THE OXIDATION OF SULPHUR DIOXIDE IN GAS FLAMES.

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The formation of sulphur trioxide in the combustion of fuels containing small amounts of sulphur compounds is a subject of considerable industrial importance, particularly in relation to corrosion by the products of combustion. It has been under investigation as part of a programme of research into boiler deposits and corrosion carried out by the Boiler Availability Committee.† Previous work [1] on the release of sulphur compounds from solid fuels during combustion and on the analysis of combustion gases showed that, in general, the main product is sulphur dioxide. Attention was therefore directed principally to the behaviour of SO_2 in combustion flames.

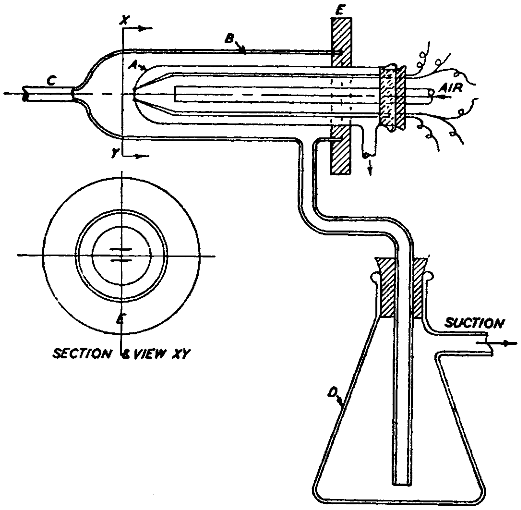

FIG. 1.—Dew point apparatus.

An extensive literature exists on the oxidation of SO_2 in gaseous systems [2] but it is almost entirely concerned with heterogeneous reactions on catalytic surfaces. There is also a growing volume on the oxidation of sulphurous acid and solutions of sulphites. On the other hand, little has been published on the homogeneous oxidation of SO_2 in the gas phase. Norrish and Axford,[3] using a polarographic method for the estimation of sulphate, have, however, recently found that oxidation of SO_2 takes place in a CO-air flame, and when the air is replaced by argon-air, the percentage oxidation is lower.

A primary requirement in studying the formation of SO_3 in combustion reactions is a method for the accurate determination of traces of SO_3 (0 to 100 p.p.m.) in the presence of small but relatively much larger concentrations of SO_2 (0·05 % to 0·20 % by volume) and of water vapour, the amount of which will vary with the hydrogen content of the combustible gas. The effect of such small proportions of SO_3 in raising the

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[1] Burdick and Barkley, *U.S. Bureau of Mines, I.C.*, May, 1939, 7065.

[2] Dooley, *B.C.U.R.A. Monthly Bulletin*, Oct., 1944, 285.

[3] Norrish and Axford, *Private communication.*

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† The Boiler Availability Committee is representative of the Central Electricity Board, the Water Tube Boilermakers' Association, the Electricity Undertakings, the Fuel Research Board, and B.C.U.R.A.

dewpoint, first emphasised by Johnstone,[4] is now widely recognised as a leading factor in promoting corrosion by flue gases in combustion plant. It has been demonstrated quantitatively by Taylor,[5] by vaporising sulphuric acid solutions into an air stream, and his curves showing the relation between dewpoint and SO_3 concentration are referred to later in the paper (Fig. 2).

At an early stage in the investigation, attention was therefore focussed upon two problems: the direct chemical estimation of SO_3 in the presence of excess of SO_2, and the determination of the dewpoint of combustion gases. Suitable techniques for use on boiler plant have been developed in both cases and details will shortly be published. The application of these to "clean" gases, free from suspended dusts, is simpler than to plant flue gases and has enabled the present investigation on the oxidation of SO_2 in flames of town gas, carbon monoxide, methane and hydrogen to be made.

