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Nucleation and Growth in a Photosensitive Glass*

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The nucleation and growth of particles can be independently determined by simultaneous measurement of two quantities having different functional dependencies upon particle number and size. Light scattering and optical absorption are the two quantities chosen to observe the precipitation kinetics of a gold colloid. When an exposed photosensitive glass is treated at high temperatures, gold precipitates on a fixed number of sites. On the other hand, increasing the concentration of reactants causes spontaneous gold precipitation in which growth sites form continuously throughout the precipitation process. This indicates that the photosensitive reaction forms nuclei in a supersaturated solution which cannot nucleate spontaneously. In agreement with this, the experiment shows that the number of growth sites increases with exposure while the growth rate is the same for all exposures. Finally, assuming that the particles are spheres, absolute values are derived for the initial change of particle size with time and for the number of nuclei as a function of exposure.

INTRODUCTION

GLASSES offer two advantages over other media for studying the nucleation and growth of particles by light scattering. First, the nucleating substance precipitates in a transparent medium; and second, the precipitation process is greatly slowed by the high viscosity of the medium. This second advantage makes long times available for measuring precipitation kinetics and also stops the precipitation process when samples are cooled to room temperature for convenience of measurement.

The scattered light can be interpreted most easily in the initial stages of precipitation when the particles are so far apart that they scatter independently. At this time the particles are small compared to a wavelength of light and the scattered intensity is proportional to the number of particles times the square of their volume. Thus, in observing precipitation kinetics by the scattered intensity, it is not possible to differentiate between changes in number and changes in volume. This difficulty can be circumvented by simultaneously measuring a second quantity which depends

in a different functional way upon the number and volume. With metallic colloids the optical absorption is such a quantity since it is proportional to the number of particles times the first power of their volume.¹ Therefore, simultaneous measurement of the two quantities, scattering and absorption, permits a differentiation between number and volume—or nucleation and growth—in metallic colloid precipitation. This paper deals with the application of this method to the study of a photosensitive glass in which a gold colloid forms.

In most photosensitive glasses, exposure to electromagnetic radiation and subsequent heating to around the softening temperature causes a metallic colloid (gold, silver, copper, etc.) to precipitate.² The radiation is thought to furnish photoelectrons which neutralize metal ions dissolved in the glass. Aggregates of these reduced metal ions (neutral atoms) form a colloid. X-rays may be used for irradiation but if the glass contains cerium, photosensitive effects may be obtained with radiation in the near ultraviolet. Cerous ions are thought to furnish photoelectrons at these lower energies. Also, one or more of a group of multivalent elements (antimony, tin, etc.) called thermoreducing

* The cover picture shows a glass exposed to ultraviolet light as viewed in the direction of the light and perpendicular to it. Higher exposures result in greater penetration of the light and consequent precipitation.

¹ R. Gans and H. Happel, *Ann. Physik* **29**, 277 (1909).

² S. D. Stookey, *Ind. Eng. Chem.* **41**, 856 (1949).

agents are often present. The function of these materials in colloid precipitation—in gold ruby glasses, for example—has been clarified by Stookey.³ At melting temperatures the metal is oxidized and both metal and thermoreducing agent are present as dissolved ions. At lower temperatures, near the glass softening point, the metal ions are reduced by the thermoreducing agent and precipitate as a colloid of neutral atoms. That is, the process depends on the relative temperature dependence of the oxidation-reduction potentials of the metal and thermoreducing agent. This paper shows the following connection between the thermal and photosensitive reduction of gold. When initially cooled from melting temperatures, a glass with thermoreducing agent and gold consists of a supersaturated solution that precipitates rather slowly. In a photosensitive glass, the nucleation of the supersaturated solution occurs so slowly that it is negligible unless the photosensitive action is present to form additional nuclei.

THEORY

The theoretical expressions used in describing the data are applicable only to the initial stages of precipitation when the particles are so few that they are created and grow independently of each other. In addition, it is assumed that under these same conditions the particles are so few that they are optically independent and scatter light incoherently. Thirdly, the theoretical optical expressions will characterize the particles as small compared to a wavelength of light. Although all of these assumptions will tend to make the analysis a poorer approximation as the precipitation progresses, they are obviously valid if observations are made in the initial stages. For this reason they will not be mentioned further.

