

that the acid distils at 104° – 122° from the contents of the retort having a temperature of 165° ; and that the nitric acid, which is received during this phase, has been partly decomposed and forms the yellow- or red-colored acid.

The conclusions drawn from the foregoing experimental work, may be expressed as follows :

(1) At the common temperature, or below 20 , neither concentrated sulphuric acid nor the polysulphate act on sodium nitrate; the reaction is, at least, so very slow, that during a contact of three to four days, only traces of free nitric acid can be observed.

(2) At a higher temperature the nitrate is decomposed by sulphuric acid and the reaction is finished at temperatures below 100° , free nitric acid and $\text{NaH}_3\cdot 2\text{SO}_4$ resulting.

(3) The trisulphate acts on the nitrate at temperatures over 165° , products of the reaction being again free nitric acid and sodium bisulphate.

(4) The nitric acid, resulting during this phase at the corresponding high temperature, is always decomposed; its vapors, in distilling over, show a temperature of about 120° – 123° , and this acid was formerly considered the second hydrate of nitric acid, $(\text{H}_2\text{O})_2\text{N}_2\text{O}_5$ (the $(\text{HO})_2\text{NO}_5$ of old).

Under the conditions of the described experimental work, the water can be the result of decomposition only of nitric acid, and I have also shown that this can take place only during the second phase of the process.

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ON THE FERROCYANIDES OF CADMIUM.

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IT has already been shown¹ that the results obtained in titrating cadmium by potassium ferrocyanide in a neutral or slightly acid solution do not agree with any of the formulas given for the precipitate, while the values obtained in an ammoniacal solution agree very closely with the formula $\text{K}_2\text{CdFe}(\text{CN})_6$.

The present work was undertaken to study the variation in composition under different conditions and, if possible, to assign

¹ Miller and Fisher: This Journal, Sept., 1900.

definite formulas to the precipitates so formed. To cover the ground as completely as possible, the following series of precipitates was made :

- A.* Neutral solution, cadmium in excess.
- B.* Neutral solution, ferrocyanide in excess.
- C.* Acid with hydrochloric, 10 cc. (sp. gr. 1.20) per liter, cadmium in excess.
- D.* Acid with hydrochloric, 10 cc. (sp. gr. 1.20) per liter, ferrocyanide in excess.
- E.* Acid with acetic, 10 cc. 50 per cent. acetic acid per liter, cadmium in excess.
- F.* Acid with acetic, 10 cc. 50 per cent. acetic acid per liter, ferrocyanide in excess.
- G.* Alkaline with ammonia,¹ cadmium in excess.
- H.* Alkaline with ammonia,¹ ferrocyanide in excess.

The precipitates were all formed in large beakers, in the cold and allowed to stand, then washed with water, water containing hydrochloric acid, water containing acetic acid, water and ammonia, respectively, so that the conditions of precipitation were maintained, then washed with water till free from excess of cadmium or of ferrocyanide. The work was begun in June, 1900, and the precipitates analyzed a year later.

In general, whenever the cadmium was in excess the precipitates settled well, and when ferrocyanide was in excess, very badly. The salts used for this series of precipitations were cadmium nitrate and potassium ferrocyanide.

The method of analysis was in all cases the same, and the object was to obtain the ratio between iron and potassium and cadmium. Some attempts were made at first to dry the precipitates to constant weight, but as decomposition resulted no attempt was made to weigh the portions taken for analysis but all the determinations were expressed as ratios.

The precipitates were repeatedly evaporated in casseroles with nitric and sulphuric acids till decomposition was complete, the residue was dissolved in water, the excess of sulphuric acid neutralized with ammonia and the cadmium precipitated as sulphide in a very weak hydrochloric acid solution, dissolved and de-

¹ The cadmium hydroxide was dissolved in an excess of ammonia before the potassium ferrocyanide was added.

terminated as phosphate.¹ In the filtrate the iron was, after oxidation, precipitated as hydroxide and weighed as ferric oxide. The filtrate from the iron was evaporated, the ammonium salts expelled and the potassium weighed as sulphate. In the determination of cadmium as phosphate, weighing as pyrophosphate, and as cadmium ammonium phosphate ($\text{CdNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$) were tried and the weighing as cadmium ammonium phosphate adopted as more convenient.

