The Heats of Formation of Complex Ions containing Ethylenediamine.

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A calorimeter is described for the accurate measurement of the heats of reactions which take place rapidly in solution, and of heats of solution, neutralisation, and dilution. Its capabilities have been tested by measurement of the heat of neutralisation of sodium hydroxide by hydrochloric acid and of the heat of solution of potassium chloride. In favourable circumstances an accuracy of 0·1% is possible. The calorimeter has been used to measure the two heats of neutralisation of ethylenediamine, and the heats of formation of complex ions of ethylenediamine and copper, nickel, cadmium, and zinc. By carrying out experiments with varying proportions of metal and amine, heats of formation have been obtained for the ions $M(en)_2^{++}$ and (except for copper) for the ions $M(en)_3^{++}$. These heats of formation have been combined with the known free-energy changes to evaluate the entropies of formation of the ions. The results are discussed, with special reference to the significance of the entropy change in complex-ion formation of this kind.

In recent years, increasing interest has been shown in the physical chemistry of complex-ion formation. In particular, numerous measurements have been made of the stability constants of complex ions and hence of their free energies of formation. If their heats of formation are also known the corresponding entropy change can, of course, be evaluated. Usually, however, either these heats of formation have not yet been determined, or else the only values available are those calculated from stability-constant measurements at more than one temperature. The reliability of such values often seems to be questionable, primarily because the range of temperatures over which the measurements were made has almost always been too small. It is undoubtedly better to measure the heats of formation calorimetrically, preferably under more or less the same conditions of concentration and ionic strength as those used in the measurement of the stability constants.

Some direct determinations of the heats of formation of metal–ammonia complex ions in solution have recently been carried out by Fyfe (*J.*, 1952, 2023), with an accuracy of $\sim\pm3\%$. These determinations were made upon rather concentrated solutions ($\sim$1M). We now describe a calorimeter for the measurement of heats of complex-ion formation with which a greater precision can be obtained while using more dilute solutions, so that the results can be combined with measurements of stability constants made in this laboratory by H. M. N. H. Irving and his co-workers (and by others elsewhere), using solutions of the same order of dilution. The accuracy of the calorimeter has been carefully tested by measuring (*a*) the heat of solution of potassium chloride in water and (*b*) the heat of neutralisation of sodium hydroxide by hydrochloric acid (which are processes involving accurately known heat-content changes), and in favourable circumstances the calorimeter is capable of a precision of $\pm0{\cdot}1\%$. The calorimeter has been used to determine the heats of formation of complex ions formed from ethylenediamine and nickel, cupric, zinc, and cadmium ions. Since, in general, any one metal forms more than one complex ion with ethylenediamine, it is necessary to know the successive stability constants for each system, and also to carry out measurements using different proportions of the metal and the diamine, in order to evaluate the heats of formation of the several complex ions. Inaccuracy in the values of the stability constants, therefore, has an effect on the values derived for the corresponding heat-content changes and, for some at least of the systems we have studied, the uncertainty in the stability constants is such that the values ultimately derived for the entropy changes may be wrong by several entropy units. We shall therefore present our thermochemical data in a way which will permit heats of formation to be recalculated from them with other values of the stability constants than those selected by us.

Finally, we report the results of measurements of the first and the second heat of neutralisation of ethylenediamine. These were carried out because of the discrepancy between the published values obtained indirectly from dissociation-constant measurements. The existence of this discrepancy means that not only must some of the values reported for these dissociation constants be wrong, but also stability constants estimated by methods which require a knowledge of these dissociation constants.

