[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

AZIDO-DITHIOCARBONIC ACID. I. FORMATION, PREPARATION AND PROPERTIES[1]

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With Microscopical Studies by C. W. MASON

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In view of the readiness with which carbon disulfide reacts with salts of hydronitric acid to form the azido-dithiocarbonates,[2] it was thought possible that it might react directly with free hydronitric acid to form azido-dithiocarbonic acid, as expressed by the equation

$$HN_3 + CS_2 = HSCSN_3 \qquad (1)$$

Formation.—Aqueous solutions of hydronitric acid, when shaken with carbon disulfide for several minutes, or when allowed to remain in contact with this substance for several hours at room temperature, yield solutions in which the presence of azido-dithiocarbonic acid may be demonstrated by treatment (1) with a solution of silver nitrate, which precipitates the explosive silver azido-dithiocarbonate, distinguishable from silver trinitride by reason of its insolubility in ammonium hydroxide; (2) with solutions of iodine and hydronitric acid, the reaction between which is strongly catalyzed, as by a solution known to contain azido-dithiocarbonic acid, and (3) with a solution of mercuric chloride, which yields a white precipitate of the explosive mercuric azido-dithiocarbonate. Anhydrous liquid hydrogen trinitride[3] reacts with carbon disulfide to form a light yellow product which in its explosive character and in its mode of decomposition closely resembles azido-dithiocarbonic acid.

From sufficiently concentrated aqueous solutions of an azido-dithiocarbonate, mineral acids precipitate the free azido-dithiocarbonic acid. Dilute nitric or sulfuric acid (1:6) acts in this way, but concd. nitric acid oxidizes the azido-acid first liberated, forming some azido-carbondisulfide as an intermediate product, and finally oxidizing at least a part of the sulfur to sulfuric acid.

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[2] (a) Sommer, *Ber.*, **48,** 1833 (1915). (b) Browne and Hoel, THIS JOURNAL, **44,** 2106, 2315 (1922). (c) Currier with Browne, *ibid.*, **44,** 2849 (1922). (d) See also Oliveri-Mandalà, *Gazz. chim. ital.*, **52,** II, 139 (1922). This paper was not seen by the authors until after the manuscript of the present article had been submitted for publication.

[3] The experiments with anhydrous hydrogen trinitride were performed in this Laboratory by Dr. A. E. McKinney and Mr. R. C. Houck, to whom the authors take this occasion to express their appreciation.

Preparation.—A convenient and satisfactory method for the preparation of azido-dithiocarbonic acid involves treatment of 6 g. of recrystallized sodium trinitride, dissolved in a small amount of water, with 6 cc. of purified[4] carbon disulfide. The mixture is allowed to react in a small, tightly-corked bottle at 40° for about 48 hours. The resulting solution of the azido-salt is filtered, chilled with ice, and treated with cold concd. hydrochloric acid,[5] which precipitates the azido-acid. The white, crystalline precipitate is washed three or four times by decantation with ice water, is drained on a Büchner funnel and is finally dried on a porous plate. It is preserved over phosphoric anhydride in a desiccator protected from the light, and kept at a temperature below 10°.

Analysis.—The sulfur was determined by oxidizing weighed samples of the azido-acid, first in alkaline solution with bromine, and then with fuming nitric acid and potassium chlorate, finally weighing the sulfur in the form of barium sulfate.

Analyses. Subs., 0.1851, 0.1903: $BaSO_4$, 0.7278, 0.7422. Calc. for $HSCSN_3$: S, 53.80. Found: 54.00, 53.56.

The nitrogen was determined in accordance with the usual Dumas method by combustion with copper oxide in a stream of pure carbon dioxide. The sample of the acid was mixed with about 20 g. of fine copper oxide and was heated gradually.

Analyses. Subs., 0.1019, 0.1186: N_2, 27.91 cc. (0.03519 g.), 33.08 cc. (0.04170 g.). Calc. for $HSCSN_3$: N, 35.26. Found: 35.12, 35.16.

The hydrogen was determined by titration of solutions containing weighed amounts of the solid acid with standard sodium hydroxide solution using methyl orange as indicator.

Analyses. Subs., 0.2587, 0.1087: H, 0.00221, 0.00091. Calc. for $HSCSN_3$: H, 0.846. Found: 0.856, 0.835.

