877. *The Thermodynamics of the Formation of Complex Ions of Ethylenediaminetetra-acetic Acid and Bivalent Cations.*

By R. A. CARE and L. A. K. STAVELEY.

Calorimetric measurements have been made of the heats of formation of the complex ions of ethylenediaminetetra-acetic acid (EDTA) with nine bivalent cations. The values obtained refer to solutions of known and comparatively small ionic strength and are considered to be more accurate than any previously published figures. They have been combined with stability-constant data to give the entropy change for the formation of the complex ion. The sum of this entropy change and the standard entropy of a metallic ion is neither constant nor shows a steady change with increasing size of the metallic ion. Possible reasons for this are considered. The values of the heats and entropies of formation of the complexes are also discussed in the light of what is known of the interaction of the cations with ethylenediamine molecules and with acetate ions.

Some experiments have been carried out on copper, nickel, and zinc in solutions of higher pH in which appreciable quantities of hydroxy-complexes of the type $MY(OH)^{3-}$ are formed, where Y is the anion of EDTA. From these experiments approximate quantitative inferences have been drawn about the thermodynamics of the formation of such hydroxy-complexes.

THE property possessed by ethylenediaminetetra-acetic acid (EDTA) of forming stable complexes with many metallic ions has important practical consequences, in both analytical and applied chemistry. In addition, the equilibria between the complexes and the free EDTA anions and the metallic ions have considerable physicochemical interest. This paper deals with the thermodynamics of the equilibria for the following bivalent cations: magnesium, calcium, strontium, barium, nickel, copper, zinc, cadmium, lead.

Schwarzenbach and his collaborators [1] have measured accurately the formation constants for the complex ions MY^{2-} in the reaction

$$M^{2+} + Y^{4-} \rightleftharpoons MY^{2-} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Y^{4-} is the EDTA anion, *i.e.*,

$$(O_2C\cdot CH_2)_2N\cdot CH_2\cdot CH_2\cdot N(CH_2\cdot CO_2)_2{}^{4-}$$

These formation constants were determined at 20° and at an ionic strength of 0·1. We have determined calorimetrically the heats of formation (ΔH_f) of the ions MY^{2-} for the metals listed. Hence it has been possible to evaluate the entropy changes for reaction (1). When the thermochemical experiments were begun, the only values available for ΔH_f were those obtained by Carini and Martell [2] for the alkaline-earth metals from the temperature variation of the formation constants over a range of 30°. Values so obtained are usually less reliable than those determined directly. While our work was in progress, Charles [3] published the results of calorimetric measurements at 25° of ΔH_f for all the metals we have studied, and for some others. The precision aimed at in his measurements was not as high as we have attempted to achieve. Moreover, we have paid rather more careful attention to the experimental conditions. It was highly desirable to make the conditions as nearly as possible the same as those under which the formation constants were determined. This requires that the ionic strength should be controlled, and also that the concentrations of EDTA should be made as low as is consistent with the generation of temperature changes on the formation of the complex which are still large enough for accurate measurement. It is also necessary to control the pH of the solutions, since, as Schwarzenbach's work has shown, at high and low pH values complexes other than MY^{2-} can be formed, namely, complexes of the type MHY^- at low pH values and of the type $M(OH)Y^{3-}$ at high. For some metals, *e.g.*, barium, the range of pH values over which the formation of the hydrogen and hydroxy-complexes can be disregarded is very limited.

EXPERIMENTAL

The calorimeter used was that described by Davies, Singer, and Staveley.[4] The metal was contained in the calorimeter in about 1 l. of an approximately 0·01M-solution, and the small bottle within this held a known quantity of a relatively concentrated solution of the tetrapotassium salt of EDTA which contained about 10% more of this salt than that stoicheiometrically required for complete complex-formation of the metal ions. The temperature change, which was usually between 0·05° and 0·10°, was measured with a resistance thermometer, and the associated quantity of heat evolved or absorbed deduced from this by the usual calibration experiments carried out with electrical heating. All measurements were made at 20°.

Although we have used metal and EDTA concentrations considerably smaller than those employed by Charles, they are nevertheless much higher than those used by Schwarzenbach in the determination of the stability constants of the complexes. Since complex formation involves combination of ions of opposite charge, this means that there is an appreciable change in ionic strength accompanying this process. In our experiments, a constant background concentration of neutral salt was maintained by making both the metal solutions and the more concentrated solutions of the complexing agent always 0·1N in potassium nitrate. The final ionic strength μ in a complex-forming experiment was approximately 0·17. We shall present our results in such a way that μ can be exactly estimated in any particular case.

