

**THERMODYNAMIC RELATIONSHIPS OF COMPLEX FORMATION.
Part I. Non-linear free energy relationships (NLFER) in Ag(I) complex
formation in aqueous solutions ***

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ABSTRACT

The free energy changes for Ag(I) single and mixed ligand complex formation in water solution at $T = 25^\circ\text{C}$ and ionic strength $\mu = 1$ for KNO_3 has been examined.

Ionic charges of both the substratum and ligand in the reaction $\text{Sub} + \text{L} = \text{Sub-L}$ do not play the most prominent role in driving the formation of these complexes in the investigated medium.

The mutual substratum-to-ligand chemical affinity depends of course on the nature of the central ion and the ligand but also on the nature of their chemical environment. The already coordinated ligand (ligands) modify the ability of the central ion to form further coordinative bonds in inverse ratio to the overall thermodynamic stability of the substratum.

On these bases, the occurrence of Non-Linear Free Energy Relationships are postulated.

This paper presents some conclusions following the author's extensive research on the thermodynamics of Ag(I) complex formation with two and three different ligands [1–7]. The results presented here are not intended to be definitive and many questions remain. In spite of this the conclusions are sufficiently interesting to present them here with the principles on which they are based. This may stimulate further research and theoretical contributions in the same directions.

In water solution, the investigated metal ion, Ag(I), has a typical soft behaviour, but the ligands (see Table 1) encompass a very large range of softness from the very soft thiosulphate ion to the hard chloride or ammonia [8,9].

The three-ligand systems were such that the Ag(I) species formed remained in solution. This is accomplished by the presence of one or two ligands which form soluble complexes with Ag(I) (thiourea and/or thio-

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TABLE 1

Investigated ligands arranged in three-ligand systems for the complex formation with Ag(I) in water solution at various temperatures and ionic strength = 1 for KNO₃

Ligands:		
Thiourea (Tu)	Thiosulphate (Ts)	Thiocyanate (Tcy)
Chloride	Bromide	Iodide
Ammonia		
Three-ligand systems:		
Thiourea-thiosulphate-X (X = thiocyanate, chloride, bromide, iodide)		
Thiourea-thiocyanate-X (X = Chloride, bromide, iodide)		
Thiosulphate-thiocyanate-ammonia		

sulphate ion in the present case). Hence the identified chemical equilibria refer to complex formation in a homogeneous (solution) phase. The data for the reactions $\text{Ag(I)} + \text{X} = \text{AgX}$ (X = halides or thiocyanate) are pertinent to AgX in solution and do not refer to the solubility-product-controlled solid-solution equilibria.

The complex formation was studied by potentiometry. The ionic strength, μ , was adjusted to 1 by KNO₃. The free energy data are interpolated from original values within the temperature range 0–50°C. More details on the experimental conditions and procedures can be found in earlier papers.

From the results of the investigation, free energy relationships for about 25–30 reaction series of Ag(I) complex substrata with different pairs of ligands can be evaluated for both coordination or displacement reactions. In these series, linear (or roughly linear) conditions are met and they can be interpreted in the traditional way.

A detailed analysis of the free energy data suggests the existence of Non-Linear Free Energy Relationships (NLFER). This is also supported by a priori considerations on the mutual dependence of the free energy changes on the thermodynamic stability of the reacting substrata for ligand coordination reactions.

Figure 1 shows the affinity sequence ($-\Delta G$) at $T = 25^\circ\text{C}$ and $\mu = 1$ between Ag(I) and the various ligands in the 1:1 = Ag(I):L complex formation reactions. As previously stated, the data refer to homogeneous reactions. The ordinate indicates the free energy changes (kcal mol^{-1}) for the reactions $\text{Ag(I)} + \text{X} = \text{AgX}$ (here after charges are omitted). The abscissa is a discrete (not continuous) variable arranged in decreasing affinity order.

