VAPOUR PRESSURE, SURFACE TENSION AND DENSITY OF OSMIUM TETROXIDE.

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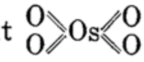
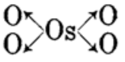
Introduction.

There are two different theories on the constitution of osmium tetroxide. Sugden says that it must be a semi-polar compound while Sidgick asserts that it must be a covalent compound. Sidgick states, according to his valency theory, as follows. As the elements of first subgroup of 8th group, iron, ruthenium and osmium, have eight electrons more than an innert gas, they might be expected to show the valency of eight, especially in 8-covalent compounds which could be formed directly without coordination. But by the covalency rule it appeares that the maximum covalency of an atom is 2 for hydrogen, 4 for the elements from lithium to fluorine, 6 for the elements from potassium to bromine, and 8 for the elements from rubidium to uranium. So the elements which can form 8-covalent compounds directly without coordination are ruthenium and osmium only. We find that osmium formes an octafluoride OsF_8 which is very stable and volatile compound, having the vapour pressure 552.5 mm. at 38.0°C.

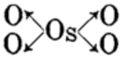
It is at least probable that we should assign a similar 8-covalent structure to osmium in the tetroxide OsO_4, and write it  $\begin{smallmatrix}O\\O\end{smallmatrix}\!\gg\!Os\!\ll\!\begin{smallmatrix}O\\O\end{smallmatrix}$ and not  $\begin{smallmatrix}O\nwarrow\\O\swarrow\end{smallmatrix}\!>\!Os\!<\!\begin{smallmatrix}\nearrow O\\\searrow O\end{smallmatrix}$. This is supported by the fact that ruthenium, which also can be 8-covalent, likewise forms a volatile tetroxide, while iron, which is limited to a covalency of six, does not.

But the result of the measurement of parachor by Sugden and the isolation of the compounds by Krauss which indicate that osmium tetroxide must be unsaturated coordination compound are strong objections to the covalency theory. Sugden got 154.0 as the parachor of osmium tetroxide using the data measured by Wartenberg. If we assume that the osmium has an octet, there must be four semi-polar links (or coordinate links according to Sidgick) in the molecule. And the value for osmium will be :

$$Os = 154.0-4\times 20.0+4\times 1.6 = 80.4\,.$$

On the other hand, if the molecule is analogous to OsF_8, and has four true double links, we should have, according to Sugden's values:

$$Os = 154.0 - 80.0 - 4 \times 23.2 = -18.8\,.$$

Sugden said that there is no other evidence of the value of parachor of osmium, but from rough data for the neighbouring elements it should be between 60 and 100. Hence he concluded that the formula  $\begin{smallmatrix}O\\O\end{smallmatrix}\begin{smallmatrix}\nwarrow\\ \swarrow\end{smallmatrix}Os\begin{smallmatrix}\nearrow\\ \searrow\end{smallmatrix}\begin{smallmatrix}O\\O\end{smallmatrix}$ is correct. According to Sidgick, Sugden's argument seems at first sight conclusive, but on close examination it will be noted that there is some difficulty. In the first place, the close agreement between theory and observation which he obtained with the other substances cannot be adduced here, for lack of other data as to the parachor of osmium. Secondly, in all the substances for which the agreement was found to be close, there is the evidence of the presence (in every atom except hydrogen) of an octet.

Hence Sidgick said that there is no proof that his values hold good when the valency group exceeds eight, it should be expected that this would affect the molecular volume, and that in addition to the constitutive factors of the parachor already mentioned, another would be needed to allow for the change in size of the valency group. This would presumably be negative: the high stability and screening effect of the octet as compared with any other arrangement of the outer electrons suggest that when there is a larger valency group the external field is stronger, and the attached atoms are more closely held; just as it is found that in zinc, where the group next to the valency electrons is eighteen, the volume is much smaller than in calcium, where it is eight. In osmium tetroxide, if the metal is really eight covalent, there is an extreme case of this effect, since the valency group has expanded from eight to sixteen, and it may be concluded that if this occurred, it would considerably reduce the parachor, so that the fact that such a formula would give a negative value for the parachor of osmium if no allowance is made for the change in the valency group, is not conclusive evidence that the formula is wrong.

