

A NOTE ON THE BEHAVIOR OF COBALTOUS HYDROXIDE.

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If excess of sodium hydroxide solution is added to a solution of a cobalt salt, a blue compound, generally considered to be a basic salt, is precipitated. If the cobalt is pure this blue compound changes quickly to a pink substance supposed to be the normal hydroxide.

Benedict¹ called attention to the fact that if a small amount of nickel salt is present the change in color is retarded depending on the amount of nickel present (table 1).

TABLE 1—Time required for color change in cobalt hydroxide when varying amounts of nickel salt was added.

cc. 2N NaOH solution	cc. .25N CoCl ₂ solution	mg. Ni.	Change began	Change complete
10	10	0	3 sec.	20 sec.
10	10	0	3 sec.	23 sec.
10	10	4	5 sec.	210 sec.
10	10	4	6 sec.	210 sec.
10	10	10	10 sec.	20 min.
10	10	10	11 sec.	20 min.

He suggested this as a test for nickel in the presence of cobalt and claimed to be able to detect 5 per cent of nickel in 10 cc. of a normal cobalt solution. This was probably the most accurate method then known for the detection of nickel in the presence of cobalt.

The effect can hardly be due to the color of the nickel hydroxide, and Benedict suggested as an explanation the formation of nickel cobalite which, being suitable, gradually broke up allowing the normal Co(OH)₂ to form.

Some years ago while using Bailey and Cady's Manual with classes in qualitative analysis my attention was called to the fact that students were reporting nickel when none was present. Upon investigation it was concluded that the difficulty lay in the NaOH used, and some experiments were begun to determine if possible what impurity was retarding the color change.

It was found that the strength of the base played an important part, a considerable excess always being necessary for rapid change. Using 10 cc. of .25 N. CoCl₂ and 10 cc. NaOH the maximum rate of change occurred when the base was 2 N or stronger. It was further observed

¹ Jour. Amer. Chem. Soc. 26, 1904, p. 695.

that freshly prepared NaOH solution gave satisfactory results, but if the solution had stood sometime in a bottle, the color change was apt to be noticeably retarded. Carbonates and calcium salts when present had no effect on the change and it seemed more probable that it might be due to silicates.

Sodium hydroxide, which had been heated in a bottle eight hours on a water bath, showed a very marked retardation of the color change (table 2). Water glass solution added to the NaOH solution had the same general effect (table 3). Sodium silicate made by fusing SiO_2 with pure NaOH showed a marked retardation of the color change when a quantity of it containing 20 mg. of SiO_2 was added to the NaOH solution.

TABLE 2. Time required for color change in cobalt hydroxide when freshly prepared sodium hydroxide is used compared with sodium hydroxide heated eight hours in a bottle on a water bath and containing by analysis 16mg. SiO_2 in 10cc.

cc. .25N CoCl_2 solution	10cc. 2N NaOH solution	Change began	Change complete
10	Fresh	5 sec.	25 sec.
10	Heated	16 sec.	8 min.
10	Heated	17 sec.	8 min.

TABLE 3. Time required for color change in cobalt hydroxide when varying amounts of sodium silicate were added.

cc. .25N CoCl_2 solution	cc. 2N NaOH solution	mg. SiO_2	Change began	Change complete
10	10	0	5 sec.	25 sec.
10	10	0	4.5 sec.	20 sec.
10	10	10	16 sec.	Indefinite
10	10	10	12 sec.	Indefinite
10	10	20	No change	} Complete next morning.
10	10	20	No change	

CONCLUSIONS.

It is evident that unless the sodium hydroxide used is freshly prepared or reasonably pure this method cannot be depended upon for the detection of nickel in the presence of cobalt, since soluble silicates also retard the rate of color change in cobalt hydroxide.

The blue color probably cannot be due to the simple mixing of cobalt silicate formed with cobalt hydroxide or the pink color would not finally appear.

Since soluble silicates have the same effect as nickel salts it seems likely that Benedict was wrong in assuming that cobaltites were first formed.