I THE OXIDATION STATE OF ARGENTIC SALTS IN ACID SOLUTION

II THE MERCURY SENSITIZED PHOTO-REACTION BETWEEN AMMONIA AND OXYGEN

III THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN SELENIDE

Thesis by

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ABSTRACT

I. THE OXIDATION STATE OF ARGENTIC SALTS IN ACID SOLUTION

The argentic salt produced in solution by oxidizing with ozone argentous nitrate dissolved in concentrated nitric acid at 0°C. is shown to contain the silver almost entirely in the bipositive form. One of the three independent methods used involves the determination of the magnetic moment of the argentic silver ion. A value of 1.98 Bohr magnetons is found for its magnetic moment.

II. THE MERCURY SENSITIZED PHOTO-REACTION BETWEEN AMMONIA AND OXYGEN

Experiments which were made in two different reaction vessels give evidence of a surface reaction. The contradictory results of two former pairs of investigators are discussed and the present results are shown to be in accord with both previous pieces of work.

III. THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN SELENIDE

The results are given of a study of the photodecomposition of hydrogen selenide at a series of pressures from 8 to 60 mm. A unit quantum yield was found, constant over this pressure range. A mechanism for the decomposition is offered.

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Argentic Salts in Acid Solution. II. The Oxidation State of Argentic Salts

BY ARTHUR A. NOYES, KENNETH S. PITZER AND CLARENCE L. DUNN

Purpose of this Investigation

In the preceding article Noyes, Hoard and Pitzer[1] described the general nature and the rates of the reactions by which argentic salt is produced by the ozone oxidation of acid argentous nitrate, and by which it is reduced by water. Before proceeding further with the description of these researches, however, it seemed essential to establish the state of oxidation, whether bipositive or tripositive, in which argentic silver exists in nitric acid solution. To a description of experiments made with this purpose this article is devoted.

It is remarkable that this question has remained unanswered so long in the case of a readily obtainable oxidation state of a common element—an oxidation state, moreover, that explains the striking catalytic effects of silver salts. Furthermore, the question is of much theoretical interest in relation to the valence states compatible with the periodic system, inasmuch as copper exists mainly unipositive and bipositive, and gold unipositive and tripositive.

Previous Investigations

The most definite indications previously existing as to the oxidation state of argentic silver in its solutions were furnished by the composition of the solid phases that separate in preparing or

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(1) Noyes, Hoard and Pitzer, THIS JOURNAL, **57**, 1221 (1935).

in diluting the solutions or upon adding other substances to them, but these indications seem contradictory.

First, it may be mentioned that Barbieri[2] found upon mixing an aqueous solution of potassium peroxysulfate with a solution of silver nitrate in pyridine (Py) that orange-colored crystals separated of the composition $\mathrm{AgS_2O_8{\cdot}4Py}$, and that this compound forms isomorphous crystals with the previously prepared cupric compound $\mathrm{Cu_2S_2O_8{\cdot}4Py}$, both these facts showing the existence of a complex salt containing bipositive silver, as is more clearly expressed by the formula $[\mathrm{Py_4Ag}]^{++}\mathrm{S_2O_8}^{=}$. There have since been prepared[3] complex salts of bipositive silver with various other bases (having coördination numbers four or six) and with other anions than peroxysulfate.

On the other hand, several investigators (Higson,[4] Yost,[5] Barbieri,[6] Jirsa[7]) have shown that argentic solutions give precipitates with water of solid basic salts that contain tripositive silver. This is proved by the fact that they yield on drying compounds such as $\mathrm{AgONO_3{\cdot}Ag_2O_3{\cdot}4AgO}$ or $\mathrm{(AgO)_2SO_4{\cdot}6AgO}$. Such salts are precipitated even from a solution prepared by dissolving pure silver oxide in nitric acid, and even though this dissolving is attended by evolution of oxygen (Jirsa). The results obtained by Yost[5] and by Carman[8] are especially significant, in that they show that all the silver is originally precipitated in the tripositive state. Thus the compounds prepared by them from neutral potassium peroxysulfate and silver nitrate contain per atomic weight of silver 2.0 oxidation equivalents (measured with reference to reduction to argentous salt). Carman showed, however, that if the precipitates stood one to three hours before filtering, the ratio drops to a fairly constant value of 1.51–1.53, corresponding to about equal quantities of bipositive and tripositive silver.

The fact that the rate of oxidation of argentous salt by peroxysulfate, as well as by ozone, is proportional to the first power, not to the square, of the argentous concentration, indicating that the mechanism involves primarily the production of tripositive silver, has also doubtless aided in creating a presumption that this is the form of silver that predominates in the solution; but in reality this fact would be fully accounted for by the existence of only a very small proportion of tripositive silver.

The Oxidation State Determined by a Solubility Method

Principle of the Method.—The principle of this method of determining the oxidation state of the silver is illustrated by the following description of the preliminary experiments which were made by K. S. Pitzer. Oxygen containing 5–7% ozone was passed for twelve hours through a gas bottle (without a porous plate) containing about 200 ml. of 10 or 16 *N* nitric acid and a great excess (25 g.) of crystalline silver nitrate at 0°. Known volume samples of the (approximately) steady-state mixture were then drawn off and analyzed: (1) for oxidizing power, correcting the result for the dissolved ozone, and (2) for total silver (unipositive plus bipositive plus tripositive). Then, by an experiment in which (to agitate the liquid) oxygen instead of ozonized oxygen was passed for forty hours, the solubility of argentous nitrate was determined in a solution of the same acid content at the same temperature, and this (unipositive) silver was subtracted from the total silver found in the steady-state mixture.

This method was fairly precise because the solubility of silver nitrate in strong nitric acid was found to be unexpectedly small (0.12–0.36 *f* at 0°). It involves the assumption that this solubility is not appreciably affected by the argentic silver, which, however, was present at only 0.22 to 0.25 formal.

The Results of the Preliminary Experiments.—These are given in Table I. It will be seen that in the more accurate, second experiment the

TABLE I

OXIDATION STATE OF ARGENTIC SILVER DETERMINED BY A SOLUBILITY METHOD; PRELIMINARY RESULTS AT 0°

Expt.	$\mathrm{HNO_3}$ Volume-formal	$\mathrm{AgNO_3}$ Solubility	Reaction mixture (Σ Ag)	($\mathrm{Ag^{II}}$) + ($\mathrm{Ag^{III}}$)	Oxid. Equiv.	Ratio of oxid. equiv. to ($\mathrm{Ag^{II}}$) + ($\mathrm{Ag^{III}}$)
1	15.2	0.119	0.366	0.247	0.217	0.89
2	10.0	.357	.583	.226	.218	.96
			.583	.226	.222	.98
			.588	.231	.222	.96

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[2] Barbieri, *Atti accad. Lincei*, [5] **21**, 560–563 (1912); *Gazz. chim. ital.*, **42**, 7 (1912).

[3] Hieber and Mühlbauer, *Ber.*, **61**, 2149 (1928); Morgan and Burstall, *J. Chem. Soc.*, **132**, 2594 (1930); Barbieri, *Ber.*, **60**, 2424–2427 (1927), and *Atti accad. Lincei*, [6] **16**, 44–47 (1932).

[4] Higson, *J. Chem. Soc.*, **119**, 2048 (1921).

[5] Yost, THIS JOURNAL, **48**, 152–164 (1926).

[6] Barbieri, *Atti accad. Lincei*, [6] **13**, 882–887 (1931).

[7] Jirsa, *Z. anorg. Chem.*, **148**, 130–140 (1925); **158**, 33–60, 61–66 (1926).

[8] Carman, *Trans. Faraday Soc.*, **30**, 566–577 (1934).

number of oxidation equivalents was 97% of the number of formula weights of the total argentic salt, indicating that this salt was substantially all in the bipositive state.

Procedure for the Final Determination.—A final experiment was then made with great care under more favorable conditions. In this experiment we were fortunate in having the detailed coöperation of Professor Isaburo Wada, Director of the Wada Research Laboratory, of Tokio, who was then visiting this Institute. In developing the analytical methods and in making the analyses we were ably assisted also by Messrs. C. D. Coryell and Alexander Kossiakoff. In this direction we are also indebted to Professor E. H. Swift for important suggestions.

The principle involved in determining the state of oxidation of the silver was the same as before. The temperature at which the solubility of silver nitrate was determined and at which the steady-state mixture was prepared was −5.8 ± 0.2°, instead of 0°, concentrated nitric acid (15.2 *N* at 20°) being used, as in one of the previous experiments. These conditions made possible much greater experimental accuracy, for at this lower temperature the ratio of argentic to argentous silver is much larger, and the spontaneous decomposition of the argentic silver is much slower. Moreover, precise analytical methods whose reliability had been well tested were used, and the quantities of the samples were all determined by weight, not by volume.

The Procedure in Detail.—The solutions were prepared in glass-stoppered gas absorption bottles with porous sintered glass plates, of the kind described in the preceding article,[1] to which reference may be made also for the details of the ozonizer, thermostat, and other features of the apparatus. In one gas bottle were placed 7 g. of fine silver nitrate crystals and 150 ml. of a nitric acid solution 15.55 *N* (by volume) at 0° (or 15.19 *N* at 20°), and in another bottle were placed 20 g. of silver nitrate crystals and 200 ml. of the same nitric acid; and these bottles were kept in a large alcohol–water bath at −6.15° for twenty-four hours, and then at −5.8 ± 0.2° for forty-eight hours more. During this whole period there was passed steadily a slow current of oxygen through the first bottle (to stir its contents), and of ozonized oxygen through the second bottle (to produce the steady-state mixture). Before entering the latter bottle (so as to avoid evaporation of the oxidized solution and to determine the solubility of the ozone) the ozonized oxygen was passed through a bottle containing only nitric acid of the same strength.

The partial pressure of the ozone was found to be 0.0625 atm. and its solubility at −5.8° in the nitric acid (15.2 *N* at 20°) was found to be 0.00321 mole per liter of solution. These quantities were determined by driving the gas, by means of a current of carbon dioxide, out of a gas bottle of known volume, filled first with the ozonized oxygen, and second containing known volumes of this gas and of its saturated solution in 15.2 *N* nitric acid. The expelled gas was passed in each case into a 0.5 *f* potassium iodide solution saturated with sodium hydrocarbonate; then the mixture was acidified, and the liberated iodine titrated with thiosulfate.