As will be shown, it was necessary in our work to use the third and fourth dissociation constants of EDTA, and although these have been determined by Schwarzenbach and Ackermann,[5] and by Carini and Martell,[6] it seemed advisable to measure them ourselves at the ionic strength

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[1] Schwarzenbach, Gut, and Anderegg, *Helv. Chim. Acta*, 1954, **37**, 937.

[2] Carini and Martell, *J. Amer. Chem. Soc.*, 1954, **76**, 2153; Schwarzenbach and Ackerman, *ibid.*, 1947, **30**, 1798.

[3] Charles, *ibid.*, p. 5854.

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

[5] Schwarzenbach and Ackerman, *Helv. Chim. Acta*, 1947, **30**, 1798.

[6] Carini and Martell, *J. Amer. Chem. Soc.*, (*a*) 1952, **74**, 5745; (*b*) 1953, **75**, 4810.

of our calorimetric experiments. Since we need to calculate the actual amounts of the ions of EDTA from pH readings obtained with a glass electrode, we need to know the "hybrid" ionisation constants :

$$K_3 = \{H^+\}[HY^{3-}]/[H_2Y^{2-}] \text{ and } K_4 = \{H^+\}[Y^{4-}]/[HY^{3-}]$$

where $-\log_{10}\{H^+\}$ is the pH measured with the glass electrode. These constants were obtained by making pH measurements during the titration of pure EDTA with a standard carbon-dioxide-free potassium hydroxide solution made by shaking carbon dioxide-free potassium chloride solution with silver oxide.[7] These titrations were carried out at such concentrations and in the presence of so much potassium nitrate that μ reached the desired value when the pH became pK for the ionisation constant under investigation. The average results obtained from several experiments for the hybrid ionisation constants K_3 and K_4 at 20° were as follows: pK_3 = 6·23 at μ = 0·184 and 6·23 at μ = 0·147; pK_4 = 10·21 at μ = 0·234 and 10·27 at μ = 0·175. Values of pK_4 at the slightly different ionic strengths encountered in the calorimetric experiments were obtained from these values by assuming a linear relation between pK_4 and $\mu^{\frac{1}{2}}$. Owing to hydrolysis, to calculate K_4 from the titration curve it is necessary to have a value for the hybrid ionic product of water at 20°, this quantity being the product of the hydrogen-ion activity and hydroxyl-ion concentration, at a known ionic strength. (A knowledge of this ionic product is also necessary in working out the ionic composition of the solutions later designated as solutions B.) From experiments on solutions containing known amounts of carbonate-free alkali this hybrid ionic product was found to be $1{\cdot}23\ (\pm 0{\cdot}09) \times 10^{-14}$ at 20° and μ = 0·213.

Potassium nitrate was preferred to potassium chloride as a neutral salt since the tendency of transition-metal ions to form ion pairs or complexes is smaller with the nitrate ion than with the chloride ion. In the experiments with lead, however, since there is some evidence that this metal forms complexes with nitrate ions,[8] potassium perchlorate was used instead. For each metal a concentrated solution in 0·1M-potassium nitrate of one of its pure salts was prepared and analysed for its metal content. For magnesium, cadmium, copper, nickel, and zinc, sulphates were used, for barium and calcium the chlorides, for strontium the nitrate, and for lead the perchlorate. All these solutions except that containing magnesium were analysed gravimetrically. Cadmium and zinc were determined as their 8-hydroxyquinoline complexes, strontium and barium as the sulphates, lead as the chromate, nickel as the dimethylglyoxime derivative, copper by electrolytic deposition, and calcium by precipitation of the oxalate followed by ignition to carbonate. The magnesium content of the magnesium sulphate solution was estimated by titration, with eriochrome-black as indicator, against an EDTA solution which had been standardised against standard calcium and zinc solutions. The solutions of copper, nickel, and zinc were made 0·02N with sulphuric acid to repress hydrolysis. The lead perchlorate solution contained a known excess of perchloric acid for the same reason.

