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HOW TO DISTINGUISH BETWEEN INNER AND OUTER SPHERE COMPLEXES IN AQUEOUS SOLUTION. THERMODYNAMIC AND OTHER CRITERIA

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A. EXPECTED DIFFERENCES IN THE THERMODYNAMICS OF COMPLEX FORMATION IN THE INNER AND OUTER SPHERE

The formation of complexes between hard, or class *a*, acceptors and hard donors in aqueous solution is generally entropy-controlled, i.e. the decrease of the free energy is wholly, or at least mainly, due to a large gain of entropy[1,2]. The enthalpy change is, as a rule, positive, often fairly strongly so, and thus will more or less strongly counteract the reaction. The pattern is especially pronounced for the first complex; as the complex formation proceeds, the changes of both entropy and enthalpy generally become less positive or, in the end, even negative[3,4].

These thermodynamic characteristics of hard–hard interactions have been interpreted as follows[1–4]. Hard acceptors, as well as hard donors, are characterized by a high charge/radius ratio. The bonds formed between them are essentially electrostatic. In aqueous solution, they also interact strongly with the water dipoles, ordering them into hydrate structures. When a complex is formed, these structures are, to a large extent, broken. This results in a large gain of entropy which is not compensated for by the loss due to the formation of the complex. On the other hand, dehydration requires a large amount of energy which is not fully regained by the union of acceptor and donor. For each step, however, the charge of the acceptor decreases, and hence its capability to order the water molecules. The entropy to be gained will therefore generally decrease for each consecutive step of the complex formation. If, finally, negatively charged complexes form, hydrate structures again build up which may result in a net loss of entropy for the last steps. Simultaneously, the energy required for the dehydration decreases with each step, and may finally even change sign, as new hydrates are formed. This implies a decrease of the enthalpy change, as is in fact generally found. This trend may be more or less counterbalanced, however, by a simultaneous decrease of the energy gained by the coordination of the ligand.

The thermodynamic pattern of hard–hard interactions in aqueous solution is thus interpreted as essentially due to the profound changes of hydration accompanying the complex formation. Consequently, this pattern should only be found when such changes occur to their full extent, i.e. when the donor enters the inner coordination sphere of the acceptor If the donor remains in the outer sphere, the change of hydration is very much smaller No large entropy gain will then result, nor will any large amount of energy be spent on dehydration Both the entropy change, ΔS°, and the enthalpy change, ΔH°, should therefore be much less positive when an outer sphere complex is formed It should be possible to use these differences in order to distinguish between inner and outer sphere complexes

It should be emphasized, however, that the generalizations stated above do not apply to the formation of complexes between soft, or class *b*, acceptors and soft donors Such complexes are invariably enthalpy-controlled, i e the decrease of the free energy, ΔG°, is wholly, or at least mainly, due to a large decrease of enthalpy while the entropy term is either unimportant or fairly strongly negative, thus counteracting the reaction[1,2] The large negative values of ΔH° are due to the formation of essentially covalent bonds Such a process evidently presumes that the donor enters the inner coordination sphere of the acceptor If it stays in the outer sphere, no covalent bond energy will be involved and ΔH° will consequently be much more positive than for the corresponding inner sphere complex The change will thus be in the direction opposite to that found for hard–hard interactions Once a soft donor has been relegated to the outer coordination sphere, the electrostatic attraction will be its only means for complex formation, i e it will be bonded in the same way as a hard donor The bonding will generally be weaker, however, as the charge/radius ratio is lower for most soft donors

The poor electrostatic attraction of typically soft donors, as well as of many soft acceptors, also means a weak hydration of such species The change of ΔH° and ΔS° due to dehydration will therefore be of much less importance in soft–soft interactions than in hard–hard ones

The criteria for distinguishing between inner and outer sphere complexes, as stated originally, are therefore applicable only when hard species are involved A further condition for their safe use is that it is reasonably well known which values of ΔH° and ΔS° to expect for the two alternatives Owing to the lack of really reliable information on this point, all discussions conducted so far along the lines indicated have suffered from a certain vagueness This difficulty may be overcome, however, by considering such systems where the inner and outer sphere complexes can be formed separately, i e systems where the inner sphere complexes are inert

B FORMALLY ANALOGOUS INNER AND OUTER SPHERE COMPLEXES OF CHROMIUM(III) AND COBALT(III)

