The Linear Free-energy Relation in the Thermodynamics of Complex Formation. Part I. Correlations involving Enthalpy Changes on Complex Formation of Silver(I) and Mercury(II) with ' Soft ' Donor Ligands

By **Robert D. Hancock** * and **Fabrizio Marsicano**, National Institute for Metallurgy, Private Bag 7, Auckland Park 2006, South Africa

The free energies of complex formation of various metal ions with ligands having ' soft ' donor atoms P, As, S, Se, and I^-, Br^-, Cl^-, and CN^- form linear free-energy relations (l.f.e.r.s) involving all these ligands. A potentiometric and calorimetric study has been made in which one l.f.e.r., for the pair of cations Ag^+ and Hg^{2+}, has been analyzed in terms of the separate enthalpy and entropy contributions. A linear enthalpy relation (l.e.r.) has been found which lies parallel to the l.f.e.r., but, unlike the l.f.e.r., does not pass through the origin. The intercept of the l.e.r. is rationalized in terms of the Powell, Latimer, and Cobble model for the partial molar entropies of complexes in aqueous solution.

THE linear free-energy relation (l.f.e.r.) involving free-energy changes on complex formation of metal ions with organic ligands has come to be recognised as a general phenomenon in inorganic chemistry.[1] However, such relations are usually of the Hammett sigma-function type, so that one of the pair of ' metal ' ions is invariably the proton. In addition, the ligands have nearly always been restricted to a single type, *e.g.* differently substituted pyridines or benzoates, *etc.* Where l.f.e.r.s have involved ' metal ' ions other than the proton, the ligands have been few and restricted in type,[2] or have involved a mixture of uni- and poly-dentate ligands.[3] This latter approach is not completely rigorous, since, as pointed out by Adamson,[4] a considerable proportion of the stability of complexes of polydentate ligands arises from the asymmetry of the standard state, which is an artifact.

In a recent paper [5] it was shown that for the d^{10} metal ions Cu^I, Ag^I, Au^I, Hg^{II}, and Cd^{II} fairly simple behaviour was observed when l.f.e.r.s were plotted with the use of all the available data for complexes of unidentate ligands with these ions. Several l.f.e.r.s were formed when any of the above metal ions were used, the division into different l.f.e.r.s being dependent on the nature of the donor atom. A single l.f.e.r. was found that contained all the ligands which would be described as ' soft ' in the Pearson hard and soft acids and bases (h.s.a.b.) classification,[6] namely ligands with phosphorus, arsenic, sulphur, and selenium donor atoms, and CN^-, I^-, Br^-, and Cl^-. In further separate l.f.e.r.s ligands having nitrogen and oxygen donor atoms were found. The relative positions of these l.f.e.r.s were explained in terms of h.s.a.b. concepts. Since considerable additional data have appeared in the literature since the previous publication,[5] which has considerably clarified the position, the l.f.e.r.s for free-energy changes of Au^I and Cu^I on complex formation with soft donor ligands, plotted against the free-energy changes for the analogous silver(I) complexes, have been reproduced in Figure 1. The l.f.e.r. for Hg^{II} against Ag^I is similar to those for Au^I–Ag^I or Cu^I–Ag^I, but is more complicated in that several of the charged ligands, such as $[SO_3]^{2-}$, $[S_2O_3]^{2-}$, $[SCN]^-$, and Cl^-, are displaced from the soft-ligand line in a direction suggesting increased hardness, or at least increased affinity for the more highly charged Hg^{II}.

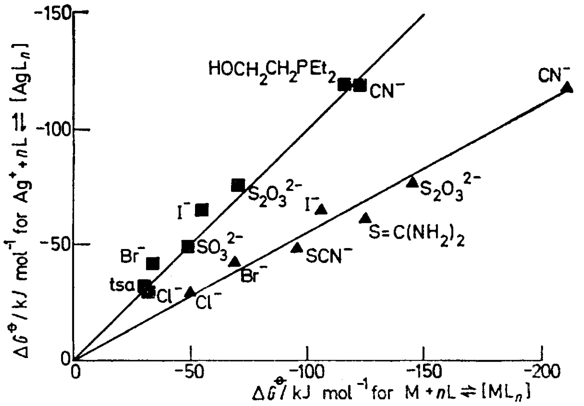

FIGURE 1 Linear free-energy relations between the free energies of formation of $[ML_2]$ complexes of Au^I (▲) and Cu^I (■) and the free energies of formation of the analogous silver(I) complexes

It was felt that some insight into factors governing complex formation might be gained if one of these l.f.e.r.s was analyzed in terms of the separate entropy and enthalpy contributions. As a starting point, since these ions appeared to offer the least experimental difficulty, the enthalpies of formation of several complexes of Ag^I and Hg^{II} were determined calorimetrically. Ligands were selected so as to include both neutral and charged, and a wide range of donor atoms. The calorimetric study of sulphur-donor ligands is reported elsewhere.[7] This paper describes a calorimetric study on the 4-(diphenylphosphino)benzenesulphonate (dbs) and tris-(3-sulphophenyl)arsine (H_3tsa) complexes of Ag^I and Hg^{II}. These results, and those determined previously,[7]

---

[1] J. R. Chipperfield in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum, London and New York, 1972.

