

- (26) It is assumed that the 44-31G method would produce an energy difference between the bent and the planar $c\text{-S}_4$ quite similar to that predicted by the STO-3G method. For cyclobutane, both STO-3G and 4-31G calculations give very similar results.¹⁹
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Contribution from the Technical University of Denmark,
Chemistry Department A, DK-2800 Lyngby, Denmark

Lower Oxidation States of Selenium. 2. Potentiometric Study Involving Tetravalent Selenium, Tetraselenium (2+), Octaselenium (2+), and Three Other Low Oxidation States of Selenium in a Chloroaluminate Melt

RASMUS FEHRMANN and NIELS J. BJERRUM*

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The solvated entities Se_4^{2+} and Se_8^{2+} have been identified in reaction mixtures of dilute SeCl_4 and elementary selenium by a potentiometric method supplemented by a spectrophotometric method. The three other low oxidation states of selenium are believed to be Se_2^{2+} , Se_{12}^{2+} , and Se_{16}^{2+} . The solvent is low-melting NaCl-AlCl_3 (37:63 mol %) at 150 °C. pK values (based on molar concentrations) are given for the reactions $2\text{Se}^{4+}(\text{soln}) + 3\text{Se}_4^{2+}(\text{soln}) \rightleftharpoons 7\text{Se}_2^{2+}(\text{soln})$ (1), $4\text{Se}^{4+}(\text{soln}) + 7\text{Se}_8^{2+}(\text{soln}) \rightleftharpoons 15\text{Se}_4^{2+}(\text{soln})$ (2), $\text{Se}_4^{2+}(\text{soln}) + \text{Se}_{12}^{2+}(\text{soln}) \rightleftharpoons 2\text{Se}_8^{2+}(\text{soln})$ (3), and $\text{Se}_8^{2+}(\text{soln}) + \text{Se}_{16}^{2+}(\text{soln}) \rightleftharpoons 2\text{Se}_{12}^{2+}(\text{soln})$ (4). For the four equilibria the potentiometric method gave pK values of 7.9, -12.5, -2.9, and 0.0 with nonlinear confidence limits (95%) of 4.7 to 9.1, $-\infty$ to -12.4, $-\infty$ to -2.5, and -0.2 to 0.2, respectively. Calculation based on earlier spectrophotometric data at 150 °C for equilibria 3 and 4 gave pK values of -2.0 and -0.8 with nonlinear confidence limits (95%) of $-\infty$ to -0.7 and $-\infty$ to +2.4, respectively; no pK value was determined for the first reaction and no well-defined pK value could be determined for the second reaction; however, the nonlinear confidence limits (95%) could be determined for the second reaction to be $-\infty$ to -5.5.

Introduction

In a previously published paper¹ it was shown that four species were formed by reduction of a solution of SeCl_4 in an acidic NaCl-AlCl_3 (37:63 mol %) melt with elementary selenium. The two highest oxidation states of these species were found to be $+1/2$ and $+1/4$ (or possibly $+4/17$), whereas no accurate value could be calculated for the two lowest oxidation states. As possible formulas for these species Se_4^{2+} , Se_8^{2+} , Se_{12}^{2+} , and Se_{16}^{2+} were proposed. In the present paper good evidence (based on potentiometric measurements) is given for Se_4^{2+} and Se_8^{2+} and the existence of Se_{12}^{2+} and Se_{16}^{2+} is shown to be reasonable. Furthermore the results indicate that there is a fifth low oxidation state of selenium present, probably Se_2^{2+} . The presence of Se_4^{2+} and Se_8^{2+} is in agreement with the results found in sulfuric acid by Gillespie and co-workers.² The results obtained by Corbett and co-workers³ seem to indicate that the same two ions are formed in chloroaluminate melts. The structure of Se_4^{2+} in $\text{Se}_4(\text{HS}_2\text{O}_7)_2$ is square planar⁴ and the structure of Se_8^{2+} in $\text{Se}_8(\text{AlCl}_4)_2$ is bicyclic.⁵

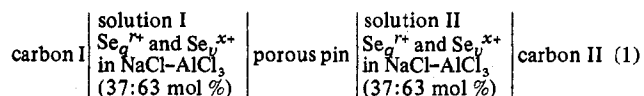
Experimental Section

The chemicals used in the present work were prepared in the same way as in the previous work on selenium.¹ The experimental technique was the same as described in a recent article about the lower oxidation states of tellurium,⁶ where an electrochemical cell with inert electrodes of glassy carbon was used for the potentiometric measurements.⁷ The furnace used has been described in detail in connection with a method for determination of densities of molten salts.⁸ The materials that made up a melt were weighed in a nitrogen-filled glovebox, where the water content was ca. 5 ppm. To avoid decomposition of the SeCl_4 used it was kept in small sealed glass tubes until used.

Results and Discussion

Cell Potentials. As demonstrated in a previous publication about low oxidation states of tellurium,⁶ an electrode cell made of Pyrex with vitreous carbon fused into the bottom can be used to measure redox potentials of the different tellurium species. The same type of cell can also be used to measure redox potentials of the low oxidation states of selenium.

