# On the "Entropy Effect" in Chelating Processes

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The available data on entropies of chelate compounds indicate that an important factor in the so-called "chelate effect" is the difference in number between monodentate and chelate molecules in a chelating reaction. The entropy differences between complex ammonia metal ions and chelate metal ions are found to be relatively small.

Let a reaction between a metal ion and a monodentate ligand be represented by the equation
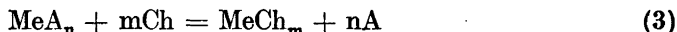
$$\text{Me(H}_2\text{O)}_n + n\text{A} = \text{MeA}_n + n\text{H}_2\text{O} \tag{1}$$
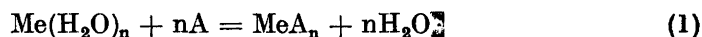
and that of a metal ion and a chelating agent by

$$\text{Me(H}_2\text{O)}_n + m\text{Ch} = \text{MeCh}_m + n\text{H}_2\text{O} \tag{2}$$
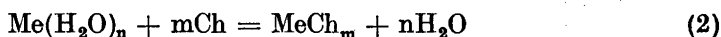
where n is the characteristic coordination number.

The equilibrium constant of (2) is generally much higher than that of (1) and there has been much discussion in the literature on the nature of this "chelate effect".

Let us consider a reaction:

$$\text{MeA}_n + m\text{Ch} = \text{MeCh}_m + n\text{A} \tag{3}$$

which is formally independent of the solvent.

The entropy change is given by

$$\Delta S = n\ S^{\ominus}(\text{A}) - m\ S^{\ominus}(\text{Ch}) + S^{\ominus}(\text{MeCh}_m) - S^{\ominus}(\text{MeA}_n)$$

The $S^{\ominus}$s are the partial molar entropies of the species in an arbitrarily chosen standard state at the temperature in question.

In most experiments in complex chemistry the standard state is the hypothetical one molar solution in a neutral salt medium. It is sometimes stated (*e. g.* Young [1]) that equilibrium data obtained in a constant salt medium do not

give "*true thermodynamic*" values. Of course the laws of thermodynamics are applicable also to reactions occurring in a constant salt medium and the thermodynamic data obtained are true enough although more or less different from those determined at extreme dilution.

The partial molar entropies of each of the reactants may in principle be measured using the third law of thermodynamics.

Unfortunately no data exist which permit a complete calculation of the entropies of complex reactions. Not even the entropies of most of the ligands are known. An exception is ammonia. According to *Selected Values of Chemical Thermodynamic Properties* [2] the partial molal entropy of ammonia in water at 25° C is 26.3 cal/degree mole. The atmospheric molar entropy of ammonia gas is 46.01 cal/degree mole at 25° C. Using the vapour pressure measurements of J. Bjerrum [3] and the heat of solution determined by Becker and Roth [4] the partial molar entropy of ammonia in a 2 M NH_4NO_3 solution is calculated to be 25.9 cal/degree mole.

In principle the entropy of a gaseous species may be calculated from statistical mechanics provided that the appropriate spectroscopic data are known. For most of the ligands of complex chemistry no such data are available. Empirical equations have been found, however, which permit a calculation of entropies of many gaseous substances with fair accuracy. Powell and Latimer [5] have proposed an equation which bases the aqueous entropy of neutral species upon the molar volume of the pure liquid state of the solute.

Cobble [6] has combined the different empirical equations and has obtained the following expression for the partial molal entropy in aqueous solution

$$S^{\oplus} = 10 + \frac{3}{2}R\log M + 9.2N - S^{\circ}_{(S)} - 0.22 V_m.$$

M is the molecular weight, N represents the number of "skeletal" bonded atoms in the compound (number of bonded atoms — number of hydrogens), $S^{\circ}_{(S)}$ is the entropy loss caused by double bonds, rings and branched chains, and V_m is the molar volume of the pure liquid compound.

For details and for references the reader is referred to the original paper.

For lack of experimental data we shall use this equation for the calculation of the partial molar entropies of ethylenediamine (en) and 1,3-diaminopropane (tn). We get the following values

$$S^{\oplus}(en) = 45 \text{ cal/degree mole at 1 M and } 25° C$$

$$S^{\oplus}(tn) = 50 \text{ cal/degree mole at 1 M and } 25° C$$

The equation yields for ammonia: $S^{\oplus}(NH_3) = 24$ cal/degree mole while the experimental value is 26. The entropy of gaseous en must be almost equal to that of *n*-butane, which is according to Pitzer [7] 74.17 cal/degree mole (25° C, 1 atm.). In Ref. [2] the entropy of vapourization of en is given as 23.8 cal/degree mole at 117° C and 760 mm Hg. Therefore the entropy of liquid en at 25° C must be about 50 cal/degree mole. It has been found by Copp and Everett [8] and others [9] that the excess entropy of mixing of amines and water is negative. Hence the value calculated for $S^{\oplus}(en)$ seems reasonable.