As the second evidence that supports Sugden's theory F. Krauss and D. Wilken(1) reported the isolation of following compounds which indicate that osmium tetroxide is unsaturated co-ordination compound, namely:

$K_2[OsO_4(OH)_2]$, $Cs_2[OsO_4(OH)_2]$, $(NH_4)_2[OsO_4(OH)_2]$,

$Ba[OsO_4(OH)_2]$, $Cs_2[OsO_4, F_2]$, $Rb_2[OsO_4, F_2]$,

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(1) *Z. anorg. allgem. Chem.*, **145** (1925), 151.

This fact is a strong objection to Sidgick's theory. In short, this question is not yet solved. It is very desirable to measure the parachor of osmium octafluoride. But the measurements of surface tensions and densities are very difficult according to its nature. But if we assume that osmium octafluoride has the same surface tension and density as osmium tetroxide, so we shall find as its parachor 212. Hence the parachor of osmium is

$$212.0-25.7\times 8 = 6.4 .$$

The author wanted to carry out more accurate measurements on parachor and measured surface tensions and densities of osmium tetroxide between its melting point and boiling point. Krauss also reported the enantiotropic isomerism of ruthenium tetroxide and osmium tetroxide. The author wanted to investigate this point thoroughly and measured vapour pressure of osmium tetroxide by the statical method using a spring manometer.

Existence of Enantiotropic Isomers of Osmium Tetroxide. The chief points by which Krauss asserts the existence of enantiotropic isomers of osmium tetroxide are as follows.

(I) Existence of white and yellow isomers. The melting point of the white one is 39.5°C. and the yellow is 41.0°C.

(II) Different vapour pressure of them.

(III) Formation of both compounds by raising or lowering the temperature.

But the present author could not recognize isomers by his experiments which will be described in details in the following lines.

(I) By Krauss osmium tetroxide obtained by heating the metal in oxygen stream is crystals of white needles and melts at 39.5°C. It solidifies in light yellow mass on cooling. When heated again, the solidified yellow mass does not melt at 39.5°C., but melts at 41.0°C.

According to the author's results, osmium tetroxide obtained by sublimation is white needles, and by heating it melts to a yellow transparent liquid. It solidifies in transparent light yellow mass or white opaque mass, according to its quantity and its cooling velocity. The melting point was observed under a microscope which is kept in a thermostat providing a thermometer standardized at P. T. R. The sublimated white needles did not melt at 39.5°C., but melted at 40.6—40.7°C. The solidified light yellow mass gave the same melting point.

(II) Krauss measured vapour pressures up to its melting point by Hüttig's(1) method and indicated that the white compound has higher vapour pressure than yellow as follows.

White osmium tetroxide.

I		II		III	
0°	2.0 mm.	0°	2.0 mm.	0°	2.0 mm.
10°	3.5	13°	4.0	8°	3.0
18°	5.0	31°	7.5	18°	5.0
29°	7.0	34°	8.5	24°	6.0
36°	9.0			32°	8.0

Yellow osmium tetroxide.

I		II		III	
0°	0.5 mm.	0°	0.5 mm.	0°	0.5 mm.
12°	2.0	8°	1.5	18°	2.5
18°	3.0	16°	2.5	23°	4.0
28°	5.0	31°	6.0	26°	4.5
35°	7.5			36°	8.5

His result of each experiment shows good coincidence and both vapour pressure curves coincide at 41.0°C. But it will be seen later that there are wide differences between these and the author's results, which have been obtained by statical measurements. So the author considers that the above result may not represent the saturated vapour pressures.

(III) Further by Krauss the yellow osmium tetroxide changes into the white form in liquid air and becomes very breakable with a glass rod. This white form also melted at 39.5°C. According to the author's result, however, the yellow form did not change its colour by leaving in liquid air for twenty hours and melted at 40.6°C.

Therefore, the enantiotropic isomerism of osmium tetroxide will be denied by the present author.

Experimental.