Two simple models are employed in analyzing the observations. The first model consists of N identical sites per unit volume which begin to grow early in the process with no further sites being created (heterogeneous nucleation). The volume of the particles is taken proportional to the time raised to a power p so that

$$V = Gt^p$$

and

$$\alpha = ANGt^p \quad (1)$$

$$R_u(90) = RNg^2t^{2p} \quad (2)$$

where α is the absorption coefficient, $R_u(90)$ is Rayleigh's ratio, and G a growth constant. The constants A and R involve the shape of the particle and its optical constants. If either the shape or optical constants change with size, then A and R will be functions of time. This is assumed not to occur. Equation (2) neglects the scattering by the depleted matrix. This is permissible for the present case where the solution is

dilute causing the depleted matrix to scatter largely in the forward direction and where the refractive index contribution of the solute increases greatly with precipitation. If the data follow the curves

$$\alpha = at^p \quad (3)$$

$$R_u(90) = rt^{2p} \quad (4)$$

where a and r are empirical values obtained from the measurements, then

$$G = \frac{A}{R} \frac{r}{a} \quad (5)$$

$$N = \frac{R}{A^2} \frac{a^2}{r} \quad (6)$$

These equations give the two constants characterizing the nucleation and growth process in its initial stages. As already mentioned, it is possible to derive both G and N because the absorption and scattering depend on these quantities in a different way. If A and R are known, the absolute values can be obtained. Even if A and R are not known, relative values can be obtained when the same type particle is precipitating in the systems to be compared.

The second model will assume that particles are being created at a constant rate I per unit volume per unit time (homogeneous nucleation). Then

$$\alpha = A \int_0^t IV(t-\tau) d\tau \quad (7)$$

$$R_u(90) = R \int_0^t IV^2(t-\tau) d\tau \quad (8)$$

where t is the time of observation and τ is the time at which a particle was created. The expression $V(t-\tau)$ is the notation for the particle volume at a time $(t-\tau)$ after the particle was created so that, similarly to the first model,

$$V = G(t-\tau)^p.$$

The assumptions for (7) and (8) are the same as for (1) and (2). Substituting the volume expression into (7) and (8) and integrating gives

$$\alpha = \frac{AIG}{p+1} t^{p+1} \quad (9)$$

$$R_u(90) = \frac{RIG^2}{2p+1} t^{2p+1}. \quad (10)$$

If the empirical curves are

$$\alpha = at^{p+1} \quad (11)$$

$$R_u(90) = rt^{2p+1} \quad (12)$$

³ S. D. Stookey, J. Am. Ceram. Soc. 32, 246 (1949).

then

$$G = \frac{2p+1}{p+1} \frac{A}{R} \frac{r}{a} \quad (13)$$

$$I = \frac{(p+1)^2}{2p+1} \frac{R}{A^2} \frac{a^2}{r}. \quad (14)$$

The constants A and R are the same as those used in the first model so that the relative growth constant in the two models, in terms of the ratio A/R , can be compared when the same particle is nucleated in different ways. This fact is utilized later. The exponent p can be obtained from the time dependence for either absorption or scattering. However, a comparison between the absorption and scattering time dependence is first necessary in order to establish whether the nucleation is homogeneous or heterogeneous.

The first section of this paper discusses only relative values of growth where values for the constants A and R need not be known. The last section derives absolute values for the particle number and growth on the assumption that the particles are spheres. For this case the theory of Mie⁴ gives

$$A = \frac{36\pi m^3}{\lambda} \frac{nk}{(n^2 - k^2 + 2m^2)^2 + 4n^2k^2} \quad (15)$$

$$R = \frac{9\pi^2 m^4}{2\lambda^4} \frac{(n^2 - k^2 - m^2)^2 + 4n^2k^2}{(n^2 - k^2 + 2m^2)^2 + 4n^2k^2} \quad (16)$$

where λ is the free space wavelength, n and k are the optical constants of the metal, and m is the refractive index of the medium surrounding the spherical particle. A proper choice of the metal optical constants to use in (15) and (16) is difficult since published values show wide differences and the true values probably depend on the way the sample is prepared.

The assumptions can be discussed somewhat further. First, since small metal particles are studied, it is possible that the electron mean free path affects the optical characteristics of the particle. If free path effects do enter into these experiments, they would have to be small to prevent invalidating the assumption that the optical properties of the particles are invariant with size. Investigation has shown the bulk properties appropriate down to dimensions of 100 to 200 Å.^{5,6} Second, computations for spheres have been made to investigate the effect of neglecting higher order terms. For increasing size, the second-order terms enter into the coefficient of absorption before the scattering so that this was the quantity examined. Retaining only the terms a factor of y^2 ($y = 2\pi mr/\lambda$ with r the sphere radius) higher than the first-order terms gives an

⁴ G. Mie, Ann. Physik 25, 377 (1908).

⁵ B. Pogany, Ann. Physik 49, 531 (1916).

⁶ Turkevich, Garton, and Stevenson, J. Colloid Sci. Suppl. 1, 26 (1954).

TABLE I. Ratio of second-order to first-order terms in the Mie theory absorption coefficient. The ratio is given for various values of the metal optical constants.

