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The Formation Conditions and the Properties of Copper, Zinc, Ammonium Sulfites*

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On the reaction of an ammonium sulfite solution with a mixed solution of cupric sulfate and zinc sulfate, ten or more complex sulfite salts have been identified by chemical analysis and X-ray diffraction, and their formation regions have been shown with equilateral triangle coordinates. Their crystallographic properties have been examined through optical observation and X-ray diffraction. Usually some of them are formed simultaneously, but sometimes only one of them is formed, depending on the reaction conditions. The newly-found compounds are as follows:

$Cu_2SO_3\cdot 7(NH_4)_2SO_3\cdot 9H_2O$	Tetragonal
$Cu_2SO_3\cdot ZnSO_3\cdot 6(NH_4)_2SO_3\cdot 10H_2O$	Tetragonal
$Cu_2SO_3\cdot 2ZnSO_3\cdot 5(NH_4)_2SO_3\cdot 12H_2O$	Monoclinic
$Cu_2SO_3\cdot 4ZnSO_3\cdot 3(NH_4)_2SO_3\cdot 12H_2O$	Hexagonal

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The authors have already proposed a new hydrometallurgical process for copper, a process includes the sulfatizing roasting of copper sulfide ores, the extraction of cupric sulfate, the reduction of cupric sulfate with ammonium sulfite, the separation of metallic copper, and the recovery of ammonium sulfate.1) In the case of simple sulfide ores, there is no technical problem in the process, but in the case of complex sulfide ores containing zinc, lead and other heavy metals besides copper, the reduction of cupric sulfate proceeds unsatisfactorily. The reason for this trouble seems to be due to the formation of inactive complex copper-zinc-ammonium sulfites, which are easily produced with both metal sulfates and ammonium sulfite in an aqueous solution.

In the present paper, an effort will be made to determine the composition, the properties, and the formation conditions of the complex sulfites.

Experimental

Procedure.—A mixed solution of cupric sulfate and zinc sulfate, prepared by the dissolution of an E. P. reagnt, was placed in a 200-ml. Erlenmeyer flask; then a freshly-prepared ammonium sulfite solution was added drop by drop to the sulfate solution until the three component salts reach a desirable mole fractions. The mixture was vigorously shaken, sealed tightly and allowed to stand for 1—20 days. The crystals which formed were separated from the solution, washed with water and then with methyl alchohl, and dried for 30 min. in a vacuum.

Analysis.—The complex salts formed in the reaction were dissolved by treatment with bromine water. The solution was then boiled on a sand bath until the bromine was completely expelled. The copper and zinc contents were determined by iodometry and by chelatometry respectively. The ammonia content was determined by alkalimetry after distillation, and sulfurous acid, as barium sulfate by oxidation.

Results and Discussion

Complex Sulfite Salts and the Conditions of Their Formation.—When an ammonium sulfite solution is added to a mixed solution of the two metal sulfates, an amorphous, yellowish-brown precipitate is immediately formed, this then gradually changes into transparent crystals. When the mixture is vigorously stirred, the amorphous precipitate tends to coagulate into a plastic mass, one which seems very stretchable without any trace of recovery. If more than a 0.78 mol. fraction of the ammonium sulfite solution is added, the amorphous precipitate is dissolved again, and a wine-red solution is obtained.

The complex salts formed in the reaction are listed in Table I, among which the compounds from III to VI have not been previously reported in the literature; their analytical values are shown in Table II. Besides, the existence of other complex sulfites, XII, XIII, XIV and XV, were recognized by means of X-ray diffraction, but regrettably, these compounds could not be isolated or identified.

