equation (i), it follows that the non-electrolytic dissociation of ammonium cyanate cannot be regulated by the law of mass. It must also be remembered that the opinion recently expressed by Walker in his Presidential Address to the Chemical section of the British Association, that in a strong electrolyte the ions behave normally and the undissociated portion of the salt abnormally, implies that the undissociated part exerts a pressure considerably greater than that calculated from its concentration, and that such an implication, if it can be justified, will obviously necessitate a drastic modification of the hitherto accepted concept of a molecule.

D. L. C.

XX.—*Copper Salts and their Behaviour with Alkalis.*

By Spencer Umfreville Pickering, M.A., F.R.S.

In searching for cupri-compounds suitable for the elucidation of those points which have been dealt with in previous communications (Trans., 1910, **97**, 1837; 1911, **99**, 169, 1347), the action of alkali on a number of copper salts was examined, and the results, which in many cases throw further light on the nature of these compounds, are embodied in the present communication. That those cupri-compounds wherein the copper is in the non-carboxylic portion of the molecule, contain it as CuOH displacing hydrogen in alcoholic hydroxyl, has already been established in such cases as have been examined, and that alcoholic groups are necessary for the formation of such compounds has now been proved, by finding that in the nineteen cases in which no such group is present, no cupri-salt is formed by the action of alkali, but a basic salt is precipitated instead; whereas in the thirteen other cases, where alcoholic hydroxyl groups are present, a cupri-salt is formed; sometimes accompanied with the formation of some basic salt also, in amounts depending on the proportion of water present.

The presence of alcoholic hydroxyl, however, should not necessarily be requisite for the formation of cupri-compounds with $:Cu^{IV}O$ in the carboxylic portion of the molecule, yet in no such case has a cupri-compound been obtained by the direct action of potassium hydroxide; and, apparently, the copper may take up this position owing to the presence of alcoholic hydroxyl, even when the latter remains unaffected (malate, citrate). Cupri-compounds have, however, been obtained by other means in the case of some acids containing no alcoholic hydroxyl (maleic, carbonic).

With a potassium cupri-salt of a monobasic acid, none of the copper can be in the carboxylic portion of the molecule, and such compounds are evidently less stable than those which contain some copper in the carboxylic position. This has already been noticed in the case of the quinate, and other instances will be found in the case of the glycerate, lactate and salicylate. Potassium cupriglycollate, already described (*loc. cit.*), is, however, comparatively stable.

Preparation of the Normal Copper Salts.

The normal cupric salts, in cases where they were sparingly soluble, were prepared by adding an equivalent of the potassium or sodium salt to copper sulphate; in other cases, by dissolving copper carbonate in the acid, and precipitating by alcohol.

With the former method a sulphate compound is liable to be formed if the mixed liquids are evaporated (for example, saccharate and malate); in the latter, the precipitate often consists of an imperfect emulsion, which on exposure to air partly liquefies; this may be avoided by placing it promptly in small quantities in a vacuum.

A few hitherto unrecorded data respecting some of these salts may be mentioned.

Propionate.—A solution of copper carbonate in slight excess of propionic acid yields dark bluish-green crystals of the normal salt, similar to the product obtained by Strecker (*Annalen*, 1854, **92**, 89), but if the solution is neutral, tough, rounded masses of light blue, acicular crystals are obtained, consisting of

$$(C_3H_5O_2)_2Cu,CuO,$$

anhydrous at 100°, but retaining $1H_2O$ over sulphuric acid. The normal salt is too soluble to be prepared by double decomposition, as it cannot be washed free from sulphate without being almost entirely dissolved.

Methylsuccinate (Pyrotartrate).—A dark greenish-blue, minutely crystalline, and nearly insoluble salt, which loses all its water at 100°, instead of retaining it, as generally stated. A double salt, $(C_5H_6O_4)_3Cu_2K_2$ (anhydrous), has previously been mentioned (Trans., 1911, **99**, 810 *) as a product of the action of potassium methylsuccinate on copper acetate, and another, $(C_5H_6O_4)_2CuK_2$, with $3H_2O$, which it parts with at 100°, has recently been obtained. The main product of the reaction, however, is either normal copper methylsuccinate, or this salt mixed with a certain amount of basic salt. Enough copper passes into solution to form a deep blue liquid, from which one or other of the double salts separates, the former in greenish-blue, and the latter in violet-blue, crystals. These are decomposed by water, giving normal copper methylsuccinate. No double salt is formed by digestion of copper methylsuccinate with potassium methylsuccinate.

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* The words "pyrotartrate" and "protocatechuate" were accidentally transposed in the passage referred to.

On diluting and heating the liquid containing the double salts, a light blue basic salt containing nearly 2CuO is thrown down.

Fumarate.—A light blue solid retaining $2H_2O$ at 100°, which it parts with slowly at 150°.

Maleate.—This may be obtained either by double decomposition or by digestion of an equivalent of copper carbonate with maleic acid. In either case it forms small, hard, hexagonal plates of a very strong, rather dark blue colour, and agrees with the formula $C_4H_2O_4Cu,H_2O$. Büchner (*Annalen*, 1844, **49**, 60) obtained this salt by the action of maleic acid on copper acetate. It retains the water in a vacuum and at 100°, but loses nearly all ($0{\cdot}8H_2O$) at 165—170°, and becomes of a fine, deep purple-blue colour, suggestive of its being, not an ordinary cupric salt, but a copper cuprimaleate (see Trans., 1911, **99**, 811).

When copper carbonate was treated in the cold with excess of maleic acid a crop of small, light blue, tetrahedral crystals was obtained, agreeing fairly well with the formula for an acid salt,

$$(C_4H_2O_4)_2CuH_2,8H_2O.$$

They lost $4H_2O$ at 100°, and the remainder of their water at 170°, becoming dark blue, but not purple like the normal salt. This is probably identical with the salt stated to be obtained by dissolving copper acetate in maleic acid.