[2] H. Irving and H. Rossotti, *Acta Chem. Scand.*, 1956, **10**, 72.

[3] A. M. Erenburg and B. I. Peschevitskii, *Zhur. neorg. Khim.*, 1969, **14**, 2714.

[4] A. W. Adamson, *J. Amer. Chem. Soc.*, 1954, **76**, 1578.

[5] R. D. Hancock and N. P. Finkelstein, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 477; *J. Inorg. Nuclear Chem.*, 1974, **36**, 2539.

[6] ' Hard and Soft Acids and Bases,' ed. R. G. Pearson, Dowden, Hutchinson and Ross, Pennsylvania, 1973.

[7] F. Marsicano and R. D. Hancock, *J. Co-ordination Chem.*, in the press.

are combined with existing literature data,[8-10] as discussed below, for analysis of the Hg^{II}–Ag^{I} soft-donor l.f.e.r. in terms of enthalpy and entropy changes on complex formation.

EXPERIMENTAL

The measurements in this study were made at 298.15 ± 0.05 K in an aqueous medium of ionic strength $I = 0.01$ mol dm^{-3} for the ligand dbs, and $I = 0.50$ mol dm^{-3} for the ligand tsa. Sodium perchlorate was used as background electrolyte.

Materials.—Stock solutions of $Ag[NO_3]$ and $Hg[ClO_4]_2$ were prepared as described previously.[7] Sodium 4-(diphenylphosphino)benzenesulphonate, Na(dbs), and the trisodium salt of tris(3-sulphophenyl)arsine, Na_3(tsa), were prepared as described by Ahrland *et al.*[11] (Found: C, 53.55; H, 7.45; O, 4.55; S, 7.80. $C_{18}H_{14}NaO_3PS{\cdot}2H_2O$ requires C, 54.0; H, 7.7; O, 4.5; S, 8.0. Found: C, 35.2; H, 2.05; O, 24.45; S, 14.65. $C_{18}H_{12}AsNa_3O_9S_3$ requires C, 35.3; H, 2.00; O, 23.5; S, 15.7%). Solutions of Na(dbs) were found to decompose slowly, and so were freshly prepared before each determination. The salt Na_3(tsa) was hygroscopic, so that the elemental analysis was carried out after heating the compound to 130 °C *in vacuo* for 24 h. Because of its hygroscopic properties, solutions of Na_3(tsa) were analyzed by dissolving a known weight of the material in water and passing this solution through an ion-exchange column packed with Dowex 50W-X8 resin in the protonated form, so that protons were exchanged for sodium ions. The amount of acid displaced from the resin was subsequently determined.

Potentiometric Apparatus and Procedure.—Stability constants involving silver were determined with the use of an electrochemical cell consisting of a silver-indicating electrode and silver chloride reference electrode, together with a salt bridge to prevent contamination of the reaction solution with chloride ions. The junctions between the reference electrode and the salt bridge, and between the salt bridge and the solution, were made with sintered-glass discs from Ingold reference electrodes. Junction potentials were minimized by the use of 0.5 mol dm^{-3} sodium perchlorate in the salt bridge, and by making up the ionic strength of the solution in the reference electrode itself to 0.5 mol dm^{-3} with $Na[ClO_4]$. Thus, a typical reference electrode consisted of an Ingold silver wire coated with AgCl dipping into a reference solution which was 0.01 mol dm^{-3} NaCl + 0.49 mol dm^{-3} $Na[ClO_4]$. A drop of a dilute solution of $Ag[ClO_4]$ was added so that the reference solution would be saturated with AgCl. Presaturated nitrogen was bubbled through the cell to exclude oxygen and carbon dioxide, and the cell potential was measured with the use of a Radiometer PHM 64 research pH-meter.

Stability constants involving mercury were determined with a J-type mercury-indicating electrode described in the literature.[12] The J tube was siliconed to prevent solution from creeping down the sides of the mercury pool. Contact on the long arm of the J tube was made with a short length of platinum wire sealed into a glass tube so that the whole length of the wire was immersed in the mercury. The remainder of the cell was the same as that described for the silver measurements.

Calorimetric Apparatus and Procedure.—The enthalpy changes were determined with the use of a titration calorimeter, the construction and testing of which have been described previously.[13] The way in which the calorimetric determinations are corrected for heat exchange, difference in temperature between titrant and titrate, and for ' non-chemical ' heat effects has been described by Eatough *et al.*[14]

Calculations.—Stability constants were calculated from potentiometric data with the use of the ETITR form of the LETAGROP VRID suite of programs.[15] These calculations were checked with the use of the MINIQUAD program of Sabatini *et al.*[16] Enthalpy changes on complex formation were calculated from the calorimetric data and from known stability constants with the use of the KALLE form [17] of LETAGROP VRID.

