2. In general, the volume change is a contraction which is largest (a) at higher temperatures and (b) at lower concentrations.
3. The increase in volume change (contraction) with temperature is greater at lower concentrations.
4. Below 30° the volume change tends towards an expansion in volume, which is in agreement with the fact that under some circumstances rubber suffers a change in density in the neighborhood of 30°.
5. In the case of xylene sols, here considered, the condition of the rubber as regards milling or plasticizing appears to have no marked effect on the volume change.

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THE PREPARATION AND PROPERTIES OF COLLOIDAL AND MONOCLINIC SULFUR IN ORGANIC LIQUIDS[1]

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Among the first studies of non-aqueous colloids were those of Graham,[2] in which he replaced the water in silicic acid jelly by alcohol, and sulfuric, nitric and formic acids. More recent workers have studied non-aqueous sols but only a few of them have selected sulfur as the substance to be dispersed. Svedberg[3] prepared a dispersion of sulfur in *iso*butyl alcohol and in ethyl ether by means of an oscillatory electric discharge. Von Weimarn and Kagan[4] prepared sulfur sols in alcohol by freezing supersaturated solutions and then allowing them to melt. Von Weimarn[5] prepared dispersions of sulfur in various alcohols and studied their colors and other properties. Sekera[6] prepared colloidal sulfur by spraying solutions into carbon disulfide.

The purpose of this investigation is to study the factors affecting the production of sulfur dispersions in organic liquids and to determine the properties of such dispersions, also to identify crystals which were formed in some of the dispersions.

Preparation of the Dispersions

Experiments were carried out to determine the liquids most suitable for dispersion media, and the best method for the production of the sulfur dis-

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[1] This paper is an abstract of a thesis submitted by Florence M. Colt in partial fulfilment of the requirements for the degree of Master of Science at Rutgers University.

[2] Graham, *Proc. Roy. Soc.* (London), **13**, 335 (1864).

[3] Svedberg, *Ber.*, **39**, 1705 (1906).

[4] Von Weimarn and Kagan, *J. Russ. Phys.-Chem. Soc.*, **42**, 480 (1910).

[5] Von Weimarn, *ibid.*, **45**, 1689 (1913); **47**, 2133 (1915).

[6] Sekera, *Kolloid Z.*, **31**, 148 (1922).

persion. A method which has been used to produce sulfur hydrosols was finally chosen and the same procedure was used with several liquids. A typical example of this procedure is as follows.

Hydrogen sulfide and sulfur dioxide were prepared by the reaction of hydrochloric acid on ferrous sulfide and sodium bisulfite, respectively. These gases were washed with water and passed into 50 cc. of benzene contained in a 150cc. conical flask. The mixture was shaken frequently, and after a short time it began to appear slightly opalescent, then yellow. Its color changed rapidly until it became a deep, opaque yellow and

TABLE I

INFLUENCE OF CERTAIN VARIABLES ON THE PRODUCTION OF SULFUR DISPERSIONS IN BENZENE

Sol	Purity of benzene	Method of stirring	Other variables	Sulfur, %
1	Commercial	Occasional shaking	Satd. C_6H_6 with H_2S; passed in SO_2 to pptn. (30 min.)	0.9
2	Commercial; b. p., 82–84°		Satd. C_6H_6 with H_2S; passed in SO_2 for 15 min.	.6
3		Mechanical	Gases passed in together for 3 hrs.	.4
4			Gases passed in together for 3 hrs.; C_6H_6 contained 1.7% of roll sulfur	1.9 (total)
5			Gases passed in together on 3 days, 3 hrs. each; container covered	0.8
6	B. p., 79.5–82°		Gases passed in together on 3 days, 3 hrs. each; gases driven off before standing	.7
7			Gases passed in together on 4 days, 3 hrs. each; gases driven off before standing	.6
8	Treated with H_2SO_4; b. p., 80–82°		Gases passed in together on 4 days, 3 hrs. each; slow; drop of H_2O added after 2 days	.6
9		None	Gases passed in together for 20 min.; stoppered and let stand	.6
10	Thiophene-free; b. p., 79.5°	Occasional shaking	Gases passed in together for 20 min.; no color; let stand until pptn.	.04
11			Gases passed in together for 40 min.; filtered at once	.1
12			Same as 11; filtered after 4 hrs.	.3
13			Gases passed in together for 60 min.; filtered at once	.6
14			Same as 13; filtered after 4 hrs.	.7
15			Satd. with H_2S (45 min.); passed in SO_2 to pptn. (30 min.); filtered at once	.3
16			Same as 15; filtered after 2 hrs.	.3
17			Satd. with SO_2 (45 min.); passed in H_2S to pptn. (10 min.); filtered at once	.4
18			Same as 17; filtered after 2 hrs.	.4

