A Proposed Approach to the "Chelate Effect"

by Arthur W. Adamson

A number of investigators have made experimental and theoretical contributions with respect to the entropy change accompanying the formation in aqueous solution of complex ions and of ion-pairs. Fyfe[1] was able to

1 W. S. Fyfe, J. Chem. Soc., 2018, 2023 (1952)

account for the average value of three or four entropy units per ammonia added in the formation of metal amine complexes by employing entropy values for "bound" ammonia and water. These last represented approximate averages of the spread of values for the entropy of ammonia and of water in solid ammoniate and hydrates. Latimer and Jolly[2] employed a similar approach

2 W. F. Latimer and W. J. Jolly, THIS JOURNAL, 75, 1548 (1953)

in treating the fluoride complexes of Al(III), although in so doing were led to the conclusion that the difference in charge and radius between $Al(H_2O)_6^{+3}$ and AlF_6^{-3} did not contribute importantly to the entropy change. Evans and Nancollas[3], as well as Fyfe[1], made use of cycles referring the

3 M. C. Evans and G. H. Nancollas, Trans. Far. Soc., 49, 363 (1953)

process from the aqueous to the gas phase, but as the former observed, estimation of the ΔS^0 (gas) must include important rotational entropy changes as well as the translational entropy change given by the Sackur equation.

Entropy values for "bound" ligands are qualitative since it is uncertain whether the data for solid hydrates, ammoniates, etc., are always germane, and if so, whether a simple average is appropriate. The alternative procedure of constructing the entropy change for the gaseous species from translational, rotational, etc., contributions may eventually be the most fruitful approach in estimating absolute ΔS^0 values.

The suggestion is made here, however, that for the purpose of present correlations entropies of complex ion formation to some extent can be accounted for by recognizing that for a process of the type

$$M(H_2O)_n + pX = M(H_2O)_{n-p} X_p + p H_2O \tag{1}$$
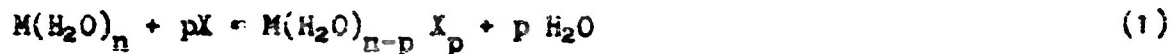
the usual choice of standard states is asymmetric. The hypothetical one molal state is employed for solutes while for the solvent the pure substance is chosen. In comparing a series of processes of type (1), of varying n and p values, not only are the magnitudes of ΔS^0 and ΔF^0 dependent upon the choice of standard states, but also their relative values or positions in a sequence. If the effect of standard state choice is regarded as primarily one of varying the translational entropy contributions, a brief can be made for the use of the hypothetical mole fraction unity state for the solutes. Such a state is one of minimum translational entropy for a solute retaining the properties it possesses in dilute solution. The conversion factors are:

$$\Delta S^{0\prime} = \Delta S^0 - 7.9\Delta n$$

$$\Delta F^{0\prime} = \Delta F^0 + 2360\Delta n \text{ (at } 25^0C)$$

the primed quantities are based on the hypothetical mole fraction unity state, and Δn denotes the moles of products minus those of reactants, exclusive of solvent.

Applying the above to the process studied by Latimer and Jolly[2]

$$Al(H_2O)_6^{+3} + 6F^- = AlF_6^{-3} + 6 H_2O \qquad \Delta S^0 = 91, \Delta S^{0\prime} = 138 \text{ E. U.}$$
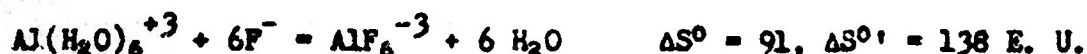
Employing their empirical equation for the charge-radius contribution to ionic entropies, the above $\Delta S^{O'}$ value is accounted for by taking the crystal radii of 0.50 and 1.36 A^O for aluminum and fluoride ions, and the reasonable value of 0.70 A^O for AlF_6^{-3}.

The present proposal is of especial value in comparing groups of reactions for which Δn differs but for which charge effects, etc. are a minimum. Thus the average ΔS^O for the formation in aqueous solution of $Cu(NH_3)_4^{+2}$ and $Zn(NH_3)_4^{+2}$ is - 15 ± 1.2 E. U., while for $Ni(NH_3)_6^{+2}$ and $Co(NH_3)_6^{+2}$, it is - 27 ± 0.3 E. U.[1] The corresponding $\Delta S^{O'}$ values are 17 and 21, and it is seen that a large measure of the difference in entropy of formation has been accounted for.