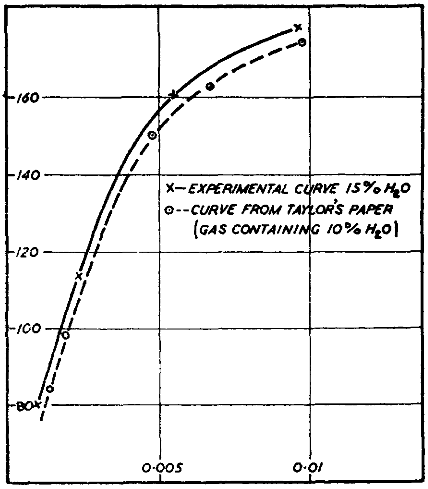

FIG. 2.—Relation between H_2SO_4 content and dew point. Bunsen flame giving 15 % H_2O in products of combustion. Ordinate: dew point °C. Abscissa: % H_2SO_4 by volume in dry gas.

Experimental.

Method of Measurement.—The direct determinations of SO_3 were made by a method devised by Dooley and Flint.* Briefly, the gases were drawn through an absorbent containing *iso*-propyl alcohol (which serves to inhibit the oxidation of dissolved SO_2), then through a sintered Pyrex filter to trap sulphuric acid mist formed during absorption, and finally through a hydrogen peroxide solution for absorption of SO_2.

Dewpoints were determined by an electrical conductivity method similar to that used by Johnstone,[4] using an improved type of instrument. Two thermocouples are fused into the external surface of a glass thimble and a potential difference of 60 volts applied between them. When the element is placed in a gas stream containing water vapour and the thimble cooled internally, the onset of condensation is indicated by an increase in conductivity. The apparatus used is illustrated in Fig. 1. A Pyrex thimble "A," 1·5 cm. in diameter and 4·5 cm. long, is mounted in an outer tube "B," 3 cm. in diameter and 6 cm. long, through which samples of gas are withdrawn via the narrow tube "C" inserted into one of the side arms. The hot gases pass from the outer tube to the large conical flask "D," the purpose of which is the observation of H_2SO_4 mist. The platinum-platinum/rhodium thermocouples, 0·2 mm. in diameter, are mounted in the end of the thimble "A" at a distance apart of 2 mm. The leads pass inside and are secured to terminals on an ebonite block "E." The convex surface of the end of the thimble is carefully polished so that the thermocouples lie correctly in the glass surface. Cooling air is directed through a jet on to the inside of the thimble. A potential

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[4] Johnstone, *Univ. of Illinois, Eng. Exp. Stn.*, Circ. No. 20, Nov., 1929.
[5] Taylor, *J. Inst. Fuel*, 1942, **16**, 25.
* To be published.

difference of 60 volts is applied across the gap between the thermocouples and any current passing is measured on a microammeter. As is necessary in all methods of dewpoint determination, a standard procedure is followed as regards rate of sampling and rate of cooling. The dewpoint is recorded as the temperature at which the conductivity first commences to increase. With methane flames, the deposition of a sooty film tends to interfere with the detection of acid films. However, the conductivity of sooty films decreases as the temperature is lowered further and it is not difficult in practice to disentangle the effects due to the two kinds of films.

Types of Flame.—Two types of flame were used. Town gas was burnt in an ordinary Bunsen burner, while diffusion flames of CH_4, H_2 and CO in air were burnt at a quartz jet.

In order to facilitate the introduction of flame inhibitors and catalysts the metal tube of the burner was replaced by a quartz tube of the same diameter (1·5 cm.) fitted with a side arm. This latter was connected through a stop-cock to the supply of pure, re-distilled reagent, generally a volatile liquid maintained at a predetermined temperature through which a stream of air was passed.

CO_2, H_2 and CH_4 were all obtained from cylinders and were used undried and without further purification. SO_2 was supplied from a syphon and was allowed to mix with the combustible gas before the burner, the volumes of the various gases being measured on flowmeters containing paraffin oil. In order that samples of gas might be withdrawn from or above the flame, a Pyrex tube, 3 cm. in diameter and 30 cm. long, fitted with side arms, was placed so as to surround the flame. The primary air supplied to the burner was controlled at the port: it was not possible to control the secondary air, which was drawn up with the flame.

Oxidation of SO_2 in Town Gas Flames.

