XCV.—*The Action of Light on Potassium Ferrocyanide.*

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ALTHOUGH the decomposition of potassium ferrocyanide by light has long been known, no close investigation of the reactions involved appears to have been made. The experiments described in this paper are a continuation of those mentioned by Prof. F. Haber (*Zeit. Elektrochem.*, 1905, 10, 847) in his note to the Bunsen Gesellschaft in 1905.

Berthelot (*Ann. Chim. Phys.*, 1900, [vii], 21, 204) noticed that ferrous sulphide is precipitated from a solution containing potassium ferrocyanide and an alkali sulphide. He makes no mention of the action of light, but explains the reaction by supposing that potassium ferrocyanide tends to decompose slowly into potassium cyanide and ferrous cyanide; the latter, reacting with the alkali sulphide present, gives alkali cyanide and ferrous sulphide. He says, further, that the presence of the alkali cyanide diminishes the dissociation of the ferrocyanide and a state of equilibrium is soon reached, so that the amount of sulphide precipitated is very small.

This cannot be the correct explanation, since ferrous sulphide dissolves quantitatively in potassium cyanide, forming potassium ferrocyanide.

Matuschek (*Chem. Zeit.*, 1901, 25, 565) remarked that potassium ferrocyanide precipitates ferric hydroxide on exposure to sunlight and that potassium cyanide is afterwards present in the solution. He did not study the reaction further.

Haber has proposed the view that potassium ferrocyanide not only dissociates in the usual way, thus :

but that on exposing the solution to light the complex ion, $\text{Fe}(\text{CN})_6'''$, dissociates to some extent into iron-ions and cyan-ions :

In the absence of light, the latter dissociation proceeds from right to left. The fundamental action thus appears to be reversible and photochemical.

The iron-ions set free in this dissociation are precipitated by an alkali sulphide or by oxygen and water as ferrous sulphide or ferric hydroxide.

The experiments were made with alkaline solutions of potassium ferrocyanide. As will be seen later, in neutral or acid solutions interference due to the formation of ferricyanide may be expected.

The energy of the reaction given by the equation

is obtained by the use of van't Hoff's expression :

$$A = RT \log_e K - RT \log_e \frac{C_{\text{Fe}(\text{CN})_6}^4 \cdot C_{\text{HO}}}{C_{\text{Fe}(\text{CN})_6}^4 \cdot C_{\text{O}_2} \cdot C_{\text{H}_2\text{O}}^2}.$$

Here A may be regarded as a measure of the "tendency" of the reaction to take place in the direction left to right, that is, towards the formation of ferricyanide. If now $C_{\text{OH}'}$ is diminished, A is increased, and hence the tendency towards the formation of ferricyanide increases. If $C_{\text{OH}'}$ increases, A decreases, and ferricyanide is less liable to be formed.

By taking the numerical values (Haber, *Thermodynamik Technischer Gasreactionen*, 1905, 160) for the oxygen electrode (Nernst and Wartenberg, *Göttinger Nachrichten*, 1905, No. 1) and for the ferri-, ferrocyanide electrode, the latter from determinations by Schaum and von der Linde (Haber, *Zeit. Elektrochem.*, 1901, 7, 1043), it may be shown that A is large in acid solutions and has a small value only in alkaline solutions. Hence, in the latter, ferrocyanide is oxidised to a very small extent.

EXPERIMENTAL.

In the first experiments, the source of light was a "Uviol" lamp, made by Schott and Genossen, of Jena; details of this lamp and of the experiments are given in Prof. Haber's note (*loc. cit.*). Some experiments were also made in sunlight. In the later experiments, a much more powerful lamp, kindly lent by W. C. Heraeus, of Hanau, was used. This is a mercury vapour lamp of quartz, and is shown in the accompanying sketch.

The essential part is a small bore tube, *A*, of quartz, bent into a U-shape with the arms close together. The upper ends are bent over and end in bulbs, which are filled with pure mercury up to the level shown. Platinum contact wires pass down two other tubes which are sealed into the bulbs at the back.

The bulbs, inlet tubes for the wires, and part of the U-tube are all enclosed in a brass casing, *C*, which has a glass front not shown in the sketch. The projecting part of the U-tube is enclosed in a thin-walled quartz tube, *B*, which is cemented into the brass casing. Close behind the U-tube a nickel tube enters, through which water flows. The water fills the whole of *B* and *C* and is carried away by another tube at the top, so that a water-jacket surrounds the lamp and keeps it quite cool. It is interesting to note that the ultra-violet light or radiation passes easily through this water-jacket.

