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A PRELIMINARY STUDY OF THE COBALTICYANIDES.

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SEVERAL years ago during the course of an investigation of the ferrocyanides of zinc and manganese,[1] it was suggested that a study of the reactions between potassium cobalticyanide and solutions of metallic salts might be of interest and that, possibly, this compound might be found useful as a reagent in either qualitative or quantitative analysis. A careful search through the literature showed that the subject had not been thoroughly investigated; that the cobalticyanides of many metals were unknown and that the properties, especially the solubilities, of the known cobalticyanides were but incompletely recorded. Apparently no work has been done on these compounds for many years, while most of the investigations bear dates prior to 1857.

The general procedure adopted in this work was:

First.—To try the action of a half-normal solution of potassium cobalticyanide[2] on half-normal solutions of all the common metals. They were first added to each other in equal quantities and the filtrate tested to see which reagent was in excess; and, having found the amount of potassium cobalticyanide needed to precipitate a given metal, to work in subsequent experiments with quantities which gave a slight excess of the precipitant. Although these solutions were only approximately half-normal, they were made with sufficient care to distinguish in the resulting precipitates between a normal cobalticyanide and a double potassium-metallic cobalticyanide. The indications show that in nearly every case a normal salt is produced by a reaction of simple double decomposition.

Second.—The solubility of the precipitates so obtained was tested in every instance in nitric, hydrochloric, sulphuric, acetic, and oxalic acids, in ammonium hydroxide and caustic potash; in all cases both cold and hot.

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[1] This Journal, 19 547 (1897).

[2] Based on the hydrogen equivalent in grams per liter.

These tests were made by adding the acid or alkali to the original liquid containing the precipitate, and, in each instance, an amount of solvent equal in volume to the original liquid was employed. A few precipitates were filtered and their solubilities tested in concentrated acids.

The special solutions used were of the following strengths:

$K_3Co(CN)_6(N/2)$	55.52 grams per liter.			
HNO_3	(1 : 3)	sp. gr.	1.135	= 22 per cent.
HCl	(1 : 1)	" "	1.10	= 20 " "
H_2SO_4	(1 : 4)	" "	1.20	= 28 " "
$HC_2H_3O_2$		" "	1.03	= 22 " "
$H_2C_2O_4$	saturated solution			= 10± " "
NH_4OH	(1 : 2)	sp. gr.	0.96	= 10 " " NH_3.
KOH		" "	1.11	= 10 " " K_2O.

No highly colored or characteristic precipitates have as yet been found which can be employed as indicators to show an excess of potassium cobalticyanide, nor do the precipitates settle readily enough to allow this point to be determined by cautious additions of cobalticyanide to the clear supernatant liquid or by spot tests. In every precipitation the potassium cobalticyanide was added to the metallic salt solution and the presence of either substance in excess had usually to be determined in a few drops of the filtrate from the resulting precipitate. The experimental part of our work will show that, in general, the cobalticyanides insoluble in water, are also insoluble in and unaffected by acids, but are soluble in or decomposed by alkalies. None of them are decomposed by boiling as is the case with several ferricyanides. There is little similarity in either solubility or appearance between the corresponding ferri- and cobalticyanides. The metals except those of the alkalies and alkaline earths were taken up in their qualitative sequence, beginning with the silver-lead-mercury group.

Silver Cobalticyanide.—When equal volumes of half-normal silver nitrate and potassium cobalticyanide solutions are mixed, the silver is completely precipitated as silver cobalticyanide, a white curdy precipitate, which settles and filters well; is insoluble in all the acids used, being transposed by hydrochloric acid; is soluble in ammonia and decomposed by potassium hydroxide giving a precipitate consisting mostly of silver oxide.

Lead Cobalticyanide.—Neither lead acetate nor nitrate are precipitated by potassium cobalticyanide, either in neutral or acid solutions. Zwenger[1] made it from lead carbonate and cobalticyanhydric acid. This salt, crystallizing in laminated crystals containing 4 molecules of water, he says, is soluble in about 3 parts of water from which solution it is precipitated by ammonia as a basic salt.

Mercurous Cobalticyanide.—Mercurous nitrate gives with potassium cobalticyanide a white, flocculent precipitate, which settles quickly. It was therefore possible to use concentrated ammonia as an indicator. Spot tests on porcelain showed a black precipitate as long as there was an excess of mercurous nitrate. Mercurous cobalticyanide is transposed by hydrochloric acid and seems to be partly changed by hot sulphuric acid but not by oxalic acid. It is unaffected by nitric and acetic acids, but decomposed by alkalies. Mercurous cobalticyanide is probably a normal salt, having the formula, $Hg_3Co(CN)_6$.

