LI.—*Double Carbonates of Sodium and Potassium with the Heavy Metals.*

By Malcolm Percival Applebey and Kenneth Westmacott Lane.

The combination of alkali carbonates with carbonates of the heavy metals to form crystalline double salts has been long known, many of these compounds having been prepared by Deville (*Ann. Chim. Phys.*, 1851, [iii], **33**, 75) by digesting the precipitated metallic carbonate with excess of a concentrated solution of the alkali carbonate. Double carbonates of cobalt, nickel, zinc, and magnesium with potassium, and of copper, magnesium, cobalt, nickel, and zinc with sodium, were thus prepared, whilst several double bicarbonates were obtained in a similar manner. Owing to the method of preparation adopted, Deville's compounds must have been contaminated with normal and basic metallic carbonates, but his products were sufficiently pure to make possible a general characterisation of this group of substances. A somewhat more satisfactory method of preparation was adopted by Reynolds (T., 1898, **73**, 262), who ground the solid acetate of the metal with a concentrated solution of potassium carbonate. Under these conditions, complete solution takes place, and the crystalline double carbonate is subsequently deposited in a fairly pure state. In this way, Reynolds succeeded in obtaining the double carbonate of copper and potassium which Deville had failed to prepare owing to its great solubility. The analyses of Reynolds's copper compounds show rather high values for the copper content, and suggest the presence of basic carbonate. Gröger (*Ber.*, 1901, **34**, 429) afterwards demonstrated the advisability of adding bicarbonate to the alkaline carbonate solution, a modification which, as was pointed out by Wood and Jones (*Proc. Camb. Phil. Soc.*, 1907, **14**, 71), represses the hydrolytic dissociation of the copper carbonate. The potassium and sodium copper carbonates prepared by Gröger nevertheless contained considerable amounts of basic carbonate, the potassium salt being particularly impure. This was, however, probably due to the subsequent treatment of the salts.

The nature of the deep blue solutions from which the copper salts are deposited has been examined by Luther and Kršnjavi (*Zeitsch. anorg. Chem.*, 1905, **46**, 170), who proved by transport experiments the presence of a deep blue complex negative ion containing copper. The conditions under which crystallisation of double salts from such solutions takes place have also been discussed by Deville and by Gröger. No quantitative study of these conditions has yet, however, been attempted, although the case is one of particular interest, since it relates to a double salt of which one constituent is practically insoluble in water. The authors therefore undertook a study of the solubility equilibria in the case Na_2CO_3–$Na_2Cu(CO_3)_2$–$CuCO_3$, which is typical of double salt equilibria of this kind. It was hoped that a parallel investigation of the equilibria in the formation of the potassium cobalt compound would be of interest. Unfortunately, owing to the difficulties of analysis in the latter case and to the enforced suspension of the work under present conditions, it has not been found possible to bring this part of the investigation to a satisfactory conclusion. The present communication therefore deals almost entirely with the sodium copper carbonate equilibrium.

Preparation and Properties of the Double Salts.

The salts prepared for the purpose of this investigation were all obtained by a method which, whilst not giving so good a yield as could be obtained by Reynolds's method, was preferable for the purpose in view, since it gave products of greater purity, analysis showing that the amount of basic carbonate present was small.

Sodium Copper Carbonate.—A solution was prepared containing about 100 grams of sodium carbonate (anhydrous) and 40 grams of sodium bicarbonate in a litre. To this solution, at a temperature of about 50°, a concentrated solution of cupric acetate was added from a burette with a fine point, the liquid being stirred continually during the addition. A clear, deep blue solution quite free from suspended basic carbonate is obtained in this way. The amount of cupric acetate solution to be added is found by trial; if too much is added, precipitation of basic carbonate occurs; if too little, there is no crystallisation. The solution is filtered and left to remain overnight, when a deposition of well-formed crystals of the double salt takes place. These are collected, rapidly washed with pure alcohol, and dried in a desiccator. The mother liquor can be used for a further preparation, and gives a rather better yield.