EXPERIMENTAL

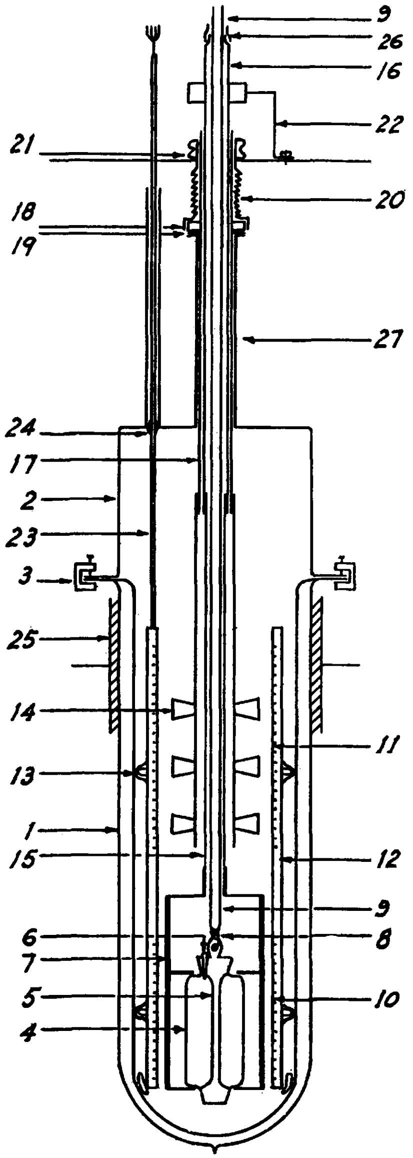
In its main features, the calorimeter is similar to that described by Pitzer (*J. Amer. Chem. Soc.*, 1937, **59**, 2365), but differs from his in not having an evacuated ground-glass stopper and in the arrangements made for introducing the solution or component present in smaller amount. Its construction is shown in the figure. The top of the Dewar vessel 1, which held about 1 l., was closed with a brass cap 2 resembling a top hat. This was about 3 in. high so as to increase the length of the tubes passing through a central hole in its roof into the liquid in the calorimeter, thereby reducing the thermal gradient along these tubes. The flange on the brass cap was held by four screw clips 3 to a flange on the top of the Dewar vessel, the joint being made water-tight with a little Vaseline.

The component present in smaller amount was contained in a bottle 4 with ground-glass stoppers at top and bottom, which were sealed to a glass rod 5. The bottle was filled through a small hole in the upper stopper (later closed by a ground-glass plug 6). When in place in the calorimeter, the bottle fitted loosely in a gold-plated metal frame 7. A loop of platinum wire was attached to the upper stopper and also to the hook 8 on the bottom of the central glass tube 9. When the upper end of this glass tube was pulled, the bottle therefore opened at both ends and its contents were quickly swept out by the current of liquid moving upwards round the bottle. There was no detectable "heat of opening." The stirrer was rotated throughout the whole experiment at a constant speed of 160 rev./min., so that (as is customary in calorimetry of this kind) it was assumed in the evaluation of the temperature change caused by the reaction or by electrical heating that the rate of generation of the heat of stirring (which in fact was very small) was constant. It must be clearly understood that the only moving part of the calorimetric assembly is the stirrer 14 and the shaft 17 bearing it. The framework 7 holding the bottle 4 is fixed, since the glass tube 15 supporting the framework is cemented to the brass tube 16, which is firmly held by the clamp 22. The tube 17 therefore rotates between the two fixed tubes 27 and 16.

The heater 10 and resistance thermometer 11 were contained within two sealed concentric copper cylinders 12 which were gold-plated on the outside, and kept central by rubber-protected projections 13.

Energy input was determined by using a potentiometer to measure the current through the manganin heater and a Venner electrically-operated stop-watch to measure (to 0·02 sec.) the time of passage of the current. Changes in the resistance of the copper resistance thermometer were measured by using the circuit described by Pitzer. All resistances were kept in a thermostat. Temperature changes of $5 \times 10^{-5\circ}$ could be detected. The actual temperature changes were $\sim 1^\circ$ in the heat of solution experiments, $\sim 0{\cdot}3^\circ$ in the heat of neutralisation experiments, and between 0·05 and 0·25° in the experiments on complex ions.

