

THE CHEMICAL BEHAVIOUR OF SULPHUR COMPOUNDS

Part III. Kinetics of the Gaseous Reaction Between Hydrogen Sulphide and Sulphur Dioxide*

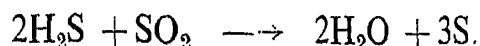
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INTRODUCTION

THE demonstration of the rapid reaction between hydrogen sulphide and sulphur dioxide in the presence of water was a common lecture-room experiment as early as 1812. Cluzel¹ noticed that no combination would result if the gases were first dried over calcium chloride. Many investigators² have studied the reaction in a more or less qualitative way, but their results throw little light on the nature of the gaseous reaction, because they permitted water to condense in the reaction system. The overall reaction is known to be



Lewis and Randall³ studied the equilibrium in the reaction, at the temperature of boiling sulphur. Later, Randall and Bichowsky⁴ investigated the equilibrium in this system at a temperature above 800° C. and noticed that at this temperature, hydrogen was present in small quantities, in the equilibrium mixture.

H. A. Taylor and W. A. Wesley⁵ measured the velocity of the combination of hydrogen sulphide and sulphur dioxide in pyrex reaction tubes at temperatures ranging from 370° C. to 730° C. The velocity was found to be proportional to the surface area of the reaction chamber. This proved that the glass surface acted as a contact catalyst.

B. S. Rao⁶ noticed that silver sulphide could act as an efficient catalyst for the union between the two gases, provided it was activated by a certain amount of moisture. To catalyse the union of the two gases at the surface of glass, a very much higher vapour pressure of water was found to be necessary than was the case with silver sulphide.

* Part of the Thesis submitted by A. R. Vasudeva Murthy for the M.Sc. Degree of the Mysore University.

The investigations described in this paper, constitute a study of the kinetics of the reaction between hydrogen sulphide and sulphur dioxide in an all-glass apparatus, wherein the vapour pressure of water was kept sufficiently low with the aid of an appropriate hygrometer, so that, while no detectable reaction took place at the surface of glass, there was adequate union at the silver sulphide. In order to maintain constant humidity at different levels, various hygrometers were used.

EXPERIMENTAL

In the study of the kinetics of this reaction, it was found essential to have a constant pressure of water vapour, and uniform composition of the gaseous mixture, throughout the system. These two conditions were secured by using a hygrometer and an all-glass, gas circulation pump.

Hygrometer.—The hygrometer consisted of a mixture of a crystal hydrate and its anhydrous salt or a lower hydrate. The following hygrometers⁷ were used to obtain different vapour pressures of water, in the reacting system:—

	<i>V.P. of water in mm. of Hg at 25 °C.</i>
(1) Oxalic acid. $(\text{COOH})_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons (\text{COOH})_2 + 2\text{H}_2\text{O}$.. 2.20
(2) Sodium bromide. $\text{NaBr} \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{NaBr} + 2\text{H}_2\text{O}$.. 5.47
(3) Barium bromide. $\text{BaBr}_2 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{BaBr}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$.. 10.56
(4) Magnesium sulphate. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{MgSO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$.. 12.46
(5) Sodium sulphate. $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$.. 19.15

PREPARATION OF HYGROMETERS

(1) *Oxalic acid.*—Oxalic acid was dehydrated by the method recommended by Clarke and Davis⁸ involving the use of boiling carbon tetrachloride for dehydration of the crystals. (Cf. Villiers^{9a}; Rising and Stieglitz^{9b}.)

(2) *Sodium bromide.*—The anhydrous salt was obtained by heating the crystals for 24 hours at 110° C.¹⁰

(3) *Barium bromide.*—The monohydrate was obtained by heating the hydrate at 80° C. for 24 hours.

(4) *Magnesium sulphate.*—Magnesium sulphate hexahydrate was obtained by heating the heptahydrate for 24 hours at 40° C.

(5) *Sodium sulphate.*—Sodium sulphate decahydrate was heated in an oven at 110° C. for 24 hours.

The following catalysts were used in the present investigation:—

- (1) Silver sulphide.
- (2) Cobalt thiomolybdate.
- (3) Cobalt sulphide.
- (4) Molybdenum sulphide.

(1) *Silver sulphide.* The silver sulphide was prepared by the reaction between silver oxide and sodium thiosulphate solution.