Hard–hard interactions involving inert species are limited to reactions of chromium(III) and cobalt(III) The data available for comparison are, therefore, not very numerous (Table 1) Moreover, they all refer to the first complex formed. In spite of these limitations, however, the general trends stand out so clearly that quite a few important conclusions can safely be drawn Thus, the inference above that both ΔH° and ΔS° are less positive for outer sphere than for inner sphere complexes is amply borne out The order of magnitude

TABLE 1

Thermodynamics of the formation of corresponding inner- and outer-sphere complexes of hard acceptors First step of complex formation, inner-sphere complex inert

Ligand	Method[a] for ΔH°	t (°C)	I (M)	Inner			Outer			Ref
				ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	
$Cr(H_2O)_6{}^{3+}$										
Cl^-	Cal	25	5.1	0.9[b]	6.6	19[b]				5
	T 30–95	25	4.4	0.9	6.1	17				6
	T 30–60	44	0.42	1.08	7.4	20				30
	T 40–80	60	4	0.15	5.6	16				7
		60	1	0.75	6.0	16				7
										7
	T 10–50	25	1				0.08	−0.4	~2	8
		40	1	0.9			0.10			8
Br^-	T 45–75	60	0.5	3.3	7.5	13				9
		60	4	2.7	6.5	11				9
	T 0–45	25	2	3.6	5.1	5				10
	T 25–45	25	4.1				0.9	~0	~−3	9
$SO_4{}^{2-}$	T 48–84	60	1	−2.58	7.2	29	−1.6	~0	~5	11
$Co(NH_3)_5H_2O^{3+}$										
$SO_4{}^{2-}$	T 4–49[c]	25	0	−4.3	4	28	−4.47	~0	~15	12, 13
	T 25–45	25	1	−1.49	3.7	17	−1.43	−0.3	4	12, 13
$Co(NH_3)_6{}^{3+}$										
$SO_4{}^{2-}$	T 4–49	25	0				−4.53	0.4	17	13

[a] In this column "Cal" means a calorimetric determination and "T" a determination from the variation of the equilibrium constant between the temperatures stated (°C)

[b] If ΔG° is assumed to have the same value (0.9 kcal/mole) at I = 5.1 M as at I = 4.4 M, the quoted value of ΔS° = 19 cal/deg results

[c] For the inner complex 25–44°C

of these differences is 5 kcal for ΔH° and 20 cal/deg for ΔS°. For outer sphere complexes, $\Delta H^\circ \simeq 0$, independent of the ionic strength I, while ΔS° approaches zero only at fairly high values of I. When $I = 0$, the value of ΔS° is markedly higher, ~ 15 cal/deg, which implies a sharp increase in the stability of the outer sphere complexes as $I \rightarrow 0$.

As pointed out by Gorski[14], the fairly high values of ΔS° encountered when outer sphere complexes are formed at low ionic strength are most probably due to a fairly extensive dehydration of the ligand. For the sulphate ion, a complete dehydration would give ΔS° = 23.5 cal/deg for $I = 0$. As the ionic strength increases, the ordering due to the sulphate ion decreases, on account of the competition for the water molecules from other ions present in increasing amounts. The entropy increase due to its dehydration should thus become smaller, as is in fact found.

The differences between the values of ΔH° and ΔS° found for inner and outer sphere complexes varies somewhat with the acceptor and donor involved which is certainly not unexpected. The decrease of ΔS° in particular varies with the nature of the ligand, in the order $SO_4^{2-} > Cl^- > Br^-$. This order evidently reflects a corresponding decrease in the hydration of the ligand. On the whole, however, the pattern found is surprisingly uniform. It should therefore be possible to apply the result to labile systems, in order to find out whether predominantly inner or outer sphere complexes are formed.

C. APPLICATION OF THE RULES FOUND TO LABILE CHLORIDE AND SULPHATE SYSTEMS

Chloride complexes of hard acceptors are all fairly weak and therefore difficult to measure. The few existing data are moreover often contradictory, as for Zn^{2+} (cf. refs. 15, 16). Reliable results seem to be available for Fe^{3+} and Eu^{3+}, however (Table 2). The values of ΔH° and ΔS° found for $FeCl^{2+}$ evidently indicate an inner sphere complex while those found for $EuCl^{2+}$ clearly point to an outer sphere complex. The latter conclusion has been reached previously by Choppin et al.[18,19], mainly from the low value of ΔS°. The low value of ΔH° seems to provide an even more convincing proof, however, in view of the fact that ΔH° is much less sensitive than ΔS° to variation of the ionic medium.

