CXLIX.—*The Action of Thiosulphates on Cupric Salts.*

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THE following investigation arose out of an observation of the late Henry Bassett, senior, that the filtrate from cuprous sulphide, precipitated by adding sodium thiosulphate to a hot acid solution of a cupric salt, contained a considerable quantity of pentathionic acid.

A considerable amount of work has been done on the interaction of sodium thiosulphate and metallic salts, especially by Vortmann, who (*Monatsh.*, 1886, **7**, 418) proposed to use this thiosulphate instead of hydrogen sulphide as a laboratory reagent, since copper, mercuric, and bismuth salts together with the chlorides of antimony, arsenic, and tin are converted into sulphides when warmed with excess of thiosulphate in acid solution.

The present communication is concerned with copper only. The reactions involved in this case are of particular interest, because they furnish an excellent method for precipitating copper quantitatively as cuprous sulphide and of separating it from cadmium and zinc and from other metals of analytical group IV. As a rule, a more perfect separation is obtainable than with hydrogen sulphide. The method is described in several text-books (Classen, "Ausgewählte Methoden der Analytischen Chemie," 1901, I, 73; Beringer, "Text-book of Assaying," 10th ed., 1906, p. 183; Fresenius, "Quantitative Analysis," 7th English ed., 1876, p. 459, where early references to the method are given).

The reduction of copper to the cuprous condition is accompanied by oxidation of thiosulphate to tetrathionate. This was shown by Rammelsberg (*Pogg. Ann.*, 1842, **56**, 321) in the case of potassium thiosulphate, and by Zettnow (*Z. anal. Chem.*, 1867, **6**, 438) in the case of the sodium salt. According to von Renesse (*Ber.*, 1877, **10**, 1682), the reaction is as follows :

$$2CuSO_4 + 3Na_2S_2O_3 = Cu_2S_2O_3 + Na_2S_4O_6 + 2Na_2SO_4.$$

Vortmann (*Monatsh.*, 1888, **9**, 165) stated that sulphuric acid is not produced as had been asserted independently by Sievert (*Pogg. Ann.*, 1842, **56**, 321) and Kessel (*Ber.*, 1877, **10**, 1677, 2000; 1878, **11**, 1581). None of these workers appears to have made quantitative determinations of the tetrathionate which is produced. C. and I. Bhaduri (*Z. anorg. Chem.*, 1898, **17**, 1) refer to Vortmann (*loc. cit.*, 1888), who obtained a bright yellow, crystalline salt to which he assigned the formula $3Cu_2S_2O_3,2Na_2S_2O_3,8H_2O$, and they give the following reaction as occurring when this salt is heated :

$$3Cu_2S_2O_3,2Na_2S_2O_3,8H_2O = 3Cu_2S + 2Na_2SO_4 + H_2SO_4 + 2S + 2SO_2 + 7H_2O.$$

We have arrived at this reaction from our bright yellow salt, which contains 6 instead of 8 molecules of water, and have found that the relative formula-weights of cuprous sulphide, sulphur, and sulphuric acid are exactly as 3 : 2 : 1. We have also made a quantitative determination of the amount of tetrathionate produced during the formation of the white salt, $Na_2S_2O_3,Cu_2S_2O_3,H_2O$, and find that it tallies with that required for the reaction

$$2CuCl_2 + 4Na_2S_2O_3 + H_2O = Na_2S_2O_3,Cu_2S_2O_3,H_2O + Na_2S_4O_6 + 4NaCl,$$

in which no sulphuric acid is produced.

Any sulphuric acid which may have been found by Sievert and Kessel was probably due to partial decomposition of one of the double salts. Von Renesse's reaction would suggest that cuprous thiosulphate is actually produced, but our work has shown that double salts are immediately formed and that cuprous thiosulphate itself, if it exists at all, is exceedingly unstable.

Investigation of the sodium cuprous thiosulphates formed in the reaction has thrown some interesting sidelights on other sodium cuprous double salts.