The following is a brief description of the precipitates formed and the results obtained from their analysis expressed as an atomic ratio:²

A (neutral solution, cadmium in excess). Yellowish white, settled well, was washed (nine times) till free from cadmium; when dry, was yellowish-white, apparently slightly oxidized to ferricyanide. Gave, on analysis, $\text{Fe} : \text{K} : \text{Cd} :: 1 : 1.14 : 1.42$ or $7 : 8 : 10$, corresponding to $\text{K}_8\text{Cd}_{10}(\text{Fe}(\text{CN})_6)_7$.

B (neutral, ferrocyanide in excess). White, settled partially after five months, was washed at intervals for a year. It was the most tedious of all but did not give evidence of decomposition. The ratio was $\text{Fe} : \text{K} : \text{Cd} :: 1 : 1.80 : 1.08$.

C (hydrochloric, cadmium in excess). Dull orange-yellow, settled very well; on washing with water containing 10 cc. concentrated hydrochloric acid per liter, the supernatant liquid became greenish with evident decomposition of the precipitate. A second lot was made under the same conditions; the precipitate, at first white, became yellow within a few seconds. The yellow precipitate is also formed when cadmium is dissolved in hydrochloric and a little nitric acid, then neutralized, 2 cc. of hydrochloric acid added, and then titrated by potassium ferrocyanide. It is not due to the presence of any nitroprusside and is undoubtedly due to the oxidation of part of the cadmium ferrocyanide to ferricyanide, which is brownish yellow, by the nitrate present in both cases. This precipitate was not analyzed.

D (hydrochloric, ferrocyanide in excess). The precipitate, at first yellowish, became white when an excess of potassium ferrocyanide was present; it settled quite well at first but badly after washing, like the others when an excess of ferrocyanide is

¹ Miller and Page: *School of Mines Quarterly*, July, 1901, and *Ztschr. anorg. Chem.*, **28**, 233 (1901).

² These values are obtained by dividing the calculated weights of iron, potassium, and cadmium, by their atomic weights and then multiplying by $\frac{1}{\text{wt. iron}}$.

present, and showed a greenish-yellow color after washing, evidently due to a slight decomposition. The results were $\text{Fe}:\text{K}:\text{Cd}::1:1.933:0.991$, corresponding to $\text{K}_2\text{CdFe}(\text{CN})_6$.

E (acetic, cadmium in excess). The precipitate was nearly white, settled well, and on drying was white. The ratio was $\text{Fe}:\text{K}:\text{Cd}::1:1.21:1.392$, corresponding quite closely to $\text{K}_6\text{Cd}_7(\text{Fe}(\text{CN})_6)_5$.

F (acetic, cadmium in excess). Creamy white precipitate which settled badly and on drying was slightly greenish on the surface. The iron cadmium ratio was $1:0.95$, corresponding approximately to $\text{K}_2\text{CdFe}(\text{CN})_6$.

G (ammonia, cadmium in excess). A pure white precipitate which gave considerable trouble in testing for an excess of cadmium, as owing to the excess of cadmium dissolved in ammonia, a point was reached where either FeCN_6''' or Cd'' ions gave a precipitate. The precipitate on washing became flocculent and settled immediately; it was washed six times with water containing ammonia and then with water until no test for cadmium was obtained. The analytical results gave the ratio $\text{Fe}:\text{K}:\text{Cd}::1:0:3.33$, a result impossible for a ferrocyanide. After rewashing with strong ammonia to dissolve out the excess of cadmium, which was undoubtedly present as either hydroxide or carbonate and which gave the flocculent character to the precipitate, the ratio became $\text{Fe}:\text{Cd}::1:1.94$, agreeing approximately with the normal ferrocyanide $\text{Cd}_2\text{Fe}(\text{CN})_6$.

H (ammonia, ferrocyanide in excess). Pure white precipitate which settles well at first, but poorly after washing.¹ In this case only, the iron cadmium ratio was determined; the figures obtained were $1:0.97$, corresponding to $\text{K}_2\text{CdFe}(\text{CN})_6$.

