39. *Physicochemical Studies of Complex Formation Involving Weak Acids. Part XIII. The Reactions of Malonic Acid with Typical Metallic Bases.*

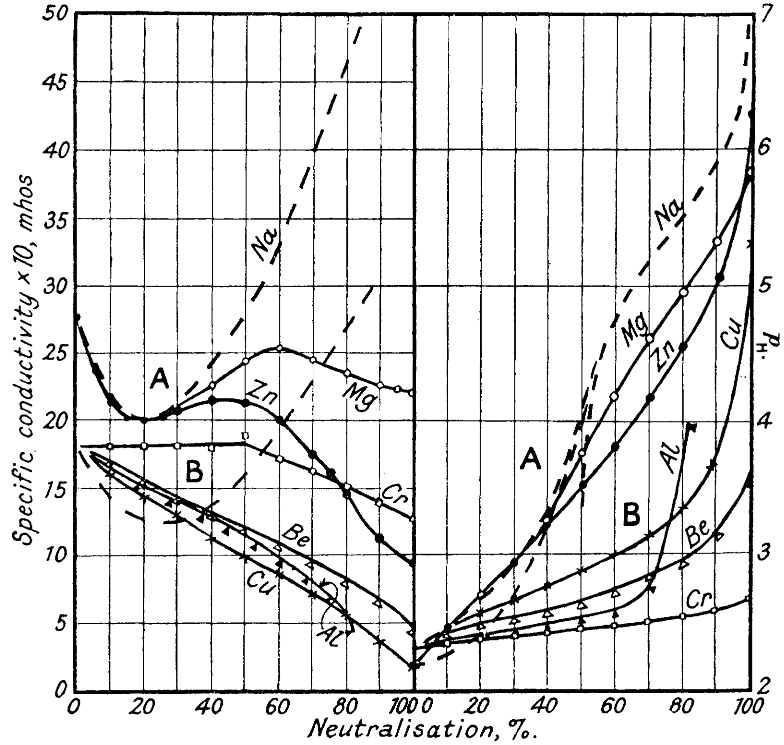
By H. T. S. Britton and Maurice E. D. Jarrett.

According to Britton (J., 1925, **127**, 1909), K_2 of malonic acid at 18° is $4{\cdot}4 \times 10^{-6}$, from which it might be expected that normal combination is not possible with those metallic bases which are precipitated at p_{H} values below $p_{K_2} + 2$, *i.e.*, p_{H} 7·36. Yet it is possible to prepare well-defined crystalline malonates from, *e.g.*, zinc and copper hydroxides, which undergo precipitation from sulphuric, hydrochloric, or nitric acid solution on reaching p_{H} 6·8 and 5·3 respectively. Combination with such bases, therefore, must be accompanied by some kind of complex formation which produces a substantial diminution in the metallic-ion concentration in order to prevent the separation of some of the base on dissolution of the salt in water.

As the methods used by Riley and his co-workers (J., 1928, 2985; 1929, 1307, 2006; 1930, 1307, 1642; 1931, 1998) in investigating the malonates and substituted malonates of zinc and copper, and by Sidgwick and Lewis (J., 1926, 2538) with beryllium malonate, do not furnish any precise information regarding the ions actually taking part in the equilibria, especially hydromalonate ions, we have studied particularly the concentrations of hydrogen ions in order to elucidate the equilibria from which they arise.

EXPERIMENTAL.

Neutralisation of Malonic Acid with Metallic Bases.—Solutions were prepared that were either 0·04M (Table IA) or 0·02M (Table IB) with respect to malonic acid, free and combined, and contained increasing amounts of the bases indicated. The specific conductivities were measured at 25°, and the p_{H} values at 18° by an electrometric method, the glass electrode in conjunction with an electrometer triode valve being used in those instances where the hydrogen and the quinhydrone electrodes were inapplicable. The data recorded in Table I for each successive 10% of neutralisation (N, %) by the various bases are compared with those set up by similar molecular proportions of sodium hydroxide. In the fig. (left) the specific conductivities are compared with those corresponding to the neutralisation with sodium hydroxide (broken line), whilst in the right-hand diagram the p_{H} values are similarly plotted.



