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THE DENSITY AND MOLECULAR STATE OF THE VAPORS OF TELLURIUM DIBROMIDE, TELLURIUM TETRABROMIDE AND SELENIUM DIOXIDE

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Introduction

Earlier investigations on tellurium tetrabromide by those interested in atomic weight determinations¹ indicated that at higher temperatures the decomposition into the dibromide and bromine is appreciable; but the extent of this decomposition, with all the substances in the vapor phase, has not been studied. Such studies have been made on selenium tetrachloride² and tetrabromide³ and they were found to be completely decomposed, in the vapor phase, into the dihalide and halogen. It has recently been established by Simons⁴ that tellurium tetrachloride undergoes no appreciable decomposition up to 500°, beyond which the dissociation into the dichloride and chlorine increases with the temperature. It was considered of interest to extend these studies to the tellurium bromides, and thus complete this phase of the chemistry of these substances.

The vapor-pressure measurements carried out by J. Meyer and Jannek⁵ on selenium dioxide in the temperature range 70 to 320° yielded results which indicate that the vapor may be more or less polymerized. The only existing value for the vapor density is one made some time ago by Mitscherlich⁶ who did not give the temperature of the experiments and which is too inaccurate to permit any decision to be made concerning any possible polymerization.

In this paper are presented the results of experiments made on tellurium dibromide and tetrabromide over the range of temperatures from 440 to 1000°, together with the results obtained for the vapor density of selenium dioxide between 350 and 500°.

Experimental Procedure and Preparation of the Materials

The vapor densities were determined by the Dumas method, using the procedure described in a former paper.³ This procedure consists in heating to a definite temperature a tube of known volume containing accurately

¹ Cf. Abegg, Auerbach and Koppel, "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, 1927, Vol. IV, Part 1, Section 1, pp. 812, 894.

² Yost and Kircher, *THIS JOURNAL*, **52**, 4680 (1930).

³ Yost and Hatcher, *ibid.*, **53**, 2549 (1931).

⁴ Simons, *ibid.*, **52**, 3488 (1930).

⁵ Jul. Meyer and Jannek, *Z. anorg. Chem.*, **83**, 62 (1913).

⁶ E. Mitscherlich, *Ann. chim. phys.*, [2] **55**, 5 (1833).

weighed portions of tellurium and bromine only and subsequently allowing the excess of vapor to escape until the contents of the tube are at atmospheric pressure. In the case of the selenium dioxide experiments, the hydrated material was introduced into a tube of known weight and volume, the material was carefully dried by heating while under a vacuum, and the tube was subsequently sealed off and again weighed, the difference in the weight being the weight of selenium dioxide. For the experiments carried out above 600° quartz tubes were used. At temperatures above 1000° appreciable errors may arise as a result of losses in the weights of the quartz tubes. The temperatures were measured by means of a chromel-alumel thermocouple which had been carefully calibrated.

The bromine used was prepared and purified in the manner described elsewhere.³ A commercial grade of metallic tellurium which contained copper and selenium was carefully purified using the method described in detail by Schuhmann.⁷

Selenium dioxide was prepared as follows. Carefully purified selenium² was treated with concentrated nitric acid, the resulting solution of selenious acid was evaporated to dryness, the residue redissolved in water and the solution was filtered and again evaporated to dryness. The resulting material was then sublimed and only those portions free from color were used for filling the vapor-density tubes.

Results of the Tellurium Bromide Experiments.—In Table I are presented representative results selected from the thirty vapor-density measurements made on tellurium dibromide and tetrabromide. The values for the apparent molecular weight M given in the last column of the table were calculated from the formula $M = 760 \times 82.07mT/pv$, where m is the mass of material in grams remaining in the tube at the absolute temperature T and barometric pressure p (in millimeters), and v the volume of the tube in cubic centimeters. It is assumed, of course, that the vapor obeys the perfect gas laws. The initial amounts of dibromide and tetrabromide in the tubes varied from 0.2491 to 0.6584 g.

As may be seen from the table, the molecular weight of tellurium dibromide is, within the limits of experimental error ($\pm 2\%$), the same as its formula weight up to a temperature of approximately 750°. Above this temperature the values are definitely lower, thus indicating decomposition into tellurium and bromine. Owing to the fact that the errors involved at the higher temperatures are appreciable, it was not thought significant to carry out any thermodynamical calculations using these results. For the same reason no corrections were made for the dissociation of bromine.

The color of the solid dibromide is black, and that of the vapor below 650° is violet and closely resembles that of iodine vapor. At higher temperatures the color of the gas shades from reddish brown to salmon

⁷ Schuhmann, *THIS JOURNAL*, **47**, 356 (1925).

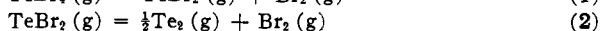
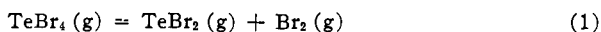
TABLE I

VAPOR DENSITIES OF TELLURIUM DIBROMIDE AND TETRABROMIDE						
Formula weight of TeBr ₂ , 287.34			Formula weight of TeBr ₄ , 447.17			
Experi- ment	Compound	Material left in tube, m, g.	Barometric pressure, p, mm.	Vol. tube v in cc.	Temp., °C.	Molecular weight M, calcd.
1	TeBr ₂	0.1921	741.5	41.4	458	285
3	TeBr ₂	.1744	741.5	41.4	533	286
5	TeBr ₂	.1704	740.0	46.3	640	283
6	TeBr ₂	.1330	740.0	46.3	883	280
7	TeBr ₂	.1191	742.0	46.3	950	264
8	TeBr ₂	.1029	742.0	46.3	1013	240
20	TeBr ₄	.1703	740.0	42.2	432	240
9	TeBr ₄	.1688	741.5	42.9	444	238
26	TeBr ₄	.1590	739.4	41.2	470	242
29	TeBr ₄	.1503	739.4	41.8	500	235
10	TeBr ₄	.1498	741.5	42.9	505	229
16	TeBr ₄	.1373	741.5	40.8	541	231
30	TeBr ₄	.1331	739.4	41.8	578	229
12	TeBr ₄	.1311	741.5	42.9	595	224
32	TeBr ₄	.1417	740.0	48.3	620	221
33	TeBr ₄	.1041	739.4	48.3	930	219
34	TeBr ₄	.0995	742.0	48.3	997	220
35	TeBr ₄	.0844	742.0	48.3	1034	192

pink, the lighter color occurring at the higher temperatures. It must be pointed out, however, that this change in color does not in itself necessarily show the formation of a new compound.

