

INTERACTION OF SULPHUR DIOXIDE AND HYDROGEN UNDER SILENT ELECTRICAL DISCHARGE

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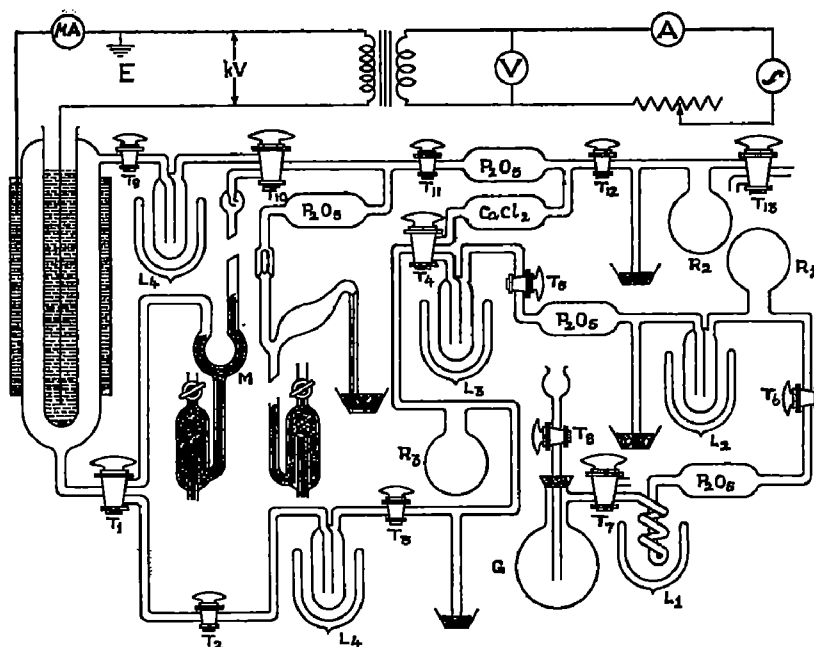
Interaction of SO_2 and H_2 under silent electric discharge is time-continuous and irreversible. An initial rapid fall of the pressure (p) is followed by a slower change and the attainment of a stationary stage. The time variation of the conductivity, i , is synchronous with but less pronounced than that of p . The formation of SO as an unstable intermediate product is suggested. Besides H_2 and undecomposed SO_2 , the reaction products consist of sulphur, H_2SO_3 , H_2SO_4 , SO_3 , O_2 , O_3 and H_2S . Ozone is produced prior to H_2S . The decrease of p is attributed to the condensation of the products of decomposition or/and their 'clean up' by the annular film of sulphur produced under the discharge. In agreement with the general finding due to Joshi the current i , at a given applied potential V , depends on $V - V_m$, where V_m is the 'threshold potential'. Production of SO and SO_3 reduces V_m and tends to increase i . The deposition of sulphur on the annular walls inhibits the reaction.

During the reaction between nitrous oxide and hydrogen, subjected to a silent discharge, observation was made of a remarkable 'periodic effect' in which the gas pressure, the current i , wattage dissipated in the system, as also the nature of the glow showed marked and synchronous discontinuities repeated over as long as 20 hours of exposure (Joshi, *Proc. Indian Sci. Cong.*, 1943, Part II, pp. 70-75 ; Joshi and Deshmukh, *Nature*, 1945, 155, 483). According to Joshi (*Curr. Sci.*, 1946, 15, 281) 'wall effect', formation of condensed products, and a spontaneous reaction reversal (despite constancy of exciting conditions,) constitute *inter alia* chief determinants of the 'periodic effect'. A reaction reversal was also observed in the interaction of sulphur and nitrogen (Deshmukh and Sirsakar, *Proc. Ind. Acad. Sci.*, 1948, 28A, 175). Present work was undertaken since condensed products appeared likely in the reduction under discharge of SO_2 which might produce the periodic phenomenon mentioned above.

EXPERIMENTAL

The general arrangement of the apparatus and the electrical circuit employed are shown in Fig. 1. This consists of a generator G for preparing SO_2 , the reservoirs R_1 , R_2 and R_3 to

FIG. 1



store SO_2 , H_2 and their mixture respectively, liquid air traps L_1 - L_5 for freezing out SO_2 and other condensible products of decomposition, a Siemens' type glass ozoniser, a Töpler pump to evacuate any or all parts of the apparatus, a manometer M to record the pressure of the gaseous mixture in the ozoniser and drying tubes containing phosphorus pentoxide and calcium chloride.

