XXVII.—*Compounds of Iron, Manganese, Lead and the Metals of Group II.*

By Spencer Umfreville Pickering.

In a previous communication (T., 1915, **107**, 942) it has been shown that cobalt and nickel form metallo-compounds analogous to those of copper; a similar examination is being made in the case of other metals, and the present communication deals with manganese, iron, lead, and all the elements of the periodic group II.

To establish the mere fact of the formation of such compounds, it has not been necessary to examine every case in detail; the existence of a metallo-compound may be first indicated by ascertaining whether alkalis react with an organic salt of the metal in question to form a soluble compound, instead of an insoluble basic salt, and then established by proving that the organic salts of the metal exist in two different forms, one a very sparingly soluble crystalline compound, the normal salt, the other a much more soluble salt of the same composition, non-crystalline, and generally obtained in the form of an emulsion, this soluble form changing spontaneously into the normal salt. The methods of preparation adopted were by (1) dissolving the hydroxide or carbonate in the acid, and precipitating by alcohol, the acids used

being tartaric, malic and citric; in some cases, also, racemic: (2) mixing solutions of the chloride, or other inorganic salt, of the metal with a potassium salt of the acid in question. Analysis of the product was not necessary in every case, since in many instances it had already been obtained and analysed by former investigators; * indeed, if the product of such reactions is found to contain no acid, no potassium, and no chlorine, it must necessarily consist either of the normal salt or of a substance differing from this only by the elements of water, and, as already pointed out (*loc. cit.*, p. 945), determining the water present leads to no useful results.

Action of Alkalis.

Those metallo-compounds, which corresponded with, and are convertible into, the normal salts, have been represented as being derived from the latter by the introduction of water into the molecule, and the union of the metal, which becomes quadrivalent, with one of the carbon atoms, as in I.
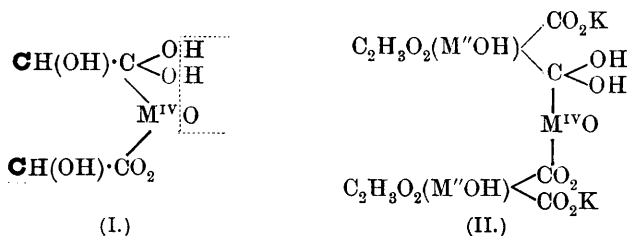
* TARTRATES.—*Iron*, Dulk, *Annalen*, 1832, **2**, 62 ; Méhu, *Jahresber.*, 1873, 569.   *Manganese*—Pfaff, *J. Chem. Phys.*, 1811, **4**, 377.   *Lead*—Abegg, "*Handbuch d. anorg. Chem.*," Erdmann, *Annalen*, 1837, **21**, 14. *Magnesium*—Mayer, *Annalen*, 1857, **101**, 166 ; Dulk, *Annalen*, 1832, **2**, 59 ; Makovetzki, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 769 ; Johnsen, *Jahrb. Min.*, 1907, **23**, 246.   *Zinc*—Zchiff, *Annalen*, 1863, **125**, 146 ; Frisch, *Jahresber.*, 1866, 400 ; Cantoni and Zachoder, *Bull, Soc. chim.*, 1905, [iii], **33**, 747 ; Werther, *J. pr. Chem.*, 1844, **32**, 385. *Cadmium*—Stromeyer, *Schw. J.*, 1818, **22**, 362. *Mercury* —Rose, *Ann. Phys. Chem.*, 1841, [ii], **53**, 127.   *Calcium*—Cantoni and Zachoder, *loc. cit.* ; Herz and Muhs, *Ber.*, 1903, **36**, 3716 ; Anschütz, *Annalen*, 1884, **226**, 197 ; Dulk, *J. Chem. Phys.*, 1832, **64**, 180, 193 ; Neumann, *ibid.*, p. 206 ; Eppler, *Zeitsch. Kryst. Min.*, 1899, **30**, 134.   *Strontium*—Cantoni and Zachoder, *Bull. Soc. chim.*, 1904, [iii], **31**, 1122 ; Marignac, *Ann. Min.*, 1859, [v], **15**, 280 ; Dulk and Neumann, *J. Chem. Phys.*, 1832, **64**, 180, 193 ; Scacchi, *Ann. Phys. Chem.*, 1860, [ii], **109**, 373.   *Barium*—Cantoni and Zachoder, *loc. cit.* ; Hertz and Muhs., *loc. cit.*

RACEMATES.—*Iron* and *Manganese*. Fresenius, *Annalen*, 1842, **41**, 1.