500 ml. of 0.5 N sodium hydroxide was carefully added to 500 ml. of 0.5 N silver nitrate solution with constant stirring, in a 2 litre beaker and to the freshly precipitated silver oxide, 500 ml. of 0.5 N sodium thiosulphate was added gradually, when all the silver oxide was converted into silver sulphide. The solution was boiled for a few minutes. The precipitate was filtered and washed several times with distilled water, then with alcohol and dried at 100° C. for 24 hours. The sulphide was finely powdered in an agate mortar to pass through a sieve of 200 mesh, and kept in a well stoppered bottle.

(2) *Cobalt thiomolybdate.*—Through 20% solution of ammonium molybdate made alkaline with ammonia, hydrogen sulphide was passed for a long time. A red solution of ammonium thiomolybdate was obtained.¹¹ The solution was concentrated by slow evaporation when blood red crystals, appearing green in reflected light, were obtained.

These crystals were dissolved in distilled water and treated with a solution of 20% cobalt sulphate. The solution was chilled in a refrigerator, causing the precipitate to settle. The solution was filtered at the pump and the precipitate washed with distilled water several times, and finally with alcohol. The precipitate was dried at 110° C. for 24 hours. The dark mass obtained, was powdered to pass through a 200-mesh sieve.

(3) *Cobalt and Molybdenum sulphide.*—These sulphides were precipitated with hydrogen sulphide from their corresponding sulphates. The sulphides were powdered to pass through a 200-mesh sieve.

Hydrogen sulphide.—Hydrogen sulphide was prepared by the action of water on aluminium sulphide. The gas was frozen by liquid air, the impurities pumped off, and the solid allowed to evaporate. The gas was collected and stored in glass globes.

Sulphur dioxide.—Sulphur dioxide obtained from a cylinder of commercial liquid sulphur dioxide, was frozen by liquid air, the impurities pumped

off, and the solid allowed to evaporate. The gas was collected and stored in glass globes.

CONSTRUCTION OF THE CIRCULATING PUMP

Porter, Bardwell and Lind¹² designed an all-glass, double acting, electromagnetic pump. This was improved upon by Funnel and Hoover.¹³ Though this improved type had greater capacity, it was found that its horizontal valve system was not satisfactory. Livingston¹⁴ overcame this defect by replacing the horizontal valve system with a vertical valve system, thereby minimising the friction. He also added a third solenoid. The three solenoids acted in succession and controlled the vertical movement of the piston. When this pump was constructed in this laboratory and worked, the piston had a tendency to fall down and smash the whole apparatus. Furthermore, the entire system formed a single unit which could not be easily cleaned. In order to avoid these difficulties, three ground glass joints were introduced in the solenoid unit and four such joints in the valve system. A separate vertical valve unit was constructed, which could be easily removed for cleaning. These solenoids were introduced in the horizontal position. The middle one acted as a controlling field and kept the piston movements under check. Details of the set-up of the pump are given in Fig. 1.