The lamp is lighted by inverting it slowly, so that the two threads of mercury in the U-tube meet at the bend. On turning the lamp in the reverse direction, the arc is struck, and fills the whole of the U-tube up to the mercury in the bulbs. A starting resistance is necessary owing to the momentary short circuit which occurs when the mercury threads meet. The lamp requires 230—240 volts, and uses 5—6 amperes.

The solutions were contained in a large tube, *D*, similar to a large test-tube, which was fitted to *B* by means of an india-rubber stopper. Two glass tubes passing through this allowed gases to be bubbled through the solutions.

The lamp gives a very large amount of ultra-violet radiation; when burning in air, a very powerful odour of ozone is perceived, and the radiation can be distinctly felt on the hand. If a *N*/1000 solution of potassium permanganate containing 9 per cent. of sulphuric acid is exposed to this light in the tube *D*, it is completely decolorised in ten minutes with evolution of oxygen. A solution of potassium iodide (0.09*N*) and starch becomes absolutely black in two minutes.

Action of Light on Potassium Ferrocyanide Solution in Presence of Oxygen.

The experiments mentioned in Haber's note to the Bunsen Gesellschaft were all carried out with the "Uviol" lamp. In each

case, 300 c.c. of *N*/10 potassium ferrocyanide solution were used. The results are shown in the following table :

No. of ex-periment.	Strength of potash solution. Normal=1.	Time of exposure in hours.	Iron, gram, precipitated as $\text{Fe}(\text{OH})_3$.	(CN) as KCN, gram.	Fe : CN
1	0.1	4.5 } 9.0	0.0196 } 0.0390	0.1039	1 : 5.72
2	0.5	3.0	0.01756	0.04855	1 : 5.95
3	1.0	3.0	0.0169	0.04529	1 : 5.75

The equation requires the proportion 1 : 6 for Fe : CN.

In the first experiment, after exposure for four and a half hours, the solution was filtered and exposed for a further period of four and a half hours. The iron hydroxide was collected, washed, and dissolved in dilute sulphuric acid and estimated by the method of Storch (*Zeit. Elektrochem.*, 1901, 7, 715).

The iron precipitate always dissolved without any odour of prussic acid, blue coloration, or any other sign of the presence of cyanide. The cyanide in the filtrate was estimated by titration with *N*/10 silver nitrate after addition of a small quantity of potassium iodide as indicator; the exactness of this method was tested by the titration of a mixture of potash and potassium ferrocyanide containing a known quantity of potassium cyanide.

From the foregoing table, it will be seen that roughly 5 milligrams of iron per hour are precipitated as hydrate. On repeating these experiments, using the quartz lamp, a much stronger action takes place, as the following numbers show :

		Fe precipitated as $\text{Fe}(\text{OH})_3$, gram.	Fe : CN.
Exposure, one hour	{	0.0132	1 : 4.9
		0.0097	1 : 5.1
		0.0083	1 : 4.1

The solutions of ferrocyanide and caustic potash were decinormal, and in each experiment about 100 c.c. of solution were exposed for one hour in a stream of oxygen. Some of the ferric hydroxide is deposited as a film on the wall of the lamp; this reduces the intensity of the light to some extent, and thus causes variations in the amount of hydroxide precipitated.

In these experiments, the relation of iron to cyanide is considerably below the theoretical 1 : 6. The experiments were made in strong alkaline solution, and at the ordinary temperature, so that the loss of cyanogen cannot be accounted for by supposing it to be expelled by the stream of oxygen. It appeared probable that hydrolysis of the cyanide took place under the influence of light. The following experiments were then carried out :

(a) One hundred c.c. of a solution containing 30 c.c. of $N/10$ potassium cyanide and 10 c.c. of $N/10$ potassium hydrate were exposed for one hour in a stream of oxygen. The quantity of cyanide in the solution diminished by 15 per cent.

(b) Another experiment was made, using a solution of the same composition. After exposure, the solution was divided into two equal parts. The first part was titrated with silver nitrate, and it was found that 23.5 per cent. of the cyanide had disappeared. The other half of the solution was acidified and distilled into a solution of caustic potash. The same amount of cyanide was found in this potash solution as in the first half, showing that all cyanide had distilled over. The residue was made strongly alkaline, and again distilled into water. A considerable quantity of ammonia passed over, and was titrated with $N/10$ hydrochloric acid. The amount of cyanide corresponding to this ammonia was 20.9 per cent. of the original quantity used; hence nearly all the missing cyanide was accounted for.

(c) Control experiments were made by passing a stream of oxygen through the solutions for an hour in absence of light; the correct quantity of cyanide was found in each case and no ammonia was detected. The conclusion is that the cyanide is oxidised by oxygen under the influence of light with formation of cyanate, which on boiling with acid is decomposed, yielding the ammonium salt of the acid used.

