

634. *The Decomposition of Sulphuric Acid in Town's Gas Flames.*

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Dew-point measurements of the combustion products have been used to determine the degree of decomposition of sulphuric acid injected into pre-mixed town's gas flames. The initial concentration of acid in the gases was in the range 0.006—0.12% (by vol.), and 94—98% is decomposed in Bunsen-type flames. Studies on separated flames show that the decomposition occurs almost entirely in the inner cone. The mechanism of decomposition is discussed with particular reference to the reaction between sulphur trioxide and atomic hydrogen.

THERE is evidence that the behaviour of sulphuric acid and sulphur trioxide, arising from the combustion of sulphur-bearing fuels, is of importance in relation, not only to the corrosive nature of the combustion products, but also to formation of carbon in flames of burning hydrocarbons. Thus it has been shown (Whittingham, *Nature*, 1945, **156**, 207) that the addition of 4% of sulphur dioxide to a town's gas diffusion flame inhibited carbon formation. This effect was confirmed by Gaydon and Whittingham (*Proc. Roy. Soc.*, 1947, *A*, **189**, 313), and Parker and Wolfhard (*Fuel*, 1950, **29**, 235), and the latter authors also showed that sulphur trioxide behaved in the same way as sulphur dioxide in diffusion flames. Whittingham (*Trans. Faraday Soc.*, 1948, **44**, 141) observed that the production of tar in the slow combustion of hexane-air-sulphur dioxide mixtures coincided with the appearance of sulphuric acid in the combustion products, and the significance of production of sulphur trioxide in relation both to deposition of carbon and to corrosive wear in engines has been discussed by several workers (Cloud and Blackwood, *Soc. Automotive Engrs.*, 1943, **51**, 408; Broeze and Wilson, *Inst. Mech. Engrs.*, 1948—49, 128).

A knowledge of the stability of sulphuric acid at high temperatures is essential to the fuller understanding of its effect on combustion processes. Information exists on its heterogeneous dissociation over a limited temperature range (*e.g.*, Mellor, "Treatise on Theoretical and Inorganic Chemistry," Vol. 10, p. 396) but the rate of decomposition in flame processes has not previously been investigated. The subject has been examined in the present work, with particular reference to pre-mixed town's gas flames.

EXPERIMENTAL

Controlled amounts of sulphuric acid were sprayed into various flames by a spray burner of the type described by Stockton (*J. Sci. Instr.*, 1949, **26**, 157) and the sulphuric acid dew-point of the products of combustion was measured. In the first series of experiments Bunsen-type flames were used, and in a second series the apparatus was modified to act as a Smithells separator so that the lower and the upper cone could be separately examined.

The two assemblies used are illustrated in Fig. 1. In the first, the supplies of town's gas and primary and secondary air fed to the burner were measured by capillary flowmeters, and the amount of acid entering the flame was varied by altering the concentration of acid in the solution in the reservoir. A side-arm attached to the base of the Pyrex chimney enabled sulphur dioxide to be introduced from a syphon, so that its behaviour could be compared with that of sulphuric acid. In the experiments with separated flames, the mixture fed to the burner was deficient in air, and the products of the primary reaction burned to completion as a diffusion flame at the top of the chimney. The amount of air diffusing into this flame was not measured but it was possible to calculate it from the water-vapour content of the interconal gases and the final products. The water-vapour content was obtained from measurement of the water dew-point and an Orsat apparatus was used to analyse the interconal gases for carbon dioxide, carbon monoxide, and oxygen.

The dew-point technique used to determine the quantities of sulphur trioxide and water in the combustion products was the same as that previously described (Flint, *J. Inst. Fuel*, 1948, **21**, 248). The essential feature of the apparatus is an air-cooled glass element, in which are mounted two platinum-platinum-rhodium thermocouples for measurement of the temperature and electrical conductivity of the surface. The element is placed in contact with the hot gases and cooled by a stream of air directed against its under side. Condensation is indicated by a

