THE SOLUBILITY OF PRECIPITATED BASIC COPPER CARBONATE IN SOLUTIONS OF CARBON DIOXIDE.

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Introduction.—Investigations on the effect of mine detritus in irrigation waters have been in progress in the Arizona Agricultural Experiment Station for several years, and in connection therewith it became necessary to know the solubility of precipitated basic copper carbonate (hydrated) in water carrying varying quantities of carbon dioxide, as well as the extent to which this solubility is affected by the presence of certain salts usually found in irrigation waters.

Determinations of the solubility in carbon dioxide solutions of one of the copper carbonates (malachite) have been made by Jahn,[1] Lassaigne,[2] and Wagner,[3] but none of these investigators has recorded the amount of carbon dioxide, and there is also considerable doubt as to the exact composition of the copper compound used. Favre's[4] data are not quantitative. In the absence[5] therefore of satisfactory data in the literature, the investigation here reported was undertaken and its results are deemed of sufficient general interest to render separate publication desirable. The much discussed question of the influence of carbon dioxide on the solubilities of the carbonates[6] is still far from solved, and data bearing on it may be of interest to other investigators.

Composition of the Precipitated Copper Carbonates.—Not the least of the difficulties in investigating the precipitated copper carbonates is the obtaining of a precipitate of definite and constant composition. Precipitates from solutions of copper salts and soluble carbonates are invariably basic, and their degree of basicity seems to vary with the conditions of precipitation, hence the large number of compounds reported in the literature.[7] The precipitate obtained by mixing solutions of, say, copper sulphate and sodium carbonate is light bluish green and very voluminous, but begins to consolidate at once, with loss of carbon dioxide and takes on a malachite green color. This consolidation is hastened by gentle heat, but if the heat be too intense, the precipitate turns black.

Gröger,[8] one of the most thorough investigators in this field, thinks

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[1] *Ann.*, 28, 111–114 (1838).

[2] *J. chim. med. pharm. tox.*, 4, 312 (1848).

[3] *Z. anal. Chem.*, 6, 167 (1867).

[4] *Ann. Chim. Phys.* [3], 10, 116–120 (1844).

[5] With the exception of the work of Skinner with solutions of $CaH_2(CO_3)_2$ and $NaHCO_3$, to be referred to later.

[6] See Raikow, *Chem. Ztg.*, 31, 55, 87, 141 (1907).

[7] See Moissan: *Traité de Chimie Minérale*, 5, 106–8 (1906).

[8] *Z. anorg. Chem.*, 24, 127–138 (1900).

that the original bluish green precipitate is a colloidal copper carbonate containing a variable amount of water and with a Cu: CO_2 ratio (molecular) of 2 : 1. The final malachite green substance he considers to be $6CuO.3CO_2.4H_2O$, which therefore differs from natural malachite ($2CuO.CO_2.H_2O$) only in containing one-third more water. Early in the course of the present investigation it was discovered that the precipitate prepared by simply mixing the solutions of copper salt and carbonate was not of the same composition in different preparations and that it changed its nature under the action of carbon dioxide and water in such a way as to markedly decrease its solubility in the carbon dioxide solution. Different preparations of the precipitate when allowed to dissolve in solutions of carbon dioxide in pure water gave solubilities ranging from 107 to 52 parts of copper per million (with approximately 1,200 parts carbon dioxide per million, or 0.12 per cent.). These same samples after being treated for four or five days with water containing carbon dioxide *all* gave solubilities of approximately 35 parts per million. Repetitions of the treatment with carbon dioxide solution produced no further change in solubility. This would indicate either that there had taken place a chemical change from a variable to a constant composition or that a transient abnormally high solubility, due to the presence of very finely divided material, had disappeared owing to the increase in the crystal size.[1] Possibly both of these actions take place side by side. At least some chemical change is very probable, as is indicated by the analyses given below. This change, under the action of carbon dioxide, takes place with precipitates produced under many different conditions of temperature and concentration as well as with precipitates from bicarbonate ($NaHCO_3$ and $Ca(HCO_3)_2$) solutions, and even in the case of the black precipitate, formed by overheating the ordinary green compound. The final solubility is always the same and probably the composition is also; this has not been tested by analyses. For purposes of comparison two samples of the purest obtainable natural malachite were ground to an impalpable powder in an agate mortar and their solubilities determined in the same way as with the artificial compounds. One sample gave 29 parts of copper per million of solution, the other 31, with approximately 1,200 parts free carbon dioxide per million in each case. The solubility of natural malachite is therefore slightly less than that of the artificial compound. This indicates a possibility that on very long standing in solutions of carbon dioxide the compound used in these experiments might be converted into true malachite. It was impossible to investigate this experimentally. It is of course pos-

