Entropies and Heat Capacities of Gaseous Selenium Molecules Se_n ($n = 5 \ldots 12$)

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Thermodynamic functions are calculated for gaseous Se_8 molecules from spectroscopic and structural data and listed for temperatures up to 3000 K. Entropy (S^0) and heat capacity ($C_p{}^0$) data for Se_n molecules ($n = 5, 6, 7, 9, 10, 11, 12$) are obtained from linear relationships between both S^0 and $C_p{}^0$ and ring size n which are derived from the corresponding values of Se_2 and Se_8.

The presumably cyclic molecules Se_5, Se_6 and Se_7 are the main constituents of saturated selenium vapor at temperatures up to 400 °C as well as of the vapor above freely subliming trigonal selenium, and cyclic Se_8 molecules can be prepared as various crystalline modifications [1]. Small selenium rings are also discussed as constituents of liquid and amorphous selenium obtained by quenching the liquid or the vapor [1]. To determine the equilibrium concentrations of the various Se_n molecules ($n > 2$) in the liquid and gaseous state, their entropies and heat capacities are needed, but no experimentally determined values have been published so far. Drowart and Smoes [2] as well as Keller et al. [3] calculated the entropies for $n = 3 \ldots 8$ using the well known statistically-thermodynamic equations [4] but no information was given concerning the molecular structures and vibrational frequencies used, which had to be assumed since only the molecular structure [5] and vibrational spectra [6–10] of solid Se_8 are known.

The vibrational spectra of Se_8 have recently been assigned and force constants have been calculated [11]. Provided neither the fundamental frequencies nor the structural parameters change on vaporization of the Se_8 molecule, the thermodynamic functions given in Table 1 can be calculated assuming rigid rotator, harmonic oscillator and ideal gas behavior. The obtained entropies differ from the estimated literature data [2] by less than 0.2%. The principal moments of inertia amount to $I_A = 4380$ and $I_B = I_C = 2410$ (in 10^{40} g · cm²; obtained with the structural data cited in [11]).

The molecular structures of Se_8 and S_8 are very similar, and there are many structural parallels between analogous homoatomic sulfur and selenium compounds. The ionization potentials and electron affinities of S and Se atoms are practically identical, leading to identical electronegativities. It is therefore not surprizing that eight- and twelve-membered sulfur-selenium mixed rings exhibit the same molecular structures as the corresponding homocyclic sulfur species [12–15]. It, therefore, can be assumed that the cyclic molecules Se_n ($n = 5 \ldots 12$) have the same molecular symmetries as the corresponding sulfur rings [16].

The heat capacities ($C_p{}^0$) and entropies (S^0) of the sulfur rings S_n ($n = 6, 7, 8, 12$) have been calculated from the known structural and spectroscopic data [18], and it was observed that the values of both $C_p{}^0$ and S^0 at a given temperature linearly depend on the ring size n of the molecule S_n. Even the S_2 molecule fits the linear relationships if its entropy is lowered by the contribution of the two unpaired electrons (9.1 J/mol · K) [18]. These linear rela-

Table 1. Thermodynamic functions of gaseous cycle-octaselenium (Se_8; symmetry D_{4d}). S_T^0 standard entropy, C_p^0 heat capacity, H enthalpy, G free enthalpy; values in J/mol · K.

Temp. (K)	S_T^0	C_p^0	$\frac{H_T - H_0}{T}$	$-\frac{(G_T - H_0)}{T}$
100.0	361.2	129.3	80.2	281.0
200.0	464.4	164.4	115.5	348.9
273.2	517.0	172.4	129.8	387.2
298.2	532.2	174.0	133.5	398.7
300.0	533.3	174.1	133.7	399.6
400.0	583.9	177.8	144.3	439.6
500.0	623.8	179.6	151.2	472.6
600.0	656.7	180.6	156.0	500.6
700.0	684.5	181.2	159.6	524.9
800.0	708.8	181.6	162.3	546.4
900.0	730.2	181.9	164.5	565.7
1000.0	749.3	182.1	166.2	583.1
1100.0	766.7	182.2	167.7	599.0
1200.0	782.6	182.3	168.9	613.7
1300.0	797.2	182.4	169.9	627.2
1400.0	810.7	182.5	170.8	639.9
1500.0	823.3	182.5	171.6	651.7
2000.0	875.8	182.7	174.4	701.5
2500.0	916.6	182.8	176.0	740.6
3000.0	949.9	182.8	177.2	772.8

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tionships allow the estimation of $C_p{}^0$ and S^0 values for molecules of intermediate size by interpolation.

Assuming that analogous relationships exist for the cyclic Se_n molecules as well as Se_2, the following equations can be obtained from the heat capacities and entropies of Se_8 and Se_2 (298 K; entropy of Se_2 lowered by 9.1 J/mol · K):

$$C_p{}^0(\mathrm{J/mol \cdot K}) = 22.17\,n - 3.33\,, \tag{1}$$

$$S^0(\mathrm{J/mol \cdot K}) = 49.6\,n + 135.4\,. \tag{2}$$

Similar equations can be derived for other temperatures. The $C_p{}^0$ and S^0_{298} values of the molecules Se_n ($n = 5, 6, 7, 9, 10, 11, 12$) calculated from these equations are presented in Table 2. While the entropies calculated this way differ by only 0.2 to 0.8% from the estimated literature data for Se_5, Se_6 and Se_7 [2, 3], the heat capacities for unknown reasons show larger deviations (up to 6%) from the values calculated by Drowart and Smoes [2]. From the experience with sulfur rings [18] it is however concluded that the present data are more reliable.

Table 2. Entropies S^0 and heat capacities C_p^0 of gaseous cyclic selenium molecules Se_n at 298 K obtained from equations (1) and (2); values in J/mol · K.

	S^0_{298}	C^0_p		S^0_{298}	C^0_p
Se_5	383.4	107.5	Se_9	581.8	196.2
Se_6	433.0	129.7	Se_{10}	631.4	218.4
Se_7	482.6	151.9	Se_{11}	681.0	240.5
Se_8	(532.2)	(174.0)	Se_{12}	730.6	262.7

It has further been found that at given temperatures T_1 and T_2 ($T_1 > T_2$) the function $H_{T_1} - H_{T_2}$ of the sulfur molecules S_2 [2], S_6, S_7, S_8 and S_{12} [18] also depends on the number n of atoms in the molecule. For example, the following equation holds for $H_{400} - H_{298}$ (correlation coefficient 0.999):

$$S_n\colon\ H_{400} - H_{298} = 2.215\,n - 1.196 \quad (\text{in kJ/mol})\,. \tag{3}$$

Assuming an analogous relationship for Se_n molecules, a corresponding equation can be derived from the data of Se_2 [2] and Se_8 (Table 1):

$$Se_n\colon\ H_{400} - H_{298} = 2.278\,n - 0.317 \quad (\text{in kJ/mol})\,. \tag{4}$$

Equations of these types allow to calculate $H_{T_1} - H_{T_2}$ for molecules S_n and Se_n ($n = 5 \ldots 12$) at any temperatures T_1 and T_2. It should be pointed out, however, that it may not be allowed to apply equations (1) to (4) to molecules with $n = 3$ or 4 which are likely to be non-cyclic.

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