When *N*-solutions of cupric chloride, sulphate, or nitrate are mixed with *N*- or 2*N*-solutions of sodium thiosulphate in proportions to satisfy the equation

$$4Na_2S_2O_3 + 2CuA_2 = Na_2Cu_2(S_2O_3)_2 + Na_2S_4O_6 + 4NaA,$$

a yellow solution is produced which soon deposits bright yellow, prismatic crystals at the ordinary temperature. This yellow salt in the case of copper nitrate corresponds exactly with the formula $2Na_2S_2O_3,3Cu_2S_2O_3,6H_2O$. When prepared from cupric chloride solution, the yellow double thiosulphate first formed soon changes into a white salt, the change being complete in a few hours. This white salt is crystalline (prisms) and perfectly homogeneous under the microscope, but always contains a considerable quantity of chloride. The analytical figures agree perfectly with a compound $Na_2Cu_2(S_2O_3)_2,H_2O$ containing varying amounts of isomorphous $Na_2Cu_2Cl_4,H_2O$ in solid solution. This particular complex cuprous chloride does not appear to have been prepared, although a number of others have been (see Abegg's "Handbuch," 1908, II, i, 550). The amount of chloride present in these preparations is always greater than the amount of sulphate which in similar circumstances appears in the yellow salt obtained from copper sulphate. It is less in presence of free hydrochloric acid than in its absence. These are both results which might be expected. It is well known that solid cuprous sulphate cannot exist in presence of water, as it breaks up into cupric sulphate and metallic copper. As the "neutral part" of a complex ion, it is more stable and the opportunity of entering into solid solution in the double thiosulphate would still further protect it. No double cuprous sulphates appear to have been actually prepared, but it seems clear that they are capable of existence under favourable conditions. The existence of complex cuprous sulphate-ions in aqueous solution has been proved by Abel (*Z. anorg. Chem.*, 1901, **26**, 361).

Double nitrates practically only exist when one of the constituent metals is tervalent; hence the freedom from contaminating nitrate in the double thiosulphate prepared from cupric nitrate is not surprising. The tetrathionate formed in the reaction might have had some tendency to form similar solid solutions to the above, but no evidence for this has been found, although specially looked for.

The formation of solid solutions of sodium cuprous chloride in sodium cuprous thiosulphate is of interest in connexion with the compounds $CuX,NH_4X,4(NH_4)_2S_2O_3$ ($X = Cl,Br,I,CNS$) obtained by Rosenheim and Steinhäuser (*Z. anorg. Chem.*, 1900, **25**, 103) by the action of saturated solutions of ammonium thiosulphate on cuprous chloride, etc. (see also Canneri and Luchini, *Gazzetta*, 1922, **52**, ii, 261, for similar sodium compounds).

The following list of double cuprous thiosulphates, with references, is given by Vortmann (*loc. cit.*, 1888):

(1) Bright yellow salt, first obtained by von Hauer (*Sitzungsber. Akad. Wiss. Wien*, 1854, [ii], **13**, 443) and erroneously considered to be $Cu_2S_2O_3,2H_2SO_3$. This undoubtedly is the same salt to which Vortmann assigns the formula $2Na_2S_2O_3,3Cu_2S_2O_3,8H_2O$. (2) A white salt obtained by Russel (*Chem. Ztg.*, 1894, **9**, 233) from copper chloride—formula $Na_2S_2O_3,Cu_2S_2O_3,H_2O$. He does not give details of preparation or analysis. (3) A pale greenish-yellow salt consisting of very small prisms, obtained by Vort-

mann from copper sulphate—formula $Na_2S_2O_3,Cu_2S_2O_3,3H_2O$. (4) $2Na_2S_2O_3,Cu_2S_2O_3,4H_2O$. (5) $2Na_2S_2O_3,Cu_2S_2O_3,2H_2O$. (6) $3Na_2S_2O_3,Cu_2S_2O_3,2H_2O$. (7) $4Na_2S_2O_3,Cu_2S_2O_3,6H_2O$. Apparently Lenz (*Annalen*, 1841, **40**, 99), Rammelsberg, Russel, Jochun (*Inaug. Diss. Berlin*, 1885), and Vortmann agree as to the existence of the last four. C. and I. Bhaduri (*loc. cit.*) quote all these and three more double salts.

