54. *The Cause of the Variation of the Colour of Crystals of Commercial Sodium and Potassium Ferrocyanide [Cyanoferrate(II)].*

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The results of experiments on the action of light, heat, and air on solutions of the ferrocyanides [cyanoferrates(II)], acid, alkaline, and neutral, together with suggestions for the reactions taking place in the formation of pentacyanoaquoferrate-(II) and -(III) and ferricyanide [cyanoferrate(III)] are recorded. Methods for detecting and estimating small amounts of the aquo-salt and ferricyanide in ferrocyanide solutions are described. It is shown that the amber-coloured crystals sometimes found in commercial ferrocyanide are caused by the presence of traces of colloidal ferric hydroxide. Briggs's explanation that the amber colour is due to the presence of small quantities of pentacyanoaquoferrate(II), and Irving and Cherry's implied suggestion that it is caused by traces of colloidal Prussian-blue, are shown not to be correct for commercial potassium or sodium ferrocyanide.

The colour of ferrocyanide crystals sometimes varies from light yellow to amber. To account for this variation, Briggs (J., 1911, **99**, 1019, 1038) suggested that there were two stereoisomeric forms differing in shade. It was shown later by Piutti (*Ber.*, 1912, **45**, 1831) that the absorption spectra of the supposed isomerides were indistinguishable, and by Bennett (J., 1917, **111**, 490) that the two types were of crystallographic identity and therefore could not be isomerides. Stereoisomerides, however, have been found amongst the organic ferrocyanides (Hartley, J., 1913, **103**, 1196) and are theoretically possible with the metallic salts. A close examination of commercial ferrocyanides manufactured in different ways, and of laboratory-prepared samples, has failed to detect any variations in the crystals except from the presence of small amounts of impurities. Briggs (J., 1920, **117**, 1026) has attributed the amber colour of the crystals to the presence of a small proportion of pentacyanoaquoferrate(II)—a strongly coloured substance—formed in acid solutions. These salts are isomorphous with the ferrocyanide of the same base and crystallise with it.

Amber-coloured crystals can be prepared as described by Briggs, by acidifying a solution of the ferrocyanide saturated at 40°, and allowing it to cool out of contact with air; they contain small quantities of the aquo-salt, varying from 0·5 to 0·8% of the potassium and 0·3 to 0·5% of the sodium ferrocyanide.

Pentacyanoaquoferrate(II) only occurs in ferrocyanide crystals obtained from acid solutions, or neutral solutions that have been exposed to light for some time. The prussiates of commerce are never crystallised from acid solutions, the liquor being kept alkaline to restrain decomposition. Pentacyanoaquoferrate-(II) or -(III) cannot exist in hot alkaline solution, being completely converted into ferro- or ferri-cyanide. It is obvious, therefore, that Briggs's explanation is not the complete solution of the problem.

Many amber-coloured crystals have been examined, including those obtained from solutions that had undergone long boiling, or been left exposed to light in alkaline solution. These sometimes contained a minute amount of aquo-salt, but the majority were entirely free from that compound. From a study of these crystals and the solutions from which they were obtained, it was concluded that the amber colour was due to traces of colloidal ferric hydroxide formed by the action of light or heat on the alkaline solution.

Irving and Cherry (J., 1941, 25) suggest that the amber colour found in some crystals of Bunsen's salt, $(NH_4)_4Fe(CN)_6,2NH_4Cl$, including those prepared by Briggs's method, may be due to the presence of a trace of colloidal Prussian-blue. Although this explanation may be possible in some cases for ammonium ferrocyanide and its double salts, owing to the somewhat different behaviour of solutions of this salt, it does not apply to the salts of alkalis for reasons given below; it also fails for amber crystals of the ammonium salt obtained from acid solutions, or neutral solutions that have been exposed to light, these crystals invariably containing the aquo-salt. As commercial ferrocyanide crystals have all been obtained from hot alkaline solutions, they must be free from Prussian-blue also; in fact, if a trace of Prussian-blue is added to a ferrocyanide solution so as to give a green tinge, a short exposure to light will precipitate red-brown ferric hydroxide: the same reaction will take place on heating. A freshly prepared solution of potassium or sodium ferrocyanide is faintly alkaline to phenolphthalein, and if such a solution containing a drop of the indicator solution is neutralised with dilute acetic acid until the colour is just discharged, and exposed to light and air, the solution will be coloured pink in 2—3 minutes' exposure, and deep red in an hour or so. If again neutralised and re-exposed, it again becomes alkaline. This series of operations may be repeated until ferrous ferrocyanide is precipitated. If the original neutralised solution is kept in the dark, no coloration develops after several days. The reaction is probably expressed as follows:

