

CCLXX.—*The Electrolytic Dissociation of Transitional-metal Salts. Part I. Copper, Zinc, and Nickel Malonates.*

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A PRELIMINARY study of the electrical conductivities of aqueous solutions of the malonates of magnesium, copper, zinc, and cadmium (Riley and Fisher, J., 1929, 2006) indicated that further work on the dissociation of "transitional-metal" salts was highly desirable. In this term we include all those metals which occupy the centre positions in the long periods of the periodic classification and readily form complex ions. In extending this work our aim is threefold, *viz.* :

1. To determine whether or not there is any definite relationship between the dissociation of a simple salt, MA, and that of the corresponding complex anion,  $[M(A)_x]'$ . Although it is well known that the anions of "weak" acids co-ordinate more readily than those of "strong" acids, so few data on the electrolytic dissociation of transitional-metal salts are available, that it is impossible to say whether or not such a fundamental relationship exists.

2. To determine the extent to which transitional-metal cations control the degree of dissociation of their salts. One of the most striking results of the preliminary study (Riley and Fisher, *loc. cit.*) was the great difference shown to exist between the degree of dissociation of copper and of zinc malonate, the latter having a dissociation constant at  $v = 800$  approximately 100 times greater than the former. When it is remembered that copper and zinc sulphates are dissociated to approximately the same extent over a large range of dilution, and that copper and zinc are adjacent elements in the periodic classification, this great difference in the malonates appears anomalous. Any comprehensive theory of the mechanism of electrolytic dissociation must account, not only for the "anomaly of strong electrolytes," but also for this anomalous behaviour of copper malonate and the similar behaviour of certain mercury and cadmium salts, which are also feebly dissociated.

3. To determine the effect of changes in the nature of the anion upon the degree of dissociation of transitional-metal salts. This phenomenon of feeble dissociation of certain transitional-metal salts is, in all probability, due, not only to the nature of the cation, but also to that of the anion. It is hoped, by studying various series of similar anions, to throw some light on the part played by the anion. In view of modern theories regarding the polarity of organic molecules, the effects of substitution on the electrolytic behaviour of organic acid ions is of particular interest.

Measurements have already been made (J., 1930, 1642) on the effect of alkyl substitution on the degree of dissociation of the dimalonatocupriate complex, so it was decided to commence the present studies with measurements of the dissociations of the same series of normal copper salts by the electrical conductivity method, and in view of the anomalous result already recorded in the case of copper malonate, to compare also a similar series of zinc salts.

#### EXPERIMENTAL.

*Bridge.*—As the extension of this work to a large number of salts is contemplated, a bridge capable of precise measurement has been assembled. It consists of a Leeds Northrup drum bridge, a Cambridge resistance box, a Sullivan oscillator and a two-valve, transformer-coupled amplifier used in conjunction with the telephones. The use of the amplifier has many definite advantages: (a) it facilitates the attainment of extremely sharp minima—with the extension coils in use, readings reproducible to 0.001% of the total length of the bridge may be taken; (b) the oscillator voltage may be cut down so that difficulties due to heating effects and polarisation are greatly reduced; (c) the working range of a conductivity cell is increased greatly as the “minimum audibility current” is reduced (compare Washburn, *J. Amer. Chem. Soc.*, 1916, **38**, 2431). An attendant disadvantage is, however, the increased sensitivity of the apparatus to external electrical disturbances, necessitating the removal of the oscillator to a distance, the enclosure of both oscillator and amplifier in earthed metal boxes, and the screening of as many connexions as possible. It was essential, also, to earth the water of the electrically heated thermostat, and to provide a master switch to isolate the entire apparatus from the mains whilst taking readings. The moving contact of the bridge was also earthed.

For balancing the capacity in the cell arm of the bridge, a 0.0015 micro-farad variable condenser, together with a range of fixed condensers, was used.

The Leeds Northrup bridge was carefully calibrated by a modification of the method of Strouhal and Barus (*Bull. U.S. Geol. Survey*, II, 664). Ten approximately equal resistances were employed to obtain the main calibration curve, and intermediate points were calibrated by the use of 9, 8, 7, and 6 resistances, which were matched as nearly as possible. Further intermediate points were obtained, and the above calibrations checked, by the Carey-Foster method.

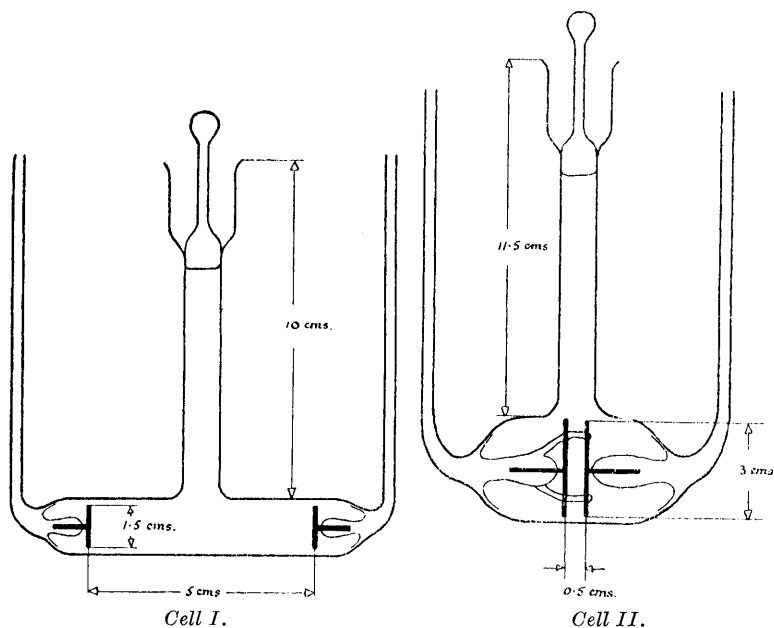
The Cambridge resistance box was also carefully calibrated, and all the calibrations were checked from time to time during the work.