The gas used in these experiments had the average composition by volume: CO_2 3·5 %, CO 11·2 %, CH_4 23·3 %, H_2 46·1 %, O_2 0·7 %, hydrocarbons 2·9 % and N_2 12·3 %. After complete combustion in a Bunsen burner, this gave a gas which was found experimentally (by freezing in a solid CO_2 trap) to contain 15·0 % of H_2O. This corresponds to a theoretical dewpoint of 55·5° C. Measurement of the dewpoint above the flame gave values 10-15° C. higher, the difference fluctuating from day to day. Determination of the SO_3 content of the Bunsen flame showed that sufficient SO_3 was produced from the small quantities of sulphur compounds present in the gas to account for this. It was found that, after burning, 25 % of the total sulphur occurred as SO_3, the actual concentration of the latter being about 0·0006 % of the dry products of combustion. This small amount of SO_3 was sufficient to give a very faint mist of sulphuric acid when the hot gases were bubbled through water. On the introduction of SO_2 to the flame, a much denser mist was produced and the production of such a mist was, in fact, found to provide a rough indication of the amount of SO_3 present in the gases.

(*a*) Variation of Oxidation with the Amount of Added SO_2.—The amount of SO_2 added to a fully aerated flame was progressively increased and the dewpoint and SO_3 content determined simultaneously at a point just above the tip of the flame. This gave information not only as to the variation of SO_3 produced with concentration of SO_2 but also confirmed the relationship between the dewpoint and SO_3 content of the gases. This is shown in Fig. 2, which includes a curve taken from Taylor's [5] paper giving the dewpoint —H_2SO_4 relationship for gases containing 10 % water vapour.

Table I shows how the conversion to SO_3 varies with the concentration of SO_2 in the flame.

The interesting feature of these results is the decrease in percentage conversion to SO_3 as the concentration of SO_2 increases. It is known from the work of Emeleus [6] and Ritchie and Ludlam [7] that SO_2 and SO_3 act as inhibitors or chain breakers in the oxidation of sulphur vapour and it is possible that a similar role is played by SO_2 here.

The addition of SO_2 to an aerated flame brought about a small but definite change in the colour of the flame. The inner cone did not appear to change in colour for small additions, but a purple colour was imparted to the normally dark blue outer cone. As the amount of SO_2 increased, this purple tint became more intense and the outer cone was visibly reduced in extent. With about 5 % SO_2 added, the flame tended to be unstable and was ultimately extinguished as the SO_2 increased beyond this amount.

TABLE I.

Per cent. SO_2 in Exit Gases.	Per cent. Oxidation to SO_3.	Dewpoint °C.
0·02	10·0	110
0·04	8·2	140
0·11	4·5	165
0·15	3·8	170
0·50	1·8	176
1·00	1·0	180

(*b*) Effect of Flame Conditions on the Formation of SO_3.—The concentration of SO_2 in these tests was adjusted in each case to 0·05 % of the hot gases and the primary air supplied to the town gas was varied by closing the port of the burner. With the port fully closed, giving a luminous, smoky flame, very little oxidation of the SO_2 occurred and the dewpoint just above the flame was 65° C. As the port was gradually opened, the percentage conversion to SO_3 increased, until with a fully aerated flame it was 6·5 %, corresponding to a dewpoint of 150° C.

By adding about 4-5 % SO_2 to a non-aerated flame, it was possible to reduce the luminosity to a considerable extent and the originally smoky flame took on a blue colour, reminiscent of burning sulphur. When a water-cooled tube was held above this flame, a yellowish white deposit was collected, and physical and chemical tests showed this to be sulphur. Spectroscopic examination of the flame showed a series of bands in the blue region and the emitter appeared to be the S_2 molecule.

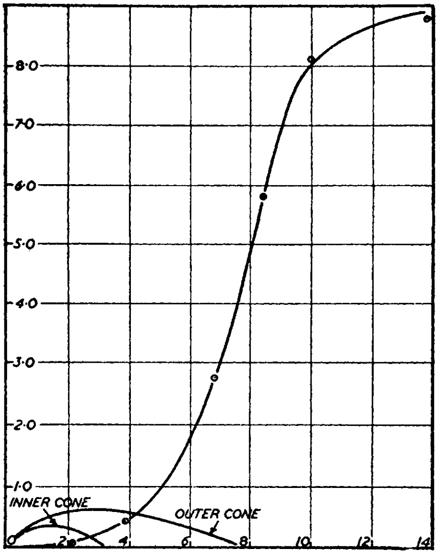

FIG. 3.—Variation in % oxidation with position in aerated flame containing 0·05 % SO_2 (with approximate flame zones superimposed). Ordinate: % oxidation. Abscissa: distance in cm. from rim of burner.

