54. *The Relative Affinities of Co-ordinating Atoms for Silver Ion. Part I. Oxygen, Sulphur, and Selenium.*

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Water-soluble sulphonated aromatic ethers, sulphides, and selenides were prepared and the stability constants of their complexes with silver ion determined. These are listed in Table 1. The ether oxygen has little if any tendency to co-ordinate, but the sulphides and selenides form complexes of moderate stability up to $\bar{n} = 4$ without the stop, usually considered characteristic of silver complexes, at $\bar{n} = 2$. The replacement of the bivalent sulphur atom by selenium in *p*-$SPh\cdot C_6H_4\cdot SO_3Na$ increases the first stability constant from 47 to 430 l. mole^{-1}, equivalent to about 1·3 kcal. mole^{-1} in $\Delta G°$. The replacement of the phenyl group by an ethyl group similarly increases the stability constant.

THERE is little quantitative information on the relative tendencies of molecules containing donor atoms from Groups V and VI of the Periodic Table, other than nitrogen and oxygen, to form complexes with acceptor molecules and ions. This, and the qualitatively observed stabilities of complex compounds, together with extensive quantitative data on the stabilities of halide complexes, indicate that acceptor atoms are of two general types: (*a*) those which form their most stable complexes with the first atoms of each Group of donor atoms in the Periodic Table (*viz.* N, O, and F); and (*b*) those which form their most stable complexes with the second (*viz.* P, S, and Cl) or a subsequent donor atom of each Group. In this context each oxidation state of a metal atom must be regarded as a different acceptor atom, *e.g.*, Co^{2+} is a different acceptor atom from Co^{3+}.

The few quantitative data about complex formation by the heavier donor atoms have been obtained mainly from vapour-phase equilibria and concern solely atoms of class (*a*), *e.g.*, Al, or of only very weak class (*b*) character,[1] *e.g.*, B in BH_3. Our present objects are (i) to measure quantitatively the tendencies of ligands containing donor atoms from Groups V and VI, other than nitrogen and oxygen, to form complexes with metal ions in class (*b*); and (ii) to obtain information on the relative double-bonding tendencies of the heavier donor atoms, since class (*b*) character appears to be associated with d_π or dative π-bonding between the metal and ligand.

Most of the metals of class (*b*) form inert non-volatile complexes which, in general, cannot be examined by equilibrium methods. Of those which form labile complexes, silver(I) appears to be the most promising for study, and it is preferable to examine its tendency to form complexes in aqueous solution because most existing stability-constant data relate to that medium.

Our knowledge of the formation of complexes in aqueous solution is based largely on measurements involving halide ions and ligands in which nitrogen and oxygen are the donor atoms. The pioneer work in this field by J. Bjerrum,[2] Leden,[3] Schwarzenbach,[4] Calvin,[5] and their co-workers has been followed by a flood of such data. The extension of their methods to organic ligands containing the heavier donor atoms of Groups V and VI has been slow because such ligands are often spontaneously oxidised by air and are insoluble in water; their complexes are also insoluble. Recently, by methods similar to those used by J. Bjerrum, some quantitative data regarding the co-ordination of sulphur

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[1] See Graham and Stone, *J. Inorg. Nuclear Chem.*, 1956, **3**, 164, and references therein.

[2] J. Bjerrum, " Metal Ammine Formation in Aqueous Solution," Haase and Son, Copenhagen, 1941.

[3] Leden, *Z. phys. Chem.*, 1941, *A*, **188**, 160.

[4] Schwarzenbach, Kampitsch, and Steiner, *Helv. Chim. Acta*, 1945, **28**, 828, 1133.

[5] Calvin and Wilson, *J. Amer. Chem. Soc.*, 1945, **67**, 2003.

ligands with a few metal aquo-ions have been obtained by employing chelating sulphido- and mercapto-amines and acids.[6, 7, 8] The use of chelating ligands with Ag^I is not desirable because they cannot accommodate themselves to the linear co-ordination which occurs in the usual 2-co-ordinated silver complexes but give rise to polynuclear complexes.[9] Unidentate ligands are thus essential; to obtain sufficient resistance to oxidation we chose phenyl derivatives, and their insolubility in water was overcome, but only just, by the introduction of one or more sulphonic acid groups. We now record observations on the formation of silver complexes by the sulphonated ether, organic sulphides, and the selenide listed in Table 1.

These sulphonated ligands each contain three different types of co-ordinating groups: (i) the ether oxygen and bivalent sulphur and selenium atoms respectively, (ii) the benzene nucleus, and (iii) the sulphonate ion group. To determine whether the last two were of any consequence, the formation of silver ion complexes by sodium benzenesulphonate was examined. Its co-ordinating capacity was negligible compared with that of the sulphonated sulphides and selenide, and so we may safely assume that complex formation takes place through their bivalent sulphur and selenium atoms. The formation of silver complexes by the sulphonated ether was of the same low order as that by sodium benzenesulphonate, and so the co-ordinating atom or group in the ether has not been established.

The formation of labile complexes by a ligand, L, and hydrated metal ion, M, in aqueous solution occurs through a series of rapidly established equilibria which may be defined by the equilibrium or stability constants, K_1, K_2, etc., or β_1, β_2, etc., as follows. The charges associated with the ions and metal ion have been omitted for clarity.

$$\begin{array}{lll}
\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML}; & K_1 = [\mathrm{ML}]/[\mathrm{M}][\mathrm{L}]; & \beta_1 = K_1 \\
\mathrm{ML} + \mathrm{L} \rightleftharpoons \mathrm{ML}_2; & K_2 = [\mathrm{ML}_2]/[\mathrm{ML}][\mathrm{L}]; & \beta_2 = [\mathrm{ML}_2]/[\mathrm{M}][\mathrm{L}]^2 = K_1K_2 \\
\text{etc. to} & \text{etc. to} & \text{etc. to} \\
\mathrm{ML}_{N-1} + \mathrm{L} \rightleftharpoons \mathrm{ML}_N; & K_N = [\mathrm{ML}_N]/[\mathrm{ML}_{N-1}][\mathrm{L}]; & \beta_N = [\mathrm{ML}_N]/[\mathrm{M}][\mathrm{L}]^N = K_1K_2 \ldots K_N
\end{array}$$

The K's are known as " stepwise " or " consecutive " stability constants and the β's as " gross " or " cumulative " stability constants. The stability constants β_1, β_2, etc., were determined at 25° by potentiometric titration of silver perchlorate with the sodium salts of the ligands, L, by use of Ag,AgCl or Ag,AgBr electrodes to determine the free $[Ag^+]$ in solution.

