

CCLXII.—*The Electrolytic Dissociation of some Metal Malonates.*

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FROM refractometric evidence, Fajans, Kohner, and Geffcken (*Z. Elektrochem.*, 1928, **34**, 1) conclude that strong electrolytes are incompletely dissociated in aqueous solution, and that they differ in degree only from weak electrolytes, so that no sharp line of demarcation can be drawn between them. It is also held by Fajans (*ibid.*, p. 502) that there are two limiting forms of chemical combination involving (1) ideal undeformable ions and (2) complete non-polar combination. If Fajans's views be correct, the distinctions now drawn between the various types of valency are purely

arbitrary and the fundamental electronic mechanism involved in each type of valency is probably the same, differences in properties being due to polar factors and not to any fundamental difference in the mode of linkage. That the distinction between strong and weak electrolytes has ever arisen is probably due to the fact that the vast amount of work which has been carried out on the conductivity of electrolytes has been confined almost exclusively to two extreme types of compound, *viz.*, alkali and alkaline-earth salts and compounds such as weak acids and bases. The very nature of these two types of compound would, on the basis of electronic theory, lead one to anticipate extremely marked differences in the extent of their electrolytic dissociations in aqueous solution. In the present paper it will be shown that normal salts exist (probably a very large number, although only four have been studied), which, although of the same type as the so-called strong electrolytes, behave as weak or intermediate electrolytes in aqueous solution, so lending strong support to Fajans's contention that the classification of electrolytes as "strong" and "weak" is arbitrary. This gradation in the extent of electrolytic dissociation is known to exist in certain series of similar organic acids, *e.g.*, acetic and the chloroacetic acids. The hydrogen ion is, however, unique with respect to its volume, and although it would be unsafe to draw deductions as to the nature of electronic linkage from the above compounds, there is apparently no reason to assume that the weak acetic acid is of a fundamentally different nature from the strong trichloroacetic acid.

Consideration of the phenomenon of electrolytic dissociation indicated that, apart from the polar nature of the solvent and the dimensions of the ions concerned, two factors are probably very important in determining the extent of dissociation, *viz.*, (1) the tendency of the kation to act as an acceptor of electrons and (2) the tendency of the anion to act as a donor. Complex-salt chemistry indicates that in the kations of those elements which depart considerably from the inert-gas structure, the excess positive charge, instead of being uniformly distributed over the surface of the ion (as is probably the case with the alkali and alkaline-earth ions), is highly localised, either actually, or potentially. If this be so in complex salts, there is no reason to suppose that this property of acting as an acceptor is absent in ordinary normal salts, and consequently this localisation of the positive charge on the kation will tend to reduce considerably the degree of dissociation. The tendencies of anions to act as donors vary considerably. The magnitude of the tendency is probably a polar factor depending on the electronic structure of the anion. It appears reasonable to suppose that an anion which readily forms stable complex salts,

i.e., salts containing complex ions which are undissociated in aqueous solution, will still possess this "donor" property in its normal salts, with a consequent tendency to decrease the degree of dissociation of the normal salts.

The data available on electrical conductivity, although containing nothing contradictory to the above views, supply little positive evidence. The behaviour of mercuric cyanide and thiocyanate in aqueous solution is, however, in agreement with them. Both compounds possess the mercury kation which departs considerably from the inert-gas structure, and both the cyanide and the thiocyanate ion readily act as donors. Other dissociations which are worthy of notice are those of magnesium oxalate (27.3% dissociated in $N/100$ -aqueous solution at 18°) and of cadmium, zinc, and copper sulphates (all approximately 62% dissociated in $N/100$ -solution at 18°). With the view to extend the data of the electrical conductivities of compounds of this type (*i.e.*, those which on the above theory would be expected to show dissociations far from complete), it was decided as a preliminary study to measure the conductivities of aqueous solutions of copper, zinc, cadmium, and magnesium malonates. These compounds are admirably suited for this purpose with regard to both solubility and stability. The malonate ion possesses the donor property to a fairly high degree, as is shown by the formation of the stable disodium diaquodimalonatocupriate (this vol., p. 1307). The copper, zinc, and cadmium ions all depart considerably from the inert-gas structure, and consequently there will be a high degree of localisation of the excess positive ionic charge. It can therefore be anticipated that the normal malonates of these elements will not behave as "strong" electrolytes, and that their dissociations will be far from complete. The magnesium ion approaches the inert-gas structure much more closely than the other ions, and it can therefore be anticipated that magnesium malonate will be more highly dissociated than the other malonates under consideration. The malonate ion possesses the donor property to a less degree than the oxalate ion (this vol., p. 1307), so it can also be predicted on the above views that magnesium malonate will be more highly dissociated than the oxalate.

The results obtained are illustrated in Fig. 1. The mobilities of the magnesium, copper, zinc, and cadmium ions being almost equal, the variation of equivalent conductivity with dilution illustrates approximately the degree of dissociation of the various salts at different dilutions.

