Conductance and Equilibrium Studies on the System Se-Cl

II. Equilibrium Studies on the System Se-Cl

MARGARETA LUNDKVIST and MATI LELLEP
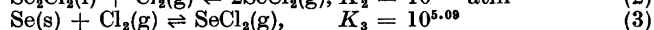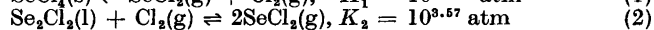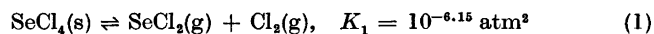
*Department of Inorganic Chemistry, Royal Institute of Technology (KTH),
Stockholm 70, Sweden*

The temperature dependence of the reaction $Se_2Cl_2(l) \rightleftharpoons SeCl_2(g) + Se(s)$ (5) has been studied in the interval $20-75°C$. $\log p(SeCl_2)$ in atm (over Se_2Cl_2 saturated with Se) *versus* T^{-1} follows the equation
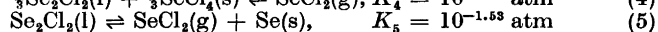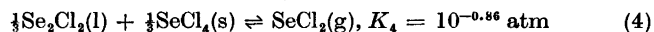
$$\log p(SeCl_2) = -2947 \cdot T^{-1} + 6.74$$

From pressure measurements and determinations of solubility of Se(s) in $Se_2Cl_2(l)$ it is concluded that ΔH for (5), ΔH_5, is approximately 16.7 kcal.

At 75°C equilibria have been studied by means of pressure and solubility measurements. The following equilibrium constants were deduced:
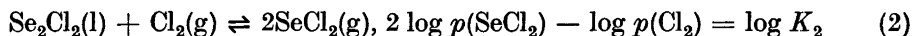
$$SeCl_4(s) \rightleftharpoons SeCl_2(g) + Cl_2(g), \quad K_1 = 10^{-6.15} \text{ atm}^2 \qquad (1)$$
$$Se_2Cl_2(l) + Cl_2(g) \rightleftharpoons 2SeCl_2(g), \quad K_2 = 10^{3.57} \text{ atm} \qquad (2)$$
$$Se(s) + Cl_2(g) \rightleftharpoons SeCl_2(g), \quad K_3 = 10^{5.09} \qquad (3)$$

Knowing K_1, K_2, and K_3, K_4 and K_5 can be calculated:

$$\tfrac{1}{3}Se_2Cl_2(l) + \tfrac{1}{3}SeCl_4(s) \rightleftharpoons SeCl_2(g), \quad K_4 = 10^{-0.86} \text{ atm} \qquad (4)$$
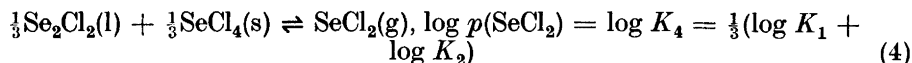$$Se_2Cl_2(l) \rightleftharpoons SeCl_2(g) + Se(s), \quad K_5 = 10^{-1.53} \text{ atm} \qquad (5)$$

Earlier data on the Se-Cl system have shown that two selenium chlorides exist in a condensed form, $SeCl_4(s)$ and $Se_2Cl_2(l)$. From gas density measurements of vaporized $SeCl_4(s)$ [1] it was concluded that the gas phase contained $SeCl_2(g)$ and $Cl_2(g)$. A study of the gas above $Se_2Cl_2(l)$ [2] showed that it consisted of $SeCl_2(g)$ and that a residue of Se(s) was left when vaporizing the $Se_2Cl_2(l)$. When the $SeCl_2(g)$ condenses, $SeCl_4(s)$ and $Se_2Cl_2(l)$ are formed.