After three days the ozone was displaced from the steady-state mixture by passing a rapid current of oxygen through it for about five minutes, and duplicate samples of the pure silver nitrate solution and of the steady-state mixture were removed from the respective bottles through their side-arms (so that the crystals of undissolved silver nitrate would be retained by the porous plate near the bottom of the bottles).

The samples of unozonized silver nitrate were run into empty weighed flasks, and those of the steady-state mixture into weighed flasks containing 1.8 g. of thallous nitrate, placed in the cold bath. After coming to room temperature these flasks and their contents were weighed, thus giving the weights of the samples, which were later analyzed as will now be described.

Methods of Analysis.—The solubility of the silver nitrate in the pure nitric acid solution was determined by diluting this solution, nearly neutralizing it with ammonium hydroxide, and adding a 2% excess of sodium chloride solution. The precipitated silver chloride was collected in a weighed porous plate filter funnel, dried at 200°, and weighed. It was proved that even the very large quantity of ammonium nitrate present did not dissolve a significant quantity of silver chloride.

The determination of the oxidizing power of the steady-state mixture involved much preliminary study, owing to the presence in the mixture of concentrated nitric acid and owing to the rapid decomposition of argentic silver when the solution is diluted or allowed to warm up. It was necessary to find some reducing substance not oxidized by concentrated nitric acid, but oxidized instantaneously, even at −5.8°, by argentic silver—a substance, furthermore, whose oxidation product could afterward be analyzed for with accuracy. After many experiments thallous nitrate was found to be well suited for this purpose. It is not oxidized by cold nitric acid, but reduces argentic silver at −5.8° within a few seconds, as was shown by the flash-like disappearance of the black color as soon as the cold sample of the steady-state mixture was run onto the solid thallous nitrate and the mixture was shaken. It was shown, moreover, by an experiment in a small eudiometer that this reaction is attended by no oxygen evolution, and therefore by no spontaneous or catalytic decomposition of the argentic silver.

After a long study of possible thallium determinations (made mainly by Mr. C. D. Coryell) it was found that the quantity of thallic salt produced could be determined by neutralizing the nitric acid in the cooled sample with 15 *N* ammonium hydroxide, filtering off and washing the brown thallic hydroxide, dissolving this in cold 3 *N* sulfuric acid, and analyzing the solution for its thallic content. This last analysis was made by using the method described by Kolthoff[9] and by Zintl and Rienäcker[10] for titrating thal-

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[9] Kolthoff, *Rec. trav. chim.*, **41**, 189 (1922).

[10] Zintl and Rienäcker, *Z. anorg. allgem. Chem.*, **153**, 278 (1926).

TABLE II

ANALYSIS OF SATURATED SILVER NITRATE SOLUTION AND OF THE STEADY-STATE MIXTURE PRODUCED AT −5.8°

Solution	Sample withdrawn, g.	Determinations of total silver			Determinations of oxidation–equivalents		
		% of sample analyzed	AgCl obtained, mg.	At. wt. Ag per kg. solution	% of sample analyzed	$KBrO_3$ used, ml.	Oxid. eq. per kg. solution
Satd. $AgNO_3$ solution	36.78	100	316.3	0.0600	...	...	....
	74.01	100	632.2	.0597	...	...	....
Steady-state mixture	38.36	51.05	851.5	.3033	26.31	45.96	0.2334
	38.36	48.81	812.4	.3027	38.54	67.22	.2331
	38.36	...	...	...	34.98	61.13	.2335
	38.45	51.66	859.1	.3017	35.32	61.78	.2331
	38.45	48.19	803.9	.3014	30.05	52.51	.2329
	38.45	...	...	....	34.19	59.75	.2329
				Mean 0.3023			Mean 0.2332

lous thallium with standard bromate solution with the aid of methyl orange as an oxidation indicator. This is possible since under proper conditions this indicator is decolorized only after an excess of bromate over that required to oxidize the thallous salt has been added.

In detail this thallic determination was carried out as follows. The thallic sulfate solution (about 140 ml.) obtained by dissolving the thallic hydroxide from each of the two samples of the steady-state mixture was divided by weighing into three nearly equal portions. To each of these portions were added 11 g. of solid potassium chloride and one drop of 0.2% methyl orange solution, and, after heating the solution to 50–60°, bromate solution (standardized against pure thallous chloride) was run in from a buret until the indicator was decolorized, thus estimating any thallous thallium (in fact about 2%) that was carried down in the thallic hydroxide precipitate. Then the solution was heated nearly to boiling, and sulfur dioxide gas was passed through it for ten minutes, after which the solution was boiled for ten to fifteen minutes to expel the sulfur dioxide, and was titrated at 50–60° with the bromate solution, adding one drop of methyl orange solution as the end-point was approached. The amount of bromate required to decolorize the indicator and the amount added before reducing the thallic salt with sulfur dioxide were subtracted, thus giving the oxidizing power of the thallic sulfate solution and hence of the original argentic solution. Test analyses, made with weighed samples of pure thallous chloride oxidized to the thallic form, had previously shown this analytical procedure to be remarkably precise.

The total silver present in the same samples of the steady-state mixture was determined by acidifying the filtrate from the thallic hydroxide precipitate, adding sodium chloride, and weighing the precipitated silver chloride, as in the case of the pure silver nitrate solution.

Experimental Results and Final Value of Oxidation State.—The experimental data for all the determinations so made are given in Table II. The headings are all self-explanatory, except that the bromate solution used was 0.05124 *N* (in an oxidation sense).

The mean values derived from all the data of Table II, and the final values of the oxidation state, are shown in Table III. In order to be able to refer the mean values of the quantities of silver and of the oxidation equivalents to 1 kg. of acid, as well as to 1 kg. of solution, the latter values have been corrected by subtracting from the weight of the solution that of the solid silver nitrate calculated to have been dissolved, and (in the case of the steady-state mixture) also that of the oxygen calculated to have been absorbed in producing the argentic silver. The nitric acid used was 15.2 *N* at 20°.

TABLE III

FINAL MEAN VALUES OF THE SOLUBILITY OF SILVER NITRATE AND OF THE COMPOSITION OF THE STEADY-STATE MIXTURE AT −5.8°

Solution	Atomic weights of silver		Oxidation equivalents		Ratio of oxid. eq. to argentic salt
	In kg. of solution	Per kg. of 15.2 *N* HNO_3	In kg. of solution	Per kg. of 15.2 *N* HNO_3	
Steady-state mixture	0.3023	0.3193	0.2332	0.2463	...
Satd. $AgNO_3$ solution	.0598	.0604	.0	.0	...
Difference	.2425	.2589	.2332	.2463	0.951

The difference 0.2589 between the number of equivalents of silver in the steady-state mixture and in the pure silver nitrate solution (referred to the same weight of nitric acid) evidently corresponds, at least approximately, to the argentic silver in the mixture, and the ratio 0.2463/0.2589 of the oxidation equivalents to this difference, which equals **0.951**, shows how much the oxidation number of the argentic silver exceeds that of argentous silver. This corresponds to an oxidation number of 1.951 for the silver in the argentic salt. The silver is therefore *bipositive* in the argentic compound existing in the steady-state mixture produced at −5.8° in nitric acid 15.2 *N* at 20°.

The difference between 1.95 and 2.00 may be reasonably attributed to the spontaneous decomposition of the compound during the time required for removal of the ozone from the mixture and for the addition of the sample to the thallous nitrate. And there is doubtless some inaccuracy in the assumption that the amounts of argentous nitrate present as such in the pure solution and in the steady-state mixture are identical.

The Oxidation State Determined by Displacement of the Steady State

EXPERIMENTS BY CLARENCE L. DUNN

Principle of the Method.—A second principle employed in these researches for determining the oxidation state of argentic silver involves displacement of the steady state. Namely, since argentic solutions have been prepared under conditions where the ratio of oxidation equivalents to total silver is already not very far from unity (which would correspond to complete conversion to the bipositive state), one may expect to determine, upon making the conditions progressively much more favorable, whether this ratio approaches unity asymptotically, or whether it goes through this value without any noticeable discontinuity. For example, starting with the fact that with 0.025 *f* silver nitrate in 12 *N* nitric acid 0.93 oxidation equivalents of argentic silver are produced at 0° for each formula weight of (total) silver present when the solution is brought to a steady state with ozone at 0.06 atm., one might determine upon increasing the ozone partial pressure, say to 0.4 atm., whether the equivalents of argentic salt increased only from 0.93 to nearly 1.00, or whether they increased up to values much above unity. This evidently involved on the experimental side making ozone at these higher partial pressures, saturating acid silver nitrate solution with it, and analyzing the mixture.

Preparation of Ozone Gas at High Concentration and Oxidation of the Silver Solution.—The concentrated ozone gas needed for these experiments was made from tank oxygen which was purified by passing it through an all-glass train of tubes containing an electrically heated platinum wire, soda-lime, strong sulfuric acid and phosphorus pentoxide, and through a very fine sintered glass filter (to remove particles of dust, rubber, etc.). This gas after emerging from the ozonizer, when it contained about 6% of ozone by volume, was fractionally condensed in a 15-ml. cylindrical bulb sealed to the ozonizer. This bulb had a sealed-in entrance tube delivering 5 cm. above the bottom of the bulb and had a side-arm near the top out of which the gas issued. The bulb was placed within a Dewar tube containing liquid air, which could be brought to any desired level by raising or lowering the Dewar tube. During the liquefaction the tube was kept so low as to condense ozone containing very little oxygen, the composition of the condensate being judged by the depth of its blue color. After about 2 ml. of liquid had condensed, requiring about three hours, the liquid was distilled at a moderate rate for a period of about three hours into a 12 *N* nitric acid solution exactly 0.025 *f* in silver nitrate, contained in a gas bottle in a thermostat at 0°. This solution had been previously treated with 6% ozone until the steady state corresponding thereto had been practically reached. The gas emerging from the reaction bottle contained at the end of one hour about 40% of ozone, and at the end of two and one-half hours about 65% of ozone by volume. A concentration of 12 *N* nitric acid was used, since this had been found to be approximately that at which the largest fraction of argentic salt was produced with 6 to 8% ozone. The small silver concentration of 0.025 formal was used, since the oxidation is larger the more dilute the silver, and since on the other hand this is the smallest concentration that would give sufficient analytic accuracy.