The entire assembly was tested initially for vacuum for at least 48 hours. Sulphur dioxide was prepared in G by the action of sulphuric acid on sodium bisulphite. The gas was purified by fractionation over liquid air in L_1 and the middle fraction was stored in R_1 . Hydrogen was obtained from a commercial cylinder. The gas was bubbled slowly through traps filled with a freshly prepared solution of alkaline pyrogallol. It was dried carefully over P_2O_5 and CaCl_2 and was finally admitted through the tap T_{13} to the reservoir R_2 . The gaseous mixture was prepared by solidifying SO_2 in L_3 cooled by liquid air. T_5 was now closed. Hydrogen was introduced in R_3 through T_{12} and T_4 . R_3 was then connected with L_3 by proper manipulation of T_4 . The liquid air bath was removed carefully and sulphur dioxide allowed to vaporise. Results now reported refer to two stock mixtures: (1) consisting of 32% H_2 and 68% SO_2 and (2) containing 83% H_2 and 17% SO_2 .

Single phase alternating current of 50 cycles frequency obtained from a rotary converter worked off 220 volt D.C. supply was fed to the primary of a 3 KVA transformer. One of its secondaries was earthed; the other was dipped in a moderately concentrated salt solution forming the H. T. terminal of the ozoniser. The outer electrode was earthed through an oxide rectifier type A. C. milliammeter (MA in Fig. 1). The applied potential expressed in kilovolts (r.m.s.) kV, was calculated from a knowledge of the step-up ratio of the transformer and the primary potential V .

The gaseous mixture was introduced in the ozoniser at a desired pressure through T_3 , T_2 and T_1 . The system was excited at a given (fixed) applied potential V . The progress of the reaction was followed by the observation of the variation of the gas pressure p , the discharge current i and the nature of the glow. Two typical sets of observations are recorded in Tables I and II. Fig. 2 shows the time variation of p and i at 6.7 kV and an initial pressure of 10.5 cm. Hg of the first stock mixture. The products of decomposition were analysed at (a) a constant pressure and (b) the maximum current stage. At the end of a given exposure to discharge the decomposition mixture was led through the trap L_4 , immersed in liquid air. The uncondensable products were collected over mercury in a gas burette by working the Töpler and were analysed for hydrogen and oxygen. The liquid air bath was removed and the condensable products allowed to vaporise. These were collected in another gas burette and tested for SO_2 . The ozoniser was washed thoroughly with distilled water. This was also analysed (qualitatively) for the presence of H_2SO_3 and H_2SO_4 . The results of analysis (by volume at N. T. P.) are shown in Table III.

TABLE I

Applied potential=6.7 kV (r.m.s.) ; 50 cycles sec. ⁻¹																		
Mixture No. 1 ($\text{H}_2/\text{SO}_2=32/68$) : 18.5°																		
Time (min.)	0	5	10	15	20	25	30	35	40	45	50	60	70	80	90	100	110	150
Pressure (cm. Hg)	19.9	17.6	16.2	15.5	14.2	13.2	12.4	11.3	10.4	9.6	9.0	7.8	7.0	6.3	5.9	5.6	5.4	4.9
Current (mA)	0.1	0.11	0.13	0.12	0.14	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.15	0.13	0.13	0.12	0.12	0.12
Remarks	Manometric Hg. fouled. White deposit in the ozoniser.					Liquid droplets observed on the annular surface.					White deposit disappears in patches.			Liquid deposit disappears leaving a yellowish solid residue.				

TABLE II

Applied potential=6.7 kV (r.m.s.) ; 50 cycles sec. ⁻¹
 Mixture No. 2 ($H_2/SO_2=32/68$) ; 21°.
 An ozene trap is connected with the ozoniser.

Time (min.)	0	5	10	15	30	45	90	135	165	195	210	240	300	Discontinues. Found the black deposit on Hg to be HgS.
Pressure (cm. Hg.)	2.4	1.7	1.2	0.9	0.5	0.45	0.4	0.3	0.3	0.3	0.3	0.3	0.3	
Current (mA)	0.20	0.26	0.26	0.26	0.22	0.22	0.24	0.24	0.23	0.24	0.24	0.24	0.24	
Remarks		Manometric Hg. fouled.					Blackening of the capillary leading to the ozone trap.				A black speck appeared on the surface of Hg in ozone trap.			

