CVII.—*The Isomerism of Ferrocyanides.*

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It was shown by Locke and Edwards (*Amer. Chem. J.*, 1899, **21**, 193, 413) that potassium ferricyanide exists in two forms, namely, the ordinary red or α -ferricyanide, and an olive-green salt or β -ferricyanide, which gives a reddish-violet solution, and was obtained by the action of acids on the ordinary modification. These authors thought that the two salts might possibly be stereoisomerides; but they drew no definite conclusion with regard to this relationship, since, according to Werner's theory of complex salts, ferricyanides should exist in only one form.

In a paper on the constitution of co-ordinated compounds, I described an alternative theory (*Trans.*, 1908, **93**, 1564), according to which potassium ferricyanide should exist in two stereoisomerides having the following formulæ:

1, 2, 3.

1, 2, 6.

If this theory is correct, ferrocyanides should also exist in two stereoisomerides, namely, 1, 2, 3, 4, and 1, 2, 6, 4, using Werner's notation for the different corners of the octahedron:

1, 2, 3, 4.

1, 2, 6, 4.

It was observed that large-scale preparations of potassium ferrocyanide, as seen at the Franco-British Exhibition in 1908, varied in colour from lemon-yellow to amber-yellow, and that sodium ferrocyanide was usually quite distinct in colour from potassium ferrocyanide, although the two compounds are alkali salts of the same acid.

It was thought that these differences in colour might be due to the existence of two classes of ferrocyanides, in agreement with the above formulæ, and the investigation described below was therefore undertaken.

The work has shown that ferrocyanides exist in two modifications which are related to each other in precisely the same way as the

α - and β -ferricyanides of Locke and Edwards, and which will therefore be called α - and β -ferrocyanides. The two forms differ in colour. They also exhibit slight differences in density and solubility, and are probably stereoisomerides.

The first part of the paper contains an account of the preparation of eight ferrocyanides in the two modifications. In the second part, the relationship of the two forms is discussed.

PART I.

Potassium Ferrocyanides, $K_4Fe(CN)_6 \cdot 3H_2O$.

Potassium ferrocyanide has been investigated more particularly by Bunsen (*Pogg. Ann.*, 1835, **36**, 404), Wyrouboff (*Ann. Chim. Phys.*, 1869, [iv], **16**, 293), and Dufet (*Compt. rend.*, 1895, **120**, 377); but none of these chemists appears to have given much attention to the colour of the salt. In Dammer's *Handbuch* (Vol. III, p. 368) it is described as "zitronen- bis orangegelben . . . Kryst. (Bunsen)." In Roscoe and Schorlemmer's treatise (1895 edition, Vol. II, Part II, p. 107) the crystals are said to be "of a lemon-yellow colour, and generally opaque. Small crystals, on the other hand, are amber-coloured and transparent." As shown below, this statement is scarcely correct, since the lemon-yellow and amber-yellow crystals represent the α - and β -forms respectively, independently of the size of the crystals.

Preparation of Potassium β -Ferrocyanide.—Locke and Edwards (*loc. cit.*) prepared potassium β -ferricyanide by the action of acids on the ordinary form. In order, therefore, to prepare a second modification of potassium ferrocyanide, the action of acids on Kahlbaum's potassium ferrocyanide was studied. Two difficulties were encountered, arising from the readiness with which acid solutions of ferrocyanides oxidise in the air, becoming blue, and from the ease with which a white decomposition product is precipitated on heating. It was therefore necessary to use a minimum quantity of acid, and to work in the absence of air and at as low a temperature as possible.

(1) A solution of 60 grams of potassium ferrocyanide in 130 c.c. of water at 50° was poured into a flask, and the air above the liquid was displaced by carbon dioxide. One c.c. of glacial acetic acid diluted with 3 or 4 c.c. of water was added from a dropping funnel, and the solution allowed to cool slowly, the flask being tightly corked. The crystals which separated after some time had a bright amber colour, as distinguished from the lemon-yellow of Kahlbaum's potassium ferrocyanide. These crystals contained a

trace of the white decomposition product, in consequence of which they became green on exposure to light. The preparation was therefore modified, a cold solution of potassium ferrocyanide being used as follows.