*Thermostat.*—The temperature of the water thermostat was con-

trolled by a spiral toluene regulator of 300 c.c. capacity, which worked an electrical relay attached to a long carbon-filament heating lamp. Temperature variations caused no perceptible change in the reading of a Beckmann thermometer. The temperature was adjusted, on a standard thermometer, to exactly 25°.

*Conductivity Cells.*—The design and dimensions of the conductivity cells are shown in Fig. 1. Owing to the low conductivity and sparingly soluble nature of most of the salts studied in this first paper, cell II was used almost exclusively. Both cells were of

FIG. 1.



Pyrex glass, and the electrodes of stout grey platinised platinum. In cell II the electrodes were held rigidly by two Pyrex-glass struts sealed to the platinum. The cells were cleaned initially with nitric-chromic acid mixture, followed by prolonged steaming. During the course of the determinations, chromic acid was not used, the cell being cleaned between experiments by thorough rinsing with conductivity water, followed by prolonged steaming from boiling conductivity water. Alkaline permanganate was found to cause contamination unless very rigid precautions were taken, so its use was abandoned.

*Conductivity Water.*—The modified Bourdillon still described by Stuart and Wormwell (J., 1930, 85) was employed. The stream of

pure air required was provided by means of a water blower, which drew air from outside the laboratory through a long tube packed with cotton wool, and forced it through a purification train consisting of (a) a wash-bottle of concentrated potash solution, (b) a scrubber of the type described by Kraus and Parker (*J. Amer. Chem. Soc.*, 1922, **44**, 2429), containing Nessler's solution, (c) two 3-foot soda-lime tubes, (d) another scrubber containing phosphoric acid, and (e) a large wash-bottle containing water.

Ordinary laboratory distilled water containing a little permanganate and potash was distilled from a 30-litre copper still, and the first third was boiled off before the conductivity water was collected. Water of  $\kappa$  0.3—0.5 gemmho was obtained in the general routine. Occasionally,  $\kappa$  was as low as 0.18 gemmho. Excessive solution of air in the water, with the consequent trouble through air bubbles separating in the conductivity cell, was prevented by collecting the water at 35° in a Pyrex receiver, which was fitted with a syphon tube and completely filled at each distillation.

It was found impracticable, possibly through unfavourable atmospheric conditions, to use "equilibrium water" as recommended, e.g., by Kendall (*J. Amer. Chem. Soc.*, 1916, **38**, 2460). The "equilibrium water" obtained had a conductivity much higher than 0.8 gemmho. Experiment showed that rapid transfer from one vessel to another, and standing for prolonged periods in well-seasoned and tightly stoppered Pyrex-glass flasks, caused only slight alteration in the conductivity of the water obtained direct from the still. Moreover, it was found desirable to reduce the water correction as far as possible, especially when dealing with feebly dissociated electrolytes.

*Determination of Cell Constants.*—The values for the specific conductivity of solutions of potassium chloride determined by Melcher (see Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 454) were employed. "A.R." Potassium chloride was twice recrystallised in platinum from conductivity water, dried, and the requisite quantity fused in a weighed platinum boat in an electric furnace. After cooling in a desiccator, the boat was rapidly introduced into a weighing bottle, which was at once tightly stoppered, and the whole carefully weighed against a counterpoise after standing for some minutes in the balance case. The boat was then placed in a stoppered Pyrex flask containing water of measured specific conductivity. The flask was weighed after standing for  $\frac{1}{2}$ -hour in the balance case. When higher dilution was required, a second solution was prepared from the first by the weight dilution method. The exact volumes of the solutions at 25° were determined by density measurements.

A long-arm "atomic weight" Oertling balance, and a larger

Oertling balance sensitive to 1 mg. were used, and all weighings, which were corrected to vacuum, were carried out with the care and precautions employed in atomic-weight determinations.

*Measurement of Conductivity.*—The following is the procedure adopted in carrying out the conductivity measurements. The pyknometer was filled with the required solution and placed in the thermostat. The cell, normally kept full of conductivity water, was emptied and refilled with the solution four times, and allowed to reach a steady conductivity in the thermostat. It was then emptied and rinsed twice more, and finally filled with the solution. After it had attained the temperature of the thermostat, the conductivity of the solution was measured with as little delay as possible. Meanwhile, the pyknometer had been removed from the thermostat, dried, and allowed to remain in the balance case for 20 mins. before weighing, its counterpoise having been treated in a similar manner. Between the measurements with different solutions the cell was rinsed, filled with conductivity water, and allowed to stand for 10 mins.

Cell I gave an excellent constant over a large range, but with cell II it was impossible to avoid a little contamination with the more dilute potassium chloride solutions which manifested itself by an apparent fall in the value of the constant. The results are tabulated in Table I.

TABLE I.

Cell I.			Cell II.		
Milli-equiv./l.	Resist-ance.	K.	Milli-equiv./l.	Resist-ance.	K.
31.24	550	2.3325	2.24	233	0.07631
15.51	1075	2.3297	1.54	336	0.07628
13.61	1220	2.3286	1.14	452	0.07619
10.03	1641	2.3291	0.80	643	0.07624
9.83	1674	2.3288	0.69	745	0.07626
6.50	2506	2.3297	0.55	929	0.07620
5.15	3140	2.3297	0.50	1021	0.07620

*Preparation of Salts.*—*Copper malonates.* Pure copper oxide was obtained by dissolving electrolytic copper in "A.R." nitric acid and strongly igniting the resulting nitrate. The malonic acids were purchased and recrystallised. Further quantities of the *isopropyl*- and *diethyl*-malonic acids required, were synthesised. The copper salts were prepared by digesting the copper oxide with a solution containing 10% excess of the malonic acid. The resulting solution was filtered, and the residual cake of sparingly soluble copper salt thoroughly extracted with conductivity water. The filtrate and extracts were evaporated in a large platinum basin on a steam-bath. When sufficient salt had separated, the mother-liquor was decanted, and the crystals of salt were well washed with conductivity water.