Further evidence confirming the formula assigned to azido-dithiocarbonic acid was obtained by analysis of the silver salt, prepared by treatment of aqueous solutions of the acid with a slight excess of silver nitrate. This white, insoluble substance is highly explosive in the dry state, but may be handled with comparative safety in aqueous suspension. The precipitate was filtered on a tared Gooch crucible, and was dried at room temperature over phosphoric anhydride for 10 days. In weighing the dry salt, suitable precautions were taken to protect the operator from possible injury. The silver azido-dithiocarbonate was dissolved in fuming nitric acid, the resulting solution was evaporated nearly to dryness, and the silver was precipitated and weighed as silver chloride by the usual procedure.

Analyses. Subs., 0.3765, 0.3767: AgCl, 0.2379, 0.2380. Calc. for $AgSCSN_3$: Ag, 47.73. Found: 47.56, 47.51.

The foregoing analytical results, considered in connection with the data obtained in a study of the decomposition of azido-dithiocarbonic acid, strongly confirm the structural formula assigned to this compound, $H—S—C(=S)—N=N=N$.

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[4] Ref. 2c, p. 2851.

[5] Sommer (Ref. 2a, p. 1841) obtained a white precipitate, which he surmised to be free azido-dithiocarbonic acid, by treatment of a cold, concentrated solution of sodium azido-dithiocarbonate with concd. hydrochloric acid. No evidence was submitted in support of this belief, however, and no further work in this direction was reported.

Properties.—Azido-dithiocarbonic acid is a white or very light yellow crystalline solid. It is fairly soluble in water, and is much more soluble in ethyl alcohol, methyl alcohol, diethyl ether, benzene, carbon disulfide, and glacial acetic acid. If the $SCSN_3$ group be considered as a unit, azido-dithiocarbonic acid may be regarded as a halogenoid hydracid that bears the same relation to azido-carbondisulfide[6] that hydrochloric acid bears to free chlorine. It may be titrated with a standard alkali solution using methyl orange or methyl red as indicator. By electrometric titration[7] it has been found to be nearly as strong an acid as hydrochloric acid. Determinations of the molecular weight of the acid in aqueous solution by the cryoscopic method gave results ranging from 72 to 87, which indicate that the compound is highly dissociated, doubtless in accordance with the expression

$$HSCSN_3 \rightleftharpoons H^+ + SCSN_3^- \qquad (2)$$

Aqueous solutions of azido-dithiocarbonic acid react with various oxidizing agents including, for example, iodine in potassium iodide solution, nitric acid of suitable concentration, ferric chloride, potassium persulfate, hydrogen peroxide, manganese dioxide, and potassium permanganate, with formation of azido-carbondisulfide which appears as a white, microcrystalline precipitate. This formation of the free halogenoid by oxidation of the halogenoid hydracid takes place as expressed by the equation

$$2HSCSN_3 + O = (SCSN_3)_2 + H_2O \qquad (3)$$

and corresponds with the liberation of chlorine by oxidation of hydrochloric acid.

Azido-carbondisulfide is itself oxidized by the stronger oxidizing agents, and this substance is, therefore, formed only as an intermediate product when the acid is treated with an excess of such substances as concd. nitric acid or potassium permanganate. In these cases the chief final products of oxidation are sulfuric acid, carbon dioxide and nitrogen.

Solutions of such salts of the heavy metals as silver nitrate, mercuric chloride, lead nitrate and copper nitrate, when treated with a solution of the azido-acid yield the insoluble azido-dithiocarbonates, all of which are highly explosive in the dry state. The acid has only a very slight solvent action upon freshly precipitated ferric hydroxide.

Microscopic Examination.—Crystals of azido-dithiocarbonic acid formed on the microscope slide (1) by interaction of a concd. aqueous solution of the potassium salt and concd. hydrochloric acid, and (2) by re-

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[6] See Browne, Hoel, Smith and Swezey, THIS JOURNAL, **45**, 2541 (1923).

[7] The experimental work on this topic has been carried out by Mr. George H. Brandes, Instructor in Analytical Chemistry at Cornell University. The data will be published in the near future, in connection with an investigation of the electrical conductance of azido-dithiocarbonic acid and certain of its salts, now nearing completion in this Laboratory.

crystallization of samples of the acid previously prepared on a large scale, were found to be identical in appearance.

The simplest setting would place them in the monoclinic system with the forms clino pinacoid (010), basal pinacoid (001) and unit prism (110) represented. The angle β is about 56°. The angle between the prism faces in the basal plane is about 83°. Twinning is frequent on the basal plane.