(2) Twenty-five grams of potassium ferrocyanide were dissolved in 100 c.c. of water, and the cold solution was treated with 2.5 c.c. of diluted acetic acid (1 vol. glacial acetic acid diluted to 10 vols. with water). The liquid was then poured into a flask, which it completely filled, no air space remaining, and the flask was tightly stoppered. After twenty-four hours the solution was filtered and mixed with alcohol, and the pure potassium β -ferrocyanide was obtained as a cream-coloured, crystalline precipitate. This was collected, washed with alcohol until free from traces of acid, and dried with ether.

Preparation of Potassium α -Ferrocyanide.—The white decomposition product obtained by the action of acids is probably potassium ferrous ferrocyanide or ferrous cyanide, resulting from a slight dissociation of the salt into simple cyanides (compare Berthelot, *Ann. Chim. Phys.*, 1900, [vii], 21, 204). It was thought that the addition of potassium cyanide as well as acid in the preparation of potassium β -ferrocyanide might prevent this decomposition by reducing the tendency to dissociate into simple cyanides. This proved to be the case, and no white precipitate separated, but the crystals obtained from a solution containing potassium cyanide as well as acid were lemon-yellow, and paler in colour than Kahlbaum's salt. A clue was thus obtained to the preparation of potassium α -ferrocyanide. Twenty-five grams of potassium ferrocyanide (Kahlbaum) and 0.25 gram of potassium cyanide were dissolved in 100 c.c. of water, and the solution was allowed to remain for a day. Alcohol was then added, and potassium α -ferrocyanide was obtained as a pure white, crystalline precipitate, which was collected, washed well with alcohol, and dried with ether.

Analysis.—Eight preparations were analysed: (1) was Kahlbaum's salt (chiefly α -ferrocyanide), recrystallised once from water; (2) was a slightly paler specimen (α -ferrocyanide), obtained by recrystallising Kahlbaum's salt from a solution containing potassium hydroxide (see p. 1025); (3) was potassium α -ferrocyanide, prepared from a solution containing potassium cyanide; (4), (5), (6), (7), (8) were potassium β -ferrocyanide, obtained from Kahlbaum's salt by the action of acetic (4 and 5), hydrochloric, sulphuric, and nitric acids respectively, in the manner already described.

Nitrogen was determined by decomposing the salt with concentrated sulphuric acid, and estimating the ammonia produced in the usual way.

Iron was determined by titration with *N*/10-permanganate, and water by dehydration in the steam-oven.

No.	(1).	(2).	(3).	(4).	(5).	(6).	(7).	(8).	Required for $K_4Fe(CN)_6 \cdot 3H_2O$.
N ...	19.96	19.98	20.2	19.86	19.87	—	—	—	19.90
Fe ...	13.29	13.27	13.29	13.22	13.25	13.28	13.24	13.28	13.22
H ₂ O	12.73	12.66	12.66	12.98	12.82	—	—	—	12.80

It is evident from these results that the deeper colour of the β -modification is not caused by the presence of an impurity which can be detected by quantitative analysis. It might, however, be due to a trace of very highly coloured impurity, too small in amount to affect the analysis. This possibility is discussed and disproved below (p. 1033).

Crystalline Form.—No crystallographic examination has been made. As the salts crystallise together in all proportions, and are generally so very similar in properties, marked crystallographic differences are not to be expected. There is, however, a distinct difference in the appearance of the crystals; possibly a difference in habit. Potassium ferrocyanide separates from solution in thin plates of various shapes. The most usual are shown diagrammatically in Fig. 1.

When a solution of potassium β -ferrocyanide is slowly evaporated over sulphuric acid, the square plates shown in *a* are generally produced, the four corners of which are clearly defined. From a solution of α -ferrocyanide the plates have the shape given in *b*. With a mixture of the two, the shorter edges of the irregular octagon are not so strongly marked, the appearance approaching more to *a*. The six-sided plates marked *c* are obtained from solutions of each form, but usually from the α -ferrocyanide.

Fig. 2 shows crystals of the β -ferrocyanide obtained by slow evaporation over sulphuric acid. Fig. 3, for which I am indebted to Mr. Howard Priestman, is a photo-micrograph of crystals obtained by spontaneous evaporation of a solution of the α -ferrocyanide on a microscope slide. The crystals are mostly the six-sided plates marked *c* in Fig. 1.

A remarkable difference in the capillary properties of the crystals of the two ferrocyanides was observed. When a concentrated

FIG. 2.

