LXIX.—*The Blue Salt of Fehling's Solution and other Cuprotartrates.*

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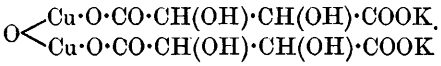
Electrolytic Experiments.

IN the course of the investigation by one of us of a new method for the direct comparison of ionic velocities (*Phil. Trans.*, 1899, **192**, 331), it became desirable to ascertain whether the blue salt of Fehling's solution owes its colour to its positive, or, as seemed more likely, to its negative ions. In the experiment adopted to test this question, it was necessary to have the blue solution as free as possible from excess of alkali. It was therefore prepared in the following manner. Pure cupric tartrate was made by mixing solutions of cupric sulphate and Rochelle salt in the proper proportion, and washing the sparingly soluble, blue, crystalline precipitate ($CuC_4H_4O_6 + 3H_2O$). This was then mixed with a little water, and caustic potash solution was added slowly, with continual shaking, until almost, but not quite, the whole of the precipitate was dissolved. The clear, filtered liquid had the appearance of Fehling's solution, but was perfectly neutral to litmus. Two flasks, provided with side necks, were connected with each other by a straight, horizontal glass tube, 12 cm. long and of narrow bore, the ends of which were covered with short pieces of rubber tubing and thus made to fit tightly into the necks. Before making this connection, however, the tub was filled with a transparent jelly containing sodium chloride in the proportion of a normal solution and 12 per cent. of gelatine. Platinum electrodes were placed in the flasks, which were now filled with the deep blue neutral solution, and the electrodes were connected with a battery giving an E.M.F. of about 40 volts. The apparatus was placed in a bath of cold water, deep enough to cover the tube and reach to the shoulders of the flasks, in order to counteract the heating effects of the current. It soon became manifest that deep blue anions were travelling through the tube, and that the cathions of the solution (presumably K) were colourless. The experiment was continued for some hours without affecting this result. The platinum cathode was then found to be plated with copper, which was undoubtedly due to secondary action of the discharged Na ions, for the blue ions had been visibly travelling away from the cathode all the time. The experiment is an easy one to carry out, and illustrates very prettily the theory of the formation of secondary products in electrolysis and its application to electro-plating.

A second experiment was then performed, in which the flasks containing the anode and the cathode were filled respectively with cupric sulphate solution and with the deep blue solution, the tube being filled with the jelly as before. Two blue boundaries were now seen to advance through the tube in opposite directions, a deep blue one moving from the cathode end, as in the first experiment, and a paler blue one moving towards it from the anode cell. Thus the contents of the tube became divided visibly into three parts—light blue cupric chloride jelly at the anode end, colourless sodium chloride jelly in the middle, and deep blue sodium-cuprotartrate jelly at the cathode end—of which the coloured parts were gradually increasing in length at the expense of the intermediate colourless one. The tube was graduated, and from experiments which are fully discussed in the paper already referred to, it was known that the visible boundaries should travel with velocities having a certain relative value (approximately 2 : 3), and should therefore meet at a certain point in the tube, *provided that they were the only boundaries* in the jelly, and that no invisible anions, except those of the chlorine of the original jelly, were travelling ahead of the dark blue ones. It soon was evident, however, that the expected ratio of velocities was not being maintained; and the cause of this was manifest when the light blue boundary, on reaching the calculated mark, while the dark blue boundary was still some way off, suddenly formed a pale blue precipitate as a septum across the tube. This proved that the dark blue solution contained, besides the coloured anions, some other, faster, colourless kind, which had the power of forming an insoluble cupric salt. The probability was that they were the ordinary tartaric ions; and, if so, the reaction between copper tartrate and caustic potash, by which the deep blue neutral solution was prepared, could not be so simple in its character as was at first assumed.*

Synthetical Experiments.