$$(1)\quad K_4Fe(CN)_6 + 2H_2O \rightleftharpoons H^{\cdot} + OH' + K^{\cdot} + K_3Fe(CN)_5 + H_2O + CN' \rightleftharpoons HCN + KOH + K_3[Fe(CN)_5,H_2O]$$

$$(2)\quad 12K_3[Fe(CN)_5,H_2O] + 4KOH + O = 10K_4Fe(CN)_6 + Fe_2O_3 + 14H_2O$$

Baudisch (*Ber.*, 1929, **62**, 2706) found that pentacyanoaquoferrate(II) is produced when neutral solutions of ferrocyanide are exposed to light in the absence of air. In the presence of air the aquo-salt is oxidised to the violet aquo-salt, which reacts with ferrocyanide to give more complicated, pale yellow compounds. Baur (*Helv. Chim. Acta*, 1925, **8**, 403) obtained similar results, and concluded that the discoloration was due to the formation of colloidal ferric hydroxide.

Solutions of different ferrocyanides in different concentrations and acid, alkaline, or neutral, were exposed to the air and diffused daylight, and corresponding solutions exposed to the air in the dark. The solutions acidified with acetic acid and exposed to the light and air developed aquo-salt(II) and ferricyanide: after 6—7 weeks 70—75% of the ferrocyanide of a 10% solution was so converted. The amount of aquo-salt(II) increased with increasing amounts of acetic acid until sufficient was added to combine with one atom of the base of the ferrocyanide; further addition of acid had no accelerating effect, but increased the proportion of insoluble, green iron cyanogen compounds. In neutral solutions the same action takes place, much more slowly, and in alkaline solutions it is inhibited.

The rate of formation of the two salts in acid, neutral, or alkaline solution during 30 days' exposure to light and air is shown in the following results:

	Aquo-salt (II), %.	Ferricyanide, %.
Acidified with HOAc	31·09	32·00
With no addition	3·41	1·84
Alkaline with K_2CO_3	0·17	0·16

The above figures are calculated as the equivalent amount of ferrocyanide converted. The alkaline solution showed no change after 10 days, and only the slightest trace after 20 days.

In the acidified solution the rate of formation of these two salts was increased by exposing a larger surface of the solution to the air, or by blowing air through, which removed the hydrogen cyanide as it was formed, and oxidised the salt. In the dark, exposure to air caused the same reactions, but more slowly, those in the neutral solutions being negligible.

The formation of pentacyanoaquoferrate(II) in the acidified solution may be expressed as follows :

$$(3)\quad K_4Fe(CN)_6 + HOAc \rightleftharpoons KOAc + HK_3Fe(CN)_6 \rightleftharpoons K_3Fe(CN)_5 + H^{\cdot} + CN' + H_2O \rightleftharpoons K_3[Fe(CN)_5,H_2O] + HCN$$

When the warm, saturated, acidified solution is allowed to cool out of contact with air, as in Briggs's method, the aquo-salt(II) is found both in solution and in the crystals. The equivalent amount of free hydrogen cyanide may be estimated in the solution. No further change takes place on keeping during many weeks, and no ferricyanide is formed without exposure to the air. Ferro- and ferri-cyanides and pentacyanoaquoferrate-(II) and -(III), together with a small green precipitate of iron cyanogen compounds, were the only compounds found in these solutions.