The salt, which crystallises in needles or rosette-like agglomerations, dries to a constant weight in a desiccator. It is, in fact, a more stable substance than might be expected, since microscopic examination fails to show any alteration in the transparency of the crystals after they have been kept at the temperature of boiling water for a considerable time. At higher temperatures, the substance loses water and carbon dioxide, passing through a stage when it has a purple colour, and giving finally a mixture of cupric oxide and sodium carbonate. It is decomposed by water, but dissolves in and can be recrystallised from a concentrated solution of sodium carbonate containing bicarbonate. This observation, which is in direct contradiction to the experience of Gröger (*loc. cit.*), has been fully established by repeated tests.

The copper in the compound was determined by the sulphide method and also electrolytically, the sodium as sulphate after precipitation of the copper. Carbon dioxide and water were estimated directly in the usual manner.

Found: $Cu = 22{\cdot}05$; $Na = 16{\cdot}05$; $CO_3 = 42{\cdot}52$; $H_2O = 19{\cdot}62$.

$Na_2Cu(CO_3)_2,3H_2O$ requires $Cu = 22{\cdot}40$; $Na = 16{\cdot}21$; $CO_3 = 42{\cdot}37$; $H_2O = 19{\cdot}02$ per cent.

It will be seen that the substance has the formula

$$Na_2Cu(CO_3)_2,3H_2O,$$

as was found by Deville, Gröger, and Wood and Jones (*loc. cit.*). The amount of water of crystallisation in this salt is somewhat anomalous, as the large number of double carbonates of potassium investigated by Reynolds, and the sodium cobalt compound to be described later, all crystallise with four molecules of water.*

Sodium Cobalt Carbonate.—This substance was prepared in exactly the same manner as the copper compound, except that the cobalt was added in the form of nitrate solution. The double salt crystallises in crusts of fine crystals of a very bright reddish-purple colour. It can be recrystallised from a solution of sodium carbonate and bicarbonate, but it is difficult to obtain well-formed crystals.

The salt was analysed by dissolving a weighed quantity in excess of standard acid and titrating with standard alkali, using methyl-orange as indicator. The colour of the solution is not sufficiently intense to affect the accuracy of this determination, which gives the total basic equivalent of the sodium and cobalt in the compound. Another weighed sample is then ignited until it is completely con-

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* The potassium copper salt can also be obtained anhydrous and with one molecule of water, but not with three.

verted into a mixture of cobalt oxide and sodium carbonate, of which the latter can be extracted with hot water and estimated by titration. This gives the percentage of sodium in the compound and the percentage of cobalt by comparison with the determination of total basic value. The sodium was also determined as sulphate (*a*). The water was determined in the usual way and the carbon dioxide by difference.

Found: Co = 20·42; Na = 15·03, 15·26(*a*); CO_3 = 40·79; H_2O = 23·64.

$Na_2Co(CO_3)_2,4H_2O$ requires Co = 19·85; Na = 15·52; CO_3 = 40·38; H_2O = 24·25 per cent.

The substance evidently has a formula corresponding with the double potassium salts described by Reynolds, and is therefore unlike the sodium copper carbonate, which has only three molecules of water of crystallisation. Deville also obtained a double sodium cobalt carbonate with ten molecules of water, but this substance was not formed under the conditions described in this paper.

Potassium Cobalt Carbonate.—This salt is obtained in an analogous manner to those previously described, the solution used for the preparation containing about 400 grams of potassium carbonate and 100 grams of potassium bicarbonate per litre. On addition of cobalt nitrate solution, a dark, reddish-purple solution is obtained very similar in appearance to that from which the sodium salt is deposited. The crystalline double salt is, however, different in habit and in appearance from the corresponding sodium compound. The crystals are well formed and do not mass together in compact crusts. They present the appearance of six-sided tables which have not the bright purple tint of the sodium salt. Large crystals formed by evaporation of solutions saturated with the double salt have a red colour resembling ordinary cobalt compounds, whilst the smaller crystals deposited from the purple solutions are a lighter red, or in some cases a pale pink. The differences in colour between different specimens at first led to the belief that the cobalt potassium compound occurred in several forms differing either in composition or in crystalline form. Repeated analyses and measurements of solubility failed, however, to show any difference between the differently coloured specimens, nor did either the red form or the pink form grow at the expense of the other when both were kept in contact with a saturated solution for several months. The authors are therefore bound to conclude that the differences of colour referred to are not due to differences of composition, structure, or crystalline arrangement. They are probably to be explained by occlusion of different amounts of some colloidal substance, such as cobalt carbonate. This conclusion is supported by the observation that increase in the concentration of bicarbonate in solution tended to favour the production of the lighter coloured variety. The effect is probably quite parallel with the well-known changes in the colour of many metallic salts when crystallised from solutions of varying acidity; these changes have been shown to be due to the occlusion of varying quantities of metallic hydroxides under different conditions.

