

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

AZIDO-DITHIOCARBONIC ACID. III. AZIDO-DITHIOCARBONATES OF LITHIUM, SODIUM, RUBIDIUM AND CESIUM¹

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WITH MICROSCOPICAL STUDIES BY C. W. MASON

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The halogenoid character of azido-carbondisulfide, $(\text{SCSN}_3)_2$, insures some degree of similarity, at least, between the azido-dithiocarbonates on the one hand, and the corresponding halides, as well as such other halogenoid salts as the thiocyanates, trinitrides and cyanides, on the other. Numerous preliminary experiments with the various salts of azido-dithiocarbonic acid have brought to light many indications of the existence of this analogy, and have suggested the desirability of a more thorough and extended study of this series of compounds.

The only azido-dithiocarbonates of the alkali metals hitherto described are a hydrated sodium salt,² $\text{NaSCSN}_3 \cdot 4\text{H}_2\text{O}$, and the anhydrous potassium salt,³ KSCSN_3 . In the present article are recorded the results obtained in the preparation and investigation of five new compounds: $\text{LiSCSN}_3 \cdot \text{H}_2\text{O}$, $\text{NaSCSN}_3 \cdot 2\text{H}_2\text{O}$, NaSCSN_3 , RbSCSN_3 and CsSCSN_3 .

Methods of Preparation.—The alkali salts of azido-dithiocarbonic acid may be obtained as products of the (1) interaction of the free acid with the hydroxides or carbonates of the metals, (2) double decomposition of barium azido-dithiocarbonate and the alkali sulfates and (3) union of carbon disulfide with the metallic trinitrides. Because of the insolubility of silver azido-dithiocarbonate, recourse cannot be had to metathesis between this substance and the alkali halides.

In the preparation of the compounds herein described, the third method, as previously outlined,³ has been exclusively employed.⁴ The alkali

¹ For the earlier articles of this series see (a) Smith and Wilcoxon with Browne, *THIS JOURNAL*, **45**, 2604 (1923). (b) Browne and Smith, *ibid.*, **47**, 2698 (1925). The current article is based upon a part of the thesis presented to the Faculty of the Graduate School of Cornell University by L. F. Audrieth in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The investigation was reported both orally and in abstract at the Ithaca meeting of the American Chemical Society, in September, 1924.

² Sommer, *Ber.*, **48**, 1833 (1915).

³ Browne and Hoel, *THIS JOURNAL*, **44**, 2315 (1922).

⁴ The addition of ethyl alcohol to the reactants in quantity sufficient to insure miscibility of the carbon disulfide and aqueous trinitride solution has been found by F. H. Swezey and others in this Laboratory to result in a marked acceleration of the reaction velocity. Since the alcohol seems to accelerate also the rate of decomposition of azido-dithiocarbonates to thiocyanates and to confer upon the final product in each case the odor of a mustard oil, its use in the present work seemed inadvisable.

trinitrides required for the work were prepared by the method used by Dennis and Benedict.⁵

Method of Analysis.—The metallic constituent was invariably determined as the sulfate. Prior thermal decomposition of the SCSN_3 radical was effected in the presence of small amounts of water, in view of the violence of the reaction between the azido-dithiocarbonates and concd. sulfuric acid. The resulting thiocyanates were fumed down with the acid and in the cases of the lithium and sodium salts small amounts of ammonium carbonate were added to insure conversion to the normal sulfate. The SCSN_3 radical was determined in every case by the Volhard method, as already described.⁶ The results obtained clearly demonstrate in each instance the composition of the substance, but show in some cases a deviation from theory somewhat larger than ordinarily expected. It is believed that such deviations are not due to experimental error in the analysis, but rather to the difficulties encountered in preparing and handling compounds as unstable as those under investigation.