The monoalkylated salts were redissolved in conductivity water and again recrystallised. It was impossible to repeat the crystallisation in the case of the dialkylated salts, owing to hydrolysis occurring in the hot aqueous solutions. After crystallisation, the salts were dried in air, very finely powdered, washed three times by decantation with absolute alcohol and three times with conductivity water. The salts were dried on well-scrubbed porous tiles, finely ground a second time, and exposed to the air for two days before use. Experiment showed that drying in a vacuum or by heating was impracticable, owing to the very slow loss of water of crystallisation and the danger of decomposition. A complete analysis of each salt and conductivity measurements over a large range of concentration were made. A second treatment of grinding and washing and a further series of measurements on the conductivity of the solutions indicated that the above method of purification is extremely effective. The copper determinations were carried out by the salicylaldoxime method described by Ephraim (*Ber.*, 1930, **63**, 1928). The following is a brief description of the properties of the individual salts.

Copper malonate is a blue crystalline salt more soluble in water than the other alkylmalonates. It contains 3 molecules of water of crystallisation,  $2\frac{1}{2}$  of which are lost, very slowly, after several days in a vacuum over concentrated sulphuric acid (Found: Cu, 29.0; C, 16.5; H, 3.6. Calc. for  $\text{CH}_2\cdot\text{C}_2\text{O}_4\cdot\text{Cu}\cdot 3\text{H}_2\text{O}$ : Cu, 28.9; C, 16.5; H, 3.7%).

*Copper methylmalonate* is rather less soluble and of a lighter shade of blue than the malonate. It contains only one molecule of water of crystallisation, which is not lost in a vacuum over concentrated sulphuric acid (Found: Cu, 32.3; C, 24.2; H, 3.0.  $\text{CHMe}\cdot\text{C}_2\text{O}_4\cdot\text{Cu}\cdot\text{H}_2\text{O}$  requires Cu, 32.2; C, 24.3; H, 3.1%).

*Copper ethylmalonate* is still a little lighter in shade and possesses a slight greenish tint. It contains  $1\frac{1}{2}$  molecules of water of crystallisation, one of which is lost in a vacuum, with deepening of colour. The solubility is slightly less than that of the methylmalonate (Found: Cu, 28.8; C, 27.2; H, 4.0.  $\text{CHEt}\cdot\text{C}_2\text{O}_4\cdot\text{Cu}\cdot 1\frac{1}{2}\text{H}_2\text{O}$  requires Cu, 28.8; C, 27.2; H, 4.1%).

*Copper n-propylmalonate* has the same colour as the ethyl salt and approximately the same solubility. It contains one molecule of water of crystallisation which is slowly lost in a vacuum, the loss being accompanied by deepening of colour to a dark greyish-blue (Found: Cu, 28.2; C, 31.6; H, 4.5.  $\text{CHPr}^n\cdot\text{C}_2\text{O}_4\cdot\text{Cu}\cdot\text{H}_2\text{O}$  requires Cu, 28.2; C, 31.9; H, 4.5%).

*Copper isopropylmalonate* crystallises anhydrous in soft, very deep blue laminae; its solubility is considerably less than those of the above malonates, being of the order of 2 g. per l. (Found: Cu, 30.7;

C, 34.5; H, 3.8.  $\text{CHPr}^\beta \cdot \text{C}_2\text{O}_4 \cdot \text{Cu}$  requires Cu, 30.8; C, 34.7; H, 3.9%.

*Copper dimethylmalonate*, in colour, crystalline form, and solubility, is indistinguishable from copper *isopropylmalonate*. It also crystallises anhydrous, but, unlike the *isopropyl* salt, it is hydrolysed somewhat when its aqueous solution is heated for a prolonged period (Found: Cu, 32.8; C, 30.9; H, 3.1.  $\text{CMe}_2 \cdot \text{C}_2\text{O}_4 \cdot \text{Cu}$  requires Cu, 32.8; C, 31.0; H, 3.1%).

*Copper diethylmalonate* crystallises as monohydrate in bright grass-green laminae, which are not dehydrated in a vacuum over concentrated sulphuric acid. It is considerably less soluble than the dimethyl salt, and the solution is hydrolysed more readily on heating (Found: Cu, 26.5; C, 35.0; H, 5.0.  $\text{CEt}_2 \cdot \text{C}_2\text{O}_4 \cdot \text{Cu}, \text{H}_2\text{O}$  requires Cu, 26.5; C, 35.0; H, 5.0%).

*Copper dipropylmalonate* is very similar to the diethylmalonate, but is of a slightly brighter green and even less soluble in water. A saturated solution of this salt is approximately 0.0005*N*. It contains one molecule of water of crystallisation which is not lost in a vacuum. The aqueous solution is also readily hydrolysed on boiling (Found: Cu, 23.8; C, 40.7; H, 6.1.  $\text{CPr}_2 \cdot \text{C}_2\text{O}_4 \cdot \text{Cu}, \text{H}_2\text{O}$  requires Cu, 23.7; C, 40.3; H, 6.0%).

It will be noticed that there is a general decrease in the solubility of these salts as the number of carbon atoms present increases. The *isopropyl*-, *dimethyl*-, *diethyl*-, and *dipropyl*-malonates are all very soft and difficult to powder. The *diethyl*- and *dipropyl*-malonates do not wet easily, forming a dry surface scum when water is added. On shaking solutions of the *ethyl* and *propyl* salts stable air emulsions are formed, and it is necessary to subject them to reduced pressure in order to remove the air. Considerable foaming occurs during the process.

