880. *Thermochemical Studies. Part III.* Heats and Entropies of Reaction of Transition Metal Ions with Ethylenediamine.*†

By M. Ciampolini, P. Paoletti, and L. Sacconi.

The heats of formation for the successive steps in complex-formation of Mn(II), Fe(II), Co(II), Ni(II), and Zn(II) with ethylenediamine in M-potassium chloride have been measured. From these values and published values of the free-energy changes, the corresponding entropy changes have been calculated. In most of the systems studied the heats for the successive steps are fairly constant. Addition of successive ethylenediamine molecules is accompanied by a decrease in the entropy change. The chelate effect is discussed and the values of ΔH and ΔS for the complexes of ethylenediamine and ammonia are discussed. Plots of atomic number against the experimental values of ΔH and those corrected for the crystal field stabilisation energy are similar to that for the heats of hydration. For Ni(II) and Zn(II) in M-potassium nitrate the influence of the ionic medium becomes evident.

While there are many data for the formation constants for complexes, the published work on heat (ΔH) and entropy changes (ΔS) for such reactions is still scanty. Moreover, most of the heats of formation of complexes have been obtained from the temperature-dependence of the stability constants. It is known that the values of ΔH thus obtained are not very accurate and, when many steps are involved, even unreliable. Further, values of ΔH are needed for the development of crystal-field theory and to check its predictions. The only series of heats of formation used hitherto for this purpose is that of the hexa-aquo-complexes of bi- and ter-valent ions of metals of the first transition series.[1,2] Ethylenediamine forms sexico-ordinate complexes with these metal ions which, because of their octahedral symmetry, have been the object of intense study in terms of crystal-field theory. In the absence of heats of formation for such complexes, however, the various authors have used the available free energies for their discussions on the rather optimistic assumption that ΔS remains constant within the series.[1]

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* Part I and II, Sacconi, Paoletti, and Ciampolini, *J. Amer. Chem. Soc.*, 1960, **82**, 3828, 3831.

† Presented at the International Conference on Co-ordination Chemistry, London, April, 1959; Chem. Soc. Special Publ. No. 13, 1959.

[1] Orgel, Reports Tenth Solvay Conf., Brussels, 1956.

[2] Orgel, *J.*, 1952, 4756; Griffith and Orgel, *Quart. Rev.*, 1957, **11**, 381; Holmes and McClure, *J. Chem. Phys.*, 1957, **26**, 1686; Basolo and Pearson, " Mechanism of Inorganic Reactions," John Wiley & Sons, Inc., New York, 1958.

It appeared, therefore, desirable to investigate calorimetrically the equilibria in aqueous solution between ethylenediamine and the bivalent ions of metals of the first transition series from manganese to zinc. In order to obtain the heats and the entropies of formation for the three successive stages of complex formation, one must carry out the experiments in the ionic medium used for the measurement of the equilibrium constants. As the only complete set of equilibrium constants has been measured in M-potassium chloride, we chose that medium for the calorimetric measurements.

The only published calorimetric values of the heats of formation for the above complexes are those of Poulsen and Bjerrum [4] for nickel and copper in M-potassium nitrate, and of Davies *et al.*[5] for nickel and zinc in 0·1M-potassium chloride. The latter authors point out that their values for the 1 : 1 complexes are so inaccurate as to be unreliable.

There appears to be no datum for the heat of reaction of the metal ions which are oxidised in an alkaline medium: Yatsimirskii and Astasheva's values for iron and cobalt refer to the gaseous state.[6]

EXPERIMENTAL

Materials.—Reagent-grade metal sulphates were used for preparation of approximately molar stock solutions. The ferrous sulphate solution was also made *ca.* 0·015M with respect to hydrochloric acid and reduced with hydrogen in presence of indigotetrasulphonate and a few drops of 2% colloidal palladium suspension. This solution was stored under hydrogen pressure.

The metal contents of the various solutions were determined by conventional methods: manganese as pyrophosphate, cobalt and zinc as anthranilate, nickel as the dimethylglyoxime derivative, and iron by titration with permanganate. Hydrochloric acid in the iron solution was determined by potentiometric titration against sodium hydroxide under nitrogen.

Ethylenediamine was distilled over sodium through a Todd fractionating column; the fraction used was titrated against hydrochloric acid and proved to be 99·7% pure. ~3M-Solutions of this base were made up with carbon dioxide-free M-potassium chloride or nitrate and standardised by potentiometric titration.

The hydrogen or nitrogen used was purified by passage over copper gauze at 400°.