According to these observations we may write the equilibrium conditions in terms of the master variables $p(SeCl_2)$ and $p(Cl_2)$. For equilibria with one condensed phase, we have

$$SeCl_4(s) \rightleftharpoons SeCl_2(g) + Cl_2(g), \log p(SeCl_2) + \log p(Cl_2) = \log K_1 \qquad (1)$$

$$Se_2Cl_2(l) + Cl_2(g) \rightleftharpoons 2SeCl_2(g), 2\log p(SeCl_2) - \log p(Cl_2) = \log K_2 \qquad (2)$$

$$Se(s) + Cl_2(g) \rightleftharpoons SeCl_2(g), \log p(SeCl_2) - \log p(Cl_2) = \log K_3 \qquad (3)$$

and with two condensed phases, by combination of $(1-3)$

$$\tfrac{1}{3}Se_2Cl_2(l) + \tfrac{1}{3}SeCl_4(s) \rightleftharpoons SeCl_2(g), \log p(SeCl_2) = \log K_4 = \tfrac{1}{3}(\log K_1 + \log K_2) \tag{4}$$

$$Se_2Cl_2(l) \rightleftharpoons SeCl_2(g) + Se(s), \log p(SeCl_2) = \log K_5 = \log K_2 - \log K_3 \tag{5}$$

This work deals to a great part with studies of these reactions at 75°C. In the interval 109—180°C studies of the pressure of vaporized $SeCl_4(s)$ have been performed by Yost and Kircher.[1] If the straight line relationship for $\log p$ *versus* T^{-1} obtained in this interval is extrapolated to 75°C, $\log K_1 = -6.15$ is obtained. The enthalpy for (1) is also given, $\Delta H_1 = 35.4$ kcal.

Some calorimetric investigations have also been performed concerning the selenium chlorides. Thomsen [3] has given ΔH for the reaction

$$Se_2Cl_2(l) + 3Cl_2(g) \rightarrow 2SeCl_4(s), \Delta H_6 = -70.2 \tag{6}$$

and Petersen [4] has given ΔH for the reaction

$$2Se(s) + Cl_2(g) \rightarrow Se_2Cl_2(l), \Delta H_7 = -20.0 \tag{7}$$
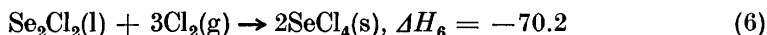
Out of these enthalpies, ΔH for (5), ΔH_5 can be calculated

$$\Delta H_5 = \Delta H_1 + \tfrac{1}{2}\Delta H_6 - \tfrac{1}{2}\Delta H_7 = 10.3 \text{ kcal}$$

This investigation started with a study of the temperature dependence of $p(SeCl_2)$ for reaction (5) in the interval 20—75°C. These data were necessary for our studies of the influence of chlorine on the conductivity of liquid selenium (part I).[5] The more extensive study of the whole system at 75°C was perhaps not necessary for the conductivity measurements, but seemed interesting and worthwhile.

EXPERIMENTAL

Apparatus. The pressure measurements have been performed using a flow method with N_2 as the carrier gas. A schematical drawing of the apparatus is given in Fig. 1. The purification of the N_2 and the flow measuring device have been described in Part I. The N_2 was then passed through a mixture of $Se_2Cl_2(l)$ and $Se(s)$ in some experiments, and through a mixture of $Se_2Cl_2(l)$ and $SeCl_4(s)$ in other experiments. In both cases the mixture was kept in two washbottles to ensure saturation of N_2 with $SeCl_2$ of equilibrium pressure. In a third group of experiments the condensed system contained $SeCl_4(s)$ only, which was then kept in a glass tube in a horizontal position.
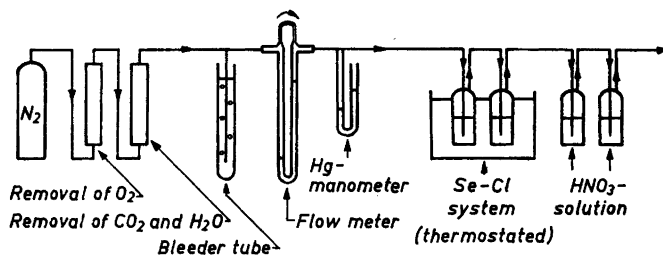

Fig. 1. Sketch of the apparatus.

