

It is to be noted that oxygen appears to the first power in the second term of the rate expression (11). Formerly<sup>1</sup> this term was expressed as  $k(\text{Cu}^{++})(\text{O}_2)^{1/2}$ . While it is true that the autocatalytic reactions at pH 11 in which the maximum rates occurred near the end of the experiments indicated a half order with respect to oxygen, it is now felt that this apparent agreement with the half power law is fortuitous and that equation (11) with its more general applicability is preferable.

**Acknowledgment.**—The authors are indebted

to Professor Max Kleiber for the use of the Warburg apparatus.

### Summary

1. The rate of absorption of oxygen by glutathione in the pH range 13 to 13.3 and in the presence of copper sulfate catalyst has been measured. The effects of changes in copper sulfate and glutathione concentrations and oxygen pressure are presented.

2. The rate law is given and a mechanism proposed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## Addition Compounds of Sulfur Dioxide<sup>1</sup>

BY NOEL F. ALBERTSON AND W. CONARD FERNELIUS<sup>2</sup>

Sulfur dioxide forms numerous addition compounds with organic substances. While almost all of these compounds are formed with nitrogen bases,<sup>3</sup> a few are formed with oxygen-containing substances: ether,<sup>4</sup> camphor,<sup>5</sup> methanol,<sup>6</sup> acetone,<sup>7</sup> and trimethylamine oxide.<sup>3,8</sup>

In the first three cases, the existence of these addition compounds has been established by thermal analyses.

The main object of the present investigation was the determination of the temperature-composition diagrams of several systems comprising sulfur dioxide and some simple oxygen-containing compound. In this way some idea of the generality of the formation of addition compounds of sulfur dioxide with oxygen compounds could be established.

### Experimental

**Preparation of Materials.**—Sulfur dioxide was distilled from a small commercial cylinder directly into a storage

ampoule after drying over barium oxide and phosphorus pentoxide. The observed melting point was  $-74.9^\circ$ .

Acetone was purified by refluxing for three and one-half hours with potassium permanganate and potassium hydroxide. It was then distilled through a long fractionating column and a small middle fraction was taken. The observed melting point was  $-94.1^\circ$  as compared to literature values<sup>9</sup> of  $-93.9^\circ$  to  $-94.6^\circ$ .<sup>10</sup>

Dioxane was refluxed with sodium hydroxide and distilled from sodium. It was then treated with a small amount of fuming sulfuric acid and fractionated. Additional refluxing with sodium and distillation from sodium gave a product melting at  $11.6^\circ$ . The literature values have been summarized by Hess and Frahm.<sup>11</sup> They report a melting point of  $11.80 \pm 0.01^\circ$ .

Other compounds were purified by distillation. A boiling point of  $75^\circ$  at 53 mm. was observed for anisole.

**Apparatus.**—The apparatus was essentially the same as that described by Booth and Martin.<sup>12</sup>

### The System Sulfur Dioxide-Ethylene Oxide

The formation of an addition compound between sulfur dioxide and dimethyl ether is best explained by assuming that the ether oxygen atom shares a pair of its electrons to form a covalent bond with the sulfur dioxide molecule.<sup>13</sup> It seemed very likely that ethylene oxide should also form an addition compound.

The results of the thermal analyses are shown in Fig. 1. The maximum due to the 1:1 addition compound is at  $-95^\circ$ . Eutectics occur at 33 and 91 mole per cent. ethylene oxide at  $-115.5^\circ$  and  $-114.2^\circ$ , respectively. Solutions containing 0.556 and 0.559 mole fraction of

(1) From a dissertation presented by Noel F. Albertson (1941) for the Degree of Doctor of Philosophy. Presented before the Division of Physical and Inorganic Chemistry at the Buffalo meeting of the American Chemical Society, September, 1942.

(2) Present address: Purdue University, West Lafayette, Indiana.

(3) (a) For examples see J. R. Bright and W. C. Fernelius, *THIS JOURNAL*, **65**, 637-9 (1943). (b) For compounds of  $\text{SO}_2$  with  $(\text{CH}_3)_3\text{N}$  and  $(\text{CH}_3)_3\text{NO}$  see A. B. Burg, *ibid.*, **65**, 1829 (1943).

(4) G. Baumé, *Compt. rend.*, **148**, 1322 (1909); *J. chim. phys.*, **12**, 216-224 (1914).

(5) I. Bellucci and L. Grassi, *Gazz. chim. ital.*, **44**, 559-564 (1914).

(6) G. Baumé and G. Pamfili, *Compt. rend.*, **152**, 1905 (1914); *J. chim. phys.*, **12**, 256-269 (1914).