To keep activity coefficients as constant as possible the solutions were adjusted with sodium perchlorate to the same initial ionic strength, I. In the case of the sulphonated sulphides and selenide the ionic strength was limited by the solubilities of the salts involved, and rather low ionic strengths of 0·1 and 0·2M were used. The limit in the case of the *p*-ethylthiobenzenesulphonate ion was set by the rather poor solubility of the sodium salt in sodium perchlorate solutions of more than 0·2M, and in the case of the *p*-ethylselenobenzenesulphonate ion by that of the silver salt. Nevertheless, both ligands form complexes sufficiently strongly for the main part of complex formation to take place within the limited available range of concentrations, [L], of the free ligands. For comparison the two sulphonated diphenyl sulphides were investigated at the same ionic strength. The more strongly co-ordinating monosulphonate gave a sufficient range of concentration to cover most of the complex-formation function, but the values of K_n/K_{n+1} are so small that the second and third complexes ($n = 2$ and $n = 3$) have only a very short range of existence (Fig. 1), and so are always in equilibrium with relatively large quantities of the first and fourth complexes. This means that K_2 and K_3 cannot be accurately determined. Using the more weakly co-ordinating disulphonate we could cover only the first part of the formation function. Even so, valuable conclusions may be drawn. K_1, which is the

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[6] Gonick, Fernelius, and Douglas, *J. Amer. Chem. Soc.*, 1954, **76**, 4671.
[7] Fielder, Rescigno, and Radicca, *Gazzetta*, 1955, **85**, 453.
[8] Ågren and Schwarzenbach, *Helv. Chim. Acta*, 1955, **38**, 1920.
[9] Schwarzenbach, Ackermann, Maissen, and Anderegg, *Helv. Chim. Acta*, 1952, **35**, 2337.

most accurately determined constant, is also the most reliable constant from which to determine the relative affinities of the various heavy donor atoms for Ag^+, since steric and other extraneous factors are least important when the addition of the first molecule of ligand to the hydrated metal ion takes place. For the very weakly co-ordinating benzenesulphonate and *p*-methoxybenzenesulphonate ions the range of concentration of the free ligand, [L], had to be extended considerably, and fortunately solubility relationships allowed this. A higher ionic strength was thus necessary and 1·0M was used for these two ligands.

The stability constants, K, for the various ligands, L, were calculated by Leden's[3] method as developed by Fronaeus[10] (Table 1): log K_1, also listed, gives a relative measure of the affinities of the various ligands for silver ion.

TABLE 1. *Concentration stability constants, K (l. mole^{-1}), of the ligands,* L, *with silver ion at an ionic strength I* (M) *and* 25°.

Ligand " L "	I	K_1	K_2	K_3	K_4	log K_1
$PhSO_3^-$ *	1·0	0·9	—	—	—	−0·04
p-$MeO{\cdot}C_6H_4{\cdot}SO_3^-$ *	1·0	0·76	0·8	—	—	−0·12
p-$Et\mathbf{S}{\cdot}C_6H_4{\cdot}SO_3^-$ †	0·1	415	48	~25	—	2·62
	0·2	390	49	17	11	2·59
p-$Ph\mathbf{S}{\cdot}C_6H_4{\cdot}SO_3^-$ †	0·1	47	22	13	40	1·67
	0·2	47	12	16	85	1·67
$\mathbf{S}(C_6H_4{\cdot}SO_3^-$-*p*$)_2$ †	0·2	25	8	~45	—	1·40
p-$Ph\mathbf{Se}{\cdot}C_6H_4{\cdot}SO_3^-$ †	0·1	430	180	35	170	2·63

* The donor atoms which take part in complex formation are not known with certainty, but are probably oxygen atoms of the SO_3^- group.

† The donor atoms taking part in complex formation are those in heavy type.

Several interesting points emerge from the constants listed. (1) The class (*b*) character of silver, well known from its general complex chemistry, is apparent. The ether oxygen atom is attached only very weakly, if at all, to silver ion in dilute aqueous solution, whereas the sulphides and selenides give much more stable complexes.

(2) In comparison with the common ligands which give very stable silver complexes, the sulphides and selenides listed in Table 1 give complexes of only moderate stability. The K_1's ranging from 25 to 430 l. mole^{-1} indicate that the complexes have a stability of the same order as the silver–pyridine complex[11] ($K_1 = 110$ l. mole^{-1}), and are much weaker than those of primary aliphatic amines,[11] ammonia,[12] and the halide ions:[13,14,15] for $L = NH_2Et$, $K_1 = 2340$; for $L = NH_3$, $K_1 = 1740$; for $L = Cl^-$, $K_1 = 700$; for $L = Br^-$, $K_1 = 14{,}000$; and for $L = I^-$, $K_1 = 1·3 \times 10^8$ l. mole^{-1}. In making these rough comparisons no allowance was made for the differences in ionic strength at which the constants were measured, or for slight differences in temperature.

(3) Silver(I) ion is usually considered to have a characteristic co-ordination number of 2, although 3 is not unknown[16] and 4 occurs in some of its solid complexes[17] and in halide[13,14,15] and cyanide[18] solutions. Usually, where successive stability constants have been determined, it is found that the first two monodentate ligands are attached strongly to the silver ion, and in those few cases where further ligand molecules are taken up by the ion they are comparatively weakly held, *i.e.*, there is a definite " stop " in complex formation after two ligand molecules have been taken up. We shall discuss this subject in the light of further examples in a later paper, but here merely note the absence

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[10] Fronaeus, " Komplexsystem hos Koppar," Gleerupska Univ.-Bokhandeln, Lund, 1948, p. 18 *et seq.*

[11] Bruehlman and Verhoek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401.

[12] Ref. 2, p. 130.

[13] Berne and Leden, *Svensk kem. Tidskr.*, 1953, **65**, 88.

[14] Berne and Leden, *Z. Naturforsch.*, 1953, **8a**, 719.

[15] Leden, *Acta Chem. Scand.*, 1956, **10**, 535.

[16] See Cass, Coates, and Hayter, *J.*, 1955, 4007.

[17] Mann, Wells, and Purdie, *J.*, 1937, 1828.

[18] Jones and Penneman, *J. Chem. Phys.*, 1954, **22**, 965.

of any major stop in the formation of silver complexes by the sulphide and selenide ligands until four ligand molecules have been accommodated, and the very short range of existence of the second complexes ($n = 2$) (see Fig. 1). This agrees with Lindqvist and Strandberg's[19] observation that silver appears to be reluctant to form linear complexes containing sulphur as ligand atoms. In this respect selenium evidently resembles sulphur. With sodium *p*-ethylthiobenzenesulphonate there is a very slight retardation after the addition of the first ligand, but generally all the ligand molecules are taken up uniformly. In the case of the dianion of di-(*p*-sulphophenyl) sulphide ($p\text{-}^-O_3S{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}SO_3^-\text{-}p$), where only three complexes can be proved in the range of concentration of L which we investigated, addition of the fourth ligand molecule might be delayed. To determine whether this is so would require the investigation of higher values of ligand concentration and a higher ionic strength, but solubility relationships do not allow this.

FIG. 1. *Regions of stability of the complex ions* AgL_n *showing the percentages of the total silver content in the form of the various complexes and their variation with* [L] *at* 25°.

A, L = $p\text{-EtS}{\cdot}C_6H_4{\cdot}SO_3^-$, $I = 0{\cdot}2$.
B, L = $p\text{-PhS}{\cdot}C_6H_4{\cdot}SO_3^-$, $I = 0{\cdot}1$.
C, L = $p\text{-}^-O_3S{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}SO_3^-\text{-}p$, $I = 0{\cdot}2$.
D, L = $p\text{-PhSe}{\cdot}C_6H_4{\cdot}SO_3^-$, $I = 0{\cdot}1$.

The regions labelled +, 1, 2, 3, 4 refer to those occupied by Ag^+, AgL_1, AgL_2, AgL_3, AgL_4 respectively.