Further experiments were then made in order to ascertain whether compounds more complex than cyanates were also produced. The solutions were exposed to light and then distilled as before, being first acidified and then rendered alkaline. The residue after these distillations was twice evaporated with concentrated hydrochloric acid. By this means, tricyanate and other polymerides would be decomposed with formation of ammonium chloride. On making alkaline and again distilling, ammonia should pass over. Repeated experiments with solutions exposed for three hours always gave ammonia at this third distillation, though the amount was small.

On comparing the experiments made with the "Uviol" lamp with those with the quartz lamp it is seen that in the former case the relation $\text{Fe}:\text{CN}$ is very near the theoretical value, although the exposure was longer. Thus the oxidation of cyanide to cyanate and other compounds takes place appreciably only in very strong light.

The foregoing experiments do not, however, explain how the ferric hydroxide is precipitated. Either the ferrocyanide may be decomposed, and the ferro-ion oxidised and precipitated, or the ferrocyanide may first be oxidised to ferricyanide, and the iron precipitated from this by hydrolysis, according to the equation:

That this hydrolysis takes place to a certain extent seems to be proved by the fact that a neutral solution of ferricyanide precipitates a small amount of ferric hydroxide on exposure in a stream of oxygen; no ferrocyanide is formed. This hydrolytic effect may be expected to be the same in an atmosphere of hydrogen, but in this case, owing to the reduction of the ferricyanide to ferrocyanide and the formation of acid, blue and green compounds are formed which prevent the detection of ferric hydroxide.

The hydrolysis of ferricyanide must proceed very slowly, otherwise a much larger amount of ferric hydroxide would be precipitated on exposure to light in presence of oxygen. If the formation of ferricyanide is an intermediate step in the precipitation of ferric hydroxide from ferrocyanide in alkaline solution, such a solution would contain ferricyanide after exposure: this is, however, not the case. Solutions of alkaline ferrocyanide, after exposure, were filtered to remove the precipitated ferric hydroxide [0.0015 gram (calculated as Fe) per 130 c.c.], acidified, and then tested for ferricyanide with pure ferrous sulphate or silver nitrate, but no trace of ferricyanide was found. We may thus conclude that ferric hydroxide is precipitated from the ferrocyanide without intermediate formation and subsequent hydrolysis of ferricyanide.

In order to ascertain if oxygen is necessary for the precipitation of ferric hydroxide, the alkaline solution was made up as before, and, after having been boiled and cooled in an atmosphere of hydrogen, was exposed. No trace of hydroxide was found, and the solution remained clear. On admitting oxygen in place of hydrogen, the solution at once became turbid, and in a few minutes deposited a considerable quantity of ferric hydrate.

This experiment also shows that no ferrous hydrate is precipitated in absence of oxygen. The dissociation represented by the equation $\text{Fe}(\text{CN})_6''' \rightleftharpoons \text{Fe}^{++} + 6\text{CN}'$ would lead to the precipitation of ferrous hydrate if the concentration of the Fe-ions became large enough to make the product $(\text{C}_{\text{Fe}^{++}} \times \text{C}_{\text{OH}^{--}}^2)$ greater than the solubility product of ferrous hydrate. From the experiment, it is evident that the dissociation does not go far enough, and even in very strong light is too small. Haber (*loc. cit.*) has explained the theory which connects this view with the high velocity of ionic reactions.

It was also found that exposure to light does not increase the conductivity of the alkaline ferrocyanide solution to any appreciable extent. Different methods of determining the conductivity were tried, but all gave the same values, both when the solution was exposed to and protected from light.

Experiments with Alkali Sulphide and Ferrocyanide.

If a solution containing ferrocyanide, potassium sulphide, and an alkali is exposed to sunlight or the light from the quartz lamp, it turns brown or green, depositing after some time a black precipitate of ferrous sulphide. Here we have undoubtedly a reaction of ferrocyanide, since any ferricyanide would be immediately reduced by the potassium sulphide to ferrocyanide. It is well known that the green solution contains colloidal ferrous sulphide.

The experiments were all made in an atmosphere of hydrogen.

It often happened that, on exposure to light, a brown solution was obtained, which, only after being further exposed for a considerable time, turned green and gave the precipitate of ferrous sulphide. It was found that a higher temperature always accelerated the change from brown to green, and the precipitate was formed in much less time. A brown solution may be obtained if a very dilute solution of ferrous sulphate is mixed with an alkali sulphide and alkali. The brown solution is quite stable at 0° , but on warming the colour changes to dark green, and finally a precipitate of ferrous sulphide is formed. If freshly precipitated ferric hydroxide is dissolved in very strong alkali and an alkali sulphide added, a clear red solution is obtained (*Zeit. Elektrochem.*, 1901, 7, 724), which slowly changes to brown, and ferrous sulphide is precipitated. These brown solutions, in whichever way prepared, all turn green and deposit ferrous sulphide.

