375. *Complex-ion Formation. Part II.* The Entropies of Formation of Some Metal Ammines.*

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The heats of ammination of some metal ions have been measured, and with existing free-energy data the entropies of ammination have been calculated. These results are discussed in relation to hydration numbers of ions.

The heats of ammination of the silver, cupric, nickel, mercuric, cadmium, zinc, lithium, and magnesium ions have been measured. These data have been combined with the free-energy data found by Bjerrum ("Metal Ammine Formation in Aqueous Solution," Haase, Copenhagen, 1941) to give the entropies of formation of the ammines from the aquo-cations. The results are summarised in Table 1, where the units are kcal./mol. The measured entropy changes are concerned with the reaction

$$[M(H_2O)_m]^{z+} + nNH_3 = [M(NH_3)_n]^{z+} + mH_2O$$

where *m* and *n* may or may not be equal. It was thought that a study of these entropies might throw some light on the problem of ionic hydration numbers.

Table 1.

Ion	No. of ligands	$-\Delta H$	$-\Delta G$	$-\Delta S$	Ion	No. of ligands	$-\Delta H$	$-\Delta G$	$-\Delta S$
H^+ *	1	12·4	12·6	−0·5	Cd^{++}	6	15·2	7·1	27·0
Ag^+	2	13·5	9·96	12·4	Hg^{++}	4(2)	28·5	26·2	7·7
Cu^{++}	4	21·1	16·4	16·2	Li^+	(3)	0·5	3·26	12·6
Ni^{++}	6	18·9	10·6	27·7	Mg^{++}	(6)	0·1	4·48	19·0
Zn^{++}	4	15·9	11·8	13·7					

* Everett and Wynne-Jones, *Trans. Faraday Soc.*, 1939, **35,** 1380.

An approach may be made to the interpretation of the entropy data in a similar manner to that used by Ulich (*Z. Electrochem.*, 1930, **36,** 497), who considered the absolute entropy of hydration of ions, and compared the entropies of certain salt hydrates with those of the

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* Part I, preceding paper.

anhydrous salts and recognised that the average contribution to the entropy of the solid for each water molecule added was about 9 kcal./mol. This value is similar to the entropy of ice at 298°. The examples quoted by Ulich, with the addition of more recent cases, are listed in Table 2, where S = entropy at 298° and Δn = change in number of water molecules in hydrate.

TABLE 2.

Salt	S	$\Delta S/\Delta n$	Salt	S	$\Delta S/\Delta n$	Salt	S	$\Delta S/\Delta n$
Al_2O_3,H_2O [a]	23·15		$MgCl_2$ [a]	21·4		$ZnSO_4$ [b]	30·6	
,, $,3H_2O$	33·5	5·17	,, $,H_2O$	32·8	11·4	,, $,6H_2O$	86·9	9·4
$Al_2(SO_4)_3$ [a]	57·2		,, $,2H_2O$	43·0	10·8	,, $,7H_2O$	92·9	6·0
,, $,6H_2O$	112·1	9·1	,, $,4H_2O$	63·1	10·4	LiOH [c]	10·23	
$CdSO_4$ [a]	31·3		,, $,6H_2O$	87·5	11·0	,, $,H_2O$	17·07	6·84
,, $,H_2O$	39·7	8·4	MnS_2O_6 [a]	45		$NaH_2PO_4,7H_2O$ [d]	102·4	
$CaSO_4$ [a]	25·9		,, $,2H_2O$	66·7	10·8	,, $,12H_2O$	150·5	9·6
,, $,\frac{1}{2}H_2O$	31·2	10·6	,, $,6H_2O$	110	11	$K_4Fe(CN)_6$ [d]	109	
,, $,2H_2O$	46·4	10·25	Na_2SO_4 [a]	33·7		,, $,3H_2O$	143	11·3
$CuSO_4$ [a]	25·3		,, $,10H_2O$	140·5	10·48	$(CO_2H)_2$ [d]	28·7	
,, $,H_2O$	33	7·7				,, $,2H_2O$	49·9	10·35
,, $,3H_2O$	52·4	9						
,, $,5H_2O$	70·2	9						

[a] U.S. Bureau of Mines Bull. 477, 1948. [b] Barieau and Giauque, *J. Amer. Chem. Soc.*, 1950, **72**, 5676. [c] Bauer, Johnston, and Kerr, *ibid.*, p. 5174. [d] Ulich, *loc. cit.*