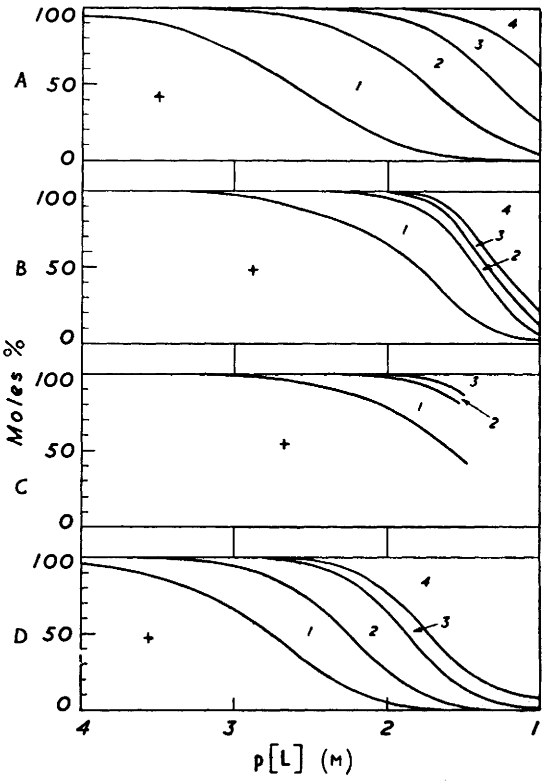
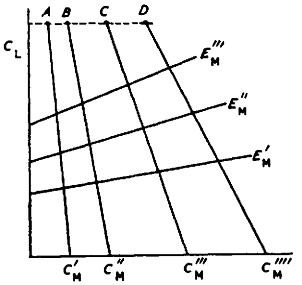


FIG. 2.



(4) Qualitatively, Coates[20] has shown that the stabilities of complexes formed by organic sulphides, selenides, and tellurides with silver iodide increase in that order. Our quantitative measurements confirm this order for sulphide and selenide complexes, and show that the difference in stability is represented in our complexes by a factor of 9 in the first stability constants, K_1, equivalent to about 1·3 kcal. mole^{-1} in $\Delta G°$. This order of stabilities may be contrasted with that qualitatively observed in the platinous chloride series, where dialkyl sulphide complexes are undoubtedly very much more stable than the corresponding selenide complexes.[21]

(5) It is generally observed qualitatively that aliphatic derivatives of the heavier donor atoms form more stable complexes than the aromatic. We have confirmed this and

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[19] Lindqvist and Strandberg, *Acta Cryst.*, 1957, **10**, 173.
[20] Coates, *J.*, 1951, 2003.
[21] Chatt and Venanzi, *J.*, 1955, 2787.

obtained a quantitative measure of the difference. The replacement of the phenyl group by an ethyl group in *p*-ethylthiobenzenesulphonic acid increases the stability constant by a factor of about 9, *i.e.*, about 1·3 kcal. mole^{-1} in ΔG°.

Generally it can be seen from Fig. 1 that the formation of silver complexes in aqueous solution by organic sulphides and selenides contrasts markedly with their formation by ammonia and primary amines. The important difference is the absence of a "stop" in complex formation at $\bar{n} = 2$. This "stop" has hitherto been considered to be characteristic of the formation of silver(I) and related complexes [*e.g.*, mercury(II)]. In most respects the silver ammines appear to represent one extreme type of silver complex and the sulphide and selenide complexes another, with the chloride and bromide ion complexes truly intermediate between these two types.

This work has now been extended to the sulphonated aromatic amines, a phosphine, and an arsine and so a detailed discussion of the shapes of the complex-formation curves is being deferred until that work is described.

EXPERIMENTAL

Microanalyses are by Messrs. W. Brown and A. G. Olney of these laboratories.

Sodium Sulphonates.—Prepared as below and dried, their purity was established by analyses and equivalent weight. The latter was determined by running a known quantity of the sodium salt in hot aqueous solution through a column containing the acid form of a cation-exchange resin (Zeo-Karb 225), eluting, and then titrating the liberated acid.

Commercial sodium benzenesulphonate was twice recrystallised from 70% aqueous methanol and dried *in vacuo* at 80—100° (Found: equiv., 180·2. Calc. for $C_6H_5O_3SNa$: equiv., 180·2). Sodium *p*-methoxybenzenesulphonate was prepared by direct sulphonation of anisole with concentrated sulphuric acid at 90° (Found: C, 39·8; H, 3·4%; equiv., 210. Calc. for $C_7H_7O_4SNa$: C, 40·0; H, 3·4%; equiv., 210). Sodium *p*-ethylthiobenzenesulphonate [22] was prepared by the action of sodium ethyl sulphide on an alcoholic suspension of the solid diazonium salt of *p*-sulphanilic acid (Found: C, 39·8; H, 4·0%; equiv., 241. Calc. for $C_8H_9O_3S_2Na$: C, 40·0; H, 3·8%; equiv., 240). Sodium *p*-phenylthiobenzenesulphonate and the *pp'*-disulphonate were prepared as described by Chatt and Williams.[23]

Sodium p-*phenylselenobenzenesulphonate.* A solution of sulphanilic acid (35 g.), sodium hydroxide (8·8 g.), and sodium nitrite (8·5 g.) in water (320 c.c.) at 0° was slowly added with stirring to dilute sulphuric acid (50 c.c. of concentrated acid in 600 c.c. of water) with cooling, so that the temperature did not exceed 3°. The explosive diazonium salt, $N_2{\cdot}C_6H_4{\cdot}SO_3$, separated as a granular precipitate and was filtered off, washed with ice-water and drained in the Buchner funnel for 30 min. It was not pressed down during this operation. The solid was then very gently removed and suspended in ethanol (100 c.c.). To this suspension was added with stirring a solution of sodium phenyl selenide and free selenophenol (PhSeH, 21 g.; NaOH, 3·75 g.) in aqueous ethanol (water 30 c.c.; EtOH, 85 c.c.). Vigorous nitrogen evolution occurred throughout the addition and when this had subsided concentrated aqueous sodium hydroxide was slowly added until the solution was permanently red. The solution was now warmed (water bath) until it became clear (5 min.) and then kept in a freezing mixture. The *product* separated as a yellow solid, which was filtered off, washed with alcohol, then ether, and dried (24 g.). It was twice recrystallised from aqueous ethanol and so obtained as a pale cream solid (6 g.) (Found: C, 42·6; H, 3·0%; equiv., 335·0. $C_{12}H_9O_3SNaSe$ requires C, 43·0; H, 2·7%; equiv., 335·2). The *benzyl*iso*thiuronium* salt, recrystallised from aqueous ethanol, had m. p. 154—155° (Found: C, 50·3; H, 4·3; N, 6·1. $C_{20}H_{20}O_3N_2S_2Se$ requires C, 50·1; H, 4·2; N, 5·85%).

Determination of the Stability Constants.—Leden's method [3] as modified by Fronaeus [10] was used, and since the modification used has appeared only in Swedish we summarise the relevant part in an Appendix, where terms not defined below are also given.

Experimental Technique.—Silver perchlorate solution of a concentration C_M' in the right-hand half-cell (Appendix) was titrated with ligand solution of a concentration C_L'. The free silver-ion concentration [Ag$^+$] (= M) was measured by means of silver halide electrodes, as pure

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[22] Stadler, *Ber.*, 1884, **17**, 2077.
[23] Chatt and A. A. Williams, *J.*, 1956, 3246.

silver electrodes are unsatisfactory.[24] Both chloride and bromide electrodes were used. They were prepared according to Brown,[25] from wire of 1 mm. diameter and about 2 cm. long. Both kinds of electrode gave the same potentials when immersed in the same solution, and from the initial potentials E_0 measured in solutions of known $[Ag^+]$ $(= C_M)$ they were shown to obey Nernst's law.

