# MOLECULAR STRUCTURE OF SOME SELENIUM COMPOUNDS DETERMINED BY MAGNETIC METHOD

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THE use of the magnetic method for determining the molecular structure is based on Pascal's investigations who showed that the susceptibility of a molecule $(\chi_m)$ can be calculated from the atomic susceptibilities of the constituent atoms $(\chi_A)$ and the constitutive constant $(\lambda)$ for different bindings. Also Bhatnagar and co-workers[1] have shown that in electrovalent salts, in which the ions have complete inert gas configuration the molecular susceptibility can be considered to be the sum of the susceptibilities of ions which constitute the molecule.

Pascal and Kido's experimental data provide the values of susceptibilities for a number of ions and atoms and for various types of bindings. In cases wherein they are not known they can be worked out, for diamagnetic atoms or ions, from Langevin equation

$$\chi_A = - a \Sigma_n \, r^2$$

where $\Sigma_n \, r^2$ is a function of the valency state of the ion and '$a$' is a constant, equal to $\dfrac{e^2 \, z}{6 \, mc^2}$. The mode of calculation of the value of $\Sigma \, r^2$ is shown in the discussion of this paper.

The magnetic method has been employed by Farquharson[2] to determine the change in polarity of some *of the linkages. Gray and Cruickshank[3] determined from the additivity law the depression in susceptibility due to various chemical bonds and used the data thus obtained to calculate the susceptibilities of several organic compounds. From the close agreement between the theoretical and experimental values they showed that the magnetic method can be employed not only to determine the structure of compounds but also to differentiate between isomeric structures and those which involve resonance. The same plan was employed by Clow[4] to elucidate the structure or urea and its several derivatives. He showed that a change in the parent molecule from a resonating zwitterion in urea itself through an amino-imino structure in N-monosubstituted urea to carbamide

in tetra-substituted molecules takes place, and that when there is a C: : N group in the molecule, it resonates between the structure C: : N̈ : and C⁺ : N̈⁻ : ·

Bhatnagar and Bahl[5] measured the magnetic susceptibilities of a large number of trivalent bismuth salts and on applying Pascal's law calculated the ionic susceptibility of $Bi^{+3}$ which is in agreement with that calculated from Pauling's theoretical consideration. In the same manner Bhatnagar and Khanna[6] determined from its several salts the ionic susceptibility of rubidium which agrees with the theoretically calculated value. Bhatnagar, Nevgi and Sharma[7] determined the ionic susceptibilities of tin in di- and tetra-valent states and Bhatnagar, Prakash and Hamid[8] and Bhatnagar, Prakash and Maheswari[9] fixed up the valency states of chromium and manganese in their several compounds.

Varadachari and Subramaniam[10] have determined the susceptibilities of a number of sulphur compounds and by comparing their experimental values with those obtained on theoretical considerations have assigned proper valencies to sulphur in these compounds. Selenium belongs to the same group as sulphur and, like sulphur, though normally bivalent, can acquire more than one valency state.

An attempt has been made in this investigation to employ the magnetic method for the elucidation of the much debated molecular constitution of some of the selenium compounds in which Se may exist in several valency states. The molecular constitutions found by this method have been discussed along with the already known constitutions for these substances.

### Experimental

The measurements of the magnetic susceptibilities were made by the modified form of Gouy's balance[11] and calculated by the usual formula,

$$\chi_{d_2} = \frac{1}{m d_2} \left[ (\chi_{d_1} m_{d_1} - \chi_a m_{ad_1}) \frac{p d_2}{p d_1} + \chi_a m_{ad_2} \right]$$

where

$\chi_{d_2}$ = magnetic susceptibility of the specimen being investigated,

$m_{d_2}$ = mass of the substance under investigation,

$\chi_{d_1}$ = magnetic susceptibility of the standard substance,

$m_{d_1}$ = mass of the standard substance,

$\chi_a$ = magnetic susceptibility of the medium which is air,

$m_{ad_1}$ = mass of air displaced by the standard substance,

$p_{d_1}$ = decrease in weight due to the standard substance,

and     $p_{d_2}$ = decrease in weight due to the specimen under investigation.

Kahlbaum's extra pure potassium chloride (magnetic susceptibility $= -0.516 \times 10^{-6}$) was used as the standard substance. All the necessary precautions for the use of the apparatus were taken. To test the working of the apparatus the susceptibilities of pure substances from Kahlbaum were measured. The results obtained are given in Table I.