Mercuric Cobalticyanide is unknown. There is no precipitate formed when potassium cobalticyanide is added to mercuric chloride either in neutral or acid solution.

Arsenic, in hydrochloric, sulphuric, or ammoniacal solution gives no precipitate.

Antimony in a solution sufficiently acid to prevent the precipitation of a basic salt, gives no precipitate.

Stannous salts in neutral, acid, or potassium hydroxide solution are not precipitated by potassium cobalticyanide. Gmelin[2] states that stannous but not stannic salts are precipitated, but does not give the conditions under which he obtained the precipitation.

Cupric Cobalticyanide.—When a solution of copper sulphate is completely precipitated by potassium cobalticyanide solution, there results a turquoise-blue compound. This salt, apparently $Cu_3Co_2(CN)_{12}$, is insoluble in all acids, cold or hot; very soluble in ammonia, and with caustic potash it turns green, becoming darker and darker until black cupric oxide separates. The ammoniacal solution upon evaporation gives small shining blue crystals to which Zwenger,[3] who first worked with this

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[1] *Ann. Chem.* (Liebig), 62, 158.

[2] "Handbook of Chemistry" (1852), Vol. VII, p. 495.

[3] *Loc. cit.*

compound, assigns the formula $Cu_3Co_2(CN)_{12} . 2NH_3 . 5H_2O$.

Cuprous Cobalticyanide, of which no mention is found in the literature, results from the precipitation of cuprous chloride by means of potassium cobalticyanide. It is a faintly yellow precipitate which filters badly; it is insoluble in acids and cold ammonia but soluble in hot, dilute ammonia. It is partly decomposed by potassium hydroxide in the cold and completely when hot. It is slowly oxidized by nitric acid, giving the blue cupric cobalticyanide.

Bismuth Cobalticyanide.—A solution of bismuth nitrate, rather strongly acid with nitric acid, is precipitated by potassium cobalticyanide giving a dense white precipitate, very soluble in hydrochloric but insoluble in the other acids and ammonia. Potassium hydroxide gives in the cold $Bi(OH)_3$, which, on boiling, may be changed to yellow Bi_2O_3. The original precipitate seems to be a normal cobalticyanide, but it has not yet been analyzed and no mention of such a compound was found in the literature.

Cadmium Cobalticyanide.—The statement appears in Gmelin's "Chemistry" (1852) that with cadmium sulphate, potassium cobalticyanide forms a brown precipitate, turning white later, soluble in excess of cobalticyanide and also in acids. In our experiments cadmium chloride was employed; the precipitate was white and amorphous, not soluble in excess of cobalticyanide nor in any acid except warm hydrochloric acid, from which it reprecipitates on cooling. To determine whether it is changed or not during this treatment will require quantitative work. It is completely soluble in cold ammonia but potassium hydroxide decomposes it, giving cadmium hydroxide.

Solutions of gold, platinum, titanium, vanadium, uranium, or zirconium are not precipitated by potassium cobalticyanide.

Aluminum chloride and chromium salts gave no precipitate with cobalticyanide. Certain double ammonio-chromic cobalticyanides have been described by Christensen[1] and by Braun.[2]

Ferric Cobalticyanide.—When potassium cobalticyanide is added to a solution of ferric chloride no precipitate forms at first, but the solution assumes a light green tint and on standing a

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[1] *J. prakt. Chem.* [2], 23, 52.

[2] *Ann. Chem.* (Liebig), 125, 153 *et seq.*

few minutes becomes cloudy and iridescent. The precipitation increases with the formation of an amorphous yellow precipitate which runs through the filter. By boiling, it becomes canary-yellow and flocculent, filtering fairly well. The precipitation does not seem to be complete; it is retarded by the presence of an excess of cobalticyanide or by large quantities of ammonium salts. The precipitate once formed is not soluble in cobalticyanide solution, nor in mineral acids, cold or hot, dilute or concentrated. Hydrochloric acid changes the color of the precipitate and renders it almost impossible to filter. Insoluble in acetic acid, cold or hot; when freshly precipitated it is instantly soluble in oxalic acid but reprecipitates on boiling. It seems that at least two different compounds are produced; they differ both in color and solubility; the greenish one is soluble in oxalic acid and the yellow one insoluble. The latter is formed by long standing in the cold or rapidly by heating. Both give ferric hydroxide with ammonia or potassium hydroxide in the cold. If the ferric salt and the cobalticyanide solutions are mixed hot, precipitation of the yellow compound is instantaneous, no matter which reagent is in excess. The well-washed ferric cobalticyanide gives no red color with ammonium thiocyanate.