The bromide electrodes were the more useful because they could be used in solutions of much lower $[Ag^+]$ without being perceptibly dissolved. In fact, the chloride electrodes were markedly dissolved at the highest concentration of *p*-phenylselenobenzenesulphonate used, but the bromide electrodes were satisfactory throughout the whole investigation.

Both kinds of electrode gave much the same reproducibility, as a rule 0·1 mv at low values, and 0·3—0·4 mv at higher values of E_M. Every solution was measured with two electrodes, and every titration series repeated at least once. The mixing of the solutions during the titrations was brought about by a stream of pre-saturated nitrogen free from oxygen.

The reference electrode was a gold–quinhydrone electrode in 0·01M-perchloric acid containing sodium perchlorate to the same ionic strength as the other half-cell. The bridge joining the half-cells contained sodium perchlorate solution of the same ionic strength.

At every point during the titrations C_M and C_L were known from the compositions of the solutions used. As the ligand solution did not contain any silver ions, C_M continuously decreased as C_L increased. The difference between the e.m.f. E at a definite point in the titration, and the initial e.m.f., E_0', due to the reduction of the silver-ion concentration, was therefore caused by dilution as well as by the formation of complexes. To find the difference E_M defined in eqn. (7) (Appendix) as due only to the formation of complexes, a correction was necessary, as follows:

The initial e.m.f. E_0' is given by equation (i) [cf. (6); Appendix]:

$$E_0' = E_k + (\boldsymbol{RT/F}) \ln C_M' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

If the electrode vessel initially contained " *a* " c.c. of silver solution (concentration C_M') and " *v* " c.c. of the ligand solution were then added, the total silver concentration would decrease to $C_M = C_M' \,.\, a/(a + v)$. Hence

$$E_0' = E_k + (\boldsymbol{RT/F}) \ln C_M + (\boldsymbol{RT/F}) \ln [(a + v)/a] = E_0 + (\boldsymbol{RT/F}) \ln [(a + v)/a]$$

and

$$E_M = E_0 - E = E_0' - E - (\boldsymbol{RT/F}) \ln [(a + v)/a] \quad . \quad . \quad . \quad . \quad (ii)$$

At least three different silver concentrations, C_M', were titrated, except when the ligand had little affinity for the metal ion; in this case $C_L \approx [L]$, and only two concentrations were needed.

When E_M is plotted against C_L a family of curves is obtained similar to those of Fig. 3 (Appendix), but with the total silver concentration C_M decreasing along each curve. By combining $C_M = C_M' \,.\, a/(a + v)$ and $C_L = C_L' \,.\, v/(a + v)$ the following linear connection between C_M and C_L is found:

$$C_M = C_M' - (C_M'/C_L')C_L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii)$$

In obtaining a plot of C_M against C_L at constant E_M [cf. Fig. 4 (Appendix)) either this formula could be used, or, more simply, C_M' plotted against C_L by using a contracting abscissa as in Fig. 2. This is most readily constructed by plotting the points *A*, *B*, etc. corresponding to $v = a$, where $C_L = \frac{1}{2}C_L'$ and $C_M = \frac{1}{2}C_M''$, etc., then joining the appropriate points *A* to C_M', *B* to C_M'' etc. The required C_M points lie along those lines at the known values of C_L. The points of constant E_M are then joined and the lines extrapolated to cut the C_L axis to give [L] as described in the Appendix.

Systems Investigated.—The experimental results are recorded in the Tables. Concentrations are millimolar (mM) and e.m.f.'s in mv. The temperature was 25° c. Other terms are as follows: C_L, total concentration of ligand in the right-hand half-cell; C_L', concentration of the ligand solution added; C_M', concentration of silver ion in the right-hand half-cell before the addition of ligand solution; E_M, difference between the e.m.f. of the cell containing the ligand C_L, and its e.m.f. had no ligand been present [eqns. (7, Appendix) and (ii)]; β and K, stability constants defined on p. 265; [L], concentration of free ligand; and X, X_1, etc., functions defined as in eqns. (3), (4), and (7) (Appendix).

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[24] Leden, *Svensk kem. Tidskr.*, 1946, **58**, 129.

[25] Brown, *J. Amer. Chem. Soc.*, 1934, **56**, 646.

Sodium benzenesulphonate has a very weak affinity for silver ion and so the measurements had to be made at high ligand concentrations, necessitating a high ionic strength. In these circumstances, at moderate concentrations of silver ion (<20 mM) $[\mathrm{L}] \approx C_\mathrm{L}$ and is thus independent of C_M. Since E_M is a function of [L] only [eqns. (3) and (7)], E_M should also be independent of C_M, unless polynuclear complexes are formed. Polynuclear complexes would be formed if both the sulphonic acid group and the benzene nucleus took up silver ion. In fact, E_M was independent of C_M and the experimental values are recorded in Table 2. X_1 is constant, indicating that complex formation does not proceed beyond the first complex over the range of C_L studied.

Sodium *p*-methoxybenzenesulphonate has a weak affinity for silver ion and a high ionic strength was necessary as with the benzenesulphonate. E_M was not quite independent of C_M and the constants were calculated in the normal manner from three values of C_M' (Table 3).

TABLE 2. *The system silver ion–benzenesulphonate ion* ($C_\mathrm{L}' = 1$M; $I = 1$M).

$C_\mathrm{L} = [\mathrm{L}]$	13·17	38·5	62·6	117·8	116·7	210·5	250
E_M	0·3	0·8	1·3	2·5	3·5	4·4	5·3
X	1·012	1·032	1·052	1·102	1·146	1·186	1·229
X_1	0·91	0·83	0·83	0·86	0·87	0·88	0·92

$\beta_1 = K_1 = 0{\cdot}9 \pm 0{\cdot}1$ l. mole⁻¹.

Sodium *p*-ethylthiobenzenesulphonate was too insoluble in sodium perchlorate solutions to be used at ionic strengths greater than about 0·2M. The first determinations were made at an ionic strength of 0·1M (Table 4), but a sufficient range of ligand concentrations to determine all the constants could not be covered at this low ionic strength and a further determination at an ionic strength of 0·2M was made (Table 5). No crystalline precipitate was obtained during any of these experiments, but a slight cloudiness developed at high ligand concentrations.

Sodium and silver *p*-phenylthiobenzenesulphonates were so slightly soluble in 0·1M-sodium perchlorate that measurements were limited to solutions of low silver ($C_\mathrm{M}' = 5$ mM) and ligand concentrations. At higher silver concentrations the *silver salt* was precipitated (Found: C, 38·6; H, 2·45; Ag, 28·7. $C_{12}H_9O_3S_2Ag$ requires C, 38·6; H, 2·4; Ag, 28·9%). In spite of the short range of concentrations available most of the complex-formation curve was covered during the titration, but owing to the very small amounts of the second and third complex in the equilibrium mixture (see Fig. 1) the second and third constants (K_2 and K_3) are known only approximately (Tables 6 and 7).

TABLE 3. *The system silver ion–*p*-methoxybenzenesulphonate ion* ($C_\mathrm{L}' = 1$M; $I = 1$M).

