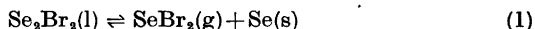


Conductance and Equilibrium Studies on the System Se-Br

KERSTIN HÖGBERG and MARGARETA LUNDQVIST

*Department of Inorganic Chemistry, Royal Institute of Technology (KTH),
S-100 44 Stockholm 70, Sweden*

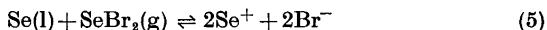
The temperature dependence of the reaction



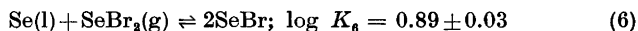
has been studied in the interval 20–75°C. The partial pressure $p(\text{SeBr}_2)$, of $\text{SeBr}_2(\text{g})$ in equilibrium with $\text{Se}(\text{s})$ and $\text{Se}_2\text{Br}_2(\text{l})$ saturated with Se , varies with temperature according to the equation

$$\log p(\text{SeBr}_2) = -3278 T^{-1} + 6.44 \quad (3)$$

Studies of the conductivity of $\text{Se}(\text{l})$ in equilibrium with $\text{SeBr}_2(\text{g})$ at 280°C indicate that four charge carriers are formed per added SeBr_2 . The reaction may be written schematically



Studies of the dependence of the total Br concentration on the partial pressure of $\text{SeBr}_2(\text{g})$ indicate that a second reaction predominates, schematically



K_6 is given in $(\text{mole}/1000 \text{ g})^2 \text{ atm}^{-1}$.

The conductivity of solid and liquid selenium is known to be influenced by the addition of other elements. An investigation of the influence of chlorine has recently been published,¹ in which the increase in conductivity of selenium melts equilibrated with $\text{SeCl}_2(\text{g})$ at various partial pressures was studied. The present investigation of the influence of bromine on the conductivity of $\text{Se}(\text{l})$ has been performed in very much the same way. Conductivity data have been used to give information on what charged species are formed when $\text{Se}(\text{l})$ is equilibrated with $\text{SeBr}_2(\text{g})$. The data have been interpreted by analogy with conductivity data of dilute aqueous solutions. Thus the contribution to the conductivity caused by the formation of a charge carrier is assumed to be proportional to its concentration. A more detailed comparison with aqueous solution has been given earlier.¹

Earlier studies of the conductivity of liquid selenium have been summarized in the paper¹ on Se-Cl.

EXPERIMENTAL

Most of the apparatus and the procedures are exactly the same as in the Se—Cl work,^{1,2} so only a short summary will be given here.

Pressure measurements with $\text{SeBr}_2(\text{g})$ in equilibrium with $\text{Se}_2\text{Br}_2(\text{l})$ saturated with Se and Se(s) according to the reaction



have been performed using the same flow method as for the corresponding $p(\text{SeCl}_2)$ measurements.² $\text{Se}_2\text{Br}_2(\text{l})$ saturated with Se(s) was prepared by adding $\text{Br}_2(\text{l})$ dropwise with stirring to Se(s) until all solid seemed to have disappeared, and then adding excess Se(s). A measured flow of purified nitrogen was used as carrier gas and passed through the equilibrium mixture. The N_2 saturated with $\text{SeBr}_2(\text{g})$ was afterwards passed through two HNO_3 solutions to dissolve the SeBr_2 . To determine $p(\text{SeBr}_2)$ the solutions were separately analysed for Se. Only about 1 % of the total amount of Se was usually found in the second solution so it is supposed that practically all the $\text{SeBr}_2(\text{g})$ had dissolved in the first.

The conductivity measurements were performed using a cell consisting of a fused silica tube with electrodes of vitreous carbon. These were the only two materials in contact with the melt. Other materials like pyrex glass and electrodes of platinum, gold, graphite, and wolfram interfere with the measurements.

The gas equilibration equipment consisted of nitrogen as inert atmosphere the flow and pressure of which were measured before it was passed through a mixture of $\text{Se}_2\text{Br}_2(\text{l})$ and Se(s) to saturate it with $\text{SeBr}_2(\text{g})$. The gas mixture was then passed into the conductivity cell.