In the experiments on complex-ion formation, a solution of ethylenediamine in 0·1M-potassium chloride was placed in the double-stoppered bottle 4, the weight of the solution being found from the increase in the weight of the bottle. (In experiments in which ethylenediamine or sodium hydroxide was used, great care was taken to exclude atmospheric carbon dioxide from all solutions.) A fixed volume ($\sim$1 l.) of 0·1M-potassium chloride was siphoned into the Dewar vessel 1, and a known amount of a concentrated solution of the metallic sulphate (also in 0·1M-potassium chloride) was added to it from a weight pipette. The calorimeter was then assembled outside the thermostat, transferred to the thermostat (which was maintained at 25·00° ± 0·005°), and the contents of the calorimeter were heated electrically until they were at a suitable temperature below 25°. Never in a run did the temperature within the calorimeter exceed 25°. The experiment was then carried out with fore and after periods of at least 10 min.; mixing seemed to be complete within 10 sec. of opening the bottle, since after this period, linear time–temperature relationship was re-established. The calorimeter was then cooled to about the same temperature as before the bottle was opened; this was conveniently done by dropping powdered solid carbon dioxide down the central glass tube 9, and the " electrical energy equivalent " experiment was carried out. Usually three determinations of the " electrical energy equivalent " were made. The heat generated in the chemical experiment was then calculated by standard methods (see, *e.g.*, Sturtevant in Weissberger, " Technique of Organic Chemistry," Interscience Publ., 1949, Vol. I, Physical Methods, Part I, p. 731). It was found by experiment that the heat of dilution of ethylenediamine under the conditions of the experiments was negligible.



1, Silvered Dewar vessel.
2, Brass cap with plane flange.
3, Screw clips.
4, Bottle, capacity ~25 c.c.
5, Glass rod, sealed to both stoppers.
6, Filling hole and plug.
7, Gold-plated frame with detachable base, and shelf to restrict upward movement of bottle.
8, Glass hook.
9, Central glass tube.
10, Heater of 32 s.w.g. manganin, resistance ~100 ohms, with leads of 24 s.w.g. copper.
11, Copper resistance thermometer, 42 s.w.g., resistance ~96 ohms at 25°, with 23 s.w.g. manganin leads.
12, Hollow gold-plated copper cylinder.
13, Rubber-protected projections to centre cylinder.
14, Glass stirrer, sending liquid up the inside of the gold-plated cylinder.
15, Glass tube cemented to the frame 7.
16, Brass tube cemented at lower end to glass tube 15.
17, Brass tube cemented at lower end to glass stirrer 14.
18, Detachable collar.
19, Greased leather washer.
20, Flexible drive fixed to collar 18 by grub screws.
21, Pulley.
22, Clamp to hold tube 16 rigid.
23, Thin-walled brass conduit for leads.
24, Rubber seal.
25, Detachable brass clamp for support of calorimeter.
26, Rubber sleeve.
27, Brass tube soldered to brass cap 2.

The possibility of evaporation from inside the calorimeter was prevented by the washer 19 and the rubber seals 24 and 26, and by making the central brass tubes (which were greased) as close a fit as possible.

The level of liquid in the Dewar vessel was about 1 cm. above the top of the cylinder 12, and that of the water in the thermostat about 5 cm. above the top of the cap 2.

The metallic salt solutions were made up from " AnalaR " samples, and their concentrations determined by standard gravimetic methods. Ethylenediamine was dried over potassium hydroxide pellets and then twice fractionated.

In the heat of neutralisation experiments a known amount of hydrochloric acid (which had been standardised gravimetrically by silver chloride precipitation) was placed in the bottle, and about 1 l. of dilute carbon dioxide-free sodium hydroxide solution (representing a slight excess) in the Dewar vessel. In the measurements of the heat of solution of potassium chloride, the salt required about 10 min. to dissolve completely, and the fore and after periods were accordingly prolonged. The thermal exchange corrections were therefore larger here than for the more rapid reactions, and consequently the precision of the heat of solution measurements is not quite as high as that of the heat of neutralisation measurements.

Results.—The unit in which all results are expressed is the thermochemical calorie (=4·1833 international joules, =4·1840 absolute joules).