When excess of potassium ferrocyanide solution is shaken with some violet aquo-salt, the latter is immediately reduced, and an equivalent quantity of ferrocyanide is oxidised to ferricyanide. In the absence of ferrocyanide, ferricyanide oxidises aquo-salt(II) to the violet aquo-salt(III). As judged from the colour of the solutions, it would appear that but little of the violet aquo-salt(III) existed in solution until the ferrocyanide content became small. When the solution is precipitated with lead acetate, the lead ferrocyanide carries down with it about 2—3% of its weight of the aquo-salt(II), any remaining aquo-salt(II) being converted into the violet-salt(III) by the ferricyanide if present. The reaction

$$(4)\qquad K_3Fe(CN)_6 + K_3[Fe(CN)_5,H_2O] \rightleftharpoons K_4Fe(CN)_6 + K_2[Fe(CN)_5,H_2O]$$

proceeds from left to right in the absence of ferrocyanide and in the reverse direction if it is present in excess. The pentacyanoaquoferrate(II) precipitated with the lead ferrocyanide may be completely recovered as the violet aquo-salt(III) by washing it with a solution of a ferricyanide containing lead acetate. If the ferricyanide in the original solution is in excess of the yellow aquo-salt(II), none of the latter will be found in the precipitated lead ferrocyanide.

An examination of the potassium and sodium ferrocyanide of current British and Continental makes has shown that they seldom contain more than a very slight trace of aquo-salt(II), the majority being entirely free from it. Traces of carbonylferrocyanide [pentacyanocarbonylferrate(II)] are very occasionally found in potassium ferrocyanide crystals obtained by extracting the cyanogen compounds from " spent oxide " or " cyanogen mud "—products obtained in the purification of coal gas—with lime.

Analysis of five different makes of commercial potassium ferrocyanide, both British and Continental, are given below :

	1.	2.	3.	4.	5.
Potassium carbonylferrocyanide, %	—	0·04	—	—	0·23
Potassium pentacyanoaquoferrate(II), %	—	—	0·03	—	—
Potassium chloride, %	0·05	0·04	0·05	0·02	0·19
Potassium sulphate, %	0·01	sl. tr.	v. sl. tr.	—	tr.
Potassium carbonate, %	0·05	0·01	0·02	0·007	0·14
Potassium formate, %	—	—	—	—	—
Potassium thiocyanate, %	0·005	—	—	v. sl. tr.	0·023
Potassium ferricyanide, %	—	—	v. sl. tr.	—	—

If the ferrocyanide solution is boiled with a little potassium cyanide and filtered and crystallised, very pale crystals are obtained as described by Briggs (*loc. cit.*); they are entirely free from aquo-salt(II), ferricyanide, or ferric hydroxide. In a similar manner, sodium ferrocyanide may be obtained in faint yellow, almost white, crystals. This reaction suggests that the normal colour of the crystals is partly due to occluded ferric hydroxide, and the variations in shade to differences in proportion.

The amber-coloured crystals are probably formed in the following manner. During the evaporation of the solution some decomposition always takes place, with formation of ferric hydroxide as described below. This hydroxide is first formed in colloidal solution and finally separates as a flocculent precipitate. When the hot solution is run into a crystalliser, the precipitate settles to the bottom or may be filtered off before crystallisation takes place, and crystals of the salt of normal colour separate on cooling. If the solution is left for some time, particularly in the presence of light and air, the cold solution darkens slightly owing to colloidal ferric hydroxide, as concluded by Baur (*loc. cit.*). The crystals partly dissolve and recrystallise owing to minor fluctuations of temperature and other causes, and after some days the larger crystals will be of an amber colour, particularly on the outer edges owing to occluded ferric hydroxide. If the solution is alkaline, these crystals will be free from aquo-salt(II) or ferricyanide. Amber-coloured crystals may be prepared by adding a dilute emulsion of Prussian-blue to a warm saturated solution of a ferrocyanide so long as it is decomposed on shaking, and allowing the filtered solution to crystallise.

A solution of ferrocyanide saturated with sulphur dioxide, exposed to light and air for several days, will be converted to the extent of 40—50% into pentacyanosulphitoferrate(II). This action takes place in the absence of light, but much more slowly. Similarly, exposure to diffused daylight of a ferrocyanide solution containing a little sodium nitrite produces nitroprusside, tests with ammonium sulphide being positive after ½ hour and strong after 3 hours. In the dark, the mixed solution does not respond to the test even after 24 hours. If the solution also contains aquo-salt(II), the test is positive in a short time in the light or the dark.