(*c*) The Region of Formation of SO_3 and the State of Sulphur Compounds in the Flame.—For the measurement of SO_3 content and dewpoint in the flame, gas was sampled through a quartz tube, 2 mm. in diameter, inserted into the flame at various heights above the burner tube. As

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[6] Emeleus, *J.C.S.*, 1928, 1942.
[7] Ritchie and Ludlam, *Proc. Roy. Soc., A*, 1932, **138**, 635.

Fig. 3 shows, there was little oxidation in the inner cone of the Bunsen flame. As the sampling point moved up the flame, the percentage conversion to SO_3 increased and appeared to reach a maximum value well above the visible limit of the flame.

In view of the well-known catalytic influence of solid surfaces on SO_2 oxidation, some attention was paid to the possible effect of the quartz sampling tube on the oxidation. Some experiments were carried out in which air containing 0·05 % SO_2 was passed, at the same sampling rate as in the tests described above, through a length of electrically heated quartz tube 2 mm. in diameter. No oxidation was detected until the quartz reached 1000° C., when 0·5 % conversion to SO_3 was obtained. In view of the fact that the length of quartz heated in these tests was much greater than when sampling from the flame, it was concluded that the effect of the sampling tube was negligible and that the oxidation takes place in and above the outer cone.

Whilst sampling from the inner cone of the flame, it was noticed that a yellowish-white deposit collected in the cool parts of the sampling line, and the absorbing solution became turbid. Examination of this material showed it to be sulphur. Experiments were then made to ascertain the nature of the sulphur compounds in the inner cone. A Smithell's separator consisting of two concentric quartz tubes of 1 cm. and 1·5 cm. bore was used for this. A cork enabled the inner tube to be slid down until its top was about 5-6 cm. below that of the outer tube and a side arm in the outer tube enabled samples to be withdrawn from the inter-conal region.

Measurement of the dewpoint of the gases in this region showed that no oxidation of SO_2 was taking place and qualitative tests showed that sulphur, hydrogen sulphide, carbon disulphide and unchanged SO_2 were the principal products, together with smaller amounts of carbonyl sulphide and other sulphur compounds. The quantitative analysis of such a complex mixture is difficult and tedious and only a partial analysis was attempted.

A sample was drawn through a cooled tube packed with glass wool to remove sulphur, and H_2S was determined by bubbling the gas through cadmium acetate solution. With 0·05 % SO_2 added to the town gas-air mixture, it was found that 10 % of the sulphur added as SO_2 occurred as elementary sulphur, and 25 % as H_2S in the inter-conal region.

In other experiments the reduction of SO_2 in the inner cone was avoided by injecting the SO_2 through a quartz jet into the tip of the flame. When 0·05 % SO_2 was added in this way, the proportion oxidised to SO_3 at a point above the outer cone was only a little less than when it was introduced in the normal way (6·0 % compared with 6·5 %).

An interesting effect was observed when the supply of SO_2 (added in the normal way) and of town gas was suddenly cut off and the flow of air through the sampling tube continued. The acid mist in the flask *increased* in density over a period of 2-3 seconds before it gradually disappeared. This result appears to indicate that active chain centres are produced in the flame which have a life of the order of seconds and are capable of oxidising the traces of SO_2 still present in the gas zone.

(*d*) **Effect of Flame Inhibitors and Catalysts.**—If, as the above results suggest, the oxidation of SO_2 is due to its participation in reaction chains involved in the combustion processes, the presence of inhibitors or catalysts should have some influence on the oxidation. Whilst the action of CCl_4 and similar substances in reducing flame speeds is by no means completely understood, such inhibitors appear to act either by de-activating energised molecules or by reacting with the oxygen atoms responsible for the propagation of chains. The possibility suggests itself that the oxidation of SO_2 may be diminished by competition of other inhibitors for oxygen atoms.