Analysis of the Reaction Mixture.—Before taking a sample for determining the oxidizing power the dissolved ozone was removed from the gas bottle by subjecting it for one minute to the reduced pressure of a water pump and then drawing a rapid stream of oxygen through it for half a minute more. A blank experiment with 12 *N* nitric acid saturated with ozone showed that the ozone remaining after this treatment was negligible. Then there was withdrawn from the gas bottle with a cooled pipet 50 ml. of the reaction mixture, and this was delivered into a two-fold excess of 0.05 *f* thallous nitrate solution at 0°. The mixture was analyzed for thallic thallium as was described in the earlier part of this article, except that hydrochloric acid was used for dissolving the ammonium hydroxide precipitate of thallic hydroxide, instead of sulfuric acid; approximately 0.05 *N* potassium bromate was used as before for titrating the thallium after reducing it by sulfur dioxide.

Experimental Results and Conclusion as to the Oxidation State.—A series of experiments was first made to determine the steady state resulting with 9 or 6% ozone at 0° in 12 *N* nitric acid solutions 0.025 *f* in silver nitrate. Such solutions were treated with ozonized oxygen of this strength for several days till no further change in their oxidizing power took place. The ratio of oxidation equivalents to total silver equivalents had at the steady state in different experiments the following percentage values: with 9% ozone, 97.4, 96.5, 98.4%; with 6% ozone, 93.0% (84.0% when 15 *N* nitric acid was used).

Then eight other experiments were made with 12 *N* nitric acid 0.025 *f* in silver nitrate at 0°, by carrying the oxidation at first only to 34 to 83% with 6% ozone, and afterward making it as complete as possible by treatment with 40 to 65% ozone for three hours in the way described above. The percentage ratios of oxidizing power to total silver obtained with the 6% and the 40–65% ozone are those shown in Table IV in the first and second rows, respectively.

TABLE IV

OXIDATION OF SILVER BY CONCENTRATED OZONE AT 0°

Ozone used, %	Percentage of oxidation equivalents to total silver equivalents							
6	83.2	81.0	80.4	80.0	56.5	49.0	48.0	34.1
40–65	100.0	100.8	98.1	99.0	99.1	103.0	90.0	98.6

It will be seen, irrespective of the oxidation (83–34%) attained with the 6% ozone, that the more concentrated ozone raised the percentage of oxidation equivalents to equivalents of total silver (except in one case) only to 98.1 to 103.0%—never to any larger value such as would correspond to any considerable proportion of tripositive silver. (Incomplete removal of ozone probably accounts for the one slightly high value of 103%.) The conclusion seems, therefore, justified that under the conditions here involved (12 *N* nitric acid, 0.025 *f* silver nitrate, 0°) even fairly concentrated ozone converts little, if any, of the silver into a state more highly oxidized than the bipositive state.

The Oxidation State of Argentic Silver Determined from the Magnetic Susceptibility of its Solutions

EXPERIMENTS BY CLARENCE L. DUNN

Theoretical Principle of the Method.—A third method of studying the state of oxidation of argentic silver was suggested by Professor Linus Pauling. This rests upon the fact that the magnetic moment of the silver ion in its different valence states and the corresponding change in the susceptibility of the solution may be expected to afford a direct indication of the oxidation state of the silver.

The theoretical principle involved in the method is the simple one, valid for certain types of atoms, that the magnetic moment of an atom or ion is determined primarily by the spin of its unpaired electrons, and therefore by the number of such electrons, being 1.73 Bohr magnetons for one such electron, 2.83 Bohr magnetons for two, and so forth.[11] The univalent silver ion has a complete sub-shell of 10 outer (4d) electrons and has no spin magnetic moment, but only a diamagnetic one. The bivalent silver ion with only nine of these outer electrons has an odd and therefore an unpaired electron, and has a spin moment of 1.73 magnetons. The trivalent silver ion with eight outer (4d) electrons probably has only paired electrons, and is probably therefore diamagnetic; for this has been shown by Janes[12] to be true of bivalent palladium, which has the same electronic configuration. It is, however, possible, though less likely, that the tripositive silver ion, like the structurally similar bivalent nickel ion (with eight 3d electrons), has two unpaired electrons, in which case it would be paramagnetic, but would have a spin moment (2.83 magnetons) different from that of the bivalent silver ion.

While in an ion having unpaired electrons the spin of such electrons usually gives to the ion its main magnetic moment, yet the orbital motion of such electrons may produce a large additional moment. Much of this orbital moment, however, is usually found (except in the rare-earth group) to be quenched by the surrounding molecules. This quenching of the orbital moment of a bivalent silver ion may be expected to occur to about the same extent as does that of the similarly constituted cupric ion, for which in solution several investigators[13] have found a total moment of about 1.92 magnetons. Moreover, Sugden[14] has found that this moment lies between 1.74 and 2.16 magnetons for various solid salts of bipositive silver with pyridine. On the other hand, the trivalent silver ion, if it is not diamagnetic, would probably have a total moment like that of the bivalent nickel ion, which has been found by Cabrera and Duperier[15] to have a total moment of 3.19 magnetons in the solution of its nitrate.

Experimental Method of Determining Susceptibilities.—The effect of oxidizing the silver upon its magnetic moment was derived by comparing the susceptibilities of appropriate solutions. These susceptibilities were measured by Gouy's method in the form described by Shaffer and Taylor,[16] with an apparatus set up and used in this Laboratory by Dr. E. B. Wilson, Jr., and Dr. G. W. Wheland. The process consists in weighing the solution in a vertical glass tube between the pole-pieces of an electromagnet both before and after the magnet is activated. Then the two weighings are repeated under identical conditions with a substance of known susceptibility (pure water). The ratio of this known value to the change in weight observed gives the constant of the apparatus, by which other observed weight differences can be multiplied to give susceptibilities.

Experimental Procedure in Detail.—In detail the experiments were made in the following way. Solutions of a

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[11] Stoner, *Phil. Mag.*, **8**, 250 (1929); Pauling, THIS JOURNAL, **53**, 1391 (1931).

[12] Janes, *ibid.*, **57**, 472 (1935).

[13] Liebknecht and Wills (1900), Jacobsohn (1916), Cabrera and Moles (1914–1917), Cherbuliez (1917). For a curve showing their results, see Birch, *J. phys. radium*, **9**, 138 (1928).

[14] Sugden, *J. Chem. Soc.*, 161–170 (1932).

[15] Cabrera and Duperier, by Barnett, "International Critical Tables," 1929, Vol. VI, p. 352.

[16] Shaffer and Taylor, THIS JOURNAL, **48**, 844 (1926).

definite amount of silver nitrate in 10 *N* nitric acid were made, and the larger part of each was treated with ozone at 0° for twenty-four hours. The rest of the unoxidized solutions was reserved for comparative susceptibility measurements.

Samples of the oxidized and unoxidized solutions were placed in a tube of about 7 mm. bore fitted with a ground-glass top and of the design described by Shaffer and Taylor, and were weighed in and out of the magnetic field. The same tube was then charged with conductivity water, and the weighing repeated, this serving as a standard of known susceptibility.

The oxidized solution, before it was weighed, had been brought to 22° and the ozone had been removed by a current of air. The concentration of the oxidized silver in the solution was determined by removing samples for analysis just before and just after making the weighing with the field on, and taking the mean of the two results, this being done to eliminate the effect of the rather rapid decomposition of the oxidized silver. Each sample was run into a weighed flask containing standard thallous nitrate solution, the flask was reweighed to give the weight of the sample, and the amount of thallous salt unoxidized was determined with bromate by the method described above.

As a check the oxidized solution was allowed to decompose spontaneously in the weighing tube, and measurements were made on the resulting solution. The susceptibility of this solution was found to be identical with that of the original unoxidized solution.

Accuracy in the magnetic measurements required that the concentration of oxidized silver be as high as possible, yet the available ranges of concentrations of acid and of total silver were very limited, owing to the fact that the percentage of the silver oxidized by 6% ozone is large only when the acid is concentrated, and then the silver nitrate is only moderately soluble. A number of measurements were made with each of two silver solutions, 10 *N* in nitric acid, in which the percentage of oxidized silver was varied in the different experiments by allowing decomposition to take place or by retreating the solution with ozone at 0°.

The Experimental Data and the Calculated Magnetic Moments.—The data of the measurements at 22° are given in the first seven columns of Table V, and the change in susceptibility upon oxidation and the magnetic moments of the oxidized silver atom, calculated as described below, are given in the last three columns. The symbols have the following significance.

c_1 and c_2 are the equivalents of argentic silver per gram of sample found in the oxidized solution just before and just after it was weighed in the magnetic field; and the mean of these values is the concentration to which the observed change in weight is considered to correspond. As given in the table these quantities are multiplied by 10^6.

Δw_{UN} is the increase in weight in milligrams which the unoxidized sample showed when the magnetic field was on over that when it was off; Δw_{OX} is the corresponding increase in weight which the oxidized sample (with the same total silver concentration) showed under the same conditions; and $\Delta w_{\mathrm{H_2O}}$ is the increase in weight which pure water showed under these conditions.

$\chi_{\mathrm{OX}} - \chi_{\mathrm{UN}}$ is the change in susceptibility per cubic centimeter (in cgsm. units) produced by oxidizing the sample. This is calculated by the expression $-7.49 \times 10^7(\Delta w_{\mathrm{OX}} - \Delta w_{\mathrm{UN}})/\Delta w_{\mathrm{H_2O}}$, the numerical factor being the volume susceptibility of water against air at 22°. μ is the increase in magnetic moment, expressed in Bohr magnetons, attending the conversion of one atom of argentous silver into argentic silver, calculated from the data in the way described below, first assuming the silver to be bipositive, and second, assuming it to be tripositive.

Experiments 1–6 were made with a solution containing 0.252 formula weight and experiments 7–12 with one containing 0.257 formula weight,

TABLE V

SUSCEPTIBILITY MEASUREMENTS AND THE MAGNETIC MOMENT OF ARGENTIC ION

Expt.	Equivalents of $Ag_{\mathrm{OX}} \times 10^6$ per g.			Δw_{UN} in mg.	Δw_{OX} in mg.	$\Delta w_{\mathrm{H_2O}}$ in mg.	$\chi_{\mathrm{OX}} - \chi_{\mathrm{UN}} \times 10^7$	μ in magnetons	
	$10^6 c_1$	$10^6 c_2$	Mean					For Ag^{II}	For Ag^{III}
1	61.2	56.6	58.9	−20.9	−16.7	−22.5	1.30	1.97	2.78
2	91.0	83.5	87.2	20.6	14.8	22.5	1.93	1.97	2.78
3	85.8	76.7	81.2	19.5	14.2	21.3	1.87	2.01	2.84
4	116.0	108.1	112.0	20.5	12.9	22.4	2.54	1.99	2.82
5	92.1	84.6	88.4	20.4	14.4	22.3	2.02	2.00	2.83
6	65.1	60.1	62.5	20.7	16.5	22.6	1.39	1.97	2.79
7	32.5	31.4	31.9	20.4	18.3	22.3	0.705	1.96	2.78
8	63.0	62.0	62.5	20.4	16.2	22.3	1.41	1.98	2.81
9	67.1	60.5	63.7	20.0	15.8	21.8	1.44	1.99	2.81
10	105.9	98.5	102.2	19.5	13.0	21.3	2.28	1.97	2.79
11	110.3	97.3	104.8	19.5	12.8	21.3	2.36	1.98	2.80
12	88.5	73.5	81.0	19.8	14.3	21.7	1.90	2.02	2.86
								Mean 1.98	2.81

of total silver per kilogram of solution. The densities at 22° of the two (unoxidized) solutions were 1.343 and 1.350, respectively.