On account of the oxidation and decomposition of some of the precipitates just described, a second set of eight was made under exactly the same conditions, using cadmium chloride instead of nitrate. These were made in December, 1900, and are marked *A'*, *B'*, etc., so as to be readily compared with the preceding series.

A' (neutral, cadmium in excess). White precipitate, which settled well and was completely washed in a month. On analysis, the ratio found was $\text{Fe}:\text{K}:\text{Cd}::1:1.14:1.448$ or $7:8:10$, agreeing with the results obtained in *A* and the formula $\text{K}_8\text{Cd}_{10}(\text{Fe}(\text{CN})_6)_7$.

¹ Washed six times with ammonia and water, then with water till free from ferrocyanide.

B' (neutral, ferrocyanide in excess). A slightly yellowish precipitate which did not settle at all; various methods were tried to hasten the settling, but without effect, so it was finally abandoned.

C' (hydrochloric, cadmium in excess). White precipitate which settled well, gave iron to cadmium 1:1.46 and 1:1.44. Results very similar to those obtained from *A* and agreeing with a ratio of Fe : K : Cd of 7 : 8 : 10.

D' (hydrochloric, ferrocyanide in excess). A greenish precipitate which would not settle. Separation by a centrifugal was tried as well as other methods such as the addition of sodium chloride but without effect, finally it became so decomposed as to be worthless.

E' (acetic, cadmium in excess). White, settled well, leaving a turbid solution; gave on analysis Fe : K : Cd :: 1 : 1.078 : 1.383.

F' (acetic, ferrocyanide in excess). This precipitate became very green on standing and was rejected.

G' (ammonia, cadmium in excess). A perfectly white curdy precipitate which settles immediately, leaving a clear colorless liquid and differs entirely in physical properties from the preceding. It gave on analysis the ratio 1 : 0 : 2.27, showing, as in *G*, no potassium, and the presence of cadmium in excess of the possible ratio for a ferrocyanide.

H' (ammonia, ferrocyanide in excess). A creamy white precipitate which settles well and has the consistency of clay, requiring considerable force to stir it up, and differing entirely in physical properties from the others. It gave, on analysis, Fe : K : Cd :: 1 : 2.07 : 1.048 or nearly 1 : 2 : 1, corresponding to $K_2CdFe(CN)_6$.

It remained to obtain precipitates to take the places of *B'*, *D'*, and *F'*. So in March, 1901, these precipitates were made again under the conditions already described, but in dark brown glass bottles and were kept in the dark. This greatly lessened the decomposition and by sacrificing a large proportion of the precipitates with the wash-water by July, residues were obtained which were free from excess of ferrocyanide and only slightly bluish in color.

B'' (neutral, ferrocyanide in excess). Ratio, 1 : 1.81 : 1.12, agreeing fairly with *B* and with $K_{18}Cd_{11}(Fe(CN)_6)_{10}$.

D'' (hydrochloric, ferrocyanide in excess). Ratio, 1 : 2.02 : 0.955, confirming *D* and corresponding to $K_2Cd Fe(CN)_6$.

F'' (acetic, ferrocyanide in excess). Ratio, 1 : 2.03 : 0.95, confirming *F* and corresponding to $K_2CdFe(CN)_6$.

The abnormal results in *G* and *G'*, probably due to cadmium hydroxide being carried down in varying quantities, necessitated a repetition of this work, so in July, 1901, *G'''* was made under the same conditions but was treated repeatedly with very large quantities of ammonia before washing with water and then analyzed at once.

G''' (ammonia, cadmium in excess). The iron cadmium ratio was determined in duplicate and found to be 1 : 1.496, corresponding to $K_2Cd_3(Fe(CN)_6)_2$.

When this precipitate was being washed it was noticed that there was a portion which did not settle as well as the rest; this was decanted from the part which settled well, washed and analyzed, giving a ratio of exactly 1Fe : 1Cd.

In the results already given the duplicates on *C'* and the ratios on *E* and *E'* did not check satisfactorily, so these precipitates were made again (July, 1901) and as they settled well (cadmium being in excess) they were washed and analyzed within a week.