Calorimetric Measurements.—The calorimeter was described in a previous paper [7] and is similar to that of Davies, Singer, and Staveley.[5] Its efficiency was checked during the measurements by determinations of the heat of solution of potassium chloride. In the experiments carried out with manganous, ferrous, and cobaltous ions, oxidation was prevented by bubbling a slow stream of nitrogen into the calorimetric liquid through two holes made at the bottom of the central glass tube. In this way no detectable oxidation took place. Controls showed that gas-bubbling does not affect the result of the measurements.

In each experiment two determinations of the electrical-energy equivalent were made and the reproducibility of this quantity was usually better than ±0·2%. The calorimeter was placed in a thermostat-bath at 25·000° ± 0·005°. At the end of the reaction the temperature was in the range 24·8—24·9° and no attempt was made to correct the heat change values to 25°.

For each run the bottle was filled with a weighed amount (*ca.* 25 ml.) of the stock metal-salt solution. For manganese and cobalt, presaturated nitrogen was bubbled, for 20 min., through the solution placed in the bottle: the bottle was then stoppered in a nitrogen atmosphere and weighed. In the case of the iron solution, the bottle was filled in a hydrogen atmosphere. A weighed amount of the ethylenediamine stock solution and, in the case of buffered systems, M-hydrochloric or nitric acid, were placed in the Dewar flask. Carbon dioxide-free M-potassium chloride or nitrate was then added, to give a resulting weight of *ca.* 930 g. The final volumes reported in Tables 1 and 2 were evaluated from the known weights of the reactants and the final density of the calorimetric liquid. The heats of dilution were measured by diluting a weighed sample (*ca.* 25 ml.) of the test solution of metal salt in about 930 g. of M-potassium

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[3] Bjerrum, Schwarzenbach, and Sillén, "Stability Constants," Part I, *Chem. Soc. Special Publ.* No. 6, 1957.

[4] Poulsen and Bjerrum, *Acta Chem. Scand.*, 1955, **9**, 1406.

[5] Davies, Singer, and Staveley, *J.*, 1954, 2304.

[6] Yatsimirskii and Astasheva, *Zhur. obshchei Khim.*, 1950, **20**, 2139.

[7] Sacconi, Paoletti, and Ciampolini, *Ricerca Sci.*, 1959, **29**, 2412.

chloride or nitrate. The heat of dilution of the ethylenediamine solution by the water contained in the metal-salt solution was found to be negligible in every case.

Procedure and Calculations.—In order to determine the total and stepwise heats of formation for individual complexes, it is necessary to know the actual ionic composition of the solution in each experiment. In fact the species M^{2+}, $M\,en^{2+}$, $M\,en_2{}^{2+}$, $M\,en_3{}^{2+}$, $en\,H^+$, $en\,H_2{}^{2+}$, en, H^+, and OH^- are usually present to a greater or smaller extent (en = ethylenediamine). The ionic composition can be calculated from a knowledge of the stability constants of the three complex ions, as well as of the two basicity constants of ethylenediamine.[3]

The stability constants used in the calculations were corrected, where necessary, to 25°, by using approximate ΔH values.

The experimental results for ethylenediamine–metal ion systems are recorded in Tables 1 and 2. The fourth column gives the amount of hydrochloric or nitric acid added to the amine solution to avoid precipitation of the hydroxides in the experiments carried out at low $\bar{n}$ values ($\bar{n}$ = average number of ligands attached to the metal) and in all experiments with manganese. The values of the heat (Q) evolved in each experiment, corrected for the heat of dilution of the