We have confirmed the existence of the first three salts. We find (1) contains only 6 molecules of water, (2) is always contaminated with chloride, whilst (3) agrees in every particular with Vortmann's description and analysis.

We have reason to believe that several of the other salts are merely mixtures, and are hoping soon to complete our study of the system $Na_2S_2O_3$–$Cu_2S_2O_3$–H_2O.

The mother-liquors from the preparations of double thiosulphates always contain excess of thiosulphate in addition to sodium tetrathionate and nitrate (chloride or sulphate), and some copper is still present in solution. This was the case in all experiments made with varying proportions and concentrations of the reactants. Some atmospheric oxidation of cuprous copper appears to occur during the reaction, but as long as sodium thiosulphate is in excess the cupric copper will be again reduced.

In all experiments in which acid was used there was strong evidence of the formation of pentathionic acid. This was traced to the action of mineral acid liberating sulphur from sodium thiosulphate. Some of this sulphur unites with the tetrathionate present. Pentathionic acid is very stable in presence of hydrogen-ions.

We are endeavouring to prepare double pentathionates starting with concentrated solutions of cupric nitrate and ammonium thiosulphate. When these solutions are mixed, a light yellow liquor is formed from which a bright yellow salt separates. This very rapidly changes to a white, crystalline salt having the formula $3(NH_4)_2S_2O_3,2Cu_2S_2O_3,H_2O$.

All the above double thiosulphates are decomposed by mineral acids, slowly in the cold, more quickly on warming, with formation of cuprous sulphide, sulphur, sulphurous and sulphuric acids. When using thiosulphate for precipitating copper quantitatively as cuprous sulphide, the sodium thiosulphate is usually added to the hot acid solution containing copper, and the formation and the decomposition of the sodium cuprous thiosulphate occur practically simultaneously. The filtrate from the precipitated cuprous sulphide and sulphur contains large amounts of polythionates, mainly pentathionate, but possibly some unaltered tetrathionate as well. If other metals are to be estimated, it is frequently advisable first to remove these polythionates by concentrating the filtrate, adding strong nitric acid, and filtering off the liberated sulphur after digesting the mixture for some time so as to render the sulphur capable of filtration. If this is not done, sulphur will be liberated from the pentathionate on addition of ammonia, and this may cause trouble.

Those who have had much experience in this method of separating copper will have noticed that a trace of copper is frequently left in solution, although its amount is usually far too minute to be of any consequence. We have found that this occurs most readily from chloride solutions, less readily from sulphate, and not at all with nitric acid solutions, provided too much acid is not present. The explanation is to be sought in the tendency to form complex cuprous chlorides or sulphates. These cannot decompose to give cuprous sulphide; only the complex cuprous thiosulphate can do that. At any moment there will be some sort of equilibrium in the solution between the complex cuprous thiosulphates and chloride or sulphate. As the former decomposes and more sodium thiosulphate is added, the amount of complex cuprous chloride or sulphate remaining in the solution will rapidly diminish, but a trace will probably remain. Comparative experiments have shown that the most suitable acid to use in this method of estimating copper is sulphuric acid—because nitric acid, if above half-normal concentration, causes slight oxidation of copper when the solution is at the boiling point, whereas sulphuric acid, if used in considerable excess and heated with any copper salt before adding the thiosulphate, prevents the formation even of the complex cuprous chlorides, and no trace of copper appears in the filtrate from the black precipitate. If hydrochloric acid is used instead of sulphuric, it may be exceedingly difficult to precipitate all the copper.

EXPERIMENTAL.

Action of Sodium Thiosulphate on Cupric Chloride in Presence of Hydrochloric Acid.