*Zinc malonates*. The zinc salts were prepared in a similar manner by digesting "A.R." zinc oxide with a solution containing 10% excess acid. They were purified by the grinding and washing method already described. Again, this was found to be remarkably effective, the second treatment not once being found to have any appreciable effect on the conductivity. Complete analyses were again carried out and the results are summarised in Table II.

In solubility these salts followed the same order as the copper salts, the malonate being more soluble than copper malonate and the *diethyl*- and *dipropyl*-malonates even less soluble than the corresponding copper salts.

*Nickel malonate* was prepared by dissolving nickelous hydroxide in excess of malonic acid solution. The nickelous hydroxide used was made by adding a hot solution of "A.R." potassium hydroxide

TABLE II.

Sub- stituent.	No. of mols. of H <sub>2</sub> O of cryst.	H <sub>2</sub> O lost in vacuum.	Analysis.					
			Found, %.			Required, %.		
			Zn.	C.	H.	Zn.	C.	H.
H <sub>2</sub> .....	2	1—1½	32.1	17.8	3.2	32.1	17.7	3.0
CH <sub>3</sub> , H ...	1	0	33.0	23.7	3.0	32.8	24.1	3.0
C <sub>2</sub> H <sub>5</sub> , H ...	2½	2	27.3	24.9	4.4	27.3	24.9	4.6
n-C <sub>3</sub> H <sub>7</sub> , H	1	0	28.8	31.3	4.2	29.0	31.6	4.4
iso-C <sub>3</sub> H <sub>7</sub> , H	1	0	29.0	31.6	4.4	29.0	31.6	4.4
(CH <sub>3</sub> ) <sub>2</sub> .....	1	0	30.5	28.1	3.7	30.6	28.1	3.8
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ...	2	1—1½	25.2	32.1	5.0	25.2	32.4	5.4
(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> ...	2	1	22.6	37.6	6.1	22.7	37.6	6.3

to a boiling solution of excess of cobalt-free nickel sulphate. The precipitate was washed by decantation with hot water several times, and finally on the filter until the washings were free from dissolved salts. The purification of the nickel malonate was carried out in the manner described for the copper and zinc salts. It is a pale bluish-green crystalline solid containing two molecules of water of crystallisation which are not lost in a vacuum over concentrated sulphuric acid. It is fairly soluble in water and dissolves readily when the solution is heated, but only very slowly in the cold (Found : Ni, 29.7; C, 18.2; H, 3.0. CH<sub>2</sub>·C<sub>2</sub>O<sub>4</sub>·Ni, 2H<sub>2</sub>O requires Ni, 29.8; C, 18.3; H, 3.1%).

*Conductivity Measurements.*—The procedure was essentially the same as that described in the determination of the cell constants. Owing to the sparingly soluble nature of most of the salts studied, it was not possible to employ the weight method of preparing solutions advocated by Whetham (*Phil. Trans.*, 1900, A, 194, 321). The Ostwald method of successive dilutions by weight, accompanied by density determinations, was employed. Except in the case of the copper and zinc malonates, prolonged shaking was necessary in order to effect solution. The sparingly soluble diethyl- and di-propyl-malonates required shaking for periods up to a week in order to yield solutions containing an appreciable amount of dissolved salt. The uncertainty of the results consequent on the above experimental difficulties was countered by carrying out a much larger number of determinations over the restricted range of concentration available.

*Water Correction.*—According to Wynne-Jones (*J. Physical Chem.*, 1927, 31, 1647), “the criterion of a true water correction is the constancy of the results obtained with different samples of solvent.” It was found that if half the normal water correction was subtracted from the conductance values, much closer agreement was obtained between the results of separate measurements with water of different conductivity. For example, a series of 41 measurements was made on solutions of copper isopropylmalonate, using water of specific conductivities 0.41, 0.64, 0.88, and 1.54 gemmhos. The values



obtained were corrected (a) by subtracting the full water correction, (b) by subtracting half the water correction, and then plotted against the concentration. Smooth curves were drawn through the two sets of points, and the differences between the ideal and the actual ordinates noted in the case of each point. The mean value of the differences when half the normal water correction was applied was 0.08, and when the full correction was applied, 0.17. A similar procedure with no water correction at all gave a mean difference of 0.24. These results support the above view that it is advisable to apply an empirical correction for the conductivity of the solvent.

*Calculation of Dissociation Constants.*—For purposes of comparison of the various salts, the degrees of dissociation ( $\alpha$ ) have been calculated from the simple Ostwald dilution law,  $\alpha^2/(1 - \alpha)v = K$ , where  $v$  = dilution in litres and  $\alpha = \lambda/\lambda_\infty$ . Although an application of the Onsager-Debye-Hückel corrections for interionic attraction to the more soluble salts brings about an improvement in the constancy of the mass-action constants, particularly in the more concentrated solutions, it is felt that the publication of such corrected results would be premature, for the following reasons. (a) It is not possible to apply the corrections to the sparingly soluble diethyl- and dipropylmalonates with any certainty owing to the very restricted range over which conductivities can be measured accurately. (b) The accurate values of  $\lambda_\infty$  of the salts studied are not known. (c) It is anticipated that the continuation of this work will lead to modifications in the interionic attraction theory, for, from a knowledge of the dissociation constants of the complex ions of the type  $[\text{Cu}(\text{CH}_2\text{C}_2\text{O}_4)_2]$  already measured (J., 1930, 1642), it is possible to calculate the percentages of complex ion in solutions of the normal salts. In the stronger solutions, these are considerable and probably account to a large extent for the increase in the value of the mass-action constant as the dilution decreases, particularly in the case of copper malonate and the *mono*-substituted copper malonates (*i.e.*, those salts whose anions have the greater co-ordinating tendency).

