that the solution undergoes a slow chemical reaction, yielding long sulfane chains of unknown length. In a study (*14*) of sulfur solubility in gaseous hydrogen sulfide at pressures between 40 and 400 atm., results indicate increased sulfur transport by high pressure gas. It is not yet established whether sulfanes form. In the present work our attention is directed towards the system liquid hydrogen sulfide-solid sulfur, which has been least studied. Several publications (*1, 3, 6, 7, 11*) before 1934 mention it in a vague fashion, without reporting numerical data. No recent data are available.

The purpose of the present study is to determine the general behavior of the system, rather than to record very accurate data. Three types of experiments were performed, to establish solubility limits, to explore the critical region of H_2S in the presence of sulfur, and to study possible reactions and reaction products, especially sulfanes.

EXPERIMENTAL

Dried Matheson C.P. grade hydrogen sulfide was condensed into a reservoir bulb and vacuum-distilled into the sample tubes. High purity filtered sulfur (99.99%) was donated by the Freeport Sulphur Co.

For the solubility determination, sulfur was measured into a glass tube 6 cm. long and 6 mm. in o.d., which was then connected to a vacuum system. After evacuation, a known amount of hydrogen sulfide was condensed in the tube at 77° K., and the tube was evacuated and sealed. The elemental sulfur content was determined in either of two ways: Sulfur crystals were weighed in the tube or a known volume of a solution of sulfur in carbon disulfide was transferred into the tube and the solvent evaporated on the vacuum line. Both procedures led to the same solubility measurements. This indicates that residual CS_2 was not present in any of the samples.

The tubes were put through several temperature cycles in temperature baths at −78°, −63.5°, −45°, −22°, 0°, 25°, 40°, 60°, and 80° C. The tubes were maintained at each temperature for several hours. The solubilities were determined by visually observing a series of tubes containing various amounts of sulfur and hydrogen sulfide. The sulfur concentrations were chosen so that at any temperature at least two tubes contained excess sulfur, and at least two contained only solution. Precipitation and dissolution temperatures were observed. On cooling, excess sulfur formed white crystalline needles. On warming, the last fraction of a needle disappeared within an hour. Solutions of originally amorphous sulfur always equilibrated quickly, but originally crystalline samples dissolved slowly. Two complete sets of tubes plus several independent samples were used to verify the reproducibility.

For reaction studies commercial NMR tubes were used. For experiments at temperatures above 100° C. U-tubes were fashioned from 6-mm. o.d. glass, and filled as above. Instead of being immersed in a temperature bath, the entire sample was straddled upside down over two containers, each of which could be kept at a separate temperature. One regulated the hydrogen sulfide pressure, the other fixed the sulfur temperature. In this way hot liquid sulfur could be equilibrated with hydrogen sulfide at different pressures.

Figure 1 shows a cross section of the experimental setup used to observe the critical point of H_2S. Sulfur and hydrogen sulfide were sealed in a 4-mm. o.d. tube prepared as described above. The tube was then placed in another tube made from 7-mm. o.d. glass, which contained enough sulfur dioxide to maintain a liquid phase at all temperatures. A spacer was inserted to raise the inner tube above the liquid SO_2 level. At 100°C., the critical point of H_2S, the pressure in the center tube was 88.6 atm., in the outer tube at 27.3 atm., and the pressure differential between glass walls remained safe.

NMR spectra were taken on a Varian A-60 spectrometer, and occasionally on a Varian HA-100. For photolysis, the tubes were quartz, or thin-walled commercial NMR tubes, and were immersed in an ultraviolet-transparent constant temperature bath.

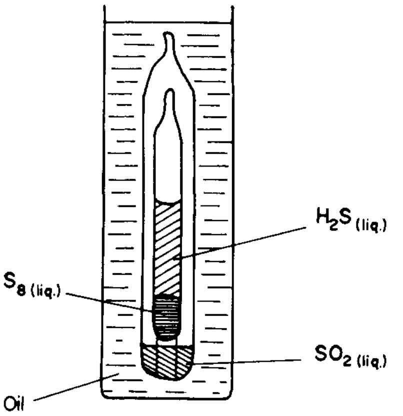

Figure 1. Cross section of experiment with double tube containing liquid sulfur and liquid hydrogen sulfide at 100° C. and 89 atm.