Double refraction is strong; the extinction angle (clino-pinacoidal view) is about 30°, and the basal view shows parallel extinction. The index of refraction for vibrations 30° to c is estimated at 1.6; for vibrations transverse to this, 1.35+. Such interference figures as were obtainable indicate biaxial character, 2 E large. Z is apparently the acute bisectrix, making the crystals optically positive (+). Probable orientation: $X \Lambda c = 30°; Y \perp a; Z = b$.

Contact with a hot wire (below red heat) causes the acid to detonate with a puff of smoke and sulfurous odor, but the detonation is much less violent than that of azido-carbondisulfide. The residue consists of a pale yellow oil from which gas is evolved in considerable amount. Minute prismatic, strongly birefringent crystals, probably of azido-carbondisulfide, showing parallel extinction are a product of the detonation, and are found in colorless masses, vesicular because of the oily material in the interstices. These crystals disappear on standing in contact with the oily material, with evolution of gas, and formation of more oily material. This oil gradually darkens in color and increases in viscosity, with ultimate formation of a red-orange, vesicular, brittle substance, very similar in appearance to the end-product of the decomposition of azido-carbondisulfide.

At room temperature the solid azido-dithiocarbonic acid decomposes slowly, with evolution of gas and formation of a small amount of a fine-grained anisotropic crystalline material together with the yellow oil. Within 24 hours the whole sample is transformed into a yellow, vesicular, tenacious "dough" of viscous material, which after 2 or 3 days becomes brittle and is found to contain no crystalline material.

When brought into immediate, intimate contact with freshly prepared dry azido-dithiocarbonic acid, the yellow detonation product appears to accelerate appreciably the rate of decomposition. This was demonstrated by evaporating a solution of the acid to a crystalline film on a microscope slide. Upon this film was placed a small amount of the coarsely crystalline acid, which was then carefully detonated with the aid of a hot wire. Care was taken to avoid contact between the wire and the microcrystalline film, which as a result of the explosion of the coarse, supernatant material, was spattered with the yellow oil. Wherever this substance came into contact with the undecomposed acid an erosion of the crystals and evolution of gas took place at a rate more rapid than that of the normal, slow decomposition, and quite distinct from the last evolution of gas from the detonation product itself.

The yellow oil obtained as an intermediate product of the decomposition of the azido-acid catalyzes not only the spontaneous decomposition of the acid itself, but also that of the related compound, azido-carbondisulfide. Conversely, the very similar yellow oil obtained from the azidodisulfide catalyzes not only the decomposition of this substance itself but also that of the azido-acid.

Decomposition.—Azido-dithiocarbonic acid is sensitive both to shock and to heat. The dry crystals detonate when broken in a porcelain mortar, when rubbed on a porous plate, or when heated on an asbestos board. The explosion is in no case so violent, however, as that of azido-carbondisulfide under similar conditions. It is accompanied by the liberation of much heat with considerable smoke and flame, as well as a characteristic odor resembling that of sulfur monochloride.

Below 10° the compound is relatively stable, especially when protected from the light. Even at 0°, however, it undergoes slow decomposition when exposed to the action of daylight. At room temperature, and exposed to diffused daylight, the white or very light yellow azido-dithiocarbonic acid spontaneously passes through a series of color changes which may be formulated as YT1, Y, and OY on the Milton Bradley chart.[8] During the course of these changes the dry crystalline material becomes viscous in texture, and puffs up, as a result of the liberation of gas, to several times its original volume. Weighed samples of the acid were found to undergo a loss of weight somewhat in excess of that corresponding to the evolution of 2 atoms of nitrogen per molecule. The presence of appreciable quantities of thiocyanic acid was established by allowing the gaseous products of decomposition to impinge upon filter paper moistened with a solution of ferric chloride. The resulting deep red color was discharged by a solution of mercuric chloride, but not by dil. hydrochloric acid, indicating the presence of thiocyanic acid and the absence of hydronitric acid. Thiocyanic acid vapor accelerates the spontaneous decomposition of azido-dithiocarbonic acid. This was demonstrated by allowing the vapor obtained by treatment of ammonium thiocyanate with dil. sulfuric acid to impinge upon a sample of the azido-acid. It was further shown in unexpected fashion when 5 samples of the solid acid, each of which weighed from 0.5 to 1.0 g., contained in small porcelain crucibles placed close together and covered with one large enamelled iron basin, detonated successively, after shortening time intervals, owing to the increasing concentration of thiocyanic acid in the surrounding atmosphere. The accumulation of the liquid (or solid) products of decomposition in close contact with the still undecomposed portion of the sample also results in greatly decreasing the stability of the azido-acid. Rela-

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[8] Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1st ed., **1905**, vol. I, p. 232.

tively large samples of the compound and samples piled up or closely packed together are more subject to spontaneous explosion than are smaller portions or thin layers, owing to the greater opportunity for adsorption of the catalytic agent in the former case. Such samples have been observed to explode, in some instances even at the temperatures of the ice chest, after the accumulation of catalyst during several hours of slow, spontaneous decomposition.

