147. *Thermodynamics of Ion Association. Part II.* Alkaline-earth Acetates and Formates.*

By G. H. Nancollas.

Thermodynamic equilibrium constants for the association, in aqueous solution, of magnesium, calcium, strontium, and barium ions with acetate and formate ions have been obtained from potentiometric measurements at 25° and 35°. ΔG, ΔH, and ΔS for the reaction $M^{2+} + A^- \rightleftharpoons MA^+$ have been calculated, and the anomalous complex-forming behaviour of the magnesium ion is interpreted in terms of a hydration effect. Calculated hydration entropies of the ion pairs are compared with values obtained from empirical relations.

Ions of the alkaline-earth series in their association with inorganic and organic anions have especially interesting properties. The absence of reliable heat and entropy data has restricted discussion to a consideration of the association constants at one temperature and, if it is assumed that the complexes are formed as a result of electrostatic interactions between the oppositely charged ions, the order of stability of the complexes for a given ligand should be in the inverse order of the radii of the cations, *i.e.*, $Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$. Colman-Porter and Monk [1] have shown that the stabilities of a number of organic salts of calcium, strontium, and barium fall in this sequence. The position of magnesium, however, which is the most hydrated alkaline-earth cation, is by no means certain. Williams,[2] in a survey covering both inorganic and organic salts of the alkaline-earths, has shown that the stability constants of organic acid complexes of magnesium are very often smaller than those of the calcium complexes.

In a previous paper,[3] it was shown that the entropy of association of a single cation with different anions depends largely on the entropy of hydration of the anion. The present work is a continuation of a proposed systematic study of the thermodynamic properties of ion association in aqueous solution and deals with systems in which the cation is varied. The derived thermodynamic data provide information concerning the behaviour of the hydrated magnesium ion as a complexing reagent.

Experimental

" AnalaR " acids and alkaline-earth chlorides were used without further purification: stock solutions were analysed volumetrically ($\pm 0{\cdot}1\%$) for acid by alkalimetry using carbon dioxide-free sodium hydroxide, and for chloride by the Mohr titration.[4] Conductivity water, prepared by mixed-bed deionisation,[5] and Grade A glassware were used throughout.

pH measurements were made with a glass electrode incorporated in the complete cell:

Ag/AgCl, HCl(0·2M)|glass|Solution under study¦sat. KCl¦Calomel electrode

The liquid junction was formed in a special apparatus which has been described elsewhere.[6] The glass electrodes were made from Corning 015 glass and had resistances of 10—20 megohms. Potentials were measured on a Tinsley potentiometer reading to 0·1mv, with a valve voltmeter as null-point indicator. The cell was contained in an oil-bath (thermostat), and reproducibility was greatly improved by maintaining the cell at its working temperature for at least 12 hr. before use. The electrode system was standardised before and after each set of measurements, with the buffer solutions: 0·05M-potassium hydrogen phthalate,[7] pH 4·005 at 25° and 4·021 at 35°; B.D.H. tabloid phosphate buffer, pH 6·99 at 25° and 6·97 at 35°. The procedure consisted in determining the pH of solutions containing known amounts of the monocarboxylic acid, sodium

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* Part I, *J.*, 1955, 1458.

[1] Colman-Porter and Monk, *J.*, 1952, 4363.
[2] Williams, *J.*, 1952, 3770.
[3] Nancollas, *J.*, 1955, 1458.
[4] Vogel, " Quantitative Inorganic Analysis," Longmans, 1947, p. 311.
[5] Davies and Nancollas, *Chem. and Ind.*, 1950, **7**, 129.
[6] Dunsmore and Speakman, *Trans. Faraday Soc.*, 1954, **50**, 236.
[7] Brit. Stand., 1647, 1950.

hydroxide, and metal chloride; these solutions were prepared immediately before use, and E.M.F. readings were reproducible to within $\pm 0{\cdot}1$ mv.

Results.—The pH being defined by $-\log f_1[\mathrm{H}^+]$, where f_1 is the mean activity coefficient for univalent ions, standardisation of the electrode system was checked by measurements with acetic acid–sodium acetate buffer solutions at 25° and 35°. The calculated thermodynamic acid dissociation constants, K_a, were within $\pm 1\%$ of the values, $1{\cdot}754 \times 10^{-5}$ at 25° and $1{\cdot}728 \times 10^{-5}$ at 35°, which were obtained by Harned and Ehlers.[8] For formic acid,[9] $K_a = 1{\cdot}772 \times 10^{-4}$ at 25° and $1{\cdot}747 \times 10^{-4}$ at 35°.