Measurement of Vapour Pressure of Osmium Tetroxide. Vapour pressures were measured by Ruff and Tschirch(2), and Wartenberg.(3) The values

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(1) *Z. anorg. allgem. Chem.*, **114** (1920).

(2) *Ber.*, **46** (1913), 929.

(3) *Ann.*, **440** (1924), 97.

measured by Ruff using the dynamical method of A. Smith and A. Merzies⁽¹⁾ are as follows.

Temperature °C.	95°	115°	125°	135°
Pressure mm.	275	482*	640.4	779

The values measured by Wartenberg extend over a wide range above and below the melting point. He measured vapour pressures of solid osmium tetroxide by dynamical method passing the stream of ozone at the temperatures 0°, −19.6° and −38.0°C.

Temperature °C.	0°	−19.6°	−38.0°
Pressure mm.	0.775	0.115	0.0137

The empirical formula is

$$\log P_{atm} = -13500/4.57\,T + 7.83\,.$$

Therefore the mean heat of sublimation is 13500 cal.

The values of vapour pressures of liquid osmium tetroxide were obtained by the dynamical method of A. Smith.

Temperature C°.	40.2	51.0	51.6	62.0	62.2	67.8	91.0	96.2	96.8	132.0	136.4
Pressure mm.	11.0	32.0	33.0	59.5	61.0	79.0	205.4	250.4	258.4	714.6	757.4

The August's empirical formula is

$$\log P_{atm} = -10100/4.57\,T + 5.49\,.$$

He gave 40.1°C. as the melting point and 129.0°C.** as the boiling point from the above values.

The author carried out the following experiment in order to obtain the more accurate values, as there are marked differences between the values of Ruff and Wartenberg.

Preparation of Osmium Tetroxide. It was prepared by heating the metal in oxygen stream. The sublimated tetroxide condenses at the cold part. It is necessary to shut off the moistures, as the tetroxide decomposes by small quantity of water giving the violet substance. (It may be osmium dioxide).

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(1) *J. Am. Chem. Soc.*, **32** (1920), 907.

* We find in the original paper the value 182 instead of 482.

** The melting point should be above 136.4 according to vapour pressures.

Method of Measurement. As the tetroxide has a strong oxidizing power and attacks mercury violently staining its surface, so it is impossible to measure pressures directly with mercury. Therefore the author used a glass spring manometer. On its preparation and employment he owes much Mr. K. Arii,⁽¹⁾ Assistant Professor of Tohoku Imperial University, and wishes to express his sincere thanks.

At first the whole apparatus is evacuated to a high vacuum such as 0.0005 mm. Hg. Then B, containing the tetroxide, is connected and by warming B the tetroxide is distilled into A, which is cooled with freezing mixtures of sodium chloride and ice, and the whole apparatus evacuated again (Fig. 1). Then sealed at a. After keeping the vacuum of 0.0005 mm. for 30 minutes the apparatus is sealed at b and c. The position of the needle d, that indicates the zero-point, is determined accurately by means of a fixed telescope, before introducing the tetroxide. The sensibility of a spring manometer used is 0.01 mm. Hg. The thermometer used was compared with a P.T.R. thermometer. The temperature of the thermostat is carefully regulated. For example, at 130°C. it is regulated within ± 0.02°C. The internal diameter of the mercury manometer is 15 mm. A cathetometer was used for the reading of pressure.

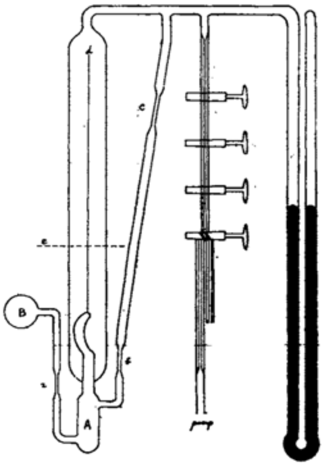

Fig. 1.

Results. There was no difference between the value after 2 hours and after 24 hours even at the lowest temperature 15.89°C. This proves that the time necessary to reach the equilibrium is very short. The values observed at each temperature are mean values of several observations for one day and night. Though osmium tetroxide is very stable compound, for precaution's sake, for example, from 70.15°C. the temperature was turned back to the previous temperature 60.10°C. and the value was compared with the former value in order to examine whether or not the dissociation takes place. Results are all negative. The pressures given in Table 1 were added necessary corrections. The relation between $\frac{1}{T}$ and $\log P$ is given in Fig. 2.

