XXV.—*Chemical Properties of Concentrated Solutions of certain Salts. Part I. Double Potassium Carbonates.*

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IN the course of some experiments on the preparation of potassium percarbonate recently discovered by Messrs. Constam and Von Haussen (*Zeit. fur Elektrochem.*, 1897, p. 455, and *Moniteur Sc.*, August, 1897), I noticed that copper sulphate would dissolve in the concentrated solution of potassium carbonate employed, yielding a deep blue liquid; as nothing appeared to be known about the compound thus formed, attempts were made to isolate it.* It was soon found that the salts of several other metals will also dissolve in this solution to a greater or less extent, and that from such solutions crystalline compounds could in most cases be obtained which on analysis proved to be double carbonates.

Most of the information we possess about the double carbonates we owe to Deville (*Ann. Chim. Phys.*, [iii], 33), who found that by digesting metallic nitrates with a saturated solution of potassium hydrogen carbonate at the ordinary temperature, compounds of the type $\text{MKH}(\text{CO}_3)_2$ were formed, where M is cobalt, nickel, or magnesium, and that if the solutions are heated for some hours they passed into $\text{MK}_2(\text{CO}_3)_2$; he also obtained the sodium double salts of the latter type with cobalt, nickel, copper, and magnesium.

As the result of a large number of experiments, I find that the best general method of preparing the compounds is the following. To the concentrated solution of potassium carbonate (sp. gr. about 1.55) the finely powdered acetate is added and the solution set aside; the crystals which form are then separated from the mother liquor by draining on a disc of toughened filter paper placed on a Buchner filter plate, employing a water pump to diminish the pressure beneath. The crystals are washed with a mixture consisting of two volumes of alcohol and one of glycerol (which floats on the salt solution and does not mix with it) until all the mother liquor is displaced, when the washing is completed with alcohol only until all the glycerol is removed.

The crystals can be dried in a vacuum at the ordinary temperature over sulphuric acid.

The acetates are most convenient as, owing to the solubility of potassium acetate, the deposition of crystals of other potassium salts

* The solutions of copper potassium carbonate introduced by Soldaini (*Gazzetta*, 1876, 6, 322) and afterwards modified by Ost (*Ber.*, 1890, 23, 1035 and 3003) for use in sugar analysis contain potassium hydrogen carbonate.

can be avoided. The freshly precipitated carbonates and hydrated basic carbonates have been used in several cases, but their employment is attended with some difficulty.

These compounds are decomposed by water alone, more or less rapidly, and alcohol alone causes the deposition of potassium carbonate upon the surface of the crystals of the new salt; hence the necessity for the use of the mixture already referred to. In one case, however, namely, that of the ferric salt, this mixture was found to decompose the compound and petroleum was substituted for it, as, notwithstanding its lower density and immiscibility with aqueous liquids, it served to displace the mother liquid.

Copper Potassium Carbonate.—This is very soluble in the strong solution, and a considerable quantity of copper acetate has to be added to get any crystals. The salt crystallises in three ways, namely, in the anhydrous form, with $1\text{H}_2\text{O}$ and with $4\text{H}_2\text{O}$; the three forms can be obtained from the same solution, provided the right proportions are employed. Thus, a solution made by adding to 70 c.c. of potassium carbonate solution of sp. gr. 1.35, 13 grams of finely powdered copper acetate, at 65° , filtering and cooling, deposited, after 48 hours, (a) dark, blue six-sided plates of the anhydrous salt, (b) light blue, silky, clustered needles of the salt with $1\text{H}_2\text{O}$, and (c) large greenish-blue, square tables of the salt with $4\text{H}_2\text{O}$. The last could be picked out by hand and freed from the liquid by means of filter paper. The compounds (a) and (b) appear to be deposited indifferently from solutions of the same strength and temperature, and I have not been able to find the conditions under which the individual compound could be obtained with certainty.

To prepare (a) or (b), the solution of potassium carbonate (sp. gr. 1.53) is added to the finely powdered copper acetate in a mortar, and after being triturated a few seconds to break up any lumps, when practically all dissolves, it is filtered rapidly through glass wool and set aside. A mixture of 36 grams of the acetate and 100 c.c. of the solution begins to crystallise in 2 or 3 minutes, and after about 10 minutes those crystals which have been formed should be separated and the remainder in two or three fractions, to prevent the solution becoming clogged. Thirty grams and 100 c.c. and separation in two instalments; or 17 grams and 100 c.c. all at once, are convenient quantities. The proportion of 12 grams to 100 c.c. generally requires some hours before crystals appear.

