even in the annealed samples, we are led to conclude that a platinum silver compound crystallizes out which reacts against the liquid during solidification, giving a soluble or partially soluble product, which in turn further reacts or is transformed. The explanation of the abnormal solubilities of these alloys and of the widely differing results of the different investigators therefore lies in the presence of varying amounts of these constituents, depending both upon the composition and rate of cooling of the alloy.

CONCLUSIONS.

(1) The separation of platinum from gold, iridium, etc., in one operation by means of alloying with silver and parting with nitric acid is impossible.

(2) Analytical results on platinum silver alloys, based on parting with concentrated sulphuric acid, are incorrect for alloys containing 20 per cent. or more of platinum, unless correction is made for the undissolved silver remaining with the platinum.

(3) The existence of platinum silver compounds is probably the explanation of the irregular results obtained in parting with nitric acid.

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THE INSOLUBLE CHROMICYANIDES.[1]

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As the potassium salt of hydrochromicyanic acid was used to precipitate the others, the methods of preparing the salts were first considered.

In 1903 L. O. Beatty investigated the method of preparation of potassium chromicyanide, and found that the methods of Böckmann,[2] Stridsberg,[3] Kaiser[4] and Christensen[5] did not give

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[1] Read at the May Meeting of the New York Section of the American Chemical Society.

[2] Traité de Chimique Organique, J. Liebig, Vol. I, p. 174; Gmelin's "Handbook of Chemistry," Vol. VII, p. 420; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 1864, Vol. XVII, p. 302.

[3] Jahresb. 1864, Vol. XVII, p. 304; N. Arch. ph. nat. XXII, p. 151.

[4] Ann. Chem. Pharm. III suppl., p. 163; Gmelin Handb. 4

satisfactory results. The method finally adopted by him was a modification of the method of Christensen, which is as follows:

The chromium chloride and potassium chloride obtained by reduction of 50 grams of potassium dichromate with alcohol and hydrochloric acid, after evaporation, were dissolved in 150 cc. of water. This solution was heated, and added slowly to a hot solution of 100 grams of potassium cyanide dissolved in 200 cc. of water, stirring constantly. The mixture was digested hot for several hours. This was filtered, and evaporated *in vacuo* to concentration, filtered from the separated chromium hydroxide, and cooled in an ice mixture. The crystals were filtered off, and washed first with dilute (50 per cent.), and then with strong alcohol (95 per cent.). No alcohol was used for precipitating the salt. The salt was recrystallized as often as necessary to free it from potassium chloride. Contrary to what Kaiser states, Beatty says that the potassium chromicyanide is decomposed by boiling even in a vacuum.

His yield was less than 50 per cent.

EXPERIMENTAL.

In carrying out this work, we are indebted to Mr. L. O. Beatty, who furnished some of the potassium chromicyanide. This salt was purified by recrystallizations over sulphuric acid in a vacuum.

Some potassium chromicyanide was prepared by Beatty's method, but the method finally used, after also testing Christensen's method, was a modification of the former. Sixty grams of chromium trioxide were dissolved in 150 cc. of concentrated hydrochloric acid, and 75 cc. of water. Seventy-five cc. of 95 per cent. alcohol were added to the mixture, a little at a time, and then the solution was evaporated to dryness. The residue was dissolved in 225 cc. of boiling water, and added slowly to a hot solution of 150 grams of potassium cyanide dissolved in 300 cc. of water. The solution was stirred vigorously after each addition of the chromium solution. The mixture was digested for several hours, and then filtered on a Büchner funnel. The filtrate was allowed to evaporate in the air, large yellow crystals

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aufl. 4, 335; Gmelin's "Handbook of Chemistry," VII, p. 429; "Handwörterbuch d. Chem. Fehling," p. 663; Jähresb. 1864, Vol. XVII, p. 302; Chem. Centrbl., 1865, p. 259.

[5] J. pr. Chem. 139, 2, 31, 163 (1885); [2] 23, 52.

of potassium chromicyanide forming, which were very pure, and consequently required only one or two recrystallizations.

If a large excess of potassium cyanide is used, a thick, deep red solution is obtained, from which alcohol will not precipitate potassium chromicyanide, but a syrup is formed at the bottom of the dish.

The salt heated five hours at 100° in a water-jacketed air-bath did not lose in weight. When heated at 102° in an air-bath for three hours, there was no loss in weight.

Three grams heated to 147° lost 0.7 mg. At this temperature the salt has a deep reddish yellow color.

At 159° the salt began to decompose, losing 2.3 mg. in weight, the crystals turning dark in spots. The temperature was increased, and at 196° the total loss in weight was only 3.2 mg. On ignition at a red heat the substance becomes black, and melts, the residue finally having a green color (Cr_2O_3). The crystals decrepitate when strongly heated.

One gram of pure potassium chromicyanide was dissolved in 300 cc. of water, and the solution allowed to stand in the light for several weeks at the ordinary temperature. The salt slowly decomposed, the solution becoming cloudy.

One gram of the salt heated red hot in a porcelain boat in a glass tube gave no water of crystallization.

0.7026 gram of the salt was analyzed by the following method: It was decomposed by boiling with aqua regia, the solution being boiled down with concentrated hydrochloric acid several times to get rid of the excess of nitric acid. The solution was finally diluted with water, and the chromium precipitated three times from the boiling hot solution by ammonium hydroxide in slightest excess. The filtrates were evaporated to dryness, and ignited to drive off the ammonium salts, the residue taken up with water, evaporated again, and ignited. The weight of the impure potassium chloride gave 36.3 per cent. of potassium.