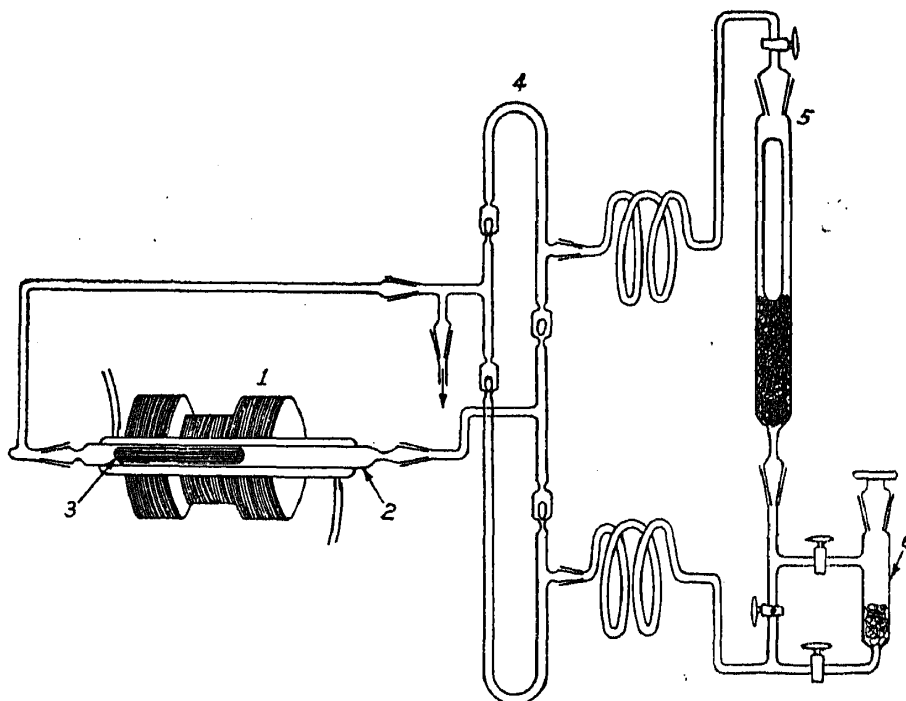


FIG. 1. All Glass Circulation Pump

- | | | |
|--------------|-----------------|---------------------|
| 1. Solenoids | 3. Piston | 5. Hygrostat Tower |
| 2. Barrel | 4. Valve System | 6. Catalyst Chamber |

The cylinder was 80 cm. long, and had an internal diameter of 1 cm. The piston was 25 cm. long and fitted the barrel fairly snugly. Enclosed in the piston were lengths of soft iron wire, embedded in paraffin. The valves consisted of very thin glass bulbs (about 4 mm. in diameter and about 0.5 gm. in weight). They were unground and rested in carefully made constrictions, in 5 mm. tubing. The valve system could be easily detached from the solenoid portion.

The solenoids were 7.5 cm. long and were separated by fibre disks. They were formed from 2,500 turns of enamelled copper wire on a brass tube which was also used as a water jacket. The tube was mounted on a wooden frame. The outer solenoids were excited alternately, 45 to 60 times per minute, by means of a rotating commutator, driven by an electric motor. The middle solenoid was continuously in action.

When adjusted to make 45 strokes a minute, this pump forced 20 litres of air per hour at atmospheric pressure against a head of 0.5 cm. of concentrated sulphuric acid. The pump circulated dry air in a closed system (containing a sulphuric acid bubbler) at all pressures down to 3 mm. of mercury. In order to overcome the heating in the solenoid and maintain the pump at room temperature, water was continuously passed through the jacket.

CONSTRUCTION OF THE REACTION CHAMBER

The outlet and the inlet of the circulating pump were connected by means of ground glass joints to the reaction vessel. The reaction vessel consisted of a tower, partially filled with the hygostat, and a catalyst chamber as shown in Fig. 1.

PROCEDURE

The circulation pump and the reaction vessel were thoroughly cleaned. The vessels were dried by rinsing with anhydrous methyl alcohol, followed by purified carbon tetrachloride. A current of hot air was employed to sweep off the carbon tetrachloride vapours. 10 g. of the hygostat mixture was kept in the tower, over plugs of glass wool (that had been previously cleaned with acid, washed and dried). The catalyst chamber had 5 g. of the catalyst, supported over plugs of glass wool.

The reaction vessel along with the circulation pump, was evacuated for half an hour and tested for vacuum tightness. The catalyst chamber was then shut off. A measured quantity of sulphur dioxide (about 100 ml. at a pressure of 35 cm. of mercury) was let into the pump. The appropriate quantity of hydrogen sulphide was then allowed into the reaction vessel,

The mixture of the two gases was circulated in the hygostat chamber for about 45 minutes to ensure that the mixture had acquired the vapour pressure of the hygostat. The reaction mixture was then passed through the catalyst chamber.

The initial pressure reading was noted down, after bringing the level of mercury in the gas burette to the reference mark, so that the volume of the reacting gases was constant, when the pressure was read. The progress of the reaction was measured at frequent intervals by noting the fall in pressure. The pressures were read with the aid of a cathetometer.

RESULTS

The rate of reaction between the hydrogen sulphide and the sulphur dioxide could be calculated from the pressure readings. The sulphur produced during the reaction was retained by the catalyst and the water evolved was taken up by the hygostat. The volume of the system had been previously determined by allowing a known volume of dry air (100 ml.) at atmospheric pressure to expand into the evacuated reaction vessel. The volume of the reaction vessel could be varied, when necessary, by introducing sealed glass tubings into the hygostat tower. In the present series of experiments, the volume of the vessel was adjusted to be about 400 ml.