The red solution obtained by dissolving ferric hydroxide in strong alkali and adding an alkali sulphide most probably contains a double sulphide of iron and potassium. The brown solutions may contain either a double salt or a colloidal form of ferrous sulphide; most probably, however, they consist of a mixture of the two.

In solutions exposed to the lamp, the brown colour is only formed at temperatures below 30° . For this reason, and in order to obtain an appreciable precipitate of ferrous sulphide, the tube containing the solution was, in the later experiments, immersed in a water-bath and kept warm. A temperature of $30-40^{\circ}$ was found to be sufficient, but about 80° is most advantageous. At this temperature, very little colloidal green solution is formed, and a considerable precipitate of ferrous sulphide is obtained.

Even at this increased temperature, the reaction is photochemical. One hundred and thirty c.c. of a solution containing $N/10$ ferrocyanide, $N/2$ alkali, and $N/2$ alkali sulphide gave, after three-quarters of an hour's exposure at 42° , 0.012 gram Fe precipitated as ferrous sulphide, whilst a similar solution heated for one and a half hours to 75° without exposure gave no trace of ferrous sulphide, but remained absolutely clear and colourless.

Ferrous sulphide dissolves easily in a solution of potassium cyanide forming ferrocyanide: hence it was to be expected that the green solutions on standing would become clear, owing to the solution of the sulphide by the potassium cyanide formed in the reaction. This did not occur, and on standing twenty-four hours the solutions were still green, although a considerable quantity of sulphide had precipitated. If ferrous sulphide, prepared by precipitation of ferrous sulphate, is shaken with excess of potassium cyanide in alkaline solution, it is completely dissolved. If the sulphide is in excess, the cyanide disappears. Hence, if cyanide is added to the solution of ferrocyanide, alkali, and alkali sulphide, no precipitation should take place on exposure. After prolonged exposure at 80° , no trace of ferrous sulphide was formed. This showed that cyanide, formed from the ferrocyanide during precipitation of sulphide, must be removed in some secondary reaction. On distilling the exposed solutions after the separation of the sulphide, in most cases no cyanide was found, and in others only very little. The distillation was carried out by Feld's method (Feld, *Journ. für Gasbeleucht.*, 1903, 564) with lead nitrate. Control experiments with a mixture of ferrocyanide, a known amount of cyanide, and alkali sulphide gave the correct amount of cyanide.

In the gas issuing from the solution, ammonia in sufficient quantity to react with litmus paper was found. Part of the cyanide is thus hydrolysed with formation of this gas. The exposed solutions were also tested for sulphocyanide in the following manner. The ferrocyanide, alkali, and alkali sulphide were precipitated as Prussian blue, iron hydroxide, and iron sulphide by excess of ferric chloride; after separation, the filtrate showed the deep red colour of iron sulphocyanide.

In order to investigate this formation of sulphocyanide further, an experiment was made in which a solution composed of $N/10$ potassium cyanide, $N/2$ potassium sulphide, and $N/10$ caustic potash was exposed in a current of hydrogen for three hours. It was found that 32 per cent. of the cyanide had disappeared and the solution had become pale yellow. On extraction with ether and subsequent evaporation, a red liquid was obtained having a strong and unpleasant odour of onions. This suggests the formation of complex sulphocyanides by interaction of the cyanide and alkali sulphide under the influence of light. No cyanide is found in the green solutions, since it is all used in the formation of sulphocyanides or is hydrolysed.

In conclusion, it may be stated that the precipitation of ferric hydroxide or ferrous sulphide from potassium ferrocyanide by alkali or alkali sulphide under the influence of light takes place in the following manner:

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Potassium ferrocyanide is dissociated in solution in absence of light into potassium-ions and the ferrocyan-ions, thus :

Under the influence of light, the complex ferrocyan-ion dissociates into iron-ions and cyan-ions,

The existence of these iron-ions can be demonstrated in the ordinary manner by precipitation with alkali and oxygen or alkali sulphide. The concentration of Fe^{2+} ions is too small to exceed the solubility product of $\text{Fe}(\text{OH})_2$ or to be found directly by conductivity measurements. It is ferrocyanide which is decomposed in this manner, not ferricyanide. The small quantity of ferric hydrate obtained from neutral solutions of ferricyanide is produced by hydrolysis, which may take place according to the equation :

Potassium cyanide is easily oxidised in presence of light by oxygen, forming cyanate and polymerides. The cyanide which is formed when iron is precipitated as sulphide from ferrocyanide under the influence of light, reacts with alkali sulphide present, producing sulphocyanide and complex sulphocyano-compounds.

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