Results on the heat of solution of potassium chloride are presented in Table 1. Since the concentration of the solution produced varied slightly from one experiment to another, small corrections have been applied to give values at an arbitrarily fixed dilution of 1 mole of salt to 167 moles of water. Two reviews of previous determinations of the heat of solution of this salt have recently been published, one by Miščenko and Yu. Ya. Kaganovich (*J. Appl. Chem., U.S.S.R.*, 1949, **22**, 1078; *Chem. Abs.*, 1950, **44**, 921), and the other by Rossini (" Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, 1952). The values given by these authors, corrected to our dilution, are included for comparison in Table 1.

TABLE 1. *Heat of solution of potassium chloride at* 25°.

x = Moles of water per mole of salt; ΔH = heat absorbed (in cal./mole) at this dilution; $\Delta H_{\text{corr.}}$ = heat of solution corrected to x = 167.

x	166·7	165·7	166·6	175·4	167·1
ΔH	4193	4195	4174	4183	4179
$\Delta H_{\text{corr.}}$	4193	4196	4174	4180	4179

Mean = 4184 ± 8

Miščenko and Yu. Ya. Kaganovich give 4187; Rossini gives 4194.

Four measurements of the heat of neutralisation of sodium hydroxide by hydrochloric acid were made, exactly the same concentrations being used throughout, that of the alkali being about N/30. After correction to infinite dilution, using for this purpose the same data as Pitzer (*loc. cit.*), the individual values were: −13,345, −13,355, −13,378, −13,344 cal./mole. The mean is −13,356 ± 12. The value derived from a critical examination of other data (Rossini, *Bur. Stand. J. Res.*, 1931, **6**, 855), when converted to 25° by Pitzer, was −13,352 cal./mole. Pitzer himself recorded a measured value of −13,363 ± 16 cal./mole.

TABLE 2. *Heat of mixing of hydrochloric acid and ethylenediamine.*

A = Moles of hydrochloric acid × 10^3; B = moles of ethylenediamine × 10^3; Q = heat evolved (in cal.).

A	24·48	24·36	24·19	9·865	9·863	9·890	9·884	9·800	9·796
B	9·637	9·618	9·620	11·51	11·56	11·57	11·58	11·49	11·52
Q	219·7	220·0	220·2	116·0	116·2	118·5	119·0	116·0	117·5

In Table 2 we present the results for the heat evolved on mixing of solutions of ethylenediamine and hydrochloric acid of different concentrations. From these results, values of ΔH_1 and ΔH_2 have been calculated, these being the heat content changes in the processes $(en)H^+ \rightleftharpoons (en) + H^+$, $(en)H_2^{++} \rightleftharpoons (en)H^+ + H^+$, respectively, in aqueous solution at 25° in 0·1M-potassium chloride. In these experiments, the constituent present in excess furnished the more dilute solution before mixing. In the first three experiments, the acid was in such excess that the doubly charged cation was virtually completely formed. The mean value for $(\Delta H_1 + \Delta H_2)$ per g.-ion is 22,850 ± 40 cal. In the remaining experiments, about 99% of the amine was converted into the singly charged ion, and the remainder into the doubly charged ion. To allow for the latter, the amounts of the two ions were calculated by using the dissociation constants at 25° given by Everett and Pinsent (*Proc. Roy. Soc.*, 1952, *A*, **215**, 416). The resulting mean value for ΔH_1 is 11,910 ± 100 cal./g.-ion, whence ΔH_2 = 10,940 ± 140 cal./g.-ion. The values of ΔH_1 and ΔH_2 are compared with others in Table 3.

Of the last four sets of values, only those of Berthelot were determined directly. The others are derived from the temperature variation of the ionisation constants. The agreement of these values with ours is satisfactory.

TABLE 3. *Heat-content changes in reactions between hydrochloric acid and ethylenediamine.*

Source	ΔH_1	ΔH_2	Ref.
This work	11,910	10,940	
Everett and Pinsent	11,820	10,870	*Loc. cit.*
Williams	13,100	10,150	Thesis, Oxford, 1948
Dickens	11,450	10,900	Personal communication
Berthelot	12,400	10,800	*Ann. Chim. Phys.*, 1900, **20**, 163