If we look at one redox pair which we will call Se_q^{r+} and Se_v^{x+} (r, q, v , and x are integers), the composition of the cell can be given as



At each electrode we have the equilibrium



where e^- is the electron and n is the number of electrons. Analogous to the calculation performed on the tellurium system⁶ it can be shown that the potential of the concentration cell is given by

$$\Delta E = \frac{RT}{F} \ln \frac{[\text{Se}_q^{r+}]_{\text{II}}^{v/n} [\text{Se}_v^{x+}]_{\text{I}}^{q/n}}{[\text{Se}_q^{r+}]_{\text{I}}^{v/n} [\text{Se}_v^{x+}]_{\text{II}}^{q/n}} \quad (3)$$

where R , T , and F have their usual meaning. The variation in the activity coefficients has been neglected in the present work. This is based on the same arguments as given in the recent article dealing with the tellurium system.⁶

A plot of the measured ΔE vs. the $\text{Se}:\text{SeCl}_4$ formality ratio (designated R) is given in Figure 1. The formality is defined as the initial molar amount of any of the added substances dissolved in 1 L of the melt. The plot in Figure 1 shows some of the same features as the spectrophotometric plot for the same system in the same R range.¹ It is for example clear that there must be a sharp change in concentrations of the species around a formality ratio of 15. It is furthermore important to notice that there is no change in ΔE after a formality ratio of ca. 31 is reached; this must mean that the melt is saturated above this formality ratio.

As in the work on the low oxidation states of tellurium⁶ the compositions in the two cell compartments were increased alternately, while interchanging the compartments used for measurement and reference. A small difference in composition

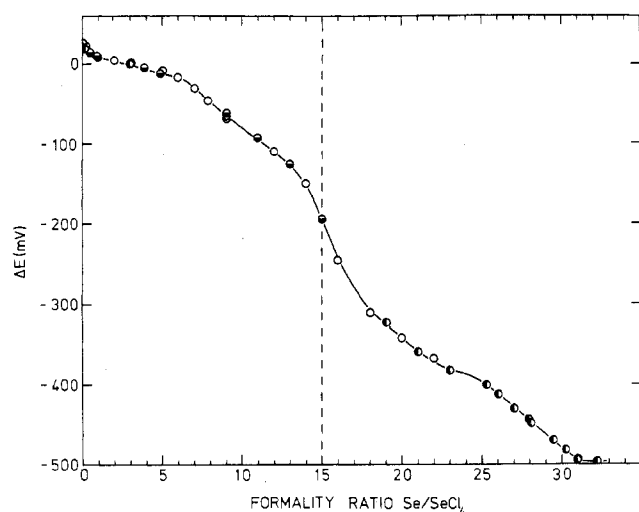


Figure 1. Measured ΔE values as a function of the Se:SeCl₄ formality ratio. Values are taken from Table I: horizontally half-filled circles, cell no. 1; vertically half-filled circles, cell no. 2; open circles, cell no. 3.

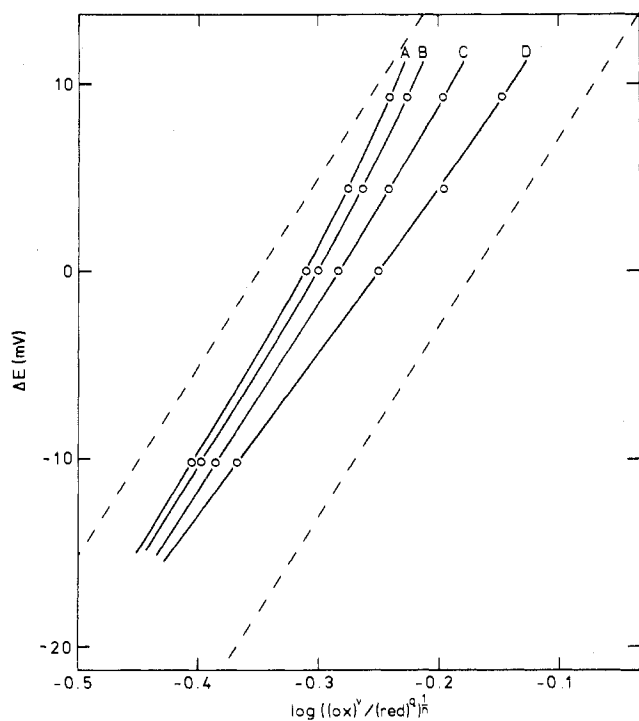


Figure 2. Relation between the measured ΔE taken from Table I (cell no. 3) and the calculated value of $\log ([\text{Ox}]^v/[\text{Red}]^q)^{1/n}$ for the formality ratio range 0.97₉ to 5.02₈. Formulas for Ox and Red and values of v , q , and n : (A) Se^{IV}, Se₈⁴⁺, 8, 1, 28; (B) Se^{IV}, Se₆³⁺, 6, 1, 21; (C) Se^{IV}, Se₄²⁺, 4, 1, 14; (D) Se^{IV}, Se₂⁺, 2, 1, 7. The dashed lines have the theoretical slope.

between the two cell compartments will reduce the possibility of vapor transport of material from one chamber to the other. In Table I all ΔE values refer to the original reference compositions called the basic reference melts.

First we decided to look at the ranges in which the spectral measurements¹ indicated that only two species were present. Two such two-species ranges are present, one with a formality ratio (Se:SeCl₄) of 0 to ca. 7 and another with a formality ratio of ca. 7 to ca. 11.5. If only two species are present the concentrations of the two chosen species (Se_q^{r+} and Se_v^{x+}) can be calculated from the formality ratio (Se:SeCl₄) and the formality of SeCl₄. If the correct formulas of Se_q^{r+} and Se_v^{x+}

Table I. Values of Cell Potential at Different Formalities of Selenium and SeCl₄ in Molten NaCl-AlCl₃ (37:63 mol %)^a at 150 °C