A well crystallised double salt, $(C_4H_2O_4)_3Cu_2K_2$, with H_2O retained at 100°, has been mentioned (Trans., *loc. cit.*, p. 810).* It was obtained by dissolving copper acetate in a concentrated solution of potassium maleate, and evaporating the deep blue liquid formed.

Found: $Cu=22{\cdot}48$; $K=13{\cdot}95$. Ratio $=1:1{\cdot}01$.

$(C_4H_2O_4)_3Cu_2K_2$ requires $Cu=22{\cdot}49$; $K=13{\cdot}83$ per cent.

On other occasions the evaporation of the liquid yielded an uncrystallisable syrup, from which alcohol precipitated a very fine emulsion, which on drying gave values corresponding with $(C_4H_2O_4)_2CuK_2,CuO$: this, from its great solubility, cannot be a basic salt, but is, no doubt, a cupri-compound, with a constitution similar to that of the cuprimalate (p. 186). It is decomposed by water, some of the copper going into solution, and the rest being thrown down as a light blue basic salt.

Glycerate.—Copper glycerate presents features of great interest. When a solution of the carbonate in glyceric acid is precipitated by alcohol, only a portion of the copper is thrown down; but the precipitation may be completed by the addition of ether. The precipitate is generally in the form of a viscid mass, but under

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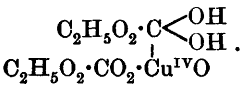
* Where there is a misprint of "malate" for "maleate," and of "$(C_3H_2O_4)$" for "$(C_4H_2O_4)$."

certain conditions it may be obtained as an emulsion. After washing with alcohol and drying rapidly in a vacuum, it may be heated at 100°.

There is a very small further loss of water at 125°, above which temperature decomposition begins, and becomes considerable at 160°. On exposure to air the dried salt remains quite constant in weight. Five different preparations dried at 125° gave, respectively, Cu=21·41, 21·02, 21·43, 20·90, 21·18: mean, 21·19, which agree fairly well with the monohydrate, $(C_3H_5O_4)_2Cu,H_2O$. (Calc., Cu=21·72 per cent.).*

The solubility of this salt is practically infinite; but when a solution of it is kept for a day or more, a mass of small, light blue crystals separates, and continues to do so even after some weeks. These on drying lose only a trace of water, and suffer no decomposition at 160°. On exposure to air, no alteration in weight occurs. Analyses of four preparations gave Cu=22·54, 22·66, 22·79, 22·84: mean, 22·71, showing it to be anhydrous copper glycerate (Cu=23·23 per cent.), the values, as in the previous case, being about 0·5 per cent. below the calculated. It is soluble to the extent of 1·23 grams (=0·28 gram Cu) in 100 c.c.†

It seems clear that the relationship of the two compounds cannot be that of an anhydrous salt to its monohydrate; a highly soluble hydrated salt could never be dehydrated by dissolving it in water; added to which, the supposed monohydrate cannot be deprived of its water without complete decomposition. A difference in constitution can be assigned, however, by representing the anhydrous compound as normal copper glycerate, and the other as a cupriglycerate, analogous to the cupritartrates, etc., previously described; thus:



$$\begin{array}{l} \qquad C_2H_5O_2\cdot C\!<^{OH}_{OH} \\ \qquad\qquad\quad\;\; | \\ C_2H_5O_2\cdot CO_2\cdot Cu^{IV}O \end{array}.$$

This view is further supported by the fact that the molecular colour-intensity of the cupriglycerate in solution (the precipitate obtained by alcohol) is three times greater than that of the normal copper glycerate, an increased depth of colour being one of the characteristics of cupri-compounds. These two substances are capable of existing independently as such in the dissolved condition; and, moreover, the cupriglycerate when in solution may be converted by heat into the normal copper glycerate, a solution

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* One sample, which separated very slowly from the alcoholic liquid, contained an additional $6H_2O$ at 100°, losing it at 125°.

† The normal salt was prepared by Huppert (*Chem. Centr.*, 1863, 835) and by Garzarolli (*Annalen*, 1876, **182**, 190) by the interaction of lead glycerate and copper sulphate.

of it when boiled having three times less colour-intensity than it had before, and remaining permanently lighter. The details of these observations are reserved for a further communication dealing with the colour of copper compounds generally.

A concentrated solution of cupriglycerate when heated for some time over a water-bath yields a light blue precipitate containing Cu = 27·91 after drying at 100°, probably consisting of

$$[(C_3H_5O_4)_2Cu]_3,CuO,$$

which requires Cu = 28·24 per cent. It dissolves to a certain extent in water, begins to decompose at 125°, and on exposure to air gains weight, and becomes darker. It was not further investigated.

Malate.—With a suitable strength of solution, this, made from the carbonate and acid, may be precipitated by alcohol and dried in the manner mentioned above, without melting; but if the solution is too strong it is precipitated as a viscid mass. After being dried at 100° the salt agrees with the formula

$$(C_4H_4O_5Cu)_2,H_2O,$$

the water not being entirely eliminated below 150°, above which temperature decomposition begins.

It dissolves easily and quickly in water, but the solution, whether concentrated or dilute, deposits after a time a crystalline basic salt. On heating, also, this same basic salt gradually separates in comparatively large, bluish-green plates. After drying at 100°, three preparations of this salt gave the following numbers on analysis, the water being eliminated at 140°, beyond which temperature decomposition began:

	Percentage.		Ratio.
	Cu.	H_2O.	Cu : H_2O.
I.	33·73	11·56	1 : 1·21
II.	33·63	11·50	1 : 1·21
III.	33·64	—	— —
Calculated	32·77	11·14	1 : 1·2

The values calculated are for $(C_4H_4O_5Cu)_4,CuO,6H_2O$, but do not agree very well, except as regards the ratio, with those found.*

Aconitate.—By double decomposition a greenish-blue precipitate of $(C_6H_3O_6)_2Cu_3,2H_2O$ is obtained, after which dark green, hexagonal plates of $(C_6H_3O_6)_2Cu_3,3H_2O$ separate. This trihydrate is converted into the dihydrate at 165°.

