Association States of Selenium in the Gas Phase

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Abstract

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Association States of Selenium in the Gas Phase

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According to the generally accepted view, based on the only study determining the density of vapors (^{1}), two kinds of molecules are present in selenium vapor: Se_2 and Se_6, which are in equilibrium with one another. However, the results of calculations of the equilibria of reactions involving elemental selenium, carried out using the data of the cited work, are in contradiction with experiment (^{2}).

In order to clarify the matter, we investigated the densities of selenium vapors by the static method, in a quartz apparatus, in the temperature interval 550°–900° and in the pressure range from tens of millimeters of mercury to 1 atm.

Compensating diaphragm manometers, similar to the manometer of Brooks (^{3}), with a sensitivity of 0.5–0.1 mm Hg, were used. The manometer and the transition capillary were thermostated at 700°. The reaction vessel, of volume about 56 ml, was placed in a furnace consisting of a steel cylinder weighing 12.4 kg, drilled along its axis. Into the opening of the cylinder a quartz tube was introduced, suspended on the end faces of the furnace, into which the reaction vessel was placed; consequently it retained an unchanged position despite the thermal deformation of the cylinder that was sometimes observed. The construction of the furnace for thermostating the manometer was analogous (weight of the cylinder 4.2 kg). Each of the furnaces had five independent electric windings.

The reaction vessel was provided with four ampoules, which made it possible to carry out five experiments with one charge of selenium. The volume of the vessel, ampoules, and capillary was determined by calibration with mercury, and that of the manometer with water. The possible error was $\Delta V_1 \pm 0.02$ ml. Temperature measurements were made with platinum–platinum-rhodium thermocouples calibrated by us, by the compensation method. The accuracy of the measurements was ±1°. The temperature in the large furnace was measured at six points by moving the thermocouple along a sheath fused into the reaction vessel. The axial gradient usually did not exceed 2°. The accuracy of pressure measurements with the mercury manometer was ±0.3 mm Hg.

The investigation was carried out with selenium containing 0.004–0.008% nonvolatile impurities and 0.001–0.002% tellurium, which was additionally distilled eight times in a high vacuum. It was introduced into the reaction vessel by distilling under vacuum an accurately weighed amount from a sealed vessel. After charging, the working part of the apparatus was sealed off from the vacuum

Figure 1

Figure 1: Figure 1

part.

The change in pressure as the temperature of the large furnace rises follows the vapor-pressure curve. After complete evaporation of the substance, the vapor enters the unsaturated region. In our 11 experiments, in the saturated-vapor region we made 39 measurements, which lay well on a single curve. By the method of least squares we derived the dependence expressed by the formula:

$$\lg P_{\text{mm}} = -\frac{4987.3}{T} + 8.0783. \tag{1}$$

This formula is almost identical with the Brooks formula, which may serve as a criterion of the accuracy of our measurements.

Pressure measurements in the region of unsaturated vapors were carried out both as the temperature was raised and as the temperature was lowered. The points fell very well on the same curves, which proves that equilibrium states were attained.

From the pressures of the unsaturated vapors, values of ν (the mean number of atoms in the molecule) were calculated with the aid of the gas equation of state:

$$\nu_1 = \frac{RT}{AP\nu_1}\left[m - \frac{PA}{R}\left(\frac{\nu_2\nu_2}{T_2} + \frac{\nu_3\nu_3}{T_3}\right)\right], \tag{2}$$

where the subscripts 1, 2, and 3 refer, respectively, to the reaction vessel, the manometer, and the capillary. The values ν_2 and ν_3 were calculated beforehand by a threefold approximation.

Figure 1 presents the dependences of ν on P. From the shape of the curves one can judge the nature of the dissociation processes in the systems under consideration (4–6). In the case of simple decomposition $X \rightleftarrows X_n$ for $n > 2$, as Smith has shown

Fig. 1. Dependence of ν on P: a —for complex decomposition, b —for simple decomposition; 1 —experimental points of Preuner and Brockmöller (1), 2 —experimental points of the authors

(6), the curves should have an S-shaped form, and from the position of the inflection point on these curves one can determine the value of n. From our experimental data it is difficult to draw an unambiguous conclusion about the position of the inflection point on the ν–P isotherms. Qualitatively, the character of our curves does not contradict the generally accepted view (1). However, the constants of the simple decomposition $Se_6 = 3Se_2$, calculated by the formula (Table 1)

$$K = \left(\frac{6-\nu}{4}P\right)^3 : \frac{\nu-2}{4}P, \qquad (3)$$

at high temperatures show a tendency to increase with increasing P. This increase exceeds the possible deviations ΔK, which are easily estimated by calculating the values of $\Delta\nu$. In calculating $\Delta\nu$ from equation (2), we adopted the indicated accuracies of the measurements of P, T_1, and ν_1, and assumed accuracies of the measurements of T_2 and T_3 of ± 10 and $\pm 20°$. The errors Δm_3, $\Delta\nu_2$, and $\Delta\nu_3$, owing to their small magnitude, were neglected, while $\Delta\nu_2$, estimated separately for each point according to spe-