Potassium β -ferrocyanide.

Crystals obtained by slow evaporation of solution over H_2SO_4 .
Half natural size.

FIG. 3.

Potassium α -ferrocyanide.

Photo-micrograph (H. Priestman).

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solution of potassium β -ferrocyanide was allowed to remain in a basin placed in a desiccator over sulphuric acid, in a few days the desiccator was filled with a moss-like, efflorescent growth of crystals. This was caused by the mother liquor creeping over the surface of the crystals as they were deposited at the edge of the liquid. The crystallisation then proceeded over the interior and exterior of the basin, and on the walls of the desiccator. Potassium α -ferrocyanide did not behave in this way. A similar difference in the capillary properties of the crystals of potassium α - and β -ferrocyanides was recorded by Locke and Edwards (*loc. cit.*, p. 198).

Colour.—Potassium α -ferrocyanide is lemon-yellow when the crystals are large, and pure white when the crystals are very small. Potassium β -ferrocyanide is orange-coloured when the crystals are large and transparent, and amber-coloured when seen in bulk. It is cream-coloured when the crystals are very small. The difference in colour persists in solution, the β -ferrocyanide giving a more intensely coloured solution than the α -ferrocyanide. When one modification is transformed into the other in solution, a corresponding change in colour is observed.

Density.—The densities were determined in carbon tetrachloride at 20°. The specimens were obtained by precipitation of a cold aqueous solution with alcohol, in order to ensure homogeneity of the trihydrate (compare Müller and Diefenthäler, *Zeitsch. anorg. Chem.*, 1910, **67**, 418).

No.	1.	2.	3.	4.	5.	6
D 20°/4°	1·882	1·883	1·882	1·888	1·889	1·890

1, 2, and 3 were potassium β -ferrocyanide, obtained as described in preparation (2) above (p. 1021), the acidified solution having been allowed to remain for one, two, and three days respectively before precipitation with alcohol. Number 4 was Kahlbaum's ferrocyanide dissolved in water, and precipitated by alcohol. 5 and 6 were both α -ferrocyanide obtained by the method given above, the solution containing potassium cyanide having been allowed to remain for one day and four days respectively before precipitation with alcohol.

The difference in density is analogous to that observed by Levy for the isomeric barium platinocyanides (*Trans.*, 1908, **93**, 1446). It is evident from Levy's work that the green platinocyanides correspond with the α -ferrocyanides, and the yellow platinocyanides with the β -ferrocyanides.

Solubility.—Three preparations of each form were investigated. The determinations were made at 20°, a weighed quantity of the saturated solution being titrated with *N*/10-permanganate. The

results are expressed as grams of potassium ferrocyanide trihydrate in 100 grams of the saturated solution at 20°:

α .	α .	α .	β .	β .	β .
25.0	25.0	24.9	24.5	24.8	24.6

According to these results, potassium β -ferrocyanide is rather less soluble than potassium α -ferrocyanide at 20°; but the difference is very small, and a much more extensive series of observations would be required to determine this difference accurately. Locke and Edwards state that potassium β -ferricyanide is more soluble than potassium α -ferricyanide, but they do not give any data.

Precipitation Reactions.—The precipitation reactions of the α - and β -ferrocyanides are not so distinctive as those of the α - and β -ferricyanides described by Locke and Edwards. The insoluble ferrocyanides may be divided into two classes according to their colour. The first class includes those in which the yellow colour of the ferrocyanide radicle is present, more or less modified by the metal with which it is combined. The ferrocyanides of lead, zinc, cadmium, nickel, and cobalt are examples. The α -ferrocyanides of this first class are different in colour from the β -ferrocyanides. The second class consists of those ferrocyanides which have an intense and characteristic colour, such as is not usually associated with either the acid or the basic part of the molecule, including the dark blue ferric ferrocyanide, the deep brown ferrocyanides of copper and uranyl, and the bright yellow thallic ferrocyanide. There is no perceptible difference in colour between the α - and β -ferrocyanides of the second class.

With solutions of lead, zinc, and cadmium salts, potassium α -ferrocyanide gives pure white precipitates, and potassium β -ferrocyanide gives yellowish-white precipitates. A more striking difference is observed when the α - and β -ferrocyanides of potassium are added to hot concentrated solutions of barium chloride. A pure white, crystalline precipitate is obtained with the α -ferrocyanide, and a straw-coloured precipitate with the β -ferrocyanide (see $K_2BaFe(CN)_6 \cdot 3H_2O$ below).