TABLE I. THE COMPLEX SALTS FORMED IN THE REACTION

Compd. No.	Chemical formula
I	$7Cu_2SO_3 \cdot 2CuSO_3 \cdot 3(NH_4)_2SO_3 \cdot 24H_2O$
II	$Cu_2SO_3 \cdot 7(NH_4)_2SO_3 \cdot 10H_2O$
III	$Cu_2SO_3 \cdot 7(NH_4)_2SO_3 \cdot 9H_2O$
IV	$Cu_2SO_3 \cdot ZnSO_3 \cdot 6(NH_4)_2SO_3 \cdot 10H_2O$
V	$Cu_2SO_3 \cdot 2ZnSO_3 \cdot 5(NH_4)_2SO_3 \cdot 12H_2O$
VI	$Cu_2SO_3 \cdot 4ZnSO_3 \cdot 3(NH_4)_2SO_3 \cdot 12H_2O$
VII	$ZnSO_3 \cdot (NH_4)_2SO_3$
VIII	$Cu_2SO_3 \cdot (NH_4)_2SO_3$
IX	$Cu_2SO_3 \cdot CuSO_3 \cdot 2H_2O$ (Chevreul's salt)
X	$ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ (Tutton's salt)
XI	$ZnSO_3 \cdot 2.5H_2O$
XII	Unknown (Cotton-like crystal)
XIII	Unknown (Calcite-like crystal)
XIV	$Cu_2SO_3 \cdot 5ZnSO_3 \cdot (NH_4)_2SO_3 \cdot 18H_2O$
XV	Unknown (Chevreul's salt-like crystal)
XVI	Non-recoverable plastic mass

The region where the complex salts are formed is shown in Figs. 1(a) and (b). The three component salts are placed at the vertexes of the coordinates, while the mole fractions of their salts in the original mixture are indicated on the internal points. The regions where the complex salts are formed are regularly distributed in the order of II, III, IV, V and VI, from the region rich in ammonium sulfite to the region of little ammonium sulfite.

Properties and Methods of Preparation.—Since some of the above salts contain copper as cuprous sulfite, they are easily oxidized with atmospheric oxygen.

Compound I: $7Cu_2SO_3 \cdot 2CuSO_3 \cdot 3(NH_4)_2SO_3 \cdot 24H_2O$.2) — Colorless, transparent, square, thin plates, or an aggregate of spherical microcrystals observed as a yellowish-green powder by the naked eye. This salt is easily formed in a very wide region, together with other salts, and it is slowly converted into Chevreul's salt in a low-mole fraction of copper ion. That is, in the region where the mole fraction of cupric sulfate is less than 0.1, the formation of this salt takes place first with an extreme decrease in the quantity of copper ions; consequently, both ramentum-like crystals of compound XIII and Tutton's salt of zinc, $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, appear. Besides, in the region where the mole fraction of ammonium sulfite is about 0.65, compound VI appears, as a result of the change in the

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1) T. Okabe and H. Ito, *Tech. Repts, Tohoku University*, **29**, 157 (1964).

2) T. Okabe, A. Kanbe and S. Hori, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **64**, 2091 (1961).

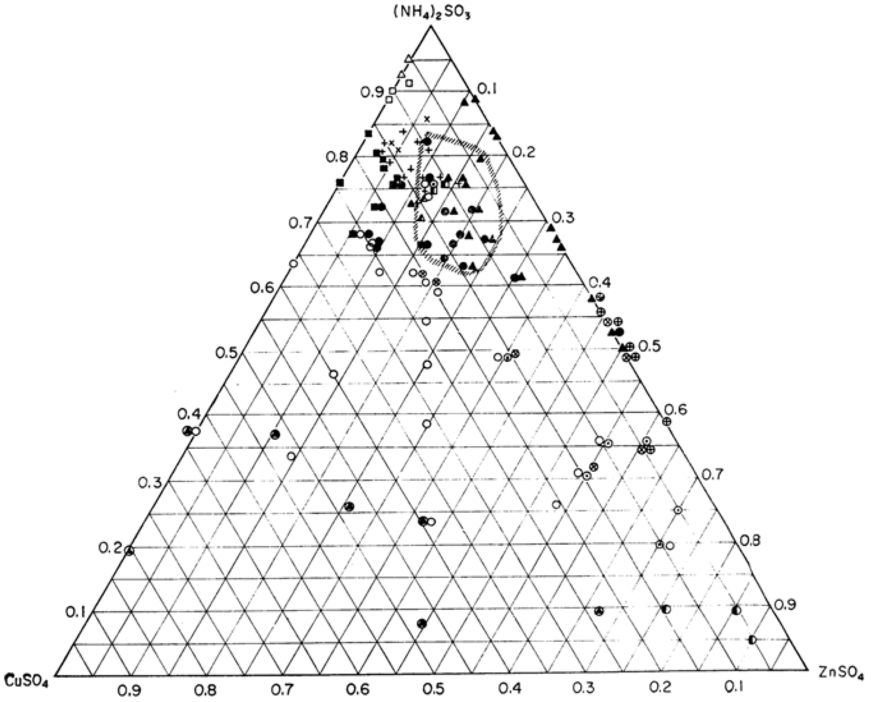

Fig. 1. (a). The formation region of copper, zinc, ammonium sulfites.