TABLE I

| Substance | $-\chi_a \times 10^6$ observed | $-\chi_a \times 10^6$ from other authors |
|---|---|---|
| Potassium persulphate .. .. .. .. | 0·371 | 0·3748 *Int. Crit. Tab.* |
| Selenium .. .. .. .. .. | 0·322 | 0·320 ,, |
| Tellurium ... .. .. .. .. | 0·323 | 0·320 ,, |
| Barium sulphate .. .. .. .. | 0·306 | 0·306 ,, |
| Glycerine .. .. .. .. .. | 0·538 | 0·538 ,, |

*Results*

The magnetic susceptibilities obtained for the selenium compounds are given in Table II. These values are the mean of three independent observations.

TABLE II

| Substance | Molecular formula | $\chi_a \times 10^6$ | $\chi_m \times 10^6$ |
|---|---|---|---|
| Selenium monobromide .. .. .. .. | $Se_2Br_2$ | $-0.3544$ | $-112.8$ |
| Selenium monochloride .. .. .. .. | $Se_2Cl_2$ | $-0.4134$ | $-94.79$ |
| Selenious acid .. ... .. .. .. | $H_2SeO_3$ | $-0.3515$ | $-45.41$ |
| Silver selenite .. .. .. .. .. | $Ag_2SeO_3$ | $-0.293$ | $-102.2$ |
| Selenosyl chloride .. .. .. .. | $SeOCl_2$ | $-0.2929$ | $-48.65$ |

All the Selenium compounds except silver selenite were obtained either from Kahlbaum or from Theoder Schuchardt and were of extra pure quality. Silver selenite was prepared in the laboratory by adding selenious acid to an aqueous solution of silver nitrate. The Selenite, precipitated out as a white powder, was crystallised from a dilute solution of nitric acid and the crystals obtained in the form of long needles were analysed (Ag found $= 62.77\%$; theory requires $62.90\%$).

### Discussion of Results

Langevin Equation assumes the form $\chi_a = -2 \cdot 832 \times 10^{10} \Sigma_n \, \bar{r}^2$, when the values of the known constants are substituted. Van Vleck[12] and Pauling[13] have independently derived a quantum mechanical expression whereby $\chi$ for a single electron is given by

$$\chi = -0 \cdot 79 \times 10^{-6} \left\{ \tfrac{5}{2} \, n^2 - \frac{3 \, l \, (l+1) - 1}{2} \right\}.$$

The application of this expression has been extended by Pauling who by introducing appropriate screening constants for each $(n, 1)$ group of electrons, finds that

$$\chi_{nl} = -0 \cdot 79 \times 10^{-6} \frac{2 \, l \, (l+1) \, n^2}{(z - \sigma_{nl})} \left\{ \tfrac{5}{2} \, n^2 - \frac{3 \, l \, (l+1) - 1}{2} \right\}.$$

The susceptibility of an atom or of an ion can be obtained by summing over all the sub-groups present in the atom or the ion.

An approximate method for the calculation of the value of $\Sigma \bar{r}^2$ has been more recently attempted by Slater[14] for a limited number of atoms. He takes the radial part of the curve function due to a single electron and finds that

$$\bar{r}^2 = \frac{(n')^2 \, (n' + \tfrac{1}{2}) \, (n' + 1)}{(z - s)^2}$$

where $n'$ and $(z - s)$ are, respectively, the effective quantum number and the effective nuclear charge. The susceptibility obtained by summing over all the electrons, is given by

$$\chi_A \times 10^6 = -0 \cdot 79 \, \Sigma \, \frac{(n')^2 \, (n' + \tfrac{1}{2}) \, (n' + 1)}{(z - s)^2}.$$

Similar rules have been given by Slater for calculating the values of $(z - s)$ and $(n')$ for any electronic group.

Values for $\Sigma \bar{r}^2$ and ionic susceptibilities for Se in various valency states have been calculated as described above and the results obtained are given in Table III. Angus[15] has introduced a slight modification in Slater's method for calculating the screening constant. Slater takes the $s$ and $p$ electrons together while Angus takes them separately. Results obtained according to Angus give lower values, as in this case, the effective charge for $s$ electrons is increased. Consequently better agreement is obtained for heavier atoms, in which case Slater's method yields values which are a bit too high, while it is impaired in the case of lighter atoms. Values of $\Sigma \bar{r}^2$ and ionic susceptibilities calculated according to Angus are also given in Table III.