ΔE , mV	c'_{Se} (formality of Se)	$c'_{\text{Se(IV)}}$ (formality of SeCl ₄)	R (Se:SeCl ₄ formality ratio)
26.7 ₇ ^b	0.0054 ₉	0.2435 ₇	0.022 ₆
21.5 ₂ ^b	0.023 ₅	0.2434 ₉	0.096 ₆
18.5 ₅ ^c	0.014 ₁	0.0930 ₂	0.15 ₁
17.8 ₂ ^b	0.061 ₆	0.2431 ₁	0.25 ₃
14.6 ₇ ^b	0.125 ₆	0.2430 ₁	0.51 ₇
11.2 ₂ ^b	0.220 ₇	0.2425 ₆	0.91 ₀
9.3 ₁ ^d	0.095 ₇	0.0977 ₁	0.97 ₉
4.4 ₂ ^d	0.195 ₄	0.0975 ₂	2.00 ₄
0.0 ₀ ^c	0.279 ₀	0.0925 ₄	3.01 ₅
0.0 ₀ ^d	0.294 ₈	0.0973 ₃	3.02 ₈
-5.7 ₁ ^b	0.939 ₆	0.2391 ₉	3.92 ₈
-10.1 ₂ ^d	0.487 ₅	0.0969 ₇	5.02 ₈
-11.9 ₅ ^b	1.176 ₈	0.2380 ₈	4.94 ₃
-17.0 ₂ ^d	0.582 ₂	0.0967 ₉	6.01 ₅
-30.4 ₆ ^d	0.642 ₄	0.0916 ₁	7.01 ₃
-46.3 ₃ ^d	0.761 ₃	0.0961 ₀	7.92 ₁
-62.5 ₂ ^b	2.095 ₁	0.2328 ₂	9.00 ₀
-65.3 ₂ ^d	0.865 ₅	0.0959 ₁	9.02 ₄
-67.8 ₂ ^c	0.824 ₉	0.0915 ₄	9.01 ₁
-93.5 ₂ ^b	2.573 ₉	0.2338 ₂	11.00 ₈
-109.8 ₂ ^d	1.086 ₆	0.0908 ₂	11.96 ₆
-126.2 ₂ ^b	3.014 ₃	0.2317 ₃	13.00 ₈
-150.4 ₂ ^d	1.267 ₀	0.0904 ₉	14.00 ₁
-193.9 ₂ ^b	3.446 ₆	0.2296 ₉	15.00 ₆
-245.8 ₂ ^d	1.440 ₈	0.0901 ₈	15.97 ₆
-311.3 ₂ ^d	1.618 ₁	0.0898 ₇	18.00 ₆
-322.5 ₂ ^c	1.698 ₃	0.0893 ₈	19.00 ₂
-343.9 ₂ ^d	1.796 ₁	0.0895 ₅	20.05 ₇
-359.3 ₂ ^c	1.879 ₃	0.0895 ₃	20.98 ₈
-367.9 ₂ ^d	1.968 ₂	0.0892 ₄	22.05 ₉
-383.0 ₀ ^c	2.052 ₃	0.0892 ₂	23.00 ₄
-400.8 ₂ ^c	2.231 ₂	0.0884 ₃	25.23 ₃
-411.8 ₂ ^c	2.300 ₂	0.0883 ₀	26.04 ₉
-430.4 ₂ ^c	2.300 ₂	0.0886 ₁	27.02 ₂
-445.3 ₂ ^c	2.477 ₅	0.0884 ₆	28.00 ₆
-447.5 ₂ ^c	2.472 ₂	0.0880 ₀	28.09 ₄
-468.6 ₀ ^c	2.604 ₀	0.0882 ₄	29.51 ₂
-481.5 ₂ ^c	2.653 ₃	0.0876 ₈	30.26 ₃
-495.3 ₂ ^c	2.729 ₉	0.0880 ₁	31.01 ₈
-495.3 ₂ ^c	2.719 ₉	0.0875 ₇	31.05 ₂
-497.5 ₂ ^c	2.824 ₄	0.0875 ₇	32.25 ₅

^a In each cell compartment was ca. 10.30 g of NaCl-AlCl₃ melt.

^b Potentiometric cell no. 1 composition of basic reference melt: $R = 3.00_9$, $c'_{\text{Se(IV)}} = 0.2435_5$. ^c Potentiometric cell no. 2 composition of basic reference melt: $R = 3.01_3$, $c'_{\text{Se(IV)}} = 0.0920_5$.

^d Potentiometric cell no. 3 composition of basic reference melt: $R = 3.01_7$, $c'_{\text{Se(IV)}} = 0.0924_0$.

are used for the species in cell compartment II and the measured ΔE values are plotted vs. $\log ([\text{Se}_q^{r+}]_{\text{II}}^{v/n}/[\text{Se}_v^{x+}]_{\text{II}}^{q/n})$, one should obtain a straight line with the slope $RT(\ln 10)/F$. Such a plot is shown in Figure 2 for the first two-species range. The formality ratio range is here 0.97₉ to 5.02₈. Since Se_q^{r+} has a higher oxidation state than Se_v^{x+}, they are designated Ox and Red, respectively. The basic reference with formality ratio of 3.01₇ and formality of SeCl₄ of 0.0924₀ is here used as solution I. We have in agreement with the spectrophotometric measurement assumed that the oxidation state of Se_v^{x+} is +1/2 in this range. The formula for Se_q^{r+} is of course Se^{IV} (present as the SeCl₃⁺ ion⁹). As before we assume that the formal charges on these species are not higher than 4+ (a survey of the chemical literature shows that few compounds have a positive charge higher than 4+).¹ As seen from Figure 2 none of the plotted reaction schemes give straight lines. This was unexpected since in the same range for the similar tellurium system straight lines are obtained. However, the plot made from the assumption that Se_v^{x+} is equal to Se₂²⁺ has a slope closest to the theoretical value. A similar plot for the other two-species range is shown in Figure