C''' (hydrochloric, cadmium in excess). White, no decomposition; gave Fe : Cd : : 1 : 1.07 and 1 : 1.065.

E''' (acetic, cadmium in excess). White, no decomposition; gave Fe : Cd : : 1 : 1.07 and 1 : 1.06.

We see in these two a total lack of agreement in composition with those which were allowed to stand many months before analysis, indicating a change in composition after precipitation. On the other hand these last results are in exact agreement with the titration ratios in slightly acid solution;¹ for if the theory for $1K_4Fe(CN)_6$ or 1Fe : 1Cd² gives for the strength of the ferrocyanide solution 1 cc. = 0.00671 gram cadmium, then, if the ratio in the precipitate is 1 : 1.07, the strength of the solution in terms of cadmium becomes 1.07×0.00671 or 0.00718, while the average result of titration was 0.00717.

For ease of comparison let us disregard for the present the potassium, which has been found to be present always in the proper amount to satisfy the remaining valency of the ferrocyanogen radical and consider only the iron cadmium ratios.

¹ Miller and Fisher : This Journal, 21, 542 (1900).

² Based on Hermann's formula $K_2Cd Fe(CN)_6$.

Character of solution.	Cadmium in excess.		Ferrocyanide in excess.	
	Fe : Cd.		Fe : Cd.	
Neutral	1 : 1.42 A		1 : 1.08 B	
	1 : 1.44 [§] A'		1 : 1.12 B''	
Hydrochloric	1 : 1.462 C'		1 : 0.99 D	
	1 : 1.44 C'		1 : 0.955 D''	
	1 : 1.07 C''' ¹		
	1 : 1.065 C''' ¹		
Acetic.....	1 : 1.392 E		1 : 0.95 F	
	1 : 1.383 E'		1 : 0.95 F''	
	1 : 1.07 E''' ¹		
	1 : 1.06 E''' ¹		
Ammonia	1 : 3.33 G		1 : 0.97 H	
	1 : 1.94 G ²		1 : 1.048 H'	
	1 : 2.27 G'		
	1 : 1.496 G'''		
	1 : 1.496 G'''		
	1 : 1 G''' ³		

We see from the work described that :

(1) The results when ferrocyanide is in excess are entirely different from those where cadmium is in excess.

(2) In either acid or ammoniacal solution, ferrocyanide being in excess, the ratio is 1 iron to 1 cadmium or the precipitate is $K_2CdFe(CN)_6$, while in a neutral solution the cadmium ratio is higher.

(3) With cadmium in excess, in either neutral or hydrochloric acid solution the final composition is the same, corresponding to $K_6Cd_{10}(Fe(CN)_6)_7$, while in an acetic acid solution the final composition corresponds to $K_6Cd_7(Fe(CN)_6)_5$.

(4) With cadmium in excess, in an acid solution the composition alters on standing with an increase of cadmium in the ratio, but when freshly precipitated the ratio agrees exactly with the results by titration.

(5) With cadmium in excess, in an ammoniacal solution the ratio exceeds the normal, but after washing with ammonia corresponds to $Cd_2Fe(CN)_6$; when freshly precipitated and washed quickly with ammonia, the part which settles badly being removed by decantation, the composition agrees exactly with $K_2Cd_3(Fe(CN)_6)_2$, while the part decanted corresponds to $K_2CdFe(CN)_6$.

¹ Analyzed within a week of precipitation.

² After treatment with ammonia.

³ Decanted portion.

(6) The constancy of the final composition of these precipitates does not favor the theory that potassium ferrocyanide is merely dragged down.

The results obtained when cadmium was in excess in an ammoniacal solution were so extraordinary that they deserved further study. The precipitate G''' , $K_2Cd_3(Fe(CN)_6)_2$, was treated seven times with strong ammonia (sp. gr. 0.90) to see whether a change could be effected by a difference in solubility in ammonia as the $K_2CdFe(CN)_6$ seemed the more soluble. In this way, a creamy white residue was obtained which gave on analysis $Fe : Cd :: 1 : 1.99$, showing $Cd_2Fe(CN)_6$ which was also obtained in G after rewashing with ammonia.