Normal solutions of the above were mixed together in the volume proportions 2 : 1 : 1. A white, crystalline salt appeared after a few hours and after a few days the salt was drained through a Büchner funnel, washed with a little water, then with alcohol, and air-dried (Found: Na = 11·35; Cu = 31·25; S = 27·30. 90% of $Na_2Cu_2(S_2O_3)_2,H_2O$ + 10% of $Na_2Cu_2Cl_4,H_2O$ requires Na = 11·35; Cu = 31·35; S = 27·75 per cent.). Chlorine and water, the presence of which was proved qualitatively, were not estimated.

The prismatic crystals, examined under the microscope, were seen to be colourless and homogeneous. In these and in subsequent experiments copper was precipitated as cuprous sulphide by warming with sulphuric acid and was weighed either as such or after ignition to oxide; the sulphur was estimated as barium sulphate, thiosulphate by iodine titration, and sodium as sulphate in a platinum dish. In every case, except with the double thiosulphates prepared from cupric nitrate, it was found that a small amount of copper remained with the fused sodium sulphate. This was estimated and allowed for.

Action of Sodium Thiosulphate on Cupric Chloride in Absence of Acid.

Normal solutions were mixed in the volume proportions

$$Na_2S_2O_3 : CuCl_2 : : 2 : 1$$

and left at room temperature. A bright yellow precipitate soon separated, but this disappeared within two days, giving place to white crystals. After five days, the white deposit became slightly blue on the surface owing to atmospheric oxidation. This small blue portion having been removed, the remainder was washed with water and with alcohol and dried in the air (Found: Na = 11·55; Cu = 31·89; S_2O_3 = 44·66; Cl = 7·42; H_2O (by diff.) = 4·48. 82·6% of $Na_2Cu_2(S_2O_3)_2,H_2O$ + 17·4% of $Na_2Cu_2Cl_4,H_2O$ requires Na = 11·56; Cu = 31·90; S_2O_3 = 44·58; Cl = 7·42; H_2O = 4·52 per cent.).

Owing to the fact that the salt is decomposed at temperatures below 100°, a direct estimation of the water was not made. The salt, when heated in a hard glass tube, after discharging water, sulphur dioxide, and excess of sulphur as vapour, left a residue (75·28 per cent.) consisting chiefly of sodium sulphate and cuprous sulphide but containing also sodium chloride. If the whole of the copper from $Na_2Cu_2Cl_4,H_2O$ is converted into cuprous sulphide, the residue by theory should be 74·33 per cent.; if none of it is so converted, the residue should be 76·39 per cent.; if half of it is converted, the residue should be 75·36 per cent.

The fact, previously noted, that copper is found in the fused sodium sulphate (after treatment with acid and precipitation of cuprous sulphide) is explained by supposing that this double chloride escapes complete conversion into cuprous sulphide.

Examination of the Filtrate from the White Salt.—Fifty c.c. of *N*-cupric chloride were left for six days with 100 c.c. of *N*-sodium thiosulphate, and the whole of the filtrate was then collected (136 c.c. without wash water). The copper in the precipitate, in the wash water, and in aliquot portions of the filtrate was estimated, the results agreeing well with the known weight in the original solution. Five estimations were made each with 10 c.c. of the filtrate, giving sulphur (as thiosulphate) 0·0620, sulphur (total) 0·2054, copper 0·0488, chlorine 0·1077, and sodium 0·1477 gram.

Assuming chlorine to be present as cuprous chloride and sodium chloride, and sodium as sodium chloride, sodium thiosulphate, and sodium tetrathionate, these figures show that the amounts of sodium and of sulphur in excess of those required to produce the cuprous chloride, sodium chloride, and sodium thiosulphate are 0·0511 gram and 0·1434 gram, respectively. The theoretical ratio for sodium tetrathionate is 0·0511 of sodium to 0·1422 of sulphur. This affords evidence for the fundamental reaction:

$$4Na_2S_2O_3 + 2CuCl_2 = Na_2Cu_2(S_2O_3)_2 + Na_2S_4O_6 + 4NaCl.$$

Further evidence was obtained by preparing the salt $Na_2S_4O_6,2H_2O$ and comparing its properties with those of filtrates from double sodium copper thiosulphate precipitates.