The residue was dissolved in hot water, an excess of chlorplatinic acid added, and the solution evaporated. More chlorplatinic acid was added, then alcohol, until about 75 per cent. by volume, and the solution allowed to stand over night in a platinum dish. The potassium chlorplatinate was filtered, washed, dissolved by boiling water into a weighed platinum dish, and after evaporation, weighed. Weighing the potassium as sulphate did not give satisfactory results.

The precipitate of chromium hydroxide was washed into a porcelain casserole, and treated with an excess of sodium peroxide. The solution was boiled for fifteen to twenty minutes, after the addition of more peroxide.

The solution was allowed to cool, and then diluted with water to 500 cc. volume. This was made acid by 10 cc. of concentrated sulphuric acid in excess, and titrated by a standard solution of ferrous sulphate (64.052 grams per liter), using a spot test, with a very dilute, freshly prepared solution of potassium ferricyanide. The ferrous sulphate was standardized at the same time by titration against a weighed quantity of potassium chromate, using the above conditions. This was the method used for the determination of chromium throughout the work.

Before this method was decided upon, 0.5207 gram of potassium chromate was dissolved in water, the chromium reduced in a hydrochloric acid solution by alcohol, and precipitated as chromium hydroxide. This was treated as above (sodium peroxide, etc.), and required the same number of cubic centimeters of ferrous sulphate solution as the same weight of potassium chromate, both solutions being titrated under the same conditions.

The addition of an excess of Mohr's salt to the acid chromate solution, and subsequent titration with a standard potassium permanganate solution, did not give accurate results, as the end point was obscured by the green chromium salt formed. When the precipitated chromium hydroxide was ignited and the chromium weighed as sesquioxide, the results were slightly high, due to the occlusion of salts by the hydroxide, sulphates especially causing this trouble.

The nitrogen was determined by the Kjeldahl method, using 0.5005 gram for analysis.

		Calculated. Per cent.	Found. Per cent.
3K	117.45	36.05	36.01
Cr	52.1	15.99	16.03
6C	72.0	22.1	by difference 21.97
6N	84.24	25.86	25.99
		100.00	100.00

The formula $K_3Cr(CN)_6$ is therefore confirmed.

The following reagents were used for determining the chemical properties of the chromicyanides.

Concentrated hydrochloric acid, sp. gr. 1.20; concentrated nitric acid, sp. gr. 1.42; concentrated sulphuric acid, sp. gr. 1.84; dilute hydrochloric acid, sp. gr. 1.0815; dilute nitric acid, sp. gr. 1.232; dilute sulphuric acid, sp. gr. 1.186; acetic acid, sp. gr. 1.017; ammonium hydroxide (strong), sp. gr. 0.900; ammonium hydroxide (dilute), sp. gr. 0.9775.

Double normal sodium hydroxide; double normal sodium carbonate; normal potassium cyanide; aqua regia (1 part concentrated nitric + 3 parts concentrated hydrochloric acid); sodium peroxide; ammonium sulphide.

Potassium chromicyanide is decomposed by boiling with water and sodium peroxide. The solution, made acid with acetic acid, gives a yellow precipitate with lead acetate.

It is decomposed by concentrated hydrochloric acid, in the cold, more readily on boiling, giving a green solution.

It is decomposed by concentrated nitric acid, giving a green solution on boiling.

It dissolves slowly in concentrated sulphuric acid, giving a yellow solution, which, on boiling, decomposes, giving a red, violet, and then a green solution.

It is decomposed by dilute sulphuric, hydrochloric or nitric acids, giving a green solution readily on boiling.

Aqua regia decomposes the salt more readily on heating.

Cadmium Chromicyanide, $Cd_3Cr_2(CN)_{12}$.—According to Kaiser[1] cadmium salts give a white precipitate. We prepared the salt, first, by adding a 4 per cent. solution of cadmium chloride to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 2 per cent. solution of cadmium chloride. In both cases, a white precipitate with a slightly greenish tinge immediately formed. This was washed thoroughly by decantation and dried at 100°.

The compound decomposed readily on ignition in a porcelain crucible, giving cadmium oxide and metallic cadmium which deposited on the cover of the crucible. Consequently, this method could not be used for decomposing the compound for analysis.

For analysis about 0.4 gram of the substance was decomposed by dissolving in dilute hydrochloric acid and evaporating twice

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[1] Ann, III Suppl., p. 170.

to a small bulk to secure complete decomposition. The cadmium was then precipitated as sulphide, the latter dissolved in dilute hydrochloric acid, and after evaporation, neutralization and the addition of 1 gram of potassium cyanide, the solution was electrolyzed by 0.17 ampere and 3.75 volts. The chromium was determined as already described.

The analyses gave: Cd, 41.45, 41.72; Cr, 12.76, 12.93. Calculated for $Cd_3Cr_2(CN)_{12}$: Cd, 44.73; Cr, 13.82. Ratio of Cr to Cd: I, 2:3.01; II, 2:2.99.

The formula given to the compound, therefore, is $Cd_3Cr_2(CN)_{12}$.

Cadmium chromicyanide is readily soluble in an excess of potassium cyanide, and ammonium hydroxide.

Concentrated hydrochloric acid immediately decomposes it, giving a red solution, which becomes green. This takes place more quickly on boiling. Concentrated nitric acid has the same effect, but the action is slower in the cold. Concentrated sulphuric acid acts more slowly than either of the above.

