407. Physicochemical Studies of Complex Formation involving Weak Acids. Part XIV. Complex Formation between Malonates of the Heavy Metals and of Sodium.

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Although the normal malonates of the weaker metallic bases such as ferric, aluminium, and chromium hydroxides have not been isolated in good crystalline form, yet well-defined complex malonates with the alkali metals are known; those formed from tervalent metals (R) are of the constitution $Na_3[R(CH_2{<}C_2O_4)_3]$, and by analogy with the corresponding complex oxalates, they are usually considered to be salts of complex tribasic acids, $H_3[R(CH_2{<}C_2O_4)_3]$. Riley (J., 1929, 1310) prepared the similar sodium cuprimalonate, which he represented as $Na_2[Cu(CH_2{<}C_2O_4)_2(H_2O)_2]$, and by means of the copper electrode he measured the " instability constant " of the anion (J., 1930, 1642).

In the case of the weakest bases, *e.g.*, ferric hydroxide, it happens that aqueous solutions of the bases alone in malonic acid have many properties in common with the complex alkali malonates; for instance, the ferric-ion concentrations of both acid ferric malonate and alkali ferrimalonate solutions are exceedingly small, treatment with potassium thiocyanate yielding but faint colorations, if any. Stronger bases, *e.g.*, magnesium, manganous, and zinc hydroxides, show no such tendencies to complex formation. The present work was therefore carried out to ascertain whether the mode of formation of complexes could be attributed to the weakness of the metallic base, as shown by the p_H value at which it is precipitated under normal conditions, and of the two dissociation constants of malonic acid. We have already shown (Part XIII, this vol., p. 168) that many of the weaker bases are unable to react with the second stage of malonic acid.

This work consists chiefly of two series of electrometric titrations: (*a*) of heavy-metal salts by sodium malonate, and (*b*) of malonic acid solutions containing various amounts of metallic bases by sodium hydroxide. The reactions of the crystalline complex salts in solution have also been compared with those of similar complex malonates formed in the course of the titrations.

It was hoped that the malonate-ion concentrations might be ascertained by means of the electrode $Ag|CH_2(CO_2Ag)_2$, just as Abegg and Schäfer (*Z. anorg. Chem.*, 1905, **45**, 293) used the silver–silver oxalate electrode in their study of complex oxalate solutions. Potentiometric determinations of the solubility product of silver malonate showed, however, that this salt is much too soluble both in water and in complex malonate solutions to be of service.

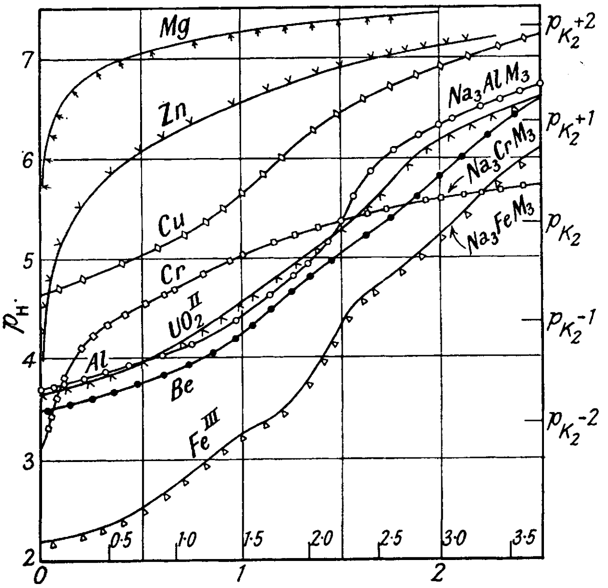
Experimental.

I. *Double Decomposition Reactions between Heavy-metal Salts and Sodium Malonate.*—The reactions occurring during the progressive addition of sodium malonate to dilute solutions of either the chloride or the sulphate of various metals have been studied by measuring the p_H values with the glass electrode. If simple double decomposition takes place, immediately the stoicheiometric amounts of alkali malonate are added the p_H values of the solutions should rise to values corresponding to the presence of free sodium malonate, *viz.*, to $p_H = \frac{1}{2}(p_{K_2} + p_{K_w} + \log c) = 9{\cdot}78 + \frac{1}{2} \log c$, where c is the concentration of the excess of added sodium malonate. Fig. 1 gives the variations in p_H which occur on adding either $0{\cdot}05M$- or $0{\cdot}1M$-sodium malonate to 100 c.c. of each of the solutions given in the first column of Table I; for both $0{\cdot}02M$-magnesium sulphate and 0·02*M*-zinc sulphate, 0·05*M*-sodium malonate was used. The copper, ferric, and aluminium salt reactions were also followed conductometrically at 25°, the specific conductivities corresponding with varying excesses of sodium malonate being recorded in Table I. In Fig. 1 the p_H values are plotted against mols. of sodium malonate per atom of heavy metal.

