ON THE THERMOCHEMISTRY OF STEPWISE COMPLEX FORMATION

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If a metal ion, M, can bind n ligands, A, to form a complex, MA_n, this complex is, if $n > 1$, always built up by stepwise reactions. All the species MA_j, $0 \leqslant j \leqslant n$, exist in equilibrium with each other. At a given concentration of free ligand the metal is distributed over all the species in a way which depends only on the equilibrium constants. In many systems even the maximum concentration of an intermediate species is less than 50 per cent of the total concentration of M. This means that, if an aqueous solution of a simple salt, say a perchlorate, is mixed with a solution containing a ligand, the resulting mixture will contain a whole series of complex species besides the starting components. It is, therefore, convenient to perform a calorimetric study of the formation of the complex by means of titrations. The heat evolved at each step in such a titration is the sum of the heats of several reactions, all of which are often far from quantitative. Such a titration calorimeter has been built by Sillén's group in Stockholm[1] and a similar one has been used in Lund[2]. The heat of reaction for each step of formation of the complex can be computed by simple graphical methods (see, *e.g.*, ref. 3) or by some least square method, for which a high speed computer must be used (Sillén *et al.*[4]). Generally, the calorimetric studies have been performed on systems for which the stability constants have been previously determined by equilibrium studies. The standard free energy change for each step is then known from the equation:

$$-\Delta G_j^\circ = RT \ln k_j \tag{1}$$

where:

$$k_j \leqslant \frac{[MA_j]}{[MA_{j-1}]\,[A]} \tag{2}$$

in solutions with constant activity factors. The well-known connection between enthalpy, free energy and entropy may be written:

$$-\Delta G_j^\circ = -\Delta H_j^\circ + T \cdot \Delta S_j^\circ \tag{3}$$

Complex formation is favoured by large positive values of $-\Delta G_j^\circ$. Hence, large values of $-\Delta H_j$, *i.e.* highly exothermic reactions, and large values of $T \cdot \Delta S_j^\circ$ favour formation of the complex. For a reaction at constant temperature and pressure in a condensed system there are some difficulties in interpreting the enthalpy and entropy terms if we try to connect them with simple models of the reaction between the metal ion and the ligands. In spite of this, a crude approach will be made below, where results from some complex formation reactions are compared.

Metal ions in aqueous solutions are hydrated. This means that some water molecules are bound closely around the metal ion in an inner sphere, so that they form, for example, the corners of a regular octahedron. In an outer sphere a cloud of further water molecules (an "iceberg" in the nomenclature of Frank and Evans[5]) is held in a more-or-less ordered structure by the influence of the charge on the metal ion. Especially if the charge is large, this cloud, with a more orderly arrangement of its water molecules than in bulk water, could be rather extensive. In a reaction between such a hydrated metal ion and a ligand to yield a complex, one or more water molecules are expelled from the inner shell and are replaced by the ligand. It would also be expected that the number of water molecules in the outer sphere would decrease, especially if the ligand is negatively charged so that the charge of the complex becomes smaller than that of the metal ion.

The approach in comparing enthalpy values should then be that $-\Delta H_j{}^\circ$ could be regarded as a measure of the difference between the energy gained from the binding of a ligand to a metal ion, and the energy lost by breaking bonds between the metal ion and water molecules in the inner and outer hydration sphere.

When discussing the entropy and the free energy terms we must first of all remember that these depend on the formulation of the law of mass action. Let us consider the first step in the complex formation (charges omitted):

$$M(H_2O)_x + A(H_2O)_y \rightleftharpoons MA(H_2O)_z + (x + y - z)H_2O \qquad (4)$$

The mass action law for this reaction is often written as in equation (2) ($j = 1$) with concentrations in M. This means that the activity of water is put equal to 1. This results in a cratic part[6] in both the entropy and the free energy term depending on the different standard states of the solvent and the solutes. This cratic part corresponds to $R\cdot(x + y - z)$ ln 55·6 e.u. = 7·9 $(x + y - z)$ e.u. A comparison of different types of system is therefore difficult on account of the unknown number of water molecules liberated in the reaction.

In the following comparisons we shall regard hydrated metal ions with high charge as a source of positive entropy change for complex formation. This will result in large positive values of $\Delta S_1{}^\circ$, hence $\Delta S_j{}^\circ$ is smaller for the further steps. The reason for this is that the water cloud diminishes as formation of the complex proceeds.

The lanthanide series provides a unique possibility for comparison of thermodynamic functions for similar systems. Calorimetric studies of the whole lanthanide series (except Pm) have been carried out by Grenthe[7–9]. The discussions above and below are mostly collected from his papers.

