V.—*On the Basic Carbonates of Copper, with some Remarks upon the Carbonates of Nickel and Cobalt.*

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In a paper upon this subject, lately published in the "Chemical News," and in Abstract at page 70 of this volume, the singular effect of a strong solution of carbonate of soda upon malachite was mentioned, together with the action of boiling water upon the same mineral. In both instances it speedily becomes black, being converted into the black oxide, with brisk evolution of carbonic acid. When the blue carbonate of copper (azurite) $3\text{CuO} \cdot 2\text{CO}_2 \cdot \text{HO}$ is subjected to similar treatment, exactly the same phenomenon occurs, the whole of the carbonic acid being expelled, the action of pure water facilitating the decomposition far more readily than the solution of carbonate of soda. In a memoir upon the carbonates of copper, Rose* informs us, that the green carbonate formed on adding a salt of copper to carbonate of soda, is converted into the oxide by long digestion with boiling water, but no blue compound is obtained. Artificial malachite may, however, be formed from azurite, by heating the latter for some little time in a rather concentrated solution of bicarbonate of soda. A bright blue liquid is produced, which, after lengthened ebullition, deposits a green powder, containing exactly the amount of oxide of copper which is found in malachite; it is this precipitate, which has a similar composition to that which is produced by boiling a solution of malachite in carbonate of soda, does not part with its water under a temperature of 380°F , and is evidently formed by the elimination of 1 atom of carbonic acid from 2 atoms of azurite, one atom of water at the same time taking the place of the carbonic acid—

Dewille† mentions that when a salt of copper is gradually added to a strong solution of carbonate of soda, nearly the whole of the alkali is precipitated with the copper, in brilliant crystals of the double carbonate. In all my experiments, warm solutions were employed, in which case no double compound was formed, but a highly basic carbonate, and subsequently black oxide, were alone produced.

* Pogg. Ann. lxxxiv, 461; Ann. Ch. Pharm. lxxx, 236.

† Ann. Ch. Phys. [3], xxxiii, 75

Carbonate of Cobalt. The various carbonates of cobalt have been intimately studied by Rose,* who remarks that the composition of these compounds depends very much upon the concentration of the solutions, and upon the temperature employed during the precipitation. When sulphate of cobalt is mixed with carbonate of soda, a precipitate is formed having the formula $2(\text{CoO} \cdot \text{CO}_2) + 3(\text{CoO} \cdot \text{HO}) + \text{Aq.}$, either from concentrated or from weak solutions, and it is only when dilute solutions are decomposed at the boiling point, that a precipitate is obtained which approximates to $\text{CoO} \cdot \text{CO}_2 + 2(\text{CoO} \cdot \text{HO})$, Aq. The same chemist further informs us, that when sulphate of cobalt is treated with an excess of bicarbonate of potash in the cold, there is formed, with brisk evolution of carbonic acid, a voluminous precipitate, which by long standing is transformed into a mass of tolerably distinct crystals, having for their composition $\text{KO} \cdot \text{CO}_2 + \text{CoO} \cdot \text{CO}_2 + 9\text{HO}$. The rather curious phenomena exhibited by the addition of dilute copper-salts to a strong solution of carbonate of soda, the latter in great excess, led me to investigate the reaction induced upon the salts of cobalt under similar circumstances. When dilute nitrate of cobalt is added to bicarbonate of soda, no precipitate occurs, until a considerable quantity has been introduced. The solution has a beautiful violet colour, and can be brought to ebullition, and even maintained at a boiling temperature for some time without undergoing complete decomposition. The precipitate which forms after a further addition of the cobalt-salt, has a pure pink colour, which scarcely changes its tint, even when the liquid in which it is suspended is boiled for several hours. This compound appears to hold carbonate soda with remarkable tenacity; indeed it seems impossible to free it from the latter by any amount of ordinary washing. When the filtrate no longer shows signs of alkalinity to test-paper, the precipitate removed from the filter and heated with a fresh portion of distilled water, still yields an alkaline solution. On filtering off the carbonate of soda, and heating with water as just described, the pink colour quickly vanishes, and it becomes brown. When nitrate of cobalt is added to an excess of carbonate of soda, carefully freed from all excess of carbonic acid, the precipitate is not pink but blue, maintains its colour with some persistency as long as the supernatant liquid is strongly alkaline, and is quite as difficult to free