A double salt, $C_6H_3O_6CuK$ (inadvertently described, *loc. cit.*, as an acid salt), was obtained by dissolving copper acetate in potassium

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* Acid and basic malates have been described (Hagen, *Annalen*, 1841, **38**, 257; Braconnot, *Ann. Chim.*, 1817, [ii], **6**, 239; Liebig, *Annalen*, 1838, **26**, 137; and Traube, *Zeitsch. Kryst. Min.*, 1899, **31**, 160), but it is doubtful whether the normal salt has been obtained hitherto. That obtained by Braconnot, which is described as such, was a green, amorphous salt, of which no analysis was made.

aconitate solution, and evaporating. It formed large, blue, rhombic plates, becoming light blue at 100°, at which temperature it retained about $\frac{1}{2}H_2O$, which was liberated at 150°. Probably the salt is slightly decomposed by the water present during its preparation, for two different samples of it indicated a deficiency of potassium.

	Per cent.	Per cent.	Ratio.
Copper	22·50	12·49	1·00
Potassium..............	12·63	12·89	0·92
Water	3·86	—	0·61

No combination occurs when copper aconitate is digested with a solution of potassium aconitate.

Citrate.—When copper carbonate is dissolved in citric acid, the solution deposits after a time, or immediately on heating, a somewhat dark green, crystalline deposit, which, when dried in the air, consists of $(C_6H_5O_7)_2Cu_3,CuO,5H_2O$. At 100° it loses $3H_2O$, and turns to a light lavender-blue; this is the citrate of commerce. If, however, the freshly prepared solution is precipitated by alcohol, the normal salt is obtained; and this, after being dried rapidly in a vacuum, may subsequently be heated at 100° without decomposition. It retains $2H_2O$ at that temperature, and becomes anhydrous at 150°, decomposing at a slightly higher temperature. It dissolves easily and entirely in water, but the solution after a few minutes deposits a copious precipitate of light, greenish-blue needles, consisting of the basic salt in a nearly anhydrous condition (Found, Cu=45·80. Calc., Cu=46·38 per cent.), instead of the green hydrate previously described. If the emulsion of the normal salt, obtained on precipitation by alcohol, is left exposed to air, it liquefies, and then dries to a blue glass, which on heating, or on being kept for some time, decomposes into the basic salt. The emulsion, also, when left in the liquid from which it has been precipitated, begins to change into the basic salt after a few days.

The colour changes of the basic salt are remarkable, and are somewhat more complex than above stated. The green pentahydrate is converted in a vacuum into a light blue dihydrate, which on heating at 100° undergoes a well marked change to lavender-blue, without any further loss in weight. The peculiar colour of this compound suggested that it was really a copper cupricitrate, forming the final member of a series of which most of the other members had been isolated (Trans., 1910, **97**, 1847). To ascertain whether there was any difference in its heat of formation from that of the blue dihydrate, 4 grams of each were dissolved in 600 c.c. of a 10 per cent. solution of hydrochloric acid, when the molecular heats of dissolution were found to be, as a result of duplicate determination:

Blue salt..................	19,726 cal.
Lavender salt............	19,553 ,,

the difference is practically nil, as it represents errors of only 0·0017°.

The $2H_2O$ retained by this salt is probably constitutional water, as it is not eliminated below the decomposition temperature, 170°. The difference between the two forms may be of a similar nature to that between the two glycerates previously described.

The fact that the somewhat dark green pentahydrate becomes light blue on partial dehydration is remarkable, the general rule, so far as we are aware, being that when any such change occurs it is in the reverse direction, the copper salts being blue when hydrated, and turning green on dehydration.

Saccharate and *Mucate* (see Trans., 1911, **99**, 176).

Glycollate (see Trans., 1911, **99**, 1348).

Toluate.—The normal salt is a fairly light blue precipitate, obtained by double decomposition. Anhydrous at 100°.

Cinnamate.—A light blue precipitate obtained by double decomposition. It apparently contains some basic salt, as its copper content was 19·19, instead of 17·77 per cent.

Salicylate.—Piria (*Ann. Chim. Phys.*, 1855, [iii], **44**, 52) obtained the tetrahydrated normal salt by decomposing barium salicylate with copper sulphate.

When 10—15 grams of potassium salicylate are mixed with an equivalent of copper sulphate, the volume of the liquid being about 200 c.c., in a few minutes light, rather dirty blue, acicular crystals of the tetrahydrate begin to form.

Air-dried.—Found: Cu = 15·76. $(C_7H_5O_3)_2Cu,4H_2O$ requires Cu = 15·52 per cent.

Dried at 100°.—Found: Cu = 19·00. $(C_7H_5O_3)_2Cu$ requires Cu = 18·83 per cent.

If, in preparing it, the solutions were more concentrated, or were hot, a small quantity of a greenish-yellow, and almost insoluble, basic salt was first formed, after which the normal salt separated, either as the blue tetrahydrate or as a green (approximately) anhydrous salt (Found, Cu = 17·93. Calc., Cu = 18·83 per cent.), which latter on washing or exposure to moist air became changed into the blue tetrahydrate. The anhydrous salt sometimes changes spontaneously and suddenly in the liquid to the blue hydrated salt. Both forms of the normal salt dissolve to the extent of 0·17 gram (= 0·03 gram Cu) in 100 c.c., the solution being green, and its colour-intensity approximately seventeen times that of copper sulphate. On prolonged heating at 100° the salt loses some of its acid, and becomes brownish-yellow. A solution of it suffers no decomposition on boiling, but prolonged heating in an open dish leads to the loss of acid and the formation of a little basic salt, which, according to Piria, is $(C_7H_5O_3)_2Cu,CuO$.