A study of the entropy change is most interesting. In *Figure 1* $T\cdot\Delta S_1{}^\circ$ is shown for the first step of complex formation between acetate, diglycolate, dipicolinate and EDTA with lanthanides. In all cases the $T\cdot\Delta S_1{}^\circ$ has lower and approximately constant values for the lower atomic number elements of the series and higher and again about constant values for the higher atomic number elements. In the middle of the series there is a steep and steady increase in the entropy term. This shows that there is no simple connection between the steadily decreasing radius of the lanthanide ions and the thermodynamic functions. On the other hand this behaviour of the entropy change is in striking agreement with several other physical properties of the lanthanide

ions, *e.g.* molar volume, activity factors, heats of dilution *etc.*[10] which also divide the lanthanide ions into two separate groups. It thus seems as if the entropy change should have a distinct physical meaning. It is indeed tempting to try to connect it with changes in the structure of the water cloud of the metal ions occurring at some critical ionic radius, which happens to be that for a

Figure 1. $T\Delta S_1^\circ$ for the first step of complex formation of the lanthanide ions (and Y) with EDTA (x), dipicolinate (□), diglycollate (○) and acetate (△): 25°, 0·5 M $NaClO_4$

lanthanide ion somewhere in the middle of the series. It is also obvious from *Figure 1* that the entropy change is smallest for the monodentate acetate ion with the charge −1 and highest for the hexadentate EDTA ion with the charge −4, where all the entropy is exhausted in a single step. Other effects, which could be expected to appear in the entropy term would be translational effects and differences of vibration between free and bound ligands. For similar systems these effects should cancel out. Ligand field effects on the *f*-electrons are too small to be of importance. This is obvious from the fact that yttrium in all cases gives values of the entropy (and enthalpy) terms close to the values for, say, dysprosium, whose ionic radius is similar. Furthermore, no apparent loss in enthalpy is noticed for the gadolinium complexes.

The enthalpy change for the same system is shown in *Figure 2*. In the two

ranges where the entropy change is about constant, $-\Delta H_1{}^\circ$ increases slowly, when the atomic number of the lanthanide ion increases, *i.e.* as the radius decreases. According to our model this should mean a greater gain of enthalpy when the central ion has a small radius. In the middle of the series, where the entropy term increases, $-\Delta H_1{}^\circ$ drops rapidly (*Figure 2*). The reason

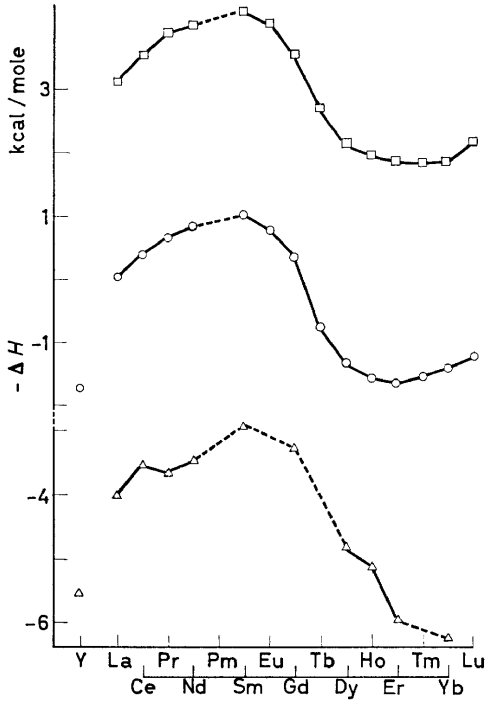

Figure 2. The enthlapy change $\Delta H_1{}^\circ$ for the complex formation of lanthanide ions (and Y) with dipicolinate (□) and diglycollate. For the corresponding acetate systems (△) $\Delta H_1{}^\circ + \Delta H_2{}^\circ$ is given; 25°, 0·5 M $NaClO_4$

for this is the great loss of energy on account of rearrangement and expulsion of water molecules from the hydration spheres. Such a counteraction of enthalpy and entropy effects seems to be rather general as can be seen from several of Grenthe's results[7–9]. At a first glance it seems rather astonishing that $-\Delta H_j{}^\circ > -\Delta H_1{}^\circ$ ($j > 1$) for the diglycolate and dipicolinate systems, since it would be expected that the binding of the first ligand to a metal ion would involve the gain of more energy than the last. The larger entropy term for the first step would mean, however, that much more energy is lost by loss of water at the first step than say at the third, and so the net result becomes $-\Delta H_j{}^\circ > -\Delta H_1{}^\circ$.

It is also seen in *Figures 1* and *2* how similar are both the entropy and enthalpy changes for the reactions, even though the ligands are quite dissimilar. This is an indication that it is the physical properties of the metal ions, which

mainly determine the variation of the thermodynamic functions within the lanthanide series.

