722. *The Stability of the Complexes of the Group* IIA *Metal Ions.*

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An account is given of the factors which affect the stability of the complex ions of the alkaline-earth metals. It is shown that a simple theory based on purely electrostatic interactions is not sufficient to explain the data available and that short-range repulsion forces must also be considered. Further, it is suggested that the latter interaction terms account for the low stability of many magnesium complexes. A brief outline of the significance of entropy changes in affecting the stability of complexes is also incorporated. Finally, reference is made to the extension of these ideas to the activity coefficients and the solubilities of the salts of the metals in aqueous solution.

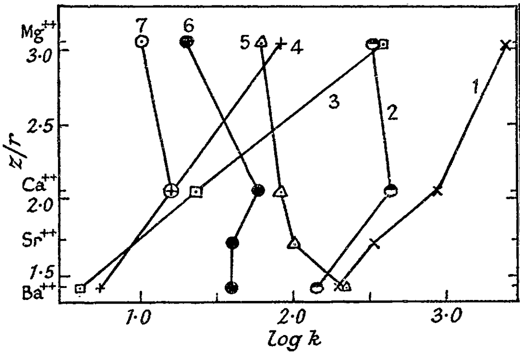
THEORETICAL discussions of the properties of the compounds of the Group IIA metals usually characterise them as arising from the electrostatic interactions between the bivalent cations and oppositely charged ions or orientated dipoles. This treatment is supported by various types of evidence: the close agreement between the experimentally observed lattice energies and those determined by the use of the Born–Haber cycle which assumes (see p. 3772) that only electrostatic forces exist between the interacting ions (Born and Mayer, *Z. Physik*, 1932, **75**, 1); the very small differences between the experimental heats of hydration and those calculated from a simple ionic model (Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515); the low ionisation potentials of the metals which are thought strictly to limit covalency; the activity coefficients of the bivalent ions in halide salt solutions which are those to be expected from the activity laws (Stokes, *Trans. Faraday Soc.*, 1948, **44**, 295); the values of the dissociation constants of some of the complexes of these metals (Jones, Monk, and Davies, *J.*, 1949, 2693); and the practically complete absence of complexes with uncharged ligands such as ammonia (Bjerrum, " Metal Ammine Formation in Aqueous Solution," Hasse and Son, Copenhagen, 1941). Nevertheless, a simple explanation of the chemistry of aqueous solutions of magnesium, calcium, strontium, and barium ions is impossible (cf. Table 1). The stability constants for complexes of these metals are true thermodynamic constants and all the values from different authors are therefore directly comparable. In a second compilation (Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314) the stability constants of the complexes of the alkaline-earth metals are internally consistent but inconsistent with those in Table 1, for they are uncorrected for the ionic strength of the medium in which the measurements were made. However, despite the difference in absolute values, the same relations are apparent between the constants of both sets. For this reason the data have been used later in this paper (Table 3). In Table 1 the constants, log k_M, *i.e.*, the logarithm of the stability constant of a metal with a given ligand, are taken from the literature and refer to aqueous solution. The stability constant, k_M, for a complex with a unidentate ligand, *e.g.*, the acetate ion or the sulphate ion, has not the same meaning as that for a polydentate ligand, *e.g.*, the oxalato-group, because the latter can co-ordinate through two groups forming a chelate ring. However, this distinction cannot be made satisfactorily, for the number of oxygen atoms through which each co-ordinating group combines is not always known.

A second difficulty arises because it has become customary to call many of these complexes "ion-pairs" in order to differentiate them from the more covalent complexes. Although the necessity for some such distinction is apparent, it is clear that the process of complex formation can be described in two stages :

$$M(H_2O)_n + L \rightleftharpoons \underset{\text{Ion-pair}}{M(H_2O)_nL} \rightleftharpoons \underset{\text{Complex}}{ML(H_2O)_m} + (n - m)H_2O$$