TABLE 2

Formation of the first chloride complex of Fe^{3+} and Eu^{3+} at 25°C

Acceptor	Method[a] for ΔH	I (M)	ΔG°	ΔH°	ΔS°	Ref.
Fe^{3+}	Cal	1	−0.63	4.2	16	17
	T 14–44	1	−0.63	4.4	17	
	T 25–45	1	−0.64	4.1	16	
	Cal	3.7	−1.40	3.4	16	
Eu^{3+}	T 0–48	1	0.13[b]	−0.05	−0.6	18

[a] See Table 1.

[b] Calculated from the value $K_1 = 0.8\ M^{-1}$ originally given[18]. The value of ΔG° quoted in ref. 19 is not quite consistent with this value of K_1.

The sulphate complexes of hard acceptors are generally much stronger than the chloride complexes. The investigations referring to sulphate systems are therefore much more numerous, and they include acceptors of all charges between +1 and +4. Data are also often available both for $I = 0$, and for higher ionic strength, $I = 1$ or $2\ M$ (Table 3).

As is certainly to be expected from the structural determinations of hydrogen sulphates

TABLE 3

Formation of the first sulphate complex of various acceptors at 25°C. Values of ΔH° are determined calorimetrically, if not otherwise stated

Acceptor	ΔG°	ΔH°	ΔS°	Acceptor	ΔG°	ΔH°	ΔS°
$I = 0$ [a]							
H^+	−2.71	5.74	28.4	Sc^{3+}	−5.51	6.31	39.6
Mn^{2+}	−3.90	0.61	15.2	Y^{3+}	−4.56	3.61	27.4
Fe^{2+}	−3.00	0.56	12.0	La^{3+}	−4.77	3.24	26.9
Co^{2+}	−3.67	0.50	13.9	Ce^{3+}	−4.75	3.46	27.6
Ni^{2+}	−3.83	0.41	14.1	Sm^{3+}	−4.80	3.70	28.6
Cu^{2+}	−3.08	1.22	14.6	Eu^{3+}	−4.83	3.64	28.4
Zn^{2+}	−3.40	0.63	13.5	Gd^{3+}	−4.75	3.59	28.0
Cd^{2+}	−3.48	0.98	15.0	Tb^{3+}	−4.73	3.60	28.0
Al^{3+}	−4.11	2.29	21.4	Dy^{3+}	−4.68	3.69	28.1
Ga^{3+}	−3.78	4.71	28.4	Yb^{3+}	−4.54	3.60	27.3
In^{3+}	−4.15	6.95	37.2	Lu^{3+}	−4.76	3.29	27.4
$I = 1$ [b]							
H^+	−1.45	5.61	23.7	UO_2^{2+}	−2.46	4.36	22.9
$I = 2$ [c]							
H^+	−1.47	5.54	23.5	Y^{3+}	−1.68	4.04	19.2
Cu^{2+}	−0.80	1.74	8.5	La^{3+}	−1.76	3.72	18.4
Cd^{2+}	−0.86	1.90	9.2	Ce^{3+}	−1.69	4.27	20.0
				Sm^{3+}	−1.77	4.27	19.7
Am^{3+}	−2.0	4.4	21 [d]	Eu^{3+}	−1.87	3.88	19.3
Cm^{3+}	−1.8	4.1	20 [d]	Gd^{3+}	−1.81	3.95	19.3
Cf^{3+}	−1.9	4.5	21 [d]	Tb^{3+}	−1.74	4.24	20.1
				Dy^{3+}	−1.68	4.41	20.4
Th^{4+}	−4.49	5.00	31.9	Yb^{3+}	−1.57	4.14	19.2
Np^{4+}	−4.79	4.4	31 [d]	Lu^{3+}	−1.48	4.25	19.2

[a] Data referring to $I = 0$ from ref. 20, except for H^+, where values quoted in ref. 2 have been entered.

[b] Data referring to $I = 1\ M$ from ref. 21.

[c] Data referring to $I = 2\ M$ from ref. 22 (all M^{3+} ions), ref. 23 (Cu^{2+}, Cd^{2+}) and ref. 2 (H^+, Th^{4+}, Np^{4+}).

[d] ΔH° determined from temperature coefficient, T 0–55 for Am^{3+}, Cm^{3+}, Cf^{3+}; T 10–35 for Np^{4+}.