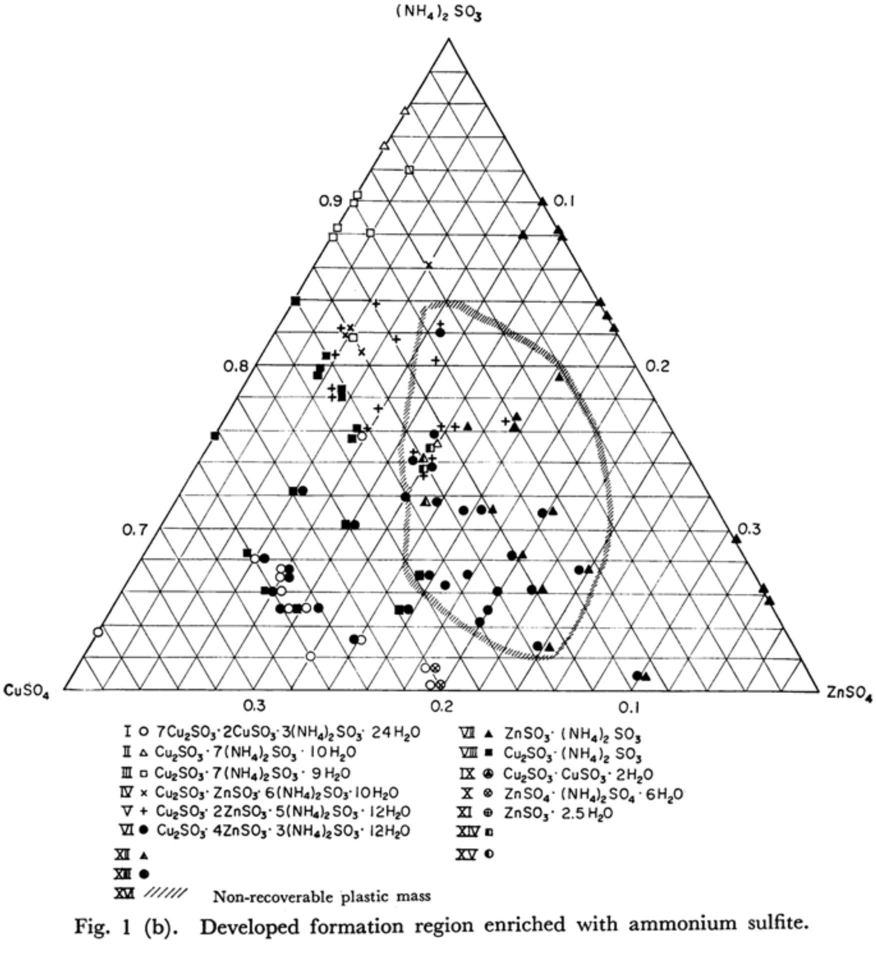

Fig. 1 (b). Developed formation region enriched with ammonium sulfite.

TABLE II. ANALYTICAL VALUES OF THE NEW SULFITES (%)

Compd. No.	Found					Calcd.				
	NH_4	Zn	Cu	SO_3	H_2O	NH_4	Zn	Cu	SO_3	H_2O
III	20.84	—	10.59	54.18	13.76	21.36	—	10.74	54.17	13.73
IV	16.68	5.30	9.93	52.85	15.24	17.60	5.32	10.33	52.10	14.65
V	13.93	10.10	9.81	49.46	16.70	13.40	9.97	9.85	50.20	16.58
VI	8.00	19.32	9.39	47.32	15.97	7.91	18.75	10.01	47.71	15.62

composition of the solution, in the zinc-rich region after the formation of the compound I.