Dilute hydrochloric, nitric and sulphuric acids decompose the compound, giving off hydrocyanic acid, and forming green solutions quickly on boiling, but slowly in the cold. Aqua regia dissolves it quickly. On boiling with sodium peroxide, it is decomposed.

The compound is decomposed by ammonium sulphide, sodium hydroxide and sodium carbonate.

Acetic acid decomposes the compound slowly on boiling.

Cobalt Chromicyanide, $Co_3Cr_2(CN)_{12}$.—Berzelius[1] states that cobalt salts give a brown precipitate, which remains brown when dry. As given in Watts' Dictionary,[2] chromicyanide of cobalt is a blue precipitate. According to Gmelin,[3] salts of protoxide of cobalt yield a blue precipitate with sesquicyanide of chromium. Kaiser[4] states that cobalt salts give with potassium chromicyanide a flesh-colored precipitate insoluble in acids, but soluble in ammonium hydroxide, giving a yellow solution. The salt was prepared, first, by adding a 4 per cent. solution of cobalt nitrate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a

[1] Berzelius Lehrbuch, 1845, Vol. III, p. 1075.

[2] Watt's Dict. Chem., Vol. II, 1872, p. 205.

[3] Gmelin's "Handbook of Chemistry," Vol. VII, p. 495.

[4] Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663: Jahresb., 1864, p. 302.

4 per cent. solution of cobalt nitrate. In both cases a light rose-colored precipitate was formed. These were washed thoroughly by decantation, magnesium chloride being added from time to time when the precipitate became colloidal, and dried at 100°. The color of the dried sample was yellowish brown.

For analysis, 0.3 to 0.5 gram was ignited in a porcelain crucible, and fused with sodium peroxide. The fusion was leached out with water, and the precipitate filtered, washed and dissolved in dilute sulphuric acid. After neutralization, 100 cc. of ammonium hydroxide and 3 grams of ammonium sulphate were added, and the solution electrolyzed by 2.5 amperes and 4.75 volts. The chromium was determined as before.

The analyses gave: Co, 22.86, 21.64; Cr, 13.59, 12.65. Calculated for $Co_3Cr_2(CN)_{12}$: Co, 29.81; Cr, 17.55. Ratio of Cr to Co: I, 2:97; II, 2:3.02.

The formula $Co_3Cr_2(CN)_{12}$ is therefore given to the compound when precipitated either by an excess of the cobalt salt or the potassium chromicyanide.

Cobalt chromicyanide is readily soluble in an excess of potassium cyanide. It is decomposed by boiling with sodium peroxide, giving a black precipitate, and a yellow solution of chromate. It is also decomposed by ammonium sulphide. Ammonium hydroxide decomposes the compound, but does not entirely dissolve it. Sodium hydroxide decomposes the compound rapidly, sodium carbonate slowly. It is insoluble in cold or boiling acetic acid. Concentrated sulphuric acid, and concentrated hydrochloric acid dissolve it in the cold, very readily on boiling. It is not readily soluble in concentrated nitric acid, even on boiling.

Aqua regia decomposes the compound, but it is not entirely dissolved, even on boiling. It is very slowly soluble in dilute sulphuric, hydrochloric, or nitric acids, being least soluble in the last. On boiling, dilute sulphuric and hydrochloric acids readily dissolve it, but nitric acid, only slowly.

Cuprous Chromicyanide, $Cu_3Cr(CN)_6$.—Kaiser[1] states that by treating cupric chromicyanide with a stream of hydrogen sulphide, or by sulphurous acid, a red compound is formed, which is probably cuprous chromicyanide ($3Cu_2Cy.Cr_2Cy_3$, equivalent to $Cu_3Cr(CN)_6$ at present).

One gram of potassium chromicyanide was treated with a

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[1] Ann. III Suppl., p. 166.

slight excess of a solution of cuprous chloride, in about 75 cc. bulk. An orange-yellow precipitate immediately formed, which was filtered, washed thoroughly, and dried at 100°. For analysis, about 0.5 gram was dissolved in dilute nitric acid, evaporated to low bulk, water added, and a little ammonium hydroxide, and the solution electrolyzed, using a current of 0.35 ampere and 2.1 volts.

Some chromium was oxidized by the current to chromate. Consequently, after all the copper was deposited, the electrolyte was boiled with alcohol, and then the chromium precipitated as chromium hydroxide, and determined as before.

The analysis gave: Cu, 45.01; Cr, 12.24. Calculated for $Cu_3Cr(CN)_6$: Cu, 47.80; Cr, 13.05. Ratio of Cr to Cu, 1:3.01. The formula of the compound is therefore $Cu_3Cr(CN)_6$.

Cuprous chromicyanide is readily soluble in an excess of potassium cyanide and readily dissolved by concentrated nitric acid in the cold or on boiling. Dilute nitric acid dissolves it, very quickly on boiling. It is readily decomposed by aqua regia, giving a green solution. It is decomposed by concentrated hydrochloric acid, slowly going into solution in the cold, but quickly on boiling. The dilute acid acts similarly.

Cold concentrated sulphuric acid dissolves it slowly, but quickly on boiling. The dilute acid acts similarly, but more slowly than with the concentrated acid. On boiling with the dilute acid it dissolves quickly, giving a green solution.