A. E_M as a function of C_L.

$C_\mathrm{M}' \rightarrow$	20	10	5	$C_\mathrm{M}' \rightarrow$	20	10	5	$C_\mathrm{M}' \rightarrow$	20	10	5
C_L	E_M	E_M	E_M	C_L	E_M	E_M	E_M	C_L	E_M	E_M	E_M
13·2	0·6	0·6	0·6	116·7	7·9	7·9	8·0	348	17·9	18·1	18·4
38·5	1·7	1·7	1·8	210·5	10·2	10·2	10·3	400	21·2	21·4	21·9
62·5	2·9	2·8	2·9	250	12·3	12·4	12·6	444	24·1	24·4	25·0
90·9	4·2	4·2	4·3	285	14·3	14·4	14·7	500	28·0	28·4	29·1
117·6	5·5	5·4	5·6	318	16·2	16·3	16·6	571	33·6	34·2	35·1

B. Calculation of [L] *and derivation of the stability constants.*

$C_\mathrm{M}' \longrightarrow$	20	10	5	0			
E_M	C_L	C_L	C_L	$C_\mathrm{L} = [\mathrm{L}]$	X	X_1	X_2
0·5	26	26	26	26	1·020	0·77	
1·0	51	51	51	51	1·040	0·78	
1·5	77	76	76	76	1·060	0·79	
2·0	102	101	100	100	1·081	0·81	0·50
3·0	153	151	150	149	1·124	0·83	0·47
4·0	203	200	197	197	1·168	0·85	0·46
5·0	253	246	240	238	1·215	0·90	0·59
6·0	299	291	284	282	1·263	0·93	0·60
7·0	346	337	326	322	1·313	0·97	0·65
8·0	395	381	367	360	1·365	1·01	0·69
10·0	490	469	448	440	1·476	1·08	0·73
12·0	582	554	527	516	1·595	1·15	0·76

$\beta_1 = K_1 = 0{\cdot}76 \pm 0{\cdot}05$ l. mole⁻¹; $\beta_2 = 0{\cdot}6 \pm 0{\cdot}2$ l.² mole⁻²; $K_2 = 0{\cdot}8$ l. mole⁻¹.

TABLE 4. *The system silver ion–ethylthiobenzenesulphonate ion* ($C_{\rm L}' = 0{\cdot}03$M; $I = 0{\cdot}1$M).

A. $E_{\rm M}$ as a function of $C_{\rm L}$.

$C_{\rm M}' \rightarrow$	10	5	2	$C_{\rm M}' \rightarrow$	10	5	2	$C_{\rm M}' \rightarrow$	10	5	2
$C_{\rm L}$	$E_{\rm M}$	$E_{\rm M}$	$E_{\rm M}$	$C_{\rm L}$	$E_{\rm M}$	$E_{\rm M}$	$E_{\rm M}$	$C_{\rm L}$	$E_{\rm M}$	$E_{\rm M}$	E$_{\rm M}$
0·395	0·9	1·4	2·5	3·53	8·7	13·8	19·9	10·44	32·5	41·8	48·8
0·779	1·7	2·8	4·8	5·00	13·1	20·0	27·0	13·33	43·5	52·3	58·2
1·154	2·5	4·2	6·9	6·32	17·4	25·5	33·0	17·15	57·5	64·7	69·4
1·875	4·2	6·9	10·9	7·50	21·6	30·3	37·9	18·75	63·3	69·8	—
2·73	6·5	10·5	15·7	8·57	25·6	34·7	42·2				

B. Calculation of [L] *and derivation of the stability constants.*

$C_{\rm M}' \longrightarrow$	10	5	2	0			
$E_{\rm M}$	$C_{\rm L}$	$C_{\rm L}$	$C_{\rm L}$	$C_{\rm L}$ = [L]	X	X_1	X_2
2	0·91	0·55	0·31	0·17	1·081	(480)	
4	1·79	1·10	0·64	0·36	1·169	(470)	
7	2·94	1·90	1·18	0·72	1·313	430	
10	3·96	2·62	1·72	1·11	1·476	430	
15	5·60	3·82	2·60	1·73	1·793	458	
20	7·05	5·00	3·55	2·52	2·178	468	21,000
25	8·42	6·17	4·57	3·40	2·646	484	20,300
30	9·77	7·41	5·63	4·33	3·214	511	22,200
40	12·43	9·97	8·03	6·63	4·745	565	22,600
50	15·10	12·65	10·82	9·32	7·002	644	24,600
60	17·84	15·66	13·95	12·62	10·33	740	25,700

$\beta_1 = 415 \pm 20$ l. mole^{-1}.
$\beta_2 = (2{\cdot}0 \pm 0{\cdot}2) \times 10^4$ l.^{2} mole^{-2}.
$\beta_3 \approx 5 \times 10^5$ l.^{3} mole^{-3}.

$K_1 = \beta_1$.
$K_2 = 48$ l. mole^{-1}.

TABLE 5. *The system silver ion–*p-*ethylthiobenzenesulphonate ion* ($C_{\rm L}' = 0{\cdot}2$M; $I = 0{\cdot}2$M).

A. $E_{\rm M}$ as a function of $C_{\rm L}$.

$C_{\rm M}' \rightarrow$	10	5	2	$C_{\rm M}' \rightarrow$	10	5	2	$C_{\rm M}' \rightarrow$	10	5	2
$C_{\rm L}$	$E_{\rm M}$	$E_{\rm M}$	$E_{\rm M}$	$C_{\rm L}$	$E_{\rm M}$	$E_{\rm M}$	$E_{\rm M}$	$C_{\rm L}$	$E_{\rm M}$	$E_{\rm M}$	$E_{\rm M}$
1·32	2·9	4·8	7·3	18·18	44·5	57·1	66·2	57·2	113·0	122·9	129·2
2·64	5·9	9·7	14·3	23·56	56·5	69·1	77·9	63·6	121·5	130·8	137·2
3·92	8·9	14·4	20·3	28·6	66·8	79·1	87·5	69·6	128·7	137·5	
5·20	12·1	19·0	26·1	33·4	75·9	88·1	95·9	80·0	140·5	148·5	
7·70	18·3	27·6	35·7	37·8	83·8	95·6	103·0	88·8	149·7	157·2	
10·14	24·5	35·3	44·0	42·2	90·9	102·4	109·6	100·0	160·5	167·5	
12·52	30·5	42·1	51·4	50·0	102·9	113·5	120·3				

B. Calculation of [L] *and derivation of the stability constants.*

$C_{\rm M}' \longrightarrow$	10	5	2	0					
$E_{\rm M}$	$C_{\rm L}$	$C_{\rm L}$	$C_{\rm L}$	$C_{\rm L}$ = [L]	X	X_1	$10^{-3}X_2$	$10^{-5}X_3$	$10^{-6}X_4$
5	2·25	1·37	0·90	0·55	1·215	391			
10	4·37	2·73	1·82	1·16	1·476	411			
15	6·37	4·11	2·80	1·87	1·793	424			
20	8·35	5·50	3·84	2·68	2·178	439			
30	12·33	8·45	6·18	4·56	3·214	486	21·1		
40	16·35	11·78	8·96	7·00	4·745	535	20·7		
50	20·5	15·50	12·05	10·0	7·002	600	21·0		
60	25·1	19·2	15·5	13·2	10·33	707	24·0	3·8	
70	30·2	24·0	19·8	17·1	15·28	835	26·0	4·1	
80	35·5	29·0	24·7	22·0	22·52	978	26·8	3·5	
90	41·6	34·6	29·9	26·8	33·24	1208	30·6	3·8	
100	48·2	40·6	35·8	32·3	49·04	1487	34·0	4·6	4·3
110	55·0	47·5	42·5	39·2	72·4	1821	36·7	4·5	3·3
120	62·5	54·9	49·9	46·4	106·8	2280	40·8	4·7	3·2
130	70·5	63·0	57·7	53·9	158·4	2920	47·0	5·2	3·7
140	79·5	71·8	66·1	62·5	232·7	3707	53·2	5·5	3·7
150	89·0	81·5	—	72·9	343·5	4720	59·7	5·6	3·3
160	99·4	91·4	—	82·0	507·0	6171	70·6	6·3	3·8