Titrations of the zinc and copper sulphate solutions with sodium malonate were carried out at 18° with zinc-amalgam and copper electrodes respectively and the normal calomel electrode, saturated solutions of potassium chloride being interposed to eliminate the diffusion potentials in both cases.

The curves in Fig. 1, except those of magnesium, zinc, and chromium, are inflected at a point corresponding with slightly more than the stoicheiometrical amount of sodium malonate. Comparison of the p_H values thereafter set up with those of $p_H = p_{K_2}$ of malonic acid, given at the right of Fig. 1, shows that some of the hydrogen ions of the second stage of dissociation of malonic acid could not have reacted with the heavy-metal bases. The curves for the two strongest bases studied, *viz.*, magnesium and zinc, indicate, however, p_H values in the region of $p_{K_2} + 2$, showing that in these cases the concentrations of hydromalonate ions were exceedingly small. The data also show that in the presence of excess of sodium malonate the zinc and copper solutions were on the verge of precipitating their respective hydroxides; for computations based on the potentials of the zinc-amalgam electrode and the p_H values led to ionic products, $[Zn^{\bullet\bullet}][OH']^2$, between 10^{-18} and 10^{-17}, which is of the same order as that of the solubility product, 1×10^{-17} (Britton and Robinson, *Trans. Faraday Soc.*, 1932, **28**, 542). Table I also shows that the ionic products $[Cu^{\bullet\bullet}][OH']^2$ lie between $10^{-19\cdot5}$ and 10^{-20}. Calculation from the p_H values, measured with the quinhydrone electrode, during the precipitation of the basic salt $CuSO_4,3Cu(OH)_2$ on adding 0·1*N*-sodium hydroxide to 0·02*M*-copper sulphate led to an average value of $10^{-20\cdot2}$ for the solubility product, $[Cu^{\bullet\bullet}][OH']^2$, the extremes being $10^{-20\cdot34}$ and $10^{-19\cdot95}$ (see also *idem, ibid.*, p. 541).

FIG. 1.



Sodium malonate, mols. per atom of tervalent metals (upper legend).
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The failure of sodium malonate to precipitate a heavy-metal base, even though the p_H at which the base is normally precipitated may be exceeded, as in the ferric, aluminium, and copper salt titrations, may be due to the retention of the hydroxide in solution as a basic hydromalonate, stabilised in some way by the alkali malonate, or else to the formation of complex anions. Thus, if we assume with Riley that cuprimalonate ions, CuM_2'', are formed when an excess of sodium malonate is added to copper sulphate, the copper-electrode potentials lead to constant values of the instability constant, *viz.*, $\overline{K} = [Cu^{\bullet\bullet}][M'']^2/[CuM_2'']$ (recorded as $-\log\overline{K}$

TABLE I.