Diam (Å)	I $n=1.73$ $k=1.72$	II $n=1.40$ $k=1.88$	III $n=1.71$ $k=1.03$
100	0.01	0.01	0.00004
200	0.05	0.04	0.0002
300	0.12	0.09	0.0004
400	0.20	0.15	0.0008
500	0.32	0.24	0.0012

approximate value of the error involved up to diameters of 400 Å or so. Unfortunately, the results are obscured by the wide choice of bulk optical constants. Table I gives the ratio of second-order to first-order terms for three sets of optical constants—the first column constants were used by Mie, the second were given by Schulz,⁷ and the third were obtained by interpolation from the International Critical Tables. The log log graphs used in the analysis below are not very sensitive to changes in the data so that a ratio of 0.05 to 0.10 could occur without significantly changing the slopes of the curves and hence the conclusions. Therefore, it appears that higher order terms in Eqs. (1) and (7) can be neglected to sizes of 200 Å and possibly beyond.

EXPERIMENTAL DETAILS

The experiments were made with a photosensitive glass of batch composition (by weight) 71.5% SiO₂, 23% Na₂O, 4% Al₂O₃, 1% ZnO, 0.3% Sb₂O₃, 0.13% CeO₂, 0.01% Au. A glass which precipitated spontaneously (warmed-in) was made by increasing the concentration of the thermoreducing agent. This had the same batch composition with 1.5% Sb₂O₃. After melting, the glasses were analyzed chemically for antimony and gold. The antimony content was approximately equal to that calculated from the batch composition but the gold values were lower, with the photosensitive glass containing 0.003 weight percent gold and the "warm-in" glass 0.0045%. Both glasses had a refractive index of 1.50 and a density of 2.44 g/cm³.

In exposing the photosensitive glass, x-rays were employed so that the samples would receive the same irradiation through their thickness. Relatively penetrating x-rays were obtained by passing radiation from a tungsten target tube operated at 250 kv through a 2-mm copper filter. Five samples cut from the same block were first measured for absorption and scattering, and then given 12 500 r; 17 500 r; 25 000 r; 50 000 r; and 75 000 r. The data obtained during precipitation were corrected by subtracting the initial absorption and scattering at 436 mμ. The initial coefficient of absorption for all the samples was about 0.01 cm⁻¹ and the initial Rayleigh's ratio was about 3 × 10⁻⁶ cm⁻¹.

Each sample was treated at high temperatures for

⁷ L. G. Schulz, J. Opt. Soc. Am. 44, 357 (1954).

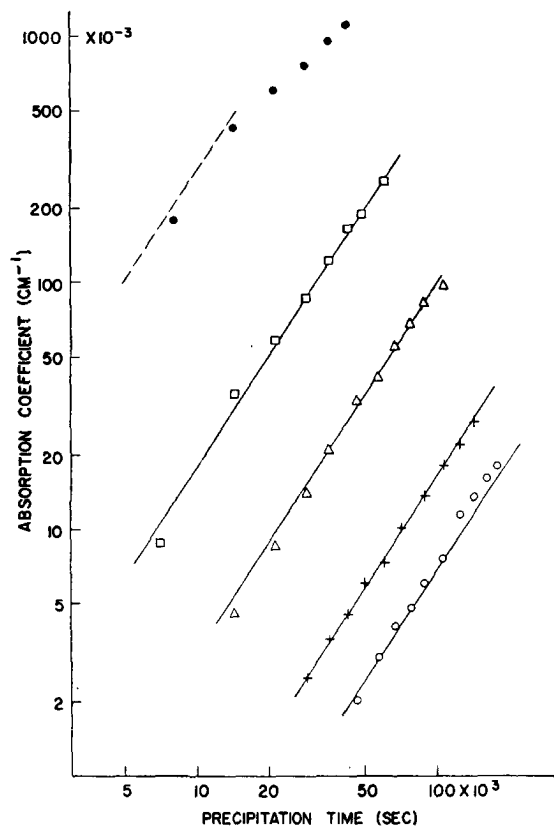


FIG. 1. Absorption coefficient at $436\text{ m}\mu$ versus precipitation time in a photosensitive glass with five different exposures. \circ —12 500 r; +—17 500 r; Δ —25 000 r; \square —50 000 r; \bullet —75 000 r. The solid lines are drawn with a slope of $\frac{3}{2}$.

progressive intervals of time with intervening cooling to room temperature for measurement. Precipitation, or development, was carried out at 530°C where the glass viscosity was about 4×10^{11} poises. A furnace with a fast heating and cooling rate was used so that each interval of development could be accurately controlled. Thermocouples near the samples indicated that the temperature was within 1°C of the final value after the furnace had been held at the development temperature for five minutes. Since the shortest development interval was 2 hours, this effective time was known within a few percent. With the furnace held at constant temperature, the spatial variation of temperature within the sample cavity was about $\pm 1^\circ\text{C}$. Heating and cooling did not greatly affect the kinetics since no systematic difference was found between samples heated for intervals with intervening cooling and samples heated continuously for the same length of time.