In alcohol it dissolves to the extent of 4·7 grams of copper in 100 c.c., giving a very deep green solution, and from this on keeping there separates a crop of dark green crystals, consisting of an acid salt, $(C_7H_5O_3)_2Cu,C_7H_5O_3H$, which may be dried at 100° without sensible decomposition, provided the heating is not too prolonged. (Found, Cu = 13·43. Calc., Cu = 13·36 per cent.)

If some water is added to the alcoholic solution, the tetrahydrated normal salt gradually crystallises (Found, Cu = 15·70 on air-dried sample, 18·70 on that dried at 100°. Calc., Cu = 15·76 and 18·83 per cent.), but in green, rectangular plates, which rapidly become opaque, and are converted into a mass of the blue, acicular crystals constituting the ordinary form of the tetrahydrate.

When a large bulk of water is added to a strong alcoholic solution of the salicylate, a green, viscid mass is obtained, which soon solidifies. After washing with alcohol and drying at 100°, this was found to contain Cu = 42·69, agreeing approximately with $(C_7H_5O_3)_2Cu,3CuO$ (Calc., Cu = 44·12 per cent.), a basic salt, which has been obtained by other means (p. 189).

Thus, besides this and the first-mentioned basic salt of undetermined composition, there are four crystalline salicylates of copper, the anhydrous normal and acid salts, and two modifications of the tetrahydrate, these differing completely in colour and crystalline form.

Protocatechuate.—A red, insoluble salt, obtained by double decomposition in a very finely divided state. It was not analysed.

Gallate.—A red, insoluble salt, which, after drying at 100°, consisted of $(C_7H_5O_5)_2Cu,CuO$.

Tannate.—A pale brown, insoluble salt, which gave values indicating that it was a mixture of the normal and monobasic salts.

Quinate.—The salt formerly obtained (Trans., 1911, **99**, 178) by boiling quinic acid with copper carbonate was a green, crystalline, slightly soluble basic salt, $(C_7H_{11}O_6)_2Cu,CuO,8H_2O$; but if excess of acid is present, the solution on evaporation yields the normal salt in very light blue, wart-like masses of crystalline needles, which contain $2H_2O$ on drying at 100°, becoming anhydrous, and then decomposing, at 145°. The same salt may be precipitated by alcohol from an acid solution.

Phthalate.—The normal salt obtained by double decomposition is a light blue, almost insoluble compound, which becomes anhydrous very slowly at 100°. Hermann (*Annalen*, 1869, **151**, 78) obtained it in crystals with $1H_2O$, which it lost at 160°. A double salt, $(C_8H_4O_4)_2CuK_2$, and also a basic salt, have been mentioned as products of the action of potassium phthalate on copper acetate (Trans., 1911, **99**, 810), and a further investigation of the action has added a basic double phthalate to the list.

A solution of 60 grams of potassium phthalate in 100 c.c. was ground up with various quantities of copper acetate. The latter dissolved entirely when not more than one equivalent was used, forming a deep blue solution, which soon became almost solid through the formation of crystals of the double salt. The solubility of this salt in water is about 0·7 gram (=0·09 gram Cu) in 100 c.c., but it is insoluble in concentrated potassium phthalate solution. Solutions of it on evaporation and subsequent cooling generally yield a crop of the salt in large, rhombic crystals of a fine, full blue colour, although there is generally at first a separation of the mixed basic salts mentioned below. The crystals retain water at 100°, and become anhydrous at 155°. Four preparations of it gave closely concordant values, of which the mean was:

	Percentage.			Ratio.
	Cu.	K.	H_2O	Cu : K : H_2O
Found	12·60	15·55	6·23	1 : 2·01 : 1·74
Calculated	12·68	15·56	6·29	1 : 2·0 : 1·75

The proportion of water, as will be seen, necessitates the formula $4[(C_8H_4O_4)_2CuK_2],7H_2O$.

The basic salt mentioned above has every appearance of being a mixture of two substances of different intensities of blue, and analyses of it, as on previous occasions, gave values (Cu = 33·96) intermediate between $(C_8H_4O_4)_2Cu,2CuO$ and $(C_8H_4O_4)_2Cu,3CuO$ (Cu = 31·23 and 39·18 per cent. respectively). It is probably a mixture of these two.

The normal double salt when washed for some time on the filter changes somewhat suddenly to a very light blue, semicrystalline substance, and solutions of it when allowed to remain in the cold for some time give a more or less copious precipitate of the same substance. Analyses of different preparations of this precipitate after drying at 100°, and subsequent heating at 165°, gave:

	Percentage.			Ratio.
	Cu.	K.	H_2O.	Cu : K : H_2O.
I.	25·08	4·63	(4·95)	1 : 0·301 : (0·70)
II.	24·25	4·65	8·16	1 : 0·312 : 1·19
III.	23·88	4·45	9·57	1 : 0·296 : 1·41
Mean	24 40	4·58	8·87	1 : 0·303 : 1·30

The water eliminated at 165° varies somewhat, and in No. 1 the elimination was only partial; but the ratio Cu : K is fairly constant, and represents a substance of considerable complexity. The values on the anhydrous salt are Cu = 26·78 and K = 5·03, and it is impossible to accept it as a double salt, $(C_8H_4O_4)_7Cu_6K_2$, with the ratio Cu : K = 1 : 0·333, for such a salt would contain Cu = 23·72 and K = 4·86 per cent. Taking the ratio, as found, to be Cu : K = 10 : 3, the minimum molecular weight of the anhydrous salt will be 2354, which will not admit of the presence of more than ten phthalic nuclei, leaving an excess of base. The formula which this suggests is $(C_8H_4O_4)_{20}Cu_{17}K_6,3CuO$, with a molecular weight of 2 × 2417. The phthalates seem to be very complex, and their constitution requires further investigation.

Action of Potassium Hydroxide.

