importance might be made, but it seems undesirable to make changes too frequently.

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SOME PHYSICAL CONSTANTS OF SULFUR TRIOXIDE. MELTING AND BOILING POINTS, DENSITY, COEFFICIENT OF EXPANSION AND MOLECULAR WEIGHTS.[1]

BY D. M. LICHTY.

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The existence of two forms of sulfur trioxide, distinguished as the α- and β-forms, has been generally recognized. The same method of distinguishing the two forms will be used in this paper. The former has a definit melting point, while the latter probably does not melt at all under atmospheric pressure, but on being heated changes to vapor, whose condensation gives rise to the α-form, which may later go over into the β-form.

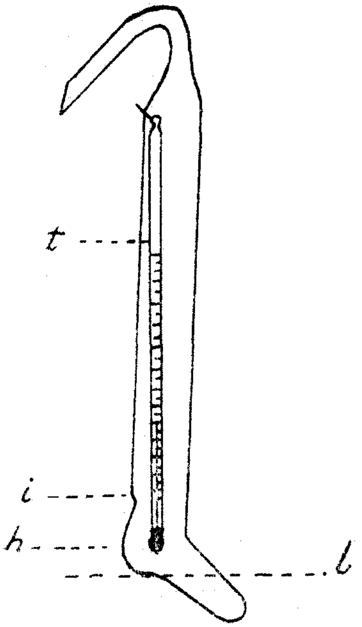

Fig. 1.—First made by Mr. H. P. Eastman, to whom I wish here to acknowledge my indebtedness.

The sulfur trioxide used in this work was prepared by repeated distillation of it, from phosphoric anhydride, in an evacuated and sealed apparatus like that previously described.[2] For the purpose of taking the melting and boiling points, the receiver was given the form shown in Fig. 1. When the trioxide had been quite thoroughly dehydrated, there was distilled enough of it to fill the receiver to the line *l*. Dry air[3] was now slowly admitted to atmospheric pressure, and then the neck of the receiver was bent through considerably more than a right angle and sealed off.

Melting Point and Boiling Point.

On being cooled to 10 or 12°, such a specimen froze to a mass of what looked like parallel lying rods. After slight

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[1] Read at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

[2] THIS JOURNAL, **30,** 1835–37.

[3] *Ibid.*, 1837.

melting these became embedded in the resulting liquid, which made possible a good contact with the bulb of the thermometer, when the container was inclined so as to bring its charge into the heel *h*. The dent *i* served to keep the thermometer bulb out of contact with the walls of the vessel. Repeated tests with three different samples of trioxide gave the same value for the melting point. The passage of a part of one sample over into the β-form of crystals, after the melting point had been repeatedly measured, did not modify the melting point of the remainder. One of the three samples was prepared from commercial trioxide obtained from J. T. Baker & Co., the other two from trioxide from Kahlbaum. The corrected melting points, taken when the room temperature was not above 17.5°, are given in Table I, and show that by the method used, sulfur trioxide of uniform purity[1] can be obtained.

As soon as the melting point measurements of a sample were completed, its boiling point was taken at the reigning atmospheric pressure. The curved neck of the container served to prevent any sulfuric acid formed in its outlet from flowing back into the trioxide. The formation of β-crystals in one sample during the boiling had no effect on the boiling point, which had been already repeatedly read. The boiling points found are given in column 3 of Table I, the corresponding pressures in column 4.

TABLE I.

No.	M. P.	B. P.	Pressure, mm.
1	16.80°	44.23°	740.7
2	16.78°	44.21°	740.0
3	16.80°	44.36°	744.5
	Mean, 16.79°		

The melting points given in the literature on sulfur trioxide vary from 14.8°[2] to 29°.[3] Knietsch[4] found it at 17.7°. In text-books 14.8° or 15° is quite generally given.

For small successive increments in the pressure, totaling about 20 mm., the rise in the boiling point will be approximately proportional to the increase in pressure. Since a rise of 4.5 mm. in pressure causes a rise of 0.15° in the boiling point, one of 20 mm. would cause a rise of 0.67°. At 760 mm. pressure, the boiling point of sulfur trioxide is therefore about 44.88°. The value generally given is 46°.[5] The first two samples were boiled over a small free flame, the third by heating in a water bath at 60–65°.

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[1] For evidence of purity, see THIS JOURNAL, **30**, 1841–42.