It was evident that further light might be thrown on the question of what occurs in this reaction by ascertaining the exact quantity of alkali required for the production of the neutral blue solution. The following experiments were therefore performed, using caustic soda as the alkali, and may be taken as confirmatory of Kahlenberg's statement (*Zeit. physikal. Chem.*, 1895, **17**, 590), that when caustic potash acts on copper tartrate, 63 per cent. of its equivalent (that is, $CuC_4H_4O_6$ takes 0·63 of 2KOH) is required to completely dissolve the salt and to develop an alkaline reaction. Kahlenberg, however, maintained that the blue salt is produced by interaction, in the proportion $CuC_4H_4O_6$: KOH, and represented its constitution by the formula



$$\mathrm{O}<\begin{array}{l}\mathrm{Cu{\cdot}O{\cdot}CO{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOK}\\ \mathrm{Cu{\cdot}O{\cdot}CO{\cdot}CH(OH){\cdot}CH(OH){\cdot}COOK}\end{array}.$$

It will be shown that this theory does not correctly represent the facts.

Precipitated copper tartrate was thoroughly washed and dried at 105°. At this temperature, it loses its water of crystallisation without further decomposition, as was proved by combustion:

0·5151 gave 0·4290 CO_2 and 0·0999 H_2O. $C = 22·71$; $H = 1·96$.
$CuC_4H_4O_6$ requires $C = 22·69$; $H = 1·90$ per cent.

Small quantities of this dry salt were then tested in stoppered flasks

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* After the experiments described above had been performed and some further progress had been made with this investigation, the May (1898) number of the Journal was received containing an abstract of a paper in the *Zeitschrift für Elektrochemie* on Ionic Reactions, by F. W. Küster (Abstr., 1898, **74**, ii, 205), in which the negative character of the blue ion of Fehling's solution is proved by an experiment similar in principle to ours. Küster's original paper is not obtainable in Melbourne. Earlier, but less direct, evidence of the same fact was given by Louis Kahlenberg (*Zeit. physikal. Chem.*, 1895, **17**, 586) in an important paper on complex tartrates.

with N/2 caustic soda solution. In each case, the alkali was added in successive portions, and the flask was well shaken and then left after each addition in order to give the salt every chance of dissolving. As the end of the reaction (complete solution) was approached, the undissolved salt had a tendency to remain suspended in the deep blue liquid as a silky turbidity, which slowly settled down as a precipitate if more alkali were required, or equally slowly went into solution if enough had been added. This made it possible to hit the end point with fair accuracy, the resulting solutions being tested with litmus paper, which was then rinsed with water to remove the blue copper compound. The following results were obtained:

	Grams of $CuC_4H_4O_6$.	C.c. of N/2 NaOH.	Ratio, $\frac{NaOH}{CuC_4H_4O_6}$.	Reaction to litmus.
A	1·470	17·12	1·23	Neutral.
B	1·149	13·65	1·26	Faint alk.
C	1·238	14·63	1·25	Faint alk.
D	0·584	6·73	1·22	Neutral.

A fifth experiment on a small scale was made by mixing copper sulphate and tartaric acid solutions, in molecular proportion, and running in sufficient caustic soda to first neutralise the acid and then dissolve the precipitated tartrate. The result showed, as is natural, that the action is not altered by the presence of sulphates, which must be present when Fehling's solution is prepared in the ordinary way, for the ratio of total NaOH to $CuSO_4$ was 3·17 : 1, or that of the extra NaOH to $CuC_4H_4O_6$ was 1·17 : 1. The fact that there was a considerably larger relative volume of water present in this case may explain the small difference between it and the other experiments, for cupric tartrate has a distinct, although small, solubility of its own, which is given as 1 in 1700 in Watts' Dictionary. If an approximate correction for this is applied, it is evident from all the experiments that the true ratio for the action producing the neutral blue salt is very close to $NaOH : CuC_4H_4O_6 = 1·25 : 1$.

This result was confirmed by preparations on a larger scale in which both caustic soda and caustic potash were used for the solution of pure cupric tartrate. Thus it was found necessary to employ 325·5 c.c. of normal caustic soda for the complete solution of 54·18 grams of the salt, and 331·0 c.c. of normal caustic potash for that of 56·02 grams, giving the ratios respectively as 1·27 and 1·25 (as compared with Kahlenberg's potash ratio, namely, 1·26), the action with litmus showing that there was a slight excess of alkali used in the former case.

These synthetical experiments, read in the light of the second electrolytic experiment, which suggested that a tartrate is formed at he same time as a blue cuprotartrate, make it probable that the action may be such as is expressed by the equation :

$$5NaOH + 4CuC_4H_4O_6 = Na_2C_4H_4O_6 + Na_3C_{12}H_7Cu_4O_{18} + 5H_2O,$$

in which, however, the formula of the second product may require modification by the inclusion of more or less of the $5H_2O$. That such an equation really expresses the reaction has been fairly well established by the analytical work to be described in the sequel.

