The conductance values were found to be greater than those of any of the compounds studied by Plotnikow, none of which are typical electrolytes.

The values of $m$ and $D$ for trimethylammonium chloride are in fair agreement with those usually found for solutions in different solvents.

The conductance follows the dilution equation of Kraus and Bray.

WORCESTER, MASS.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

# A PRELIMINARY STUDY OF REVERSIBLE REACTIONS OF SULFUR COMPOUNDS.

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Before publishing the details of a number of investigations which have extended over a period of eight years and which have finally permitted the calculation of the free energy of important sulfur compounds, we shall discuss briefly the nature and difficulties of the problem, and shall describe a large number of preliminary experiments. Designed as a means of orientation, these experiments were for the most part rough and qualitative. Some were selected for extensive quantitative investigation, and of these a few led to the successful results to be described later. They all help to throw light upon the extremely complicated behavior of sulfur compounds.

Sulfur is an element which appears in so many various types of compounds, in which it displays different valences, that the difficulty in obtaining data suitable for free energy calculations is due not to the paucity but to the wealth of reversible reactions. Indeed here, as with the nitrogen compounds, it is hard to find a reversible reaction which is not attended by numerous side reactions.

In studying the oxygen compounds of sulfur, the first important substance to consider is sulfur dioxide. Its free energy could be determined most directly from measurements of its thermal dissociation. Deville[1] passed sulfur dioxide through a "hot-cold" tube, and found evidence of a slight dissociation at 1200° C. We have, however, repeated these experiments between 1000 and 1500° and found, even at the highest temperatures, that the dissociation is too small to furnish a reliable method for obtaining the free energy of formation.

Turning, therefore, to a more complicated system, we have studied equilibria is *systems* containing sulfur, oxygen and hydrogen. *This system,* under varying conditions, yields, besides hydrogen and oxygen, gaseous $S_8$, $S_6$, $S_2$, S, the numerous solid and liquid forms of sulfur, steam,

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[1] Deville, *Ann. chim.*, **145**, 94 (1865).

hydrogen sulfide, sulfur dioxide, sulfur trioxide, sulfuric acid vapor, and, in the presence of liquid water, sulfurous acid, sulfuric acid, and numerous thionic acids. We have, however, studied this system at the boiling point of sulfur, where sulfur and water vapor react to form small amounts of hydrogen sulfide and sulfur dioxide, without any disturbing side reaction, and between 900 and 1400°, where the only substances present in large amount are hydrogen, sulfur as $S_2$, hydrogen sulfide, steam and sulfur dioxide. These investigations are described in detail in the following papers.

In place of sulfur, silver sulfide was treated with water vapor at high temperatures, and since large amounts of hydrogen sulfide and sulfur dioxide were at first obtained, a somewhat extensive investigation of the equilibria in this reaction was undertaken, but had to be abandoned when it was discovered that the silver sulfide which was employed, and which was ostensibly of the highest purity, contained an excess of sulfur. When this excess was removed the reaction took place to no measurable extent up to 800°, where other phases besides pure solid silver and silver sulfide appear.

**Sulfur as a Reducing Agent.**—At room temperatures sulfur is not a highly reactive substance. In at least one case it is known to act as an oxidizing agent. The reaction

$$S + 2HI = H_2S + I_2$$

has been investigated, and furnishes one of the methods by which the free energy of formation of hydrogen sulfide has been obtained. As a reducing agent sulfur becomes noticeably reactive between 100° and 200°, as shown by the following experiments in aqueous solutions, carried out in evacuated and sealed glass or quartz tubes, heated for some hours to about 160°.

Cations whose sulfides are insoluble in strong acids, such as silver, mercurous, cupric, bismuth, lead, were slowly but quantitatively precipitated as sulfides.[1] Oxidizing cations such as mercuric, ferric, stannic, were quantitatively reduced.

The anions, nitrate, permanganate, iodate, bromate, were reduced to nitric oxide, manganese dioxide, iodine, bromine, respectively. Two days' heating at 180° showed no reduction of sulfates, periodates, or perchlorates. Chlorates appeared to be very slowly reduced. It seems at first paradoxical that in solutions in which reduction by sulfur occurred a strong test for hydrogen sulfide was usually obtained. This seems to indicate that the reaction

$$2H_2O + 3S = 2H_2S + SO_2,$$

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[1] Cf. Geitner, *Pharm. Ann.*, **129**, 350 (1864); Filhol and Senderens, *Compt. rend.*, **94**, 152 (1881); *Ber.*, **14**, 2415 (1881).

