

dynamic foundations because (4.10) satisfies the first and the second law of thermodynamics.

5. Conclusions

The concept of length in the thermodynamics of elastic bodies which has been deduced in this paper for a PES should be extended to the general case of an elastic body. It will be the modulus κ of (3.2) which must, in a general theory, be applied to all components of the empirical deformation tensors. A construction which is analogous to that of physical length will then provide a physical deformation tensor. The thermodynamic interpretation of physical deformation tensors will give the same linkage relations between pairs of conjugated quantities as Gibbs¹⁰ has deduced. Specific internal energy of elastic bodies, however, is no

longer a function of state, and a quantitative conversion of chemical into mechanical work of reservoirs during cyclic processes with elastic bodies is not possible.

As soon as physical length or physical deformation tensors are experimentally established, one must discuss the theory of dynamic equilibria again since the force of inertia depends on accelerations, *i.e.*, length changes, in a field of force. Such increases can perhaps be measured with the modulus κ , which is universal in the thermodynamics of elastic bodies. It is certain that one has to introduce into the statistical theory of elastic bodies a new probability factor which accounts for the necessary randomness of length. This probability factor is either a consequence of the elementary dynamic laws or it is a property of mechanical ensembles. In such ways eq 3.2, with its classical beauty, may give us new physical insights.

Kinetics of Formation and Growth of Colloidal Silver Bromide Particles. II¹

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The kinetics of formation and growth of colloidal particles of silver bromide has been investigated. In sols formed both in aqueous medium and in the presence of ethanol or of acetone, the number of particles at a given time is proportional to the initial supersaturation, over wide limits. The rate of particle growth due to Ostwald ripening has been determined over the period 2 min to 1 day.

Introduction

Studies on the kinetics of formation and growth of colloidal particles of silver bromide have been reported previously in which light-scattering methods were used for the continuous measurement of particle size as a function of time.² The present paper gives results of further study of this problem, the main emphasis being on the effects of concentration of sol and of the presence of complexing agents, colloid stabilizer, and organic solvents upon number of colloid particles, particle size, and growth. The unexpected

result has been found that over wide limits the number of colloidal particles is directly proportional to the initial supersaturation, described already in a brief communication.³ Also, the rate of particle growth as a result of Ostwald ripening has been determined.

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(2) E. J. Meehan and W. H. Beattie, *J. Phys. Chem.*, **65**, 1522 (1961).

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Experimental Section

Reagents and Preparation of Sols. Analytical reagent grade potassium bromide and silver nitrate, dried at 110° for 2 hr, were used to prepare 0.1 *M* stock solutions in redistilled water. The solutions were filtered through 0.45- μ pore size Millipore filters and were stored in polyethylene bottles. Acetone was AR grade. Ethanol and ammonia were reagent grade. Disodium dihydrogen ethylenediaminetetraacetate (EDTA, Eastman Kodak Co.) was recrystallized. Polyvinylpyrrolidone (PVP, Antara Chemicals) was Type NP-K30 with a number-average molecular weight of 4×10^4 . It was used without purification. The pH of a 1% aqueous solution was 3.7. The scattering at an angle of 90° was negligible compared to that of the most dilute sol investigated, and the solution was transparent (1 cm thickness) over the range 240–1000 $m\mu$. Potentiometric measurements (± 0.5 mv) using a silver electrode in solutions of silver nitrate in the absence and presence of PVP (up to 0.01%), compared to control measurements in solutions of silver nitrate, potassium cyanide, and PVP, indicated that no reaction occurred between Ag(I) and PVP.

The solutions of silver and bromide, plus other reagents when used, were brought to 25°. Under dim white light one solution was added either by pipet or microburet to 25 ml of the other solution contained in a 250-ml beaker and stirred as described previously.² The use of Pyrex or polyethylene beakers gave the same results. Time was measured from the beginning of the addition, which took about 30 sec; the first measurement was made at about 2 min. The sols were kept in the dark at 25° between measurements. Ethanol or acetone, when present, was added in equal amounts to both silver and bromide before mixing. The concentrations of ethanol and acetone are expressed as per cent by volume. Several of the radius-time curves given in this paper have been found to be reproducible within 10% by various workers in this laboratory over a period of several years, indicating that dust or impurities in the reagents do not affect the results.