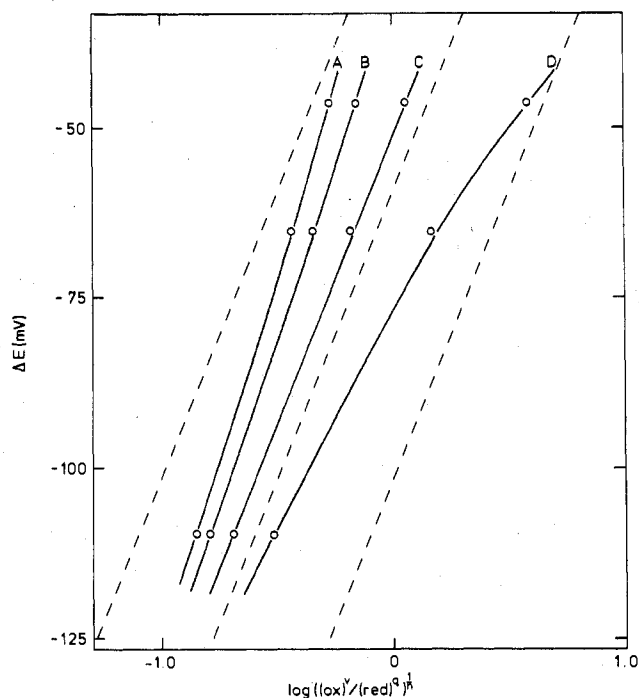


Figure 3. Relation between the measured ΔE taken from Table I (cell no. 3) and the calculated value of $\log ([\text{Ox}]^v/[\text{Red}]^q)^{1/n}$ for the formality ratio range 9.92₁ to 11.96₅. Formulas for Ox and Red and values of v , q , and n : (A) Se_4^{2+} , Se_{16}^{4+} , 4, 1, 4; (B) Se_4^{2+} , Se_{12}^{3+} , 3, 1, 3; (C) Se_4^{2+} , Se_8^{2+} , 2, 1, 2; (D) Se_4^{2+} , Se_4^{+} , 1, 1, 1. The dashed lines have the theoretical slope.

3. The formality ratio range is here 7.92₁ to 11.96₅. According to the spectrophotometric examination of the system a species with oxidation state $+1/2$ (i.e., Se_2^{2+}) is present together with a species with the oxidation state $+1/4$. As can be seen from Figure 3 one of the models gives an almost straight line with a slope close to the theoretical value. This line is calculated with Se_4^{2+} as Ox and Se_8^{2+} as Red. The possibility that one is not dealing with a species with oxidation state $+1/2$ in the nonlinear cases can be excluded since this is in complete disagreement with the spectrophotometric results. A more likely possibility is that in the R range from 0 to 7 there is a third species present in a small concentration together with Se^{IV} and a species with oxidation state $+1/2$. An examination of the plots in Figure 2 indicates that the deviation from the theoretical slope is most pronounced at low formality ratios. Since spectrophotometric measurements have only been performed on a few compositions at low formality ratios, a reinvestigation of the spectrophotometric measurements seemed appropriate. In Figure 4 plot A represents the formal absorptivity (i.e., the absorptivity divided by the formality of SeCl_4) measured at $21.9 \times 10^3 \text{ cm}^{-1}$ (the same as in the spectrophotometric work¹); one point with a formality ratio of 2.99 is new. As can be seen a straight line is still obtained. If one, however, plots the formal absorptivity of SeCl_4 for the same composition at $26.7 \times 10^3 \text{ cm}^{-1}$, there seems to be a deviation from the straight line in the R range from 0 to ca. 4 making more than two species a possibility. If we now exclude the potentiometric measurements with R below 3 (below 4 would have been better but not many measurements were available), this corresponds to removal of the upper two rows of points in Figure 2. An examination of the slopes defined by the remaining two rows of points shows that the slope of curve C is very close to the theoretical value. Curve C is based on the formation of Se_4^{2+} .

If three species are present (according to the spectrophotometric work this is the situation outside the two-species ranges), one has to start with the mass action relation which

Table II. Variances Based on Potentiometric Measurements for Models^a with Oxidation States in the Range +4 to $+1/2$ ^b

Oxidn state	Formal charge			
	1+	2+	3+	4+
+4				
+3			1.7×10^5	
+2		6.7×10^4		(1.2×10^5)
$+3/2$			7.3×10^4	
+1	$3.4 \times 10^{3*}$	$4.7 \times 10^{3*}$	1.7×10^4	1.6×10^4
$+4/5$				$(3.7 \times 10^3)^c$
$+3/4$			$(1.7 \times 10^3)^c$	
$+2/3$		1.2×10^2 ^c		$6.3 \times 10^{3*}$
$+3/5$			1.8×10^4	
$+4/7$				5.1×10^4
$+1/2$				

^a Other species in the equilibria assumed to be Se^{IV} and Se_4^{2+} .

^b Number of measurements 5; formality ratio range 0.022₆ to 3.00₉; asterisks indicate values based on $F_{0.10}(4.4) = 4.11$. Parentheses indicate that no minima were found; the values given are then equilibrium constants of either 10^{+60} or 10^{-60} . ^c Corresponding equilibrium constant large (i.e., in disagreement with spectrophotometric measurements).

in the recent spectrophotometric work was given as



For each model equation one has to start with an arbitrarily chosen equilibrium constant (as explained in the recent article about the lower oxidation states of tellurium⁶), calculate the concentration of each species and introduce the calculated concentrations in eq 3. By varying systematically the equilibrium constant for the particular model equilibrium we are considering it is possible to minimize the deviation (least squares) between the formality ratios directly calculated from the weighting scheme and the calculated ratios. In Table II calculations by this method are given for the R range 0.022₆ to 3.00₉. The solution with an R value of 0.25₃ has been chosen to represent solution I. All the possible oxidation states between +4 and $+1/2$ with formal charges not higher than 4+ are given in this table; the two other species are assumed to be Se^{IV} and Se_4^{2+} . Se^{IV} is selected as Ox and the new species as Red. For the models where no minima were found the variances were calculated from equilibrium constants of either 10^{+60} or 10^{-60} . Since the variances varied very little with respect to the equilibrium constants at these extreme values, the given variances are assumed to be correct. In a few cases the equilibrium constant for eq 4 was found to be very large. This cannot be the case since an extrapolation of the curves A and B in Figure 4 in the formality ratio range 4 to 7 will go through the origin. This must mean that the unknown species is only obtaining an appreciable concentration around $R = 3$. The calculations in Table II are based on a series of measurements where increasing amounts of materials have been added to the same cell. The sum of squares for each model have therefore been weighted by the inverse of the associated variance for each formality ratio, calculated from an estimated average error of ± 0.14 mg in the weight of selenium and of ± 0.40 mg in the weight of SeCl_4 . This procedure is similar to the procedure used for the tellurium system⁶ and has been used in all calculations in this work.

