

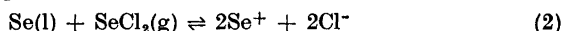
Conductance and Equilibrium Studies on the System Se-Cl

I. The Influence of Cl on the Conductivity of Liquid Se

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Studies of the conductivity of Se(l) in equilibrium with $\text{SeCl}_2(\text{g})$ at 280°C indicate that four charge carriers are formed per added $\text{SeCl}_2(\text{g})$ according to the reaction



The equilibrium constant for (2) was determined from solubility and conductivity data, $\log K_2 \approx -5.4$ (< -4.2)

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



with the equilibrium constant $\log K_8 \approx -0.09$ (< 0.02).

K_2 is given in $(\text{mole/kg})^4 \text{ atm}^{-1}$ and K_8 in $(\text{mole/kg})^2 \text{ atm}^{-1}$.

The conductivity of solid and liquid selenium is reported to be influenced considerably by nonmetals, such as oxygen and especially chlorine. The present work was started with the long-range aim of getting from conductivity studies added information on dissolved species in liquid selenium. Another aim was to see if it was possible to use conductivity measurements to analyse for impurities in liquid Se. One avoids disturbances from grain boundaries by using liquid instead of solid Se, and the liquid is more rapidly equilibrated with various gases.

Commonly conductivity data of Se are interpreted from the usual point of view of physicists, but in this study a chemical reasoning will be used analogous to that applied, for instance to aqueous solutions. The charge carriers will be assumed to be defined chemical species, for instance Se_n^{2+} , Se_n^+ , Se_nCl^- . This chemical picture is equivalent to a physical picture with electron holes of positive charge and excess electrons connected with the Cl. From studies of dilute aqueous solutions it is not possible to deduce how many solvent (water) molecules are bound to each dissolved species. Similarly, from studies of this type, the number of Se atoms that travel with the charge

carrier cannot be determined. For this reason the simplest possible formulas will be used: Se^{2+} , Se^+ , Cl^- etc., with the understanding that each species contains in addition an unknown number of Se atoms.

EARLIER DATA

The first study of the conductivity of liquid Se seems to be that reported by Marc¹ in 1907. He was mainly interested in the conductivity of solid Se, but also made a single measurement on liquid Se just above the melting point, 220°C.

In 1921 Pélabon² made a series of measurements between 390 and 690°C.

In the beginning of 1940 Borelius and co-workers³ made an extensive series of measurements on liquid Se, as part of a research program on the physical properties of Se.

Lizell⁴ in 1952 studied the conductivity of Se and Se-Te mixtures. The effect of Cl, Br, I, P, and Hg was investigated by Henkels⁵ in 1950, and the effect of Br and O by Eckart⁶ in 1954. Henkels and Eckart made their experiments at atmospheric pressure, while Lizell had an evacuated conductivity cell. The data on pure Se of Henkels and Eckart agree quite well with those of Lizell, but disagree with those of Borelius:

Author	$-\log \kappa_0$ (280°C, $\text{ohm}^{-1}\text{cm}^{-1}$)
Borelius ³	≈ 5.9
Lizell ⁴	6.72
Henkels ⁵	6.77
Eckart ⁶	6.43

κ_0 means the conductivity of pure liquid Se.

EXPERIMENTAL

Apparatus. A sketch of the conductivity cell is given in Fig. 1. The material in contact with the melt is fused silica and the electrodes consist of so-called vitreous carbon.⁷

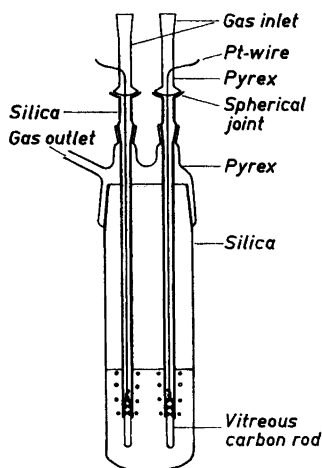


Fig. 1. Sketch of the conductivity cell.