The vapour pressure of water inside the system was constant, and was taken into account in computing the reduction in pressure due to the reaction between sulphur dioxide and hydrogen sulphide.

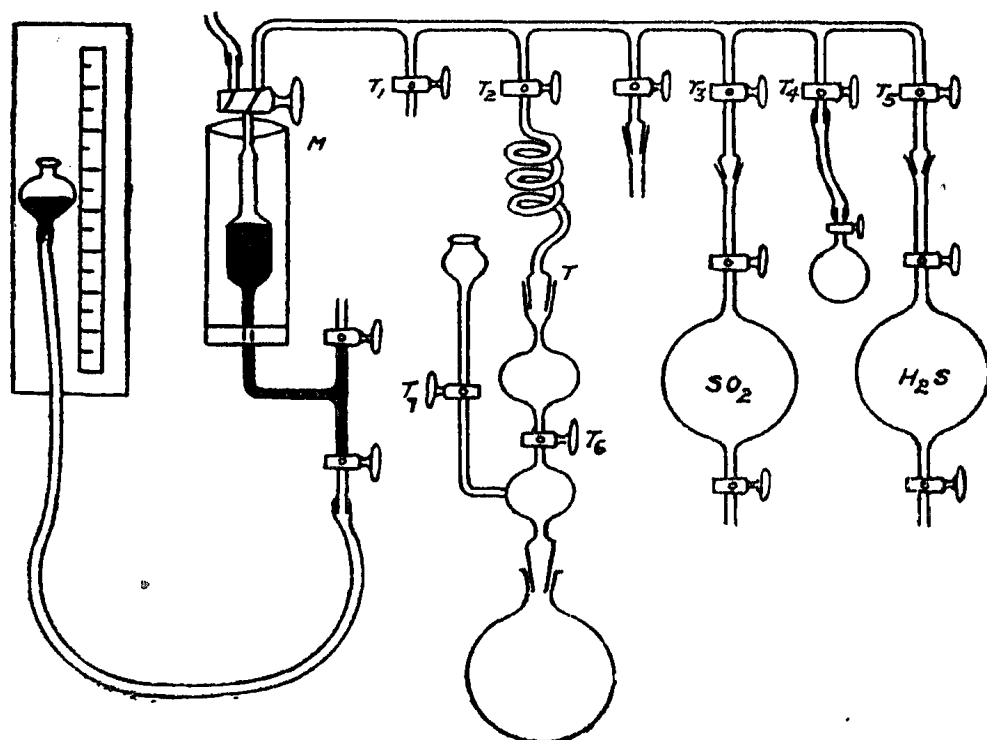


FIG. 2

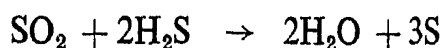
After the reaction was over, the residual gas was pumped out and absorbed in 30% caustic soda solution using the arrangement shown in Fig. 2. To ensure complete absorption of the two gases by the alkali, dry hydrogen was let into the reaction chamber and conveyed to the absorption vessel. This procedure was repeated several times. The sulphide and sulphite of sodium produced in the absorption vessel were estimated by the method of Kurtenacker and Wollak.¹⁵ These analytical values served as a check on the volumes of the residual gases as measured by the fall in pressure.

The order of the reaction could be determined by finding out the time required to undergo a definite fraction of the original concentration, employing the equation

$$\frac{T_2}{T_1} = \frac{C_1^{n-1}}{C_2},$$

where n was the order of the reaction. Time required to undergo half the reaction was calculated in a representative experiment. Invariably the ratio $\frac{T_2}{T_1}$ was found to be equal to $\frac{C_1}{C_2}$ so that n was always equal to 2. This indicated that the reaction was of the second order. Values of K calculated on the assumption that the reaction was (a) unimolecular and (b) termolecular were not constant and it was therefore clear that the reaction was bimolecular.