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(1) *Bull. of the Institute of Phys. and Chem. Research,* Vol. **8**, No. 7.

Table 1.

Temperature °C.	T	$\frac{1}{T}$	$P_{\text{mm.}}$	$\log P$
15.89	288.99	0.0034603	5.37	0.72997
21.92	295.02	33896	7.95	0.90037
26.95	300.05	33328	11.03	1.04258
31.97	305.07	32778	15.08	1.17840
36.99	310.09	32249	21.05	1.32325
40.01	313.11	31938	25.09	1.39950
43.02	316.12	31634	28.84	1.46000
47.04	320.14	31236	35.64	1.55194
53.07	326.17	30659	47.12	1.67321
60.10	333.20	30012	64.44	1.80916
70.15	343.25	29133	100.18	2.00078
85.22	358.32	27908	181.04	2.257776
100.29	373.39	26782	300.46	2.477784
115.00	388.10	25767	483.89	2.684751
130.00	403.10	24808	746.18	2.872848

Melting Point. The melting point determined by the relation between $\frac{1}{T}$ and $\log P$ is 40.7°C., and that from a microscopic observation is 40.6° or 40.7°C.

Wartenberg determined it as 40.1°C. from the vapour pressure curve, but this value is not correct, because his vapour pressure curve is somewhat different from author's result. The author can not agree with Krauss' values 39.5° and 41.0°C. owing to above reason.

Boiling Point. The value obtained by the graph is 131.2°C. Krauss' value is 134°C.

Empirical Formula below Melting Point. The August's formula has been obtained by an assumption that the heat of sublimation is constant in the range of temperature measured. The calculated values well coincide with the observed ones.

$$\log P = -\frac{2542.01}{T} + 9.51791 .$$

Table 2.

Temp.	15.89	21.92	26.95	31.97	36.99	40.01
$P_{obs.}$	5.37	7.95	11.02	15.08	21.05	25.09
$P_{calc.}$	5.27	7.97	11.11	15.33	20.90	25.07

Therefore the mean heat of sublimation is 11640 cal.

Empirical Formula above Melting Point. The relation between log P and $\frac{1}{T}$ was indicated in Fig. 2. It is composed of two straight lines intersecting at about 72°C. It cannot be decided with this result only, whether any change takes place in a liquid at 72°C. or the actual relation is not a straight line, but is a curve owing to gradual decrease of the heat of vaporization. If we assume a transition point at about 72°C. and apply August's formula, we obtain the following two relations.

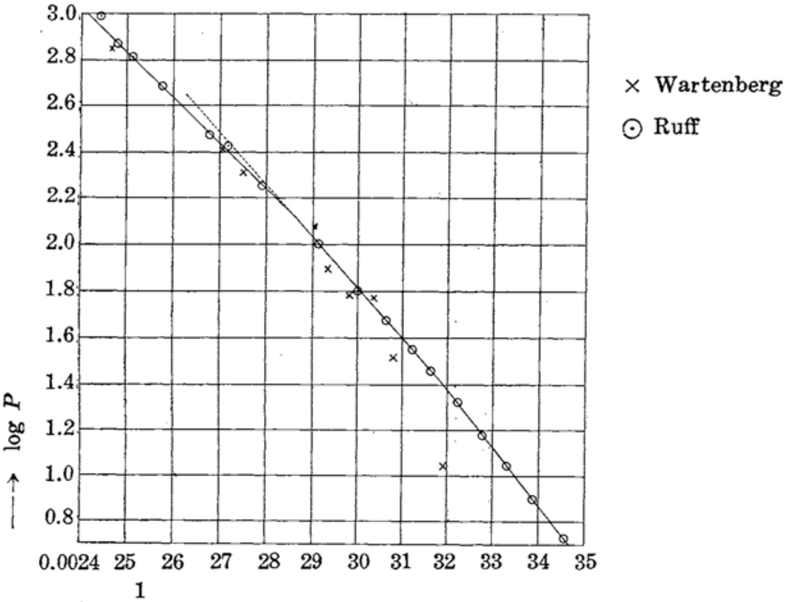

Fig 2.

