VOL. XXII. [SEPTEMBER, 1900.] NO. 9.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 27.]

NOTES ON LEAD AND CADMIUM FERROCYANIDES.

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Received June 29, 1900.

LEAD FERROCYANIDE.

THE following series of experiments were made in order to ascertain whether the composition of lead ferrocyanide is invariably $Pb_2Fe(CN)_6$, or whether, like the ferrocyanides of manganese and zinc, it is affected by the conditions of precipitation.

The precipitates were made as follows: Lead acetate was dissolved in water and heated to boiling, to this a hot aqueous solution of potassium ferrocyanide was added, and acid in some cases as is noted later. The precipitates were allowed to settle and were washed by decantation until free from lead or ferrocyanide as indicated by hydrogen sulphide, or by ferric chloride. They were then dried at 105° C. to constant weight. The method of analysis was in all cases as follows: About one gram was dissolved in dilute nitric acid in a casserole, and after the addition of sulphuric acid, evaporated to fumes. One evaporation was found to effect complete decomposition. The residue was taken up with 1 per cent. sulphuric acid to which half its volume of alcohol was added. The lead sulphate was washed with 1 per cent. sulphuric acid containing alcohol, filtered and weighed in a Gooch crucible. The iron was precipitated in the filtrate by ammonia, after boiling out the alcohol and adding ammonium chloride, filtered, washed, and weighed as Fe_2O_3. The filtrate from the iron was evaporated to dryness in platinum, the ammonia salts volatilized and the potassium sulphate weighed.

A. Precipitate formed in a neutral solution with lead in excess, settles rapidly. The analytical results are:

	I.	II.	III.	Average.
Lead	66.03	66.15	66.09	66.09
$Fe(CN)_6$	34.07	33.98	33.85	33.97
Potassium	0.50	0.48	0.45	0.47
				100.53

B. Solution neutral, ferrocyanide in excess, the precipitate settles slowly. It gave on analysis:

	I.	II.	III.	Average.
Lead	66.26	66.06	65.98	66.10
$Fe(CN)_6$	33.54	33.77	33.90	33.70
Potassium	0.62	0.55	0.58	0.58
				100.38

C. Solution slightly acid with acetic acid, lead in excess. The precipitate settles rapidly. On analysis the following results were obtained:

	I.	II.	III.	Average.
Lead	64.42	64.55	64.62	64.53
$Fe(CN)_6$	35.48	35.33	35.37	35.39
Potassium	0.84	0.81	0.80	0.82
				100.74

D. Solution slightly acid with acetic acid, ferrocyanide in excess. Precipitate settles rapidly. The results on analysis were almost identical with those obtained from the preceding precipitate.

	I.	II.	III.	IV.	Average.
Lead	64.43	64.28	64.38	64.58	64.42
$Fe(CN)_6$	35.47	35.62	35.69	35.60	35.59
Potassium	0.82	0.76	0.86	0.79	0.81
					100.82

E. Solution strongly acid with acetic acid, ferrocyanide in excess. Precipitate settles badly. The results are:

	I.	II.	Average.
Lead	63.73	64.02	63.87
$Fe(CN)_6$	35.51	35.02	35.26
Potassium	0.76	0.96	0.86

These and the following are results calculated from the determination of potassium, lead, and iron in undried portions and consequently, when calculated from the ratio of Fe : K : Pb, add up to 100 per cent.

F. Solution strongly acid with hydrochloric acid, ferrocyanide in excess, precipitated hot as usual.

	I.	II.	Average.
Lead	63.02	63.39	63.21
$Fe(CN)_6$	34.74	34.48	34.61
Potassium	2.24	2.12	2.18

When the analysis is made on a sample dried to constant weight, it invariably adds up to a little over 100 per cent. This is probably caused by the fact that on drying, the precipitates become either bluish or greenish in color due to a slight decomposition so that the percentages of $Fe(CN)_6$ which are calculated from the iron are high.[1]

It is evident from these results that the precipitate varies in composition under different conditions of precipitation, and as the acidity increases the percentage of potassium increases and that of lead diminishes.

Also, that when the acidity is the same the composition is the same whether ferrocyanide or lead is in excess.