Results for the metal ion–ethylenediamine systems are given in Table 4. In general, in any of these systems, there are three complex ions to consider, namely $M(en)^{++}$, $M(en)_2^{++}$, and $M(en)_3^{++}$. To evaluate the heat of formation of each of them, it being assumed that the three stability constants are known, at least three determinations of the heat evolved for different ratios of metal ion and ligand must be made. These heats of formation cannot be evaluated with equal precision from our experiments, and in fact the figures obtained for the ions $M(en)^{++}$ are almost worthless since only very small amounts of these ions were formed under the conditions employed, which were such that the pH of the final solution invariably exceeded 8. [To convert appreciable quantities of the metal into $M(en)^{++}$ without precipitation of the hydroxide would have meant buffering the reaction to a much lower pH.] As it was particularly desirable to obtain the best possible estimates of the heat of formation of the ion $M(en)_2^{++}$, since a comparison could then be made for nickel, copper, zinc, and cadmium, at least three measurements were made for the last three metals of the heat evolved at fixed concentrations chosen so that as much of the ion $M(en)_2^{++}$ was formed as possible. With zinc and cadmium, the mean of the results of the set of three experiments was combined with the results of at least two other experiments at different concentrations to obtain values for the heats of formation of all the complex ions. In experiments with nickel, which forms a more stable 3 : 1 complex, three determinations were made of the heat change when the ethylenediamine was in a slight excess of this ratio. In the choice of stability constants we have had the benefit of the advice of Dr. H. M. N. H. Irving and Mr. J. E. Dickens, to whom we are very grateful. From plots of stability constants obtained by different workers against ionic strengths, the following values of stability constants have been selected as the best available for the ionic strengths used by us :

TABLE 4. *Heat of reaction between metals and ethylenediamine.*

M = No. of g.-ions of metal × 10^3; *B* = no. of moles of ethylenediamine × 10^2; *V* = total vol. (c.c.) of solution after mixing; *Q* = heat evolved (in cal.); ΔH = heat content increase per g.-ion of metal on formation of complex from metal and ethylenediamine.

	M	*B*	*V*	*Q*	ΔH
Nickel.					
1 [a]	4·916	1·742	972	136·6	
2	4·900	0·960	972	86·8	$Ni(en)^{++}$ = −15,000 [b]
3	4·902	0·962	972	85·6	$Ni(en)_2^{++}$ = −17,250 [b]
4	4·904	1·125	974	100·3	$Ni(en)_3^{++}$ = −28,010 [b]
5	4·902	1·295	976	116·9	
Zinc.					
6 [a]	4·963	1·016	975	51·4	$Zn(en)^{++}$ = +9,800
7	4·956	1·464	985	59·2	$Zn(en)_2^{++}$ = −11,450
8	4·952	2·868	981	66·4	$Zn(en)_3^{++}$ = −18,460
Cadmium.					
9 [a]	4·898	1·012	977	60·7	$Cd(en)^{++}$ = −1,200
10	4·911	1·452	966	69·8	$Cd(en)_2^{++}$ = −13,330
11	4·870	2·881	978	78·8	$Cd(en)_3^{++}$ = −19,700
Copper.					
	—	—	—	—	$Cu(en)_2^{++}$ = −25,160 [c]

[a] This is the mean of the data for three almost identical experiments. [b] Mean of values calc. for the following combinations of *Q* values : 1, 2, 4; 1, 3, 4; 1, 4, 5; 2, 4, 5; 3, 4, 5. [c] By using a slight excess of ethylenediamine, copper ion is completely converted into $Cu(en)_2^{++}$. The individual values for four experiments under these conditions were : −25,280; −25,120; −24,920; −25,310.