General Properties of the Alkali Azido-dithiocarbonates

All of the compounds prepared are white, crystalline solids. The anhydrous sodium salt, although the least soluble of all the alkali azido-dithiocarbonates, is readily soluble in water, and deliquesces in air saturated with water vapor at ordinary temperatures. With the exception of the lithium salt, which is very soluble and extremely deliquescent, the compounds studied seem to show increase in solubility with rise in atomic weight of the alkali metal. In methyl and ethyl alcohol, ether and acetone, the hydrated lithium and sodium salts are fairly soluble, while the anhydrous rubidium and cesium salts are but slightly soluble. The anhydrous sodium salt is fairly soluble in all of these solvents except ether, in which the solubility is but slight. In carbon disulfide, chloroform, carbon tetrachloride and benzene none of the compounds shows appreciable solubility.

All of the alkali azido-dithiocarbonates tend to decompose slowly at room temperature, and more rapidly at higher temperature, in accordance with the general equation $M'SCSN_3 = M'SCN + S + N_2$. Beginning with the sodium salt, which shows, particularly in the hydrated form, the lowest sensitivity to friction or impact, these substances show a sensitivity and, when detonated, a violence of explosive action, which appear to vary directly with the atomic weight of the metal. The hydrated lithium salt is, however, distinctly more explosive than either the hydrated or the anhydrous sodium salt.

⁵ Dennis and Benedict, *THIS JOURNAL*, 20, 225 (1898); *Z. anorg. Chem.*, 17, 18 (1898).

⁶ Ref. 1 b, p. 2700.

Under the microscope the salts may usually be seen to dissolve in water with perceptible evolution of gas, as a result, no doubt, of their tendency to retain a part of the nitrogen formed by prior slow decomposition at room temperature, occluded in the crystals. After a time sulfur is precipitated from the solution, and is also formed by decomposition of the dry salt, as evidenced by the appearance of characteristic crystals either on the solid salt, or as a residue after solution has been effected.

When detonated on the microscope slide the salts all appear to behave similarly. The miniature explosion results in each case in the liberation of a gas or vapor possessing a characteristic sulfurous odor. A yellow, highly viscous, vesicular product, probably a polymer of free thiocyanogen, is left on the slide. This substance, which becomes brittle on standing, is found to contain very fine anisotropic particles. In some experiments, portions of the sample that escaped explosive decomposition were observed to melt and later, on cooling, to crystallize in the manner peculiar to the original salt.

Lithium Azido-dithiocarbonate Monohydrate, $\text{LiSCSN}_3 \cdot \text{H}_2\text{O}$.—Considerable difficulty was experienced in effecting the crystallization of this extremely deliquescent substance from aqueous solution. Concentrated solutions yielded no crystals when cooled with solid carbon dioxide, or when treated with methyl or ethyl alcohol, ether or acetone, but began to crystallize slowly after standing for several days in a vacuum desiccator over phosphorus pentoxide. Recrystallizations for microscopic study were of necessity made in a special type of desiccator slide containing this drying agent.

Anal. Subs., 0.2136, 0.2602: SCSN_3 , 0.1769, 0.2146. Calcd. for $\text{LiSCSN}_3 \cdot \text{H}_2\text{O}$: SCSN_3 , 82.6. Found: 82.8, 82.5.

Subs., 0.3275, 0.2326; Li_2SO_4 , 0.1295, 0.0915. Calcd. for $\text{LiSCSN}_3 \cdot \text{H}_2\text{O}$: Li, 4.84. Found: 4.99, 4.97.

The salt crystallizes in acute, rhombic plates, either separate or in clusters. The terminal angle is 58° . The thicker forms show the symmetry of the monoclinic system, which is also indicated by the slightly oblique extinction observed with some views of the crystals. Birefringence is strong, and the crystals are biaxial. The optical character was not determined.