On the basis of these facts, Ulich considered that when a water molecule becomes bound to a cation the average entropy change will be approximately equal to the entropy of fusion of water at 298°, or 6 kcal./mol. (In this discussion rounded entropy figures will be used as present data do not justify a more accurate treatment.) To obtain hydration numbers he divided the absolute entropy of hydration of the gaseous ion by 6. Such an approach must be an over-simplification, for the different strengths with which water molecules may be bound to a cation are not considered. The strength of the linkage must influence the degrees of freedom of the water molecule.' Latimer (*J. Amer. Chem. Soc.*, 1951, **73**, 1480) also uses the figure of 9 kcal./mole as being the average contribution to the entropy of a hydrate per water molecule.

It is now generally considered that entropy effects accompanying hydration of an ion consist of two major parts: an electrostatic effect arising from orientation and restriction of translational freedom of water molecules due to ion–dipole interaction, and secondly, restriction due to the formation of true covalent bonds between a donating centre of the solvent and the ion. It might be expected that where covalent bonding occurs, the entropy decrease per water molecule would be greater than in the case where only electrostatic interaction occurs. With most anions, and the cations of the most electropositive metals, the electrostatic effect will probably account for most of the entropy of hydration, while with more electronegative metals, where covalent bonding will occur, the second effect may well be the more important. Hydrogen bonding must play an important part where this can occur as it will with the fluoride and chloride anions, and at the outside of the first hydration shell with cations. However, in the case of most cations the small additional positive charges on peripheral hydrogen atoms of first-shell water molecules will probably make hydrogen bonding only slightly stronger than in the bulk of the solvent and restrictional entropy decreases with these molecules should be small.

With ionic crystals, the degrees of freedom of the positive and negative ions will depend to some extent on the electrostatic field in which the ions are situated. This factor will be dependent on the size of the constituent ions. When the ions in a crystal become fully hydrated, the field intensity will be very considerably decreased, and this will greatly increase the entropy of the ions. This factor must be taken into account if the entropies of anhydrous and hydrated salts are compared. In effect, the loss of degrees of freedom by water molecules is greater than that assumed on the simple Ulich picture, for, although the water molecules are losing freedom, the ions are gaining freedom owing to the dilution of the potential field. The figures for the entropies of salt hydrates and anhydrous salts listed in Table 2 indicate that the entropy of the water molecules is far from being constant but varies from 6 to 11 entropy units.

The value used by Ulich of 6 kcal./mole for the entropy change accompanying solvation must be considered the smallest possible change, and it is of interest that if for the more electronegative metals an entropy decrease of about 10 kcal./mole is used, then very reasonable hydration numbers are obtained. For example, the transition-metal ions would have a hydration number of 6, the silver ion 2, etc. The case of the very small hydrogen ion must be considered separately. If we accept Eastman's value (*J. Amer. Chem. Soc.*, 1928, **50**, 292) for the absolute entropy of the chloride ion, then the absolute entropy of hydration of the hydrogen ion is —23 kcal./mole. From the considerations mentioned above, the formation of the hydroxonium ion would account for a decrease of approximately 10 kcal./mole; this ion is still very small and woud be expected to have an entropy of hydration similar in magnitude to that of an alkali-metal ion which would easily account for remaining entropy decrease.

The suggestion that the degrees of freedom, and hence entropy, of a water molecule bound to a cation are less than those in ice does not appear unreasonable when it is considered that around an ion there may be a tightly packed system of 6 or more molecules bound with much stronger linkages than the hydrogen bonds in ice. Rotational degrees of freedom must be very slight indeed.

Similar considerations may now be applied to the entropies of ammination. We may as a first approximation suggest that the entropy of ammonia bound to a cation will be similar to the entropy of an ammonia molecule in solid ammonia. From an extrapolation of the data on the specific heat of ammonia found by Overstreet and Giauque (*ibid.*, 1937, **59**, 255) the entropies of solid and liquid ammonia at 298° were calculated to be 16 and 25 kcal./mole, respectively. Thus the entropy of fusion is approximately 9 kcal./mole. This idea was also tested by calculating approximately the entropy of hexa-amminonickel nitrate from Long and Toettcher's specific-heat data (*J. Chem. Phys.*, 1940, **8**, 504) which gave a value of 140 kcal./mole compared with that of nickel nitrate, 50 kcal./mole calculated by Latimer's approximation method (*loc. cit.*). The average entropy of the ammonia molecules in the ammine is thus approximately 15 kcal./mole. This is in good agreement with the Ulich model. Once more, however, the actual losses per molecule will be greater.