Nickel	$\log_{10}k_1$ = 7·32	$\log_{10}k_2$ = 6·06	$\log_{10}k_3$ = 4·1
Zinc	$\log_{10}k_1$ = 5·50	$\log_{10}k_2$ = 4·55	$\log_{10}k_3$ = 1·35
Cadmium	$\log_{10}k_1$ = 5·2	$\log_{10}k_2$ = 4·2	$\log_{10}k_3$ = 1·7
Copper	$\log_{10}k_1$ = 10·72	$\log_{10}k_2$ = 9·31	

As mentioned earlier, a linear temperature–time relation in the after-period of a calorimetric experiment was normally reached very quickly, within 10 sec. of opening the bottle. For one system, however, this steady state was only reached after about 3 min. This was the system nickel–ethylenediamine under conditions such that a small but appreciable amount of the ion $Ni(en)_3^{++}$ was formed in the presence of a larger amount of the ion $Ni(en)_2^{++}$. This suggests that the formation of one of the complex ions has an appreciable activation energy. If the addition of the ethylenediamine molecules takes place in stages, it might be expected that that with the largest activation energy would be the final one in which the third molecule of ethylenediamine enters the complex if, as is probable, this involves the formation of an ion with three octahedrally disposed diamine molecules from one with two planar diamine molecules. All signs of the slow reaction disappeared in the presence of excess of ethylenediamine above that required for the stoicheiometric formation of the 3 : 1 complex, presumably because of a simple mass-action effect.

DISCUSSION

In Table 5 are given our values of ΔH, the values of ΔG corresponding to the values of the formation constants already quoted, and the derived values of ΔS. These quantities refer to the formation of the complex ion at 25° in water containing neutral salt to give an ionic strength of 0·1. In the column headed $(\Delta S + S_{aq.})$, $S_{aq.}$ is the standard entropy of the cation. The following values for $S_{aq.}$ have been taken from Powell and Latimer (*J. Chem. Phys.*, 1951, **19**, 1139): Cu^{++} −23·6; Zn^{++} −25·45; Cd^{++} −14·6 cal./° C. They do not quote a figure for Ni^{++}. For this ion, Rossini (*op. cit.*) gives −38·1, which is described as a calculated value though the details are not given. This seems a surprisingly large (negative) value. A figure of −29·3 cal./° C was proposed by Barvinok (*J. Gen. Chem., U.S.S.R.*, 1950, **20**, 208), and as this seems more likely we have used it in evaluating $(\Delta S + S_{aq.})$ for nickel in Table 5: but even this figure of −29·3 is lower than that of any of the neighbouring transition metals.

Values of $(\Delta S + S_{aq.})$ are not, of course, the actual entropies of the complex ions on the conventional scale, but they are in the same relation as these entropies for ions of the same metal : amine ratio. Thus, the values of $(\Delta S + S_{aq.})$ for the ions $M(en)_2^{++}$ all differ by a constant amount from the standard entropies of these ions. The values for the ions $M(en)_3^{++}$ may similarly be compared with each other, but not with those for the ions $M(en)_2^{++}$.

Results for the 1 : 1 complex ions have been omitted from Table 5, since they are too inaccurate to justify their inclusion and discussion. We must once more stress that, owing to uncertainty in the values for some of the stability constants, there may be errors of several units in some of the ΔS values.

The entropy of an ion in solution depends on its interaction with the solvent molecules. If this is essentially electrostatic, then the greater the ionic size the less powerful is the field of force near the ion, and hence the interaction with neighbouring molecules is weaker. So the larger the ion, the larger its entropy: the quantitative relationship has been discussed by Powell and Latimer (*loc. cit.*). Thus the standard entropy of the cadmium ion exceeds that of the zinc ion by nearly 11 e.u. On the other hand, if we consider the ions $Zn(en)_3^{++}$ and $Cd(en)_3^{++}$, in which the metallic atom is surrounded by three octahedrally co-ordinated ethylenediamine molecules, these ions are much larger than the simple cations, and moreover, although the ion containing cadmium is presumably still the bigger of the two, the relative difference in size is now very much less. We must therefore expect that the standard entropies of these complex ions (after allowance for the contribution from the internal degrees of freedom of the chelated molecules) will not only be much larger than those of the simple ions, but will also be much more nearly equal. In fact, $(\Delta S + S_{aq.})$ is approximately the same for the ions $Zn(en)_2^{++}$ and $Cd(en)_2^{++}$, while for the 1 : 3 ions of these two elements the difference of 5 e.u. may well be due to errors in the formation-constant values. It is interesting that ΔH is numerically greater for the two complex cadmium ions than for the corresponding zinc ions, while the reverse is true of ΔG. It is probable that the interaction of transition-metal ions with water, and still more with amines, is not a simple electrostatic interaction, but that some degree of covalent bonding is involved. From the general chemical behaviour of zinc and cadmium, we should expect that covalent bonding would play a larger part with cadmium than with zinc, and hence that cadmium would form relatively stronger bonds with ethylenediamine than zinc. It is therefore not surprising that the cadmium complexes are formed with a greater evolution of heat than are those containing zinc. That the latter are nevertheless the more stable is due to the entropy term ΔS. This is larger for zinc than for cadmium because the entropy gain when the water molecules surrounding the metallic ion are replaced by ethylenediamine molecules is greater for the smaller ion.

