[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 267]

THE VAPOR PRESSURES OF SELENIUM TETRACHLORIDE. THE EXISTENCE OF SELENIUM DICHLORIDE

BY DON M. YOST AND CHARLES E. KIRCHER

RECEIVED JULY 30, 1930 PUBLISHED DECEMBER 18, 1930

Introduction

The former studies of the physical properties of selenium tetrachloride have been restricted to vapor density measurements and to the determination of its heat of formation from the elements. There is considerable lack of agreement between the results of the measurements of the vapor density made by different investigators, although in all cases the evidence for dissociation is fairly conclusive. Ramsay and Evans,[1] as a result of measurements by the method of Victor Meyer, give the degree of dissociation as zero at 200°, 0.19 at 210°, and 0.65 at 350°, while Clausnizer[2] finds complete dissociation at the temperature (not given) at which he worked, the vapor density being just one-half that calculated from the formula $SeCl_4$.

The recently published results of the very interesting experiments made by Simons[3] show definitely that the vapor density of selenium tetrachloride is one-half that to be expected from the formula over the temperature range from 200 to 600° and at atmospheric pressure.

The present investigation was undertaken to determine the extent and nature of this reported dissociation.

Experimental Method and Procedure

Owing to the corrosive action of selenium tetrachloride it was necessary to carry out the necessary pressure measurements in an all-glass apparatus. For this purpose the substance was placed in a cylindrical pyrex bulb at one end of which was sealed a so-called click-gage[4] also of pyrex. The gage was enclosed in and sealed to another glass tube, the latter being connected to the barometer used for measuring the pressures necessary to cause the gage to click. The whole assembly, reaction bulb and gage, being of one piece was placed in an electric furnace. The furnace was equipped with a copper core and auxiliary end coils for maintaining a

---

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

[2] Clausnizer, *Liebig's Ann. Chem.*, **196**, 265 (1879).

[3] Simons, THIS JOURNAL, **52**, 3483 (1930). This article appeared after the present work was completed. The present results, in so far as they are concerned with the vapor density, are in complete agreement with those of Simons. The temperature range over which selenium dichloride exists is shown by our results to be different than that suggested by him, his conclusions being based solely on observations of color changes.

[4] Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, **1929**.

uniform temperature in the central region and a slightly higher one at the end near which the bulb of the gage rested. It was thus possible to maintain the temperature of the reaction bulb constant, while that of the gage was kept slightly higher to prevent any condensation of solid material on it.

The temperature range investigated lay between room temperature and 230°. It was accordingly necessary first to investigate the characteristics of pyrex click-gages over this range. Small but definite changes in the pressure differences necessary to cause clicking were found at the higher temperatures, and, in fact, some gages ceased to operate after having reached the highest temperature. The gage eventually used suffered no great changes in its click constants even after repeated heating and cooling, the variations amounting on the average to about 2 mm. of mercury.

In making the measurements the temperature of the furnace was raised or lowered to some definite value and held there until the pressure remained constant. That equilibrium had been reached was established by varying the temperature above and below the selected one until the pressure changes responded to such variations. Equilibrium was approached from temperatures considerably above and below those at which measurements were made.

For the purpose of making vapor-density measurements the initial quantity of solid selenium tetrachloride taken was such that at the higher temperatures it would be completely vaporized. Moreover, after complete vaporization, the manner in which the pressures increased with increase in temperature was observed in order to determine the extent of any dissociation of the vapor itself. Thus it was found possible to make measurements of the vapor pressures, the vapor density and the degree of dissociation by a rather simple experimental device.

The accidental errors involved in the values given for the pressures consist of those arising from measurements of the temperature and pressure and do not exceed 3%. The absolute errors due to small losses of selenium tetrachloride during preparation, changes in the volume of the bulb and gage as a result of sealing it, and to the already mentioned variations of the click constant of the gage, do not exceed 2%, and most of this is to be ascribed to the two former causes. The accuracy of the vapor pressure measurements is probably greater than that of the vapor density.

Preparation of Materials

Great care was taken in the preparation of the selenium tetrachloride. The selenium itself was first purified by dissolving the C. P. material in concentrated nitric acid, filtering, evaporating almost to dryness, dissolving in concentrated hydrochloric acid and then precipitating with sulfur dioxide. The precipitate was washed repeatedly with cold water, and then with boiling water. This process[5] yields selenium free from

---

[5] A. A. Noyes and W. C. Bray, "Qualitative Analysis for the Rare Elements," The Macmillan Company, New York, **1927**, p. 381; Keller, THIS JOURNAL, **19**, 771 (1897).

tellurium and was applied twice. The material so obtained was again dissolved in concentrated nitric acid, the solution evaporated almost to dryness, diluted to 400 cc. with water, filtered, and then treated with hydrazine hydrochloride. The resulting precipitate was thoroughly washed as before and finally dried and melted, and the melt poured into cold water in such a way that small spheres with diameters of 2 mm. and smaller were formed. This material was then dried.

