

ART. II. — *The Influence of Hydrochloric Acid on the Precipitation of Cuprous Sulphocyanide*; by R. G. VAN NAME.

[Contributions from the Kent Chemical Laboratory of Yale University.—CV.]

IN a previous contribution to this Journal* the writer gave the results of a series of experiments upon the estimation of copper by precipitating and weighing as cuprous sulphocyanide. It was concluded from this work that the process did not lose greatly in accuracy even when quite large amounts of sulphuric or hydrochloric acid were present. In discussing the results obtained, however, no distinction was made, as should have been done, between free acid originally present in the solution and that remaining in the free state after the addition of the precipitants, ammonium bisulphite and ammonium sulphocyanide.

With hydrochloric acid the effect of the bisulphite, as will be shown, is to convert a definite quantity of acid into ammonium chloride, so that by increasing the bisulphite the free acid present when the copper is precipitated may be diminished to any desired extent.

The results obtained by precipitating copper in solutions containing various amounts of hydrochloric acid, weighing as cuprous sulphocyanide, and determining the copper in the filtrate, are given in Table I.

In neutral or faintly acid solutions cuprous sulphocyanide is precipitated in a very finely divided state and often shows a tendency to pass through the filter with the wash water as soon as the latter becomes nearly free from dissolved salts. This may be prevented by washing with a salt solution. For this reason the precipitates were washed with decinormal ammonium sulphocyanide, a medium in which cuprous sulphocyanide is even less soluble than in pure water.

An electrolytically standardized copper sulphate solution of about $\frac{1}{3}$ normal strength was measured out in portions of 50^{cm}³ for the first seven determinations. For the last four, like quantities of approximately $\frac{1}{20}$ normal copper sulphate were taken. The required amount of strong hydrochloric acid of specific gravity 1.17–1.18 was then added, followed, after diluting, by ammonium bisulphite and ammonium sulphocyanide in the order named, the last in measured portions of a standardized decinormal solution. The ammonium bisulphite solution was prepared by saturating aqueous ammonia with sulphur dioxide.

After precipitation the mixture was allowed to stand for

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TABLE I.
Final volume 200^{cm}³.

	Cu taken, gm.	HCl sp. grav. 1.17-1.18. cm ³ .	HNH ₄ SO ₃ sat. sol. cm ³ .	NH ₄ SCN approx. %/10. cm ³ .	Cu ₂ S ₂ (CN) ₂		Error, gm.	Cu in filtrate and NH ₄ SCN washings.		Cu in alcohol washings.		Total Cu found, gm.
					found, gm.	Calc. as Cu, gm.		grav. gm.	color. gm.	grav. gm.	color. gm.	
1.	.3163		5	60	.6085	.3180	+ .0017					.3180
2.	.3163	2	5	60	.6076	.3176	+ .0013	.0001	.00005	.0001	none	.3177
3.	.3163	4	5	60	.6083	.3179	+ .0016	.0000	.00006	.0001		.3181
4.	.3163	6	5	60	.6072	.3173	+ .0010	.0001	.00015	.0001	.00004	.3175
5.	.3163	8	5	60	.6081	.3178	+ .0015	.0002		.0000	.00007	.3181
6.	.3163	8	5	60	.6078	.3177	+ .0014	.0003	.0005	.0000	.00009	.3183
7.	.3163	12	5	60	.6069	.3172	+ .0009	.0004	.0004	.0002	.00002	.3176
8.	.0793	12	5	120	.1521	.0795	+ .0002	.0002	.00018		.00008	.0798
9.	.0793	25	5	120	.1512	.0790	- .0003	.0008	.00054		.00004	.0796
10.	.0793	12	2	120	.1518	.0793	.0000					.0801
11.	.0793	25	2	120	.1495	.0781	- .0012					.0798

Cu in NH₄SCN washings, color. gm.

Cu in alcohol washings, color. gm.

Cu in filtrate, color. gm.

Cu in NH₄SCN washings, color. gm.

Cu in alcohol washings, color. gm.

forty-eight hours or more before filtering, the final volume being in every case 200^{cm}³.

The precipitates were collected upon asbestos in a perforated platinum crucible, washed thoroughly with a decinormal solution of ammonium sulphocyanide and then with alcohol to remove any excess of the ammonium sulphocyanide, dried at 105° and weighed. It should be mentioned in this connection that no distinct instance of the apparent tendency of cuprous sulphocyanide to increase slightly in weight on prolonged heating at 110°, described in the article before referred to, was noticed during the present investigation.

