THE VACUUM PHOTOLYSIS OF SILVER BROMIDE

BY GEORGE W. LUCKEY

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The photolysis of silver bromide crystals, slabs and evaporated films in vacuum has been studied by measuring the pressure The photolysis of silver bromide crystals, slabs and evaporated films in vacuum has been studied by measuring the pressure of the photolytic bromine. The quantum yields at 27° were independent of intensity in the range extending from about 10^{14} to 10^{16} quanta/sec./cm.². The quantum yields increased with decreasing wave length in the region extending from 280 to 436 m_{\mu} at 27°. Increasing the temperature decreased the quantum yields at all wave lengths, but the decrease was greater at short wave lengths. Bromination and evacuation of previously irradiated samples at 200° either did not affect or de-creased the room temperature quantum yield at 365 m_{\mu}. In general, the quantum yield of evaporated films increased with exposure at 365 m_µ, while the yield of fused samples remained constant or decreased slightly. The maximum decomposition in the experiments was about 0.1%. The data indicate that vacuum is a good halogen acceptor and that the quantum yield of the silver bromide decomposition is near unity when the concentration of electron traps is high enough. In the relatively thick crystals studied, the decomposition which produced measurable quantities of bromine occurred in a thin surface layer. At high temperatures, the trapped electrons are not stable and some recombination with positive holes occurs occurs.

I. Introduction

The photolysis of silver bromide has been studied by many workers, who have shown that the products of the decomposition are silver and bromine and that the primary quantum yield is approximately unity.¹⁻⁴

The quantum yield of silver production in silver bromide-gelatin emulsions was first determined by Eggert and Noddack in 1921.⁵ Since that time, a large number of studies have been made by Eggert and his co-workers⁶ and later by Meidinger.⁴ The most recent measurements by Meidinger⁷ showed that the quantum yield of silver production in emulsions containing no halogen acceptors was about 0.1 at 365 and 436 m μ . Lippmann emulsions had much lower yields. Addition of halogen acceptors such as nitrite ion increased the quantum yield about 6-fold in emulsions of large grain size at 20°, and yields near 1 were obtained by heating such emulsions to 100° during photolysis.

The quantum yield of silver production for precipitated silver bromide was measured by Kieser⁸ in the absence of protective colloid, but with water present. He found that the yield was unity at $436 \text{ m}\mu$ if nitrite ion was present or 0.05 to 0.07 if it was not.

Hilsch and Pohl⁹ and later Stasiw and Teltow¹⁰ measured the quantum yield of silver formation in 0.1-1-mm. thick silver bromide crystals optically. Stasiw and Teltow found that the quantum yield at 436 m μ was about 0.02 in large pure crystals and showed that this yield could be increased by addition of a few hundredths of a per cent. of silver sulfide to values of 0.2 to 0.5. The values obtained by

(1) C. E. K. Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942, Chapter IV. (2) W. Meidinger, "Das latente Bild," in "Fortschritte der Photo-

graphie," Bd. III, edited by E. Stenger and H. Staude, Akad. Verlag., Leipzig, 1944, pp. 1-72.

(3) W. Meidinger, ibid., Bd. I, 1938, pp. 1-40.

(4) W. Meidinger, Phot. Korrespondenz, 79, 20, 35 (1943).

(5) J. Eggert and W. Noddack, Sitzber. preuss. Akad. Wiss., 631 (1921).

(6) Reviewed by W. Meidinger in "Die theoret. Grundlagen d. phot. Prozesse," in "Handbuch wiss. angew. Photographie," Bd. V, edited by A. Hay and M. von Rohr, J. Springer, Vienna, 1932.

(7) W. Meidinger, Z. wiss. Phot., 44, 1 (1949).

(8) H. Kieser, ibid., 26, 1 (1928).

(9) R. Hilseh and R. W. Pohl, ibid., 30, 255 (1931).

(10) O. Stasiw and J. Teltow, Nachr. Ges. Wiss. Göttingen, Math. Phys. Kl., 100 (1941); Ann. Physik, 40, 181 (1941); Z. wiss. Phot., 40, 157 (1941).