The pH of acetate and formate buffer solutions in the presence of the bivalent metal chlorides, which are known to be highly dissociated, can be satisfactorily interpreted in terms of the formation of only one complex, MA^+. The concentrations of the ionic species present in solution were obtained from the equations: (*a*) for the total concentration of bivalent metal, $T_m = [\mathrm{M}^{2+}] + [\mathrm{MA}^+]$; (*b*) for the total acid concentration, $T_a = [\mathrm{HA}] + [\mathrm{A}^-] + [\mathrm{MA}^+]$; (*c*) for electroneutrality, $[\mathrm{Na}^+] + [\mathrm{H}^+] = [\mathrm{MA}^+] + [\mathrm{A}^-]$; and (*d*) for the dissociation constant of the acid, $K_a = [\mathrm{H}^+][\mathrm{A}^-]f_1^{\,2}/[\mathrm{HA}]$.

Thermodynamic association constants, K, were obtained by successive approximations of I, the ionic strength, from the equation

$$\log K = \log\,[\mathrm{MA}^+]/[\mathrm{M}^{2+}][\mathrm{A}^-] + 2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I],$$

where $I = 3T_m + 2[\mathrm{A}^-] - [\mathrm{Na}^+] - [\mathrm{H}^+]$.

K values are given in Table 1, together with the concentrations of ionic species in millimoles/l.

TABLE 1. pH *Determinations* (*concns. in mmoles/l.*).

T_a	T_m	NaOH	pH	HA	A^-	MA^+	M^{2+}	I	K
				Magnesium acetate at 25°					
20·14	9·99	10·76	4·705	9·36	10·00	0·78	9·14	39·1	17·6
20·14	9·99	9·04	4·559	11·07	8·40	0·67	9·25	37·5	17·5
20·14	6·95	9·98	4·655	10·13	9·45	0·56	6·39	29·7	17·6
20·14	4·96	9·98	4·668	10·13	9·59	0·41	4·55	24·0	17·0
20·14	3·97	11·34	4·791	8·78	10·96	0·40	3·57	22·2	18·0
4·02	9·92	2·04	4·672	1·96	1·90	0·165	9·76	31·8	17·3
4·03	9·92	1·361	4·375	2·62	1·290	0·116	9·80	31·2	17·8
4·03	9·92	1·134	4·277	2·81	1·098	0·096	9·82	30·9	17·5
4·03	9·92	0·907	4·160	3·03	0·906	0·083	9·84	30·8	18·0
4·03	9·92	0·680	4·035	3·24	0·725	0·062	9·86	30·4	17·5
								Mean	17·6
				Magnesium acetate at 35°					
20·08	9·89	12·88	4·907	7·19	12·02	0·87	9·02	40·8	16·6
20·08	9·89	11·81	4·811	8·25	11·05	0·78	9·11	40·1	16·1
20·08	9·89	10·73	4·715	9·33	10·00	0·75	9·14	39·3	16·9
20·08	9·89	9·01	4·568	11·04	8·44	0·60	9·29	37·5	15·6
10·04	6·93	7·52	5·147	2·51	7·14	0·39	6·54	27·8	15·9
10·04	6·93	6·02	4·851	4·00	5·71	0·33	6·60	26·1	16·2
								Mean	16·2
				Calcium acetate at 25°					
20·14	9·98	10·76	4·705	9·36	10·00	0·78	9·20	39·1	17·5
20·14	9·98	10·21	4·659	9·91	9·49	0·74	9·24	38·7	17·2
20·14	9·98	9·04	4·559	11·07	8·40	0·67	9·31	37·7	17·5
20·14	6·99	11·34	4·771	8·78	10·76	0·60	6·39	31·1	17·0
20·14	4·99	12·47	4·883	7·66	11·98	0·50	4·49	26·5	17·3
20·14	3·99	13·61	4·998	6·52	13·20	0·42	3·57	24·8	16·4
10·07	4·99	8·39	5·376	1·67	8·02	0·37	4·62	23·6	18·4
								Mean	17·5
				Calcium acetate at 35°					
20·08	9·95	12·88	4·905	7·19	11·95	0·93	9·02	40·8	18·4
20·08	9·95	11·81	4·806	8·25	10·96	0·87	9·08	39·9	18·3
20·08	9·95	10·73	4·712	9·33	9·95	0·80	9·15	39·3	18·3
20·08	9·95	9·01	4·564	11·04	8·35	0·70	9·25	37·5	18·6
10·04	6·97	7·52	5·147	2·51	7·10	0·43	6·54	27·7	17·7
10·04	6·97	6·02	4·847	4·00	5·66	0·38	6·59	26·0	18·8
								Mean	18·4