The tests for copper in the filtrates were made by evaporating the solution with nitric acid to a small bulk, heating in a platinum crucible over a radiator to expel sulphuric acid and decompose interfering substances, dissolving the residue in nitric acid, filtering, electrolyzing and weighing the copper.

As the gravimetric results thus obtained were not sufficiently accurate for small amounts of copper, the copper was also determined by the following colorimetric method.

The electrolytic deposit was dissolved in nitric acid and the solution, contained in a small beaker of about 15^{cm}³ capacity placed against a white background, was neutralized with ammonia and made faintly acid with acetic acid. A dilute solution of potassium ferrocyanide was then added, a few drops at a time, until no further deepening of the brown color was observed. Another beaker of the same size containing the same amount of potassium ferrocyanide was placed beside the first, and after diluting its contents to a like volume a copper sulphate solution containing .00025 gm. of copper per cubic centimeter was added drop by drop from a pipette graduated to hundredths of a cubic centimeter until the brown color was identical with that in the first beaker. With amounts of copper less than .0001 gm., this method is correct to within .00002 gm. Its accuracy, however, naturally grows less as the amount of copper increases. The results obtained by the gravimetric and colorimetric methods appear in the table in adjacent columns.

Small amounts of copper were in nearly every case found in the alcohol washings, due to traces of the precipitate passing through the filter with the alcohol. Although it was difficult to entirely prevent loss in this way, in only a few instances was the quantity thus carried through large enough to cause distinct cloudiness in the filtrate. Water might have been used instead of alcohol to wash out the ammonium sulphocyanide, but the chances of loss seemed on the whole to be considerably less when alcohol was employed.

The values obtained by the weighing as cuprous sulpho-

cyanide show, with all but the largest amounts of acid, considerable positive errors. On comparing with these the values in the last column, which represent the total amounts of copper found and are obtained by adding to the figures in the sixth column the amounts of copper in the filtrates and washings as determined by the comparative method, it appears that the positive errors persist throughout. This seems to be due to the method of washing, which apparently fails to remove all the soluble impurities present, for in a number of cases where water alone was used to wash precipitates obtained from these same solutions the results were close to the theory. The use of this method of washing is however justified in this case because it reduces the chances of mechanical loss to a minimum, and accuracy in determining the amounts of copper precipitated is for the present purpose less desirable than accuracy in estimating the amounts remaining in solution.

In the first seven determinations the ammonium bisulphite and sulphocyanide were kept constant and the hydrochloric acid gradually increased. The effect is shown by the weights of copper in the filtrate, which rise fairly steadily to 0.005 gm. with the largest amounts of acid. A part of the hydrochloric acid, however, as already stated, reacts with the bisulphite forming ammonium chloride and liberating sulphur dioxide, and a similar reaction probably takes place with the ammonium sulphocyanide. As hydrochloric acid has a far greater solvent effect upon cuprous sulphocyanide than the equivalent amount of ammonium chloride, the result in both cases would be to diminish the amount of copper held in solution, unless, as hardly seems probable, the sulphur dioxide or sulphocyanic acid liberated is more active in holding up the copper than the corresponding amount of hydrochloric acid. That the weights of copper held in solution do actually decrease with an increase of either the bisulphite or sulphocyanide is readily proved.

The relation between the bisulphite and hydrochloric acid is apparent upon comparing the amounts of copper in the filtrates of the last four determinations of the table. The conditions under which Nos. 8 and 9 were made were respectively the same as those for Nos. 10 and 11 except that the quantity of bisulphite solution used was 5^{cm} for the first pair and 2^{cm} for the second. The losses are distinctly greater with the smaller amount.

Increasing the ammonium sulphocyanide while the bisulphite and hydrochloric acid remain constant has a similar effect. For the first seven experiments of the table the amount of ammonium sulphocyanide theoretically required was about 50^{cm} of the decinormal solution. The excess present was therefore about 10^{cm} or 0.076 gm. of the dry salt. In Nos. 8

and 9 the theory required about 13^{cm^3} of the decinormal solution, and the excess was consequently 107^{cm^3} or 0.815 grm. Making due allowance for the large amounts of acid present in these two experiments, the losses are much less than in the preceding ones.