is the primary reaction and that the sulfur dioxide thus produced (existing in solution not chiefly as such but in the form of thionic acids) is the reducing agent. Even after heating sulfur with pure water or dilute irreducible acids the odor of hydrogen sulfide is very noticeable,[1] but no test for sulfur dioxide could be obtained, nor did any of the recognized tests for thionic acids give positive results. The failure of these tests does not, however, show conclusively the absence of thionates in small amounts.[2]

Although we are therefore unable to state the composition of the solution obtained by heating sulfur and water, an interesting observation was made which bears upon this question. When sulfur is heated in quartz with dilute neutral or slightly alkaline solutions of non-reacting salts such as potassium chloride, sodium sulfate, magnesium sulfate or tripotassium phosphate, a blue color of the shade of indigo appears, and is first noticeable, in a tube of 0.5 cm. diameter, at about 130°. The intensity of the color increases rapidly with the temperature. On cooling, the color disappears and milky sulfur is precipitated. Pure water in quartz gives no color with sulfur, but in glass the color appears, owing doubtless to the dissolved alkali. In the presence of acid this color does not appear. We find that this colored solution was described by Geitner[3] in 1864, but no satisfactory explanation has been given. The fact that the color is inhibited by acid indicates that it is not due to an elementary molecular species of sulfur, but to some compound formed by interaction with the solvent or with hydroxyl ion. The close analogy between water and ammonia as solvents indicates that the colored solutions of sulfur in water and those discovered by Moissan[4] in liquid ammonia are to be similarly explained. In fact we have found that under certain circumstances sulfur solutions in liquid ammonia are rendered colorless by a substance which is an acid in that solvent, namely ammonium chloride. Colored solutions of sulfur in sulfur trioxide,[5] boron oxide,[6] phosphorous pentoxide, potassium thiocyanate,[6] potassium cyanide,[6] glycerine,[7] ethyl alcohol,[8] and acetone,[8] have been found.

**The Reduction of Sulfuric Acid by Sulfur.**—The apparently mysterious

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[1] The action of sulfur on water and the formation of $H_2S$ has also been studied by Gerard, *Compt. rend.*, **56**, 797 (1863); Gelis, *Ann. Pharm.*, **129**, 350 (1864); *Compt. rend.*, **56**, 1014 (1864); Cross and Higgins, *J. Chem. Soc.*, **35**, 249 (1879); *Ber.*, **12**, 846 (1879); Geitner, *Loc. cit.*

[2] Takamatsu and Smith, *J. Chem. Soc.*, **37**, 608 (1880).

[3] Geitner, *Loc. cit.*, see also Colson, *Bull. soc. chim.*, [2] **34**, 66 (1880); Senderens, *Ibid.*, [3] **6**, 80 (1891).

[4] Moissan, *Compt. rend.*, **132**, 510 (1901).

[5] Discovered by Buchholz, Gehlen's *Neues J. Chem.*, **3**, 7 (1804); see Gmelin Kraut, "Handbuch," Heidelberg, **1**, 1, 436 (1907).

[6] Hoffman, *Z. Chem. Ind. Kolloid*, **10**, 275 (1912).

[7] Hoffman, *Loc. cit.*; also *Z. angew. Chem.*, **19**, 1089 (1909).

[8] Paterno and Mazzucchelli, *Atti Accad. Lincei*, [1] **16**, 465 (1907).

disappearance of sulfur dioxide in the experiments just mentioned, which is even more striking in other experiments which we shall discuss shortly, was explained by the discovery of a reaction which, although mentioned by Preistley in 1775 and re-discovered by numerous investigators,[1] is at present little known. In sealed tubes containing sulfur dioxide and water and heated to about 150°, sulfur is formed at a noticeable rate according to the reaction

$$3SO_2 + 2H_2O = S + 2H_2SO_4.$$

The reverse of this reaction can be readily obtained by heating sulfur with sulfuric acid, and this evidence of the reversibility of the reaction led to a study of the equilibrium in the reduction of concentrated sulfuric acid by sulfur. The result of the investigation will be given in a later paper.

**The Reduction of Carbon Dioxide by Sulfur.**—One of the most direct methods of determining the free energy of formation of sulfur dioxide would be the study of the equilibrium in the reaction

$$S + 2CO_2 = SO_2 + 2CO.$$

As a preliminary to this investigation, Lewis and Lacey[2] studied the equilibrium between carbonyl sulfide, carbon monoxide and sulfur. Further work in this direction was discontinued when it was learned that similar experiments were being carried on in the Geophysical Laboratory of the Carnegie Institution. This work has just been brought to a successful conclusion,[3] and the results obtained will later afford us one of the most important methods of determining the free energy of sulfur dioxide.

**The Reduction of Sulfates.**—We have just spoken of the reduction of $H_2SO_4$ by sulfur. We shall consider now certain other reactions which show the action of other reducing agents upon sulfates and sulfate ion.