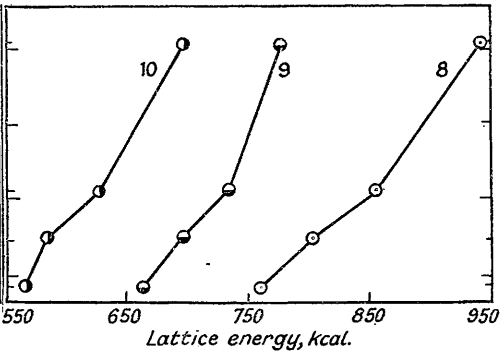
As it is not possible to say, as yet, to what extent each of these processes occurs in some cases, it has been necessary to discuss the stability constants initially in terms of the overall reaction, as this leads to a simpler examination of the data. It seems likely, however, that in some systems the stability-constant data refer to different stages of the above reaction even in the series of the alkaline-earth metals, and that they might easily refer, for example, to the formation of an ion-pair in the case of the magnesium salt and to a complex in that of the barium salt with the same anion. The general argument outlined here is not invalidated by such considerations, as shown later (p. 3775), but the distinction is of importance for the discussion of the activity coefficients and the solubility of the salts of the Group IIA metals as the degree of hydration may vary with the concentration of the solution. If now the basic assumption is made that the complexes are formed as the result of the electrostatic interactions between the cations and the negative charge of the ligands, then 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 > Ca > Sr > Ba :

FIG. 1. *Plot of the logarithm of the stability constant of some of the complexes (Table* 1) *against* z/r, *where* z *is the charge on the metal ion and* r *its radius.*



1, Oxalate. 2, Malate. 3, Hydroxyl. 4, Alanine. 5, Thiosulphate. 6, Tartrate. 7, Glycylglycine.

FIG. 2. *Plot of the lattice energies of some of the salts of the alkaline-earth metals against* z/r. (*cf. Fig.* 1).



8, Oxides. 9, Sulphides. 10, Fluorides.

N.B. The tartrate data are not strictly comparable with the others (see notes to Table 1).

	Mg	Ca	Sr	Ba
Ionic radius, Å	0·66	0·99	1·15	1·37

Furthermore, a linear relation between the free-energy change for the formation of the complex, which is proportional to log k_M, and the ionic potential, z/r, where z is the charge on the cation and r its radius, might well have been expected (see Davies, *J.*, 1951, 1256). It is clear from Fig. 1 that no such simple relation exists, and that deviations to low magnesium stabilities often occur. For organic acid complexes the values of log k_M of the magnesium complex are increasingly smaller than those of the calcium complex the greater the number of the groups through which the ligand can co-ordinate. An exception to this appears in the glycine complexes (Table 1) but in this case the ligand contains a highly polarisable amino-group. In the iodate, thiosulphate, nitrate, and possibly the sulphate complexes the indications are that the stability sequence is completely reversed (Table 1).

A somewhat similar effect can be observed in the lattice energies of the Group IIA metal salts (Table 2) when they are plotted against z/r (Fig. 2). However, in this case although the values for the magnesium salts are low, no change of the expected order occurs. The relatively low values of the lattice energies of the magnesium salts here arise through the increasing repulsion forces between the anions concomitant with the diminishing size of the cation. This is particularly important in the case of magnesium, for the size of its ion is such that the anions come into " contact " with one another before they come into " contact " with the central ion : this has been discussed at length by Pauling (" Nature of the Chemical Bond," pp. 352—372, Cornell Univ. Press, 1941). Likewise, in the calculation of heats of hydration of these cations, Bernal and Fowler (*loc. cit.*) obtained agreement with the experimental data by allowing for similar repulsion terms.

These ideas on the effect of repulsion between non-bonded atoms cannot be extended directly to the discussion of the formation of a complex in solution, for in this case the stability of the bond is measured relative to the hydrate stability (Jones, Monk, and Davies, *loc. cit.*). However, the effect of this complication can be seen from the differences, Δ, between the lattice energies of salts with a constant anion and the heats of hydration of the corresponding cations (Table 2). The values of Δ fall in no particular sequence. In the replacement of water by a ligand in a complex, therefore, repulsion terms are likely to destroy the order expected of stabilities as given by the ionic potential.

TABLE 1. *Stability constants, log* k_M, *of complexes of the alkaline-earth metals.*

Ligand	Mg	Ca	Sr	Ba	Zn
Oxalate[2]	3·43	3·00	2·54	2·33	4·89
Malonate	2·85	2·49	—	1·71	3·68
Succinate	2·15	2·00	—	1·70	2·70
Malate	2·52	2·66	—	2·19	3·70
Acetate	1·05	1·00	0·97	0·93	1·57
Propionate	1·08	1·04	0·97	0·88	1·55
Butyrate	1·07	1·05	0·90	0·84	1·54
β-Hydroxybutyrate	1·14	1·14	1·01	0·97	1·60
Glycine	3·44	1·43	—	0·77	5·52
Alanine	1·96	1·24	—	0·77	5·21
Glycylglycine	1·06	1·24	—	—	3·80
Tartrate[1]	1·36	1·80	1·65	1·62	2·68
Nitroacetate[9] ...	−0·17	−0·30	—	—	—
Citrate[10]	—	3·17	2·92	2·98	—
o-Phthalate[10] ...	—	1·07	—	0·92	—
Salicylate[10]	—	0·14	—	0·0	—
Maleate[11]	—	2·43	—	2·26	—
Fumarate[11] ...	—	2·00	—	1·59	—
Hydroxide[3]	2·58	1·40	—	0·64	—
Iodate[4]	0·72	0·89	—	1·05	—
Sulphate[5]	2·15	2·28	—	—	—
Thiosulphate[6]	1·84	1·92	2·04	2·33	—
Nitrate[7]	0·00	0·28	—	0·92	—
$P_3O_9^{---}$[8].........	3·32	3·46	—	3·35	—
Polyphosphate[12]	3·2	3·0	2·8	3·0	—
HPO_4^{--}[13]	2·5	2·4	—	—	—