The values of  $\lambda_\infty$  used in the calculations have been assumed to be equal to the sum of the mobilities of the constituent ions. The malonate ion mobilities are those recorded by Vogel (J., 1929, 1476), those of isomeric ions being taken as equal. The values for the mobilities of  $\frac{1}{2}\text{Cu}''$ ,  $\frac{1}{2}\text{Zn}''$ , and  $\frac{1}{2}\text{Ni}''$  are those recorded in Landolt-Börnstein "Tabellen," the values for  $\frac{1}{2}\text{Zn}''$  and  $\frac{1}{2}\text{Ni}''$  at 25° having been calculated from those recorded at 18° by the use of the formula  $a_{18} = \left(\frac{1}{l} \cdot \frac{dl}{dt}\right)_{18} = 0.0254$ , where  $a$  = temperature coefficient and  $l$  = the mobility.

The results at rounded dilutions are recorded in Tables IV, V, and

TABLE III.

*Zinc isopropylmalonate.*

<i>v.</i>	$\kappa \times 10^6.$	$\lambda.$	$100a. K \times 10^3.$		<i>v.</i>	$\kappa \times 10^6.$	$\lambda.$	$100a. K \times 10^3.$	
274.8	121.7	33.43	32.1	0.55	2,563	26.60	68.17	65.4	0.48
431.4	106.1	36.21	34.7	0.54	3,629	20.49	74.35	71.3	0.49
460.8	86.64	39.93	38.3	0.52	3,994	18.96	75.72	72.6	0.48
652.3	69.27	45.19	43.3	0.51	5,013	15.81	79.25	76.0	0.48
656.2	68.60	45.01	43.2	0.50	6,204	13.37	82.94	79.6	0.50
898.5	55.66	50.01	48.0	0.49	6,540	12.64	82.67	79.3	0.47
938.1	53.89	50.55	48.5	0.49	8,757	10.02	87.74	84.2	0.51
1285	43.73	56.19	53.9	0.49	9,242	9.50	87.80	84.2	0.49
1316	42.89	56.43	54.1	0.49	11,669	7.73	90.20	86.5	0.48
1599	37.31	59.66	57.2	0.48	14,388	6.52	93.81	90.0	0.56
2237	29.54	66.07	63.4	0.49	17,730	5.30	93.97	90.1	0.47

TABLE IV.

<i>v.</i>	$\kappa \times 10^6.$	$\lambda.$	$100a. K \times 10^5.$		$\kappa \times 10^6.$	$\lambda.$	$100a. K \times 10^5.$		
<i>Copper malonate.</i>				<i>Copper methylmalonate.</i>					
20	196.5	3.930	3.45	6.17					
50	80.90	4.045	3.55	2.62					
100	42.55	4.255	3.74	1.45	46.14	4.614	4.19	1.83	
200	23.82	4.764	4.18	0.91	25.77	5.154	4.68	1.15	
400	14.37	5.748	5.05	0.67	15.60	6.240	5.67	0.85	
600	10.98	6.585	5.78	0.59	11.91	7.146	6.49	0.75	
800	9.17	7.336	6.44	0.56	9.94	7.952	7.22	0.70	
1,000	8.05	8.050	7.07	0.54	8.70	8.700	7.90	0.68	
1,200	7.24	8.688	7.63	0.52	7.81	9.372	8.51	0.66	
1,400	6.62	9.268	8.14	0.52	7.16	10.02	9.10	0.65	
1,600	6.16	9.856	8.66	0.51	6.66	10.66	9.67	0.65	
1,800	5.78	10.40	9.14	0.51	6.25	11.25	10.21	0.65	
2,000	5.49	10.98	9.64	0.51	5.90	11.80	10.71	0.64	
2,500	4.92	12.30	10.80	0.52	5.25	13.13	11.92	0.65	
3,000	4.49	13.47	11.83	0.53	4.78	14.34	13.02	0.65	
4,000	3.95	15.80	13.88	0.56	4.15	16.60	15.07	0.67	
6,000	3.25	19.50	17.13	0.59	3.41	20.46	18.58	0.71	
8,000	2.84	22.72	19.96	0.62	3.01	24.08	21.86	0.77	
10,000	2.53	25.30	22.22	0.63	2.70	27.00	24.51	0.80	
$\infty$		113.85				110.15			
<i>Copper ethylmalonate.</i>				<i>Copper propylmalonate.</i>					
100	47.90	4.790	4.59	2.21	51.82	5.182	5.02	2.66	
200	26.59	5.318	5.10	1.37	28.05	5.610	5.43	1.56	
400	15.75	6.296	6.04	0.97	16.23	6.492	6.29	1.06	
600	11.90	7.140	6.85	0.84	12.12	7.272	7.04	0.89	
800	9.91	7.928	7.60	0.78	9.98	7.984	7.73	0.81	
1,000	8.68	8.680	8.33	0.76	8.63	8.630	8.36	0.76	
1,200	7.78	9.336	8.96	0.73	7.71	9.252	8.96	0.74	
1,400	7.10	9.940	9.53	0.72	7.03	9.842	9.53	0.72	
1,600	6.59	10.54	10.11	0.71	6.53	10.44	10.11	0.71	
1,800	6.10	10.98	10.53	0.69	6.09	10.96	10.62	0.70	
2,000	5.80	11.60	11.13	0.70	5.75	11.50	11.14	0.70	
2,500	5.14	12.84	12.33	0.69	5.10	12.75	12.35	0.70	
3,000	4.70	14.10	13.53	0.70	4.65	13.95	13.51	0.70	
4,000	4.02	16.08	15.42	0.70	4.02	16.08	15.57	0.72	
6,000	3.24	19.44	18.65	0.71	3.26	19.56	18.94	0.74	
8,000	2.80	22.40	21.49	0.73	2.86	22.88	22.16	0.79	
10,000	2.50	25.00	23.98	0.76	2.53	25.30	24.50	0.80	
$\infty$		104.25				103.25			

TABLE IV (contd.).