Independent observations on more dilute vapor at 300° with a visual spectrometer showed that the gas possesses a banded absorption spectrum stretching from the region 6700 to 5300 Å. It was found by Professor R. M. Badger of this Institute, with the aid of a grating spectrograph of large dispersion, that these bands possess no observable fine structure.

In the case of tellurium tetrabromide, the dissociation into the dibromide and bromine is quite extensive, even at the lowest temperature of 432°, where it amounts to more than 90%. At about 600° the dissociation is practically complete, and the calculated molecular weight M is, within the limits of experimental error ($\pm 2\%$), one-half the formula weight. Further decomposition into tellurium and bromine does not take place to an appreciable extent at temperatures lower than 1000°, as is shown by the fact that the molecular weights remain nearly constant up to this point. This behavior is in complete accord with the greater decomposition of the dibromide at the higher temperatures and the mass action law, since the partial pressure of bromine in the tetrabromide experiments is much greater. The decomposition in both cases may be represented by the chemical equations



The vapor pressure of tellurium at 750°⁸ is sufficient to exclude the possibility of the presence of liquid tellurium.

The results given do not exclude the possibility of a decomposition at the lower temperatures taking place with the formation of the unknown tellurium monobromide, Te₂Br₂, and bromine in accordance with the chemical equations



That tellurium dibromide does not decompose to form the monobromide and bromine is shown by the fact that no bromine bands were observed in its absorption spectra. From this it appears that a mixture of the monobromide and bromine is not stable with respect to the formation of the dibromide, and hence the products of reaction (3) could not exist as such. It may be concluded, therefore, that the dibromide vapor is normal and that the tetrabromide decomposes to form the dibromide and bromine. It is assumed of course that all reactions come rapidly to equilibrium, and this assumption is probably correct since the temperatures involved are rather high.

At temperatures above 650° the color of the tetrabromide vapor is, to the eye, the same as that observed in the case of the dibromide at the same temperature. At lower temperatures the vapor has a reddish brown color, and on solidifying there results first dark orange crystals which become bright yellow at some point below 100°.

Results of the Selenium Dioxide Experiments

The vapor densities of selenium dioxide over the range of temperatures from 360 to 500° are given in Table II. The initial amounts of selenium dioxide used varied from 0.1994 to 0.3189 g. As may be seen from the last column of the table, the values of the molecular weights, calculated as before, are, within the limits of experimental error ($\pm 1\%$), the same as the formula weight. It is clear from this that there is no appreciable polymerization of selenium dioxide vapor in this temperature range. If, then, the abnormal character of the vapor pressure curve is due to polymerization,

TABLE II
VAPOR DENSITIES OF SELENIUM DIOXIDE
Formula weight of SeO₂, 111.2

Experiment	Material left in tube, m, g.	Barometric pressure, p, mm.	Vol. of tube, v in cc.	Temp., °C.	Molecular weight M, calcd.
3	0.0852	742.5	40.7	359	111
4	.0817	742.5	40.7	400	114
1	.0785	743.6	41.2	426	112
5	.0708	742.5	40.7	496	112
2	.0705	742.5	41.2	500	111

⁸ Doolan and Partington, *Trans. Faraday Soc.*, 20, 342 (1924).

the present results show that this effect can be appreciable only at the lower temperatures.

Independent experiments were made on the color of selenium dioxide vapor, these being carried out at 400° in a series of three tubes having a volume of 56.5 cc. and containing 0.1370 g. of selenium dioxide each. Oxygen at pressures of 0, 100 and 330 mm., respectively, was introduced in order to repress the formation of any free selenium or oxides containing more selenium than the dioxide. So far as could be determined visually, there was no marked difference either in the shade or intensity of the color in any of these tubes. Moreover, the color of the vapor in the vapor-density experiments was essentially that observed in these independent experiments. These results show that the color is not due, as has been suggested (*Cf.* Ref. 1, p. 733), to free selenium, a molecule containing more than one atom of selenium, a lower oxide, nor a polymerized molecule. The color of the vapor is green-yellow; and on cooling, white feathery crystals are deposited on the sides of the tubes.

Summary

The vapor densities of tellurium dibromide and tetrabromide have been determined over the range of temperatures from 440 to 1000° . The dibromide vapor was found to be normal up to about 750° ; but above this temperature appreciable dissociation into tellurium and bromine sets in. The tetrabromide is more than 90% decomposed at the lowest temperature (432°) into the dibromide and bromine, and complete dissociation into these substances is reached at about 600° . Appreciable dissociation of the resulting dibromide into tellurium and bromine does not take place until a temperature of about 1000° is reached.

Vapor-density determinations on selenium dioxide showed its vapor to be normal over the temperature range 360 to 500° . Observations on the color at these temperatures, in the absence and presence of oxygen, showed that the color is not due to elementary selenium, to a polymerized molecule, to a lower oxide, nor to a molecule containing more than one atom of selenium.

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