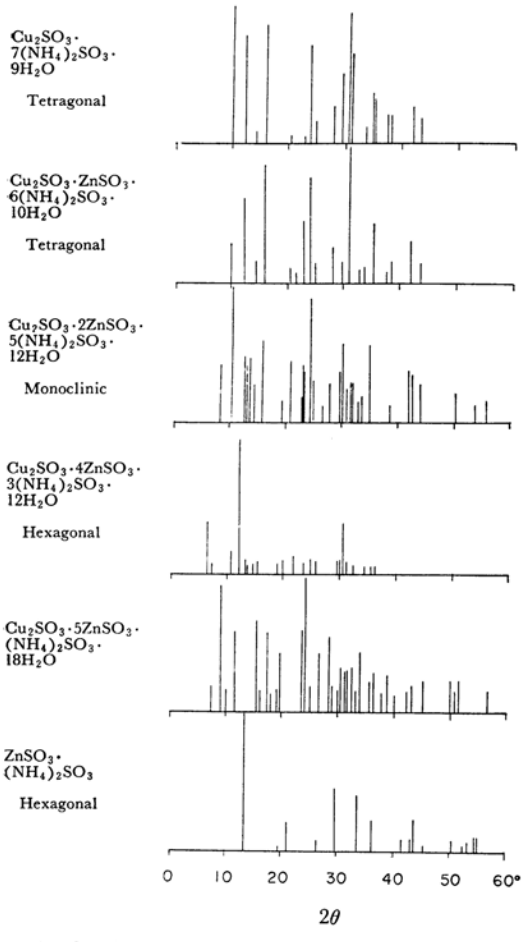

Fig. 2. The X-ray diffraction patterns of some complex sulfites.

Compound II: $Cu_2SO_3 \cdot 7(NH_4)_2SO_3 \cdot 10H_2O$.²⁾— Transparent, colorless needles. Very soluble in water. This salt is prepared easily by the drop-by-drop addition of a cupric sulfate solution to a 3-mol./l. or a more concentrated solution of ammonium sulfite in the region where the mole fraction of cupric sulfate is less than 0.06.

Compound III: $Cu_2SO_3 \cdot 7(NH_4)_2SO_3 \cdot 9H_2O$.— Tetragonal (4/m 2/m 2/m). $c=0.3223$. Soluble in water. This salt is formed in a pale wine-red solution at about a 0.9 in mole fraction of ammonium sulfite. When zinc ions are absent in the solution, this salt is obtained as transparent, colorless plates as a result of the good development of the (110) face, and also occasionally as large crystals with a sandglass structure of a wine-red color, while in the presence of a few zinc ions in the solution, this salt is obtained as prisms, as is shown in Fig. 3. This salt bears a resemblance to the compound II and to the $Cu_2SO_3 \cdot 7(NH_4)_2SO_3 \cdot 14H_2O$ reported by Svensson³⁾ in composition; apparently, however, these salts are not the same, for their chemical properties, X-ray diffraction patterns and formation regions are different.

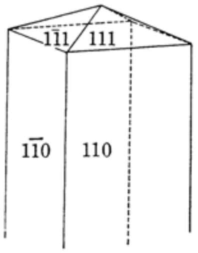

Fig. 3. Cuprous, ammonium sulfite, III.

Compound IV: $Cu_2SO_3 \cdot ZnSO_3 \cdot 6(NH_4)_2SO_3 \cdot 10H_2O$.—Tetragonal, transparent, colorless prisms. Soluble in water. When this salt is oxidized in moist air, it gradually turns yellow. The X-ray diffraction pattern is almost equal to that of the compound III except for the peak corresponding to d: 2.88 Å. This salt is obtained in the region where the amount of zinc ions is larger than that in the formation region of the compound III. This salt is obtained as transparent prisms, for example, in a mixed solution of metal sulfates to which 2—2.5 mol./l. ammonium sulfite solution is added until the mole fractions of cupric sulfate zinc sulfate and ammonium sulfite reach 0.08, 0.06 and 0.86 respectively, and which has stood for several days.

Compound V: $Cu_2SO_3 \cdot 2ZnSO_3 \cdot 5(NH_4)_2SO_3 \cdot 12H_2O$.—Monoclinic prisms, as are shown in Fig. 4 and in Photograph 1. $a:b:c=0.9325:1:0.4557$, $\beta=93°$ or 87°. Easily soluble in water. The solution of this salt is yellowish green. This salt is formed slowly as large crystals, together with the plastic mass in the region where the mole fraction of cupric sulfate is nearly equal

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3) N. Svensson, *Ber.*, **4**, 713 (1871).

