

CCCLXXXVI.—*The Chemical Nature of Precipitated Basic Cupric Carbonate.*

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THE author has previously studied (J., 1925, 127, 1007) the mechanism of the changes which occur when precipitated cupric carbonate is kept in contact with the resulting solution. Special attention has now been directed towards the initial process which occurs on admixture of solutions of copper sulphate and sodium carbonate, the concentrations of which are systematically varied, with the object of gaining definite information as to the chemical nature of precipitated cupric carbonate, the composition of which is well known to depend on certain arbitrary factors, such as temperature of precipitation, relative proportions of admixed reagents, and time elapsing between precipitation and analysis. Serious analytical discrepancies have also been found to arise through inefficient mixing of the reacting solutions. In order to minimise such variations in the composition of the precipitate, a special mode of procedure was adopted in the present work.

If an excess of copper sulphate is used in the precipitation, and more especially if the sodium carbonate is added to the copper sulphate, the precipitate contains basic sulphate admixed with the basic carbonate. If the copper sulphate is added to excess of sodium carbonate, the precipitate consists of the basic carbonate, and the solution may contain carbonic acid, sodium hydrogen carbonate, or sodium carbonate, or mixtures of these compounds, according to the excess of sodium carbonate employed. On the other hand, with efficient stirring, and if the copper sulphate is

added to an equimolecular proportion of the sodium carbonate, the precipitate contains a relatively small percentage of basic sulphate, whilst the solution contains only carbonic acid and a small amount of dissolved copper.

The possibility of decomposition of the precipitate through subsequent drying or other further treatment was minimised by carrying out the analyses immediately after the reaction. The results thus obtained were reproducible, the effect of small temperature changes being unimportant.

In order to render the investigation as complete as possible, determinations have been made of copper and carbonic acid in the precipitate and in the solution after the reaction; of sodium carbonate remaining in solution, and adsorbed in the precipitate; and of adsorbed sulphate.

#### EXPERIMENTAL.

The solutions employed in the precipitations were all prepared by dilution from *M*-solutions. The cupric sulphate (A.R.) was used to standardise the sodium thiosulphate used in the subsequent copper estimations, and in the preparation of the *M*-cupric chloride solution. The cupric chloride employed was free from sulphate, but contained 22.9% of water; the solution was therefore made a little stronger than *M*, titrated against the standard thiosulphate solution, and diluted with the calculated amount of water. The *M*-sodium carbonate solution was standardised against the oxalic acid used in the carbon dioxide estimations, which had been previously standardised against pure sodium carbonate from bicarbonate. The oxalic acid was also employed in the estimations of sodium carbonate in solution. The potassium carbonate was prepared from bicarbonate and its titration against the oxalic acid confirmed the accuracy of the previous standardisation against sodium carbonate (Titration found: 27.65 c.c. Calc.: 27.67 c.c.). The barium hydroxide solution used in the estimations of carbon dioxide was preserved in an apparatus for titration in the absence of carbon dioxide. It was standardised against the oxalic acid.

The more dilute solutions were prepared in every case by dilution with water free from carbon dioxide and air. The volumes of the solutions employed were adjusted to yield a convenient quantity of precipitate, and varied from a minimum of 50 c.c. to a maximum of 1000 c.c. Equimolecular quantities of sodium carbonate and copper sulphate were used.

The experimental method adopted in the precipitations was similar to that described by Gröger (*Z. anorg. Chem.*, 1900, **24**, 127). The solution of copper sulphate was added in a fine stream

to that of sodium carbonate, violent mechanical stirring being employed throughout the addition. All the precipitations were carried out at room temperature (20°). The solution was filtered immediately after flocculation (5—10 minutes) through a Buchner funnel by means of the water-pump, and the precipitate was washed rapidly with cold water free from carbon dioxide and air.