Hilsch and Pohl were ascribed to disorder in their crystals.

Mutter¹¹ studied silver bromide precipitates prepared in the absence of gelatin. Water was present in his experiments. The quantum yield of bromine production at 436 m μ decreased with increasing exposure from 0.16 to 0.14. The more recent experiments of Wolff¹² are not in disagreement with these data.

Experiments by Meidinger¹³ have shown that the quantum yield of silver produced in emulsions in the presence of water is about twice that produced in a dry emulsion.

All these quantum-yield measurements were made with some water and air present, and a large number were made in the complex gelatin-water-air-silver bromide system. Volmer,¹⁴ Strömberg,¹⁵ and Hartung¹⁶ have studied the vacuum photolysis of silver bromide by weighing the decomposing crystal with a microbalance. Volmer's data were criticized by Strömberg, who showed that the effects observed were probably due to heating of the silver bromide films by the incident light. Har-tung, by use of much higher light intensities and dark weighing, was able to show that vacuum photolysis of silver bromide produced silver and gaseous bromine, and that photolytic silver recombines with bromine. No quantum-yield measurements were made by any of these workers.

The purpose of the present investigation is to study the mechanism of photographic latent-image formation as a function of crystal structure, crystal environment, foreign-ion concentration and wave length of the absorbed radiation. The first step of this investigation was to measure the quantum yield of bromine evolution in the vacuum photolysis of silver bromide with various types of silver bromide crystals.

II. Experimental

(a) The silver bromide was prepared from Eastman Kodak Co. C.P. silver nitrate and redistilled hydrobromic Three types of samples were used: evaporated films, acid.

(11) E. Mutter, ibid., 26, 193 (1929).

(12) H. Wolff, Z. Elektrochem., 53, 82 (1949).
(13) W. Meidinger, Physik. Z., 38, 905 (1937).

(14) M. Volmer, Dissert., "Photographische Umkehrungserscheinungen," Leipzig, 1910.

(15) R. Strömberg, Z. wiss. Phot., 22, 165 (1923).

(16) E. J. Hartung, J. Chem. Soc., 121, 682 (1922); ibid., 125, 2198 (1924); ibid., 126, 2691 (1925).

films fused between two quartz or Pyrex plates, and slabs fused in an atmosphere of nitrogen without a quartz plate eovering the top surface.

The evaporated films used in these experiments were prepared by evaporation of precipitated silver bromide from a boat-shaped filament onto quartz or Pyrex microscope slides.¹⁷ The slides were cleaned by washing in sodium hydroxide and nitric acid, rinsing in distilled water and drying with lens tissue. The films were uniform, transparent to red light, and between 0.5 and 8 μ in thickness.

Spectroscopic analysis of the coatings¹⁸ showed that they all contained some impurities from the filament used in the evaporation. However, as will be seen below, these probably did not affect the photolysis. The silver bromide films fused between quartz slides were

The silver bromide films fused between quartz slides were also optically clear, and were between 5 and 250 μ in thickness.¹⁹ They contained spectroscopic quantities of copper, calcium, iron, magnesium and silicon.

Finally, several fused slabs were prepared in a nitrogen atmosphere and slowly annealed in nitrogen.²⁰ These slabs had two or three grain boundaries, but large areas were transparent to red light. The thickness was between 2 and 3 mm.

(b) Some of the bromine used in these experiments was prepared by the method of Baxter and Grover.²¹ The rest was Baker and Adamson Reagent Grade. Similar results were obtained with both products. The bromine was dried with sodium which had been distilled twice in vacuum. After drying, the bromine was degassed and stored as described below.

(c) The reaction system consisted of a Pyrex or quartz cell, a platinum-iridium Pirani gage tube, and a Langmuir gage. This system was isolated from the diffusion pump by a Monel-glass-Teflon valve, a liquid nitrogen trap, and a 9-mm. bore vacuum stopcock. The bromine storage system was isolated from the reaction system by a Monel-glass-Teflon valve.