The potassium hydroxide solution used contained 0·035 gram per c.c.,* and phenolphthalein was used as indicator. Wherever the copper salt was sufficiently soluble, a solution of it was used; in other cases the solid salt was treated with the alkali in a mortar under continual grinding. It is difficult to ensure complete action in such cases, unless excess of alkali is present during part of the time, and as such excess tends to decompose any basic salt into hydroxide, the less soluble the copper salt is, the less exact are the values obtained. The solubilities are given in the second column of table I, in which the results with those salts which form no cupri-compounds are given. The proportion of potassium hydroxide required to produce an alkaline reaction is, of course, sufficient to determine the formula of the basic salt formed when none of the copper remains in solution. In no case was there any indication of different basic salts being formed in succession, as happens with copper sulphate under like conditions (Trans., 1907, **91**, 1982).

Of the nineteen salts examined, two are without action, and in four others either copper hydroxide, or a very highly basic salt of uncertain composition, is precipitated. The basic salts in the other thirteen cases form three groups: two have 1CuO, four have 3CuO, and seven have 7CuO, that is, the prevalent proportion of total copper in these salts, including the normal salt, is 1, 2, 4, or 8 atoms. What significance attaches to this fact is not clear.

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* The action of concentrated aqueous potassium hydroxide is not considered in the present communication; its action on all copper salts, organic or inorganic, results in some of the copper passing into solution at first, probably as a cuprite, and the subsequent decomposition of this into copper oxide, unless a cupri-compound is formed.

TABLE I.

Solubility, and Reaction of Copper Salts with Potassium Hydroxide.

Salt.	Solubility, grams Cu in 100 c.c.	Mols. KOH to precipitate each Cu.	Product.
Carbonate	0·00	no reaction	—
Oxalate	0·00	,, ,,	—
Acetate	2·30	[1·90	$(C_2H_3O_2)_2Cu,19CuO$]
Propionate	3·81	[1·95	$(C_3H_5O_2)_2Cu,39CuO$]
*iso*Butyrate	0·30	[1·97	Copper hydroxide]
Oleate	0·00	[2·12 *	,, ,,]
Butyrate	1·8	1·72	$(C_4H_7O_2)_2Cu,7CuO$
Valerate	0·012	1·77	$(C_5H_9O_2)_2Cu,7CuO$
*iso*Valerate	0·047	1·74	$(C_5H_9O_2)_2Cu,7CuO$
Succinate	0·012	1·77	$C_4H_4O_4Cu,7CuO$
Methylsuccinate	0·009	1·75	$C_5H_6O_4Cu,7CuO$
Maleate	0·017	1·74	$C_4H_2O_4Cu,7CuO$
Toluate	0·053	1·78	$(C_8H_7O_2)_2Cu,7CuO$
Formate	1·73	1·50	$(CHO_2)_2Cu,3CuO$
Fumarate	0·003	1·50	$C_4H_2O_4Cu,3CuO$
Aconitate	0·011	1·54	$(C_6H_3O_6)_2Cu_3,9CuO$
Benzoate	0·18	1·52	$(C_7H_5O_2)_2Cu,3CuO$
Cinnamate	0·003	(0·92 *)	$(C_9H_7O_2)_2Cu,CuO$
Phthalate	0·03	1·01	$C_8H_4O_4Cu,CuO$

* Uncertain. Some alcohol must be present for the alkali to react with the oleate.

Similar data respecting the salts which form cupri-compounds are given in table II.

TABLE II.

Solubility, and Reaction of Copper Salts with Potassium Hydroxide.

Copper partly precipitated.			None of the copper precipitated.		
Salt.	Solubitity, grams Cu in 100 c.c.	Mols. KOH.	Salt.	Solubility, grams Cu in 100 c.c.	Mols. KOH.
Glycollate	0·061	1·62	Tartrate	0·015	1·34
Lactate *	2·15	2·0	Saccharate	0·007	1·49
Citrate †	∝ ?	1·17—1·25	Mucate	0·000	1·59 ‖
Protocatechuate	0·000	(1·04)	Quinate ¶	0·02	0·67—1·0 ‖
Salicylate ‡	0·114	1·94	Glycerate	∝	1·02
Tannate §	0·000	(0·9)	Malate	∝	1·00
			Gallate ¶	0·000	1·6

* If the solution is concentrated, no precipitate.

† If the solution is dilute, no precipitate.

‡ A crystalline precipitate forms eventually.

§ Contained some basic salt.

‖ The solution soon gelatinises.

¶ A basic salt.

The glycollate, tartrate, saccharate, mucate and quinate have been dealt with in previous communications.

Glycerate.—The proportion of potassium hydroxide required to produce alkalinity is about 1KOH for every atom of copper, the whole of the copper remaining in solution whether there is much or little water present. On the addition of alcohol a light blue emulsion is precipitated, which, when dried in a vacuum and then at 100°, forms a dark blue, brittle solid. It begins to decompose at 135°. An analysis of it is given under *A*. On dissolving it in water and reprecipitating, only a small proportion is thrown down, and this (*B*) is much poorer in potassium than the first precipitate. The values are similar to those obtained in the case of the quinate, suggesting that potassium cupriglycerate, $C_2H_4(CuOH)O_2{\cdot}CO_2K$, is the first product, and that this, by the action of water, becomes converted into copper cupriglycerate:

	A.	Theory for potassium cupriglycerate.	*B*.	Theory for copper cupriglycerate.
Cu...........	29·83	28·42	37·18	44·0
K	13·10	17·48	8·89	0·0

When excess of potassium hydroxide (2—3KOH) is added to copper glycerate, alcohol precipitates from the mixture a few drops of dark blue liquid, and causes a small, crystalline deposit to form on the sides of the vessel; but these products were not obtained in sufficient quantity for examination.

The crystalline compound obtained by the interaction of potassium glycerate on copper acetate, corresponding with the formula $(C_3H_5O_4)K(CuO)_4$ (Trans., 1911, **99**, 810), also requires further examination.