Some difficulty was experienced in dissolving the weaker bases at room temperature by prolonged mechanical agitation. Recourse to heating was avoided, where possible, as it was considered that such treatment would lead to a loss in the reactivity of the base towards malonic acid, particularly with its second stage.

The magnesium and zinc solutions were prepared by adding the requisite amounts of the oxide to malonic acid solutions and heating on a water-bath; but as only 95% and 90% respectively of the acid could thus be neutralised, solutions corresponding to 100% neutralisation were prepared from the isolated normal salts, $ZnC_6H_4O_8,2H_2O$ and $MgC_6H_4O_8,2H_2O$.

For the preparation of the aluminium and chromium solutions an acidic aluminium malonate (Al, 9·1; $C_3H_2O_4''$, 63·11%) and the heptahydrate of normal chromium malonate (Cr, 19·59; $C_3H_2O_4''$, 57·2%) were isolated by saturating 10% malonic acid solutions with the freshly

TABLE I.

A. *Neutralisation of* 0·04*M-Malonic Acid.*

	NaOH.		Mg(OH)$_2$.		Zn(OH)$_2$.	
N, %.	p_H.	$10^3\kappa$.	p_H.	$10^3\kappa$.	p_H.	$10^3\kappa$.
0	2·17	2·79	2·17	2·79	2·17	2·79
10	2·24	2·21	2·45	2·12	2·45	2·15
20	2·47	2·01	2·69	1·99	2·72	2·00
30	2·72	2·12	2·96	2·07	2·96	2·07
40	3·21	2·41	3·26	2·27	3·19	2·16
50	4·00	2·80	3·75	2·44	3·52	2·13
60	4·80	3·32	4·17	2·53	3·79	2·00
70	5·19	3·96	4·61	2·44	4·17	1·74
80	5·53	4·64	4·95	2·33	4·55	1·43
90	5·90	5·30	5·32	2·26	5·07	1·13
100	9·06	5·94	5·85	2·20	6·27	0·94

B. *Neutralisation of* 0·02*M-Malonic Acid.*

	NaOH.		Cr(OH)$_3$.			Be(OH)$_2$.			Al(OH)$_3$.			Cu(OH)$_2$.		
				$10^3\kappa$.			$10^3\kappa$.			$10^3\kappa$.			$10^3\kappa$.	
N, %.	p_H.	$10^3\kappa$.	p_H.	obs.	calc.	p_H.	obs.	calc.	p_H.	obs.	calc.	p_H.	obs.	calc.
0	2·35	1·82	2·35	1·82	1·82	2·35	1·82	1·82	2·35	1·82	1·82	2·35	1·82	1·82
10	2·45	1·41	2·40	1·80	1·63	2·42	1·70	1·56	2·37	1·65	1·66	2·46	1·59	1·40
20	2·67	1·27	2·41	1·83	1·60	2·49	1·54	1·33	2·42	1·51	1·52	2·58	1·39	1·07
30	2·94	1·30	2·41	1·78	1·58	2·53	1·41	1·20	2·47	1·37	1·38	2·68	1·24	0·85
40	3·36	1·39	2·43	1·78	1·53	2·59	1·28	1·05	2·53	1·25	1·20	2·77	1·11	0·69
50	4·10	1·59	2·47	1·78	1·37	2·66	1·15	0·89	2·55	1·12	1·15	2·88	0·98	0·53
60	4·81	1·94	2·48	1·70	1·34	2·74	1·02	0·75	2·60	0·98	1·02	3·00	0·85	0·41
70	5·12	2·32	2·51	1·59	1·27	2·88	0·87	0·53	2·77	0·80	0·69	3·14	0·71	0·29
80	5·42	2·69	2·55	1·51	1·16	2·96	0·72	0·41	3·71	0·49	0·10	3·35	0·55	0·18
90	5·91	3·07	2·59	1·38	1·04	3·16	0·56	0·28	—	—	—	3·70	0·36	0·08
100	—	—	2·68	1·27	0·84	3·57	0·375	0·11	—	—	—	5·31	0·16	0·01

precipitated hydroxides, heating for some hours in a water-bath, filtering the solution, evaporating it to dryness, and drying at 100° for some hours. The residue was extracted with ether and redried at 100° for 6 hrs. During preparation, both substances passed through a syrupy condition, the first being finally obtained as a very hard white amorphous substance, and the second as an amorphous, dark green, friable mass (cf. Werner, J., 1904, **85**, 1438).

