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36. Enthalpy and Entropy Changes by Formation of Different Types of Complexes[1]

by **Sten Ahrland**[2]

(27. X. 66)

Ligands coordinated to acceptors termed (*a*), or hard, are generally held by bonds of an essentially electrostatic character, while the less numerous group of acceptors termed (*b*), or soft, form bonds which are markedly covalent.

The facts supporting this statement may be summarized as follows [1]: With a certain group of ligands of the same charge, *e.g.* the halide ions, the complexes formed by (*a*)-acceptors are invariably stronger, the smaller the ligand. The complexes also become stronger the higher the charge and the smaller the radius of the acceptor involved. For (*b*)-acceptors on the other hand, the strongest complex is not formed by the smallest ligand of a series, but by a succeeding one. Strong complexes are often formed with uncharged ligands of low polarity, or even no polarity at all, such as olefins. For several elements, the (*b*)-character increases with decreasing charge of the acceptor, and even becomes most pronounced in the zero oxidation state.

For typical (*b*)-acceptors, the bonds become strongly covalent, especially when the ligands are also very soft, *i.e.* very prone to covalent bonding. Such ligands as a rule exert only weak electrostatic attraction, and are therefore not coordinated by hard acceptors. Hard ligands on the other hand, *i.e.* those held mainly by electrostatic forces, are coordinated to all acceptors surrounded by a sufficiently strong field, irrespective of whether they are hard or soft.

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The formation of complexes thus depends upon two different factors, which operate fairly independently of each other; a certain acceptor may well be able to form strong covalent bonds while exerting only a quite feeble electrostatic attraction, and *vice versa.*

It may then be presumed that the two terms which together make up the free energy of complex formation, *viz.* the enthalpy and the entropy, are influenced in different ways depending upon whether the bonds formed are predominantly electrostatic, or covalent. The following survey will show that this is really the case, and moreover that important conclusions about the bonding within the complexes can be drawn from this fact.

Only aqueous systems are considered here, and the complex formation is therefore in fact a substitution of water molecules for ligands within the inner coordination sphere of the acceptor. The reaction thus involves not only the formation of acceptor-to-ligand bonds, but also the breaking of acceptor-to-water bonds, and hence a liberation of water molecules. Especially for acceptors of high charge and/or small radius, which are able to coordinate water also in outer hydration spheres, the coordination of a ligand presumably causes a considerable structural break-down, resulting in the liberation of several water molecules for each ligand bonded.

Furthermore the formation of an accepter-to-ligand bond will more or less completely move the ligand out of its previous hydration sphere. In the case of very hard ligands, such as the fluoride ion, which by the formation of strong hydrogen bonds exert an ordering influence upon the water structure [2] [3], this means that water molecules are set free also from the ligands. Most ligands are structure-breaking, however, and among them the heavier halides. This implies that the interactions between the ligands and the water molecules are so weak that the resulting structure will be less ordered than that of pure water, which does not exclude, of course, that the ligand-to-water interaction may be quite strong, as is certainly still the case for chloride [4]. The interaction becomes markedly weaker with increasing radius of the halide [2], *i.e.* with increasing softness [1]. The transfer of a structure-breaking ligand into a complex will thus make it possible for the water to attain a more well-ordered structure. For the series of halide ions, this improvement of order, or loss of freedom, will evidently increase with increasing softness; for the first member, the hard fluoride ion, the net result of the solvent rearrangement will even be a decrease of order, as has already been stated.

Whether the total process of complex formation will be exothermic, implying that the enthalpy change favours the reaction, will depend upon if more energy is gained by formation of new bonds than is spent for breaking existing ones. Likewise, whether a net gain of entropy will result, favouring the complex formation, will depend upon the balance between gains and losses accompanying the various process steps. Of these, the formation of the acceptor-to-ligand bond involves a loss of entropy which is, at least in the case of acceptors of high charge and/or small radius, more than offset by the gain resulting from the liberation of water from the acceptor. The net result will then evidently depend very much upon the term connected with the ligand-to-water interaction, which can be foreseen to be positive for structure-producing ligands but negative for structure-breaking ones. Other sources of entropy exist, however, as will be further discussed below.