[2] Weber, *Pogg. Ann.*, **159**, 313; Rebs, *Ann.*, **246**, 379.

[3] Buff, *Ann. Supl.*, **4**, 151–2.

[4] *Ber.*, **34**, 4100.

[5] Schultz-Sellak, *Ber.*, **3**, 215; Buff, *loc. cit.*; Weber, *loc. cit.*

It was the character of the two results, namely, a decidedly higher melting point and a lower boiling point than those generally accepted, both evidences that my material possessed a higher degree of purity than that upon which the usually accepted melting point and boiling point are based, that induced me to study other physical properties of sulfur trioxide.

Density and Coefficient of Expansion.

With 158.253 grams (corr.) of α-sulfur trioxide enclosed in a flask with a graduated and calibrated neck, data were obtained for calculating its densities and coefficients of expansion. In Table II are given the observations, and the densities referred to water at 4°; in Table III, the coefficients of expansion found by me as well as some found by others.

TABLE II.

Temp.	11.8°	15°	20°	25°	30°	35°	40°	48°
Vol. in cc.	81.333	81.480	82.297	83.204	84.187	85.225	86.363	88.305
Density	1.9457	1.9422	1.9229	1.9020	1.8798	1.8569	1.8324	1.7921

Schenck[1] gives the densities at 11° and 35.3° as 1.944 and 1.849, respectively.

TABLE III.—COEFFICIENTS OF EXPANSION.

		By Schenck.[1]	
Temp.	Coeff.	Temp.	Coeff.
11.8– 15°	0.000676	....	....
15 – 20°	0.002005	....	....
20 – 25°	0.002204	11.0–35.3°	0.0023
25 – 30°	0.002363	35.3–60.4°	0.0030
30 – 35°	0.002466	60.4–78.3°	0.0031
35 – 40°	0.002671	78.3–80.3°	0.0028
40 – 45°	0.002754[2]	80.3–100°	0.0028
40 – 48°	0.002805	....	....
11.8– 35°	0.002066	....	....
		Schultz-Sellak.[3]	
25 – 48°	0.002665	25.0–45.0°	0.0027

According to Schenck,[4] α-sulfur trioxide attains constant volume very slowly at 35.3°, whether approached from a higher or a lower temperature. This observed peculiarity he ascribes to a slow molecular change. In one instance, for example, on cooling from 60.4°, constancy was not reached in 2 hours, while at 60.4° and 78.3° constancy was always reached in 20 to 25 minutes. The addition of sulfuric acid was observed by him to hasten the attainment of constancy of volume at 35.3°. His observations were made with 4.872 cc. in a dilatometer whose capillary was graduated in 0.01 cc. With a dilatometer containing a sample of about

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[1] *Ann.*, 316, 1.

[2] By interpolation.

[3] *Ber.*, 3, 215.

[4] *Loc. cit.*

84 cc. of α-trioxide, whose free surface lay in a capillary not over 2.5 mm. in diameter, and such, therefore, that 2 mm. of its length scarcely represented 0.01 cc., the writer observed no change in volume in a bath at 35° after 50–60 minutes, whether the temperature rose from 20° or fell from 45°. The trioxide had been kept at the starting temperature during two or more hours before the test. Considering the quantity of trioxide used, it seems fair to conclude that there is no peculiarity connected with its change in volume as its temperature approaches 35.3°. It may be added that at 20° and 25° constant volume was readily reached whether these temperatures were approached from above or below.

That an unusual change does occur in α-sulfur trioxide as its temperature rises, is shown by the rapid increase in its coefficient of expansion and the consequent rapid decrease in its density. The most rapid change observed in its coefficient of expansion occurs between 15° and 20°, the temperature interval in which the freezing point lies. The successive increments in the significant figures in the coefficient for successive increments of 5° in temperature are 329, 191, 159, 103, 105, and 83, and show a decreasing value with rise in temperature. The greatest observed change in the density occurred, of course, where the coefficient of expansion is the highest.

Molecular Weight.

1. Historical.—The molecular weight of sulfur trioxide in a state of vapor has long been known to be about 80, corresponding to the formula SO_3.[1] From the depression of the freezing point of phosphorus oxychloride,[2] caused by sulfur trioxide, Oddo[3] found the molecular weight as given in column 3, Table IV. Although he found, experimentally, 70.16[4] for the value of the molecular depression constant, he used 69 in his calculations.