The hydroxides were precipitated with ammonium hydroxide from hot chloride solutions, washed with dilute ammonia until free from chloride, and then with water until free from ammonia. Sidgwick and Lewis (*loc. cit.*) obtained turbid solutions of beryllium malonate by dissolving basic beryllium carbonate in solutions of malonic acid, but clear solutions can be obtained by dissolving the so-called crystalline beryllium hydroxide (produced by boiling dilute alkaline beryllate solutions, see Britton, *Analyst*, 1921, **46**, 359) in malonic acid solution with gentle heating on a water-bath. 0·02*M*-Malonic acid dissolved more than the equivalent quantity of beryllium hydroxide, and data obtained with such clear basic solutions are given below:

N, %.	Composition of solute.	p_H.	$10^3\kappa_{25°}$.	(*a*).	(*b*).
100	$BeO,C_3H_4O_4$	3·57	0·375	9·38	9·38
110	$BeO,0{\cdot}91C_3H_4O_4$	4·69	0·267	6·68	6·07
120	$BeO,0{\cdot}83C_3H_4O_4$	5·05	0·288	7·20	6·00
130	$BeO,0{\cdot}77C_3H_4O_4$	5·29	0·321	8·03	6·19
140	$BeO,0{\cdot}71C_3H_4O_4$	5·59	0·409	10·23	7·12

The last two columns give the equivalent conductivities calculated with respect to the concentrations of (*a*) malonate and (*b*) beryllium. For a solution of beryllium malonate of concentration comparable to that corresponding to the first line of the table, Sidgwick and Lewis found $\Lambda = 7{\cdot}51$, and it would appear from the table that their beryllium malonate must have been slightly basic; this also seems probable in view of their method of preparing the solutions (from the basic carbonate).

The copper solutions were prepared in the cold by dissolving copper malonate in the acid. The trihydrated salt was obtained by dissolving pure copper hydroxide, prepared by Dawson's method (J., 1909, **95**, 370), in a 20% excess of 10% solution of malonic acid on a water-bath; after partial evaporation, small, well-defined crystals separated on standing. They were purified by recrystallisation from 0·2—0·4% malonic acid solution, washed, dried, powdered, and re-washed with water and alcohol (Found: Cu, 29·04; $C_3H_2O_4''$, 44·5. Calc.: Cu, 28·96; $C_3H_2O_4''$, 44·4%). The copper was determined gravimetrically as oxide, and the malonate volumetrically by direct titration of a boiling solution to phenolphthalein. Attempts to determine the copper iodometrically led to low and variable results owing to complex formation;

by adding an excess of sodium malonate to copper sulphate the concentration of copper ions can be so depressed that excess of potassium iodide fails to produce a precipitate.

It was intended to study the reaction between an extremely weak base, *viz.*, ferric hydroxide, and malonic acid, but much difficulty was experienced in preparing a complete series of solutions owing to the limited solubility of the base and the ease with which the salt undergoes hydrolysis on heating. Two solutions, both giving p_H *ca.* 2·4, were obtained: (*a*) 0·024*M*-malonic acid containing half the amount of hydroxide required for the normal salt, and (*b*) 0·0432*M*-malonic acid containing two-thirds of the amount. The latter was prepared directly from a pale green powder of composition $Fe_2(C_3H_2O_4)_3,2Fe(C_3H_3O_4)_3,1{\cdot}5H_2O$ (Found: Fe, 19·16; $C_3H_2O_4''$, 78·0%), obtained by saturating malonic acid solution at 100° with pure, freshly precipitated ferric hydroxide, evaporating the solution to dryness at room temperature, drying in air, grinding the solid, and extracting it with boiling ether; such a substance can scarcely be regarded as a definite acid salt. Dissolution in water was slow at the ordinary temperature, giving a green solution, and warming caused hydrolysis with separation of a brown precipitate, which, however, redissolved on cooling and shaking. Its ionisation was abnormal, for potassium thiocyanate yielded only a very pale coloration: none of the iron was in the reduced state. Solution (*a*), which was prepared from the same substance and malonic acid, had $\kappa = 1{\cdot}734 \times 10^{-3}$ mho, indicating that the greater part of the acid was free.