0·05*M*-Na_2M, c.c.		40	60	80	100	120	140
Na_2M, excess, mols.		0	0·5	1·0	1·5	2·0	2·5
0·02*M*-$CuSO_4$	p_H	5·65	6·45	6·91	7·16	7·26	7·32
	[HM′]/[M″]	0·56	0·09	0·03	0·02	0·01	0·01
	HM	—	0·98	0·98	0·99	0·99	0·99
	$p_{Cu^{\cdot}}$	3·09	4·16	5·03	5·59	6·07	6·41
	$p_{[Cu^{\cdot\cdot}][OH']^2}$	20·07	19·54	19·49	19·55	19·83	20·05
	p_K	—	—	—	8·14	8·09	8·13
	$\kappa_{obs.} \times 10^3$, mho	3·27	3·72	4·22	4·71	4·97	5·47
	$\kappa_{calc.} \times 10^3$,,	3·20	3·85	4·42	4·95	5·30	5·75
	$\kappa_{diff.} \times 10^3$,,	+0·05	−0·13	−0·20	−0·24	−0·33	−0·28
0·02*M*-$BeSO_4$	p_H	4·26	5·03	5·80	6·59	6·97	7·19
	[HM′]/[M″]	13·8	2·34	0·40	0·06	0·03	0·02
	HM	—	0·73	0·84	0·95	0·93	0·98
0·02*M*-UO_2Cl_2	p_H	4·55	5·28	6·22	6·72	6·93	7·05
	[HM′]/[M″]	7·01	1·32	0·24	0·048	0·030	0·022
	HM	—	0·80	0·89	0·96	0·97	0·97
0·10*M*-Na_2M, c.c.		30	40	50	60	70	80
Na_2M, excess, mols. (per atom of Al, Cr, Fe)		0	1	2	3	4	5
0·02*M*-$Al_2(SO_4)_3$	p_H	4·45	4·92	5·83	6·32	6·59	6·79
	[HM′]/[M″]	8·91	3·02	0·372	0·120	0·065	0·041
	HM	—	1·20	1·34	1·41	1·44	1·45
	$\kappa_{obs.} \times 10^3$, mho	4·50	4·85	5·32	5·89	6·46	7·05
	$\kappa_{calc.} \times 10^3$,,	4·50	5·50	6·53	7·30	7·95	8·60
	$\kappa_{diff.} \times 10^3$,,	0·0	−0·65	−1·21	−1·41	−1·49	−1·55
0·02*M*-$CrCl_3$	p_H	5·02	5·28	5·46	5·61	5·73	5·80
	[HM′]/[M″]	2·40	1·32	0·87	0·62	0·47	0·40
	HM	—	1·30	1·17	1·14	1·12	1·08
0·02*M*-$FeCl_3$	p_H	3·23	3·75	4·67	5·25	5·85	6·20
	[HM′]/[M″]	148	44·7	5·37	1·41	0·36	0·16
	HM	—	1·02	0·77	0·88	1·20	1·31
	$\kappa_{obs.} \times 10^3$, mho	5·30	5·30	5·66	6·19	6·70	7·20
	$\kappa_{calc.} \times 10^3$,,	5·13	6·17	6·99	7·75	8·36	8·91
	$\kappa_{diff.} \times 10^3$,,	+0·17	−0·87	−1·33	−1·56	−1·66	−1·77

or p_K), which are in accord with those found by Riley; [M″], the malonate-ion concentration, refers to the concentration of sodium malonate in excess of that required to form CuM_2'', whereas [CuM_2''] is taken equal to the total copper concentration, all the copper being assumed to have entered the complex anion. Similar calculations made for the zinc solutions, however, did not give constant values for the instability of the hypothetical ZnM_2'', and these ranged from $10^{-7 \cdot 09}$ to $10^{-5 \cdot 69}$ as the excess of sodium malonate was increased. This divergence might have been caused by failure of the zinc-amalgam electrode to behave in a reversible manner, although the potentials set up were reproducible.

Riley found that the instability constants of the cupri-diethyl- and -dipropyl-malonate ions were about 1000 times greater than that of the cuprimalonate ion. Moreover, the addition of the corresponding sodium malonates to copper sulphate solutions resulted in slight precipitation. According to Gane and Ingold (J., 1929, 1691), these substituted acids ionise appreciably more in their first stage than does malonic acid, but their second stages of ionisation are about 100 times weaker, $\overline{K}_2$ being of the order of 10^{-8}. Their alkali salts are therefore appreciably more alkaline, and this, coupled with the stronger first stages, will either lead to precipitation of copper hydroxide from copper sulphate solutions or else cause the base to be retained in solution in an unstable manner.