As the reaction between the bisulphite and hydrochloric acid gives rise to a gaseous product (sulphur dioxide), it would naturally be expected that equilibrium would only be reached when one or the other of the reagents was nearly exhausted. If this is true, the measure of the amount of hydrochloric acid which can be converted into ammonium chloride by a definite quantity of bisulphite solution is the weight of combined ammonia which the latter contains. This value was found to be 0.1757 grm. per cubic centimeter for the bisulphite solution used in the above experiments. This means that if equal quantities of the bisulphite solution and of hydrochloric acid of sp. grav. 1.18 act upon one another, nearly nine-tenths of the acid may be converted into ammonium chloride. It is, however, not necessary to assume that this reaction is complete under the conditions of the experiments of the table. If with a given amount of hydrochloric acid it progresses farther when the quantity of bisulphite is increased, the results are sufficiently explained.

The limit of the reaction between the ammonium sulphocyanide and hydrochloric acid is entirely indefinite, but an increase in the amount of this salt must, as in the case of the bisulphite, cause the neutralization of a greater amount of acid and thus bring about a more complete precipitation of the copper. Very probably, the reduction in the solubility of the precipitate in the acid solution caused by the presence of an excess of ammonium sulphocyanide,* also contributes to this effect.

From these results it is evident that even in strongly acid solutions the copper may be almost completely precipitated by sufficiently increasing the amounts of ammonium bisulphite and sulphocyanide. As far as could be judged from a limited number of determinations made in sulphuric acid solution, the above holds true for sulphuric as well as hydrochloric acid. Cuprous sulphocyanide is, however, somewhat soluble in solutions of ammonium salts, and in cases where the amount of acid is very large this may become an important factor.

The solubility of cuprous sulphocyanide in various solutions is shown in the following table, but the figures must be understood to be only approximate. Weighed amounts of cuprous sulphocyanide prepared by precipitation in the usual way,

* See Table II.

thoroughly washed, and dried at 105°, were allowed to stand in the solutions to be tested from 40 to 50 hours. After careful filtering through asbestos the copper in the clear filtrate was estimated by the battery or, in cases where the amount was small, by the colorimetric method described above.

TABLE II.
Volume of liquid, 200^{cm}³.

Cu ₂ S ₂ (CN) ₂ taken. gram.	HCl sp. grav.. 1.18 cm ³ .	NH ₄ SCN gram.	Cu in filtrate. gram.
0.3			0.00035
0.3			0.00040
0.3		10.	0.0050
0.25		1.52 $\left(\frac{n}{10}\right)$	0.00018
0.3		0.76 $\left(\frac{n}{20}\right)$	0.00007
0.3		0.19 $\left(\frac{n}{80}\right)$	0.00004
0.3	2		0.0019
0.3	2	2.5	0.0013
0.3	2	1.77*	0.0009
0.3	2	0.19	0.0006
	NH ₄ Cl gram.		
0.3	10		0.0031
0.3	10	0.19	0.00013
0.3	1 $\left(\frac{n}{10}\right)$ †		0.00045
0.3	1	0.19	0.00005

The solubility is lowest in dilute solutions of ammonium sulphocyanide, and the presence of a small amount of this salt lessens the solubility in hydrochloric acid, and in solutions of ammonium chloride. In decinormal ammonium chloride the solubility is greater than in ammonium sulphocyanide of like strength, but this order is reversed in more concentrated solutions.

The results of the investigation may be summarized as follows: In the presence of free‡ hydrochloric acid the precipitation of cuprous sulphocyanide by a small excess of ammonium sulphocyanide is incomplete, but not injuriously so unless the

* Equivalent to the amount of hydrochloric acid present.

† Approximately.

‡ By free acid is here to be understood that acid which remains in the free state after the interaction with the ammonium bisulphite.

amount of the concentrated acid exceeds about 0.5 per cent of the total volume. By employing a considerable excess of ammonium sulphocyanide the precipitation can be made practically complete, at least after a few hours standing, even when the amount of acid is several times the above figure. The use of a decided excess of the sulphocyanide is advisable not only in the presence of acid but also when the solution contains much ammonium salts, on account of the reduction in the solubility of the precipitate thus brought about.*

The result of an increase in the ammonium bisulphite in the presence of hydrochloric acid is, except for the liberation of sulphur dioxide, exactly the same as the effect produced by a partial neutralization of the acid by ammonia, namely, the formation of ammonium chloride at the expense of the acid. Unless the amount of acid thus neutralized is quite large, the solubility of the cuprous sulphocyanide in the ammonium salts formed is too small to interfere materially with the completeness of the precipitation. There is, moreover, no objection to the use of ammonia in addition to the bisulphite to neutralize an excess of acid, and where sulphur dioxide is employed in place of ammonium bisulphite, ammonia is in many cases desirable. If, finally, the amount of acid is very large it is unquestionably better to remove the greater part before precipitating the copper.

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* See the last four determinations of Table II.