The calculated specific conductivities given in Table IB were deduced from the p_H values, it being assumed that only the first-stage dissociation of malonic acid was involved, and that the contribution due to the ionised acid, $H_2M = H^{\cdot} + HM'$, is given by $\kappa_{calc.} = [H^{\cdot}](l_{H^{\cdot}} + l_{HM'})/1000$ ($l_{H^{\cdot}} = 349{\cdot}7$, $l_{HM'} = 58{\cdot}9$; see Vogel, J., 1929, 1486). Such an assumption is justified by the position of the p_H curves (see fig.) of the weak bases, *viz.*, chromium, beryllium, aluminium, and copper, with respect to the second section of the sodium curve, which gives the p_H values that would obtain with weak bases if (*a*) they reacted normally with malonic acid and (*b*) their salts were completely ionised. The observed and the calculated specific conductivities during the reactions with the weak bases (Table IB) are of the same order, the calculated being, in general, but slightly smaller than the actual conductivities. It appears that the hydrolysed malonic acid is responsible for the major portion of the conductivity of the solutions, and therefore that the products of the combination of the weak bases and the malonic acid are but feebly ionised.

The conductivity curves (*A*) corresponding to the two stronger bases, magnesium and zinc hydroxides, show, as do also the p_H curves, that the reaction of malonic acid with the first 0·5 equiv. of base tends to be normal, in that the curves almost coincide with the sodium curve, the variations in specific conductivity introduced by the different mobilities of the kations being negligible at such dilutions. This shows that the bases are able to combine with the first stage to form magnesium and zinc hydrogen malonates, which ionise to an extent similar to sodium hydrogen malonate at the same dilution. Between 25 and 50—60% neutralisation, the conductivities fall below that of the sodium salt and, after attaining maxima, decrease as more magnesium and zinc malonate are formed. The fact that zinc hydroxide is a weaker base than magnesium hydroxide is apparent from the greater diminution in conductivity in the case of zinc. Except for the p_H values of magnesium and zinc malonate solutions, *i.e.*, at 100%, the weakness of magnesium and zinc hydroxides compared with that of sodium seems also to be reflected in the relative positions of the p_H curves between 50 and 100% neutralisation, the zinc curve again lying below that of magnesium. As the p_H values result from the equilibrium $HM' \rightleftharpoons H^{\cdot} + M''$, it follows that the lower p_H values represented by the zinc and magnesium curves indicate much lower ratios of malonate to hydrogen malonate ions. This must be attributed chiefly to diminished concentrations of malonate ions which originate from the substances formed by the reaction of the zinc and magnesium hydrogen malonates with further amounts of the respective base. The effect of the much weaker second stage is thus made apparent.

The conductivity and p_H curves (*B*) of the series of the yet weaker bases, when compared with the appropriate sodium curves, show that the equilibrium $H_2M \rightleftharpoons HM' + H^{\cdot}$ is now the controlling factor.