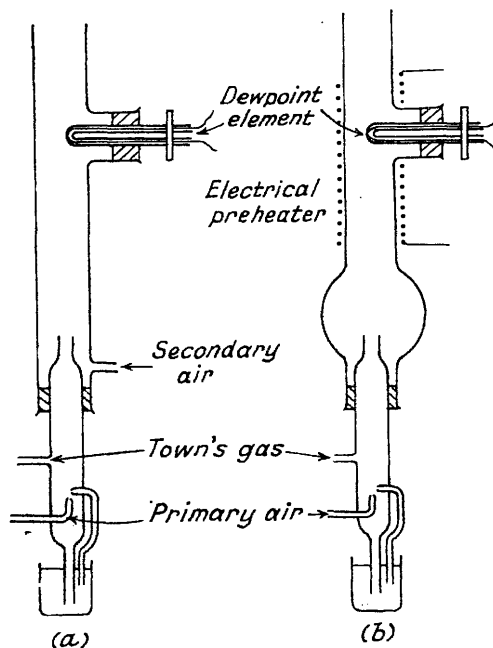
rapid increase in conductivity. Data (Taylor, *J Inst. Fuel*, 1942, 16, 25; Dooley and Whittingham, *Trans. Faraday Soc.*, 1946, 42, 354) on gases having a wide range of sulphuric acid and water contents were used to obtain the acid content from the measured dew-point.

RESULTS

Bunsen-type Flames.—Town's gas and primary and secondary air were supplied at the rates of 4.5, 11.25, and 34.25 l. min.⁻¹ respectively. The town's gas had the average composition by volume: CO₂ 3.6, O₂ 0.4, C_nH_m 4.6, CO 15.0, CH₄ 23.7, H₂ 42.4, and N₂ 10.3%. If C_nH_m is assumed to be C₄H₈, the calculated composition of the combustion products was CO₂ 5.6, H₂O 10.0, O₂ 10.0, N₂ 74.4%, giving a theoretical water dew-point of 46°, whereas the measured dew-point was 50°. The difference was attributed to the presence of traces of residual sulphur compounds in the gas, which oxidise to sulphur trioxide and thereby produce a slightly higher dew-point.

The quantities of acid induced into the flame, for various solutions in the reservoir, are shown

FIG. 1. Apparatus used for (a) Bunsen-type flames, (b) separated flames.



in Table 1. The reduction in the rate of spraying, as the concentration of acid in solution increased, was due to the increasing density and viscosity of the solution.

When acid was sprayed into the flame, carbon was deposited on the walls of the mouth of the burner over a length of about 0.5 cm., and with the 20% and 40% solution a shower of carbon particles appeared in the flame. The sulphuric acid concentration of the combustion products

TABLE 1.

H ₂ SO ₄ in solution (% by vol.)	Rate of spraying (c.c./hr.)	Amount of acid introduced (% by vol. of air-gas mixture)
2.5	16.5	0.0060
5.0	15.0	0.0110
10.0	12.0	0.0176
20.0	11.0	0.0322
40.0	6.0	0.0351

is plotted against the ingoing sulphuric acid in Fig. 2. The lower curve shows the amount of acid produced for a range of sulphur dioxide additions.

Separated Flames.—Town's gas and air were supplied to the lower cone at the rates of 3.35

and 8.7 l. min.⁻¹ respectively and the range of acid additions was as before. Analysis of the combustion products from this flame, when uncontaminated, gave the average values CO₂ 7.6, CO 9.7, O₂ 0.0, H₂O 11.5, and N₂ 71.2% (by difference). Because of the cooling of the products of the lower flame as they traversed the chimney and the large amounts of dilution air induced in the upper diffusion flame, it was difficult to maintain a stable flame. Some degree of stability was achieved by electrical preheating of the interconal gases by about 200°.

The measured water dew-point of the final combustion products was 41°, corresponding to 7.0% of water. When acid solution was sprayed into the flame, the water content of the interconal gases increased to a maximum of 14%, depending on the rate of spraying, and that of the final products increased to 7.5%. Production of carbon on the burner walls and in the lower cone was again evident and when traces of alkaline impurities were present in the acid solution there was a yellow luminescence, extending well beyond the boundaries of the

FIG. 2. Variation in H₂SO₄ content of combustion products with amount of H₂SO₄ or SO₂ added to Bunsen-type flame.