To prepare a metal solution for a calorimetric experiment a known weight of the concentrated solution was mixed with 941·5 ml. of a carbon dioxide-free solution of 0·1M-potassium nitrate in the calorimeter, and a few ml. of 0·5N-nitric acid added. The resulting solution will be referred to as solution A. The precise amount of 0·5N-nitric acid added in any particular case was that which trial experiments had shown would lead to a suitable final pH after the addition of the EDTA to solution A. Except in the experiments with lead, the concentrations of the metals in solutions A were approximately 0·01M. With lead, where potassium perchlorate was used instead of potassium nitrate, to avoid precipitation of potassium perchlorate on the addition of the EDTA the concentrations of the lead and the complexing agent were reduced to about half their usual values.

As the sodium ion forms complexes with EDTA while the potassium ion does not, we have preferred to use the tetrapotassium rather than the tetrasodium salt and make a correction, as Charles did. The commercial acid was dissolved in carbonate-free potassium hydroxide, the solution filtered, and the acid then slowly reprecipitated from dilute solution by adding an equivalent quantity of nitric acid. The precipitate was washed and then the whole process was repeated once. The purified acid so obtained was then dissolved in carbonate-free potassium hydroxide in 0·1M-potassium nitrate, about 5% more alkali being used than was just required for complete formation of the tetrapotassium salt. We shall call this solution B.

In order to determine ΔH_f for the reaction (1) a minimum of two calorimetric experiments

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[7] Schwarzenbach and Biedermann, *Helv. Chim. Acta*, 1948, **31**, 331.

[8] Bale, Davies, and Monk, *Trans. Faraday Soc.*, 1956, **52**, 816.

was required. The first consisted in measuring the heat absorbed, ΔH_C, when a known amount (about 21 ml.) of solution B was added to the solution A to give a final solution C. Immediately solution C was removed from the calorimeter its pH (pH_C) was measured at 20° by using a glass electrode and a " Cambridge " pH meter. The second experiment consisted in measuring the heat absorbed ΔH_D when exactly the same amount of solution B was added to a solution containing none of the metal but otherwise identical with solution B and therefore containing the same amount of free acid. The pH (pH_D) of this second final solution (D) was also measured. The successive dissociation constants of EDTA being known, the ionic composition of solution D was estimated. Even when pH_D was between 10 and 11 (when solution D contained a considerable quantity of hydroxyl ion), owing to the very small value of the fourth dissociation constant, while most of the complexing reagent was present as the Y^{4-} ion, some 20—30% was there as HY^{3-}. (The amount present as H_2Y^{2-} in solution D was always negligible.) Likewise, for solution C, pH_C, the formation constant of MY^{2-}, and the total amounts of metal and complexing agent being known, it was possible to calculate the ionic composition. Conditions were so chosen that at pH_C the metal was virtually completely in the form of the complex MY^{2-}. (With copper, nickel, and zinc a rather more extended series of experiments was carried out to investigate the behaviour at high pH.) The surplus complex-forming agent at pH_C was usually present mostly as HY^{3-} with small amounts of Y^{4-} and H_2Y^{2-}. The difference $\Delta H_C - \Delta H_D$ gives the heat-content change ΔH_2 for the process

$$M^{2+} + H^+{}_D + Y^{4-}{}_D + HY^{3-}{}_D + OH^-{}_D \longrightarrow$$
$$MY^{2-}{}_C + Y^{4-}{}_C + HY^{3-}{}_C + H_2Y^{2-}{}_C + OH^-{}_C + H^+{}_C \quad . \quad (2)$$

Since the amounts of all the ions in process (2) are known, the quantity sought, ΔH_f, can be evaluated from ΔH_2 by allowing for the heat-content changes due to the following processes :

$$H^+ + HY^{3-} \rightleftharpoons H_2Y^{2-} \quad +\Delta H_3 \quad . . . . \quad (3)$$
$$H^+ + Y^{4-} \rightleftharpoons HY^{3-} \quad +\Delta H_4 \quad . . . . \quad (4)$$
$$H^+ + OH^- \rightleftharpoons H_2O \quad +\Delta H_5 \quad . . . . \quad (5)$$

For ΔH_3 and ΔH_4 we have used the values Carini and Martell [6(b)] derived from the temperature variation of the dissociation constants, and for ΔH_5 the value of 13,610 cal. calculated for 20° from Pitzer's formula.[9]

The thermal capacity of the calorimeter was virtually the same for all experiments so that once it had been established it was not necessary to determine the electrical energy equivalent after each measurement, though check determinations were made from time to time.