Calculation of the Magnetons per Atom of Argentic Silver.—The calculation of the magnetic moment from the data was made as follows.

(1) The magnetic changes in weight are first converted into change in susceptibility per cubic centimeter (in cgsm. units) in the way described above. Thus is calculated the quantity $\chi_{OX} - \chi_{UN}$, recorded in the table.

(2) This change in susceptibility per unit volume is then converted into susceptibility per equivalent of argentic salt produced. This is done by multiplying it by $1/cd$, since this is the volume of one equivalent when d represents the density and c (equal to the mean of c_1 and c_2 in the table) represents the equivalents of argentic salt per gram of the given sample. The expression $(\chi_{OX} - \chi_{UN})/cd$ so obtained is evidently also that for the susceptibility per atomic weight of oxidized silver produced in case this be bipositive, and twice this quantity is this susceptibility in case the silver be tripositive.

(3) Now an expression for the atomic susceptibility in terms of the magnetic moment of the atom is given by the Langevin formula.[17] Namely, the change in susceptibility (in cgsm. units) per atomic weight of an element each of whose atoms increases its magnetic moment from 0 to μ cgsm. units is by this formula equal to $N_A^2\, \mu^2/3RT$, where N_A is Avogadro's number. This expression is therefore equated with that for each of the two atomic susceptibilities obtained in (2), these equations are solved for μ, and the values are multiplied by $10^{21}/9.23$ to convert them from cgsm. units into Bohr magnetons. There are thus obtained the expressions:

For bipositive silver

$$\mu = \frac{10^{21}}{9.23\, N_A} \sqrt{(\chi_{OX} - \chi_{UN})\, 3RT/cd}$$

For tripositive silver

$$\mu = \sqrt{2} \times \text{this quantity}$$

The Magnetic Moment of the Argentic Ion.—From the next to last column of Table V it is seen that the mean value found for the magnetic moment of the argentic ion is 1.98 magnetons if the argentic silver be provisionally assumed bipositive. This is not greatly different from the value 1.92 for the bivalent copper ion, and it lies between the values 1.74 and 2.16 found for the solid salts of bivalent silver with pyridine. Moreover, it is only 0.25 magneton larger than the value (1.73 magnetons) predicted theoretically for the magnetic moment arising from the spin of an unpaired electron, such as the bivalent silver and copper ions possess, this excess of 0.25 unit being no greater than may well arise from the contribution of the unquenched orbital moment of the electron. This all points to the conclusion that the argentic silver is in fact largely in the bivalent state.

Before drawing this conclusion, however, it is necessary to show that the results are not also consistent with the conclusion that the argentic silver is tripositive. The last column of Table V shows that the measured susceptibilities lead to the magnetic moment 2.81 Bohr magnetons if the argentic silver be provisionally assumed to be tripositive. Now from a theoretical standpoint, as has been already mentioned, there are two possibilities to be considered for trivalent silver: either the eight outer 4d electrons are all paired, or two of them are unpaired. The first case is by far the more probable, because this structure is possessed by bivalent palladium, which is diamagnetic in all of its compounds which have been studied magnetically, including palladous nitrate as crystals and in dilute solution,[12] and because trivalent silver presumably has exactly the same structure as bivalent palladium, in that the number of electrons and types of electron orbits available are just the same in the two atoms. The observed susceptibility for the argentic solutions leads, however, to a large calculated moment (2.81 magnetons) instead of to the value zero, showing that the argentic silver is not present as trivalent silver with the electronic structure that is to be expected for it.

We may however also consider the second, less probable, alternative that the trivalent silver is similar in structure to the bipositive nickel ion, in that it contains two unpaired electrons (4d for silver, 3d for nickel). In this case the contribution of the orbital moment to the susceptibility would be expected to be about the same for the tripositive silver ion as for the bipositive nickel ion. But for the latter ion Cabrera and Duperier[15] have found, by susceptibility measurements of solutions of nickel nitrate, a total moment of 3.19 magnetons, which is 0.38 magnetons larger than that derived for tripositive silver from our measurements.

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[17] See Van Vleck, "Electric and Magnetic Susceptibilities," Oxford Press, 1932. p. 226.

Molecular State of Argentic Compounds in Acid Solutions

The above-established conclusion that in concentrated nitric acid solutions of the argentic compounds produced by ozone the silver is present almost wholly in the bipositive oxidation state is in accord with the above-cited results of Barbieri and others, which showed that organic bases, such as pyridine, precipitate complex salts of bipositive silver from argentic solution. This conclusion and these results, however, must be reconciled with the fact also above cited that the solid phases separating from acid solutions contain all the silver in the tripositive state. This reconciliation can be made with the aid of the following hypothesis.

Though argentic compounds in strongly acid solutions contain the silver very largely in the form of the Ag^{++} ion, yet this ion is involved in a rapidly established equilibrium with appreciable quantities of Ag^+ ion and Ag^{+++} ion, which last however probably mainly exists as a hydrolyzed product, such as AgO^+. Thus, for definiteness it may be assumed, as was done in the preceding article on the reaction rates, that the following reaction quickly attains equilibrium

$$2Ag^{++} + H_2O \rightleftharpoons Ag^+ + AgO^+ + 2H^+$$

In that case the mass action expression $(Ag^{++})^2 = K(Ag^+)(AgO^+)(H^+)^2$ would determine the various concentrations prevailing in the solution.

From this mass action expression it follows that upon diluting an acid argentic solution with water the concentration of AgO^+ would increase until the solution became saturated with some compound produced out of this tripositive silver radical. This tripositive compound is shown to be a basic salt by the fact that it yields upon drying (which results incidentally in partial reduction of the tripositive silver) substances like $AgONO_3 \cdot Ag_2O_3 \cdot 4AgO$ or $(AgO)_2SO_4 \cdot 6AgO$ which contain the acidic constituent of the solution.

The proportion of tripositive silver that as a result of this reaction is present in more dilute (1 to 4 *N*) nitric acid has not been determined by any of the three above-described methods, for these could be used only in presence of concentrated acid (10–15 *N*). In the following article on the argentous–argentic electrode potential, however, evidence is presented (by a fourth method) that the tripositive silver even in 1 to 4 *N* nitric acid is relatively small.

Summary

The argentic salt produced in solution by oxidizing with ozone argentous nitrate dissolved in concentrated nitric acid at 0° has been shown to contain the silver almost entirely in the bipositive form. This has been done by three independent methods.

1. The total silver content and the oxidizing power of the steady-state mixture produced in contact with an excess of solid silver nitrate was determined, and from the total silver was subtracted the unipositive silver present as determined by measuring the solubility of silver nitrate in the same strength of nitric acid.

2. Total silver and oxidizing power determinations showed that, though 85–90% of the silver is converted (stoichiometrically) into bipositive silver by passing 5–8% ozone into a 0.025 *N* solution of silver nitrate in 12 *N* nitric acid, yet the use of even 40–65% ozone results in converting only 98 to 103%.

3. The change in magnetic susceptibility resulting when an argentous solution is partially oxidized was measured, and from this the magnetic moment of the argentic ion was computed. This was found to have a magnitude (1.98 magnetons) that corresponded with that to be expected for the bivalent silver ion (1) from its structural similarity with the bivalent copper ion and (2) from the susceptibilities of solid salts of bipositive silver with pyridine previously measured by Sugden. It is shown that the alternative assumption of trivalent silver leads to an experimental value (2.81 magnetons) of the magnetic moment entirely inconsistent with the diamagnetism of the presumably almost indentical bivalent palladium ion, and discordant even with the magnetic moment (3.19 magnetons) of the less closely related bivalent nickel ion.

These results are in accord with the well-established fact that organic bases, such as pyridine, precipitate salts of bipositive silver from argentic solutions. To account also for the well-known fact that from such solutions water precipitates basic salts of trivalent silver, the hypothesis is proposed that in more dilute acid solutions an equilibrium rapidly establishes itself, such as: $2Ag^{++} + H_2O = Ag^+ + AgO^+ + 2H^+$. This hypothesis has already proved useful in explaining the mechanisms of the silver oxidation and reduction reactions.

PASADENA, CALIFORNIA RECEIVED MAY 6, 1935

THE MERCURY SENSITIZED PHOTO-REACTION BETWEEN AMMONIA AND OXYGEN

Introduction

The photochemical reaction between ammonia and oxygen was first studied qualitatively by Berthelot and Gaudechon[1] who exposed, for long periods of time, mixtures of the two gases to the total radiation of a mercury arc. They found nitrogen, hydrogen, and water as the products. More recently Bacon and Duncan[2] studied the reaction in greater detail, using radiation of λ2050Å. They found as products besides nitrogen, hydrogen and water, considerable quantities of ammonium nitrate and small quantities of ammonium nitrite. About twenty percent of the total ammonia oxidized was converted to nitrate while one percent went to nitrite. A rather variable quantum yield always less than unity was found. These investigators maintained that the failure of Berthelot and Gaudechon to obtain nitrate and nitrite was due to the photochemical decomposition of these ammonium salts by the prolonged irradiation of the entire reaction system.

The following investigation of the mercury sensitized oxidation of ammonia is believed to point to the conclusion that the reaction is a surface reaction and the difference in results of the former workers could be attributed to this factor.

Preparation of Ammonia and Oxygen

Tank ammonia was purified by repeated distillation from a trap surrounded by a carbon dioxide-alcohol mixture to one surrounded by liquid air. The gas was stored in a flask over freshly fused potassium hydroxide. Oxygen was obtained by electrolysis of a sodium hydroxide solution and was subsequently purified by being slowly passed over a glowing platinum wire eighteen inches in length, then through tubes of soda lime and magnesium perchlorate into a storage flask containing the latter dessicant.