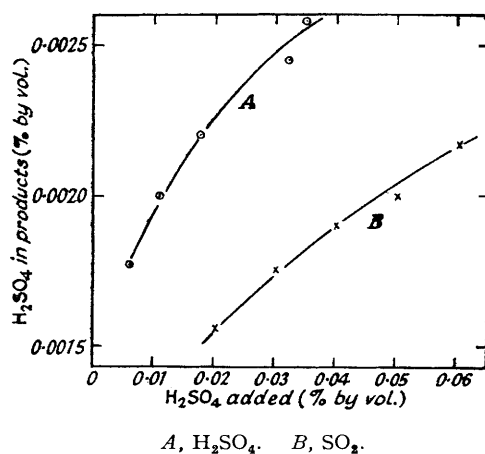
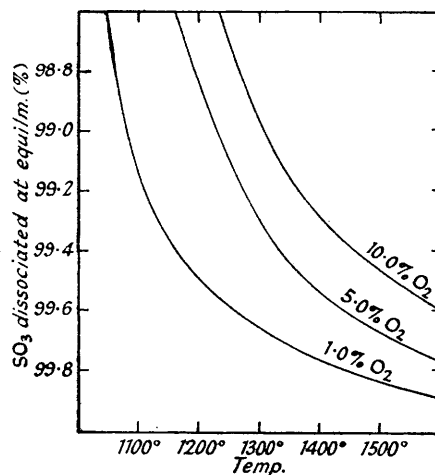


FIG. 3. Equilibrium degree of dissociation of SO₂ at various temperatures.



(uncontaminated) flame. The upper cone remained clear. These phenomena have been described and discussed in detail by Arthur and Littlejohn (*Nature*, 1952, 169, 288).

The results of the dew-point measurements on the interconal gases and on the final combustion products are shown in Table 2. The figures in column 4 were derived from those in

TABLE 2. Dew-point and equivalent H₂SO₄ concentration of interconal and final products of combustion.

H ₂ SO ₄ introduced (% by vol.)	Interconal gases		Upper cone		
	Dew-point	H ₂ SO ₄ , %	H ₂ SO ₄ , Initial concn., %	Dew-point of products	H ₂ SO ₄ in products, %
0.023	146°	0.0043	0.0011	74°	0.0008
0.040	164	0.0072	0.0018	108	0.0017
0.070	166	0.0076	0.0019	110	0.0018
0.082	170	0.0081	0.0020	114	0.0020
0.120	177	0.0110	0.0025	116	0.0022

column 3 and the volumes of the interconal gases and the air entering the upper diffusion flame. The accuracy of dew-point measurements, over the temperature range encountered, is $\pm 2^\circ$ and the sulphuric acid concentrations in the final column are estimated to be within $\pm 0.0001\%$.

DISCUSSION

We consider first the behaviour of sulphuric acid in the Bunsen-type flame. Fig. 2 shows that the amount of sulphuric acid in the combustion products is 10–15% of that added to the flame. Now, the decomposition of sulphuric acid produces sulphur dioxide, and

Dooley and Whittingham (*loc. cit.*) have previously shown that oxidation of the latter to sulphur trioxide occurs in diffusion and pre-mixed flames to an extent which depends on the concentration of dioxide, the fuel : air ratio, and the nature of the fuel burned. To obtain the true degree of decomposition of sulphuric acid it is therefore necessary to subtract from the measured acid content of the gases that amount of acid arising from re-oxidation of sulphur dioxide in and above the outer cone. This can be obtained from the lower curve in Fig. 2, and Table 3 shows how the true degree of decomposition varies with the initial

TABLE 3. *Relation between the degree of decomposition and the initial concentration of acid.*

H ₂ SO ₄ added, %	0.0110	0.0176	0.0322	0.0351
Decompn., %	94.1	96.5	97.7	97.8

concentration of acid. It is evident that the decomposition process is almost of first-order with respect to sulphuric acid concentration. The temperature of the flame, when contaminated with acid, was calculated to be 1290°, and from the flame dimensions and the rates of flow of town's gas and air the overall time of passage of a volume element of mixture through the complete flame zone was estimated at 5×10^{-2} sec. It is of interest to compare the above values for the degree of decomposition with the equilibrium degree of dissociation of sulphur trioxide according to the system $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$. Fig. 3, based on the work of Bodenstein and Pohl (*Z. Elektrochem.*, 1905, **11**, 373), shows the amount of trioxide existing under equilibrium conditions over the range 1000—1500°. It is seen that for gases containing 10% of oxygen the degree of dissociation at 1290° is 99.0%.