Transformation of the α - and β -Ferrocyanides.

When potassium α -ferrocyanide is allowed to remain in aqueous solution for some time it is slowly converted into the β -modification. A similar change is caused by 1 per cent. of acetic acid in twenty-four hours. The effect appears to be due to the hydrogen ions, since other acids (hydrochloric, sulphuric, and nitric) behave in the same way.

The reverse transformation is brought about by cyanides, alkalis, and ammonia, cyanides having the strongest action.

It is probable that in solution the two forms attain a state of equilibrium:

and that acids accelerate the reaction towards the right, whereas cyanides, alkalis, and ammonia increase the reaction towards the left. These transformations are precisely analogous to those observed by Levy with the green and yellow platinocyanides (*loc. cit.*). Locke and Edwards (*loc. cit.*) attributed the change from potassium α -ferricyanide to potassium β -ferricyanide in the presence of acids to the effect of the hydrogen ions. They do not appear to have studied the conditions of the reverse transformation, except for the observation that the β -ferricyanides readily change into the α -salts, especially on heating. I found, however, that potassium β -ferricyanide prepared according to their method was rapidly converted into α -ferricyanide when its solution was treated with a little potassium cyanide, potassium hydroxide, or ammonia. The effect of these reagents was beautifully seen in the colour change from the reddish-violet β -ferricyanide to the bright yellow α -ferricyanide, as well as in the precipitation reactions of the solution, before and after treatment.

In addition to the potassium salt, the following seven ferrocyanides have been obtained in the two modifications, which are related to each other in the same way as the potassium α - and β -ferrocyanides. The two forms when soluble in water give differently coloured solutions. These undergo the same transformations and changes in colour when treated with acids and cyanides respectively, as were found with the solutions of the potassium salts. It should be observed that in the salts of sodium, potassium, ammonium, and caesium the difference in colour of the two modifications, and also the colour change on transformation in solution, become more strongly marked with increase in the atomic volume of the positive atoms, being least with the sodium salts, and greatest with the caesium compounds.

Sodium Ferrocyanides, $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$.

Pebal (*Annalen*, 1886, **233**, 165) describes the salt as crystallising in large, transparent crystals, of the colour of sulphur crystallised from carbon disulphide. Bunsen (*Pogg. Ann.*, 1835, **36**, 413) refers to the colour as "hell weingelb."

Sodium α -Ferrocyanide.—The preparation was made from 20 grams of Kahlbaum's sodium ferrocyanide and 0.2 gram of sodium cyanide in 100 c.c. of water, the procedure being the same

as with potassium α -ferrocyanide. A pure white, crystalline powder was obtained, which was collected, and dried with alcohol and ether. When recrystallised from warm water it gave large, pale yellow crystals.

Sodium β -Ferrocyanide was prepared by the action of 2 c.c. of dilute acetic acid (1 vol. of glacial acid made up to 10 vols. with water) on a cold solution of 20 grams of Kahlbaum's sodium ferrocyanide in 100 c.c. of water, in the same way as described for potassium β -ferrocyanide (preparation (2) above, p. 1021).

The sodium β -ferrocyanide was obtained as a yellowish-white powder, which on recrystallisation gave large, bright yellow crystals.

Analysis:

	Required for $\text{Na}_4\text{Fe}(\text{CN})_6 \cdot 10\text{H}_2\text{O}$.	Found, α .	Found, β .
Fe	11.54	11.62	11.59
N	17.36	17.01	17.37
H_2O	37.22	36.84	36.85

Ammonium Ferrocyanides, $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.

The ammonium ferrocyanide was prepared by neutralising hydrogen ferrocyanide with ammonia, and evaporating the filtered solution in a vacuum over potassium hydroxide. The salt was obtained in very thin, greenish-yellow plates.

Ammonium α -Ferrocyanide:—Five and a-half grams of the preparation and 0.05 gram of sodium cyanide were dissolved in 5 c.c. of water. After twenty-four hours the liquid was decanted from a small quantity of blue precipitate, and poured into a large volume of alcohol, when the ammonium α -ferrocyanide was obtained in yellowish-white crystals. Bunsen's preparation (*Pogg. Ann.*, 1835, **36**, 404) was evidently α -ferrocyanide, the colour being "weiss, ins Gelbliche spielend."