A cold solution of ferrocyanide, when made alkaline and shaken with some precipitated mercuric oxide and protected from the light, forms a little mercuric cyanide, but when the filtered solution is exposed to the light, ferric hydroxide is rapidly precipitated, the solution becoming cloudy in about 30 seconds.

Light also has a powerful effect on the neutral or alkaline solutions of the ferrocyanides. A solution of the potassium salt, made alkaline with potassium hydroxide and exposed to direct sunlight, first darkens and then soon becomes cloudy, precipitating ferric hydroxide. A neutral solution behaves in a similar manner but more slowly. No ferricyanide or aquo-salt(II) is formed in alkaline solution, or, if formed, it is immediately decomposed. Both salts are, however, formed in the neutral solution. No such action takes place in the absence of light.

A solution of 2% each of potassium ferro- and ferri-cyanide, made alkaline with potassium hydroxide, rapidly decomposed in sunlight, ferric hydroxide being precipitated with reduction of the ferricyanide. A portion of the same mixture kept in the dark was unaltered after several days.

Ferricyanide solutions are rapidly reduced in the cold when exposed to light (Vogel, *Ber.*, 1871, **4**, 96). When a dilute solution of potassium ferricyanide containing lead acetate or cerous sulphate is exposed to direct sunlight, a cloudiness due to the formation of the corresponding ferrocyanide is observed in 3—4 minutes; a heavy deposit separates later.

Hauser and Biesalski's suggestion (*Ber.*, 1912, **45**, 3516) that the supposed isomeric " β " ferricyanide of Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193,413) was due to occluded Prussian-blue in the crystals is possibly correct in some cases. Freshly prepared solutions of potassium ferricyanide are not alkaline to phenolphthalein, and do not become so on exposure to light or on heating. Nevertheless, Briggs's explanation that these darker crystals contain the violet aquo-salt(III) is in the majority of cases correct. Pentacyanoaquoferrate(III) will occur in the solution of the ferricyanide, not only after treatment by Briggs's method, but also on exposure of the neutral or acidified solution to the light, and by over oxidation in the preparation of the salt from ferrocyanide. The violet aquo-salt(III) may sometimes be found in the commercial salt, and crystals of the darker shade almost invariably contain this aquo-salt and not Prussian-blue.

Pentacyanocarbonylferrate(II) decomposes rapidly in dilute solutions when exposed to light, with precipitation of ferric hydroxide and conversion into normal ferrocyanide. Solutions of carbonylferrocyanides mixed with a little lead acetate or cerous chloride—the carbonyl salts of which are soluble—when exposed to light rapidly decompose with precipitation of the insoluble ferrocyanide and ferric hydroxide.

The violet ferric aquo-salt also fades and turns blue in the light, contrary to Lecocq's statement (*Bull. Soc. chim. Belg.*, 1911, **25**, 72). These reactions do not take place in the absence of light. A solution of pentacyanocarbonylferrate(II) acidified with acetic acid and kept in the dark, or more rapidly in the light, decomposes with replacement of the carbonyl by water to form the aquo-salt(II), together with ferrocyanide and a precipitate of Prussian-blue.

Cobalticyanide appears to be unaffected by light in either alkaline or neutral solution. In acid solution, a deeper yellow colour occurs, which is possibly due to the formation of some pentacyanoaquocobaltate(III).

Decomposition occurs when solutions of the ferrocyanides are boiled under atmospheric pressure, with loss of cyanogen and precipitation of ferric hydroxide. The extent of decomposition increases with dilution. This decomposition is inhibited by potassium hydroxide, carbonate, and cyanide. The solution of pure ferrocyanide after boiling usually contains some formate and carbonate, together with a little ferricyanide and a suspension of ferric hydroxide.