At 25°C, iodide is the most strongly interacting ligand amongst those investigated, followed by thiosulphate ion, thiourea, Chloride closes the sequence at the opposite end with its affinity for Ag(I) slightly lower than that of NH₃. Iodide and chloride, at either end of the sequence, encompass singly charged (bromide, thiocyanate), doubly charged (thiosulphate) and neutral (thiourea, ammonia) ligands in random order with respect to the

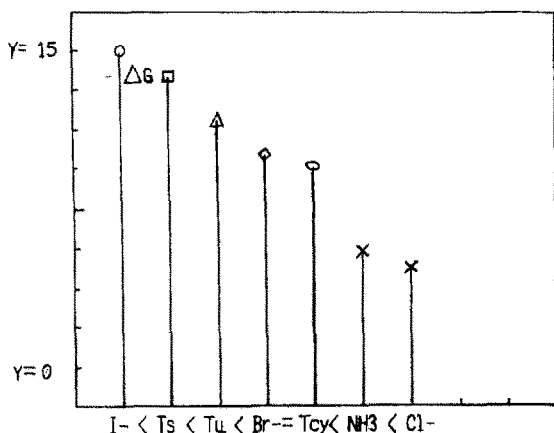


Fig. 1. Free energy changes (kcal mol^{-1}) for the homogeneous reaction $\text{Ag(I)} + \text{X} = \text{AgX}$ in aqueous solution at ionic strength $\mu = 1$ for KNO_3 and $T = 25^\circ \text{C}$.

ionic charge. The strongest interacting, the singly charged ligand I^- , is followed by $\text{S}_2\text{O}_3^{2-}$ and then by a neutral ligand (thiourea). In other words, the uniform increase in the free energy changes is not accompanied by a regular change in the ionic charges of the ligands, although the substratum (Ag(I)) remains constant within the series. It is obvious that the affinity sequence cannot be easily explained in terms of the ionic charge of the reacting ligand.

The abscissa sequence in Fig. 1 is very important in the following analysis.

When coordinated substrata interact with the entering groups, the mutual chemical affinities between the central ion and the incoming ligand are lower, except in some cases [10], than between the "free" (solvated) ion and the same ligand. How the mutual substratum-to-ligand chemical affinity alters as a consequence of changes in the coordination sphere of the substratum is a question which embraces both qualitative (the model and the conditions under which it occurs) and quantitative aspects (how much the affinity is changed as an immediate consequence of the characterization of the model).

Figure 2 shows the stability sequence for reactions of variously monocoordinated substrata interacting with thiosulphate ion. The series is characterized by the same entering group but has different singly coordinated Ag(I) substrata. The ligand in the coordination sphere of the reactant Ag(I) complexes can be used to identify the term of the series; this is shown on the abscissa of Fig. 2 (in Fig. 1, the abscissa refers to the entering ligand). Iodide (chloride) ion, with the highest (lowest) chemical affinity toward the solvated Ag(I) of the ligands investigated, has a negative effect on the affinity of Ag(I) substrata towards thiosulphate ion as second entering group: the effect is highest for iodide and lowest for chloride. The free energy changes for the

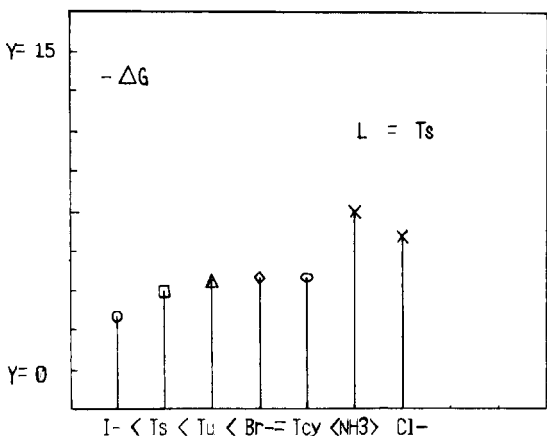


Fig. 2. Free energy changes (kcal mol⁻¹) for the homogeneous reaction between monocoordinated AgX substrata and thiosulphate as entering ligand ($\mu = 1$ for KNO₃; $T = 25^\circ\text{C}$).