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[8] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, **55**, 652.
[9] Harned and Embree, *ibid.*, 1934, **56**, 1042.

TABLE 1. (*Continued.*)

T_a	T_m	NaOH	pH	HA	A^-	MA^+	M^{2+}	I	K
			Strontium acetate at 25°						
20·14	9·99	15·06	5·121	5·07	14·19	0·88	9·11	43·3	14·5
20·14	9·99	11·84	4·806	8·28	11·15	0·71	9·28	40·5	14·3
20·14	9·99	10·76	4·711	9·36	10·10	0·68	9·31	39·2	14·9
20·14	9·99	9·04	4·563	11·07	8·49	0·58	9·41	37·9	14·8
10·07	6·99	7·96	5·245	2·10	7·59	0·38	6·61	28·3	14·5
10·07	6·99	6·03	4·845	4·02	5·76	0·29	6·70	26·4	13·9
								Mean	14·5
			Strontium acetate at 35°						
20·08	9·96	12·88	4·909	7·19	12·09	0·80	9·16	41·2	15·1
20·08	9·96	11·81	4·814	8·25	11·11	0·72	9·24	40·3	14·6
20·08	9·96	10·73	4·716	9·33	10·05	0·70	9·26	39·2	15·6
20·08	9·96	9·01	4·571	11·04	8·47	0·57	9·39	37·9	14·7
10·04	6·97	7·52	5·150	2·51	7·16	0·37	6·60	28·0	15·0
10·04	6·97	6·02	4·850	4·00	5·72	0·32	6·65	26·3	15·5
								Mean	15·1
			Barium acetate at 25°						
20·14	9·99	10·76	4·710	9·36	10·12	0·66	9·33	39·4	14·5
20·14	9·99	10·21	4·662	9·91	9·59	0·64	9·35	38·8	14·7
20·14	9·99	9·04	4·564	11·07	8·51	0·56	9·43	37·9	14·2
20·14	6·99	11·34	4·776	8·78	10·85	0·51	6·48	31·3	14·1
20·14	4·99	12·47	4·886	7·65	12·06	0·43	4·56	26·7	14·5
20·14	3·99	13·61	4·999	6·52	13·24	0·38	3·61	24·8	14·5
10·07	4·99	8·39	5·379	1·67	8·11	0·29	4·70	22·8	13·5
10·07	4·99	6·12	4·872	3·93	5·91	0·23	4·76	20·6	14·2
								Mean	14·2
			Barium acetate at 35°						
20·08	9·96	12·88	4·914	7·19	12·21	0·68	9·28	41·4	12·7
20·08	9·96	11·81	4·816	8·25	11·20	0·63	9·33	40·4	12·7
20·08	9·96	10·73	4·721	9·33	10·19	0·56	9·40	39·5	12·5
20·08	9·96	9·01	4·574	11·04	8·53	0·51	9·45	37·9	13·0
10·04	6·97	7·62	5·176	2·41	7·31	0·32	6·65	27·9	12·5
10·04	6·97	6·02	4·857	4·00	5·80	0·24	6·75	26·4	12·0
								Mean	12·5
			Magnesium formate at 25°						
19·64	9·92	10·76	3·729	8·66	9·85	1·13	8·79	38·5	26·9
19·67	9·92	9·07	3·585	10·30	8·39	0·98	8·94	37·2	26·3
19·64	9·92	9·04	3·583	10·29	8·34	1·01	8·91	37·1	27·7
19·67	6·95	9·75	3·660	9·66	9·20	0·81	6·14	29·3	27·1
19·67	3·97	11·34	4·027	5·95	13·06	0·66	3·31	24·3	27·8
9·84	4·96	8·39	4·439	1·41	7·90	0·53	4·43	22·3	27·0
9·84	4·96	6·12	3·906	3·58	5·86	0·40	4·56	20·3	26·2
								Mean	27·0
			Magnesium formate at 35°						
19·59	9·89	12·88	3·934	6·57	11·82	1·20	8·69	40·3	24·3
19·59	9·89	11·81	3·834	7·60	10·87	1·12	8·77	39·4	24·3
19·59	9·89	10·73	3·740	8·64	9·87	1·08	8·81	38·6	25·4
19·59	9·89	9·01	3·595	10·28	8·40	0·91	8·98	37·2	24·1
9·79	6·93	7·52	4·191	2·20	7·00	0·59	6·34	27·2	25·2
9·79	6·93	6·02	3·886	3·62	5·69	0·48	6·45	26·0	24·1
								Mean	24·5
			Calcium formate at 25°						
19·64	9·98	10·76	3·729	8·66	9·85	1·13	8·85	38·7	26·7
19·67	9·98	10·21	3·682	9·22	9·38	1·07	8·91	38·2	26·1
19·64	9·98	9·04	3·583	10·29	8·34	1·01	8·97	37·3	27·5
19·67	6·99	11·34	3·788	8·14	10·62	0·91	6·07	34·1	27·8
19·67	4·99	12·47	3·912	7·05	11·90	0·72	4·27	26·2	26·3
19·67	3·99	13·61	4·027	5·95	13·08	0·64	3·35	24·4	26·5
9·84	4·99	8·39	4·439	1·41	7·90	0·53	4·46	22·3	27·2
9·84	4·99	6·12	3·905	3·58	5·85	0·41	4·58	20·4	26·8
								Mean	27·0
			Calcium formate at 35°						
19·59	9·95	12·88	3·929	6·57	11·67	1·35	8·60	40·2	28·1
19·59	9·95	11·81	3·831	7·60	10·70	1·29	8·66	39·3	28·8
19·59	9·95	10·73	3·735	8·64	9·79	1·16	8·80	38·6	27·2
19·59	9·95	9·01	3·588	10·27	8·29	1.03	8·92	37·2	28·4
9·79	6·97	7·62	4·215	2·10	7·04	0·65	6·32	26·9	28·0
9·79	6·97	6·12	3·900	3·52	5·69	0·58	6·39	25·9	28·9
								Mean	28·5