TABLE 1. *Systems* MSO_4 + en *in* M-*potassium chloride.*

Metal	Metal (10^{-5} mole)	en (10^{-5} mole)	HCl (10^{-5} mole)	Q (cal. mole^{-1})	$Q_{corr.}$ (cal. mole^{-1})	$\bar{n}$	$-\Delta H_a$ (kcal. mole^{-1})
Mn^{2+}	2463	106,900	5830	274·9	0·1	2·89	3·60
(V 924 ml.)	2756	109,300	5850	288·8	0·2	2·89	3·63
	2597	30,240	13,610	211·3	8·6	2·43	3·45
	2597	29,540	13,590	212·1	9·4	2·42	3·39
	2516	21,520	13,570	161·4	3·9	2·03	3·23
	2591	21,410	13,720	158·9	4·7	2·02	3·13
	2595	15,650	11,400	115·0	9·8	1·57	3·06
	2672	15,680	11,410	115·4	10·7	1·56	3·03
	2589	12,250	8730	96·2	9·5	1·39	2·94
	2551	12,160	8740	96·4	9·2	1·37	3·01
	2596	12,050	8740	94·2	10·3	1·35	2·99
	2578	12,040	8750	94·1	11·6	1·34	3·02
Fe^{2+}	2318 *	35,050		363·7	−1·1	2·97	5·26
(V 909 ml.	2417 *	35,050		383·1	−1·2	2·97	5·32
	2309 *	9976	5796	237·0	12·5	2·07	5·22
	2286 *	9880	5732	234·4	12·3	2·07	5·21
	2384 *	7194	10,724	104·2	45·2	1·22	5·13
	2350 *	7243	10,583	103·5	44·5	1·23	5·14
Co^{2+}	2582	17,810		569·5	−1·8	2·99	7·35
(V 933 ml.)	2574	17,870		570·1	−1·8	2·99	7·38
	2578	17,700		572·9	−1·8	2·99	7·41
	2570	5450	310	362·2	0·2	2·00	7·05
	2588	5483	313	362·8	0·2	2·00	7·02
	2519	5338	304	353·0	0·2	2·00	7·02
	2561	3079	822	172·0	4·5	0·99	6·94
	2517	3026	806	166·9	4·5	0·99	6·85
	2575	7224	8278	138·6	40·5	1·01	6·87
Ni^{2+}	2707	8559		770·4	−4·0	2·99	9·47
(V 933 ml.)	2782	10,520		791·9	−3·3	3·00	9·46
	2555	5111		473·3	−3·8	2·00	9·19
	2563	5128		470·8	−3·8	2·00	9·11
	2567	3770	2390	208·8	18·3	0·99	8·94
	2562	3764	2384	209·3	18·3	0·99	8·97
	2646	2579	1299	208·4	20·0	0·96	8·98
Zn^{2+}	2193	3669		448·5	−0·8	2·95	6·92
(V 933 ml.)	2196	3706		447·4	−0·8	2·95	6·89
	2194	3694		448·6	−0·8	2·95	6·85
	2191	5776	1325	304·2	0·6	2·02	6·89
	2189	5804	1326	304·8	0·6	2·02	6·87
	2192	5774	1325	302·7	0·6	2·02	6·85
	2187	5557	5126	139·3	32·0	1·16	6·76
	2194	5580	5150	140·0	32·2	1·16	6·76
	2190	5566	5036	143·2	31·4	1·18	6·76

* These solutions contain $1·424 \times 10^{-2}$ mole of hydrochloric acid per mole of metal ion.

metal salt, given in column 5, are corrected additionally in column 6 for the heat effects due to the reactions:

$$\text{en H}^+ + \text{OH}^- \longrightarrow \text{en} + \text{H}_2\text{O} \quad \Delta H = -1500 \text{ cal. mole}^{-1} \text{ (in unbuffered systems)}$$

$$2\,\text{en H}^+ \longrightarrow \text{en} + \text{en H}_2{}^{2+} \quad \Delta H = 1590 \text{ cal. mole}^{-1} \text{ (in buffered systems)}$$

which take place on complex-formation. These values were obtained from our heats of neutralisation of ethylenediamine in M-potassium chloride, which are to be reported elsewhere. The last column gives the values of ΔH_a, *i.e.*, the average heat of reaction per mole of ethylenediamine bound to the metal ion. The values of ΔH_a for $\bar{n}$ values close to each other give an indication of the reproducibility of the measurements.

The heat of stepwise complex-formation for the separate complexes was obtained by combining the results of three runs carried out at different $\bar{n}$ and solving the set of three simultaneous equations:

$$Q_m = \alpha_1 \Delta H_1 + \alpha_2 \Delta H_{1-2} + \alpha_3 \Delta H_{1-3}$$

where Q_m is the heat evolved per g.-ion of metal added and α_1, α_2, and α_3 are the degrees of formation of the three complexes in the reaction mixture. The relative accuracies of the three heat changes ΔH_1, ΔH_{1-2}, and ΔH_{1-3} are not the same. In fact, for each metal ion, measurements were carried out with a large excess of ethylenediamine. Under these conditions practically only 3 : 1 complexes are present with all metal ions except manganese. In the last case the amount of 3 : 1 complex present is only about 89%, even in M-solutions of ethylenediamine. Therefore, the accuracy of the ΔH_{1-3} values for the complexes of iron, cobalt, nickel, and zinc is of the same order of magnitude as the reproducibility of the calorimetric measurements, while the values of ΔH_1 and ΔH_{1-2} (and the ΔH_{1-3} for the manganese complex) are less accurate because of their critical dependence on the values of the stability constants chosen. Further, they depend mainly on the experiments carried out at lower values of $\bar{n}$ in which the thermal effects measured are due to a large extent to the heat of buffering. The estimated errors are: ±200 cal. mole^{-1} for ΔH_1 and ΔH_{1-2}, and ±150 cal. mole^{-1} for ΔH_{1-3}.