Note.—The measurement in refs. 1, 12, and 10 are not directly comparable with the other data in the table as the former are " constants " uncorrected for the ionic strength of the medium in which they were obtained

[1] Cannan and Kibrick, *loc. cit.* [2] Monk, *Trans. Faraday Soc.*, 1951, **47**, 297. [3] Davies, *J.*, 1951, 1257. [4] Jones, Monk, and Davies, *loc. cit.* [5] Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609. [6] Denney and Monk, *ibid.*, 1951, **47**, 789. [7] Righellato and Davies, *ibid.*, 1930, **26**, 390. [8] See ref. 4. [9] Pedersen, *Acta Chem. Scand.*, 1949, **3**, 676. [10] Joseph, *J. Biol. Chem.*, 1946, **164**, 529. [11] Topp and Davies, *J.*, 1940, 87; see also Peacock and James, *J.*, 1951, 2233. [12] Van Vazer and Campanella, *J. Amer. Chem. Soc.*, 1950, **72**, 655. [13] Greenwald, Redish, and Kibrick, *J. Biol. Chem.*, 1940, **135**, 65.

(References in this table are often to papers in which some of the data were originally tabulated; in these papers there are very many detailed references.)

To return to the data in Table 1 and in Fig. 1, the stability of the hydroxides increases almost linearly with the ionic potential and hence the repulsion terms must be small. The same sequence occurs in the mono- and di-carboxylic acid complexes, but the linear relation is not obeyed presumably owing to the repulsion around the cation between the ligand and an unknown number of water molecules. For the chelated complexes two factors alter as the ring size increases. First, the stability of the ring diminishes—this appears in the fall in the stability constants for all the metal complexes through the series oxalate, malonate, succinate, and glutarate despite the fact that the changes in the acid dissociation constants favour stronger complexes as the ring size is increased. Secondly, the volume occupied by the liquid around the central ion increases slightly with the size of the ring. It is observed, as expected, that this has the greatest effect in the magnesium complexes, *e.g.*, in the replacement of oxalate by succinate (Table 3). The effect of the introduction of further groups into the ligand is seen in the hydroxy-dicarboxylic acid complexes. In the tartrates the magnesium ion is the least able of all the cations to form a complex. As all the tartrates are more stable than the succinates, despite the lower acidic constants, the hydroxy-groups must play some part in the complexes (Table 3). It is interesting too that the order of the stability of the magnesium complexes follows the order of the acid dissociation constants from malate to tartrate, but the converse is true of the barium and strontium complexes. A similar difference between magnesium and the other three ions appears in the hydroxy-monocarboxylic acid complexes in which there can be no doubt that the hydroxy-groups play some part. The complexes of the larger cations gain most in stability from the substitution of hydroxy-groups in the simple acid anions. These points can be simply interpreted in terms of the suggested " crowding " effect.

TABLE 2.* *Theoretical lattice energies* (*kcal.*) *of some salts.*

Salt	Mg	Ca	Sr	Ba
Fluoride	699·2	620·2	581·8	558·9
,, (exptl.)	692·3	621·0	585·2	549·8
Oxide	946·3	846·8	803·0	755·1
Sulphide	781·0	726·4	692·2	660·3
Selenide	—	701·5	671·5	641·3
Hydration (heat)	464·0	381·9	349·8	316·2
Δ (Salt — Hydrate) (see p. 3772)				
Fluoride	235·2	238·3	232·0	232·7
Oxide	482·3	464·9	453·2	438·9
Sulphide	317·0	344·5	342·4	344·1
Selenide	—	319·6	321·8	325·1

* The data in this table are from Paul (" Principles of Chemical Thermodynamics," McGraw-Hill, New York, 1951, p. 158).