<i>v.</i>	$\kappa \times 10^6.$	$\lambda.$	$100a.$	$K \times 10^3.$	$\kappa \times 10^6.$	$\lambda.$	$100a.$	$K \times 10^3.$
	<i>Copper isopropylmalonate.</i>				<i>Copper dimethylmalonate.</i>			
100	50.63	5.063	4.09	2.53	53.80	5.380	5.16	2.80
200	26.00	5.200	5.04	1.34	32.22	6.444	6.18	2.03
400	13.85	5.540	5.37	0.76	20.30	8.120	7.78	1.62
600	9.86	5.916	5.73	0.58	15.87	9.522	9.13	1.53
800	7.88	6.304	6.11	0.50	13.45	10.76	10.31	1.48
1,000	6.70	6.700	6.49	0.45	11.87	11.87	11.38	1.46
1,200	5.91	7.092	6.87	0.42	10.75	12.89	12.36	1.45
1,400	5.35	7.490	7.25	0.41	9.87	13.82	13.24	1.44
1,600	4.89	7.824	7.58	0.39	9.16	14.66	14.05	1.43
1,800	4.51	8.118	7.86	0.37	8.60	15.48	14.83	1.44
2,000	4.22	8.440	8.17	0.36	8.13	16.26	15.58	1.44
2,500	3.70	9.250	8.96	0.35	7.22	18.05	17.30	1.45
3,000	3.31	9.930	9.62	0.34	6.57	19.71	18.89	1.47
4,000	2.85	11.40	11.04	0.34	5.72	22.88	21.93	1.54
6,000	2.31	13.86	13.42	0.35	4.67	28.02	26.85	1.64
8,000	2.04	16.32	15.81	0.37	4.05	32.40	31.05	1.75
10,000	1.86	18.60	18.02	0.40	3.62	36.20	34.69	1.84
$\infty$		103.25				104.35		
	<i>Copper diethylmalonate.</i>				<i>Copper di-n-propylmalonate.</i>			
1,000	9.02	9.02	8.77	0.85				
1,200	8.07	9.68	9.42	0.82				
1,400	7.40	10.36	10.08	0.81				
1,600	6.89	11.02	10.72	0.81	6.47	10.35	10.83	0.82
1,800	6.49	11.68	11.36	0.81	6.02	10.84	11.34	0.81
2,000	6.18	12.36	12.02	0.82	5.70	11.40	11.93	0.81
2,200	5.90	12.98	12.63	0.83	5.44	11.97	12.52	0.81
2,400	5.69	13.66	13.28	0.85	5.22	12.53	13.11	0.82
2,600	5.48	14.25	13.86	0.86	5.00	13.00	13.60	0.82
2,800	5.31	14.87	14.46	0.87	4.83	13.52	14.15	0.83
3,000	5.17	15.51	15.09	0.89	4.69	14.07	14.72	0.85
3,500	4.85	16.98	16.51	0.93	4.38	15.33	16.04	0.87
4,000	4.62	18.48	17.98	0.98	4.15	16.60	17.36	0.91
5,000	4.26	21.30	20.72	1.08	3.77	18.85	19.72	0.97
6,000	3.97	23.82	23.17	1.17	3.50	21.00	21.97	1.03
8,000	3.56	28.48	27.70	1.33	3.12	24.96	26.11	1.15
10,000	3.29	32.90	32.00	1.51	2.88	28.80	30.13	1.30
$\infty$		102.8				95.6		

TABLE V.

<i>v.</i>	$\kappa \times 10^6.$	$\lambda.$	$100a.$	$K \times 10^3.$	$\kappa \times 10^6.$	$\lambda.$	$100a.$	$K \times 10^3.$
	<i>Zinc malonate.</i>				<i>Zinc methylmalonate.</i>			
100	232.6	23.26	20.3	0.51	301.0	30.10	27.1	1.01
200	153.9	30.77	26.8	0.49	193.7	38.74	34.9	0.93
400	99.59	39.84	34.7	0.46	123.2	49.28	44.3	0.88
600	77.31	46.39	40.4	0.46	93.60	56.16	50.5	0.86
800	64.32	51.46	44.8	0.46	76.52	61.22	55.1	0.84
1,000	55.52	55.52	48.3	0.45	65.19	65.19	58.7	0.83
1,200	48.90	58.68	51.1	0.45	57.03	68.44	61.6	0.82
1,400	43.97	61.58	53.6	0.44	50.65	70.94	63.8	0.80
1,600	40.20	64.32	56.0	0.45	45.81	73.30	66.0	0.80
1,800	37.10	66.78	58.2	0.45	41.82	75.28	67.7	0.79
2,000	34.42	68.84	59.9	0.45	38.49	76.98	69.3	0.78
2,500	29.48	73.70	64.2	0.46	32.38	80.95	72.8	0.78
3,000	25.80	77.40	67.4	0.46	27.83	83.49	75.1	0.76
4,000	20.85	83.40	72.6	0.48	22.03	88.12	79.3	0.76
6,000	15.22	91.32	79.5	0.51	15.79	94.74	85.3	0.82
8,000	12.02	96.16	83.7	0.54	12.20	97.60	87.8	0.79
10,000	10.00	100.00	87.1	0.59	10.11	101.1	91.0	0.92
$\infty$		114.85				111.15		

TABLE V (contd.).