Ferrous Cobalticyanide.—Ferrous sulphate and potassium cobalticyanide seem to give a normal ferrous cobalticyanide,—a slightly yellow, amorphous, slow-settling precipitate. When an excess of cobalticyanide is present there is no oxidation or change of color in the ferrous cobalticyanide, even upon long boiling. The precipitation is complete and filters well. With nitric acid, cold and hot, and with hydrochloric and sulphuric acids, hot, there is oxidation. The precipitate darkens in varying degrees, most with nitric and least with sulphuric acid. After treatment with these acids the precipitate filters badly. No change is noticed with acetic or oxalic acids; in the presence of the latter it filters very well. With ammonia the precipitate is partially decomposed in the cold, becoming bluish, and by boiling is completely converted into ferrous hydroxide. With potassium hydroxide it gives a greenish tint, darkening on standing, becoming slate-colored by boiling, forming probably a mixture of ferrous and ferroso-ferric hydroxides.

Manganese Cobalticyanide.—This precipitate, apparently normal, is pure white and filters well. It is insoluble in all cold acids but not absolutely so in hot mineral acids. Alkalies decompose it giving first $Mn(OH)_2$ and later by oxidation, $Mn_2O_2(OH)_2$.

Zinc Cobalticyanide is formed when a solution of zinc sulphate is precipitated by potassium cobalticyanide. It is pure white, settles quickly and filters well ; insoluble in hot water, cold or hot acids, except that a trace seems to dissolve in hot sulphuric acid. This precipitate as well as a few others, *e. g.*, ferrous and ferric cobalticyanides, on boiling with hydrochloric acid passes into a condition which renders it impossible to filter even on double filters. It is very soluble in alkalies.

Cobalt Cobalticyanide.—From solutions of cobaltous chloride, potassium cobalticyanide precipitates a rose-pink, amorphous, rather gelatinous precipitate which is insoluble in cold and hot acids. At 100° or even lower it looses water and becomes blue. This fact was noted by Zwenger, who also states that he formed this compound by heating cobalticyanhydric acid with concentrated sulphuric acid and diluting with water before the decomposition was complete. A peculiarity of many cobalticyanides is the large amount of water which they retain after drying at 100° C. Zwenger noticed that the blue anhydrous cobaltous-cobalticyanide rapidly absorbs moisture from the air and that when water is poured upon it, there is a considerable evolution of heat. We found that the ferrocyanides of zinc and manganese acted in the same way. When cobaltous-cobalticyanide is treated cold with ammonia, it gives a brown solution and pink residue ; on boiling, the solution becomes pink and the residue greenish-brown. The presence of ammonium salts increases the solubility of this compound in ammonia ; it is completely soluble in concentrated ammonia. Caustic potash gives first blue basic salts and on standing or boiling rose-colored cobaltous hydroxide.

Nickel Cobalticyanide results when potassium cobalticyanide is added to solutions of nickel salts. Zwenger states that this precipitate cannot be washed free from potassium salts and that the pure nickel cobalticyanide, $Ni_3Co_2(CN)_{12}$, must be made from cobalticyanhydric acid and a nickel salt. The precipitate is