TABLE III

Mixture No.	Initial press. (cm. Hg)	Applied kV.	Duration of discharge (min.)	Stage of analysis.	Total vol. of gas collected at N.T.P.	Vol. of SO_2 at N.T.P.	Vol. of H_2 at N.T.P.	Vol. of O_2 at N.T.P.	% SO_2 .	% H_2 .	% O_2 .
1. ($H_2/SO_2=32/68$)	10.4	6.7	185	Const. press.	3.4 c.c.	1.88c.c.	1.40c.c.	0.12c.c.	55.3	41.1	3.5
	10.2	6.7	41	Max. current	5.0	2.88	1.95	0.17	57.6	39.0	3.4
2. ($H_2/SO_2=83/17$)	10.5	6.7	90	Const. press.	3.93	0.54	3.30	0.1	13.6	84.1	2.3
	10.4	6.7	28	Max. current	4.0	0.71	3.2	0.1	17.8	80.0	2.2

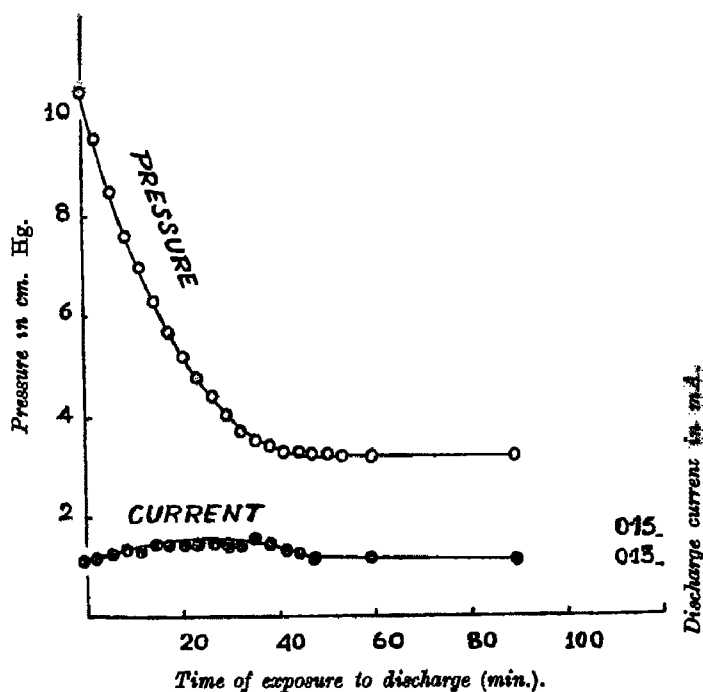
DISCUSSION

Results in Fig. 2 and Tables I and II indicate that the interaction of SO_2 and H_2 under electrical discharge is time-continuous and irreversible. The pressure—time curve in Fig. 2 (which is but typical of a series of results) shows an initial rapid fall, followed by slower change and the attainment of a stationary minimum stage. Thus *e.g.* at 6.7 kV pressure decreased from 10.5 to 4.0 cm. Hg. *i.e.* by 62% in 30 minutes and from 4.0 to 3.2 cm. *i.e.* by about 20% in 24 minutes of exposure to discharge. p remained sensibly constant at this stage even after prolonged exposure to discharge for about 100 minutes. The discharge current i flowing through the reaction vessel varied synchronously with p though not in the same sense. i increased initially from 0.135 to 0.15mA *i.e.* by 11% in 15 minutes, remained stationary for the next 24 minutes and decreased again to the initial minimum of 0.135 mA in 9 minutes of exposure to discharge. The attainment

of the constant stage was more or less simultaneous in both the pressure—time and current—time curves (cf. Fig. 2).

FIG. 2

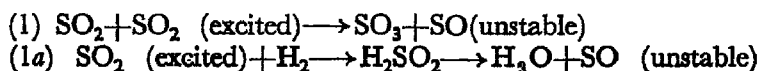
Pressure-current variation during SO₂-H₂ interaction at 6.7kv; 50 cycles sec. ⁻¹