Cupric Chromicyanide, $Cu_3Cr_2(CN)_{12}$.—Kaiser[1] states that in the cold, copper sulphate gives a blue precipitate, containing a little potassium, as shown by his analysis, and which he calculates to copper. By mixing at 75° a concentrated solution of a copper salt with dilute potassium chromicyanide solution, the precipitate was free from potassium.

From his analysis he gives the formula $3CuCy.Cr_2Cy_3$, corresponding to $Cu_3Cr_2(CN)_{12}$ at the present time.

On heating this compound formed in the cold, at 40°, it loses water irregularly, and if the temperature is raised, it changes from blue to blue-green, green, yellow-green, and finally reddish-gray at 100°, carrying variable amounts of water. This red salt, on being treated with water, will not become blue again. It is

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[1] Ann. III Suppl., p. 166; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

insoluble in cold acids, dilute or concentrated, but dissolves on heating. Also insoluble in cold ammonium hydroxide, and sodium hydroxide. On boiling with the latter, dark brown copper oxide is finally precipitated.

Comey[1] gives the formula $Cu_3(Cr(CN)_6)_2$ to the cupric compound, and states that it is a precipitate insoluble in dilute or concentrated acids, except on heating; insoluble in ammonium or potassium hydroxides plus water.

We prepared the salt, first, by adding a 3 per cent. solution of copper sulphate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 3 per cent. solution of potassium chromicyanide to a 2 per cent. solution of copper sulphate. In both cases, a precipitate immediately formed, having a robin's egg-blue color, which changed to green on standing. Both precipitates were thoroughly washed by decantation, potassium sulphate and magnesium chloride being used with the latter as it became very colloidal, and dried at 100°. The color of the dried substance was reddish purple.

For analysis, about 0.5 gram was dissolved in dilute nitric acid, and after boiling for about two hours, the solution was electrolyzed. The chromium was precipitated as hydroxide, and determined as usual.

The analyses gave: Cu, 32.23, 30.96; Cr, 17.50, 16.96. Calculated for $Cu_3Cr_2(CN)_{12}$: Cu, 31.41; Cr, 17.15. Ratio of Cr to Cu: I, 2 : 3.02; II, 2 : 2.99.

The formula $Cu_3Cr_2(CN)_{12}$ is therefore given to this compound, being precipitated either by an excess of the copper salt, or *vice versa.*

Cupric chromicyanide is readily soluble in an excess of potassium cyanide. It is decomposed by an excess of ammonium hydroxide in the cold, giving a blue solution, and a precipitate. Ammonium sulphide gives a black precipitate of copper sulphide. It is decomposed by sodium hydroxide, and by sodium carbonate, the latter giving a blue solution, and a yellowish green precipitate.

It is dissolved by aqua regia; readily by concentrated sulphuric acid in the cold, giving a red solution, which becomes violet, and finally green. Concentrated hydrochloric acid readily dissolves it in the cold, more quickly on boiling. Concentrated nitric acid decomposes it, but only gives a clear green solution on boiling. It

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[1] "Dictionary of Solubilities," 1896.

is very slowly soluble in cold dilute hydrochloric, nitric, and sulphuric acids, while on boiling the first two readily dissolve it, but the sulphuric acid dissolves it only slowly. It is insoluble in cold acetic acid.

Boiled with sodium peroxide and water, it is decomposed, giving a green solution. On the addition of acetic acid, a precipitate formed. This was removed by filtration and then lead acetate added to the filtrate, and a yellow precipitate of lead chromate obtained.

Ferrous Chromicyanide, $Fe_3Cr_2(CN)_{12}$.—According to Kaiser,[1] potassium chromicyanide gives with ferrous solutions, a red, very pulverulent precipitate. If precipitated at 70° it is practically potassium-free, two analyses averaging 0.25 per cent. of potassium. If heated to 100° there is a great loss of hydrocyanic acid, and the black mass resulting no longer dissolves by warming with hydrochloric acid, while the compound dried over sulphuric acid readily dissolves in hydrochloric acid. To the substance dried over sulphuric acid he gives the formula $3FeCN.Cr_2(CN)_3.20Aq.$, corresponding to $Fe_3Cr_2(CN)_{12}.20Aq.$ at the present time, but states that the point at which the compound has not yet lost any water is very difficult to determine accurately, because the substance contains so much water of crystallization. The substance is decomposed by shaking with sodium hydroxide. Liebig[2] states that potassium chromicyanide gives a brick-red precipitate with ferrous salts. Watts[3] states that the precipitate is brick-red, while Storer[4] gives the formula $3FeCN.Cr_2(CN)_3$ (?), equivalent to $Fe_3Cr_2(CN)_{12}$ at present.

We prepared the salt, first, by adding a 7 per cent. solution of Mohr's salt to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 4 per cent. solution of Mohr's salt. In both cases, two drops of concentrated sulphuric acid were added. A brick-red granular precipitate formed immediately in each case, which was washed thoroughly by decantation, and dried at 100°. The color of the dried substance was dark green.

[1] Ann. III Suppl., p. 169: "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

[2] "Traité de Chimique Organique," J. Liebig, Vol. I, p. 174.

[3] Watt's "Dictionary of Chemistry," 2, 205 (1872).

[4] Storer: "Dictionary of Solubilities," 1864.

For analysis, from 0.3 to 0.5 gram was ignited in a porcelain crucible, fused with sodium peroxide, and the fusion leached out with water. The precipitate was filtered, washed, dissolved in sulphuric acid, and the iron determined by titration with permanganate. The chromium was determined as before.