In view of the increasing tendency exhibited by the stronger bases, *viz.*, magnesium and zinc hydroxides, to combine normally with the first equivalent of malonic acid, the conductivities and p_H values of solutions of magnesium, zinc, and copper hydrogen malonates were determined in a series of dilutions. Col. 1 of Table II gives *v*, the number of litres containing 1 g.-equiv. of the metallic base. The p_H values (col. 2) were measured at 18° and the conductivities at 25°. The columns headed "α,$Mg(HM)_2$," etc., give the apparent degrees of ionisation, *viz.*, the conductance ratio, Λ_v/Λ_∞; Λ_∞ for magnesium, zinc, and copper hydrogen malonates was taken as 111·9, 114·9, and 113·8, respectively, these values being based on the mobility of the hydromalonate ion, 58·9 (Vogel, J., 1929, 1476), and on those of the respective metallic ions (Landolt–Börnstein, "Tabellen"). The degrees of ionisation of magnesium hydrogen malonate are compared with those of its sulphate and chloride under similar conditions, and those of the zinc and copper hydrogen malonates are each similarly compared with two salts of the metal.

The p_H values of the magnesium and zinc solutions are slightly lower than those of sodium hydrogen malonate solutions at the same concentrations. From the dissociation constants, $K_1 = 10^{-2\cdot70}$ and $K_2 = 10^{-5\cdot36}$, obtained by Britton, it would appear that the p_H of a sodium hydrogen malonate solution should be approximately 4·03 but his constants refer to 0·023*M*-malonic acid. A quinhydrone titration of 100 c.c. of *M*/1600-malonic acid with 0·00495*N*-sodium hydroxide at 18° gave slightly smaller constants, *viz.*, $K_1 = 10^{-3\cdot03}$ and $K_2 = 10^{-5\cdot75}$, and the p_H at the mid-point, *i.e.*, corresponding to a solution of 0·000555*M*-sodium hydrogen malonate, was 4·68. Such a concentration is a little lower than those of magnesium, zinc, and copper hydrogen malonates at $v = 800$. It may be noted that the equation $K_1K_2[H^\cdot]^2$, as assumed by Auerbach and Smolczyk (*Z. physikal. Chem.*, 1924, **110**, 83), does not hold at such low concentrations, for it is here that the hydrogen-ion concentration is not negligible when compared with either K_1 or the concentration of the salt (see Britton, J., 1925, **127**, 1909). Calculation of K_2 from the p_H values and $K_1 = 10^{-3\cdot03}$ by means of the general formula (Britton, *loc. cit.*) gives $K_2 = 10^{-5\cdot86}$, which agrees fairly well with the values of K_2 obtained from the p_H values prevailing during the progressive conversion of sodium hydrogen malonate into the normal malonate.

TABLE II.

Magnesium hydrogen malonate.

v.	p_H.	$\kappa \times 10^4$.	Λ,Mg(HM)$_2$.	α,Mg(HM)$_2$.	Λ,MgM.	α,MgM.	α,MgSO$_4$.	α,MgCl$_2$.
25	3·78	25·52	63·8	0·57	34·2	0·31	0·60	0·87
50	3·89	14·15	70·8	0·63	42·4	0·38	0·68	0·90
100	4·00	7·73	77·3	0·69	52·3	0·47	0·75	0·95
200	4·10	4·26	85·7	0·76	63·6	0·57	0·82	0·97
400	4·24	2·30	92·0	0·82	77·4	0·69	0·87	0·97
800	4·58	1·25	100·0	0·90	88·4	0·79	—	—

Zinc hydrogen malonate.

v.	p_H.	$\kappa \times 10^4$.	Λ,Zn(HM)$_2$.	α,Zn(HM)$_2$.	Λ,ZnM.	α,ZnM.	α,ZnSO$_4$.	α,Zn(NO$_3$)$_2$.
25	3·48	21·74	54·3	0·47	14·7	0·13	0·54	0·83
50	3·63	12·39	61·8	0·54	18·5	0·16	0·62	0·87
100	3·73	7·16	71·3	0·62	23·9	0·21	0·70	0·88
200	3·89	4·05	81·0	0·71	31·5	0·27	0·77	0·90
400	4·06	2·34	92·4	0·80	42·7	0·37	0·82	0·91
800	4·24	1·25	100·0	0·87	55·7	0·49	—	—

Copper hydrogen malonate.