Corrections were made for any reactions known to be taking place in the experiment, *e.g.* hydrolysis of the metal ions and ligand protonation. Hydrolysis of the metal ions occurs because, for $[SO_3]^{2-}$, the ligand has sufficient basicity to raise the pH of the solution significantly. For Ag^+, the metal hydroxide stability constant [18] of log β_1 3.02 is relatively low, leading to negligible corrections for metal hydrolysis. Values of the hydroxylation constants and enthalpies of hydroxylation of cadmium and mercury,

TABLE 1

Metal hydroxide stability constants and enthalpies for Cd^{2+} and Hg^{2+}, together with the ion product of water, and the enthalpy of combination of H^+ and OH^-

Reaction	log β	I mol dm^{-3}	Ref.	$\Delta H^{\ominus}$ kJ mol^{-1}	I mol dm^{-3}	Ref.
$Cd^{2+} + [OH]^- \rightleftharpoons [Cd(OH)]^+$	6.08	0	19	−1.67	3	22
$Hg^{2+} + [OH]^- \rightleftharpoons [Hg(OH)]^+$	10.04	0.5	20	−24	3	23
$Hg^{2+} + 2[OH]^- \rightleftharpoons Hg[OH]_2$	21.18	0.5	20	−68	3	23
$H^+ + [OH]^- \rightleftharpoons H_2O$	13.74	0.5	21	−56.90	0.5	24

---

[8] L. G. Sillén and A. E. Martell, ' Stability Constants of Metal–Ion Complexes,' *Special Publ.* no. 17, The Chemical Society, London, 1964.

[9] L. G. Sillén and A. E. Martell, ' Stability Constants of Metal–Ion complexes,' *Special Publ.* no. 25, The Chemical Society, London, 1971.

[10] J. J. Christensen and R. M. Izatt, ' Handbook of Metal Ligand Heats and Related Thermodynamic Quantities,' Marcel Dekker, New York, 1970.

[11] S. Ahrland, J. Chatt, N. R. Davies, and A. A. Williams, *J. Chem. Soc.*, 1958, 276.

[12] P. Brooks and N. Davidson, *J. Amer. Chem. Soc.*, 1960, **82**, 2118.

[13] K. Lowe, A. W. Forbes, and F. Marsicano, ' The Construction and Testing of a Precision Calorimeter,' National Institute for Metallurgy, Johannesburg, report 1582, 1973.

[14] D. J. Eatough, J. J. Christensen, and R. M. Izatt, *Thermochim. Acta*, 1972, **3**, 219.

[15] P. Brauner, L. G. Sillén, and R. Whiteker, *Arkiv. Kemi*, 1969, **31**, 365.

[16] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53.

[17] R. Arnek, *Arkiv. Kemi*, 1970, **32**, 81.

[18] A. O. Gubeli and J. Ste-Marie, *Canad. J. Chem.*, 1967, **45**, 827.

together with the value of the ion product of water and the heat of combination of H^+ and OH^-, used in this investigation are shown in Table 1.[19-24] The error introduced by the fact that the data given in Table 1 for Cd^{2+} and the enthalpies of hydroxylation of Hg^{2+} were determined at an ionic strength other than 0.5 mol dm^{-3} is second order and can be neglected. It has been shown[20] that, at ionic strengths and concentration conditions similar to those used in this work, no polynuclear mercury hydroxide species are formed. The formation of mercury(I) ions according to the reaction $Hg^{2+} + Hg(l) \rightleftharpoons [Hg_2]^{2+}$ was taken into account by use of a reported[25] value of 130 for the equilibrium constant of this reaction.

RESULTS

In Table 2 the experimental data for the potentiometric titrations are given, and in Table 3 the data obtained from the calorimetric titrations are given. Any special features encountered with the various systems will be discussed separately. Values for the thermodynamic properties of complex formation are listed in Table 4. The estimated error limits are three times the standard deviations given by the LETAGROP ETITR and KALLE programs.

TABLE 2

Potentiometric measurements. Experimental data for the calculation of stability constants. The potential $E_{cell}^{\ominus}$ comes from the equation $E_{cell} = E_{cell}^{\ominus} + (RT/nF) \ln [M^{n+}]$; the subscript 0 refers to the titrate, and t refers to the titrant. The concentrations of background electrolyte are omitted for simplicity. The volume–e.m.f data are given as pairs (V_t, E_{cell}) separated by semi-colons, in units of cm^3 and mV respectively

(*i*) $Ag^+ + Na_3(tsa)$

$E_{cell}^{\ominus} = 440.6$ mV; $[H]_0 = 0$, $[Ag]_0 = 1.99 \times 10^{-3}$, $[tsa]_0 = 0$, $[H]_t = 0$, $[Ag]_t = 0$, $[tsa]_t = 0.010\,05$ mol dm^{-3}; $V_0 = 20.00$ cm^3