The scattering measurements were made with incident light of $436\text{ m}\mu$ using an experimental arrangement previously described.⁸ Rayleigh's ratio was obtained by comparison with benzene which was assumed to have a value of $48.4 \times 10^{-6}\text{ cm}^{-1}$ at $436\text{ m}\mu$.⁹

⁸ R. D. Maurer, *J. Chem. Phys.* **25**, 1206 (1956).

⁹ Brice, Halwer, and Speiser, *J. Opt. Soc. Am.* **40**, 768 (1950).

The observed scattered intensity had to be corrected for the absorption of the sample. This correction was minimized by reducing the path length traveled by the incident beam from the sample face to the scattering volume being observed. Nevertheless, the light path through the sample could not be reduced below about 1 cm so that the correction for absorption eventually became quite large as evidenced by the absorption values given below. This means that the Rayleigh ratio values at high absorption are not as accurate as the values for the same sample at low absorption.

DISCUSSION OF DATA

Photosensitive Gold Precipitation

The absorption and scattering results for the five different exposures in the photosensitive glass are shown in Figs. 1 and 2. The solid lines drawn through the data have a slope of $\frac{3}{2}$ for the absorption and 3 for the scattering. In the case of the highest exposure, the dashed lines were drawn with these same slopes and positioned to be asymptotic to the observations. The data fit these lines fairly well although, in the scattering curves, two of the samples indicate a somewhat less steep slope. It would require extensive work to determine whether this effect is real or due to experimental error, but it is believed that the lines drawn are within the accuracy of the data.

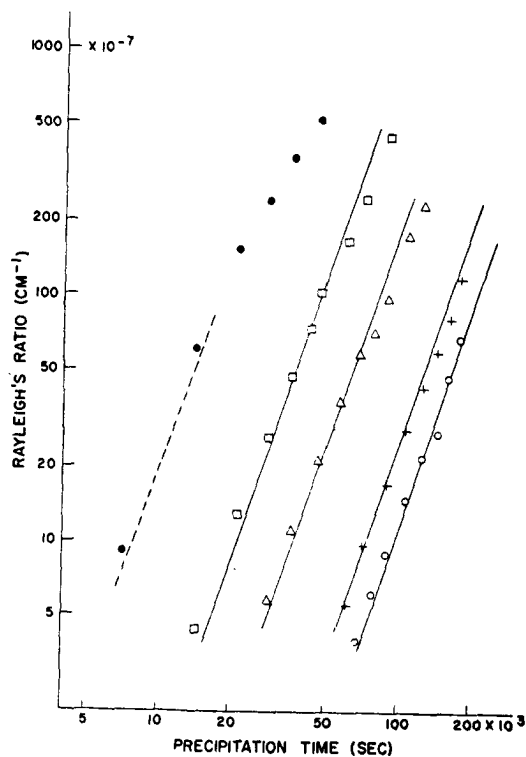


FIG. 2. Light scattering at $436\text{ m}\mu$ versus precipitation time in a photosensitive glass with five different exposures. \circ —12 500 r; +—17 500 r; Δ —25 000 r; \square —50 000 r; \bullet —75 000 r. The solid lines are drawn with a slope of 3.

The observations conform to a fixed number of sites growing with $p = \frac{3}{2}$, as represented by Eqs. (3) and (4). This is a heterogeneous nucleation description and suggests the possibility that the exposure of the glass served to activate sites upon which the gold precipitated. There is also the possibility that the sites were already activated but the exposure acted to reduce the dissolved gold ions. It will be shown that the first suggestion is correct.

Figure 3 shows scattering data later in the precipitation process for the 25 000 r, 50 000 r, and 75 000 r exposures. When the last data were taken at 9.70×10^6 seconds (270 hours), the absorption coefficients were 2.0, 1.8, and 2.1 cm^{-1} , respectively. The absolute scattering values may be in error because of the large correction for absorption but the relative values are correct since the absorption is about the same for all the samples. Even though precipitation is not yet complete, it is clear that in the final state the lower exposures will scatter more light and hence must contain larger particles.