The values in Table II marked with asterisks indicate that the variances for these models are within the 90% probability range (based on an F test) of the lowest obtained variances. In this connection it was assumed that there were only as many degrees of freedom as there were different melt compositions minus 1. From Table II it can be seen that three formulas (Se^+ , Se_2^{2+} , and Se_6^{4+}) are possible. From the chemical point of view Se_2^{2+} is the most likely formulation for this species since Te_2^{2+} is found in chloroaluminate melts with high

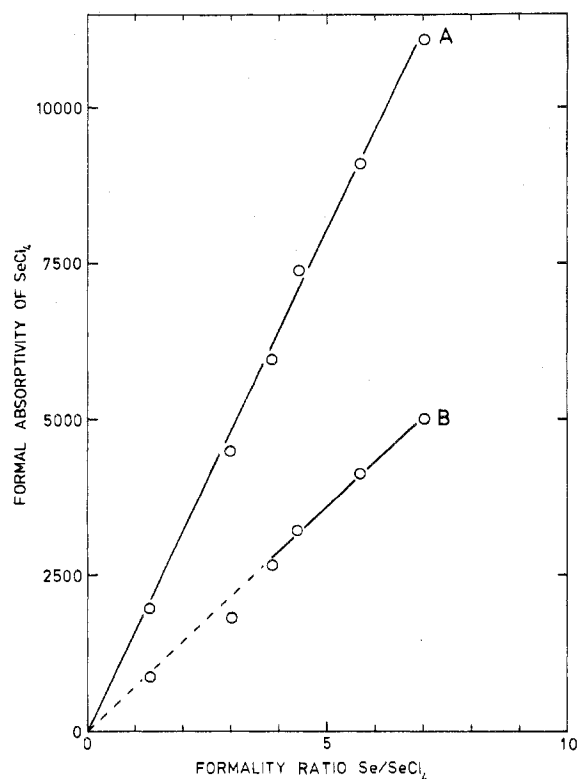


Figure 4. Relation between the formal absorptivity of SeCl_4 and the $\text{Se}:\text{SeCl}_4$ formality ratio in the range 0 to 7 measured at two different wavenumbers: (A) at $21.9 \times 10^3 \text{ cm}^{-1}$; (B) at $26.7 \times 10^3 \text{ cm}^{-1}$. The dashed line shows where a deviation from Beer's law is a possibility.

Table III. Variances Based on Potentiometric Measurements for Models^a with Oxidation States Close to $+1/2$ ^b

Oxidn state	Formal charge			
	1+	2+	3+	4+
$+2/3$		(2.0×10^3)		(3.5×10^3)
$+3/5$			(1.2×10^3)	
$+4/7$				(1.0×10^3)
$+1/2$	$2.4 \times 10^2*$	$8.6 \times 10^*$	$1.9 \times 10^2*$	3.6×10^2
$+4/9$				$2.8 \times 10^2*$
$+3/7$			4.4×10^2	
$+2/5$		(1.1×10^3)		1.2×10^3

^a Other species in the equilibria assumed to be Se^{IV} and Se_6^{2+} .

^b Number of measurements 6; formality ratio range 3.02₈ to 11.96₅; asterisks indicate values based on $F_{0.10}(5.5) = 3.45$. Parentheses indicate that no minima were found; the values given are then for equilibrium constants of either 10^{+60} or 10^{-60} .

chloride ion activity (i.e., basic melts).¹⁰

In Table III are similarly given the variances for models with oxidation states close to $+1/2$; the other species in the equilibrium are assumed to be Se^{IV} and Se_8^{2+} just as in the case of the spectrophotometric measurements. The species with oxidation state close to $+1/2$ is selected as Ox and Se_8^{2+} as Red. The R range has been chosen to be 3.02₈ to 11.96₅. Below $R = \text{ca. } 3$ there is too much of the species likely to be Se_2^{2+} in comparison with the other low oxidation states and according to the previous spectrophotometric measurements there is too much of the species believed to be Se_{12}^{2+} above $R = \text{ca. } 12$. The composition with $R = 9.02_4$ is used as solution I. From Table III it can be seen that four formulas under the above conditions will have to be taken into account. A comparison with the similar calculations for the spectrophotometric measurements will exclude one of these possibilities. We are therefore left with the species Se_2^{2+} , Se_4^{2+} , and Se_6^{3+} . From the table it is clear that the variance for Se_4^{2+} is quite a bit lower than for the other species. If we instead

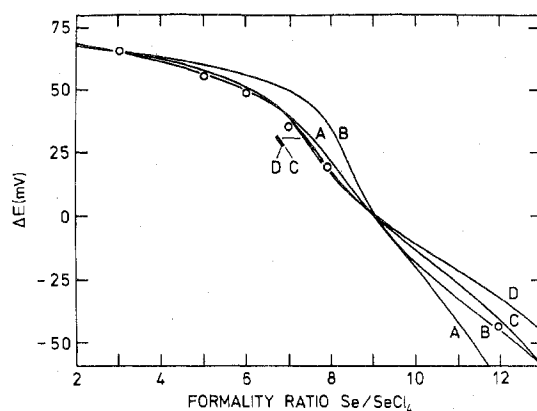


Figure 5. Measured ΔE values taken from Table I (open circles, cell no. 3) as a function of the $\text{Se}:\text{SeCl}_4$ formality ratio compared with values (full lines) calculated from the weighted experimental data for the four reaction schemes with the lowest variances in Table III. Species in equilibrium with Se^{IV} and Se_8^{2+} : (A) Se_2^{2+} ; (B) Se_9^{4+} ; (C) Se_4^{2+} ; (D) Se_6^{3+} .