<i>v.</i>	$\kappa \times 10^6$ .	$\lambda$ .	$100a. K \times 10^3$ .		$\kappa \times 10^6$ .	$\lambda$ .	$100a. K \times 10^3$ .	
	<i>Zinc ethylmalonate.</i>				<i>Zinc propylmalonate.</i>			
150	—	—	—	—	219.5	32.92	31.6	0.97
200	—	—	—	—	182.6	36.52	35.0	0.94
250	165.3	41.32	39.3	1.02	—	—	—	—
400	121.0	48.40	46.0	0.98	115.5	46.20	44.3	0.88
600	91.87	55.12	52.4	0.96	87.29	52.37	50.2	0.85
800	74.92	59.94	57.0	0.94	71.47	57.18	54.9	0.83
1,000	63.79	63.79	60.6	0.93	60.84	60.84	58.4	0.82
1,200	55.78	66.94	63.6	0.93	53.39	64.07	61.5	0.82
1,400	49.62	69.50	66.0	0.92	47.58	66.64	63.9	0.81
1,600	44.80	71.68	68.1	0.91	43.00	68.80	66.0	0.80
1,800	41.00	73.80	70.1	0.91	39.27	70.69	67.8	0.79
2,000	37.73	75.46	71.7	0.91	36.20	72.40	69.5	0.79
2,500	31.58	78.95	75.0	0.90	30.17	75.43	72.4	0.76
3,000	27.20	81.60	77.5	0.89	26.00	78.00	74.8	0.74
4,000	21.50	86.00	81.7	0.91	20.53	82.12	78.8	0.73
6,000	15.20	91.20	86.7	0.94	14.59	87.54	84.0	0.73
8,000	11.87	94.80	90.1	1.02	11.41	91.28	87.6	0.77
10,000	9.69	96.90	92.1	1.07	9.46	94.60	90.7	0.89
$\infty$		105.25				104.25		
	<i>Zinc isopropylmalonate.</i>				<i>Zinc dimethylmalonate.</i>			
250	128.9	32.23	30.9	0.55	216.2	54.05	51.3	2.16
400	95.93	38.37	36.8	0.54	153.4	61.36	58.2	2.03
600	73.02	43.81	42.0	0.51	113.6	68.16	64.7	1.98
800	60.03	48.02	46.1	0.49	91.00	72.80	69.1	1.93
1,000	51.74	51.74	49.6	0.49	76.31	76.31	72.4	1.90
1,200	45.70	54.84	52.6	0.49	65.92	79.10	75.1	1.89
1,400	41.11	57.58	55.2	0.49	58.14	81.43	77.3	1.88
1,600	37.40	59.84	57.4	0.48	52.09	83.34	79.1	1.87
1,800	34.36	61.85	59.3	0.48	47.10	84.78	80.5	1.84
2,000	31.90	63.80	61.2	0.48	43.00	86.00	81.6	1.81
2,500	27.12	67.80	65.0	0.48	35.50	88.75	84.2	1.80
3,000	23.69	71.07	68.2	0.49	30.20	90.60	86.0	1.76
4,000	18.99	75.96	72.9	0.49	23.50	94.00	89.2	1.85
6,000	13.63	81.78	78.5	0.48	16.21	97.26	92.3	1.85
8,000	10.71	85.68	82.2	0.47	12.34	98.72	93.7	1.74
10,000	8.81	88.10	84.5	0.46	9.95	99.50	94.5	1.61
$\infty$		104.25				105.35		
	<i>Zinc diethylmalonate.</i>				<i>Zinc dipropylmalonate.</i>			
2,500	28.61	71.53	68.9	0.61	27.91	69.78	72.2	0.75
3,000	24.57	73.71	71.0	0.58	24.00	72.00	74.5	0.73
4,000	19.35	77.40	74.6	0.56	18.88	75.52	78.2	0.70
6,000	13.69	82.14	79.1	0.50	13.28	79.68	82.5	0.65
8,000	10.64	85.12	82.0	0.47	10.29	82.32	85.2	0.61
10,000	8.68	86.80	83.6	0.43	8.40	84.00	87.0	0.58
$\infty$		103.8				96.6		

TABLE VI.

*Nickel malonate.*

<i>v.</i>	$\kappa \times 10^6$ .	$\lambda$ .	$100a. K \times 10^4$ .		<i>v.</i>	$\kappa \times 10^6$ .	$\lambda$ .	$100a. K \times 10^4$ .	
100	169.1	16.91	14.3	2.38	1,800	28.96	52.13	44.0	1.92
200	111.4	22.29	18.8	2.18	2,000	27.09	54.18	45.7	1.93
400	73.43	29.37	24.8	2.04	2,500	23.40	58.50	49.4	1.93
600	57.58	34.55	29.2	2.00	3,000	20.82	62.46	52.7	1.96
800	48.20	38.56	32.6	1.96	4,000	17.22	68.88	58.2	2.12
1000	42.00	42.00	35.5	1.95	6,000	12.98	77.88	65.7	2.10
1200	37.59	45.11	38.1	1.95	8,000	10.60	84.80	71.6	2.25
1400	34.06	47.68	40.3	1.94	10,000	8.71	87.10	73.5	2.04
1600	31.28	50.05	42.3	1.93	$\infty$		118.45		

TABLE VII.

