PHYSICO-CHEMICAL INVESTIGATIONS ON THE BASIC CORBONATE OF COBALT

BY D. S. Bhardwaj and A. R. Vasudeva Murthy
(Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-12)

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ABSTRACT

The composition and nature of the precipitate obtained by the addition of a solution of sodium carbonate to a solution of cobalt sulphate is examined by chemical analysis and potentiometric studies. The effect of ageing on the precipitate has been studied with respect to its composition as well as to its surface properties determined by methylene blue dye adsorption method. The effect of different desiccants on the composition of the basic carbonate has been studied by thermogravimetric method. These studies have shown that it is possible to prepare samples of basic carbonates of cobalt in solid condition with the following compositions—

(i) $4\text{CoCO}_3 \cdot 5\text{Co(OH)}_2 \cdot 5\text{H}_2\text{O}$ and
(ii) $4\text{CoCO}_3 \cdot 5\text{Co(OH)}_2 \cdot \text{H}_2\text{O}$

It has been shown earlier that when a solution of a nickel salt is treated with a solution of alkali hydroxide, the entire quantity of nickel present in solution is thrown down as a precipitate with about 1.66 equivalents of alkali added$^{1,1(a)}$. On the other hand, if an alkali carbonate is added, the complete precipitation of the nickel from the solution takes place only if the molar ratio of the alkali carbonate and nickel salt taken is at least 2.5. This behaviour was explained on the basis of the formation of aquo nickel ion complexes, which are precipitated as the basic salts of nickel. A similar observation was made with cobalt solutions and a detailed investigation was undertaken and the results are reported in this paper.

EXPERIMENTAL

1. Reagents. (a) Cobalt sulphate solution:—A stock solution (1M) of cobalt sulphate was prepared with a Merck’s sample of the hydrated salt (CoSO$_4 \cdot 7\text{H}_2\text{O}$). The strength of the solution was determined, by estimating the cobalt content in an aliquot by anthranilic acid method$^{3-5}$. The stock solution was suitably diluted and standardised before use in all other experiments by analysis.

(b) Standard sodium hydroxide and standard sodium carbonate solutions were prepared and their strengths were determined as described earlier.$^{6-7}$
2. **Potentiometric titration:** (a) **Alkali hydroxide against cobalt sulphate**—A Beckmann pH meter with a glass electrode was used to follow the potentiometric titration of cobalt sulphate solution (0.05192M) with 0.1N sodium hydroxide. A known amount of cobalt sulphate solution was taken in a 250 ml. beaker and the solution was stirred mechanically during the dropwise addition of small volumes of alkali hydroxide solution from a burette. Stirring was continued for a minute after the addition of alkali was over and then stopped. The corresponding pH (or potential) was measured. The titration was continued till an excess of sodium hydroxide had been added, indicated by the high pH value of 11. The titration was carried out at room temperature (24 ± 1°C) which did not vary beyond 1° during the experiment. The results are presented graphically in Figure I.

![Potentiometric titration of cobalt sulphate](image)

From the potentiometric curve (Figure I) a₁, it is seen that initial pH of the cobalt sulphate solution is 4.90, owing to hydrolysis². The pH, when precipitate first appears is 7.90. The amount of alkali consumed, before precipitate first appears, corresponds to 0.098 equivalents of sodium hydroxide. At the point of inflexion, obtained from the differential plot, a₂, the pH is 9.4 and 1.718 equivalents of sodium hydroxide are consumed. Therefore, only 1.620 equivalents of the alkali hydroxide are consumed for the complete precipitation of cobalt.
(b) *Alkali carbonate against cobalt sulphate:* Similar potentiometric studies were conducted using cobalt sulphate and sodium carbonate instead of sodium hydroxide, and the results are presented in the curves b₁ and b₂ of Figure 1. Here again, a small quantity of the alkali carbonate is consumed before the actual precipitation takes place at pH 7.9. All the cobalt in solution is removed when the alkali carbonate added is about 2.5 times the molar concentration of the cobalt taken, which corresponds to the attainment of end point in the potentiometric titration.

Reference to the potentiometric data indicates that, when $5.192 \times 10^{-4}$ mole of cobalt sulphate solution is titrated against sodium carbonate, no precipitate is visible when $2.795 \times 10^{-5}$ mole of sodium carbonate is added. With the progressive addition of sodium carbonate, the amount of precipitate formed increases and all the cobalt is thrown out of the solution when $12.70 \times 10^{-4}$ g. mole of sodium carbonate is added. The precipitate formed at this stage was analysed for any sulphate contamination. However, no sulphate was present in the precipitate, indicating that the precipitate obtained is not basic sulphate, but only basic carbonate.