An attempt was made to calculate the composition of the heavy-metal malonate present in these sodium malonate solutions from the p_H values, on the assumption that the weaker bases are able to react with only the first stage of malonic acid. Thus with copper sulphate, in consequence of the weakness of copper hydroxide and of the second-stage dissociation of malonic acid, the following reaction might take place: $H_2O + CuSO_4 + Na_2M \longrightarrow Cu(OH)(HM) + Na_2SO_4$; and similarly for aluminium sulphate: $3H_2O + Al_2(SO_4)_3 + 3Na_2M \longrightarrow Al_2(OH)_3(HM)_3 + 3Na_2SO_4$. Hence, when equivalent quantities of sodium malonate are added, there exist in the solutions what are virtually basic hydromalonates, probably in the state of very feebly ionised micelles. It is possible that the hydromalonate might react further with the metallic bases, especially if the basic aggregates are not in the state of true solution. Of a number, y, of mols. of sodium malonate added in excess per heavy metal atom, suppose a number, x, reacted in accordance with the equation $x\mathrm{Na_2M} + x\mathrm{H_2O} + \mathrm{Cu(OH)(HM)} \longrightarrow 2x\mathrm{NaHM} + \mathrm{Cu(OH)}_{1+x}\mathrm{(HM)}_{1-x}$, then $[\mathrm{NaHM}]/[\mathrm{Na_2M}] = 2x/(y - x) = [\mathrm{HM}'/[\mathrm{M}'']$, if the ionisation of the sodium malonate and hydromalonate is assumed to be complete. This ratio can be calculated from the expression $p_{\mathrm{H}} = p_{K_2} + \log [\mathrm{HM}']/[\mathrm{M}'']$, K_2 being $10^{-5 \cdot 4}$. In Table I the values of $[\mathrm{HM}']/[\mathrm{M}'']$ are given for the various excess amounts of sodium malonate added (per atom of heavy metal), from which HM, the amount of radical combined with each molecule of the heavy metal base existing in solution, has been obtained. Table I shows that, whilst the heavy-metal salts are appreciably basic in the presence of small amounts of sodium malonate, they become less and less basic as the excess of alkali malonate is increased. This is true of copper, beryllium, and uranium, the final complexes of which might be represented as $\mathrm{Cu(OH)_{1 \cdot 01}(HM)_{0 \cdot 99}}$, $\mathrm{Be(M)_{1 \cdot 02}(HM)_{0 \cdot 98}}$, and $\mathrm{UO_2(OH)_{1 \cdot 03}(HM)_{0 \cdot 97}}$. Similarly, $\mathrm{Al(OH)_{1 \cdot 54}(HM)_{1 \cdot 46}}$ and $\mathrm{Fe(OH)_{1 \cdot 65}(HM)_{1 \cdot 35}}$ refer to the weaker bases. Chromium, however, becomes increasingly basic. The specific conductivities set up with various excesses of sodium malonate are recorded in Table I as $\kappa_{\mathrm{obs.}}$, and are compared with the calculated conductivities, $\kappa_{\mathrm{calc.}}$. The latter are based on the assumptions that simple metathesis occurs, and that the conductivity of the solutions is due to the sodium malonate in excess of the amount required to form the heavy-metal malonate, together with the equivalent amount of sodium sulphate or chloride simultaneously formed, the contribution of the heavy malonate not being considered. The very small differences between the observed and calculated conductivities, $\kappa_{\mathrm{diff.}}$, show that this view is sensibly correct in the case of copper and aluminium, the larger discrepancy in the case of iron being probably caused by a little hydrolysed malonic acid. It would appear, therefore, that the heavy-metal basic hydromalonates existing in solution are but slightly ionised. With excess of sodium malonate the calculated conductivities are seen to be higher than the observed, the differences being greater for aluminium and iron than for copper. These diminished conductivities are evidently caused by the retention of the heavy metals in solution. In certain reactions hydromalonate ions were present: they could have but little effect on the conductivity.

II. *Electrometric Titrations with Sodium Hydroxide of Malonic Acid Solutions of Typical Bases.*—Figs. 2 and 3 illustrate the variations in p_{H} taking place when malonic acid solutions, previously neutralised with a heavy-metal base to the extent indicated by the first point on each curve, are titrated with $0 \cdot 1N$-sodium hydroxide. The curves have been constructed so as to emphasise the changes in p_{H} during the process of (*a*) neutralisation of the malonic acid, the abscissa representing the total percentage of neutralisation, *i.e.*, with both heavy-metal base and sodium hydroxide, and (*b*) precipitation, the abscissa giving the percentage amount of the stoicheiometrical quantity of sodium hydroxide required to precipitate the metallic hydroxide from malonates of the heavy metals after the malonic acid has been completely neutralised. The curves are those of glass-electrode titrations of solutions, details of which are recorded in Table II; the arrows on them denote the incidence of precipitation, and the p_{H} values at which it occurs are compared in Table II with those at which the respective bases are usually precipitated. Except for magnesium and zinc hydroxides, the precipitation p_{H} values for malonate solutions are considerably higher, showing that the metal-ion concentrations of the malonate solutions of the weak bases are exceedingly low, owing either to the existence of feebly ionised basic hydromalonates or to the bases being present in complex malonate ions. Potential measurements have already demonstrated the low concentrations of copper ions, and Table II shows that the greater the ratio of free malonic acid to copper malonate the higher is the p_{H} value to be reached before precipitation ensues. A similar effect was observed with acid ferric malonate solutions; *e.g.*, the ferric hydromalonate solution, the titration curve of which is illustrated by Curve *K* (Fig. 2), gave but a slight indication of ferric ions with potassium thiocyanate. On the addition of alkali the concentration rapidly diminished, so much so that when the solute acquired the composition represented by $\mathrm{Na_3FeM_3}$, the ferric ions had entirely disappeared.