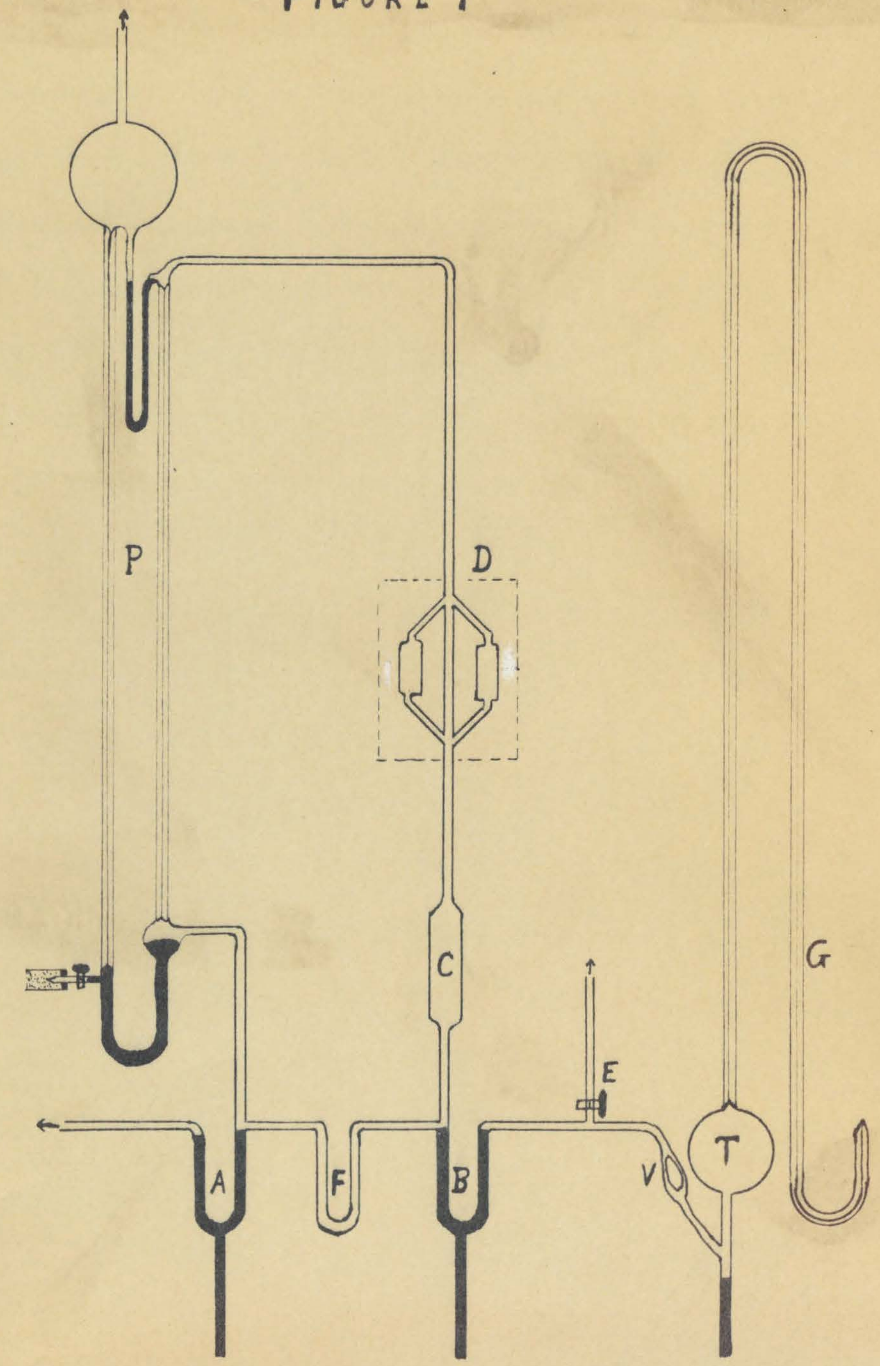
Experimental Apparatus and Procedure

A static system was used and the procedure followed was to irradiate a mixture of ammonia and oxygen for a convenient period of time and to analyze the reaction mixture for ammonia, oxygen, hydrogen, water and nitrogen. No hydrogen was found in any experiment and as the analysis in the first few experiments showed that the ammonia and oxygen used in the reaction could be quantitatively accounted for by such an analysis, it was concluded that water and nitrogen were the only products of the reaction. Consequently in all later experiments the mixtures were analyzed only for these two substances together with the initial reactants.

The source of radiation was a water cooled, magnetically deflected quartz mercury lamp. A shield and shutter device was used so that only a small portion of the reaction vessel was exposed to the radiation. Two cylindrical quartz reaction vessels, each approximately 2.5 x 10 cm. were used during the course of this work. The first was a simple vessel while the second was provided with a double quartz jacket for the circulation of cooling water and for holding an acetic acid filter.

The all glass apparatus used for the reaction and for the analysis of the products is represented in Figure 1 below.

FIGURE 1



After irradiating the reactants in cell C for about one hour, the condensable gases, ammonia and water, were frozen out by circulating the mixture through trap F surrounded by liquid air. The circulating device was an automatic Sprengel pump somewhat similar to that described by Waran[3]. It had a capacity of approximately 100 ml. per minute. With the pump P idle and all mercury cut-offs at a fixed height, the pressure of the noncondensable gases in the system was measured on cut-off A by means of a cathetometer, reading to 0.1 mm. When no further pressure decrease was observed, by lowering cut-off B the noncondensable gases were allowed to expand into a Toepler pump T which had been previously evacuated through E by means of a mercury diffusion pump. The portion of gas in T was driven through the capillary G into the small atmospheric pressure storage tube of a gas micro-analysis apparatus very similar to that described by Blacet and Leighton[4]. V, a glass valve, prevented mercury from passing toward E. By the addition of a known volume of hydrogen and a combustion procedure, the percentage of oxygen and nitrogen in the noncondensable gas was determined. Freshly dehydrated calcium chloride was used for the absorption of water vapor after the combustion. This analytical method was thoroughly tested and found to be accurate to less than one percent.

The portion of noncondensable gas remaining in the reaction system was removed through A by means of the mercury diffusion pump, the system again closed by raising cut-offs A and B, and the condensable gases allowed to volatilize.

Water vapor and ammonia were separately determined by absorbing the former with freshly fused potassium hydroxide and the latter with anhydrous magnesium perchlorate. D represents diagramatically an apparatus consisting of two absorption tubes with appropriate cut-offs so that the gases might be circulated through neither, either, or both of the tubes. By considering the small change in volume on including the absorption tubes in the system, the pressure decrease attending absorption gave in each case the amount of water and ammonia in the condensable gases. As might be expected, the removal of both water and ammonia reduced the pressure in the system to a value not detectable by means of the cathetometer.

Experimental Results

Table 1 contains the results of eighteen experiments. When a mixture of ammonia and oxygen in the presence of mercury vapor is irradiated by the full radiation of a cooled mercury lamp, several reactions are possible. Among them is the direct photochemical formation of ozone by the small amount of radiation of $\lambda 1849\text{Å}$. This ozone, besides oxidizing the ammonia, could results in the formation of mercuric oxide. This same end could be attained by the mercury sensitized formation of ozone.

The first two experiments, which were carried out with the full radiation of the mercury lamp, show that roughly one fourth of the oxygen used in the reaction did not appear in the analysis. That this oxygen had been used for the oxidation of mercury was indicated by the appearance of a deposit in the reaction vessel which disappeared on heating.

TABLE 1

Exp. No.	Cell & Filter	Init. Press (mm)		% Used		Loss (in % of Used)		
		NH_3	O_2	NH_3	O_2	O_2	N_2	H_2
1.	1-N.F.	23.4	13.8	9.9	16.5	23.0	0	0
2.	1-N.F.	22.2	13.1	20.2	32.8	21.7	0	0
3.	1-HAc	20.8	10.3	5.0	7.5	0	0	0
4.	1-HAc	22.2	14.1	8.5	10.0	0	0	0
5.	1-HAc	20.7	12.8	2.3	2.8	0	0	0
6.	1-N.F.	20.6	17.2	33.0	33.5	25.0	11.7	13.8
7.	1-N.F.	22.9	13.9	14.5	22.5	24.5	19.0	5.1
8.	2-HAc	27.7	19.8	34.7	40.5	33.7	13.5	21.5
9.	2-HAc	23.0	15.5	40.0	47.5	27.0	21.6	21.0
10.	2-HAc	24.7	17.8	32.0	44.3	39.5	8.5	28.0
11.	2-HAc	23.1	15.2	32.5	47.5	9.4	0	10.3
12.	2-HAc	28.0	14.2	39.2	59.4	42.0	13.8	46.0
13.	2-N.F.	26.9	14.5	18.8	29.7	35.0	23.5	35.2
14.	2-N.F.	25.2	13.0	28.2	55.5	43.0	0	23.0
15.	2-N.F.	25.0	13.1	20.0	40.0	42.0	-9.0	18.7
16.	1-N.F.	23.8	12.3	59.0	95.5	36.6	-5.7	29.5
17.	1-N.F.	26.7	12.6	21.0	47.5	41.7	-18.0	15.5
18.	2-HAc	27.0	12.7	15.0	34.0	42.0	-13.0	17.8

Experiments 3, 4, and 5 show that when a 50% acetic acid filter was placed between the lamp and the reaction vessel, in order to remove all radiation less than 2400Å, this loss in oxygen was eliminated and the analysis for ammonia, water, oxygen and nitrogen accounted for all the initial amounts of nitrogen, hydrogen and oxygen. These three experiments, together with the first two, led to the continuation of this investigation, for it appeared that the oxidation of ammonia proceeded very simply to nitrogen and water.

Experiments 6 and 7 were conducted without an acetic acid filter and the loss in oxygen is evident together with an apparent loss in both nitrogen and hydrogen. The loss in these latter two elements was not seriously considered at the time, but was attributed to possible analytical mistakes. These first seven experiments were carried out in the simple reaction vessel designated as #1.

Reaction vessel #2 was installed to provide for water cooling of the reaction mixture and for a convenient filter surrounding the entire vessel. Experiments 8 to 15 inclusive show that with or without the acid filter no balance in oxygen, hydrogen or nitrogen could be attained in this reaction vessel. Between experiments 12 and 13 the vessel was removed and cleaned with both acids and alkali and later thoroughly rinsed and torched out. The entire analytical procedure was also thoroughly checked. Experiments 16 and 17 show that, when vessel #1 was reinstalled, the discrepancies, previously observed in experiments 6 and 7, persisted.

