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Dissociation Energies of Group VIa Gaseous Homonuclear Diatomic Molecules. II. Selenium*

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The dissociation energy of $Se_2(g)$ has been determined by the simultaneous Knudsen-torsion effusion method. The equilibrium, $Se_2(g) \leftrightharpoons 2Se(g)$, has been studied with a double-oven, alumina effusion cell; one oven contained elemental selenium and supplied vapor to the hot oven from which the effusion occurred. The value of $D_0°$ found in this study is 75.7±2.5 kcal/mole; this value is in excellent agreement with values determined in mass-spectrometric equilibrium studies and in good agreement with a value from a spectroscopic experiment.

INTRODUCTION

The dissociation energy of $Se_2(g)$ has been investigated previously by spectroscopic, by thermochemical, and by mass-spectrometric techniques. The results of these investigations have been reviewed recently by Drowart and Goldfinger.[1] They concluded that $D_0°$ was 72.94±0.05 kcal/mole, a value based mainly on spectroscopic data and the analysis of Barrow, Chandler, and Meyer.[2] Drowart and Goldfinger[1] stated that this value is confirmed by the value of 74.5±2 kcal/mole which they reported from the mass-spectrometric determination of Detry.[3]

The present paper reports the experimental determination of the dissociation energy by the simultaneous Knudsen-torsion method. This method, not being subject to the same assumptions or errors as the previous experimentation, would yield an independent value.

EXPERIMENTAL

Apparatus

A description of the Knudsen-torsion apparatus, the double-oven alumina effusion cells, the orifice parameter and torsion fiber calibration procedures, and the experimental procedure are described in a previous paper.[4] Effusion cell A-10 was used in all the experiments with selenium; orifice parameters for this cell were given previously.[4] Two torsion fibers were used with values of the torsion constant sufficiently different to permit an appreciable range of pressure variation.

A heating lamp was used to prevent condensation of selenium on the mirror and apparatus wall. With this arrangement no significant condensation occurred on the suspension system. After several runs, only a very slight deposit was noted by a faint yellow on the damping plate.[4]

Sample

The sample of selenium used in this study was obtained from American Smelting and Refining Company, South Plainfield, New Jersey, and had a stated purity of 99.999+%. The impurities were Te, Cu, As, and Si in amounts less than 0.0001% each.

RESULTS

The experimental results for selenium consist of a low-temperature set which shows nearly no dissociation and a set at temperatures above 1277°K for which dissociation was definitely measurable. The set for the undissociated $Se_2(g)$ is given in Table I. The values for the pressures calculated from the Knudsen equation, P_K, and those calculated from the torsion equation, P_T, agree with each other within ±1.4%. The set of results for experiments in which dissociation was significant is reported in Table II. The "third-law" dissociation energy of $Se_2(g)$ for each run was calculated through the equation,

$$D_0° = \Delta H_0° = -RT \ln K_p - T\{2[(G_T° - H_0°)/T]_{Se} - [(G_T° - H_0°)/T]_{Se_2}\}, \quad (1)$$

where K_p is the measured equilibrium constant for the dissociation reaction, and $(G_T° - H_0°)/T$ is the free energy function. Values for the free energy functions were taken from Stull and Sinke.[5] The average of the individual third-law values for $D_0°$ is 75.7 kcal/mole with a standard deviation of ±2.5. The solid line in Fig. 1 is based on this value and the cited free energy functions.

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* Abstracted from a thesis submitted by P. Budininkas to the Illinois Institute of Technology in partial fulfillment of the requirements for the Ph.D. degree, June 1967. Presented at the 152nd National American Chemical Society Meeting, New York City, September 1966.

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[5] D. R. Stull and G. C. Sinke, *Thermodynamic Properties of the Elements* (American Chemical Society, Washington, D.C., 1956).

TABLE I. Comparison of P_K and P_T.

Temp (°K)	t (sec)	m (g)	β (rad)	P_T (atm×10^5)	P_K (atm×10^5)	$[(P_T-P_K)/P_T]10^2$ (%)
			Gaseous species essentially dimer			
1043[a]	10 842	0.0173	0.1656	0.960	0.971	−1.1
1050[b]	6 955	0.0224	0.0874	2.033	1.97	+3.1
1077[b]	6 364	0.0158	0.0663	1.542	1.54	+0.1
					Average	±1.4

[a] Torsion constant, $D=0.65878$ g-cm^2 sec^{-1}·rad^{-1}.

