136. *The Interaction of Sulphur Monoxide with Nitrous and Nitric Acids.*

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Solutions of nitrous and nitric acids in sulphuric acid are reduced irreversibly by sulphur monoxide. Nitrogen is liberated from nitrous acid in accordance with the equation $3SO + N_2O_3 = 3SO_2 + N_2$.

THE isolation of sulphur monoxide by Schenk (*Z. anorg. Chem.*, **1933**, **211**, 150) and the demonstration that this compound is formed in 1% yield when a mixture of sulphur vapour, sulphur dioxide, and air is passed through a tube heated to 700°, reopens the question of chemical loss of nitrogen in sulphuric acid manufacture by the lead-chamber process. Such a loss occurs if there is irreversible reduction of the nitrate, *e.g.*, to nitrous oxide or to nitrogen. Recently, Schenk (*ibid.*, **1937**, **233**, 385) examined the reaction of nitric oxide and sulphur monoxide and concluded that the formation of a higher oxide of nitrogen and elementary sulphur does not occur. In the present work, sulphur monoxide has been allowed to react with nitrogen compounds such as exist in the lead-chamber plant, and the fate of these compounds determined.

Table I gives the results of experiments to determine whether, when sulphur monoxide reacts with nitric acid, irreversible reduction occurs. Potassium nitrate was dissolved in 78% sulphuric acid and allowed to react either with a stream of pure sulphur dioxide or with a similar quantity of sulphur dioxide containing about 12% of sulphur monoxide. The residual nitrate or nitrite left in the reaction vessel or carried over into absorption vessels was estimated as ammonia after reduction with Devarda's alloy. Any loss of nitrogen is an indication of reduction of nitrate to nitrous oxide or nitrogen.

TABLE I.

Gas.	Initial KNO_3, g.	KNO_3 left, g.	KNO_3 carried over, g.	Total KNO_3 recovered, g.	KNO_3 lost, g.
SO_2	0·3877	0·1960	0·1911	0·3871	0·0006
SO_2	0·0972	0·0122	0·0831	0·0953	0·0019
$SO_2 + SO$	0·2355	0·0378	0·1743	0·2121	0·0234
$SO_2 + SO$	0·3320	0·0561	0·2543	0·3104	0·0216
$SO_2 + SO$	0·0905	0·0151	0·0639	0·0790	0·0115
$SO_2 + SO$	0·3000	0·1339	0·1156	0·2495	0·0505
$SO_2 + SO$	0·4867	0·0081	0·4411	0·4492	0·0365
SO_2	0·1256	0·0037	0·1183	0·1220	0·0036
SO_2	0·2632	0·0189	0·2448	0·2637	−0·0005
$SO_2 + SO$	0·1430	0·0918	0·0434	0·1352	0·0078
$SO_2 + SO$	0·2128	0·0300	0·1489	0·1789	0·0339

It appears from these figures that, whenever the monoxide was present, there was a loss of nitrate–nitrite many times greater than is observed in the control experiments when sulphur dioxide alone was used. Irreversible reduction of a much larger proportion of the nitric acid was achieved by allowing the acid to remain in contact with the sulphur dioxide or monoxide mixture in a 5-l. flask for 2 hours. The results obtained are given in Table II. In this set of experiments some sulphur separated on the surface of the solution of nitrate in sulphuric acid. No such separation occurred when the gas bubbled through the liquid as in the experiments of Table I.

TABLE II.

	$SO + SO_2$.	SO_2.	SO_2.	$SO + SO_2$.	SO_2.	$SO + SO_2$.
KNO_3, initial	0·0444	0·0447	0·0707	0·0653	0·1954	0·0380
KNO_3, recovered ...	0·0089	0·0403	0·0660	0·0350	0·1904	0·0061
KNO_3, loss	0·0355	0·0044	0·0047	0·0303	0·0050	0·0319

A mixture of sulphur monoxide and dioxide of known sulphur monoxide content was then passed through a solution of sodium nitrite in sulphuric acid, and the extent of the irreversible reduction determined. The results are given in Table III. The values for the loss of nitrite lie close to the broken line (Fig. 1) which represents the theoretical loss if the equation $3SO + N_2O_3 = 3SO_2 + N_2$ represents the reaction.

TABLE III.

Weight of SO used, g.	0·0049	0·0150	0·0145	0·0074	0·0312
Loss of $NaNO_2$, g.	0·0055	0·0155	0·0165	0·0061	0·0246
Density of H_2SO_4	1·78	1·78	1·71	1·71	1·71

FIG. 1.