The resistance measurements were carried out on a new a.c. conductivity meter type Autobalance Universal Bridge from the Wayne Kerr Co. Ltd., Sycamore Grove, New Malden, Surrey, England. The accuracy is claimed to be ± 0.1 % in the range 10–10⁸ ohm.

Reagents. The Se used was so-called "Special selenium" obtained from Boliden's mining company, Skelleftehamn, Sweden. This Se has been used without further purification both for the conductivity measurements and for the preparation of $\text{Se}_2\text{Br}_2(\text{l})$.

Analyses for total bromine content of quenched melts were performed in the following way. The sample was powdered and dried in a desiccator. About 30 g of the sample was put in a solution with excess Ag^+ -ion, HNO_3 was added and the solution was heated to dissolve the sample. A precipitate of AgBr was formed and after all the Se had dissolved the solution was filtered and the AgBr was dried and weighed. To check the method, known amounts of bromide were melted with Se and treated in the same way as above. The analyses of these samples agreed within ± 2 % of the known Br content.

Procedure. About 80 g of Se(s) was put in the cell, melted and heated to 280°C. A stream of pure N_2 was then passed through the Se(l) and the conductivity of pure liquid Se, κ_0 , was read after about 5 h of N_2 -bubbling. Then the $\text{SeBr}_2(\text{g})$ -bubbling was started by passing the N_2 through the mixture of $\text{Se}_2\text{Br}_2(\text{l})$ and Se(s) initially thermostated at 20°C, before it reached the conductivity cell. After about 24 h the conductivity had increased to a constant value and κ could be read. $p(\text{SeBr}_2)$ was then increased stepwise every 24 h by increasing the temperature of the $\text{Se}_2\text{Br}_2(\text{l}) + \text{Se}(\text{s})$ mixture and κ was read after each equilibration.

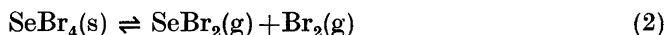
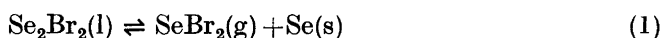
When the melt was to be analysed for Br, separate runs had to be performed for each $p(\text{SeBr}_2)$ value. When equilibrium was reached the melt was quenched by pouring it into distilled water.

RESULTS AND DISCUSSION

The temperature dependence of the reaction $\text{Se}_2\text{Br}_2(\text{l}) \rightleftharpoons \text{SeBr}_2(\text{g}) + \text{Se}(\text{s})$. Earlier data³ on phase equilibria in the Se—Br system show that it behaves in a manner similar to the Se—Cl system. Two condensed selenium bromides exist, $\text{SeBr}_4(\text{s})$ and $\text{Se}_2\text{Br}_2(\text{l})$. Neither of these bromides exist in a gas phase, but dissociate upon vaporization according to the reactions:

Table 1. $p(\text{SeBr}_2)$ for equilibrium (1) in the temperature range 20–75°C.

$t^\circ\text{C}$	$10^3/T$	$\log p(\text{SeBr}_2)$			
20	3.411	-4.76,	-4.78,	-4.72,	-4.82
30	3.298	-4.38,	-4.38,	-4.38,	-4.37
40	3.193	-4.01,	-4.03,	(-4.04),	-4.00
50	3.094	-3.74,	-3.70,	-3.76,	-3.72
60	3.001	(-3.39),	(-3.38),	-3.44,	-3.43
75	2.872	(-2.91),	-2.97,	-2.99,	-3.00

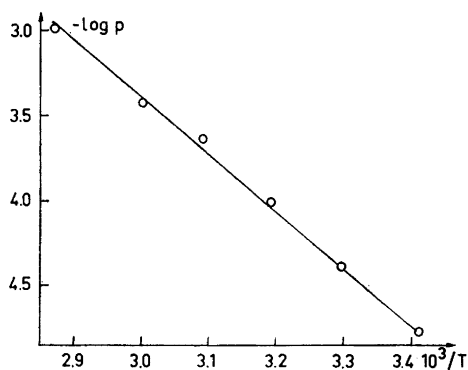
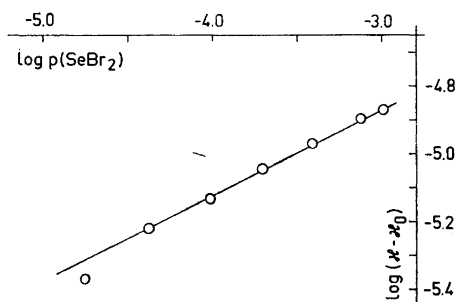