The analyses gave: Fe, 22.12, 22.06; Cr, 13.85, 13.75. Calculated for $Fe_3Cr_2(CN)_{12}$: Fe, 28.70; Cr, 17.83. Ratio of Cr to Fe: I, 2:2.98; II, 2:2.99. Therefore, the formula of the compound is $Fe_3Cr_2(CN)_{12}$.

Ferrous chromicyanide is decomposed by sodium hydroxide and ammonium hydroxide, giving a brown precipitate, by sodium carbonate giving a green precipitate, and by ammonium sulphide. Potassium cyanide immediately turns the precipitate dark-red, but does not dissolve it. It is decomposed by boiling with sodium peroxide and water.

Aqua regia immediately decomposes the compound, in the cold or on boiling. It is most soluble in hydrochloric acid, concentrated or dilute acid slowly dissolving it in the cold, but very quickly on boiling, giving a green solution.

Dilute or concentrated nitric acid, in the cold, decomposes it, giving a precipitate of a dirty yellow color. On boiling with the dilute acid, a clear solution is obtained, but the precipitate does not dissolve on boiling with the concentrated acid, except when diluted with water. Concentrated sulphuric acid immediately decomposes it, hot or cold. Cold dilute sulphuric acid acts more slowly than hydrochloric acid but, on boiling, a clear solution is quickly obtained. It is not decomposed by cold acetic acid.

Manganous Chromicyanide, $Mn_3Cr_2(CN)_{12}$.—Kaiser[1] states that the manganese salt is white, crystalline, and insoluble in dilute acids.

We prepared the salt, first, by adding a $3^1/_2$ per cent. solution of manganese chloride to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 2 per cent. solution of manganese chloride. In both cases, a greenish white precipitate immediately formed, which, under the microscope, appeared to consist of small crystals, apparently isometric. The precipitates were washed thoroughly, and dried at 100°; when dried, the color was light brown.

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[1] Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

If the compound is dried in a desiccator, in a vacuum, over sulphuric acid, it has a buff color.

The compound was analyzed by several methods. A portion was ignited in a porcelain crucible, and then fused with sodium peroxide, but this introduced silica and alumina, which had to be subsequently separated, and the results were very poor. Another portion was dissolved in hydrochloric acid, and the chromium precipitated four times by ammonium hydroxide. The manganese could not be separated from the chromium by this method. The filtrates were combined, the manganese separated, and potassium determined, giving only a trace.

Finally, about 0.5 gram of the compound was dissolved in dilute hydrochloric acid, and after two evaporations to low bulk with acid, sodium peroxide was added, and the solution boiled. The precipitate was filtered, washed, and dissolved in dilute hydrochloric acid and sulphurous acid. The sulphur dioxide was boiled out of the solution, and the preceding process repeated four times until the manganese was free from chromium, when it was determined as manganese pyrophosphate. The chromium was determined as before.

The analyses gave: Mn, 23.06, 23.14; Cr, 14.58, 14.69. Calculated for $Mn_3Cr_2(CN)_{12}$: Mn, 28.37; Cr, 17.91. Ratio of Cr to Mn, I, 2 : 2.99; II, 2 : 2.98.

The compound has, therefore, the formula $Mn_3Cr_2(CN)_{12}$.

The compound is decomposed by sodium peroxide, giving a precipitate of manganese dioxide, and a yellow solution of chromate; decomposed by boiling with concentrated hydrochloric, nitric or sulphuric acid or aqua regia, giving a green solution; readily soluble in an excess of potassium cyanide; decomposed by an excess of ammonium hydroxide, sodium hydroxide, sodium carbonate and ammonium sulphide; dissolves very slowly in dilute hydrochloric, nitric or sulphuric acid, but readily on boiling, giving a green solution; only slightly soluble in cold acetic acid, more so on boiling.

Mercurous Compound.—According to Berzelius,[1] mercurous salts give a white precipitate with potassium chromicyanide, which makes the solution at the bottom brown, while the precipitate becomes dark. The color of the liquid soon disappears,

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[1] Berzelius' "Lehrbuch," Vol. III, p. 1075 (1845).

and a compound of chromium cyanide with a little mercury remains behind.

Kaiser[1] states that mercurous nitrate gives a dark gray precipitate with potassium chromicyanide, insoluble in nitric acid and ammonium hydroxide.

We dissolved 0.5 gram of potassium chromicyanide in 50 cc. of water, and quickly added 100 cc. of a 2 per cent. solution of mercurous nitrate.

A yellowish white precipitate formed, which quickly darkened, turning finally to gray, and which settled rapidly. The solution did not then smell of hydrocyanic acid. One hundred cc. of water were added, and the solution stirred. The precipitate settled rapidly, leaving the supernatant liquid reddish-yellow, which rapidly became darker in color. The precipitate darkened, becoming smaller in volume, and on stirring the solution hydrocyanic acid could be readily detected. On standing for a day or so the solution became green, due to the color of the chromium salt. The gray precipitate proved to be nothing but metallic mercury in a very finely divided state. This was filtered and washed, dissolved in dilute nitric acid, part of the acid neutralized by ammonium hydroxide and the solution electrolyzed by a current of 0.18 ampere, and 2.3 volts.

Total weight of mercury found was 0.4679 gram.

The reaction takes place probably in the following steps: First, mercurous chromicyanide is precipitated, which then decomposes, giving mercurous cyanide, which then decomposes, giving mercuric cyanide, which slowly dissolves, and metallic mercury.