$$\log P = -2167.22/T + 8.31658 \text{ (below 72°C)} \quad \ldots\ldots\ldots\ldots \quad \text{I}$$

$$\log P = -1977.39/T + 7.77704 \text{ (above 72°C)} \quad \ldots\ldots\ldots\ldots \quad \text{II}$$

The mean heat of vaporization will be obtained by these equations

$$\varDelta H = 9923 \text{ cal.} \qquad \text{(from I)}$$

$$\varDelta H = 9054 \text{ cal.} \qquad \text{(from II)}$$

The difference between them indicates the heat of transformation.

If the relation between $\log P$ and $\frac{1}{T}$ is not a straight line, the following Nernst's formula will be obtained.

$$\log P = -2592.66/T + 1.75 \log T - 0.0062662\,T + 7.26716\,.$$

Table 3 shows the comparisons between observed and calculated values.

Table 3.

C°	$P_{obs.}$	$P_{calc.}$ by I or II	$P_{calc.}$ by Nernst's formula
43.02	28.84	28.89	28.53
47.04	35.64	35.24	35.24
53.07	47.12	47.00	47.10
60.10	64.44	64.91	65.00
70.15	100.18	100.65	100.10
85.22	181.04	181.36	180.40
100.29	300.46	302.83	305.52
115.00	483.89	480.73	484.61
130.00	746.18	743.93	739.37

Further, the heat of vaporization in a narrow range of temperature is given by the following relation

$$\varDelta H = 4.5787 \frac{T_1 T_2}{T_2 - T_1} \log \frac{p_2}{p_1}\,.$$

As the range is narrow, $\varDelta H$ may be assumed as a heat of vaporization at a mean temperature instead of a mean heat of vaporization within this range of temperature.

The heat of vaporization at the melting point found from the above data by extrapolation is 10100 cal. The difference (1540 cal.) between the heat of sublimation (11640 cal.) and the heat of vaporization (10100 cal.)

shows the heat of fusion of osmium tetroxide. If we put the heat of vaporization at boiling point equals to that at 122.5°C., we get as Trouton's constant,

$$\frac{\varDelta H}{T} = \frac{8982}{404.3} = 22.2\,.$$

The heat of vaporization obtained by extrapolation, from Table 4 is $\varDelta H = 8700$ cal. and Trouton's constant becomes

$$\frac{\varDelta H}{T} = \frac{8700}{404.3} = 21.5\,.$$

Table 4.

Temperature range	Mean temperature	ΔH
43.02— 60.10	51.56	9859 cal
60.10— 85.22	72.66	9763
85.22—115.00	100.11	9129
115.00—130.00	122.50	8982

Thus we know that osmium tetroxide is a normal liquid at its boiling point.

By Wartenberg's measurement the heat of vaporization is 10100 cal. and the heat of sublimation is 13500 cal., so the heat of fusion is 3400 cal. This value coincides well with his value 3410±2% cal. obtained by a calorimetric observation.

The author cannot agree with 10100 cal. for the heat of vaporization at the melting point, because the heat of vaporization decreases as the temperature rises. The mean heat of vaporization between 51.0° and 62.0°C. using Wartenberg's value becomes 12170 cal. The difference between 13500 cal. and 12170 cal. is 1330 cal. So we know that the heat of fusion measured by Wartenberg is incorrect.

The vapour pressure at 25°C. obtained by interpolation is 9.91 mm. So

$$\mathrm{OsO_4(s)} = \mathrm{OsO_4(g)}\,, \qquad \varDelta F_{298.1} = 2572\,.$$

Further, the vapour pressure at 25°C. of the super-cooled liquid obtained also by extrapolation is 11.02 mm.

$$\mathrm{OsO_4(l)} = \mathrm{OsO_4(g)}\,, \qquad \varDelta F = 2509\,.$$

Thus the free energy change between solid and liquid tetroxide at 25°C. is

$$\mathrm{OsO_4(s)} = \mathrm{OsO_4(l)}\,, \qquad \Delta F_{298.1} = 63\,.$$

The specific heats of liquid and solid osmium tetroxide are unknown. If we assume that there are no differences between them.

$$\Delta H_0 = 1540 \text{ cal.}\,, \qquad \Delta F = 1540 + IT\,.$$

And $\Delta F = 0$ at 40.7°C., then $I = -4.91$.