SO_2 pressure in outer tube 23 atm.

RESULTS AND DISCUSSION

Solubility of Solid Sulfur in Liquid Hydrogen Sulfide. Table I shows at once that sulfur is soluble in H_2S, and that the solubility increases with temperature. In this work we are concerned with recording upper and lower limits for solubilities, and, therefore, neglect the volume of undissolved sulfur. The density of liquid H_2S at equilibrium pressure (*2, 12*) decreases from 0.938 gram per cc. at the melting point to 0.680 gram per cc. at 58° C. This includes thermal expansion and compressibility. The volume increase in this temperature range is 40%. In the same range the gas pressure increases from 1 to 42 atm., and the gas density increases accordingly. Thus, the decrease of gas volume is compensated by the gas density, and there is little net transfer of H_2S from liquid to gas phase. Therefore, the weight of the liquid phase is probably constant within the accuracy of the present observations.

The plot of the logarithm of solubility of sulfur in H_2S *vs.* $1/T$ (Figure 2) is within experimental accuracy a straight line, as expected for a nonreactive solution. A least squares fit of the data gives a straight line whose slope yields a heat of solution of $\Delta H_S = 2.1 \pm 0.1$ kcal. per mole. On the basis of this fit, the solubility can be

Table I. Solubility of Sulfur in Liquid H_2S

T,°C.	Solubility, Mole S_8 /Gram H_2S		
	Lower limit	Upper limit	Least Squares
−78	. . .	5.32×10^{-6}	. . .
−63.5	. . .	5.32×10^{-6}	6.92×10^{-6}
−45	1.05×10^{-5}	1.18×10^{-5}	1.02×10^{-5}
−25	1.18×10^{-5}	1.34×10^{-5}	1.52×10^{-5}
0	1.34×10^{-5}	2.08×10^{-5}	2.22×10^{-5}
10	2.08×10^{-5}	2.27×10^{-5}	2.54×10^{-5}
20	2.27×10^{-5}	3.38×10^{-5}	2.74×10^{-5}
40	3.38×10^{-5}	3.91×10^{-5}	3.62×10^{-5}
60	3.91×10^{-5}	5.84×10^{-5}	4.42×10^{-5}
80	5.84×10^{-5}		

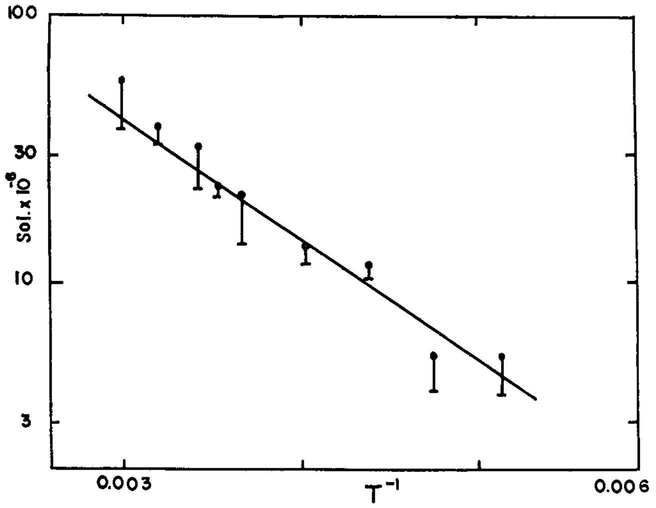

Figure 2. Plot of log solubility *vs.* $1/T$ for sulfur in liquid hydrogen sulfide

Straight line represents least squares fit of data computed from the equation $\log S = \frac{-4.52 \times 10^2}{T} - 3.00$ for the temperature range of −80° to +80° C. The fact that saturated solutions are quickly produced by cooling, and that saturation after long cycling is reached reversibly, by cooling and by heating, is a further indication that irreversible or slow reactions do not occur.

Mixtures at Critical Point of Hydrogen Sulfide. Between 100° and 119° C., solid sulfur and gaseous hydrogen sulfide are expected to coexist, but in the presence of H_2S at equilibrium pressure sulfur melts at 98° C. Liquid H_2S and liquid sulfur do not mix. At the critical temperature, the meniscus between liquid and gaseous hydrogen sulfide disappears, and a dew of liquid sulfur settles on the walls of the tube where the liquid disappeared. Obviously, the solubility of sulfur decreases during the phase transition.