TABLE 2. *Systems* MSO_4 + en *in* M-*potassium nitrate.*

Metal	Metal (10^{-5} mole)	en (10^{-5} mole)	HNO_3 (10^{-5} mole)	Q (cal. mole^{-1})	$Q_{corr.}$ (cal. mole^{-1})	$\bar{n}$	$-\Delta H_a$ (kcal. mole^{-1})
Ni^{2+}	2609	9285		714·6	−3·3	3·00	9·10
(V 916 ml.)	2505	8647		688·2	−3·1	3·00	9·12
	2248 *	8610		622·7	−2·8	3·00	9·20
	2250 *	8695		624·2	−3·2	3·00	9·21
	2499	5030		455·8	−3·8	2·01	8·99
	2500	5007		453·0	−3·8	2·00	8·97
	2502	3726	2414	206·9	18·6	0·99	9·09
	2503	3720	2408	206·6	18·6	0·99	9·08
Zn^{2+}	2395	20,080		396·9	−1·5	2·91	5·67
(V 903 ml.)	2378	20,050		397·0	−1·5	2·91	5·72
	2502	17,500		415·5	−1·6	2·89	5·73
	2495	17,490		412·0	−1·6	2·89	5·70
	2525	7246		352·8	−2·6	2·44	5·69
	2374	6839		334·8	−2·8	2·43	5·74
	2378	6199	1431	286·9	1·2	2·02	6·00
	2377	6197	1450	284·3	1·3	2·02	5·96
	2569	6518	1451	302·2	1·7	2·00	5·91
	2508	7281	3009	222·9	9·9	1·95	6·00
	2558	8629	7394	203·4	50·3	1·56	6·34
	2377	8013	7372	188·5	46·3	1·55	6·37
	2397	10,760	14,860	133·7	43·0	1·14	6·50
	2379	10,560	14,750	128·9	41·8	1·11	6·44
	2452	10,770	14,990	134·4	43·6	1·12	6·49
	2459	10,730	14,970	132·1	43·3	1·11	6·45

* These measurements were carried out with nickel nitrate. From these data $\Delta H_{1-3} = -27{\cdot}61$ kcal. mole^{-1} is obtained.

Spectrophotometric Measurements.—The spectrum of the $[\text{Fe en}_3]^{2+}$ ion was measured with a

TABLE 3. *Spectrophotometric data of absorption of* [Fe en_3]$^{2+}$ *ion.*

$\nu_{max.}$ (cm.$^{-1}$)	11,420	19,490	21,830	24,450
ε	2·26	0·17	0·15	0·17

Beckmann DU spectrophotometer fitted with 1 cm. stoppered silica cells. The spectral data are given in Table 3. For the standardisation of the wavelength scale, a mercury lamp was used.

A solution of ferrous sulphate in 0·1N-hydrochloric acid was reduced with hydrogen in the presence of one drop of colloidal platinum suspension which flocculated immediately. Ethylenediamine was then added in a nitrogen atmosphere until the solution was about 3M in ethylenediamine, 0·8M in [Fe en_3]$^{2+}$ and 0·05M in en H^+, thus containing virtually pure hexa-ammine complex.

The cell was filled with this solution under nitrogen; in this way no detectable oxidation was observed. The solution used as a control contained the same concentration of base and its hydrochloride as the test solution.

RESULTS

Table 4 reports the values for the thermodynamic functions ΔH, ΔG, and ΔS relative to the three successive reaction steps. Our values of heats of reaction often differ by a few kcal. mole^{-1} from the non-calorimetric values reported in the literature.[8]

Comparison of our heats of formation for the complexes of nickel and zinc with accurate calorimetric values of Davies *et al.*,[5] and Poulsen and Bjerrum,[4] shows the dependence of these values on the ionic medium employed; Yatsimirskii and Milyukov [9] found that ΔH of formation for complex ammines of zinc and cadmium becomes more negative with increase in the ionic strength of the medium. This difference is particularly evident with the ethylenediamine complexes of zinc. In fact, the values of $-\Delta H_{1-2}$ and $-\Delta H_{1-3}$ given by Davies for 0·1M-potassium chloride are lower than ours for M-potassium chloride by 2·30 and 2·24 kcal. mole^{-1} respectively. This difference can be attributed, at least in part, to the endothermic formation of chloro-complexes, as shown by the fact that the heat of dilution of the stock solution of zinc sulphate in M-potassium chloride is positive and relatively large, while it is negative in M-potassium nitrate. The heats of dilution of all the other stock solutions in M-potassium chloride are negative. The stepwise formation constants for zinc complexes reported in the literature differ from each other,[3] but they all indicate an appreciable degree of formation of chloro-complexes in M-potassium chloride.

TABLE 4. *Thermodynamic functions and spectral data for metal*(II)*–ethylenediamine systems in* M-*potassium chloride at* 25°.