Analysis by the method used for the sodium cobalt compound gave:

Found: $Co=17{\cdot}85$; $K=24{\cdot}05$; $CO_3=21{\cdot}60$; $H_2O=36{\cdot}50$.

$K_2Co(CO_3)_2,4H_2O$ requires $Co=17{\cdot}91$; $K=23{\cdot}72$; $CO_3=21{\cdot}89$; $H_2O=36{\cdot}45$ per cent.

This substance also clearly belongs to the normal type with four molecules of water of crystallisation, as was previously found by Reynolds.

Both the sodium and potassium cobalt salts have properties very similar to those of the sodium copper carbonate. They are quite stable in the cold, but lose water and carbon dioxide on heating. They are decomposed by water, but, like the copper compound, can be recrystallised from concentrated solutions of alkali carbonate and bicarbonate.

Formation of the Double Salts.

The formation of the double salts from the intensely coloured solutions has already excited some interest. Deville remarked upon the deep colour of the solutions, and doubted whether this colour could possibly be due to the small quantity of double carbonate which in the solid state is not more highly coloured than ordinary copper salts. A very striking experiment illustrating Deville's argument consists in acidifying a solution of the double carbonate containing 0·1 to 0·2 gram of copper per litre. This solution, which is bright blue, becomes almost colourless when the complex ion is destroyed by acidification, and even the addition of ammonia only produces a colour very much fainter than that of the original solution. Deville was so much impressed with the intense colour of the solutions that he regarded it as possible, if not probable, that the solutions contained some substance much more intensely coloured than the double carbonate into which it was slowly transformed during the crystallisation of the latter.

Other phenomena now to be discussed give considerable support to Deville's hypothesis. The crystals of the double salt are formed slowly from the solution when the latter has been kept for several hours, but the solution is not supersaturated in the ordinary sense.

This is shown by the fact that addition of crystalline nuclei does not appreciably hasten the separation. Gröger, who noted this phenomenon, also describes a remarkable experiment, which the authors have been unable to confirm. According to him, if a solution supersaturated with sodium bicarbonate is used in the preparation of the copper solution, addition of the crystalline double salt brings about no crystallisation, but sowing with a fragment of sodium bicarbonate not only induces crystallisation of the bicarbonate itself, but also brings about the rapid separation of the double salt along with it. This would constitute a remarkable type of supersaturation; attempts to repeat the experiment, however, never led to the result described, only bicarbonate being obtained as solid phase, whilst no appreciable fall in copper concentration took place.

It was thought that evaporation or absorption or loss of carbon dioxide might be a determining factor. Experiments were therefore entered on to test these points, but the results were entirely negative. Whether the solutions were left to crystallise in the open, in sealed flasks, or in a desiccator connected to a Kipp's apparatus for carbon dioxide, no appreciable difference in the rate of crystallisation was observed. It is therefore tentatively suggested that the behaviour of the solutions is due to one of the following causes:

(1) The rate of crystallisation is very small, and there are no stable supersaturated solutions.

(2) An intermediate compound is formed in the solutions which changes only slowly into the practically insoluble double salt.

In the latter case, the change from intermediate compound to double salt is reversible, since the double salt can be recrystallised from a solution of carbonate and bicarbonate.

The Solubility Equilibria.

In undertaking this investigation, the authors were faced at the outset with the difficulty that solutions of the double salts are unstable in absence of bicarbonate. Repeated attempts to obtain a solution saturated with sodium carbonate decahydrate and with the sodium copper carbonate in absence of bicarbonate all led to failure. When the solids were stirred in a constant-temperature bath at 18°, a blue solution was obtained, but decomposition with precipitation of basic compounds always occurred before the experiment had proceeded a sufficiently long time to ensure the attainment of equilibrium. It was therefore decided that the work must be carried out exclusively with solutions containing bicarbonate.