*Analysis.*—(a) *Precipitate.* The moist precipitate was transferred to an apparatus for the estimation of carbon dioxide in carbonates (following the author's modification of Van Slyke's method, *Analyst*, 1926, **51**, 622), and analysed at once, loss of carbon dioxide from the precipitate through exposure to the air being thus eliminated. Copper was determined in the hydrochloric acid solution (remaining after the carbon dioxide estimation) by dilution, addition of sodium acetate in excess and of potassium iodide, and titration against standard sodium thiosulphate. Each determination was carried out in duplicate, except in Expts. 7 and 8 (Table I), where the amount of precipitate obtained was insufficient.

In the estimations of the adsorbed material in the precipitate, about 1 g. of the air-dried material was ignited to cupric oxide, extracted with boiling water, the filtrate concentrated, and titrated against 0.1*N*-oxalic acid for sodium carbonate (compare Applebey and Lane, J., 1918, **113**, 611). The remaining precipitate was dissolved in hydrochloric acid and added to the aqueous extract; the sulphate in the combined solution was then estimated as barium sulphate. (The solution was made up to 100 c.c. and 10 c.c. were titrated against the standard thiosulphate to determine the copper present, the remaining 90 c.c. being employed in the sulphate estimation.)

(b) *Filtrate.* A large volume of the filtrate was concentrated, whereby the copper was completely precipitated, with evolution of carbon dioxide; it was filtered off, dissolved in acetic acid, and titrated as usual. This filtrate was further concentrated and its sodium carbonate was estimated by titration in boiling solution against standard oxalic acid, phenolphthalein being used as indicator. Carbon dioxide in solution was determined by difference.

The results of the complete series of experiments (over a concentration range of *M* to 0.00625*M*) are given in Table I. The carbon dioxide content of the precipitate appears to vary continuously with the concentration of the reagents employed in the precipitation. The percentage of adsorbed copper sulphate at concentrations varying from 0.5*M* to 0.05*M* is small and erratic in nature; its variation is parallel to that in the concentration of the sodium carbonate remaining in solution (see Table V). The

TABLE I.

Expt. No.	Initial conc. (mols./litre).	Composition of precipitate.				Adsorbed $\text{CuSO}_4$ , %.
		$\text{CO}_2$ , g.	$\text{CuO}$ , g.	Value of $x$ in $2\text{CuO}, x\text{CO}_2$ .		
				$x$ .	Mean.	
1 a	1.00	0.1013	0.3480	1.052	1.044	—
b	"	0.03704	0.1295	1.035		
2 a	0.50	0.09204	0.3146	1.058	1.052	0.16
b	"	0.07145	0.2473	1.045		
3 a	0.25	0.05790	0.2200	0.952	0.945	1.84
b	"	0.04290	0.1656	0.937		
4 a	0.10	0.0681	0.2845	0.906	0.902	2.25
b	"	0.04508	0.1818	0.897		
5 a	0.05	0.02122	0.09572	0.802	0.798	2.21
b	"	0.04296	0.1957	0.794		
6 a	0.025	0.03038	0.1476	0.744	0.737	—
b	"	0.03833	0.1894	0.732		
7	0.0125	0.02004	0.1068	0.678	0.678	—
8	0.00625	0.02522	0.1463	0.623	0.623	—

percentage of adsorbed sodium carbonate is negligible. It seems probable that these small quantities of adsorbed material play no essential part in the reaction, and they have therefore been ignored in the following discussion.

The solubility of carbon dioxide in water at  $20^\circ$  corresponds with a concentration of  $0.039M$  (Landolt-Börnstein, Tables, 5th Edn., 1923, 768). The solution resulting from admixture of approximately  $0.25M$ -solutions of copper sulphate and sodium carbonate should therefore (from calculations based on the composition of the precipitate) be saturated with carbon dioxide; no effervescence occurred, however, on admixture of such solutions at  $20^\circ$ , whilst the effervescence was very slight in the case of  $0.5M$ -solutions, and violent with  $M$ -solutions. The liquid in equilibrium with the precipitate from  $0.5M$ -solutions appears, therefore, to be supersaturated with carbon dioxide, the concentration of carbon dioxide deduced from the composition of the precipitate being  $0.119M$ . It was observed that the analytical figures for the precipitates from  $0.5M$ -solutions and above were more variable than those for precipitates from more dilute solutions. This would be in accordance with the essential instability of supersaturated solutions and their sensitiveness towards small temperature changes. It will be noted particularly that the carbon dioxide content of the precipitates increases continuously until the concentration  $0.5M$  is reached, but oscillates when this concentration is exceeded, suggesting a definite connexion between the concentrations of carbon dioxide in the liquid and the solid phases. It has accordingly been assumed that the concentration  $0.119M$  for carbon dioxide in equilibrium with the precipitate was the maximum value possible.