The negative losses of nitrogen appearing in experiments 15 to 18 inclusive mean that more nitrogen appeared in the analysis that was initially put into the system. No explanation is available for this unless it was that hydrogen was one of the products in these experiments. Since it did not appear in the first few experiments and was not analyzed for in these later runs, hydrogen would appear in the analysis as residual nitrogen.

At the end of experiment 18, the reaction vessel was removed, rinsed with distilled water and the resulting solution tested for nitrate and nitrite by the phenol-sulphonic[5] and Griess[6] methods respectively. Nitrate was found present together with smaller amounts of nitrite. The presence of these two ions coupled with the serious discrepancies of experiments 6 to 18, inclusive, indicated that the reaction, which appeared very simple in the first few experiments had become extremely complex. Due to the lack of time no further work was attempted.

Discussion

It is believed that this set of experiments indicates that a surface reaction is involved in the mercury sensitized oxidation of ammonia. Reaction vessel #1 initially gave a very straightforward reaction as indicated by the first five experiments. Later, the reaction in this same vessel changed in nature and in vessel #2 it was likewise very complex. Vessel #1 was made of new quartz and had never been used for any purpose, while vessel #2 had been used for previous work. The most obvious explanation of the results of these experiments is that the reaction between ammonia and oxygen is a surface reaction, proceeding differently on a fresh quartz surface than on an old quartz surface. This belief may be corrolated with the results of earlier investigators. As mentioned previously, Bacon and Duncan[2] explained the results of Berthelot and Gaudechon[3] by the statement that due to the continued irradiation of the entire system any nitrate or nitrite initially formed was decomposed photochemically. The results of the first five experiments of the present work can not be explained in the same manner. Only a small portion of the reaction vessel was illuminated and the reaction was continued for only short periods of time. Thus it appears that the results of the previous pairs of workers may have differed because of different surface conditions.

REFERENCES

1. Berthelot and Gaudechon, Compt. rend., 150, 1932, (1910)
2. Bacon and Duncan, J.A.C.S. 56, 336, (1934)
3. Waran, Proc. Phys. Soc., 34, 3, 120, (1922)
4. Blacet and Leighton, Ind.Eng.Chem., Anal.Ed., 3, 266,(1931)
5. Chamot,Pratt and Redfield, J.A.C.S. 33, 381, (1911)
6. Treadwell and Hall, "Analytical Chemistry", John Wiley & Sons Eighth Ed. Vol. II, Page 317.

THE PHOTOCHEMICAL DECOMPOSITION OF HYDROGEN SELENIDE

Introduction

The absorption of light by hydrogen selenide was first studied qualitatively by Plücker[1]. Several later investigators[2] showed that the dry gas is decomposed by ultraviolet light. Recently Goodeve and Stein[3] determined the absorption spectra of hydrogen selenide and after illumination of the gas found red amorphous selenium on the windows of the absorption tube. The gas was found to exhibit a threshold of absorption with light of wavelength 3290Å. Using data from various sources Goodeve and Stein calculated that light of this wavelength had just sufficient energy to dissociate a hydrogen selenide molecule into a normal hydrogen molecule and a metastable ^1D selenium atom. Apparently on the basis of this calculation, they made the statement that it was evident that this dissociation into a hydrogen molecule and an excited selenium atom was the primary process in the photochemical decomposition of the gas and that this process was followed by recombination of the selenium atoms probably on the wall of the reaction vessel.

The present work involves a more or less detailed study of the photochemical decomposition of hydrogen selenide.

Preparation of Hydrogen Selenide

Pure hydrogen selenide was prepared by the action of acid on aluminum selenide which was obtained igniting with a burning magnesium ribbon a powdered mixture of the pure metals. C.P. aluminum powder was used without further purification as it contained no impurities that would appear in the hydrogen selenide. Selenium of rather doubtful purity and probably containing tellurium was very carefully purified.

Impure selenium dioxide was obtained by evaporation of a nitric acid solution of the metal. The dioxide was purified by sublimation which remove most foreign metals including tellurium, as tellurium dioxide does not sublime. As a further precaution, the selenium dioxide was dissolved in eight normal hydrochloric acid and reduced in this concentration of acid with sulfur dioxide. In such an acidity, tellurium remains in solution. As a final precaution against the presence of either sulfur or tellurium, the precipitated selenium was dissolved in dilute acid, filtered and reduced with hydroxylamine, which does not reduce tellurium in acid solution. The ignition of selenium and aluminum was carried out in a porcelain crucible. In an all-glass apparatus the aluminum selenide was decomposed by slowly dropping phosphoric acid on the solid and sweeping the hydrogen selenide, by means of a current of hydrogen, through a long tube of phosphoric pentoxide into a trap surrounded by liquid air. The generator and drying tubes were then sealed off from the remainder of the apparatus, and, after pumping off the noncondensable gas, the hydrogen selenide was twice distilled from a trap surrounded by a carbon dioxide-alcohol mixture to one surrounded by liquid air. The gas was then stored over phosphoric pentoxide in a blackened storage flask.

PART I

DECOMPOSITION STUDY

Apparatus and Procedure

A diagram of the apparatus is shown below in Figure 1.

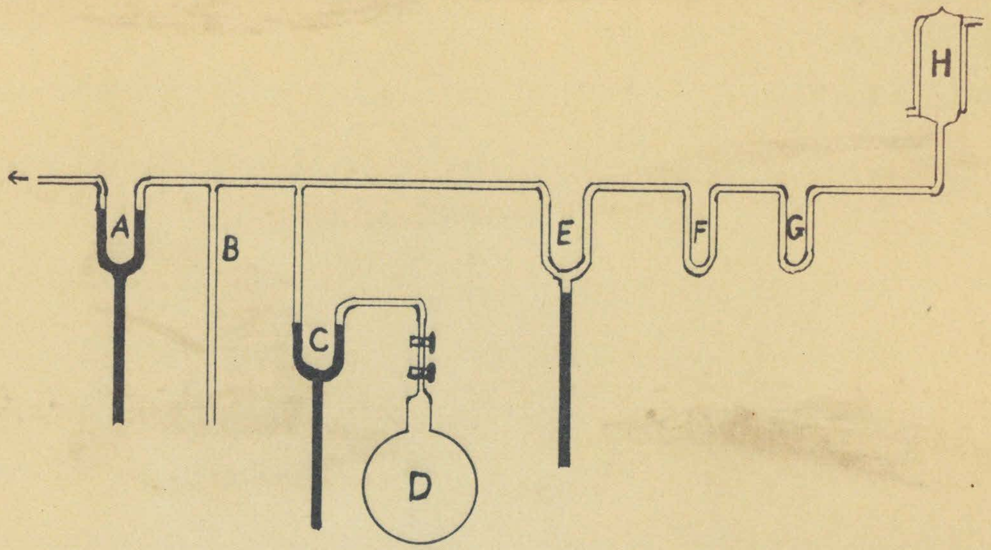


FIGURE 1

Since the radiation from a cooled quartz mercury lamp was used for most of the experiments, it was necessary to be certain that all traces of mercury vapor was removed from the reaction cell, in order to prevent any possible mercury sensitized decomposition of the hydrogen selenide. With liquid air on trap F, reaction vessel H was carefully torched out before each experiment, and after the system had cooled a carbon dioxide-alcohol mixture was put around trap G. This cold mixture on G was not removed at any time thereafter until the end of the run. The desired portion of hydrogen selenide was removed from the storage flask D and condensed in trap F. Traces of noncondensable gas were pump off through A by means of a mercury diffusion pump. Cut-off E was raised and the liquid air surrounding trap F was quickly replaced with a mixture of carbon dioxide-alcohol, which allowed the hydrogen selenide to volatilize. Reaction vessel H was a cylindrical quartz cell 2.5 x 10 cm. and was surrounded by a quartz jacket containing a filter consisting of 5 mm. of 50% acetic acid, to remove all radiation less than $\lambda 2400 Å$. With this filter the principal radiation from the mercury lamp which is absorbed by hydrogen selenide is $\lambda 2537 Å$.

Since there is no change in total pressure attending the conversion of hydrogen selenide into hydrogen and solid selenium, it was necessary to apply liquid air on trap F and, after the hydrogen selenide had condensed, to measure the pressure of noncondensable hydrogen. Since this pressure was in most cases quite small it was read by lowering cut-off E and allowing the gas to expand into a McLeod gage connected at B.

Preliminary Observations

When hydrogen selenide at pressures from 5 to 50 mm. was irradiated by a cooled mercury lamp, as outlined above, a red film of selenium was deposited on the walls of the reaction vessel. Measuring the pressures on cut-off E by means of a cathetometer reading to 0.1 mm, no change in total pressure was observed. A gas noncondensable in liquid air was formed. With pressures of hydrogen selenide less than 0.2 mm., the decomposition was carried out with cut-off E open and cut-offs A and C closed, so that the pressures could be read on the McLeod gage. With this means of detecting slight pressure changes, a small decrease in total pressure was observed. Even when hydrogen selenide at several centimeters pressure was irradiated for a long period so that nearly all the gas was decomposed, the change in total pressure was even then not detectable by means of the cathetometer. In the case of small pressures read on the McLeod gage, the rate of loss of total pressure was the greatest during the initial stages of the decomposition and gradually became less.

The above behavior suggested that the loss might be due to clean-up of hydrogen atoms on the freshly torched quartz surface of the reaction vessel. To prove that the possible hydrogen atoms were not produced by the mercury sensitized dissociation of hydrogen molecules, the acetic acid filter was removed and the mercury lamp replaced by a cadmium vapor lamp, the radiation from which contained considerable light of $\lambda 2288\text{Å}$. That the cadmium contained no mercury was determined spectroscopically. A small loss in total pressure was observed when hydrogen selenide was irradiated with this lamp.

To prove that the pressure loss was due to hydrogen clean-up, the walls of the reaction vessel were saturated with hydrogen atoms by irradiating, with a cooled mercury lamp, hydrogen gas in the presence of mercury vapor until no further pressure decrease was observed. Then on irradiating hydrogen selenide by the cadmium lamp, no pressure decrease was detected.

This foregoing set of experiments points to the conclusion that atomic hydrogen is produced by the photochemical decomposition of hydrogen selenide. At the pressures used for all studies in this work, the hydrogen clean-up on the walls of the reaction vessel was a negligible percent of the total hydrogen produced.

