

<i>x</i> .	Per cent. CaCO ₃ . $y = \frac{0.0642}{x - 0.3}$	Per cent. CaO. $y = \frac{0.0360}{x - 0.3}$	Per cent. H ₂ SO ₄ . $y = \frac{0.0590}{x}$	Per cent. SO ₃ . $y = \frac{0.0432}{x}$
12.1	0.00543	0.00305	0.00488	0.00398
12.2	0.00539	0.00303	0.00484	0.00395
12.3	0.00535	0.00300	0.00480	0.00392
12.4	0.00531	0.00298	0.00476	0.00389
12.5	0.00526	0.00295	0.00472	0.00386
12.6	0.00522	0.00293	0.00468	0.00383
12.7	0.00517	0.00290	0.00465	0.00380
12.8	0.00513	0.00288	0.00461	0.00377
12.9	0.00509	0.00285	0.00457	0.00374
13.0	0.00505	0.00283	0.00454	0.00371
13.2	0.00498	0.00279	0.00447	0.00364
13.4	0.00490	0.00275	0.00440	0.00359
13.6	0.00483	0.00271	0.00434	0.00354
13.8	0.00476	0.00267	0.00427	0.00349
14.0	0.00469	0.00263	0.00421	0.00344
14.2	0.00462	0.00259	0.00415	0.00339
14.4	0.00455	0.00255	0.00410	0.00335
14.6	0.00449	0.00251	0.00404	0.00330
14.8	0.00443	0.00248	0.00399	0.00326
15.0	0.00437	0.00245	0.00393	0.00321
15.5	0.00422	0.00237	0.00381	0.00311
16.0	0.00409	0.00229	0.00369	0.00301
16.5	0.00396	0.00222	0.00358	0.00292
17.0	0.00384	0.00216	0.00347	0.00284
17.5	0.00373	0.00209	0.00337	0.00276
18.0	0.00363	0.00203	0.00328	0.00268
18.5	0.00353	0.00198	0.00319	0.00261
19.0	0.00343	0.00192	0.00311	0.00254
19.5	0.00334	0.00187	0.00303	0.00247
20.0	0.00326	0.00183	0.00295	0.00241

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, No. 22.]

UPON BISMUTH COBALTCYANIDE.

BY J. A. MATHEWS.

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IN a recent article entitled "A Preliminary Study of the Cobalticyanides,"¹ by E. H. Miller and myself, mention was made of bismuth cobalticyanide. It was stated that "the original precipitate seems to be a normal cobalticyanide, but it has not been analyzed and no mention of such a compound is found in the

¹ This Journal, 22, 65 (1900).

literature." It was further stated that as lead cobalticyanide is exceedingly soluble in water, there might be a possibility of effecting a separation of bismuth from lead in pig-leads by the use of potassium cobalticyanide. I have analyzed the cobalticyanide of bismuth, noted carefully its properties, and determined the most favorable conditions for its precipitation. The results have not been favorable to its use in the analysis of pig-leads but it may still be found useful in the analysis of lead-bismuth alloys, "fusible metals" such as Wood's alloy, etc.

The precipitate of bismuth cobalticyanide is crystalline, settles and filters well, and contains more or less water which is not completely given up below 165° C. The anhydrous compound has the formula $\text{BiCo}(\text{CN})_6$. The theoretical percentage of bismuth for this compound is 49.17. The average of three determinations gave 49.05 per cent. bismuth. When freshly precipitated and before filtering, the precipitate appears white but on the filter it has a slight greenish tint. During the process of dehydrating the color becomes blue, getting darker as the temperature rises; then upon exposure to the air it reabsorbs water rapidly and the color becomes pink. This behavior seems to indicate some decomposition of the cobalticyanide radical at the temperature required for complete dehydration, and this view is strengthened by the fact that different samples exhibit differences of tint and that, in general, after exposing the anhydrous samples to the air, the depth of the pink tint is proportional to the depth of blue in the sample exposed.

A sample of bismuth cobalticyanide dried below 100° C. and exposed to the air for one week, lost by subsequent heating to 162° C., 19.5 per cent. Two portions dried to constant weight at 100° C. lost, by heating to 165° C., 4.35 per cent. and 4.24 per cent. respectively, corresponding to one molecule of water. The samples upon exposure to the air reabsorbed about 16.25 per cent. of water, the actual percentage fluctuating slightly from day to day.