All the experiments of Table I were carried out with copper sulphate and sodium carbonate. Precipitations with 0.5*M*- and 0.05*M*-cupric chloride and sodium carbonate, and with 0.5*M*- and 0.05*M*-copper sulphate and potassium carbonate, were also carried out, in order to ascertain whether the composition of the precipitated basic cupric carbonate was influenced to any extent by the acid and basic radicals associated with the cupric and carbonate ions (Table II). Although the results are not identical, and indicate some specific action of foreign ions, the composition of the precipitate approximates to the same value in each case.

TABLE II.

Precipitants used.	Composition of precipitate.	
	Value of $x$ in $2\text{CuO}, x\text{CO}_2$ for	
	0.5 <i>M</i> -Sols.	0.05 <i>M</i> -Sols.
$\text{CuSO}_4, \text{Na}_2\text{CO}_3$	1.052	0.798
$\text{CuCl}_2, \text{Na}_2\text{CO}_3$	1.011	0.850
$\text{CuSO}_4, \text{K}_2\text{CO}_3$	0.999	0.833

#### Discussion.

The composition and the chemical nature of precipitated cupric carbonate have been investigated previously by several authors, and there is some divergency in the views expressed by them.

Gröger (*loc. cit.*) has studied the effect upon the carbon dioxide content of precipitated cupric carbonate, of steadily increasing the molecular proportion of sodium carbonate relative to copper sulphate. In his experiments, all the precipitations were carried out with *N*-solutions, and the concentration was not systematically varied as in the author's experiments, but the method of procedure was otherwise very similar. The products were air-dried before analysis. When the molecular ratio  $\text{Na}_2\text{CO}_3 : \text{CuSO}_4$  was increased from 1:1:1 to 2:1, the carbon dioxide content was very much lowered (from  $2\text{CuO}, 1.012\text{CO}_2$  to  $2\text{CuO}, 0.802\text{CO}_2$ ). With a molecular ratio of 4:1 the carbon dioxide content was reduced still further ( $2\text{CuO}, 0.748\text{CO}_2$ ). The composition of the precipitate from approximately equimolecular quantities (1.1:1) of 0.5 *M*-solutions corresponds with  $2\text{CuO}, 1.012\text{CO}_2$ , in close agreement with the author's result at this concentration,  $2\text{CuO}, 1.052\text{CO}_2$ .

Employing sodium bicarbonate in place of the normal carbonate, Gröger found the carbon dioxide content of the precipitate to be increased—with approximately equimolecular solutions, the composition of the product corresponded with  $2\text{CuO}, 1.244\text{CO}_2$ . He apparently regards the precipitated basic cupric carbonate as the decomposition product of the normal carbonate, for he states

(*loc. cit.*, p. 134) that it is not improbable that normal cupric carbonate is first formed and passes into the basic carbonate with loss of carbon dioxide. The high results for the carbon dioxide content of precipitates from sodium bicarbonate are held to agree with this view, by increasing the available carbon dioxide content of the reagent used, and so diminishing the extent of the decomposition. On the other hand, Gröger formulates the above product from bicarbonate as a definite compound,  $8\text{CuO},5\text{CO}_2,7\text{H}_2\text{O}$ .