Blank experiments proved that there was no dark decomposition of gaseous hydrogen selenide.

It was also found that when the reaction vessel, having a freshly deposited thin film of selenium on its walls and containing hydrogen gas but no mercury vapor, was irradiated by the mercury lamp no hydrogen selenide was formed by the combination of the two elements.

Tests showed that when hydrogen selenide at a pressure of 20 mm. and containing 0.01 mm. of hydrogen was condensed in a trap surrounded by liquid air no hydrogen was included in the condensed phase.

Dependence of Rate on Pressure

A series of experiments were made to determine the effect of pressure on the rate of decomposition. A charge of hydrogen selenide at the desired pressure was confined in the reaction vessel and the pressure read on cut-off E. With mercury vapor excluded from the cell and an acetic acid filter in place, the gas was illuminated for a definite period of time by the mercury lamp which was in a fixed position. The hydrogen produced was read as usually on the McLeod gage, after condensing out the residual hydrogen selenide. After each experiment the selenium film was removed by torching out the cell and the acid filter was replace by fresh acid. The time of illumination was adjusted so that in each experiment approximately the same thickness of selenium film was deposited on the walls of the reaction vessel. This film was so thin that when it was not removed but the same charge of hydrogen selenide was illuminated for a second period, the rate was only two percent less than that in the first experiment.

Figure 2 gives the results of irradiating samples of hydrogen selenide at ten different pressures. The rate of formation of hydrogen expressed as millimeters per second is plotted against total pressure of the selenide. The linearity of the first portion of the curve indicates that the quantum yield is independent of pressure.

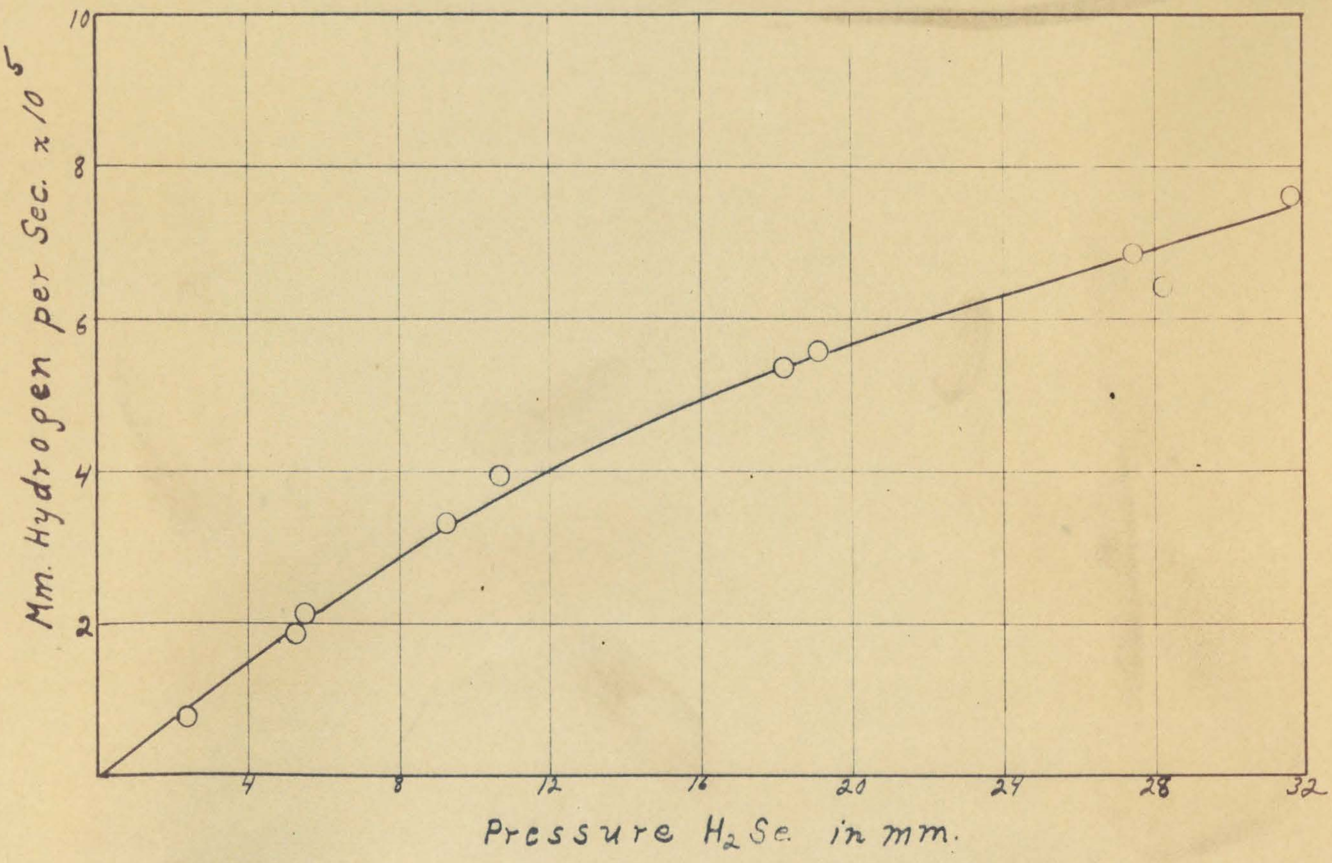


FIGURE 2

Dependence of Rate on Hydrogen Pressure

Experiments were made to test the effect of hydrogen pressure on the rate of decomposition. The procedure was to irradiate a sample of hydrogen selenide for a definite period of time with the mercury lamp in a fixed position, measure the hydrogen produced and then after admitting a measured pressure of hydrogen, repeat the irradiation under identical conditions except for the presence of the added hydrogen. Pressures larger than 0.3 mm. were read on a mercury cut-off by means of a cathetometer while smaller pressures were read on the McLeod gage. Between the two portions of an experiment, while the hydrogen selenide was kept frozen in the trap, the cell walls were cleaned of the slight film of selenium by torching.

Table 1 gives the results of a series of four experiments.

TABLE 1

Selenide Press.(mm.)	Initial Hydrogen(mm.)	Hydrogen Increase(mm.)
47.0	0	0.0212
47.0	0.2175	0.0205
25.0	0	0.3035
25.0	2.45	0.3000
23.75	0	2.6
23.75	22.2	2.5
26.3	0	2.5
26.3	27.0	2.6

It is seen that, within the limits of accuracy of pressure readings, the presence of hydrogen in amount even greater than that of the hydrogen selenide has no effect on the rate of decomposition of the selenide.

Dependence of Rate on Intensity

In a series of experiments a sample of hydrogen selenide at 28.0 mm. pressure was irradiated for definite periods of time with the mercury lamp at increasing distances. After each period of illumination the residual selenide was frozen out and the hydrogen measured on the McLeod gage. The hydrogen was pumped off and the selenium removed from the cell walls before the hydrogen selenide was allowed to volatilize for the next illumination. The periods of illumination were adjusted so as to give approximately the same amount of decomposition in each case.

Table 2 gives the results of five experiments. It is seen that except for small distances where the inverse square law no longer accurately applies, the term $\frac{P_{H_2}}{t}\left(\frac{d}{d_o}\right)^2$ is a constant, indicating that the rate of decomposition is directly proportional to the intensity of radiation.

TABLE 2.

Time t (sec.)	Distance d (mm.)	Press. H_2 mm. x 10^3	$\frac{P_{H_2}}{t}\left(\frac{d}{d_o}\right)^2$
210	90 = d_o	8.84	42.1
420	136	7.31	39.8
1800	246	9.49	39.4
2580	320	8.10	39.8
6480	530	7.36	39.5

Deposition of Selenium at High Temperatures

Work has been done at this Institute[4] in which selenium was rapidly volatilized in vacuo and deposited on a metal bar along which a temperature gradient existed. It was found that at a point on the bar corresponding to 74°C a very definite and sharp break occurred in the nature of the deposit. At temperatures lower than 74° red monoclinic selenium was formed, whereas at higher temperatures black hexagonal selenium was deposited. During the present investigation, experiments were made to determine if the above phenomenon could be observed when selenium, formed by the photochemical decomposition of hydrogen selenide, was deposited on quartz. Using the jacketed quartz vessel previously mentioned, hydrogen selenide at 50 mm. pressure was decomposed by radiation from a cadmium vapor lamp. By rapidly circulating hot water through the jacket of the vessel and careful determining the temperature of the water as it entered and as it left the jacket, the temperature of the cell walls was known to within 0.3 degree C. Experiments were made at a series of temperatures, namely, 25°, 70°, 78°, and 90° C. The character of the selenium deposit was determined both by its appearance and by its solubility in carbon disulfide. Red selenium is soluble in this organic liquid, giving a yellow solution, while black selenium is insoluble. With short periods of illumination the selenium deposited even at the highest temperature was found to be the red form. If the illumination of the hydrogen selenide even at room temperature was continued for two or three hours, it was found that while most of the deposit was soluble in carbon disulfide, there remained a slight black residue. This is in accord with the well known fact that on irradiation with ultra-violet light, red monoclinic selenium slowly changes into the black hexagonal variety.

PART II

QUANTUM YIELD DETERMINATION

Apparatus

The reaction system was very similar to that represented in Figure 1 except that the cylindrical jacketed vessel was replaced by a rectangular cell of fused quartz with flat polished front and rear quartz windows.

The source of radiation was a water cooled and magnetically deflected quartz mercury lamp. Monochromatic radiation of wavelength 2537Å was obtained by means of a Bausch and Lomb monochromator. The beam of light emerging from the monochromator passed through two converging cylindrical lenses, through the reaction cell onto the vane of a vacuum thermopile. The thermopile was connected to a Leeds and Northrup high sensitivity galvanometer which was set up in conjunction with an automatic recording device so that continuous records were made of the galvanometer deflections. It was found that, after the lamp had attained a steady condition, the intensity of radiation λ2537Å did not vary more than 2 to 3 percent over a period of three hours. For this reason no means was provided for continuously measuring the energy flux incident on the front window of the reaction vessel. A measure of this energy was obtained just before and just after each run.