TABLE IV.—MOLECULAR WEIGHTS.

Conc.	Depression.	Mol. wt.	Mol. wt.[5]
	α-Trioxide in separate portions of solvent.		
2.2902	2.096	75.4	83.95
2.0643	1.882	78.1	80.96
	β-Trioxide in a series.		
2.0360	0.843	166.6	185.5
3.1505	1.347	161.38	179.7
3.8400	1.682	157.58	175.5
	Mean,	161.85	180.2

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[1] Schultz-Sellak, *loc. cit.*; Perman, *Proc. Roy. Soc.*, **48**, 45.

[2] F. P. of the phosphorus oxychloride given as —1.782° (*Gazz. chim.*, 31, II, 139, 148).

[3] *Ibid.*, **163**, 165.

[4] *Ibid.*, 141.

[5] Walden's constant, page 12.

These results naturally led to the conclusion that the β-variety of sulfur trioxide is a polymeric form of the α-variety. Oddo called it disulfuric anhydride.

It is interesting to note that the α-variety used by Oddo, although sealed in a tube, changed at room temperature to the β-variety, and that to preserve it unchanged, he kept it in a water bath at 30°. It was made from Kahlbaum's crystallized fuming sulfuric acid by distillation from a retort into a receiver sealed to the former and kept at 27–30°. The receiver was pipet-like in shape, its projecting end being drawn to a length of 10 cm. and a diameter of 1 mm., and, in charging the cryoscopic tube, served as a kind of Beckmann pipet. The apparatus used by Oddo for preparing the β-trioxide was like that used for preparing the α, except that the open end of the receiving tube was ground to hold a valve of sulfuric acid during the preparation and afterwards to receive a well fitting stopper. At 15–18°, the temperature at which the receiver was kept during the distillation, the distillate solidified to a fibrous mass, which however was not immediately polymerized, as the molecular weight of the recently prepared product showed. Only after the sealed-off and securely stoppered receiver stood[1] until its wall was covered with long asbestos-like crystals, did the molecular weight found indicate complete polymerization (Table IV). From this container, he afterwards pulled small portions of the crystals by means of a hook of clean bright iron wire, and placed them in separate weighing glasses. This procedure necessarily exposed a large surface of the brush-like masses to moisture, which may have had some effect on the values found for the molecular weight.

2. *Experimental.*—That there exists a crystallin asbestos-like sulfur trioxide (which I will call β-trioxide), whose molecular weight is the same as that of the persistently liquid or α-trioxide, will appear from the results of my research presented below. To collect the trioxide in small samples suitable for molecular weight determinations, the receiver was made out of an ordinary 20 cm. test tube in which were placed, in an inverted position, a number of weighed glass bulbs, distinguishable by differences in length of stem and by a straight, a zigzag or otherwise irregular stem. The bulbs used for collecting the α-trioxide were well dried and filled with dry air before they were placed in the receiver. There they were repeatedly rinsed with the trioxide, a process which was easily accomplished by proper variation of the pressure in the distilling apparatus. After each rinsing the liquid was poured back upon the dehydrating material and redistilled. To obtain the β-trioxide the bulbs were not especially dried or rinsed. In this way enough moisture

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[1] In order that the sulfuric acid, formed by union of sulfur trioxide and water in the capillary space around the stopper, should not flow upon the crystals, the tube was kept in an inverted position. The acid also prevented ready entrance of moisture.

was left in them, probably mainly in the adsorbed condition, to cause **ready change of the** α- to the β-**variety.** These samples will be referred to as β.

In addition to the β-form collected in bulbs, there were used two other sets of samples. One set was obtained by permitting the vapor from ordinary solid trioxide, contained in a flask, to condense in a whorl of smaller flasks sealed to it. These samples consisted of long lustrous needles and will be referred to as β_2. The other set, β_3, was obtained from a bunch of crystals hanging like a rod from the apex of the neck of a flask of sulfur trioxide, most of which was liquid. These crystals had the usual asbestos-like luster of the ordinary solid trioxide. When they were removed from the flask they were flexible, but after a very few minutes of exposure to the air they lost their distinctly crystallin appearance and became so brittle that they were easily broken with the fingers. Two pieces were sealed up in long necked flasks.