Choice of Systems for Comparison. – For the purpose envisaged, the contributions from the changes of standard enthalpy, ΔH^0, and standard entropy, ΔS^0, to the standard free energy change, ΔG^0, should be compared for suitably chosen complex formation reactions. The ligands should preferably be small, of the same charge, and as simply and similarly built as possible, having only one donor atom. Most important, however, they should constitute a sequence, ranging from extremely hard to extremely soft donors, In this way the bonding will be kept free from chelate effects, and also to a high degree from steric influences, which may change markedly between various acceptors. Furthermore the identical charge will make it easier to estimate the electrostatic attraction exerted by the various ligands.

Obviously the halide ions form the sequence of ligands which most closely conforms to the conditions set forth. They are small monoatomic ions of charge -1, ranging from the hardest ligand known, F^-, through Cl^- and Br^-, of very moderate softness, to the fairly soft I^-. In order to extend the comparison to a very soft ligand, the pseudohalide CN^- has also been included. This seems permissible, because its complex formation occurs according to the same pattern as for the soft halides, as far as the acceptors compared here are concerned (Cd^{2+} and Hg^{2+}, *cf.* [5]).

For the ligands chosen, the ability for covalent bonding, *i.e.* the softness, thus increases in the order

$$F^- \ll Cl^- < Br^- < I^- < CN^-,$$

while the electronegativities, and hence the strength of the electrostatic interactions between ligand and acceptor, as well as between ligand and water, increase in the reverse order, at least for the halides. In this respect, the position of the cyanide ion is somewhat uncertain, as will be further discussed below.

The acceptors should also preferably range between extremely hard and extremely soft ones for both types of ligands. In these acceptor sequences, however, some elements will inevitably be found missing. Thus, very soft ligands do not form complexes at all with very hard acceptors. Also, the hard ligand F^- forms only very weak complexes with acceptors, mostly soft ones, which combine low charge and large radius. For these combinations, where practically no reaction takes place, an experimental determination of thermodynamic quantities is of course impossible.

Choice of Data for Comparison. – Two of the three quantities ΔG^0, ΔH^0 and ΔS^0, related according to

$$\Delta G^0 = \Delta H^0 - T\Delta S^0, \qquad (1)$$

must be known for the intended comparison to be possible.

As regards the standard free energy change ΔG^0, the cumulative constants β_n and the consecutive ones K_n have been determined for very many systems, allowing the calculation of

$$\Delta G_n^0 = -RT \ln K_n \qquad (2)$$

or

$$\Delta G_{\beta n}^0 = -RT \ln \beta_n \qquad (3)$$

referring to the *n*th step, or the first *n* steps, respectively.

For the standard enthalpy change ΔH^0, on the other hand, the data are still rather scarce. Furthermore, most of them have been found from the variation of β with T. By this procedure a good value of ΔH^0 can result only if β is measured very accurately over a sufficiently wide interval of T. Very often these conditions have not been observed. Even if they have, however, the ΔH^0 found may still be in error, because only fairly large values of ΔH^0 can be correctly determined by this method unless ΔC_p, the difference between the heat capacities of the formed and reacting species, is very small, which as a rule is not the case[3]).

An inherently much better way of determining ΔH^0 is by direct calorimetric measurement. This method has been increasingly used in later years, as the futility, in many cases, of the temperature coefficient method has been realized (*cf. e.g.* GERDING *et al.* [7], ROSSOTTI [8], p. 68).