(e g ref 24), HSO_4^- in aqueous solution is no doubt an inner sphere complex, its formation being characterized by high positive values of ΔH° and ΔS° The same is also true for UO_2SO_4 formed by the divalent UO_2^{2+}

On the other hand, for most of the divalent transition metal ions, ΔH° is only ~ 0 5 kcal at $I = 0$, while $\Delta S^\circ \simeq 15$ cal/deg, values which are compatible throughout with predominant formation of outer sphere complexes The values of ΔH° found for Cu^{2+} and Cd^{2+} at $I = 0$ are markedly higher than for the other ions, however At $I = 2\ M$, slightly higher values still of ΔH° are found for these two ions Most probably, the proportion of inner sphere complexes is significantly larger for Cu^{2+} and Cd^{2+} than for the other divalent transition metal ions appearing in Table 3

The trivalent ions of Table 3, especially Sc^{3+} and In^{3+}, show such high values of both ΔH° and ΔS° that dominance of inner sphere complexes may be safely postulated For all the rare earth ions, including Y^{3+}, and the actinide ions, inner sphere complexes are also probably predominant The same is certainly true for Ga^{3+} For Al^{3+}, on the other hand, both ΔH° and ΔS° are markedly lower than for the other trivalent ions In this case, inner and outer sphere complexes may exist in roughly the same proportions

With the tetravalent ions Th^{4+} and Np^{4+}, the values of ΔH° and ΔS° strongly indicate inner sphere sulphate complexes

For all acceptors which have been measured at various values of I, viz H^+, Cu^{2+}, Cd^{2+} and the rare earths, it is observed that ΔH° varies only slightly between $I = 0$ and $I = 1$ or $2\ M$ Generally, an increase of the order of magnitude 0 5 kcal is found between $I = 0$ and $2\ M$, except for H^+ where a small decrease occurs The value of ΔS°, on the other hand, decreases markedly between $I = 0$ and $2\ M$, viz with about 5, 6 and 8 cal/deg for H^+, Cu^{2+} and Cd^{2+} and the rare earths, respectively These trends are evidently independent of whether inner or outer sphere complexes are formed, as is further confirmed by the behaviour of the inert acceptor $Co(NH_3)_5^{3+}$ In this case the same values of ΔH° are found for $I = 0$ and $1\ M$, while ΔS° decreases by some 11 cal/deg for both the inner and the outer sphere complex Very similar conditions are found for the formation of the first complex in fluoride systems (ref 1, Table 1) The decrease of ΔS° between $I = 0$ and $0\ 5\ M$ is ~ 6 cal/deg while ΔH° often stays approximately constant In some cases, however, a significant decrease of ΔH° seems to occur, e g for H^+ It should be remembered, however, that the sulphate complex of this acceptor behaves in the same way.

The values of ΔH°, and consequently ΔS°, quoted in Table 3 for the divalent transition metal ions, and for La^{3+} and Ce^{3+}, differ appreciably from those listed previously[2]. The new values are no doubt the more dependable as they have been determined by a direct calorimetric method while the old values were calculated from the temperature coefficients of the stability constants, a method which is not only generally less precise but sometimes yields quite erroneous results[1] In the present case, the accuracy of the old values, in contrast to the new, would not allow any reliable answers to the question of whether inner or outer sphere complexes are formed For the divalent transition metal ions, the old values favoured, if anything, the presumably false view that the proportion of inner sphere complexes was quite considerable[2]

D COMPARISON OF THE RESULTS BASED ON THERMODYNAMIC CRITERIA WITH THOSE FOUND BY NON-THERMODYNAMIC METHODS

It is evidently of great interest to investigate whether the results found above can be confirmed by other, non-thermodynamic methods Among these, infrared and ultrasonic absorption spectra have been applied specifically for the purpose of distinguishing between inner and outer sphere complexes

(i) Infrared absorption spectra

When a composite ligand, such as $SO_4{}^{2-}$, is coordinated in the inner coordination sphere of an acceptor, more or less extensive changes in the electronic distribution within the ligand take place as a result of the formation of the new bond This causes a shift in the infrared absorption frequencies of the internal ligand bonds Moreover, the infrared active stretching vibrations of a highly symmetrical ligand such as $SO_4{}^{2-}$ are triply degenerate. On coordination, this degeneracy is at least partly removed, which results in a splitting of the bands characteristic of the free sulphate ion while other previously inactive vibrations may become active, giving rise to new bands[25,26]

On the other hand, if the ligand stays in the outer coordination sphere, its electronic distribution is only slightly perturbed Consequently, no great change in the infrared spectrum is observed[25,26]