This can be understood if the reduction of gold in the growth process does not involve the exposure, which merely serves to activate sites on which the gold precipitates. The gold in the growth process can be reduced by the antimony, as in a gold ruby glass. A lower exposure would activate fewer sites upon which a fixed amount of gold would precipitate (determined

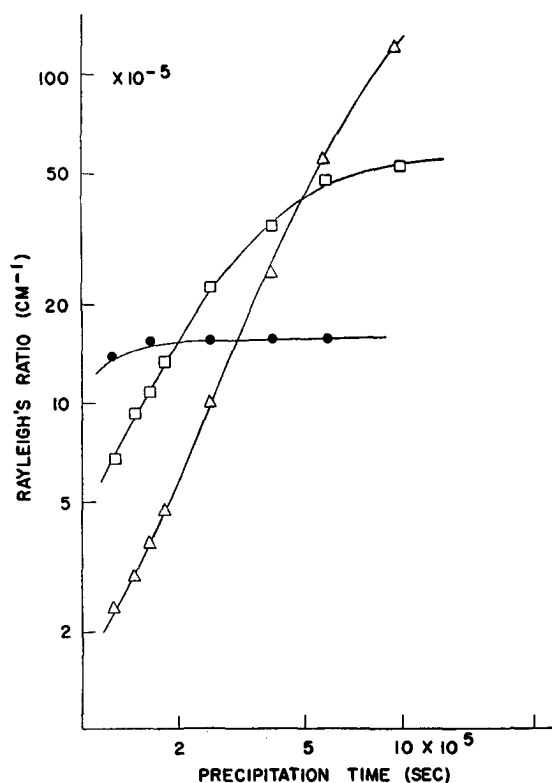


FIG. 3. Light scattering at 436 $m\mu$ versus precipitation time in a photosensitive glass with three different exposures. Δ —25 000 r; \square —50 000 r; \bullet —75 000 r. Data show the lower exposures scatter more light when the precipitation nears completion.

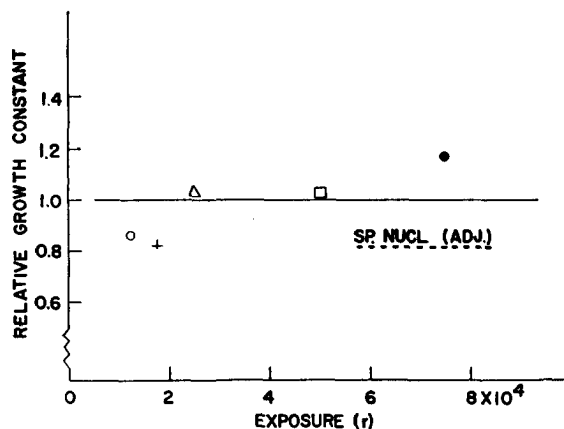


FIG. 4. Relative growth constant versus exposure for a photo-sensitive glass. Symbols correspond to data in Figs. 1 and 2. Also shown is the growth constant for particles nucleated spontaneously after data were corrected for variation in gold concentration.

by the antimony-gold equilibrium). Therefore, larger particles would result from a lower exposure.

Such a view is confirmed by the following experiment. Samples with exposures of 37 500 r, 50 000 r, and 75 000 r were treated until precipitation was complete—the absorption and scattering no longer changed with time. They were then re-exposed to twice the highest initial exposure. Additional heat treatment after this second exposure failed to precipitate any more gold in any of the samples. Evidently, after precipitation ceases an equilibrium state independent of exposure has been attained. It follows that the exposure acts to nucleate a supersaturated solution of antimony and gold ions.

Further confirmation of this deduction comes from the relative growth constants computed from the data of Figs. 1 and 7 using Eq. (5). The results are shown in Fig. 4. The growth constant appears independent of exposure, as would be expected if the role of exposure is only in nucleation.

Spontaneous Gold Precipitation

The deductions of the previous section were pursued further by investigating the spontaneous precipitation of gold that occurs with an increase in antimony concentration. The composition of this glass is given above. It was shown above that in a photosensitive glass a supersaturated solution of gold ions and antimony ions is present. This solution cannot nucleate without the photosensitive reaction. Increasing the concentration of antimony should increase the rate of the nucleation reaction and result in spontaneous precipitation. This is actually the case.

Figures 5 and 6 show the absorption and scattering data. The lines drawn through the data have slopes of $\frac{5}{2}$ and 4, respectively. Therefore, these data fit the homogeneous nucleation model, Eqs. (11) and (12), with $p = \frac{3}{2}$ —the same time dependence for growth