The actual amount of sodium tetrathionate produced from a mixture of 50 c.c. of *N*-cupric chloride and 50 c.c. of 2*N*-sodium thiosulphate was estimated by Kurtenacker and Fritsch's method (*Z. anorg. Chem.*, 1921, **117**, 202), using standard potassium cyanide, whereby tetrathionate is reconverted into thiosulphate. The results confirmed our suspicion that oxidation by air and subsequent reduction of the copper by thiosulphate take place, since the ratio of tetrathionate to copper was found to be higher than would have been the case if such alternating action had not occurred. In the examination of the above filtrate it was proved that one-quarter of the copper originally taken had been subjected to this alternating action, since the total copper corresponded to 1·6 as compared with 2 grams of tetrathionate sulphur found.

Examination of the Temporary Yellow Precipitate.—This examination was made after establishing the formula of the permanent yellow precipitates formed when copper sulphate and copper nitrate are used. The precipitate formed by mixing 50 c.c. of *N*-cupric chloride with 50 c.c. of 2*N*-sodium thiosulphate was collected after standing for five hours, drained with suction, washed with water and with alcohol, and air-dried as in all other similar preparations [Found: Cu = 31·74; S_2O_3 = 47·23; Cl = 2·26; residue on heating = 69·19. 70% of the yellow salt

$$(2Na_2S_2O_3,3Cu_2S_2O_3,6H_2O) +$$

30% of the white salt (analysis given above; 17·4% double chloride) requires Cu = 32·84; S_2O_3 = 47·72; Cl = 2·23; residue after heating = 69·27 per cent.].

Portions of this precipitate, examined under the microscope, were seen to consist of a mixture of yellow and white crystals.

It is evident that the change from the yellow to the white salt begins to take place at an early stage, although the yellow colour requires about two days to disappear completely. Earlier attempts to prepare white salts when using copper sulphate and copper nitrate were unsuccessful, but if 2*N*-copper nitrate is mixed with 4*N*-thiosulphate, Vortmann's pale yellow salt,

$$Na_2S_2O_3,Cu_2S_2O_3,3H_2O,$$

will be produced at room temperature.

Action of Sodium Thiosulphate on Copper Sulphate.

One hundred c.c. of *N*-sodium thiosulphate, mixed with 50 c.c. of *N*-copper sulphate, gradually deposited yellow crystals for eight days. The yield was 53 per cent., that is, 47 per cent. of the copper remained in the filtrate—and the ratio of thiosulphate in this filtrate to that from the white salt was 3 : 2. The air-dried yellow crystals were seen under the microscope to be perfectly homogeneous [Found : Na = 8·20; Cu = 33·49; S (as S_2O_3) = 26·58; S (as SO_4) = 0·66; S (total) = 27·24; residue after heating = 67·22. 93% of $2Na_2S_2O_3,3Cu_2S_2O_3,6H_2O$ + 7% of

$$2Na_2SO_4,3Cu_2SO_4,6H_2O$$

requires Na = 8·13; Cu = 33·71; S (total) = 27·16; residue after heating = 67·02 per cent.].

Action of Sodium Thiosulphate on Copper Nitrate.

One hundred c.c. of *N*-sodium thiosulphate, mixed with 50 c.c. of *N*-copper nitrate, deposited yellow crystals as in the last case, but here no nitrate could be detected in the yellow salt either by brucine or by other tests (Found : Na = 8·00; Cu = 33·28; S = 27·86; residue after heating = 67·41. $2Na_2S_2O_3,3Cu_2S_2O_3,6H_2O$ requires Na = 8·06; Cu = 33·39; S = 28·04; residue after heating = 67·70 per cent.).

These results correspond with the pure salt. The residue after heating strongly consists entirely of cuprous sulphide and sodium sulphate. Larger quantities of this salt were prepared for subsequent experiments.