[b] Torsion constant, $D=2.6467$ g-cm^2 sec^{-1}·rad^{-1}.

DISCUSSION

Reliability Tests

The tests discussed in the previous paper[4] were performed. (1) The cell body, which constituted the hot "oven" from which effusion occurred, was heated to operating temperature while the sample reservoir was unheated and, hence, was not supplying vapor to the cell body. There was no rotation of the suspended cell and, therefore, no anomalous torque. (2) Effusion measurements were made under conditions of temperature and pressure which assured that only the $Se_2(g)$ species was present. The Knudsen and torsion pressures agreed within ±1.4%. (3) Measurements were performed at several total pressures varying over a factor of 9. There was no variation of values for $D_0°$ with total pressure, and this is assurance that there was equilibrium between the $Se(g)$ and $Se_2(g)$ species. (4) The measured dissociation energy of $I_2(g)$, as was reported in the previous paper,[4] was 36.17±0.77 kcal/mole in agreement with the accepted value of 35.538 kcal/mole.[6] The additional check[4] of the effect of variation of orifice size was not performed with selenium; the absence of a pressure dependence in the calculated $D_0°$ values was a sufficient assurance that dissociative equilibrium had been achieved.

The Dissociation Energy of $Se_2(g)$

A summary of reported values of the dissociation energy of selenium is presented in Table III. There is remarkable agreement of the value of $D_0°$ obtained in this work with the values by Detry,[3] and by Berkowitz and Chupka.[7]

The value of the dissociation energy found by Berkowitz and Chupka[7] was recalculated using the free energy functions for $Se(g)$ and $Se_2(g)$ by Stull and Sinke.[5]

TABLE II. Dissociation energy of $Se_2(g)$.

Temp (°K)	t (sec)	m (g)	β (rad)	p_T (atm×10^5)	Degree of dissociation[a]	K_p[a] (atm×10^5)	$-\Delta(G_T°-H_0°)/T$ (cal/deg·mole)	$\Delta H_0°$[a] (kcal/mole)
1277	5 976	0.0200	0.0978	2.263	0.012	0.00142	24.98	77.8
1355	5 678	0.0218	0.1192	2.756	0.069	0.0530	25.08	72.9
1355	4 675	0.0153	0.1044	2.412	0.121	0.143	25.08	70.2
1405	4 622	0.0204	0.1447	3.339	0.138	0.261	25.15	71.2
1441	4 651	0.0242	0.1663	3.834	0.063	0.0614	25.20	77.3
1442	4 636	0.0199	0.1409	3.249	0.114	0.172	25.20	74.4
1473	3 686	0.0203	0.1839	4.238	0.127	0.279	25.24	74.6
1493	4 150	0.0216	0.1736	3.998	0.110	0.198	25.26	76.7
1498[b]	5 606	0.0066	0.1640	0.9401	0.188	0.138	25.27	78.0
1523[b]	16 664	0.0105	0.1012	0.5795	0.543	0.968	25.30	73.5
1529	4 582	0.0198	0.1542	3.549	0.230	0.789	25.31	74.4
1547	3 764	0.0203	0.1961	4.511	0.259	1.30	25.33	73.8
1560[b]	9 173	0.0093	0.1537	0.8800	0.341	0.464	25.35	77.6
1571	2 963	0.0186	0.2199	5.056	0.158	0.520	25.36	77.8
1576	4 700	0.0177	0.1359	3.123	0.218	0.626	25.37	77.5
1602[b]	8 359	0.0086	0.1682	0.9620	0.518	1.41	25.40	76.2
1623	4 742	0.0191	0.1532	3.517	0.308	1.48	25.43	77.1
1629	5 558	0.0189	0.1287	2.956	0.293	1.11	25.43	78.4
1639	2 978	0.0180	0.2260	5.188	0.255	1.44	25.44	78.0
				Average	$\Delta H_0°=75.7\pm2.5$ kcal/mole			

[a] A small but basically required correction has been applied to the data reported by P. Budininkas, Ph.D. thesis, Illinois Institute of Technology, 1967.

