theory is applicable to the usual electrodes as well as to oxidation–reduction electrodes.

The writer wishes to express his thanks to Professor A. E. Brodsky both for suggesting the problem and for help in carrying it out. Part of the material presented appeared in *Z. Elektrochem.*, **39**, 220 (1929). Slight corrections are necessary to part of the published data; the corrections have been applied in this report.

Summary

1. The methods of preparation of silver–silver chloride and silver–silver bromide electrodes have been studied, and it has been found that the procedure recommended by Noyes and Ellis is to be preferred.

2. Measurements have been made of the e. m. f. of the cell Ag | AgCl, KCl (c_1) | KBr (c_2) ($c_1 = c_2$), AgBr | Ag in water and in ethyl and methyl alcohol–water mixtures of various concentrations.

3. The results obtained justify the application of Nernst's osmotic theory to non-aqueous solutions, as has been carried out by Professor A. E. Brodsky.

DNIEPROPETROVSK, EKATERINOSLAW, U. S. S. R.

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

THE PROPERTIES OF SELENIUM TETRACHLORIDE[1]

BY J. H. SIMONS

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The tetrahalogen compounds of the electronegative elements in group number six of the periodic table are of considerable interest from the point of view of molecular structure. On the Lewis theory the central atom should be represented with a shell of ten electrons, four pair of which are shared with the halogen atoms and one pair which is not shared. Henley and Sugden[2] propose a shell of eight electrons with two of the halogen atoms held by single electron bonds.

Of these compounds the following are known: SCl_4, SF_4, $SeBr_4$, $SeCl_4$, SeF_4, TeI_4, $TeBr_4$ and $TeCl_4$. The formulas of most of these have, however, been assigned from only an analysis of the crystalline compound. The molecular weights and therefore the number of atoms in the molecule have not been determined. In fact, a number of these compounds are very unstable crystalline substances, the crystal structures of which are not known. The stability of these compounds increases in the expected man-

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

[2] Henley and Sugden, *J. Chem. Soc.*, 1058 (1929).

ner as one proceeds from the iodide to the fluoride and also as one changes the central atom from sulfur to tellurium. SI_4, SBr_4 and SeI_4 are not known, undoubtedly because they are too unstable to exist under any ordinary laboratory conditions. SCl_4, $SeBr_4$ and TeI_4 are known only as very unstable solids which decompose upon heating. $SeCl_4$ and $TeBr_4$ are crystalline solids which can be sublimed. SF_4, SeF_4 and $TeCl_4$ form liquids under ordinary pressures. TeF_4 would be expected to be a stable compound but it has not yet been isolated.

Before these compounds can be used in a discussion of molecular structure, it is necessary that more information be obtained about them. In this paper a report of a study of selenium tetrachloride will be given.

Several attempts have been made to determine the molecular weight of selenium tetrachloride. Clausnitzer[3] reports that the vapor density by the Dumas method is one-half the normal value for $SeCl_4$ but does not record the temperature of the determination. Evans and Ramsay,[4] however, found the vapor density normal below 200° and the material half decomposed at 288°. Chambrie[5] finds the vapor density at 360° to be one-half normal. Beckmann[6] determined the freezing point lowering of selenium tetrachloride in acetic acid at 16.5° and obtained molecular weights varying from 142 to 152 depending on the concentration. He made very modest claims for these determinations, for he accounted for the results by a reaction with the solvent, a dissociation of the selenium tetrachloride, or a reaction with water in the solvent.

Preparation of Selenium Tetrachloride.—Elementary selenium was treated with pure dry chloride in a pyrex glass apparatus, which consisted of several tubes sealed into one another. The selenium was placed in the first tube, the air in the apparatus was flushed out with chlorine, and then the tube containing the selenium was placed in a small electric furnace. By proper control of the temperature the tetrachloride could be sublimed into the first tube out of the furnace, at the same time that a chlorine stream entered the tube in the furnace. When all of the selenium had reacted, the entire apparatus was heated to drive out any oxychloride that might be present. After this the apparatus was allowed to cool, admitting more chlorine to keep out air and then it was evacuated and sealed off. After the product had been sublimed out of the first tube, this was sealed off, and the second one placed in the furnace to sublime the product into the small tubes in which it was to be contained for storage and use. These small tubes could then be sealed off and preserved.