TABLE 1. (*Continued.*)

T_a	T_m	NaOH	pH	HA	A^-	MA^+	M^{2+}	*I*	*K*
Strontium formate at 25°									
19·64	9·99	15·06	4·155	4·50	13·75	1·39	8·60	42·3	24·9
19·64	9·99	11·84	3·827	7·62	10·90	1·12	8·87	39·8	24·1
19·64	9·99	10·76	3·733	8·66	9·96	1·02	8·97	38·9	24·0
19·64	9·99	9·04	3·587	10·29	8·40	0·95	9·04	37·4	25·4
9·82	6·99	7·96	4·297	1·80	7·40	0·62	6·37	27·9	24·6
9·82	6·99	6·03	3·888	3·64	5·72	0·46	6·53	26·1	23·0
								Mean	24·4
Strontium formate at 35°									
19·59	9·96	12·88	3·932	6·57	11·78	1·24	8·72	40·5	25·2
19·59	9·96	11·81	3·834	7·60	10·84	1·15	8·81	39·6	25·1
19·59	9·96	10·73	3·739	8·64	9·87	1·08	8·88	38·7	25·3
19·59	9·96	9·01	3·594	10·28	8·40	0·91	9·05	37·4	24·4
9·79	6·97	7·52	4·190	2·20	6·98	0·61	6·36	27·3	26·0
9·79	6·97	6·02	3·885	3·62	5·67	0·50	6·46	26·0	25·2
								Mean	25·2.
Barium formate at 25°									
19·64	9·99	10·76	3·732	8·66	9·95	1·03	8·96	38·9	23·7
19·67	9·99	10·21	3·684	9·22	9·42	1·03	8·96	38·4	24·9
19·64	9·99	9·04	3·587	10·29	8·40	0·95	9·04	37·4	25·4
19·67	6·99	11·34	3·799	8·14	10·70	0·83	6·16	30·8	24·2
19·67	4·99	12·47	3·913	7·06	11·91	0·70	4·29	26·2	25·0
19·67	3·99	13·61	4·031	5·95	13·14	0·58	3·41	24·5	23·6
9·84	4·99	8·39	4·440	1·41	7·94	0·49	4·50	22·4	24·1
9·84	4·99	6·12	3·908	3·58	5·90	0·36	4·63	20·5	23·0
								Mean	24·2
Barium formate at 35°									
19·59	9·96	12·88	3·938	6·57	11·93	1·09	8·87	40·7	21·5
19·59	9·96	11·81	3·839	7·60	10·97	1·02	8·94	39·8	21·5
19·59	9·96	10·73	3·742	8·64	9·95	1·00	8·96	38·8	22·9
19·59	9·96	9·01	3·599	10·28	8·53	0·78	9·18	37·6	21·0
9·79	6·97	7·52	4·198	2·20	7·07	0·52	6·45	27·4	22·0
9·79	6·97	6·02	3·889	3·62	5·73	0·44	6·53	26·2	22·0
								Mean	21·8