For a system of consecutively formed, mononuclear complexes the total enthalpy change per mol, $\overline{\Delta H}$, is given by

$$\overline{\Delta H} = \frac{\sum\limits_{n=1}^{N} \Delta H^0_{\beta n}\,[\mathrm{ML}_n]}{C_M} = \frac{\sum\limits_{n=1}^{N} \Delta H^0_{\beta n}\,\beta_n [\mathrm{L}]^n}{1 + \sum\limits_{n=1}^{N} \beta_n [\mathrm{L}]^n}. \tag{4}$$

Formally it should be possible to calculate both sets of constants, β_n as well as $\Delta H^0_{\beta n}$, from $\overline{\Delta H}$ as a function of [L]. In practice, however, this generally cannot be achieved, as has been repeatedly shown for the equivalent functions obtained when spectrophotometry is applied to complex equilibria [9]. It can be done if not more than two or, at most, three various species of M are present simultaneously in perceptible amounts, but even then the accuracy of the constants found tends to be somewhat restricted [9] [10] [11]. Generally it is far better to determine the constants β_n by some reliable, separate method, using equ. (4) only for the determination of $\Delta H^0_{\beta n}$.

In the following, the reasoning has primarily been founded on calorimetrically determined ΔH^0. In several cases, however, seemingly sound values calculated from temperature coefficients have been used as supporting evidence.

The values of the standard entropy change ΔS^0 have, as a rule, been calculated from equ. (1). For iron(III) cyanide, however, $\Delta S^0_{\beta 6}$ has been calculated from other entropy data [12] [13] and then combined with a value of $\Delta H_{\beta 6}$, found from a set of calorimetric determinations [12], to yield a value of $\Delta G^0_{\beta 6}$ (Table 3). From this quantity and the standard potential [14] of the couple $\mathrm{Fe(CN)}_6^{3-}/\mathrm{Fe(CN)}_6^{4-}$, it is possible to find $\Delta G^0_{\beta 6}$ for the iron(II) cyanide system. The value of $\Delta H^0_{\beta 6}$ for this system having been determined calorimetrically [12], $\Delta S^0_{\beta 6}$ can finally be calculated.

As to the halide systems, the first step of the complex formation, *i.e.* the reaction $\mathrm{M} + \mathrm{L} \rightleftharpoons \mathrm{ML}$, has primarily been selected for comparisons, *cf.* Tables 1 and 2. The most important reason is that the data referring to this step are by far the most numerous, and, as a rule, also the most reliable. It can also be argued that the first step should be less sensitive than any of the following ones to changes of co-ordination number and configuration between various acceptors. Such changes will often make comparisons between later steps somewhat questionable.

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[3]) For weak, monobasic acids, HARNED & ROBINSON [6] have found that $K(T)$ can be described by an empirical expression which allows the simultaneous evaluation of both ΔH^0 *and* ΔC_p.

In the case of fluoride, the original data often refer to the equilibrium $M^- + HF \rightleftharpoons MF + H^+$, characterized by the stability constant K_1^* (corresponding to a free energy change ΔG_1^{0*}) and an enthalpy change ΔH_1^{0*}. These have been recalculated to ΔG_1^0 and ΔH_1^0 needed for Table 1 by means of the values of ΔG_1^0 and ΔH_1^0 for the hydrogen fluoride system, given first in that Table. For the ionic strength $I = 0$, the values of ΔH_1^0 (and ΔS_1^0) reported are from a direct calorimetric determination [15]. For $I = 0.5$ M, no such determination exists, so ΔH_1^0 has to be calculated from the temperature coefficient of K_1. Several sets of K_1 in fair agreement with each other are available [16] [17] [18], however, so it is believed that the values reported for ΔH_1^0 and ΔS_1^0 are quite reliable also for $I = 0.5$ M.