From stoichiometric considerations, two equivalents of sodium hydroxide are required per mole of cobalt sulphate to precipitate cobalt as $\text{Co(OH)}_2$. As indicated earlier, 1.62 equivalents of sodium hydroxide are actually taken up for the precipitation of cobalt and a corresponding quantity of $\text{Co(OH)}_2$ is precipitated. The rest of the cobalt gets precipitated along with the $\text{Co(OH)}_2$ as basic sulphate. Thus the composition of the precipitate can be taken as $\text{Co(OH)}_{1.62} \text{Co(SO}_4)_{0.38}$ or $\text{CoSO}_4 \text{Co(OH)}_2$. The formation and isolation of a similar basic sulphate of nickel has been reported.

The formation of the basic sulphate may be explained on the basis of hydrolysis of the aquo cobalt ion, $[\text{Co(H}_2\text{O)}_6]^{++}$. The coordination of the bivalent Co$^{++}$ion varies with the nature of the ligands and the experimental conditions and, invariably, is less than six. The $\text{H}^+$ions liberated due to hydrolysis of the salt consumes the sodium hydroxide added initially before the basic salt starts precipitating. This may account for the rise of pH from 4.9 to 7.9 initially. The precipitation of the basic sulphate before the addition of the stoichiometric quantity of NaOH occurs probably due to the lower solubility of the basic sulphate than that of the $\text{Co(OH)}_2$.

In the potentiometric titration of sodium carbonate against cobalt sulphate, the following reaction is likely to take place:

$$\text{CoSO}_4 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{CoCO}_3 + \text{Na}_2\text{SO}_4$$

In addition to this the sodium carbonate added undergoes hydrolysis.

$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NaHCO}_3 + \text{Na}^+ + \text{OH}^-$$

The Co (OH)$_2$ formed is unable to furnish OH$^-$ ions to convert the HCO$_3^-$ to CO$_3^{2-}$, as its solubility is very low ($3.2 \times 10^{-6}$ gm/ml). Therefore, the CO$_3^{2-}$ ion
produced is neutralised only by the OH⁻ ion obtained by hydrolysis of Na₂CO₃. Consequently, the amount of CoCO₃ produced, the amount of CoCO₃ hydrolysed and the amount of CO₃²⁻ neutralised, continuously change. The inflexion point in the potentiometric curve starts at a pH of 8.75 which is nearly the pH for the first stage of neutralisation of H₂CO₃.

On continuing the potentiometric titration beyond the point of inflexion, the increase in pH is slow, showing a buffering action of the solutions. A large excess of sodium carbonate has to be added to precipitate all the cobalt, to have a sufficiently high pH. As a result of this, more than 2.5 equivalents of sodium carbonate are to be added to precipitate the cobalt completely at a pH nearing 11. This accounts for the formation of the basic carbonate of cobalt. The composition of the precipitate thus obtained has been found by analysis to be 4CoCO₃. 5Co(OH)₂. From stoichiometric considerations, formation of this basic salt may be written as:

\[
9 \text{CoSO}_4 + 14 \text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O} \rightarrow 4\text{CoCO}_3 \cdot 5\text{Co(OH)}_2 + 9 \text{Na}_2\text{SO}_4 + 10 \text{NaHCO}_3
\]

This requires that the molar ratio of CoSO₄ : Na₂CO₃ should be 9 : 14 or 1 : 1.55 for complete precipitation of CoSO₄ as the basic carbonate. However, it is found, in an actual experiment, that only 93.55 per cent of the cobalt is precipitated, when the reagents are added in that proportion. In order to overcome the buffering action of the solution containing a bicarbonate (produced by the hydrolysis), a considerably large excess of the carbonate has to be added such that all the cobalt from the solution may be thrown out completely.

3. Precipitation of Basic Carbonate of Cobalt:—It was felt of interest to find out the cobalt thrown out as precipitate by the addition of sodium carbonate in different proportions. A known volume of cobalt sulphate solution was treated with a solution of sodium carbonate in different amounts under identical experimental conditions. The violet precipitate was separated from the mother liquor and the cobalt content of the precipitate and filtrate were determined. The unconsumed alkali carbonate present in the filtrate was also estimated. The results of a set of experiments are given in Table I.

An examination of the table shows that when the molar ratio of the cobalt salt to sodium carbonate added is 1 : 1, only 59.3% of the cobalt is precipitated, while the rest of the metal remains in solution. With the progressive increase in the amount of sodium carbonate added, the amount of cobalt precipitated also increases. The complete precipitation of all the cobalt takes place only when the ratio of the cobalt sulphate to sodium carbonate is more than 1 : 2.5. The analytical results lend further support to the findings from the potentiometric titrations.