Potassium and Sodium Cuprotartrates.

When about twice the volume of strong alcohol is added to the deep blue neutral solution obtained as already described, a crystalline blue precipitate separates, leaving a colourless, supernatant liquid. If the solution prepared with caustic potash, instead of caustic soda, is used, the blue salt tends to separate as a gummy mass, but this may be avoided by adding the alcohol gradually. It was found, in both cases, that the clear liquid, on standing, yields a growth of delicate, colourless acicular crystals. A complete separation of these from the blue salt is easily accomplished by washing the latter repeatedly with dilute alcohol (2 vols. alcohol to 1 vol. water) in which it is quite insoluble, so that there is no difficulty in obtaining the cuprotartrate in a pure state. The colourless crystals obtained in the caustic soda reaction were carefully tested by comparison with sodium tartrate crystallised from dilute alcohol and also by conversion into the calcium and silver salts, and their identity with sodium tartrate was thus placed beyond question. The quantity of this product is always small in comparison with that of the blue salt, and, so far as could be judged without exact quantitative estimation, the proportion is in keeping with requirements of the equation just given.

The purified cuprotartrates of the alkali metals are freely soluble in water, giving perfectly neutral solutions of the characteristic deep blue colour. Although precipitated by alcohol, they contain water of crystallisation, which they lose, or partly lose, at 100° ; anhydrous salts cannot be prepared in this way, however, as the dehydration is accompanied by a decomposition involving formation of cuprous oxide, which subsequently separates on treatment with water. This reducing action also occurs to an appreciable extent when the fresh solution of the pure salt is boiled for a few minutes, or when it is left at the ordinary temperature for a few days. The solid sodium and potassium salts apparently differ in their degree of hydration ; the former may be exposed to the atmosphere without change, but the latter slowly deliquesces and forms dark blue, oily drops which eventually form an enamel-like solid. When a solution of the potassium salt is poured over a smooth plate, it rapidly dries to a glassy, blue varnish which cracks off in a form exactly similar to that of the so-called scale preparations of the British Pharmacopœia, and differing from them only in colour. This behaviour is doubtless due to the formation of a higher hydrate than the crystalline one obtained by precipitation with alcohol.

When heated below redness, these salts undergo rapid decomposition, and scatter in a manner suggestive of mercury sulphocyanate, leaving a residue of mixed alkali carbonate and copper oxide.

The potassium salt, precipitated and purified by alcohol, dried on a porous tile, and subsequently left for eight days over sulphuric acid in a vacuum, was analysed in the following manner. Two portions were used for combustion which gave the total hydrogen and all the carbon not retained as carbonate in the residue. This residue could not be weighed, as it was impossible to prevent it from scattering beyond the porcelain boat. Two other portions were very carefully heated in covered porcelain crucibles and finally ignited strongly without the lid. The residues, after weighing, were dissolved in nitric acid, and the solutions used for estimating the copper by electro-deposition and the potassium as sulphate. In all four experiments, it was found that the porcelain boat or crucible was slightly attacked. This meant necessarily a higher percentage of carbon in the combustion than that calculated from the formula and a correspondingly smaller amount of carbon in the residue, since some of the carbonate of the latter was converted into silicate. The difficulty could hardly be avoided, as it was thought unsafe to use platinum: it seemed fairest, therefore, to calculate the CO_2 of the residue, not from the equivalent of the K_2O, but by difference after deducting the K_2O and CuO; its quantity was insufficient for direct estimation.

I. 0·3496 gave 0·1864 CO_2 and 0·0644 H_2O.
II. 0·4639 „ 0·2448 CO_2 „ 0·0860 H_2O.
III. 0·9895, on ignition, gave 0·5569 residue, yielding 0·2804 Cu and 0·2944 K_2SO_4.
IV. 0·7855, on ignition, gave 0·4344 residue, yielding 0·2216 Cu and 0·2338 K_2SO_4.

These figures give the percentage results tabulated below. Consideration of the carbon results and of the figures for the residues after ignition show that the action of the alkali carbonate on the porcelain fully explains the only notable discrepancies between the found and calculated values.