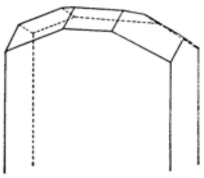
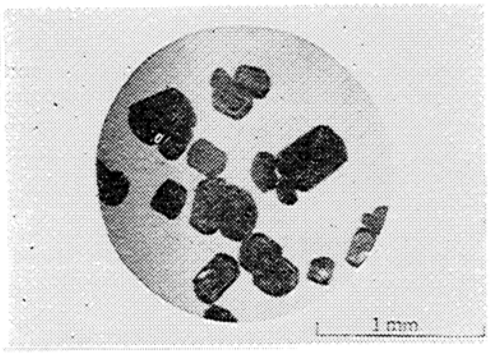
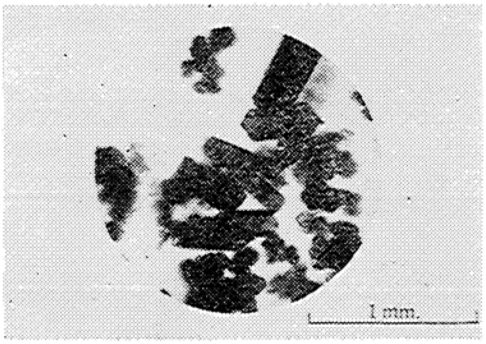


Fig. 4. Cuprous, zinc, ammonium sulfite, V.



Photograph 1.

to that of zinc sulfate and where the mole fraction of ammonium sulfite is 0.75—0.83. When the number of zinc ions is large, the compound VII, $ZnSO_3\cdot(NH_4)_2SO_3$, is formed, while when the number of copper ions is large, the compound VIII, $Cu_2SO_3\cdot(NH_4)_2SO_3$, is formed.



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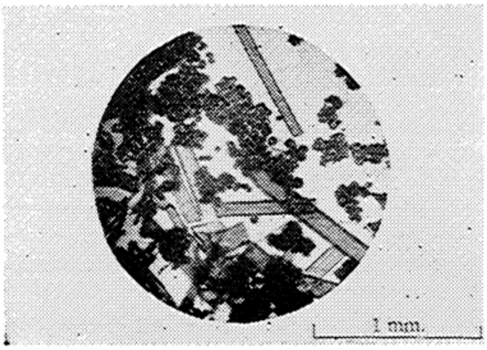

Photograph 3.

Compound VI: $Cu_2SO_3\cdot4ZnSO_3\cdot3(NH_4)_2SO_3\cdot12H_2O$. — Hexagonal crystals, as are shown in Photographs 2 and 3. Insoluble in water and stable in the air. This salt is formed as plates since the $(10\bar{1}0)$ face grows well in the region where the mole fraction of ammonium sulfite is 0.63—0.73. This salt is prepared by adding a 2 mol./l. ammonium sulfite solution to a mixed solution of metal sulfates until the mole fractions of cupric sulfate, zinc sulfate and ammonium sulfite become 0.15, 0.20 and 0.65 respectively. At this state, the mixture must be shaken sufficiently to dissolve the plastic mass and then allowed to stand for a few days, isolated from the atomsphere.

Compound VII: $ZnSO_3\cdot(NH_4)_2SO_3$.[4]—Hexagonal, transparent and colorless crystals. Slightly soluble in water and relatively stable in the air. The X-ray diffraction pattern and the Miller indices of this salt resemble those of the monohydrate registered on the ASTM X-ray Card 7-0426, but the results of the chemical analysis are apparently different from that of the monohydrate. This salt is formed easily at a 0.25 molar ratio between zinc sulfate and ammonium sulfite. Hexagonal plates are formed in the presence of copper ions, and bipyramidal plates, in the absence of copper ions or at a low concentration of ammonium sulfite. The primary formation of this salt is usually followed by that of the compound V or VI. (Found: NH_4, 13.19; Zn, 25.19; SO_3, 61.55%).

Compound VIII: $Cu_2SO_3\cdot(NH_4)_2SO_3$.[5]—Rhombohedral, $c=9.0139$. Insoluble in water and stable in the air. Bipyramidal crystals are formed in the presence of zinc ions, and hexagonal plates, in the absence of zinc ions. This salt is obtained over a wide region by adding cupric sulfate to an ammonium sulfite solution until the molar ratio of cupric sulfate to ammonium sulfite becomes nearly 0.25.

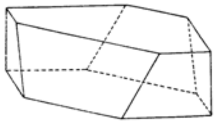

Fig. 5. Cuprous, ammonium sulfite, VIII.