The results on separated flames (Table 2) show that about 80—90% of the acid introduced is decomposed in the inner cone (calc. flame temperature 1470°), where partial combustion of the hydrocarbons and hydrogen occurs, whereas the further decomposition in the upper, diffusion flame is very much less.

Attention can now be given to the various processes involved when acid spray is injected into the flames. These are: (i) evaporation of acid droplets; (ii) dissociation of acid vapour into sulphur trioxide and water; and (iii) further dissociation of sulphur trioxide into dioxide and oxygen.

Before (ii) and (iii) are considered in detail it is necessary to estimate the time required for the initial process of evaporation. The rate of evaporation of single drops in still and in moving air streams of varying temperature has been studied by several workers (Frössling, *Z. Geophysik*, 1938, **52**, 170; Sjenitzer, *Inst. Mech. Engrs.* "General Discussion on Heat Transfer," 1951, Part I; E. G. Richardson, *ibid.*), but in the present system the experimental conditions are very dissimilar, as a cloud of drops is heated by radiation from a flame front. Detailed information on the drop-size distribution curve, which is of more significance than the average drop diameter, for the type of spray burner used, has not yet been obtained by us. Initial measurements indicate that the maximum droplet size is of the order of 100 μ although these large drops are but few in number and only occur with the strongest acid solutions. It is believed that the carbon "streamers" observed when spraying concentrated acid into the flame are due to rapid reactions between the hydrocarbons in the flame and incompletely evaporated drops. Calculations show that for droplets of 1- μ diameter the time of evaporation is approximately 10^{-3} sec. and is less than the time of passage of a volume element of mixture from the burner-mouth to the flame-front of the inner cone.

Bodenstein and Katayama (*Z. Elektrochem.*, 1909, **15**, 354) obtained the following relation for the variation in dissociation of sulphuric acid vapour with temperature:

$$\log K = -5000/T + 0.75 \log T - 0.00057T + 4.086$$

where

$$K = [\text{SO}_3][\text{H}_2\text{O}]/[\text{H}_2\text{SO}_4]$$

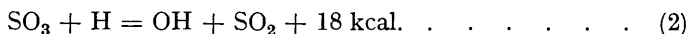
At flame temperatures, the rate of dissociation is extremely fast and it is unlikely that any undissociated sulphuric acid passes through the flame. It is evident from the

results that the further decomposition of sulphur trioxide is also an extremely fast process and there are various possibilities for the reaction mechanism. The bimolecular reactions $2\text{SO}_3 \longrightarrow 2\text{SO}_2 + \text{O}_2$, either in the gas phase or surface-catalysed, can be eliminated because of the high activation energies required (≈ 44 kcal. and ≈ 25 kcal. respectively) and the absence of surfaces in contact with the flame. Moreover, the experimental results indicate a first-order reaction with respect to sulphur trioxide.

Consideration of the various molecular and atomic species present in the flames provides the following possibilities :



where M = CO, H₂, or CH₄



Little information exists on the rate of the homogeneous reactions between sulphur trioxide and other molecular species, although it is known that when M = CO, the equilibrium concentration of trioxide according to $\text{CO} + \text{SO}_3 \rightleftharpoons \text{CO}_2 + \text{SO}_2$ is extremely small at temperatures exceeding 1000° (Johnstone, Univ. Illinois, Eng. Exp. Stn. Circ. No. 20, Nov., 1929). By analogy with other free-radical reactions, the activation energy of process (2) is likely to be low, of the order of 5–6 kcal., and recent work (Linnett and Pickering, *Trans. Faraday Soc.*, 1951, **47**, 1101) shows that the concentration of hydrogen atoms in hydrocarbon flames may be quite high. Arthur and Littlejohn (*loc. cit.*) recently suggested that the conditions existing in the inner cone of separated flames are particularly conducive to a high concentration of hydrogen atoms.

On the assumption that a partial pressure of hydrogen atoms of 1 mm. exists in the inner cone of pre-mixed town's gas flames—a not unreasonable estimate—calculation shows that 95% of the sulphur trioxide is destroyed in *ca.* 10⁻³ sec. The low degree of dissociation of trioxide in the upper cone of the separated flames examined can be mainly attributed to the low temperature of the flame, which contained a large excess of air, and the low concentration of hydrogen atoms likely to occur. It is not possible to state to what extent sulphur dioxide was re-oxidised in this flame, and this matter is under investigation.

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