In the reaction:—



for every ml. of sulphur dioxide consumed, 2 ml. of hydrogen sulphide would be utilised. The velocity of the reaction was therefore

$$-\frac{dx}{dt} = K(a-x)(b-2x)$$

where a and b were the initial concentrations of sulphur dioxide and hydrogen sulphide respectively. The following equation obtained on integration:

$$K = \frac{2 \cdot 303}{t(2a-b)} \cdot \log \cdot \frac{(a-x)b}{(b-2x)a}$$

could be used to calculate K , the velocity constant of the reaction. The total fall in the pressure would be $3x$. The results of various experiments are indicated in the following tables;—

EXPERIMENT NO. 1. *Silver Sulphide Catalyst*

V. pres. of barium bromide hygostat = 10.56 mm. Temp. 25° C.
 Initial partial pressure of SO₂ in cm. of Hg = pSO₂ = 4.75 ; pH₂S = 7.18

Time in minutes	Net pres.*	Fall in pres.	K × 10 ³
0	11.93
5	10.49	1.44	3.18
10	9.28	2.55	3.15
15	8.48	3.45	3.12
20	7.68	4.25	3.11
25	6.98	4.95	3.26
35	6.23	5.70	3.13
45	5.33	6.60	3.13
60	4.88	7.45	3.15
75	3.83	8.10	3.19
90	3.38	8.85	3.17
180	1.73	10.20	3.12
240	1.73

* This is the pressure reading less partial pressure of moisture.

EXPERIMENT NO. 2. *Silver Sulphide Catalyst*

V. pres. of magnesium sulphate hygostat = 12.46 mm. Temp. 25° C.
 pSO₂ = 4.1, pH₂S = 8.2

Time in minutes	Net pres.*	Fall in pres.	K × 10 ³
0	12.30
5	10.65	1.65	3.78
10	9.40	2.90	3.81
15	8.35	3.95	3.86
20	7.55	4.75	3.83
30	6.30	6.00	3.87
45	5.05	7.25	3.86
60	4.25	8.05	3.86
90	3.20	9.10	3.84
120	2.55	9.75	3.80
240	0.10	12.20	..

EXPERIMENT NO. 3. *Silver Sulphide Catalyst*

V. pres. of sodium sulphate hygostat = 19.15 mm. Temp. 25° C.
 pSO₂ = 6.3, pH₂S = 6.3

Time in minutes	Net pres.*	Fall in pres.	K × 10 ³
0	12.6
5	10.35	2.25	4.61
10	8.85	3.75	4.62
15	7.70	4.90	4.57
20	6.90	5.70	4.50
30	5.70	6.90	4.57
45	4.65	7.95	4.51
60	4.10	8.50	4.52
90	3.55	9.05	4.57
120	3.50	9.10	..
240	3.50	9.10	..

EXPERIMENT NO. 4. *Cobalt Thiomolybdate Catalyst*

V. pres. of barium bromide hygrostat = 10.56 mm. Temp. 25° C.

pSO₂ = 5.95, pH₂S = 5.95

Time in minutes	Net pres.*	Fall in pres.	K × 10 ³
0	11.90
5	9.80	2.10	5.93
10	7.85	4.05	5.84
15	6.65	5.25	5.93
20	5.90	6.00	5.85
30	4.85	7.05	5.91
45	4.44	7.90	5.84
60	3.55	8.35	5.87
90	3.10	8.80	..
120	3.10	8.80	..
240	3.10	8.80	..

EXPERIMENT NO. 5. *Cobalt Thiomolybdate Catalyst*

V. pres. of magnesium sulphate hygrostat = 12.46 mm. Temp. 25.8° C.

pSO₂ = 4.3, pH₂S = 8.6

Time in minutes	Net pres.*	Fall in pres.	K × 10 ³
0'	12.90
5	10.10	2.80	6.35
10	8.35	4.55	6.35
15	7.05	5.85	6.41
20	6.15	6.75	6.37
30	4.85	8.05	6.40
45	3.70	9.30	6.33
60	3.00	9.90	6.39
90	2.15	10.75	6.42
240	0.05	12.80	..

EXPERIMENT NO. 6. *Cobalt Thiomolybdate Catalyst*

V. pres. of sodium sulphate hygrostat = 19.15. Temp. = 26° C.

pSO₂ = 4.40, pH₂S = 8.80

Time in minutes	Net pres.*	Fall in pres.	K × 10 ³
0	13.20
5	10.00	3.20	7.21
10	8.10	5.10	7.15
15	6.75	6.45	7.24
20	5.70	7.50	7.47
30	4.50	8.70	7.38
45	3.40	8.80	7.30
60	2.70	10.50	7.37
90	1.95	11.25	7.28
240	0.05	13.15	..