Ammonium β -Ferrocyanide:—This salt was prepared from 5.5 grams of the ammonium ferrocyanide, 5 c.c. of water, and 0.5 c.c. of dilute acetic acid (1 vol. of glacial acid diluted to 10 vols. with water). The mixture was allowed to remain for twenty-four hours in a small, tightly-stoppered cylinder, and was then precipitated by pouring into a large volume of alcohol. The ammonium β -ferrocyanide separated as a mass of bright amber-coloured crystals, which readily became green on exposure to light. Analysis:

	Required for $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.	Found, α .	Found, β .
H_2O	16.0	16.8	16.0
N	41.4	40.0	40.3

The low percentage of nitrogen was due to the presence of a

small quantity of potassium, probably derived from the hydrogen ferrocyanide used in the preparation of the salts.

Double Salts of Ammonium Ferrocyanide and Ammonium Chloride,
 $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 2\text{NH}_4\text{Cl}.$

The double salt was described by Bunsen (*loc. cit.*) as

Etard and Bémont (*Compt. rend.*, 1885, **100**, 108) give the formula $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 2\text{NH}_4\text{Cl}$, which is confirmed by the present experiments.

The preparations were made from Kahlbaum's ammonium ferrocyanide. This also contained a little potassium, the effect of which is seen in the analyses.

α-Salt:—Fifteen grams of ammonium ferrocyanide were dissolved in 15 c.c. of water, and 0.15 gram of sodium cyanide was added to the solution, which was allowed to remain twenty-four hours. It was then mixed with a solution of 7.5 grams of ammonium chloride in 12 c.c. of warm water. The double salt separated on cooling as a yellowish-white, crystalline powder.

β-Salt:—Fifteen grams of ammonium ferrocyanide in 13 c.c. of water were mixed with 1.5 c.c. of diluted acetic acid (1 vol. of glacial acid in 10 vols.). The solution was placed for twenty-four hours in a stoppered cylinder, which it filled completely, and was then mixed with a solution of 7.5 grams of ammonium chloride in 12 c.c. of warm water. The *β*-salt separated as a deep amber-coloured, crystalline powder. Analysis:

	Required for $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 2\text{NH}_4\text{Cl}$	Found, <i>α.</i>	Found, <i>β.</i>
N.....	42.9	41.8, 41.8	42.3
Fe	14.27	14.02	14.05

These salts show the difference in colour of the *α*- and *β*-ferrocyanides to the greatest extent of any which have been prepared. When the mother liquors from the above-mentioned preparations were evaporated over sulphuric acid in a vacuum, very large, transparent crystals were obtained. The crystals of the *α*-double salt were pale orange, and the crystals of the *β*-double salt were brown. The *β*-double salt resembled ammonium *β*-ferrocyanide in the ease with which it became green on exposure to light. The *α*-compounds also became green, but more slowly.

Cæsium Ferrocyanides.

Cæsium hydroxide was neutralised with hydrogen ferrocyanide, and the filtered solution was concentrated on the water-bath and precipitated with alcohol.

The α - and β -caesium ferrocyanides were obtained from this preparation by the method described above for the potassium salts (p. 1020).

When dehydrated in the steam-oven, the α -salt lost 12.0 per cent. of water, and the β -salt 12.2 per cent. $2\text{Cs}_4\text{Fe}(\text{CN})_6, 11\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=11.8$, and $\text{Cs}_4\text{Fe}(\text{CN})_6, 6\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=12.7$ per cent. Nitrogen was determined in the dehydrated salts.

	Required for $\text{Cs}_4\text{Fe}(\text{CN})_6$.	Found, α .	Found, β .
N	11.3	11.4	11.3

The difference in colour of equivalent solutions of the caesium compounds, and the colour change when one modification is transformed into the other, are very marked, and more distinctive than the differences observed with the sodium and potassium compounds.

Potassium Barium Ferrocyanides, $\text{K}_2\text{BaFe}(\text{CN})_6, 3\text{H}_2\text{O}$.