v.	p_H.	$p_{Cu^{\cdot\cdot}}$.	$\kappa \times 10^4$.	Λ,Cu(HM)$_2$.	α',Cu(HM)$_2$.	α,Cu(HM)$_2$.	α,CuSO$_4$.	α,CuCl$_2$.
50	2·84	2·75	10·04	50·2	0·18	0·44	0·62	0·87
100	3·00	2·93	6·56	65·6	0·24	0·58	0·73	0·90
200	3·17	3·13	4·14	82·8	0·30	0·73	0·81	0·93
400	3·34	3·31	2·56	102·4	0·39	0·90	0·85	0·95
800	3·57	3·44	1·50	120·0	0·58	1·05	—	—

Copper malonate.

v.	p_H.	$p_{Cu^{\cdot\cdot}}$.	Λ,CuM.	α',CuM.	α,CuM.	$p_{[Cu^{\cdot\cdot}][OH']^2}$.
25	5·54	3·07	—	0·009	—	20·2
50	5·50	3·38	4·05	0·010	0·036	20·6
100	5·48	3·59	4·25	0·010	0·037	20·9
200	5·36	3·79	4·76	0·013	0·042	21·3
400	5·26	3·96	5·75	0·017	0·051	21·7
800	5·19	4·24	7·34	0·019	0·064	22·1

The fact that both magnesium and zinc hydrogen malonates ionise largely as normal salts is evident from a comparison of their degrees of ionisation with those of salts formed from strong acids, which were computed from the conductivities given in the International Critical Tables. Thus it is seen that α,Mg(HM)$_2$ is but slightly lower than α,MgSO$_4$, whilst α,MgSO$_4$ is appreciably smaller than α,MgCl$_2$; the latter inequality is probably to be associated with the slight weakness of sulphuric acid in its second stage of dissociation, K_2 being 2×10^{-2}, and it is also probable that this is the reason why the ionisation of magnesium hydrogen malonate should be comparable with that of magnesium sulphate, the stage of the malonic acid involved having a constant of 2×10^{-3}. Similar remarks apply to the comparison of the zinc salts. The equivalent conductivities of magnesium, zinc, and copper malonates and their conductance ratios, α,MgM, etc., obtained by Riley and Fisher (J., **1929**, 2006) and Ives and Riley (J., **1931**, 1998), are inserted to show that the ionisation of these salts is considerably less than that of the respective hydrogen malonates and, moreover, that, when compared with one another, α,MgM > α,ZnM > α,CuM, which brings out clearly the effect of the strengths of the three metallic bases.

It might be held that consideration should have been given to the possible effect of the subsequent ionisation of the hydromalonate ion and also of any free malonic acid due to hydrolysis. Calculations, based on the p_{H} values and the mobilities of the hydrogen, hydromalonate, and malonate ions, reveal, however, that these effects are relatively small for magnesium hydrogen malonate, slightly greater for the zinc salt, and, owing to the low p_{H} values, comparatively large for copper hydrogen malonate; *e.g.*, in the dilutions investigated, the corrected conductance ratios range from 0·56 to 0·81 for the magnesium salt, compared with 0·57—0·90 as given in Table II, whereas for the zinc salt they vary from 0·44 to 0·77 instead of 0·47 to 0·87.

The low p_{H} values of the copper hydrogen malonate solutions indicate that much of the malonic acid had failed to combine with the weak base, and consequently the conductance ratios, α,Cu(HM)$_2$, can have no real significance. It was found that the potentials set up when a copper electrode was immersed in these solutions were quite steady and reproducible, and col. 3 gives the negative exponent to the base 10 of the copper-ion concentrations calculated therefrom. In the column headed α',Cu(HM)$_2$, the ratios of [Cu$^{\cdot\cdot}$] to salt concentration are much smaller than the corresponding conductance ratios, and evidently indicate the extent to which the unhydrolysed copper hydrogen malonate was ionised. The retention of copper hydroxide in these solutions is seen to be possible from a consideration of the ionic products, $[\mathrm{Cu}^{\cdot\cdot}][\mathrm{OH}']^2$, which are much smaller than the solubility product of copper hydroxide, *viz.*, *ca.* 10^{-20}.