The saturated N_2 was afterwards passed through two bottles with HNO_3-solution, which will dissolve $SeCl_2$. After a run the solutions were analysed for Se to determine $p(SeCl_2)$ in the gas.

Reagents. $Se_2Cl_2(l)$ saturated with Se(s) was prepared by passing $Cl_2(g)$ over Se(s) in a flask, and stirring till all solid seemed to have disappeared. The product was $Se_2Cl_2(l)$, really with some excess of Se or Cl. To this solution excess Se was added.

$Se_2Cl_2(l)$, saturated with $SeCl_4(s)$ was prepared in much the same way, but Cl_2 was passed over the solution till $SeCl_4(s)$ was seen to crystallize on the walls.

When pure $SeCl_4(s)$ was prepared the Cl_2-stream was passed over the $Se_2Cl_2(l)$ till it was entirely converted to white $SeCl_4(s)$. The rate of reaction was increased by gentle heating.

During these preparations care was taken so that no moisture contaminated the substances. N_2 was used as an inert atmosphere.

Analyses. The Se content of the above mentioned HNO_3-solutions was determined as follows. Each of the solutions was neutralized with NaOH-solution. Elementary Se was precipitated by adding hydrazinium sulfate. The solution with the precipitate was then placed on a waterbath for at least 2 h to convert the red, colloidal Se into gray, stable Se, which was more easily filtered. The precipitate was filtered, dried at 105—110°C and weighed.

The solubilities of Se(s) and $SeCl_4(s)$ in $Se_2Cl_2(l)$ at 75°C have been determined by analyses. The $Se_2Cl_2(l)$ was first equilibrated for about 24 h with Se(s) or $SeCl_4(s)$. After that, the solid was allowed to sink to the bottom of the flask and then about 300 mg of the solution was sucked up through a capillary into a glass ampoule and the ampoule sealed. The filled ampoule was weighed and then broken while immersed in HNO_3-solution, which dissolved the selenium chloride. The glass was filtered off and weighed, and the Se content of the solution determined as described above. The Cl content was taken as the difference.

Procedure. The determinations of $p(SeCl_2)$ were performed as follows. First the pressure drop across the washbottles with the condensed phases, Δp_1, in torr, was measured with the Hg-manometer, in a constant flow of N_2. Then the two HNO_3-bottles were connected and the time-measuring started. The total pressure drop, Δp_2, could then be read on the manometer. The experiment went on till a large enough amount of Se (at least 50 mg) had been obtained. Afterwards the two solutions were analysed one at a time. Each experiment was repeated several times using different flow rates to ensure that N_2 was saturated with $SeCl_2(g)$. For flow rates up to 80 ml min^{-1}, constant $p(SeCl_2)$-values were obtained. At higher flow rates, $p(SeCl_2)$ decreased.

The number of mmoles of N_2, $n(N_2)$, passed through the system and $p(SeCl_2)$ in atm was calculated from

$$n(N_2) = \frac{Q \cdot \tau (P_{air} + \Delta p_2)}{R \cdot T(N_2)} \tag{8}$$

$$p(SeCl_2) = \frac{n(Se) \cdot (P_{air} + \Delta p_2 - \Delta p_1)}{(n(N_2) + n(Se)) \cdot 760} \tag{9}$$

Q = flow rate in ml min^{-1}
τ = time of a run in min
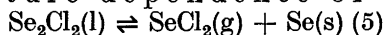P_{air} = atmospheric pressure in torr
R = the gas constant = 62.361 l torr $deg^{-1}mole^{-1}$
$T(N_2)$ = temperature of N_2 in °K
$n(Se)$ = Se amount in mmoles found by analysis

RESULTS AND DISCUSSION

The temperature dependence of the reaction
$$Se_2Cl_2(l) \rightleftharpoons SeCl_2(g) + Se(s) \quad (5)$$

As has been mentioned Wehrli [2] has shown that the gas above $Se_2Cl_2(l)$ consists of $SeCl_2(g)$ only. To make a rough check of this statement experiments have been performed, totally vaporizing a small amount of $Se_2Cl_2(l)$.