1.50, 269.5; 2.00, 264.3; 2.50, 257.5; 3.00, 249.0; 3.50, 237.6; 4.00, 220.4; 4.50, 200.2; 5.00, 184.3; 5.50, 174.2; 6.00, 165.6; 6.50 159.6; 7.00, 154.1; 7.50, 149.6; 8.00, 146.2; 8.50, 142.9; 9.00, 139.9; 9.50, 137.2; 10.00, 134.7; 10.50, 132.6; 11.00, 130.5; 11.50, 128.5; 12.00, 126.9; 12.50, 125.3; 13.00, 123.7; 13.50, 122.3; 14.00, 120.7; 14.50, 119.5; 15.00, 118.2; 15.50, 117.1; 16.00, 115.9; 16.50, 114.8; 17.00, 113.8; 17.50, 112.8; 18.00, 111.7; 18.50, 110.8; 19.00, 110.0; 19.50, 109.2; 20.00, 108.3

(*ii*) $Hg^{2+} + Na_3(tsa)$

$E_{cell}^{\ominus} = 491.3$ mV; $[H]_0 = 0.010\,0$, $[Hg]_0 = 1.768 \times 10^{-3}$, $[tsa]_0 = 0$, $[H]_t = 0$, $[tsa]_t = 0.010\,05$ mol dm^{-3}; $V_0 = 22.02$ cm^3

0.50, 354.5; 1.00, 343.5; 1.50, 341.4; 2.00, 338.8; 2.50, 335.7; 3.00, 331.7; 3.50, 326.8; 4.00, 317.5; 4.50, 304.0; 5.00, 285.7; 5.50. 273.6; 6.00, 264.0; 6.50, 255.5; 7.00, 246.4; 7.50, 235.7; 8.00, 224.1; 8.50, 211.4; 9.00, 196.4; 9.50, 184.4; 10.00, 174.1; 10.50, 167.1; 11.00, 161.6; 11.50, 156.6; 12.00, 152.9; 12.50, 149.5; 13.00, 146.2; 13.50, 143.5; 14.00, 141.2; 14.50, 139.2; 15.00, 137.2; 15.50, 135.3; 16.00, 133.8; 16.50, 132.1; 17.00, 130.8; 17.50, 129.4; 18.00, 128.0; 18.50, 126.9; 19.00, 125.8; 19.50, 124.6; 20.00, 123.7

TABLE 3

Calorimetric measurements. Experimental data for calculation of enthalpy changes. The subscript 0 refers to the titrate and t refers to the titrant. The concentrations of background electrolytes are omitted for simplicity. The data for volume per incremental heat liberated are given as pairs (V_t,q) separated by semi-colons, in units of cm^3 and J respectively

(*i*) $Ag^+ + Na(dbs)$

$[Ag]_0 = 0$, $[dbs]_0 = 0.005\,024$, $[Ag]_t = 0.100\,1$, $[dbs]_t = 0$ mol dm^{-3}; $V_0 = 95.00$ cm^3

0.26, 5.61; 0.56, 6.84; 0.87, 6.87; 1.18, 6.23; 1.49, 4.23; 1.79, 1.08; 2.10, 0.36; 2.41, 0.36; 2.72, 0.42; 3.33, 0.48; 3.64, 0.20; 3.95, 0.20; 4.26, −0.03; 4.56, 0.20

$[Ag]_0 = 0$, $[dbs]_0 = 0.005\,024$, $[Ag]_t = 0.100\,1$, $[dbs]_t = 0$ mol dm^{-3}; $V_0 = 95.00$ cm^3

0.24, 5.27; 0.53, 6.30; 0.81, 6.43; 1.10, 5.95; 1.39, 4.50; 1.67, 2.03; 1.96, 0.41; 2.25, 0.36; 2.53, 0.31; 2.82, 0.42; 3.11, 0.25; 3.39, 0.31; 3.68, 0.26; 3.97, 0.26; 4.25, 0.03

(*ii*) $Hg^{2+} + Na(dbs)$

$[H]_0 = 0$, $[Hg]_0 = 0$, $[dbs]_0 = 9.98 \times 10^{-4}$, $[H]_t = 0$, $[Hg]_t = 0.019\,68$, $[dbs]_t = 0$ mol dm^{-3}; $V_0 = 95.00$ cm^3

0.23, 1.01; 0.54, 1.44; 0.85, 1.24; 1.15, 1.32; 1.46, 1.17; 1.77, 0.74; 2.08, 0.60; 2.39, 0.42; 2.69, 0.03; 3.00, −0.03; 3.31, 0.03; 3.62, 0.03; 3.93, 0.03; 4.23, 0.03; 4.54, 0.03