EXPERIMENT NO. 7. *Cobalt Sulphide Catalyst*

V. pres. of barium bromide hygostat = 10.56 mm. Temp. = 25.3° C.
 $p\text{SO}_2 = 5.80$, $p\text{H}_2\text{S} = 5.80$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	11.60
5	9.80	1.80	4.24
10	8.50	3.10	4.21
15	7.55	4.05	4.36
20	6.80	4.80	4.15
30	5.60	6.00	4.29
45	4.70	6.90	4.10
60	4.10	7.50	4.15
90	3.40	8.20	4.22
120	3.05	8.55	4.24
240	2.95	8.65	..

EXPERIMENT NO. 8. *Molybdenum Sulphide Catalyst*

V. pres. of barium bromide hygostat = 10.56 mm. Temp. 25.7° C.
 $p\text{SO}_2 = 4.20$, $p\text{H}_2\text{S} = 8.40$

Time in minutes	Net pres.*	Fall in pres.	$K \times 10^3$
0	12.60
5	10.45	2.15	4.85
10	9.00	3.60	4.76
15	7.85	4.75	4.78
30	5.95	6.90	4.80
45	4.50	8.10	4.76
60	3.70	8.90	4.79
90	2.70	9.90	4.85
120	2.15	10.45	4.79
240	0.05	12.50	..

* This is the pressure reading less partial pressure of moisture.

It was found that when oxalic acid and sodium bromide hygostats were used, there was no indication of any reaction in presence of the various catalysts.

In view of the catalytic effect of boron trifluoride and of aluminium chloride on certain chemical reactions, it was considered to be of interest, to find out if boron trifluoride or aluminium chloride would activate the silver sulphide.

The boron trifluoride was prepared by the method described by Booth and co-workers.¹⁶ The vessel in which the reaction between hydrogen sulphide and sulphur dioxide in presence of boron trifluoride was tried, was a 100 ml. flask fitted with a ground glass joint and connected to the gas burette system (Fig. 2),

It was found that even after 24 hours there was no reaction at all. In another experiment silver sulphide was kept in the reaction flask and boron trifluoride let in. It was found that no reaction at all took place between the hydrogen sulphide and the sulphur dioxide. Boron trifluoride therefore did not activate the silver sulphide.

Experiments were carried out in a similar way to find out if anhydrous aluminium chloride would catalyse the reaction between hydrogen sulphide and sulphur dioxide. It was noticed that there was no detectable reaction between the two gases even after 24 hours. The chloride had thus no activating influence on silver sulphide.

SUMMARY OF THE RESULTS

Catalyst	Hygrostat	V. pres. of hygrostat in mm. of Hg at 25° C.	K × 10 ³
1 Silver sulphide ..	Oxalic acid	2.20	No reaction
2 " ..	Sodium bromide	5.47	"
3 " ..	Barium bromide	10.56	3.13
4 " ..	Magnesium sulphate	12.46	3.82
5 " ..	Sodium sulphate	19.15	4.52
6 Cobalt thiomolybdate ..	Oxalic acid	2.20	No reaction
7 " ..	Sodium bromide	5.47	"
8 " ..	Barium bromide	10.56	5.80
9 " ..	Magnesium sulphate	12.46	6.43
10 " ..	Sodium sulphate	19.15	7.31
11 Cobalt sulphide ..	Barium bromide	10.56	4.21
12 Molybdenum sulphide ..	Barium bromide	10.56	4.83
13 Silver sulphide and Boron trifluoride	No reaction

DISCUSSION

The results show that certain metallic sulphides can catalyse the union between hydrogen sulphide and sulphur dioxide but the sulphides have always to be activated by moisture before they can function as catalysts. The vapour pressure of water in the oxalic acid or sodium bromide hygrostats is evidently insufficient to activate the silver sulphide or cobalt thiomolybdate. The vapour pressure of the barium bromide hygrostat, however, is adequate. The catalytic activity increases with a rise in the vapour pressure of water in the system, as can be gathered from the higher values of the velocity constant, in the magnesium sulphate hygrostat. The highest values for K are obtained in the sodium sulphate hygrostat.

Silver sulphide has the least catalytic activity. Cobalt sulphide and molybdenum sulphide are better and cobalt thiomolybdate is the best catalyst

of the four metallic sulphides tried. Cobalt thiomolybdate, it is of interest to note, is known to be a good catalyst for the oxidation of hydrogen sulphide.