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Zn^{2+}
$-\Delta H_1$ (kcal. mole^{-1})	2·80	5·05	6·90	8·90	6·65
$-\Delta H_{1-2}$,, ...	6·00	10·40	13·95	18·25	13·75
$-\Delta H_{1-3}$,, ...	11·05	15·85	22·15	28·35	20·70
$-\Delta G_1$ (kcal. mole^{-1})	3·75 [a, d]	5·90 [a, d]	8·10 [b]	10·50 [b]	7·90 [c, d]
$-\Delta G_{1-2}$,, ...	6·65 [a, d]	10·45 [a, d]	14·55 [b]	19·20 [b]	14·40 [c, d]
$-\Delta G_{1-3}$,, ...	7·90 [a, d]	13·25 [a, d]	18·65 [b]	25·10 [b]	16·80 [c, d]
ΔS_1 (cal. deg.$^{-1}$ mole^{-1})	+3·0	+3·0	+4·0	+5·5	+4·0
ΔS_{1-2} ,, ,, ...	+2·0	0·0	+2·0	+3·0	+2·0
ΔS_{1-3} ,, ,, ...	−10·5	−8·5	−12·0	−11·0	−13·0
$Dq[M(H_2O)_6]^{2+}$ (cm.$^{-1}$)	—	1040 [e]	900 [f]	850 [e]	—
Dq [M en_3]$^{2+}$ (cm.$^{-1}$)	—	1140	1100 [f]	1160 [e]	—
$-\Delta H_{1-3\ cryst.}$ (kcal. mole^{-1})	0	1·15	4·55	10·60	0
$-\Delta H_{1-3\ corr.}$ (kcal. mole^{-1})	11·05	14·70	17·60	17·75	20·70

[a] Bjerrum, "Metal Ammine Formation," P. Haase & Son, Copenhagen, 1941. [b] Edwards, Diss., Univ. Michigan, 1950. [c] Carlson, McReynolds, and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1334. [d] Corr. at 25°. [e] Jörgensen, Reports Tenth Solvay Conf., Brussels, 1956. [f] Ballhausen and Jörgensen, *Acta Chem. Scand.*, 1955, **9**, 397.

On the other hand, even the heats of formation, $-\Delta H_{1-2}$ and $-\Delta H_{1-3}$, for nickel, where the

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[8] Calvin and Bailes, *J. Amer. Chem. Soc.*, 1946, **68**, 949; Spike and Parry, *ibid.*, 1953, **75**, 2726, 3770; Cotton and Harris, *J. Phys. Chem.*, 1955, **59**, 1203; McIntyre, jun., Block, and Fernelius, *J. Amer. Chem. Soc.*, 1959, **81**, 529.

[9] Yatsimirskii and Milyukov, *Zhur. neorg. Khim.*, 1957, **2**, 1046.

formation of chloro-complexes in M-potassium chloride is excluded, are higher than the corresponding values in 0·1M-potassium chloride by 1 and 0·34 kcal. mole^{-1} respectively.[5] In order to study the influence of the " inert salt " we have measured the heats of formation for complexes of ethylenediamine with nickel and zinc in M-potassium nitrate. This study could not be extended to other ions because of the lack of formation constants in this ionic medium.

The values of the thermodynamic functions ΔH, ΔG, and ΔS, determined in M-potassium nitrate are given in Table 5. The values of $-\Delta H_{1-3}$ and $-\Delta H_{1-2}$ are lower than the corresponding values in M-potassium chloride for both metal ions. For nickel the only data comparable with ours are those of Poulsen and Bjerrum.[4] These authors find a small dependence of the heat of formation on the ionic strength of the medium: they give ΔH_{1-3} for nickel in 1·2M-potassium nitrate (−27·96 kcal. mole^{-1}) and in water (−27·24 kcal. mole^{-1}). After correction for the heat of dissociation of the base and linear interpolation, one obtains ΔH_{1-3} −27·69 kcal. mole^{-1} in M-potassium nitrate. This value, however, is higher than ours by 0·29 kcal. mole^{-1} (~1%).

TABLE 5. *Thermodynamic functions for some metal*(II)*-ethylenediamine systems in* M*-potassium nitrate at* 25°.

	Ni^{2+}	Zn^{2+}		Ni^{2+}	Zn^{2+}
$-\Delta H_1$ (kcal. mole^{-1})	9·05	7·00	ΔS_1 (cal. deg.$^{-1}$ mole^{-1})...	4·0	3·5
$-\Delta H_{1-2}$,, ...	17·90	11·90	ΔS_{1-2} ,, ,, ...	3·5	10·5
$-\Delta H_{1-3}$,, ...	27·40	17·10	ΔS_{1-3} ,, ,, ...	−8·5	2·0
$-\Delta G_1$ (kcal. mole^{-1})	10·25 [a]	8·05 [b]			
$-\Delta G_{1-2}$,, ...	18·90 [a]	15·10 [b]			
$-\Delta G_{1-3}$,, ...	24·90 [a]	17·65 [b]			

[a] Ref. 4. [b] Bjerrum and Andersen, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, 1945, **22**, No. 7.