## TABLE III

*Diamagnetic Susceptibilities of Se in Various Valency States Calculated from Various Methods*

| Valency states | $\Sigma r^2$ calculated by Slater's method | $-\chi \cdot 10^6$ calculated by Slater's method | $\Sigma r^2$ calculated by modification in Slater's method | $-\chi \cdot 10^6$ calculated by modification in Slater's method, using constant 0.790 instead of 0.807 | $\Sigma r^2$ calculated by Angus's method | $-\chi \cdot 10^6$ calculated by Angus's method | $\Sigma r^2$ calculated by modification in Angus's method | $-\chi \cdot 10^6$ calculated by modification in Angus's method using constant 0.790 instead of 0.807 |
|---|---|---|---|---|---|---|---|---|
| Se divalent .. | 28·32 | 22·86 | 34·59 | 27·32 | 26·75 | 21·59 | 32·09 | 25·34 |
| Se tetravalent | 17·60 | 14·20 | 19·18 | 15·15 | 17·52 | 14·14 | 16·10 | 15·09 |
| Se hexavalent | 9·85 | 7·95 | 8·61 | 6·800 | 9·77 | 7·881 | 8·52 | 6·732 |

The values of $\Sigma r^2$ and ionic susceptibilities have also been calculated after introducing slight empirical changes, as given below, in Slater's and Angus's formulæ;

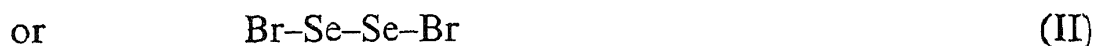(A) giving the value 0·85 to the lower groups and not to the shells while calculating the screening constants,

(B) making no distinction between the $d$ and $f$ groups as compared with the ones containing $s$ and $p$,

(C) taking 0·790 (given by Slater) instead of 0·807 (given by Angus).

These values have been employed in the discussion of the molecular constitution of different compounds and have been represented as follows:

$(\chi_a)_1$ and $(\chi_m)_1$ .. Specific and molecular susceptibilities in different states calculated according to Slater's method.

$(\chi_a)_2$ and $(\chi_m)_2$ .. Specific and molecular susceptibilities in different states calculated according to the modifications in Slater's method.

$(\chi_a)_3$ and $(\chi_m)_3$ .. Specific and molecular susceptibilities in different states calculated according to Angus's method.

$(\chi_a)_4$ and $(\chi_m)_4$ .. Specific and molecular susceptibilities in different states calculated according to the modifications of Angus's method.

$(\chi_a)_E$ and $(\chi_m)_E$ .. Experimental values of the author.

$(\chi_a)_0$ and $(\chi_m)_0$ .. Values observed by others.

1. *Selenium monobromide* $(Se_2Br_2)$.—The constitution of this compound may be formulated as

$$Se = Se \underset{\searrow Br}{\overset{\nearrow Br}{}} \qquad (I)$$

or        Br–Se–Se–Br        (II)

Reactions of this substance with organic compounds, notably Grignard reagent, indicate that these two forms are likely to co-exist, thus representing an example of inorganic tautomerism (Morgan and Burstall, *Inorganic Chemistry*, p. 170). The calculated and the experimental magnetic values for the two constitutions are given in the following Table. In these calculations the value for $Br^-$ ion is taken as $-32 \cdot 5 \times 10^{-6}$ (Stoner, *Magnetism and Matter*, p. 468).

TABLE IV

| Constitutional formula | (I) $Se = Se \overset{\nearrow Br}{\searrow Br}$ | (II) Br–Se–Se–Br |
|---|---|---|
| $(\chi_a)_1$ | $-0 \cdot 3208 \times 10^{-6}$ | $-0 \cdot 3479 \times 10^{-6}$ |
| $(\chi_m)_1$ | $-102 \cdot 06 \times 10^{-6}$ | $-110 \cdot 72 \times 10^{-6}$ |
| $(\chi_a)_2$ | $-0 \cdot 3379 \times 10^{-6}$ | $-0 \cdot 3674 \times 10^{-6}$ |
| $(\chi_m)_2$ | $-107 \cdot 47 \times 10^{-6}$ | $-119 \cdot 64 \times 10^{-6}$ |
| $(\chi_a)_3$ | $-0 \cdot 3163 \times 10^{-6}$ | $-0 \cdot 3400 \times 10^{-6}$ |
| $(\chi_m)_3$ | $-100 \cdot 73 \times 10^{-6}$ | $-108 \cdot 18 \times 10^{-6}$ |
| $(\chi_a)_4$ | $-0 \cdot 3313 \times 10^{-6}$ | $-0 \cdot 3636 \times 10^{-6}$ |
| $(\chi_m)_4$ | $-105 \cdot 43 \times 10^{-6}$ | $-115 \cdot 68 \times 10^{-6}$ |
| $(\chi_a)_E$ | | $-0 \cdot 3544 \times 10^{-6}$ |
| $(\chi_m)_E$ | | $-112 \cdot 6 \times 10^{-6}$ |

It is clear from the above that all the calculated values of $\chi_a$ and $\chi_m$ for the constitution II agree fairly well with the experimental values. Hence the constitution of $Se_2Br_2$ is Br–Se–Se–Br.