[b] Torsion constant, $D=0.65878$ g-cm^2 sec^{-1}·rad^{-1}. All others, torsion constant, $D=2.6467$ g-cm^2 sec^{-1}·rad^{-1}.

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[6] W. H. Evans, T. R. Munson, and D. D. Wagman, J. Res. Natl. Bur. Std. **55**, 147 (1955).

[7] J. Berkowitz and W. A. Chupka, J. Chem. Phys. **45**, 4289 (1966).

TABLE III. Dissociation energy values for $Se_2(g)$ obtained by various methods.

Method	$D_0°$ (kcal/mole)	Investigator or reviewer
Spectroscopic	64.5	Gaydon[a] (reviewer)
	72.94±0.03	Barrow, Chandler, and Meyer[2] (investigators)
Thermochemical	71.5	Nernst[b, c] and von Wartenberg[d] (investigators)
Mass spectrometric	75±2	Detry[3] (investigator)
	75.3±2	Berkowitz and Chupka[7, e] (investigators)
Knudsen-torsion effusion	75.7±2.5	This work (investigators)

[a] A. G. Gaydon, *Dissociation Energies and Spectra of Diatomic Molecules* (Chapman and Hall, Ltd., London, 1953), 2nd ed.

[b] W. Nernst, Z. Electrochem. **9**, 622 (1903).

[c] P. Goldfinger, M. Jeunehomme, and B. Rosen, Nature **138**, 205 (1936).

[d] H. von Wartenberg, Z. Anorg. Chem. **56**, 320 (1908).

[e] Recalculated using Stull and Sinke's free energy functions for Se_2.

There was apparent confusion about the ground electronic state of $Se_2(g)$ which led Berkowitz and Chupka to use other free energy functions. The ground electronic state of $Se_2(g)$ used by Stull and Sinke is $^3\Sigma$ which is in agreement with the magnetic-susceptibility measurements of Massen, Weijts, and Poulis.[8] Thus, the Stull and Sinke[5] free energy functions for $Se_2(g)$ appear to use the correct ground electronic state.

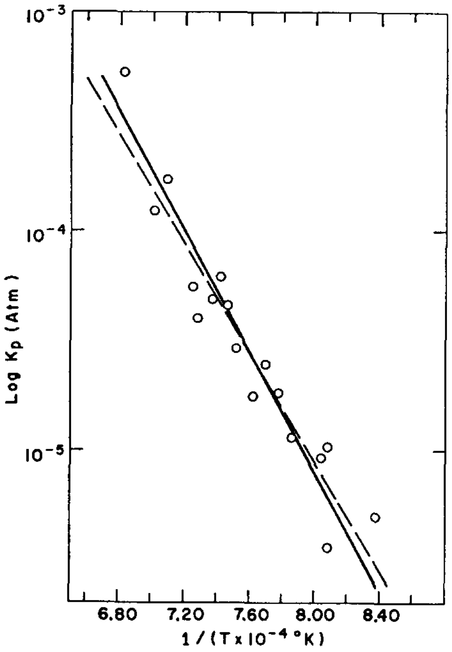

FIG. 1. Equilibrium constants as a function of temperature for $Se_2(g) \rightleftharpoons 2Se(g)$. ——, calculated from the derived $\Delta H_0° = 75.7$ kcal/mole and the free energy functions[5]; – – –, calculated by least-squares treatment of the data shown ("second law").

It is to be noted that all of the mass-spectrometric data and the result of the present study for $D_0°$ have assigned uncertainties of ~2 kcal/mole. Thus, all of these values are in agreement with the spectroscopic value of Barrow, Chandler, and Meyer.[2] The fact that all of the dissociation energies from these three equilibrium studies yield an average value of 75.3 kcal/mole within 0.4 kcal/mole suggests that the uncertainty may be much smaller than the assigned 2 kcal/mole. There is little basis for preference between the spectroscopic value and the noted average value. If the spectroscopic value chosen by Barrow *et al.*[2] is correct and also the mass-spectrometric and Knudsen-torsion experiments are valid, then the free energy functions used to calculate the results for the latter would have to be incorrect.

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[8] C. H. Massen, A. G. L. Weijts, and J. A. Poulis, Trans. Faraday Soc. **60**, 317 (1964).