Our measurements with nickel nitrate, made by Poulsen and Bjerrum's method, in M-potassium nitrate gave a value of $-\Delta H_{1-3}$ of 27·61 kcal. mole^{-1}, as given in Table 2.

Thus, changing the anion of the metal salt causes a fairly small change in the heat of formation of the ethylenediamine complexes.

It is known that in solution metal sulphates are more associated than nitrates,[10] and it is likely that this association may change slightly on going from the hexa-aquo-cation to the trisethylenediamine cation.

DISCUSSION

In Fig. 1 the experimental ΔH_{1-3} values in M-potassium chloride (upper line), as well as the values corrected for crystal field stabilisation energy (lower line), are plotted against the atomic number of the metal. The $\Delta H_{1-3\,\mathrm{cryst.}}$ corrections were calculated according to the formula:

$$\Delta H_{1-3\,\mathrm{cryst}} = (4n_\epsilon - 6n_\gamma)(Dq_{6\mathrm{H_2O}} - Dq_{3\mathrm{en}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For iron, cobalt, and nickel the term $Dq_{6\mathrm{H_2O}} - Dq_{3\mathrm{en}}$ is not constant but increases in the ratio 1 : 2 : 3. The corrected values increase regularly from manganese to zinc, but all the values lie above the line joining manganese to zinc. A similar trend is observed in the corrected heats of hydration for these metal cations: [1,2,14] the points are slightly above the line joining manganese to zinc. Yatsimirskii [11] puts forward the hypothesis that in the case of the hexa-aquo-cations the difference observed can be attributed to a Jahn–Teller effect. This, however, cannot be true in the case of nickel. On the other hand, if metal–ligand bonds have a partially covalent character, the value of the crystal field stabilisation energy calculated on the basis of eqn. 1 cannot be completely correct.[12]

Further, crystal field theory does not require that the corrected values must lie on a straight line, but only that they should increase steadily. Orgel [1] suggested that in order to obtain heats of formation corrected for crystal field stabilisation energy " . . . . the most suitable procedure would be to draw a curve through the values for Mn^{2+} and Zn^{2+}

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[10] Nair and Nancollas, *J.*, 1959, 3934.

[11] Yatsimirskii, *Zhur. neorg. Khim.*, 1958, **3**, 2244.

[12] Jörgensen, *Discuss. Faraday Soc.*, 1958, **26**, 185.

as nearly parallel to the curve for hydration energy as possible," but in order to avoid ambiguity he preferred to use linear interpolation between Mn^{2+} and Zn^{2+}.

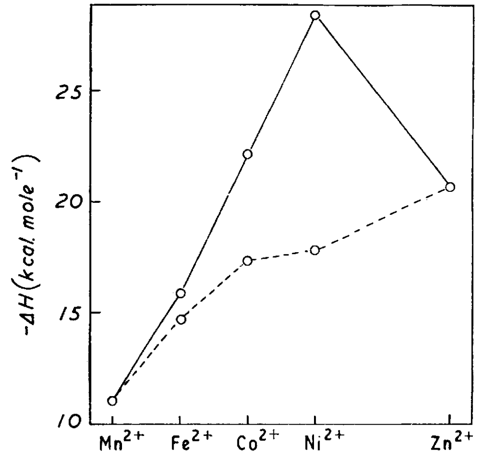
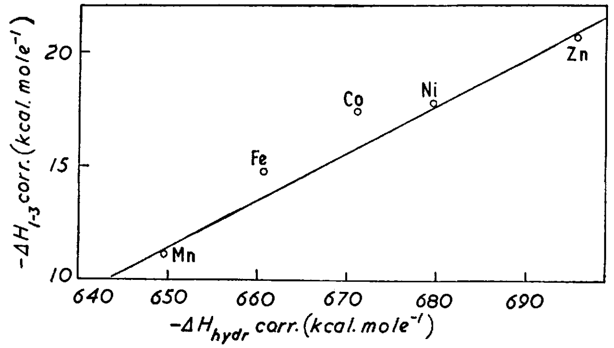


FIG. 1. *Experimental* (——) *and corrected* (*crystal field stabilisation energy*) (– – – –) *heats of formation of* [M $en_3]^{2+}$ *ions.*

FIG. 2. *Corrected heats of formation of* [M $en_3]^{2+}$ *ions plotted against the corrected heats of formation of* $[M(H_2O)_6]^{2+}$ *ions.*



Our curve for the corrected ΔH values, however, is not exactly parallel to that for the corrected heats of hydration, as shown by Fig. 2 where the values of $\Delta H_{\text{hydr. corr.}}$ [13] are plotted against our values $\Delta H_{1-3\,\text{corr.}}$; this does not give a straight line. The values for manganese, nickel, and zinc are on a straight line, but those for iron and cobalt are slightly above it. If there were appreciable Jahn–Teller stabilisation in the aquo-complexes of iron and cobalt, as postulated by Yatsimirskii,[11] the deviation from straight-line relationship for iron and cobalt could be attributed to the effect of an even greater stabilisation in the ethylenediamine complexes.