Malate.—Copper malate, either in dilute or concentrated solution, required almost exactly 1KOH to show alkalinity, no precipitation occurring. This indicates the formation of

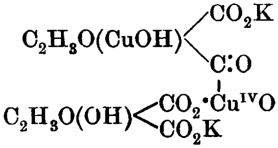
$$(C_4H_4O_5)_2CuK_2,CuO,$$

and on evaporation a viscid liquid was obtained, from which after a time dark blue, non-deliquescent, microscopic crystals separated; these, after dehydration at 160°, gave values agreeing with the above formula, the mean results from six different preparations being:

	Copper.	Potassium.	Ratio.
Found...............	26·12	16·76	2 : 21
Calculated	26·19	16·11	2 : 2

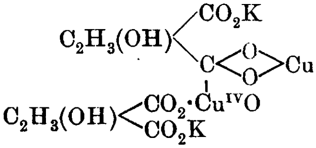
It was obtained in two different crystalline forms, one squat and rounded, these crystals being anhydrous, the other prismatic, containing approximately $2H_2O$. The addition of alcohol to the liquid precipitated this same substance as a viscid mass or very imperfect emulsion.

This substance is a further instance of the inacceptability of the view that in these cupri-compounds a copper atom displaces two hydrogen atoms of the alcoholic hydroxyls, for this would necessitate the substance after heating at 160° being still hydrated, thus, $C_4H_6CuO_2(CO_2)_4CuK_2,H_2O$, which is highly improbable; and that it can be regarded as a basic salt is scarcely possible, owing to its great solubility, its solution at 15° containing 50 grams per 100 c.c. That it contains copper in the alcoholic hydroxyl group, represented in formula (I) below, also seems improbable, as none of these compounds have been found to crystallise as this substance does, and such a formula does not agree with the analytical results, as it requires Cu = 25·26 and K = 15·53 per cent. It therefore would seem to be a compound with the formula (II), analogous to the



$$\begin{array}{l} C_2H_3O(CuOH)\left\langle\begin{array}{l}CO_2K\\ C{:}O\end{array}\right.\\ \qquad\qquad\qquad\quad | \\ C_2H_3O(OH)\left\langle\begin{array}{l}CO_2\cdot Cu^{IV}O\\ CO_2K\end{array}\right. \end{array}$$

(I.)



(II.)

cupricitrate No. 6 (Trans., 1910, **97**, 1846); and in further support of this view there is the fact that maleic acid (which contains no alcoholic hydroxyl) yields an excessively soluble compound with a precisely similar formula (p. 176).

Attempts to obtain other cuprimalates failed. The addition of excess of potassium hydroxide to copper malate precipitated a basic malate with, approximately, 5CuO.

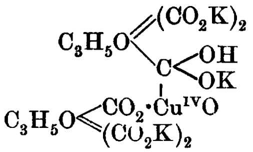
Citrate.—On adding potassium hydroxide to copper citrate in dilute solution, about 1·17KOH for each atom of copper was required to produce alkalinity, and no precipitation occurred, either with this or a larger proportion of alkali. When there was only very little water present, 1·25KOH was required, and about one-third of the copper was precipitated as a basic salt, insoluble in excess of alkali, and this, on drying, formed a brittle, olive-green substance, giving values on analysis agreeing exactly with $(C_6H_5O_7)_2Cu_3,6CuO$, or copper orthocitrate. It retained about $3H_2O$ at 100°, which it lost at 140°.

The copper which remained in solution was precipitated by alcohol as an imperfect emulsion or viscid mass, varying in composition in different experiments, and containing copper and potassium in the atomic ratios of 3 : 4 to 3 : 5.

When excess of alkali, 2 to 10 KOH, is added to copper citrate, and the liquid separated from the basic precipitate, and treated with alcohol, a very small crop of alkaline, viscid, rather large crystals is obtained. The most satisfactory preparation gave, after drying:

	At 100°.		At 130°.	Theory.
Cu	9·44	= 1·00	10·24	9·72
K	29·28	= 5·04	31·76	29·89
H_2O	7·82	= 2·92	—	—

these values agreeing with the cupricitrate No. 3 (Trans., 1910, **97**, 1842), which was not previously isolated with any certainty. As representing the first step in the formation of a cupricitrate by the action of potassium hydroxide, such a compound is of importance, the formula assigned to it being:



Unfortunately, in other cases it was only obtained contaminated with what was evidently potassium citrate precipitated by the alcohol.

Potassio-cupric citrate on treatment with potassium hydroxide requires exactly 1KOH for each atom of copper to produce alkalinity, indicating the formation of potassium citrate and the cupricitrate No. 6 (*loc. cit.*, p. 1846), according to the equation:

$$2KOH + 2[(C_6H_5O_7)_2CuK_4] = 2C_6H_5O_7K_3 + (C_6H_5O_7)_2K_4Cu,CuO.$$

Lactate.—No satisfactory results have so far been obtained with this salt. In weak solution (0·4 per cent. Cu) potassium hydroxide gave a precipitate when the proportion reached 1KOH, and alkalinity when it reached 2KOH. About 14 per cent. of the copper remained in solution, and the precipitate consisted of, approximately, $(C_3H_5O_3)_2Cu,5CuO$. From the liquid, alcohol caused the separation of a viscid mass, in which the proportion Cu : K = 1 : 1·4. If deficit of alkali had been added (1KOH), the precipitate by alcohol contained Cu : K = 1 : 0·76.

When solid copper lactate is treated with potassium hydroxide, the proportion required to dissolve it is 0·8KOH for each Cu. This solution, after twenty-four hours, deposits a copious precipitate of a basic salt approximating to $(C_3H_5O_3)_2Cu,CuO$.