For cyanide systems, however, the data pertaining to the first step are much too few to allow any comparison. In part, this is certainly due to experimental difficulties. It has also been found, however, that the first complex has an abnormally low stability for several cyanide systems (Ni^{2+}, Zn^{2+}), in comparison with what would be expected from the very strong overall complexity [19] [20]. For these reasons, it seems preferable to consider the fourth complex, formed according to $M + 4\,L \rightleftharpoons ML_4$. As to these equilibria, data exist for several acceptors, *viz.* the group Zn^{2+}, Cd^{2+} and Hg^{2+}, all forming tetrahedral complexes, and also Ni^{2+}, with square planar configuration. Fortunately, $\Delta G_{\beta 4}^0$ and $\Delta H_{\beta 4}^0$ have also been determined for the analogous complexes formed by Cd^{2+} and Hg^{2+} with the heavier halides, and a comparison between these donors and CN^- is therefore possible, *cf.* Table 3. In the same Table, the cyanide complexes formed by H^+, with $N = 1$, and by Fe^{3+} and Fe^{2+}, with $N = 6$, have also been reported, providing further material for a comparison between cyanide complexes of various configurations.

In Tables 1–3, values of ΔG^0 and ΔH^0 are given in kcal mole^{-1} and of ΔS^0 in cal degree^{-1} mole^{-1} (e. u.). The method column states how ΔH^0 was determined, *viz.* calori-

Table 1. *ΔG_1^0, ΔH_1^0 and ΔS_1^0 for fluoride complexes, 25°C*

Acceptor	Method ΔH^0	I	ΔG^0	ΔH^0	ΔS^0	Ref.
H^+	*T* 0–50	0.5	−3.96	2.93	23,1	[16] [17] [18]
	cal	0	−4.33	3.18	25.2	[21] [15]
Be^{2+}	*T* 5–50	0.5	−6.88	−0.4	22	[18]
		0	−8.17	−0.2	27	
Al^{3+}	*cal*	0.5	−8.37	1.1	32	[22]
		0	−9.54	2.1	39	[22] [23]
Sc^{3+}	*T* 15–35	0.5	−8.40	0.6	30	[23]
Y^{3+}	*T* 15–35	0.5	−5.34	2.2	25	[24]
		0	−6.53	2.3	30	
Fe^{3+}	*cal*	0.5	−7.05	2.35	31.5	[17] [25]
	T 15–35	0	−8.23	3.4	39	[17] [23]
Ga^{3+}	*T* 5–50	0.5	−6.06	1.8	26	[18]
		0	−8.4	1.9	34	
In^{3+}	*T* 15–35	0.5	−5.11	2.4	25	[26] [23]
		0	−6.30	3.5	33	
UO_2^{2+}	*T* 10–40	2	−6.0	~ -2	~ 13	[27]
Zn^{2+}	*T* 15–35	0.5	−1.0	~ 1.5	~ 8	[28]
Cd^{2+}	*cal*	3	−0.78	1.02	6.0	[29] [30]
		1	−0.63	1.23	6.2	
Hg^{2+}	*T* 15–35	0.5	−1.39	~ 0.9	~ 8	[23]

metrically (*'cal'*) or by determining the equilibrium constant over a certain temperature range (*'T* 15–35', in the range 15–35 °C). All data refer to a temperature of 25 °C. The ionic strength (I; in M) is given for each set of data. An effort has been made to select data valid for the same medium. To a certain extent, this can be achieved for systems of the same ligand, but it cannot be helped that most of the data, and moreover some of the most reliable ones, refer to a much higher ionic strength (3 or 4 M) for the heavier halides than for fluoride (0 or 0.5 M). For quite a few systems, however, data are available for different media, and it is comforting to find that a change of medium, though altering the figures perceptibly, does not in any case change the overall picture.

Discussion. – *Fluoride Complexes* (*Table 1*). For the extremely hard fluoride ion, the entropy term is all-important for the formation of the first complex. The enthalpy term is either insignificant, or even markedly counteracting the decrease of free energy. The latter occurs *e.g.* for H^+. For tervalent ions, as well as for Be^{2+} and H^+, of lower charge but with very small radius, ΔS_1^0 has quite a high value, around 30 cal degree^{-1}, which is enough to ensure a strong complex formation in spite of the unfavourable value of ΔH_1^0. For divalent ions of ordinary size, ΔS_1^0 is much lower, with the result that the complex formation becomes quite weak.