After further evaporation Sol 6 contained 1.0% of sulfur; 7, 1.8; 8, 1.8; 9, 1.6%.

a dense precipitate began to settle out. After allowing the mixture to stand for a short time, it was filtered and a clear yellow dispersion remained. The per cent. of sulfur in these dispersions was as follows: benzene, 0.6; toluene, 0.5; xylene, 0.4; acetone, 0.6; kerosene, 0.7; ethyl acetate, 0.2%; ethyl alcohol became milky, then yellow, and all the sulfur crystallized out within 48 hours; the glycerol resembled the alcohol in that all of the sulfur eventually settled out.

From this list of liquids, benzene was selected and a further study was made of the effect of certain variables on the production and stability of its sulfur sol. The results are shown in Table I.

From these experiments it seems that the concentration of sulfur obtainable is largely independent of the purity of the benzene, the order in which the gases are introduced, and the method of stirring; although the last factor affects the time required to reach the maximum. It was concluded that the easiest and most rapid way to prepare a sulfur sol in benzene is to pass hydrogen sulfide and sulfur dioxide, without stirring, into benzene contained in a closed vessel, until a precipitate is formed and then, after filtering off the precipitate or allowing it to settle, to concentrate the sol by evaporation. The time required to reach the maximum is about one hour. The impurities are traces of hydrogen sulfide, sulfur dioxide, water and possibly some thionic acids. Gases are, for the most part, driven out of those sols concentrated by evaporation.

A sample of the sol standing over anhydrous copper sulfate for several days showed only a trace of water. The concentration of acid was determined by washing 25 cc. of the sol with three 25cc. portions of distilled water and titrating the washings with 0.0111 *N* alkali. The washings required 1.36 cc. of alkali.

Properties of the Sol

A sulfur sol in benzene, prepared in the above manner, is a clear, deep yellow liquid in marked contrast to the very slight yellow tinge which is observed in a saturated solution of roll sulfur in benzene. All the sols prepared from the purer benzene were slightly lighter in color.

All the sols were exceedingly stable. A sample kept in a tightly stoppered test-tube for four months gave no indications of any coagulation or precipitation. Electrolytes had very little effect on the sol. Concd. potassium hydroxide solution, when left in contact with it for a few weeks, formed a white emulsion. Hydrogen sulfide, sulfur dioxide, hydrogen chloride, formic acid, benzoic acid, β-naphthol, resorcinol, ammonium hydroxide, pyridine, *o*-toluidine, ethyl alcohol, benzaldehyde and sodium chloride were tried as coagulants, with no effect. Some substances, such as phosphorus pentoxide, metallic sodium, copper, silver and calcium entered into a chemical reaction with the sulfur in the sol in the same manner as with sulfur dissolved in benzene. The dehydrating agents, copper sulfate, calcium chloride, sodium carbonate and sulfuric acid, caused no coagulation.

When the sol was heated the benzene evaporated, leaving a yellow, sticky residue, which was not redispersed after six days' standing in benzene with occasional shaking.

Samples of the sol and of sulfur dissolved in benzene were kept at 3° for an hour. At the end of this time rhombic crystals of sulfur had settled out of the sulfur solution, while no precipitate or cloudiness was perceptible in the sol. The samples were cooled to —10° until both were frozen. When the sulfur solution was melted, a larger precipitate was found in the bottom of the tube than settled out at 3°. This redissolved when left in the benzene for several days. When the sol melted it appeared slightly cloudy. After the sol was repeatedly frozen a small amount of yellow precipitate settled out. This did not redisperse after several weeks' standing.

A sol which contained 1.6% of sulfur was allowed to stand in a test-tube sealed with paraffin for several days, over powdered roll sulfur. At the end of this time it contained 3.3% of sulfur, 1.7% more than it originally contained. Benzene saturated with sulfur in this same manner contained 1.8%.