(7) Bossneck, German Patent 47,093, Jan. 28, 1888; *Ber.*, **22**, c. 303 (1889); R. Bayer, Chemische Fabrik, German Patent 464,010, July 26, 1928; *Chem. Abst.*, **22**, 4131 (1928).

(8) M. Delépine and R. Demars, *Bull. sci. Pharmacol.*, **30**, 577-9 (1923).

(9) A. Ladenburg and C. Krügel, *Ber.*, **33**, 638 (1900).

(10) L. F. Guttman, *THIS JOURNAL*, **29**, 347 (1907).

(11) K. Hess and H. Frahm, *Ber.*, **71B**, 2633 (1938).

(12) H. S. Booth and D. R. Martin, *THIS JOURNAL*, **64**, 2198-2205 (1942).

(13) The possible structure of sulfur dioxide addition compounds has been discussed by J. R. Bright and J. J. Jasper, *ibid.*, **63**, 3487 (1941).

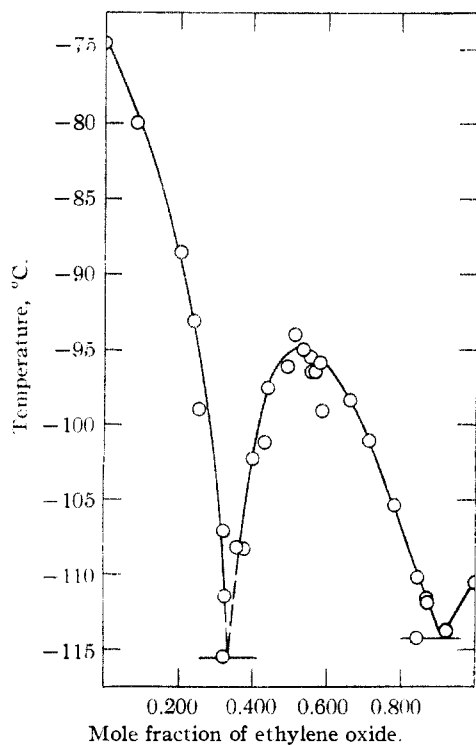


Fig. 1.—The system ethylene oxide-sulfur dioxide.

ethylene oxide exhibited unusual cooling curves. The first half of the cooling curve was perfectly normal but, after the temperature had dropped a few degrees below the melting point, it suddenly rose and a constant temperature was again maintained for several minutes before the solution started to cool once more. No other mixtures gave results of this nature. The solutions are colorless.

#### The System Dioxane-Sulfur Dioxide

Dioxane has two oxygen atoms (ether linkage) which should be capable of acting as electron donors. Figure 2 indicates that dioxane does form both the 1:1 and 1:2 compound with sulfur dioxide. The 1:2 compound is very unstable; the 1:1 compound is more stable, but even it is highly dissociated at the melting point. The maxima are at 0° and 2.5°. The region between 30 and 36 mole per cent. dioxane tends to deposit the metastable 1:1 compound in preference to the 1:2 addition product. This is shown by the fact that the second break in the cooling curve sometimes occurs at a higher temperature than the first break. Solutions containing more than 80% sulfur dioxide undercool slightly. The addition compounds are colorless.

#### The System Anisole-Sulfur Dioxide

An oxygen atom joining a phenyl and an alkyl group appears to have less power to form a third covalent bond than does an oxygen atom joining two alkyl groups. In this connection it seemed interesting to compare the anisole-sulfur dioxide system with the dimethyl ether-sulfur dioxide system.

A very unstable 1:1 compound was found to exist between anisole and sulfur dioxide at  $-70^{\circ}$  (Fig. 3). Solu-

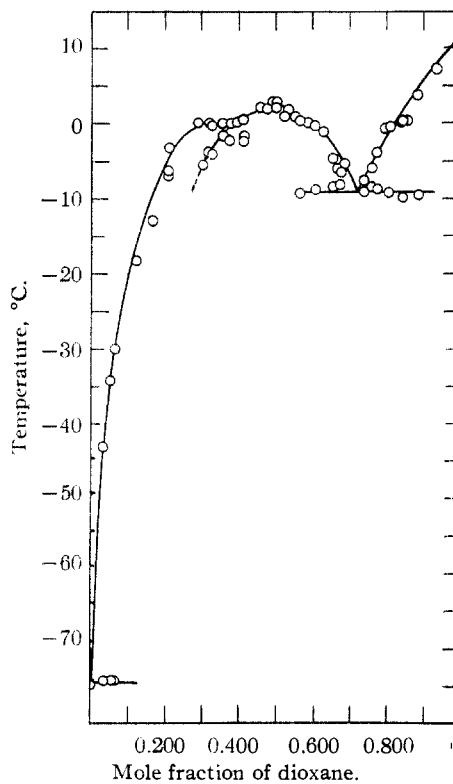


Fig. 2.—The system dioxane-sulfur dioxide.

tions in the neighborhood of the eutectic give glasses upon cooling.

