[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, CAMBRIDGE, ENGLAND, AND THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PROPERTIES OF TELLURIUM TETRACHLORIDE[1]

BY J. H. SIMONS

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In a former paper[2] the author has pointed out the fact that although the tetrahalogen compounds of sulfur, selenium and tellurium are of considerable interest in theories of molecular structure, very little is known about them.

A study of tellurium tetrachloride has added interest because of the recent investigation of Drew[3] in which he showed that $Te(CH_3)_2X_2$ went over readily to a double salt $Te(CH_3)_3X\cdot TeCH_3X_3$. This indicates that the compound has a tendency to get away from the unstable ten electron shell by two molecules associating, giving an eight electron shell to one tellurium atom and a twelve to the other. It would be interesting to see whether tellurium tetrachloride has double molecules in the gas phase.

Michaelis[4] made Victor Meyer determinations of the vapor density of tellurium tetrachloride with the following reported results.

Temp., °C.	Vapor density Experimental		Calcd. $TeCl_4$ (referred to air at same temperature)
448	9.028	9.224	9.32
530	8.859	8.464	9.32

Preparation of Tellurium Tetrachloride.—The tellurium tetrachloride was prepared in a similar manner and in an apparatus similar to that used for selenium tetrachloride.[2] As the tellurium compound distils rather than sublimes, the necks of the small reserve bulbs were restricted to facilitate sealing off. One more distillation was obtained by having an additional distilling bulb in the chain.

Melting and Boiling Points.—The melting point was obtained from the cooling curve after the material had been fused in a small electric furnace. The melting point thus determined is 225°.

The boiling point was obtained by using a glass jacketed thermocouple immersed in the vapor above the boiling liquid. The boiling point thus determined is 390° at 755.6 mm.

Solubility Relations.—Tellurium tetrachloride was found not to dissolve appreciably in carbon tetrachloride by sealing a small amount of the compound in a tube containing the dry solvent and heating in a bath of boiling water. It was found to react with solvents which would be expected to dissolve it, such as CH_3CN. No convenient solvent was found in which to determine its conductivity and freezing point lowering. Its solubility relations indicate that it is a polar compound, salt-like in nature.

Vapor Density.—The apparatus and method used to measure the vapor density of

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[1] Part of this work was done while the author was a National Research Fellow at Cambridge University.

[2] Simons, THIS JOURNAL, 52, 3483 (1930).

[3] Drew, *J. Chem. Soc.*, 560 (1929).

[4] Michaelis, *Ber.*, 20, 1780 (1887).

tellurium tetrachloride was the same as that for selenium tetrachloride. The results as shown in Table I give higher values below 500° for the apparent molecular weight than the theoretical for $TeCl_4$, and lower values at more elevated temperatures. The higher values may be due either to association of the molecules or to some difficulty in removing the material from the bulb as, for example, due to its adsorption on the walls.

TABLE I

VAPOR DENSITY OF TELLURIUM TETRACHLORIDE

Bulb No. 1				Bulb No. 2			
Temp., °C.	Vapor density (H_2 = 2.016)	Temp., °C.	Vapor density (H_2 = 2.016)	Temp., °C.	Vapor density (H_2 = 2.016)	Temp., °C.	Vapor density (H_2 = 2.016)
420	290.3	522	269.1	429.5	297.3	528	265.6
434.5	286.9	535	267.2	441	289.9	541	261.4
450	283.1	548	263.6	457.5	284.4	554	258.9
464	280.2	561	260.2	473	276.8	568	254.9
480	277.7	573	257.3	486	276.2	581	251.8
493	273.3	587	253.6	501.5	272.9	595	246.6
507	273.2	601	250.5	515.5	268.4		

The latter explanation was suggested by the difficulty experienced in boiling out the material from the bulb at a few degrees above the boiling point. Repeated determinations gave similar results to those recorded here. As the apparatus and method functioned very well for selenium tetrachloride, it was thought that the difficulty might be due to the fact that tellurium tetrachloride is a polar liquid, and as such would be difficult to remove from the glass surface.

Above 500° the color of the vapor in the bulb became darker with higher temperature. This indicated dissociation, for $TeCl_2$ is dark red.