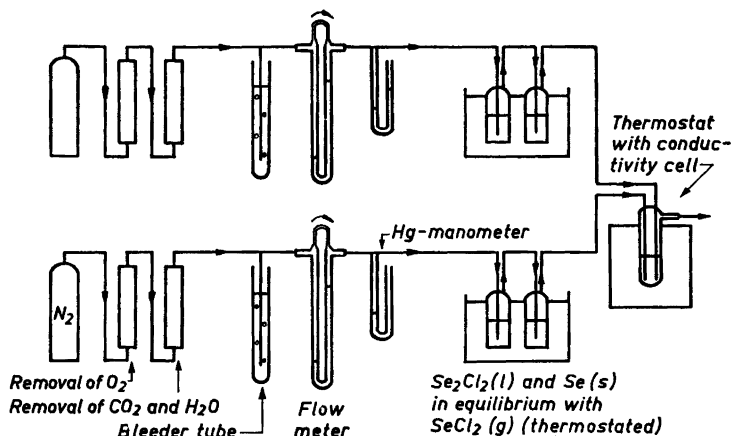


Fig. 2. Sketch of the whole apparatus.

The vitreous carbon rods, which have a quadratic cross-section, are kept in narrow silica tubes, from which about 2 cm of the rods stick out. Platinum wires are wound tightly in grooves in the upper part of the electrodes and run inside the silica tubes up to the pyrex part of the cell, where they are sealed through the pyrex glass. The gas, with which the liquid Se is equilibrated, is introduced into the melt through the electrode tubes. In this way, only those parts of the electrodes sticking out of the silica tubes are in contact with the melt, the rest being surrounded by gas.

In Fig. 2 a schematical drawing of the whole apparatus is given. Two gas leads are needed; one for each electrode tube of the cell. The nitrogen, which is used as inert atmosphere, is taken from cylinders, passed through electrically heated tubes containing active copper on kieselguhr at about 180°C to remove O₂, then through tubes filled with ascarite and dehydrite to remove CO₂ and H₂O. The gas flows are measured by means of flow meters consisting of a capillary and a manometer containing butyl phthalate; the pressure drop through each flow meter is maintained constant by bleeder tubes at set levels below the surface of butyl phthalate in the outer tubes. The flow meters were calibrated against a soap film meter giving Q , the flow rate in ml min⁻¹, as a function of the pressure drop read on the butyl phthalate manometer.

The pressure of the system is measured with a Hg manometer before the N₂ is passed through the two bottles containing a mixture of Se₂Cl₂(l) and Se(s), which is in equilibrium with SeCl₂(g) according to the reaction (see Part II)



It has been found that two bottles must be used to ensure that the N₂ is saturated with SeCl₂(g). The partial pressure of SeCl₂(g), $p(\text{SeCl}_2)$, is maintained constant by keeping the bottles containing the above mentioned mixture in a thermostat. The N₂, saturated with SeCl₂(g), is then passed through the conductivity cell with Se(l). In order to avoid condensation of SeCl₂(g) all glass tubes are heated using thermocords, to a temperature above that of the mixture of Se₂Cl₂(l) and Se(s). To keep the temperature of the liquid Se constant at 280°C a thermostat filled with oil (Shell Nassa Oil 89) is used. The temperature of the oil bath can be kept constant within $\pm 0.3^\circ\text{C}$.

The resistance measurements were carried out on an a.c. conductivity meter type LBR from Wissenschaftlich-technische Werkstätten GmbH, Weilheim, Oberbayern. The bridge could be read to better than $\pm 1.5\%$.

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. Se₂Cl₂(l) saturated with Se(s) was prepared by passing Cl₂(g) over Se(s) in a flask

till all solid seemed to have disappeared. The product was really $\text{Se}_2\text{Cl}_2(\text{l})$ with excess of Se or Cl. To this solution excess Se(s) was added. During the preparation and afterwards care must be taken that no air or moisture is introduced into the reaction vessel.

Analysis. Chlorine analyses of quenched melts have been performed by Boliden's Mining Company in the following way. The sample was dissolved in HNO_3 in the presence of Ag^+ , which precipitated the chlorine as $\text{AgCl}(\text{s})$. The precipitate was converted to $\text{Ag}(\text{l})$ by heating it in the presence of Pb at 900°C . The sample was then cupellated twice and the remaining Ag weighed.

Procedure. About 80 g of Se(s) was put into the cell, melted and heated to 280°C . Then a stream of pure N_2 , with a flow rate of about 70 ml min^{-1} for each gas lead, was passed through the Se(l). The conductivity of pure liquid Se, κ_0 , was taken as the practically constant value obtained after at least 5 h of N_2 -bubbling. In the beginning of an experiment the conductivity was somewhat high, probably due to the presence of dissolved oxygen.