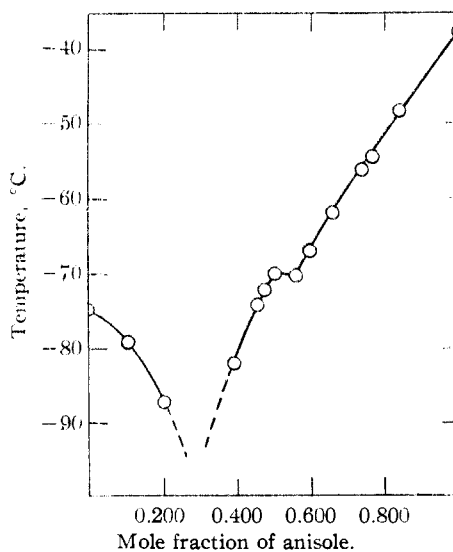


Fig. 3.—The system anisole-sulfur dioxide.

#### The System Acetone-Sulfur Dioxide

Compounds of ketones and aldehydes have been reported previously,<sup>14</sup> but phase diagrams have not been given.

(14) See ref. 7; Von G. Weissenberger and H. Hadwige, *Z. angew. Chem.*, **40**, 734 (1927).

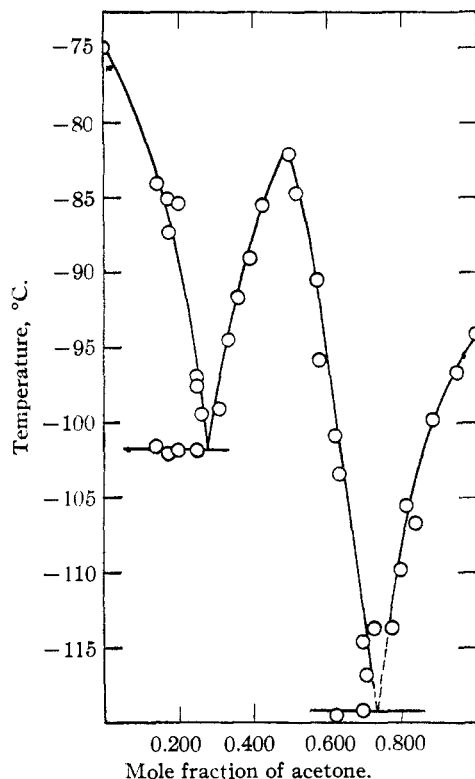


Fig. 4.—The system acetone-sulfur dioxide.

Figure 4 gives the results of a thermal study of the sulfur dioxide-acetone system. A 1:1 compound is formed melting at  $-82.1^{\circ}$ . Mixtures in the neighborhood of the eutectics are difficult to crystallize without undercooling. The solutions are colorless. Eutectics occur at 28 and *ca.* 73 mole per cent. acetone at temperatures of  $-102^{\circ}$  and *ca.*  $-119^{\circ}$ , respectively.

#### The System Diethyl Sulfide-Sulfur Dioxide

Since sulfur dioxide forms addition compounds with molecules containing oxygen and nitrogen atoms capable of sharing an electron pair, one would expect that compounds containing some of the other donor atoms (*e. g.*, F, P, S) would also form coordination compounds with sulfur dioxide.

To indicate the possibilities, the system diethyl sulfide-sulfur dioxide was investigated. A 1:1 compound exists between these two substances. The observed maximum is at  $-48^{\circ}$ , but the system shows such a great tendency to undercool that all of the points between the eutectics are believed to be low. The observed undercooling decreases in a regular fashion on either side of the 1:1 mixture. There can be no doubt about the existence of a compound, however, as is shown by the character of the curve (Fig. 5). Eutectics occur at 16 and 83 mole per cent. diethyl sulfide at temperatures of  $-84.1^{\circ}$  and  $-104.5^{\circ}$ , respectively.

Glasses are normally obtained in the range from 60 to 80 mole per cent. diethyl sulfide. It will be noted that dimethyl ether gives glasses with sulfur dioxide in the 60 to 70 mole per cent. ether range.