Properties of Disodium Tricuprous Thiosulphate.—This salt crystallises in bright yellow needles, those deposited during the early stages of the preparation being larger than those forming later on. If left in presence of the mother-liquor, the deposit will remain bright yellow for several weeks. The air-dried salt, if perfectly free from traces of tetrathionate, appears to be quite permanent, but if the crystals are not well washed (about 200 c.c. of water for a 40-gram yield), the salt will slowly decompose and eventually become quite black. When the salt was strongly heated in absence of air, the decomposition was shown to agree with the reaction $3Cu_2S_2O_3,2Na_2S_2O_3,6H_2O = 3Cu_2S + 2Na_2SO_4 + H_2SO_4 + 2SO_2 + 2S + 5H_2O$. C. and I. Bhaduri (*loc. cit.*) arrived at the same reaction, assuming 8 instead of 6 molecules of water to be present.

The solubility of the salt in water at 10° appears to be 3 parts in 1000. After some time, a white cloud separates (possibly cuprous thiosulphate is formed and sodium thiosulphate dissolved). After twelve hours at 11°, the white suspension begins to hydrolyse —$Cu_2S_2O_3 + H_2O \longrightarrow Cu_2S + H_2SO_4$—after forty-eight hours, the hydrolysis has proceeded to the extent of 52 per cent. When the temperature is raised to 80°, this brown mixture becomes black and the extent of hydrolysis reaches 75 per cent., whilst after boiling for ten minutes it reaches 95 per cent.

The action of acids and of sodium thiosulphate—separately and together—on the salt has been studied with the view of finding a method which completely removes copper as cuprous sulphide from solution. From these experiments, it appears that the complete separation cannot be effected in presence of hydrochloric acid, but that it can be effected by excess of sodium thiosulphate in presence of nitric acid, provided the latter is not highly concentrated. The desired result can also be attained in sulphuric acid solution if sufficient acid be present to prevent the formation of complex double chloride or (less readily formed) double sulphate.

The Action of Ammonium Thiosulphate on Copper Nitrate.

On mixing $5N$-ammonium thiosulphate and $2{\cdot}5N$-cupric nitrate in equal volumes, a bright yellow liquid was immediately produced, but no deposit was obtained after twenty hours' standing. Solutions of the preceding strength were concentrated and cooled separately, and then mixed together; after a short time, solidification occurred quite suddenly. The purple-grey, crystalline solid obtained was proved to contain traces of products of decomposition.

To another portion of the bright yellow liquid above mentioned an equal volume of alcohol was added. This immediately produced a bright yellow, crystalline solid, which became white in less than two minutes; it was separated, washed, and air-dried. (The wash-water was bright yellow and on the addition of alcohol again deposited white particles.) When dry, the white product assumed a pale buff colour [Found: $NH_4 = 11{\cdot}54$; $Cu = 27{\cdot}25$ (as Cu_2S), $27{\cdot}09$ (as CuO); $S_2O_3 = 58{\cdot}34$, $58{\cdot}34$; residue after heating $= 34{\cdot}12$. $3(NH_4)_2S_2O_3,2Cu_2S_2O_3,H_2O$ requires $NH_4 = 11{\cdot}49$; $Cu = 27{\cdot}02$; $S_2O_3 = 59{\cdot}57$; residue on heating $= 33{\cdot}83$ per cent.].

These figures indicate triammonium dicuprous thiosulphate. The proportions in which the solutions were mixed were, as in all previous cases here cited, such as to favour the production of a double salt in *equi*molecular ratio. This salt appears to resemble the former white salt in crystallising with 1 molecule of water. The residue after strongly heating is pure cuprous sulphide. The filtrate from the separated salt contains ammonium tetrathionate.

Formation of Pentathionic Acid.