Solid sulfates are reduced by hydrogen gas at moderate temperatures. Hydrogen was passed over sodium sulfate at 220–250°. The gas emerging gave a marked test for hydrogen sulfide with lead acetate, and deposited elementary sulfur. The residue was distinctly alkaline and contained no sulfide. At 300° silver sulfate is similarly reduced, the reaction being obviously complex. The issuing gas gave fumes and smelled strongly of sulfur dioxide. At the end of about an hour the silver sulfate was com-

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[1] Berthelot, *Mem. l'Acad.*, **1872**, 599; Fourcroy and Vacquelin, *Ann. chim.*, **24**, 234; Geitner, *Ann.*, **129**, 140 (1864); Hautefeuilles, *Bull. soc. chim.*, [2] **7**, 1867; Tyndall, *Chem. News*, **18**, 266 (1868); Morreu, *Compt. rend.*, **69**, 397 (1869); Walden and Centnerszwer, *Z. physik. Chem.*, **42**, 432 (1902); Sainte Pierre, *Compt. rend.*, **74**, 52 (1872); Jungfleisch and Brunel, *Ibid.*, **156**, 1719 (1913); **157**, 257 (1913); Berthelot, *Compt. rend.*, **96**, 298 (1883).

In spite of this rather extensive reference list this reaction is little known, Berthelot, Fourcroy and Vacquelin, Geitner and Sainte Pierre were each apparently unaware of the older work on the subject.

[2] Lewis and Lacey, THIS JOURNAL, **37**, 1976 (1915).

[3] Ferguson, *Proc. Nat. Acad. Sci.*, **3**, 371 (1917).

pletely destroyed and the residue, though black in color, was doubtless chiefly metallic silver, and dissolved in dilute nitric acid. Thallous sulfate at a somewhat higher temperature was also reduced by hydrogen. The gas gave a copious white precipitate with lead acetate, this precipitate being soluble in dilute nitric acid, showing that in this case sulfur dioxide was produced but no hydrogen sulfide. At lower temperatures (about 150°) sulfate ion in aqueous solution is reduced even by mild reducing agents. These miscellaneous experiments on the reduction of sulfates were discontinued in favor of the two reversible reactions which will be discussed in later papers, namely, the reduction of sulfuric acid by sulfur and by mercury.

**Potential of the Sulfur Dioxide Electrode.**—Instead of reducing sulfuric acid by a chemical agent, the reduction may be made by the aid of the electric current, and we shall describe in this section unpublished experiments made in connection with this investigation by the late Arthur Edgar[1] with the purpose of testing the reversibility of a sulfur dioxide-sulfate-ion electrode. An iridized platinum electrode over which bubbled sulfur dioxide (diluted with air) was used in a solution of sulfuric acid. The other electrode was of mercury covered with mercurous sulfate in the same acid. This cell was measured at 25° with a view of determining the free energy of the reaction

$$SO_2 + Hg_2SO_4 + 2H_2O = 2H_2SO_4 + 2Hg.$$

The cell so constituted behaved in a fairly satisfactory manner. Equilibrium conditions apparently were not reached with great rapidity, but, upon standing, steady values were obtained reproducible to within about a millivolt.

TABLE I.

Electromotive Force of the Cell Pt, $SO_2$, $H_2SO_4$, $Hg_2SO_4$, Hg.

| Mol % $H_2SO_4$. | Pressure of $SO_2$ in atmospheres. | E. M. F. | E. M. F. calculated $[SO_2] = 1$ atm. |
|---|---|---|---|
| 0.09555 | 0.01328 | 0.301 | 0.356 |
| 0.09555 | 0.00689 | 0.295 | 0.358 |
| 0.8946 | 0.1091 | 0.274 | 0.302 |
| 0.8946 | 0.05080 | 0.266 | 0.305 |
| 0.8946 | 0.02479 | 0.259 | 0.306 |
| 0.8946 | 0.01328 | 0.251 | 0.306 |
| 0.8946 | 0.00689 | 0.238 | 0.302 |
| 0.915 | 0.969 | 0.324 | 0.324 |
| 0.915 | 0.969 | 0.324 | 0.324 |
| 4.618 | 0.02489 | 0.200 | 0.247 |
| 4.618 | 0.01333 | 0.192 | 0.247 |
| 10.303 | 0.9814 | 0.189 | 0.189 |

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[1] These experiments were made in the Research Laboratory of Physical Chemistry of the Mass. Institute of Technology.