MALATES.—*Iron*, Rosenthaler and Siebeck, *Arch. Pharm.*, 1908, **246**, 55. *Manganese*—Traube, *Zeitsch. Kryst. Min.*, 1899, **31**, 60.   *Lead*—Otto, *Annalen*, 1863, **127**, 177.   *Magnesium*—Traube, *loc. cit.*, p. 160 ; Hagen, *Annalen*, 1841, **38**, 265 ; Liebig, *Annalen*, 1833, **5**, 148.   *Zinc*—Traube, *loc. cit.*, and *Jahrb. Min., Beil. Bd.*, 1898, **11**, 627 ; Liebig, *loc. cit.*; Hagen, *loc, cit.*   *Calcium*—Traube, Liebig, and Hagen, *loc. cit.* ; Iwig and Hecht. *Annalen*, 1886, **233**, 168. *Strontium*—Traube and Hagen, *loc. cit.*   *Barium*— Liebig, *Annalen*, 1833, **5**, 149 ; 1838, **26**, 136.

CITRATES —*Iron*, Heldt, *Annalen*, 1843, **47**, 157, Kämmerer, *Annalen*, 1868, **148**, 294 ; 1873, **170**, 176 ; Siboni, 1906, **1**, 65. *Manganese*—Heldt and Kämmerer, *loc. cit.* ; Power, *Pharm. J.*, 1901, **13**, 135. *Lead, Magnesium, Zinc, Cadmium, Calcium, Strontium, Barium*, Helt and Kämmerer, *loc. cit.*

In many instances these investigations bear ample evidence, at any rate in the light of the present work, that the substance in question must exist in two different forms.

$$\mathbf{C}H(OH)\cdot C\!\!<^{O\!\vdots H}_{O\!\vdots H}$$
$$M^{IV}\!\vdots O$$
$$\mathbf{C}H(OH)\cdot CO_2$$

(I.)

$$C_2H_3O_2(M''OH)\!\!<^{CO_2K}_{C<^{OH}_{OH}}$$
$$M^{IV}O$$
$$C_2H_3O_2(M''OH)\!\!<^{CO_2}_{CO_2K}$$

(II.)

In that case, the action of potassium hydroxide should produce an analogous substance, with KHO instead of HHO, the alkali reacting with the organic salt in the proportions of $K:M''$; also, the compound produced should be slightly alkaline. Neither of these results obtained in the case of copper tartrate (T., 1911, **99**, 169); the proportion of alkali absorbed by the tartrate before any alkalinity appeared (and it appeared quite sharply) gave the ratio $4K:3Cu$, and the compound produced contained the metals in the ratio $2K:3Cu$, the equation for its formation being

$$3C_4H_4O_6Cu + 4KOH = (C_8H_4O_{12}Cu_2)CuK_2 + C_4H_4O_6K_2.$$
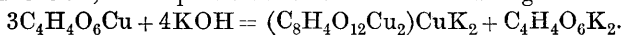
By the addition of alcohol this substance was precipitated; it differed considerably in physical properties from the more simple cupri-compounds, and the formula II was suggested for it.

It appears now, however, that the behaviour of copper is exceptional, in that the first stage of the reaction is suppressed, and that a secondary product alone is obtained. The results on adding alkali to seven other tartrates show that the ratio of alkali to metal is generally $1:1$, and that the product, although neutral to phenolphthalein, is really slightly alkaline, as evidenced by its action on litmus, even when the addition of alkali does not exceed about 0.1 $KOH:M''$. The results, given below, show a mean of $0.99:1$ for the ratio $KOH:M''$ on the first appearance of alkalinity towards phenolphthalein, manganese giving lower results, which are omitted. Such low results might be expected in some cases, owing to the slight alkalinity of the product.

Ratio of $K:M$ *at Alkalinity to Phenolphthalein.*

	Tartrate.		Citrate.	
	First.	Full.	First.	Full.
Copper	1·34	1·34	1·92	1·02
Cobalt	1·00	1·09	—	—
Nickel	0·99	1·23	(0·24)	(0·89)
Manganese	(0·68)	1·07	0·72	0·98
Iron	0·99	1·34	0·90	0·93
Zinc	1·08	1·24	0·91	0·97
Cadmium	0·87	0·97	0·88	1·00
Lead	1·03	1·27	0·77	0·98
Mean	0·99	—	—	0·97

In all these cases, unlike that of copper, the initial alkalinity is not sharply marked, and increases only very gradually with further additions of alkali; full alkalinity is reached, so far as it is possible to judge, only with the proportions indicated in the second column. In four of the cases the latter values evidently approximate to that obtained with copper $(3M'':4K)$, indicating the formation of the secondary product II. With cobalt, manganese and cadmium the reaction does not appear to proceed beyond the first stage. With cobalt, however, the second product has been isolated by digesting the tartrate with potassium hydroxide and precipitating with alcohol (*loc. cit.*, p. 952); it was also obtained in an impure condition in the case of nickel. Attempts to isolate it in the other cases have not been made.