In many respects, the simplest plan and that promising results of most interest was to work with solutions saturated with sodium carbonate or with sodium bicarbonate, and the determinations made by the authors relate only to such solutions. The equilibria investigated are therefore those of (1) sodium copper carbonate and sodium bicarbonate with solutions containing increasing quantities of sodium carbonate; (2) sodium copper carbonate and sodium carbonate decahydrate with solutions containing decreasing quantities of bicarbonate. In each of these regions we are dealing with a system univariant at constant temperature with two solid phases. At the point of intersection we have at constant temperature a non-variant system with three solid phases.

The concentration of copper in the equilibrium solutions is in all cases very small in comparison with the concentrations of the sodium salts. The latter may consequently be considered as influenced only to an inappreciable extent by the presence of copper. The determinations therefore serve also to characterise the equilibrium of sodium carbonate and sodium bicarbonate at the temperature of experiment. They may be compared with the results of McCoy and Test (*J. Amer. Chem. Soc.*, 1911, **33**, 473) at 25°.

The solutions were prepared in a stirring-bottle closed with a mercury seal and maintained at 18° by means of a constant-temperature bath regulating to 0·02°. The time allowed for equilibrium to be established was never less than forty hours, preliminary experiments having shown that this was a satisfactory minimum period. When saturation was complete, the stirrer was stopped and the solution was allowed to settle. The stirrer was then removed and replaced by an inverted filter, through which the saturated solution was blown into a clean flask, from which samples were taken for analysis. Filtration of the solutions was necessary, as in some cases a solid substance, probably a basic carbonate, was present in a state of very fine suspension.

The concentration of copper in the solutions was found by direct titration of the solutions with a potassium cyanide solution, standardised against alkaline copper solutions of known strength, due allowance being made for the variation in the titre of the solutions ocasioned by variation in bicarbonate concentration. The cyanide titration of these solutions is much sharper than in the case of ammoniacal copper solutions of equal copper content (*Analyst*, 1918, **43**, 268).

The carbonate and bicarbonate were determined by dilution of the solutions by means of carefully standardised pipette and flask, and titration by Winkler's method. A modification of this method which proved serviceable consisted in running in *N*/10-sodium hydroxide solution until the bicarbonate was almost completely changed into carbonate, the amount necessary being found by a preliminary trial. Excess of neutral barium chloride solution and a drop of phenolphthalein were then added, and the titration with sodium hydroxide was completed. This modification is preferable in point of convenience to Winkler's method of adding excess of sodium hydroxide, then adding barium chloride and phenolphthalein, and titrating back, and appears to be quite as accurate, although, of course, several titrations of each solution must be carried out. If the quantity of sodium hydroxide solution first added is sufficiently near the quantity required for complete conversion (within 0·2 or 0·3 c.c.), there appears to be no difficulty occasioned by the decomposition of the barium bicarbonate which must be formed on adding barium chloride.

The following tables give the results of the several experiments made with the sodium copper solutions (table I) and with the potassium cobalt solutions (table II). No determinations of the cobalt content of the latter solutions are given, as sufficiently trustworthy values were not obtained at the time when the experiments were interrupted. The concentration of cobalt in the equilibrium solutions was in the neighbourhood of 0·1 to 0·2 gram per litre, and appeared to pass through a minimum value at a concentration of potassium carbonate equal to about 200 grams per litre. A similar variation is not found in the case of the sodium copper compound, with which the copper content of the equilibrium solutions increases continually with increase of the carbonate concentration.

TABLE I.