If the reaction takes place as above stated, 0.5 gram of the potassium salt would precipitate 0.4605 gram of mercury, while 0.4679 gram was found.

Nickel Chromicyanide, $Ni_3Cr_2(CN)_{12}$.—Kaiser[1] states that solutions of nickel salts give a bluish-green precipitate, very voluminous, becoming green on boiling, insoluble in dilute acids, but soluble in ammonium hydroxide with a grayish green color.

The salt was prepared, first, by adding a 4 per cent. solution of nickel nitrate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 4 per cent. solution of nickel nitrate. In both

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[1] Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

cases a voluminous light greenish blue precipitate formed immediately which was washed thoroughly by decantation, with the aid of 8 grams of magnesium chloride, added from time to time, when it became too colloidal. The precipitates were dried at 100°, when they became black in color.

Five-tenths gram of the substance was dissolved by dilute nitric acid, and the separation of the chromium from the nickel attempted by the addition of ammonium hydroxide, in the presence of ammonium chloride, and reprecipitation of the chromium. The results were inaccurate. Finally 0.3 to 0.6 gram was ignited in a porcelain crucible, fused with sodium peroxide, and the fusion leached out with water. The precipitate was filtered, washed, and dissolved in dilute sulphuric acid. After the addition of 3 grams of ammonium sulphate, and 100 cc. of ammonium hydroxide in excess, the solution was electrolyzed by a current of 2.5 amperes and 3 volts. The chromium was determined as before.

The analyses gave: Ni, 24.25, 18.13; Cr, 14.37, 10.76. Calculated for $Ni_3Cr_2(CN)_{12}$: Ni, 29.71; Cr, 17.58. Ratio of Cr to Ni, I, 2:3.00; II, 2:2.99. Number II was not dry when analyzed.

The formula $Ni_3Cr_2(CN)_{12}$ is, therefore, given to the compound, being precipitated either by an excess of nickel salt or of potassium chromicyanide.

The substance is readily soluble in an excess of potassium cyanide and ammonium hydroxide. It is readily decomposed by ammonium sulphide. It dissolves slowly in the cold in dilute hydrochloric, nitric or sulphuric acid, but readily on boiling, giving a clear green solution.

It is slowly soluble in concentrated hydrochloric, nitric, or sulphuric acid, being much more soluble in concentrated sulphuric acid than in either of the other two. On boiling, all three acids readily dissolve it, forming clear green solutions.

It is slowly decomposed by aqua regia in the cold, quite readily on boiling, giving a green solution after a few minutes.

On boiling with sodium peroxide and water, it is decomposed, but not very readily, precipitating green nickel hydroxide. The filtrate contains sodium chromicyanide. Sodium hydroxide behaves similarly. Sodium carbonate decomposes it slowly in the cold. The compound is insoluble in cold acetic acid, but is slightly soluble on boiling.

Silver Chromicyanide, $Ag_3Cr(CN)_{12}$.—Berzelius[1] states that silver salts give a white precipitate with potassium chromicyanide, which is gray when dry.

Kaiser[2] states that silver chromicyanide is of a deep yellow color, and in the dry state unaffected by light. It is noted for its stability, being unaffected after twelve hours' treatment with hydrochloric acid, nitric acid, or ammonium hydroxide. He says that the only solvent is potassium cyanide, and that hydrochloric acid reprecipitates silver chromicyanide. Dried at 20° to 30°, it retains its yellow color, while at 100° it has a rose-red color, and loses 0.6 per cent. of its weight. He gives the formula $3AgCN.Cr_2CN_3$, equivalent to $Ag_3Cr(CN)_6$ at present, and states that there was some undecomposed substance in the silver chloride, making the percentage of silver high and the chromium low. According to Watts,[3] silver nitrate gives a white precipitate.

Stover[4] gives chromicyanide of silver $3AgCN.Cr_2(CN)_3$, equivalent to $Ag_3Cr(CN)_6$ at present, as a precipitate. Comey[5] says that silver chromicyanide $Ag_3Cr(CN)_6$ is insoluble in all solvents excepting potassium cyanide.

Böckmann[6] states that potassium chromicyanide forms a white precipitate with silver salts similar in composition to the potassium salt. When heated, it decomposes into cyanogen gas, metallic silver and chromium cyanide. Hydrogen sulphide passed through the solution containing silver chromicyanide in suspension, gives silver sulphide, and hydrochromicyanic acid.

We prepared the salt by adding a 4 per cent. solution of silver nitrate to a 2 per cent. solution of potassium chromicyanide. An orange-yellow voluminous precipitate immediately formed, which settled rapidly, and was easily washed by decantation, and dried at 100°; when dry, it was rose-red in color.

Difficulty was encountered in the analysis of this compound.

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[1] Berzelius' "Lehrbuch," Vol. III, 1075-76 (1845).

[2] Ann. III Suppl., p. 167; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

[3] Watts' "Dictionary of Chemistry," **2**, 205 (1872).

[4] "Dictionary of Solubilities," 1864.

[5] "Dictionary of Solubilities," 1896.

[6] Gmelin's "Handbook of Chemistry," Vol. VIII, p 31; "Traité de Chimique Organique," J. Liebig, Vol. I, p. 174.