In order to investigate the material in the gas phase at lower temperatures to determine whether or not the molecules were associated, the following work on the vapor pressure was done.

Vapor Pressure.—The apparatus, as shown in Fig. 1, consisted of a pyrex tube containing a sealed-in bubbler joined to another tube by a ground-glass connection. The latter tube had an outlet to the air. This apparatus was placed in a furnace so that the lower end of the second tube projected below the end of the furnace. This was to allow the vapor to condense.

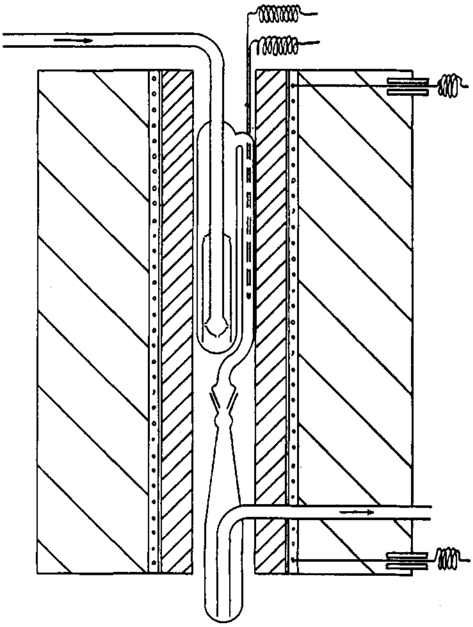

Fig. 1.—Apparatus for determining the vapor pressure of tellurium tetrachloride.

The dynamic vapor pressure method was used. A known quantity of purified and dried nitrogen was passed slowly through the apparatus while it was kept at a constant temperature in the furnace. The decrease in weight of the tube containing the tellurium tetrachloride gave the amount carried off by the nitrogen. The rate of passage of the gas was sufficiently slow to reach equilibrium with the tetrachloride, as shown by the fact that increasing or decreasing the rate had no influence on the results.

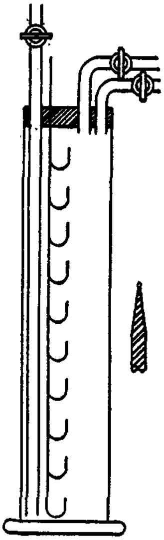

Fig. 2.—Gas measuring cylinder.

The cylinder used to measure definite volumes of nitrogen is shown in Fig. 2. Small glass points fixed in position and pointing upward provided the measuring device. A light reflected from the surface of the water showed very easily whether the point was just raising the surface of the water or was just below it. The volumes between the points could be calibrated closer than to one-hundredth of a cubic centimeter, but this was more than sufficient for our purpose. By test it was found that the eye could detect a difference in height of the water of about one three-hundredths of a millimeter, when the surface was just touching the point.

The results of these determinations are given in Table II. When the molecular weight is assumed to be the formula weight of $TeCl_4$ and the logarithms of the vapor pressure, calculated by using this assumption, are plotted against the reciprocal of the temperature, a straight line results, and this line includes the point given by the boiling point of the compound. This curve is shown in the graph. The point marked * is the boiling point. If double the formula weight is used as the assumption in the calculations, then the curve as shown by the crosses results. The true vapor pressure should give a straight line on this graph, the slope being a measure of the heat of vaporization, by the equation, $\partial \ln p/\partial(1/T) = \Delta H/R$.