The driving force for the formation of strong complexes by hard ligands is thus the huge entropy gain derived from the simultaneous breaking of strong acceptor-to-water *and* strong ligand-to-water bonds. On account of the large energy required to break these bonds, which for most systems is by far not compensated by the energy gained on formation of the acceptor-to-ligand bond, the total process will as a rule be fairly strongly endothermic. In the case of hydrofluoric acid, it was recognized already by ROTH [31], that the strong hydration of the fluoride ion caused the *dissociation* of the acid to be strongly *exothermic*.

In all cases ΔS_1^0 is perceptibly lower for $I = 0.5$ M than for $I = 0$. One interpretation of this fact would be that the presence of strongly structure-breaking ions (ClO_4^- or, in a few cases, NO_3^-) [2] disrupt the outer hydration shells of the acceptors so that fewer water molecules are set free on complex formation.

Chloride, Bromide and Iodide Complexes (*Tables 2 and 3*). In the case of chloride, the complex formation is due exclusively to a favourable entropy term only for typically hard acceptors, *i.e.* for acceptors which are not very capable of forming covalent bonds. Thus for Ce^{3+}, Cr^{3+} and Fe^{3+}, Table 2, the enthalpy term is still strongly counteracting the reaction, seemingly even more than for any fluoride system yet investigated. In spite of the fairly positive value of ΔS_1^0, just under 20 e. u., the complexes formed are therefore quite weak.

With increasing softness of the acceptors, however, the enthalpy change becomes more and more favourable for the complex formation, as pointed out earlier by LEDEN [32]. Already for border cases, such as Tl^+, Cd^{2+} and Bi^{3+}, ΔH_1^0 is around zero, and for typically soft acceptors, such as Hg^{2+}, Tl^{3+} and Pd^{2+}, it is strongly negative. The entropy change seems on the whole to decrease with decreasing charge and/or increasing radius of the acceptor, as for the fluoride systems. The degree of softness of the acceptor does not influence ΔS_1^0 very conspicuously, as already pointed out by KING *et al.* [33]. Several irregularities appear among the data, however, and it is not easy to

Table 2. ΔG_1^0, ΔH_1^0 *and* ΔS_1^0 *for ligands of increasing softness, 25° C*

	Ligand →		Cl⁻			Br⁻			I⁻			Ref.
Acceptor	Method ΔH^0	I	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	
Ce^{3+}	*cal*	var	0.0	5.4	18							[34]
Cr^{3+}	*cal*	5.1	0.9	6.6	19							[35]
	T 30–95	4.4	0.9	6.1	17	3.6*	5.1*	5				[36]
Fe^{3+}	*cal*	1	−0.63	4.2	16							[37]
Tl^{+}	T 15–80	4	0.00	−1.1	−4							[38]
	T 5–45	0	−0.92	~0	3	−1.43	−2.5	−4				[39]
Sn^{2+}	T 0–45	3	−1,56	2.6	14	−0.99	1.4	8				[40]
Bi^{3+}	T 25–65	3	−3.0	~0	10							[41]
Ag^{+}	T 15–35	0	−4.5	−2.7	6							[42]
Cd^{2+}	*cal*	3	−2.16	−0.10	6.9	−2.40	−0.98	4.7	−2.84	−2.26	2.0	[29] [30]
Hg^{2+}	*cal*	3	−9.60	−5.79	12.8	−12.79	−9.57	10.8				[11]
		0.5	−9.2	−5.5	12	−12.3	−10.2	7	−17.5	−18.0	−2	[43] [44]
		0.5	−9.15	−5.9	11							[43] [45]
Tl^{3+}	*cal*	4	−10.20	−6.04	13.9	−12.96	−8.96	13.4				[46]
Pd^{2+}	T 21–38	0	−8.3	−8	~0							[47]

* T 0–45; $I = 2$

decide, whether they should all be ascribed to experimental inaccuracies. The observed overall increase of the stability of chloride complexes as the acceptor softens is, however, exclusively due to a very marked decrease in ΔH_1^0.