TABLE 3. *Differences of complex stability on the exchange of ligands.*

Ligands exchanged	Mg	Ca	Sr	Ba
Acetate/Glycollate	0·41	0·58	0·37	0·27
Propionate/Lactate	0·39	0·57	0·27	0·21
Butyrate/Hydroxybutyrate	0·07	0·09	0·11	0·12
Propionate/Glycerate	0·32	0·68	0·46	0·46
Butyrate/Gluconate	0·17	0·70	0·64	0·64
Malonate/Malate	−0·36	0·34	0·20	0·07
Succinate/Tartrate	0·16	0·60	0·59	0·59
Oxalate/Succinate *	−1·28	−1·00	—	−0·63

Note. The differences of stability, log k_{M}, listed in this table are those between the metal complexes of the second- and of the the first-named ligand with the same metal ion. (Data from Cannan and Kibrick, *J. Amer. Chem. Soc.*, 1938, **60**, 2314, except that those marked * are from Table 1.)

In Table 1 there are also some stability constants for amino-acid complexes. The crowding effect would seem to be the cause of the low magnesium stability in the glycylglycine complex, compared with its high stability in the glycine and alanine complexes.

The zinc ion has a radius of 0·72 Å, whence the effect of steric factors on the stability of its complexes should be similar to that for magnesium. This is shown by the data in Table 1—despite the much greater overall stability of the zinc complexes through greater covalency.

In Table 4, another set of data, due to Schwarzenbach *et al.*, is presented. A dominating feature is the reduction of the stability of any chelate complex consequent upon an increase in the ring size. More important for present purposes is the reduction of the stability of the magnesium complexes relatively to those of calcium and the other cations, upon increase in the number of positions through which the ligand can co-ordinate. This factor is sometimes sufficient to reverse the stability order expected from the ionic potentials for magnesium and calcium complexes. The alternations in the relative stability of the complexes of these two metals as a new ligand group is substituted *ortho, meta,* and then *para* to the original group in a benzene ring, is very significant of the size of this steric factor.

However, throughout all the series of these ligands there is no change in the order of stabilities Ca>Sr>Ba.

From the above discussion it is possible to understand why the stability of the magnesium complex is sometimes lower than that of the other ions, but no explanation has been given for the stability sequences observed with the anions of the strong inorganic acids, *e.g.*, with the iodate, nitrate, and thiosulphate ions (Table 1). In this connection it is interesting to examine the free-energy change, ΔG, occurring on the formation of a complex by reaction (1):

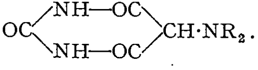
$$M(H_2O)_n + L \longrightarrow ML + nH_2O \quad \ldots \ldots \quad (1)$$

ΔG is the sum of the heat and entropy changes of this reaction, whence

$$\Delta G = -\boldsymbol{R}T \ln k_M = \Delta H - T\Delta S$$

The entropy change will always be such as to favour the formation of the complex as a neutralisation of charge is involved (cf. Frank, *J. Chem. Phys.*, 1945, **13**, 478); *e.g.*, in the formation of the barium thiosulphate complex, $\Delta S = -18{\cdot}8$ cals./°c, $\Delta H = -2{\cdot}6$ kcal. (Davies and Wyatt, *Trans. Faraday Soc.*, 1949, **45**, 770); in the formation of the zinc malonate complex $\Delta S = -27{\cdot}5$ cal./°c, $\Delta H = -3{\cdot}1$ kals. (James, *J.*, 1951, 153). Further examples are provided by the work of Davies on the lanthanum ferricyanide complex (*Proc. Poy. Soc.*, 1948, **195**, *A*, 116) and of Rabinowitch and Stockmayer on the ferric complexes with chloride, bromide, and hydroxyl ions (*J. Amer. Chem. Soc.*, 1942, **64**, 335). The gain in entropy arises from the partial loss of hydration on complex formation, and for a series of alkaline-earth complexes with a given ligand it should be proportional to the entropy of hydration of the cations, *i.e.*, in the order Mg > Ca > Sr > Ba (cf. Rabinowitch and Stockmayer, *loc. cit.*). However, the heat energy changes in these reactions, ΔH, can be either positive or negative as has been shown by measurements on the hydrogen-ion complexes (Latimer, *Chem. Reviews*, 1936, **18**, 349; Pitzer, *J. Amer. Chem. Soc.*, 1937, **59**, 2365) and by the work cited in the above references. Now it is the sum of the heat and

TABLE 4. *The stability constants, log* k_M, *of some further Group* IIA *metal complexes.*