In one experiment N_2 was passed over a weighed amount of a solution of Se_2Cl_2(l) with dissolved Se. According to analysis and the known weight, the sample contained 1.03 mmoles of Se_2Cl_2(l) with 0.11 mmoles of Se dissolved. When apparently only Se(s) was left the residue was weighed, dissolved in HNO_3 and analysed for Se. It was found that the residue consisted almost entirely of Se and the amount was 1.14 mmoles. This was what could be expected if the reaction is

$$Se_2Cl_2(l) \rightarrow SeCl_2(g) + Se(s)$$

The determinations of $p(SeCl_2)$ for the reaction were performed at some temperatures in the interval 20—75°C using the flow method described above.

Table 1. $p(SeCl_2)$ for equilibrium (5) in the temperature range 20—75°C.

Temp. (°C)	$10^3/T$ (°K)	$p(SeCl_2)$ (atm)	$\log p(SeCl_2)$	Temp (°C)	$10^3/T$ (°K)	$p(SeCl_2)$ (atm)	$\log p(SeCl_2)$
		4.533×10^{-4}	-3.34			4.041×10^{-3}	-2.39
		4.969×10^{-4}	-3.30			4.060×10^{-3}	-2.39
20	3.411	4.917×10^{-4}	-3.31	50	3.094	4.040×10^{-3}	-2.39
		5.204×10^{-4}	-3.28			3.932×10^{-3}	-2.40
		1.041×10^{-3}	-2.98			8.421×10^{-3}	-2.07
		1.071×10^{-3}	-2.97			7.798×10^{-3}	-2.11
30	3.298	1.009×10^{-3}	-3.00	60	3.001	7.854×10^{-3}	-2.10
		1.040×10^{-3}	-2.98			7.687×10^{-3}	-2.11
		2.303×10^{-3}	-2.64			1.817×10^{-2}	-1.74
		2.230×10^{-3}	-2.65			1.848×10^{-2}	-1.73
40	3.193	2.195×10^{-3}	-2.66	75	2.872	1.842×10^{-2}	-1.73
		2.214×10^{-3}	-2.66			1.780×10^{-2}	-1.75

The results are given in Table 1, and Fig. 2 shows $\log p(SeCl_2)$ *versus* T^{-1}. The equation of the straight line drawn in the diagram is
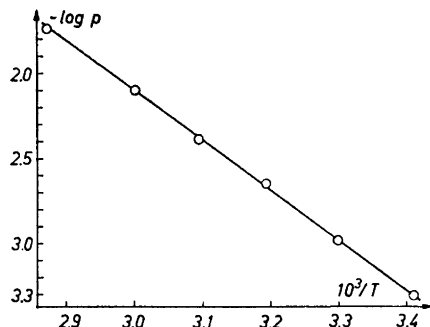
$$\log p(SeCl_2) = -2947 \cdot T^{-1} + 6.74 \tag{10}$$

Fig. 2. log $p(SeCl_2)$ *versus* T^{-1} for equilibrium (5).