A fairly favourable ΔS_1^0 is *a priori* to be expected for the formation of chloride complexes, as the structure-breaking properties of the chloride ion are not very marked, implying that the entropy loss due to this source must be modest (*cf.* p. 307). For the fluoride ion on the other hand, the term is strongly positive. The net gain of entropy should therefore be much smaller for chloride than for fluoride systems, as is in fact observed.

As long as the electrostatic interaction dominates the acceptor-to-ligand bond, *i.e.* for typically hard acceptors, ΔH_1^0 should have a value not very different from that found for the fluoride systems, *i.e.* fairly positive. Admittedly, the partial dehydration of the ligand may be an exothermic process in the case of chloride which it certainly is not in the case of fluoride, but on the other hand the gain of energy on the formation of the acceptor-to-ligand bond will be much less for chloride than for fluoride. These two opposing tendencies should largely cancel each other. As mentioned, ΔH_1^0 is in fact more positive for chloride than for fluoride complexes of hard acceptors; evidently the gain of energy due to the easier dehydration of the chloride ion cannot even quite make up for the loss due to the weaker acceptor-to-ligand interaction.

The sharp decrease of ΔH_1^0 with increasing softness of the acceptor means that the formation of an essentially covalent bond is accompanied by a large evolution of heat, as has also been inferred by ROSSOTTI [8] (p. 27) and by GERDING [30].

The trends encountered in the formation of chloride complexes are further strengthened for bromide and, in a still higher degree, for iodide complexes, *cf.* Tables 2 and 3. The values of ΔS^0 continue to decline, reflecting the decreasing strength of interaction between ligand and solvent. For the formation of iodide complexes, the part played by ΔS^0 is insignificant.

Simultaneously, the values of ΔH^0 become increasingly more negative as the bond grows more covalent with increasing softness of the ligand, and of the acceptor. For typically hard acceptors, however, even the bromide complexes seem to have strongly positive values of ΔH_1^0, of the same order of magnitude as those found for fluoride and chloride complexes of such acceptors, to judge from the value reported for Cr^{3+}. It is thus once more confirmed that the decrease of ΔH_1^0 with increasing softness of the acceptor is mainly due to a growing covalency of the acceptor-to-ligand bond. If the acceptor is not able to form such a type of bond, no decrease of ΔH_1^0 will occur.

Also between chloride and bromide, the expected decrease of hydration enthalpy as the ligand becomes softer is evidently largely compensated by the simultaneous decrease of the electrostatic interaction between acceptor and ligand, exactly as is the case between fluoride and chloride.

The value of ΔH^0 will thus provide a fairly good measure of the covalency of a bond: *the lower ΔH^0, the more covalent the bond.*

It should be noted that quite the same picture emerges, whether the formation of the first complex is considered, or the gross reaction leading to the fourth complex, at least for all systems where a comparison has been possible (Tables 2 and 3, respectively).

Table 3. *$\Delta G^0_{\beta 4}$, $\Delta H^0_{\beta 4}$ and $\Delta S^0_{\beta 4}$ for ligands of increasing softness*[a]*), 25 °C*