Ligand	Mg	Ca	Sr	Ba	Ref.
NHR_2 *	3·66	3·41	—	1·67	1
	8·85	8·77	7·6	6·8	2
$Ph{\cdot}NR_2$	1·15	0·6	—	—	3
o-$C_6H_4(SO_3H){\cdot}NR_2$	2·68	4·57	3·50	3·48	
m- ,,	1·26	1·26	—	—	
p- ,,	1·15	0·95	—	—	
o-$C_6H_4(CO_2H){\cdot}NR_2$	3·91	5·06	3·91	3·57	
m- ,,	1·38	1·46	$\leqslant$1·00	<1·00	
p- ,,	1·30	1·30	<1·0	<1·0	
o-$C_6H_{10}(NR_2)_2$ †	10·3	12·5	—	—	4
m- ,,	4·64	4·77	—	—	
p- ,,	4·30	4·19	—	—	
NR_3	5·41	6·41	4·94	4·82	5
$NR_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$	5·28	5·04	3·87	3·40	
$[CH_2]_2(NR_2)_2$	8·69	10·59	8·63	7·76	6, 7
$[CH_2]_3(NR_2)_2$	6·02	7·12	5·18	4·24	
$NR_2{\cdot}CH_2{\cdot}PO_3H$	6·28	7·18	5·59	5·35	5
$NR_2{\cdot}CH_2{\cdot}CH_2{\cdot}PO_3H$	6·33	5·44	4·10	3·64	
$NR_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H$	3·48	4·15	3·26	3·01	
$[CH_2]_4(PO_3H)_2$	2·77	2·54	—	2·28	8

OC<(NH—OC)(NH—OC)>CH·NR₂

* $R = CH_2{\cdot}CO_2H$. † C_6H_{10} = 1 : 2-*cyclo*Hexylene residue.

[1] Schwarzenbach, Kampitsch, and Steiner, *Helv. Chim. Acta*, 1945, **28**, 1133. [2] *Idem, ibid.*, 1946, **29**, 364. [3] Schwarzenbach, Willi, and Bach, *ibid.*, 1947, **30**, 1303. [4] Schwarzenbach and Ackermann, *ibid.*, 1949, **32**, 1682. [5] Schwarzenbach, Ackermann, and Ruckstuhl, 1949, **32**, 1175. [6] Schwarzenbach and Ackermann, *ibid.*, 1948, **31**, 1029. [7] *Idem, ibid.*, 1947, **30**, 1798. [8] Schwarzenbach, Ruckstuhl, and Zurc, *ibid.*, 1951, **34**, 455.

entropy changes that controls the individual values of k_M and thence the order of the stabilities. As ΔS is expected to follow the fixed order of the ionic potential of the cations, the heat changes must produce the different observed orders, and in the case of the complexes with the strong-acid anions they must therefore decrease as the ionic potential of the cation increases, *i.e.*, the energy of interaction $M-H_2O$ must be increasingly greater than that of M–L the smaller the cation. This argument is supported (see below) by a discussion of the activity coefficients and the solubilities of the salts of the alkaline-earth cations.

No mention has been made yet of possible ion-pair formation :

$$M(H_2O)_n + L \longrightarrow M(H_2O)_nL \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Provided all the cations were equally hydrated, the expected stability of such ion-pairs would fall in the same sequence as the stability of the complexes M–L, because the size of the hydrated ions would then follow the size of the bare ions. However, it is very probable that the cations of Group IIA are decreasingly hydrated as their size increases, and so the experimentally determined stability constants might well refer to different degrees of hydration of the different cations. This difference in the nature of the "complexes" could lead to an order of stabilities opposed to the order of the ionic potential as the bare barium ion is smaller than the hydrated magnesium ion $Mg(H_2O)_6^{++}$; but this is only another expression of the fact that the ligand may not be able to displace the water of hydration from the smaller cations as easily as from the larger, and if the experimental stabilities do refer to the formation of ion pairs, $M(H_2O)-L$, of the smaller cations, their complexes, M–L, must be even less stable than is apparent. Evidence will now be discussed which would suggest that the different cations do, in fact, form "complexes" of different degrees of hydration with the strong-acid anions and that this is not so with the weak acid anions in general.