The copper electrode, which was in the form of a small copper plate, was covered with a fine bright deposit of copper from a 10% solution of copper sulphate using a cathodic *C.D.* of about 1 amp./dm.^{2}. When tested in 0·01*M*-copper sulphate, which was taken as 62·9% ionised (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 475), a normal electrode potential (*N*-H = 0) of + 0·341 volt at 18° was obtained. Hydrogen was bubbled through the electrode chamber during the measurement of the *E.M.F.* of the cell, the junction liquid being a saturated solution of potassium chloride, and the normal calomel electrode being the standard half-element.

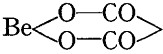
The last section of the table referring to copper malonate solutions shows that the apparent degree of ionisation, α,CuM, of the normal salt is exceedingly small, and once again α',CuM = [Cu$^{\cdot\cdot}$]/[CuM] is still smaller. These solutions, unlike those of the acid salt, were on the verge of precipitating copper hydroxide, as will be seen from the values of $p_{[\mathrm{Cu}^{\cdot\cdot}][\mathrm{OH}']^2}$ given in the last column, although there appears to be a distinct tendency for the product of the ionic concentrations to fall below the solubility product as the dilution of the salt is increased.

DISCUSSION.

The electrometric curves in the fig. show clearly that, although the majority of the bases studied are able to combine with malonic acid as far as its first stage of ionisation is concerned to an extent depending upon the precipitation p_{H} of the base in question (see Britton, J., 1925, **127**, 2110, 2120, 2148; Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 531) and the magnitude of K_1, yet they do not combine with the second stage in a strictly normal way. This is even true of the strongest base investigated, *viz.*, magnesium hydroxide, which does not begin to be precipitated until p_{H} 10·5 is reached; as this is higher than $p_{\mathrm{H}} = p_{K_2} + 2 = 7{\cdot}36$, the acid should have ample scope for complete neutralisation with this base, but Table I shows that the p_{H} of 0·04*M*-magnesium malonate is only 5·85, whereas the p_{H} of 0·04*M*-sodium malonate solution is 9·05. A p_{H} value of 5·85 indicates that the solution contains hydromalonate ions and malonate ions in approximately the ratio 1 : 3, and therefore that the former ions originate from equilibria represented by

$$2\mathrm{MgM} + 2\mathrm{H_2O} \rightleftharpoons 2\mathrm{Mg(OH)HM} \rightleftharpoons \mathrm{Mg(HM)_2} + \mathrm{Mg(OH)_2}.$$

With a weaker base, such as copper hydroxide, combination with the second stage becomes very limited and even the reaction with the first stage is incomplete. This would be expected from the p_H (*ca.* 5) at which copper hydroxide normally begins to be precipitated and K_1 and K_2 of the acid. That some malonic acid fails to combine in a copper hydrogen malonate solution, is evident from its low p_H and also from the fact that the ratio of the cupric-ion concentration to that of the total copper is smaller than the conductance ratio, α. The same is true of the copper malonate solution. Metallic bases that precipitate from still more acidic solutions become increasingly unable to react with the first stage and fail completely with the second stage.

Those bases which form " soluble basic salts " (Britton, J., 1925, **127**, 2120) behave mainly as very weak bases. Examples are beryllium and chromium hydroxide, and their inability to react seems to be related to the fact that 1 equiv. of each of the bases is only able to enter into a loose kind of combination with strong acids. Towards weak acids, this capacity to combine appears to be non-existent. As Table I shows, those products of the little combination that occurs possess low conductivities, for the conductivities of the solutions arise largely from the uncombined acid. As already expressed by Britton (*loc. cit.*), these bases are probably held in solution in a pseudo-colloidal form. This view has been contested by Sidgwick and Lewis (J., 1926, 1287, 2540) on the grounds that basic beryllium salt solutions have not the ordinary properties of colloidal solutions. Moreover, they contend that McBain's views on colloidal electrolytes cannot apply to beryllium malonate solutions, because the viscosities and conductivities are small, and they therefore suggest that beryllium hydroxide must be held in the solutions in a non-polar cyclic form,  $Be{<}\genfrac{}{}{0pt}{}{O{-}CO}{O{-}CO}{>}CH_2$, and that the abnormal constancy of conductivity on dilution is due to the ionisation $2BeM = Be^{\cdot\cdot} + [BeM_2]''$, the complex anion containing the stable 4-covalent beryllium. Such an hypothesis is not in accord with the low p_H value, 3·57, of 0·02*M*-beryllium malonate, which shows that the solution contains a relatively large proportion of hydromalonate to malonate ions, and that more than one-quarter of the very small conductivity is to be attributed to the hydrolysed acid.