Therefore $\mathrm{OsO_4(s)} = \mathrm{OsO_4(l)}\,, \quad \Delta F_{298.1} = 77\,.$

The results obtained from both calculations are concordant.

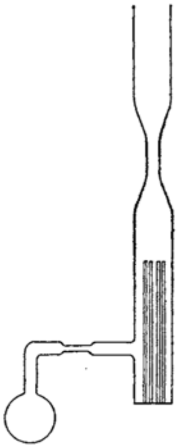

Fig. 3.

Measurement of Surface Tension. It was found by the above experiment that the decrease of the heat of vaporization of osmium tetroxide is remarkable with the rise of temperature. To ascertain this point on the one hand and to make sure Wartenberg's value on the other hand, its surface tensions and densities were measured. The measurements were carried out by the method of a capillary rise in a sealed tube. The glass capillary used has the same radius at its both ends. The radius of the wider tube was calibrated by measuring the weight and length of the mercury thread put into it. A good concordant value, 0.611 mm., was obtained.

The radius of the narrow one was calculated from the surface tension of benzene. Benzene used was "Kahlbaum zur Analyse" and dehydrated by sodium. The difference in height was 8.52 mm. at 25°C.

$$a^2 = \frac{H}{\dfrac{1}{b_1} - \dfrac{1}{b_2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where a^2 is the specific cohesion; H is the difference in height between the lowest points on the menisci; and b_1, b_2 are the radii of curvature at these points respectively. On the other hand

$$a^2 = \frac{2\gamma}{g(D-d)}\,.$$

where γ is the surface tension and D and d are the densities of liquid and vapour respectively. The surface tension of benzene is 28.23 at 25.00°C. The densities of liquid and vapour are 0.87345 and 0.00044 respectively. Hence

$$a^2 = 0.06592 \ .$$

If we put $\frac{1}{b_2} \doteqdot \frac{1}{r_2}$ in the equation (1), we obtain as $\frac{1}{b_1}$ 2.898. Hence b_1 is 0.345 mm. If we put $b_1 \doteqdot r_1$ and approximately calculate twice from Bashforth and Adam's table, we obtain $r_1 = 0.343$ mm. as a mean value. From these values of r_1 and r_2, we obtained the value of the surface tension of water as 70.93 at 34.32° while Richards' value by the method of the capillary rise is 70.72.

Osmium tetroxide was distilled into the tube which has two capillary tubes in it, Fig. 3, and the apparatus was sealed at a and kept in vacuum of 0.0005 mm. for 30 minutes and sealed at b. Thus we measured the capillary rise under its own vapour pressure. The apparatus was kept in a thermostat at a constant temperature and after 15 minutes several observations were carried out. The results obtained are shown in Table 5.

Table 5.

t° C.	$H_{\text{mm.}}$	a^2mm.^{2}	γ dyne/cm.	$\gamma^{5/6}$
43.00	3.05	0.02323	49.24	25.72
50.00	3.00	0.02284	48.10	25.23
58.00	2.97	0.02261	47.25	24.85
67.00	2.91	0.02214	45.87	24.24
75.00	2.88	0.02191	45.03	23.87
85.00	2.79	0.02120	43.15	23.04
95.00	2.72	0.02066	41.62	22.36
105.00	2.65	0.02021	40.13	21.69
115.00	2.58	0.01956	38.59	20.99
130.00	2.44	0.01845	35.79	19.71
150.00	2.33	0.01760	33.32	18.57

The surface tensions at 50.0° and 100.0°C obtained by Wartenberg are 49.8 and 42.2 respectively.