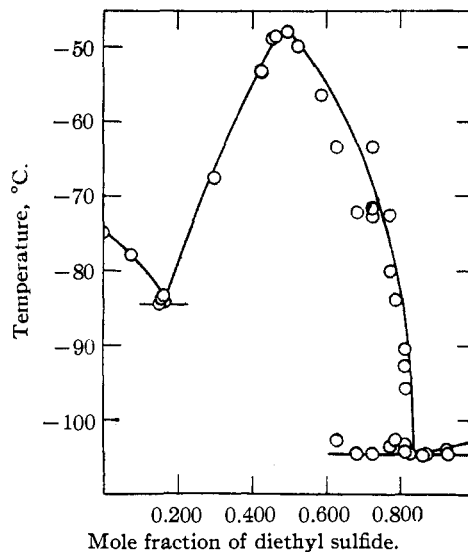


Fig. 5.—The system diethyl sulfide-sulfur dioxide.

#### The System Methylaniline-Sulfur Dioxide

Vapor pressure measurements on the system methylaniline-sulfur dioxide<sup>15</sup> gave evidence of a 1:1 addition compound melting close to  $31^{\circ}$  to give an orange red liquid. Bright had investigated part of this system, and showed that there was no compound having a 2:1 ratio of amine to sulfur dioxide.<sup>16</sup>

The study of this system has now been extended to slightly higher mole percentages of sulfur dioxide. With the permission of Dr. Bright his data for this system have been included in Fig. 6. There is a great tendency to form glasses over all concentration ranges. The region between 82 and 100 mole per cent. methylaniline could

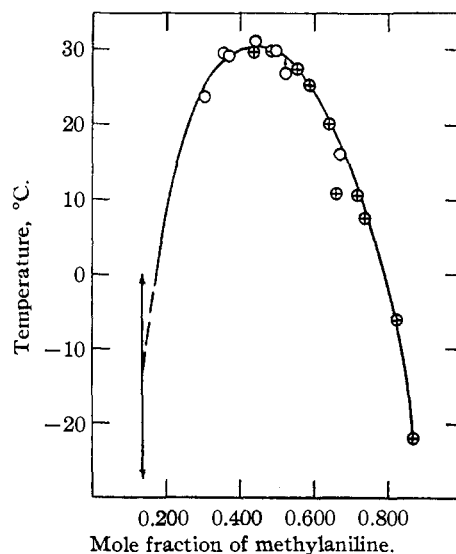


Fig. 6.—The system methylaniline-sulfur dioxide; ⊕, data recorded by J. R. Bright.

(15) H. W. Foote and J. Fleischer, *THIS JOURNAL*, **56**, 870 (1934); A. E. Hill and T. B. Fitzgerald, *ibid.*, **57**, 250 (1935).

(16) J. R. Bright, personal communication.

not be crystallized.<sup>17</sup> Between 0 and 30 mole per cent. methylaniline, the pressure in the melting point tube became too great to avoid loss of sulfur dioxide. The solutions are orange and the solids are golden yellow, although the 50 mole per cent. solution gave a bright red solid.

### Summary

Phase diagrams are presented for binary sys-

(17) J. C. Swallow and R. O. Gibson, (*J. Chem. Soc.*, 20 (1934)), obtained a glass on cooling methylaniline while F. M. Jaeger (*Z. anorg. allgem. Chem.*, **101**, 146 (1917)) claims to have crystallized this substance at  $-57^{\circ}$ .

tems of sulfur dioxide with ethylene oxide, acetone, dioxane, anisole, diethyl sulfide and methylaniline.

The following new compounds are reported: dioxane-sulfur dioxide (1:1 and 1:2), ethylene oxide-sulfur dioxide, anisole-sulfur dioxide and diethyl sulfide-sulfur dioxide.

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## Mechanism of the Reaction between Hydrogen Sulfide and Sulfur Dioxide in Liquid Media

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It has been known for some time that sulfur dioxide and hydrogen sulfide will not react with each other in either the gas or liquid phase unless an appropriate third substance is present. The reaction between these two gases to give sulfur and water progresses readily in a number of liquid media, but does not take place at all in the presence of others. Previous work in the investigation of the effect of various liquids upon this reaction has been carried out by Klein<sup>2</sup> and by Mathews.<sup>3</sup>

These workers have demonstrated that the catalytic effect is not dependent upon the dielectric constant of the liquid. Klein believed that an unstable compound must be formed between one or the other of the two gases and the liquid medium, but was unable to establish which reactant must form the addition compound. Mathews does not favor this viewpoint since methyl salicylate does not promote the reaction whereas methyl benzoate does. Mathews suggests that the activity of the catalyst depends upon its ability to dissolve the sulfur dioxide and the hydrogen sulfide. In the course of an examination of the reaction in this Laboratory additional data were obtained which make possible a proposed theory and explanation of which liquids will act as catalysts and which will not.