The Pyrex cell used in most of the experiments could be electrically heated to 400°. Its temperature was measured with chromel-alumel thermocouples and a glass-enclosed thermometer. Samples were introduced by opening a vacuum seal consisting of two 1.5-in. diameter Corning Glass pipe flanges and a No. 820 Snap-On-Teffon Gasket.²² This seal was held together by the usual pipe fittings, and its leak or degassing rate was less than 0.2×10^{-6} mm. of mercury per minute after three hours of evacuation. The samples were supported in the cell by two Pyrex holders.

The Langmuir gage²³ used in the cent by two Fyrex holders. The Langmuir gage²³ used in these experiments was capable of measuring pressures of 10^{-6} mm. of mercury. Because it was incapable of following rapid pressure changes at low pressures, an additional vacuum gage was necessary. A platinum-iridium Pirani gage was designed by B. B. Dayton and constructed by A. Miller, of Distillation Products Industries. The gage was capable of measuring 10^{-5} mm. of mercury and its sensitivity remained constant throughout the experiments. The zero varied to some extent, but this effect was corrected by use of the Langmuir gage as a standard.

gage as a standard. The Langmuir gage was calibrated by comparison with a McLeod gage at various pressures of dry nitrogen gas. Mercury vapor from the McLeod gage was condensed in a liquid nitrogen trap. The data were in good agreement with the relation given by Dushman²³

$$P(M)^{1/2} = (B/t) - C \tag{1}$$

The ratio of C/B was determined by evacuating the system and measuring the time necessary for damping. The value of B was obtained from the slope of the pressure vs. 1/t plot. The final gage calibration was

Bromine pressure in $\mu = (102.6/t) - 0.0204$ (2)

(17) These films were prepared by J. F. Hamilton and L. Brady of these Laboratories.

where t is the time in seconds required to reach a fixed amplitude of vibration.

By comparison with the Langmuir gage it was found that one Pirani gage scale division corresponded to 1.93×10^{-6} μ of bromine pressure. Comparison with the McLeod gage showed that one Pirani gage scale division corresponded to $1.58 \times 10^{-5} \mu$ of nitrogen pressure, and the ratio of Pirani gage sensitivity for bromine to that for nitrogen was about 0.82. Since this value was not in agreement with that predicted by Yarwood and Le Croissette,²⁴ the gage calibration was checked chemically as described below.

The volume of the reaction system was measured gasometrically and by filling with water at a known temperature. From this volume and the Pirani gage calibration it was found that one Pirani gage scale division corresponded to 1.25×10^{15} atoms of bromine at 25°.

An additional calibration was provided by freezing a measured amount of bromine in a sample bulb which was then sealed off from the system. The bromine was kept at liquid nitrogen temperature until the seal cooled and then analyzed in the following manner.²⁵ The bulb was broken under a 50% water solution of potassium iodide which had been titrated to an oxidation-reduction end-point before use with either oxidant or reducer to eliminate a blank. The iodine liberated from the potassium iodide was titrated with a 10⁻⁴ N solution of arsenous oxide, a platinum electrode pair being used to detect the end-point. When applied to solutions of known iodine concentration, the method was accurate to ± 1 micrograms, so that the results were subject to a possible error of about 3%. This method showed that one Pirani gage scale division corresponded to about 1.27 \times 10¹⁶ atoms of bromine.

Since the cell volume was an appreciable fraction of the reaction volume, a change in cell temperature affected the calibration calculated above. It was therefore necessary to calibrate the system at various cell temperatures. At 120°, for example, one Pirani gage scale division corresponded to 1.12×10^{15} atoms of bromine.

The error in the Pirani gage readings was about 0.2 scale divisions, so that it was possible by this method to measure 10^{16} atoms of bromine with an error of about 5%.

The Monel-glass-Teflon valve used in these experiments was so designed that only glass and Teflon surfaces were exposed in the reaction system. Analytical measurements showed that no detectable amount of bromine was absorbed by the Teflon in the pressure range studied. The valve maintained a vacuum of 10^{-6} mm. of mercury on one side when the other side was open to air at 760 mm. pressure.