Ligand →		Cl⁻			Br⁻			I⁻			CN⁻			Ref.
Acceptor	I	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	ΔG^0	ΔH^0	ΔS^0	
Zn^{2+}	1											−27.0		[50]
	0										−22.75	−24.7	−6.5	[48] [49]
Cd^{2+}	3				−5.05	0.47	18.5	−8.89	−7.00	6.3	−25.64	−29.3	−12.3	[29] [30] [51]
	0										−26.77	−27.8	−1.0	[20]
Hg^{2+}	3	−21.88	−14.79	23.8	−30.26	−26.20	13.6				−55.5[b])	−59.5	−13	[11] [49] [52]
	0.5	−20.66	−14.9	19.4	−28.5	−27.7	2.7	−40.6	−44.3	−12.4				[43] [45]
	0										−53.1	−63.3	−34	[54]
	0										−56.4			[53]
Tl^{3+}	4	−26.50	−11.34	50.8	−36.05	−21.77	47.9							[46]
	3	−24.91	−11.25	45.8										[33]
	0.25											−44.3		[19]
Ni^{2+}	0										−41.1	−43.2	−7	[19]
		ΔG^0_1, ΔH^0_1 and ΔS^0_1:												
H^+	0										−12.53	−10.4	7	[55]
		$\Delta G^0_{\beta 6}$, $\Delta H^0_{\beta 6}$ and $\Delta S^0_{\beta 6}$:												
Fe^{2+}	0										−50.6	−85.77	−118	[12] [13] [14]
Fe^{3+}	0										−59.9	−70.14	−34.3	[12] [13]

[a]) All ΔH^0 determined calorimetrically [b]) $I = 0.1$ M, recalculated from 20 °C with $\Delta H^0 = -60$ kcal

This is true for all ligands discussed, and for acceptors exhibiting very different complex formation functions, as do *e.g.* Cd^{2+} and Hg^{2+} [4]).

Contrary to what was found for the fluoride systems, the values of ΔS^0 for the heavier halides tend to increase with I, at least as far as can be judged from the few instances where reliable data exist for more than one medium. It is probably significant, however, that for all systems quoted I is quite high, 3 or 4 M, in at least one of the media, and it may therefore be that ΔS^0 goes through a minimum around an I of about 0.5 or 1 M, reflecting the minimum found for the activity coefficients in that region.

Cyanide Complexes (*Table 3*). The high stability of the complexes formed by the extremely soft cyanide ion with various acceptors is entirely due to a very negative ΔH^0, while ΔS^0 counteracts the complex formation for all metal ion acceptors investigated so far, and most markedly for the six-coordinated iron systems. Especially the formation of the iron(II) complex is accompanied by a huge decrease of entropy, consuming not far from half of the enormous enthalpy decrease. The only acceptor exhibiting a positive ΔS^0 is the proton, though even in this case ΔH^0 is the completely dominating term.

The large negative values of ΔH^0 conform to the view that the cyanide ion is coordinated by covalent bonds of unusual strength. It is a very soft ligand; much softer even than iodide, softest among halides, to judge from the data of Table 3. It is especially striking that the cyanide ion can form strongly covalent bonds with acceptors which are otherwise reluctant to participate in such bonds. This is the case with Zn^{2+}, Fe^{3+} and, at least as far as the heavier halides are concerned, also with Fe^{2+}, Ni^{2+} and H^+. These acceptors, which usually tend to be hard, or, at most, border-line cases, suddenly turn quite soft when approached by cyanide ions.

The small, or even strongly negative values of ΔS^0 certainly suggest only a very weak ligand-to-water interaction; the cyanide ion would thus be an even more pronounced structure-breaker than the iodide ion. For the formation of cyanide complexes, however, there are further sources of entropy that must be considered before a conclusion on this point can be reached. First, the complex formation of the diatomic cyanide ion involves a loss of rotational entropy which has no counterpart for the monoatomic halide ions ([8], p. 20). Second, the extremely strong covalent bonding in cyanide complexes may possibly lead to a further loss of vibrational entropy, as compared with the less tightly held heavy halides.

It is not easy to assess the relative importance of these three sources of decrease of ΔS^0. It seems reasonable to assume, however, that the first one, which depends upon the strength of the ligand-to-water interaction, will be fairly well measured by the hydration enthalpy of the cyanide ion.