This result, together with the fact that the portion first obtained by decantation when the precipitate was originally treated with ammonia, gave a ratio of $Fe : Cd$ of exactly $1 : 1$ shows that the original precipitate can be resolved into the two simple ferrocyanides $Cd_2Fe(CN)_6$ and $K_2CdFe(CN)_6$, and affords important confirmation of the theory that these complicated precipitates are mixtures, advanced several years ago in connection with the ferrocyanides of zinc and manganese.¹

Now, if this is true for the precipitate in an ammoniacal solution, it ought also to be true of those more complicated ones formed in acid solutions; accordingly, C''' , which gave $1 : 1.07$ when freshly precipitated, was treated in the same way with strong ammonia, and the residual cream-colored portion analyzed. This gave a ratio of $1 : 1.90$, showing that the same change had taken place, though it was not entirely complete.

To test this further, precipitate A (neutral, cadmium in excess, made June, 1900) was treated eight times with strong ammonia and the residue analyzed. This gave the ratio of $1 : 1.99$, agreeing almost perfectly with $Cd_2Fe(CN)_6$.

In order to ascertain whether the change which takes place on standing can be hastened by heating, the precipitate E''' (acetic, cadmium in excess), which when washed quickly and analyzed gave a ratio of $1 : 1.07$, was heated with water containing acetic acid on a water-bath for three days and then analyzed. The result was $Fe : Cd :: 1 : 1.40$ compared with $1 : 1.383(E')$ after standing six months in the cold and $1 : 1.392(E)$ after one year.

This precipitate (E''' after heating) was next treated eight

¹ This Journal, 19, 556 (1897).

times, with strong ammonia, and the residual portion analyzed. The result was Fe : Cd : : 1 : 1.97, showing again the presence of the normal cadmium ferrocyanide.

These experiments show that the ferrocyanides undergo a change in composition after precipitation which progresses to the same point under the same conditions and which is hastened by heating. The action of ammonia on these precipitates (cadmium in excess) has been confirmatory of the idea that they are either mixtures or else very easily decomposable double salts made up of $K_2CdFe(CN)_6$ and $Cd_2Fe(CN)_6$.

Written in this way the results are expressed as follows :

Character of solution.	Cadmium in excess.	Ferrocyanide in excess.
Neutral	$4K_2CdFe(CN)_6, 3Cd_2Fe(CN)_6$	$9K_2CdFe(CN)_6, Cd_2Fe(CN)_6$
Hydrochloric ..	$14K_2CdFe(CN)_6, Cd_2Fe(CN)_6^1$ $4K_2CdFe(CN)_6, 3Cd_2Fe(CN)_6$	$K_2CdFe(CN)_6$
Acetic	$14K_2CdFe(CN)_6, Cd_2Fe(CN)_6^1$ $3K_2CdFe(CN)_6, 2Cd_2Fe(CN)_6$	$K_2CdFe(CN)_6$
Ammonia	$K_2CdFe(CN)_6, Cd_2Fe(CN)_6^1$	$K_2CdFe(CN)_6$

It would be premature to advance these formulas as representing relations of these complicated and variable precipitates, but the facts seem to warrant this as a working hypothesis, to be used in a further study of the other insoluble ferrocyanides.

Although the results are not all that are desired, many of the precipitates are so easily oxidized, readily decomposed and impossible to filter, that it seemed very doubtful whether any better results could be obtained if the work were repeated.

On comparing the results obtained on cadmium with those on zinc previously published² and with those of Stone and Van Ingen³ we see some cases of remarkable agreement as well as some discrepancies, but a discussion of these results is postponed as it is proposed to continue this work by a similar investigation of the ferrocyanides of the other metals of the periodic group containing cadmium and zinc and also of the analytical group containing zinc, manganese, nickel and cobalt so that, taking zinc as a starting-point, we can see whether the variations in composition have any connection with the analytical grouping or the periodic law and also possibly obtain more knowledge of their constitution.

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¹ Freshly precipitated.

² This Journal, **19**, 547 (1897)

³ *Ibid.*, **19**, 542 (1897).