The remainder of the vacuum system was of conventional type. The liquid nitrogen traps were either glass spirals or U-tubes to prevent thermomolecular effects²⁶ from interfering with the calibration measurements.

(d) A General Electric Type AH-6 water-cooled mercury arc was used as a light source. The light from this arc passed through a diaphragm and a quartz lens, forming a parallel beam about 2 square centimeters in area. In some of the experiments, the 365 m μ mercury line was isolated by means of a Kodak Wratten 18A Filter and a 1-cm. thickness of 5% cupric chloride solution in water. In other experiments, the light passed through a Bausch and Lomb 500 mm. focal length grating monochromator. In both cases, the resultant light was photographed with a Hilger medium quartz spectrograph. The filtered light consisted of a band of wave lengths extending from 365 to 385 m μ . The light transmitted by the monochromator at the slit settings used consisted of a band of wave lengths about 10 m μ wide.

(e) The light intensity was measured by several methods. A Cambridge circular thermopile with an area of 30.4 square millimeters was calibrated with Bureau of Standards No. C52 radiation standard. The thermopile was then used with appropriate window corrections to measure the intensity of the mercury arc. This intensity was much larger than the calibrating intensity, and was reduced by means of calibrated neutral-density filters so that the galvanometer deflections were similar for both intensities.

A Weston Model 594 Photronic Cell was calibrated by

- for these analyses.
- (26) D. W. Stops, J. Sci. Instruments, 29, 121 (1952).

⁽¹⁸⁾ These coatings were analyzed by J. Moore, of these Laboratories.

⁽¹⁹⁾ The crystals were prepared by W. West, of these Laboratories.

⁽²⁰⁾ The slabs were prepared by P. Goddard of these Laboratories.
(21) G. P. Baxter and F. L. Grover, J. Am. Chem. Soc., 37, 1029

^{(1915).}

⁽²²⁾ Manufactured by the United States Gasket Company.

⁽²³⁾ S. Dushman, "Scientific Foundations of Vacuum Technique," John Wiley and Bous, Inc., New York, N. Y., 1949, p. 283.

⁽²⁴⁾ J. Yarwood and D. H. Le Croissette, Vacuum, 1, 37 (1951).
(25) The author is indebted to R. S. Miller, of these Laboratories,

comparison with the thermopile and was used to measure the incident intensity in some experiments.

(f) The total light absorption of the films was calculated from the total reflection and transmission which were measured with a General Electric Recording Spectrophotometer and a Model 11 MS Cary Recording Spectrophotometer. The usual reflection was between 15 and 23%, and the transmission was usually negligible at the wave lengths used in photolysis.²⁷

The transmission of the cell window was measured before installation. By use of this transmission and the absorption calculated above, the light absorbed by the silver bromide was calculated. The reflection and absorption were affected by the formation of photolytic silver, so that measurements were made before and after photolysis. The probable error of the absorption values was between 5 and 20%, depending on the wave length region studied. The absorption coefficients calculated from the absorption measurements agreed within 15% with the values determined by Slade and Toy.²⁸

(g) It was important to determine whether appreciable amounts of photolytic bromine would be adsorbed by the glass and by the vacuum gages. Bromine vapor at 200 mm. pressure was introduced into a previously evacuated and degassed bulb containing one-half gram of Pyrex glass wool. The bromine was then removed by evacuation at room temperature, and the bulb was sealed and analyzed for bromine. Less than one microgram of bromine was retained by the glass wool. This experiment and the agreement between the chemical and gasometric methods of calibration indicate that very little adsorption by the walls occurred. Pressures of bromine in the photolytic region could be maintained for 30 minutes without measurable change in the photolysis system with the Pirani gage in operation, indicating that there was no appreciable reaction with the gage. (h) The quantum yield measured in these experiments

(h) The quantum yield measured in these experiments was the yield of bromine molecules which escaped from the surface of the decomposing silver bromide crystal. These yields were converted to bromine atom yields by multiplying them by two. It should be emphasized that this is a secondary yield. The primary yield of bromine atom production within the crystal was undoubtedly larger.