	I.	II.	III.	IV.	Means.	Calculated.
K	—	—	13·33	13·34	13·33	13·03
Cu	—	—	28·34	28·39	28·36	28·24
C′	14·54	14·39	—	—	14·47 }	13·98 }
C″	—	—	1·30	1·16	1·23 }	2·00 }
H	2·05	2·06	—	—	2·05	1·90
O	—	—	—	—	(40·56)	40·85
					100·00	100·00
Residue after ignition	—	—	56·38	55·32	55·85	58·33

The calculated percentages are those corresponding to the formula, $K_3C_{12}Cu_4H_7O_{18} + 5H_2O$, already suggested by the synthetical experiments; it may, therefore, be regarded as established, although the possibility exists that a portion of the $5H_2O$ is present, not as water of crystallisation, but as part of the acid radicle.

Insoluble Cuprotartrates.

A solution of potassium or sodium cuprotartrate gives insoluble, or sparingly soluble, amorphous precipitates when mixed with solutions of the following salts :—

$Ba(NO_3)_2$. Granular, light blue precipitate, soluble in excess of the alkali salt.

$AgNO_3$. Light blue precipitate, very sparingly soluble in water; decomposes on exposure to light.

$Pb(NO_3)_2$. Light blue precipitate, very sparingly soluble in water, or in excess of either solution.

$CuSO_4$. Blue precipitate, darker than any of the others; fairly soluble in water and in excess of the alkali salt; not formed with dilute solutions.

$ZnSO_4$. Light blue precipitate; more soluble than the copper salt.

$FeCl_3$. On slowly adding dilute ferric chloride solution, the following characteristic changes occur: first a green solution is formed, then a bright green precipitate, dissolving in excess to a clear yellow solution, which, on standing, quickly deposits a copious yellow precipitate.

Whilst the last of these reactions probably involves more complicated changes, the others seem to depend simply on the formation of cuprotartrates, in which the heavy metals take the place of the potassium or sodium of the blue soluble salt. Only the lead and silver salts have been examined with much care as yet, and of the others the copper cuprotartrate is interesting as presumably containing the same metal in two capacities.

Lead Cuprotartrate was prepared by precipitating the potassium salt with lead nitrate solution. The precipitate, after thorough washing, was dried over sulphuric acid in a vacuum, and when analysed gave numbers which indicated that its composition corresponded to that required for the formula $Pb_3(C_{12}H_9Cu_4O_{19})_2 + 24H_2O$. It is doubtful, however, whether the salt examined can be regarded as a definite hydrate, and, moreover, it contained some impurity, probably lead nitrate, arising from the well known habit that some precipitates have of carrying down soluble salts and refusing to part with them on washing.

Silver Cuprotartrate.

This was prepared by adding silver nitrate solution to potassium cuprotartrate, a rather large excess of the former being found necessary for complete precipitation. It was washed, dried on a porous tile, and placed in a vacuum desiccator for two days, the work being carried out in a dark room, as it was found necessary to guard the salt from the action of light. Two portions were then subjected to combustion, and the residue from one of these was dissolved in nitric acid for the estimation of silver as chloride and of copper electrolytically after removal of chlorine. A third portion was ignited and used similarly for silver and copper estimations, another portion being employed for estimating the water lost by heating at 100° in the dark for 2 hours, no further loss occurring after heating for an additional $2\frac{1}{2}$ hours.

I. 0·6530 salt gave 0·2840 CO_2 and 0·1331 H_2O.
II. 0·7869 ,, ,, 0·3451 CO_2, 0·1605 H_2O, and 0·4194 residue, which gave 0·2704 AgCl and 0·1724 Cu.
III. 0·7663 salt, on ignition, gave 0·4102 residue, which gave 0·2643 AgCl and 0·1663 Cu.
IV. 0·5997 lost 0·0807 H_2O.