Results.—The unit in which all results are expressed is the thermochemical calorie (= 4·1833 international joules = 4·1840 absolute joules). The accuracy of which the calorimeter is capable has been discussed in a previous paper.[4] In favourable cases it can reach 0·1%, but this has not been achieved here, since to keep the ionic strength down it was necessary to work with comparatively dilute solutions. We consider that our average ΔH_f value for any one metal is reliable to ±150 cal./mole, though the limits of accuracy are not easy to assess, since a value of ΔH_f depends not only on the thermal, pH, and quantity measurements but also on the values adopted for the third and fourth ionisation constants of EDTA appropriate to the ionic strength used and on the heat-content changes associated with these ionisation stages. Our results are accordingly presented in Tables 1 and 2 in sufficient detail to permit recalculation from them of ΔH_f by use of different values for the ionisation constants and associated heats of ionisation, should these be revised by later work.

There were slight variations from one metal to another in μ for the solutions C, depending on which salt of the metal was used. For the C solutions containing magnesium, cadmium, copper, nickel, and zinc, μ was between 0·173 and 0·177, while for solutions of barium, calcium, and strontium, μ was 0·165. For the D solutions, μ was between 0·210 and 0·213. For lead, μ for solutions C and D was 0·133 and 0·157 respectively.

Some experiments were also carried out with copper, zinc, and nickel in which the final solution had a sufficiently high pH to contain appreciable quantities of the so-called hydroxy-complexes of the type $M(OH)Y^{3-}$. The results of these experiments are recorded in Table 2.

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[9] Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365.

TABLE 1.

Type *		M	pH	Q	ΔH_f
C	K_4Y = 10·70 V = 982	9·530 Mg^{2+}	8·91	7·59	+3·15
C		9·510 Mg^{2+}	8·97	7·69	+3·14
C		9·425 Ca^{2+}	8·15	97·09	−6·45
C		9·395 Ca^{2+}	7·86	96·30	−6·45
C		9·312 Ba^{2+}	8·82	81·43	−4·86
C		9·343 Ba^{2+}	9·14	81·14	−4·83
D			10·84, 10·86,	29·91, 29·42,	
D			10·85, 10·85	29·94, 29·71	
C	K_4Y = 11·20 V = 982	9·948 Sr^{2+}	9·13	79·53	−4·12
C		9·970 Sr^{2+}	8·94	79·34	−4·09
C		9·789 Cd^{2+}	8·62	135·03	−10·04
C		9·793 Cd^{2+}	7·77	135·26	−10·08
D			10·87, 10·91	31·45, 31·71	
C	K_4Y = 11·32 V = 982	9·418 Zn^{2+}	8·36	94·58	−5·68
C		9·341 Zn^{2+}	9·10	93·04	−5·61
C		9·546 Ni^{2+}	7·60	120·85	−8·31
C		9·553 Ni^{2+}	7·38	121·03	−8·39
D			10·82, 10·71	35·15, 36·47	
C	K_4Y = 10·93 V = 981	9·790 Cu^{2+}	6·16	123·27	−8·84
D			10·76	31·70	
C	K_4Y = 10·97 V = 984	9·761 Cu^{2+}	6·23	138·09	−8·78
D			10·78	48·41	
C	K_4Y = 10·93 V = 980	9·699 Cu^{2+}	7·38	116·96	−8·68
C		9·770 Cu^{2+}	7·60	116·88	−8·53
D			10·84, 10·91	27·24, 27·17	
C	K_4Y = 10·97 V = 983	9·643 Cu^{2+}	9·26	130·03	−8·53
D			10·94	43·02	
C	K_4Y = 5·495 V = 982	4·982 Pb^{2+}	9·75	88·31	−13·94
C		5·100 Pb^{2+}	8·17	90·69	−14·19
C		5·100 Pb^{2+}	9·45	90·43	−13·99
D			10·74, 10·74	11·74, 11·38	

* The letter C means that the experiment was the formation of the complex ion, while D denotes a dilution experiment (see text). K_4Y = no. of millimoles of the tetrapotassium salt of EDTA; V = total volume (ml.) after mixing or dilution; M = no. of mg. ions of metal; pH = pH of final solution; Q = heat evolved in calories on forming the solution C or D (two or more Q values given together are the results of separate experiments carried out under identical conditions); ΔH_f = calculated heat content change for the reaction $M^{2+} + Y^{4-} \rightleftharpoons MY^{2-}$ in kcal./mole (1 cal. = 4·1840 abs. joules).