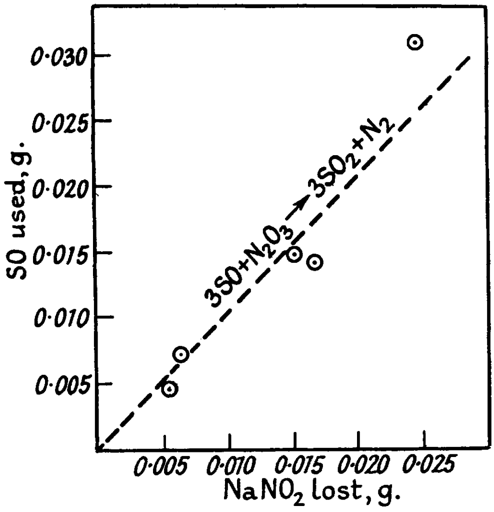
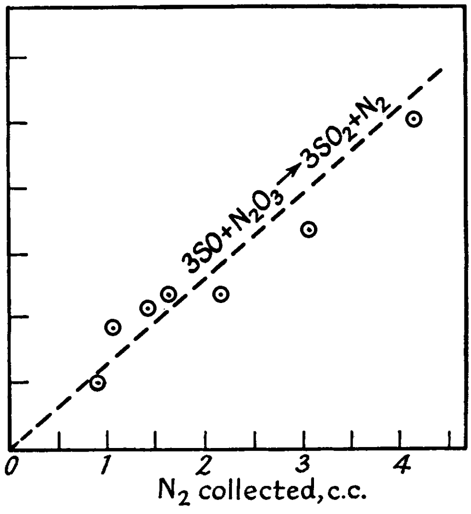


FIG. 2.



A further set of experiments was carried out to identify the products of the irreversible reduction. No evidence was obtained of the presence of ammonia, hydrazine, or nitrous oxide. Free nitrogen was, however, isolated, and its volume was found to be proportional, within experimental error, to the weight of sulphur monoxide passed through the solution of nitrite in sulphuric acid. The results (Fig. 2) are in harmony with the foregoing equation. Blank experiments in which a similar quantity of sulphur monoxide was passed through sulphuric acid indicated that the sulphur monoxide and dioxide mixture contained no appreciable nitrogen.

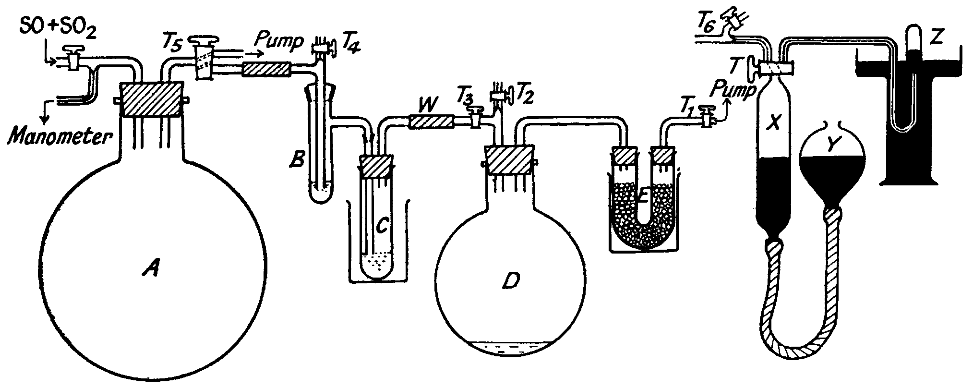
Although the present measurements have been confined to room temperature, it appears likely that if sulphur monoxide were present in the burner gases entering the Glover tower, it would react irreversibly with nitrous acid and be a contributory cause of loss of nitre. Further work is in progress on the technical aspects of the reaction.

EXPERIMENTAL.

Preparation and Estimation of Sulphur Monoxide.—Sulphur monoxide was prepared by burning sulphur in oxygen at pressures below 40 mm. (Schenk, *Z. anorg. Chem.*, **1934**, **220**, 268). It was estimated by absorbing it in 5N-potassium hydroxide and analysing the resulting solution for sulphite, thiosulphate, and sulphide by the method of Kurtenacker and Wollack (*ibid.*, **1927**, **161**, 201). For purposes of estimation, the sulphide and thiosulphate may be regarded as produced according to the equations $3SO + H_2O = 2SO_2 + H_2S$ and $2SO + H_2O = H_2S_2O_3$.