Fig. 4 shows how the percentage oxidation, measured well above the flame, was influenced for a Bunsen flame containing 0·05 % SO_2 when varying amounts of these reagents were entrained with the town gas. It will be seen that carbon tetrachloride, pyridine and ethyl nitrate were more effective in reducing the oxidation than ethyl alcohol and benzene. Ethyl nitrate is a positive catalyst (*i.e.* increases flame speeds) but it will be noted that this substance decreased the oxidation. At the same time, the periphery of the outer cone was coloured yellowish-green, suggesting the formation of oxides of nitrogen.

When CCl_4 was added to the flame, the outer cone became blue-green in colour and was gradually shortened in extent as the concentration added increased. The flame was ultimately extinguished by the addition of about 4 % CCl_4. During dewpoint determinations in this series, an extremely dense mist was observed in the flask and this was attributed to the relatively large amounts of hydrochloric acid formed in the oxidation of the tetrachloride.

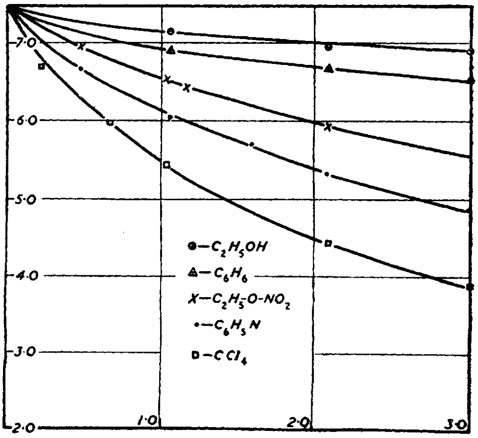

FIG. 4.—Effect of various substances on oxidation of SO_2 in bunsen flame containing 0·05 % SO_2. Ordinate: % oxidation. Abscissa: % reagent added.

(e) The Effect of Nitric Oxide.—Gaydon[8] has recently drawn attention to the continuous yellow-green emission visible when nitric oxide is injected into flames. This he attributes to reaction of NO with atomic oxygen to form nitrogen peroxide and with the release of light energy according to the expression

$$NO + O \rightarrow NO_2 + h\nu.$$

It follows that, if atomic oxygen is involved in the reactions leading to SO_3 formation in flames, the introduction of NO should have a marked influence on the amount of SO_3 formed.

TABLE II.

SO_2 in gases = 0·05 %.

Per cent. NO Added.	Per cent. Oxidation of SO_2.
0·0	7·5
0·1	7·3
0·5	6·0
1·0	4·5
2·0	4·3

In our experiments, NO (prepared by reacting $NaNO_2$, KI and H_2SO_4, and stored over water) was led, in an undried state, through a quartz jet directly into the base of the flame. As described by Gaydon, a yellowish-green colour was imparted to the periphery of the outer cone, and in a darkened room a greenish glow was seen to extend well above the normal visible limit of the flame. On the introduction of SO_2 in small amounts, there was no visible change in the intensity of the glow. With the addition of 2 % SO_2, and consequent reduction in size of the outer cone, the green tended to merge into a blue colour, and the green glow above the flame was definitely reduced in extent. Analysis of the gases sampled at a point above the flame showed a variation of the proportion of SO_2 oxidised with the amount of nitric oxide added. The results are set out in Table II.

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[8] Gaydon, *Proc. Roy. Soc., A*, 1944, **183**, 111.

It was necessary to ascertain whether the *iso*-propyl alcohol used as inhibitor for the suppression of the oxidation of SO_2 was equally effective in the presence of dissolved oxides of nitrogen. It was found that, for the concentrations of NO used in these tests, *iso*-propyl alcohol did inhibit the oxidation of sulphurous acid under these conditions.

The Oxidation of SO_2 in CO, H_2 and CH_4 Flames.

The diffusion flames of these gases in air were adjusted to be of roughly the same dimensions and SO_3 determined in the gas sampled above the flames. The results are illustrated in Fig. 5. It will be seen that, as with town gas flames, the percentage oxidation to SO_3 decreases as the concentration of SO_2 increases. There is also a marked difference between the degree of oxidation with the different flames, the order in increasing conversion being methane : hydrogen : carbon monoxide. This is the same order as that for increasing atomic oxygen concentration in these flames, as given by Gaydon [8] on the basis of the intensity of the yellow-green continuous emission in the presence of nitrogen oxides. The effect on the appearance of these flames of added NO was examined. As Gaydon had observed, the most intense yellow-green coloration was given by the CO flame.