The phosphorus oxychloride was prepared by the oxidation of phosphorus trichloride by means of potassium chlorate, the addition of the latter being continued until the product turned slightly yellow from separated chlorine.[1] Careful fractionation yielded a large fraction of practically constant boiling (106.4–106.7°) product. From this product there were frozen out four small samples. They froze at 1.132 to 1.141°, while the original froze at 1.114°.

The remainder of the distillate was subjected to fractional distillation under 40–45 mm. pressure, in a stream of air, dried by means of sulfuric acid and phosphoric anhydride. Only that oxychloride which was carried from the receiver in the form of vapor by the exhaust stream could come in contact with anything but glass. The fractions, of which there were 23, were collected by the aid of the device sketched in Fig. 2. By means of the three-way cock, which was lubricated with oxychloride, the distillate could be turned into the one or the other of the tubes *a* and *b*. When a sufficiently large sample had been collected in one of them, proper manipulation of the three-way cock and either *c* or *d* brought the pressure in the receiver to that of the atmosphere, which then permitted ready replacement of the charged receiver by an empty one. The charged receiver was at once sealed in a blast lamp flame. The freezing points (corr.) of fractions 1, 10, 16 and 23 were 0.885, 1.132, 1.174 and 1.102°, respectively, while the freezing point before fractionating was 1.114°. The first or lowest boiling fractions evidently contained an impurity of greater volatility than the oxychloride, and the last or highest boiling fraction one of less volatility.

The cryoscopic work was carried out in a Beckmann apparatus provided with an electromagnetic stirrer. The bulbs, containing the α-tri-

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[1] Dervin, *Compt. rend.*, 97, 576; Oddo, *loc. cit.*, 138.

oxide, were broken either by means of the stirrer or by pressure applied with a long glass rod. The latter procedure made possible the entrance of moist air into the freezing vessel, and also resulted in the loss of a small amount of solvent. The errors so introduced were certainly too small to affect the results appreciably. The bulbs of β-trioxide were generally very slightly cracked just before they were dropped into the apparatus.

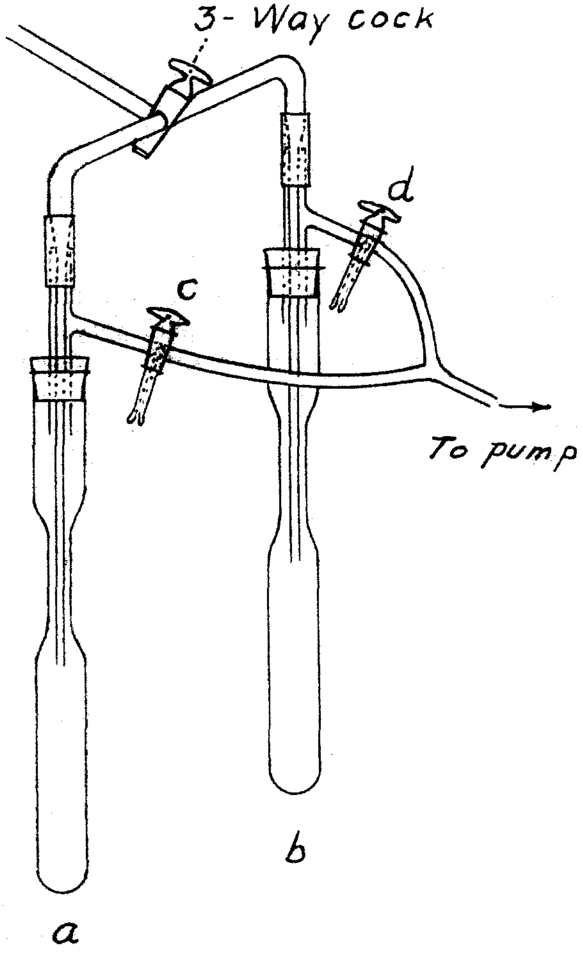

Fig. 2.

With phosphorus oxychloride, whose freezing point was about 1.15° (1.144–1.157°) instead of —1.782, the freezing point of that used by Oddo, the results given in Tables V and VI were obtained. The values given in the third column were obtained with $K = 69$, those in the next column with $K = 76.8$, a value recently published by Walden,[1] and obtained with oxychloride freezing at +1.25°. The β-variety had been kept for two to four weeks before it was used.