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[1] "On the Effect of Crystal Size on Solubility," see Rothmund *Löslichkeit und Löslichkeits Beeinflussung*, pp. 109–111 (1907).

sible that the low solubilities are due to a failure to completely attain equilibrium.[1]

In order to procure a quantity of some definite substance which could be used in the study of the dissolving action of carbon dioxide, a 0.5 *N* solution of sodium carbonate was precipitated at 50° by an equivalent quantity of 0.5 *N* copper sulphate solution. The precipitate was allowed to stand over night, filtered off, washed, suspended in water and treated with carbon dioxide under a pressure slightly greater than atmospheric for three days. For extra assurance this carbon dioxide treatment was repeated, and the precipitate then filtered off and kept suspended in water ready for use. Analyses of this compound, both before and after treatment with carbon dioxide, were kindly made by Dr. W. H. Ross, of this Station, and the results are given below in molecular ratios of CuO, CO_2 and H_2O, respectively:

	CuO.	CO_2.	H_2O.
1. Before treatment—wet	1.000	0.411	....
2. After treatment —wet	1.000	0.510	....
3. " " —air-dry	1.000	0.516	0.616[2]
4. " " —dry at 100°	1.000	0.515	0.603[2]

For the sake of comparison, the corresponding ratios[3] of natural malachite and of Gröger's compound are also given.

	CuO.	CO_2.	H_2O.
Natural malachite	1.000	0.500	0.500
Gröger's compound	1.000	0.500	0.667

The compound before treatment with carbon dioxide is thus seen to be more basic than natural malachite or Gröger's compound (the basicity of which is the same), while after treatment it is slightly less so. The compound after treatment—the only one which was analyzed in dry condition—contains more water than natural malachite but less than is called for by Gröger's formula. It seems at least possible that there may exist a whole series of these carbonates, or perhaps a series of solid solutions, and that the substances which have been analyzed by previous investigators were mixtures of indefinite composition. The compound used in this investigation has a somewhat greater claim to definiteness, since its solubility is unchanged by repeated treatment with carbon dioxide solutions, although this of course does not prove that it is a simple compound, or indeed a compound at all in the strict sense of the word. The study of these compounds ought to furnish a fruitful field for the application of the phase rule methods.

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[1] *cf.* Cameron and Bell, *Bulletin No.* 30, *Bureau of Soils, U. S. Dept. Agr.*, pp. 29–30, where it is shown that powdered minerals in water solutions attain equilibrium only very slowly.

[2] H_2O determined by difference.

[3] Calculated from the formulae.

Method of Experimentation.—In making the solubility determinations on the compound prepared as outlined above, 2 grams of the powder suspended in water were placed in a bottle holding about 750 cc. and 600 cc. of water added. Carbon dioxide gas was then passed in for the time necessary to produce the concentration of carbon dioxide desired, and the bottle was corked and shaken frequently for three days. For the higher concentrations of carbon dioxide, the air space in the bottle was entirely filled with the gas by passing in a rapid stream for one half hour, and the bottle was then connected with a reservoir of carbon dioxide kept at the pressure desired. Thus arranged, the bottle was shaken as before at frequent intervals during three days. At the end of that time the precipitate was allowed to settle, the bottle opened and samples for analysis removed with a pipette, precautions being taken to prevent loss of carbon dioxide. All experiments were made at a temperature which remained quite constant at about 30°.