Table IV. Variances Based on Potentiometric Measurements for Models^a with Oxidation States Close to $+1/4$ ^b

Oxidn state	Formal charge			
	1+	2+	3+	4+
$+1/3$	1.9×10^3	1.5×10^3	1.8×10^3	2.9×10^3
$+4/13$				5.5×10^2
$+3/10$			4.5×10^2	
$+2/7$		3.5×10^2		1.4×10^2
$+3/11$			$4.2 \times 10^*$	
$+4/15$				(1.7×10^2)
$+1/4$	2.7×10^2	8.0^*	8.8×10	(1.6×10^2)
$+4/17$				(5.8×10^2)
$+3/13$			(5.6×10^2)	
$+2/9$		5.4×10^2		(1.3×10^3)
$+3/14$			(1.5×10^3)	

^a Other species in the equilibria assumed to be Se^{IV} and Se_4^{2+} .

^b Number of measurements 4; formality ratio range 6.01₅ to 11.96₅; asterisks indicate values based on $F_{0.10}(3.3) = 5.39$. Parentheses indicate that no minima were found; the values given are then for equilibrium constants of either 10^{+60} or 10^{-60} .

of 90% probability work with 75% probability the two other species will be excluded and only Se_4^{2+} will be left. As mentioned before the existence of Se_4^{2+} is in agreement with the results from other media.

In Figure 5 is shown a graphical comparison of the four models with the lowest variance in Table III. Since the solution with an R value of 9.02₄ has been chosen to represent solution I, all of the curves cross at this value.

In Table IV are similarly given the variances for models with oxidation states close to $+1/4$. The other species in the equilibrium are Se^{IV} and Se_4^{2+} . Se_4^{2+} is selected as Ox and the species with oxidation state close to $+1/4$ as Red. The melt with $R = 9.02_4$ was used as solution I. Since very little of the species with oxidation state close to $+1/4$ (according to the spectrophotometric measurements) is present below $R = \text{ca. } 7$ and since the species selected to represent Ox and Red should be present in reasonable amount, the R range was chosen to be 6.01₅ to 11.96₅. From Table IV it can be seen that two formulas will have to be taken into account (Se_8^{2+} and Se_{11}^{3+}). A comparison with the spectrophotometric measurements will exclude Se_{11}^{3+} so we are left with Se_8^{2+} as the only possibility. In Figure 6 is shown a graphical comparison of the three models with the lowest variance in Table IV.

In Table V are given the variances for models with oxidation states close to $+1/6$. The other species in the equilibria are Se_8^{2+} and Se_{16}^{2+} . The species with an oxidation state close to $+1/6$ is selected as Ox and Se_{16}^{2+} as Red. The melt with

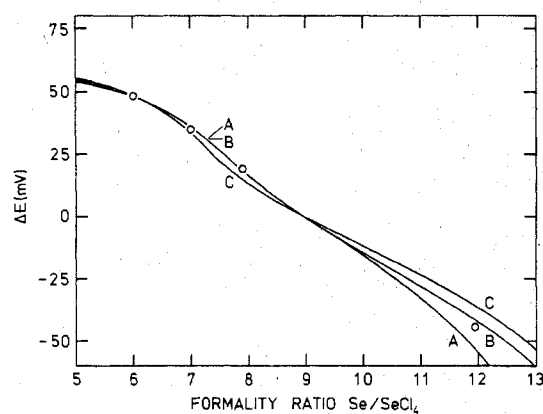


Figure 6. Measured ΔE values taken from Table I (open circles, cell no. 3) as a function of the Se:SeCl₄ formality ratio compared with values (full lines) calculated from the weighted experimental data for the three reaction schemes with the lowest variance in Table IV. Species in equilibrium with Se^{IV} and Se₄²⁺: (A) Se₁₁³⁺; (B) Se₈²⁺; (C) Se₁₂³⁺.

Table V. Variances Based on Potentiometric Measurements for Models^a with Oxidation States Close to +¹/₆^b

Oxidn state	Formal charge			
	1+	2+	3+	4+
+ ² / ₉		(1.1 × 10 ²)		8.7 × 10 ²
+ ³ / ₁₄			(2.9 × 10 ²)	
+ ⁴ / ₁₉				(4.2 × 10 ²)
+ ¹ / ₅	1.2 × 10*	1.6 × 10*	(4.9 × 10)	(1.3 × 10 ²)
+ ⁴ / ₂₁				5.4 × 10
+ ³ / ₁₆			3.1 × 10*	
+ ² / ₁₁		8.5 × 10		3.2 × 10*
+ ³ / ₁₇			9.8*	
+ ⁴ / ₂₃				2.1 × 10*
+ ¹ / ₆	1.2 × 10*	1.1 × 10*	1.5 × 10*	1.4 × 10*
+ ⁴ / ₂₅				3.6 × 10*
+ ³ / ₁₉			3.1 × 10*	
+ ² / ₁₃		2.5 × 10*		6.1 × 10
+ ³ / ₂₀			7.1 × 10	
+ ⁴ / ₂₇				8.9 × 10
+ ¹ / ₇	1.4 × 10 ²	1.8 × 10 ²	1.7 × 10 ²	1.7 × 10 ²

^a Other species in the equilibria assumed to be Se₈²⁺ and Se₁₆²⁺.