Owing to the very sparing solubility of the tartrates themselves, the above determinations were made by taking solutions of an inorganic salt of the metal mixed with excess of potassium tartrate; from 4 to 12 equivalents of the latter were necessary to prevent the precipitation of a basic salt. With nickel, a steely-grey cloudiness appears just before alkalinity is reached; with cadmium and lead, a precipitate is formed, which redissolves some time before alkalinity is attained. In the case of iron, the liquid on the addition of alkali gradually becomes of a dark bottle-green colour, 500 to 1000 times more intense than that of iron as ferrous sulphate; with more alkali this colour disappears nearly entirely, but with still more alkali it reappears, being darker than before, the liquid gradually becoming opaque, and then suddenly forming a flocculent precipitate of greenish-black ferrous hydroxide. Time plays a conspicuous part in these changes; if excess of alkali is added in the first instance, a darkening of the liquid occurs, then a loss of colour, followed by a more intense darkening, and subsequent precipitation. These liquids if exposed to the air oxidise to form the brownish-yellow ferritartrate.

Solid ferrous tartrate or potassium ferrous tartrate treated with concentrated potassium or sodium hydroxide solution dissolves entirely to form a liquid which is nearly colourless at first, although it rapidly becomes green. After some time a dirty white, viscid solid separates, or can be precipitated at once by alcohol (T., 1913, **103**, 1366); whether this is the compound I or II has not been determined; it is very oxidisable, and on attempting to purify it by dissolving in water, and reprecipitating it with alcohol, it always decomposes. An analogous compound is obtained in the case of manganous tartrate, but it is still more unstable.

The colour changes in the case of the ferro-compounds are certainly obscure. In the communication referred to above, the

absence of colour in the freshly-prepared sodium ferrotartrate, and the fact that no iron anion appeared on the electrolysis of it, led to the conclusion that ferrous iron did not form ferro-compounds analogous to the cupri-compounds. This conclusion must be withdrawn, for on submitting to a stronger current a solution of the ferrotartrate which had become coloured, a green anion made its appearance in the gelatin tube; and, as regards colour-intensity, the great intensity exhibited by cupri-, ferri-, and cobalti-compounds has been found to be by no means an essential feature of metallo-compounds; this was proved by the results with nickel (T., 1915, **107**, 942), and is still more evident from the results detailed in the present communication.

Attempts to prepare the compound I were also made in the case of zinc and cadmium by adding potassium hydroxide to the zinci- and cadmicitrates and the cadmitartrate, and then precipitating by alcohol. Emulsions were obtained in both cases, but they were of such a gelatinous character that they could not be filtered or purified for analysis.

With mercury tartrate, potassium hydroxide gives a permanent precipitate of mercuric oxide; with the other metals of group II alkalinity, of course, appears at once.

An examination of the behaviour of the citrates with alkalis gave the results shown in the last two columns on p. 237. With copper, alkalinity to litmus and to phenolphthalein appeared at the same point; in the other cases it did not, and the alkalinity to phenolphthalein made its appearance before the ratio 1:1 was reached. The latter, however, is the ratio evidently attained when the alkalinity becomes full, there being, thus, no indication of the reaction proceeding to a second stage, as in the case of the tartrates. The appearance of alkalinity before the ratio 1:1 is reached, means that the primary compound is less stable than in the case of the tartrates. With the nickel compound this is conspicuously so; but the values here varied greatly, being dependent on dilution and on some factor which could not be determined. As the citrates contain three atoms of metal in the molecule, three compounds similar to I (p. 237) are possible. Owing to the colour of the solution, no determinations were possible in the case of a cobalt.

Although none of the metallo-compounds with potassium corresponding with I has been isolated, others containing the metal and potassium in the same ratio (1:1) have been obtained; these were the cupriracemates of sodium and potassium, the cupritartrates of sodium and lithium (T., 1912, **101**, 1616), and the cobalti-tartrate of potassium (T., 1915, **107**, 952); they were obtained as slightly alkaline emulsions by digesting the racemates or tartrates

with some excess of the alkali, and precipitating with alcohol; they contained, however, only three-quarters of the proportion of tartrate nucleus required by formula I, and were represented by the empirical formula $R_2M''M'_2,RM'',2M''O,2M'OH$. These probably represent a third stage of the action of alkalis on the tartrates, for their composition agrees with that of substances composed of a molecule of I and II together, each with an OH-group displaced by OM'. The molecule can be represented as united by means of the copper or cobalt atoms. Such a formula is in harmony with their feeble alkalinity.

The malates and lactates were examined as regards their behaviour with alkali, but definite results were obtained in the case of copper only. Here alkalinity to litmus and phenolphthalein appeared at the same time: in the case of the malate, this took place at $Cu:1\cdot03K$, and in that of the lactate, at $Cu:1\cdot37K$. With nickel malate, alkalinity occurred at $1\cdot13$ to $1\cdot211K$, but the point seemed to vary with the dilution. With all the other metals a precipitation occurred.

Preparation of Metallo-compound and Normal Salt.