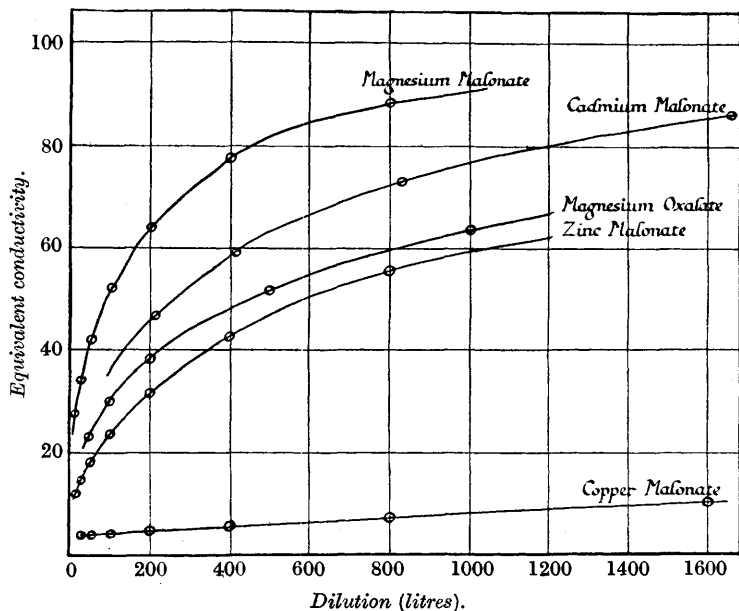
The values for the dissociation of magnesium oxalate are due to Noyes and Falk (*J. Amer. Chem. Soc.*, 1912, **34**, 475), and were determined at 18°. If they had been determined at 25°, these

values would have shown still greater differences from those of the malonate.

EXPERIMENTAL.

The conductivities of the various salt solutions were measured by the ordinary Kohlrausch method. 20 C.c. of the most concentrated solution of the salt under consideration were introduced into a Kohlrausch cell and the conductivity was determined at 25°, a meter bridge, telephones, a Post-office box, and a small induction coil being used. Dilutions were made by means of a calibrated 10-c.c. pipette.

FIG. 1.



The various salts were prepared by dissolving the corresponding oxides in excess of malonic acid and recrystallising them twice from conductivity water. The purity of the products was checked by analysis. The copper malonate crystals, $\text{CH}_2(\text{CO}\cdot\text{O})_2\text{Cu}\cdot 3\text{H}_2\text{O}$, were finely powdered and dried between filter-paper, and an exactly $N/25$ -solution was prepared by dissolving the requisite quantity of salt in conductivity water and diluting it to 250 c.c. The zinc and magnesium malonates, solutions of which were prepared in a similar manner, had been dried at 100°, and analysis showed them to have the formulæ $\text{C}_3\text{H}_2\text{O}_4\text{Zn}\cdot\text{H}_2\text{O}$ and $\text{C}_3\text{H}_2\text{O}_4\text{Mg}\cdot 2\text{H}_2\text{O}$ respectively. Owing to the sparing solubility of cadmium malonate, a litre of an

approximately $N/200$ -solution was prepared and its concentration determined by estimating the cadmium present in 500 c.c.

The results of the conductivity determinations are given below; v represents the dilution in litres, κ the specific conductivity, Λ the equivalent conductivity, α the ratio Λ_v/Λ_∞ , and K the Ostwald dilution formula $\alpha^2/(1 - \alpha)v$.

v .	$\kappa \times 10^6$.	$\Lambda \times 10^3$.	α .	$K \times 10^5$.	v .	$\kappa \times 10^6$.	$\Lambda \times 10^3$.	α .	$K \times 10^5$.
Magnesium malonate.					Zinc malonate.				
12.5	2206	27.6	0.247	648	12.5	967	12.1	0.105	98.6
25	1365	34.2	0.306	540	25	588	14.7	0.128	75.2
50	844	42.2	0.377	456	50	370	18.5	0.161	61.8
100	523	52.3	0.467	409	100	239	23.9	0.208	54.6
200	318	63.6	0.569	376	200	157	31.5	0.274	51.7
400	193	77.4	0.692	389	400	107	42.7	0.372	55.1
800	111	88.4	0.790	372	800	70	55.7	0.485	57.1
∞	—	111.86	—	—	∞	—	114.86	—	—
Cadmium malonate.					Copper malonate.				
206.9	226	46.7	0.405	133	25	160	3.99	0.0351	5.11
413.8	142	58.9	0.511	129	50	81	4.06	0.0356	2.63
827.7	88	72.8	0.631	130	100	43	4.27	0.0375	1.46
1655.4	52	86.4	0.750	136	200	24	4.78	0.0424	0.92
∞	—	115.26	—	—	400	14	5.72	0.0502	0.66
					800	10	7.60	0.0668	0.60
					1600	6.7	10.56	0.0927	0.59
					∞	—	113.86	—	—

The value of the mobility of the malonate ion is that determined by Vogel (this vol., p. 1476), and those of the magnesium, cadmium, zinc, and copper ions are taken from Landolt-Börnstein "Tabellen."

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