Pickering (J., 1909, **95**, 1409) attempted to ascertain the composition of precipitated basic cupric carbonate by adding sodium carbonate to a solution of copper sulphate sufficiently weak to ensure the retention of any carbon dioxide liberated (0.05% of copper). He found that alkalinity was attained when 1.61 mols. of sodium carbonate had been added per mol. of copper sulphate, and thence deduced the formula  $5\text{CuO},2\text{CO}_2$  (or  $2\text{CuO},0.80\text{CO}_2$ ) for the precipitated substance. Pickering apparently assumes that the composition of the precipitate is independent of the concentration employed in the precipitation. This assumption has already been shown by the author to be untenable. Further, since the sodium carbonate was added to the copper sulphate, Pickering's compound undoubtedly contained basic sulphate.

Dunnicliff and Lal (J., 1918, **113**, 718) claimed to have prepared two new basic carbonates by precipitation from cupric sulphate-sodium carbonate mixtures of stated concentration, under standard conditions. Their method consisted in the addition of a cold 10% solution of sodium carbonate to a half-saturated solution of copper sulphate. The precipitate was kept for 24 hours, washed free from sulphate, and dried at  $96^\circ$  to constant weight. The mean of a number of analyses led to the formula  $13\text{CuO},5\text{CO}_2,9\text{H}_2\text{O}$ . The second compound, prepared by adding a mixture of 5% sodium carbonate and 5% sodium bicarbonate solutions to the copper sulphate solution, corresponded to the formula  $7\text{CuO},2\text{CO}_2,5\text{H}_2\text{O}$ .

The underlying idea in the experiments of Dunnicliff and Lal appears to be that any substance of constant composition which can be prepared under standard conditions is a definite compound, but, as judged by the author's results, these so-called compounds probably form points in a continuous curve; further, they appear to have no well-marked individuality or characteristics which distinguish them from other precipitates as definite compounds.

Mond and Heberlein (J., 1919, **115**, 908) have determined the composition of basic cupric carbonate precipitated from approximately 0.05*M*-solutions, under different conditions. The results indicate, contrary to those of Gröger, that the composition of the precipitated basic cupric carbonate was constant and independent

of the molecular proportion of cupric sulphate and sodium carbonate, in mixtures containing amounts in the proportion of 1 : 1 and lower. The molecular ratio in the precipitate was  $\text{CuO} : \text{CO}_2 = 2.26 : 1$  (or  $2\text{CuO}, 0.885\text{CO}_2$ ). The amount of adsorbed material was relatively large, as is to be expected in the absence of an efficient stirrer. They concluded that no well-defined compound of copper is obtained by precipitation, the composition altering according to the conditions.

From theoretical considerations, there are a number of possibilities as to the chemical nature of the precipitated basic cupric carbonate. The simplest (Pickering; Dunncliff and Lal) is to assume that a definite compound, or series of compounds, is formed. This view appears to be untenable in the light of the present experiments. A second view (Gröger) regards the substances as a mixture of the normal carbonate and the hydrated oxide. The various products are then regarded as due to the partial decomposition of the normal carbonate, and the variations of composition observed are attributed to greater or less decomposition, under given experimental conditions. It follows from this view, by the application of the mass-action equation  $[\text{CuO}][\text{CO}_2]/[\text{CuCO}_3] = K$ , that the concentration of the carbon dioxide in solution (or of carbonic acid), after precipitation, should possess a constant value, independent of the concentrations of the initial solutions employed in the precipitations; for, since both the normal cupric carbonate and the hydrated oxide may be regarded as very sparingly soluble in water, their active masses in solution would be constant.

It follows further, from this argument, that the amount of carbon dioxide retained in the precipitate at any particular initial concentration will diminish as the concentration of the precipitating solution is diminished, in order that this limiting concentration of carbon dioxide may be attained, after which no further loss of carbon dioxide from the precipitate should take place. Further, it appears that at a certain limiting value, *i.e.*, an initial concentration which will yield a concentration of carbon dioxide in the mother-liquor just equal to the equilibrium value, the precipitate should consist of the hydrated oxide only, and be free from carbon dioxide.

The experimental results for the concentration of carbon dioxide in the mother-liquor indicate, however, that this concentration diminishes steadily with the initial concentration of the reagents employed; the experimental result is therefore directly opposed to that derived from a consideration of the theoretical basis of Gröger's idea. A similar result follows if the basic cupric carbonate is regarded as the product of hydrolysis of the normal carbonate.