No. of experiment.	Hours stirring.	Solid phases.	Na_2CO_3 grams/litre.	$NaHCO_3$ grams/litre.	Cu grams/litre.
1	48	$Na_2Cu(CO_3)_2,3H_2O$ and $NaHCO_3$	9·27	87·79	—
2	140		11·08	86·45	0·0509
3	50		11·29	86·75	—
4	50		13·44	85·27	0·0542
5	50		37·36	78·63	—
6	100		61·32	74·18	—
7	100		62·36	72·65	0·0870
8	100		96·68	65·31	0·1061
9	50		99·30	64·10	0·1061
10	70		152·63	56·24	0·1411
11	50		168·75	53·60	0·1553
12	50	$Na_2Cu(CO_3)_2,3H_2O$ $NaHCO_3$ and $Na_2CO_3,10H_2O$	185·02	53·77	—
13	50	$Na_2Cu(CO_3)_2,3H_2O$ and $Na_2CO_3,10H_2O$	193·13	17·64	—
14	50		195·57	7·48	—
15	50		197·08	18·94	0·257

TABLE II.

No. of experiment.	Hours stirring.	Solid phases.	K_2CO_3 grams/litre.	$KHCO_3$ grams/litre.
1	120	$K_2Co(CO_3)_2,4H_2O$ and $KHCO_3$	13·3	280·6
2	70		14·85	282·5
3	50		25·5	272·4
4	240		47·5	262·3
5	100		103·2	237·0
6	70		114·1	230·7
7	40		125·1	227·6
8	50		145·7	219·0
9	120		166·8	203·2
10	120		220·0	181·0
11	120		289·4	158·9
12	70		309·2	151·3
13	40		453·5	108·4
14	70		607·7	68·9
15	120		643·0	64·1
16	120		704·3	54·6
17	120	$K_2Co(CO_3)_2,4H_2O$, $KHCO_3$ and $K_2CO_3,2KHCO_3,3H_2O$	800·2	43·1
18	120	$K_2Co(CO_3)_2,4H_2O$ and $K_2CO_3,2KHCO_3,3H_2O$	805·1	40·9
19	170		822·8	35·0
20	170	$K_2Co(CO_3)_2,4H_2O$, $K_2CO_3,2H_2O$ and $K_2CO_3,2KHCO_3,3H_2O$	825·8	33·1
21	100	$K_2Co(CO_3)_2,4H_2O$ and $K_2CO_3,2H_2O$	836·2	12·2
22	170		840·8	5·9

These results are represented graphically in Figs. 1 and 2. Fig. 1, which also contains McCoy and Test's results for the sodium carbonate–bicarbonate equilibrium at 25°, shows no sign of a break corresponding with the double compound $Na_2CO_3,NaHCO_3,2H_2O$ (trona) at 18°. It is therefore probable that this compound ceases to be stable in contact with solutions at some temperature between 18° and 25°

In the course of the solubility experiments, it was noted that a distinct change in the appearance of the solid phase occurred in passing along the bicarbonate curve. The bicarbonate used in these experiments was the usual micro-crystalline variety, and this form appeared to suffer no change when left in the stirring bottle in contact with solutions ranging from pure bicarbonate to a point on the curve corresponding with about 70 grams of carbonate per litre. Beyond this point, the solid phase becomes transformed into well-formed, transparent crystals. These crystals are nevertheless pure anhydrous bicarbonate, as was established by repeated analyses. It is possible that a polymorphic change takes place, but in view of the fact that the solubility curve shows no break, and seeing that all attempts to obtain evidence of a definite transition point failed completely, the authors are inclined to think that the phenomenon is not to be explained by polymorphism. This opinion is supported by the absence of any clear distinction between the two kinds of crystals when examined under the polarising microscope. Probably the conditions of the solubility equilibrium in presence

FIG. 1.

Upper curve, McCoy and Test, 25°
Lower „ Applebey and Lane, 18°.