reactions $\text{AgX} + \text{Ts} = \text{XAgTs}$ depend on the coordinated ligand X and the affinity of the monocoordinated substrata toward thiosulphate ion and are lower with higher thermodynamic stability of the substratum ($-\Delta G$ according to the reaction $\text{Ag(I)} + \text{X} = \text{AgX}$). The affinity sequence of monocoordinated substrata for thiosulphate shows that the more strongly the solvated Ag(I) interacts with X, the weaker the affinity of AgX toward thiosulphate; the substratum sequence (expressed in terms of coordinated ligand (Fig. 2)) is exactly the reverse of that of solvated Ag(I) toward the ligand X in the reaction $\text{Ag(I)} + \text{X} = \text{AgX}$ (Fig. 1). The trend in Fig. 2 is asymptotic and cannot be rationalised in a simple way on the basis of the ionic charges of the substrata. In fact the steady increase of the monocoordinated substratum-to-ligand affinity ($\text{AgI} < \text{AgTs} < \text{AgTu} < \text{AgBr} < \text{AgTcy} < \text{AgCl} < \text{AgNH}_3$) does not correspond to any trend in the charge of the substratum ($0 > -1 < +1 > 0 = 0 < 0 < +1$).

The general behaviour of the above-considered reactions and, in particular, the sequence of the singly coordinated substrata ligands, remain essentially unaltered when the entering group is changed, as is shown in Figs. 3–6 which refer to the reaction series of monocoordinated substrata with thiourea (Fig. 3), iodide (Fig. 4), bromide (Fig. 5) and thiocyanate (Fig. 6) as the second entering group. Obviously Figs. 2–6 differ for the affinity of the single complex toward the respective incoming group.

So far, the behaviour of monocoordinated complexes toward single incoming ligands have been analysed with respect to the relationship between the stability of the substrata and the ionic charge of both the substrata and the incoming ligand.

For dicoordinated substrata, the general behaviour is essentially the same. Figure 7 shows the chemical affinity of solvated Ag(I) towards pairs of ligands (the overall thermodynamic stability of dicoordinated complexes

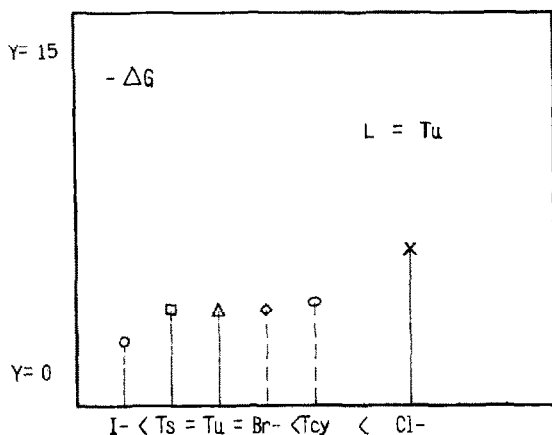


Fig. 3. Free energy changes (kcal mol^{-1}) for the homogeneous reaction between monocoordinated AgX substrata and thiourea as entering ligand ($\mu = 1$ for KNO_3 ; $T = 25^\circ\text{C}$).

with both the same or different ligands). The figure corresponds to Fig. 1 and the pairs of entering ligands are arranged (as in Fig. 1) according to the decreasing affinity of the pairs toward the central ion.

Considering the first three pairs from left to right ((I^-, Tu) , (Ts, Tu) and (Tu, Tu)) with the same ligand (Tu), the overall thermodynamic stability increases as the affinity of the variable ligand of the pair (in this case I^- , Ts and Tu) increases. For the other pair, two of them ((Tcy, Ts) and (Tcy, Tcy)) follow this behaviour. $(\text{Tcy}, \text{NH}_3)$, however, falls out of sequence, showing more affinity than (Tcy, Tcy) although $\text{NH}_3 > \text{Tcy}$ (see Fig. 1). These results suggest that the stability sequence for the simultaneous coordination of two

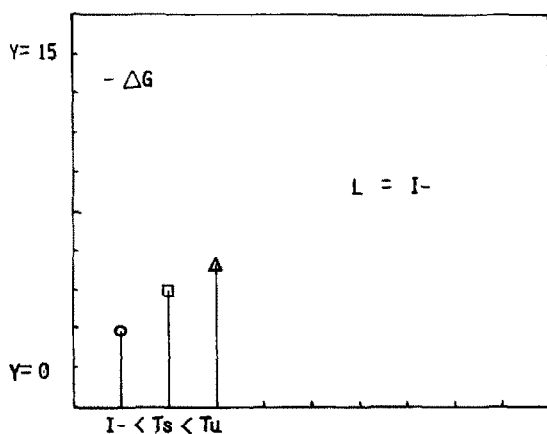


Fig. 4. Free energy changes (kcal mol^{-1}) for the homogeneous reaction between monocoordinated AgX substrata and iodide as entering ligand ($\mu = 1$ for KNO_3 ; $T = 25^\circ\text{C}$).