Table 1

Dissociation constants of simple decomposition

550°

P	ν	$\Delta\nu$	$K \cdot 10^{-2}$	$\Delta K \cdot 10^{-2}$
57,0	4,553	$±$0,050	3,31	$±$0,40
62,8	4,506	$±$0,050	3,30	$±$0,40
41,6	4,125	$±$0,050	3,35	$±$0,35
38,8	4,002	$±$0,072	3,76	$±$0,54
26,5	3,617	$±$0,065	3,69	$±$0,45

$$\overline{K} = 3{,}44 \cdot 10^2$$

600°

P	ν	$\Delta\nu$	$K \cdot 10^{-3}$	$\Delta K \cdot 10^{-3}$
170,2	4,414	$±$0,025	2,99	$±$0,17
142,5	4,288	$±$0,030	2,79	$±$0,19
134,8	4,182	$±$0,024	3,13	$±$0,16
110,3	4,017	$±$0,034	2,94	$±$0,20
85,7	3,751	$±$0,036	2,99	$±$0,21
81,2	3,670	$±$0,040	3,12	$±$0,23
54,3	3,331	$±$0,031	2,62	$±$0,15
50,9	3,213	$±$0,048	2,90	$±$0,26
34,7	2,906	$±$0,046	2,44	$±$0,23

$$\overline{K} = 2{,}86 \cdot 10^3$$

650°

P	ν	$\Delta\nu$	$K \cdot 10^{-4}$	$\Delta K \cdot 10^{-4}$
298,2	4,113	\$±\$0,023	1,77	\$±\$0,08
294,2	4,018	\$±\$0,019	2,09	\$±\$0,08
212,6	3,702	\$±\$0,021	2,01	\$±\$0,08
180,6	3,548	\$±\$0,027	1,94	\$±\$0,10
171,8	3,436	\$±\$0,022	2,16	\$±\$0,09
142,4	3,260	\$±\$0,028	2,06	\$±\$0,11
110,7	3,040	\$±\$0,029	1,91	\$±\$0,11
105,4	2,962	\$±\$0,033	2,02	\$±\$0,14
70,9	2,670	\$±\$0,026	1,73	\$±\$0,11
66,1	2,586	\$±\$0,036	1,85	\$±\$0,17
44,9	2,349	\$±\$0,035	1,77	\$±\$0,23

$$\overline{K} = 1{,}96 \cdot 10^4$$

700°

P	ν	$\Delta\nu$	$K \cdot 10^{-5}$	$\Delta K \cdot 10^{-5}$
357,9	3,403	\$±\$0,020	1,10	\$±\$0,04
369,3	3,345	\$±\$0,016	1,19	\$±\$0,04
268,6	3,051	\$±\$0,018	1,10	\$±\$0,04
229,6	2,904	\$±\$0,023	1,08	\$±\$0,05
216,5	2,837	\$±\$0,020	1,11	\$±\$0,05
179,2	2,696	\$±\$0,025	1,04	\$±\$0,06
138,3	2,529	\$±\$0,025	0,94	\$±\$0,06
131,5	2,475	\$±\$0,027	1,00	\$±\$0,08
86,4	2,290	\$±\$0,021	0,82	\$±\$0,07
80,3	2,220	\$±\$0,031	0,99	\$±\$0,16
52,4	2,103	\$±\$0,027	1,03	\$±\$0,30

$$\overline{K} = 1{,}08 \cdot 10^5$$

750°

P	ν	$\Delta\nu$	$K \cdot 10^{-5}$	$\Delta K \cdot 10^{-5}$
465,0	2,846	\$±\$0,017	5,03	\$±\$0,17
457,5	2,799	\$±\$0,015	5,36	\$±\$0,18
331,2	2,566	\$±\$0,018	4,90	\$±\$0,23

P	ν	$\Delta\nu$	$K \cdot 10^{-5}$	$\Delta K \cdot 10^{-5}$
279,3	2,474	$±$0,022	4,51	$±$0,29
262,0	2,425	$±$0,018	4,62	$±$0,27
214,4	2,340	$±$0,023	4,15	$±$0,36
163,0	2,227	$±$0,024	3,90	$±$0,48
154,0	2,196	$±$0,024	4,19	$±$0,58
98,0	2,105	$±$0,020	3,34	$±$0,72
89,9	2,069	$±$0,029	4,30	$±$1,87