Then the $\text{SeCl}_2(\text{g})$ -bubbling was started by passing the N_2 first through the mixture of $\text{Se}_2\text{Cl}_2(\text{l})$ and Se(s) and then through the Se(l). The initial temperature of this mixture in one experimental series was 6.5°C . After about 24 h equilibrium was reached, that is κ had increased to a constant value. The temperature of the $\text{Se}_2\text{Cl}_2(\text{l}) + \text{Se}(\text{s})$ mixture (and with that $p(\text{SeCl}_2)$) was increased stepwise every 24 h by about 10°C until 75°C was reached and the equilibrium values of κ were measured at each temperature.

When the melt was to be analysed for Cl, $\text{SeCl}_2(\text{g})$ of a fixed partial pressure was bubbled through the melt until equilibrium was reached and then the melt was quenched by pouring it into distilled water.

RESULTS AND DISCUSSION

Influence of cell and electrode material. Several types of cells were tried before the fused-silica vitreous carbon cell. The first cells were made of soda glass for practical convenience, but it was found that they gave a higher value of the conductivity of pure Se(l) at 280°C , κ_0 , than cells of silica. Pyrex glass also gave a somewhat high κ_0 -value.

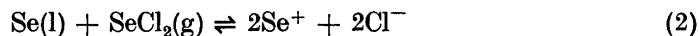
As electrode material, platinum, gold, graphite, wolfram, and vitreous carbon were tried. The effect of current density on κ_0 has been roughly tested for all of these materials except wolfram. The current was changed by connecting a ceramic resistance in series with the cell. For low current densities it was found that the apparent κ_0 decreased, which would indicate a surface resistance. However, when the current density was high enough κ_0 approached a constant value for all materials tested. The lowest permissible current densities were of the orders of magnitude $0.02 \mu\text{A cm}^{-2}$ for graphite, $0.6 \mu\text{A cm}^{-2}$ for platinum, $0.2 \mu\text{A cm}^{-2}$ for gold and $0.2 \mu\text{A cm}^{-2}$ for vitreous carbon. However, the surface of the graphite electrodes used by that time was so large that the current density became lower than permitted. One might have used smaller graphite electrodes, but at any rate they were slightly porous and hence hard to clean. Platinum and gold were later excluded for other reasons. These materials were attacked by the Se(l) and gave high values of κ_0 . A cell made of silica and with wolfram electrodes gave $\log \kappa_0 = -6.70 \pm 0.07$, the same value as for the silica-vitreous carbon cell. However, the wolfram electrodes did not work well when the melt was equilibrated with $\text{SeCl}_2(\text{g})$. Irreproducible data were obtained, which indicated that there was a reaction between the wolfram electrodes and the chlorine added. There has been no indication that the vitreous carbon electrodes are attacked by the Se(l), not

even in the presence of Cl. Data with the new cell would hence be less influenced by impurities than our earlier data.⁸

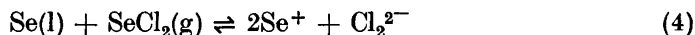
Measurements with alternating current of 50 and 3000 cycles per second gave the same values for the conductivity within the limits of error. This agrees well with the results of Lizell,⁴ who did not find any difference in the conductivity of Se(l) with DC and AC frequencies between 50 and 100 000 periods per second.

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

Now suppose that the conductivity, κ , is proportional to the number of charge carriers. Then the dependence of $\log \kappa$ on $\log p(\text{SeCl}_2)$ would be different, depending on the predominating reaction in the solution. If, for instance, the predominating charge carriers are formed by the reaction



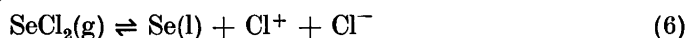
the equilibrium law predicts that $\log \kappa = \text{constant} + \frac{1}{4} \log p(\text{SeCl}_2)$, giving a slope of $\frac{1}{4}$. The reactions



would give a slope of $\frac{1}{3}$ and the reaction



and the quite unlikely



would give a slope of $\frac{1}{2}$. From the diagram $\log \kappa$ versus $\log p(\text{SeCl}_2)$ one could thus exclude certain possibilities and make reasonable guesses about the mechanism.