To prepare the tetrachloride a weighed amount (about 0.0200 g.) of selenium was placed in a small glass tube one end of which was drawn down to a long thin capillary, the other end being then sealed to a drying tube containing anhydrous barium perchlorate. After displacing the air with carbon dioxide, chlorine was passed through the apparatus for some time, the vigor of the resulting reaction being diminished at the beginning by cooling the tube with a small lump of ice. When the reaction was almost complete it was necessary to heat the tube gently with the flame of a match in order to obtain complete conversion. Following this treatment the excess of chlorine was displaced with carbon dioxide. The tip of the capillary was then sealed, the whole assembly evacuated, and finally the tube containing the selenium tetrachloride sealed off. The material was almost white and was free from the lower chlorides. The tube containing the final product was placed in the reaction bulb, the bulb and gage were thoroughly evacuated, heat being applied to the bulb to drive out any adsorbed water, and finally the reaction bulb was sealed. The tube containing the tetrachloride was broken by shaking the reaction bulb.

The vapor of selenium tetrachloride has an intense orange color and at pressures of about one-fifth atmosphere a few diffuse absorption bands in the green region were observed.

For the experiments in which an excess of chlorine was present the procedure was as follows. A weighed amount of selenium in a small evacuated tube was placed in the reaction bulb and the latter carefully dried by heating and passing a stream of dried air through it. Dried chlorine was next passed through the bulb until the air had been swept out, after which the bulb was closed by sealing it, and the tube containing the selenium broken as before. The chlorine remaining was that in excess of the amount necessary to convert the selenium to the tetrachloride and was determined in advance by the amount of selenium taken.

Experimental Results and Discussion

TABLE I

VAPOR PRESSURES OF SOLID SELENIUM TETRACHLORIDE

Temperature, °C.	Pressure, mm.	Temperature, °C.	Pressure, mm.
109	11.3	157	157.8
120	23.9	161	203.4
129.5	40.0	163.6	235.8
131	42.6	170.5	310.6
140	65.5	171	317.7
149	111.1	175.5	389.6
150	117.4	180.5	482.0

In Table I are presented the final values for the vapor pressures of selenium tetrachloride. In Table II are given the values of the pressures after all the solid had been converted to the vapor, together with the pressures calculated on the assumption that the vapor consists of $SeCl_4$. All pressures are expressed in millimeters of mercury.

TABLE II

RESULTS OF PRESSURE–TEMPERATURE EXPERIMENTS ON THE VAPOR FROM SELENIUM TETRACHLORIDE

Volume of reaction bulb and gage, 27.3 cc.
Wt. of selenium taken to prepare $SeCl_4$, 0.0188 g.
Wt. of Se calculated from gas law, assuming complete dissociation, 0.0185 g.
Wt. of Se calculated from slope of P–T curve, assuming complete dissociation, 0.0188 g.

Temp., °C.	Press. (obsd.), mm.	Pressure (calcd.) for normal $SeCl_4$ vapor, mm.	Ratio of obsd. to calcd. press.
189.2	489.6	250.7	1.95
191.5	495.3	251.9	1.97
199	502.2	256.0	1.96
199.5	502.6	256.2	1.96
208	512.1	260.9	1.96
209.5	513.4	261.7	1.96
215	520.1	264.7	1.96
223	526.6	269.0	1.96
226	533.5	270.6	1.96

The observed pressures given in Table II are, within the limits of the experimental errors involved, twice those calculated on the assumption that the vapor consists of $SeCl_4$. Moreover, the vapor obeys the simple gas law over the range where no solid is present. It may be concluded, therefore, that the selenium tetrachloride is, at these temperatures, completely dissociated in such a way that one molecule of it gives rise to two.

The vapor pressures of the solid increase very rapidly with the temperature. It was found that over the range of temperatures where the solid phase was present, the graph of $\log_{10}P_0$ plotted against the reciprocal of the absolute temperatures was a straight line. This fact indicates that the tetrachloride vapor is completely dissociated even at the lowest temperatures investigated.

There are three possible reactions that would be in accord with the results found experimentally, *viz.*

$$SeCl_4\ (s) = Se\ (s) + 2Cl_2\ (g) \qquad (1)$$
$$2SeCl_4\ (s) = Se_2Cl_2\ (g) + 3Cl_2\ (g) \qquad (2)$$
$$SeCl_4\ (s) = SeCl_2\ (g) + Cl_2\ (g) \qquad (3)$$

Inasmuch as no solid or molten selenium (m. p. 217°) could be observed either in the vapor pressure experiments or in separate experiments devised to determine whether it were ever present, it is concluded that Reaction 1 does not occur.

