

phosphorus atoms at (000) and $(\frac{1}{2}\frac{1}{2}0)$ and iodine atoms at $(0\frac{1}{2}u)$ and $(\frac{1}{2}0\bar{u})$ where u is very close to 0.40; and it is shown that no simpler structure is capable of accounting for the data. The close relation between this structure and that of the lower temperature form of ammonium chloride is shown.

PASADENA, CALIFORNIA

NOTE

The Sizes of Atoms in Diamond-Type Crystals.—It has recently been shown that the interatomic distances for substances crystallizing in the diamond type of lattice can be satisfactorily represented in terms of atomic "radii" characteristic only of the rare-gas types of atoms involved.¹ For the argon type, the value for silicon derived from the density (1.15 Å. U.) rather than that given by Debye and Scherrer² (1.18 Å. U.) was taken. Gerlach³ has recently made a careful re-determination of this constant and finds its value to be 1.17 Å. U. It, therefore, seems that this value rather than the lower one derived from the density should be adopted. For the radius of atoms of the krypton type, one-half the value for the distance between the copper and bromine atoms in cuprous bromide (1.26 Å. U.) was taken. Hull⁴ has recently found that the element germanium, which is of the krypton type, also crystallizes in the diamond lattice, the value for the atomic radius being 1.22 Å. U. The rather close agreement between the interatomic distances in gray tin and silver iodide (2.80 and 2.83 Å. U., respectively), all the atoms being of the same (xenon) type, would lead one to expect better agreement between cuprous bromide and germanium (2.52 and 2.44 Å. U., resp.). Inasmuch as cuprous bromide is undoubtedly the more difficult of the two to prepare in a pure state owing to its tendency to be decomposed by light and as the germanium value gives a little better agreement with the data (with the exception, of course, of the value for cuprous bromide), it seems best to adopt the value derived from germanium (1.22 Å. U.) as the atomic "radius" of krypton-type atoms in the diamond type of lattice. This, moreover, results in the constants all being determined from elementary substances.

The revised set of constants and the resulting values calculated for the various substances are given below.

Type		Atomic radius Å. U.
Neon	Diamond	0.77
Argon	Silicon (S, Cl)	1.17
Krypton	Germanium (Cu, Zn, Br)	1.22
Xenon	Gray tin (Ag, I)	1.40

¹ Pease, *THIS JOURNAL*, **44**, 769 (1922).

² Debye and Scherrer, *Physik. Z.*, **17**, 277 (1916).

³ Gerlach, *ibid.*, **22**, 557 (1921); **23**, 114 (1922).

⁴ Hull, American Physical Society Meeting at Washington, April 22, 1922.

Substance	Interatomic distances in Å. U.				
	Obs.	Calc.	Diff.	From Bragg's radii	Diff.
SiC.....	1.90	1.94	+0.04	1.95	+0.05
ZnS.....	2.35	2.39	+0.04	2.35	0.00
CuCl.....	2.38	2.39	+0.01	2.43	+0.05
CuI.....	2.63	2.62	-0.01	2.78	+0.15
AgI.....	2.83	2.80	-0.03	3.18	+0.35
CuBr.....	2.52	2.44	-0.08	2.57	+0.05

CONTRIBUTION FROM THE
LABORATORY OF PHYSICAL CHEMISTRY,
PRINCETON UNIVERSITY,
PRINCETON, N. J.

ROBERT N. PEASE

Another Time Reaction.—In the January, 1922, number of THIS JOURNAL an article by Forbes, Estill and Walker describes a time reaction between thiosulfuric acid and sodium arsenite or arsenate. It occurred to the writer that the same reaction, or a similar one should occur with antimony salts, and as antimony sulfide is even more highly colored than arsenic sulfide, the reaction should be even more desirable as a lecture experiment to exhibit induction periods and reaction velocity, and at the same time might throw some light on the chemical reaction which takes place, the exact nature of which seems doubtful.