The following procedure was used in the experiments.

(1) The incident light intensity and the dark leak rate were measured.

(2) The film was irradiated and the pressure increase was measured.

(3) The leak rate and light intensity were again measured.

(4) The leak rates were averaged and subtracted from the bromine production rate. The leak rates were never more than 10% of the bromine production rate and usually less than one-thirtieth.

(5) In some of the experiments, the reaction system was filled with 200 mm. pressure of bromine and the cell heated to 200°. The bromine was removed by condensation, and the system was evacuated at 200° for two hours. The cell was then cooled in vacuum. This treatment will be called "bromination."



Fig. 1.—The variation of the quantum yield of bromine production with exposure time at $365-385 \text{ m}\mu$.

The experimental error of most of the quantum-yield measurements was probably less than 15%. Measurements made with the same crystal under the same conditions were reproducible within 10%; measurements made with two different crystals from the same melt agreed within 15%. The rate of bromine evolution was not affected by condensation of the photolytic bromine with liquid nitrogen.

III. Experimental Results

A. Experiments with Filtered $365-385 \text{ m}\mu$ Radiation.—The quantum yields obtained in these experiments are given in Table I. The initial yield was calculated from the amount of bromine liberated by a one-minute exposure. The final yield was the value after an exposure time given in the table. The quantum yields of photolysis for a 2-mm. sample slowly cooled from the melt in a nitrogen atmosphere and for a typical evaporated film are plotted in Fig. 1 as a function of the exposure time.

TABLE I

Quantum Yield of Bromine Formation from Silver Bromide Photolysis at 365 m μ , 27 ° and 5 \times 10¹⁵ Quanta/Sec./Cm.²

		·····	1	posure to give final
	Crystal description	yield	Final yield	(min.)
	Evaporated	films		
1	Impurities, Cu, Zn, Mo	0.08		10
2	Impurities, Cu, Zn, Mo	.08	• • •	30
3	Impurities, Mo only	.12	0.10	10
4	Impurities, Al, Mo, Mg, Si	.02		5
5	Impurities, trace only	.027	.055	20
6	Impurities, Ca, Cu, Mg, Si	.055	, 060	15
	Fused films between	quartz s	lides	
1	Impurities, trace only	.045	.055	30
2	Impurities, trace only	.060	.070	10
3	1% lead bromide present	.021	.042	22
4	1% cadmium bromide	.047	.047	
	After bromination	.065	.099	20
5	Oriented (100)	.071	.071	
	Brominated 200°	.085	• • •	••
	Fused films prepared and	cooled in	nitrogen	
1	Untreated, HBr precipitated	.050	.101	25
2	Made from HNO ₃ treated			
	precipitate	.10	.087	15
	After 200° bromination	.014	.038	45
3	Made from HNO ₃ treated			
	precipitate	. 0 99	.093	••
	After room temperature Br ₂	.075	.094	10
	After 200° bromination	.015	.037	50
4	Made from HNO_3 treated			
	precipitate	.107	.114	7
	Short bromination 200°	084	084	

The most reproducible samples were crystals which were fused in a nitrogen atmosphere and cooled from the melt in a nitrogen atmosphere or between Pyrex plates. The quantum yields obtained with evaporated films were erratic and will not be discussed in detail. The data may be summarized as follows:

(1) The quantum yield of gaseous bromine formation from photolyzed silver bromide crystals containing small amounts of silver was 0.05-0.1 at 27°.

⁽²⁷⁾ These measurements were made under the direction of E. E. Richardson, of these Laboratories.

⁽²⁸⁾ R. E. Slade and F. C. Toy, Proc. Roy. Soc. (London), A97, 181 (1920).

(2) The addition of 1% of divalent lead or cadmium ion had little effect on the quantum yield of bromine formation.