There are comparatively few published data with which comparisons can be made. Cannan and Kibrick[10] obtained from potentiometric measurements, apparent dissociation constants for alkaline-earth acetates at an ionic strength of 0·2. Applying an approximate correction for this, we have the *K* values, Mg^{2+} 14, Ca^{2+} 14, Sr^{2+} 12, and Ba^{2+} 10. Colman-Porter and Monk[1] cite figures, obtained from solubilities of some alkaline-earth iodates, which are substantially lower, varying from 6·3 and 5·9 respectively for the formate and acetate of calcium, to 4·0 and 2·6 for those of barium. The reason for this is not clear, although, since the solubility method involves a consideration of numerous ion pairs and the solubility of some of the iodates is extremely small, the present results are probably more accurate. Dunsmore and Speakman[6] in a determination of dissociation constants by four different methods conclude that when pH measurements can be carried out rigorously, very reliable results can be expected.

DISCUSSION

The process of complex formation may be described in two stages, the first corresponding to the formation of an ion pair, $M^{2+}(H_2O)_nA^-$, and the second to the formation of a more covalent complex, $MA^+(H_2O)_{n-1}$. The latter, of course, is usually simply written MA^+. A given ligand, for example, may not be able to displace the water of hydration from the smaller magnesium ion as easily as from the larger cations. This is reflected in the abnormally low stability of magnesium complexes (Table 1); there is a small variation in *K* at 25°, more marked at 35°, in the sequence $Mg^{2+} \ll Ca^{2+} > Sr^{2+} > Ba^{2+}$.

ΔG, ΔH, and ΔS values, calculated from the experimental *K* values at 25° and 35°, are given in Table 2. The linear relation between ΔS(association) and ΔS(hydration) of the cation is shown in Fig. 1. This was predicted in Part I[3] in which a similar relation was

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[10] Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314.

TABLE 2. *Thermodynamic properties.*

Reaction	ΔG at 25° (kcal. mole^{-1})	ΔH (kcal. mole^{-1})	ΔS (cal. deg.$^{-1}$ mole^{-1})	$S_{\text{trans}}(\text{MA}^+)$ (cal. deg.$^{-1}$ mole^{-1})	$S_{\text{rot}}(\text{MA}^+)$ (cal. deg.$^{-1}$ mole^{-1})	ΔS_g (cal. deg.$^{-1}$ mole^{-1})
$Mg^{2+},H{\cdot}CO_2^-$ ...	−1·94	−1·77	0·6	38·8	24·6	−30·1
$Ca^{2+},H{\cdot}CO_2^-$	−1·94	0·98	10	39·4	25·6	−30·0
$Sr^{2+},H{\cdot}CO_2^-$	−1·88	0·59	8·3	40·7	26·5	−30·3
$Ba^{2+},H{\cdot}CO_2^-$ ...	−1·87	−1·89	−0·3	41·7	27·1	−30·0
$Mg^{2+},CH_3{\cdot}CO_2^-$ ...	−1·69	−1·52	0·6	37·5	27·7	−32·0
$Ca^{2+},CH_3{\cdot}CO_2^-$ ...	−1·69	0·91	8·7	37·9	28·6	−32·2
$Sr^{2+},CH_3{\cdot}CO_2^-$ ...	−1·58	0·74	7·8	39·0	29·4	−32·8
$Ba^{2+},CH_3{\cdot}CO_2^-$ ...	−1·57	−2·32	−2·5	39·8	30·0	−32·7