Apparatus.—The 5-l. bulb *A* (Fig. 3) was evacuated and filled with the mixture of monoxide and dioxide up to a pressure of 40—50 mm. After evacuation of the remainder of the apparatus with taps T_2, T_4 and T_5 closed, T_1 was closed and T_5 opened, so that the gas from *A* slowly bubbled through the tube *B* containing a known weight of nitrate or nitrite in sulphuric acid. The reaction products passed through 3N-alkali in *C*, and the non-acidic gases collected in the 2-l. bulb *D* containing about 50 c.c. of concentrated alkali. When sufficient gas had passed through the reaction tube *B*, taps T_3 and T_5 were closed, and T_2 and T_4 opened to admit air. The nitric oxide which had collected in *D* and *E* was oxidised and absorbed by the alkali. An hour was allowed for this absorption, but as an additional safeguard, the gases were then slowly drawn through the U-tube *E* filled with glass beads moistened with alkali. The vessels *C* and *E* were packed in ice to lessen volatilisation. The alkali in *C* contained sodium peroxide to prevent the accumulation of sulphite, the presence of which might cause reduction of nitric oxide in alkaline solution. In determination of the residual nitrogen as nitrate and nitrite, *B* and *C* were detached together, and excess of dilute alkali was added down the inlet tube of *B* to retain all the oxides of nitrogen remaining. The nitrate and nitrite in *B*, *C*, *D*, and *E* were estimated by reduction with Devarda's alloy to ammonia. Similar control experiments were carried out upon pure sulphur dioxide.

FIG. 3.



In the experiments of Table II, potassium nitrate was weighed into a large bulb fitted with a tap-funnel. After evacuation, 5 c.c. of sulphuric acid (*d* 1·71) were run in, and when the nitrate had dissolved, the sulphur monoxide–dioxide mixture was admitted. After 2 hours, the nitrogen oxides remaining were absorbed by allowing air and excess dilute alkaline peroxide to flow in. Nitrous oxide would not be absorbed.

In order to determine the weight of sulphur monoxide available for reaction with nitrous or nitric acids, two 5-l. bulbs, *A*, were filled simultaneously (only one is shown in Fig. 3). The monoxide in one was estimated by running in alkali, while the other was connected to a pressure gauge so that the fraction of gas withdrawn from it was known.

Examination of Gaseous Products of the Reaction.—The two large bulbs *A* and the sulphur combustion tube (not shown) were freed from air by evacuation to about 1 mm., filling with sulphur monoxide–dioxide mixture to 40 mm., and repeating the evacuation twice before using the gas. To collect the gaseous products of the reaction, the vessels *D* and *E* were detached at *W* and replaced by the 200-c.c. gas burette *X*. The apparatus between the closed taps T_5 and *T* was evacuated through T_6. The non-acidic gaseous reaction products collected in the upper part of *C* and in *X* and were passed from time to time into the sample tube *Z*. The nitric oxide in the sample so collected was removed by adding excess oxygen and absorbing the nitrogen dioxide with solid sodium hydroxide. The resulting mixture of oxygen, with possibly nitrogen or nitrous oxide, was then sparked with excess of hydrogen, and the residual hydrogen removed. The contractions indicated that nitrogen was present and that the amount of nitrous oxide was inappreciable.

In one typical experiment, the volume of gas collected was 13·45 c.c. After addition of 11·63 c.c. of oxygen, the volume after absorption of nitrogen dioxide was 5·60 c.c.; 9·90 c.c. (*a*) of hydrogen were added, and after sparking, a contraction of 8·70 c.c. (*b*), leaving 6·80 c.c., was observed. Excess oxygen was then added, and the contraction (*c*) after sparking was 6·16 c.c. It follows that the volume of nitrous oxide in the 5·60 c.c., after absorption of the dioxide, was $3a - 2b - 2c = -0{\cdot}02$ c.c., the volume of oxygen was $b + 2c/3 - a = 2{\cdot}91$ c.c., and that of nitrogen $5{\cdot}60 - 2{\cdot}91 = 2{\cdot}69$ c.c. Results of experiments in which the volume of nitrogen obtained was correlated with the weight of sulphur monoxide present are given in Table IV.

TABLE IV.

Vol. of gas collected, c.c.	37·00	36·90	5·12	13·50	24·25	24·30
Vol. of nitrogen, ...	4·09	1·07	0·93	1·62	3·04	1·43
SO used from *A*, g.	0·025	0·009	0·0047	0·012	0·017	0·011

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