Free (*J. Amer. Chem. Soc.*, 1908, **30**, 1366) has suggested that the precipitated basic cupric carbonates might be regarded as solid solutions of carbonic acid with hydrated cupric oxide. This view does not appear to be very probable.

Certain basic salts produced by precipitation have been subjected to phase-rule studies (compare Britton, *J.*, 1925, **127**, 2796), and the results have been held to be comparable with those obtained in initial precipitation processes. It appears to be a condition of such studies—more particularly those employing Schreinemaker's method of residues—that the liquid phase should be in equilibrium with a definite solid phase (or phases), *i.e.*, a well-characterised (probably crystalline) substance. In cases where a definite product is not obtained (*e.g.*, a colloidal substance, as obtained by Carter and Hartshorne, *J.*, 1923, **123**, 2223, in their study of the system ferric oxide-phosphoric acid) the phase-rule method yields no definite result. Further, sufficient time must be allowed in phase-rule studies to enable a definite equilibrium to be reached. When such a state has been attained, the solid phase in equilibrium with the liquid is generally found to be crystalline (compare Carter and Hartshorne, *loc. cit.*).

It appears, therefore, that the initial product in a precipitation change must be distinguished from that obtained in a phase-rule study, or, in the particular case under investigation, that the initial precipitate is entirely different in nature from the stable basic carbonate, malachite, which is obtained under special conditions (compare *J.*, 1925, **127**, 1007).

For the particular conditions maintained in the author's experiments, the final products of the precipitation at each concentration (neglecting small amounts of fortuitous impurities) consisted of a solid phase containing cupric oxide and a liquid phase containing carbon dioxide together with sodium sulphate. When the concentration of carbon dioxide in solution is plotted against the carbon dioxide content of the precipitate, Curve I (Fig. 1), is obtained. The carbon dioxide content,  $a$ , of the solid phase is evidently a continuous function of that in the liquid phase,  $c$ ; further there is an exponential relation between these two magnitudes. When the logarithms of the two quantities are plotted, the points obtained lie, within the limits of experimental error, along a straight line (Curve II; Fig. 1). These results, therefore, are in accordance with the criteria usually applied to adsorption effects.

According to Freundlich ("Colloid and Capillary Chemistry," 1926, p. 172), the general form of the adsorption isotherm is represented by the equation

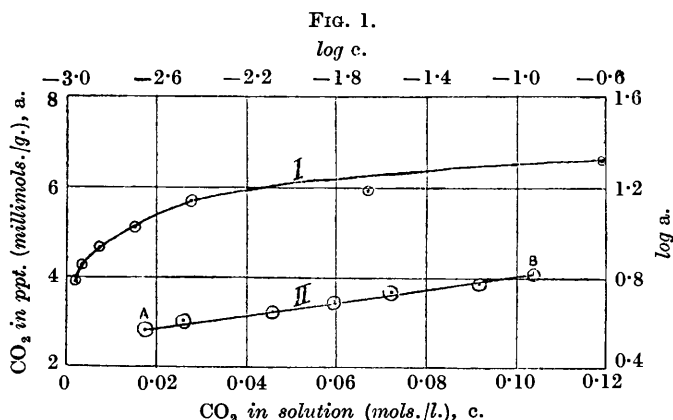
$$a = \alpha(c)^{1/n} \quad . \quad . \quad . \quad . \quad . \quad (1)$$



where  $1/n$  has a value between 0.1 and 0.5, whilst the constant  $\alpha$  may vary within wide limits. [The concentration  $c$  is given in mols. per litre, whilst the quantity  $a$  is calculated in millimols. per g. of adsorbent (anhydrous cupric oxide).] The value of  $1/n$  was calculated to be 0.130 from the co-ordinates of the points A and B, both of which fell on the logarithmic line. From this value and the observed values of  $a$  and  $c$ ,  $\alpha$  was found to be 8.75, by substitution in (1). Hence

$$a = 8.75c^{0.130} \dots \dots \dots (2)$$

By use of this equation, the theoretical values for  $a$  have been calculated at the concentrations actually employed, and compared



For Curve I, use ordinary co-ordinates.  
For Curve II, use logarithmic co-ordinates.

with the experimental figures (Table III, columns 2 and 3). The agreement appears to be satisfactory.