Completeness of the Precipitation.—By means of several series of experiments in which bismuth solutions were precipitated by potassium cobalticyanide, it was found that below a concentration of 0.0079 gram of bismuth per cubic centimeter the precipitate was under no conditions complete and that at ten times

that dilution no precipitate was produced even on long standing. By varying the ratio of bismuth to potassium cobalticyanide, it was shown that a decided excess of the latter was beneficial. The precipitation is found to be more complete if acetic acid is present. Boiling assists in the precipitation of very dilute solutions, but a solution so dilute that no precipitate forms in the cold is never completely precipitated by heating. The solubility of the precipitate does not vary much with change of temperature, and when once formed is not soluble in a quantity of water which would have prevented its formation in the beginning.

The following tables, with the remarks accompanying each, show the influence of different conditions upon the completeness of precipitation. A solution containing 0.0794 gram of bismuth per cubic centimeter in nitric acid was used in all cases.

I. VARYING RATIO OF $\text{Bi}(\text{NO}_3)_3$ TO $\text{K}_3\text{Co}(\text{CN})_6$.

	Temperature.	$\text{Bi}(\text{NO}_3)_3$, cc.	Half-normal $\text{K}_3\text{Co}(\text{CN})_6$, cc.
1	cold	5	15
2	"	3	15
3	"	1	15
4	hot	5	15
5	"	3	15
6	"	1	15

All filtrates showed a trace of bismuth with $(\text{NH}_4)_2\text{S}$: Greater in 4, 5, and 6, than in 1, 2, and 3; deepest in 1 and 4; least in 3 and 6, respectively. The insolubility is therefore increased by an excess of $\text{K}_3\text{Co}(\text{CN})_6$.

II. VARYING VOLUME. RATIO OF $\text{Bi}(\text{NO}_3)_3$: $\text{K}_3\text{Co}(\text{CN})_6$ CONSTANT.

	$\text{Bi}(\text{NO}_3)_3$, cc.	H_2O , cc.	$\text{K}_3\text{Co}(\text{CN})_6$, cc.
1	5	5	15
2	3	7	9
3	1	9 (+ $\text{H}\bar{\text{A}}$)	3 also,
[4	1	9	6]

Number 3 is very incomplete. Filtrate gave large precipitate with ammonium carbonate. 1, 2, and 4 showed only a trace of bismuth with $(\text{NH}_4)_2\text{S}$. Comparison of 3 and 4 shows the effect of increasing the amount of $\text{K}_3\text{Co}(\text{CN})_6$.

III. CONSTANT VOLUME.

	Bi(NO ₃) ₃ . cc.	H ₂ O(+H \bar{A}). cc.	K ₃ Co(CN) ₆ . cc.
1	5	5	15
2	3	12	10
3	1	19	5
4	1	21	3

In 1, 2, and 3 the ratio of K₃Co(CN)₆ to Bi(NO₃)₃ increases with the dilution. Filtrate from 3 contained 10 per cent. of the bismuth; filtrate from 4 contained 57 per cent. of the bismuth. In 1 and 2, the filtrates showed a trace of bismuth with (NH₄)₂S, greater in 2 than in 1, showing that the completeness of the precipitation increases with the concentration.

A RAPID METHOD FOR THE DETERMINATION OF CARBON IN IRON OR STEEL BY COMBUSTION.

BY GEO. WM. SARGENT.

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THE part taken by the carbon in determining the utility of steel or iron, especially the effect of slight changes in the quantity, impresses one with the need of exercising the greatest care that its estimation may be accurately made, and yet the large number of determinations required in a limited time calls for greater speed in their accomplishment.

The color method of Eggertz is probably the most rapid, but its application is so limited that it is scarcely used outside of regular furnace work where straight steels only are encountered, and the steel has undergone the same treatment, consequently the carbon is present in always the same condition. The advent of alloys of nickel, chromium, tungsten, molybdenum, titanium, etc., with iron, forces even the furnace chemist back to the most reliable method,—that of the combustion, in oxygen, of the carbon residue from the solution of the drillings. During the past three months the results obtained in this laboratory, by this method somewhat modified, have been so eminently gratifying with regard to accuracy, rapidity, and simplicity of the apparatus used, that I believe it worthy the attention of other chemists.

The apparatus as shown by the accompanying cut consists of, beginning on the right, a small copper or platinum spiral, water-jacketed at each end to prevent the burning of the rubber con-