In every case where the formation of potassium metallo-compounds was indicated by the reaction with alkali, as well as in others where no such indications were obtainable, the simple metallo-compound metameric with the normal salt has been obtained by one or other of the methods mentioned on p. 235. These may be designated for brevity sake as "by acid" or "by double decomposition."

The metallo-compound obtained by either process is an emulsion of varying degrees of solubility, although always much more soluble than the crystallised normal salt, and the latter is always deposited gradually (sometimes rapidly) from solutions of it. As seen from the following table, the lowest ratio for the solubilities of the two

Solubilities at $8°$, or where marked *, at $15°$.

	Tartrates.		Citrates.		Malates	
	Normal.	Metallo.	Normal.	Metallo.	Normal.	Metallo
Mn	$0\cdot072*$	$4\cdot5$	$0\cdot36*$	∞	$0\cdot18*$	∞
Fe	$0\cdot026$	$1\cdot3$	$0\cdot11$	∞	$0\cdot37$	∞
Mg	$0\cdot10*$	$3\cdot0*$	$0\cdot102*$	$2\cdot6*$	$0\cdot47*$	$6\cdot3*$
Zn	$0\cdot018$	$0\cdot9$	$0\cdot167$	$0\cdot9$	$0\cdot091$	$3\cdot7$
Cd	$0\cdot013$	$0\cdot8$	$0\cdot020$	$0\cdot44$	—	$0\cdot5*$
Hg	$0\cdot002*$	$0\cdot054*$	—	$0\cdot007*$	$0\cdot015$	$0\cdot06*$
Pb	$0\cdot002*$	$0\cdot006*$	$0\cdot003$	$0\cdot012$	$0\cdot012$	$0\cdot14$

Racemates.

	Normal.	Metallo.
Mn	$0\cdot018$	$1\cdot23$
Fe	$0\cdot045$	$0\cdot9$

compounds is 3:1 (lead tartrate), the ratio generally being at least 10 or 20:1.

The rapid change of the metallo-compound into the normal salt renders it impossible to obtain more than very rough values for the solubility of the former; they are generally much too low, and the entries in the table must be read as meaning merely that solutions of such a concentration have been obtained. In a few cases, even approximate values could only be obtained by precipitating the metallo-compounds, and noting the volume of water which had to be added to the mixed solutions in order to redissolve it.

In double decomposition, the bulky emulsion first precipitated may, perhaps, change directly into the compact, crystalline normal salt; but the change is generally indirect, the emulsion redissolving and the normal salt crystallising from the liquid. An explanation of this redissolution has been obtained, but cannot be dealt with in the present communication. In the cases hitherto examined, the formation of a double salt preceded or accompanied that of the normal salt (T., 1915, **107**, 948); this is not so in all those described below.

Manganese and Iron.

Tartrates. (a) *By Acid.*—The freshly-prepared carbonates were manipulated in an atmosphere of carbon dioxide. With manganese, the sole product isolated was the crystallised normal salt; with iron, a small yield of the ferrotartrate was also obtained, this drying to a nearly white, easily soluble powder.

(b) *By Double Decomposition.*—With manganese, the successive changes of the initial precipitate of metallo-compound into the double salt, and then into manganese tartrate, occur rapidly (*loc. cit.*); with iron, the latter change occupied several weeks, and is never complete at the ordinary temperature, there always being a layer of minute white needles of the double salt above the much larger, irregular yellow prisms of the single tartrate. The double salt has not been obtained pure; doubtless it is FeT,K_2T, and the product previously obtained (T., 1913, **103**, 1266), which agreed with $4FeT,Na_2T$, was a mixture. On very rapidly heating the freshly mixed reagents containing about 1 gram of iron per 100 c.c., the ferrotartrate redissolves completely, and the normal salt is precipitated at the boiling point as a well-crystallised compound of a pale straw-colour, quite free from potassium. (Found, after drying at 100°, $Fe = 27.51$. Calc., $Fe = 27.39$ per cent.). If the proportions or method of procedure are much altered, especially if the solutions are mixed while boiling, a gelatinous

or membrane-like (see p. 248) precipitate is produced which, although it cannot be washed free from potassium, is probably a modification of the single tartrate, analogous to the jellies obtained in the case of nickel tartrate, etc. (T., 1915, **107**, 953).

The normal tartrate is not easily oxidised unless it is heated when moist; treatment with certain liquids, however, which might be expected to be inert, appear to bring about oxidation: ether immediately turns it dark yellow, light petroleum does so to a somewhat less extent; chloroform, alcohol and toluene have a very slight effect of a similar character, whilst water, carbon disulphide and benzene are without action. These observations were made in view of the possible chemical action of antiseptics in the treatment of soils (*J. Agric. Sci.*, 1908, III, 35).

Racemates.   (a) *By Acid.*—The yield of metallo-compound is in both cases small. The solutions of them give crystals of the normal salt in a few hours.