Fig. 3 gives the curves for the heats of formation, both experimental and corrected, for the mixed complexes $[M(H_2O)_2en_2]^{2+}$ and $[M(H_2O)_4en]^{2+}$. The crystal field stabilisation energies were taken as two-thirds and one-third of $\Delta H_{1-3\,\text{cryst.}}$ respectively, in accordance with the rule of average environment.[14] Again for these complexes the corrected values are above the manganese–zinc straight line.

Tables 4 and 5 show the values of ΔH_1, ΔH_{1-2}, and ΔH_{1-3} to be roughly in the ratio 1 : 2 : 3; that is, the heat changes for the successive steps are fairly constant. This has been observed also in successive reaction steps for the formation of ammines of nickel,

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[13] Gill and Nyholm, *J.*, 1959, 3997.

[14] Tsuchida, *Bull. Chem. Soc. Japan*, 1938, **13**, 388, 436; Tsuchida and Kobayashi, *ibid.*, p. 471.

copper,[15] and cadmium,[9] and is in agreement with Poulsen and Bjerrum's statement that such a ratio is to be expected for all complexes with dipolar molecules which are free from steric strain and undergo no change of configuration or spin multiplicity on stepwise complex-formation. In most of the systems examined by us, however, a slight increase in the heat for each successive step is apparent. This is particularly evident with manganese, where the third ethylenediamine molecule becomes bound to the metal with evolution of heat which is greater than that for the first two. On the other hand, in the system ethylenediamine-zinc in M-potassium nitrate the value of $-\Delta H_1$ is much larger than that of either $-\Delta H_2$ or $-\Delta H_3$. Thus manganous and zinc ions behave differently, even though in both cases the crystal field stabilisation energy is zero. The anomaly of zinc might be related to the tendency of this ion to give complexes with structures which differ according to the number and type of co-ordinated ligands. The $[\mathrm{Zn\ en_2}]^{2+}$ ion might have a tetrahedral structure,[5,9,15] and thus its formation from the octahedral ion $[\mathrm{Zn(H_2O)_4\,en}]^{2+}$ would cause liberation from the first co-ordination sphere of two more water molecules than does formation of the octahedral ion $[\mathrm{Zn(H_2O)_2en_2}]^{2+}$. Even if, in a tetrahedral complex ion, the water molecules in the second hydration sphere can get closer to the metal, the total effect should still be endothermic. Thus the heat of binding of the second molecule of ethylenediamine would be lower. The low value of $-\Delta H_3$ indicates that the weak tendency of zinc to form a trisethylenediamine complex, already apparent from the relative value of ΔG, is a heat effect.

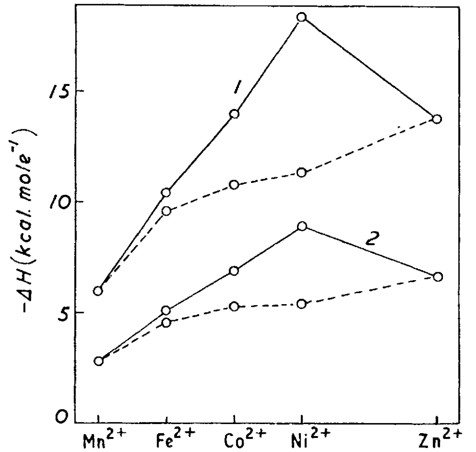

FIG. 3. (1) *Experimental* (——) *and corrected* (- - - -) *heats of formation of* $[\mathrm{M\ en_2}]^{2+}$ *ions;* (2) *Experimental* (——) *and corrected* (- - - -) *heats of formation of* $[\mathrm{M\ en}]^{2+}$ *ions.*

The course of the reaction of complex formation between zinc and ethylenediamine in M-potassium chloride appears to differ from that in M-potassium nitrate.

The regular variations of both heats and entropies of reaction observed in the first medium appear to indicate absence of structural change during formation of the bisethylenediamine complex. An octahedral structure for such a complex could possibly be stabilised by the presence of co-ordinated chloride ions.