TABLE 2.

Type		M	pH	OH^-	Q	ΔH_f	ΔH_6
C	K_4Y = 10·92 V = 977	9·809 Zn^{2+}	11·06	1·19	53·34	−5·67	0
C		9·740 Zn^{2+}	10·94	1·57	52·45	−5·66	0
C		9·848 Ni^{2+}	10·99	1·40	75·37	−7·89	+ 3·24
D			11·38, 11·44		−6·45, −6·68		
C	K_4Y = 10·93 V = 973	9·825 Ni^{2+}	11·08	0·47	76·06	−7·82	+11·04
D			11·34, 11·27		−6·55, −6·74		
C	K_4Y = 10·93 V = 978	9·790 Cu^{2+}	9·83	0·33	111·81	−8·62	—
D			10·99		20·97		
C	K_4Y = 10·93 V = 976	9·773 Cu^{2+}	10·27	0·90	140·40	−8·98	−3·37
D			11·15		11·87		
C	K_4Y = 10·92 V = 977	9·760 Cu^{2+}	10·81	1·89	85·82	−9·11	−2·27
D			11·38, 11·44		−6·45, −6·68		
C	K_4Y = 10·92 V = 977	9·619 Cu^{2+}	10·83	1·96	82·83	−9·12	−2·21
C		9·730 Cu^{2+}	10·98	1·55	85·51	−9·22	−3·45
D			11·40, 11·45		−7·89, −8·04		

For C, D, M, and K_1Y, see notes to Table 1; V = volume of solution in calorimeter, in ml., after mixing; pH = pH of the same solution; OH^- = number of mg.-ions of hydroxyl ion removed from the system as a result of complex formation; Q = observed heat evolved, in calories; ΔH_f = heat absorbed (cal.) per g.-ion of metal entering into complex formation; ΔH_6 = estimated heat-content change for the reaction $MY^{2-} + OH^- \rightleftharpoons M(OH)Y^{3-}$ per mole of the last ion.

TABLE 3.

	(1) ΔH_f	(2) ΔG	(3) ΔS	(4) $S°$	(5) $\Delta S + S°$	(6) ΔH_f (ref. 3)	(7) ΔH_f (ref. 2)	(8) r
Mg	+ 3·14	−11·65	50·5	−28·2	22·3	+ 3·1, + 3·1	−2·9	0·66
Ca	− 6·45	−14·34	26·9	−13·2	13·7	− 5·8, − 6·5	−2·5	1·01
		−14·69	28·1		14·9			
Sr	− 4·11	−11·57	25·4	− 9·4	16·0	− 4·2, − 4·2	−4·1	1·18
Ba	− 4·83	−10·40	19·0	+ 3	22	− 5·1, − 5·3	−4·1	1·34
Ni	− 8·35	−24·96	56·7	—	—	− 7·6, − 7·8	—	0·69
Cu	− 8·67	−25·20	56·4	−23·6	32·8	− 8·2, − 8·4	—	0·72
Zn	− 5·61	−22·12	56·3	−25·45	30·8	− 4·5, − 4·9	—	0·74
Cd	−10·08	−22·07	40·9	−14·6	26·3	− 9·1, − 9·3	—	0·97
Pb	−14·08	−24·18	34·5	+ 5·1	39·6	−13·1, −13·4	—	1·20

(The units of ΔH_f and ΔG are kcal./g. ion, of ΔS cal./g.-ion deg., and of r, the ionic radius, Ångstrom units.)

DISCUSSION

In Table 3 are recorded: (1) our mean values for ΔH_f at 20° for the reaction $M^{2+} + Y^{4-} \longrightarrow MY^{2-}$; (2) the values of ΔG at 20° for this reaction calculated from Schwarzenbach's formation constants [1] for $\mu = 0·1$; (3) the derived values of the entropy change, ΔS; (4) the standard entropies, $S°$, of the metal ions (taken from the National Bureau of Standards publication "Selected Values of Chemical Thermodynamic Properties," Washington, 1952); (5) values of the quantity $\Delta S + S°$; (6) the values of ΔH_f obtained by Charles at 25°, and (7) those given by Carini and Martell for 30°; and (8) the ionic radii of the metallic ions.[10]