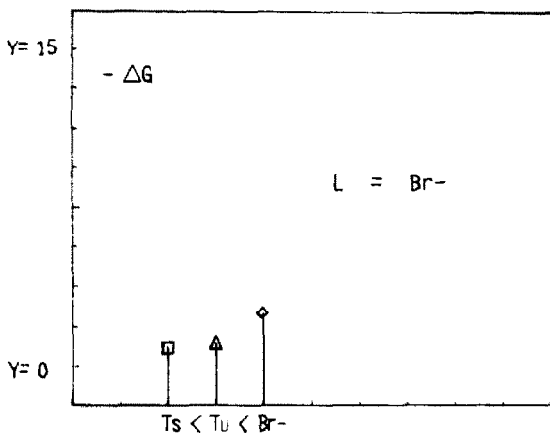


Fig. 5. Free energy changes (kcal mol^{-1}) for the homogeneous reaction between monocoordinated AgX substrata and bromide as entering ligand ($\mu = 1$ for KNO_3 ; $T = 25^\circ \text{C}$).

ligands can follow (with exceptions) from the sequence for single ligand coordination by a direct additive non-linear rule.

Once more the charge-charge interactions in solution are not the straightforward driving force in the complex formation. When a dicoordinated substratum interacts with a ligand, the interactions are weaker (stronger), the stronger (weaker) the simultaneous affinity of the solvated Ag(I) toward both coordinated ligands, independent of the ionic charge of the substratum and the entering ligand. This is demonstrated in Fig. 8 which refers to Ts as reacting ligand with dicoordinated substrata.

It is clear that, at least for the system examined in this paper in water solution, the ionic charges of both the substratum and incoming ligand are

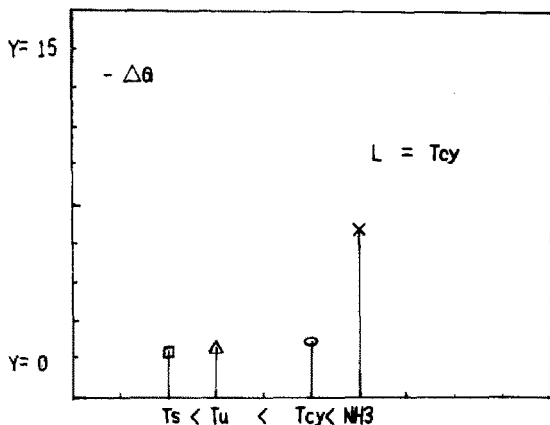


Fig. 6. Free energy changes (kcal mol^{-1}) for the homogeneous reaction between monocoordinated AgX substrata and thiocyanate as entering ligand ($\mu = 1$ for KNO_3 ; $T = 25^\circ \text{C}$).

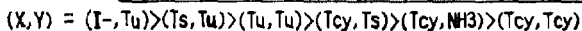
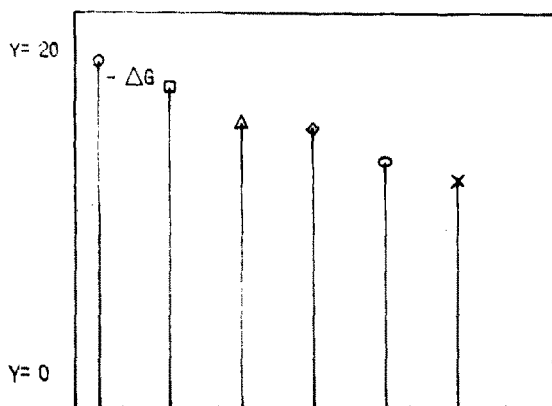


Fig. 7. Free energy changes (kcal mol^{-1}) for the homogeneous reaction $\text{Ag(I)} + X + Y = \text{AgX}_y$ in water solution ($\mu = 1$ for KNO_3 , and $T = 25^\circ\text{C}$).

not directly responsible in determining the complex formation. Charge effects in solution are mediated by the solvent medium and point charges, comparable to insulated cations or anions, are enveloped by coordinating solvent molecules in successive coordination spheres [11,12]. Moreover, the extent of a chemical reaction depends on the chemical environments of the reacting centres of the reaction partners.