TABLE II

VAPOR PRESSURE OF TELLURIUM TETRACHLORIDE

Press. N_2, mm.	Vol. of N_2, cc.	Temp. of N_2, °C.	Moles of N_2	Barometric pressure, mm.	Weight of $TeCl_4$ removed from tube, g.	Temp. of $TeCl_4$, °C.	Moles of $TeCl_4$	Vapor pressure (assuming $TeCl_4$), mm.	Vapor pressure (assuming Te_2Cl_8), mm.
760.3	493.5	23.5	0.020789	759.4	0.0800	233	0.0002975	10.8	4.8
773.5	493.5	22.7	.021211	771.3	.1270	247	.000472	16.8	8.5
768.1	493.5	24.0	.020970	767.9	.1980	260	.000735	26.0	13.3
764.9	314.9	25.2	.013273	766.3	.2257	278.5	.000837	45.5	23.4
768.3	248.2	23.3	.010577	767.1	.3016	295	.001127	73.8	38.7
770.2	210.6	24.8	.008952	770.6	.4296	313	.001597	116.7	70.4
766.0	104.3	22.6	.004440	763.4	.3540	328	.001317	174.5	98.6
761.8	104.3	27.4	.004346	766.6	.3610	328	.001342	181.0	102.7
765.4	47.07	26.0	.001980	767.6	.2880	345	.001070	269.5	165.3
766.0	47.07	25.0	.001988	766.7	.5738	360	.002132	396.5	268
763.2	37.60	19.8	.001610	757.4	1.7284	376	.00641	605.0	503
			Boiling point			390		755.6	

These results indicate that the molecules are not associated, or at least that there is very little association. If the molecules were double the formula weight, then the crosses should fall on a straight line. If association began below the boiling point, the line drawn on the assumption of single molecules should begin to curve at this point. This tends to prove that the high apparent molecular weight at the lower temperatures obtained in the vapor density measurements is not due to association, for if it were a very considerable association would be expected 200° lower at the temperatures of the vapor pressure measurements. This would at least be sufficient to cause a break in the vapor pressure curve. The heat of vaporization calculated from this curve is 18,400 calories per mole.

Density of **Liquid.**—The apparatus used in determining the density of the liquid was made of pyrex glass and is shown in Fig. 3. The volume of the lower bulb and tube connected to it was determined by filling it with mercury to various heights and weighing it. A fine scratch on the glass just above the bulb was used as a reference mark from which to measure the level of the mercury. A telescope containing cross hairs was mounted on a traveling microscope bed for the measuring device.

Tellurium tetrachloride was run into the apparatus carefully so as not to expose it to the air. The level of the liquid in the measuring bulb was adjusted by pouring the liquid from one bulb to the other. The secondary bulb was sealed off when this was accomplished. The apparatus was then placed in a furnace which was made with copper walls one-half inch thick. It had a slit in the side so that observations could be made on the apparatus inside it. The height of the liquid in the tube was noted at different temperatures.

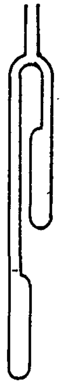
Fig. 3.—Density bulb.

The results of these determinations are given in Table III. Corrections were made both for the curvature of the meniscus and for the expansion of the glass of the bulb.

TABLE III

DENSITY OF LIQUID TELLURIUM TETRACHLORIDE

Temp., °C.	232	277	314	315	341	344	385	424	427
Density, g./cc.	2.559	2.494	2.443	2.442	2.402	2.401	2.334	2.275	2.260

Surface Tension.—A pair of capillaries which had been calibrated for surface tension measurements at room temperature were inserted in a tube which contained tellurium tetrachloride and the tube was sealed. It was then put in the above-mentioned

TABLE IV

SURFACE TENSION OF TELLURIUM TETRACHLORIDE

Temp., °C.	Surface tension, dynes/cm.	Parachor	Temp., °C.	Surface tension, dynes/cm.	Parachor
238	40.2	265.8	327	33.75	267.9
260	38.3	265.7	338.5	31.85	266.0
261	38.27	265.8	352.5	31.57	267.9
263	37.70	265.1	353	31.37	267.5
280	36.87	266.2	370	30.07	267.9
298.5	35.77	267.0	397	28.37	269.3
316	34.25	267.1	413	26.93	269.1
322	34.05	267.6	413.5	26.92	269.2

furnace; after it had been kept heated for some time to make sure that the glass was wetted, the measurements were made. These covered a considerable temperature range. A close examination gave no indication of a finite angle of contact between liquid and glass. These results are given in Table IV. Corrections were made for the expansion of the glass and for the curvature of the meniscus.

The parachors[5] were calculated from these surface tension measurements. They are given in Table IV. The density of the vapor was calculated from the vapor pressure.

In all this work the same thermocouple was used as in the work on selenium tetrachloride.