Vapor Density.—The apparatus used for measuring the vapor density is shown in Fig. 1. The furnace was made of a piece of copper pipe one and three-quarters inches inside diameter, ten inches long, and with a wall one-half inch thick. It was covered with asbestos paper, uniformly wound with nichrome wire, covered with alundum cement, packed with magnesia into a metal can and cemented at the openings with fire clay. Copper disks one-half inch thick served as base and cover. The lower one con-

[3] Clausnitzer, *Ann.*, **196**, 268 (1879).

[4] Evans and Ramsay, *J. Chem. Soc.*, **45**, 62 (1884).

[5] Chambrie, *Bull. soc. chim.*, **2**, 803 (1890).

[6] Beckmann, *Z. physik. Chem.*, **70**, 1 (1910).

tained an opening for the thermocouple and the upper one an opening for the capillary. Two loops of heavy copper wire formed handles for the cover. A copper tube one-quarter inch inside diameter, one inch outside and about six inches long was connected to nichrome wires which could be used to lift, carry or support it. This tube fitted over the capillary of the glass bulb and was kept at a higher temperature than the furnace by means of a gas flame.

The pyrex glass bulb had a volume of about 135 cc. The depression in the bottom kept the material in the bulb to the outside and so near the source of heat.

The thermocouple was of copper–constantan. The wires were slipped into a capillary tube of hard glass which was then heated and bent. To prevent oxidation of the wires the tube was filled with dry carbon dioxide and the ends were sealed with cement.

To check the uniformity of the temperature in the furnace as well as assist in the calibration of the thermocouple, a glass bulb similar in shape and size to those used in the determinations was sealed to a capillary tube which connected to a two-atmosphere open-tube manometer. The bulb was filled with dry nitrogen and used as a constant volume gas thermometer. A comparison of the calibration of the thermocouple by this means with its calibration by use of fixed points showed no deviation within the precision of the measurements. This showed that the temperature within the furnace was uniform. The fixed points used were the boiling points of water and sulfur and the freezing points of tin and lead. The thermocouple was read by a potentiometer so arranged that one scale division on the instrument corresponded to less than one-tenth of a degree centigrade.

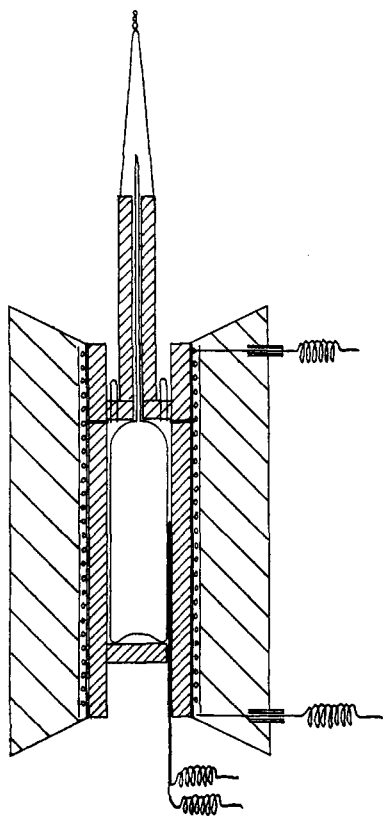

Fig. 1.—Vapor density apparatus.

A small sample tube of selenium tetrachloride with the tip opened was placed in the bulb before the capillary was drawn, the bulb at that time being filled with dry nitrogen. After the capillary was drawn, the bulb was evacuated and sealed. The excess material was allowed to escape through the capillary by opening it when the temperature of the furnace was held constant at slightly above the subliming temperature. The capillary was sealed and the bulb removed from the furnace and weighed. Repeated determinations could be made by opening the tip of the capillary with a small flame when the temperature of the furnace was ten or more degrees above the temperature of the previous determination, and the tube again sealed by removing a small piece of the capillary. The barometric pressure and the temperature of the balance case were recorded for each determination. The volume of the bulb and the weight of the glass of bulb, tips, etc., were found at the end of the series of determinations. The results are given in Table I. The calculations were made using the perfect gas law.

The color of the bulb filled with gas just as it was taken out of the furnace varied as the temperature was raised. At the lower temperatures in the vicinity or less than 250° the gas was light yellow. As the temperature was raised, it became darker and darker until it was about the density of color of bromine vapor at atmospheric pressure. This was despite the fact that the density of the gas was decreasing as the temperature was raised. Above about 500° the shade of color seemed to remain constant.