For convenient handling of the other samples of solid trioxide, the neck of each flask was constricted about 10 cm. from its body and then sealed off about 13 cm. from its body. After each flask had been weighed, its neck was warmed near the seal to vaporize traces of crystals which may have been deposited there. As soon as the neck was cold, it was carefully broken open near the end to admit about 30 grams of phosphorus oxychloride of known freezing point, or a solution of β_2 or β_3 in

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[1] *Z. anorg. Chem.*, 68, 307–16.

oxychloride, of known concentration and freezing point. Following the addition of the solvent, the flask was sealed at the constriction. If only oxychloride had been added, the increase in weight was the weight of the solvent. The greater part of the solution was now transferred to the freezing vessel, and while this solution was cooling, the flask was cleaned and dried and later it and all of the severed tubing were weighed. The difference between the first and last weights was the weight of solute. Thus were obtained data for calculating the concentration of the solution.

TABLE V.[1]

Variety.	Conc.	Depr.	Molecular weights.	
β	0.817	0.731°	77.07	85.80
β	1.479	1.343	76.00	84.61
β	2.154	2.019	73.60	81.94
α	2.902	2.796	71.63	79.85
α	3.637	3.595	69.79	77.69
		Means of first three values,	75.56	84.11
		Means of all values,	73.62	81.98

TABLE VI.[2]

Variety.	Conc.	Depr.	Molecular weights.	
α	0.882	0.813°	74.82	83.30
α	1.540	1.435	74.08	82.28
β	2.297	2.214	71.57	79.68
β	3.152	3.139	69.28	77.13
		Means of first two values,	74.45	82.79
		Means of the four values,	72.44	80.60

If the same solvent was to be used a second time, as much as possible of the solution was added to a second weighed sample of trioxide of the same source as that already in the solution. Weighings then followed in the order just stated. This time the increase in weight was the weight of solution added, but from this and the proportions of solvent and solute which it contained, the weights of these in the solution added were calculated. After having found the weight of the newly added portion of solute, the concentration of the new solution was found.

The results with samples β_2 and β_3 are given in Table VII.

TABLE VII.—WITH β.

No. of prep.	Conc.	Depr.	Molecular weights.	
2	0.441	0.494°	61.65	68.63
	A series of two.			
2	0.483	0.491°	67.92	75.61
2	0.957	1.029	64.71	72.04
	A series of two.			
3	0.263	0.224°	81.1	90.28
3	0.519	0.472	75.95	84.55

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[1] 0.177 to 0.218 g. trioxide in 26.7 g. oxychloride.

[2] 0.180 to 0.224 g. sulfur trioxide to 27.26 g. oxychloride.

The values for the molecular weights given in Table V and VI show that the two varieties of sulfur trioxide used, behave essentially alike in phosphorus oxychloride, and that the molecules of both are represented by the formula SO_3. While the first three pairs of molecular weights of the β-variety recorded in Table VII are not in good agreement with 80, they certainly do not lead to 160 as the molecular weight. The values obtained with the β-trioxide which had been exposed to moist air are higher than any others found during this work. It may fairly be questioned whether this is due to some association, to the somewhat complicated experimental process, or to partial combination with water.

These points and others regarding the physical changes which sulfur trioxide undergoes, as well as the relation between the α- and β-forms, are now under investigation.

Summary.

1. In addition to values for the melting and boiling points of α-sulfur trioxide, which seem to be more trustworthy than those heretofore obtained, new values for the density and the coefficient of expansion were obtained.
2. Nowhere between 11.8° and 45° was there observed a slow attainment of constancy of volume at fixed temperature, such as Schenck observed at 35.3° in α-trioxide.
3. It has been shown that there exists a solid sulfur trioxide, apparently identical with the ordinary solid form, and designated the β-form, whose molecular weight in phosphorus oxychloride is 80, the same as that of the persistently liquid α-variety.

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THE ATOMIC WEIGHT OF PALLADIUM.

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Berzelius in 1828 first determined the atomic weight of palladium by decomposing potassium palladiochloride in an atmosphere of hydrogen. Since that time twelve investigators have worked on this problem, nine of whom have used this method of analysis, the other three reducing by electrolysis. Two have determined chlorine also, but the vast majority of the work has been the reduction of a salt in hydrogen at an elevated temperature.

It was thought desirable to try to throw out the metal from a solution of some salt, collect the precipitate upon a filter and weigh, thus getting a ratio without using a high temperature and thereby avoiding danger of volatilizing palladium. The idea of a Munroe crucible also eliminated