4. Influence of ageing on the nature of the precipitated basic cobalt carbonate:—It is well known that gelatinous precipitates exhibit peculiar properties on ageing. Because of a large surface development, surface adsorption is very
Progressive precipitation of cobalt with sodium carbonate as precipitant.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Amount of cobalt taken (X10^4 moles)</th>
<th>Amount of Na_2CO_3 added (X10^4 moles)</th>
<th>Molar ratio Co : Na_2CO_3</th>
<th>Amount of cobalt in precipitate (X10^4 moles)</th>
<th>Amount of Na_2CO_3 used up (X10^4 moles)</th>
<th>Molar ratio Co pptd. : Na_2CO_3 used up</th>
<th>% Cobalt precipitated</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>10.290</td>
<td>2.570</td>
<td>1 : 0.25</td>
<td>1.388</td>
<td>0.883</td>
<td>1 : 0.636</td>
<td>13.50</td>
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<tr>
<td>2</td>
<td>10.290</td>
<td>5.145</td>
<td>1 : 0.50</td>
<td>3.122</td>
<td>3.674</td>
<td>1 : 1.177</td>
<td>30.35</td>
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<tr>
<td>3</td>
<td>10.290</td>
<td>7.715</td>
<td>1 : 0.75</td>
<td>4.393</td>
<td>4.868</td>
<td>1 : 1.108</td>
<td>42.70</td>
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<td>5.193</td>
<td>1 : 1.00</td>
<td>3.066</td>
<td>2.963</td>
<td>1 : 0.966</td>
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<tr>
<td>5</td>
<td>10.386</td>
<td>12.990</td>
<td>1 : 1.25</td>
<td>8.092</td>
<td>8.306</td>
<td>1 : 1.027</td>
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<tr>
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<td>15.597</td>
<td>1 : 1.50</td>
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<td>31.250</td>
<td>1 : 2.50</td>
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<tr>
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<td>30.530</td>
<td>1 : 3.00</td>
<td>10.176</td>
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<td>1 : 1.104</td>
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</tr>
</tbody>
</table>

Basic cobalt precipitates obtained under identical experimental conditions (25 ml. of 0.05 M of cobalt sulphate solution was treated with 75 ml. of 0.1N sodium carbonate) was allowed to remain in contact with the mother liquor to age from 30 minutes to 16 days. The different precipitates were analysed and their composition was found to remain the same corresponding to \([4\text{CoCO}_3.5\text{Co(OH)}_2\times\text{H}_2\text{O}]\). However, the surface properties of the precipitate aged for different periods are known to vary. Dye adsorption studies have been helpful to study the variation of these surface properties of precipitates. This technique was followed in the present investigation also.

Methylene blue was found to be the most suitable dye to study the adsorption characteristics of the wet precipitate. The same technique described earlier was employed to determine the extent of dye adsorption on the precipitate aged for different periods. It was observed that the amount of the dye adsorbed increased with the increase of the period of ageing of the wet precipitate, attaining a maximum value on ageing for a period of 190 hours. In a representative experiment it was found that 103.6 mg. of the basic carbonate precipitate adsorbed 2.564 mg. of the dye.

A rough idea of the specific surface of the cobalt basic carbonate could be obtained by assuming that the dye is adsorbed at the surface forming a monomolecular layer and assuming the cross sectional area of the methylene blue to
be 100 Å² units. On calculation the surface was found to be 4.7 square metres per gram of the basic carbonate precipitated in the wet condition, which is gelatinous and bulky. The increase in the amount of dye adsorbed on ageing for six days, during which period there is no change in the chemical composition, may be attributed to the breaking up of the gelatinous precipitate causing the exclusion of water molecules. This probably leads to the formation of more crevices and pores than were already present, thus exposing a larger surface of the precipitate to the dye molecules to occupy.

5. Preparation of the solid basic carbonate of cobalt:—It was found to be practicable to prepare a sample of basic carbonate of cobalt with a definite composition and study its properties in the solid form. The details of the preparation are given below:

To a litre of 0.05M cobalt sulphate solution in a five litre beaker, three litres of 0.1N sodium carbonate solution were added from a dropping funnel in about 5 to 6 minutes. Efficient stirring was maintained, with the help of a mechanical stirrer, during the addition and it was continued for 30 minutes more. The bulky gelatinous precipitate was separated from the mother liquor by filtering at the pump. The precipitate was washed free of alkali carbonate and then transferred to a tared watch glass. The wet precipitate was weighed and was transferred to a desiccator, and dry air was passed over it for a period of 100 to 120 hours. During this interval, the precipitate lost 90% of its weight and it contracted in volume. The dark violet mass was pulvarised into a free flowing powder and the powder was dried over calcium chloride in a vacuum desiccator to constant weight over a period of seven days. Seven different samples were prepared by changing the concentrations of the reagents, keeping the same molar ratio of CoSO₄: Na₂CO₃::: 1 : 3.