The substance was dissolved in concentrated nitric acid and dilute sulphuric acid, and heated for some time. The silver was precipitated as silver chloride, which gave about 0.7 per cent. of silver too high, and about 0.5 per cent. of chromium too low. This corresponds quite closely to the results given by Kaiser.[1] Several analyses were made with the same result. It was thought that the difficulty was with incomplete decomposition of the silver compound. Consequently, the following method was finally used, giving good results:

About 0.5 gram of the substance was treated with concentrated nitric acid and dilute sulphuric acid, the solution boiled down to low bulk, more nitric acid added, and the treatment repeated three times, finally evaporating until nearly all the nitric acid was eliminated. If the solution is evaporated too far, a sulphate of chromium will be formed, which is then insoluble on the addition of more acid and boiling. The solution was allowed to cool, and then a little dilute hydrochloric acid was added to precipitate the silver. The silver chloride was filtered on a porcelain Gooch crucible, with a piece of filter-paper on the bottom, and dried at 110° and weighed. The silver chloride was dissolved in 3.25 grams of potassium cyanide, and the solution electrolyzed.

The chromium was determined as before.

The analyses gave: Ag, from electrolysis, 60.84; from AgCl, 60.89; Cr, 9.69. Calculated for $Ag_3Cr(CN)_6$: Ag, 60.85; Cr, 9.79. Ratio of Cr to Ag: from electrolysis, 1 : 3.03; from AgCl, 1 : 3.04.

The formula $Ag_3Cr(CN)_6$ is confirmed.

Silver chromicyanide is readily soluble in an excess of potassium cyanide, giving a yellow solution. Ammonium sulphide decomposes the compound, precipitating black silver sulphide. It is decomposed by sodium hydroxide solution, and slightly by ammonium hydroxide. It is insoluble in a solution of sodium carbonate, as in hot or cold acetic acid. By boiling with sodium peroxide and water it is decomposed.

A large excess of concentrated hydrochloric acid dissolves the compound, the solution becoming red, then pink, and finally green. On dilution with water, silver chloride is precipitated. When treated with small amounts of acid the decomposition is the same,

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[1] Kaiser: Ann. III Suppl., p. 167.

only silver chloride is precipitated. With concentrated nitric acid it slowly dissolves, giving a yellow solution. On boiling it quickly dissolves, giving a green solution.

It is readily soluble in an excess of concentrated sulphuric acid, the solution becoming red, then pink and finally green.

It is decomposed by aqua regia, giving a precipitate of silver chloride. It is very slightly soluble in cold dilute hydrochloric acid, but decomposes on boiling, giving a green solution and a precipitate of silver chloride. It is slightly soluble in cold dilute nitric acid, but even on boiling is not entirely dissolved. Dilute sulphuric acid does not attack it as readily as dilute nitric acid, being only very slightly soluble in the cold, but much more soluble on boiling.

Zinc Chromicyanide, $Zn_3Cr_2(CN)_{12}$.—According to Berzelius[1] zinc salts give a white precipitate with potassium chromicyanide, bluish gray when dry.

Kaiser[2] states that the zinc precipitate is yellowish white in color, pulverulent, and easily soluble in ammonium and sodium hydroxides, but only incompletely decomposed by alkali carbonates. It is insoluble in dilute acids, but somewhat concentrated acids color the compound red, and the solution also.

Gmelin[3] says that the zinc compound is white, turning light bluish gray when dry.

Storer[4] says that chromicyanide of zinc is a precipitate.

Watts[5] states that a solution of potassium chromicyanide gives a white precipitate with zinc salts.

We prepared the salt, first, by adding a 4 per cent. solution of zinc sulphate to a 2 per cent. solution of potassium chromicyanide, and second, by adding a 4 per cent. solution of potassium chromicyanide to a 2 per cent. solution of zinc sulphate. In both cases, a yellowish white precipitate immediately formed, which, under the microscope, appeared to consist of very small crystals, apparently isometric. The precipitates were thoroughly washed and dried at 100°. When dried over sulphuric acid, at the ordinary temperature, the compound has a straw color.

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[1] Berzelius' "Lehrbuch," Vol. III, p. 1075 (1845).

[2] Ann. III Suppl., p. 169; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 302 (1864).

[3] Gmelin's "Handbook of Chemistry," Vol. VII, p. 425.

[4] Storer's "Dictionary of Solubilities," 1864.

[5] Watts' "Dictionary," Vol. II, p. 205 (1872).

About 0.5 gram of the substance was dissolved in sulphuric acid, and the chromium precipitated four times by ammonium hydroxide, dissolving the precipitate each time in a considerable excess of hydrochloric acid. From the results obtained it was found that the separation of chromium from zinc was not complete.

Another sample was analyzed as before, with the exception that the zinc was precipitated first as sulphide after taking out the chromium as before. The sulphide of zinc was dissolved in hydrochloric acid, and the zinc precipitated as before. The results again showed incomplete separation of chromium and zinc. Finally about 0.5 gram of the substance was dissolved in aqua regia, and the solution boiled down to low bulk several times in a casserole after the addition of hydrochloric acid. The solution was finally diluted with water to a volume of about 400 cc., and neutralized by ammonium hydroxide, and then made fairly acid with acetic acid, and a stream of hydrogen sulphide passed through the solution in the cold for about two hours.

The zinc sulphide was filtered, washed, and dissolved in hydrochloric acid, and the zinc determined as pyrophosphate. The chromium was determined as before. Potassium was determined as chlorplatinate, giving 0.35 per cent. of potassium, which was somewhat impure from a little organic matter from the alcohol.