observed between the entropy of association of lead ions with halide ions, and ΔS(hydration) of the anions. An even more extensive linear correlation has been suggested by Williams.[11] If the hydration shell of the Mg^{2+} ion is preserved in its association reactions, then, for comparison with the other systems, the experimental ΔS(association) will be too low by 16·7 cal. deg.$^{-1}$ mole^{-1}, the entropy of an aqueous water molecule. Fig. 1 shows that the corrected figures are approximately consistent with the same straight lines.

FIG. 1. *Relation between the entropy of association and the entropy of hydration of the cation* :
1, *acetates* (⊙) ; 2, *formates* (+).

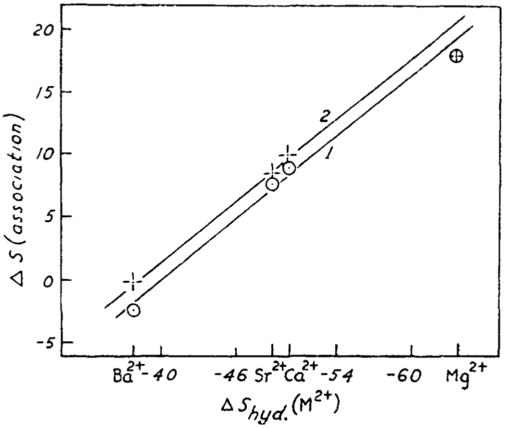
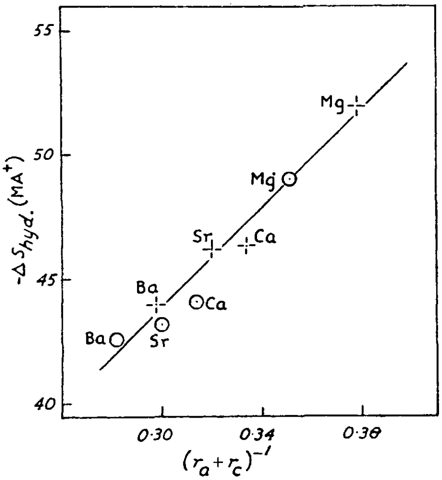


FIG. 2. *Plot of* $\Delta S_{\text{hyd}}(\text{MA}^+)$ *against* $(r_c + r_a)^{-1}$:
⊙, *acetates* ; +, *formates*



The entropy of the association reaction $M^{2+} + A^- \rightleftharpoons MA^+$ in aqueous solution may be written :[3]

$$\Delta S = \Delta S_g + \Delta S_{\text{hyd}}(\text{MA}^+) - \Delta S_{\text{hyd}}(\text{M}^{2+}) - \Delta S_{\text{hyd}}(\text{A}^-) \quad . \quad . \quad . \quad . \quad (1)$$

where ΔS_g and ΔS_{hyd} represent, respectively, the entropy of association of the ions in the gas phase, and the hydration entropy of the ion concerned.

$\Delta S_{\text{hyd}}(\text{M}^{2+})$ and $\Delta S_{\text{hyd}}(\text{H}{\cdot}\text{CO}_2^-)$ were obtained from the known standard and gas-phase entropies.[12] $\Delta S_{\text{hyd}}(\text{CH}_3{\cdot}\text{CO}_2^-)$ was estimated (—35 cal. deg.$^{-1}$ mole^{-1}) from the formate value by assuming a linear relation between $\Delta S_{\text{hyd}}(\text{A}^-)$ and the reciprocal of the ionic radius.

ΔS_g contains both translational and rotational terms and is given by

$$\Delta S_g = S_{\text{trans}}(\text{MA}^+) - S_{\text{trans}}(\text{M}^{2+}) - S_{\text{trans}}(\text{A}^-) - S_{\text{rot}}(\text{A}^-) + S_{\text{rot}}(\text{MA}^+) \quad . \quad (2)$$

Translational entropies at 25° were calculated from the Sackur–Tetrode equation, $S_{\text{trans}} =$

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[11] Williams, Proc. Symp. Co-ord. Chem., Copenhagen, 1953, 68.