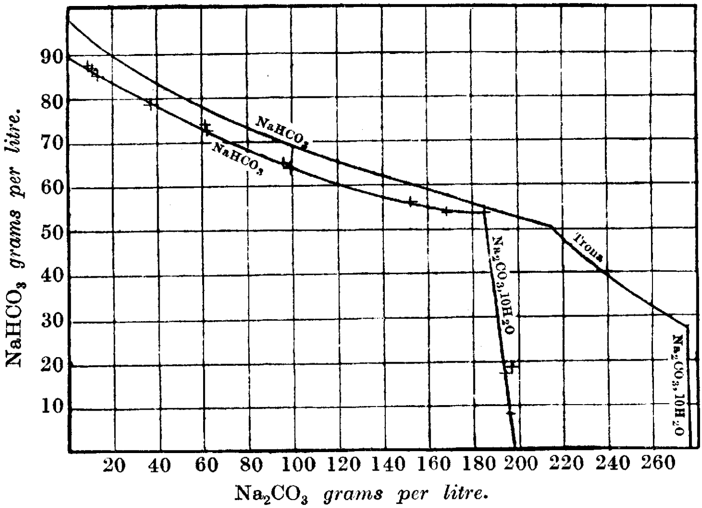
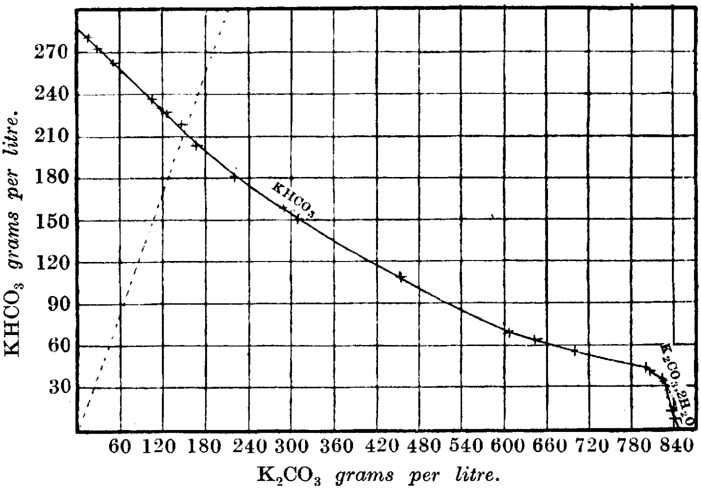


FIG. 2.



of considerable quantities of sodium carbonate are such as to facilitate the growth of the crystals.

Fig. 2, which is the corresponding diagram for potassium carbonate and bicarbonate, shows clear evidence of a double compound. This substance, the region of stability of which is very limited at 18°, is doubtless identical with the compound obtained by Bauer (*Ber.*, 1883, **16**, 1143) during the evaporation of bicarbonate solutions on a large scale in a mineral water factory. This salt was carefully analysed, and was examined crystallographically by Rammelsberg, but all attempts to obtain it synthetically have up to the present failed. Its formula is

$$K_2CO_3,2KHCO_3,3H_2O,$$

and, as the figure shows, it is only obtainable in equilibrium with a very limited range of solutions, which are very different in composition from the double salt itself.

The determinations of copper concentration in the equilibrium solutions lie on a smooth curve showing a steady increase with increase in the concentration of sodium carbonate. The copper determination of experiment 15 alone lies considerably above the curve. This point is the only determination of copper concentration in a solution in equilibrium with sodium carbonate decahydrate as solid phase, and seems to show that the rapid decrease in the bicarbonate concentration along the decahydrate curve brings about an increase in the copper content. Experiment 15 is, however, not very satisfactory, as the solution appears to have been somewhat supersaturated with carbonate owing to failure of the regulation of temperature, and the corresponding point lies at a considerable distance from the curve in Fig. 1 which connects the other points. The authors therefore content themselves with noting the observation, but lay no stress on its interpretation.

Discussion of Results.

The experimental results set forth above have several features of interest which throw some light on the nature of the equilibria involved. In the first place, it is noteworthy that the curve of copper concentrations does not approach the solubility of copper carbonate in water, which is negligibly small, as the concentration of sodium carbonate decreases, but the curves of solubility of copper carbonate and double salt appear to intersect at a copper concentration of about 0·045 gram per litre. This is unlike the normal case of double salt equilibrium in which the solubility of each component is lowered by the addition of the other. Assuming that this abnormal rise of solubility of copper carbonate in the presence of sodium carbonate is due to the formation of the complex ion $Cu(CO_3)_2$, it is easily shown that the first effect of sodium carbonate must be to depress the solubility of the other component, the solubility passing through a minimum, and subsequently rising on addition of further quantities of the sodium salt. The investigation of this curve forms no part of the present investigations. It may be noted, however, as a point of interest, that by the application of the mass-action law, which is possibly justifiable in that only very dilute solutions are under consideration, it can be readily established that the position of the minimum solubility is given by the condition.