It will be seen that Charles's results are in fair agreement with our own. The wider discrepancies between our figures and those of Carini and Martell exemplify the unreliability of ΔH values obtained by measuring stability constants over a limited temperature range. In particular, it will be noted that they give a ΔH value of the magnesium complex which is not even of the correct sign. As the quantity $\Delta S + S°$ will play a considerable part in the discussion of our results, we must draw attention to possible errors in the $S°$ values. From a survey of the data available for calculating ionic entropies, and having regard not only to the values given in the publication mentioned but also to those tabulated by other authorities (*e.g.* Kelley [11] and Latimer, Pitzer, and Smith [12]) it seems that some of the $S°$ values in Table 3 could be in error by as much as 2 e.u. Therefore the quantities $\Delta S + S°$ may be in error by 2—3 e. u.

As Charles, and Carini and Martell have pointed out, the stability of the EDTA complexes is due largely to the ΔS values which are large and positive owing to the liberation of solvent molecules previously in the hydration sphere of the component ions. If it were true for all the metals examined that, in their complexes, the EDTA ion was being fully utilised as a hexadentate ligand, then we would expect that these complexes would have essentially the same shape, differ relatively little in overall size, and hence interact with the surrounding water in much the same way. The entropy of the complex ion in solution would then be almost constant or at least show a comparatively gradual change with the radius of the metallic ion within it. The same statements would then apply to the quantity $\Delta S + S°$ since this only differs from the standard entropy of the complex ion by the constant entropy of the Y^{4-} ion. Charles suggested that the quantity $\Delta S + S°$ was in fact approximately constant by plotting ΔS against $S°$ and showing that the points conformed reasonably closely to a straight line. It is, however, clear from Table 3 that there are variations in $\Delta S + S°$ which are well outside any uncertainty in this quantity. Particularly striking is the difference in $\Delta S + S°$ for lead and strontium, two ions of approximately the same size, and also the fact that for the alkaline earths the values are neither constant nor show a simple trend with increasing size of metallic ion.

There are, however, a number of reasons for the absence of any simple regularity in the values of $\Delta S + S°$ and also of ΔH_f. We are concerned with the equilibrium

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[10] Ahrens, *Geochim. Cosmochim. Acta*, 1952, **2**, 155; *Nature*, 1954, **174**, 644.

[11] Kelley, *U.S. Bur. Min. Bull.*, 1937, No. 406; 1949, No. 477.

[12] Latimer, Pitzer, and Smith, *J. Amer. Chem. Soc.*, 1938, **60**, 1829.

$M^{2+} + Y^{4-} \rightleftharpoons MY^{2-}$, in which all three ions are hydrated, and the changes in the thermodynamic functions for this reaction may be regarded as the relatively small differences between the much larger changes in these functions when a gaseous metallic ion becomes hydrated on the one hand and on the other becomes co-ordinated with the EDTA ion. If the metallic ion in solution is particularly closely associated with, say, six water molecules, each of these is a separate entity which can individually take up such a position as to minimise the free energy of the system. In the EDTA anion, by contrast, the positions of the six atoms available for co-ordination cannot be so freely altered, and a compromise must be reached in which probably none of these six atoms is in its optimum position in relation to the metal ion. The size of the central metallic ion must affect the degree to which the bonds of the EDTA anion are distorted in forming the complex, and this will also influence the distances between pairs of oxygen atoms in different carboxyl groups, between which there will be repulsion. If atomic models are used it appears that an octahedron is most nearly approached with metallic ions neither too big nor too small, and this may be chiefly why, with the alkaline earths, the complex formed with the greatest evolution of heat is that of calcium. It may also be noted that, just as for the pair magnesium–calcium, so also for the pair zinc–cadmium (for which the change in ionic radius is much the same), there is a considerable drop in ΔH (*i.e.*, the formation of the complex becomes more exothermic) on going from the smaller to the larger cation. On geometrical grounds alone, therefore, the relation between the size of metallic cation and the heat of interaction of this gaseous ion with the EDTA anion may be more complicated than the relation between ionic size and heat of hydration. A further factor which will militate against a smooth relation between the former heat of interaction and cationic radius is that with increase of the latter a point may be reached when the anion acts as a 5- rather than as a 6-co-ordinating unit, as is indeed suggested by the experiments of Wheelwright, Spedding, and Schwarzenbach [13] with the rare earths.