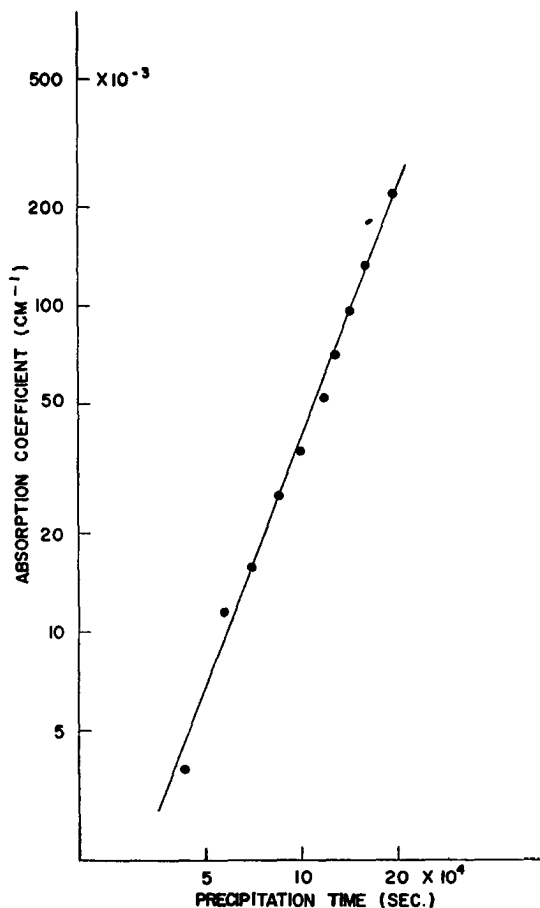


FIG. 5. Absorption coefficient at 436 $m\mu$ versus precipitation time for a glass which precipitated gold spontaneously. The solid line is drawn with a slope of $\frac{3}{5}$.

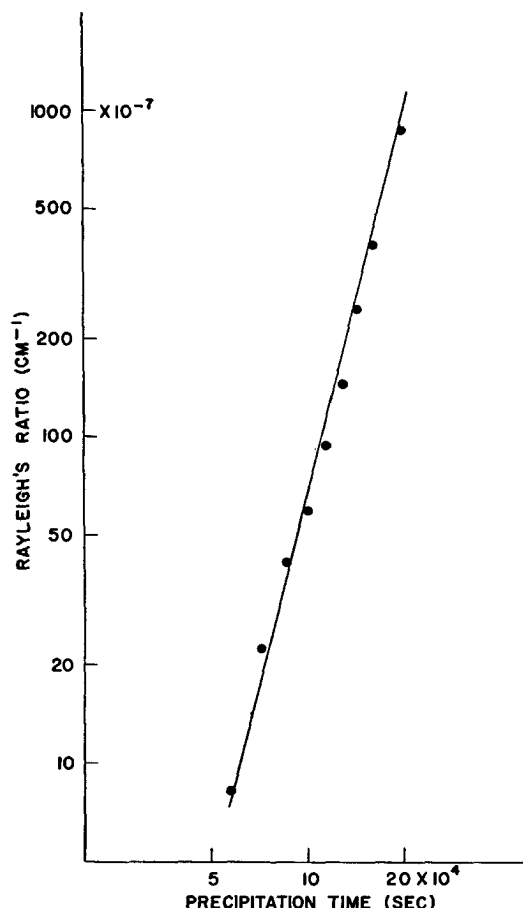
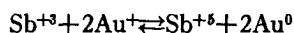


FIG. 6. Light scattering at 436 $m\mu$ versus precipitation time for a glass which precipitated gold spontaneously. The solid line is drawn with a slope of 4.

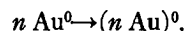
found in photosensitive glasses. Since the particles are presumably the same as in the photosensitive glass, the relative growth constant can be computed for comparison with those in Fig. 1. The value obtained from Eq. (13) is 1.51. However, the gold concentration is higher in this glass, requiring a correction that consists of dividing by the $\frac{3}{2}$ power of the relative concentrations (explained below). This gives an adjusted value of 0.82 which is shown in Fig. 4. Since a fivefold increase in antimony concentration causes little or no increase in the growth constant, the growth must be controlled by the diffusion of the metal ions. This may be a result of the relative concentrations since, stoichiometrically, there is enough antimony in the glass to neutralize a hundred times the amount of gold present.

The nucleus formation is difficult to understand if the migration of neutral gold atoms is required. Neutral gold atoms must be formed by the reaction



(which is written in terms of aurous ions for convenience). This reaction is assumed to be in equilibrium. Ordinarily the rate controlling process in nucleation is

the formation of a nucleus of stable size. With the neutral atom hypothesis, a stable nucleus of n atoms would be built up by neutral atom migration and the nucleation frequency is determined by the rate reaction



The equilibrium constant for the first reaction shows that the neutral atom concentration is proportional to the $\text{Sb}^{+3}/\text{Sb}^{+5}$ ratio which depends upon melting conditions and should not change greatly with increase in antimony concentration. Therefore, the nucleation frequency would not change with antimony concentration; this is contrary to experiment. It seems more likely that antimony and gold ions migrate and a critical size nucleus is built up by their interaction. In this case, antimony is involved in the rate controlling process so that the nucleation frequency would increase with increase in antimony concentration.