Definite colour changes were observed when SO_2 was added to these flames. The lilac-blue of the CO flame became deeper blue and eventually purple when 2 % SO_2 was present. A similar effect was noted in the H_2 flame and at the same time a deep blue inner cone was observed. When 0·1 % NO was added to the hydrogen flame, the deep blue inner cone disappeared completely. As with a luminous town gas flame, the luminosity of the CH_4 flame decreased when SO_2 was added : with 5 % SO_2, a blue flame was given which deposited sulphur on cooled surfaces.

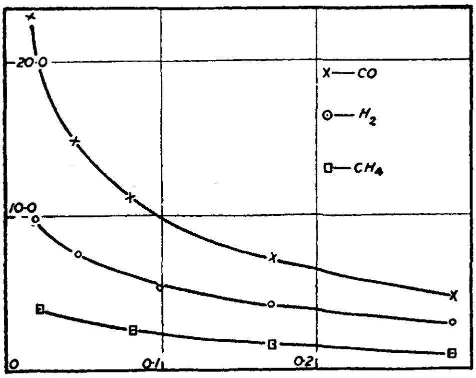

FIG. 5.—Oxidation of SO_2 in various flames. Ordinate : % oxidation. Abscissa : % SO_2 in gases.

Discussion.

It is evident from the above observations that the measured degree of oxidation of SO_2 in flames is dependent upon (*a*) the disposition of the sampling point in relation to the reaction zones, (*b*) the nature of the flame, (*c*) the concentration of SO_2 present, and (*d*) the presence of flame inhibitors and catalysts such as nitric oxide.

Analysis of the intermediate products formed in the inner reducing region of the flame indicated that SO_2 is reduced to some extent to H_2S, sulphur, CS_2 and other products. The oxidation of these substances must therefore be considered in any discussion on the mechanism of oxidation of SO_2. Thompson [9] and Farkas [10] have shown that the oxidation of H_2S occurs through chain reactions which appear to involve oxygen atoms. Sulphur monoxide is known to be an intermediate

[9] Thompson and Kelland, *J.C.S.*, 1931, 1809.
[10] Farkas, *Z. Elektrochem.*, 1931, **37**, 670.

product and the following reactions have been suggested to indicate the formation of atomic oxygen :

$$H_2S + O_2 \rightarrow H_2O + SO \quad . \quad . \quad . \quad (1)$$
$$SO + O_2 \rightarrow SO_2 + O \quad . \quad . \quad . \quad . \quad (2)$$

followed by :

$$H_2S + O \rightarrow H_2O + S$$
$$S + O_2 \rightarrow SO + O$$

these reactions being responsible for the maintenance of chains.

It is clear that reaction (2) could lead to the production of SO_3 as a secondary product of the oxidation. Chamberlin and Clarke,[11] working on the flame speed of H_2S-air mixtures, found that up to 20 % of the sulphur in the products of explosion was in the form of SO_3 and, as the concentration of H_2S in the mixture increased, the amount of SO_3 produced decreased.

Similarly, the presence of such radicals as CS as well as SO in the oxidation of CS_2 suggests an atomic oxygen chain :

$$CS_2 + O \rightarrow CS + SO$$
$$SO + O_2 \rightarrow SO_2 + O.$$

The work of Semenov and Rjabinin [12] on the oxidation of sulphur vapour (a reaction which exhibits all the characteristics of a chain process), suggests that atomic oxygen is the active species responsible for chain propagation.

The formation of SO_3 in flames to which SO_2 has been added might then be explained by the intermediate formation of H_2S, CS_2 and other sulphur compounds and the oxidation of these by the reactions indicated above. On the other hand, the fact mentioned above, that SO_2 is oxidised when injected into the tip of the Bunsen flame, suggests that SO_2 reacts directly with some active product from the combustion processes.

It is known that oxygen atoms can be formed in the combustion of CO and H_2 through some such reactions as :

$$CO + O_2 \rightarrow CO_2 + O$$
$$H + O_2 \rightarrow OH + O$$

and we are of the opinion that, when SO_2 is present, SO_3 can be formed through

$$SO_2 + O \rightarrow SO_3.$$

Very little is known about the reaction between SO_2 and atomic oxygen. Harteck and Kopsch,[13] who studied the interaction of H_2S and CS_2 with oxygen containing a high proportion of oxygen atoms, showed that these reacted vigorously, but the authors did not include SO_2 in the substances examined. In later work, Harteck and Geib [14] showed that, even at liquid air temperatures, SO_2 reacted with atomic oxygen to the extent of 8 %. Under the same conditions, CO gave 1·2 % CO_2.