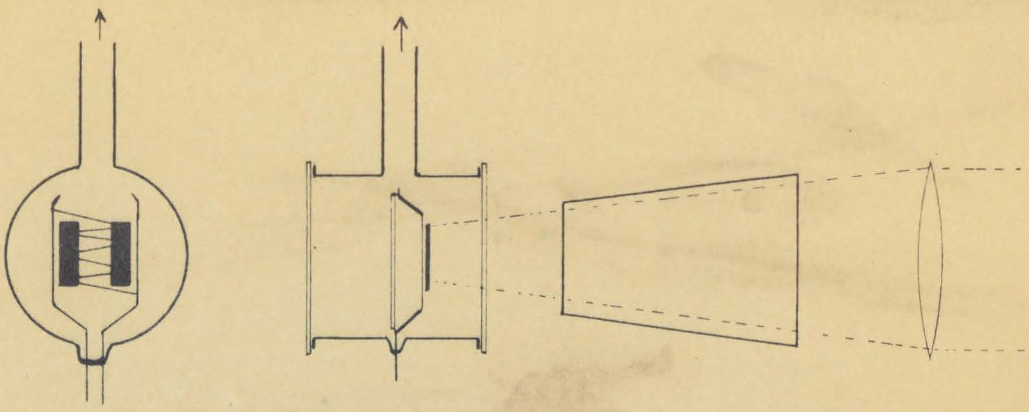


FIGURE 3

The thermopile element, illustrated above in Figure 3, consisted of six fused junctions of Bi-Sn (3% Sn) and Bi-Sb (5% Sb) alloys in series, three junctions attached to each vane. The vanes were 2.5 x 5 mm. strips of thin aluminum foil blackened with a paint of lamp and platinum black. The element was mounted in a cylindrical glass container one inch in diameter and three-quarters inch in length with a fused quartz front window and a Pyrex glass **rear** window,both attached with wax. A piece of uranium glass behind the element added in focusing the beam of radiation on the thermopile vane. The cell was enclosed in a metal box with cotton packing. The thermopile was kept evacuated to less than 10^{-5} mm. by means of an apiezon oil diffusion pump, with liquid air surrounding a trap placed between the pump and the thermopile cell.

The continuous recording device is represented below in Figure 4. A is a roll of six inch photographic paper which is pulled upward by the revolving drum D, B and C being idling rollers to provide tension. Light from an illuminated slit was reflected from the galvanometer mirror, in front of which was placed a 1-diopter plane convex cylindrical lense. Another cylindrical lense E focused this slit of light to a small spot on the photographic paper so that a sharp line was traced as the paper moved upward. The revolving drum D was driven by an induction motor with a series of enclosed gears so that the paper traveled one inch in twenty minutes. A cutting knife and shutters were provided so that, after entering the detachable upper box F, the exposed paper could be removed to the photographic dark room.

To avoid error caused by shrinkage or expansion of the paper during development, a coordinate system was printed on the paper after removal from the recorder. This was done according to the method used by Wenner and Beckman[5].

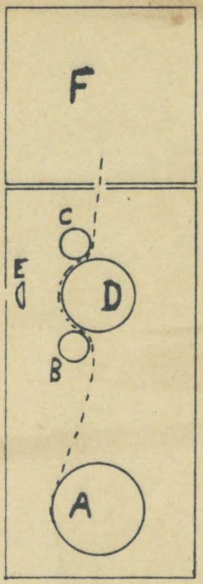


FIGURE 4

Calibration of Apparatus

The method of calibrating the thermopile and of determining the transmission factors of the quartz windows was substantially the same as outlined by Wenner and Beckman[5].

Transmission of the thermopile window to radiation λ2537Å and to that of the standard lamp was determined before assembly to be 0.860 and 0.916, respectively. As the reaction cell had been previously assembled and as several pieces of fused quartz gave within 1 percent this same transmission, the factor for the rear cell window was also taken to be 0.860. The sensitivity of the thermopile was checked three times during the course of the work and found always to be 1.80 ergs/sec./division deflection.

Procedure

The procedure followed was very similar to that outlined in Part I of this paper. Mercury vapor was excluded from the reaction cell by a carbon dioxide-alcohol mixture surrounding both traps F and G (Figure 1). Pressures of hydrogen selenide were read on cut-off E and, with all mercury cut-offs at a fixed level, the pressures of hydrogen were read on the McLeod gage. After each run the reaction cell was swung out of position and away from the thermopile so that the walls could be torched to remove the slight film of selenium. The film was so slight as to reduce the radiation reaching the thermopile by only 2 percent.

A blank run was made which was a duplicate of ordinary runs except that the monochromator shutter was kept closed.

The pressure of hydrogen selenide was 20mm. and the duration of the run was 120 minutes. A slight pressure of noncondensable gas was found. This was applied as a correction in the pressure of hydrogen recorded in column 6 of Table 3.

As a check on the entire apparatus and calibrations, a sample of hydrogen azide was prepared and the quantum yield of the mercury sensitized decomposition was determined. A value of 3.4 at 25.5 mm. pressure agrees well with the value of 3.6 obtained by Myers and Beckman[6].

An experiment was also made to determine if the procedure used was successful in removing the mercury vapor from the reaction cell. A carbon dioxide-alcohol mixture was applied as usual to the traps F and G and a sample of hydrogen azide at 5 mm. pressure was irradiated by monochromatic radiation of $\lambda 2537\text{Å}$ from a cooled mercury lamp. At the end of 15 minutes the pressure of noncondensable gases as read on the McLeod gage was only 1.6×10^{-5}mm. On removing the cold mixture from traps F and G and continuing the exposure for another 15 minutes, the pressure of noncondensables was 1.0×10^{-3}mm. This shows that, with the procedure used in the first experiment not enough mercury vapor was present to produce an appreciable amount of mercury sensitized decomposition of the hydrogen azide. It is therefore justified to assume that in the case of hydrogen selenide no appreciable mercury sensitized decomposition took place.

Method of Calculating Results

The energy E absorbed in the decomposition of hydrogen selenide was calculated as follows: S represents the duration of the run in seconds; t, the transmission factor of the quartz windows to $\lambda 2537 \mathring{A}$; C, the sensitivity of the thermopile in ergs/sec./division deflection; D, the mean galvanometer deflection during the run; and D_o, the deflection recorded with no hydrogen selenide or mercury vapor in the cell.

$$E = \frac{C\,S(D_o - D)}{t^2}$$

Since t = 0.860 and C = 1.80 and since one quanta of $2537 \mathring{A}$ is equivalent to 7.75×10^{-12} ergs, the number of quanta Q is given by the expression

$$Q = \frac{1.80\ S\ (D_o - D)}{(0.86)^2\ 7.75 \times 10^{-12}}$$

To determine the number of molecules of hydrogen selenide decomposed it was necessary to know, besides the pressure of hydrogen formed, the effective volume of the system and the temperature. The effective volume was determined by admitting a convenient amount of hydrogen into the system and measuring its pressure on the McLeod gage, the volume of which was, of course, known. Keeping this gas in the gage, the remainder of the system was evacuated, cut-offs A, B, and F were raised to a marked level, A and B being closed. With liquid air on F and carbon dioxide-alcohol on G, the gas in the gage was allowed to expand into the entire system and the resulting pressure read on the McLeod. These two pressure readings and the volume of the gage gave the effective volume of the apparatus to be 275.0 ml.

The number of molecules N decomposed is then given by the expression

$$N = \frac{275(6.06)10^{23}}{82.1(760)} \frac{P}{T}$$

where P is the pressure of hydrogen in millimeters and T is the temperature in degrees Absolute.

Table 3 gives the results of seven quantum yield determinations arranged in the order of decreasing pressure. Pressures of hydrogen selenide and hydrogen are given in millimeters and the duration of run S is given in seconds.

TABLE 3

Run	P_{H_2Se}	T	S	D_o-D	P_{H_2}	$Q \times 10^{-16}$	$N \times 10^{-16}$	N/Q
1.	65.0	298	6120	20.0	4.60	3.85	4.11	1.07
2.	39.4	300	9000	25.0	8.30	7.08	7.39	1.04
6.	37.8	300	6660	28.0	6.27	5.87	5.58	0.95
3.	34.0	300	6600	20.0	4.29	4.15	3.78	0.92
7.	24.0	299	6900	29.0	7.75	6.30	6.95	1.10
5.	13.0	299	8460	20.0	7.34	5.30	6.56	1.24
4.	8.2	300	7200	11.5	2.98	2.58	2.65	1.03

It is seen that within the limits of experimental error the quantum yield N/Q is unity. With increasing pressures there is no apparent trend in the values obtained.

Discussion

Although no analytical proof was obtained that the final products of the decomposition of hydrogen selenide were hydrogen and selenium, the experimental facts indicate that such must be the case. The fact that there is no total pressure decrease except that due to slight hydrogen clean-up, and the fact that a gas is formed which is noncondensable in liquid air eliminate the possibility of any new compound of hydrogen and selenium as a final product. Since it was found that atomic hydrogen is formed in the decomposition it is logical that molecular hydrogen should be one of the final products.

Contrary to the statement of Goodeve and Stein[3], the primary process in the photochemical decomposition cannot be the dissociation into a hydrogen molecule and an excited selenium atom. The fact that atomic hydrogen is formed in the decomposition necessitates that one of the following be the primary process

$$H_2Se + h\nu = H + H + Se$$
$$H_2Se + h\nu = H + HSe$$

From an energy standpoint the first of these reactions is impossible. Although the existence of HSe has never been reported, there is no reason why it could not exist. The following mechanism is therefore offered for the photochemical decomposition of hydrogen selenide,

$$H_2Se + h\nu = H + HSe$$
$$H + H = H_2 \qquad \text{(wall)}$$
$$HSe + HSe = H_2 + Se_2 \qquad \text{(wall)}$$

This mechanism accounts for all the experimental observed facts. The rate would be directly proportional to the radiation intensity, and independent of the hydrogen pressure. The quantum yield would be unity.

Summary

The photochemical decomposition of gaseous hydrogen selenide has been studied using radiation $\lambda 2537\text{Å}$. A constant quantum yield of unity has been found over a pressure range from 8 to 60 mm., and a mechanism for the decomposition has been proposed.

REFERENCES

1. Plücker, Pogg. Ann., <u>121</u>, 459, (1864)
2. de Forcrand and Fonzes-Diaczon, Compt.rend., <u>134</u>,171,229,281,(1902)
   Hempel and Weber, Z.anorg.Chem. <u>77</u>, 48,(1912)
   Moser and Doctor, Z.anorg.Chem. <u>118</u>, 284,(1921)
3. Goodeve and Stein, Trans.Far.Soc., <u>27</u>,393,(1931)
4. McCullough, Ph.D. thesis, Calif. Inst. Tech., 1936
5. Wenner and Beckman, J.A.C.S. <u>54</u>,2787(1932)

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