$\beta_1 = 390 \pm 20$ l. mole^{-1}.
$\beta_2 = (1{\cdot}9 \pm 0{\cdot}2) \times 10^4$ l.^{2} mole^{-2}.
$\beta_3 = (3{\cdot}2 \pm 0{\cdot}5) \times 10^5$ l.^{3} mole^{-3}.
$\beta_4 = (3{\cdot}6 \pm 0{\cdot}5) \times 10^6$ l.^{4} mole^{-4}.

$K_1 = \beta_1$.
$K_2 = 49$ l. mole^{-1}.
$K_3 = 17$ l. mole^{-1}.
$K_4 = 11$ l. mole^{-1}.

TABLE 6. *The system silver ion–*p*-phenylthiobenzenesulphonate ion* ($C_L' = 0{\cdot}095$M; $I = 0{\cdot}1$M).

A. E_M as a function of C_L.

$C_M' \rightarrow$	5	2	1	0·5
C_L	E_M	E_M	E_M	E_M
0·794	0·8	0·9	0·9	1·0
2·34	2·4	2·6	2·6	2·8
3·85	3·8	4·2	4·3	4·5
5·66	5·7	6·1	6·4	6·6
7·41	7·3	8·0	8·4	8·7
10·71	10·6	11·5	12·3	12·6
13·79	13·7	14·8	15·8	16·2
16·67	16·5	18·0	19·2	19·6
19·35	19·3	21·0	22·4	22·9
21·88	22·0	23·7	25·3	26·1
24·24	24·5	26·5	28·2	29·0
26·47	26·8	29·0	30·8	31·7
28·6	29·2	31·4	33·4	34·3
32·4	33·5	35·9	37·7	38·8
35·9	37·5	40·1	42·0	43·0
39·0	41·1	43·8	45·9	46·8
43·2	46·2	48·8	51·1	51·8
46·8	50·5	53·1	55·7	56·3
50·0	54·4	57·1	59·6	60·2

B. Calculation of [L] *and derivation of the stability constants.*

$C_M' \rightarrow$	5	2	1	0·5	0				
E_M	C_L	C_L	C_L	C_L	$C_L = [L]$	X	X_1	$10^{-1}X_2$	$10^{-2}X_3$
2	2·0	1·8	1·7	1·7	1·7	1·081	48		
4	4·0	3·7	3·5	3·4	3·3	1·169	51		
6	6·1	5·6	5·3	5·1	5·1	1·263	52		
8	8·1	7·4	7·0	6·8	6·7	1·366	55		
10	10·1	9·3	8·8	8·5	8·4	1·476	56·7	121	
15	15·2	13·9	13·1	12·7	12·5	1·793	63·5	136	
20	20·1	18·5	17·4	17·1	16·7	2·178	70·7	145	
25	24·7	23·0	21·6	21·0	20·8	2·646	79·1	157	260
30	29·4	27·3	25·7	25·0	24·7	3·214	89·6	174	288
35	33·8	31·7	30·0	29·2	29·0	3·905	100·2	185	283
40	38·1	35·8	34·2	33·3	33·2	4·745	112·8	200	292
45	42·2	40·0	38·3	37·5	37·3	5·762	127·7	218	309
50	46·4	44·2	42·3	41·6	41·3	7·002	145·3	239	329
55	50·5	48·3	46·3	45·7	45·3	8·505	165·6	263	353

$\beta_1 = 47 \pm 2$ l. mole^{-1}. $K_1 = \beta_1$.
$\beta_2 = 1000 \pm 100$ l.^{2} mole^{-2}. $K_2 = 22$ l. mole^{-1}.
$\beta_3 = (13 \pm 4) \times 10^3$ l.^{3} mole^{-3}. $K_3 = 13$ l. mole^{-1}.
$\beta_4 = (5 \pm 2) \times 10^5$ l.^{4} mole^{-4}. $K_4 = 40$ l. mole^{-1}.

TABLE 7. *The system silver ion–*p*-phenylthiobenzenesulphonate ion* ($C_L' = 0{\cdot}2$M; $I = 0{\cdot}2$M).

A. E_M as a function of C_L.

$C_M' \rightarrow$	5	2	1
C_L	E_M	E_M	E_M
2·6	2·1	2·7	2·9
7·7	6·7	7·8	8·2
12·5	11·1	12·7	13·3
18·2	16·6	18·8	19·5
23·6	21·9	24·5	25·4
33·4	32·3	35·7	36·8
42·2	42·5	46·6	47·9
50·0	52·2	57·1	58·5
57·2	60·9	66·5	68·3
63·6	68·7	74·8	76·8
69·6	75·4	81·8	84·0
80·0	86·6	93·0	95·2
88·8	95·2	101·2	103·3
100·0	104·7	109·9	111·6

B. Calculation of [L] *and derivation of the stability constants.*

$C_M' \rightarrow$	5	2	1	0					
E_M	C_L	C_L	C_L	$C_L = [L]$	X	X_1	X_2	$10^{-2}X_3$	$10^{-5}X_4$
3	3·7	2·95	2·7	2·5	1·124	49·5			
5	5·8	4·95	4·6	4·3	1·215	50·0			
7	8·0	6·9	6·5	6·2	1·314	50·6	645		
10	11·25	9·9	9·3	8·9	1·476	53·5	775		
15	16·6	14·65	14·0	13·4	1·793	59·2	940		
20	21·7	19·4	18·7	17·9	2·178	65·8	1073		
30	31·3	28·45	27·6	26·6	3·214	83·25	1378	312	(82)
40	40·55	37·2	36·1	34·9	4·745	107·2	1736	341	(74)
50	48·3	44·7	43·8	42·5	7·002	141·2	2226	396	71
60	56·4	52·2	51·1	49·8	10·33	187·4	2827	457	73
70	64·7	59·9	58·5	56·9	15·28	251·0	3592	534	78
80	73·8	68·0	66·2	64·1	22·51	335·5	4507	616	82
90	83·3	77·2	75·2	73·0	33·24	441·7	5412	665	79
100	94·4	87·7	85·0	82·4	49·20	584·9	6533	726	77
105	100·5	93·4	90·9	88·2	59·6	664·0	7000	731	73

$\beta_1 = 47 \pm 2$ l. mole^{-1}. $K_1 = \beta_1$.
$\beta_2 = 550 \pm 100$ l.^{2} mole^{-2}. $K_2 = 12$ l. mole^{-1}.
$\beta_3 = (9 \pm 4) \times 10^3$ l.^{3} mole^{-3}. $K_3 = 16$ l. mole^{-1}.
$\beta_4 = (7{\cdot}5 \pm 2) \times 10^5$ l.^{4} mole^{-4}. $K_4 = 85$ l. mole^{-1}.