Repeated attempts to prepare the anhydrous lithium azido-dithiocarbonate by dehydration of the monohydrate were found to result in decomposition of the SCSN_3 radical, with ultimate formation of lithium thiocyanate. The monohydrate readily undergoes thermal decomposition, turning yellow when heated to 75° , and melting with decomposition between 105° and 110° . It does not explode when rubbed on a porous plate or when struck with a hammer, but detonates with a sharp report when thrown upon a hot plate or when heated in the Bunsen flame.

Sodium Azido-dithiocarbonate Tetrahydrate, $\text{NaSCSN}_3 \cdot 4\text{H}_2\text{O}$.—This compound, first prepared but only very briefly described by Sommer,² is obtained in the form of long needles by crystallization from a concentrated aqueous solution of sodium azido-dithiocarbonate at about 0° .

Anal. Subs., 0.1721, 0.2871: SCSN_3 , 0.0959, 0.1600. Calcd. for $\text{NaSCSN}_3 \cdot 4\text{H}_2\text{O}$: SCSN_3 , 55.4. Found: 55.7, 55.7.

Subs., 0.2139, 0.3746, 0.4658: Na_2SO_4 , 0.0684, 0.1269, 0.1590. Calcd. for $\text{NaSCSN}_3 \cdot 4\text{H}_2\text{O}$: Na, 10.8. Found: 10.4, 11.0, 11.1.

Although fairly stable under ordinary conditions, the tetrahydrate gradually assumes a slightly yellowish tint on long standing. Heated in a capillary melting-point tube it effloresces, and decomposes with evolution of gas at 45° to 50°. It does not detonate when rubbed upon a porous plate or when struck with a hammer. When thrown upon a hot plate it explodes with a slight puff, after melting and losing at least a part of its water of crystallization. In the attempt to effect a recrystallization of the tetrahydrate at room temperature upon the microscope slide, crystals of the dihydrate were obtained.

Sodium Azido-dithiocarbonate Dihydrate, $\text{NaSCSN}_3 \cdot 2\text{H}_2\text{O}$.—The dihydrate is readily obtainable by crystallization from aqueous solutions of sodium azido-dithiocarbonate at ordinary temperatures.

Anal. Subs., 0.2670, 0.2433: SCSN_3 , 0.1783, 0.1616. Calcd. for $\text{NaSCSN}_3 \cdot 2\text{H}_2\text{O}$: SCSN_3 , 66.7. Found: 66.8, 66.4.

Subs., 0.2698, 0.1991: Na_2SO_4 , 0.1064, 0.0792. Calcd. for $\text{NaSCSN}_3 \cdot 2\text{H}_2\text{O}$: Na, 13.0. Found: 12.8, 12.9.

The crystals, apparently of the orthorhombic system, comprise plate-like prisms and some thicker crystals. They exhibit strong birefringence, with the index of refraction for vibrations parallel to their elongation very nearly the same as that of the mother liquor. The index for perpendicular vibrations is much higher, and dispersion is marked. Yellow halos are seen at the crystal boundaries. Parallel extinction is observed from all views. When detonated under the microscope the crystals do not explode completely. The undecomposed material seems to melt in its own water of crystallization and yields, on cooling, the characteristic crystals of the dihydrate. In the capillary melting-point tube the salt undergoes fusion with decomposition, in the neighborhood of 75°. In its lack of sensitivity to friction or impact, and in its behavior on the hot plate this compound is very similar to the tetrahydrate.

Sodium Azido-dithiocarbonate,⁷ NaSCSN_3 .—Anhydrous sodium azido-dithiocarbonate may be prepared by dehydration of either the tetrahydrate or the dihydrate at room temperature over phosphorus pentoxide in a vacuum desiccator. A slight decomposition usually takes place during this operation, as evinced by the development of a fugitive pink color on the surface of the crystals, which disappears on subsequent exposure to the air.

Anal. Calcd. for NaSCSN_3 : SCSN_3 , 83.7. Found: 84.1, 83.8, 84.3. Subs., 0.1821, 0.2251: Na_2SO_4 , 0.0933, 0.1135. Calcd. for NaSCSN_3 : Na, 16.3. Found: 16.6, 16.3.