Salicylate.—On the addition of an alcoholic solution of potassium hydroxide to the solid salt, the latter is transformed into a very light green, amorphous and anhydrous substance, stable up to 145°. Various preparations gave:

	Percentage.		Ratio.
	Cu.	K.	Cu : K.
I.	15·35	18·53	1 : 1·96
II.	15·11	18·59	1 : 1·96
III.	15·21	18·49	1 : 1·98
IV.	15·37	18·65	1 : 1·97
	15·26	18·56	1 : 1·97
Calc. for *A* ...	15·23	18·90	1 : 2
,, ,, *B* ...	14·72	18·11	1 : 2

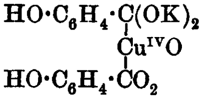
A.

Cu for H_2 in $(COH)_2$.

$(C_6H_4O)_2Cu(CO_2K)_2$

B.

A cupri-compound.



$$\begin{array}{l} HO{\cdot}C_6H_4{\cdot}C(OK)_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad Cu^{IV}O \\ \qquad\qquad\quad | \\ HO{\cdot}C_6H_4{\cdot}CO_2 \end{array}$$

The analyses agree with formula *A*; but on the addition of water, the substance gives a strong alkaline reaction, which is inconsistent with such a formula, and indicates a constitution represented by *B*. This is another instance, similar to that of the cupriglycollate and cupricitrate (Trans., 1911, **99**, 1350, 1351), wherein an alkaline cupri-compound, when anhydrous, appears to be a compound wherein the copper takes the place of hydrogen in alcoholic hydroxyl, and which can only be explained by a transformation of the one substance into the other. In the present instance both substances appear also to be capable of existing in solution, although in an unstable condition; thus, when aqueous, instead of alcoholic, potassium hydroxide (0·035 per cent.) is used, the copper salicylate dissolves completely to form a dark green *neutral* liquid, 1·94KOH (as a mean of four determinations) being required before the liquid becomes alkaline. In a few minutes a crystalline deposit begins to form, which soon becomes copious, and apparently consists of the same compound (which is alkaline) as that obtained when alcoholic potassium hydroxide is used, but in a hydrated condition (with $4H_2O$, which it loses at 145°), and slightly decomposed by the water present; in six different preparations the ratio Cu : K varied from 3 : 5 to 4 : 7. The decomposition occurring accounts for the alkali required to produce alkalinity, being only 1·94 instead of 2 KOH, as it should be according to the equations given below.

The salt prepared either by alcoholic or aqueous potassium hydroxide gives an alkaline reaction with water, a basic copper salicylate being gradually precipitated from the liquid; excess of water increases the amount of the precipitate eventually thrown down, 90 per cent. of the copper being precipitated when the total copper present amounts to 0·01 gram per 100 c.c. For each atomic proportion of copper thus precipitated, half an atomic proportion of potassium (Found, 0·48) is liberated as alkali, and the precipitate has approximately the composition $(C_7H_5O_3)_2Cu,3CuO$, similar to the basic salicylate previously described,* so that the formation and decomposition of the cuprisalicylate will be represented by the equations:

$$(C_7H_5O_3)_2Cu + 2KOH = (C_7H_5O_3)_2(OK)_2CuO + H_2O.$$

$$(C_7H_5O_3)_2(OK)_2CuO + H_2O = (C_7H_5O_3)_2Cu,3CuO + 2KOH + 6C_7H_5O_3K.$$

From the neutrality of the solutions from which this substance separates, it would appear that $(C_7H_4O)_2Cu(CO_2K)_2$ must be capable of existing as such in solution, whilst, when it dissolves with excess of water to form an alkaline solution, the fact that the basic salt is only gradually precipitated indicates that the alkaline substance, or cupri-compound, must also be capable of existing temporarily in the dissolved condition. With the cupriglycollate and cupricitrate the alkaline compounds are quite stable in weak solution, but with the cupricitrate decomposition gradually occurs if the solution is strong.

The following salts, owing to their colour or indefiniteness in composition, did not appear suitable subjects for investigation:

Protocatechuate.—This on treatment with potassium hydroxide required 1·04KOH to produce alkalinity, about 50 per cent. of the copper passing into solution.

Gallate.—The basic copper gallate, $(C_7H_5O_5)_2Cu,CuO$, required about 1·6KOH for each atom of copper to produce alkalinity, and the whole of the copper passed into solution.

Tannate.—On treatment with potassium hydroxide, about 0·9KOH to each atom of copper was required to produce alkalinity, and about 10 per cent. of the copper passed into solution.

Sulphate Compounds.

The existence of a sulphate compound has been mentioned in the case of copper saccharate, and similar compounds probably exist in many other cases; that formed by copper malate has been investigated.

When fairly strong solutions of copper malate and copper sulphate are mixed, and either gently warmed or left in the cold, a copious precipitation of greenish-blue, well-crystallised solid gradually occurs. When heated at 100°, this turns to a full, rather dark

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* Copper percentage found in the present case, 46·90, and in the former, 42·69; mean, 44·8; the above formula requiring 44·12. It contained $1H_2O$ at 100°, which it lost at 160°, remaining otherwise undecomposed at that temperature.

blue, and suffers only a trifling further loss up to 140°, above which temperature decomposition begins. Five different preparations after drying at 140° gave, as a mean value:

Cu = 39·01; SO_3 = 12·74. Ratio 4 : 1·04.

Calc., Cu = 40·34; SO_3 = 12·70. Ratio 4 : 1.

The analyses indicate a minimum molecular weight of 640, which is inconsistent with the presence of more than two malic acid groups, so that some of the copper must be present as CuO; the formula $(C_4H_4O_5Cu)_2,CuO,CuSO_4$ gives a molecular weight of 630, the percentage of copper and SO_3 in it being indicated by the values given above, and these agree fairly well with those found. What the constitution of the salt is can only be conjectured, but seeing that it contains excess of CuO, and yet is fairly soluble, it is probably a cupri-compound with $:Cu^{IV}SO_4$ entering into the molecule in a similar manner to that suggested for $:Cu^{IV}CO_3$ in the cupricarbonates (see Trans., 1911, **99**, 809).