$$[Cu^{\bullet\bullet}]=[Cu(CO_3)_2'']\text{.}$$

Passing now to the consideration of solutions saturated with the double salt, $Na_2Cu(CO_3)_2,4H_2O$, the results obtained in the present work are again at variance with the normal behaviour of double salts in that the increase of concentration of one component brings about an increase in the concentration of the other, the curve apparently rising throughout its whole course. This abnormal behaviour must, as in the case of the solubility of copper carbonate itself, be occasioned by the formation of a new constituent in the solution which removes copper from the solution equilibrium of the double salt, and so leads to an increase in its apparent solubility. The increasing solubility of the double salt with rising concentration of sodium carbonate thus constitutes a direct experimental proof of the view held by Deville that the copper in these solutions was largely present in some form chemically different from the salt which crystallises out.

Turning now to the identification of the dissolved substance, which is thus the parent of the crystalline double carbonate, a little consideration will show that if the substance is an ionisable one, the complex copper ion which forms the negative part must consist of a more heavily carbonated species, such as $Cu(CO_3)_4''''''$; the concentration of such an ion would increase with increasing concentration of carbonate. On the other hand, if such ions are present, it is very remarkable that double salts containing more than one equivalent of alkali carbonate to one of metallic carbonate never crystallise out of any of these alkali metallic carbonate solutions.

The authors are, however, of opinion that the true explanation of the solubility phenomena is to be found in the presence of a large proportion of the copper in the form of a colloidal substance, probably a normal or basic copper carbonate. This view accounts for the contrast between the colour of the solutions and that of the crystalline double salts, and is supported by the fact that coagulation can certainly be brought about, although with difficulty, by the addition of much sodium phosphate to the solutions. The possibility that the solutions are of a colloidal nature has already been considered and rejected by Luther and Kršnjavi (*loc. cit.*) on the evidence of their transport experiments, and also because the solutions can diffuse through a parchment membrane. It appears, however, that such arguments, whilst they prove the presence of complex negative ions containing copper, do not at all exclude the simultaneous presence of a positive colloid, which may, in fact, be much greater in amount than the complex ions. In fact, it is obvious that when a solution contains a colloidal substance in kinetic equilibrium with crystalloids, the colloid will diffuse through an animal membrane by first changing into the dialysable form, the colloidal form being again obtained on the other side of the membrane by the reverse change. The passage of such a solute through a membrane will doubtless be slow in comparison with the rate of dialysis of crystalloids, but when the above conditions are fulfilled, such passage must take place. The escape of colloid normally comes to an end after a small quantity has passed, owing to the disappearance of some crystalloid factor on which the change to crystalloid form depends. An example which will make the argument clear may be found in ferric chloride. A solution of this substance may be regarded as made up of colloidal ferric hydroxide, ferric ions, and hydrogen and chlorine ions. In the dialyser, the ions, including the ferric ions, immediately begin to diffuse out, and diffusion of ferric ions will, in fact, continue as long as chlorine ions remain in the solution. The concentration of chlorine ions in such a solution is, however, not very great, and their escape is fairly rapid. The result is that escape of ferric ions soon comes to an end. In the case of the alkaline copper solutions, however, the crystalloid and diffusible substance, $Na_2Cu(CO_3)_2$, is constantly regenerated, since the solutions contain much sodium carbonate, which takes a considerable time to escape from the dialyser. The escape of copper is therefore more pronounced than that of iron from a ferric chloride solution, and, in fact, is so favoured by the presence of excess of sodium carbonate that the solution simulates the behaviour of a simple crystalloid.

It is perhaps worth noting that Luther and Kršnjavi remark that the movement of the coloured boundary in their transport experiments was very slow. This may to some extent be due to the conversion of the complex ions which have crossed the boundary into the positive colloid, which travels in the opposite direction by cataphoresis.

In conclusion, the authors wish to express their indebtedness to Mr. D. H. Nagel and to Mr. D. L. Chapman for much valuable assistance and advice during the progress of this work. They have also to thank Mr. S. G. Plant for assistance in carrying out some of the analytical work.

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