TABLE III.

Equil. conc. of CO <sub>2</sub> in soltn. (mols./l.).	CO <sub>2</sub> in precipitate (millimols. per g.).		Equil. conc. of CO <sub>2</sub> in soltn. (mols./l.).	CO <sub>2</sub> in precipitate (millimols. per g.).	
	Found.	Calc.		Found.	Calc.
0.119	6.61	(6.63)	0.00789	4.63	4.66
0.0668	5.94	6.15	0.00319	4.26	4.15
0.0275	5.67	5.48	0.00215	3.92	(3.94)
0.0150	5.01	5.07			

There is a marked parallelism between these results and those of Biltz (*Ber.*, 1904, **37**, 3138) for the adsorption of arsenious oxide by hydrated ferric oxide. Biltz's figures have been recalculated according to the adsorption equation

$$a = 6.02c^{0.200} \dots \dots \dots (3)$$

and the values obtained are in Table IV.

TABLE IV.

Equil. conc. of As <sub>2</sub> O <sub>3</sub> in soltn. (mols./l.).	As <sub>2</sub> O <sub>3</sub> in precipitate (millimols. per g.).		Equil. conc. of As <sub>2</sub> O <sub>3</sub> in soltn. (mols./l.).	As <sub>2</sub> O <sub>3</sub> in precipitate (millimols. per g.).	
	Found.	Calc.		Found.	Calc.
0.0979	3.77	(3.77)	0.0125	2.51	2.51
0.0603	3.40	3.43	0.00699	2.32	2.23
0.0479	3.26	3.28	0.00427	2.21	2.02
0.0422	3.10	3.19	0.00270	1.90	1.85
0.0330	2.99	3.04	0.00114	1.59	1.55
0.0240	2.82	2.85	0.00025	1.15	(1.15)
0.0178	2.75	2.69			

TABLE V.

Conc. of original solution (mols./litre).	Equil. conc. of CO <sub>2</sub> (mols./litre).	Conc. of Cu in solution (mols./litre).	% Cu not pptd.	Conc. of Na <sub>2</sub> CO <sub>3</sub> in solution (mols./litre).	% Na <sub>2</sub> CO <sub>3</sub> not pptd.
1.00	—	0.0047	0.94	0.0030	0.60
0.50	0.119	0.0049	1.98	0.0007	0.28
0.25	0.0668	0.0036	2.9	0.0014	1.1
0.10	0.0275	0.0018	3.6	0.0009	1.8
0.050	0.0150	0.0011	4.4	0.00034	1.4
0.025	0.0079	0.00071	5.6	0.00031	2.5
0.0125	0.0032	0.00050	8.0	Trace	—
0.00625	0.0022	0.00026	8.6	„	—

Further, the values for  $1/n$  are within the limits laid down by Freundlich for typical adsorptions, but somewhat lower than the average (0.3—0.5), whilst the constant  $\alpha$  is in both cases well within the range of values usual for such phenomena. A further parallelism appears in the nature of the adsorbed substance. The cases of adsorption from aqueous solution which have been investigated most thoroughly are those of the weak organic acids by charcoal, and in the present case the adsorbed substance is apparently carbonic acid, a weak acid the strength of which is of the same order of magnitude as those of the organic acids.

The precipitated cupric oxide appears to be present, when initially precipitated, in a very finely divided condition, as is indicated by the abnormally large solubility in the carbon dioxide in solution. Such a large effective surface would facilitate large and rapid adsorption.

The author therefore puts forward the view that the formation of precipitated cupric carbonate is due, not to dissociation of the normal carbonate, but to adsorption of un-ionised carbonic acid by hydrated cupric oxide in a very active state.