Larsson[26] has found that the SO stretching frequency ν_3, active in the free sulphate ion, is not actually split, but somewhat broadened when a complex is formed with a divalent transition metal ion Simultaneously, a very feeble activation of the stretching frequency ν_1 is also observed. This is interpreted as indicating that inner sphere complexes are formed only to a minor extent, the complexes are predominantly of the outer sphere type, as concluded from the thermodynamic criteria If the broadening of the ν_3-band is taken as a measure of the relative concentration of inner sphere complexes, their contribution would increase in the order $Ni^{2+} < Mn^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+} < Cd^{2+}$, while the integrated absorption of the new ν_1-band would suggest $Mn^{2+} < Zn^{2+} \simeq Co^{2+} < Ni^{2+} < Cu^{2+} \simeq Cd^{2+}$ Apart from the position of Ni^{2+}, the two sequences agree fairly well Both confirm the conclusion drawn above that the relative concentration of inner sphere complexes is largest in the Cu^{2+} and Cd^{2+} systems

Using certain crude assumptions regarding the magnitude of the molar absorption for the inner sphere complex, Larsson[26] calculates from the ν_1-band that the relative amount of such complexes is about 10% for the first step in the sulphate systems of divalent transition metal ions This result is, of course, entirely compatible with the conclusions drawn from the thermodynamic criteria

On the other hand, the same approach for the first step in the sulphate systems of In^{3+} and Ce^{3+} yields only 50% and 12% inner sphere complexes, respectively This is definitely much less than indicated by the thermodynamic criteria It may be that the assumptions mentioned are not fulfilled in these cases

(ii) Ultrasonic absorption measurements

As pointed above, the formation of an inner sphere complex from oppositely charged ions involves a very extensive break-up of the hydrate structures. The water molecules thus set free bring about a considerable increase of the solution volume. The formation of an outer sphere complex is accompanied by a much less extensive dehydration, and hence by a much smaller increase in volume. Consequently, the equilibrium between the inner and outer sphere complexes will be dependent upon the pressure.

Pressure changes can be brought about by exposing the solution to ultrasonics. This method has been successfully developed for the present problem by Eigen et al.[27,28] The sound absorption is measured as a function of the frequency. Within the frequency range available, the function often passes through two maxima, reflecting the existence of inner as well as outer sphere complexes. From the value of the absorption in the maximum, or the maximum of lower frequency if two are present, the constant for the equilibrium between inner and outer sphere complexes can be determined. From the position of the maximum, the relaxation time and hence the rate constants for the dissociation and formation of the inner sphere complex can be found.

In this way the sulphates of the divalent transition metal ions from Mn^{2+} to Zn^{2+} have been investigated by Eigen and Tamm[27], and the lanthanide sulphates (except that of Pm) by Fay et al.[29] (Table 4). As to the divalent ions, the amount of inner sphere complex is estimated to be about 10% for Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}, in fair agreement with the result arrived at both from the thermodynamic criteria and from the infrared spectra. For

TABLE 4

Relative amounts of inner- and outer-sphere complexes in various sulphate systems, as determined by ultrasonic absorption measurements. $M(H_2O)SO_4 \rightleftharpoons MSO_4$, $K_{43} = k_{34}/k_{43} = [MSO_4]/[M(H_2O)SO_4]$

Acceptor	$k_{34} \times 10^{-7}$	$k_{43} \times 10^{-7}$	K_{43}	% inner
Mn^{2+}	0.4	2	0.2	17
Fe^{2+}	0.1	0.6	0.17	15
Co^{2+}	0.02	0.25	0.08	7
Ni^{2+}	0.0015	0.01	0.15	13
Cu^{2+}	> 1	20		
La^{3+}	21	5.6	3.8	79
Ce^{3+}	33	7.0	4.7	83
Pr^{3+}	44	6.4	6.9	87
Nd^{3+}	52	8.8	5.9	85
Sm^{3+}	74	14.0	5.3	84
Eu^{3+}	66	14.6	4.5	82
Gd^{3+}	67	12.8	5.2	84
Tb^{3+}	52	9.6	5.4	85
Dy^{3+}	42	5.2	8.1	89
Ho^{3+}	28	3.5	8.0	89

Cu^{2+} and Zn^{2+}, the rates of transition between the inner and outer sphere complexes are too fast to allow any determination For the trivalent lanthanide ions, a much higher relative concentration of inner sphere complexes is found, 80–90%. Evidently, this vindicates the conclusions drawn from the thermodynamics of the complex formation rather than those based on the semi-quantitative evaluation of the infrared spectra.

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