This constitution is in agreement with the fact that organo-selenium compounds obtained as a result of the reaction between selenium monobromide and organo-magnesium compounds have a chain structure, –Se–Se–, (*cf.* Pieroni and Coli, *Gazzetta*, 1914, **44**, 349; Pieroni and Balduzzi, *ibid.*, 1915, **45**, 106).

2.  *Selenium monochloride* ($Se_2Cl_2$).— It has been definitely shown by cryoscopic measurements of solutions of selenium monochloride in ethylene di-bromide that its molecular weight is in accordance with the molecular formula $Se_2Cl_2$ (Beckmann, *Zeit. anorg. chem.*, 1908, **63**, 63). However, its constitution is still uncertain. Its constitution may be represented either as

$$Se\!\cdot\!\cdot Se\!\!\begin{array}{c} \diagup Cl \\ \diagdown Cl \end{array} \qquad \text{(I)}$$

$$\text{or} \qquad Cl\text{-}Se\text{-}Se\text{-}Cl \qquad \text{(II)}$$
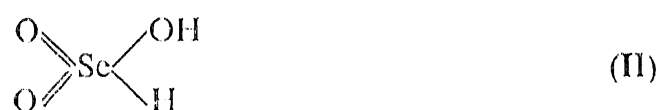
The calculated and experimental values for the two constitutions are given in the following Table. The value for Cl ion used in these calculations is taken as $-22.2 \times 10^{-6}$ (Leiterer, *Z. physical chem.*, (B), 1937, **36**, 332; Bhatnagar, Prakash and Hamid, *Jour. Chem. Soc.*, 1938, 1433).

TABLE V

| Constitutional formula | (I) $Se\!\cdot\!\cdot Se\!\!\begin{array}{c}\diagup Cl\\\diagdown Cl\end{array}$ | | (II) Cl-Se-Se-Cl | |
|---|---|---|---|---|
| $(\chi_a)_1$ | $0.3552$ | $10^{-6}$ | $-0.3930$ | $10^{-6}$ |
| $(\chi_m)_1$ | $81.46$ | $10^{-6}$ | $90.12$ | $10^{-6}$ |
| $(\chi_a)_2$ | $0.3788$ | $10^{-6}$ | $0.4319$ | $10^{-6}$ |
| $(\chi_m)_2$ | $86.87$ | $10^{-6}$ | $99.04$ | $10^{-6}$ |
| $(\chi_a)_3$ | $0.3494$ | $10^{-6}$ | $0.3819$ | $10^{-6}$ |
| $(\chi_m)_3$ | $80.13$ | $10^{-6}$ | $87.58$ | $10^{-6}$ |
| $(\chi_a)_4$ | $0.3709$ | $10^{-6}$ | $0.4145$ | $10^{-6}$ |
| $(\chi_m)_4$ | $84.83$ | $10^{-6}$ | $95.04$ | $10^{-6}$ |
| $(\chi_a)_5$ | | | $0.4134$ | $10^{-6}$ |
| $(\chi_m)_5$ | | | $94.79$ | $10^{-6}$ |

The above results show a good agreement for the constitution Cl-Se—Se-Cl and thus establish a similarity in the constitution of $Se_2Cl_2$ and $Se_2Br_2$.

3.  *Selenious acid* ($H_2SeO_3$).— Nothing is definitely known regarding the constitution of selenious acid. Two possible structures are given below:

$$O\!=\!Se\!\!\begin{array}{c}\diagup OH\\\diagdown OH\end{array} \qquad \text{(I)}$$

$$\begin{array}{c}O\\O\end{array}\!\!>\!\!Se\!\!\begin{array}{c}\diagup OH\\\diagdown H\end{array} \qquad \text{(II)}$$

In (I) selenium is quadrivalent and both Hydrogen atoms belong to hydroxyl groups while in (II) selenium is hexavalent. The acid is classed amongst the pseudo acids in which changes can take place in their constitution. Karve[16] has studied the absorption spectra and the catalytic activity of this acid and has concluded that it is an associated pseudo acid in the pure condition. The aqueous solution of the acid contains large proportion of the pseudo acid and only a small percentage of the hydrate of the true acid.