Very small samples of the azido-acid, heated in open melting-point tubes, appear to melt between 50° and 65° to a yellow oil, in reality a decomposition product, which undergoes further transformation, with evolution of gas and formation of the final orange-yellow solid product. Many samples have exploded under this treatment, sometimes with sufficient violence to shatter the melting-point tube, and in two instances, the thermometer as well. When heated above 70° samples of the azido-acid have almost invariably exploded, usually within a few seconds.

In aqueous solution azido-dithiocarbonic acid undergoes decomposition, with evolution of nitrogen and formation of the usual orange-yellow product which is insoluble in water. The solution becomes turbid at first probably owing to the formation of small amounts of an insoluble intermediate product, rather than to the formation of sulfur, as the substance was found to be soluble in hydrochloric acid. In certain nonaqueous solvents such as carbon disulfide, benzene, and ethyl alcohol, the azido-acid undergoes a similar decomposition with formation, apparently, of the same final product, which is insoluble also in these liquids.

A quantitative nitrometric study of the isothermal decomposition of azido-dithiocarbonic acid in aqueous solution at 25° has been made over a period of about 218 hours, during which the volume of nitrogen evolved was read at frequent intervals. A sample of the solid acid weighing 0.1024 g. and treated in the nitrometer tube with an amount of water just about sufficient to dissolve it, yielded 19.22 cc. (corr.) of nitrogen gas, corresponding to 1.991 atoms of nitrogen per molecule of the azido-acid. The data are shown in part in Fig. 1, Curve A. They indicate that the azido-acid decomposes in aqueous solution at a continually decreasing rate, owing to the diminishing concentration of the reacting substances present in the solution. The differential equation

$$\frac{dx}{dT} = 0.04368\,(2 - x) \qquad (4)$$

where T is the time in hours, and x the number of atoms of nitrogen evolved per molecule of the azido-acid, expresses the approximate velocity of the reaction. This is the type equation of a simple monomolecular reaction. The integrated form

$$T = \frac{1}{0.04368}\left(ln\,\frac{2}{2 - x}\right) \qquad (5)$$

makes it possible to calculate the amount of decomposition at any specified time. Curve B, Fig. 1, was plotted from data calculated by means of Equation 5. From the close agreement between the experimental and the calculated data it is evident that the spontaneous decomposition of azido-dithiocarbonic acid in aqueous solution is to be regarded as a simple, monomolecular reaction that shows no effect of catalytic action.

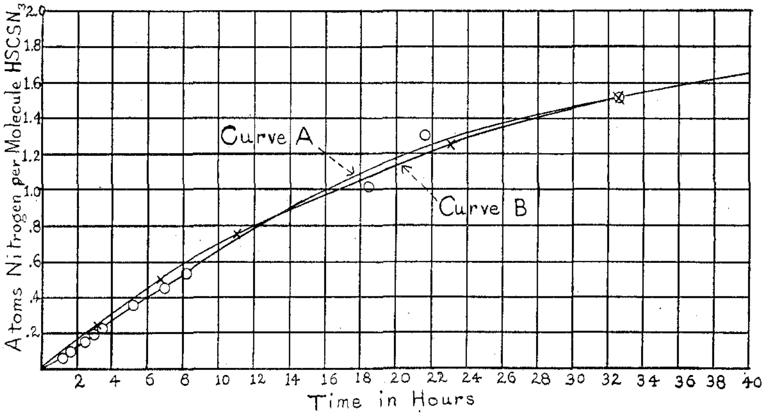

Fig. 1

A similar investigation of the isothermal decomposition of the dry azido-acid at 25° covered a period of 48 consecutive hours, during which a sample weighing 0.1055 g. yielded 18.76 cc. (corr.) of nitrogen, or 1.987 atoms per molecule of the acid. The course of the decomposition during the first 10 hours is shown in Fig. 2.