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The stepwise complex formation between ammonia and metal ions proceeds according to the reaction:

$$\mathrm{Me}\,(\mathrm{H_2O})_x\,(\mathrm{NH_3})_j + \mathrm{NH_3} \rightleftharpoons \mathrm{Me}\,(\mathrm{H_2O})_y\,(\mathrm{NH_3})_{j+1} + (x-y)\mathrm{H_2O} \qquad (5)$$

Yatsimirskii[11] and co-workers have determined the enthalpy change for such reactions and the free energy change has also been determined by Bjerrum[12]. Some typical results are shown in *Table 1.* For nickel, copper and cadmium the

Table 1. $\Delta H_j°$ and $-\Delta G°$ for reaction 5 at 27°

	$-\Delta H_j°$ (kcal/mole)	$-\Delta G_1°$ (kcal/mole)	j
Ni^{2+}	3·5	3·6	1–6
Cu^{2+}	5·5	5·7	1–5
Cd^{2+}	3·5	3·6	1–6

enthalpy change is practically constant for all values of j. This could perhaps be expected for a complex formation up to the "characteristic coordination number" in Bjerrum's nomenclature ($n = 4$ for copper and cadmium, $n = 6$ for nickel), if the formation of the complex proceeds so that one water molecule is replaced by one ammonia molecule at each step without any other changes in the hydration sphere. Hence $x - y = 1$ in all the reactions. This is in accordance with the fact that $-\Delta H_1° = -\Delta G_1°$ (so there is no entropy change for the first step). From pure statistical reason $\Delta G_j°$ is expected to change for the following steps and since $-\Delta H_j°$ does not vary with j, $T{\cdot}\Delta S_j°$ decreases regularly for increasing j as much as $-\Delta G_j°$ decreases. Bjerrum[12] has expressed this by saying that there are only small residual effects in the free energy term for the stepwise formation of ammonia complexes as long as there are no serious changes in the structure of the complex, *i.e.* when the "characteristic coordination number" has not been exceeded. When the structure changes a comparison becomes complicated, *inter alia* because $x - y$ probably $\neq 1$, but it is perhaps a little surprising that $-\Delta H_j°$ now also remains constant.

The picture is similar for other uncharged ligands, such as ethylenediamine, even though $\Delta S_j° \neq 0$ in this case. Here we have probably a cratic effect, since a bidentate ligand such as ethylenediamine probably expels two water molecules so that the total number of particles is changed by the reaction.

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Other simple examples of complex formation are those between halide ions and metal ions. It has been pointed out[13, 14] that the metal ions may be

divided into two groups depending on the order of strength of their halide complexes. Halide systems have been extensively studied by Ahrland[15]. Most metal ions form their most stable halide complex with fluoride ions so that the strength decreases in the order $F^- \gg Cl^- > Br^- > I^-$. There is a minority of metal ions, however, found in a more or less triangular area in the periodic system, which form their strongest halide complexes with iodide ions[13, 14]. Examples of these metals are Cu(I), Ag, Hg(II), the platinum metals, Cd(II) and Tl.

Aluminium(III) and iron(III) are typical examples of the first group. From *Table 2* it is obvious that the aluminium and ferric fluoride complexes owe

Table 2. The change of enthalpy, $\Delta H_j°$ in kcal/mole and entropy $\Delta S_n°$ in e.u. for the reaction $MeX_{n-1} + X \rightleftharpoons MeX_n$ at 25°

Me	X	$j \rightarrow$	1	2	3	4	5	6	*Salt medium*	*Ref.*
Al^{3+}	F^-	$\Delta S_j°$	32	26	18	13	5	−3	0·5M KNO_3	20
Fe^{3+}	F^-		31	24	23				0·5M $NaClO_4$	21
Fe^{3+}	Cl^-		35						→ 0	22
Al^{3+}	F^-	ΔH_j	1·1	0·8	0·2	0·3	−0·7	−1·5	0·5M KNO_3	20
Fe^{3+}	F^-		2·3	1·8	3·0?				0·5M $NaClO_4$	21
Fe^{3+}	Cl^-	ΔH_1	8·5						→ 0	22

their high stability to the large entropy terms, which within experimental error are the same for the corresponding steps in the two systems. The enthalpy change is more unfavourable to the formation of the complex at the first step in the ferric system. The general trend within the fluoride systems is that both $\Delta H_j°$ and $\Delta S_j°$ decrease when j increases. The reason for this may be the same as with the lanthanides. The hydrated aluminium and ferric ions act as a large entropy source, which is gradually exhausted as formation of the complexes proceeds. The opposition of enthalpy and entropy changes is obvious. Also the ferric chloride system has about the same high value of $\Delta S_1°$ as that for the fluoride. But the large value of $\Delta H_1°$ is so unfavourable for complex formation that $FeCl^{2+}$ gives a very weak complex.