One may take the nonformation of a selenium analogue of thiosulphuric acid on heating selenium with a selenite solution as an evidence in favour of the formula I. This view is also supported by the formation of ethyl selenite

$$O = Se \underset{\diagdown OC_2H_5}{\overset{\diagup OC_2H_5}{}}$$ by the action of (i) sodium ethoxide on selenosyl chloride and

(ii) ethyl iodide on silver selenite (Michaelis and Landmann, *Ber.*, 1880, **13**, 656; 1887, **20**, 625).

Recently the constitution of this compound has been investigated by Venkateswaran[17] who studied Raman spectra of the solid crystalline acid and of its aqueous and alcoholic solutions of varying concentrations. He also studied the Raman spectra of sodium biselenite and sodium selenite. His results point to the existence of both types of molecules, namely, the forms (I) and (II), in dynamical equilibrium with each other. In the solid state and in solution in methyl alcohol the form (II) is predominant while in aqueous solution almost the whole of the acid exists in the form (I). This shows that in the solid state selenium is hexavalent and in aqueous solutions it is tetravalent.

The results given in the Table below refer to solid selenious acid. In order to calculate the magnetic susceptibility of this acid the following values for the groups present are used.

$$OH = - 7 \cdot 54 \times 10^{-6} \text{ (Pascal)}.$$

$$H = - 3 \cdot 05 \times 10^{-6} \text{ (\textit{Int. Crit. Tab.})}$$

and the results obtained are given under A of Table VI.

Although there is a very good agreement between the author's experimental value and that given in the *International Critical Tables* it will be seen that it does not agree with any of the calculated values. This discrepancy may be due to oxygen atoms whose atomic susceptibility varies with the mode of combination. If binding between oxygen and other atoms is strong, it produces ionic deformation and consequently introduces a high paramagnetic term in the total molecular susceptibility. The ionic magnetic

## TABLE VI

| Constitutional formula | A (I) $O = Se{<}^{OH}_{OH}$ $-\chi \times 10^6$ | A (II) $O{=}Se{<}^{OH}_{H}$ (with $O$ double bonds) $-\chi \times 10^6$ | B (I) $O = Se{<}^{OH}_{OH}$ $-\chi \times 10^6$ | B (II) $O{=}Se{<}^{OH}_{H}$ $-\chi \times 10^6$ |
|---|---|---|---|---|
| $(\chi_a)_1$ .. .. | 0·2531 | 0·1954 | 0·3284 | 0·3470 |
| $(\chi_m)_1$ .. .. | 32·64 | 25·26 | 42·43 | 44·34 |
| $(\chi_a)_2$ .. .. | 0·2599 | 0·1866 | 0·3357 | 0·3382 |
| $(\chi_m)_2$ .. .. | 33·59 | 24·11 | 43·88 | 43·69 |
| $(\chi_a)_3$ .. .. | 0·2522 | 0·1949 | 0·3278 | 0·3465 |
| $(\chi_m)_3$ .. .. | 32·58 | 25·191 | 42·37 | 44·77 |
| $(\chi_a)_4$ .. .. | 0·2595 | 0·1861 | 0·3353 | 0·3376 |
| $(\chi_m)_4$ .. .. | 33·53 | 24·042 | 43·32 | 43·62 |
| $(\chi_a)_E$ .. .. | .. | .. | .. | 0·3515 |
| $(\chi_m)_E$ .. .. | .. | .. | .. | 45·41 |
| $(\chi_a)O_1$ .. .. | .. | .. | .. | 0·36 |
| $(\chi_m)O_1$ .. .. | .. | .. | .. | 46·51 |
| $(\chi_a)O_2$ .. .. | .. | .. | .. | 0·3948 |
| $(\chi_m)O_2$ .. .. | .. | .. | .. | 51·00 |
| $(\chi_a)O_3$ .. .. | .. | .. | .. | 0·4149 |
| $(\chi_m)O_3$ .. .. | .. | .. | .. | 53·6 |

$O_1$ refers to *Int. Crit. Tables.*

$O_2$ refers to Rao's values (*loc. cit.*)

$O_3$ refers to the value calculated by Kido's data (*Sci. Rep. Tohoku, Imp. Univ.*, 1933, **22**, 835).