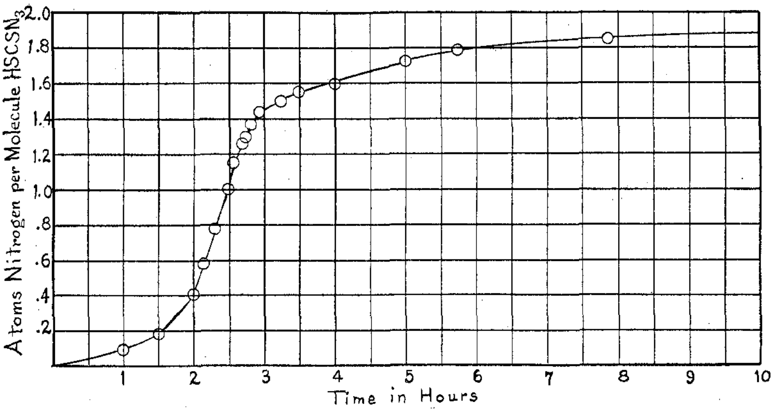

Fig. 2

The form of the curve tends strongly to confirm the experimental observations upon the catalytic action of the yellow intermediate product recorded above, and points toward the conclusion that the decomposition of dry azido-dithiocarbonic acid takes place after the fashion of a monomolecular reaction catalyzed by one of its own products. It has not been found possible to formulate this autocatalytic reaction mathematically by means of the type equation $dx/dt = kx(A - x)$, probably for one or more of the following reasons: (1) at least a part of the catalyst is initially evolved as a gas, HSCN, the adsorption and polymerization of which takes place to a degree largely dependent upon the mechanical and physical condition of the sample; (2) the reacting mixture is only partially in liquid form, with the result that its behavior cannot be satisfactorily interpreted in terms of the mass law; and (3) light may exert a catalytic effect upon the reaction as indicated by certain qualitative observations. Further investigation of this topic is in progress.

In the case of the decomposition of the azido-acid in aqueous solution the catalyst is but slightly soluble in water and is, therefore, removed from the sphere of action as soon as it is formed. Very dilute aqueous solutions of the unpolymerized thiocyanic acid seem to exert no appreciable catalytic influence upon the reaction.

It might be argued that at higher temperatures the rapid progress of the exothermic decomposition would maintain the sample of azido-acid at a temperature appreciably above that of the thermostatic bath, thus producing an apparent autocatalytic effect due to the action of heat. At ordinary temperatures, however, the thermal gradient established in this manner may be regarded as negligible, in view of the relatively long period of decomposition, especially in cases where small samples of the azido-acid are used.

Various lines of evidence justify the conclusion that azido-dithiocarbonic acid, both in the dry state and in aqueous solution, decomposes as expressed by the equation

$$HSCSN_3 = HSCN + S + N_2 \qquad (6)$$

This is in conformity with the results of independent investigations of the decomposition of the potassium azido-salt,[9] which yields potassium thiocyanate, sulfur and nitrogen; and of azido-carbondisulfide,[10] from which are obtained free thiocyanogen, sulfur and nitrogen.

The brittle, vesicular, orange-yellow, final product was found[11] to be somewhat soluble in hot water, but practically insoluble in cold water. It dissolves readily in solutions of potassium, sodium or ammonium hydroxide. It loses little or no weight when stored for days in a desiccator over phosphorus pentoxide. It is apparently but slightly soluble in ethyl alcohol, acetic acid, and acetone.

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[9] Ref. 2b, p. 2318.

[10] Ref. 6, p. 2543.

[11] In connection with this work the authors acknowledge with pleasure the assistance rendered by Mr. D. P Murray.

Four determinations of the total amount of sulfur in both free and combined forms showed an average of 70.18%, confirming the theoretical value, 70.35%, calculated for the mixture $(HSCN)_x + xS$. The sulfur appears to be very intimately and rather uniformly mixed with the polymerized thiocyanic acid, possibly forming a molecular mixture or solid solution with it. In an attempt to extract the sulfur with carbon disulfide it was found that the extract contained some thiocyanic acid, showing a tendency on the part of this liquid to dissolve or depolymerize the residue. A fair separation was accomplished by digestion of the mixture with a 5% solution of sodium hydroxide. This dissolved the polymerized acid, and left much, though probably not all, of the sulfur undissolved. After removal of the sulfur by filtration, the yellow filtrate was acidified with nitric acid in slight excess, with the result that a heavy orange-yellow precipitate, similar in appearance to the original mixture, was obtained. The percentage of sulfur in different samples of this product was found to vary between 53 and 55%, but the average of several determinations, 54.21%, agrees closely with the theoretical value, 54.26% calculated for thiocyanic acid, indicating that the product is a fairly pure polymerized thiocyanic acid. It probably resembles the substance already described as dithiocyanic acid, $H_2C_2N_2S_2$;[12] while the orange-yellow solid regarded by the authors as a *mixture* of free sulfur and polymerized thiocyanic acid shows certain of the characteristics of the substance known as perthiocyanic acid, $H_2N_2C_2S_3$,[13] or as isopersulfocyanic acid, $H_2C_2N_2S_3$.[14]