$$\overline{K} = 4{,}86 \cdot 10^5$$

800°

P	ν	$\Delta\nu$	$K \cdot 10^{-6}$	$\Delta K \cdot 10^{-6}$
548,2	2,415	$±$0,015	2,12	$±$0,10
385,7	2,278	$±$0,017	1,72	$±$0,13
320,2	2,234	$±$0,021	1,47	$±$0,16
299,4	2,194	$±$0,019	1,60	$±$0,19
242,4	2,147	$±$0,022	1,43	$±$0,24
180,3	2,097	$±$0,023	1,24	$±$0,31
169,5	2,072	$±$0,025	1,49	$±$0,57
105,9	2,032	$±$0,020	1,37	$±$0,64
96,8	2,005	$±$0,029	*	
61,2	1,965	$±$0,025	*	

$$\overline{K} = 1{,}78 \cdot 10^6$$

850°

P	ν	$\Delta\nu$	$K \cdot 10^{-6}$	$\Delta K \cdot 10^{-6}$
625,9	2,188	$±$0,014	7,36	$±$0,66
427,3	2,128	$±$0,017	5,08	$±$0,71
351,3	2,110	$±$0,021	4,11	$±$0,86
226,8	2,081	$±$0,019	4,97	$±$1,29
202,8	2,058	$±$0,023	4,57	$±$1,83
193,3	2,032	$±$0,024	*	
180,8	2,027	$±$0,026	*	
111,8	2,005	$±$0,021	*	
102,0	1,983	$±$0,029	*	

$$\overline{K} = 5{,}65 \cdot 10^6$$

900°

P	ν	$\Delta\nu$	$K \cdot 10^{-7}$	$\Delta K \cdot 10^{-7}$
678,7	2,089	$±$0,014	1,91	$±$0,32
456,3	2,065	$±$0,018	1,22	$±$0,33
374,6	2,057	$±$0,021	0,95	$±$0,35
347,5	2,027	$±$0,020	*	
277,8	2,018	$±$0,022	*	
203,2	2,008	$±$0,024	*	
190,0	2,005	$±$0,026	*	
117,1	1,991	$±$0,020	*	
106,8	1,968	$±$0,030	*	

$$\overline{K} = 1{,}39 \cdot 10^7$$

* Calculation of these constants was not meaningful because of the large values of ΔK.

the initial graph, was of the order of ±0.1. To the error in determining the total mass Δm we assigned, for the first and last experiment of each series, the value ±0.00004 g, and for the intermediate experiments the values ±0.00012 and 0.00009 g, equal to half the differences between the initial weighed portions and the sums of the sealed-off masses of selenium.

The decrease of the constants with decreasing pressure indicates the presence of an intermediate association stage of selenium between Se_2 and Se_6.

If one assumes the dissociation $Se_6 \rightleftarrows Se_4 \rightleftarrows Se_2$, then in this case $(6-\nu)P : 4 = P_2 + P_4 : 2$ and $(\nu-2)P : 4 = P_6 + P_4 : 2$, where P_2, P_4, and P_6 are the partial pressures of the corresponding associates. Hence the constant calculated from equation (3) is in fact equal to

$$K = \frac{P_2(2 + K_4' P_2)^3}{4(K_4' + 2K_6' P_2)}, \tag{4}$$

where $K_4' = P_4 : P_2^2$, and $K_6' = P : P_2^3$.

It follows from equation (4) that, with increasing P_2, proportional to the total pressure, the constant should increase, as is the case under consideration. It is easy to show that if, in addition to Se_2 and Se_6, Se_8 were present in the system, the constants would have to decrease.

The theoretically justified method for calculating the constants of complex equilibria requires knowledge of the dependences of ν on P as $P \to 0$. In our case such a calculation would have involved an excessively arbitrary extrapolation. We therefore used a fitting method, in which we took into account the values of the constants determined in calculating the simpler dissociation.

The constants of the three-stage dissociation describe well only the isotherms 700–900°. The constants of the four-stage dissociation describe all the isotherms well, which agrees with the constancy of the constants of the simple dissociation $Se_6 \rightleftarrows Se_2$ for temperatures 550–650°, at which the influence of Se_4 molecules is compensated by the influence of Se_8.

In selecting the constants of the four-stage dissociation, analogous to dissociation in sulfur vapor (^{7}), we arbitrarily assumed the independence of the thermal effects from temperature, which, of course, is not entirely correct.

The equations for the dependences of $\lg K$ on $1/T$ have the following form:

$$\lg K_4 = -\frac{36700}{4.576\,T} + 11.31; \qquad \lg K_6 = -\frac{62700}{4.576\,T} + 19.23;$$

$$\lg K_8 = -\frac{93900}{4.576\,T} + 29.41.$$

Somewhat doubtful is the excessively large value of ΔH in the first equation. Fig. 1 shows the calculated dependences of ν on P: by solid lines for the complex dissociation and by dotted lines for the simple dissociation. The latter were calculated from the weighted-average constants from Table 1. It should be noted that the points of Preuner and Brockmöller are widely scattered at elevated pressures, precisely in the region where the accuracy should be greatest.

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