The broken lines in Figs. 2 and 3 represent the neutralisation of malonic acid with sodium hydroxide. It will be seen that during the second stage of the neutralisation of solutions of malonic acid containing the metallic bases, the curves corresponding to the weakest bases, *e.g.*, ferric and aluminium hydroxides, depart most from the broken curves. Incidentally, the conductivities were almost equal to those which would have been caused by the sodium malonate formed. It appears, therefore, that the weak bases must have been present in the form of very feebly ionised basic hydromalonate complexes. Hence the changes in p_{H} during the neutralisations shown in Figs. 2 and 3 result from the neutralisation of any free malonic acid that may have been present, and also from the gradual decomposition of the basic complexes.

In view of the low metal-ion concentrations of malonic acid solutions of weak metallic bases, it might, for instance, be held that those solutions in which the solutes correspond with the hydromalonates of copper, aluminium, ferric iron, and chromium contain, respectively, the complex acids, H_2CuM_2, H_3AlM_3, H_3FeM_3, and H_3CrM_3, so that on adding 1 equiv. of sodium hydroxide (per mol. of malonic acid), the corresponding complex sodium salts are formed. As shown by Figs. 2 and 3, the variations in p_H during the neutralisation of the acid solutions give no evidence of any such complex acids being present. The p_H value of the solution in which sodium cuprimalonate was formed was 7; aluminimalonate, 7; ferrimalonate, 5·6; chromimalonate, 5·45. Only negligible concentrations of hydromalonate ions were present in the first two solutions, whilst the low p_H values of the last two reveal that the salts were decomposed somewhat, giving malonate and hydromalonate ions. Figs. 2 and 3 also illustrate the addition of sodium hydroxide and hydrochloric acid to solutions of sodium aluminimalonate (curves *a* and *b* respectively) and ferrimalonate (curves *M* and *N* respectively), the initial solutions having been prepared from the crystalline complex malonates. It will be seen that the p_H values of these solutions are almost the same as those set up during the titrations of the acid solutions, and moreover, that on treatment with alkali the salts underwent similar attack resulting in precipitation. Curves *N* and *b* show that the complex malonates are decomposed by hydrochloric acid.

FIG. 2.

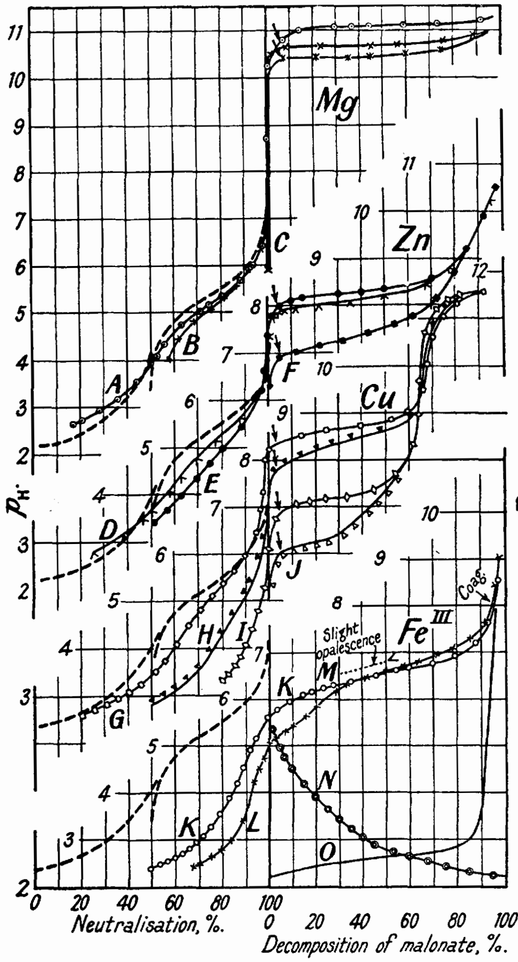

FIG. 3.