The fact that the composition of the basic cupric carbonate precipitated from 0.5*M*-solutions approximates to the formula  $2\text{CuO}\cdot\text{CO}_2$ , independently of the particular salt of copper employed suggests that a definite compound is produced at this concentration. Further, this composition represents the maximum value for the

carbon dioxide content when the precipitations are carried out with sodium carbonate and copper sulphate. According to the views put forward by the author, however, the agreement of the analytical figures at this concentration with the formula for malachite is only a coincidence. The carbon dioxide content of the precipitate is conditioned by its concentration in the liquid phase, and the maximum value of this concentration is further limited by the solubility of carbon dioxide in water, which may, however, be affected by the formation of supersaturated solutions. If the solubility of carbon dioxide in water could be made to exceed this value, the carbon dioxide content of the precipitate would be expected to be higher. This prediction finds support in Gröger's results for precipitations with bicarbonate: in the presence of sodium bicarbonate the solubility of carbon dioxide is increased, and the concentration of un-ionised carbonic acid is further increased by the excess of bicarbonate ions, according to the relation  $[H^+][HCO_3^-]/[H_2CO_3] = K_1$ . Actually, under these conditions the carbon dioxide content of the precipitate was increased.

The author has carried out a number of experiments with the object of approaching the equilibrium from the other side, *viz.*, from hydrated cupric oxide and aqueous solutions of carbon dioxide, but certain difficulties rendered it impossible to obtain definite results. Primarily, it was not found possible to prepare hydrated cupric oxide free from notable amounts of cupric sulphate, without the occurrence of blackening, due to traces of alkali. It is thought that more definite results might be obtained by the use of a more stable hydrogel, *e.g.*, hydrated ferric oxide.

The idea that certain basic salts might be adsorption compounds has recently been tentatively put forward by Britton (J., 1926, 125) to explain the fact that the thorium hydroxide precipitated from thorium nitrate by addition of potassium chromate contained large amounts of chromic anhydride, the presence of which was attributed to "a process akin to adsorption, in which the chemical tendencies of the weak acid and the weak base played an important part." Although no further experimental verification of this statement was adduced, the idea is analogous to that now suggested by the author.

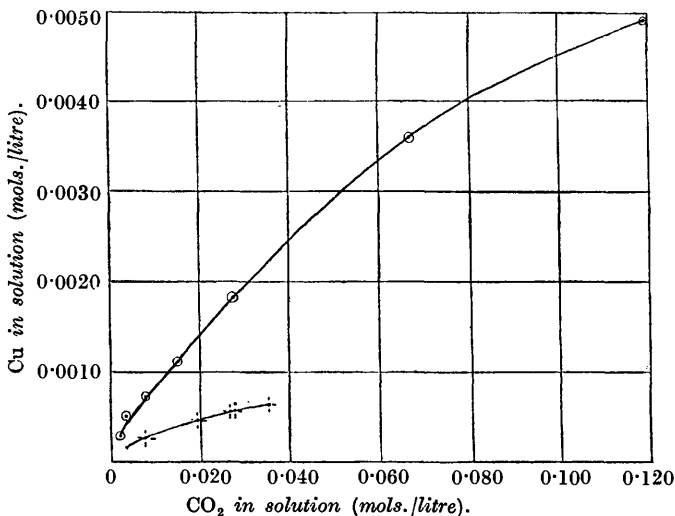
#### *The Copper in Solution.*

At every concentration at which the precipitation was carried out, it was found that a definite concentration of copper in solution was attained, after precipitation, dependent upon the concentration of carbon dioxide in the final solution. The relation between these two concentrations is represented by a smooth curve, shown in Fig. 2. The regularity of the results is striking, in view of the fact

that the carbon dioxide contents of the precipitates obtained at each concentration were widely divergent, the value of  $x$  in the formula  $2\text{CuO}, x\text{CO}_2$  varying from 1.052 to 0.623; in spite of this, these precipitates behave in the same way as regards their solubility in aqueous solutions of carbon dioxide, which suggests that they are of very similar chemical nature. Such would be the case if each precipitate consisted of hydrated cupric oxide with variable quantities of adsorbed carbon dioxide.

Mond and Heberlein (*loc. cit.*) have determined the concentration of copper in the solution remaining after a precipitation from

FIG. 2.