For the other 1 : 3 ion in Table 5, namely $Ni(en)_3^{++}$, $(\Delta S + S_{aq.})$ is markedly different from the values for the zinc and cadmium analogues. Unfortunately, as already stated, there is some ambiguity about the value of $S_{aq.}$ for nickel, and a redetermination of this quantity as well as a re-examination of the formation constants of the ethylenediamine complexes would be desirable.* It must, however, not be forgotten that we can only expect the entropies of the ions $M(en)_3^{++}$ to be equal if they have identical shapes. If, in an ion of this type, two ethylenediamine molecules are strongly bound, but the third only weakly, it is possible that this last molecule would be attached at one end only. The entropy of such an ion need not then be the same as that of an ion in which all three ethylenediamine molecules are chelated. Of the three ions under discussion, the most stable is that formed by nickel, and though the cadmium and zinc complexes are weaker it is doubtful if the differences in ΔG for the 1 : 2 and 1 : 3 zinc and cadmium ions are small enough to make it likely that the third molecule is only attached to the metal at one nitrogen atom.

TABLE 5. *Thermodynamic data for metal complexes of ethylenediamine.*

	ΔH	ΔG	ΔS	$(\Delta S + S_{aq.})$		ΔH	ΔG	ΔS	$(\Delta S + S_{aq.})$
$Ni(en)_2^{++}$	−17,250	−18,250	+ 3·4	−25·9	$Cd(en)_2^{++}$	−13,330	−12,820	− 1·7	−16·3
$Ni(en)_3^{++}$	−28,010	−23,840	−14·0	−43·3	$Cd(en)_3^{++}$	−19,700	−15,140	−15·3	−29·9
$Zn(en)_2^{++}$	−11,450	−13,710	+ 7·6	−17·9	$Cu(en)_2^{++}$	−25,160	−27,280	+ 7·1	−16·5
$Zn(en)_3^{++}$	−18,460	−15,550	− 9·8	−35·3					

Turning to the ions of formula $M(en)_2^{++}$, these can now differ in shape and so need not necessarily have almost the same entropies. Thus, we should expect that the two ethylenediamine molecules in a $Cu(en)_2^{++}$ ion in solution are coplanar, whereas in a $Zn(en)_2^{++}$ ion in solution they are probably tetrahedrally disposed round the zinc. The interaction of the complex ion with water molecules may differ according to whether it is planar or tetrahedral. Thus, two water molecules might get fairly close to the metal ion in the planar complex by filling the two vacant octahedral sites, which is not possible with the tetrahedral ion. The extent to which the complex ion orders neighbouring water molecules (and also the extent to which it disorganises the water structure) will therefore depend on its shape; $(\Delta S + S_{aq.})$ is, in fact, about the same for the planar $Cu(en)_2^{++}$ as for the (probably) tetrahedral $Zn(en)_2^{++}$ and $Cd(en)_2^{++}$, while once again it appears to be the nickel ion which is out of line. It seems, therefore, that the entropies of the two types of 1 : 2 ion do not differ very much : but it would be very interesting to have really accurate relative entropy figures for a larger number of these ions, to see if in fact these entropies tend to fall into two groups, according to the shape of the complex.