(b) *By Double Decomposition.*—The gelatinous precipitate of the metallo-compound rapidly becomes opaque, rendering the whole mixture semi-solid with the double salt; it liquefies in a few hours, leaving a deposit of large crystals of the impure single racemate. This may generally be obtained free from potassium by heating the mixed reagents.

To ascertain whether there existed two forms of the normal racemate, as in the case of cobalt (T., 1915, **107**, 953), crystals obtained under various conditions were examined: although differing somewhat in colour, they were found not to differ in crystalline form or behaviour; when dried at atmospheric pressure, and also at 100°, they contained, in the case of manganese, $2H_2O$ (Found, $Mn = 22 \cdot 66$—$22 \cdot 97$.   Calc., $Mn = 22 \cdot 98$ per cent.); at 135° they were anhydrous (Found, $Mn = 27 \cdot 25$—$27 \cdot 46$.   Calc., $27 \cdot 06$ per cent.), and were not decomposed below 200°, whilst the values obtained for their solubility varied only from $0 \cdot 016$ to $0 \cdot 019$ gram of manganese in 100 c.c. at 10°. In the case of iron, the palest (of a clear, pale yellow) and darkest both contained $5H_2O$ when air-dried (Found, $Fe = 19 \cdot 16$—$18 \cdot 92$.   Calc., $Fe = 19 \cdot 04$ per cent.), retained H_2O at 100° (Found, $Fe = 25 \cdot 84$—$25 \cdot 67$. Calc., $Fe = 25 \cdot 23$ per cent.), and became anhydrous at 150°, with slight decomposition.

Citrates.   (a) *By Acid.*—The sole product is the metallo-compound.   The emulsions are difficult to dry without liquefaction. Solutions of them yield crystals of the normal salt after some hours, and, when evaporated at 100°, they yield a residue of "scales," which, in the case of manganese, is the scale preparation sold as manganese citrate.   Repeated redissolution and re-evapora-
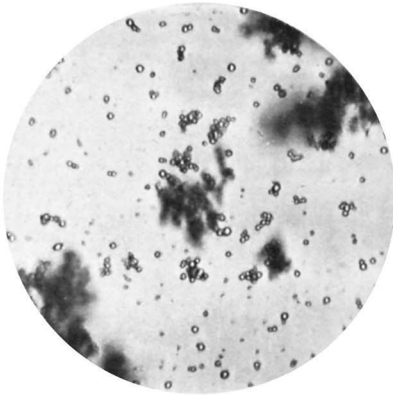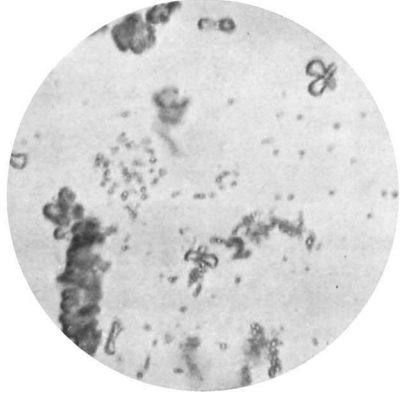
FIG. 1.

FIG. 2.

FIG. 3.

Plumbicitrate changing into lead citrate.
Magnification 200 *diameters.*

tion converts it into the normal salt. The iron compound is not easily oxidised.

(b) *By Double Decomposition.*—With manganese, the gelatinous precipitate of the metallo-compound first formed redissolves at once, and no crystallisation occurs. With iron, there is no temporary precipitate, but minute white flakes of the normal salt eventually form : these retain $2H_2O$ at $100°$.

Both manganese and iron form citrates of the type MK_4Cit_2, similar to those in other cases (T., 1915, **107**, 943). They consist of minute white crystals of great solubility, dissolving, in the case of iron, to form a dark, greenish-yellow, oxidisable solution.

Malates. (a) *By Acid.*—The metals remain entirely dissolved. The precipitated emulsions cannot be dried without the globules coalescing. Solutions of them deposit crystals of the nearly white normal salts, and on evaporation they leave residues of scales and glass.

(b) *By Double Decomposition.*—Nothing is observed until crystallisation of the normal salt begins after three or four days. Ferrous malate in solution is very oxidisable.

Lead.

Distinctive features in this case are the non-formation of a double salt, and the sparing solubility of the emulsions of the metallo-compounds.

Tartrate, Citrate and Malate. (1) *By Acids.*—The crystallised normal salt is the sole product with tartaric acid ; in the other two cases the solutions, on cooling, deposit much flocculent precipitate consisting of an emulsion, and a further yield is obtainable by adding alcohol. (Plumbicitrate, after drying at $100°$, contained $Pb = 62\cdot24$. Calc., $Pb = 62\cdot17$ per cent.) In time, or more rapidly when boiled with water, they change (indirectly, however, after first redissolving) into the nearly insoluble, crystalline, normal salts.