The sample for the determination of carbon dioxide was placed in an ordinary evolution apparatus, sulphuric acid added and the evolved gas collected in standard barium hydroxide solution, the last traces of carbon dioxide being driven over by boiling and passing a current of air through the apparatus. When evolution was complete the barium hydroxide solution was removed and titrated against oxalic acid with phenolphthalein as indicator. The carbon dioxide absorbed was calculated from the difference in the values of the barium hydroxide solution. This method gives, of course, the total carbon dioxide in solution. The free carbon dioxide was calculated by subtracting the amount which would be combined with the copper present in the solution, assuming the $Cu:CO_2$ ratio (molecular) in the dissolved compound to be 2 : 1. When carbonates other than copper were present, a correction was made for the carbon dioxide thus combined. The values given in the tables are in all cases free or uncombined carbon dioxide.

Copper was determined by evaporating a sample of the solution to dryness with nitric acid, redissolving and precipitating the copper electrolytically in acid solution. When large quantities of other salts (Na_2SO_4, $CaCl_2$, etc.) were present, the copper was precipitated by hydrogen sulphide, dissolved in nitric acid and electrolyzed. When small quantities of sodium chloride were present the sample was heated with sulphuric acid to drive off the hydrochloric acid and then electrolyzed. Small quantities of sodium sulphate or carbonate or of calcium salts were ignored. When no weighable quantity of copper was found, traces were detected by electrolyzing, using the point of a platinum wire as cathode. Since the nature of the copper compound existing in solution is open to question, the results are given in parts of metallic copper per million parts of solution.

Solubility in Solutions of Carbon Dioxide.—The solubilities in water containing varying quantities of carbon dioxide (but no salts) are given in Table I.

TABLE I.—SOLUBILITY IN SOLUTIONS OF CARBON DIOXIDE ONLY—PARTS PER MILLION.

Free CO_2.	Metallic Cu.	Free CO_2.	Metallic Cu.
0 (pure water)	1.5	961	31.0
157	8.3	1158	33.7
277	13.7	1224	34.8
348	17.0	1268	35.3
743	25.7	1549	39.7
859	28.0		

The last two results were obtained in solutions saturated with carbon dioxide at partial pressures slightly greater than 760 mm. That the carbon dioxide values are lower than those usually given for the solubility of this gas in water is due to the relatively high temperature (30°) at which the present experiments were conducted. The normal atmospheric pressure at Tucson is also somewhat below 760 mm. on account of the altitude. During these experiments it ranged from 698 mm. to 705 mm., with an average of 702 mm. The solubility of carbon dioxide in pure water under the conditions of the experiments was found, by trial, to be 1200 parts per million, which agrees quite well with the value of 1259 parts per million found by Bohn and Bock for 30° and 760 mm.[1]

Rapidity of Solution and Reprecipitation of the Copper.—It was found that in solutions of approximately 1200 parts per million of carbon dioxide the copper compound dissolved quite rapidly. The solubility attained its full value in about three hours. The reprecipitation of this copper, as carbon dioxide was lost from the solution, was observed by exposing the solution to the air and testing it at intervals. The results are given in Table II.

TABLE II.—RATE OF PRECIPITATION OF COPPER AS CARBON DIOXIDE IS LOST FROM THE SOLUTION—PARTS PER MILLION.

Days exposed.	Free CO_2.	Metallic Cu.[2]
0	1412	68
1	1370	64
3	1096	61
7	739	56
13	228	41
23	54	33

It is apparent that the fall of the copper content does not keep pace

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[1] Landolt and Börnstein, Third Edition., p. 602.

[2] The high values for the copper are due to the fact that the copper salt used in this experiment was not from the stock sample but was especially prepared, and lacked the preliminary treatment with carbon dioxide and water (See p. 1368). This does not vitiate the general conclusions.

with the loss of carbon dioxide. There is a tendency for the copper once dissolved to remain so, even when the dissolving agent (the carbon dioxide) has been removed. In time, however, it would probably be almost entirely precipitated, especially if the solution were stirred.

Solubility in Solutions of Carbon Dioxide and Sodium Chloride.—The experiments leading to Table I were repeated with solutions containing 100 parts per million of sodium chloride. The results are given in Table III.