The view that the oxidation of SO_2 in flames takes place through reaction with the chain propagators (atomic oxygen) implies that it is an inhibitor of the combustion process. Drop [15] in fact showed that SO_2 is an explosion inhibitor.

The effect of organic flame inhibitors and nitric oxide in suppressing the oxidation of SO_2 can be explained on the basis of the competitive reactions :

$$X + O \rightarrow XO \rightarrow$$
$$SO_2 + O \rightarrow SO_3.$$

[11] Chamberlin and Clarke, *Ind. and Eng. Chem.*, 1928, **20**, 1017.
[12] Semenov and Rjabinin, *Z. physik. Chem.*, *B*, 1928, **1**, 192.
[13] Harteck and Kopsch, *Z. Elektrochem.*, 1930, **36**, 714.
[14] Harteck and Geib, *Trans. Faraday Soc.*, 1934, **28**, 131.
[15] Drop, *Rec. Trav. Chim.*, 1937, 56, 71-85, 86-96.

Carbon tetrachloride, pyridine and benzene are known from the work of Harteck and Kopsch to react vigorously with oxygen atoms. Melville[16] was able to calculate from the effect on the upper critical pressure of the phosphorus oxidation the probability of the reaction between oxygen atoms and SO_2, benzene, acetylene and related compounds classed as "poisons." He gave 6×10^{-5} as the efficiency of inhibition collisions for SO_2, as compared with 8×10^{-5} for benzene and 5×10^{-1} for iron pentacarbonyl.

The extent to which SO_3 is formed in flames of CO, H_2 and CH_4 can be correlated with the concentration of atomic oxygen in these flames according to the work of Gaydon,[8] suggesting that atomic oxygen is involved. The slight extent of the oxidation observed with methane does not, however, necessarily indicate a very low concentration of atomic oxygen, because the carbon particles present in the flame may adsorb sulphur oxides.

One other factor which remains to be considered is the possible role of nitrogen oxides in the oxidation of SO_2. That oxides of nitrogen are formed in flames is well known and the work of Bone and Newitt[17] on the combustion of CO in air at high pressures has demonstrated that they may be formed in large quantities under these conditions. There is reason to believe that appreciable quantities are not found at atmospheric pressure. There appears to be no published work on the catalytic influence of oxides of nitrogen on the gas phase oxidation of SO_2.

We have suggested that the effect of nitric oxide on the oxidation in flames can be attributed to the removal of oxygen atoms through

$$NO + O \rightarrow NO_2 + \text{light energy},$$

but the sensitising effect of NO_2 on many oxidation processes, due to its role in providing oxygen atoms, may result in the order of the concentration of nitrogen oxides determining the over-all effect observed.

It is not improbable that further elucidation of the reaction

$$SO_2 + O \rightarrow SO_3$$

would enable the oxidation of SO_2 in combustion flames to be used as a measure of atomic oxygen concentration, as the SO_3 formed can readily be measured, even when present in small quantities.

The authors are indebted to the Boiler Availability Committee for permission to present this paper, to Dr. D. H. Bangham for his close interest and many suggestions, and to L. Lorenz, A. Cave and D. Flint for assistance in some aspects of the experimental work.

Summary.

The oxidation of SO_2 in combustion flames has been studied, using a dewpoint meter and a direct method of analysis. The amount of SO_3 formed varies with (*a*) the concentration of SO_2, (*b*) the nature of the gas burned, (*c*) position of the sampling point, (*d*) the presence of organic flame inhibitors and (*e*) the presence of nitric oxide. Various mechanisms for the oxidation of SO_2 in flames are discussed, and it is considered that atomic oxygen is responsible.

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[16] Melville, *Trans. Faraday Soc.*, 1932, **28**, 308.
[17] Bone and Newitt, *Proc. Roy. Soc., A*, 1927, **115**, 41.