A view more in harmony with the observations is to regard the hydrogen malonates as tending to correspond with the normal salts of strong acids and to undergo hydrolysis in the case of weak and very weak bases (*e.g.*, copper and aluminium hydroxides, respectively), *e.g.*, $Cu(HM)_2 + 2xH_2O = xCu(OH)_2 + (1 - x)\ Cu(HM)_2 + 2xH_2M$. The normal malonates hydrolyse in the first place in accordance with the scheme $2H_2O + 2CuM \rightleftharpoons Cu(HM)_2 + Cu(OH)_2$, the hydrogen malonate then hydrolysing still further as shown above. Support for this hypothesis is to be found in the fact that copper malonate solutions are saturated, or nearly so, with respect to copper hydroxide, inasmuch as their ionic products, $[Cu^{\cdot\cdot}][OH']^2$, are comparable with its solubility product. It is probable that some of the copper hydroxide is associated in solution with the hydrogen malonate, thus forming aggregates of basic copper hydrogen malonate which are feebly ionised and are maintained in solution in a highly dispersed state owing to their tendency to ionise (cf. the " solution link " of Thomas and Frieden, *J. Amer. Chem. Soc.*, 1923, **45**, 2522).

Ives and Riley (J., 1931, 1998) observed that the conductance ratios of the malonates and numerous alkylmalonates become smaller in passing through the series magnesium, zinc, nickel, copper. They attempted to explain this, but without success, on the basis of Riley's electronic hypothesis of localised ionic charges; and considered that the greater ionisation of zinc than of copper malonate must be regarded as an anomaly in view of the relative positions of the two metals in the periodic system.

It happens, however, that the order found by Ives and Riley is also that of the precipitation p_H's of the respective bases, that of copper hydroxide being the lowest. Such p_H values impose a limit upon the extent to which a weak acid may react in forming a normal soluble salt. The foregoing work shows that *normal* combination with the first stage of malonic acid is only possible when the precipitation p_H is higher than $p_{K_1} + 2$, and with the second stage when it is higher than $p_{K_2} + 2$. Malonates of such weak bases, however, can be isolated in crystalline form from acid solutions, but on dissolution in water much hydrolysis occurs in which the second stage of ionisation is largely involved.

Ives and Riley regard it as " highly significant " that the secondary dissociation constants of diethyl- and dipropyl-malonic acids (Gane and Ingold, J., 1929, 1691) should be so very much smaller than that of malonic acid or of the other substituted acids of the series. They state that the failure of these constants to affect the dissociation of the malonato-cupriate complex ion is probably the result of the formation of a complete electron grouping round the central copper ion. The fact is that copper hydroxide is much too weak a base to react normally with the second stage of any of these acids, and consequently, it could scarcely be considered that any variation in the already small secondary dissociation constants would be perceptible.

In conclusion, the above work shows that any theory which purports to account for the relatively low dissociation of the salts formed from weak acids and heavy-metal bases must incorporate the dissociation constants of the acids and the strength of the base—the precipitation p_H of the base probably being the closest approach yet possible to the measure of the basic strength. Until these factors have been considered, it is premature to ascribe differences to the localisation of ionic charges, which in the case of salts studied by Riley is without any experimental support.

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UNIVERSITY COLLEGE, EXETER.

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