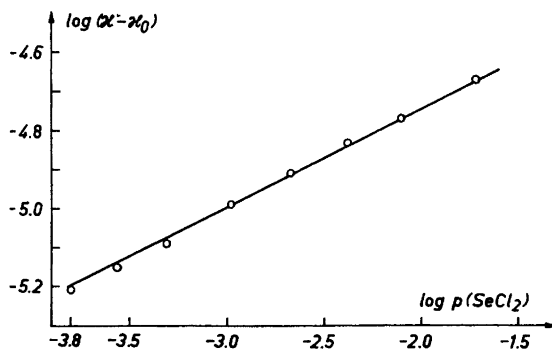


Fig. 3. $\log (\kappa - \kappa_0)$ versus $\log p(\text{SeCl}_2)$.

Up to now we have neglected the fact that even pure Se(l) contains some charged species which give rise to the conductivity κ_0 . If none of the conducting species formed by adding $\text{SeCl}_2(\text{g})$ is identical with any of the ions of the pure solvent one may expect the contribution from these species, κ_{Cl} , simply to be added to κ_0 ; thus the contribution κ_{Cl} would be $\kappa - \kappa_0$. On the other hand if any of the ions formed is identical with one of the solvent ions, κ_{Cl} would be within the limits $\kappa - \kappa_0$ and κ . Using $\kappa - \kappa_0$ for κ_{Cl} will at any rate cause only a small error since even the lowest value of κ used in this investigation is about 30 times greater than κ_0 .

Fig. 3 gives a plot of $\log(\kappa - \kappa_0)$ versus $\log p(\text{SeCl}_2)$ for one series of experiments. The data are given in Table 1, where κ is given in $\text{ohm}^{-1} \text{cm}^{-1}$ and $p(\text{SeCl}_2)$ in atm. The straight line drawn in the diagram corresponds to the equation

$$\log(\kappa - \kappa_0) = \frac{1}{4} \log p(\text{SeCl}_2) - 4.25 \quad (7)$$

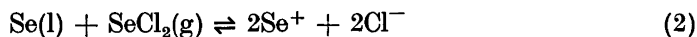
$\log \kappa_0$ equals -6.70 .

Table 1. Values of the temperature of the $\text{Se}_2\text{Cl}_2(\text{l}) + \text{Se}(\text{s})$ mixture, of $\log p(\text{SeCl}_2)$ obtained from the relationship, $\log p(\text{SeCl}_2) = -2947 \cdot T^{-1} + 6.74$, and the corresponding conductivity values.

$t^\circ\text{C} (\text{Se}_2\text{Cl}_2 + \text{Se})$	$\log p(\text{SeCl}_2)$	$\log(\kappa - \kappa_0)$
6.5	-3.80	-5.21
13	-3.56	-5.15
20	-3.31	-5.09
30	-2.98	-4.99
40	-2.67	-4.91
50	-2.38	-4.83
60	-2.10	-4.77
75	-1.72	-4.67

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

From the value of the slope, $\frac{1}{4}$, it follows that in the main reaction giving rise to charged particles, for each SeCl_2 added four dissolved particles are formed. The only reasonable reaction of that kind seems to be ^{8a}



As has been mentioned, it is not possible to say how many molecules of the solvent (Se) are attached to each particle so that the formulas might more correctly be written Se_n^+ and Se_nCl^- .

It is possible that an important contribution to the conductivity comes from electron jumps; that is a rapid shift of an electron hole through the solution. The analogy to aqueous solutions is very close. The two fastest ions in aqueous solutions are $\text{H}^+(\text{H}_2\text{O})_n$ and OH^- . It is generally thought that their high mobility comes, not from a high mobility of the whole group, but rather from proton jumps. What is described as the mobility of OH^- is the sum of 1) the relatively small contribution from the movement of the

OH^- ions as such in the electrical field, and 2) the rapid shift of a proton hole across the solution. The situation is similar with H^+ . Nevertheless, the contribution to conductivity is proportional to concentration, and one can use such measurements for determining equilibrium concentrations, which has been done with considerable success.

Table 2. Values of $p(\text{SeCl}_2)$ and corresponding values of the total chlorine concentration, C .