TABLE III.—SOLUBILITY IN SOLUTIONS OF CARBON DIOXIDE AND SODIUM CHLORIDE. CARBON DIOXIDE VARIABLE. SODIUM CHLORIDE = 100 PARTS PER MILLION.

Free CO_2 (parts per million).	Metallic Cu (parts per million).
0	1.5
228	15.3
876	29.3
1026	35.0
1326	35.5
1608	37.0

The results are not essentially different from those obtained for water and carbon dioxide alone (Table I).

The effect of varying amounts of sodium chloride in solutions containing about 1200 parts carbon dioxide per million was also studied and the results are given in Table IV.

TABLE IV.—SOLUBILITY IN SOLUTIONS OF CARBON DIOXIDE AND SODIUM CHLORIDE SODIUM CHLORIDE VARIABLE.

NaCl (parts per million).	Free CO_2 (parts per million).	Metallic Cu (parts per million).
0	1268	35
10	1404	38[1]
50	1158	35
100	1326	36
500	1255	39
10000[2]	1276	58

The results seem to indicate an increase of solubility in the presence of large amounts of sodium chloride.

Solubility in Solutions of Carbon Dioxide with Sodium Sulphate, Sodium Carbonate, Calcium Sulphate, Calcium Carbonate.—The solubilities in solutions containing approximately 1200 parts per million of carbon dioxide and varying quantities of the salts named are given in the following tables:

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[1] High value due to large amount of carbon dioxide present.

[2] A value was obtained for 1000 parts sodium chloride per million, but was discarded on account of known analytical errors.

TABLE V.—SOLUBILITY IN SOLUTIONS OF CARBON DIOXIDE AND SODIUM SULPHATE. FREE CARBON DIOXIDE = APPROXIMATELY 1200 PARTS PER MILLION.

Na_2SO_4 (parts per million).	Metallic Cu (parts per million).
0	35
10	32
100	37
1000	47
10000	58

TABLE VI.—SOLUBILITY IN SOLUTIONS OF CARBON DIOXIDE AND SODIUM CARBONATE. FREE CARBON DIOXIDE = APPROXIMATELY 1200 PARTS PER MILLION.[1]

Na_2CO_3 (parts per million).	Metallic Cu (parts per million).
0	35
10	27
100	10
1000	1
10000	0.7

TABLE VII.—SOLUBILITY IN SOLUTIONS OF CARBON DIOXIDE AND CALCIUM SULPHATE. FREE CARBON DIOXIDE = APPROXIMATELY 1200 PARTS PER MILLION.

$CaSO_4$ (parts per million).	Metallic Cu (parts per million).
0	35
10	32
100	32
2085 (saturated)	36

TABLE VIII.—SOLUBILITY IN SOLUTIONS OF CARBON DIOXIDE AND CALCIUM CARBONATE. FREE CARBON DIOXIDE = APPROXIMATELY 1200 PARTS PER MILLION.[1]

$CaCO_3$ (parts per million).	Metallic Cu (parts per million).
0	35
10	25
100	7
1125	1.4

In connection with a paper on the effects of copper salts in irrigating waters, Skinner[2] gives determinations of the amount of copper held in solution by saturated solutions of sodium bicarbonate and calcium bicarbonate as 953 and 207.1 parts per million, respectively. These values are so much higher than those found in the present investigation that they require somewhat extended notice. The experiments were made by preparing a clear solution saturated with sodium carbonate

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[1] The presence of sodium carbonate materially decreases the amount of free carbon dioxide dissolved by water, and hence the solutions containing the larger amounts of sodium carbonate had to be treated with carbon dioxide at pressures greater than were usually employed in order that 1200 parts per million of *free* carbon dioxide might be absorbed. The same is true, though in less degree, of the solutions containing calcium carbonate. It is not probable that this increase of pressure would in itself have any effect on the solubility of the copper salt.