When copper chloride, sulphate or nitrate, is treated with excess of sodium thiosulphate in presence of any mineral acid, there is evidence to show that pentathionic acid is produced and remains in solution after cuprous sulphide and excess of sulphur have been thrown out by boiling. This must be due to interaction between sodium tetrathionate, sodium thiosulphate, and the mineral acid: $Na_2S_4O_6 + Na_2S_2O_3 + 4HA' = H_2S_5O_6 + 4NaA' + H_2O + SO_2$. The tests applied, which were those tabulated by Tamakatsu and Smith (T., 1880, **37**, 608) and by Debus (T., 1888, **53**, 297), gave positive results with the solutions here considered and also with mixtures prepared by adding sodium thiosulphate and acids to sodium tetrathionate, prepared from sodium thiosulphate and iodine (von Klobukow, *Ber.*, 1885, **18**, 1871).

Tests which Differentiate Pentathionic Acid from Colloidal Sulphur.—It is well known that certain chemists have been sceptical as to the existence of pentathionic acid. The literature up to 1887 was summarised by Debus (*loc. cit.*) and since then further papers have appeared from Berthelot, Spring, Hertlein, Lang and Carson, Valeton, Casolari, Maclaurin, W. Fell, and recently a longer paper by Riesenfeld and G. W. Fell (*Z. anorg. Chem.*, 1921, **119**, 252). Among thirty authors, four only are sceptical, namely, Spring, Curtius, Pfeiffer, and Valeton. Valeton (*Chem. Weekblad*, 1907, **4**, 553) states that colloidal sulphur gives all the tests usually ascribed to pentathionates. We have confirmed this statement in so far as the following tests are concerned, which may be termed the " positive " tests of Debus :

1. Ammoniacal silver nitrate: immediate darkening (due to Ag_2S).
2. Caustic potash : immediate deposition of sulphur.
3. Ammonia alone : less rapid deposition of sulphur.
4. Ammonia containing H_2S : immediate deposition of sulphur.
5. Mercuric cyanide in aqueous ammonia : black precipitate forming slowly in the cold, rapidly on warming.

All these tests were equally successful with pentathionic acid (in presence of a trace of hydrochloric acid) and with colloidal sulphur prepared according to Svedberg (*Z. Chem. Ind. Kolloide*, 1909,

4, 49) (a concentrated solution of sodium thiosulphate is slowly added to concentrated sulphuric acid, the temperature being kept below 25°, and the precipitated sulphur is repeatedly centrifuged, separated, dissolved in water, reprecipitated by sodium chloride, and finally dissolved in pure water).

Among the " negative " tests given by Debus are: pentathionic acid gives *no* precipitate with HCl, $CuCl_2$, $FeCl_3$, $CuAc_2$, $CuSO_4$, or $Co(NO_3)_2$. We found this to be the case, but each of the above reagents gave an immediate precipitate of sulphur when added to the colloidal solution. Comparative experiments were also made with a number of other salts. The most delicate was that with didymium chloride; the merest trace of the tervalent cation precipitated sulphur from the colloidal solution, but a considerable amount failed to have any effect on pentathionic acid. Pentathionic acid, therefore, is unaffected by electrolytes provided the solution is not rendered alkaline. In this respect, it differs from colloidal sulphur. Another way to differentiate them is to boil each for a short time with hydrochloric acid and then apply Debus's " positive " tests involving alkali. It will be found that pentathionic acid responds to all the tests, and what *was* colloidal sulphur to none of them.

The solution containing pentathionic acid used in the above experiments was obtained by adding 10 c.c. of 2*N*-hydrochloric acid to 10 c.c. of *N*-cupric chloride, followed by 20 c.c. of 2*N*-sodium thiosulphate, concentrating to half the volume, and filtering from cuprous sulphide, the last two operations being repeated after the addition of another 10 c.c. of 2*N*-hydrochloric acid; a clear, colourless, acid solution remained. Valeton's statement may be modified by saying that pentathionic acid, when rendered alkaline, liberates colloidal sulphur.