Figures 2–6 and 8 also demonstrate that the free energy changes for single ligand coordination depend on the overall thermodynamic stability of both the substratum and the ligand. The greater the overall stability of the substratum, the lower its affinity toward the entering ligand. Moreover, the lower its affinity toward an entering ligand the less the free energy change

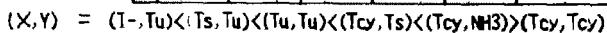
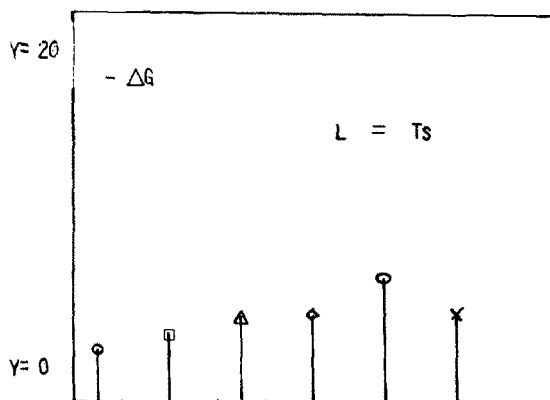


Fig. 8. Free energy changes (kcal mol^{-1}) for the homogeneous reaction between dicoordinated AgX substrata and thiosulphate as entering ligand ($\mu = 1$ for KNO_3 ; $T = 25^\circ\text{C}$).

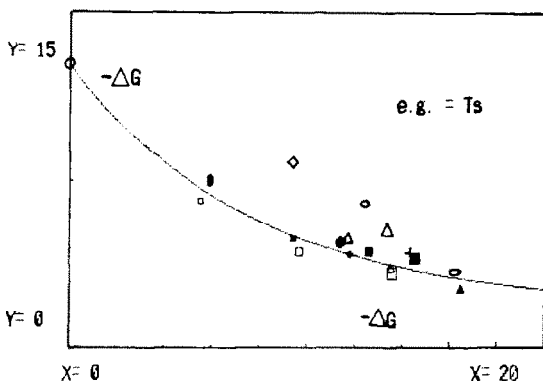


Fig. 9. Relationship between the stepwise free energy change for the coordination reaction of thiosulphate ion to Ag(I) free, single coordinated substrata or dicoordinated substrata and their overall stability in aqueous solution ($\mu=1$ for KNO_3 ; $T=25^\circ\text{C}$).

for single further coordination can be modified. This holds for both mono- and dicoordinated substrata, independent of their ionic charges, and is also true going from monocoordinated to dicoordinated complexes and leads to an exponential model for the relationships between the affinities toward an entering group (the step-wise free energy change) and the overall stability of the reacting substrata (model: $y = A + B \exp(-Cx)$; $y = -\Delta G$ for the reaction $\text{AgX}_i\text{Y}_j + \text{Z} = \text{AgX}_i\text{Y}_j\text{Z}$; $x = -\Delta G$ for the reaction $\text{Ag(I)} + i\text{X} + j\text{Y} = \text{AgX}_i\text{Y}_j$).

Figures 9–11 shows the relationships between the affinities of the substrata, both monocoordinated and dicoordinated, toward thiosulphate, thiourea and thiocyanate, respectively, as incoming ligand versus the overall stabilities of the substrata. The lines drawn were deduced by non-linear

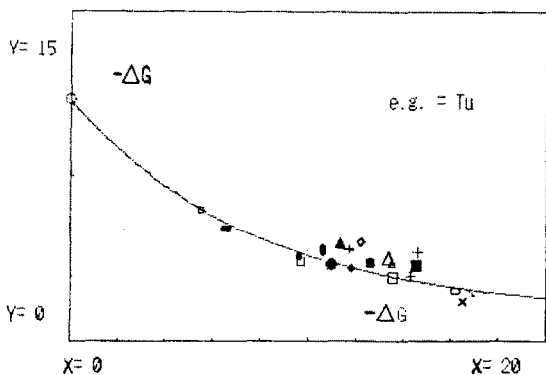


Fig. 10. Relationship between the stepwise free energy change for the coordination reaction of thiourea ion to Ag(I) free, single coordinated substrata or dicoordinated substrata and their overall stability in aqueous solution ($\mu=1$ for KNO_3 ; $T=25^\circ\text{C}$).