The formation of a salt containing excess of cupric oxide from the neutral malate and sulphate involves the simultaneous formation of free acid, or of an acid salt, and the mixture, as a matter of fact, becomes strongly acid.

A solution of it on protracted boiling deposits an impure basic copper malate, and the addition of alcohol to a mixture of copper malate and sulphate precipitated a mixture of variable composition containing free malic acid.

The air-dried salt in four cases was found to contain H_2O = 27·72 (27·45 to 28·19), corresponding with $13·88H_2O$, and the dried salt on exposure to air re-absorbed this amount exactly. In two other cases the water present corresponded with only $8H_2O$, and this amount only was re-absorbed when the dehydrated salt was exposed to air, implying some difference between this and the other dehydrated specimens. The heat of dissolution of the two forms was determined, dissolving 4 grams in 600 c.c. of a 10 per cent. solution of hydrochloric acid, but the values obtained were 42·7 and 44·6 cal. per gram, respectively, and, as the difference between these values corresponded with only 0·007°, there was nothing to substantiate any difference in the nature of the substances.

Summary.

Copper salts of organic acids containing no alcoholic hydroxyl react with alkalis to form insoluble basic salts, whilst those of the oxy-acids form soluble cupri-compounds, with the copper in either the carboxylic or non-carboxylic portion of the molecule; in some cases a certain amount of basic salt is also formed. Cupri-salts of

monobasic acids, when the copper is in the non-carboxylic position, are, in nearly every case, very unstable.

Further evidence that copper in most cupri-salts is present as CuO, and not as copper displacing hydrogen, was obtained in several cases, especially in that of the salicylate and malate, the latter being of importance, because in the compound in question the copper must be in the carboxylic position, and former evidence applied chiefly to compounds with the copper in the non-carboxylic position.

In the case of copper glycerate a cupri-compound has been obtained differing in composition from the normal salt only by the elements of water, but certainly not being a hydrate. The two compounds have very different solubilities, colours, and temperatures of decomposition; and, in solution, the cupri-compound may easily be converted into the normal salt.

Similar modifications appear to exist in the case of basic copper citrate.

Two modifications of tetrahydrated copper salicylate were obtained, but there was nothing to suggest either of these being a cupri-compound. An alkaline potassium cuprisalicylate was obtained, which, like the corresponding cupriglycollate and cupricitrate, appears to change on dehydration into a neutral compound, the copper moving into the place of the hydrogen in the alcoholic hydroxyl.

Potassium cupri-compounds of malic and maleic acids were obtained, which might be represented as basic salts, but their great solubility shows that some other constitution must be assigned to them.

Amongst other compounds obtained, one which may be represented as consisting of basic copper malate with copper sulphate, is probably also a cupri-compound.

Thirteen basic salts, precipitated by alkali from salts of acids containing no alcoholic hydroxyl, conform to formulæ representing 1, 3, or 7 CuO united with a molecule of the normal salt. Besides these, the following compounds have been obtained:

Propionate.—A basic salt, $(C_3H_5O_2)_2Cu,CuO$, also with H_2O.

Methylsuccinate.—The normal salt; anhydrous. A double salt, $(C_5H_6O_4)_2CuK_2,3H_2O$.

Fumarate.—The normal salt; anhydrous, and as a dihydrate.

Maleate.—The normal salt; anhydrous, and as a monohydrate. An acid salt, $(C_4H_2O_4)_2CuH_2$, anhydrous, and with 4 and 8 H_2O. A cupri-compound, $(C_4H_2O_4)_2CuK_2CuO$.

Glycerate.—The normal anhydrous salt, and a salt corresponding with a monohydrate, but which is, apparently, a cupri-compound.

A basic salt, approximately $[(C_3H_5O_4)_2Cu]_3,CuO$. A potassium cupriglycerate, $C_2H_4(CuOH)O_2,CO_2K$.

Malate.—The normal salt in the anhydrous and monohydrated condition. A basic salt, $(C_4H_4O_5Cu)_4,CuO,6H_2O$, and another, approximately $C_4H_4O_5Cu,5CuO$. A cupri-salt,

$$(C_4H_4O_5)_2CuK_2Cu^{IV}O,$$

anhydrous and with $2H_2O$. A sulphate compound,

$$(C_4H_4O_5Cu)_2CuO,CuSO_4,$$

anhydrous and with 8 and 14 H_2O.

Aconitate.—The normal salt, anhydrous, and with 2 and 3 H_2O.

Citrate.—The normal salt, anhydrous, and with $2H_2O$. The basic salt, $(C_6H_5O_7)_2Cu_3,CuO$, anhydrous, and with 2 and 5 H_2O, one of these being probably a cupri-compound. A basic salt, or orthocupric citrate, $(C_6H_5O_7)_2Cu_3,6CuO,3H_2O$.

Lactate.—Two basic salts, approximately $(C_3H_5O_3)_2Cu,5CuO$ and $(C_3H_5O_3)_2Cu,CuO$.

Tannate.—The normal salt, anhydrous.

Salicylate.—The anhydrous normal salt, and two distinct modifications of a tetrahydrate of it. An acid salt,

$$(C_7H_5O_3)_2Cu,C_7H_5O_3H.$$

A basic salt, $(C_7H_5O_3)_2Cu,3CuO$. A potassium cuprisalicylate, $(C_6H_4O)_2Cu(CO_2K)_2$, anhydrous, and with $4H_2O$.

Gallate.—A basic salt, $(C_7H_5O_5)_2Cu,CuO$.

Phthalate.—The normal salt, and a double salt,

$$4[(C_8H_4O_4)_2CuK_2],7H_2O.$$

A mixture of basic salts, probably containing 2CuO and 3CuO. A double salt of basic character with the empyrical formula

$$(C_8H_4O_4)_{20}Cu_{17}K_3,3CuO.$$

HARPENDEN,
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