[2] THIS JOURNAL, 28, 361–8 (1906).

or calcium carbonate, and with carbon dioxide at atmospheric pressure, and adding to it a solution of copper sulphate until a precipitate began to form. This precipitate was then allowed to settle for 48 hours and copper determined in the supernatant solution. It is therefore evident that the conditions were quite different from those of the present investigation. It was pointed out on page 1366 that the compound first formed on mixing solutions of a copper salt and a carbonate, is a blue precipitate of uncertain, and probably indefinite, composition, which changes on standing, and undergoes still further change under the action of carbon dioxide and water. It is probable that 48 hours is insufficient for these changes to take place, and the determinations therefore refer not to the presumably constant green compound used in the present experiments, but to one of the first formed, transient substances, whose solubilities, as mentioned above, are higher than that of the final compound.

In addition to this effect of the presence of more soluble copper compounds, it is probable that Skinner's values are too high on account of supersaturation of the solution even with respect to these more soluble salts. As shown on page 1371, the copper in these compounds, when once dissolved, tends to remain so, and since in his experiments the copper was added in the dissolved condition, it is probable that it would require more than 48 hours for complete precipitation, especially as the solutions were apparently not agitated after the initial mixing. To test this point more directly a solution was prepared by adding a copper sulphate solution to a saturated solution of calcium carbonate and carbon dioxide, and allowing it to stand. At the beginning it contained 67 parts of copper per million,[1] but after five days' standing this had fallen to 14 parts of copper per million, and after 20 days less than 1 part of copper per million was present. The fall in copper content would no doubt be much more rapid if the solution were agitated.

Skinner's results are therefore higher than those of the present investigation, because, as shown above, insufficient time was allowed for the formation of a stable copper salt, and because the solution was probably supersaturated. The presence of sulphate ions in the solution may also have had a slight effect in increasing the amount of copper dissolved. It is very doubtful if the conditions of agitation, etc., in a running stream would permit the permanent retention in solution of amounts of copper anywhere nearly so large as indicated by the figures under consideration.

Summary and Discussion.—The general conclusions of the present investigation may be summarized as follows:

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[1] That this value is lower than Skinner's is probably due to some accidental variation in the manner of precipitation. Slight differences in conditions of precipitation would produce differences of composition and consequently of solubility.

(1) The compounds produced by precipitation of copper solutions by carbonates are unstable and possess varying solubilities in solutions of carbon dioxide.

(2) On treatment with solutions of carbon dioxide these substances pass over into an apparently stable compound possessing a definite solubility in solutions of carbon dioxide of definite concentration, which solubility increases with the concentration of carbon dioxide.

(3) The addition of small amounts of sodium chloride or sodium sulphate causes no decided change in the solubilities. Larger amounts of these salts increase the solubilities.

(4) The action of calcium sulphate is not decidedly in either direction.

(5) Sodium carbonate and calcium carbonate both decrease the solubility strongly, and in about the same ratio.

The results with soluble salts are in line with what would be expected from the standpoint of the electrolytic dissociation theory. If the dissolved copper be supposed to exist in some combination which gives a carbonate ion on dissociation, the presence of the same ion derived from sodium or calcium carbonates ought to depress the solubility of copper—as it does. On the other hand, the presence of an ion which forms a soluble copper salt, as Cl^- or $SO_4^=$, ought to increase the solubility —as it does.

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THE ELECTROLYTIC FORMATION OF SELENIC ACID FROM LEAD SELENATE.

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This paper gives the results of a series of experiments that were made to determine the best conditions for electrolytically changing lead selenate into metallic lead and selenic acid. It is a well known fact that many insoluble metallic salts, when in contact with the cathode, are changed into the metal and the acid by the nascent hydrogen that is formed during the electrolysis. Many of the salts of lead are decomposed in this manner. Lead oxide is easily reduced at the cathode.[1] The commercial process of Salom[2] for the electrolytic reduction of galena depends upon the fact that lead sulphide resting upon the cathode in a dilute solution of sulphuric acid is changed into metallic lead and hydrogen sulphide. Lead sulphate can also be changed into metallic lead and sulphuric acid as is shown by the negative plates of storage batteries during charging. In a

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[1] Lodyguine, *Trans. Am. Electrochem. Soc.*, 7, 221 (1905).

[2] J. W. Richards: *Electrochem. Met. Ind.*, 1, 18 (1902). A. J. Weightman: *Trans. Am. Electrochem. Soc.*, 1, 931 (1902).