Light-Scattering Measurements. A calibrated Aminco light-scattering microphotometer was used to measure scattered intensity at 436 and 546 $m\mu$. Transmission measurements were made in a Beckman DU spectrophotometer fitted with 4-mm aperture plates, using cells of path length from 0.1 to 50 cm as required. The methods used for size determination were specific forward scattering, specific turbidity, dissymmetry, and polarization ratio, the choice being determined by particle size and concentration.⁴ Exact Mie scattering calculations for the appropriate range of

size and refractive index are available.⁵ For calculations in ethanol-water or acetone-water mixtures, the Mie functions corresponding to silver bromide in water were used. From the refractive indices of the solvents, the maximum resulting error in radius for small particles is calculated to be 3%.

Results

Figures 1–5 present typical radius-time curves for sols prepared under a variety of conditions. In the presence of an excess of bromide (Figures 1 and 2) the initial growth became more rapid with decreasing concentration of sol. In 10^{-5} – 10^{-6} *M* sols (10% excess of bromide) all the particle growth occurred within 2 min or less. The effect of preparing a sol (10^{-3} *M*) in the presence of ethanol is shown in Figure 3. In up to 50 vol % ethanol the 2-min radii decreased slightly with increasing ethanol content, but soon after mixing, the radius-time curves became practically parallel. In 90% ethanol, however, the rate of growth after the initial period was substantially larger than in 0–50% ethanol. The effect of acetone (not shown) was determined only in dilute sols. As compared to the growth pattern in water, the presence of acetone caused a pronounced reduction in the initial rate of growth and slow growth occurred for several hours after mixing.

Presence of ammonia during formation of a 10^{-3} *M* sol (Figure 4) changed the growth pattern to that of a very dilute sol in the absence of ammonia; practically all the growth occurred in 2 min. Qualitatively similar results were obtained in 10^{-4} and 10^{-5} *M* sols (not shown). The behavior in the presence of EDTA was completely different. In a typical experiment 2.2×10^{-4} *M* potassium bromide was added to an equal volume of 2.0×10^{-4} *M* silver nitrate containing 4×10^{-3} *M* EDTA. The pH of the mixture was 9.4. The main silver species in solution was calculated⁶ to be 2.6×10^{-6} *M* AgY^{3-} , where Y is the anion of EDTA. The radius at 2 min was only 0.011 μ and the particles grew rapidly; after 3 hr the radius was 0.15 μ and the sol began to settle.

Effect of PVP. Under certain conditions PVP is an effective stabilizer for silver halide sols.^{7,8} Under some circumstances the rapid growth that occurs after mixing the reactants (Figures 1 and 2) could be pre-

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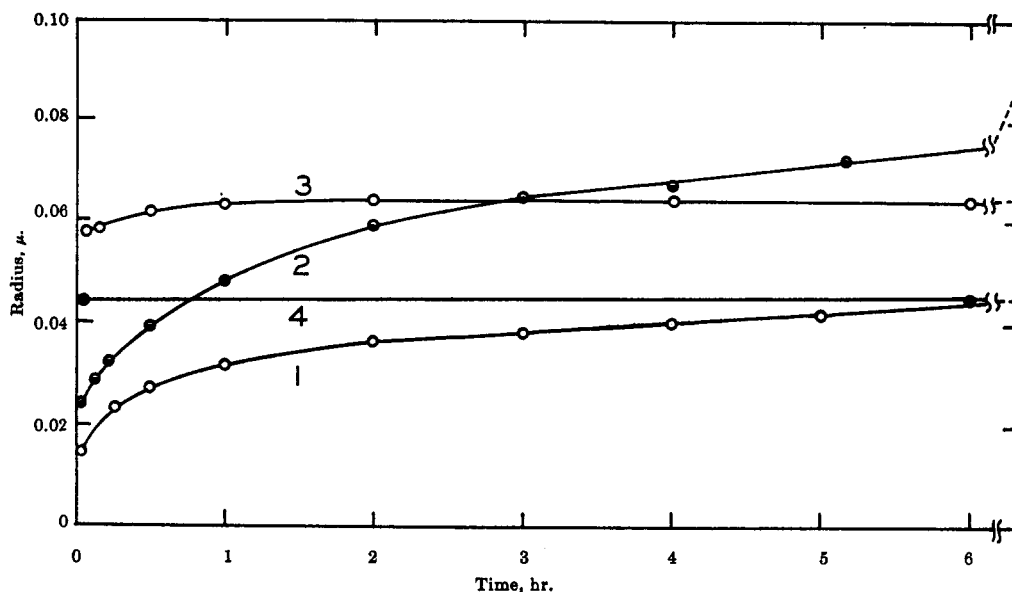


