The Journal of the American Chemical Society

with which has been incorporated
The American Chemical Journal
(Founded by Ira Remsen)

VOL. 48 NOVEMBER, 1926 No. 11

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF IOWA]

THE FORMATION OF SULFUR TRIOXIDE DURING THE BURNING OF SULFUR

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RECEIVED MARCH 29, 1926 PUBLISHED NOVEMBER 5, 1926

In the extensive literature[1] relating to the chemistry of sulfur are found many allusions to the fact that small quantities of sulfur trioxide are formed during the ordinary burning of sulfur, but up to the present time neither a satisfactory theory nor consistent analytical data concerning the quantities of sulfur dioxide and sulfur trioxide found in the gases of combustion has been offered. Kastle and McHargue,[1c] whose results are typical, report duplicate sulfur trioxide analyses which vary by 2% in a total of about 7%. Further, the percentage of sulfur recovered compared with the quantity burned varies from 94 to 107. A closer regulation of experimental conditions suggests itself as a corrective.

In the work here described the authors have attempted three objectives: (1) to burn sulfur in the vapor phase and within rather narrow temperature limits; (2) to secure consistent results in analyzing sulfur dioxide—sulfur trioxide mixtures in the presence of large excess of air or oxygen; (3) to make qualitative observations concerning the origin of the sulfur trioxide observed.

Burning Sulfur under Controlled Conditions

This was done in the following manner. The middle of a piece of glass combustion tubing 1 meter long and 2.5 cm. in diameter was placed in an ordinary three-unit electric combustion furnace. To the entering end of this tube was attached a drying train. This same end also allowed the admission of a thermocouple, one junction of which was near the burning

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[1] (a) Berthelot, *Ann. chim.*, [5] **22**, 422 (1881). (b) Hempel, *Ber.*, **23**, 1455 (1890). (c) Kastle and McHargue, *Am. Chem. J.*, **38**, 465 (1907). (d) Nestell and Anderson, *J. Ind. Eng. Chem.*, **8**, 258 (1916). (e) Ferguson, THIS JOURNAL, **39**, 364 (1917). (f) Norrish and Rideal, *J. Chem. Soc.*, **123**, 696 (1923).

sulfur. The effluent end of the combustion tube was attached to an absorption train to be described later. The sulfur, previously purified by four distillations, was placed in a test-tube of Pyrex glass, which was then sealed except for a pin-point opening. The sulfur tube thus prepared was placed within the combustion tube at about the middle of the furnace. Air or oxygen was then drawn through the apparatus while the temperature was slowly raised to about 460°, as indicated by the thermocouple. Under these conditions no sulfur could leave the sealed tube except in the vapor phase. The sulfur burned spontaneously at the pin-point outlet with a bright blue, jet-like flame of about 2 to 3 mm. long. This arrangement eliminated the possibility of liquid sulfur influencing the action. The total quantity of air or oxygen passed for a single run was 3 to 4 liters, while the duration of a single run was two to three hours. The quantities of sulfur used and the other data obtained are found in Table I.

Analysis of Gases Containing Sulfur Dioxide and Sulfur Trioxide

An analysis of the effluent gases of combustion obtained, as described above, was made by the iodine-absorption method. The gases from the combustion tube were passed through a train consisting of first, a series of glass bulbs containing 0.1 *N* iodine solution which absorbed the sulfur dioxide and part of the sulfur trioxide; second, a wash bottle containing a potassium iodide solution which retained any iodine carried from the first member of the train; and third, a Hawley filter[2] which caught and retained the sulfur trioxide fumes not held in the preceding solutions. At the close of each run the entire contents of all the units of the absorption train along with the washings from the inside of the combustion tube were placed in a 0.5-liter Erlenmeyer flask. The resulting solution was titrated to approximate neutrality by means of a 0.5 *N* sodium hydroxide solution.

This reduction of acidity lessened the probability of air oxidation of the hydriodic acid present. The solution was next titrated with 0.1 *N* sodium thiosulfate solution, using starch as indicator. After the sodium thiosulfate titration, phenolphthalein was added to the solution and the sodium hydroxide titration continued to an end-point. Obviously, the iodine consumed before addition of the thiosulfate solution represents sulfur dioxide

TABLE I

COMPOSITION OF GASES FROM BURNING SULFUR VAPOR IN AIR AS OBTAINED BY THE IODINE-ABSORPTION METHOD

S burned, g.	SO_2 found, g.	SO_3 found, g.	S recovered, g.	S as SO_2, %	S as SO_3, %	Total S recovered, %
0.2657	0.5101	0.0254	0.2654	96.07	3.83	99.90
.2454	.4739	.0209	.2455	96.64	3.42	100.06
.2522	.4846	.0241	.2522	96.16	3.82	99.98
			Av.	96.87	3.69	99.98

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[2] Hawley, *Eng. Min. J.*, **94**, 364 (1912).

changed to sulfur trioxide, while the total sodium hydroxide represents sulfur dioxide plus sulfur trioxide. From these data, the sulfur trioxide and the sulfur dioxide present in the gases of combustion are easily computed.