The Activity Coefficients of the Salts of the Bivalent Metal Ions.—Many of the stability constants quoted in Table 1 were obtained from consideration of the negative deviations of the activity coefficients of the corresponding salts from the theoretical values for dilute solutions as given by the Debye–Hückel equation. At higher concentrations these and other salts show positive deviations from the same equation, and this has been explained in terms of the degree of hydration of the ions by Stokes and Robinson (*J. Amer. Chem. Soc.*, 1948, **70**, 1870), who attribute a large positive deviation to a high degree of hydration, and, assuming complete dissociation, they calculate the number of water molecules associated with the ions of different salts. In this treatment no account is taken of complex or ion-pair formation, since the salts discussed are those that behave in a theoretical manner at high dilution. The theory does not explain the following points.

(*a*) The activity coefficients of the cobaltous and nickel halides are very similar to those of the magnesium halides, and yet the activity coefficients of manganous chloride lie close to those of strontium chloride, and those of copper chloride close to those of barium chloride, and the values for zinc chloride differ entirely from those of the other 2 : 1-electrolytes. All the ions of these transition metals have similar radii and yet the above treatment would lead to very different apparent hydration of these ions.

(*b*) The activity coefficients of the halides of Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}, Co^{II}, and Zn^{II} increase in the order chloride < bromide < iodide. The above authors therefore suggest an *increase* in hydration following this, the increasing order of the anionic radii. The activity coefficients of the cadmium salts increase in the opposite sequence.

(*c*) The activity coefficients of the nitrates, perchlorates, chlorides, bromides, and iodides decrease in the order $Mg > Ca > Sr > Ba$, at both very high and low dilution, but the activity coefficients of the weak-acid salts must decrease in the opposed order, at least in dilute solution, as shown by the stability data given on p. 3772. A similar distinction arises between the weak- and strong-acid salts of the Group IA metals (Robinson and Harned, *Chem. Reviews*, 1941, **28**, 419). Amongst the transition-metal salts of the bivalent ions there is a general order of stability of their complexes with the anions of weak acids, $Mn < Fe < Co < Ni < Cu > Zn$ (Irving and Williams, to be published) but this order is not followed by the stability constants of the complexes or the activity coefficients of the salts of the strong acids, *e.g.*, the chlorides and sulphates. (All these data are given by Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1950, 2nd edn., Chap. 13.)

Consider point (*b*) : many factors would show that the hydration of the gas ions of the halogens must be in the order Cl > Br > I (Bockris, *Quart. Reviews*, 1949, **3**, 173). Hence, the inverse of this order obtained by the above authors implies that their hydration values are not those of the completely dissociated salts. This is confirmed by the data on the transition-metal salts. Complex formation in the zinc halides, in the order Cl > Br > I, and in the cadmium halides, in the order I > Br > Cl, explains the negative deviations of the activity coefficients of these salts from ideal behaviour in dilute solution but also would account for the order of their positive deviations (and the resulting low apparent hydration) in concentrated solution. Cobaltous chloride is increasingly associated with increasing concentration of its solutions as determined by the change in its absorption spectrum, but cobaltous bromide is not equally associated (Job, *Ann. Chim.*, 1936, **6**, 97). This agrees with the decreasing activity coefficients of the cobaltous salts through the order I > Br > Cl (Robinson, McCoach, and Lim, *J. Amer. Chem. Soc.*, 1950, **72**, 5783). The activity coefficients of magnesium chloride solution fall between those of cobaltous chloride and bromide, and it seems difficult to avoid the conclusion that the low apparent hydration of all these salts relatively to the iodides is due to association, as ion-pairs in the more dilute solutions and increasingly as complexes in the more concentrated solutions. A similar postulate would also account for the anomalous order of hydration of the halides of calcium, strontium, and barium as given by Stokes and Robinson, *i.e.*, the hydration reflects complex formation in the order $I^- < Br^- < Cl^-$.