(3) The effect of exposure (intensity \times time of irradiation) depended on the sample. In general, the quantum yields of evaporated samples increased with exposure, while the quantum yields of fused samples decreased slightly or did not change with exposure.

(4) Bromination of the crystals, followed by evacuation at 200°, either did not affect or decreased the quantum yield.

Some typical data on the effect of light intensity are summarized in Table II. It was found that the quantum yield of bromine formation was almost independent of the light intensity in the intensity range extending from 4×10^{14} to 6×10^{16} quanta/ sec./cm.². There was some indication that the yield increased at the lowest intensities measured, but the accuracy of the experiments was not sufficient to establish this conclusively. In these cases, the increase was less than 10%.

TABLE II

Variation of Quantum Yield of Bromine Formation with Intensity at 365 m μ , 27 °

Absorbed intensity

Sample description	in quanta/min./cm. ²	Quantum yield (ϕ)
Evaporated film No. 3	$3.6 imes10^{17}$	0.12
Evaporated film No. 3	$6.5 imes10^{16}$. 12
Evaporated film No. 3	$2.4 imes10^{16}$.12
Fused film (oriented)	$5.2 imes10^{17}$.08
Fused film (oriented)	$5.7 imes10^{18}$.08
Fused film (oriented)	$8.7 imes10^{18}$.08
Evaporated film No. A	$3.5 imes10^{18}$.05
Evaporated film No. A	$2.0 imes10^{18}$.05
Evaporated film No. A	$2.0 imes10^{17}$.05
Evaporated film No. A	$8.8 imes10^{17}$.05

The effect of temperature on the quantum yield of bromine production was tested with three samples which had not been brominated. The results are given in Table III. The ratio of the quantum yield at 120° to that at 25° for the three samples was between 0.5 and 0.6. The large value of the yield obtained with the evaporated film at 25° was produced by oxygen annealing at 300° . This treatment usually increased the quantum yield, but the results were dependent on the sample and will not be presented at this time.

TABLE III

Effect of Temperature on the Quantum Yield of Bromine Formation at 365 $m\mu$

Sample description	Temp., (°C.)	Quantum yield (ø)	$\frac{\phi 120}{\phi 25}$
Fused film (nitrogen)			
HNO ₃ treated, No. 3	25	0.112	0.59
HNO ₃ treated, No. 3	120	.066	
Fused film (quartz)	25	.058	. 55
Fused film (quartz)	122	.039	
Evaporated film No. 3	25	.185	.54
Evaporated film No. 3	121	. 10	
Evaporated film No. 3	190	.01	

As previously mentioned, the rate of recombination of photolytic bromine with photolytic silver was never larger than 10% of the rate of bromine evolution. The recombination rate increased with increased temperature and with increased silver content. In samples which had been brominated and evacuated at 200°, the recombination rate was not measurable in the initial exposures even at 120°.

B. Experiments at Various Wave Lengths Isolated by the Monochromator.—The quantum yields obtained in these experiments are given in Table IV. The table gives the method of sample preparation (in nitrogen or between glass plates) and a sample number, the thickness, the temperature of the measurements and, in the case of the nitrogen samples, whether the nitrogen or quartz side of the sample was exposed. In cases where the same sample was used several times, it was brominated and evacuated at 200° between exposures. All of the samples except number 14 were supported in such a way that bromine could escape from both crystal faces. This sample was supported by a Pyrex microscope slide which probably hindered the evolution of bromine from the rear surface. The quantum yields of most of these samples were independent of exposure in the range studied. With thin crystals, the quantum yield sometimes decreased with increasing exposure. This decrease was most pronounced at short wave lengths. The yield could be restored to its original value by bromination and evacuation at 200°.

These results may be summarized as follows.

(1) The quantum yields increased with decreasing wave length and were independent of intensity in the range from 1×10^{14} to 3×10^{15} quanta/sec. at 27°.

(2) An increase in temperature decreased the short wave length yield more than the long wave length yield.