$p(\text{SeCl}_2) \times 10^3$ (atm), $C \times 10^3$ (mole/1000 g); 0.49, 2.38; 0.49, 2.54; 0.49, 2.85; 1.05, 3.58; 1.05, 3.81; 1.05, 3.74; 2.14, 4.96; 2.14, 5.17; 2.14, 5.01; 4.17, 7.47; 4.17, 6.81; 7.94, 10.10; 7.94, 8.96; 14.13, 13.16; 14.13, 12.07; 19.05, 13.73; 19.05, 13.85.

The variation of total chlorine content with $p(\text{SeCl}_2)$. From the analyses we obtained C , the total chlorine concentration in mole/kg in the Se(l) (Table 2). If $\text{SeCl}_2(\text{g})$ dissolves only by reaction (2) one would expect that $\log C$ plotted versus $\log p(\text{SeCl}_2)$ would also give a line of slope $\frac{1}{4}$. However, this is not the case. The best straight line for $\log C$ versus $\log p(\text{SeCl}_2)$ has a slope near to $\frac{1}{2}$. The predominating reaction would then give two dissolved particles per SeCl_2 and they must be uncharged, since the conductivity is not influenced. This would indicate the reaction

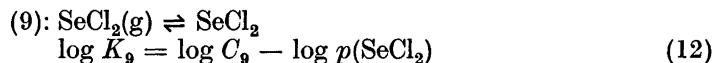
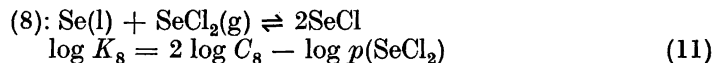
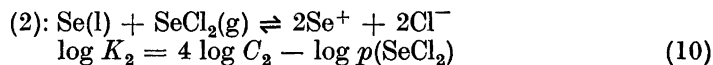


where as usual the SeCl may be solvated by more Se. There may also be to some extent a reaction such as



If this were the main reaction it would give a slope of 1 in $\log C$ ($\log p$).

We may hence consider the following three reactions and equilibrium constants:



where C_2 is the concentration of Se^+ and Cl^- , C_8 the concentration of SeCl and C_9 the concentration of SeCl_2 in the Se(l).

The data have been treated using the computer program Letagropvrid.⁹ If all three reactions are important the solubility C takes the form

$$C = k_2 p^{1/4} + k_8 p^{1/2} + k_9 p \quad (13)$$

$$\text{where } k_2 = K_2^{1/4}, k_8 = K_8^{1/2} \text{ and } k_9 = 2K_9 \quad (13a)$$

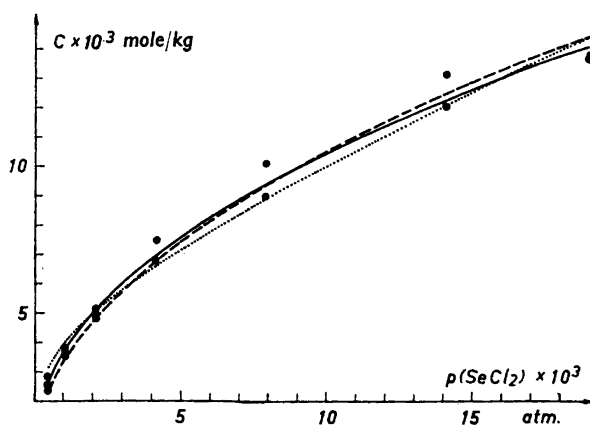


Fig. 4. Experimental points C versus $p(\text{SeCl}_2)$ and calculated curves.

The program 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 . In the output, the "best" set of constants is given together with the calculated value C_{calc} for each experimental p -value.

When all three constants were varied at a time k_2 and k_9 were found to have negative values at the minimum for U . The program is so constructed that negative equilibrium constants, here k_2 and k_9 , are set equal to zero and the remaining constants, here k_8 , recalculated to give minimum U . As a result of this is obtained:

$$k_8 = 1.05 \pm 0.15, U = 12.72 \quad (14)$$

where ± 0.15 is the standard deviation $\sigma(k_8)$. In the diagram in Fig. 4 the dashed line shows C_{calc} versus $p(\text{SeCl}_2)$ for this case where $C_{\text{calc}} = k_8 \cdot p^{1/2}$.