From a stoichiometric viewpoint the above data are in far better agreement than any similar data previously reported. Incidentally, we may add that results of the above consistency were obtained only after extended effort and then only when the Hawley filter was used on the end of the absorption train. The facility with which sulfur trioxide, even in the small concentrations here represented, would pass through absorbing solutions for as much as the distance of a meter was quite surprising. Also, we noted that some iodine was retained on the Hawley filter.

Qualitative Observations

1. During the progress of nearly every run, drops of a viscous liquid having the appearance of sulfur trioxide formed in the cooler parts of the tube. These drops disappeared during the "sweeping out" process concluding each run.

2. Whenever the temperature of the furnace rose, the rate of emission of sulfur vapor, and also the size of the flame increased. Whenever the flame exceeded about 5 mm. in length, sulfur passed through the flame and was deposited in the cooler parts of the tube. This solid sulfur reacted with the viscous, liquid sulfur trioxide to give a mixture of bright blue, yellow and brown crusts such as form when sulfur and sulfur trioxide react. (None of the data recorded in the table are based on runs where these phenomena were observed.)

These two observations show that some sulfur trioxide is formed before the effluent gases reach the absorption device.

3. Supposing that the walls of the combustion tube might catalyze some action, such as $2SO_2 + O_2 = 2SO_3$, runs were made in which sulfur was omitted and sulfur dioxide was mixed with the entering oxygen or air. In some cases moisture was added to incoming gas mixtures. In no case was any sulfur trioxide found (by the Hawley filter). These results indicate that sulfur trioxide is not formed after leaving the flame by catalytic oxidation of sulfur dioxide. These experiments offer no evidence concerning secondary actions that might follow from introduction of sulfur trioxide and free sulfur from the flame.

Summary

1. We have described a device for burning sulfur vapor in the absence of liquid sulfur at 460°.

2. We have shown by absorption in the iodine solution that about 3.6% of the sulfur in the gases of combustion is present as sulfur trioxide and the remainder as sulfur dioxide.

3. We have qualitatively shown that under experimental conditions, sulfur trioxide is not formed by catalytic action of the vessel walls.

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THE MANIFESTATION OF INTERFACIAL FORCES IN DISPERSED SYSTEMS

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Received April 26, 1926 Published November 5, 1926

For the present purpose, a definition of heterogeneity will be confined to that degree of this state lying outside of the molecular or ionic and will therefore comprise colloidal dispersions. As an introduction, it will be briefly recalled that heterogeneous dispersates differ from the homogeneous in their behavior under capillary shear.[1] While homogeneous fluids within certain fairly wide limits of applied stress (pressure) conform to Poiseuille's equation in capillary shear, heterogeneous systems depart from this and Hooke's law in yielding parabolic P/V relationships according to the proximate equation

$$P/V^{\phi} = \text{constant} \qquad \text{(A)}$$

where ϕ is fractional and less than unity. A further difference between homogeneous and heterogeneous systems lies in the fact that many if not all of the latter show a property of static rigidity which is exponentially variable with the applied stress.[2] The complete equation defining the behavior of a plastic on shearing through a capillary has been shown[3] to be

$$\pi R^4 g(P - fe^{-PR/2l})/8V^{\phi}l = \eta \qquad \text{(B)}$$

where the static rigidity or elasticity ("yield value") at infinite rest is denoted by f, e = log base, and the negative exponent in the numerator corresponds to the stress applied under the conditions defined. It will be noted that f remains constant under all conditions of stress, but the entire exponential term in the numerator, which may be denoted as F the elasticity or yield value under any condition, diminishes as the stress

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[1] de Waele, *J. Oil Colour Chem. Assoc.*, **6**, 33 (1923).

[2] de Waele, *Kolloid-Z.*, **36**, 332 (1925).

[3] Criticisms have been advanced as to the dimensional validity of Equation B on the score of the exponent of V in the denominator. Consideration of the underlying principles of the mechanism of the extrusion of heterogeneous dispersates to be found in the last reference will show that of the two variables, that corresponding to V or the volume in cc. per sec. cannot in itself have the identity demanded by the definition of viscosity, since it does not correspond with an efflux volume that has been extruded under a continuous velocity gradient, but comprises both sheared and slipping zones. The equation may be written in the form $\pi r^4(P - fe^{-PR/2l})/8\eta l = V^{\phi} = Q$. Thus, of the total efflux extruded as a mixed regime, that fraction only corresponding to V^{ϕ} or Q has accounted for the loss of hydrostatic pressure applied as shear. The application of the exponent ϕ then must be regarded as being merely equivalent to the use of a factor.