Under the microscope the anhydrous salt was found to present a distinctly powdery appearance. No definite crystal form could be assigned to the samples examined.

When rubbed on a porous plate rather vigorously it explodes, without great violence. It is not very sensitive to shock. No explosion resulted when several 0.05g. samples in small test-tubes were heated in boiling water for ten minutes. When heated to temperatures between 139° and 143°, or when thrown upon the hot plate, however, the material was invariably found to detonate with a loud report.

Rubidium Azido-dithiocarbonate, RbSCSN_3 .—Crystals of anhydrous rubidium azido-dithiocarbonate may be obtained by adding ethyl alcohol to a concentrated solution of the azido salt, cooled well below 0° by means of an ice-salt freezing mixture. Repeated attempts to crystallize fair-sized samples of the compound from aqueous solution by evaporation at room temperature have invariably resulted in violent explosions.

Very thin films of the solution will crystallize upon a flat surface, but portions of

⁷ A part of the experimental work upon this salt was performed by Dr. R. C. Houck, to whom the authors wish to express their appreciation of his assistance.

appreciable depth, especially on a curved surface like that of a cover glass, decompose on evaporation to dryness with a succession of puffs. This tendency to detonate spontaneously is probably attributable to friction between the growing crystals, and is particularly noticeable when the crystallization proceeds from several directions toward a central point.

Anal. Subs., 0.2100, 0.1841: SCSN_3 , 0.1237, 0.1081. Calcd. for RbSCSN_3 : SCSN_3 , 58.0. Found: 58.9, 58.75 (1.015 and 1.013 moles of SCSN_3 per atom of Rb).

Subs., 0.1234, 0.1227: Rb_2SO_4 , 0.0803, 0.0793. Calcd. for RbSCSN_3 : Rb, 42.0. Found: 41.7, 41.4 (0.993 and 0.986 atoms of Rb per mole).

The rubidium salt, normally colorless, gradually assumes a light red tint, RT2 on the Milton Bradley Standard,⁸ on exposure to diffused daylight. In the dark this color slowly fades and ultimately disappears entirely. In the dry state the salt is extremely sensitive to friction and to impact. Crystals detonate when gently rubbed upon a porous plate, when struck lightly with a hammer, or when thrown upon a hot plate. Small samples heated either in test-tubes or in Thiele melting-point tubes were found to decompose explosively, without melting, at temperatures between 115° and 120°.

Under the microscope, crystallization of rubidium azido-dithiocarbonate seems to take place in two stages. At first very thin rhombic plates are formed, which show symmetrical extinction, with parallel extinction when viewed edgewise, and terminal angles of about 35°. On further evaporation these appear to undergo solution and subsequent transformation into thicker crystals of a different habit, but probably still of the orthorhombic system. The terminal angles are 55° in one position and 85° in another. The forms represented might be called unit prism, basal pinacoid and macrodome.

Cesium Azido-dithiocarbonate, CsSCSN_3 .—The cesium salt crystallizes in anhydrous form from concentrated solutions cooled with a freezing mixture or treated with ethyl alcohol. Evaporation of solutions at ordinary temperatures has invariably resulted in explosions of even greater violence than those of rubidium salt, under comparable conditions. The inner walls of apparatus in which such an explosion had occurred were found to be coated, whenever the apparatus survived the shattering effect of the detonation, with a yellow solid composed chiefly of polymerized thiocyanogen, sulfur and cesium sulfide. In case phosphoric anhydride or sulfuric acid had been used as the dehydrating agent, hydrogen sulfide, liberated no doubt from the cesium sulfide, was easily detected among the products of the reaction. The rapid change of phase resulting when the supersaturated solution begins to crystallize indubitably produces stresses and strains in the crystal mass, and is manifestly accompanied by considerable friction which is conducive to further explosive decomposition.