As a first approach to the calculation of the entropies of ammination we might consider that the entropy change for each molecule of water replaced by an ammonia molecule will equal the difference in the entropies of fusion of ammonia and of water at 298°, or approximately —3 kcal./mole. By using this approximation and assuming that the number of water molecules in the aquo-cation is equal to the number of ammonia molecules in the ammine, the figures in Table 3 were obtained.

TABLE 3.

Ion	No. of ligands	$-\Delta S$ (calc.)	$-\Delta S$ (found)	Ion	No. of ligands	$-\Delta S$ (calc.)	$-\Delta S$ (found)	Ion	No. of ligands	$-\Delta S$ (calc.)	$-\Delta S$ (found)
H	1	3	−0·5	Ni	6	18	27	Hg	4(2)	6(12)	8
Ag	2	6	12·4	Zn	4	12	14	Li	3	9	12
Cu	4	12	16	Cd	6	18	27	Mg	6	18	19

The results calculated are of reasonable magnitude and suggest that each of the ions carries no more water molecules covalently bound than ammonia. If the ion carried more water, then the calculated entropy change would be more positive whereas in fact, except for the hydrogen ion, the measured results are more negative. The large decrease in entropy on ammination may in part be attributed to the shortening of the linkages in the ammines which would be accompanied by more configurational restrictions.

A more fundamental approach may be made by consideration of the following entropy cycle :

$$\begin{tikzcd}
 & {[M(H_2O)_m]^{z+}_g + n(NH_3)_g} \arrow[rrr, "\Delta S_2"] & & & {[M(NH_3)_n]^{z+}_g + m(H_2O)_g} \arrow[dd, "\Delta S_3"] & \\
\Delta S_{1a} & & \Delta S_{1b} & \Delta S_{3a} & & \Delta S_{3b} \\
 & {[M(H_2O)_m]^{z+}_{aq.} + n(NH_3)_{aq.}} \arrow[uu, "\Delta S_1"'] & & & {[M(NH_3)_n]^{z+}_{aq.} + m(H_2O)_{aq.}} \arrow[lll, "\Delta S_4"'] &
\end{tikzcd}$$

where $\Delta S_1 = -\Delta S$ of hydration of gaseous ion $+(-\Delta S)$ of hydration of gaseous ammonia; $\Delta S_2 =$ entropy of ammination in the gas phase; $\Delta S_3 = \Delta S$ of hydration of complex ion $+$ entropy of condensation of water; $\Delta S_4 = -\Delta S$ measured in the liquid phase; $\Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = 0$.

If the first three of these steps could be calculated, ΔS_4 could be obtained. With present data only very approximate calculations can be made. Primarily we may assume that the entropy of hydration of the aquo-cation and of the ammine will be similar. This should be reasonable, particularly for larger ions with large values of n and m, as these ions will be of similar size, and Latimer (*Chem. Rev.*, 1936, **18**, 349) has demonstrated that the entropy of hydration of a gaseous ion is a function of its size. Thus ΔS_{1a} and ΔS_{3a} will be considered approximately equal and will cancel out. The entropy of hydration of ammonia was calculated from free-energy data (Lewis and Randall, "Thermodynamics," McGraw-Hill, 1923), and heat of solution data (Bichowsky and Rossini, "Thermochemistry," Reinhold, 1936) and gave a value of —20 kcal./mole. At 298°, ΔS_{3b} is approximately —29 kcal./mole. Considering ΔS_2, we may assume that the general translational degrees of freedom of the complex ions remain unchanged and that the entropy changes are restricted to loss of degrees of freedom by the ammonia molecules and gain by the water molecules. As a first approximation we may consider that both gases when bound have an entropy equal to that in the solid state. As at 298° the entropies of gaseous ammonia and of gaseous water are 45 and 46 kcal./mole, respectively, and those of the solids are 9 and 16 kcal./mole, then ΔS_2 will equal $36m - 30n$.