The method used by the original investigators in conducting the reaction is not applicable due to the insolubility of sodium antimonite and antimonate, and even the potassium salts of these acids are not sufficiently soluble for the purpose. Tartar emetic was considered but its solubility is low (5.26 g. per 100 cc. of water) and the reaction periods were found to be too long. It was necessary to devise a solution which would hold a sufficient amount of antimony to give reaction periods of a satisfactory duration without at the same time introducing too high a concentration of acid which would be undesirable for the same reason. The only solution which could be found capable of doing so was one containing a relatively large amount of free potassium hydroxide. Accordingly, a solution containing potassium hydroxide and Rochelle salts was used as a solvent for antimony trioxide, and was found to be satisfactory for the main purpose. It had the disadvantage, however, that only by using a constant volume of it, was it possible to keep the acid concentration constant without an amount of trouble that was unwarranted, as the reaction has very little value save as a lecture experiment.

Method and Observations

1. Approximately molar sodium thiosulfate solution was prepared and standardized against iodine.
2. One liter of a solution containing 1.67 moles of potassium hydroxide

and 0.67 moles of Rochelle salts was saturated with carefully purified antimony trioxide, and then analyzed by the method of Treadwell and Hall for tartar emetic, with appropriate modifications. It was found to contain 44.46 g. of antimony per liter.

3. 4 *M* hydrochloric acid (also acetic) was prepared and standardized against sodium hydroxide which had previously been standardized for another purpose.

Distilled water and the required amount of each solution to give the required concentration in a volume of 100 cc. were run into beakers from burets, and the time of reaction was taken as the time of appearance of the first turbidity after mixing. The end of the induction period is sharp if the time is short, and the precipitate comes out at once with the characteristic orange color of antimony sulfide. If the reaction period is long it takes 45 seconds or more for the first yellow turbidity to become deep orange.

For lecture purposes the above solutions made up approximately should be used in parts by volume as follows: 40 of (1), 20 of (2), and 10-15 of (3), the acid always being added last. The reaction will occur sharply at the end of 30 to 60 seconds. Longer periods can be determined in advance by rough experiment with these solutions.

In one set of experiments the following times were obtained. The concentrations are expressed in millimoles per liter.

HCl	Na ₂ S ₂ O ₃	Sb	Time Sec.
172	102	148	30
172	204	148	27
172	306	148	23
172	408	148	20
172	510	148	17

From these values it is apparent that the length of the induction period is roughly varying linearly with the concentration of the thiosulfate over the range studied, a conclusion not quite the same as that arrived at in the case of arsenic.

When it was attempted to vary the amount of the stock antimony solution used, the amount of acid solution remaining constant, the acid concentration varied also, and the observed reaction times exhibited no regular variation, as would not of course, be expected. It was, however, observed that with the amount of the stock solution relatively small with respect to the concentrations of the other two, an immediate precipitate of sulfur was obtained, followed later by the appearance of the color of the sulfide.

In contrast with the results observed by Forbes, Estill, and Walker with arsenic it was found that the use of acetic acid lengthened the induction

period to such an extent that it was not possible to obtain satisfactory times of reaction.

Vortman¹ who originally discovered the fact that the sulfides of the metals could be obtained by boiling thiosulfate solutions of various metals, notably copper, mercury, arsenic, antimony, and under the proper conditions, zinc, as mentioned in the article already quoted, did not mention the fact that these were time reactions with quite definite induction periods. In addition to these metals, the experiment was also tried with tin and gold which apparently do not undergo the reaction, although lead salt solutions will, upon long standing, deposit small amounts of lead sulfide. I have also found that while copper exhibits this reaction, its induction period is not at all sharp, and the resultant solution undergoes some remarkable color changes. The addition of sodium thiosulfate to a copper salt solution decolorizes it, due probably to the formation of a complex salt, and subsequent acidification produces a bright orange-red solution which passes over a longer or shorter period through deep red, brick-red, brown and green, and eventually precipitates a pronouncedly greenish-black copper sulfide.