An extension of this interpretation can be made to the activity coefficients of the oxy-acid salts in concentrated solution. In the nitrates of the Group IIA metals the activities are considerably lower than those of the corresponding chlorides, and the properties of even dilute solutions are best interpreted in terms of association (see Table 1). In the strontium and barium nitrate solutions the activity coefficients are lower than those of zinc chloride, and the variation of the coefficients with concentration suggests very low hydration consequent upon complex formation. The hydration of the smaller cations would still appear to be considerable, however. In the sulphates the activity coefficients of even the small cations are as low as the values for the cadmium halides. Now this is also the case for the sulphates of the bivalent ions of the transition metals, and the similarity in the values suggests a common property. Spectrophotometric studies in cupric sulphate solutions (Näsänen, *Acta Chem. Scand.*, 1949, **3**, 179) indicate definite complex formation. Thus it is again very probable that complex formation can take place in the salts of Group IIA metals. The fact that the order of the stability of the transition-metal sulphates is not that of the decreasing ionic radius or of the increasing ionisation potential (*i.e.*, Mn < Fe < Co < Ni < Cu > Zn) is a strong indication that the increments in stability of the $M^{++}–SO_4^{--}$ bond are less than the decrements in hydration energy upon complex formation on moving from one member of this series to another of smaller radius (Irving and Williams, *loc. cit.*). The parallel with the Group IIA metals leads again to the argument of increasing *complex* formation, M–L, in the sequence Ba > Sr > Ca > Mg, and its further extension to the nitrates, iodates, bromates, and halides of these metals seems increasingly likely. These conclusions are in accord with the form in which the salts crystallise from solution. For instance, the barium and strontium salts of the strong acids, even the chlorides, form lattices in which the cation lies adjacent to the anion, but the magnesium salts are invariably highly hydrated, the cation being surrounded by six water molecules (Jensen, "Krystallinske Salthydrater," Nordlundes, Copenhagen, 1948). Similarly, manganous and ferrous chloride crystallise with lower hydration than cobalt and nickel chloride, whereas cupric and zinc chlorides, in solutions of which complex formation is well recognised, crystallise with only two molecules of water. In the lattice, of course, the problems of packing are more than in solution, but the following discussion illustrates some similarities between the two states of aggregation.

The Solubility of the Alkaline-earth Metal Salts.—The solubility of a salt in water is related to the stability of the corresponding complex in aqueous solution in certain circumstances (cf. Irving and Williams, *Nature*, 1948, **162**, 746); *e.g.*, by assuming that the lattice energy of the compound, MOx_2, a metal " oxinate " (8-hydroxyquinoline complex), was independent of the metal ion M^{++}, as any effect that this ion could produce would be screened by the large organic ligands, it was predictable that the stability of the 8-hydroxyquinoline complexes would control the order of their insolubilities : this was observed by Mellor and Maley (*Australian J. Sci. Res.*, 1949, **2**, 92). Now it is also found that the order of the insolubility of the hydroxides of these metals follows the order of the stability of the hydroxide complexes. This would apparently imply either that the lattice free energy along the series of hydroxides was constant, or even that it followed the same sequence. In these lattices, however, there is a continuous assembly. This makes an examination of the insolubility of the salts of the Group IIA metals particularly interesting, as very many of these salts crystallise in a continuous lattice. It is noteworthy that the salicylates should form a lattice of discrete molecules, in which case the insolubility and the complex stability should be directly relatable. The data so far available agree with this (Tables 1 and 5).

The solubility data are given in Table 5. The absence of any unique order is apparent, but the order obtaining is often the same as that of the complex stabilities, *e.g.*, in the hydroxides, nitrates, thiosulphates, and iodates. However, the orders are not the same in the dibasic acid salts, *e.g.*, the oxalates. It has already been pointed out that in the complexes with these ligands " crowding " effects are likely to be imposed upon the expected order of stabilities. When a lattice is built up from these ligands further co-ordination takes place in order to build a continuous assembly and simultaneously the crowding of the ligands around the central ion is increased (cf. Table 1 and Fig. 2). This should reduce in particular the stability of the magnesium lattice, and therefore explains the higher solubility of this salt than of those of the other alkaline-earth oxalates. Similar repulsion effects must appear in the fluoride lattices, *e.g.*, Pauling (*op. cit.*) considers that packing difficulties force the magnesium salt to adopt a lattice of lower co-ordination than the other fluorides. Such a low lattice stability would account for the solubility of the magnesium salt being greater than that of the calcium salt although the stabilities of their complexes are in the order Ca > Mg.

The number of water molecules of crystallisation has been mentioned as evidence of the inability of the ligand to replace water around the cation. In the strong-acid salts, such as the sulphates, nitrates, and halides, the magnesium and calcium salts are invariably more hydrated than the strontium and barium salts. With the simple weak-acid salts, fluoride, hydroxide, oxalate, and carbonate, this difference does not appear. However, with the complicated anions of the hydroxy-acids, the smaller cations again crystallise with a larger number of water molecules (Table 5). The degree of hydration in

TABLE 5. *Solubility of the salts of the alkaline-earth metals, solubility products,* p*S*.*

Salt	Mg	Ca	Sr	Ba	Salt	Mg	Ca	Sr	Ba
Hydroxide	11·26	5·10	3·50	2·30	Chromate	(Sol.)	3·50	4·44	9·70
Fluoride	8·19	10·41	8·52	5·77	Iodate	(Sol.)	5·71	—	8·90
Oxalate	4·07	8·64	7·25	6·96	Bromate	(Sol.)	(Sol.)	1·0	5·26
Sulphate	(Sol.)	4·64	6·55	10·00	Nitrate	(Sol.)	(Sol.)	—	2·35
Carbonate	5·00	8·32	9·03	8·31	Thiosulphate	(Sol.)	—	3·0	4·0

* p*S* = —log $[M][R]^2$, where M = metal and R = anion (concentrations in g.-ions/l.)