The "chelate" effect arises from a still simpler situation. The observation is that, for example, etheylenediamine complexes tend to be more stable than the corresponding amine ones, and that in general the higher the dentate character of the ligand, the more stable the complex. This has been stated, in a general way, to be an entropy effect[4,5] while Schwartzenbach[6]

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4 A. E. Martell and M. Calvin, "The Chemistry of the Metal Chelate Compounds", Prentice Hall Inc., N. Y., 1952, p. 149f.
5 C. G. Spike and R. W. Parry, THIS JOURNAL, 75, 2726, 3770 (1953)
6 G. Schwartzenbach, Helv. Chim. Acta, 35, 2344 (1952)

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has, in addition, presented a detailed kinetic treatment supposing a two stage addition of a bidentate ligand with the rate of addition of the second functional group proportional to its effective concentration as estimated from its free volume. This leads to a prediction of a chain length effect roughly in accord with the meager existing data.

While specific structural aspects are undoubtedly relevant, it is suggested here that the usual "chelate" effect is largely a consequence of the arbitrary asymmetry in the usual choice of standard states. If this is true

one would expect $\Delta S^{0}{}'$ values to be small for processes of the type

$$MX_p + p/2 \; Y = MY_{p/2} + pX \tag{2}$$

where Y denotes a bidentate group. It is seen from Table I that such
$\Delta S^{0}{}'$ values (and, where not available, $\Delta F^{0}{}'$ values) tend to be symmetrical
around zero, i.e. that a large measure of the apparent extra stability of
the chelate complexes disappears with the new choice of standard states.

As has been pointed out by J. Bjerrum[7], and by Schwartzenbach[6], a

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[7] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haase and
Son, Copenhagen, 1941.

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priori or statistical factors enter also into the entropy change for processes
(1) or (2). For a fully coordinated complex, i.e. of the type MX_n, the
statistical factor is unity, however, while for complexes such as $MX_2(H_2O)_{n-2}$,
an assumption is required as to the equivalence of the various possible
isomers. This has not been attempted here.

Table I

Influence of Choice of Standard State on the "Chelate" Effect[a]

$\underline{M}$	$\underline{p}$	ΔF^0 (Kcal)	$\Delta F^{0\prime}$ (Kcal)	ΔS^0	$\Delta S^{0\prime}$

I. $M(NH_3)_p + p/2\ en = M(en)_{p/2} + pNH_3$

$\underline{M}$	$\underline{p}$	ΔF^0 (Kcal)	$\Delta F^{0\prime}$ (Kcal)	ΔS^0	$\Delta S^{0\prime}$
Co^{+2}	2	-3.2	-0.9		
Ni^{+2}		-3.7	-1.4		
Cu^{+2}		-4.3	-2.0 [b]	5.7	-2.2
		-3.3	-1.0 [b]		
Zn^{+2}		-1.6	0.7	5.7	-2.2
Cd^{+2}		-1.3	1.0	4.4	-3.5
		$\underline{-1.4}$	$\underline{1.1}$	$\underline{4.7}$	$\underline{-3.2}$ [c]
	Av.	-2.7	-0.4	5.1	-2.8
Co^{+2}	4	-7.7	-3.0		
Ni^{+2}		-8.6	-3.9		
Cu^{+2}		-10.4	-5.7 [b]	19.1	3.3
		-6.7	-2.0 [b]		
Zn^{+2}		-2.3	2.4	13.4	-2.4
Cd^{+2}		-4.0	0.7	11.8	-4.0
		$\underline{-5.6}$	$\underline{-0.9}$	$\underline{19.3}$	$\underline{3.5}$ [c]
	Av.	-6.4	-1.7	15.6	0.1
Co^{+2}	6	-12.7	-5.6		
Co^{+3}		-18.3	-11.2		
Ni^{+2}		-13.2	-6.1	24.0	0.3

II. $M(NH_3)_p + p/3\ den = M(den)_{p/3} + p\ NH_3$ [d]

$\underline{M}$	$\underline{p}$	ΔF^0 (Kcal)	$\Delta F^{0\prime}$ (Kcal)	ΔS^0	$\Delta S^{0\prime}$
Co^{+2}	3	-5.3	-0.5		
Ni^{+2}		-5.8	-1.0		
Cu^{+2}		-8.2	-3.4		
Zn^{+2}		-3.1	1.7		
Cd^{+2}		$\underline{-3.5}$	$\underline{1.3}$		
	Av.	-5.2	-0.4		

III. $M(NH_3)_p + p/4\ trien = M(trien)_{p/4} + p\ NH_3$ [e]

$\underline{M}$	$\underline{p}$	ΔF^0 (Kcal)	$\Delta F^{0\prime}$ (Kcal)	ΔS^0	$\Delta S^{0\prime}$
Co^{+2}	4	-8.2	-1.1		
Ni^{+2}		-9.1	-2.0		
Cu^{+2}		-11.6	-4.5		
Zn^{+2}		-4.6	2.5		
Cd^{+2}		$\underline{-5.3}$	$\underline{1.8}$		
	Av.	-7.8	-0.7		

a. Values from refs. 4, 5, and 7, for ca. 25°C.
b. Propylene diamine instead of en.
c. NH_2CH_3 instead of NH_3.
d. diethylenetriamine
e. triethylenetetramine

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