Generally there are a following relation in a normal liquid.

$$\gamma = \gamma_o(1-T_r)^{\frac{6}{5}}$$

where γ_0 is the surface tension at absolute zero and T_r is reduced critical temperature. On osmium tetroxide the relations between $\gamma^{\frac{5}{6}}$ and t show two straight lines of different inclinations intersecting at about 75°C. The discussion on the liquid state will be described later.

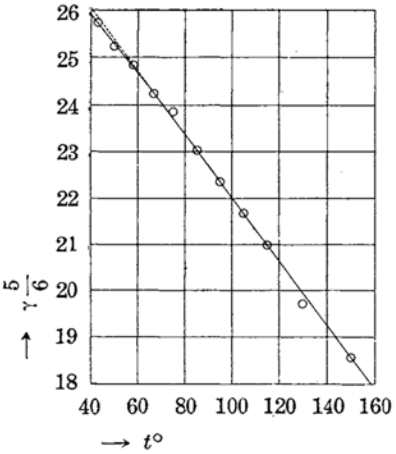

Fig. 4.

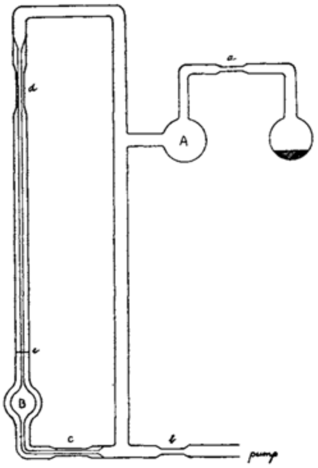

Fig. 5.

Measurement of Densities. The experiment was carried out only on liquid osmium tetroxide. After the sample was distilled into A, it was sealed at a and evacuated to vacuum of 0.0005 mm., and it was cooled with a freezing mixture of NaCl and ice and then sealed at b. By warming A the melt was transfered into B up to slightly above the mark e and was sealed at c and d. (Fig. 5). The capillary rise was read by a cathetometer with an accuracy of 0.01 mm. The apparatus was immersed in a thermostat. The capillary used has a length of about 7 cm. and its mean radius is 0.695 mm. by several observations with mercury. After the measurement ended, it was cut at a little above e and its capacity up to e is measured with water several times (V mm^3.). The coefficient of expansion of glass was taken as 2.5×10^{-5}.

The density of vapour is calculated by the following formula

$$d_b = 0.0122 \frac{M}{T_b}$$

$$\log_{10} \frac{d}{d_b} = 5\left(\frac{T}{T_b} - 1\right).$$

where d_b is the vapour density at the boiling point, M the molecular weight and T_b the boiling point.

The results are shown in Table 6. At the last column values of parachor are given, $p = \frac{M\gamma^{\frac{1}{4}}}{D-d}$. Its mean value was obtained only from the values above 75°C.

Table 6.

t °C	$V_{\text{mm.}^3}$	D	d	$D-d$	$(D-d)^{\frac{10}{3}}$	P
43.00	646.95	4.3224	0.0006	4.3218	131.46	156.2
50.00	651.14	4.2946	0.0008	4.2938	128.66	156.3
58.00	656.12	4.2620	0.0010	4.2610	125.42	156.8
67.00	661.75	4.2257	0.0012	4.2245	121.86	157.0
75.00	667.02	4.1923	0.0015	4.1908	118.67	157.5
85.00	673.49	4.1521	0.0021	4.1500	114.86	157.2
95.00	680.25	4.1108	0.0027	4.1081	111.04	157.6
105.00	687.04	4.0702	0.0036	4.0666	107.34	157.7
115.00	694.38	4.0271	0.0048	4.0223	103.49	157.9
130.00	705.81	3.9619	0.0074	3.9545	97.79	157.6
150.00	721.96	3.8733	0.0131	3.8602	90.23	158.4
						157.7

The value of parachor calculated by Sugden from Watenberg's data is 154.0 and the densities obtained by Wartenberg at 42° and 100° are 4.44 and 4.19 respectively.