The thermodynamic properties of these complexes, however, can scarcely be determined by size factors alone. They must also depend upon the nature of the interaction between the metal ion and the nitrogen and oxygen atoms of the EDTA anion. For the alkaline-earth complexes we would expect that their interaction is essentially electrostatic, whereas for elements such as copper and nickel it will have a greater degree of covalent character. According to the use made of the lone pair of electrons of the nitrogen atoms, the angles between the orbitals on these atoms will vary, and this in turn will affect spatial relations within the complex. Thus, trials with models showed that it was easier to fit the two nitrogen and four oxygen atoms approximately octahedrally round the metal atom if the orbitals of the nitrogen atoms were given the directions of 4-covalent nitrogen, rather than that of 3-covalent nitrogen. (We may add that a secondary consequence of differences in the interaction between the metal atom and the ligands will be that the effective charges on the nitrogen and oxygen atoms in the complex will vary with the nature of the metal which in turn will affect the interaction of the complex with surrounding water molecules.) Furthermore, especially with metals whose complexes involve some degree of covalent bonding between metal and ligand, preference need not always be given to an octahedral complex. For example, since copper never appears to form really stable 6-co-ordinated complexes it would seem probable that in interacting with the EDTA anion it uses only four of the available six atoms, and so $\Delta S + S^\circ$ need not necessarily be the same for the copper complex as for the complex with a cation of about the same size but which co-ordinates with all six of the atoms available in the EDTA anion.

One approach by which the operation of some of these factors might be investigated is to consider the EDTA anion as consisting, as far as its complexing powers are concerned, of one ethylenediamine molecule and four acetate ions, and then to review the thermodynamics of EDTA complexes in the light of what is known about the interaction of the same metal ions with ethylenediamine and with acetate ions. Unfortunately, reliable data for ethylenediamine complexes exist only for copper, nickel, cadmium, and zinc.[14]

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[13] Wheelwright, Spedding, and Schwarzenbach, *J. Amer. Chem. Soc.*, 1953, **75**, 4196.

[14] (*a*) Davies, Singer, and Staveley, ref. 4; (*b*) Poulsen and Bjerrum, *Acta Chem. Scand.*, 1955, **9**; 1407; (*c*) Spike and Parry, *J. Amer. Chem. Soc.*, 1953, **75**, 2726, 3770.

Although formation constants have been measured for ion pairs of an acetate ion and all of the cations of Table 3, only for magnesium, calcium, strontium, and barium have comparable measurements been made at more than one temperature, so that ΔH and ΔS are only known for these metals.[15]

For the copper ion, co-ordination of one ethylenediamine causes an evolution of heat of 13·0 kcal. per mole and an entropy increase of 5·4 (Poulsen and Bjerrum [14(*b*)]). Yet when this cation complexes with the EDTA anion, although the entropy increase is 57 e.u., the heat evolved is only 8·59 kcal., in spite of the fact that the copper ion [16] has a stronger tendency to form ion pairs with the acetate ion than any other metal in Table 3 except lead.[17] However, the values given by Bell and George [18] for ΔG, ΔH, and ΔS for ion pairs involving various anions other than the acetate ion show that ΔH is usually small and can be either positive or negative, while ΔS can vary considerably. Their results suggest that when ΔS is relatively large (leading to a ΔG which is also large numerically, but negative) the formation of the ion pair is endothermic. The results obtained by Nancollas [15] likewise show that a relatively high ΔS tends to be associated with a positive ΔH. When, therefore, the ΔG values for cation–acetate ion-pair formation (which are negative) are relatively large numerically (as for copper in particular) it may well be that the corresponding ΔS values are high, and this is primarily responsible for the large entropy increase when, say, the cupric ion forms complexes with the EDTA anion. It is possible, however, that ΔH for the ion-pair formation is positive, and that this to some extent offsets the exothermic interaction of the copper atom with the nitrogen atoms, thus causing the overall ΔH_f to be numerically less than that for the formation of a 1 : 1 copper–ethylenediamine complex. On this analysis, we might say that, roughly speaking, the heat evolved in the formation of the copper–EDTA complex arises from the reaction of the metal atom with the nitrogen atoms, while most of the entropy increase arises from the interaction with the acetate groups. Nevertheless, the observed entropy increases are larger than might be expected on this basis. Thus for the nickel–EDTA complex the heat evolved per mole is the same within 0·7 kcal. as the heat evolved when this cation co-ordinates with one mole of ethylenediamine. If this is taken to mean that for 1 : 1 ion-pair formation of the nickel ion and the acetate ion, ΔH is almost zero, it follows from the ΔG value for the ion-pair formation that the associated ΔS is only about 5 e.u., whereas for the EDTA complex of nickel the ΔS value is approximately 57 e.u. (For the 1 : 1 complex of nickel with ethylenediamine, ΔS is about 4 e.u.) It may be that in an EDTA complex desolvation is much more complete than for a simple ion pair, since in the former any one charged centre benefits from the screening effect of the rest of the EDTA ion. It would clearly be interesting to have some information about the thermodynamics, not only of ethylenediamine complexes and of metal–acetate ion-pair formation, but also of the interaction of metal ions with the anions of polycarboxylic acids.