An extensive study of Se-Cl equilibria at 75°C has been performed.² For the Se-Br system only the $p(\text{SeBr}_2)-T$ function was determined, which sufficed for interpreting the conductivity measurements. The results of the $p(\text{SeBr}_2)$ measurements at temperatures in the interval 20–75°C are given in Table 1, and Fig. 1 shows $\log p(\text{SeBr}_2)$ versus T^{-1} . The equation of the straight line drawn in the diagram is

$$\log p(\text{SeBr}_2) = -3278T^{-1} + 6.44 \quad (3)$$

Influence of $p(\text{SeBr}_2)$ on the conductivity of liquid Se. An equilibrium is considered between Br, dissolved in Se(l), and a gas phase with a known partial pressure of $\text{SeBr}_2(\text{g})$. The activity $\{\text{Br}\}$ in the melt is fixed by equilibrium with the gas so that $\log \{\text{Br}\}$ is equal to $\frac{1}{2} \log p(\text{SeBr}_2) + a$ constant.

As the conductivity is supposed to be proportional to the number of charge carriers in the melt the dependence of $\log(\kappa - \kappa_0)$ on $\log p(\text{SeBr}_2)$ is determined by the predominating reaction leading to charged species in

Fig. 1. $\log p(\text{SeBr}_2)$ versus T^{-1} for equilibrium (1).Fig. 2. $\log(\kappa - \kappa_0)$ versus $\log p(\text{SeBr}_2)$.

the solution. κ_0 is the conductivity of pure liquid Se and $\kappa - \kappa_0$ is supposed to be the contribution to the conductivity from the charged species so formed (for details see Ref. 1). In this investigation, as in the Se—Cl work,¹ it has been found that $\log(\kappa - \kappa_0)$ is equal $\frac{1}{4} \log p(\text{SeBr}_2) +$ a constant which leads to the conclusion that four charged particles are formed per added SeBr_2 .

Table 2. Values of the temperature of the $\text{Se}_2\text{Br}_2(\text{l}) + \text{Se}(\text{s})$ mixture, of $\log p(\text{SeBr}_2)$ obtained from (3), and the measured conductivity values at 280°C.

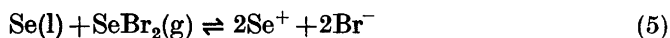
t°C, $\log p(\text{SeBr}_2)$, $\log(\kappa - \kappa_0)$; 20, -4.75, -5.37; 30, -4.38, -5.22; 40, -4.04, -5.13; 50, -3.71, -5.05; 60, -3.41, -4.97; 70, -3.12, -4.90; 75, -2.98, -4.87;

The results of one series of experiments are given in Table 2 and Fig. 2 gives the corresponding plot of $\log(\kappa - \kappa_0)$ versus $\log p(\text{SeBr}_2)$. The equation of the straight line drawn in the diagram is

$$\log(\kappa - \kappa_0) = \frac{1}{4} \log p(\text{SeBr}_2) - 4.13 \quad (4)$$

$\log \kappa_0$ equals -6.69. Other series of experiments give lines of the same slope but may be shifted by ± 0.07 units in $\log(\kappa - \kappa_0)$.

As in the Cl case the only reasonable reaction by which four charged carriers are formed, seems to be



The formulas might more correctly be written Se_n^+ and Se_nBr^- , but as has been mentioned the number of solvent atoms cannot be determined and therefore the simplest possible formulas are used.

Table 3. Values of $p(\text{SeBr}_2)$ and corresponding values of the total bromine concentration, C .