We are now able to obtain approximate values of $nS^{\ominus}(NH_3)-mS^{\ominus}(en)$ and $nS^{\ominus}(NH_3)-mS^{\ominus}(tn)$ in chelating processes of the type (3).

If the ΔS of the reaction is known we can make rough estimates of the differences $S^{\ominus}(MeCh_m)-S^{\ominus}(Me(NH_3)_n)$. Surprisingly few accurate determinations of entropies of reactions of complex compounds exist.

From the recent paper by Poulsen and Bjerrum [10] and from measurements by Bjerrum [11], Fyfe [12] and Davies, Singer and Staveley [13] one obtains the following entropy changes (Standard state 1 M, 25° C)

$$Ni(NH_3)_6^{++} + 3 \text{ en} = Nien_3^{++} + 6 \text{ NH}_3 \qquad \Delta S = 21 \text{ cal/degree mole}$$
$$Ni(NH_3)_6^{++} + 3 \text{ tn} = Nitn_3^{++} + 6 \text{ NH}_3 \qquad \Delta S = 14 \text{ » »}$$
$$Cu(NH_3)_4^{++} + 2 \text{ en} = Cuen_2^{++} + 4 \text{ NH}_3 \qquad \Delta S = 15 \text{ » »}$$
$$Cu(NH_3)_4^{++} + 2 \text{ tn} = Cutn_2^{++} + 4 \text{ NH}_3 \qquad \Delta S = 11 \text{ » »}$$
$$Zn(NH_3)_4^{++} + 2 \text{ en} = Znen_2^{++} + 4 \text{ NH}_3 \qquad \Delta S = 21 \text{ » »}$$
$$Cd(NH_3)_4^{++} + 2 \text{ en} = Cden_2^{++} + 4 \text{ NH}_3 \qquad \Delta S = 14 \text{ » »}$$

From the partial molar entropies of the three ligands we calculate the following differences:

$$6\ S^{\ominus}(NH_3)-3\ S^{\ominus}(en) = 21 \text{ cal/degree mole}$$
$$6\ S^{\ominus}(NH_3)-3\ S^{\ominus}(tn) = 6 \text{ » »}$$
$$4\ S^{\ominus}(NH_3)-2\ S^{\ominus}(en) = 14 \text{ » »}$$
$$4\ S^{\ominus}(NH_3)-2\ S^{\ominus}(tn) = 4 \text{ » »}$$

These data yield the following entropy differences:

$$S^{\ominus}(Nien_3^{++}) \ - S^{\ominus}(Ni(NH_3)_6^{++}) = 0 \text{ cal/degree mole}$$
$$S^{\ominus}(Nitn_3^{++}) \ - S^{\ominus}(Ni(NH_3)_6^{++}) = 8 \text{ » »}$$
$$S^{\ominus}(Cuen_2^{++}) \ - S^{\ominus}(Cu(NH_3)_4^{++}) = 1 \text{ » »}$$
$$S^{\ominus}(Cutn_2^{++}) \ - S^{\ominus}(Cu(NH_3)_4^{++}) = 7 \text{ » »}$$
$$S^{\ominus}(Znen_2^{++}) \ - S^{\ominus}(Zn(NH_3)_4^{++}) = 7 \text{ » »}$$
$$S^{\ominus}(Cden_2^{++}) \ - S^{\ominus}(Cd(NH_3)_4^{++}) = 0 \text{ » »}$$

The experimental ΔS values are probably uncertain at about $\pm$ (10—15) %. The estimated entropy values are probably uncertain at about 3—4 cal/degree mole.

An optimistic estimation of the uncertainties involved would yield an indeterminacy of about $\pm$ 10 cal/degree mole for the values of the entropy differences between chelate and non chelate complex ions. This means that their partial molar entropies are almost equal within the experimental uncertainty. An interpretation of the figures obtained seems rather futile.

In the chelating reactions considered the entropy change is largely due to the entropy difference between the monodentate ligands and the chelating ligands. As suggested by Calvin and Bailes [14] this entropy difference is partly caused by the different numbers of monodentate and chelate molecules taking part in the reaction. The numerical value is dependent upon the arbitrary choice of standard state. The entropy differences between the complex ions are of course independent of the standard state.

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