Anal. Subs., 0.1053, 0.1748: SCSN_3 , 0.0495, 0.0825. Calcd. for CsSCSN_3 : SCSN_3 , 47.1. Found: 47.0, 47.2.

Subs., 0.1083, 0.3257: Cs_2SO_4 , 0.0779, 0.2360. Calcd. for CsSCSN_3 : Cs, 52.9. Found: 52.8, 53.2 (0.999 and 1.006 atoms of Cs per mole).

Under the microscope, the cesium salt is seen to crystallize in the form of very well developed, rhombic tablets, similar to those of the rubidium salt. Supersaturation is likely to occur unless the solution is seeded. The axial plane of the crystals is parallel to the long diagonal of the rhomb. The crystals are probably optically negative, and show a marked dispersion of the optic axis, $v < r$. The terminal angles are 85°. The higher index of refraction is for vibrations parallel to the dome faces.

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

On exposure to direct sunlight or to diffused daylight, the white crystals assume within a few minutes a superficial, violet-red tint,⁸ VRT1-VR, of a depth of color varying directly, while the time of formation varies inversely, with the intensity of the light. That this effect is not ascribable to the action of ultraviolet light is attested by the production of an entirely similar coloration upon samples covered with a glass plate 1 cm. thick. In the dark the color gradually disappears, but it may be revived by exposure to light. Repeated alternate illumination and confinement of a given sample result in a series of cycles which may be prolonged until the usual spontaneous thermal decomposition of the azido salt into thiocyanate, sulfur and nitrogen has proceeded well toward completion.

This transitory, reversible coloration of crystals of the rubidium and cesium azido-dithiocarbonates by solar radiation may possibly be attributable to a change in the position or in the orbit of the valence electron of certain rubidium or cesium atoms, brought about by the electric or the magnetic field (or both), established in the crystals by the light waves. On the assumption that these crystals are of "non-molecular structure," and that their atoms (or radicals) "are electrically charged in the solid state as well as in solution,"⁹ it seems reasonable to suppose that the principal effect of illumination may be the neutralization of certain rubidium or cesium ions in the crystal lattice by restoration in each case of the valence electron. This would be tantamount to a liberation of atoms of the alkali metals, and of azido-dithiocarbonate radicals at various points, but no escape of these discharged ions, or displacement from their normal positions in the lattice is of necessity involved. The presence of atoms of metallic rubidium or cesium held *in situ* in the crystals should account for the observed color. Since azido-carbondisulfide is colorless, the presence of an equivalent amount of this substance should produce no color effect.

From this viewpoint the coloration is due to an incipient, reversible *photolysis*, or *actinolysis*, and may be regarded as an indication of the development of local potential differences which result in electronic migration.¹⁰ This would afford another instance of a certain parallelism between the behavior of light and that of the electric current, first recognized

⁸ Wyckoff, "The Structure of Crystals," Chemical Catalog Co., New York, 1924, p. 396.

¹⁰ Against the possible contention that the coloration may be due to the formation of a thin film of free sulfur or of free thiocyanogen on the crystals, may be cited the facts that (1) no similar coloration has been observed hitherto during decomposition of the azido-dithiocarbonate radical in the free state (as azido-carbondisulfide), or in its numerous compounds; (2) the color formation is reversible, while the decomposition of the azido-dithiocarbonate radical is irreversible; (3) the course of the thermal decomposition at a given temperature is apparently the same, and identical products are formed, whether the sample is illuminated or kept in the dark.

by Grotthuss in 1818, or between photolysis or actinolysis on the one hand, and electrolysis on the other.¹¹