If k_2 and k_8 are varied at the same time positive values are obtained:

$$k_2 = (4.51 \pm 1.50) \times 10^{-2}, k_8 = (9.03 \pm 0.48) \times 10^{-1}, U = 7.904 \quad (15)$$

The full-drawn line shows

$$C_{\text{calc}} = k_2 \cdot p^{1/4} + k_8 \cdot p^{1/2}$$

using these constants.

Also if k_2 and k_9 are varied at a time positive constants are obtained:

$$k_2 = (2.01 \pm 0.11) \times 10^{-1}, k_9 = 3.67 \pm 0.34, U = 19.70 \quad (16)$$

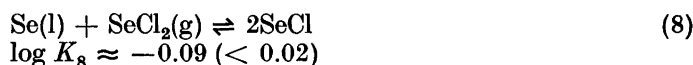
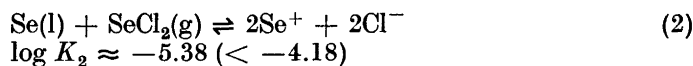
The dotted line shows

$$C_{\text{calc}} = k_2 \cdot p^{1/4} + k_9 \cdot p$$

If k_8 and k_9 are varied at the same time k_9 is given a negative value and then k_8 and U will be the same as in (14).

PROBABLE REACTIONS AND EQUILIBRIUM CONSTANTS

The conductivity data indicate that the reaction (2) really takes place. The lowest U -value and hence the best fit to the analytical data is obtained for the combination of (15) reactions (2) and (8) (full-drawn line in Fig. 4). Obviously reaction (8) predominates as the value of k_8 does not change much when (2) is not considered. One may conclude, using (13a) and (15) that the most likely reactions and equilibrium constants are



K_2 is given in (mole/kg)⁴ atm⁻¹ and K_8 in (mole/kg)² atm⁻¹. "Best" values of $\log K_i$ are given, and maximum values equal to $\log(K_i + 3\sigma(K_i))$.¹⁰

ON THE NATURE OF THE CHARGE CARRIERS

The contribution to conductivity caused by the formation of Se^+ and Cl^- may come partly from movement of whole groups Se_n^+ and Se_nCl and partly from electron jumps. The shift of positive charge from one Se^+ to another Se seems much more likely than shift of electrons between SeCl and SeCl^- of quite low concentrations. To get some information on the conduction mechanism, the apparent radius, r , of the charged species has been calculated using Stokes' law. The conductivity is assumed to be caused by the movement of spherical particles in a continuum.

$$\text{Stokes' law: } r = \frac{F}{6\pi\eta v} \quad (17)$$

r = radius of particle in cm

v = velocity of conducting particle in cm sec⁻¹

F = force acting on particle in dyne

η = viscosity in poise (dyne sec cm⁻²)

v for any field strength X volt cm⁻¹ can be calculated from the conductance and analytical data. Λ , the equivalent conductance is given by the expression

$$\Lambda = \frac{10^3(\kappa - \kappa_0)}{c} \text{ cm}^2 \text{ equiv}^{-1} \text{ ohm}^{-1} \quad (18)$$

where c is the concentration in mole dm⁻³ for the conducting species Se^+ or Cl^- , $(\kappa - \kappa_0) = 10^{-4.25} \times p^{3/4}$ is obtained from eqn. (7), $c = 4.51 \times 10^{-2} \cdot p^{3/4} \cdot 3.9$ equiv dm⁻³ is obtained from (15) and the density (3.9) of Se(l) at 280°C. Thus from eqn. (18) is obtained $\Lambda = 0.32$. The equivalent conductances of the positive and the negative ion have been approximated to be equal: $l_+ = l_- = 0.16$.

Then $v = 0.16 \cdot X / 96491$

The force F is given by:

$$F = 1.6021 \times 10^{-19} \cdot X \times 10^7 \text{ dyne}$$

η is equal to 3.3 poise for pure Se(l) at 280°C.¹¹ These values of v , F , and η are put into eqn. (17) and r is obtained.

$$r = 1.6 \times 10^{-8} \text{ cm} = 1.6 \text{ \AA}$$

This value is of the order of magnitude of the radius of one Se^+ or Cl^- ion. However, the conductivity may be caused not only by movement of these species but also by movement of larger groups and by electron jumps. If for instance an unreasonably low value of r had been obtained one could have expected the conductivity to be caused mainly by electron jumps.

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