The analyses gave: Zn, 29.42, 31.01; Cr, 15.68, 16.41. Calculated for $Zn_3Cr_2(CN)_{12}$: Zn, 32.01; Cr, 17.00. Ratio of Cr to Zn: I, 2:2.99; II, 2:3.01.

The formula of the compound is therefore $Zn_3Cr_2(CN)_{12}$.

Zinc chromicyanide is readily soluble in an excess of potassium cyanide, sodium hydroxide, and ammonium hydroxide. It is decomposed by sodium carbonate solution. Ammonium sulphide decomposes the compound, precipitating white zinc sulphide. Boiled with sodium peroxide and water it gives a clear yellow solution, which yields a yellow precipitate of lead chromate on the addition of lead acetate and acetic acid.

With concentrated hydrochloric acid it decomposes slowly, but very quickly on boiling, giving a red, then green solution. It is readily decomposed by boiling with concentrated nitric or sulphuric acid, giving a green solution in each case.

Aqua regia decomposes it quickly, giving a clear red solution, which becomes green.

Dilute hydrochloric acid in the cold easily dissolves the compound, yielding finally a green solution. Dilute sulphuric acid acts more slowly, while dilute nitric acid decomposes it very slowly. On boiling, any of the three readily yields a green solution. It is very slightly soluble in boiling acetic acid.

Lead Compounds.—Böckmann[1] states that potassium chromicyanide gives a white precipitate with basic lead acetate, but no precipitate with lead nitrate. Berzelius[2] says that lead salts give a white precipitate, which becomes blue on drying. Kaiser[3] states that the neutral lead salt is soluble in water. On evaporation, hydrocyanic acid is given off, the solution becomes green and a grayishwhite pulverulent substance separates. He says that it is easy to obtain a basic lead chromicyanide by adding to the yellow solution containing the neutral salt a mixture of lead acetate and ammonium hydroxide. Also that basic salts can be formed from hydrochromicyanic acid. He thinks that several of these basic salts exist, as on adding to the filtrates either lead acetate or ammonium hydroxide, he obtains repeatedly new compounds containing chromium. Also that the precipitates formed are sometimes easily soluble in an excess of lead solutions, or that the filtrates are precipitated by diluting with water. In other cases this did not happen. He analyzed one of the compounds, and from the results obtained concluded that it was a mixture of different basic salts. The compound was easily soluble in nitric acid and sodium hydroxide solution.

We found that tenth-normal solutions of lead nitrate and lead acetate, with a few drops of acetic acid, gave no precipitate with tenth-normal potassium chromicyanide solution, either when added in excess, or *vice versa.*

Soluble Chromicyanides.—Kaiser[3] states that mercuric chloride and stannous chloride solutions behave the same as lead. He states that aluminium, chromium, ferric iron or uranium, gives no precipitation with potassium chromicyanide in the cold, while, on heating, the potassium salt is decomposed. According to

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[1] Liebig's "Traité de Chimique Organique," Vol. I, p. 174.

[2] Berzelius' "Lehrbuch," Vol. III, pp. 1075-76 (1845); Gmelin's "Handbook of Chemistry," Vol. VII, p. 428.

[3] Ann. III Suppl., p. 170; "Handwörterbuch d. Chem. Fehling," Vol. II, p. 663; Jahresb. 17, 303 (1864).

Böckmann[1] the salts of ferric iron give no precipitate; also given by Watts.[2]

We found that tenth-normal solutions of the following reagents gave no precipitate with tenth-normal potassium chromicyanide, either when added in excess, or *vice versa.*

Aluminium sulphate, barium chloride, calcium chloride, bismuth nitrate (with enough nitric acid to prevent hydrolysis), ferric chloride, lithium chloride, magnesium sulphate, mercuric nitrate (with a few drops of nitric acid added to dissolve the salt), mercuric chloride, strontium chloride, sodium chloride, ammonium chloride, caesium chloride, rubidium chloride, chromium chloride, arsenic acid, cerous sulphate, antimony chloride (with enough hydrochloric acid to keep the antimony in solution), antimony chloride, with enough tartaric acid to keep the antimony in solution, erbium nitrate, beryllium nitrate, didymium nitrate, ammonium molybdate, lanthanum nitrate, platinum chloride (chlorplatinic acid), sodium chlorplatinate, sodium tungstate, ammonium vanadate, uranium nitrate, columbium potassium fluoride (K_2NbOF_5), tantalum potassium fluoride (a saturated solution only), arsenious acid (a saturated solution only), stannous chloride (with enough hydrochloric acid to keep the salt in solution), thorium nitrate, thallium sulphate, yttrium nitrate, zirconium nitrate (with a few drops of nitric acid to clear the solution).

A 5 per cent. solution of palladium chloride and a solution of auric chloride gave no precipitate when added in excess, or *vice versa,* to a tenth-normal solution of potassium chromicyanide.

From the foregoing results, we see that the insoluble chromicyanides, formed by the ordinary methods of precipitation, are all normal in composition, in this respect as well as regards their solubility, resembling the cobalticyanides more closely than the ferricyanides. The fact of their normal composition, and the intense red color of the ferrous compound, may lead to their use in volumetric analysis, but whether they are insoluble enough to give accurate results further investigation must decide.

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June 4, 1906.

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[1] Liebig's "Traité de Chimique Organique," Vol. I, p. 174.

[2] Watts' "Dictionary of Chemistry," Vol. II, p. 205 (1872).