Another suggestion which arises from the current hypothesis is that the photosensitivity of crystalline solids may be a function of certain inter-atomic distances within the lattice. Knowledge of such dimensions, as measured or calculated from center to center of atoms or radicals, may be of value, but would seem of less significance in this connection than information concerning the distance between the nearest points of approach to each other of the outermost orbit of the valence electron in its two locations: (a) in the negative atom or radical, and (b) in the metallic atom. This minimum distance might be regarded, in a sense, as a sort of "spark gap" across which the valence electron would travel, in one direction, under the influence of radiation, in returning to the metallic ion, and in the other during the fading of the color in the dark. *Caeteris paribus*, crystals composed of relatively large atoms or radicals should show a correspondingly smaller minimum orbital distance, unless a compensatory increase in distance from center to center has occurred.¹² In the absence of experimental data concerning the crystal structure of the azido-dithiocarbonates, no definite suggestion may yet be made with regard to the arrangement of the atoms in the negative ion. In the present belief of the authors, however, the valence electron is chiefly controlled by the sulfur atom ordinarily represented as combined with the metallic atom in the undissociated molecule of the salt. If this be true, and if the azido-dithiocarbonate ion occupies a larger volume than the halogen ion, the facility of transfer of the valence electron from negative to positive ion in the lattice should be greater for azido-dithiocarbonates of the alkali metals of higher atomic weight than for those of alkali metals of lower atomic weight, and for alkali halides in general. This would possibly account for the peculiar photosensitivity of the rubidium and cesium azido-dithiocarbonates. A further experimental study of these phenomena is now in progress.

The foregoing tentative hypothesis is not altogether inconsistent with statements made by previous investigators in the attempt to explain the coloration effected in various materials by radiation, or to account for the natural color of Stassfurt blue halite.¹³ This blue color, first noted by

¹¹ Bancroft, *J. Phys. Chem.*, **12**, 209, 318, 417 (1908); **13**, 1, 181, 269, 449, 538 (1909); **14**, 292 (1910); **17**, 596 (1913).

¹² It is believed that inter-atomic distances in crystals of the alkali metal halides increase with rise in atomic weight of either metal or halogen (Ref. 9, p. 400). Whether or not this increase is sufficient to compensate fully for the increase in the size of the individual atoms, and thus to prevent a progressive reduction in the size of the "spark gap," is not yet apparent.

¹³ (a) Meyer and Przibram [*Sitzb. Kais. Akad. Wiss. Wien Abt. IIA*, **121**, 1413 (1912); **123**, 653 (1914); *C. A.*, **3**, 1387 (1914); **9**, 411 (1915)] ascribe the coloration

Davy in 1818, and explained by Zsigmondy,¹⁴ with approval of Siedentopf¹⁵ and Svedberg,¹⁶ as due to the presence of colloidal particles of metallic sodium, may now perhaps more reasonably be attributed to atoms of metallic sodium held *in situ* in the lattice. The presence of an equal number of chlorine atoms, also held *in situ*, would insure non-alkalinity of aqueous solutions of the blue salt, as observed by various investigators.¹⁷ It seems scarcely necessary to assume, with Meyer and Przibram,^{13a} the coagulation of metallic atoms to form colloidal particles, unless the treatment is so prolonged, or the radiation so intense as to result in a partial disintegration of the lattice. In this event some halogen atoms would probably escape, and an aqueous solution of the crystals should show appreciable alkalinity. The color produced in the crystals under such conditions might be expected to vary with the degree of aggregation of the colloidal particles. The displacement of "certain groups of electrons," postulated by Lind and Bardwell^{13c} may, in the case of metallic salts or other polar compounds, at least (as may also the "abnormality in the constraint upon the valence electron," suggested by Phipps and Brode)^{13d} consist simply in the transfer of certain valence electrons from negative to positive ions in the lattice, as assumed to take place during the illumination of rubidium and cesium azido-dithiocarbonates.