ABSOLUTE VALUES FOR THE INITIAL PRECIPITATION

The preceding discussion has analyzed the data without reference to the particle shape or optical characteristics. It is necessary to be specific about these

points in order to derive absolute values of number and size.

Some information about particle shape can be obtained from depolarization measurements. Data for the various samples are given in Table II. The value for ρ_u seems to be about constant at around 0.005 throughout the process and this constancy supports the assumption that the particle shape is not changing during the growth process. All measurements of ρ_u represent an upper limit since the errors entering into the measurement make it too high. To be practical, ρ_u can be taken as zero without much error. For example, using the theory of Gans,¹⁰ a depolarization of less than 0.005 results from gold oblate spheroids with minor to major axis ratio greater than 0.9; taking the depolarization as zero approximates these particles by spheres.

A measured depolarization of approximately zero does not determine the particle shape unambiguously. This means only that the three polarizabilities are equal, which is true for both cubes and spheres as well as for more complicated shapes. Some electron microscope examination of a gold ruby glass revealed cubical particles.¹¹ On the other hand, in unusual instances spherical particles have been seen in photosensitive glasses with the aid of a microscope. Also, spherical gold particles precipitate from aqueous solution.⁵ In the analysis below the colloid will be considered to consist of spheres. This assumption makes the time dependence of growth understandable since it agrees with the theoretical prediction for diffusion-limited growth of spheres.¹²

The bulk optical constants chosen for calculation are those measured by Schulz⁷: $n=1.40$ and $k=1.88$ at 436 m μ . Using these in (15) and (16), and substituting in (5) gives $G=4.98 \times 10^{-26}$ cm³ sec⁻¹ for the average growth constant at 530°C for the five photo-

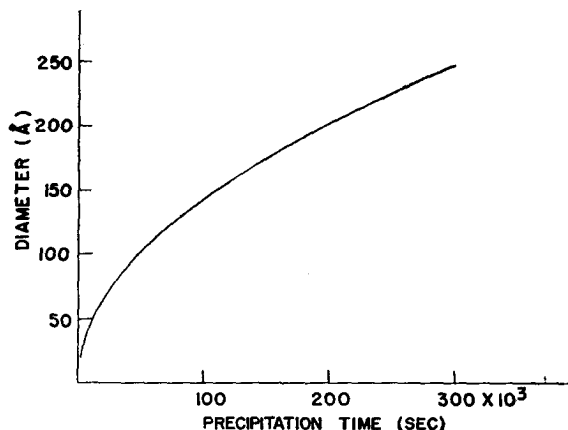


FIG. 7. Particle diameter *versus* precipitation time in a photosensitive glass computed with the assumption that the particles are spheres.

¹⁰ R. Gans, *Ann. Physik* **37**, 881 (1912); **62**, 331 (1920).

¹¹ Backman, Fisher, and Badger, *Glass Ind.* **27**, 399 (1946).

¹² C. Zener, *J. Appl. Phys.* **20**, 950 (1949).

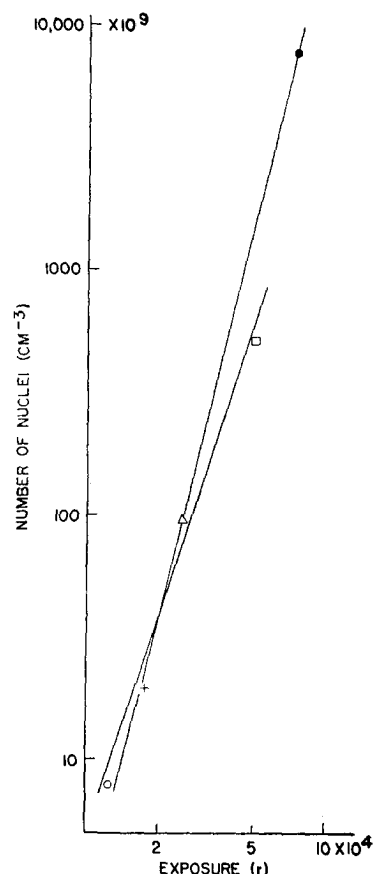


FIG. 8. Number of nuclei *versus* exposure in a photosensitive glass computed with the assumption that the particles are spheres. Symbols correspond to data in Figs. 1 and 2. The solid lines have slopes of three and four.

sensitive samples. The diameter of a sphere with this growth constant is shown as a function of time in Fig. 7. In the initial stages of precipitation, all particles will follow this growth curve. Later, competition for the available gold will deplete the solution and the growth will be somewhat less rapid than shown. The time at which competition becomes apparent in the growth depends on the number of nuclei created by the exposure.