	I.	II.	III.	IV.	Means.	Calculated.
Ag	—	25·86	25·90	—	25·89	27·04
Cu	—	21·91	21·70	—	21·80	21·25
C...........	11·87	11·96	—	—	11·92	12·02
H	2·27	2·26	—	—	2·26	2·27
O	—	—	—	—	(38·13)	37·42
					100·00	100·00
Residue on ignition	—	53·30	53·53	—	53·42	53·65
Water lost at 100°	—	—	—	13·45	13·45	13·54

The calculated percentages are those required for the formula $Ag_3C_{12}Cu_4H_9O_{19} + 9H_2O$, or for the formula $Ag_3C_{12}Cu_4H_7O_{18} + 10H_2O$ on the assumption that the salt retains one molecular proportion of water of hydration after drying at 100°. At any higher temperature, the salt is decomposed and darkened in colour. It is evident, from the proportions of silver and copper found, that the preparation was not quite pure, but the figures, on the whole, seem to confirm the formula, and may be taken as indicating that the radicle of the cuprotartrates is either $(C_{12}Cu_4H_7O_{18})'''$ or $(C_{12}Cu_4H_9O_{19})'''$, so that of the water indicated in the formula for the potassium salt at least $4H_2O$ are present as water of crystallisation.

The conclusion may thus be drawn, that the cuprotartrates are metallic salts of a definite trivalent radicle $(C_{12}H_7Cu_4O_{18})'''$ or $(C_{12}H_9Cu_4O_{19})'''$, and since none of the salts has been obtained with less hydrogen and oxygen than that indicated by the second formula without at the same time undergoing general decomposition, this may be accepted for the present, at any rate, as correct. In this case, the formulæ of the potassium salt, dried in a vacuum, and of the silver and lead salts dried at 100°, are respectively, $K_3C_{12}H_9Cu_4O_{19},4H_2O$, $Ag_3C_{12}H_9Cu_4O_{19}$, and $Pb_3(C_{12}H_9Cu_4O_{19})_2$.

Instability of Cuprotartaric Acid.

Some attempts have been made to isolate cuprotartaric acid itself, but so far without success. When a solution of the potassium salt is titrated with a dilute mineral acid, the deep blue colour gradually gives place to the colour of an ordinary copper salt solution, and when this change is complete, or nearly so, a light blue precipitate slowly forms which has the appearance and characters of cupric tartrate. One sample, prepared in this way, was analysed and proved to be slightly impure cupric tartrate. Its formation may be represented by the equation :

$$K_3C_{12}H_9Cu_4O_{19} + 5HCl = 3KCl + 3CuC_4H_4O_6 + CuCl_2 + H_2O.$$

As the precipitate is produced slowly, it is possible that this decomposition is really preceded by the formation of a very unstable cuprotartaric acid, $H_3C_{12}H_9Cu_4O_{19}$, which then reacts with more acid.

It seemed possible that a solution of the free acid might be obtained without decomposition by suspending the lead salt in water and adding just sufficient dilute sulphuric acid to remove the lead as sulphate, but this also proved unsuccessful. The pale blue solution was proved to contain positive cupric ions, and no complex blue negative ions, by electrolytic experiments similar to those described at the beginning of this paper.

Sulphuretted hydrogen solution decomposes all the cuprotartrates, precipitating cupric sulphide or a mixture of this with the sulphide of the other metal. The ease with which this occurs is a little surprising, as truly negative metallic radicles do not generally break up in this way. Indeed, in this reaction, the copper of the cuprotartrates shows in marked contrast to, say, the gold of the aurocyanides, yet the electro-negative character of the one is as certain as is that of the other. But it seems to be only the ion that can exist as such, whilst the un-ionised hydrogen cuprotartrate tends to undergo such transformation as to turn the copper back into an ordinary metallic radicle. If this is so, the action of sulphuretted hydrogen, even on the potassium salt, is explained, since a proportion of the hydrogen and cuprotartaric ions must naturally enter into combination, and more must unite to take the place of this when it is transformed.

Kahlenberg (*loc. cit.*) adduced arguments, based on physical properties, in favour of the view that the excess of alkali in Fehling's solution as usually made, or part of it, is present in the state of combination, and not merely mixed with the blue salt. We have obtained chemical evidence in proof of the truth of this contention, as the addition of alcohol to a solution made from caustic soda and cupric tartrate in the ratio $2NaOH : CuC_4H_4O_6$ throws out a strongly alkaline salt which retains this character even after the alcoholic washings have become quite neutral, and contains sodium and copper in the ratio $Na : Cu = 7 : 4$. We intend to continue this investigation, and in the meantime abstain from any discussion of the probable or possible inner constitution of the negative radicle of the cuprotartrates.

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