The mechanism of the reaction between sulphur dioxide and hydrogen sulphide has been a subject of much controversy. Dalton¹⁷ expected the production of polythionic acid along with water and sulphur. Thomson¹⁸ regarded the reacting mixture as sulphite of hydrogen sulphide (SO₂, H₂S). Lang and Carson¹⁹ stated that the union of the gases in terms of the equation $2\text{H}_2\text{S} + \text{SO}_2 \rightarrow 3\text{S} + 2\text{H}_2\text{O}$, was itself the primary reaction, in view of the fact, that even though water is absent, sulphur dioxide and hydrogen sulphide in liquid condition, slowly form sulphur. Klein²⁰ believed that a liquid surface was necessary to bring about the union between the two gases, but did not find any correlation between the dielectric constant of the liquid and its capacity to catalyse the reaction.

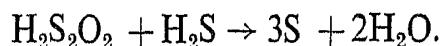
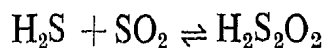
H. A. Taylor and W. A. Wesley⁵ found that the rate of reaction, between hydrogen sulphide and sulphur dioxide at elevated temperature, was proportional to the surface area of the chamber, indicating the heterogeneity of the reaction. They suggested a mechanism in which it was assumed that each of the reactants was activated by adsorption on the surface of glass and that the reaction then took place only between the activated molecules. Further, they observed that the rate of reaction at constant temperature was directly proportional to p_{SO_2} and $p_{\text{H}_2\text{S}}^{1.5}$ according to the equation

$$-\frac{dx}{dt} = K \times (p)_{\text{SO}_2} \times (p)_{\text{H}_2\text{S}}^{1.5}$$

It was thus suggested that the observed order of reaction was 2.5.

Various mechanisms have been suggested by different authors for the reaction between sulphur dioxide and hydrogen sulphide. Riesenfeld and G. W. Feld²¹ have explained the formation of polythionic acids by assuming that sulphur dioxide and hydrogen sulphide react in solution producing sulphur monoxide as the primary product. Several investigators, however, have suggested that the primary product of the reaction between the two gases is thiosulphurous acid. B. S. Rao and M. R. A. Rao²² who studied the reaction in non-aqueous solutions explained their observations on the basis of the formation of this acid. Deines and Grassman²³ in their study of the steps in the reaction between hydrogen sulphide and sulphurous acid also suggested that thiosulphurous acid was the primary product of the reaction. Thiosulphurous acid itself cannot be isolated because of its instability, but the methyl and the ethyl esters of the acid have been prepared by Meuwesen.²⁴ It is of interest to note that during their studies on the

splitting of ethylthiosulphite, Meuwsen and Gerhardt²⁵ isolated the ethyl ester of sulphylic acid. Sulphylic acid itself has not been isolated. Stamm and Wintzer²⁶ studied the hydrolysis of alkyl thiosulphites and explained the formation of certain products on the basis of the decomposition of thiosulphurous acid (the primary product of hydrolysis) into hydrogen sulphide and sulphurous acid. Stamm and Goehring²⁷ in explaining the mechanism of the formation of polythionic acid, by the interaction between hydrogen sulphide and sulphur dioxide in aqueous solution, postulate the formation of thiosulphurous acid as the primary product of the reaction and suggest its subsequent decomposition by hydrogen sulphide to yield sulphur.



Zil'berman²⁸ on the other hand explains the production of sulphur by the reaction between hydrogen sulphide and sulphur dioxide on the basis of the formation of dihydrogen sulphoxide as the primary product, the equations being:



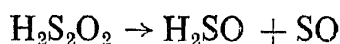
The above mechanisms have been suggested for the reaction of hydrogen sulphide and sulphur dioxide in aqueous solution and should not be considered to be equally applicable to systems studied in the present investigation where the moisture was present only in traces.