DEPARTMENT OF CHEMISTRY,
COLLEGE OF THE CITY OF NEW YORK,
NEW YORK, N. Y.

MARTIN MEYER

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The Precipitation of Metals by Hydrogen Sulfide.—In the precipitation of the hydrogen sulfide group of metals, the concentration of hydrochloric acid commonly employed is about 0.3 *N*, and yet, in spite of the infinitely small sulfide-ion concentration of such solutions, this ion is nevertheless assigned the major role in the precipitation of the heavy metal ions. This is done on the basis of the extremely minute values of the solubility products of the sulfides, and in the face of our admittedly imperfect knowledge as to the validity of the solubility product principle,¹ as well as our lack of information concerning the condition of the heavy metallic sulfides when present, in infinitely small quantities, in aqueous solutions. Furthermore, this is done without regard to the work of Linder and Picton,² who showed conclusively that sulfide precipitates obtained in the ordinary way, by means of hydrogen sulfide, from salt solutions of antimony, arsenic, cadmium, copper, gold, indium, silver and zinc, contain appreciable amounts of combined hydrogen sulfide.

In the light of these facts, the writer ventures to suggest that, *if, after*

¹ Vortman, *Ber.*, **22**, 2308 (1889).

² Cf. Stieglitz, *THIS JOURNAL*, **30**, 946 (1908). Washburn, *ibid.*, **32**, 488 (1910).

³ Linder and Picton, *J. Chem. Soc.*, **61**, 114 (1892).

a full consideration of all the evidence,³ it should still be thought best to regard the formation of these precipitates from the ionic standpoint alone, then the hydrosulfide ion should be regarded as the active precipitating agent, and not the sulfide ion.⁴ By way of emphasizing this suggestion, let us consider the constitution of a solution 0.1 *M* with respect to hydrogen sulfide and 0.2 *M* with respect to hydrogen chloride, of which the hydrogen-ion concentration is about 0.177 *M*.

The equilibrium constants for the primary⁵ and secondary⁶ ionization of hydrogen sulfide are represented by the expressions: $[H^+][HS^-]/[H_2S] = 0.91 \times 10^{-7}$, and $[H^+][S^{--}]/[HS^-] = 1.2 \times 10^{-15}$; and further, by multiplication, we obtain, $[H^+]^2 [S^{--}]/[H_2S] = 1.1 \times 10^{-22}$. With the use of these data, we arrive at the following concentration values for the solution in question: sulfide ion, $[S^{--}] = \frac{1.1 \times 10^{-23}}{0.1 \times (0.177)^2} =$

3.5×10^{-22} ; hydrosulfide ion, $[HS^-] = \frac{0.91 \times 10^{-7}}{0.1 \times 0.177} = 0.5 \times 10^{-7}$;

and non-ionized hydrogen sulfide, $[H_2S] = 0.1$. The true significance of these figures may best be made apparent by means of Avogadro's number, $N = 60.62 \times 10^{22}$; which of course represents the number of individual particles actually present in a gram molecular weight of a substance.

If we let x equal the number of individual ions or molecules in 1 liter of the solution referred to above, we have: (1) for the sulfide ion, $60.62 \times 10^{22} : 1 = x : 3.5 \times 10^{-22}$, whence $x = 212$; (2) for the hydrosulfide ion, $x = (60.62 \times 10^{22}) (0.5 \times 10^{-7}) = 30.31 \times 10^{15}$; and (3) for hydrogen sulfide molecules, $x = 60.62 \times 10^{22} \times 0.1 = 6.06 \times 10^{22}$. That is to say, a 5cc. portion of the solution under discussion contains, according to the accepted data, 300×10^{18} non-ionized molecules of hydrogen sulfide, 150×10^{12} individual hydrosulfide ions, and only 1 solitary sulfide ion. Why, then, without strong evidence to that effect, should sulfide ion be considered as the active precipitating agent?