Analysis of the anhydrous compound (a dark blue, crystalline powder).

	CO_2 .	CuO .	K_2O .	H_2O .
Found	32.92	31.54	35.39	0.06
Calculated for $\text{CuK}_2(\text{CO}_3)_2$	33.67	30.31	36.02	nil.

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Analysis of the light blue, silky needles.

	CO ₂ .	CuO.	K ₂ O.	H ₂ O (by diff.).
Found.....	30·77	29·93	32·70	6·60
Calculated for CuK ₂ (CO ₃) ₂ + H ₂ O...	31·45	28·41	33·70	6·44

(Specimens (a) and (b) probably were contaminated with a little hydrated copper carbonate.)

Analysis of the greenish-blue tables.

	CO ₂ .	CuO.	K ₂ O.	H ₂ O (by diff.).
Found.....	26·24	23·14	28·84	21·78
Calculated for CuK ₂ (CO ₃) ₂ + 4H ₂ O	26·39	23·78	28·26	21·57

The copper solution decomposes slowly when heated to 65°, and rather quickly at 85°, cupric oxide being precipitated; if, however, a large quantity of the acetate is added, no black precipitate forms even at 100°, but a green powder of the composition Cu₂(OH)₂CO₃.

Cobalt Potassium Carbonate.—A cobalt salt dissolves in the warm solution of potassium carbonate and small six sided rose-coloured crystals soon separate on cooling.

	CO ₂ .	CoO.	K ₂ O.	H ₂ O.
Found.....	26·30	22·78	28·70	22·10
Calculated for CoK ₂ (CO ₃) ₂ + 4H ₂ O	26·72	22·78	28·64	21·86

Nickel Potassium Carbonate.—A nickel salt dissolves as above, but in much smaller quantity, and pale green crystals soon form on cooling.

	CO ₂ .	NiO.	K ₂ O.	H ₂ O.
Found.....	26·68	22·64	28·82	21·86
Calculated for NiK ₂ (CO ₃) ₂ + 4H ₂ O	26·72	22·78	28·64	21·86

Magnesium Potassium Carbonate.—The magnesium compound is obtained in like manner, by adding magnesium acetate to the solution, crystals appear in a few minutes.

	CO ₂ .	MgO.	K ₂ O.	H ₂ O (by diff.).
Found.....	29·74	14·15	32·02	24·09
Calculated for MgK ₂ (CO ₃) ₂ + 4H ₂ O	29·86	13·72	32·00	24·42

The last three are identical with the compounds obtained by Deville by prolonged heating with a saturated solution of potassium hydrogen carbonate.

Manganese Potassium Carbonate.—The last three salts are best prepared from warm solutions, but this one must be prepared at the ordinary temperature, otherwise much oxidation occurs. The acetate was powdered in a mortar, and the solution added and stirred for a few seconds; the crystals separate out very quickly, as the salt is scarcely soluble in the solution.

	CO ₂ .	MnO.	K ₂ O.	H ₂ O.
Found.....	26·86	21·80	29·20	22·14
Calculated for MnK ₂ (CO ₃) ₂ + 4H ₂ O	27·03	21·82	29·03	22·12

Ferrous Potassium Carbonate.—In order to prevent oxidation, this salt must be prepared by a slight modification of the process. The following answered very well. A bottle containing about five-sixths of its volume of the solution was filled up with a saturated solution of ferrous chloride and stoppered; on mixing the two liquids by shaking, a white precipitate of FeCO₃ is at first formed, but this soon dissolves yielding a greenish solution, from which the compound FeK₂(CO₃)₂ + 4H₂O crystallises out in nearly white scales after about 10 minutes. The salt can be separated and purified in the manner already described.

	CO ₂ .	FeO.	K ₂ O.	H ₂ O (by diff.).
Found.....	26·80	21·93	28·60	22·67
Calculated for FeK ₂ (CO ₃) ₂ + 4H ₂ O	26·99	22·06	28·89	22·06

Calcium Potassium Carbonate.—This can be easily prepared by pouring the solution on to the finely powdered acetate in a mortar and triturating for some time. The crystals are anhydrous, CuK₂(CO₃)₂, and are quite different in form from the last five compounds, which contain water.

	CO ₂ .	CuO.	K ₂ O.
Found	36·55	22·40	38·94
Calculated for CuK ₂ (CO ₃) ₂	37·00	23·50	39·50

(The salt probably retained about 2 per cent. moisture.)