Bunsen described the salt $\text{K}_2\text{BaFe}(\text{CN})_6, 3\text{H}_2\text{O}$, but did not refer to the colour (*Pogg. Ann.*, 1835, **36**, 404). Wyruboff gave the formula with $5\text{H}_2\text{O}$, also without reference to the colour (*Ann. Chim. Phys.*, 1870, [iv], **21**, 279). The salts obtained in the present investigation have Bunsen's formula.

The α -salt was prepared by mixing boiling solutions of 3 grams of crystallised barium chloride in 6 c.c. of water, and 6 grams of potassium α -ferrocyanide in 7.5 c.c. of water. The salt separated on cooling as a pure white, crystalline deposit, leaving a pale yellow mother liquor.

The β -ferrocyanide was prepared in the same way from potassium β -ferrocyanide. It was obtained in straw-coloured crystals, which left a bright yellow mother liquor.

	Required for $\text{K}_2\text{BaFe}(\text{CN})_6, 3\text{H}_2\text{O}$.	Found, α .	Found, β .
N.....	17.5	17.6	17.8
Ba	28.53	28.68	28.53

Potassium Magnesium Ferrocyanides, $2\text{K}_2\text{MgFe}(\text{CN})_6, 7\text{H}_2\text{O}$.

These salts were prepared by mixing boiling solutions of 6 grams of the respective potassium ferrocyanides in 100 c.c. of water, and 3 grams of magnesium chloride hexahydrate in 100 c.c. of water. The α -ferrocyanide was pure white, and the β -ferrocyanide cream-coloured.

	Required for $2\text{K}_2\text{MgFe}(\text{CN})_6, 7\text{H}_2\text{O}$.	Found, α .	Found, β .
N.....	22.3	22.5, 22.4	22.4
H_2O	16.7	16.5	—

Robinson obtained the anhydrous compound $K_2MgFe(CN)_6$ by mixing cold concentrated solutions of potassium ferrocyanide and magnesium chloride (Trans., 1909, 95, 1353).

l-Menthylammonium Ferrocyanides.

For reasons given below (p. 1033), it was thought desirable to prepare the ferrocyanide of an optically active base, and to determine the specific rotation of the two modifications. For this purpose Professor J. B. Cohen suggested the study of *l*-menthylammonium ferrocyanide. I am also very much indebted to Professor Cohen for a quantity of pure *l*-menthylammonium chloride, with which the preparations were made, and for the use of the polarimeter in his laboratory in the Leeds University. A number of methods were attempted for the preparation of *l*-menthylammonium ferrocyanide, two of which may be described:

(1) It was proposed to obtain the salt by the two precipitation reactions:

A calculated amount of silver sulphate was boiled with barium silicofluoride and water, in order to prepare a solution of silver silicofluoride. In this process partial decomposition took place, a mixture of silver silicofluoride and silver fluoride being obtained. The solution was precipitated in the cold with *l*-menthylammonium chloride, and the silver chloride was removed by filtration. The filtrate was treated in the cold with an excess of potassium ferrocyanide and calcium ferrocyanide to precipitate silicofluoride and fluoride respectively. The resulting solution of the ferrocyanides of potassium, calcium, and *l*-menthylammonium was evaporated on the water-bath at 25°. The *l*-menthylammonium ferrocyanide separated as an oil, but the evaporation was continued until a dry solid mass remained. This was powdered, and extracted with absolute alcohol. The alcoholic solution was concentrated by evaporation at 25°, and then poured into a large volume of ether. A bright yellow, crystalline precipitate of *l*-menthylammonium β -ferrocyanide was obtained.

(2) The preparation was made according to the equations:

The method of preparation was similar to that already described, but the solid residue of almost pure *l*-menthylammonium ferro-

cyanide was extracted with absolute alcohol in two parts. The first extraction, when precipitated with ether, gave what appeared to be a mixture of the α - and β -ferrocyanides. The residue remaining after this extraction was dissolved in absolute alcohol, and the solution was evaporated over sulphuric acid in a vacuum. Long, pale greenish-yellow needles of *l*-menthylammonium α -ferrocyanide were thus obtained. These contained a molecule of alcohol of crystallisation, which was given off at 60°. The β -ferrocyanide already described did not contain alcohol. Analysis:

		Found.	Required for (C ₁₀ H ₁₉ NH ₃) ₄ Fe(CN) ₆ .C ₂ H ₅ OH.
(1) α -Salt:	N	15.78	15.88
	EtOH.....	5.39	5.22
		Found.	Required for (C ₁₀ H ₁₉ NH ₃) ₄ Fe(CN) ₆ .
(2) β -Salt:	N	16.95	16.75

The two modifications were very different in appearance and in properties. Their solutions in alcohol or in water were different in colour, dilute solutions of the α -form being almost colourless, whereas equivalent solutions of the β -salt were bright yellow. The colour of solutions of the α -salt was intensified by the addition of a trace of acid. Similarly, solution of the β -modification became paler in colour when treated with cyanides. The α -form could not be recrystallised from warm water, as solutions of the alcoholate and also of the dealcoholated salt deposited an uncrystallisable oil on cooling. The β -modification, on the contrary, separated from aqueous solution in bright yellow needles, or, if the solution was slowly evaporated over sulphuric acid, in long, transparent, deep amber-coloured prisms. Both salts decomposed without melting when heated.

The specific rotations were determined at 17° in absolute alcoholic solution, in order to avoid the effect of ionisation. Owing to the colour of the salts, the observations were rather difficult, and it was not possible to work with a solution of higher concentration than 1 per cent. when using a 2-dcm. tube.

	Vol. of solution.	Weight of salt.	α .	$[\alpha]_D^{17}$.
(1) α -Salt	50 c.c.	0.540	-0.87°	-42.4°
(2) β -Salt	50 „	0.500	0.57	28.5

Assuming these observations to be approximately correct, the addition of a trace of acid to a solution of the α -salt should bring about a fall in the rotation, resulting from the transformation of the α -form into the β -modification. This was actually observed.

The acid was prepared by diluting 0.4 c.c. glacial acetic acid to 10 c.c. with absolute alcohol; 0.1 c.c. of this solution was added

to 25 c.c. of the solution of the α -salt in experiments 3 and 4. The rotations were determined in the freshly prepared solutions, and also after twenty-four hours, a 2-dcm. tube being used.

	Vol. of solution.	Weight of salt.	α .	$[\alpha]_D^{17}$.
(3) α -Salt	50 c.c.	0.501 gram.	-0.81°	-42.6°
„ after 24 hours	50 „	0.501 „	0.65	34.2
(4) α -Salt	25 „	0.261 „	0.81	40.9
„ after 24 hours	25 „	0.261 „	0.63	31.8

It is therefore evident that the conversion of one modification into the other is accompanied by a change in specific rotation, as well as a change in colour.

PART II.

Relationship of the α - and β -Ferrocyanides.

The difference in colour of two salts of the formula

may be due to any of the following causes:

(1) Dimorphism. (Difference in the arrangement of the molecules in the crystal.) (2) Polymerism. (Difference in the state of aggregation of the molecules in the two modifications.) (3) Hydrate isomerism. (Difference in the method of attachment of the three molecules of water of crystallisation in the two forms.) (4) The presence of a coloured impurity in the β -modification. (5) Structural isomerism of the molecule $K_4Fe(CN)_6$. (Cyanide and isocyanide isomerism is the only possibility of this kind.) (6) Stereoisomerism of the molecule $K_4Fe(CN)_6$, as suggested at the commencement of the paper.

These various possibilities will be discussed separately:

Dimorphism:—If the α - and β -ferrocyanides were dimorphous, then the difference in properties should disappear when the crystal structure is destroyed by solution or by dehydration. It has already been shown, however, that the difference in properties persists in solution. It was also found that the two potassium ferrocyanides when dehydrated over sulphuric acid were still different in colour, and when the dehydrated salts were recrystallised from warm water, the α - and β -ferrocyanides were regenerated unchanged. The salts, therefore, are not dimorphous.

Polymerism:—Since the difference in properties persists in solution, freezing-point determinations should give a difference in molecular weight if one modification were a polymeride of the other. A series of molecular-weight determinations was made with the potassium salts. As shown in Fig. 4, when the results are plotted with molecular weights as abscissæ and concentrations as ordinates,

only one curve is obtained. There is, therefore, no difference in the state of aggregation of the α - and β -ferrocyanides.

α -Ferrocyanide.