The basic carbonate was then analysed for the cobalt, carbonate and water contents by standard methods already described. It was noticed that the analytical results of the above seven samples indicated that the composition was practically the same. The analytical results of a representative sample gave the following composition, \([\text{CoO} = 65.75\% , \text{CO}_2 = 16.75\% \text{ and } \text{H}_2\text{O} = 28.50\% ]\), corresponding to the molecular formula \(4 \text{CoCO}_3 \cdot 5 \text{Co(OH)}_2 \cdot 5 \text{H}_2\text{O}\).

Instead of calcium chloride, phosphorus pentoxide was used as the drying agent and the free flowing powder was obtained in a similar way. The powder, so obtained, was found to have the composition \(4 \text{CoCO}_3 \cdot 5 \text{Co(OH)}_2 \cdot \text{H}_2\text{O}\). Even when the wet precipitate was aged for a period of 1 to 16 days and then dried over \(\text{P}_2\text{O}_5\), the basic carbonate was found to have the composition \(4 \text{CoCO}_3 \cdot 5 \text{Co(OH)}_2 \cdot \text{H}_2\text{O}\).

6. Thermogravimetric behaviour of the samples:—It is quite apparent from the above results that the samples of basic carbonates containing different water of hydration could be easily prepared. This was confirmed by examining the thermogravimetric behaviour of the samples using quartz spring technique.
described earlier. The corresponding thermograms of these two samples, (a) $4\text{CoCO}_3:5\text{Co(OH)}_2:5\text{H}_2\text{O}$ and (b) $4\text{CoCO}_3:5\text{Co(OH)}_2:2\text{H}_2\text{O}$, are given in the Figure II. It may be inferred from the thermogram (a) that there is no loss in weight till the sample reaches $100^\circ\text{C}$. With further increase in temperature it suffers continuous loss till $180^\circ\text{C}$ is reached, giving off all its free water.

[corresponding to $5\text{H}_2\text{O}$]. On further heating it gives off carbon dioxide rapidly along with hydroxyl water. The sample maintains a constant weight in the range $240^\circ\text{C}-400^\circ\text{C}$. The final residue was found to be $\text{Co}_3\text{O}_4$. In the case of sample (b), its weight remains steady up to $100^\circ\text{C}$ and suffers a slight decrease in weight up to $200^\circ\text{C}$, beyond which there is a steep fall in its weight up to $240^\circ\text{C}$. Beyond $240^\circ\text{C}$, the sample attains a constant weight and the residue was found to be $\text{Co}_3\text{O}_4$.

In sample (a) free water is expelled earlier and hydroxyl water is lost at a later stage, whereas in the case of sample (b) there is no loss in the initial step due to free water, thus confirming the earlier analytical results. The hydroxyl water and carbon dioxide are driven off at higher temperatures.

It has to be pointed out that when cobalt basic carbonate is heated in an atmosphere of nitrogen, the residue left behind corresponds to $\text{CoO}$. Instead, if it is heated in air or oxygen, the residue was found to correspond to the formula $\text{Co}_3\text{O}_4$. These observations of the present authors confirm earlier reports. The net loss suffered by the samples during thermogravimetric experiments corresponds to the loss of water and carbon dioxide minus the gain in weight of the oxide to form $\text{Co}_3\text{O}_4$ from $\text{CoO}$.

![Graph](image-url)
7. Decomposition of the basic carbonate in vacuum:—It is not possible to distinguish between the stages of decomposition corresponding to the loss of hydroxyl water and loss of carbon dioxide from the thermogravimetric results. This was further confirmed by studying the decomposition of the samples in vacuum in an apparatus described earlier. The gas evolved at different temperatures was passed over phosphorus pentoxide to remove moisture and the remaining gas was collected, measured and analysed. The gas was found to be carbon dioxide.

The volume of carbon dioxide evolved at different temperatures has been plotted in the graph (Figure III). It can be made out from the graph that there was no gas evolved at 100°C and only a very small quantity was expelled up to 200°C. The expulsion of the gas became rapid beyond 250°C up to 350°C.

At 400°C, nearly 1% of carbonate still remained undecomposed. The total carbon dioxide liberated, including the gas expelled towards the last stages, correspond to the theoretical carbon dioxide content of the basic carbonate. The residue was found on analysis to be CoO.

Conclusion:—It can be easily made out from the foregoing experimental observations that contrary to the usual belief that no basic carbonate of cobalt of definite composition can be obtained by precipitation with sodium carbonate,
it has been shown that it is possible to prepare two different basic carbonates of composition:

(1) \(4 \text{CoCO}_3 \cdot 5 \text{Co(OH)}_2 \cdot 5 \text{H}_2\text{O}\) and

(2) \(4 \text{CoCO}_3 \cdot 5 \text{Co(OH)}_2 \cdot \text{H}_2\text{O}\).

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REFERENCES