$p(\text{SeBr}_2) \times 10^4$, atm, $C \times 10^4$ (mole/1000 g); 0.177, 0.766; 0.273, 1.15; 0.415, 1.58; 0.621, 1.78; 0.919, 2.72; 1.34, 3.42; 1.94, 3.93; 2.77, 4.64; 3.91, 5.42; 5.47, 6.71; 7.57, 7.79; 7.57, 7.61; 10.4, 8.82; 10.4, 9.09;

The variation of total bromine content with $p(\text{SeBr}_2)$. The results of the analyses of quenched melts are given in Table 3 together with the corresponding $p(\text{SeBr}_2)$ values. The Br-concentrations, C , are given in mole/1000 g and $p(\text{SeBr}_2)$ in atm. If reaction (5) were the only one taking place when $\text{SeBr}_2(\text{g})$ dissolves in $\text{Se}(\text{l})$ one would expect $\log C$ plotted versus $\log p(\text{SeBr}_2)$ to have a slope of $\frac{1}{4}$. However, the best straight line for $\log C$ versus $\log p(\text{SeBr}_2)$ has a slope near to $\frac{1}{2}$. The predominating reaction would then give two dissolved particles per SeBr_2 and they must be uncharged, since the conductivity is not influenced. This would indicate the reaction



where as usual the SeBr may be solvated by a number of Se atoms.

Other reactions giving rise to (7) one and (8) three (uncharged) particles per dissolved SeBr_2 have been considered and also the possibility (9) that the "pure" selenium contains impurities which contribute to the apparent C .

If all the reactions mentioned are important the solubility C takes the form

$$C = k_5 \cdot p^{1/4} + k_8 \cdot p^{1/3} + k_6 \cdot p^{1/2} + k_7 \cdot p + k_9 \quad (10)$$

The data have been treated using a special form of the computer program LETAGROPVRID,⁴ which finds the set of values for k_i that minimize the error-square sum $U = \sum (C_{\text{exp}} - C_{\text{calc}})^2$, which is a function of the k_i .

The lowest acceptable value for U was obtained with the combination (σ values given):

$$k_6 = 2.68 \pm 0.12, \quad k_7 = 4.18 \pm 4.42, \quad U = 5.64 \times 10^{-5} \quad (11)$$

which corresponds to the broken line in Fig. 3, and gives only terms with $p^{1/2}$ and $p^{1.0}$ in C . When any other k_i from (10) was added, it came out with a negative value at the minimum for U . Hence, the solubility data give no evidence for reactions giving rise to 4 or 3 particles, or for a constant term corresponding to impurities.

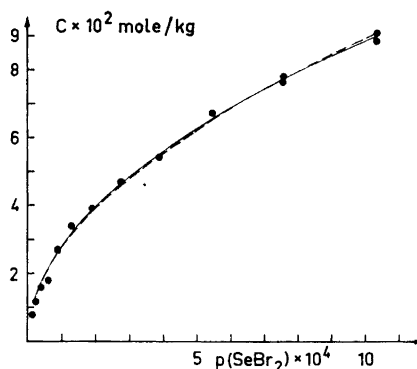


Fig. 3. Experimental points C versus $p(\text{SeBr}_2)$ and calculated curves.

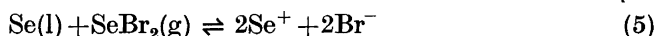
Even k_7 in (11) has a large standard deviation, and an almost as good fit is obtained if only the term $k_6 p^{1/2}$ is considered (full-drawn line, Fig. 3)

$$k_6 = 2.79 \pm 0.03, \quad U = 6.10 \times 10^{-5} \quad (12)$$

PROBABLE REACTIONS AND EQUILIBRIUM CONSTANTS

Though the conductivity data indicate that reaction (5) must take place, its contribution to C is negligible. Obviously, reaction (6) predominates and from these data all one can say about k_7 is a maximum value $\log k_7 < 1.2$.

Thus the most likely reactions are





Since $K_6 = k_6^2$ we find from (12), giving 3 σ -limits⁵

$$\log K_6 = 2 \log [\text{SeBr}] - \log p(\text{SeBr}_2) = 0.89 \pm 0.03 \quad (13)$$

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* In the paper on Se-Cl¹ there are some errors of minor importance. On p. 287 in Table 7 and p. 288 in Fig. 4, " $C \times 10^3$ mole/1000 g" should be $C \times 10^2$ mole/1000 g.

If the values of error square sums, U , (page 288) are recalculated to the unit (mole/kg Se) the right values are: (14): $U = 3.59 \times 10^{-4}$, (15): $U = 2.23 \times 10^{-4}$, (16): $U = 5.56 \times 10^{-4}$.