[12] Latimer, " Oxidation Potentials," Prentice-Hall, New York, 1952.

$1{\cdot}5\boldsymbol{R}\ln M + 26{\cdot}03$, where M = molecular weight. The rotational entropies of acetate and formate ions were obtained from the equation :[13]

$$S_{\rm rot} = 2{\cdot}287\,(3\log T + \log I_{\rm A}I_{\rm B}I_{\rm C}) - 5{\cdot}384 \quad . \quad . \quad . \quad . \quad (3)$$

the products of the moments of inertia, $I_{\rm A}I_{\rm B}I_{\rm C}$, being calculated by the method described previously :[3] at 25°, $S_{\rm rot}({\rm H{\cdot}CO_2^-}) = 20{\cdot}6$, $S_{\rm rot}({\rm CH_3{\cdot}CO_2^-}) = 23{\cdot}4$ cal. deg.$^{-1}$ mole^{-1}.

By using, for gas-phase calculations, the dimensions of solid barium formate derived from *X*-ray data by Sugawara *et al.*,[14] and assuming that the formate and the acetate complexes are similarly planar with centres of mass lying on the H–C$\cdots$M and $\rm CH_3$–C$\cdots$M axes respectively, $S_{\rm rot}({\rm MA^+})$ values have been obtained from equation 3. These are given in Table 2 together with the entropies ($\Delta S_{\rm g}$) of association of the gaseous ions.

Substitution of these calculated entropies in equation 1 permits the evaluation of $\Delta S_{\rm hyd}({\rm MA^+})$. Fig. 2 shows the good linearity of a plot of $\Delta S_{\rm hyd}({\rm MA^+})$ against $(r_{\rm c} + r_{\rm a})^{-1}$, where $r_{\rm c}$ and $r_{\rm a}$ are the radii of the cations and anions respectively. The latter are " pseudo-spherical " radii and were obtained from the calculated total volumes of the anions : for formate, $r_{\rm a} = 2{\cdot}0$; for acetate, $r_{\rm a} = 2{\cdot}2$. They may be compared with the values, 1·7 and 2·2 respectively, calculated from aqueous ionic mobilities by means of Stokes's law.

Cobble[15] has defined a corrected entropy $\bar{S}'$ of a complex ion by the equation : $\bar{S}' = \bar{S}^0 - n\bar{S}^0({\rm H_2O})$ where $\bar{S}^0$ is the partial molal entropy and n represents the number of water molecules replaced from the normal aquated ion by the complex-forming agent. When this corrected entropy and empirical relations suggested by Cobble are used, the entropy of hydration may be written :

$$\Delta S_{\rm hyd}({\rm MA^+}) = 49 - 99z{\rm F}/(r_{\rm a} + r_{\rm c}) + nS^0({\rm H_2O}) - S_{\rm g}({\rm MA^+}) \quad . \quad . \quad (4)$$

where z is the charge. The value of F, a structural factor depending upon the geometry of the ion, which best fits the data is 1·44. On the assumption that $n = 0$ for magnesium complexes which retain the hydration shell of the cation, and $n = 1$ for the other complexes, the calculated $\Delta S_{\rm hyd}({\rm MA^+})$ values are given in Table 3. The excellent agreement with the experimental values illustrates the success of these empirical methods of correlation. The accumulation of experimental thermodynamic results would thus be generally useful in predicting the properties of as yet undetermined species.

TABLE 3.

	Acetates				Formates			
	$\rm Mg^{2+}$	$\rm Ca^{2+}$	$\rm Sr^{2+}$	$\rm Ba^{2+}$	$\rm Mg^{2+}$	$\rm Ca^{2+}$	$\rm Sr^{2+}$	$\rm Ba^{2+}$
$-\Delta S_{\rm hyd}({\rm MA^+})$ (expt.)	66·1	44·3	43·3	42·6	69·1	46·3	46·4	44·2
$-\Delta S_{\rm hyd}({\rm MA^+})$ (calc.)	66	45	44	43	68	47	46	45

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[13] Herzberg, " Infra-red and Raman Spectra," Van Nostrand, New York, 1945, Chap. 5

[14] Sugawara, Kakudo, Saito, and Nitta, *X-Sen.*, 1951, **6**, 85.

[15] Cobble, *J. Chem. Phys.*, 1953, **21**, 1443, 1446.