Again, to take an extreme case, Knox⁷ gives 2.8×10^{-54} as the solubility product of mercuric sulfide. For the molal concentration of the mercuric ion, or of the sulfide ion, in the saturated aqueous solution of the salt, this figure gives at most the value 1.7×10^{-27} ; and from this value,

³ Investigations are at present under way, in this laboratory, of which so far the indications point to an interpretation of the interaction of metallic salt solutions and hydrogen sulfide in the light of the coordination theory of Werner.

⁴ In the precipitation of copper oxide from a solution of the sulfate by sodium hydroxide solution, at the boiling temperature, it is not customary even to consider the oxide ion. The formulation is, $Cu^{++} + 2 OH^- = Cu(OH)_2 = CuO + H_2O$.

⁵ Auerbach, *Z. physik. Chem.*, **49**, 220 (1904).

⁶ Knox, *Trans. Faraday Soc.*, **4**, 44 (1908).

⁷ Ref. 6, p. 48 *et seq.*

by means of Avogadro's number, an easy calculation ($x = 60.62 \times 10^{22} \times 1.7 \times 10^{-27} = 1.03 \times 10^{-3}$) indicates the presence of only one solitary positive or negative ion of mercuric sulfide in each 1000 liters of the solution. Surely, in order to maintain equilibrium with anything in this volume, these two ions would have to move with the velocity of light, and be everywhere at the same time; and this condition we know they do not fulfil.

CONTRIBUTION FROM THE UNIVERSITY OF WASHINGTON, SEATTLE, WASHINGTON
G. MCP. SMITH
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CONSTITUTION OF THE SO-CALLED DITHIO-URAZOLE OF MARTIN FREUND. I

BY PRAPHULLA CHANDRA GUHA

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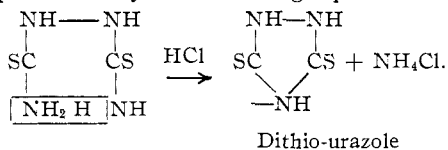
Freund and Wischewiansky¹ showed that by treating hydrazo-dithio-dicarbonamides of the type $\text{RNH} \cdot \text{CS} \cdot \text{NHNHCS} \cdot \text{RNH}$ with phosgene in toluene solution, a molecule of hydrogen sulfide is eliminated and compounds of the formula $\text{C}_2\text{H}_2\text{R}_2\text{N}_4\text{S}$ are formed for which the constitutional

formula, $\text{RHN} \cdot \text{C} \begin{array}{l} \text{N-NH} \\ \parallel \quad | \\ \text{NR} \quad \text{CS} \end{array}$ or $\text{RN} \cdot \text{C} \begin{array}{l} \text{NH-N} \\ \parallel \quad || \\ \text{NR} \quad \text{C} \cdot \text{SH} \end{array}$ containing a triazole ring was

given.

Later on, Freund with his collaborators² showed that when the hydrazo-dithio-dicarbonamides of the above type were treated with strong hydrochloric acid, instead of phosgene, the decomposition took place in two ways, yielding compounds of the formulas $\text{C}_2\text{H}_2\text{RN}_3\text{S}_2$ and $\text{C}_2\text{H}_2\text{R}_2\text{N}_4\text{S}$, respectively, the former by the loss of one molecule of NH_3 or NH_2R , as the case may be, and the latter by the loss of one molecule of H_2S , the former was acidic and the latter basic in nature.

The formation of the compound $\text{C}_2\text{H}_3\text{N}_3\text{S}_2$ of acid nature, was evidently assumed to be represented by the following equation.



¹ Freund and Wischewiansky, *Ber.*, **26**, 2877 (1893).

² Freund, *ibid.*, **27**, 1744 (1894). Freund and Imgart, *ibid.*, **28**, 946 (1895). Freund and Heilbrun, *ibid.*, **29**, 859 (1896).