A number of dialysis experiments were carried out. Collodion, collodion containing glycerol, collodion containing castor oil, cupric ferrocyanide, parchment paper, parchment paper impregnated with gelatin, sheet rubber, beef bladder and sheets of commercial cellulose acetate were tried in an attempt to find a membrane which is suitable for dialysis of the sol. Only the beef bladder and the cellulose acetate membranes were satisfactory. The collodion, paper and rubber membranes were too permeable, and the gelatin and copper salt offered mechanical difficulties. In all dialysis experiments, care was taken to guard against evaporation. A sol containing 1.6% of sulfur was dialyzed against five times its volume of pure benzene for two days. At the end of this time no sulfur had dialyzed. Under the same conditions 39% of dissolved sulfur dialyzed through the cellulose acetate membrane from a 1.8% solution. These experiments were repeated with beef bladder as the membrane, and under the same conditions 19% of the colloidal sulfur dialyzed in three days compared with 50% of the dissolved sulfur.

Discussion of Properties

The concentration of sulfur sol obtained was nearly the same as the saturation value of rhombic sulfur in benzene. Consequently, most of the experiments on properties were carried out with both sol and solution for comparison. From the results it is seen that: (1) the colors of the sol and solution are different; (2) the sol on evaporation gives amorphous sulfur (probably sulfur μ), while the solution gives rhombic crystals; (3) on freezing, a result similar to (2) is obtained; (4) the sol dissolved approximately the same amount of crystalline sulfur that benzene does;

(5) the sol dialyzes less readily than dissolved sulfur. In view of these comparative results, the dispersions are considered to be colloidal sulfur of a high degree of dispersion.

The acid present is in the approximate ratio of 1 molecule to 200 molecules of sulfur (S_8), which appears to be too little to stabilize the sols. Likewise, the small amount of water shown to be present by the copper sulfate, and the stability of the sol in the presence of dehydrating agents make the protective action of water seem doubtful.

Crystalline Sulfur

Needle-like crystals were noticed after an attempt to disperse sulfur in ethyl alcohol. The mixture first began to appear milky, then yellow, and finally a yellow precipitate formed. This mixture was filtered but the filtrate was milky. Two days later the sulfur had all settled out in needle-like crystals. Likewise when an attempt was made to obtain colloidal sulfur in alcohol by acidifying ammonium polysulfide, the crystals were obtained in about three hours. In a third case these needles, some of them 5 cm. in length, formed in a flask of alcoholic ammonium polysulfide. Finally, during recovery of benzene from various residues containing sulfur, the greater part of the benzene had been distilled off and the small portion which remained was set aside in a flask. A few days later this solution contained a great many long, needle-like crystals.

Monoclinic sulfur has been obtained below the equilibrium temperature of 96° from solutions of sulfur in alcohol, benzene and turpentine, and also by evaporating alcoholic solutions of ammonium polysulfide and, along with rhombic crystals, from solutions of sulfur in boiling alcohol, benzene and other liquids. Maquenne[7] mentions "the accidental presence of prisms" in crystallizations obtained in the cold in carbon disulfide, and he also obtained them from ether solutions. He states that sulfur crystallizes from benzene in octahedra "which often group themselves in rectilinear rows resembling opaque needles." He considered that this variety of sulfur was "a deformation of the octahedron, and that because of the apparent analogy which it manifests with monoclinic sulfur, it has often been confused with the latter." He found their density to be 2.041 and 2.049, while that of octahedral sulfur is 2.071. He was also of the opinion that the pearly rods described by Gernez[8] are octahedra grouped in rows.

There seems to be no mention in the literature of monoclinic sulfur crystals being formed in cold alcohol, though there are several references made to their formation from boiling alcohol.

To establish whether or not these were identical with the common monoclinic crystals of sulfur, they were examined under the microscope, melting points taken and densities determined.

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[7] Maquenne, *Bull. soc. chim.*, [2] **41**, 238 (1884).

[8] Gernez, *Compt. rend.*, **98**, 144 (1884).

Examined under the microscope, the freshly prepared dispersion, before the sulfur had settled out, appeared to contain spheres rather than crystals. As soon as the dispersed sulfur had settled, it was examined again. The precipitate consisted of clear, yellow, needle-like crystals, with an occasional rhombic crystal. After two days some crystals from this same sample were examined again. Some of them had become cloudy and appeared to consist of rows of rhombic crystals, but most of them remained clear. These crystals were examined from time to time for a period of several weeks, and the number of crystals that had changed to the rhombic form increased, but even after two months a small percentage of them remained as clear and transparent needles.