The change in the case of lead citrate is shown by the accompanying photographs, taken (1) at once after precipitation, (2) ten minutes, and (3) thirty minutes later. The globules redissolve, assume Brownian motion (which has interfered with the definition of 2), and the crystals simultaneously separate from the liquid. The dark patches in 1 and 2 are masses of globules which are not in focus.

(2) *By Double Decomposition.*—*Tartrate :* a mixture of prismatic crystals and globules, the latter becoming converted into crystals in a few days. *Citrate :* a mixture of globules and skin-like particles, both becoming converted into crystals in five weeks,

or more rapidly on heating. *Malate:* a very fine-grained, fairly soluble emulsion, converted into large, prismatic, sparingly soluble crystals after twenty-four hours.

Magnesium, Zinc, Cadmium, Mercury.

Most of the metallo-compounds of these metals, except mercury, are readily soluble, but, unless shaken into water in small quantities at a time, they agglomerate into a viscid mass. There is some tendency to form acid compounds where the acid process of preparation is adopted, but none to form double salts where double decomposition is employed, except in the case of mercury.

Tartrates. (1) *By Acid.*—With mercury, the main product is the normal salt in star-like clusters of crystals; in the other cases the sole primary product is the metallo-compound, which retains its solubility after drying, and from the solution of which the normal salt crystallises sooner or later. In the case of magnesium, a solution of the carbonate in the cold acid often, but not always, sets to a jelly, soluble on dilution. The mercuritartrate, when dissolved in hot water, separates as an emulsion again on cooling. Prolonged boiling decomposes it.

(2) *By Double Decomposition.*—In all cases some globules of the metallo-compound are formed, if the solutions are sufficiently concentrated; these very rapidly give place to the crystalline normal salt in the case of magnesium and zinc, and less rapidly with cadmium and mercury. With zinc, the mixed liquids, if not very concentrated, often set, after an hour, to a clear, nearly insoluble jelly, which subsequently becomes opaque, eventually leaving only a small deposit of crystals.

Citrates. (a) *By Acid.*—With zinc, some of the crystallised normal salt is produced; with the other three metals, nothing but the metallo-compound. This, in the case of mercury, separates on cooling, and also on dilution, even with hot water, without the addition of alcohol; it changes into the almost insoluble normal salt after a few days, or on continued heating, consisting then of large spheres made up of small spheres or botroidal crystals. Solutions of the other metallo-compounds yield the corresponding crystallised normal salts after a day or two, except in the case of cadmium, where the normal salt is obtained only when the solution is evaporated at the ordinary temperature; when evaporated at 100° it yields the cadmicitrate as a soluble glass, which on being moistened, breaks up into globules of emulsion. A glassy residue is likewise obtained at first in the case of magnesium and zinc, but by repeated moistening and evaporation it is converted into the corresponding normal salt. Cadmicitrate fritters at 150°. Zinci-

citrate retains $2H_2O$ at $100°$, and becomes anhydrous at $130°$ (Found, $Zn = 34·66$. Calc., $Zn = 34·16$ per cent.), remaining quite soluble. When a solution of it is boiled, some of the emulsion separates, and redissolves on cooling. The normal salt also retains $2H_2O$ at $100°$. Prolonged digestion of the carbonate with acid yields a soluble basic zincicitrate, precipitated by alcohol as an emulsion, the solution of which deposits the corresponding insoluble basic salt. The formula is $Zn_3Cit_2,Zn(OH)_2$. (Found, after drying at $170°$, $Zn = 38·93$. Calc., $Zn = 38·82$ per cent.) A similar compound was obtained in the case of cobalt (T., 1915, **107**, 947). The mercury compound obtained by the acid process is a mixture of the neutral and acid salts; it contains $Hg = 56·95$ after drying at $100°$ (slight decomposition occurs at a higher temperature), Hg_3Cit_2 requiring $Hg = 61·42$, and HgHCit requiring $Hg = 51·35$ per cent.

(b) *By Double Decomposition.*—With magnesium, globules are precipitated, which soon change into hexagonal crystals; with zinc, the normal salt alone was obtained, large square crystals forming after some days; with cadmium, a stiff jelly, consisting of skin and globules, is formed, soluble on much dilution, and changing after a few hours into crystals; with mercury, the mixture gradually becomes opaque throughout several days owing to the formation of globules, after which acicular crystals appear, but some globules still remained : both contain much potassium.

Malates. (a) *By Acid.*—With mercury, some of the emulsion separates on cooling, and more when alcohol is added; it changes into botroidal crystals in a few days. With the other metals, the emulsions precipitated by alcohol are very soluble, and in the case of cadmium, no crystallisation of the normal salt from a solution of it has been obtained. A solution of cadmimalate when heated to $60°$, and also when cooled to $10°$, becomes cloudy through the separation of emulsion—probably not of the same composition in the two cases—which redissolves at once on cooling or heating, respectively. On evaporation, the solution of it leaves a clear glass, which on moistening becomes opaque, owing to its becoming an emulsion. Zincimalate, after being dissolved, gelatinises, the jelly eventually contracting, and becoming converted into crystals of the normal salt. Dry zincimalate changes into the normal salt in the course of some weeks.