### Experimental

The general method used in this study was to bubble a mixture of hydrogen sulfide and sulfur

(1) Post-Doctorate Fellow, Southern Acid and Sulphur Co., Inc. Project with The Ohio State University Research Foundation.

(2) D. Klein, *J. Phys. Chem.*, **15**, 1-19 (1911).

(3) E. Mathews, *J. Chem. Soc.*, 2270-2273 (1926).

TABLE I

- |    |   |
|----|---|
| A. | LIQUIDS IN WHICH HYDROGEN SULFIDE AND SULFUR DIOXIDE REACT IN TWO MINUTES OR LESS   |
| a. | Water <sup>1,2,3</sup>  |
| b. | Alcohols: methyl, <sup>1,2</sup> ethyl, <sup>2,3</sup> <i>i</i> -propyl, <sup>2</sup> <i>i</i> -butyl, <sup>2,3</sup> <i>t</i> -butyl, <sup>1,2</sup> <i>n</i> -amyl, <sup>3</sup> <i>i</i> -amyl, <sup>2,3</sup> <i>t</i> -amyl, <sup>2</sup> allyl, <sup>2</sup> benzyl <sup>2</sup>              |
| c. | Basic nitrogen compounds: aniline, <sup>1,2</sup> pyridine, <sup>1</sup> dimethylaniline, <sup>1</sup> <i>o</i> -toluidine, <sup>1</sup> molten diphenylguanidine <sup>1</sup>  |
| d. | Carbonyl derivatives: acetone, <sup>1,2,3</sup> methyl ethyl ketone, <sup>2,3</sup> carvone, <sup>3</sup> benzaldehyde <sup>2,3</sup>   |
| e. | Ethers: dioxane <sup>1</sup>  |
| f. | Nitriles: benzyl cyanide <sup>3</sup>   |
| g. | Esters: propyl acetate, <sup>3</sup> amyl acetate, <sup>1,2</sup> ethyl butyrate, <sup>2</sup> bornyl acetate, <sup>2</sup> <i>i</i> -amyl nitrite <sup>1</sup>   |
| B. | LIQUIDS IN WHICH HYDROGEN SULFIDE AND SULFUR DIOXIDE REACT IN TWO TO THIRTY MINUTES   |
| a. | Alcohol: glycerol <sup>2</sup>  |
| b. | Basic nitrogen compound: benzanilide in benzene <sup>1</sup>  |
| c. | Ether: diethyl ether <sup>1,2,3</sup>   |
| d. | Nitriles: acetonitrile, <sup>1,2,3</sup> propionitrile, <sup>3</sup> valeronitrile <sup>3</sup>   |
| e. | Esters: ethyl acetate, <sup>2,3</sup> <i>i</i> -butyl acetate, <sup>3</sup> methyl benzoate, <sup>2,3</sup> amyl benzoate, <sup>2</sup> ethyl phthalate, <sup>1</sup> methyl sulfate <sup>2</sup>   |
| f. | Nitro compounds: nitromethane <sup>1,2</sup>  |
| C. | LIQUIDS IN WHICH HYDROGEN SULFIDE AND SULFUR DIOXIDE DO NOT REACT WITHIN THIRTY MINUTES   |
| a. | Hydrocarbons and halogen derivatives: carbon tetrachloride, <sup>1,2,3</sup> chloroform, <sup>1,2,3</sup> benzene, <sup>1,2,3</sup> chlorobenzene, <sup>2</sup> mineral oil, <sup>1</sup> petroleum ether, <sup>1</sup> amylene <sup>3</sup> ethyl chloride, <sup>3</sup> ethyl iodide <sup>2</sup> |
| b. | Nitro compounds: nitrobenzene, <sup>2,3</sup> 2-nitro- <i>p</i> -cymene <sup>1</sup>  |
| c. | Acid derivative: methyl salicylate, <sup>2</sup> benzoyl chloride, <sup>3</sup> acetyl chloride <sup>3</sup>  |
| d. | Sulfur compounds: ethyl disulfide, <sup>3</sup> <i>n</i> -butyl mercaptan, <sup>1</sup> carbon disulfide, <sup>2,3</sup> sulfuryl chloride, <sup>3</sup> diethyl sulfide <sup>1</sup>   |
| e. | Phosphorus compounds: phosphorus oxychloride <sup>2</sup>   |

<sup>1</sup> Present work. <sup>2</sup> Klein. <sup>3</sup> Mathews.