Summary

Five new compounds have been prepared and described: lithium azido-dithiocarbonate monohydrate, $\text{LiSCSN}_3 \cdot \text{H}_2\text{O}$; sodium azido-dithiocarbonate dihydrate, $\text{NaSCSN}_3 \cdot 2\text{H}_2\text{O}$; sodium azido-dithiocarbonate, Na -produced in the salts of the alkali and alkaline-earth metals by the rays from radium to a neutralization of the positive metallic ion in the salt by the electron, with production of a neutral metallic atom. Such atoms are believed subsequently to coagulate, yielding colloidal particles which are directly responsible for the color. (b) Newbery and Lupton [*Mem. Proc. Manchester Lit. Phil. Soc.*, **62**, No. 10 (1918)] assume primary ionization into positive and negative ions, which are of atomic dimensions, and are separated by minute distances. One of these ions is capable of producing color. (c) Lind and Bardwell [*J. Franklin Inst.*, **196**, 375 (1923)] explain the coloring produced in transparent minerals and gems by radium radiation on the assumption that "certain groups of electrons are displaced by radiation from their normal positions, and take up new metastable positions among the atoms. No displacement (or only secondary displacement) of the atom is involved." (d) Phipps and Brode [*J. Phys. Chem.*, **30**, 507 (1926)] conclude, from their spectrophotometric investigation of Stassfurt blue halite, that the blue color "may be due to an abnormality in the constraint upon the valence electron at various points in the halite lattice, and that the fading of the color with heat may come from the return of the electron to its normal constraint."

¹⁴ Zsigmondy, "Zur Erkenntnuiss der Kolloide," Gustav Fischer, Jena, 1905, p. 58.

¹⁵ Siedentopf, *Physik. Z.*, **6**, 855 (1904).

¹⁶ Svedberg, "Colloid Chemistry," Chemical Catalog Co., New York, 1924, p. 67.

¹⁷ Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, 1922, p. 530.

SCSN₃; rubidium azido-dithiocarbonate, RbSCSN₃; and cesium azido-dithiocarbonate, CsSCSN₃.

An outstanding characteristic of the rubidium and cesium salts is their extraordinary photosensitivity, in consequence of which they assume, respectively, on exposure to ordinary light, a light red or a violet-red tint, which gradually fades in the dark. It is suggested that this phenomenon may be attributed to the discharge of certain metallic and azido-dithiocarbonate ions, *in situ*, in the crystal lattice as a result of photolysis. Further work, looking toward the extension of this hypothesis to other cases of photosensitivity and radiosensitivity, is now in progress.

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THE SURFACE ENERGY AND THE HEAT OF SOLUTION OF SOLID SODIUM CHLORIDE. I

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In this paper is described a new type of calorimeter which can be used with small quantities of material to determine directly the heat of solution from high to very low concentrations, with a high degree of accuracy in all cases. The calorimeter was applied to the determination of the heats of solution of sodium chloride over a wide range of concentrations. From determinations made with finely divided sodium chloride, the surface energy of solid sodium chloride was found.

The surface energy of solids is not susceptible of direct measurement, as in the case of liquids. A few investigators, by the use of indirect methods, have arrived at a partial solution of the problem and since an excellent summary of their work will be found in Freundlich's "Colloid and Capillary Chemistry"¹ it will not be repeated here.

In the present investigation, an attempt is made to determine the surface energy of solid sodium chloride by measurement of the difference between the heat of solution of ordinary crystalline sodium chloride and that of finely divided salt at the same concentration.

If sodium chloride be subdivided into cubes 1μ in diameter, an area of 1.6×10^6 sq. cm. per mole is produced. On solution, the energy associated with this surface should appear as heat and thereby produce a larger positive heat of solution than the coarsely ground solid. Since the heat of solution of ordinary sodium chloride is negative, this means that the heat of solution of the finely divided material should be numerically smaller. The experimental procedure adopted in this investigation is detailed in the following pages, but the result may be briefly indicated here.

¹ Methuen and Co., Ltd., London, 1926, pp. 102, 155.