The results recorded in Table 2 throw some light on the thermodynamics of the formation of hydroxy-complexes in solutions of higher pH. It will be seen that in these experiments appreciable quantities of hydroxyl ions were removed from the system, consequent on the reaction

$$\mathrm{MY^{2-} + OH^- \rightleftharpoons M(OH)Y^{3-}} \qquad . \; . \; . \; . \; . \; . \; . \quad (6)$$

or alternatively

$$\mathrm{MY(H_2O)^{2-} + OH^- \rightleftharpoons M(OH)Y^{3-} + H_2O}$$

(In the experiments of Table 1, by contrast, the amount of hydrogen or hydroxyl ions which apparently disappeared was always zero within the limits of experimental error, showing that the formation of hydrogen- or hydroxy-complexes did not occur to any significant extent.)

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[15] Nancollas, *J.*, 1956, 744.

[16] Lloyd, Wycherley, and Monk, *J.*, 1951, 1786; Sircar, Aditya, and Prasad, *J. Indian Chem. Soc.*, 1953, **30**, 633.

[17] Das, Aditya, and Prasad, *ibid.*, 1952, **29**, 169; Aditya and Prasad, *ibid.*, 1953, **30**, 213; Shin Suzuki, *J. Chem. Soc. Japan*, 1953, **74**, 531.

[18] Bell and George, *Trans. Faraday Soc.*, 1953, **49**, 619.

From the data in Table 2, estimates can be made of K_6, where

$$K_6 = [MY(OH)^{3-}]/([MY^{2-}][OH^-])$$

and of ΔH_6, the corresponding heat content increase. For copper, $\log_{10} K_6 = 2{\cdot}5 \pm 0{\cdot}1$, $\Delta H_6 = -2{\cdot}7 \pm 1$ kcal./mole; for zinc, $\log_{10} K_6 = 2{\cdot}1 \pm 0{\cdot}1$, $\Delta H_6 \simeq 0$; for nickel, $\log_{10} K_6 = 1{\cdot}8 \pm 0{\cdot}3$, $\Delta H_6 \simeq$ 3kcal./mole. (Although these values are rather rough, particularly those of ΔH_6, it is obvious from Table 2 that the hydroxy-complex of copper is formed exothermically from the normal complex, while the same process for nickel is endothermic and that for zinc almost athermal.) This difference between copper and nickel is noteworthy since ΔH_f for these two metals is about the same. Differences also exist in the values of ΔS_6, the entropy increase associated with reaction (6). The above values of K_6 and ΔH_6 lead to a value of ~2 e.u. for ΔS_6 for the copper complex, and although this quantity cannot be so reliably estimated for zinc and nickel, it is clear that for zinc ΔS_6 is considerably larger than 2 e.u., and even bigger for nickel where ΔH_6 is positive. Finally, it seems very probable that for the normal MY^- complexes of tervalent metals one of the six co-ordinating positions is occupied by a water molecule. Of the bivalent metals we have studied, the same may well be true of copper, at least, in view of its well-known reluctance to form hexa-co-ordinated complexes. If this is so, the formation of the hydroxy-complex really arises from the process

$$Cu(H_2O)Y^{2-} + H_2O \rightleftharpoons Cu(OH)Y^{3-} + H_3O^+ \quad . \quad . \quad . \quad . \quad (7)$$

and the value of $\Delta H_6 = -2{\cdot}7$ kcal./mole then leads to a value of $\Delta H_7 = 10{\cdot}9$ kcal. for the heat content increase in process (7), that is, for the heat of ionisation of the bound water molecule.

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INORGANIC CHEMISTRY LABORATORY, OXFORD. [*Received, June 4th,* 1956.]