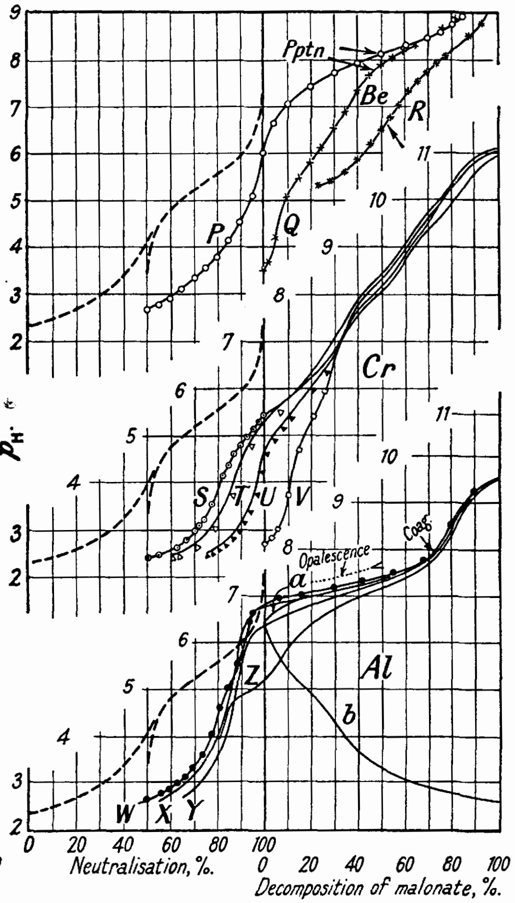

TABLE II.

Curve.	Solution titrated.	Pptn. began at p_H.	Normal pptn. p_H.
A	100 C.c. of 0·04*M*-$CH_2(CO_2H)_2$ + 17·0% $Mg(OH)_2$ ...	10·8	10·5
B	,, ,, ,, ,, 57·5% ,, ...	10·6	10·5
C	,, ,, ,, ,, 100% ,, ...	10·4	10·5
D	,, ,, ,, ,, 25% $Zn(OH)_2$ ...	7·9	*ca.* 7
E	,, ,, ,, ,, 50% ,, ...	8·0	,, 7
F	,, ,, ,, ,, 100% ,, ...	7·0	,, 7
G	,, ,, ,, ,, 20% $Cu(OH)_2$ ...	8·3	5·4
H	,, ,, ,, ,, 50% ,, ...	7·8	5·4
I	,, ,, ,, ,, 80% ,, ...	6·9	5·4
J	,, ,, ,, ,, 100% ,, ...	6·1	5·4
K	100 C.c. of 0·024*M*-$CH_2(CO_2H)_2$ + 50% $Fe(OH)_3$ ...	6·5—8·0	2 *
L	100 C.c. of 0·043*M*-$CH_2(CO_2H)_2$ + 67·7% $Fe(OH)_3$ ...	6·5—8·0	2
M	100 C.c. of 0·0133*M*-Na_3FeM_3 †	6·5—8·0	2
P	100 C.c. of 0·02*M*-$CH_2(CO_2H)_2$ + 50% $Be(OH)_2$ ...	8·2	5·7
Q	,, ,, ,, ,, 100% ,, ...	7·8	5·7
R	,, ,, ,, ,, 130% ,, ‡ ...	6·6	5·7
S	,, ,, ,, ,, 50% $Cr(OH)_3$ ...	No. pptn.	5·3
T	,, ,, ,, ,, 60% ,, ...	,,	5·3
U	,, ,, ,, ,, 75% ,, ...	,,	5·3
V	,, ,, ,, ,, 100% ,, ...	,,	5·3
W	,, ,, ,, ,, 45% $Al(OH)_3$ ...	7·5—8·0	4·1
X	,, ,, ,, ,, 52·8% ,, ...	7·5—8·0	4·1
Y	,, ,, ,, ,, 64·5% ,, ...	7·5—8·0	4·1
Z	,, ,, ,, ,, 81·7% ,, ...	7·5—8·0	4·1

* Cf. curve *O* : 0·02*M*-$FeCl_3$ + 0·1*N*-NaOH.

† Curve *N* represents the titration of this solution with 0·1*N*-HCl.