Silver Potassium Carbonate.—This can be prepared by adding powdered silver nitrate to the solution, but I found it better to add the saturated solution of the nitrate to a large excess of the potassium carbonate solution, as in the former case particles of the nitrate which have become coated over with the compound are liable to be mixed with it. The yellow precipitate at first formed soon changes into the white double salt, AgKCO₃. If exposed to light during the washing, superficial reduction takes place, due to the glycerol.

	CO ₂ .	Ag ₂ O.	K ₂ O.
Found	20·58	54·50	23·90
Calculated for AgKCO ₃	21·23	56·01	22·76

This salt has been already obtained by De Schulten (*Compt. rend.*, 1887, 105, 811).

Bismuth Potassium Carbonate.—When powdered bismuth nitrate is added to the solution, some effervescence occurs, but a considerable quantity slowly but completely dissolves; the crystalline compound that separates after a short time is mixed with crystals of potassium

nitrate and hydrogen carbonate from which it cannot be separated. It was found better, therefore, to employ the subnitrate. The crystals, which are microscopic, when prepared at the ordinary temperature are of an entirely different form from those obtained by adding the powder to the solution warmed to about 75° ; they have, however, the same composition. The commercial subnitrate contains a small quantity of a constituent which is not acted on by the solution. Most of this impurity can be got rid of by pouring the solution, after the addition of the subnitrate, into a tall cylinder and decanting from the impurity which settles down more quickly than the fine crystals. A purer product can be obtained by preparing the subnitrate from the nitrate using a small quantity of water, draining with the aid of the filter pump, and adding the precipitated salt to the concentrated solution heated to about 70° . The crystals separate almost immediately.

	Bi_2O_3 .	K_2O .	CO_2 .	H_2O (by diff.).
Found	55.00	21.86	20.26	2.88
Calculated for $\text{Bi}_2\text{OK}_4(\text{CO}_3)_4 + \text{H}_2\text{O}$	54.90	22.24	20.73	2.13

The following list contains all the salts I have been able to isolate in well-defined crystalline form.

$\text{CuK}_2(\text{CO}_3)_2$	}	Not previously known.
$\text{CuK}_2(\text{CO}_3)_2 + \text{H}_2\text{O}$		
$\text{CuK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$		
$\text{MnK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$		
$\text{FeK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$		
$\text{CaK}_2(\text{CO}_3)_2$	}	Obtained by Deville by heating the bicarbonate.
$\text{Bi}_2\text{OK}_4(\text{CO}_3)_4 + \text{H}_2\text{O}$		
$\text{CoK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$		
$\text{NiK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$		
$\text{MgK}_2(\text{CO}_3)_2 + 4\text{H}_2\text{O}$		
$\text{AgK}(\text{CO}_3)$		Obtained by De Schulten.

In addition to these, I have obtained compounds containing lead, zinc, iron (ferric) chromium, mercury, and cadmium, but not crystalline or of definite composition.

It is noticeable that the chemical behaviour of potassium carbonate in the form of a concentrated solution is quite different from that of the same salt in a dilute solution. In the latter case, normal or basic carbonates are formed, whereas, in the former, double salts are produced which may be soluble in the liquid.

The solutions and the compounds in the solid state are decomposed when diluted or brought into contact with water; in this respect, they are similar to the double sulphates, which are all decomposed by water. In the case of such compounds as $\text{CaNa}_2(\text{SO}_4)_2$ and $\text{CaK}_2(\text{SO}_4)_2$, this is

evident, since calcium sulphate is precipitated, but in the case of the soluble salts, although not so obvious, the fact of decomposition has been proved by Raoult (*Compt. rend.*, 1884, 99, 914), and also from thermochemical data.

It is noticeable that the ratio of K to CO_3 is unity in all the above compounds, and this is also the case with the double sulphates $\text{K} : \text{SO}_4$, and double oxalates $\text{K} : (\text{CO}_2)_2$, and it is possible to write the constitution of these three classes of double salts thus.

Potass. mangan.
carbonate.

Potass. mangan.
sulphate.

Potass. mangan.
oxalate.

A concentrated solution of potassium succinate behaves very like that of potassium carbonate; although the succinates of the metals, except the alkalis, are almost insoluble, yet on adding their salts to a concentrated solution of potassium succinate many of them dissolve, and crystalline double compounds are obtainable. I propose to give an account of these in a future communication.

The above investigation was carried out under the supervision of Professor Tilden, to whom I am much indebted for his advice and encouragement.

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