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$K_3Co(CN)_6$.	(1) HNO_3.	(2) HCl.	(3) H_2SO_4.	(4) $H.C_2H_3O_2$	(5) $H_2\ C_2O_4$.	(6) NH_4OH.	(7) KOH.	Remarks.
+ $AgNO_3$ white, curdy ppt.	(cold) *i* (hot) *i*	$AgCl$ $AgCl$	*i* *i*	*i* *i*	*i* *i*	partly *s* *s*	Ag_2O Ag_2O	Precipitation complete. Settles and filters well. (6) White crystalline ppt. (double salt) on evaporation. Easily sol. cold conc. $NH_4(OH)$.
+ $Hg_2(NO_3)_2$ white, flocculent ppt.	*i* *i*	Hg_2Cl_2 Hg_2Cl_2	*i* *i*	*i* *i*	*i* *i*	$NH_2Hg_2NO_3$ $NH_2Hg_2NO_3$	Hg_2O Hg_2O	(3) Seems slightly soluble hot or else is partly changed to Hg_2SO_4. (5) Not changed to oxalate.
+ $CuSO_4$ turquoise-blue ppt.	*i* *i*	*i* *i*	*i* *i*	*i* *i*	*i* *i*	*s* *s*	CuO CuO	Filters well. (6) Intense blue solution, giving double NH_3 compound on evaporation. (7) Turns green, getting darker until black CuO separates.
+ $Bi(NO_3)_3$ dense, white ppt.	*i* *i*	eas'y *s* *s*	*i* *i*	*i* *i*	*i* *i*	*i* *i*	$Bi(OH)_3$ Bi_2O_3	Precipitation done in strongly acid solution to prevent basic salts upon dilution. (6) Not transposed to $Bi(OH)_3$.
+ $CdCl_2$ white, amorphous ppt.	*i* *i*	*i* *s*	*i* *i*	*i* *i*	*i* *i*	*s* *s*	$Cd(OH)_2$ $Cd(OH)_2$	Filters badly. (2) Precipitates again on cooling.
+ Fe_2Cl_6 green, becoming yellow.	*i* *i*	*i* *i*	*i* *i*	*i* *i*	*i* *i*	$Fe_2(OH)_6$ $Fe_2(OH)_6$	$Fe_2(OH)_6$ $Fe_2(OH)_6$	(5) When freshly precipitated and greenish it is readily sol. in oxalic cold. Ammonia salts in quantity prevent precipitation and excess of $K_3Co(CN)_6$ retards it.
+ $FeSO_4$ faintly yellowish white ppt.	*i* *i*	*i* *i*	*i* *i*	*i* *i*	*i* *i*	partly $Fe(OH_2)$ $Fe(OH_2)$	$Fe(OH)_2$ $Fe(OH)_2$	(1, 2 and 3) On boiling oxidize more or less to yellow ferric cobalticyanide. (6 and 7) Some oxidation to dark-colored ferroso-ferric compounds.
+ $MnCl_2$ white ppt.	*i* *i*	*i* *i*	*i* *i*	*i* *i*	*i* *i*	$Mn(OH_2)$ and $Mn_2O_2(OH)_2$	$Mn(OH)_2$ and $Mn_2O_2(OH)_2$	(1, 2, 3, 4, and 5) Seem very slightly soluble hot.
$ZnSO_4$ dense, white ppt.	*i* *i*	*i* *i*	*i* trace *s*	*i* *i*	*i* *i*	easily *s* *s*	easily *s* *s*	(4 and 5) Bump violently on boiling.
+ $CoCl_2$ rose-pink ppt.	*i* *i*	*i* *i*	*i* *i*	*i* *i*	*i* *i*	partly *s* partly *s*	$Co(OH)_2$ $Co(OH)_2$	(6) Solubility increased by ammonium salts. Almost completely sol. in hot conc. NH_4OH. (7) At first blue basic salts, turning again pink.
+ $NiCl_2$ robin's egg blue ppt.	*i* *i*	*i* *i*	*i* *i*	*i* *i*	*i* *i*	blue sol. *s* *s*	$Ni(OH)_2$ $Ni(OH)_2$	Very voluminous precipitate, which filters poorly.
NH_4, Li, Na, Mg, Ba, Ca, Sr, Pb, Hg'', Sn''+IV, Cr, Al, Pt, Au, Zr, Ti, Mo salts.	No precipitates.							Solutions of salts of other metals are not precipitated by $K_3Co(CN)_6$ and other known cobalticyanides are easily soluble in water. Such cobalticyanides are usually made from an oxide or hydroxide acted upon by $H_3Co(CN)_6$.

robin's egg blue in color, very voluminous and dries up to a vitreous mass with conchoidal fracture. It is insoluble in water and acids, cold or hot; soluble completely in ammonia, cold or hot. Potassium hydroxide gives instantly pale green nickel hydroxide.

The effect of the reagents used on the precipitates formed by potassium cobalticyanide is shown by the accompanying table. A glance at this tabulation will show several possibilities for new separations:

1. The lead salt is exceedingly soluble, while those of silver, copper, and bismuth are insoluble in either water or nitric acid. This may find an application in the analysis of pig lead, when the separation of relatively small quantities of these impurities would be much more preferable to the separation of the lead as sulphate. The separation of the bismuth can be effected either by treatment with hydrochloric acid which dissolves the bismuth cobalticyanide and leaves the copper as cobalticyanide and the silver as chloride, or by ammonia which leaves the bismuth and dissolves the copper and silver. The bismuth compound, if not suitable for weighing, can be decomposed by potassium hydroxide and weighed as Bi_2O_3 or one of the new volumetric methods may be employed for its estimation.

2. As the precipitation of ferric cobalticyanide in the cold can be completely prevented by the presence of ammonium sulphate, and probably by other compounds, it is possible to precipitate zinc, manganese, nickel, or cobalt in the presence of iron. With zinc ores containing iron and manganese, the manganese and zinc can be precipitated as cobalticyanides and then separated by treatment with potassium hydroxide, which readily dissolves the zinc cobalticyanide and leaves the manganese as $Mn_2O_2(OH)_2$.

Another possible application is in the analysis of nickel steel, where the separation from ferric iron, if sufficiently complete, would be more convenient than the method in use, based on the solubility of ferric chloride in ether. The nickel cobalticyanide after filtration can be converted into hydroxide and then dissolved in acid for the cyanide titration or for electrolysis.

These and other possible uses of the cobalticyanides are under investigation at Columbia University.

HAVEMEYER HALL, December 6, 1899.