Dry crystals of ferrocyanide, protected from the air by a glass cover, are unchanged by light. Some dry crystals of the salt (2—3 lb.), removed from the top surface of a crystalliser and exposed to diffused daylight in a well-fitting, glass-covered case for 36 years, were entirely free from aquo-salt and ferricyanide or any other decomposition product. Dry samples of sodium, calcium, and magnesium ferrocyanide and of the sparingly soluble double salts of potassium and ammonium with calcium and barium ferrocyanide were similarly unchanged after 30 years in a corked bottle. Lithium ferrocyanide, however, changed owing to the difficulty of keeping the deliquescent crystals dry.

Experimental.

Analytical Methods.—Estimation of small quantities of aquo-salts in ferrocyanides. (1) To 10—20 ml. of the ferrocyanide solution, add a little dilute ferricyanide (if not already present), 0·25—0·5 g. of dicyanodiamide, and 5 ml. of a 5% solution of sodium hydroxide, and heat nearly to the boil. A red colour develops in the presence of pentacyanoaquoferrate(II). No colour is obtained if ammonia is substituted for the sodium hydroxide, and sodium carbonate is not so efficient. The colour may be matched against a standard ferrocyanide solution containing a known quantity of the aquo-salt. This test will detect 1 part in 30,000 parts.

(2) To 10 ml. of the solution to be tested, add 10 ml. of 20-vol. hydrogen peroxide, followed by 5 ml. of glacial acetic acid. In the presence of a trace of the aquo-salt, a brown colour develops in a few minutes owing to formation of the strongly coloured aquo-salt(III). With larger amounts of the aquo-salt the colour is purple. With very slight traces the mixture should be allowed to stand for 10—15 mins. screened from the light and air. The colour may be matched against a standard. The sensitivity is the same as in (1).

(3) To 10 ml. of the solution to be tested, add 10 ml. of a 5% solution of sodium carbonate and a few drops of a 10% solution of thiocarbamide, and let the mixture stand for a few minutes. If aquo-salt is present a reddish-violet colour develops, and is matched against a standard. The method detects 1 part in 20,000 parts. If ferricyanide is absent a few drops of a 1% solution should be added before the thiocarbamide. This method, however, is not recommended for estimation, as the colour fades rapidly. Sato (*Biochem. Z.*, 1909, **23**, 44) gave this reaction as a delicate test for thiocarbamide, and stated that the addition of thiocarbamide to a solution of potassium ferrocyanide acidified with acetic or hydrochloric acid gives a green colour changing to blue, and that if sodium carbonate be substituted for the acid a reddish-violet colour develops in a few minutes No such colorations occur with pure potassium ferrocyanide

solutions or even if they contain ferricyanide. The colorations are due to the presence of a trace of pentacyanoaquoferrate(II), and are only obtained with a ferrocyanide solution that has been exposed to light for some time or left acidified. The reaction is also given by a solution of pentacyanocarbonylferrate(II) or moist crystals that have been exposed to light. This is probably due to the replacement of carbonyl by water. The reaction is not given by the pure salt.

For the estimation of larger amounts of the aquo-salt(II), take 50 ml. of the solution, make it alkaline with sodium hydroxide, add a slight excess of hydrogen peroxide to decompose all ferricyanides, and boil the solution for 5 mins. All aquo-salt is decomposed by this method and converted into ferrocyanide with a quantitative precipitation of ferric hydroxide [equation (2)]. The latter is filtered off, washed, and estimated by any known method. The amount of ferric oxide obtained is multiplied by 24·075 to obtain the proportion of aquo-salt(II) in the solution taken, or by 31·65 for the equivalent of potassium ferrocyanide. The method is only moderately accurate. Pure potassium ferrocyanide, free from ferricyanide or aquo-salt, gives no precipitate of ferric hydroxide when boiled with the above reagents for 10 mins. if screened from the light.

Detection and estimation of small quantities of ferri- in ferro-cyanide solution. To 10 ml. of the neutral solution, add a few drops of pure 2 : 4-diaminophenol dissolved in glacial acetic acid. In the presence of a trace of ferricyanide a bright red colour is instantly formed. This may be matched against suitably prepared standards. This test will detect 1 part in 40,000 parts of solution.