(3) The quantum yields at 365 m μ measured in these experiments were somewhat higher than those found with filtered radiation. This was probably caused by the shorter wave length of the light transmitted by the monochromator.

(4) At thicknesses of 35 microns or less, the ratios of the yields at 436 and 405 m μ to those at 365 m μ increased. At thicknesses greater than 35 μ , the thickness did not have much effect on these ratios.

(5) The quantum yield of a given sample was apparently related to its purity or structure. Thick samples usually gave larger yields than thin ones. Samples prepared and treated in the same manner had similar yields.

(6) The maximum decomposition in all these experiments was about 0.1%.

IV. Discussion of Results

The most significant experimental result is the increase in quantum yield with decreasing wave length. Slade and Toy²⁸ and Fesefeldt and Gyulai²⁹ have shown that the absorption coefficient of silver bromide also increases with decreasing wave length. At short wave lengths, the incident radiation is absorbed in a thin surface layer of the silver bromide having a thickness which can be computed from the absorption coefficient. The concentration of positive holes and electrons

(29) H. Fesefeldt and Z. Gyulai, Nachr. Ges. wiss. Göttingen, Math. Phys. Kl., 228 (1929).

Sample description			Temp.	Exposed	Quantum vield at						
		Thickness	(°C.)	side	280 mµ	$302 \text{ m}\mu$	$313 m\mu$	334 mµ	365 mµ	$405 \text{ m}\mu$	436 mµ
1	N_2D241	2 mm.	27	N_2			0.76	0.36	0.16	0.05	0.012
2	N_2D241	2 mm.	82	N_2			.20	.11	.065	.019	
3	N_2D240	2 mm.	27	N_2			.71	. 41	.17	.06	.018
4	N_2D216	2 mm.	27	N_2			.49	.27	.11	.036	.014
5	N_2D216	2 mm.	27	Quartz			.52	. 29	.11	.036	.015
6	$N_{2}D216$	2 mm.	27	N_2	0.53	0.43	.37	.29	.14	.06	.018
7	N_2D214	2 mm.	27	N_2			. 19	.17	.079	.05	.021
8	N_2D214	2 mm.	27	Quartz	. 24		.16		.08	.046	. 02
9	N_2D214	2 mm.	27	Quartz			.39	.27	.12	.05	.017
10	Pyrex A	34μ	27	Glass			.52	.30	.07	.04	.015
11	Pyrex B	134μ	27	Glass			. 55	.32	.12	.03	.010
12	Pyrex C	35.4μ	27	Glass	.28		.20	.17	.088	.05	.021
13	Pyrex D	$15.8~\mu$	27	Glass	. 20	• •	. 17	.14	.075	.043	.031
14	Pyrex E	19.6 µ	27	Glass			.21	. 13	.08	.06	. 05
15	Pyrex F	132μ	27	Glass			.30	. 20	.086	.035	.010
16	Pyrex F	132μ	110	Glass			.04	.06	.05	.036	.017
17	Pyrex F	132μ	51	Glass			.31	.24	.12	.05	.018
18	Pyrex F	132 μ	27	Glass			.39	.26	.14	.07	.024
19	Pyrex G	5μ	27	Glass			.55	.43	.19	.19	. 19
20	Pyrex H	133 μ	27	Glass	••		.45	.27	.12	.046	.014

TABLE IV

QUANTUM YIELD OF BROMINE PRODUCTION AT VARIOUS WAVE LENGTHS AND TEMPERATURES

in the region of the crystal in which photolysis occurs is much greater at short wave lengths than at long, and considerable recombination should take place. The high yields at short wave lengths show, however, that such recombination does not occur and that vacuum is a very good halogen acceptor. The low yields observed at long wave lengths are therefore not due to lack of halogen acceptance at the surface of the crystal.

It is instructive to consider the results obtained by previous workers at long wave lengths. With emulsions or thin crystals produced by precipitation, the quantum yields in the presence of halogen acceptors were close to unity. In the thick crystals observed by Stasiw and Teltow, however, the yields were low and similar to those observed in these experiments.