Summary

Azido-dithiocarbonic acid, $HSCSN_3$, a new halogenoid hydracid, has been prepared by treatment of concentrated solutions of the sodium salt with hydrochloric acid. Its composition has been established by analysis, and its crystallographic and optical properties have been studied under the microscope. It is a white or very light yellow crystalline solid, fairly soluble in water, and readily soluble in various non-aqueous liquids. It shows the characteristic properties of a strong acid, and its strength approaches that of hydrochloric acid. It is easily oxidized by various reagents, yielding the free halogenoid, $(SCSN_3)_2$.

In solid form the acid is sensitive both to shock and to heat. At ordinary temperatures it undergoes spontaneous decomposition at a rate characteristic of reactions of the monomolecular type. This decomposition is catalyzed in the dry state, but not in aqueous solution, by an intermediate product or by the thiocyanic acid formed, and may be expressed

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[12] Fleischer, *Ann.*, **179,** 204 (1875).

[13] Chattaway and Stevens, *J. Chem. Soc.*, **71,** 833 (1897). See also Klason, *J. prakt. Chem.*, [2] **33,** 116 (1886); **38,** 366 (1888).

[14] Stokes, THIS JOURNAL, **29,** 443 (1907).

by the equation, $HSCSN_3 = HSCN + S + N_2$. The solid product finally formed consists of polymerized thiocyanic acid and free sulfur.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

DENSITY AND HYDRATION IN GELATIN SOLS[1]

BY THE SVEDBERG AND BRUNO A. STEIN

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Introductory and Theoretical

It is known that in the case of true solution and in colloidal solutions there is more or less combination between the solute or the particles and the solvent or dispersing phase.

Nägeli long ago advanced the idea that solution was a process in which the material was surrounded by a shell of water. Pauli[2] states, "Crystalloids are said to be hydrated (or, in general, solvated) in solution when water is attached to the dissolved molecules in a stoichiometric proportion. In some instances this hydration is sharply defined (as for sulfuric acid and ferric chloride), but in other cases the hydration is variable and shows a continual alteration with dilution and with change of temperature. We can describe such phenomena with more accuracy as addition of water (or formation of envelopes) by the particles, ..."

"Such an addition of the medium occurs on the particles of many colloids, and is described as hydration. . . . The indications of hydration of a disperse phase are a disproportionately great viscosity of the solution, a decreased activity of the movement of the particles as displayed in diffusion or in an electric field, and an alteration in volume or density in the direction of compression of the medium." Zsigmondy[3] assumes that a density increase must be due to a compression of the particle by its water layer. A contraction in volume when gelatin is dissolved in water is then an evidence of hydration. The varying amount of water in gelatinous coagula shows hydration. Zsigmondy[4] states that egg white and gelatin must have thicker layers of water than the non-soluble gold and that this assumption probably explains the stability of the former to addition of electrolytes. This exemplifies sols of the hydrophile and hydrophobe type. This author feels that this stability is due to the film of water rather than to the dispersion size of gelatin and gold. Remy also[5] ascribes a shell of water (Wasserhülle) to the ions of salts in solution.

A high degree of hydration corresponds to a high viscosity in the sol according to Pauli[6] and Hatschek.[7] At the iso-electric point of gelatin, at *P*H about 4.7, a mini-

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[1] This paper constitutes the major portion of a thesis submitted by Bruno A. Stein in partial fulfilment of the requirements for the degree of Master of Science at the University of Wisconsin.

[2] Pauli, "Colloid Chemistry of the Proteins," P. Blakiston's Son and Co., Philadelphia, **1922**, p. 10.

[3] Zsigmondy, "Kolloid Chemie," Otto Spamer, Leipzig, **1920**, 3rd ed., p. 99.

[4] Ref. 3, pp. 97–100.

[5] Remy, *Z. physik. Chem.*, **89**, 467 (1915).

[6] Pauli, *ibid.*, **89**, 529 (1915).

[7] Hatschek, "Introduction to Physics and Chemistry of Colloids," J. and A. Churchill, London, **1922**, 4th ed., p. 84.