TABLE I

VAPOR DENSITY OF SELENIUM 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)
208	110.9	360.5	110.4	202.5	113.6[a]	352	111.1
225	111.2	376	110.6	215.5	111.7	368	111.4
243	110.2	406	109.9	234	111.2	391.5	111.1
260	110.5	435.5	110.0	252	111.2	420.5	110.9
278	110.3	466	110.1	270	111.6	450	110.8
295	110.4	493	110.5	286.5	111.1	479	111.2
312	110.7	521	109.9	303	111.3	508	111.0
328	110.8	574.5	109.9	320	111.6	548.5	111.1
344.5	110.4			336	111.5	600	111.2
		Av.	110.4				111.2

[a] Not averaged.

Melting and Subliming Points.—Voigt and Biltz[7] report the only attempt at determining a melting point of selenium tetrachloride. They state that between 400 and 500° the material melted in a sealed tube but a gas was evolved and the tube exploded.

A thick-walled six-millimeter tube containing selenium tetrachloride was carefully sealed and placed in a furnace which had an opening so that the tube could be watched with a telescope. The temperature of the furnace was raised until the crystalline material seemed to melt; then the temperature was lowered until it crystallized again. This alternate melting and freezing was repeated a number of times. The average temperature of these determinations was 305 ± 3°. The liquid formed is very dark red (almost black) and this makes it difficult to observe the formation of the crystals.

To determine the temperature at which the vapor pressure of the material is one atmosphere (the subliming point), the bulb as set up for the vapor density experiments was used. Before all the solid was allowed to escape, the capillary was sealed; then, by a careful control of the temperature of the furnace, the end of the capillary was tested with a flame to see when the glass blew out a little and when it sank in. A mean of these temperatures was taken for the value. It is 196 ± 1°.

Solubility Relations.—In order to study the solubility of selenium tetrachloride in a non-polar solvent, a small amount of the solid was placed in a tube of dry carbon tetrachloride, the tube sealed, placed in a water-bath and heated to about 100°. There was no indication of any solubility. Methyl cyanide was considered for use as a polar solvent; it, however, reacted with the crystals.

Discussion

The insolubility of this compound in non-polar solvents and apparent solubility in polar solvents[6] seems to indicate that it is polar in nature. However, due to its high melting point its solubility in non-polar solvents

[7] Voigt and Biltz, *Z. anorg. allgem. Chem.*, **133**, 277 (1924).

would be small even if it were non-polar, but in that case it should be more inert to polar solvents.

The vapor density is about one-half that which the formula $SeCl_4$ would indicate. As this value remained constant for the entire temperature range of the experiments, it shows that the vapor is completely dissociated under these conditions. This confirms the results of Clausnitzer and of Chambrie but is not in agreement with those of Evans and Ramsay. This would seem to indicate a dissociation of this kind

$$SeCl_4 = SeCl_2 + Cl_2$$

However, $SeCl_2$ is not recorded in the literature. The same result for vapor density would be obtained from the reaction

$$2SeCl_4 = Se_2Cl_2 + 3Cl_2$$

as suggested by the earlier workers. There seems to be a change in the substance as heat is applied, as seen by the change in color. This is, of course, no proof but it may be an indication, for SCl_2 and $TeCl_2$ are both known, the former being red in color and the latter so dark red that it is almost black. Also SCl_2 is much deeper in color than S_2Cl_2 and so we expect $SeCl_2$ to be deeper in color than Se_2Cl_2. The author would like to suggest that the decomposition takes place to form Se_2Cl_2 at the lower temperatures (250°) and $SeCl_2$ at higher ones (500°).

As these experiments show the vapor of the material to be completely dissociated in the gas phase over the range of temperature from 200 to 600°, the mechanism of subliming must be the formation of a lower chloride and chlorine and a recombination to form the crystalline material upon cooling. The depth of color of the liquid formed by melting the crystals, as well as the very high pressure necessary, indicates a dissociation in the liquid state probably to $SeCl_2$. This may cast some doubt as to whether the molecular species $SeCl_4$ as such exists at all, for without x-ray crystal studies we do not know the molecular form in the crystal state.

Summary

A method of preparing pure selenium tetrachloride is described.

The vapor density of selenium tetrachloride has been determined from 200 to 600° at one atmosphere pressure. The vapor is completely dissociated under these conditions.

The apparent melting and subliming points of selenium tetrachloride are determined.

The solubility relations of selenium tetrachloride indicate the material to be polar in nature.

The existence of $SeCl_2$ is indicated in these experiments.

EVANSTON, ILLINOIS