^b Number of measurements 6; formality ratio range 20.98₈ to 28.09₄; asterisks indicate values based on $F_{0.10}(5.5) = 3.45$. Parentheses indicate that no minima were found; the values given are then for equilibrium constants of either 10⁺⁶⁰ or 10⁻⁶⁰.

$R = 27.02_2$ was used as solution I. An examination of the spectrophotometric measurements indicated that there was a good possibility for four species in the R range from ca. 16 to ca. 20. Therefore the R range examined is only 20.98₈ to 28.09₄. The upper limit was set at $R = 28.09_4$ in order to avoid the presence of elementary selenium. The solubility of selenium in the melt is low as demonstrated in the recent spectrophotometric work.¹ As can be seen from Table V many models are possible even if there are quite a few less than for the spectrophotometric measurements. It can be seen that the lowest variance is obtained for Se₁₇³⁺ and Se₁₂²⁺; statistically this has no importance, but the low variances seem to fall in an area around the oxidation state +¹/₆ in agreement with the spectrophotometric measurements.

In Table VI are given the variances for models with oxidation states close to +¹/₈. The other species in the equilibria are assumed to be Se₈²⁺ and Se₁₂²⁺. Se₁₂²⁺ is selected as Ox and the species with oxidation state close to +¹/₈ as Red. As before the melt with $R = 27.02_2$ was used as solution I. An R range of 20.98₈ to 28.09₄ was examined. As it can be seen from Table VI the possible formulas for the species with oxidation states close to +¹/₈ are Se₁₆²⁺, Se₃₂⁴⁺, Se₁₇²⁺, Se₂₆³⁺, Se₉⁺, and Se₁₈²⁺. A comparison with the spectrophotometric

Table VI. Variances Based on Potentiometric Measurements for Models^a with Oxidation States Close to +¹/₈^b

Oxidn state	Formal charge			
	1+	2+	3+	4+
+ ² / ₁₅		1.4 × 10 ³		(1.4 × 10 ³)
+ ³ / ₂₃			1.2 × 10 ³	
+ ⁴ / ₃₁				(9.7 × 10 ²)
+ ¹ / ₈	4.1 × 10	1.1 × 10*	2.4 × 10 ²	1.1 × 10*
+ ⁴ / ₃₃				2.9 × 10 ²
+ ³ / ₂₅			9.8 × 10	
+ ² / ₁₇		1.1 × 10*		4.2 × 10
+ ³ / ₂₆			2.2 × 10*	
+ ⁴ / ₃₅				6.9 × 10
+ ¹ / ₉	3.6 × 10*	2.9 × 10*	4.9 × 10	1.0 × 10 ²
+ ⁴ / ₃₇				(7.7 × 10)
+ ³ / ₂₈			8.9 × 10	

^a Other species in the equilibria assumed to be Se₈²⁺ and Se₁₂²⁺.

^b Number of measurements 6; formality ratio range 20.98₈ to 28.09₄; asterisks indicate values based on $F_{0.10}(5.5) = 3.45$. Parentheses indicate that no minima were found; the values given are then for equilibrium constants of either 10⁺⁶⁰ or 10⁻⁶⁰.

Table VII. pK Values^a for Different Equilibria between Selenium Species in Solution in Molten NaCl-AlCl₃ (37:63 mol %) at 150 °C

Equilibrium	Method	pK	Confidence limits for pK
2Se ⁴⁺ + 3Se ₄ ²⁺ ⇌ 7Se ₂ ²⁺	Poten ^c	7.9	4.7 to 9.1
4Se ⁴⁺ + 7Se ₈ ²⁺ ⇌ 15Se ₄ ²⁺	Poten	-12.5	-∞ to -12.4
	Spec ^d	^b	-∞ to -5.5
Se ₄ ²⁺ + Se ₁₂ ²⁺ ⇌ 2Se ₈ ²⁺	Poten	-2.9	-∞ to -2.5
	Spec	-2.0	-∞ to -0.7
Se ₈ ²⁺ + Se ₁₆ ²⁺ ⇌ 2Se ₁₂ ²⁺	Poten	0.0	-0.2 to 0.2
	Spec	-0.8	-∞ to 2.4

^a Based on molar concentrations. ^b No minimum. ^c Potentiometric. ^d Spectrophotometric.

measurements will unfortunately not exclude any of these formulas. It is seen that Se₁₆²⁺ has the lowest variance (together with Se₃₂⁴⁺ and Se₁₇²⁺); as before this has no statistical importance, but since the only corresponding sulfur compound reported is S₁₆²⁺ (in the compounds S₁₆(AsF₆)₂ and S₁₆(SbF₆)₂)¹¹ the most likely choice is Se₁₆²⁺.

In Table VII are given the equilibrium constants for reactions between the different selenium species calculated from the potentiometric measurements. The equilibrium constants are also given for the previous spectrophotometric work (with the exception of the equilibrium containing Se₂²⁺, this species was not found in the original spectrophotometric measurements). The pK values for the reaction Se₄²⁺ + Se₁₂²⁺ ⇌ 2Se₈²⁺ were calculated from three potentiometric measurements (plus one for solution I) in the R range 14.00, to 20.05₇. For this range a systematic examination of the species was not performed since the number of measurements was too low for a reasonable statistical examination. Furthermore the assumption that we are dealing only with Se₄²⁺, Se₈²⁺, and Se₁₂²⁺ in this range is not correct since an appreciable amount of Se₁₆²⁺ is present at higher R values. The pK value found must therefore be used with caution. The pK values based on spectrophotometric measurements were obtained in connection with determination of the variances given in the tables in the previous work.¹ Since it was not possible at that time to distinguish between many of the reaction schemes, the equilibrium constants were not given.