In order to secure a sharp melting point, the temperature was rapidly increased to within about five degrees of the melting point, thus eliminating, as much as possible, the chance of change during the process. As checks on the method and on the thermometer, melting points were first taken of rhombic sulfur crystallized from carbon disulfide and of monoclinic sulfur crystallized from the molten state, the latter being kept above 96° on a steam-bath. The rhombic sulfur melted at 113–114° and the monoclinic at 118.5° to 119.5°. Next, freshly prepared crystals were taken from the alcoholic solution and dried. They melted at 119–120°. After two days, crystals from this same sample melted at 119–120°. The values given in the International Critical Tables are 112.8° for rhombic sulfur and 119.0° for monoclinic sulfur.

The densities of the crystals were determined by the floating method in solutions of chloroform and ethylene bromide saturated with sulfur. One solution was made with a density of 2.07, which was that of our sample of rhombic sulfur; the other had a density of 1.95, which was that of our monoclinic sulfur. Freshly prepared crystals from the alcohol had a density of 1.95. The values given in the International Critical Tables are 2.07 for rhombic sulfur and 1.96 for monoclinic sulfur. After they had been kept for two days, a few of the crystals sank in the solution which had a density of 1.95. At the end of a month there were still some crystals which had the density of monoclinic sulfur, but the greater part of them had the density of rhombic sulfur.

When they were kept in the alcohol, some of them retained their monoclinic form for several weeks, which is unusual, since the stability of monoclinic sulfur in contact with air at ordinary temperatures is generally considered to last only a few days at most.

Summary

1. Sulfur sols in benzene, toluene, xylene, kerosene, acetone and ethyl acetate were prepared by the reaction of hydrogen sulfide and sulfur dioxide. The benzene sols had a deep yellow color and contained 1.4 to

1.8% of sulfur. At the end of four months one sample gave no indication of coagulation; it was affected little or not at all by the electrolytes and organic substances which were tried as coagulants. When the benzene was removed by evaporation, a sticky, yellow residue of amorphous sulfur remained, which could not be redispersed in benzene. It dialyzed more slowly than dissolved sulfur through membranes of beef bladder and of cellulose acetate. It seems doubtful whether either water or acids are responsible for the stability of these sols.

2. Needle-like crystals of sulfur were obtained in ethyl alcohol at room temperature. These crystals were shown to be monoclinic by microscopic examination, and by melting-point and density determinations. Some of these crystals were stable for several weeks.

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

THE VARIATION OF THE CELL CONSTANT WITH CONCENTRATION AND THE MOLAL CONDUCTANCE OF AQUEOUS BARIUM NITRATE, SODIUM SULFATE AND SULFURIC ACID AT 0°

By Merle Randall and Gordon N. Scott

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Several recent investigations[1] have shown that relatively large errors probably exist in the values of the specific and equivalent conductances reported. As the precision of conductivity measurements is great, we wished to find the procedure which would best enable us to use this method as a means of determining the concentration of dilute aqueous solutions in freezing-point measurements. Our apparatus was capable of high precision, and we shall report several observations which confirm and extend some of the conclusions reached by the above authors. The investigation, however, is confined to Pyrex cells with platinized electrodes.

We also give the values of the molal conductance of barium nitrate, sodium sulfate and sulfuric acid at 0°.

Experimental Methods

Electrical Circuit.—The conductance set was the same as that used by Randall and Vanselow,[2] except that the oscillator was entirely rebuilt on a new design and a two-stage audio amplifier was added to the bridge circuit.

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[1] (a) Schlesinger and Reed, This Journal, **41,** 1727 (1919). (b) Kraus and Parker, *ibid.*, **44,** 2422, 2429 (1922). (c) Parker, *ibid.*, **45,** 1366, (d) 2020 (1923). (e) Morgan and Lammert, *ibid.*, **45,** 1692 (1923); (f) **48,** 1220 (1926). (g) Haworth, *Trans. Faraday Soc.*, **16,** 365 (1921). (h) Parker and Parker, This Journal, **46,** 312 (1924).

[2] Randall and Vanselow, *ibid.*, **46,** 2418 (1924).