TABLE 8. *The system silver ion–dianion of di-*(p*-sulphophenyl*) *sulphide* ($C_L' = 0·0667$M; $I = 0·2$M).

A. E_M as a function of C_L.

$C_M' \longrightarrow$	5	2	$C_M' \longrightarrow$	5	2	$C_M' \longrightarrow$	5	2
C_L	E_M	E_M	C_L	E_M	E_M	C_L	E_M	E_M
0·53	0·3	0·4	11·12	6·7	6·8	23·93	14·8	15·3
1·56	1·0	1·0	12·91	8·0	8·0	26·03	16·1	16·6
2·57	1·5	1·6	14·59	9·0	9·1	28·80	17·9	18·5
3·78	2·2	2·4	16·17	10·0	10·2	31·22	19·4	20·2
4·94	3·0	3·1	17·66	10·9	11·1	33·35	20·8	21·6
7·14	4·4	4·5	19·05	11·8	12·0			
9·20	5·6	5·8	21·63	13·3	13·7			

B. Calculation of [L] *and derivation of the stability constants.*

$C_M' \longrightarrow$	5	2	0				
E_M	C_L	C_L	C_L = [L]	X	X_1	X_2	X_3
2	3·2	3·2	3·2	1·081	25·3		
4	6·5	6·3	6·4	1·168	26·3		
6	9·8	9·6	9·5	1·263	27·7	284	
8	13·0	12·8	12·7	1·365	28·7	291	
10	16·2	15·9	15·7	1·476	30·6	338	8800
12	19·5	19·1	18·8	1·595	31·6	351	8000
14	22·6	22·0	21·6	1·725	33·6	398	9200
16	25·8	25·1	24·6	1·864	35·1	411	8600
18	29·0	28·1	27·5	2·015	36·9	433	8500
20	32·2	31·0	30·1	2·178	39·1	468	8900
22	35·4	34·0	33·1	2·354	40·9	480	8500

$\beta_1 = 25 \pm 2$ l. mole^{-1}. $K_1 = \beta_1$.
$\beta_2 = 200 \pm 30$ l.^{2} mole^{-2}. $K_2 = 8$ l. mole^{-1}.
$\beta_3 = 8500 \pm 1000$ l.^{3} mole^{-3}. $K_3 = 44$ l. mole^{-1}.

TABLE 9. *The system silver ion–*p*-phenylselenobenzenesulphonate ion* ($C_L' = 0·1$M; $I = 0·1$M).

A. E_M as a function of C_L.

$C_M' \longrightarrow$	2	1	0·5	$C_M' \longrightarrow$	1	0·5	$C_M' \longrightarrow$	1	0·5
C_L	E_M	E_M	E_M	C_L	E_M	E_M	C_L	E_M	E_M
0·66	4·2	5·2	6·1	6·26	43·5	48·2	25·0	132·2	137·8
1·32	8·2	10·1	11·9	7·41	50·6	55·8	28·6	114·5	149·7
1·96	11·9	14·8	17·2	9·09	60·7	66·3	31·8	154·9	159·9
2·60	15·7	19·5	22·2	11·78	75·3	81·3	34·8	163·8	168·6
3·23	19·4	23·8	27·1	14·3	87·9	93·9	40·0	178·5	182·9
3·85	23·0	27·9	31·6	16·7	99·0	105·2	44·4	190·1	194·4
4·46	26·4	—	—	18·9	108·7	114·7	50·0	203·8	207·7
5·07	—	36·1	40·3	21·1	117·3	123·3			

B. Calculation of [L] *and derivation of the stability constants.*

$C_M' \longrightarrow$	2	1	0·5	0					
E_M	C_L	C_L	C_L	C_L = [L]	X	X_1	$10^{-3}X_2$	$10^{-6}X_3$	$10^{-8}X_4$
5	0·78	0·63	0·54	0·46	1·215	467			
10	1·62	1·29	1·11	0·95	1·476	501			
15	2·49	1·98	1·20	1·44	1·793	551	84·1		
20	3·34	2·67	2·31	1·92	2·178	598	85·3		
25	4·21	3·41	2·96	2·54	2·646	648	84·9		
30		4·16	3·63	3·10	3·214	714	91·7	4·42	
40		5·69	5·04	4·38	4·245	855	97·2	4·38	
50		7·31	6·53	5·75	7·002	1044	106·7	4·99	4·16
60		9·0	8·1	7·2	10·33	1296	120·3	5·88	4·56
75		11·7	10·65	9·6	18·53	1826	145·4	7·02	4·61
90		14·75	13·55	12·35	33·24	2610	176·6	7·98	4·37
100		16·95	15·6	14·25	49·04	3370	206·5	9·02	4·51
110		19·3	17·8	16·3	72·4	4380	242·5	10·09	4·59
120		21·85	20·25	18·65	106·8	5670	281	10·89	4·44
135		25·8	24·2	22·6	191·6	8430	354	12·22	4·27
150		30·25	28·75	27·2	343·5	12,600	447·5	13·6	4·04
160		33·5	31·9	30·3	507·0	16,720	538	15·2	4·17
170		36·95	35·3	33·65	748	22,220	648	16·95	4·27
180		40·55	39·0	37·45	1105	29,470	776	18·65	4·29
190		44·3	42·7	41·1	1630	39,650	954	21·35	4·57
200		48·3	46·8	45·3	2405	53,150	1164	24·0	4·72

$\beta_1 = 430 \pm 20$ l. mole^{-1}. $K_1 = \beta_1$.
$\beta_2 = (7·8 \pm 0·7) \times 10^4$ l.^{2} mole^{-2}. $K_2 = 180$ l. mole^{-1}.
$\beta_3 = (2·6 \pm 0·5) \times 10^6$ l.^{3} mole^{-3}. $K_3 = 33$ l. mole^{-1}.
$\beta_4 = (4·4 \pm 0·7) \times 10^8$ l.^{4} mole^{-4}. $K_4 = 170$ l. mole^{-1}.

The disodium salt of di-(*p*-sulphophenyl) sulphide was prepared in order to provide a derivative of diphenyl sulphide more soluble in water than the monosulphonate. In this way it was hoped to obtain the higher constants more accurately than was possible with the monosulphonate, but unfortunately the disulphonate was so weak a complexing agent that only three constants could be obtained (Table 8). It appears as if the formation of complexes ceases at $\bar{n} = 3$ (*i.e.*, that X_3 is constant). This may well be so since the ionic charge on the complex $[Ag\{S(C_6H_4 \cdot SO_3^-)_2\}_3]^{5-}$ would strongly repel the addition of a fourth molecule of the disulphonate, but at a higher concentration of free ligand, had solubility allowed it, the formation of complexes might have continued.

Sodium *p*-phenylselenobenzenesulphonate had sufficient affinity for silver ion to allow the whole range of complex formation to be covered at $I = 0{\cdot}1$M, but even at such a low ionic strength only very dilute solutions of silver perchlorate could be investigated. Three concentrations were used $C_M' = 0{\cdot}5$ mM, 1 mM, and 2 mM. The *silver salt* was precipitated from the 2mM-solution when the concentration of ligand reached 4·5 mM (Found: Ag, 25·6. $C_{12}H_9O_3SAgSe$ requires Ag, 25·7%). At the lower concentrations no precipitation occurred up to ligand concentrations of 50 mM. The results are listed in Table 9.