susceptibility of oxygen determined from substances characterised by strong binding is much less diamagnetic than that in compounds of weak binding in which oxygen atoms may exhibit their own magnetic properties without being affected by other atoms in the molecule. Selenious acid is a weak acid and the binding between the oxygen and selenium atoms may be weak. Pauling, Slater and Angus[18] have independently calculated the ionic susceptibility of oxygen atom on theoretical considerations and Angus has shown (*ibid.*) that these values fit in very well with experimental results. These values are $- 12 \cdot 6 \times 10^{-6}$ (Pauling), $- 13 \cdot 15 \times 10^{-6}$ (Slater) and $- 11 \cdot 25 \times 10^{-6}$ (Angus), and are fairly close to each other. Consequently magnetic susceptibility of selenious acid was calculated for the two constitutions using Slater's value for oxygen and the values obtained are given under B of the above Table.
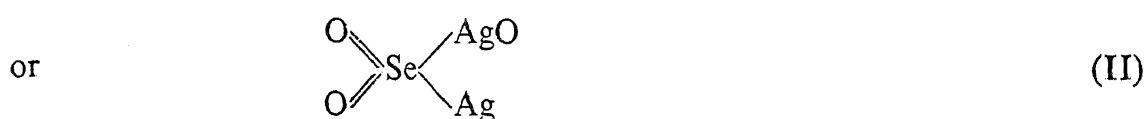
Recently Rao[19] has determined the ionic susceptibility of $SeO_3$. This value has been utilized also to calculate the magnetic susceptibility of this acid.

It is evident that the values for the constitutional formula (II) are in good agreement with the experimental values showing thereby that selenious acid

has the structure $\overset{O}{\underset{O}{>}}Se\overset{OH}{\underset{H}{<}}$ , in the solid state. The values obtained

from Kido's and Rao's data are a little higher than the experimental value obtained by the author.

4. *Silver Selenite* ($Ag_2SeO_3$).—Accepting the unsymmetrical constitution for the selenious acid it is probable that its salts will be also unsymmetrical. To test this point silver selenite ($Ag_2SeO_3$) was chosen for investigation. But it has been mentioned before that the reaction between ethyl iodide and silver selenite yields symmetrical ethyl selenite (*loc. cit.*) whose constitution has been established further by the action of sodium ethoxide on selenosyl
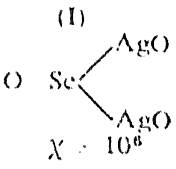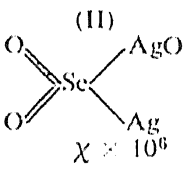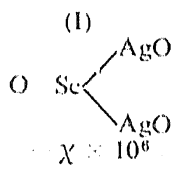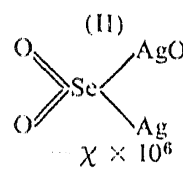
chloride which is definitely symmetrical $O = Se\overset{Cl.}{\underset{Cl.}{<}}$ This substance has

also been studied in this investigation and its discussion appears in the succeeding paragraphs. Hence silver selenite may have the constitution

$$O = Se\overset{AgO}{\underset{AgO}{<}} \qquad \qquad \text{(I)}$$

or $\qquad \overset{O}{\underset{O}{>}}Se\overset{AgO}{\underset{Ag}{<}} \qquad \qquad \text{(II)}$

The atomic and molecular susceptibilities for both the forms have been calculated and are compared with the experimental values. The value for AgO is obtained by adding the ionic susceptibilities of Ag ($- 31 \cdot 0 \times 10^{-6}$; *Int. Crit. Tables*) and O ($-4 \cdot 61 \times 10^{-6}$), since it is of the type R–O–R (Bhatnagar and Mathur, *Physical Principles and Application of Magneto-Chemistry*, p. 90). This comes out to be $- 35 \cdot 61 \times 10^{-6}$. It can be calculated from the magnetic constants of $Ag_2O$ for which $\chi_a$ is $- 0 \cdot 58 \times 10^{-6}$ (Bhatnagar and Mathur, *ibid.*, p. 214) and, therefore, $\chi_m$ is $- 66 \cdot 98 \times 10^{-6}$. Subtracting the ionic value for Ag ($- 31 \cdot 0 \times 10^{-6}$) the value for AgO comes out to be $- 35 \cdot 89 \times 10^{-6}$, which is nearly the same as obtained by the first method.
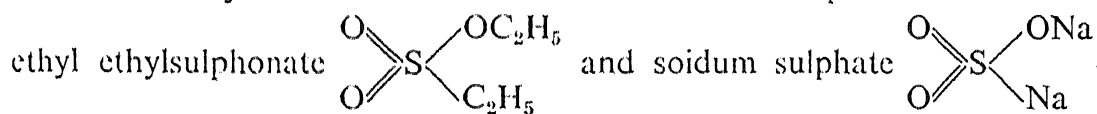
In the Table given below the calculated values under A and B are obtained by using, respectively, Pascal's and Slater's value for oxygen. Rao's (*ibid.*) value for $SeO_3$ ion has been also utilized for these calculations.