In a similar manner, the number of nuclei for the five different exposures has been calculated. Figure 8 shows the results. The lines have been drawn to have slopes of 3 and 4. Ignoring the point for the highest exposure, which is least reliable, the slope of three gives the better fit. The photoelectrons from the exposure are thought to remain trapped until the glass is heated whereupon they react with active sites to form nuclei.² Assuming

TABLE II. Depolarization, ρ_u , for the colloid measured at various times during precipitation.

Time (sec)	17 500 r	25 000 r	50 000 r	75 000 r
3.60×10^4			0.005	0.009
5.76				0.006
7.20			0.004	
12.6		0.006		
16.2	0.004			
18.0		0.006		0.006

that the reaction with the sites may be treated with the mass action law leads to the conclusion that three electrons are needed to form a nucleus since the number of photoelectrons is proportional to the exposure. This implies that either three aurous or one auric ion are involved in its formation. Since this glass contained 2×10^{18} gold ions per cubic centimeter, only about one in 10^6 ions was neutralized by the highest exposures used.

The same constants used to find the number of sites may be used with Eq. (14) to find the nucleation rate. The nucleation rate at 530°C for the glass with high antimony content was $5.25 \times 10^5 \text{ cm}^{-3} \text{ sec}^{-1}$.

Finally, the growth constant permits an estimate of the diffusion constant governing the precipitation process. Large changes in antimony concentration did not change the growth constant appreciably. Therefore, the growth appears limited by the metal ions and can be analyzed in terms of diffusion of a single species. Zener¹² has shown that diffusion-limited growth of spheres from dilute solution follows the law

$$V = -\frac{4\pi}{3} \left[\frac{2Dt(n_\infty - n_1)}{(n_0 - n_1)} \right]^{\frac{1}{2}}, \quad (17)$$

where n_∞ is the concentration at large distances, n_0 the concentration in the particle, n_1 the equilibrium concentration at the interface, and D the diffusion constant. The concentration at large distances is known from chemical analysis and the concentration within the particle is the same as bulk gold. This leaves the equilibrium concentration at the interface which may be investigated from the initial concentration in the glass and the final amount precipitated. The amount precipitated can be estimated from the optical absorption which is equal to A times the volume fraction. This equality holds for particles small compared to a wave length. The final absorption for the 75 000 r sample, which has the smallest particles, yields a precipitated gold concentration of 0.0026 weight percent. Chemical analysis showed about 0.003 weight percent. Although the calculated value depends somewhat upon the optical constants chosen for the purpose, the result indicates that a very large fraction of the gold is precipitated. Evidently antimony has a strong tendency to reduce gold and the concentration of gold in solution at the interface will be small. Therefore, n_1 will be neglected with respect to n_∞ in Eq. (17) and hence

$$G \approx -\frac{4\pi}{3} \left(\frac{2Dn_\infty}{n_0} \right)^{\frac{1}{2}}. \quad (18)$$

This equation was used above in correcting the growth

constant for variations of gold concentration. Equation (18) gives a diffusion constant of $6.8 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$. Diffusion constants measured for silver in glasses at comparable temperatures¹³ were considerably lower which may be partly due to the difference in ionic radius.

CONCLUSIONS

In a photosensitive glass, gold precipitates at a fixed number of sites while in the same glass with increased antimony concentration the growth sites form continuously during the precipitation process. Since antimony thermally reduces dissolved gold ions to form neutral atoms, the continuous formation of particles involves precipitation from a supersaturated solution. In a photosensitive glass the supersaturated solution of antimony and gold does not precipitate because negligible nucleation occurs with the lower antimony concentration. The necessary nuclei are provided by photoelectrons which reduce a few gold ions. This reduction by photoelectrons occurs early in the precipitation process and provides the fixed number of sites for subsequent growth. In agreement with this explanation, the observations show that the number of growth sites in a photosensitive glass depends upon the exposure while the early growth rate of a particle is the same for any exposure. Only a small number of photoelectrons (order of three) is involved in the formation of a nucleus, so it is necessary for photoelectrons to neutralize only about 10^{-7} to 10^{-6} of the atoms present in order to get perceptible precipitation of gold. This study does not clarify the mechanism of nucleus formation.

The action of antimony, as well as the photoelectrons, can be understood best by assuming the gold migrates as dissolved ions. Therefore, the reduction of the gold ions must take place at the particle with the result that growth occurs by the diffusion of both antimony and gold ions to the particle. For the concentrations of antimony and gold used in these glasses, the growth rate appears limited by the diffusion of gold ions. The particles grow until a fixed amount of gold precipitates. This amount is determined by the gold-antimony equilibrium and includes almost all the gold present. The final particle size will depend upon the number of growth sites, or exposure, but for conventional cases it appears to be the order of a few hundred angstroms.

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¹³ J. Halberstadt, *Z. anorg. u. allgem. Chem.* **211**, 185 (1933); O. Kubaschewski, *Z. Electrochem.* **42**, 5 (1936).