In the Irving–Williams stability order (Irving and Williams, *Nature*, 1948, **162**, 746; *J.*, 1953, 3192), the stability of complexes of the first group of transition metals reaches a maximum with copper. For the ethylenediamine complexes, this is because ΔH is numerically largest for copper, which therefore forms stronger bonds with nitrogen than do nickel and zinc. The ΔH values of Table 5 can be regarded as being the relatively small differences between the interaction energies of the unhydrated (*i.e.*, gaseous) metal ion with water on the one hand, and ethylenediamine on the other. Relative values of the heats of hydration of a series of bivalent metal cations can be evaluated if we know for each metal its heat of vaporisation, its first and second ionisation potentials, and the heat of formation of one particular compound (the same compound for all the metals) in dilute aqueous solution. (The values so obtained differ slightly according to the compound chosen, but probably the

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* Dr. Irving has pointed out to us that, on using Powell and Latimer's relation (*loc. cit.*) between ionic radius and entropy, the entropy of the nickel ion corresponding to the radius of 0·70 Å given by Pauling (" The Nature of the Chemical Bond," Cornell Univ. Press, 1945) is −24·9 e.u., and that if this value is used for $S_{aq.}$ instead of that of −29·3 e.u. which we have employed, the resulting figures for $(\Delta S + S_{aq.})$ for both nickel complexes are in much better agreement with those for the other metal complexes studied.

figures for the chlorides are the most reliable. The relation between the values about to be given is not qualitatively changed, however, by choosing other compounds for which the required information is available.) Using data from Rossini's book (*op. cit.*) for the chlorides of the transitional elements and taking −67 kcal. for the heat of hydration of the chloride ion (Kortum and Bockris, "Textbook of Electrochemistry," Elsevier Publishing Co., 1951, Vol. I, p. 124), we have the following heat of hydration figures (in kcal.): Mn^{++}, −483; Fe^{++}, −503; Co^{++}, −530; Ni^{++}, −545; Cu^{++}, −539; Zn^{++}, −529·5. In arriving at these values we have made use of recent determinations of the latent heats of evaporation of iron, cobalt, and copper carried out by Edwards, Johnston, and Ditmars (*J. Amer. Chem. Soc.*, 1951, **73**, 4729; 1953, **75**, 2467). The ion which hydrates with the greatest evolution of heat is nickel, not copper. This to some extent offsets the difference in the ΔH figures for nickel and copper in Table 5. But by combining these ΔH figures with those for the heats of hydration, we have that for the process

$$M^{++}(g.) + 2(en)(aq.) \rightleftharpoons M(en)_2{}^{++}(aq.)$$

ΔH is −562 for Ni; −564 for Cu; and −541 kcal. for Zn, so that copper must still be regarded as forming the strongest bonds with ethylenediamine.

Finally, for zinc and cadmium the ratio of the ΔH values for the 1 : 3 and 1 : 2 complexes is roughly 3 : 2, and the ratio for nickel is somewhat greater. But the corresponding ratio for the ΔG values is considerably less than 3 : 2. The reason for this is that, whereas the reaction of the hydrated metal ion to give the $M(en)_2{}^{++}$ is accompanied by an entropy increase (or with cadmium by only a *small* entropy decrease), the last stage in the formation of the $M(en)_3{}^{++}$ ion, *i.e.*, the reaction $M(en)_2{}^{++} + (en) \rightleftharpoons M(en)_3{}^{++}$, involves an entropy decrease, which with zinc and nickel amounts to 17·4 e.u. and with cadmium to 13·6 e.u. That the entropy change on formation of the $M(en)_2{}^{++}$ ion is positive (or if negative is small) is due, of course, to the release of water molecules from the hydrated ion. Since the entropy change is negative and quite large for the addition of a third ethylenediamine molecule, it would seem as if the further dehydration of the ion in this stage is a comparatively minor matter, and this is presumably why the values of $(\Delta S + S_{aq.})$ for the planar $Cu(en)_2{}^{++}$ and the presumably tetrahedral zinc and cadmium analogues are almost the same, notwithstanding what has been said on the possible dependence of entropy on ionic shape. Most of the entropy decrease of 15—17 e.u. in the third stage for nickel, zinc, and cadmium must therefore be derived from the reduction in the freedom of movement of the ethylenediamine molecule when it enters the complex.

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