As Se(s) dissolves to some extent in Se_2Cl_2(l) the equilibrium constant, K_5, is given by

$$\log K_5 = \log p(SeCl_2) - \log \{Se_2Cl_2\} \qquad (11)$$

The activity, $\{Se_2Cl_2\}$, depends on what species are formed when Se(s) is dissolved. The simplest assumption is that the solution contains single Se atoms. This does not seem very likely but may be defended since it gives mole fractions intermediate between those calculated for two chemically more plausible models: Se_n rings and $ClSe_nCl$ chains. For instance, let us consider a solution of the stoichiometric composition $1Se + 1Se_2Cl_2$. With single Se atoms, the mole fraction $b = X(Se_2Cl_2) = \frac{1}{2}$; with Se_6 rings $b = 6/7$. Finally if the species Se_4Cl_2, Se_3Cl_2, and Se_2Cl_2 are formed in equal molar amounts, then $b = 1/3$.

Here the solution has been roughly approximated to consist of an ideal mixture of single Se atoms and Se_2Cl_2 molecules. Then for reaction (5) $\{Se_2Cl_2\}$ $= b_0$, which is the mole fraction of Se_2Cl_2(l) when saturated with Se(s).

b_0 has been roughly determined by analyses, described above, at 20°C and 75°C. At 20°C the solubility of Se(s) was zero within the limits of error, but at 75°C a considerable amount of Se(s) dissolved. In Table 2 are given

Table 2. Solubility of Se(s) and $SeCl_4$(s) in Se_2Cl_2(l) at 75°C.

b_0 = mole fraction of Se_2Cl_2(l) saturated with Se(s)

a_0 = mole fraction of Se_2Cl_2(l) saturated with $SeCl_4$(s).

a_0	0.778	0.777	0.779	0.729	0.800	0.729	Average:	$a_0 = 0.77 \pm 0.03$
b_0	0.622	0.637	0.642	0.637	0.665	0.643	Average:	$b_0 = 0.64 \pm 0.03$

mole fractions of Se_2Cl_2(l) either with Se(s) dissolved, b_0, or with $SeCl_4$(s) dissolved, a_0, determined by analysis. Knowing b_0 and using eqns. (10, 11) $\log K_5 = -1.53$ at 75°C. At 20°C $\log K_5 \approx \log p(SeCl_2)$ and is obtained from

$$(10): \log K_5 = -3.31.$$

On the basis of these two values of $\log K_5$ a linear relationship can be given

$$\log K_5 = -3655 \cdot T^{-1} + 9.16 \qquad (12)$$

Using this equation the enthalpy for reaction (5) can be calculated, $\Delta H_5 = 16.7$ kcal. As a comparison, a combination of calorimetric literature data gives a value of $\Delta H_5 = 10.3$ kcal, as has been mentioned above.

Equilibrium study at 75°C

At 75°C there are three condensed species: $SeCl_4$(s), Se_2Cl_2(l), and Se(s). The gas phase consists of Cl_2(g) and $SeCl_2$(g). The equilibrium reactions involving one condensed phase are (1—3). If the activities of the condensed species $\{SeCl_4\}$ etc. are not unity, corresponding terms should be added to the right in eqns. (1—3).

When the two condensed species $SeCl_4(s)$ and $Se_2Cl_2(l)$ or $Se(s)$ and $Se_2Cl_2(l)$ are present, both $SeCl_4(s)$ and $Se(s)$ have been found to be soluble in $Se_2Cl_2(l)$. In these mixtures the activities of $SeCl_4(s)$ and $Se(s)$ are equal to unity, while in both cases the activity of $Se_2Cl_2(l)$ is less than one. The solutions will be assumed to consist of ideal mixtures of single Se atoms in $Se_2Cl_2(l)$ and of single $SeCl_4$ molecules in $Se_2Cl_2(l)$. As has been said above this may be a very rough approximation. Thus the equilibrium constants for reactions (4,5) are given by the equations:

$$\log p(SeCl_2) - \tfrac{1}{3}\log a_0 = \log K_4 \qquad (13)$$

$$\log p(SeCl_2) - \log b_0 = \log K_5 \qquad (14)$$

a_0 and b_0 are the mole fractions of $Se_2Cl_2(l)$ saturated with $SeCl_4(s)$ or $Se(s)$ (see Table 2).
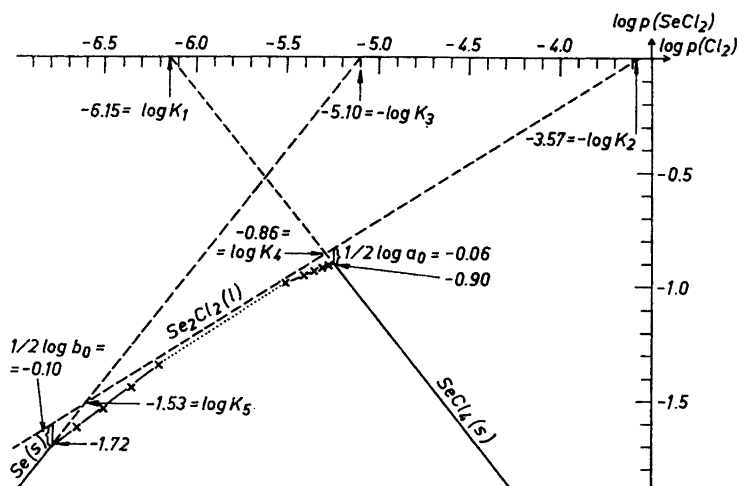
Fig. 3. log $p(SeCl_2)$ *versus* log $p(Cl_2)$ at 75°C.

In Fig. 3 a diagram log $p(SeCl_2)$ *versus* log $p(Cl_2)$ is given. The three straight lines correspond to the equilibria with one condensed phase (1—3). For the lowest values of $p(Cl_2)$ only $Se(s)$ is present. With increasing $p(Cl_2)$ a point is reached where both $Se(s)$ and $Se_2Cl_2(l)$ are present and there, according to the phase rule, the composition of the gas phase is fixed. If $p(Cl_2)$ is still increased $p(SeCl_2)$ will also increase and only $Se_2Cl_2(l)$ is present as the condensed phase. Then again a point of fixed gas composition and with two condensed species $Se_2Cl_2(l)$ and $SeCl_4(s)$ is reached. After that with increasing $p(Cl_2)$ only $SeCl_4(s)$ is present and $p(SeCl_2)$ decreases.

The value log $K_1 = -6.15$ gives the position of the $SeCl_4$-line in the diagram in Fig. 3. Control measurements for equilibrium (1) have been performed at 75°C, measuring $p(SeCl_2)$ by the flow method described. The values

Table 3. $p(SeCl_2)$ for equilibria (1) and (4) and calculated values of log K_1.

Equilibrium (1)				Equilibrium (4)	
$p(SeCl_2)$ atm	log p	log K_1		$p(SeCl_2)$ atm	log p
8.209×10^{-4}	-3.09	-6.17		1.292×10^{-1}	-0.89
1.135×10^{-3}	-2.94	-5.89		1.173×10^{-1}	-0.90
8.110×10^{-4}	-3.09	-6.18		1.248×10^{-1}	-0.90
9.034×10^{-4}	-3.04	-6.09			
9.891×10^{-4}	-3.00	-6.01		Average: log $p = -0.90$	
8.301×10^{-4}	-3.08	-6.16			
8.978×10^{-4}	-3.05	-6.09			

of log $p(SeCl_2)$ and log K_1 obtained are given in Table 3. Most of the $p(SeCl_2)$-values are slightly higher than what corresponds to log $K_1 = -6.15$, probably due to the presence of small amounts of $Se_2Cl_2(l)$. It seemed preferable to use Yost and Kircher's [1] value log $K_1 = -6.15$ rather than an average of the present not too accurate data.