* Pogg. Ann. lxxxiv. 548. Ann. Ch. Pharm. lxxx. 237.

from adhering soda as the other compound. Cobalt, it appears, differs somewhat from copper when acted upon by either the carbonate or the bicarbonate of soda. When a salt of copper, it may be remembered, is added to a strong hot solution of the former, immediate decomposition takes place, carbonic acid is evolved, and a highly basic carbonate formed, which is ultimately converted into the black oxide. When the bicarbonate is employed, a green precipitate of hydrated bicarbonate is obtained. In order to see if oxide of cobalt altogether free from carbonic acid can be procured by long-continued boiling in distilled water, solutions of the nitrate of that metal and carbonate of soda were mixed, neither being in great excess. The peach-coloured compound was well washed and suspended in a pint of water, which was brought to ebullition and maintained at that temperature for about ten hours, water being added from time to time to compensate for the loss resulting from evaporation. The precipitate soon changed colour, becoming brown, and ultimately black. After filtration, it was dried at 212° Fah. and analysed, yielding 12·34 of carbonic acid, and 78·51 black oxide of cobalt (Co_3O_4) upon intense ignition. The carbonate of cobalt, as it originally existed, was composed of $2(\text{CoO} \cdot \text{CO}_2) \cdot 3(\text{CoO} \cdot \text{HO}) + \text{Aq.}$, and by the action of water at 212° , parted with a portion of its carbonic acid, and became partially converted into the sesquioxide. A compound containing 12·21 carbonic acid, which upon ignition would yield 78·41 of the protoperoxide of cobalt, would have the following formula :—

Found.	Calculated.
$\text{CO}_2 = 12\cdot34$	$\text{CO}_2 \ 12\cdot12$
$\text{Co}_3\text{O}_4 \ 78\cdot51$	$\text{Co}_3 \ \text{O}_4 \ 78\cdot41.$

That this compound is a mixture of ordinary carbonate of cobalt with the hydrated sesquioxide, arises from the action of dilute hydrochloric acid. When this acid, diluted with three or four times its bulk of water, is added to the carbonate, the latter is almost instantaneously dissolved, with brisk disengagement of carbonic acid. Upon the sesquioxide, however, it produces little effect. When cold and comparatively weak, the liquid becomes only slightly tinged, after being in contact with it many hours. Exactly the same phenomena occur in the compound just mentioned. On the addition of dilute hydrochloric acid, the whole of the

carbonate is immediately dissolved, a black powder remaining untouched. When warm and concentrated acid is added to this, it is gradually decomposed, solution is effected, and chlorine is evolved. When nitrate of cobalt is added to a solution of bicarbonate of soda containing a small quantity of the hypochlorite of that alkali, an intense and beautiful green colour is produced, and no elimination of carbonic acid results. So strong is the colouring power of this body, that 0.2 of a grain of nitrate of cobalt will colour eight ounces of solution, a clear bright green, as dark as a tolerably concentrated solution of chloride of copper. Large quantities of oxide of cobalt can be dissolved in this way, and the liquid, if not too strong, may be boiled for some time without undergoing decomposition. When, however, the nitrate of cobalt is rather concentrated, and heat is applied, a brisk evolution of carbonic acid takes place, and sesquioxide is precipitated, which, adhering in a scaly mass to the sides of the glass, and being removed by agitation, floats about the liquid in brilliant iridescent plates, appearing at first sight to be beautifully and highly crystalline.

Cobalt cannot be separated from iron or manganese by this method, although every degree of concentration and temperature has been tried. When the solution is not sufficiently warm, a small quantity of iron is dissolved, when, on the other hand, considerable heat is applied, a small quantity of cobalt remains with the precipitate.

Carbonates of Nickel. Nickel-salts exhibit, generally speaking, the same reactions as those of cobalt in excess of carbonate of soda. I have tried in vain to procure oxide of nickel perfectly free from carbonic acid by boiling the carbonate in water, although the resulting compound was very highly basic. No peroxide however is formed, as in the case of cobalt. The carbonates of nickel, when precipitated in very strong solutions of the alkaline carbonates, appear to hold the latter with as great tenacity as the cobalt-compound.