‡ *I.e.*, BeM,0·3$Be(OH)_2$.

Alkali chromimalonates, prepared by actual crystallisation, are, however, much more stable than either the alumini- or the ferri-malonate. On dissolution in water the chromimalonates give appreciably higher p_H values than when they are prepared by metathesis in solution, and are also much more resistant to alkali. Thus 0·0067*M*-potassium chromimalonate (K_3CrM_3) has a p_H of 6·20, and on addition of a drop of alkali the solution becomes alkaline, but on standing, decomposition occurs and the p_H falls to 7·5.

With strong acids, both beryllium and chromium hydroxides form salts in which 1 equiv. of the acid appears to be more loosely bound than the remaining 1 and 2 equivs. respectively. With this peculiarity is associated the fact that the salts of the two bases resist precipitation with alkali until this loosely bound acid has been removed.

In each of the beryllium titrations, precipitation did not begin until the solute had the composition represented by BeM,$Be(OH)_2$. From the chromium solutions, precipitation did not occur, although it could be effected from the alkaline solutions by shaking with potassium chloride or by prolonged boiling. The acid solutions were deep mauve, but as alkali was added to bring them to *ca.* p_H 7 they became green, and thereafter developed the characteristic bright green colour of alkaline chromium solutions. Curve *V*, that of so-called chromium malonate, shows, by comparison with the broken curve, that about one-third of the malonic acid was either free or loosely combined, and that the basic portion, CrM(OH), could scarcely have been ionised, for it exerted very little, if any, buffering action. The acid–malonate curves, *S,T,U*, are largely those of the neutralisation of uncombined malonic acid, and it is significant that they tend to merge at about p_H 7, corresponding to the basic salt, Cr(OH)M. The decomposition of this basic malonate is difficult, as is seen from the increasing alkalinity of the solution during the addition of 35—80% of the stoicheiometrical amount of alkali required to effect its decomposition.

Uranyl malonate, $UO_2(CH_2C_2O_4)_2,3H_2O$ (Found : U, 55·8; loss at 100°, 8·04. Calc. : U, 55·87; H_2O, 8·44%) was prepared by Courtois' method (*Compt. rend.*, 1924, **158**, 1689), and the decomposition of its solution by alkali investigated, together with that of the solution of the double salt Na_2M,UO_2M, prepared by dissolving uranyl malonate in sodium malonate by the aid of heat on the water-bath. The large increase in the solubility of uranyl malonate in the presence of alkali malonates is noteworthy. The decomposition of these solutions by alkali is similar to that of the corresponding aluminium and iron malonate solutions, and hence the p_H curves were omitted from the diagrams.

III. *Equivalent Conductivities of Complex Malonates.*—In Table III the equivalent conductivities of potassium chromimalonate are compared with those of potassium malonate, whilst

Table III.

v, litres	32	64	128	256	512	1024	$\Lambda_{1024} - \Lambda_{32}$.
$\frac{1}{3}K_3Cr(CH_2C_2O_4)_3$	99·8	109·2	115·4	123·4	127·1	133·6	33·8
$\frac{1}{2}K_2CH_2C_2O_4$	112·5	117·6	123·1	125·0	126·9	128·0	15·5
$\frac{1}{3}Na_3Al(CH_2C_2O_4)_3$	80·0	87·7	92·0	97·2	105·0	117·7	37·7
$\frac{1}{3}Na_3Fe(CH_2C_2O_4)_3$	72·6	76·7	82·9	87·7	92·9	98·3	25·7
$\frac{1}{2}Na_2CH_2C_2O_4$	98·2	102·4	105·5	109·0	112·0	114·0	15·8

those of sodium alumini- and ferri-malonate are compared with the conductivities of sodium malonate. The last column gives the differences $\Lambda_{1024} - \Lambda_{32}$. These might be considered, according to the Ostwald–Walden rule, to indicate the tribasicity of the chromi- and ferri-malonate ions, but the value for the aluminium complex, 37·7, is somewhat higher than would be expected if this were a stable salt of a tribasic acid. The observed conductivities of these solutions were reproducible when freshly prepared solutions were used; after standing at, or after boiling and cooling to, 25°, they increased but very slightly. This was unexpected in the case of sodium ferrimalonate in view of the colour changes which it undergoes: solutions more concentrated than $N/64$ are pale green; $N/128$-solution is green immediately after preparation but becomes pale yellow in a few hours, whilst more dilute solutions become yellow almost immediately, the rapidity of the change and the relative intensity of the colour increasing with dilution. On boiling, the pale green $N/32$-solution becomes deep reddish-brown, although the $N/512$- and the $N/1024$-solution suffer scarcely any further change.