For constructing the Se_2Cl_2-line and the Se-line log K_2 and log K_3 have been calculated in the following way. Log K_5 has been calculated (see above) and equals -1.53. Log K_4 is given by

$$\log K_4 = \log p(SeCl_2) - \tfrac{1}{3}\log a_0 = -0.86$$

where log $p(SeCl_2)$ is given in Table 3 and a_0 in Table 2. Then log $K_2 = 3.57$ can be calculated from the equation

$$\log K_4 = \tfrac{1}{3} \log K_1 + \tfrac{1}{3} \log K_2 \qquad (15)$$

Log $K_3 = 5.10$ can be calculated from the equation

$$\log K_5 = \log K_2 - \log K_3 \qquad (16)$$

These values fix the positions of the Se_2Cl_2- and Se-lines.

Log $p(SeCl_2)$ *versus* log $p(Cl_2)$ follows the Se-line to the point where log $p(SeCl_2) = -1.72$ and also the full drawn part of the $SeCl_4$-line starting in

Table 4.

a. Calculated values of b and $p(SeCl_2)$.				b. Calculated values of a and $p(SeCl_2)$.		
log $p(Cl_2)$	b	log $p(SeCl_2)$		log $p(Cl_2)$	a	log $p(SeCl_2)$
-6.81	$0.64 \ (b_0)$	-1.72		-5.25	0.77	-0.90
-6.65	0.68	-1.62		-5.27	0.78	-0.91
-6.50	0.73	-1.54		-5.30	0.80	-0.92
-6.35	0.77	-1.45		-5.35	0.83	-0.93
-6.20	0.80	-1.34		-5.40	0.85	-0.95
-5.90	0.85	-1.20		-5.50	0.90	-0.99
-5.60	0.95	-1.03		-5.60	0.93	-1.03
				-5.70	0.94	-1.08

the point $\log p(\text{SeCl}_2) = -0.90$. The deviations from the straight lines at the intermediate area have been calculated for some $p(\text{Cl}_2)$-values and are given in Tables 4a and 4b. Table 4a shows the results if only solubility of Se(s) in $\text{Se}_2\text{Cl}_2(l)$ is considered and 4b shows the case with solution of $\text{SeCl}_4(s)$ in $\text{Se}_2\text{Cl}_2(l)$. The mole fractions b and values of $\log p(\text{SeCl}_2)$ in Table 4a are calculated from the following equations:

$$\log K_2 = 3.57 = 2 \log p(\text{SeCl}_2) - \log p(\text{Cl}_2) - \log b$$
$$\log K_3 = 5.10 = \log p(\text{SeCl}_2) - \log p(\text{Cl}_2) - \log [(1 - b)/(1 - b_0)]$$

where $(1-b)/(1-b_0)$ is equal to the Se-activity in the solution. The mole fractions and values of $p(\text{SeCl}_2)$ in Table 4b are obtained from the equations:

$$\log K_1 = -6.15 = \log p(\text{SeCl}_2) + \log p(\text{Cl}_2) - \log [(1-a)/(1-a_0)]$$
$$\log K_2 = 3.57 = 2 \log p(\text{SeCl}_2) - \log p(\text{Cl}_2) - \log a$$

where $(1-a)/(1-a_0)$ equals the SeCl_4-activity in the solution.

These calculated values are also plotted in the diagram in Fig. 3. As can be seen, there is a region where the solubility of both Se(s) and SeCl_4(s) would be appreciable, but since nothing is known about the solution mechanism a more "accurate" calculation does not seem worth-while. However, by very accurate measurements of $p(\text{SeCl}_2)$ over unsaturated solutions, one could possibly get information on what kind of species are present in the solution.

REFERENCES

1. Yost, D. M. and Kircher, C. E. *J. Am. Chem. Soc.* **52** (1930) 4680.
2. Wehrli, M. *Helv. Phys. Acta* **9** (1936) 637.
3. Thomsen, J. *Ber.* **15** (1882) 3023.
4. Petersen, E. *Z. physik. Chem.* **8** (1891) 601.
5. Lundkvist, M. *Acta Chem. Scand.* **22** (1968) 281.