As can be seen from Table VII there is good agreement between the values obtained by the two different methods (where they can be compared). From these calculated pK values it is now possible to examine some of our assumptions. For example a calculation based on the potentiometric measurements will show that the percentage of the proposed species Se^{IV}, Se₂²⁺, Se₄²⁺, Se₈²⁺, Se₁₂²⁺, and Se₁₆²⁺ at $R = 3.00$,

is approximately 37.3%, 5.9%, 56.3%, 0.5%, $10^{-16}\%$, and $10^{-10}\%$, respectively. Since Se_2^{2+} obtains its highest concentration at $R = 3$, it is seen that our assumption that Se_2^{2+} is never present in high concentrations is correct. A calculation based on the potentiometric measurements at $R = 20.98_8$ (the lower limit for the calculation in Table V and VI) will show that the percentages of the proposed species Se^{IV} , Se_2^{2+} , Se_4^{2+} , Se_8^{2+} , Se_{12}^{2+} , and Se_{16}^{2+} are approximately $10^{-13}\%$, $10^{-5}\%$, 0.1%, 46.7%, 31.7%, and 21.5%, respectively. The similar values for the upper limit, $R = 28.09_4$, are approximately $10^{-17}\%$, $10^{-6}\%$, $10^{-3}\%$, 7.0%, 22.3%, and 70.7%, respectively. Our assumption that we are dealing with only three species in the R range 20.98_8 to 28.09_4 is therefore correct; in fact the calculations show that the lower limit could have been moved down to about 18. There is no reason, however, to believe that this should have given a different picture in Tables V and VI.

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Registry No. Se^{4+} , 22541-55-5; Se_2^{2+} , 62586-31-6; Se_4^{2+} , 62586-32-7; Se_8^{2+} , 12597-34-1; Se_{12}^{2+} , 62586-33-8; Se_{16}^{2+} , 62586-34-9; Se, 7782-49-2; SeCl_4 , 10026-03-6.

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Contribution from the Department of Geosciences and Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

Crystallization of Amorphous GeS_2 and GeSe_2 under Pressure

MASAHIKO SHIMADA and FRANK DACHILLE*

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By subjecting amorphous starting materials of GeS_2 and GeSe_2 to temperatures of 300–600 °C and pressures of 0–90 kbar, three polymorphs of GeS_2 (GeS_2 -I, GeS_2 -II, and GeS_2 -III) and three polymorphs of GeSe_2 (GeSe_2 -I, GeSe_2 -II, and GeSe_2 -III) have been synthesized. The GeS_2 -I and GeSe_2 -I are isotopic orthorhombic phases listed in ASTM x-ray file cards 17-123 and 16-80, respectively. The GeS_2 -II phase synthesized under high pressure is the phase reported by Prewitt and Young.¹ The other crystalline phases are new high-pressure phases.

Experimental Section

For the preparation of the amorphous GeS_2 and GeSe_2 samples, stoichiometric proportions of high-purity Ge, S, and Se (99.99% and up) were sealed in a silica tube at about 10^{-4} torr, placed in a furnace, and raised slowly in temperature to 1000–1200 °C. After its contents reacted for 5 h with occasional shaking, the sample tube was quenched in water. The resultant materials were homogeneous and amorphous to x rays. The crystallization was done in a high-pressure apparatus where the load on the sample was applied between a pair of cylindrical "anvils", each anvil having a conical taper at one end which was terminated with a small circular surface.² The sample was compacted into a nickel ring whose outer diameter was that of the anvil's flat; the inner diameter was about 60% of the outer diameter. The ring-sample assembly was sandwiched between two disks of platinum-10% rhodium foil. Experiments demonstrated that a uniform pressure was applied to the sample that was equal to the total load divided by the area of the anvil flat when the thickness of the ring-sample + foils sandwich was between $1/22$ and $1/25$ of the diameter of the flat.³

Results and Discussion

Summaries of the experimental conditions used and the results obtained with the amorphous GeS_2 and GeSe_2 starting materials are presented in Table I, Table II, Figure 1, and Figure 2. The x-ray powder diffraction patterns for each crystalline phase and for the amorphous materials are shown in Figures 3 and 4. It will be noted that at 300 °C in the GeS_2 system crystallization did not occur after the application of pressures up to 90 kbar for 96 h; at 400 °C crystallization was not achieved with the use of pressures above 60 kbar. Although GeS_2 remained amorphous under some of the conditions noted in Table I, the x-ray diffraction traces of the

Table I. Experimental Conditions and Results for GeS_2

Sample no.	Pressure, kbar	Temp, °C	Time, h	Result
1	30	300	68	Noncrystallized
2	30	400	68	GeS_2 -II
3	30	500	41	GeS_2 -II
4	40	300	41	Noncrystallized
5	40	400	46	GeS_2 -II
6	40	500	46	GeS_2 -II
7	50	300	46	Noncrystallized
8	50	400	69	GeS_2 -II
9	50	500	69	GeS_2 -II
10	60	300	69	Noncrystallized
11	60	400	69	Noncrystallized
12	70	300	69	Noncrystallized
13	70	400	69	Noncrystallized
15	80	300	70	Noncrystallized
16	90	400	70	Noncrystallized
17	90	300	70	Noncrystallized
18	0	400	70	GeS_2 -I
19	20	400	96	GeS_2 -II
21	20	300	96	Noncrystallized
22	10	500	96	GeS_2 -II
23	10	400	96	GeS_2 -II
24	10	300	96	Noncrystallized
25	0	300	72	Noncrystallized
27	60	500	44	GeS_2 -II (50%) + GeS_2 -III (50%)
28	70	500	39	GeS_2 -III (HgI ₂ type)

amorphous quenched products provide evidence of structural changes. For example, referring to Figure 3, trace A, which is that of the starting amorphous GeS_2 , has only one broad diffuse maximum near $14^\circ 2\theta$. Trace B, of a sample held at