In Table I are given results with several concentrations of sulfuric acid and with a wide variation in the partial pressure of sulfur dioxide. If the e. m. f. is a measure of the free energy of the above reaction, we should have the equation

$$\mathbf{E} = \mathbf{E}^\circ - \frac{RT}{2\mathbf{F}} \ln \frac{(H_2SO_4)^2}{[SO_2]\,(H_2O)^2}$$

where $[SO_2]$ represents the pressure of sulfur dioxide and the terms in parenthesis represent not the concentrations but the corrected concentrations or activities of sulfuric acid and water. In as far as the effect of the pressure of the sulfur dioxide is concerned, the equation is verified as shown in the last column of the table, and this would also tend to establish the reversibility of the electrode. But when we consider the effect of change of concentration of sulfuric acid, we find the change of e. m. f. with the concentration is only about one-half what it should be according to the equation. The activities of water and of sulfuric acid used in this calculation were obtained from the measurements made by Brönsted[1] and by Dolezalek[2] and also by Edgar upon the e. m. f. of the cells $H_2$, $H_2SO_4$, $Hg_2SO_4$, Hg and Pb, $PbSO_4$, $H_2SO_4$, $PbSO_4$, $PbO_2$. The former cell has also been subjected to a more exact investigation by Randall and Cushman and their work will form a part of this series of papers. There can be no question that the e. m. f. equation given above fails. We have at present no explanation to offer for this result, except that the cell does not give reversibly the reaction under consideration.

**Reactions Involving Silver Sulfite.**—In the early stages of our investigation we hoped that important results might be obtained from a study of reversible reactions of silver sulfite, especially the two reactions

$$Ag_2SO_3 = Ag_2O + SO_2.$$
$$2Ag_2SO_3 = 2Ag + Ag_2SO_4 + SO_2.$$

Pure, dry silver sulfite was heated in a bath of boiling carbon tetrachloride at 76°. It was contained in a glass tube connecting outside the bath with a closed manometer. Sulfur dioxide was evolved until its pressure was equal to the vapor pressure of liquid sulfur dioxide, and drops of the liquid condensed in the manometer. In another experiment we actually found liquid sulfur dioxide in that part of the tube heated to 76°. The reaction is sluggish, but there may be a true equilibrium pressure not far from that of liquid sulfur dioxide at the same temperature. The experiments, however, were discontinued when it appeared that the solid phase produced in the reaction is not silver oxide but rather a basic salt or solid solution. Indeed when silver sulfite was heated at atmospheric pressure to 140°, only about one-third of the theo-

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[1] Brönsted, *Z. physik. Chem.*, **68**, 703 (1909).

[2] Doiezalek, *Z. Electrochem.*, **4**, 349 (1898).

retical amount of sulfur dioxide was evolved, and the mixture may be heated to fusion without much further loss of sulfur dioxide.

A more rapid reaction occurs according to the second of the above equations when silver sulfite is heated in the presence of water.[1] It is evident that in the reaction as written the water can take no part except as a catalyzer. When a mixture of silver sulfite and water was heated to 110° in a tube connecting with a manometer, the partial pressure of sulfur dioxide reached 4 atmos. But when the tube was heated to 132° this partial pressure fell to less than 3 atmos. This surprising result was not understood until further investigation showed that when the system is heated at constant temperature the pressure rises rapidly to a maximum and then falls off, apparently without limit, according to the law of a monomolecular reaction. This effect is in all probability due to the simultaneous occurrence of two independent reactions, the first of which we have no reason to doubt is the one written above. The second reaction we believe to be

$$Ag_2SO_4 + SO_2 + 2H_2O = 2Ag + 2H_2SO_4.$$

In fact an analysis of the mixture showed the presence of sulfuric acid. This reaction is quite analogous to the corresponding one with mercurous sulfate, which we shall discuss at length in another paper. It seems very likely that it might be possible to separate these two reactions and obtain true equilibrium conditions in the former, but we have not proceeded further in these directions.

The various reactions which have been chosen for detailed study will be discussed in other papers. In the present group will be included two papers on the reactions of sulfur dioxide, and one on the free energy of dilution of sulfuric acid, while in a later group, which we hope to publish in the near future, we shall include papers involving the free energy of formation of sulfuric acid and finally a general paper on the free energy of the sulfur compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

# EQUILIBRIUM IN THE REACTION BETWEEN WATER AND SULFUR AT THE BOILING POINT OF SULFUR.[2]

BY GILBERT N. LEWIS AND MERLE RANDALL.

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The well-known reaction between gaseous hydrogen sulfide and sulfur dioxide to give sulfur and water has been studied by numerous investi-

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[1] This reaction is mentioned in Abegg's Handbuch, 1, 714.

[2] This work was carried out in the Research Laboratory of Physical Chemistry of the Massachusetts Institute of Technology, and concluded in 1910.