(b) *By Double Decomposition.*—With magnesium, only the normal salt was obtained; with zinc, only zinc potassium sulphate; with cadmium, only a fine emulsion of the cadmimalate; with mercury, an emulsion, changing after some days into botroidal crystals of the normal salt.

L 2

Calcium, Strontium, Barium.

With these metals, the tendency to form acid compounds is very marked, these generally being the sole product when the carbonates are treated with acid; by using excess of the hydroxides, the neutral compounds may be obtained.

Solutions of the acid metallo-compounds tend to deposit the neutral instead of the acid normal salt. Sufficient evidence, however, has been obtained to show that both neutral and acid compounds exist in the two forms, but the change from the metallo-compound to the normal salt occurring on double decomposition, especially when the solutions are mixed gradually, is in many cases more complex than may appear from the present description, an emulsion being first precipitated, which then changes to a skin formation, and only eventually into the normal crystalline salt. An explanation of this has been obtained, but cannot be given without entering into results which must be reserved at present. There does not appear to be any tendency to form ordinary double salts with potassium as a step in the change of the metallo-compound into the normal salt, the latter being always quite free from potassium.

Glucinum has been examined, and it forms metallo-compounds, but they bear no resemblance to those of the calcium metals, and are, on the other hand, like those of ferric iron (T., 1913, **103**, 1358). A description of them will therefore be postponed until they can be compared with those obtained from other metals forming sesquioxides.

The solubilities of the compounds of the calcium metals (grams of metal in 100 c.c. at 15°) are as follows:

	Tartrates.		Citrates.				Malates.			
	Acid.		Neutral.		Acid.		Neutral.		Acid.	
	Nor-mal.	Me-tallo.	Nor-mal.	Me-tallo.	Nor-mal.	Me-tallo.	Nor-mal.	Me-tallo.	Nor-mal.	Me-tallo.
Ca	0·007	—	0·018	3·2	0·11	3·9	0·07	1·4	—	—
Sr	0·04	0·36	—	—	0·016	5·2	0·004	0·4?	—	—
Ba	0·01	0·59	0·096	(0·15)*	0·023	0·55	0·44	1·21	0·14	20·0

* Much too low, owing to rapid conversion into the normal salt.

Tartrates. (a) *By Acid.*—When neutralised with the hydroxide, the normal salt alone is obtained in the case of calcium, only a very small yield of metallo-compound in that of barium, and a considerable yield in that of strontium. Solutions of these metallo-compounds deposit crystals after a time. When not neutralised, calcium gives the neutral metallo-compound, which, however, cannot be dried without becoming converted into the

corresponding insoluble normal salt. (Found, after drying at 155°, $Ca = 20.83$. CaT requires $Ca = 21.30$ per cent.) It retained $2H_2O$ at 100°. Strontium under like conditions yielded an acid compound. (Found, $Sr = 28.63$. SrH_2T_2 requires $Sr = 28.45$ per cent.) It was easily soluble, the solution becoming rapidly opaque with crystals. Barium gave a mixed product. (Found, after drying at 100°, $Ba = 35.72$, indicating a mixture of 75 per cent. of the neutral compound with 25 per cent. of the acid compound.)

(b) *By Double Decomposition.*—The temporary formation of globules in the case of calcium and barium, and of globules and skin in that of strontium, is observable under the microscope. These rapidly dissolve, and crystals form.

Citrates.   (a) *By Acid.*—From the neutralised liquid the yield of metallo-citrate is very small in the case of calcium and barium, nil in that of strontium. The calcicitrate, but not the baricitrate, can be dried without conversion into the normal salt. When dried at 155°, the former gave $Ca = 23.77$; calc., $Ca = 24.12$ per cent.; it retained $2H_2O$ at 100°; the baricitrate gave $Ba = 52.42$; calc., $Ba = 52.16$ per cent. When not neutralised, the acid metallo-compounds, MHCit, are obtained. (*Calcium:* Found, $Ca = 17.61$; calc., $Ca = 17.46$. *Strontium:* Found, $Sr = 31.94$; calc., $Sr = 31.56$. *Barium:* Found, $Ba = 41.87$; calc., $Ba = 41.96$ per cent.) They are all anhydrous at 100°, and freely soluble after dehydration, solutions of them depositing the neutral salt unless further excess of acid is added, in which case acid salts of the type MHCit crystallise. If much excess of acid is present before the precipitation of the metallo-compound by alcohol, a hyperacid compound, probably MH_4Cit_2, is obtained, although not in a pure state; with calcium, the compound contained 15.4 of metal, with strontium, 26.5, and with barium, 34.8 per cent., all which values are considerably lower than those required for the salts MHCit as given above.