$[H]_0 = 0$, $[Hg]_0 = 0$, $[dbs]_0 = 9.98 \times 10^{-4}$, $[H]_t = 0$, $[Hg]_t = 0.019\,68$, $[dbs]_t = 0$ mol dm^{-3}; $V_0 = 95.00$ cm^3

0.22, 0.88; 0.48, 1.22; 0.73, 1.13; 0.99, 1.09; 1.25, 1.16; 1.50, 0.96; 1.76, 0.63; 2.02, 0.70; 2.28, 0.54; 2.53, −0.02; 2.79, 0.03; 3.05, 0.03; 3.30, 0.09; 3.56, 0.03; 3.82, 0.03

(*iii*) $Ag^+ + Na_3(tsa)$

$[Ag]_0 = 0$, $[tsa]_0 = 0.009\,497$, $[Ag]_t = 0.400\,0$, $[tsa]_t = 0$ mol dm^{-3}; $V_0 = 95.00$ cm^3

0.10, 1.39; 0.26, 2.18; 0.42, 2.30; 0.58, 2.16; 0.74, 2.12; 0.90, 2.18; 1.06, 1.98; 1.21, 1.99; 1.37, 1.95; 1.53, 1.96; 1.69, 1.97; 1.85, 1.76; 2.01, 1.67; 2.17, 1.12; 2.33, 0.29

$[Ag]_0 = 0$, $[tsa]_0 = 0.002\,062$, $[Ag]_t = 0.039\,99$, $[tsa]_t = 0$ mol dm^{-3}; $V_0 = 95.00$ cm^3

0.24, 0.39; 0.55, 0.41; 0.86, 0.37; 1.17, 0.37; 1.47, 0.49; 1.78, 0.28; 2.09, 0.51; 2.40, 0.35; 2.71, 0.41; 3.01, 0.36; 3.32, 0.37; 3.63, 0.32; 3.94, 0.44; 4.25, 0.33; 4.56, 0.22

(*iv*) $Hg^{2+} + Na_3(tsa)$

$[H]_0 = 0$, $[Hg]_0 = 0$, $[tsa]_0 = 0.001\,998$, $[H]_t = 0$, $[Hg]_t = 0.040\,0$, $[tsa]_t = 0$ mol dm^{-3}; $V_0 = 95.00$ cm^3

0.24, 0.36; 0.55, 1.02; 0.86, 1.04; 1.16, 1.06; 1.47, 1.03; 1.78, 0.94; 2.08, 0.73; 2.39, 0.36; 2.70, 0.26; 3.00, 0.21; 3.31, 0.22; 3.61, 0.23; 3.92, 0.24; 4.23, 0.07

Silver(I) *and Sodium* 4-(*Diphenylphosphino*)*benzenesulphonate*.—The stability constants of Ahrland *et al.*,[11] log β_1 8.15, log β_2 14.10, and log β_3 19.50 determined at $I = 0.1$ mol dm^{-3}, were used for the derivation of values of $\Delta H^{\ominus}$ from the calorimetric data in Table 3, which was also determined at $I = 0.1$ mol dm^{-3}. The poor solubility of the sodium and potassium salts of dbs prevented the use of 0.5 mol dm^{-3} background electrolyte. The titrations were made by adding metal-ion solution to a solution of the ligand, a procedure that favours the formation of the higher complexes. It was necessary to include a fourth complex, $[AgL_4]^{3-}$, in the calculations in order to produce a good fit to the calorimetric data. The stability constant for this complex was treated as an adjustable parameter, giving a

---

[19] V. B. Spivakovskii and L. P. Moisa, *Zhur. neorg. Khim.*, 1964, **9**, 2287.

[20] S. Hietanen and L. G. Sillén, *Acta Chem. Scand.*, 1952, **6**, 747.

[21] R. Fischer and J. Byé, *Bull. Soc. chim. France*, 1964, 2920.

[22] R. Arnek and W. Kakolowicz, *Acta Chem. Scand.*, 1967, **21**, 2180.

[23] R. Arnek and W. Kakolowicz, *Acta Chem. Scand.*, 1967, **21**, 1449.

[24] V. P. Vasil'ev and G. A. Lobanov, *Zhur. fiz. Khim.*, 1967, **41**, 838.

[25] A. Jonsson, I. Qvarfort, and L. G. Sillén, *Acta Chem. Scand.*, 1947, **1**, 461.

value of log β_4 23.3 ± 0.9. The stability constants and the thermodynamic properties of complex formation are given in Table 4.

Mercury(II) *and Sodium* 4-(*Diphenylphosphino*)*benzenesulphonate*.—The stability constants of Salvesen and Bjerrum,[26] determined at $I = 1$ mol dm^{-3}, were corrected to $I = 0.1$ mol dm^{-3} with the use of an extended Debye–Hückel equation,[27] and were used for the derivation of values of $\Delta H^{\ominus}$ from the calorimetric titration data in Table 3 to give the thermodynamic properties of complex formation (Table 4).