Compound IX: $Cu_2SO_3\cdot CuSO_3\cdot2H_2O$.[6]—Pseudo orthorhombic.

$$a=8.34\ \text{Å}$$
$$b=7.64\ \text{Å}$$
$$c=5.56\ \text{Å}$$

Insoluble in water, but slightly soluble in sulfurous acid. This salt is always formed easily in a

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[4] F. L. Hahn, H. A. Meier and H. Siegert, *Z. anorg. Chem.*, **150**, 126 (1926).

[5] A. Rosenheim and S. Steinhauser, ibid., **25**, 98 (1900).

[6] G. Brauer and M. Eichner, *Z. anorg. u. allgem. Chem.*, **287**, 95 (1956).

small mole fraction of ammonium sulfite, or in a relatively large one through the conversion of the compound I.

Compound X: $ZnSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.—This salt is formed slowly in the zinc-rich region as large crystals after the formation of zinc sulfite.

Compound XI: $ZnSO_3 \cdot 2.5H_2O$.[7]—This salt is formed when the mole fraction of ammonium sulfite is smaller than 0.55. Below a 0.4 mol. fraction of ammonium sulfite, only this salt is formed, but at about 0.45 it is accompanied by Tutton's salt.

The following compounds have also been obtained, but their properties have not been identified.

Unknown Compound XII.—This salt is obtained as a cotton-like aggregate of needles, together with a plastic mass, when a 3 mol./l. or more concentrated solution of ammonium sulfite is added to a mixed solution of the two metal sulfates. The X-ray diffraction pattern of this salt resembles that of the compound II, but the peak at d: 11.7 Å disappears and the intensity of the peak at d: 2.12 Å decreases compared with that of the compound II.

Unknown Compound XIII.—Transparent, colorless and calcite-like crystals. This salt is obtained in the same region as the compound XII is formed. However, the conditions under which only this salt is obtained could not be discovered.

Compound XIV: $Cu_2SO_3 \cdot 5ZnSO_3 \cdot (NH_4)_2SO_3 \cdot 18H_2O$.—This salt is formed as transparent and pink crystals in the clear solution after the dissolution of the plastic mass first formed. Besides, several salts with X-ray diffraction patterns similar to that of the compound II are formed in the region where the mole fraction of copper is below 0.1. (Found: NH_4, 2.56; Zn, 23.00; Cu, 8.96; SO_3, 42.18; H_2O, 23.30%).

Unknown Compound XV.—In the presence of zinc sulfate the color of the Chevreul salt formed in the reaction varies from a reddish brown through orange to yellow with the increase in the amount of zinc sulfate. The change in color may be due to the partial replacement of copper by zinc. The X-ray diffraction pattern varies with the color change until the formation of a certain pattern of this salt is established.

The Non-recoverable Plastic Mass. — Upon the drop-by-drop addition of an ammonium sulfite solution to a mixed solution of metal sulfates in the region where the molar ratio of zinc to copper is 1—2.5 and where the mole fraction of ammonium sulfite is 0.63—0.78, yellowish brown amorphous precipitates are rapidly formed at first; when stirred, these turn into a paste-like material which has no elasticity but which does have a good plasticity; this is named the "non-recoverable plastic mass."

The mass gradually hardens when the occluded water is released, and it is partly converted into the compounds I and VI within a few days or weeks.

Summary

In the reaction of an ammonium sulfite solution with a mixed solution of cupric sulfate and zinc sulfate, ten or more of the complex salts formed have been identified, and their formation regions and properties have been examined. Usually some of them are formed simultaneously, but sometimes only one is formed, depending on the reaction conditions. The newly-found compounds are as follows;

$Cu_2SO_3 \cdot 7(NH_4)_2SO_3 \cdot 9H_2O$
$Cu_2SO_3 \cdot ZnSO_3 \cdot 6(NH_4)_2SO_3 \cdot 10H_2O$
$Cu_2SO_3 \cdot 2ZnSO_3 \cdot 5(NH_4)_2SO_3 \cdot 12H_2O$
$Cu_2SO_3 \cdot 4ZnSO_3 \cdot 3(NH_4)_2SO_3 \cdot 12H_2O$

Among these salts, some may be represented by the general formula of $Cu_2SO_3 \cdot mZnSO_3 \cdot n(NH_4)_2SO_3 \cdot xH_2O$, in which $(m+n)=7$. Possibly, ammonium ions may be replaced by zinc ions to a certain extent.

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[7] T. Okabe, K. Kanzawa and S. Hori, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **81**, 531 (1960).