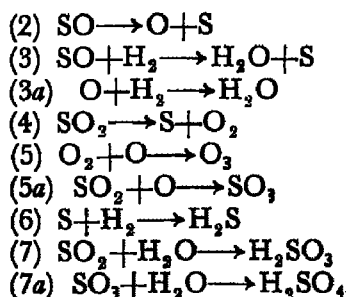


During experiments to which Table I refers, the formation of liquid droplets was observed on the annular walls of the ozoniser. It was interesting to note that the conductivity also increased to its maximum value during this stage of the reaction. The liquid product disappeared slowly leaving behind a yellowish solid residue when the current, as also the pressure of the reaction mixture, tended to reach the stationary minimum. Amongst the reactions products (besides H₂ and undecomposed SO₂) sulphur, H₂SO₃ and H₂SO₄ were detected by the usual chemical tests. The fouling of the manometric mercury during the course of the reaction indicated the presence of ozone or/and H₂S. Series of experiments (of which the results given in Table II are but typical) were therefore next made by connecting an ozone trap (not shown in Fig. 1) between the ozoniser and the tap T₁. In all these cases the detection of HgO and HgS during successive stages of the reaction showed that the formation of H₂S was preceded by that of ozone.

Data for the analysis of the products of the reaction at the constant pressure and maximum current stage for the two stock mixtures containing different proportions of SO₂ and H₂ are recorded in Table III. The results are similar except that the amounts of the gaseous products of decomposition are different due to the varying proportions of SO₂ and H₂ in the stock mixtures.

The foregoing results suggest that the following reactions constitute the overall mechanism of the interaction of SO₂ and H₂ under silent discharge :





Starting from the primary reaction (1) all the subsequent steps follow. The production of SO has been postulated by many investigators (Gordes and Schenk, *Z. Electrochem.*, 1933, **39**, 594). Harteck and Gieb (*Ber.*, 1933, **66**, 1815, ; *Z. physikal. Chem.*, 1934, **170**, 1 ; *Trans. Faraday Soc.*, 1934, **30**, 131) advanced evidence from spectroscopic and thermochemical data for the formation of SO by the decomposition of an intermediate product H_2SO_2 . (1) and (1a) are therefore suggested for the initial stage in the interaction of sulphur dioxide and hydrogen. With the exception of (6) all the reactions mentioned above may lead to the observed decrease of pressure due to the formation of condensible or/and adsorbable products of reaction such as SO_3 , H_2O and S. The reduction of p may also be due to the 'clean up' of hydrogen (Newman, *Trans. Amer. Electrochem. Soc.*, 1924, **44**, 77) and other gaseous products by the annular deposit of sulphur produced in (2), (3) and (4). Repeated observations have shown that H_2S occurs only during the last stage of the reaction. The step $\text{SO} + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{S} + \text{O}$ is therefore not considered along with (3). The production of H_2S according to this reaction at a later stage is also considered unlikely in view of the instability of SO formed during the initial stage. According to Thomson and Hinselwood (*Proc. Roy. Soc.*, 1929, **A**, **122**, 616) the presence of sulphur dioxide does not affect the $\text{H}_2 - \text{O}_2$ reaction. The production of H_2O according to (3a) is therefore suggested. Joshi and Sharma (*J. chim. phys.*, 1934, **31**, 511) studied the decomposition of sulphur dioxide under silent electrical discharge. The decomposition mixture contained SO_3 , O_2 , about 10% undecomposed SO_2 and two unidentified solid products. ' SO_2 decomposes under electrical discharge to produce S and SO_3 and the free sulphur combines with SO_3 to give a viscous liquid which absorbed SO_2 ' (Berthelot, *Ann. chim. phys.*, 1898, *vii*, **14**, 167). The occurrence of the liquid product as observed may therefore be ascribed to the condensation of SO_3 or/and the formation of absorption complexes of S, SO_2 and SO_3 on the walls of the ozoniser. The slow diminution of pressure, indicative of the retardation of the reaction, may be due, in part, to deposition of sulphur on the annular walls. The production of ozone in presence of a large proportion of hydrogen is remarkable. This agrees with the results obtained in the $\text{N}_2\text{O} - \text{H}_2$ reaction under silent discharge where ozone and a series of higher oxides of nitrogen were detected despite the presence of excess of hydrogen (Joshi and Deshmukh, *loc. cit.*).

According to Joshi (*Trans. Faraday Soc.*, 1929, **25**, 118, 137 ; *Curr. Sci.*, 1939, **8**, 548) the discharge current i depends on $V - V_m$. Since i increases with the appearance of the liquid products (obtained presumably due to condensation of SO_3), it may be assumed that its production lowers the 'threshold potential' V_m . A simultaneous decrease of i and also the corresponding reaction rate, as judged by the time variation of p , may be associated with the deposition of sulphur or/and the formation of adsorption complexes on the walls of the ozoniser.

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