If Reaction 2 or 3 takes place, chlorine should have a marked effect upon the vapor pressure of the solid. This was found by experiment to be the case. Indeed, it was found possible to establish that Reaction 3 is the correct one. If P_0 is the vapor pressure of the solid at a given temperature in the absence of excess of chlorine, and if complete dissociation takes place, then the equilibrium constants for Reactions 2 and 3 at the temperature in question are given by

$$K = \frac{27}{256} P_0^4 \quad (4) \qquad \text{and} \qquad K = \frac{1}{4} P_0^2 \qquad (5)$$

If excess of chlorine is present at the pressure p and if the total pressure is p_0, then for Reactions 2 and 3, respectively

$$P_0^4 = \frac{1}{27} (p_0 - p)(3p_0 + p)^3 \qquad (6)$$

$$P_0^2 = (p_0 - p)(p_0 + p) \qquad (7)$$

Applying Equations 6 and 7 to the results of the experiments in which excess of chlorine is present, the vapor pressure of the solid in the absence of excess of chlorine may be calculated. In Table III are given the results of such experiments together with the calculated and observed values of P_0. All pressures are expressed in mm. of mercury.

TABLE III

RESULTS OF EXPERIMENTS ON THE EFFECT OF CHLORINE ON THE VAPOR PRESSURE OF SELENIUM TETRACHLORIDE

Temp., °C.	Total press., mm.	Press. excess chlorine, mm.	P_0 (obs.) of $SeCl_4$, mm.	P_0 (calcd.) Eq. 7, mm.	P_0 (calcd.) Eq. 6, mm.
146	365.5	346.0	95.9	117.8	215.8
151	374.6	350.0	123.2	133.5	232.4
156	395.7	354.0	157.4	176.8	274.2
161	413.9	358.0	203.4	207.9	303.4
166	449.7	362.0	252.4	267.3	357.6
171	489.0	366.0	317.7	324.3	409.3
176	548.9	370.0	396.5	405.6	483.0

The results show that chlorine does have an effect on the vapor pressure of the tetrachloride, and that its magnitude corresponds to that demanded by Reaction 3, as may be seen by comparing the last three columns of Table III. It is, therefore, concluded that over the range of temperatures investigated the vapor phase consists of selenium dichloride and chlorine.

Thermochemical Results

The vapor pressures of selenium tetrachloride in equilibrium with the solid may be represented by the following formula[6]

$$\log_{10} P = -\frac{0.05223 \times 73{,}990}{T} + 11.2040$$

where P is expressed in millimeters of mercury and T is the absolute temperature.

The value of the heat of Reaction 3 is then

$$SeCl_4\,(s) = SeCl_2\,(g) + Cl_2\,(g) \quad \Delta H = 35{,}380 \text{ cal.}$$

---

[6] The formula is set up so as to conform with the usage adopted by the "International Critical Tables."

Thomsen[7] gives the heat of formation of selenium tetrachloride as 46,156 cal. Combining this with the above we find

$$\mathrm{Se\ (s) + Cl_2\ (g) = SeCl_2\ (g)}\quad \Delta H = -10{,}780\ \mathrm{cal.}$$

It may be remarked that, if Reaction 1 or 2 be assumed as true, the calculated values for the heats of formation of $SeCl_4$ or Se_2Cl_2 differ greatly from the experimentally found values of Thomsen.

Stability of Selenium Dichloride

Attempts made heretofore to prepare selenium dichloride from equivalent amounts of the two elements have always met with failure, the resulting product consisting of a mixture of the solid tetrachloride and liquid monochloride. In analogy with sulfur and tellurium, the dichloride of selenium would be expected to exist, and its tendency to decompose with the formation of the tetrachloride and monochloride under normal conditions has doubtless prevented its previous detection. From the results of the investigation described in this paper the vapor form appears to be fairly stable. It is also possible that the vapor above liquid selenium monochloride consists, in part, at least, of the dichloride, since a considerable residue of elementary selenium always results after distillation. Moreover, the reported vapor density measurements on the monochloride show that there is no increase in the number of molecules on evaporation, even though a residue of elementary selenium is left behind. These facts would be in agreement with the assumption that the vapor consists of the dichloride.

Summary

The vapor pressures of selenium tetrachloride have been measured both in the presence and absence of excess of chlorine. From these results and the results of vapor density measurements it has been shown that over the range of temperatures from 109 to 226° the vapor consists entirely of selenium dichloride and chlorine.

The vapor pressures of the solid may be computed from the following formula where P is expressed in millimeters of mercury and T is the absolute temperature.

$$\log_{10}P = -\frac{0.05223 \times 73{,}990}{T} + 11.2040$$

The heat change accompanying the decomposition of solid selenium tetrachloride into the gaseous dichloride and chlorine is $\Delta H = 35{,}380$ cal. The heat of formation of gaseous selenium dichloride was found to be $\Delta H = -10{,}780$ cal.

Pasadena, California

---

[7] J. Thomsen, "Thermochem. Untersuchungen," Leipzig, **1882-1886**; Abegg, Auerbach and Köppel, "Handbuch der anorg. Chem.," Leipzig, **1927**, IV B, Abt. I, p. 723.