TABLE 4

Stability constants, β_i, together with the free energies $\Delta G_i^{\ominus}$, enthalpies $\Delta H_i^{\ominus}$, and entropies (expressed as the entropy contributions to the free energy of complex formation, $T\Delta S_i^{\ominus}$) of complex formation of the metal M with ligand L at 298.15 K and the ionic strength indicated

Metal	Ligand	I / mol dm^{-3}	Complex	log β	$\Delta G^{\ominus}$ / kJ mol^{-1}	$\Delta H_i^{\ominus}$ / kJ mol^{-1}	$T\Delta S_i^{\ominus}$ / kJ mol^{-1}
Ag	dbs	0.1	[AgL]	8.15	−46.5	−71 ± 3	−25 ± 3
			$[AgL_2]^-$	14.10	−80.5	−131.6	−50 ± 6
			$[AgL_3]^{2-}$	19.50	−111.3	−195 ± 6	−84 ± 6
			$[AgL_4]^{3-}$	23.3 ± 0.9	−133 ± 5	−225 ± 9	−92 ± 10
Hg	dbs	0.1	$[HgL]^+$	14.5 *	−82.8	−86 ± 10	−3 ± 10
			$[HgL_2]$	24.8 *	−141.6	−174 ± 12	−32 ± 12
			$[HgL_3]^-$	29.9 *	−170.7	−217 ± 16	−46 ± 16
			$[HgL_4]^{2-}$	33.2 *	−189.5	−236 ± 35	−47 ± 35
Ag	tsa	0.5	$[AgL]^{2-}$	4.96 ± 0.03	−28.3 ± 0.2	−31 ± 2	−3 ± 2
			$[AgL_2]^{5-}$	6.7 ± 0.3	−38 ± 2	−48 ± 9	−10 ± 9
Hg	tsa	0.5	$[HgL]^-$	9.3 ± 0.1	−53.1 ± 0.6	−43 ± 12	10 ± 12
			$[HgL_2]^{4-}$	14.36 ± 0.06	−82.0 ± 0.3	−73 ± 16	9 ± 16
			$[HgL_3]^{7-}$	17.0 ± 0.3	−97.0 ± 2		

* Results of Salvesen and Bjerrum,[26] corrected to $I = 0.1$ mol dm^{-3} as described in the text.

Silver(I) *and the Trisodium Salt of Tris*(3-*sulphophenyl*)-*arsine*.—The only reported stability constant[11] for this system is log β_1 5.36 obtained at 298.15 K and $I = 0.2$ mol dm^{-3}. The Ag(I) electrode used for that determination dissolved at high ratios of ligand to metal, with the result that determination of the higher stability constants was not possible. In this study a silver-wire electrode was used, oxygen being carefully flushed out from the system before the ligand solution was brought into contact with the electrode. The potentials obtained were steady to 0.2 mV and were independent of the stirring rate, indicating no chemical process at the electrode and therefore no dissolution of the electrode. The stability constants and the thermodynamic properties of complex formation are given in Table 4.

The absence of any complexes with a co-ordination number greater than two can probably be attributed to the unfavourable energetics of packing eight or more negative charges on to one anion. The large changes in charge that occur in the reaction $Ag^+ + L^{3-} \rightleftharpoons [AgL]^{2-}$ would be expected to lead to a marked dependence of log β on the ionic strength. This may account for the discrepancy between the experimentally determined value of log β_1 4.96 ± 0.03 and the value (log β_1 5.36) reported by Ahrland *et al.*[11]

Mercury(II) *and the Trisodium Salt of Tris*(3-*sulphophenyl*)-*arsine*.—The potentiometric data for this system were consistent with the formation of only three complexes: $[HgL]^-$, $[HgL_2]^{4-}$, and $[HgL_3]^{7-}$. The absence of a fourth complex, $[HgL_4]^{10-}$, is probably due to charge repulsion making complex formation energetically unfavourable. The stability constants and thermodynamic properties of complex formation are given in Table 4.

DISCUSSION

In Figure 2 the $\Delta H_2^{\ominus}$ values for Ag^I and Hg^{II} have been plotted on the same diagram as the l.f.e.r. for complex formation of soft-donor ligand $[ML_2]$ complexes. Both enthalpy and free-energy changes on complex formation are expressed as kJ mol^{-1}. For the sake of simplicity, ligands for which the enthalpy change on complex formation was not determined are omitted from Figure 2. It is interesting to note that, with the exception of points 2 and 7, a l.e.r. exists. However, much more striking is the fact that, unlike the l.f.e.r., the l.e.r. does not pass through the origin of the diagram, but runs very nearly parallel to the l.f.e.r. with an intercept on the Ag-axis. For an explanation of this behaviour one must turn to models of the partial molar entropy of complexes in aqueous solution proposed by Cobble.[28]