Potassium chromimalonate, $K_3Cr(CH_2C_2O_4)_3,3H_2O$, was prepared by heating 15 g. of potassium dichromate with 35 g. of malonic acid in 200 c.c. of water on a water-bath, then adding sufficient potassium carbonate to neutralise the malonic acid. Crystallisation was effected by adding 30 c.c. of alcohol and 5 c.c. of ether to the hot solution (about 100 c.c.), and the dark green crystals were washed with alcohol and ether and dried in air (Found: Cr, 10·06; K, 22·01. Calc.: Cr, 9·83; K, 22·12%) (compare Jaeger, *Rec. trav. chim.*, 1919, **38**, 294; Lapraik, *J. pr. Chem.*, 1893, **47**, 321).

Sodium aluminimalonate, $Na_3Al(CH_2C_2O_4)_3$, was obtained as white rhombic crystals by evaporating on a water-bath a solution containing 10 g. of aluminium chloride and 34 g. of sodium malonate, sufficient malonic acid having been included to prevent the separation of basic salt (Found: Al, 6·81; Na, 16·91. Calc.: Al, 6·72; Na, 17·16%).

Sodium ferrimalonate, $Na_3Fe(CH_2C_2O_4)_3$, was prepared as green rhombic crystals by the methods of Matsui (*J. Coll. Sci. Tokyo*, 1908, **28**, ii, 1) and Scholz (*Monatsh.*, 1908, **29**, 439). Both methods yielded the unhydrated salt (Found: Fe, 13·06; Na, 15·85. Calc.: Fe, 12·99; Na, 16·02%), and thus there is no evidence that the salt is dihydrated, as claimed by Scholz.

IV. *Solubility Product of Silver Malonate.*—The solubility product, $[Ag^{\cdot}]^2[M'']$, was determined by means of the combination

$$Ag|50\text{ c.c. of }0{\cdot}1M\text{-}AgNO_3 + x\text{ c.c. of }0{\cdot}05M\text{-sodium malonate }|\text{Satd. }KNO_3|N\text{-Calomel},$$

the contents of the left-hand electrode vessel having been mechanically shaken at 18° until equilibrium was reached. The data obtained are given below, the total concentrations of malonate ions having been calculated from the excess of sodium malonate present and the malonate ions originating from the dissolved silver malonate, these being equal to one-half of $[Ag^{\cdot}]$. The validity of this method of calculating the malonate-ion concentrations follows from the p_H values, *ca.* 7, of the solutions when excess of sodium malonate had been added.

x.	*E.M.F.*	$p_{Ag^{\cdot}}$.	$[M''] \times 10^4$.	$[Ag^{\cdot}]^2[M''] \times 10^7$.	x.	*E.M.F.*	$p_{Ag^{\cdot}}$.	$[M''] \times 10^4$.	$[Ag^{\cdot}]^2[M''] \times 10^7$.
50	0·3928	2·19	—	1·40	65	0·3817	2·36	59·4	1·47
55	0·3902	2·22	22·25	1·44	70	0·3793	2·42	75·0	1·34
60	0·3831	2·32	41·6	1·48	75	0·3774	2·45	88·5	1·32

Mean: $[Ag^{\cdot}]^2[M''] = 1{\cdot}41 \times 10^{-7}$.

Hence it follows that the solubility of silver malonate in water is $[1{\cdot}41 \times 10^{-7}/4]^{1/3} = 3{\cdot}28 \times 10^{-3}$ g.-mol./l. This is greater than was found by Massol (*Ann. Chim. Phys.*, 1894, **1**, 196), *viz.*, $1{\cdot}79 \times 10^{-3}$ g.-mol./l.

Summary.

1. When sodium malonate is added to solutions of heavy-metal salts, the bases appear to be held in solution as feebly ionised basic hydromalonates, but these, with increasing excess of alkali malonate, probably become converted into complex anions.

2. Malonic acid solutions of heavy-metal bases, although complex in nature, do not contain definite complex acids.
3. Several complex malonates have been isolated and their solutions investigated.
4. The solubility product of silver malonate at 18° is $1{\cdot}41 \times 10^{-7}$.

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