If we consider the case of the hydrogen ion and put $n = m = 1$, then

$$\Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = 20 + 6 - 29 + \Delta S_4 = 0, \text{ and } \Delta S_4 = 3,$$

and the measured entropy change will be —3 kcal./mole. Similarly, for the cupric ion, it being assumed that $n = m = 4$,

$$\Delta S_4 = -80 -24 + 116 = 12$$

and the measured entropy will equal —12 kcal./mole. If for the latter case we use Ulich's value of 10 for the solvation number of the cupric ion, then $m = 10$ and $n = 4$, and

$$\Delta S_4 = -80 -240 + 290 = -30$$

and the measured change would be +30 kcal./mole. It will be noted that, the above constants being used, the cycle will give the same calculated results as in Table 3.

From considerations previously outlined, it appears that the entropy of a water molecule solvating the more electronegative cations is more likely to have an entropy of approximately 6 kcal./mole, and if a proportional decrease is allowed for the ammonia molecule then these new constants give much better agreement with the cases of the silver, nickel, and cadmium ions. It is obvious that, as with the salt hydrates listed in Table 2, there will be small differences in the entropies of the ammonia molecules in different cases, and as the degrees of freedom of the ammonia molecules will vary from case to case no set of constants will cover all results.

If the assumptions in the above calculations are considered reasonable, it will be seen that, in general, the condition that the number of strongly bound water molecules is equal to the number of ammonia molecules in the ammine gives the best agreement with the experimental values. Making the hydration numbers larger causes the calculated entropies to be more positive whereas actually they should be more negative.

A criticism which may be levelled at the above arguments is that in the cases considered where $m > n$ it is still assumed that the entropy of hydration of the two complex ions is the same. This assumption can hardly be valid for cases like the hydrogen ion where n and m are small. However, with larger ions such as the nickel hexaquo-cation there will be little difference in the size and presumably in the entropy of hydration on the addition of another water molecule, especially when it is remembered how small the entropies of hydration of large ions like iodide and rubidium are. As mentioned in Part I (*loc. cit.*) the charge density on large complex ions is probably very small. To make the calculations for the cupric ion invalid it would have to be assumed that the entropy of hydration of $Cu(H_2O)_{10}^{++}$ is more positive than that of $Cu(NH_3)_4^{++}$ by 42 kcal./mol., which does not appear probable when it is considered that the absolute entropy of hydration of the cupric ion of radius 0·80 Å is 62 kcal./mol. while the radius of the ammine will be approximately 3·5 Å. Again, this objection is to some extent overruled by the fact that, in general, ammines will be smaller than the aquo-complexes owing to the greater covalent character of the bonds, and this effect will tend to make the calculated entropies too positive. Owing to the more polar character of the bonds in the hydroxonium ion than in the ammonium ion, the entropy of solvation of the former may be greater than that of the latter, thus accounting for the negative value of the entropy calculated.

Experimental.—The heats of formation of the ammines were measured in Dewar flasks at room temperature (14—17°). The flasks were fitted with a stirrer and a pipette with a seal of picene wax which could be broken when desired. The pipettes were immersed below the level of one of the reagents in the flask. In most runs the flasks contained 100 c.c. of M-ammonium hydroxide and the pipette contained 10 c.c. of approximately M-metal salt. An excess of ammonia was always present. Temperatures were measured with a Beckmann thermometer and heats of reaction were normally 1—2°. Duplicate runs were reproducable to ±0·01°. Each experiment also involved the measurement of two heats of dilution so that an overall error of ±3% is possible. The flasks were calibrated both by electrical means and by measuring heats of neutralisation.

Reagents were of " AnalaR " quality, and solutions were standardised by normal analytical procedures. In the case of the mercuric ion, a solution of mercuric nitrate was prepared by dissolving mercuric oxide in nitric acid and standardising the solution with potassium chloride. Experiments using mercuric chloride gave a ΔH of approximately half that of those using the nitrate. With zinc, cadmium, mercury, and magnesium ions, the measurements were carried out in 3M-ammonium nitrate to prevent basic salt formation. With lithium and magnesium the temperature changes were 0·1° or less so that greater errors are possible. In these cases 10M-ammonium hydroxide was used.

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