When the sample is cooled, the entire vapor volume clouds before liquid condenses. Below the critical point hydrogen sulfide and sulfur are both liquid. When the temperature is further lowered, sulfur supercools and, finally, crystallizes between 95° and 90° C.

In several sample tubes, liquid sulfur and liquid hydrogen sulfide were equilibrated for several hours. The tubes were quenched in liquid nitrogen at 77°K. The content of the inner tube was dissolved in carbon disulfide. NMR spectra of the resulting solutions showed no indication of sulfanes. Thus, reaction between the two liquids does not occur, or is much slower than that reported between liquid polymeric sulfur and hydrogen sulfide gas (*5, 15, 16*) at higher temperatures.

The coexistence of the two liquids is unexpected. The temperature measurements are not accurate enough to decide whether the critical temperature of hydrogen sulfide saturated with sulfur is increased. However, the experiment established that the melting point of sulfur saturated with H_2S at 90 atm. lies at 98°C.—i.e., about 20° C. below that of sulfur in air at 1 atm.

Solid sulfur begins melting at 119.3° C., the "ideal melting point" (*8, 9*). In equilibrium with liquid, the melting point drops to 114.6° C., the "natural" value, probably because of the autodissociation of sulfur rings in the liquid. Thus, the value of the molar freezing point depression of sulfur must be substantial. A detailed study of this phenomenon exceeds the scope of this paper.

Reactivity of Sulfur–Hydrogen Sulfide. Since liquid hydrogen sulfide did not seem to react with sulfur, experiments were performed to test the effect of light. About 2 mg. of sulfur and 1 ml. of H_2S were sealed in evacuated commercial NMR tubes. In some tubes, the entire content was exposed to the full light of a General Electric AH-4 medium pressure mercury arc lamp with glass envelope removed. In other tubes, only a small fraction of the liquid was exposed to light, and the solid sulfur was carefully shielded. In all tubes, at all temperatures studied, a white suspension formed from the onset of irradiation. The white particles settled quickly and redissolved within 4 weeks at 25° C. after the irradiation was terminated. NMR signals of sulfanes were not observed, even after 90 minutes of irradiation. This means that less than 0.05% sulfanes were formed, although the observation of generous white precipitation indicates that a reaction occurred. Similar precipitation of sulfur from other solvents was observed by Wiegand and others (*8, 13*). They explained it by assuming that a new insoluble allotrope of elemental sulfur, "photosulfur," formed. The x-ray structure of photosulfur has not yet been determined, but it seems likely that it consists of polymeric sulfur. Apparently, solid polymeric sulfur is considerably less soluble in H_2S than S_8.

Polymeric sulfur forms from S_8 by chain scission and free radical reaction. That such a reaction can occur in liquid H_2S without formation of sulfanes indicates that H_2S does not react rapidly below 100°C. with sulfur radical chains with eight or more atoms. This is supported by the solubility data of H_2S in liquid polymeric sulfur, which forms in liquid sulfur at 150°C. At this temperature it dissolves about twice as much H_2S as S_8 at 124° C. Thus, sulfur radical chains increase H_2S solubility. Hyne and coworkers (*5*) and Wiewiorowski and Turro (*15, 16*) studied the system at 150° C. and reported that a very slow reaction occurs, and small amounts of sulfanes with chains larger than six can be observed after 3 to 9 hours. Using a U-tube with one arm at 120° to 400° C. and the other at −61° to 25° C., the present experiments confirmed their results, and showed that the reaction is very slow even at 20 atm.

At room temperature, sealed tubes containing liquid hydrogen sulfide and solid sulfur showed no detectable sulfanes, even after standing for 4 weeks. Similarly, the contents of tubes maintained at 110° C. and 100 atm. for 6 hours did not react. Therefore, for all practical purposes sulfur and hydrogen sulfide do not react under these conditions. In this range, the system forms true solutions, the sulfur solubility increasing with temperature. The kinetics of dissolution are slower for orthorhombic than for amorphous sulfur, and photosulfur is practically insoluble in H_2S.

These observations are limited to pressures below 100 atm. Therefore, it is possible that free radical reactions occur under more severe conditions—for example, under geochemical conditions in and around oil wells. Ionic reactions yielding sulfanes will be discussed in a later paper.

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