APPENDIX

Leden's Method [3] *as Modified by Fronaeus* [10] *for Determination of Stability Constants.*—In an aqueous solution containing a metal ion, M, and a ligand, L, a series of mononuclear complexes ML, ML_2 . . . ML_N may exist in equilibrium with the hydrated metal ion and the ligand. The total concentration of the metal ion (C_M) both free and in complexes is given by

$$C_M = [M] + [ML] + [ML_2] \dots + [ML_N] \qquad (1)$$

Using the definition of the gross concentration stability constants β_1, β_2, etc., on p. 265 we obtain a function X such that

$$C_M/[M] = 1 + \beta_1[L] + \beta_2[L]^2 \cdots\cdots\cdots \beta_N[L]^N = X \qquad (2)$$

Provided X and [L] are known over the whole range of complex formation by L then all the β's can be determined as follows. A new function X_1 is formed from eqn. (2) such that

$$X_1 = (X - 1)/[L] = \beta_1 + \beta_2[L] + \beta_3[L]^2 \cdots\cdots \beta_N[L]^{N-1} \qquad (3)$$

If X_1 is now plotted against [L] and extrapolated to cut the X_1 axis we obtain β_1 as the intercept and β_2 as the slope at the point of intersection. However, β_2 is better obtained by writing a new function X_2 similar to X_1 such that

$$X_2 = (X_1 - \beta_1)/[L] = \beta_2 + \beta_3[L] + \cdots\cdots \beta_N[L]^{N-2} \qquad (4)$$

and so obtaining β_2 which is the limiting value of X_2 as $[L] \longrightarrow 0$. The higher constants (β_3, β_4, etc.) are calculated analogously until finally a constant function $X_N = \beta_N$ is found. This indicates that ML_N is the highest complex formed in the range of concentrations used.

The values of X and [L] needed for the above calculation are found by determining the e.m.f. of the following cell with various total concentrations of metal ion, C_M, and ligand C_L, in the right-hand compartment.

$$\text{Reference electrode}\ \overset{+}{\Big|}\ \text{Bridge}\ \Big\|\ \begin{array}{l}\text{Metal ion }(C_M)\\ \text{Ligand }(C_L)\\ \text{Ionic medium }(I,\ NaClO_4)\end{array}\ \overset{-}{\Big|}\ \begin{array}{c}\text{M,MCl (or}\\ \text{M,MBr)}\end{array}$$

The e.m.f., E, is given by

$$E = E_k + (\boldsymbol{RT/nF}) \ln [M] \qquad (5)$$

where E_k includes the potential of the reference electrode, the liquid junction potentials, and activity coefficients, *i.e.*, all factors considered to remain constant throughout the measurements. When $C_L = 0$, *i.e.*, no ligand has been added to the cell, the e.m.f., E_0, is given by

$$E_0 = E_k + (\boldsymbol{RT}/n\boldsymbol{F}) \ln C_M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The addition of ligand to the cell gives a new potential E, and the difference $E_0 - E$ gives X directly according to (7).

$$E_0 - E = E_M = (\boldsymbol{RT}/n\boldsymbol{F}) \ln (C_M/[M]) = (\boldsymbol{RT}/n\boldsymbol{F}) \ln X \quad . \quad . \quad . \quad (7)$$

Since X is a function only of [L] [eqn. (2)] and E_M is a function only of X, there is for every E_M a unique value of [L], independent of the total metal concentration, C_M. To find corresponding values of E_M and [L], E_M is determined experimentally as a function of C_L at several values of C_M. A family of curves is then obtained (Fig. 3) where $C_M'''' > C_M''' > C_M'' > C_M'$. These curves are cut at a number of values of E_M, and C_M plotted against C_L for every E_M (Fig. 4). By extrapolation to $C_M = 0$, [L] (which is equal to C_L at $C_M = 0$) is found for each particular value of E_M, as the intercept on the C_L axis.

FIG. 3.

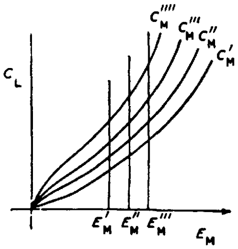
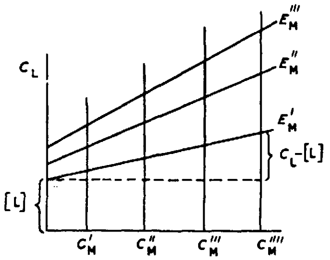


FIG. 4.



From this X is determined as a function of [L], and so the constants β_1, β_2, etc., from the eqns. (3), (4), etc.

X as a function of [L] can be determined in this manner only when the ligand has a weak or moderate affinity for the metal ion (*i.e.*, $\beta_1 \lesssim 1500$ l. mole^{-1}), as is the case here. If the affinity is strong (*i.e.*, $\beta_1 \gtrsim 1500$ l. mole^{-1}), [L] is so low when the formation of complexes takes place (or at least during the formation of the lower complexes), that the extrapolations pass too close to the origin to allow reliable values of [L] to be read. In such cases an alternative procedure described in the Appendix of Part II (following paper) has to be used.[10]

From the fact that [L] is constant along a line of constant E_M it follows that the ligand number $\bar{n}$, defined according to eqn. (8)

$$\bar{n} = (C_L - [L])/C_M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

is constant too. For when eqns. (9)

$$C_L = [L] + \sum_{n=1}^{N} n[ML_n] = [L] + [M] \sum_{n=1}^{N} n\beta_n[L]^n \quad . \quad . \quad . \quad . \quad (9)$$

and (2) are inserted in (8) we obtain

$$\bar{n} = \frac{\sum_{n=1}^{N} n\beta_n[L]^n}{1 + \sum_{n=1}^{N} \beta_n[L]^n} = \frac{\sum_{n=1}^{N} n\beta_n[L]^n}{X} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

i.e., $\bar{n}$ is a function of [L] only, and therefore constant along a line of constant [L]. Thus, at constant E_M, the relation (8) between C_L and C_M must be a straight line with the slope $= \bar{n}$, corresponding to the value of [L] found as the intercept in Fig. 3.

From the constants β_1, β_2, etc., so obtained it is possible to calculate the fraction α_n of the total metal concentration which is present in the form of each particular complex ML_n in equilibrium at each value of [L] by using equation (11):

$$\alpha_n = \frac{[ML_n]}{C_M} = \frac{\beta_n[L]^n}{X} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

By plotting the mole percentage of silver in the various complexes against log [L] it is possible to see graphically the regions of stability of each complex (Fig. 1).[26]

In the derivation of the above equations we have assumed that only mononuclear complexes are formed. If polynuclear complexes are formed as well, E_M depends on both [L] and [M], but it has been shown [10] that the intercept on the C_L axis still gives [L] corresponding to the value of X found according to eqn. (7). However, the slope of the C_L–C_M curve will then be a quantity $<\bar{n}$. Nevertheless, as X can be found as a function of [L] it is still possible to determine the stability constants of the mononuclear complexes present, and hence the true values of $\bar{n}$ according to eqn. (10). Comparison of the $\bar{n}$'s thus found with those obtained from the slopes reveals whether polynuclear complexes are formed. In our experiments we found no evidence of polynuclear complex formation.

This test for polynuclear complexes fails when a great enough range of C_M is not available, because then the curves giving E_M as a function of C_L are close together and the C_L–C_M slopes cannot be determined with any certainty. Nevertheless, the correct stability constants relating to the formation of the mononuclear complexes can still be determined according to the method above.

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[26] Cf. ref. 2, p. 287.