The hydration enthalpy for an anion L^- is defined as the enthalpy change $\Delta H_h^0(L^-)$ of the reaction $L^-(g) \rightarrow L^-(aq)$. It can be calculated from the solution enthalpy ΔH_s^0

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[4]) On the other hand, the various steps of a system may show a fairly different behaviour, as has been pointed out by LEDEN [32] and by GERDING [30]. This may sometimes depend upon the modification of the acceptor caused by successive coordination of ligands [32]; in other cases the variations seem to be very peculiar for the step in question [30]. A detailed discussion of these aspects may still be somewhat premature, however.

of a salt ML, its lattice enthalpy ΔH_l^0, and the hydration enthalpy of the cation, $\Delta H_h^0(M^+)$. Of these, ΔH_s^0 is easily determined. Furthermore, if the same M^+ is chosen for all ligands, a wrong estimation of $\Delta H_h^0(M^+)$ will cause the same absolute error in all $\Delta H_h^0(L^-)$ and thus does not impair their comparisons. The difficult point is the calculation of ΔH_l^0, especially when the pertinent formulas must be used for ligands of, after all, as different types as the monoatomic, spherically symmetrical halide ions on the one hand, and the complex cyanide ion on the other. It seems likely enough that values of ΔH_l^0 will be obtained for halide salts, yielding values of $\Delta H_h^0(L^-)$ which fairly faithfully reflect the decreasing strength of the anion-to-water bonds from F^- to I^- (*cf. e.g.* [56] [57] and references quoted therein). On the other hand, too far-reaching conclusions should certainly not be drawn from a comparison of these values with that found in the same way for the cyanide ion. Formally it will come out similar to that of the bromide ion [57], but the differences between the $\Delta H_h^0(L^-)$ of the various ligands are so small, and the possible errors so large, that it seems safest to conclude only that $\Delta H_h^0(CN^-)$ is of the same magnitude as $\Delta H_h^0(L^-)$ for the heaviest halide ions. The influence exerted on the water structure should therefore also be about the same. It thus seems likely that the extra losses of rotational, and possible also vibrational, entropy are responsible for the further decrease of ΔS^0 for cyanide complexes in comparison with the complexes of the heavy halides.

The various values entered in Table 3 also give some idea about the accuracy of the measurements available. Considerable discrepancies do exist between different investigators, but the main pattern is nevertheless not in doubt.

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SUMMARY

The different types of bonding in complexes formed in aqueous solution are clearly reflected in the values of ΔH^0 and ΔS^0 for the complex formation reaction.

In the case of essentially electrostatic bonding, most nearly realized between very hard acceptors and very hard donors, the complex formation is due to a large gain of entropy, while the enthalpy change generally counteracts the reaction. The source of this entropy gain is obviously the liberation of water molecules from the hydrate shells of the acceptor, *and* the ligand, on the formation of the complex.

In the case of essentially covalent bonding, most nearly realized between very soft acceptors and very soft donors, the complex formation is due to a large decrease of enthalpy, evidently accompanying the formation of the covalent bond. Here ΔS^0 tends to counteract the reaction, mainly because of the structure-breaking properties of soft ligands. Also the low charge and large radius of most soft acceptors will act in the same direction, however, and a further decrease of ΔS^0 may come from an extra loss of rotational and vibrational entropy suffered by the ligand.

The value of ΔH^0 thus seems to provide a good measure of the covalency of the bond between acceptor and ligand. The more negative (or less positive) ΔH^0, the stronger is generally the covalent bonding.

The value of ΔS^0 is a more complicated function of the electrostatic, as well as the covalent, bonding capacities of acceptor and ligand. On the whole, ΔS^0 tends to decrease with decreasing electrostatic interaction between acceptor and ligand, but owing to its dependence upon many various factors, it cannot be regarded as a good measure of this quantity.

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