Relative Stability of Pentathionic Acid and its Salts.—Watson Smith (T., 1883, **43**, 355) maintained that pentathionic acid is stable, but that its salts are not, since they readily decompose, yielding sulphur and tetrathionates. This difference between the acid and its salts was recognised by Debus (*loc. cit.*) and by other workers, including Riesenfeld and Fell (*loc. cit.*), who attempt to account for it on their theory, which involves " the hydrate of SO." This is stable in acid solution and polymerises to produce pentathionic acid. The theory appears to be a variant of Debus's hypothetical S_2O_2, which polymerises and then combines with water: $5S_2O_2 = 2S_5O_5$ and $H_2O + S_5O_5 = H_2S_5O_6$. Our interpretation of the matter is simply that the molecule of pentathionic acid is fairly stable, whilst its possible anions are very unstable. The following observations bear out this view:

i. On several occasions it was noticed that perfectly clear filtrates in Wackenroder preparations were rendered turbid by addition of pure water (dilution favouring ionisation).

ii. We find that any reagent that develops alkalinity immediately precipitates sulphur from pentathionic acid (salt formation).

iii. Solutions containing pentathionic acid in a slight excess of mineral acid slowly decompose in the cold with formation of sulphuric acid, deposition of sulphur, and evolution of sulphur dioxide, but in fairly concentrated mineral acid the solution may be boiled for several hours without separation of sulphur.

The potassium and barium salts were prepared by Lewis (T., 1881, **39**, 68), who found that the pure salts could be obtained from highly concentrated solution only, and Shaw (T., 1883, **43**, 351) obtained potassium pentathionate, apparently pure, only from his sixth and last crop of crystals. It seems to be a matter of great difficulty to obtain these simple pentathionates in the pure state.

These results are all in keeping with the theory of ionic dissociation coupled with the assumption that HS_5O_6' or S_5O_6'' (or both ions) is very unstable.

Summary.

1. Cupric salts are reduced at once to the cuprous state on adding excess of sodium thiosulphate. From normal or more concentrated solution, the yellow salt, $3Cu_2S_2O_3,2Na_2S_2O_3,6H_2O$, crystallises out rapidly. Sodium tetrathionate is simultaneously produced.

2. When copper nitrate is used, pure specimens of the yellow salt are obtained. With copper sulphate, the yellow salt contains $3Cu_2SO_4,2Na_2SO_4,6H_2O$ in solid solution. With copper chloride, the yellow salt soon gives place to the white salt,

$$Cu_2S_2O_3,Na_2S_2O_3,H_2O,$$

which invariably contains $Cu_2Cl_2,2NaCl,H_2O$ in solid solution. The yellow salt in this case was found to be a mixture containing some of the white salt.

3. The pure yellow salt is quite stable if kept dry and prepared perfectly free from adhering tetrathionate. When strongly heated, it yields cuprous sulphide and sodium sulphate, whilst sulphur, sulphur dioxide, and water are expelled.

4. A white salt, $2Cu_2S_2O_3,3(NH_4)_2S_2O_3,H_2O$, has been obtained from concentrated solutions containing copper nitrate and ammonium thiosulphate.

5. When copper salts in presence of excess of thiosulphates are heated with mineral acids, cuprous sulphide is precipitated, but this precipitation is not complete even after prolonged boiling if hydro-

chloric acid is employed. The reason for this appears to depend on the formation of the double chloride mentioned above, which cannot decompose into cuprous sulphide. The precipitation is complete if nitric acid is used, provided the acid concentration is less than *N*/2, and is complete with sulphuric acid, which should be fairly concentrated if any copper chloride is present.

6. In the above circumstances, pentathionic acid is produced through the interaction of thiosulphate, tetrathionate, and mineral acid.

7. We have examined previous work on pentathionic acid and its salts and have indicated some methods of differentiating pentathionic acid from colloidal sulphur. We conclude that the molecule $H_2S_5O_6$ is stable, especially in presence of high concentration of hydrogen-ions, but that its salts are very unstable, because they tend to ionise, and we believe the anions HS_5O_6' and S_5O_6'' to be very unstable.

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