In addition to these results, it has been shown that for thicknesses less than 35μ , the ratios of the yields at 405 and 436 m μ to those at 365 m μ increase.

The simplest explanation of these facts is that most of the absorption which is effective in producing gaseous bromine occurs in a thin surface layer, about one-third micron thick. As the wave length decreases, more and more of the incident radiation is absorbed in the surface layer, and the quantum yield increases. In thin crystals, the thickness is comparable with that of the active layer, and the quantum yield is large at long wave lengths. In thick crystals, more of the light is absorbed in the interior, and the quantum yield is small.

The decrease in quantum yield with increasing temperature is probably due to the decreased stability of the trapped electrons. Meidinger⁷ has shown that the quantum yield of silver formation in Agfa Rontgen SR film increased to a value of 0.99 at 100°. In emulsions, the positive holes may react directly with gelatin at high temperatures, and the rate of this reaction may be fast enough to prevent appreciable combination with the less stable trapped electrons. In vacuum, however, the rate of desorption of bromine may not be fast enough to prevent recombination with the electrons at high temperatures. The decrease in yield is most pronounced at short wave lengths where the surface concentration of holes and electrons is the largest, and this concentration is further enhanced by the increase of absorption coefficient with temperature. Therefore, the number of electrons in shallow traps will be greater at short wave lengths than at long, the rate of recombination with bromine will be greater, and the yield will decrease.

The decrease in the initial and final quantum yields caused in some cases by bromination of the crystal can be explained by the reaction of bromine with some of the surface traps. An alternative explanation is that bromination and evacuation at high temperature introduce additional positive hole traps, which would also decrease the yield of bromine evolution. It is hoped to decide this question when measurements of the effect of bromine on the conduction and photoconduction of such crystals have been completed.

It is possible to derive a kinetic expression which is consistent with the experimental results, but the data are not sufficient to justify its presentation at this time.

The presence of large concentrations of lead and cadmium ions had little effect on the rate of bromine evolution, but the data do not permit extensive interpretation. Further experiments to test the effect of impurities on the quantum yield are now in progress.

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DISCUSSION

C. C. KLICK (Naval Research Laboratory).—Is bromine evolution delayed by diffusion through the one-third micron surface layer, and can this delay be detected or estimated?

G. W. LUCKEY.—No delay was detected with the present apparatus. If the rate-limiting process is the diffusion of positive holes, the time estimated from the data of L. P. Smith and co-workers is less than one microsecond.

V. P. GUINN (Shell Development).—If the evolved bromine comes only from a thin surface layer of the silver bromide crystal, as you propose, photolysis of a crystal prepared from silver and radioactive bromine, and covered with a thin layer of inactive silver bromide, should produce only inactive bromine. This experiment, or its reverse, using inactive AgBr covered by AgBr*, might serve as a relatively simple quantitative test of the theory.

LUCKEY.—This would be a very informative experiment.

E. G. JOHNSON (Minnesota Mining and Mfg. Co.).— Is it a coincidence that the active layer thickness is approximately equal to the wave length of the incident light? LUCKEY.—This is an interesting coincidence, but there seems to be no connection between these two distances.

A. E. MILCH (Mellon Institute).—The parameter, "a," might be related to the wave length, since the bromine atom liberated by short-wave length irradiation has more residual energy than one liberated by long wave length.

LUCKEY.—This possibility cannot be eliminated because the ultraviolet absorption coefficients of silver bromide are not accurately known. The data available at present indicate that there is no variation of the parameter with wave length, but additional measurements are needed to establish this.

J. Q. UMBERGER (du Pont Co.).—In summary, you obtain low quantum yields at long wave lengths with thick crystals, because at long wave lengths you have low extinction coefficients and deep penetration of the light. This means that most of the bromine atoms formed inside the crystal cannot escape.

LUCKEY.—That is correct. Apparently, light absorbed within the crystal either does not form bromine atoms, or the atoms which are formed recombine with electrons before reaching the surface. Light that is absorbed within about one-third micron of the surface produces gaseous bromine.