Berzelius[2] states that when formed in a neutral solution with potassium ferrocyanide in excess, the composition of the precipitate is $Pb_2Fe(CN)_6$. Using the most recent atomic weights this corresponds to a percentage composition of:

Lead	66.10
$Fe(CN)_6$	33.90

Our results are, with lead in excess:

Lead	66.09
$Fe(CN)_6$	33.97

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[1] For the CN : Fe ratio is higher in $Fe(CN)_6$ than in $Fe_7(CN)_{18}$ or $Fe_5(CN)_{12}$.

[2] *Ann. Chem. Phys.*, 15, 157 (1820).

With ferrocyanide in excess:

Lead	66.10
$Fe(CN)_6$	33.70

The only statement we have found suggesting any variation in the composition of this ferrocyanide is by Gay-Lussac[1] that "the precipitate for however long a time it may have been washed, retains from 6–9 per cent. of ferrocyanide of potassium; of which it continues to give up a certain quantity to fresh portions of water." The conditions of this precipitation are not stated.

In order to compare these results with those obtained by titration, the following experiments were made. A solution of potassium ferrocyanide was very carefully standardized against metallic zinc and freshly ignited zinc oxide. The conditions being; bulk 200 cc., acidity 2 cc. concentrated hydrochloric acid, temperature about 80° C. Uranium acetate was used as an indicator on porcelain. An allowance of 0.3 cc. was made in each case for the excess necessary to affect the indicator. The results of six concordant determinations gave as the strength of this solution, 1 cc. = 0.005857 gram of zinc.

This solution was then used to titrate solutions containing known weights of lead as follows:

Neutral Solution.—Separate portions of metallic lead, of about 1 gram each, were dissolved in nitric acid, hydrochloric acid added and evaporated to complete dryness; the lead chloride was then dissolved in hot water diluted to 200 cc. and titrated. The titration in a neutral solution is not altogether satisfactory. Five determinations gave results varying from 0.02454 to 0.02461. Average, 0.02458.

Acetic Acid Solution.—Six determinations gave from 0.02450 to 0.02458; the average coinciding with the two most satisfactory titrations is 0.02454 gram.

Hydrochloric Acid Solution.—In a solution containing one drop of concentrated hydrochloric acid the results were from 0.02441 to 0.02446; average, 0.02444 gram. With 1 cc. of hydrochloric acid the results were unreliable on account of the solubility of the precipitate.

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[1] Gmelin's "Handbook of Chemistry" (London, 1852), Vol. VII, p. 490.

Assuming that the precipitates formed are in one case $Zn_3K_2(Fe(CN)_6)_2$, and in the other $Pb_2Fe(CN)_6$ or that an amount of ferrocyanide which precipitates three atoms of zinc precipitates four of lead, the factor by which the zinc standard must be multiplied to give the lead standard is 4.218. This gives by calculation from the zinc standard, 0.0247 as the lead standard of the solution.

The amounts of lead precipitated per cubic centimeter in no case reach this value and although the variations are not so great as is shown from the analyses of the precipitates, they are in exactly the same order, and so confirm the statement that increase of acidity tends to diminish the percentage of lead in the precipitate.

Our results agree closely with Low's[1] statement: that a solution containing 10 grams per liter of crystallized potassium ferrocyanide will equal 10 milligrams of lead per cubic centimeter, and are at complete variance with a statement by Furman[2] that it requires 16 grams per liter for such a solution. Furman's figure is evidently based on the assumption that this value can be determined by a direct ratio between lead and zinc.

CADMIUM FERROCYANIDE.

The potassium ferrocyanide solution, already described, was used to titrate a number of solutions containing cadmium under different conditions. Portions of cadmium oxide of 0.3 to 0.4 gram each were dissolved in hydrochloric acid, and evaporated to complete dryness, then dissolved in 200 cc. of hot water and titrated. It was found that uranium acetate on porcelain was very unsatisfactory as the precipitate reacts with the indicator as is the case with manganese, so that the end tests in these titrations were made on filter-paper placing the drops so that the precipitate of cadmium ferrocyanide did not come in contact with the uranium acetate.

The results in a neutral solution were not concordant, varying between 0.0071 and 0.00727 gram of cadmium per cubic centimeter.

In a solution containing 1 cc. of 50 per cent. acetic acid the

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[1] This Journal, 15, 550 (1893).

[2] "Manual of Practical Assaying," p. 139.

results ran from 0.00699 to 0.00702 gram of cadmium; average, 0.0070 gram.