○ Author (see Table V). ⊘ Free.

0.05M-solutions of cupric sulphate and sodium carbonate. They found this concentration to be 0.0032M (representing 8.0% of the total copper originally in solution), whereas the author's experiments at 0.05M gave 0.0011M (representing 4.42% of the original copper). Their corresponding concentrations of sodium carbonate remaining in the mother-liquor were also much higher than those found by the author. It is suggested that these high results are to be attributed to incomplete mixing owing to the lack of an efficient stirrer.

According to Mond and Heberlein, the dissolved copper is present in colloidal solution as the basic sulphate, and the sodium sulphate present in the solution may be removed by dialysis; they also state that the basic carbonate itself is not appreciably soluble in

water in the presence of carbon dioxide. In the author's opinion, these views are based upon insufficient experimental evidence, for the statement that the substance in solution is the basic sulphate appears to be founded upon one analysis of the precipitate formed after expelling carbon dioxide from the solution by boiling, whereby any carbon dioxide in the precipitate would also be removed. The black precipitate so produced contained  $\text{SO}_3 : \text{CuO} = 1 : 4$ .

The copper in solution is completely precipitated by boiling and expelling the carbon dioxide, the solution is colourless and not opalescent, and on exposure to air in an open vessel it loses carbon dioxide rapidly, with film formation of the basic carbonate on the surface. Under such conditions, it is difficult to understand how Mond and Heberlein were able to dialyse such a solution without decomposition and precipitation through loss of carbon dioxide.

Previous determinations of the solubility of basic cupric carbonate in aqueous solutions of carbon dioxide have been carried out by Free (*loc. cit.*). Precipitated basic cupric carbonate was agitated with a solution of carbon dioxide of known concentration, and the concentration of copper in solution was estimated after equilibrium had been attained. It was found that freshly precipitated basic cupric carbonate was more soluble in aqueous carbon dioxide solutions than the stable crystalline basic salt (malachite), and that the solubility of the freshly precipitated substance steadily decreased with time, finally reaching constancy at the value representing the solubility of malachite in the particular concentration of carbon dioxide. At the same time it was observed that the substance had been transformed into malachite.

The maximum value obtained by Free in any experiment was 107 parts of copper per million parts (or 0.00167 g.-atom per litre), in a solution of carbon dioxide containing 1200 parts per million. The author's result at this carbon dioxide concentration corresponds with 0.0018 g.-atom per litre. The agreement for freshly precipitated basic cupric carbonate is therefore satisfactory.

The author's results for the concentration of copper in solution are approximately three times as high as those obtained by Free for malachite (*e.g.*, for a solution containing 0.0275 mol. of  $\text{CO}_2$  per litre, the concentration of Cu in solution was 0.0018 g.-atom per litre, whereas Free's result for a solution containing 0.0278 mol. of  $\text{CO}_2$  per litre was 0.00054 g.-atom of Cu per litre). It is probable, therefore, that the freshly precipitated basic cupric carbonate is in a very finely divided condition, since below a certain limit of particle size the solubility of such precipitates is known to increase with the degree of dispersity. It may be observed, in this connexion, that Seyler (*Analyst*, 1908, **33**, 454) has attributed

the regularities found in Free's results to the formation of cupric bicarbonate in solution, and has attempted to show, by the application of ionic principles, that the solubility relationships are in accordance with this assumption.

*Summary.*

The effect of systematic variation in the concentration of the precipitants (copper sulphate and sodium carbonate) on the carbon dioxide content of precipitated basic cupric carbonate has been studied. The solutions employed were equimolecular, and the concentration ranged from  $M$  to  $0.00625M$ . The results obtained indicate that the carbon dioxide content of the precipitate is a continuous function of the concentration of carbon dioxide in solution, and that these two magnitudes are capable of representation by a Freundlich adsorption equation. The view is therefore advanced that the formation of basic cupric carbonate is due to an adsorption process, the absorbent consisting of hydrated cupric oxide in a very active state, and the adsorbed material being un-ionised carbonic acid.

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