Estimation of total oxidised salt. (1) To 10 ml. of the solution, add an excess of lead acetate and then potassium ferrocyanide until the supernatant liquor is a bright clear yellow, filter it, remove the excess lead with dilute sulphuric acid, and refilter it. The ferricyanide in the filtrate is estimated by known means. When the aquo-salt and ferricyanide are less than 3% of the ferrocyanide the addition of more ferrocyanide is unnecessary.

(2) To a measured quantity of the solution containing about 0·5 g. diluted to 500 ml., add 10 ml. of a saturated solution of zinc sulphate and a few drops of potassium iodide solution, and titrate the free iodine with 0·1 or 0·01N-sodium thiosulphate solution, using starch paste as indicator. There is no known means of separating pentacyanoaquoferrate(III) from ferricyanide.

The standard solution of the aquo-salt is prepared by dissolving a known quantity of pentacyanoaquoferrate(III) in a 10% solution of potassium ferrocyanide, the solution being kept protected from the light. The aquo-salt may be prepared by Cambi's method (*Gazzetta*, 1911, **41**, i, 157). The salt is then analysed, and a weighed portion dissolved in the 10% potassium ferrocyanide solution. For use as a standard, a measured portion is diluted with 10% solution of pure potassium ferrocyanide to the required volume.

Other Details.—The potassium ferrocyanide used in these experiments was a good commercial quality recrystallised from water twice, screened from the light, redissolved in warm water, and precipitated when cold by alcohol, dried, and kept in an amber bottle.

Effect of surface area. 100 Ml. of a 10% solution of the trihydrate were kept in (i) a cylinder and (ii) a dish of respective surface areas 15·02 and 60·1 sq. cm. for 7 days, and the content of ferricyanide was then (i) 0·220%, (ii) 0·952% : ratio of surface, 1 : 4; ratio of $K_3Fe(CN)_6$ formed, 1 : 4·21.

Effect of concentration of ferrocyanide solution on the formation of ferricyanide when exposed to air. The following data were obtained :

Concn., %.	$K_3Fe(CN)_6$, % :	after 7 days.	after 14 days.	after 21 days.
1		2·24 (0·0224)	5·6 (0·056)	10·0 (0·1)
5		0·614 (0·0307)	1·344 (0·0672)	2·0 (0·1008)
10		0·448 (0·0448)	0·728 (0·0728)	1·17 (0·117)

The figures in parentheses give the actual amount formed calculated as $K_4Fe(CN)_6,3H_2O$. 150 Ml. of 20% trihydrate solution kept in the dark for 14 days gave 0·03% of ferricyanide.

Effect of acid concentration on formation of the aquo-salt in the light. 100 Ml. of 10% ferrocyanide trihydrate gave the following percentages of aquo-salt with the stated amounts of acetic acid : 0·1 ml., 5·99; 0·5 ml., 17·65; 1·0 ml., 29·24; 2·0 ml., 42·67; 5·0 ml., 37·3; 10·0 ml., 37·2%.

100 Ml. of the same solution together with 1 ml. of acetic acid were exposed to light and gave the following data

Time, days	9	17	24	38
Aquo-salt, %	3·35	9·48	15·48	29·3
$K_3Fe(CN)_6$, %	9·52	14·84	22·8	37·3

Decomposition during boiling at atmospheric pressure. Various solutions were boiled, and the loss during successive periods of 10 hrs. determined :

Solution.	Loss, %, during :	1st 10 hrs.	2nd 10 hrs.	3rd 10 hrs.
1000 Ml. 10% $K_4Fe(CN)_6$, $3H_2O$		0·639	0·897	0·886
100 G. $K_4Fe(CN)_6,3H_2O$ in 200 ml. H_2O		0·095	0·12	0·101
25 G. $K_4Fe(CN)_6,3H_2O$ in 1200 ml. H_2O		2·319	2·17	2·318
1000 Ml. 10% $Na_4Fe(CN)_6,10H_2O$		0·482	—	—
100 G. $Na_4Fe(CN)_6,10H_2O$ in 200 ml. H_2O		0·052	—	—

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