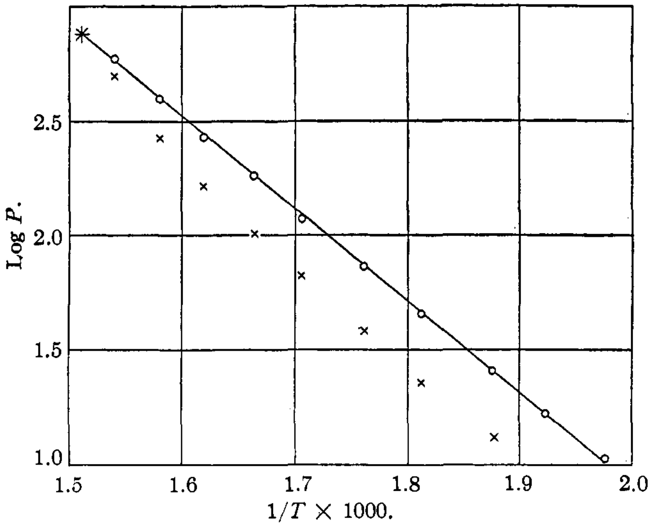

Fig. 4.—Vapor pressure of $TeCl_4$.

Discussion

These experiments show that tellurium tetrachloride exists as $TeCl_4$ in the gas phase. Three ways of explaining its structure are the ionic form $TeCl_3^+Cl^-$, the structure containing two single electron bonds as recommended by Sugden,[6] and a form in which a ten electron shell is assigned to the central atom, four pairs of these being shared by chlorine atoms. It is difficult to understand how the first form could exist in the gas phase as a normal gas. The second form involves the assumption of single electron bonds, which is an extremely questionable hypothesis. The third form gives a structure which agrees well with the properties of the compound.

Of the tetrahalogen compounds of this family of elements tellurium tetrachloride is the only one that lends itself readily for study. The only others that are stable enough to exist in anything but a crystalline form are the fluorides and these are difficult to handle due to their reactivity with glass. The properties of tellurium tetrachloride are, therefore, to be

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[5] See Sugden, *J. Chem. Soc.*, **125**, 1177 (1924).

[6] Sugden, *ibid.*, 1058 (1929).

considered as representing the general properties of ten electron shell compounds in which one electron pair of the central atom is not shared.

Summary

A method for the preparation of pure tellurium tetrachloride is described.

The melting point and boiling point of tellurium tetrachloride are determined to be 225 and 390°, respectively.

The vapor density of tellurium tetrachloride is measured from above the boiling point to 600°.

The vapor pressure of liquid tellurium tetrachloride is measured.

The heat of vaporization is determined to be 18,400 calories per mole.

The vapor of the compound is concluded to consist of single molecules of $TeCl_4$ from the melting point to about 500°, where dissociation begins.

The density of liquid tellurium tetrachloride is determined from the freezing point to above the boiling point.

The surface tension of tellurium tetrachloride is determined over the same range.

Tellurium tetrachloride is concluded to have a ten electron shell surrounding the central atom, four pairs of these being shared with the chlorine atoms.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE PEARSON CHEMICAL LABORATORY OF TUFTS COLLEGE]

THE STANDARDIZATION OF A MODIFIED OSTWALD VISCOMETER

BY H. M. CHADWELL AND B. ASNES

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A viscometer conforming essentially to Washburn and Williams,[1] modification of Ostwald's viscometer has been used by one of us[2] to determine the viscosities of several aqueous solutions, without attempting to determine how accurately the instrument reproduced true viscosities. The viscosities were calculated both by the simple law of Poiseuille and by assuming a value of 1.12 for m, the coefficient of the correction term which has been variously called the kinetic energy, Hagenbach, or inertia correction. Washburn and Williams reported experiments on changing time of flow with changing pressure, to support the conclusion that the law of Poiseuille, without a correction, should be used, but their method of calculation has since been questioned.[3] Since the magnitude of m is thought to be dependent upon the shape of the terminal of the capillary as well as

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[1] Washburn and Williams, THIS JOURNAL, **35**, 739 (1913).

[2] Chadwell, *ibid.*, **48**, 1912 (1926).

[3] Dorsey, *J. Opt. Soc. Am.*, **14**, 45 (1927).