In a solution containing 1 to 2 cc. of concentrated hydrochloric acid the average of six determinations on cadmium oxide gave 1 cc = 0.007177 gram of cadmium; this was checked by four tests with metallic cadmium which gave 0.007165 gram, or a general average of 0.00717 gram. Another set was made with only a few drops of hydrochloric acid present; these gave almost the same results. With this solution it was found possible to use uranium acetate on porcelain but drops on filter-paper are a safer end-point for cadmium titrations.

As cadmium hydroxide is soluble in ammonia it was possible to extend the titration to an ammoniacal solution by using as an indicator a 4 per cent. solution of copper sulphate, as recommended by Moldenhauer[1] for zinc. The spots are made on filter-paper, as already described; the end-point, a red line, is distinct but not as delicate as with uranium acetate. An allowance of 0.9 cc. was made for the excess necessary to affect the indicator. Four tests gave the following values for 1 cc.: 0.00669, 0.00678, 0.00674, 0.00674; average, 0.00674 gram of cadmium per cubic centimeter.

The formula usually assigned to cadmium ferrocyanide is that given by Hermann:[2] $CdK_2Fe(CN)_6$; assuming that this is the composition of the precipitate, the ratio as regards ferrocyanide is $3Zn = 2Cd$, and the strength of the ferrocyanide solution used would be 1 cc. = 0.00671 gram cadmium. The results of the titrations do not agree with this value except those obtained in an ammoniacal solution.

Other formulas have been given for cadmium ferrocyanide. Dammer gives it the normal composition $Cd_2Fe(CN)_6$ and cites Wittstein[3] as his authority, but the original article gives neither formula nor analysis.

Wyrouboff[4] gives the composition under all conditions as $K_5Cd_5(Fe(CN)_6)_4$ which has been altered in Comey's "Dictionary," so as to satisfy the valence of the $Fe(CN)_6$ radical to $K_6Cd_5(Fe(CN)_6)_4$. Assuming that this is the precipitate formed, the

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[1] *Chem. Ztg.*, 13, 1220 (1889), and 15, 223 (1891).

[2] *Ann. Chem. u. Pharm.*, 145, 235 (1868).

[3] Büchner's *Repertorium der Pharm.*, 63, 316-317.

[4] *Ann. chim. phys.* [5], 8, 449 (1878).

ratio as regards ferrocyanide becomes $6Zn = 5Cd$, and the strength of the solution used would be 1 cc. = 0.00838 gram cadmium.

Our results in acid solutions are intermediate between these values and indicate a variation in the composition of the precipitate between the formulas of Hermann and of Wyrouboff. They are confirmed by a statement by Mackay[1] that it requires about 2½ per cent. less potassium ferrocyanide to precipitate cadmium than is required by the formula $CdK_2Fe(CN)_6$ or in other words the cadmium standard is higher than would be obtained by calculation. They are again in direct contradiction to the statement by Furman that the cadmium standard can be obtained from the zinc standard by direct proportion assuming that $2Zn = 2Cd$.

In order to ascertain the composition of cadmium ferrocyanide under different conditions analyses of the precipitates must, of course, be made. This work has already been started and while no results have yet been obtained the marked difference in the physical properties of the precipitates seems to confirm the variation in composition.

COLUMBIA UNIVERSITY,
June 27, 1900.

[CONTRIBUTION FROM THE LABORATORY OF THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION.]

THE DIGESTIBILITY OF SOME NON-NITROGENOUS CONSTITUENTS OF CERTAIN FEEDING-STUFFS.[2]

BY G. S. FRAPS.

Received June 16, 1900.

THE ether extract, protein, nitrogen-free extract, and crude fiber, which are determined in ordinary feeding-stuff analyses, are groups of compounds, and are composed of various substances with different properties and different coefficients of digestibility. The ether extract may contain (besides the true fats) waxes, cholesterin, phytosterin, lecithin, hydrocarbons, coloring-matters, etc. "Protein" includes amido compounds, acid amides, organic bases, ammonia, and nitrates, besides proteids of varied nature, one of which, nuclein, is entirely indiges-

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[1] This Journal. 21, 940 (1899).

[2] This work was suggested to the author by Prof. W. A. Withers, Chemist of the Station. See Bulletin 172.