A typical example of the second group is mercury(II), which forms complexes with halide ions in the order of strength $I^- > Br^- > Cl^- \gg F^-$. In this group the complexes owe their stability mainly to the large values of $-\Delta H_j°$. For the reaction:

$$Hg^{2+}(aq.) + 2X^-(aq.) \rightleftharpoons HgX_2(aq.)$$

$-\Delta H$ equals 12·3 kcal/mole for X = Cl and 22·5 kcal/mole for X=Br, whence the $T \cdot \Delta S$ term is much smaller, 5·1 and 1·2 kcal/mole respectively[16].

The rather weak cadmium halide complexes are borderline cases, in which both the values of $-\Delta H_j°$ and $\Delta G_j°$ decrease in the order $I^- > Br^- > Cl^- > F^-$. A detailed discussion of these systems is found in Gerding's[17] paper. The complex formation of thallium(III) ions with chloride and bromide has been studied by Ryhl[18], who used the equilibrium constants determined by Ahrland *et al.*[19] In this case the values of $-\Delta H_j°$ and $T\cdot\Delta S_j°$ are of the same order of magnitude. As seen in *Table 3* all eight values of $T\cdot\Delta S_j°$ are about

Table 3. The thermodynamic functions for the reaction of thallium(III) with chloride and bromide in the medium 3M $HClO_4$ + 1M $NaClO_4$ at 25°

Reaction	X = Cl $-\Delta H$ (kcal/mole)	X = Cl $-\Delta G°$ (kcal/mole)	X = Cl $\Delta S°$ (cal/mole deg)	X = Br $-\Delta H$ (kcal/mole)	X = Br $-\Delta G°$ (kcal/mole)	X = Br $-\Delta S°$ (cal/mole deg)
$Tl^{3+} + X^- \rightleftharpoons TlX^{2+}$	5·9	10·2	14·4	8·9	13·0	13·8
$TlX^{2+} + X^- \rightleftharpoons TlX_2^+$	4·3	7·9	11·9	6·1	10·0	13·3
$TlX_2^+ + X^- \rightleftharpoons TlX_3$	0·6	4·6	13·4	4·6	7·5	9·6
$TlX_3 + X^- \rightleftharpoons TlX_4^-$	0·6	3·8	10·6	2·3	5·6	11·1

equal. The direct results of the measurements are shown in *Figure 3*, which shows the heat, *h*, evolved per mole thallium(III) at the calorimetric titration of thallium(III) perchlorate with chloride and bromide. The average number,

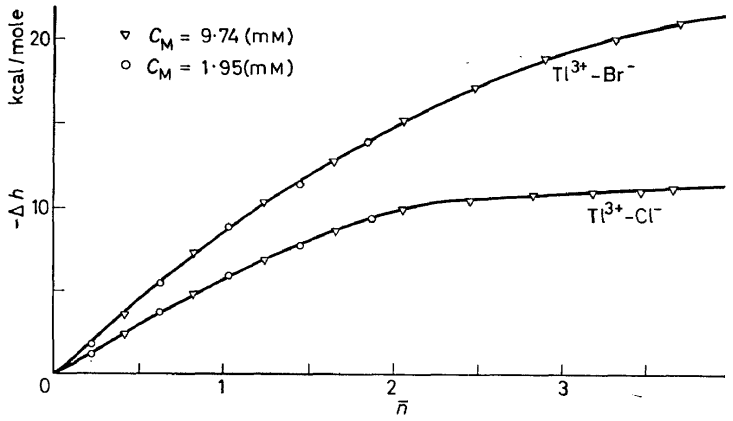

Figure 3. Calorimetric titrations of thallium(III) perchlorate with bromide and chloride in the medium 3M $HClO_4$ + 1M $NaClO_4$ at 25°

$\bar{n}$, of ligands bound per thallium(III) ion has been used as abscissa. In a mononuclear system both $\bar{n}$ and *h* are functions only of the concentration of free ligand in the solutions (see, *e.g.*, Rossotti, Rossotti[3]). A good test to show that no polynuclear species are formed is therefore to carry out titrations with different

concentrations of the central ion. This has been done for the thallium bromide system (see *Figure 3*) and also the cadmium bromide system[17].

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So far the experimental thermodynamic data are rather meagre, so that discussion may seem premature. This paper is to be regarded as a challenge to calorimetric workers for more experimental data. The need for this is also accentuated by the fact that so many unrealiable data can be found in the literature. Trials to compute enthalpy changes from the temperature dependence of the free energy must be regarded with caution. A drastic example of this is given by Rossotti[23].

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