Values taken from Latimer (" Oxidation Potentials," Prentice-Hall, New York, 1938, Appendix III).

Salt	Mg	Ca	Sr	Ba	Temp.
	Solubility (g./100 g. of water)				
Malonate	—	0·36 (4)	0·53 (0)	0·21 (2)	20°
Succinate	24·4 (5)	1·28 (1)	0·27 (0)	0·42 (0)	20
Malate	2·5 (3)	0·92 (1)	0·55 (0)	1·24 (0)	25
(+)-Tartrate	1·2 (4)	0·04 (4)	0·18 (4)	0·30 (½)	25
Citrate	—	0·96 (4)	0·1 (6)	0·06 (7)	25
Salicylate	20·4 (4)	2·29 (3)	3·04 (2)	28·65 (1)	15
Acetate	39·0 (4)	34·7 (6)	41·0 (½)	72·0 (3)	20

All values are taken from Seidell (" Solubilities of Inorganic and Metal–Organic Compounds," 3rd edn., Van Nostrand Co., New York, 1940). The numbers in parentheses are the number of molecules of water with which the salt crystallises.

the lattice roughly parallels the solubility of the magnesium salts in a manner similar to the parallel suggested between the activity coefficients and the hydration of the salts in solution (p. 3776). Both these points can be expressed in terms of the ease of complex formation, M–L, as opposed to the formation of an ion-pair $M(H_2O)_n$–L (p. 3775).

TABLE 6. *Heats of solution (kcal./mole) of anhydrous salts.*

Salt	Mg	Ca	Sr	Ba	Salt	Mg	Ca	Sr	Ba
Acetate	—	7·00	5·56	5·24	Sulphate	20·3	5·26	—	−5·4
Formate	—	0·66	0·62	−2·44	Chloride	35·9	18·0	11·15	2·07
Glycollate	4·4	−1·62	−1·20	−5·08	Bromide	43·3	24·5	16·1	4·98
Hydroxide	1·2	3·38	10·5	11·6	Iodide	49·8	27·7	20·6	10·29
Nitrate	—	3·94	−4·7	−9·47	Sulphide	38·0	26·3	27·0	27·2

Increasing values indicate increasing tendency to dissolve. All values are taken from Bichowsky and Rossini (" Thermochemistry of Chemical Substances," Reinhold Publ. Corp., New York, 1936).

Entropy of solution (cal./°c)

Salt	Mg	Ca	Sr	Ba	Salt	Mg	Ca	Sr	Ba
Fluoride	—	−32·0	—	−25·0	Hydroxide	−55·6	−35·0	—	—
Sulphate	—	−33·0	—	−25·0	Carbonate	−60·0	−46·0	—	−38·0

Increasing negative values imply decreasing tendency to dissolve (see Rice, " Electronic Structure and Chemical Binding," Reinhold Publ. Corp., New York, 1936, Section 19·5).

The solubilities of the thiosulphates, sulphates, iodates, bromates, chromates, and nitrates, all strong-acid salts, fall in the sequence Mg > Ca > Sr > Ba. Now, the entropy of solution of the different cations would favour exactly the opposite order of solubilities, and therefore it must be assumed that the heats of solution for the salts of these cations with a given strong-acid anion are in the order of decreasing radius of the cation. The available data confirm this argument for the strong-acid salts (Table 6). For the weak-acid salts, *e.g.*, those of the monocarboxylic acids, the order is the same but the differences on moving from one cation to another are very small. In the hydroxides, the order of the heats of solution is reversed, as indeed is the order of the solubilities. In Table 6 some entropies of solution are also listed and their values can be seen to be in the order expected. The whole of this discussion is exactly paralleled by that given on p. 3774 in discussing the stability orders of the complexes with weak and strong acid anions. It should also be compared with the discussion of the solubility of Group I metal halides given by Rice (*op. cit.*, Sect. 19.5).

The above arguments, although tentative in many respects, go some way to link the stabilities of the complexes, the solubilities of the salts, and the activity coefficients of the ions of those salts in aqueous solution, especially for the Group IIA metals.

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