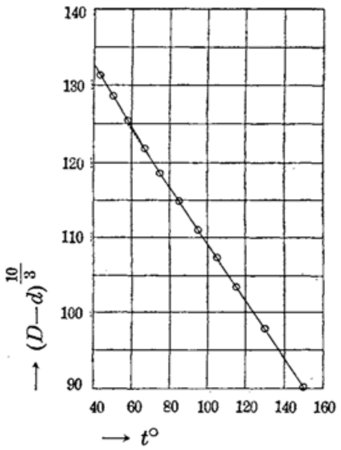

Fig. 6.

For a normal liquid, generally, there is a relation,⁽¹⁾

$$D-d = D_o(1-T_r)^{\frac{3}{10}}$$

where D_0 is the density at absolute zero, and T_r the reduced critical temperature. That is to say, there is a linear relation between $(D-d)^{\frac{10}{3}}$ and temperature. For osmium tetroxide this relation holds good at above 75°C. but the line bends below 75°C. This fact is also in parallel to the results on vapour pressure and surface tension measurements.

Liquid State of Osmium Tetroxide. It has been known by the measurement of the

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(1) Sugden, *J. Chem. Soc.*, **1927**, 1780.

vapour pressure that the relation between $\log p$ and $\frac{1}{T}$ can be expressed by two straight lines intersecting at about 70°C. The Trouton's constant is 21~2. The tetroxide, therefore, is a normal liquid at its boiling point.

In the measurement of the surface tension the relation $\gamma=\gamma_o(1-T_r)^{\frac{6}{5}}$ holds at above 75°C. and at below 70°C. separately, showing two straight lines. The same fact is observed in the measurement of densities. The relation $D-d = D_o(1-T_r)^{\frac{3}{10}}$ holds good at above 75°C.

According to Walden⁽¹⁾ there is a following relation at its boiling point for a normal liquid.

$$\frac{Ma^2}{T} = K = 1.162 .$$

where a^2 is the specific cohesion at its boiling point. For osmium tetroxide

$$a^2 = 1.867 , \qquad K = 1.177 .$$

Therefore this relation also indicates that the substance is a normal liquid at its boiling point. Putting these facts together, osmium tetroxide must be a normal liquid at above 75°C. In the following Katayama's equation which indicates the relation between a molecular surface energy and temperature, the constant K' is 2.12 for a normal liquid in most cases.

$$\gamma\left(\frac{M}{D-d}\right)^{\frac{2}{3}} = k'(T_c-T)$$

where T_c is the critical temperature. If the liquid associates, the degree of association is given by $x = \left(\frac{2.12}{k}\right)^{\frac{3}{2}}$, where k is the value found by experiment. In the following table k and x for osmium tetroxide are given.

t °C.	43.00		67.00		95.00		115.00		150.00
k		1.68		1.91		1.95		1.97	
x		1.42		1.17		1.13		1.11	

As the value of 2.12 varies somewhat according to a kind of a molecule, so it may be said that the tetroxide is a normal liquid at a high temperature. It will be concluded that the abnormalities observed in the measurements of the vapour pressure, the surface tension and the density are due to an association. This indicates that this compound has somewhat a polar character.

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(1) *Z. physik. Chem.*, **65** (1908), 129, 257.

Critical Temperature. Wartenberg measured the critical temperature and found to be of 405°C. The author extrapolated the value by the relations $\gamma = \gamma_o(1-T_r)^{\frac{6}{5}}$ and $D-d = D_o(1-T_r)^{\frac{3}{10}}$ and found the values 422°C. and 388°C. respectively. There is a great difference between them, but this is inevitable because the temperature range of measurements is narrow. The mean value of them is 405°C. We adopt this value, though it is not so accurate.

Summary.

(I) The structure of osmium tetroxide was discussed.

(II) It was made clear that the phenomenon of an enantiotropy of osmium tetroxide set forth by Krauss did not exist.

(III) The vapour pressure of osmium tetroxide was measured between 15° and 130°C. Melting point, boiling point, heat of sublimation, heat of vaporization, heat of fusion, and free energy change among solid, liquid and vapour were determined.

(IV) Surface tensions and densities from melting point up to 150°C. were determined.

(V) Osmium tetroxide in liquid state somewhat associates below 70°C., though it is a normal liquid above 75°C.

(VI) The critical temperature was determined as 405°C.

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