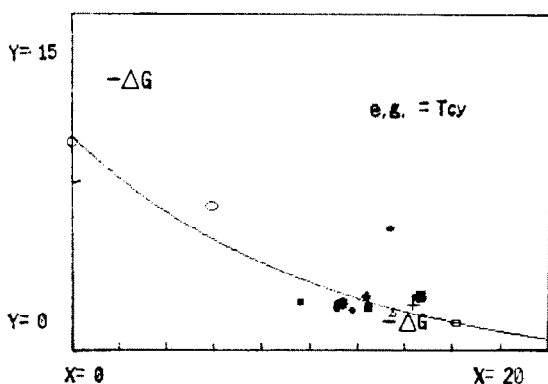


Fig. 11. Relationship between the stepwise free energy change for the coordination reaction of thiocyanate ion to Ag(I) free, single coordinated substrata or dicoordinated substrata and their overall stability in aqueous solution ($\mu = 1$ for KNO_3 ; $T = 25^\circ\text{C}$).

least-squares fitting of the exponential model on the experimental (y, x) points. The other ligands as entering groups have comparable behaviours.

Figures 9–11 clearly substantiate the hypothesis that Non-Linear Free Energy Relationships occur. At the same time, deficiencies are immediately evident in the pattern of the data concerning Ag(I) substrata with both very weak and very strong ligands. The first set of data is necessary for an improvement in the parameter C and the other is necessary to better define the horizontal asymptote A .

The results of the exponential regressions are collected in Table 2. From the above discussion and, in some cases, for a number of experimental points, the numerical values of the parameters may undergo changes with an improvement in the regression. More important than the numerical values of the parameters are their meanings and, in particular, the meaning of the

TABLE 2

Values of the parameters calculated with non-linear least-squares fitting on the experimental free energy data for the model $y = A + B \exp(-Cx)$ ($y = -\Delta G$ for the step-wise coordination of the entering group; $x = -\Delta G$ for the overall formation of the substratum) at 25°C and ionic strength = 1 for KNO_3

Entering group	I^a	A (kcal mol $^{-1}$)	B (kcal mol $^{-1}$)	C (mol kcal $^{-1}$)
Thiourea	21	1.279 ± 1.28	9.613 ± 1.34	0.128 ± 0.046
Thiosulphate	15	1.808 ± 0.9	10.801 ± 0.9	0.128 ± 0.029
Thiocyanate	13	-1.125 ± 3.4	10.713 ± 3	0.094 ± 0.06
Chloride	7	0.313 ± 0.3	5.200 ± 0.5	0.364 ± 0.15
Bromide	7	-1.561 ± 0.6	8.143 ± 0.8	0.226 ± 0.08
Iodide	6	-11.177 ± 15	24.689 ± 15	0.004 ± 0.03
Ammonia	5	-28.24 ± 257	34.76 ± 256	0.009 ± 0.07

^a I = number of experimental points.

parameters A and C which are, respectively, the asymptotic and exponential parameters of the regression line. A is given by the difference between the free energy states of the entering and leaving group plus a constant (or null) term. This means that when the central ion is strongly complexed but coordinatively unsaturated, the driving force for the coordination of one more ligand mainly depends on the incoming and leaving group in their solvated states. For the coordination reaction series $\text{Sub} + \text{X} = \text{Sub-X}$ in solution, as in the cases considered here, the leaving group is the coordinated solvent which is ejected from both the substratum and the ligand solvation spheres. C , the exponential parameter, relates to the substratum-to-ligand interactions. When the interactions depend largely on the ligand, the relationship is rather flat and C is low in value; however, when the interactions mainly depend on the nature of the reacting substratum, C assumes high values.

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