It has already been stated that moisture has an "activating influence" on the silver sulphide catalyst and that in absence of adequate moisture, the reaction between hydrogen sulphide and sulphur dioxide does not take place at a detectable rate. The influence of water may be explained on the basis that the adsorbed moisture on the catalyst, owing to its avidity for sulphur dioxide, brings about a larger concentration of this reactant at the catalyst surface and thus promotes chemical union. With a view to confirm this, the adsorption of sulphur dioxide on the catalyst surface, was measured, using the McBain-Bakr Spring technique* to register the increase in weight of catalyst due to adsorption of sulphur dioxide, the moisture in the system being controlled by the use of different hygrometers. It was found that the adsorption of sulphur dioxide per gram of catalyst was always perceptibly higher in presence of moisture. A positive correlation between the quantity of sulphur dioxide adsorbed and the partial pressure of water in the system was also noticed.

* cf. *J. Am. Chem. Soc.*, 1926, 48, 696.

The adsorption of hydrogen sulphide at the catalyst surface was also measured. It was found that the adsorption of this gas was much less. In this case also, moisture was found to increase adsorption but the influence of water was less pronounced.

The mechanism, the present authors suggest for the reaction between hydrogen sulphide and sulphur dioxide, is based on the formation of thio-sulphurous acid as the primary product of the reaction. This reaction is reversible.† But under suitable conditions, the thiosulphurous acid, instead of reverting to sulphur dioxide and hydrogen sulphide can undergo decomposition on other lines. We suggest that decomposition can also take place in the following way:—

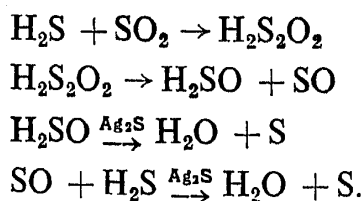


and that the silver sulphide catalyses, the decomposition of dihydrogen sulphoxide as also the union between sulphur monoxide and hydrogen sulphide, the products formed being water and sulphur, in both these reactions.

Owing to its great reactivity, dihydrogen sulphoxide has not been isolated so far, but organic sulphoxides have been prepared.‡ Dihydrogen sulphoxide, it may be pointed out, is intermediate between hydrogen persulphide and hydrogen peroxide. It is well known that hydrogen peroxide is catalytically decomposed into water and oxygen by a variety of substances. The present authors have found that silver sulphide catalytically decomposes hydrogen persulphide vapour.§ Dihydrogen sulphoxide can be expected to decompose with at least equal ease, at the surface of silver sulphide, forming water and sulphur.

The sulphur monoxide formed along with dihydrogen sulphide reacts with hydrogen sulphide in presence of silver sulphide to yield water and sulphur, as already shown by B. S. Rao and M. R. A. Rao.²⁹

The mechanism would therefore be



† *cf.* Noack, *Z. anorg. allgem. chem.*, 1925, 146, 239; also Stamm and Goehring, *Naturwiss.*, 1939, 27, 317.

‡ *cf.* Fromm and Palma, *Ber.*, 1906, 39, 3317.

§ Hydrogen persulphide vapour, obtained by the distillation under reduced pressure, of dry hydrogen persulphide, was passed over silver gauze previously coated with silver sulphide. There was marked increase in the weight of the gauze due to liberation of elemental sulphur.

Boron trifluoride and aluminium chloride did not catalyse the union between hydrogen sulphide and sulphur dioxide. Nor did the two substances have any activating effect on the silver sulphide. The inability of boron trifluoride and aluminium chloride to catalyse the reaction can perhaps be accounted for, by the fact that both of them form comparatively stable complexes³⁰ with hydrogen sulphide as well as sulphur dioxide. The formation of such complexes seems to prevent any chemical reaction between the two gases.

SUMMARY

Certain sulphides, in presence of a small amount of moisture were found to catalyse the reaction between hydrogen sulphide and sulphur dioxide. The kinetics of this reaction was studied in a closed system, using an all-glass, gas circulation pump.

The partial pressure of water in the reacting system was maintained constant with the aid of a hygostat [mixture of a hydrated salt and its anhydrous form (or lower hydrate)]. The higher the partial pressure of water, the greater was the velocity of reaction, for a given catalyst.

Of the sulphides employed, cobalt thiomolybdate was found to be the best catalyst. Cobalt sulphide and molybdenum sulphide were less efficient. Next in order of efficiency, was silver sulphide.

Boron trifluoride and anhydrous aluminium chloride were found to have no catalytic effect on the union between hydrogen sulphide and sulphur dioxide.

The mechanism of the reaction could be explained on the basis of the formation of thiosulphurous acid, as the primary product.

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