<i>w.</i>	<i>W.</i>	$\Delta T.$	M.W.	Grams $K_4Fe(CN)_6$ in 100 grams of solution.
0.487	11.76	0.62	126	4.0
0.775	11.89	0.95	130	6.2
0.644	5.37	1.52	148	10.7
1.747	13.55	1.58	153	11.4
0.169	13.32	0.24	100	1.3

β -Ferrocyanide.

0.255	11.20	0.38	113	2.2
0.659	11.26	0.83	133	5.6
1.165	11.33	1.35	143	9.3
1.744	13.74	1.54	155	11.3

FIG. 4.

O = α -Ferrocyanide, X = β -Ferrocyanide.

Hydrate Isomerism:—The difference is evidently not the result of hydrate isomerism, since ferrocyanides have been described above with various amounts of water of crystallisation (3, 6, and 10

molecules), and even without water of crystallisation (the *l*-menthylammonium compounds), but still capable of existing in the two modifications. Again, the difference does not disappear on dehydration of the two potassium salts, as it would if the salts were hydrate isomerides.

Impurity.—It was shown by the analyses of the potassium salts (p. 1022) that no appreciable amount of impurity was present in the β -modification. The deeper colour of the β -ferrocyanides might still be due, however, to a trace of very highly coloured impurity, which could not be detected by analysis. If this were the case, then the α - and β -modifications of the ferrocyanide of an optically active base should have the same specific rotation, whereas if the difference in the α - and β -ferrocyanides were due to structural isomerism or stereoisomerism, a difference in specific rotation would be expected. For this reason the *l*-menthylammonium salts were investigated, as already described. They were found to differ greatly in specific rotation, and the transformation of the α -ferrocyanide into the β -salt was accompanied by a corresponding change in rotation. It therefore follows that in the *l*-menthylammonium ferrocyanides the *l*-menthylammonium radicles are either combined with different groups in the two salts (that is to say, the salts are cyanide and isocyanide respectively), or the *l*-menthylammonium groups are situated in different positions in the two modifications, that is, the α - and β -ferrocyanides are stereoisomeric.

Cyanide and isoCyanide Isomerism.—If the salts were cyanide and isocyanide, they should display considerable differences in chemical and physical properties. The chemical and physical properties are very similar, however, as was shown by the detailed investigation of the two potassium salts already described.

Stereoisomerism therefore appears to be the most probable explanation of the difference of the α - and β -ferrocyanides, and accounts satisfactorily for the phenomena which have been observed. Two salts of the formula suggested in the previous paper (Trans., 1908, **93**, 1564):

should exist in two stereoisomeric forms:

1, 2, 3, 4.

1, 2, 6, 4.

It is evident that in solution these forms would give stereoisomeric anions:

which agrees with the observation that the difference in properties persists in solution.

Direct evidence in favour of stereoisomerism is furnished by:

(1) The ease with which one modification can be transformed into the other, and by the opposite action of acids and bases in effecting this transformation, which is analogous to their influence on the conversion of the *syn*- and *anti*-aldoximes (Hantzsch, *Grundriss der Stereochemie*, 2nd ed., p. 150).

(2) The increasing difference of the α - and β -ferrocyanides with increase in the atomic volume of the positive atoms. It is evident that the effect of transferring an atom from position (3) to position (6) and vice versa will be all the greater the greater the volume occupied by that atom.

(3) The difference in the α - and β -ferrocyanides is not so great as that between the α - and β -ferricyanides of Locke and Edwards. A study of the formulæ shows that the effect of moving one potassium atom out of three from position (3) to position (6) in the ferricyanides will be greater than that of the corresponding change in position of one potassium atom out of four in the ferrocyanides.

An absolute proof that the salts are stereoisomeric, and not cyanide and isocyanide, can only be obtained by preparing in two modifications other salts which do not contain cyanogen groups, but which are otherwise similarly constituted to the ferrocyanides. I intend to continue the investigation in this direction. Attention may be directed to the fact that many platinichlorides are said to be dimorphous (Schryver, *Proc.*, 1891, **7**, 39; Trobridge, *J. Soc. Chem. Ind.*, 1909, **28**, 230). It is not impossible that some of these instances may be really due to isomerism.

In conclusion, it may be observed that the platinocyanides, such as barium platinocyanide:

should exist in two stereoisomeric forms if Werner's "square" configuration for plato-compounds is adopted. The formulæ would be:

The yellow and green platinocyanides of Levy (*loc. cit.*) may be explained in this way.

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