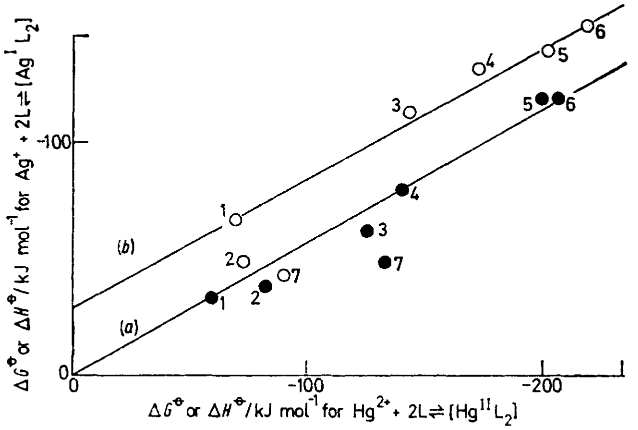

FIGURE 2 Linear free-energy (*a*) and linear enthalpy relations (*b*) between the free energies and enthalpies of formation of $[Hg^{II}L_2]$ complexes and the free energies and enthalpies, respectively, of formation of the analogous $[Ag^IL_2]$ complexes. L = Thiodiglycol (1), tsa (2), thiourea (3), dbs (4), CN^- (5), $HOCH_2CH_2PEt_2$ (6), and SO_3^{2-} (7)

---

[26] B. Salvesen and J. Bjerrum, *Acta Chem. Scand.*, 1962, **16**, 735.

[27] C. I. Nyman and T. Salazar, *Analyt. Chem.*, 1961, **33**, 1467.

[28] J. W. Cobble, *J. Chem. Phys.*, 1953, **21**, 1451.

The semi-empirical equation (1) was proposed where $\bar{S}^0$ is the partial molar entropy of the complex in solution,

$$\bar{S}^0 = 42 + (3/2R)\ln W + 38.5N - S_s{}^0 - 0.92\ V_n \quad (1)$$

W is the molecular weight of the complex, N is the number of skeletal atoms (*i.e.* hydrogen atoms are not counted), $\bar{S}_s{}^0$ is a structural factor to take into account double bonds, rings, *etc.*, and V_n is the molar volume of the complex. This equation has a fair degree of success in the prediction of partial molar entropies of complexes of neutral ligands in aqueous solution. The basic assumption made by Cobble in the development of this equation is that the charge on the central metal ion is effectively shielded from the solvent when the central metal ion is surrounded by neutral ligands. Examination of equation (1) shows that, for two analogous complexes of a pair of metal ions such as Ag^I and Hg^{II}, the only differences in $\bar{S}^0$ will arise in the $(3/2R)\ln W$ and $0.92V_n$ terms. The way in which the latter term is estimated[28] depends on the mass of the central metal ion. Even so, with bulky ligands, both of these terms combined give rise to only a relatively small difference in $\bar{S}^0$. Thus, in the complex formation (2) where x water molecules are displaced by n neutral ligands, if

$$M^{y+} + nL \longrightarrow [ML_n]^{y+} + x\ H_2O \quad (2)$$

x has the same value for $M = Ag^I$ and Hg^{II} then the difference in $\Delta\bar{S}^\ominus$ for both complex formations must be given, largely, by the difference in $\bar{S}^0$ between the two metal ions. With the use of equation (1), it has been shown[7] that, for the neutral ligands thiodiglycol and thiourea, both Hg^{II} and Ag^I do give the same value of x for a given value of n. It can also be shown that, for ligands of intermediate size, $\bar{S}^0$ for mercury(II) complexes should be *ca.* 28 J K^{-1} mol^{-1} larger than for the analogous complex of Ag^I. Values of $\bar{S}^0$ for $Ag^+(aq)$ and $Hg^{2+}(aq)$ have been reported[29] as +73.93 and −22.58 J K^{-1} mol^{-1} respectively which gives a difference of 28.7 kJ mol^{-1} in $T\Delta S^\ominus$. The intercept on the Ag^I axis, which should approximate the difference in $T\Delta S^\ominus$ for formation of analogous complexes of Ag^I and Hg^{II}, has a value of 29 kJ mol^{-1}. If the difference of 8.4 kJ mol^{-1} in $T\Delta S^\ominus$ predicted by equation (1) for analogous complexes of Ag^I and Hg^{II} is neglected, the agreement between the predicted and observed value of the intercept on the Ag^I axis is excellent, considering it to represent only the difference in $\bar{S}^0$ for $Ag^+(aq)$ and $Hg^{2+}(aq)$. Addition of the 8.4 kJ mol^{-1} predicted by equation (1) somewhat worsens the agreement. The significance of this is probably that the intercept at 29 kJ mol^{-1} is smaller than the value of 28.7 + 8.4 = 37.1 kJ mol^{-1}, since in the complexes of Ag^I and Hg^{II} under consideration Cobble's requirement that the charge on the metal ion is shielded from the solvent is not fully met. This is discussed more fully below.