*Summary of results.*

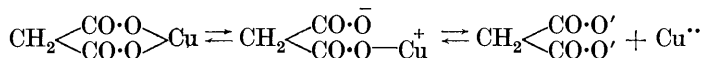
Substituent.	Dissociation constants.		
	Copper malonate. $K \times 10^5$ .	Zinc malonate. $K \times 10^3$ .	Nickel malonate. $K \times 10^4$ .
H <sub>2</sub> .....	0.51	0.45	1.9
CH <sub>3</sub> , H .....	0.65	0.79	
C <sub>2</sub> H <sub>5</sub> , H .....	0.70	0.91	
n-C <sub>3</sub> H <sub>7</sub> , H .....	0.70	0.75	
iso-C <sub>3</sub> H <sub>7</sub> , H .....	0.35	0.48	
(CH <sub>3</sub> ) <sub>2</sub> .....	1.44	1.81	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> .....	0.81	0.58	
(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> .....	0.81	0.70	

VI. These were obtained by interpolation from large-scale specific conductivity-concentration curves, plotted from approximately 30 experimental results in each case. Table III gives, for comparison, a series of experimental values.

*Discussion.*

It should be remembered that the values of the dissociation constants obtained must be considered only relatively correct until the values of  $\lambda_{\infty}$  of the various salts are known with more certainty.

Apart from the diethyl- and the dipropyl-compounds, the values of the dissociation constants of the various copper salts follow the same order as the values recorded for the constants of instability of the corresponding dimalonatocupriate complex ions (J., 1930, 1642). In the normal salt, the substitution of Me, Et, and Pr causes a small increase, Me<sub>2</sub> a larger increase, and Pr<sup>*β*</sup> a small decrease in the value of the dissociation constant. These effects are, however, not so pronounced as those recorded for the complex ions, but there can be little doubt that the underlying causes are the same in both cases, *viz.*, alterations in the extent of the localisation of negative electric charge on the carboxyl oxygen atoms. It is somewhat surprising that the dissociation constants of the diethyl- and dipropyl-salts are so little different from that of copper malonate itself, particularly when it is remembered that the substitution of these groups brings about other profound changes in the nature of the malonate, *e.g.*, change in colour of the copper salt, ease of hydrolysis with water, tendency to co-ordinate with the copper ion. This anomalous behaviour can be explained by the following theory. The electrolytic dissociation of copper malonate probably takes place in two stages :



The degree of dissociation of copper malonate will therefore be governed to some extent by the effect which the free negative pole,

formed when one of the Cu—O bonds breaks, has upon the other carboxyl oxygen atom. It can be anticipated from this view that some parallel should be observable between the dissociation constants of this series of copper malonates and the secondary dissociation constants of the free malonic acids. It is highly significant that in the results recorded by Gane and Ingold (J., 1929, 1691), the secondary dissociation constants of diethyl- and dipropyl-malonic acids are from approximately 1/30th to 1/120th of the magnitude of the secondary dissociation constants of any of the other malonic acids in this series. That this same effect does not influence in the same manner the dissociation of the malonatocuprate complex ion, is probably due to the stability of the complex depending upon the completion of an additional electron grouping round the centre copper ion, and once this is broken, the whole complex ion dissociates readily.

There is also a very close parallel between the effects of alkyl substitution in the copper series and those in the zinc series. This suggests that, if the variations observed are due to polar effects, then alkyl substitution causes a permanent alteration in the polar nature of the malonate ions, for in the feebly dissociated copper salts the effects would have been greatly enhanced, compared with the zinc salts, had alkyl substitution caused an appreciable alteration in the polarisability of the ions.

Another important aspect of these results is the great difference in the degree of dissociation of the copper and the zinc salts, and the intermediate character of the nickel salts. It has already been suggested (Riley and Fisher, *loc. cit.*) that the feeble dissociation of copper malonate is due to a high degree of localisation of the excess positive charge on the surface of the copper ion and to the co-ordinating tendency of the malonate ion, these two properties causing an intense electrostatic attraction between the two ions of this salt. Why, then, should copper sulphate and zinc sulphate dissociate to approximately the same extent in aqueous solution? Noyes and Falk (*loc. cit.*) record the percentage dissociations of these salts at 18° as follows :

Milliequivs./l.	1	2	5	10	20	50	100	200	1000
CuSO <sub>4</sub> .....	86.2	80.4	70.9	62.9	55.0	45.5	39.6	35.1	30.9
ZnSO <sub>4</sub> .....	85.4	79.9	71.0	63.3	55.6	46.4	40.5	36.0	30.9

This different behaviour of the sulphates, compared with the malonates, can be explained as follows. Although no quantitative information is available, it is highly probable from qualitative knowledge of the instability of sulphato-compounds and double sulphates generally, that the co-ordinating tendency of the sulphate ion is considerably less than that of the malonate ion. Consequently,

the sulphate ion will be far less capable than the malonate ion of breaking down the solvated sheath of solvent molecules round the copper ion. The effects of the localisation of the excess positive charge on the surface of the copper ion will be considerably reduced by solvation, the charge becoming more evenly distributed over the surface of the solvated ion. It is only when the co-ordinating tendency of the anion is sufficiently great to break down the solvated ion system that the effect of the localised charge reaches its maximum value. The behaviour of the copper and zinc sulphates is therefore explained by the view that in each case we are dealing with solvated kations possessing similar electrostatic properties.

It is interesting to compare the variation of the dissociation constants of the malonates already studied :

	Mg.	Cd.	Zn.	Ni.	Cu.
<i>K</i> .....	$0.4 \times 10^{-2}$	$1.3 \times 10^{-3}$	$0.45 \times 10^{-3}$	$1.9 \times 10^{-4}$	$0.51 \times 10^{-5}$

From the above, it can be anticipated that further work will show that the degree of localisation of the excess positive charge on the surface of a kation is dependent principally upon two factors, (*a*) the extent to which the ion departs from inert-gas structure, and (*b*) the ionic radius, localisation effects being greatest in smaller ions. These results indicate quite clearly that even with definitely metallic salts there is no sharp division between "strong" and "weak" electrolytes. It is highly probable that the localised charge on the surface of the copper ion is a contributory cause of the instability of cupric iodide.

The extension of these studies should throw considerable light upon the electronic structure of metal ions.

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