## TABLE VII

| Constitutional formula | A | | B | |
|---|---|---|---|---|
| | (I) O–Se(AgO)(AgO) $\chi \times 10^6$ | (II) (O)(O)Se(AgO)(Ag) $\chi \times 10^6$ | (I) O–Se(AgO)(AgO) $\chi \times 10^6$ | (II) (O)(O)Se(AgO)(Ag) $\chi \times 10^6$ |
| $(\chi a)_1$ .. .. | 0·2588 | 0·2370 | 0·2874 | 0·2941 |
| $(\chi m)_1$ .. .. | 88·78 | 81·28 | 98·57 | 100·86 |
| $(\chi a)_2$ .. .. | 0·2616 | 0·2336 | 0·2901 | 0·2908 |
| $(\chi m)_2$ .. .. | 88·73 | 80·13 | 99·52 | 99·75 |
| $(\chi a)_3$ .. .. | 0·2586 | 0·2368 | 0·2872 | 0·2938 |
| $(\chi m)_3$ .. .. | 88·72 | 81·21 | 98·51 | 100·84 |
| $(\chi a)_4$ .. .. | 0·2614 | 0·2334 | 0·2900 | 0·2937 |
| $(\chi m)_4$ .. .. | 89·67 | 80·06 | 99·46 | 99·692 |
| $(\chi a)_k$ .. .. | .. | 0·298 | .. | 0·298 |
| $(\chi m)_k$ .. .. | .. | 102·2 | .. | 102·2 |
| $(\chi a)O_1$ .. .. | .. | .. | .. | 0·3117 |
| $(\chi m)O_1$ .. .. | .. | .. | .. | 106·9 |
| $(\chi a)O_2$ .. .. | .. | .. | .. | 0·3193 |
| $(\chi m)O_2$ .. .. | .. | .. | .. | 109·5 |

$O_1$ and $O_2$ refer to the values calculated from Rao's and Kido's data.

It will be seen that the experimental values agree with those calculated for the constitution (II) when Slater's value for oxygen is used. This shows that the constitution of $Ag_2SeO_3$ is similar to that of selenious acid, that is, Se is hexavalent in the compound and the binding with oxygen atoms is such that only high magnetic value of oxygen is admissible. Also the magnetic data definitely proves that this salt of selenious acid is unsymmetrical. This is in conformity with the constitution of the salts of sulphurous acid such as ethyl ethylsulphonate $(O)(O)S(OC_2H_5)(C_2H_5)$ and soidum sulphate $(O)(O)S(ONa)(Na)$ .

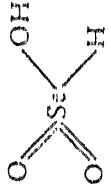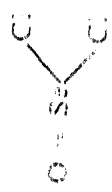5. *Selenosyl chloride or selenium oxychloride* ($SeOCl_2$).—There is no indefiniteness regarding the constitution of this compound which is represented as $O = Se\big\langle\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ as there is no alternative representation.

The interest in the study of this compound lies in the behaviour of oxygen atom. Using Pascal's value for oxygen ($-3 \cdot 36 \times 10^{-6}$) it is found that the theoretically calculated value is much higher than the experimental one. If Slater's value for oxygen ($-13 \cdot 35 \times 10^{-6}$) is used, this value is still higher. Stoner[9] (*Magnetism and Matter*, p. 473) and Bhatnagar and Mathur (*loc. cit.*) have shown that if there is only one oxygen atom in a molecule connected by double bond to other atoms, the oxygen atom will be paramagnetic ($+1 \cdot 8 \times 10^{-6}$). If this value is used, the calculated results are in better agreement with the experimental ones. But still there is a large discrepancy between the two, which may be due to the absorption of moisture by $SeOCl_2$ and its consequent decomposition into selenium dioxide and hydrochloric acid before it is introduced into the specimen tube. Even with the best care taken to transfer the liquid into the specimen tube as quickly as possible, an observation could only be taken once. For the second observation with the same filling it was found that an increase in weight of the substance had taken place, evidently due to the absorbed moisture. The results obtained are shown below:

### TABLE VIII

| Constitution $O = Se\big\langle\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$ | $\chi_a$ and $\chi_m$ obtained by using Pascal's value of $O\ (-3 \cdot 35 \times 10^{-6})$ | $\chi_a$ and $\chi_m$ obtained by using the value of $O = (+1 \cdot 8 \times 10^{-6})$ |
|---|---|---|
| $(\chi_a)_1$ | $-\ 0 \cdot 3730 \times 10^{-6}$ | $-\ 0 \cdot 3419 \times 10^{-6}$ |
| $(\chi_m)_1$ | $-\ 61 \cdot 96 \ \times 10^{-6}$ | $-\ 56 \cdot 8 \ \ \ \times 10^{-6}$ |
| $(\chi_a)_2$ | $-\ 0 \cdot 3787 \times 10^{-6}$ | $-\ 0 \cdot 3477 \times 10^{-6}$ |
| $(\chi_m)_2$ | $-\ 62 \cdot 91 \ \times 10^{-6}$ | $-\ 57 \cdot 75 \ \ \times 10^{-6}$ |
| $(\chi_a)_3$ | $-\ 0 \cdot 3727 \times 10^{-6}$ | $-\ 0 \cdot 3416 \times 10^{-6}$ |
| $(\chi_m)_3$ | $-\ 61 \cdot 90 \ \times 10^{-6}$ | $-\ 56 \cdot 74 \ \times 10^{-6}$ |
| $(\chi_a)_4$ | $-\ 0 \cdot 3784 \times 10^{-6}$ | $-\ 0 \cdot 3473 \times 10^{-6}$ |
| $(\chi_m)_4$ | $-\ 62 \cdot 85 \ \times 10^{-6}$ | $-\ 57 \cdot 69 \ \ \times 10^{-6}$ |
| $(\chi_a)_E$ | .. | $-\ 0 \cdot 2929 \times 10^{-6}$ |
| $(\chi_m)_E$ | .. | $-\ 48 \cdot 65 \ \ \times 10^{-6}$ |

## TABLE IX
### Selenium Compounds

| Compound | Constitution | | $-X_a \times 10^6$ and $-X_m \times 10^6$ observed by the authors | $-X_a \times 10^6$ and $-X_m \times 10^6$ calculated by Slater's method | $-X_a \times 10^6$ and $-X_m \times 10^6$ calculated by the modification of Slater's method | $-X_a \times 10^6$ and $-X_m \times 10^6$ calculated by Angus's method | $-X_a \times 10^6$ and $-X_m \times 10^6$ calculated by the modification of Angus's method |
|---|---|---|---|---|---|---|---|
| Se₂Br₂ | Br–Se–Se–Br | $X_a$ | 0.3544 | 0.3477 | 0.3674 | 0.3400 | 0.3536 |
| | | $X_m$ | 112.6 | 110.72 | 119.64 | 108.18 | 115.63 |
| Se₂Cl₂ | Cl–Se–Se–Cl | $X_a$ | 0.4054 | 0.2920 | 0.4310 | 0.3819 | 0.4145 |
| | | $X_m$ | 94.79 | 90.12 | 99.04 | 87.58 | 95.04 |
| H₂SeO₃ | | $X_a$ | 0.3515 | 0.3470 | 0.3352 | 0.3465 | 0.3376 |
| | | $X_m$ | 43.41 | 44.84 | 43.69 | 44.7 | 43.62 |
| | | | 0.36 | | | | |
| | | | 45.51 *(Int. Crit. Tab.)* | | | | |
| Ag₂SeO₃ | | $X_a$ | 0.283 | 0.2941 | 0.2908 | 0.2933 | 0.2957 |
| | | $X_m$ | 102.2 | 100.95 | 99.73 | 100.841 | 93.492 |
| SeOCl₂ | | $X_a$ | 0.3429 | 0.3419 | 0.3477 | 0.3416 | 0.3473 |
| | | $X_m$ | 49.43 | 56.8 | 57.75 | 56.74 | 57.62 |

It is probable that the strong binding between the oxygen and selenium atoms has the effect of reducing the diamagnetism to a greater extent than that shown by the paramagnetic value. The discrepancy in the theoretical and the experimental values observed in the case of $SeOCl_2$ is also exhibited by thionyl chloride (to be discussed in a paper to be published soon) which is analogous to it.

Table IX gives the correct constitution of various compounds of Se investigated along with the experimental and calculated values observed by the author. It will be seen that in all calculations made in this investigation Slater's and Angus's values have been found to give much satisfactory results. It may also be remarked that the choice of the value for O is an important one and depends upon the type of binding in the molecule.

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