The intercept on the Ag^I axis implies that the enthalpy changes on complex formation of Ag^I are more favourable by *ca.* 29 kJ mol^{-1} than would be expected. The extra stabilization in the enthalpy change for silver(I) complexes is cancelled by the fact that the entropy changes on formation of the analogous mercury(II) complexes are more favourable by *ca.* 29 kJ mol^{-1}, thereby permitting the l.f.e.r. to pass through the origin of the diagram. Linear free-energy relations commonly pass through the origin of the diagram, so that this cancellation of enthalpy and entropy change must be common to all such l.f.e.r. It is somewhat difficult to see why this exact cancellation should occur. If we consider the entropy, it seems clear that the constant difference is related to the stronger solvation of $Hg^{2+}(aq)$. The problem, then, is why $\Delta H^\ominus$ for the silver(I) complexes is 29 kJ mol^{-1} more favourable than expected. The enthalpy of formation of the Ag–L bond might simply be more favourable than expected by this constant amount. However, it seems more likely that this constancy should be related to the same process in the two complex formations that causes the entropy contributions to be more favourable for Hg, *i.e.* desolvation of the metal ion. Thus comparison of Hg^{II} with Ag^I shows that the complex formations of Hg^{II} have a more favourable entropy of desolvation because of the stronger solvation of Hg^{II}. However, this stronger solvation produces a less favourable enthalpy contribution from desolvation, so that the free-energy change on complex formation is smaller and counterbalances the entropy contribution.

In Figure 3, the free-energy and enthalpy changes have been plotted for the formation of complexes [ML] of Hg^{II} and Ag^I with soft-donor ligands. With so few points, it cannot be said that the existence of a l.e.r. is established. However, if a l.e.r. does exist, it does not appear to run even approximately parallel to the l.f.e.r., nor to have an intercept at 29 kJ mol^{-1}. This probably arises from the fact that the [ML] complexes are very much further than the $[ML_2]$ complexes from the requirement of (1) that the charge on the metal ion should be effectively shielded from the solvent. In fact, for most

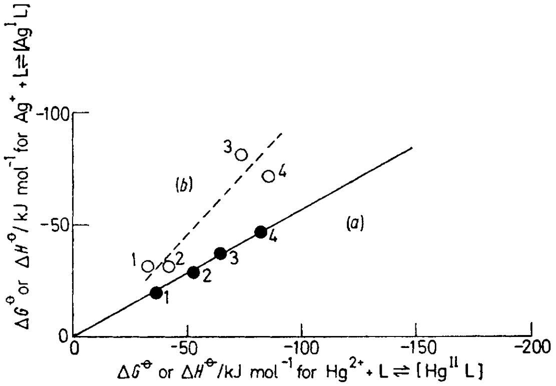

FIGURE 3 Linear free-energy (*a*) and linear enthalpy relations (*b*) between the free energies and enthalpies of formation of $[Hg^{II}L]$ complexes and the free energies and enthalpies of formation, respectively, of the analogous $[Ag^IL]$ complexes. For nature of L see Figure 2

---

[29] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, 1951, **19**, 1139.

l.f.e.r.s, comparisons are made between log K_1 values for pairs of metal ions, and will, therefore, be very far from the requirements of equation (1), so that the intercept observed on one or other axis will not be the difference between the entropies of the two metal ions, but a much smaller value.

Of course, most of the ligands in Figure 2 are charged, so that they would not necessarily be expected to have the same intercepts as those suggested by equation (1). All the same, all the ligands having charges of only 1— appear to fall on the l.e.r. but ligands such as sulphite and tsa, having charges of 2— and 3— respectively, do not. With the arsine ligand it appears that the very high charges that result on the complex have produced an unfavourable enthalpy contribution for the metal ion bearing the smaller positive charge, namely Ag^I. The same appears to be true for sulphite, with an additional difference that it appears to be different in its bonding characteristics from other sulphur-donor ligands, being higher in the spectrochemical series than ammonia.[30] Thus, the point for this ligand is also considerably displaced from the l.f.e.r., as well as from the l.e.r.

The relation between the l.e.r. and l.f.e.r. in Figure 2 implies that a linear entropy-change relation between $[ML_2]$ complexes of Ag^I and Hg^{II} will be observed with a gradient of unity and intercept of 124 J K^{-1}. This will be discussed more fully in a future paper. However, it is of interest to point out at this stage that, even though equation (1) does not predict the entropies of complexes of charged ligands correctly, it seems that the difference in $\Delta S^{\ominus}$ implied by equation (1) for complexes of Hg^{II} and Ag^I with neutral ligands is also found for complexes of charged ligands, as seen in Figure 3, except when the charge on the ligand is very high as for tsa.

This paper is published by permission of the Director General of the National Institute for Metallurgy.

[6/411 *Received, 1st March, 1976*]

---

[30] C. K. Jørgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' 2nd edn., Pergamon, Oxford, 1964, p. 109.