(b) *By Double Decomposition.*—In all cases globules are first precipitated, changing rapidly into crystals free from potassium; with barium a skin formation appears as an intermediate step in the change.

Malates.   (a) *By Acid.*—The neutral metallo-compounds are obtainable in all cases, but with strontium, only in small proportions, and the strontium compound is converted nearly entirely into the normal salt during desiccation at 155°. In the other cases this is not so. Where excess of acid was present, the products consisted of mixtures of the neutral and acid compounds. The barium compound gave no crystallisation from the solution after

many days, but on evaporation it left a glass mixed with crystals, and was converted entirely into crystals by repeated dissolution and evaporation.

(b) *By Double Decomposition.*—If the solutions are very concentrated, fine globules, changing into crystals, are observed under the microscope in the case of calcium; with strontium and barium, the formation of globules is not quite certain, and no crystallisation follows.

Emulsions, Jellies, and Membranes.

That the phenomena presented by the organic salts of the metals here examined are essentially the same as those presented by copper, nickel, cobalt and ferric iron, there can be no doubt. The limited solubility of some of the emulsions is, however, a novel feature in the case, and their true character would probably not have been recognised but for the microscopic examination of them; for this the author is indebted chiefly to Dr. H. B. Hutchinson. The behaviour of these emulsions, especially their separation from the liquid when it is cooled, as observed in many cases, finds a parallel in the behaviour of mixtures of phenol and water. At a sufficiently high temperature the solubilities of the two substances in each other will be infinite, and the mixture may be evaporated to dryness with nothing but insensible gradations between the liquid and solid conditions. This is what happens with those emulsions which yield a glass or scales when solutions of them are evaporated. There are cases (zincicitrate, cadmimalate) where the emulsion separates on rise of temperature, just as there are cases where the solubility of an ordinary salt diminishes with rise of temperature. According to the author's explanation of the nature of emulsions (T., 1907, **91**, 2014), the presence of solid particles surrounding the globules is necessary for the emulsion to be of a permanent character; in the case of these metallo-compounds the solid probably consists of particles of the normal salt, possibly of only molecular dimensions; these would be insoluble in the liquid already saturated with this salt. Such particles could effectively surround the globules only when these were in a liquid medium, and on the drying of this medium the particles would collect together, and the globules would coalesce; this explains the apparent melting of many of these emulsions during drying.

In many cases (the tartrates of zinc, magnesium and nickel, cadmium citrate, and the malates of nickel and zinc, as well as some of the copper salts) compounds have been obtained in the form of jellies, and in others (the tartrates of iron and strontium, lead and strontium malates, and barium and cadmium citrates)

they appear under the microscope to be made up of small irregular particles resembling those of skin or gelatin. These forms cannot be discussed fully at present, but it may be mentioned that the gelatinous and membranous conditions are probably identical, and that, whilst the comparative insolubility of most of the substances in this condition shows that they are not a form of the metallo-compound, the greater solubility in other cases shows that they are not a form of the normal salt, as was formerly suggested (T., 1915, **107**, 954).

Conclusion.

When first formed the metallo-compound appears to contain the elements of water in addition to the formula MR, but in many cases it can be dehydrated without losing its distinctive properties, and in this condition it is strictly isomeric with the normal salt, from which it differs markedly in physical properties, and in constitution; for electrolysis shows it to contain the metal in the anion. Over forty pairs of such compounds have been obtained, in which thirteen different metals and five acids figure, whilst the colour phenomena of copper salts leave no doubt that similar compounds exist in the case of all organic acids.

Whatever explanation is given of the existence of the metallo-form of copper salts must apply equally to those of the other metals now examined. That iron, manganese, cobalt, nickel, and, perhaps, lead should act as tetrads, is not surprising, but it may be thought otherwise in the case of the other metals. It is clear, however, that restricted views on the subject of valency are no longer possible. So-called saturated compounds combine with each other, and, therefore, must possess some affinity, and also valency; for valency, or definite points of attachment, is essential for combination in definite proportion. Such affinity and valency must belong to the atoms composing the molecule, for we cannot devise any system for attributing affinity and valency to a molecule if its constituent atoms possess neither. Now, the residual affinity of an atom when combined with another may be insufficient to bind to itself a third atom, but quite sufficient to satisfy the residual affinity of such an atom when it is already in a state of combination; hence residual affinity and higher valencies will come into play in the formation of complexes, although the lower valencies alone operate in the formation of simple compounds. Platinum in the compound $PtCl_6K_2$ has been shown to be united with all six atoms of chlorine, though in simpler compounds its maximum valency is 4. A similar fact has been established as regards cobalt and chromium, whilst the usually bivalent copper is quadrivalent in $CuCl_4K_2$. It is only in the case of carbon and

hydrogen, amongst the more familiar elements, that there appears to be no residual affinity and no higher valency values; and to this must be attributed the building up of compounds of these two elements in a manner which is impossible in any other case.

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