Comparison of the successive heats of formation for the ethylenediamine complexes of nickel (present work) and copper in M-potassium nitrate [4] with those for complex ammines in 2M-ammonium nitrate [16] shows that the chelate effect in these systems is, in part, a heat effect, the heat change being lower in the ammonia systems. This is particularly evident in the case of nickel where the differences $\Delta H_{\mathrm{Ni\,en}_x} - \Delta H_{\mathrm{Ni(NH_3)}_{2x}}$ are $-1{\cdot}05$, $-1{\cdot}90$, and $-2{\cdot}90$ kcal. mole^{-1} for $x = 1$, 2, and 3 respectively. These values are of the same order of magnitude as the differences in crystal field stabilisation energy in the two types

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[15] Rossotti, in Lewis and Wilkins, "Modern Co-ordination Chemistry," Interscience Publ., New York, N.Y., 1960, p. 25.

[16] Yatsimirskii and Milyukov, *Zhur. fiz. Khim.*, 1957, **31**, 842.

of complexes (—0·90, —1·85, and —2·75 kcal. mole^{-1} respectively). For copper the differences in heats of formation for $x = 1$ and 2 are —1·90 and —3·40 kcal. mole^{-1} respectively, but in this case these values cannot be compared with the crystal field stabilisation energies, because the latter cannot be evaluated owing to the strong Jahn–Teller effect which is operating.

If the differences in the heats of formation between the complexes of ammonia and those of ethylenediamine were due only to the crystal field stabilisation energy one would expect that for zinc these differences should be zero. The differences[9] are, however, —1·3 and +2·9 kcal. mole^{-1} for $x = 1$ and 2 respectively. The first difference could be attributed to a geometrical factor: in the complex $[Zn(NH_3)_2(H_2O)_4]^{2+}$ the two ammonia molecules are probably *trans* to each other;[9,17] thus, their replacement by one molecule of ethylenediamine would require rearrangement of the complex which, in this case, would be exothermic. On the other hand, the second difference could be steric. Molecular models of Stuart type for tetrahedral $[Zn\ en_2]^{2+}$ show the ethylenediamine molecule to be somewhat distorted; this would decrease the heat of formation with respect to that of the corresponding complex ammine, thus accounting for the sign of the difference in heat observed when $x = 2$.

The values of the entropy changes, ΔS_1 (Table 4), are all positive and vary from 3·0 to 5·5 cal. deg.$^{-1}$ mole^{-1}, indicating that the decrease in degrees of freedom of the ethylenediamine molecule on complex formation is more than compensated by the number of free particles generated during the reaction $[M(H_2O)_6]_{aq.}^{2+} + en_{aq.} \longrightarrow [M(H_2O)_4 en]_{aq.}^{2+} + xH_2O$.

The ΔS_{1-2} values are all positive and vary from zero to 3·0 cal. deg.$^{-1}$ mole^{-1}. The values of ΔS_{1-3} are, however, all negative (—8·5 to —13·0).

The gradual decrease in entropy change for each successive step appears to be typical for all metal–ligand systems.[4,5,9,16,18] This behaviour is attributed to statistical effects, but the differences observed by us, as well as those observed by Poulsen and Bjerrum,[4] are higher than those calculated on a statistical basis.

The anomalous values of ΔS_{1-2} and ΔS_{1-3} for zinc in M-potassium nitrate (Table 5) can be explained on the same lines as for the relative $-\Delta H_2$ and $-\Delta H_3$. The larger number of water molecules released in the formation of the tetrahedral $[Zn\ en_2]^{2+}$ starting from the octahedral $[Zn(H_2O)_6]^{2+}$ produces an increase of translational entropy which raises the value of ΔS_{1-2}. The positive value of ΔS_{1-3} can be accounted for in terms of the weak tendency of Zn^{2+} to bind three molecules of ethylenediamine, as mentioned above. Comparison of the zinc and the cobaltous ion is particularly revealing. They have very similar ionic radii and the same heats of hydration. Even their heats of formation for the 1 : 1 complex are the same, while the heat of formation of the 1 : 3 complex of the zinc is markedly lower than that of the corresponding cobalt complex. This leads one to conclude that the six water molecules are bound to both cations with equal strength, while the three ethylenediamine molecules are bound less strongly to the zinc than to the cobalt ion, the ratios $\Delta H_{1-3} : \Delta H_1$ being 2·4 and 3·2 respectively. As a consequence the $[Zn\ en_3]^{2+}$ ion should have a less rigid structure and thus a greater partial entropy which makes itself felt on the value of ΔS_{1-3}.

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INSTITUTE OF GENERAL CHEMISTRY, THE UNIVERSITY OF PALERMO,
PALERMO, ITALY.
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[17] Schwarzenbach, *Helv. Chim. Acta*, 1952, **35**, 2344.

[18] Latimer and Jolly, *J. Amer. Chem. Soc.*, 1953, **75**, 1548.