Figure 1. Particle radius vs. time; silver nitrate added to 10% excess of potassium bromide. Concentration of sol: 1, $10^{-3} M$; 2, $10^{-4} M$; 3, $10^{-5} M$; and 4, $5 \times 10^{-6} M$.

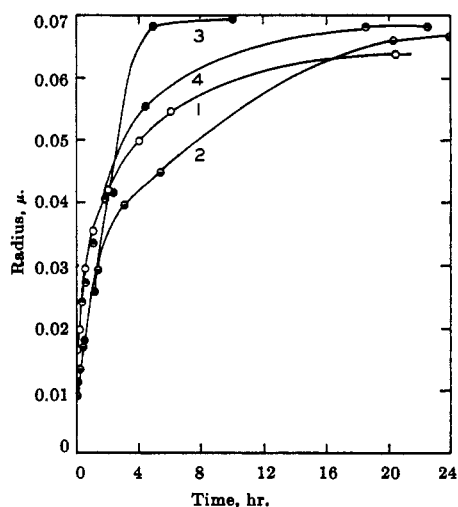


Figure 2. Particle radius vs. time: silver nitrate added to potassium bromide. Concentration of bromide in excess, $5 \times 10^{-3} M$; concentration of sol: 1, $5 \times 10^{-3} M$; 2, $5 \times 10^{-4} M$; 3, $5 \times 10^{-5} M$; and 4, $5 \times 10^{-6} M$.

vented completely by the addition of PVP. However, the effectiveness of PVP depended markedly upon the conditions of its addition, as shown by the following results. Approximately $10^{-5} M$ sols with 100% excess either of silver or of bromide were formed by adding by pipet 1 ml of $10^{-3} M$ potassium bromide (or silver nitrate) with or without PVP, the solution being stirred at 500 rpm. Stirring was continued for 20 sec. If neither solution contained PVP, 1 ml of PVP solution was added 20 sec after mixing. In all cases the final

concentration of PVP was about $10^{-5}\%$. The intensity scattered at an angle of 40° (i_{40}) was measured. In the absence of PVP, i_{40} increased at least eightfold within 30 min after mixing. Table I summarizes the results. (In this table, a sol is called "stable" if i_{40} changed by less than 1%/hr and "unstable" if i_{40} increased about as rapidly as in the absence of PVP.)

Table I: Stability of Ca. $10^{-5} M$ Sols with Ca. $10^{-5}\%$ PVP

Solution added	Solution to which addition was made	
	AgNO ₃	AgNO ₃ + PVP
KBr	Stable ^a	Unstable
KBr + PVP	Stable for a few hours	Stable for a few hours
	KBr	KBr + PVP
AgNO ₃	Stable ^a	Stable
AgNO ₃ + PVP	Unstable	Stable

^a PVP added immediately after formation of sol.

The stability of sols prepared by adding silver nitrate to a solution of potassium bromide plus PVP was remarkably dependent upon the concentration of PVP, as shown in Figure 5. The addition of silver nitrate containing PVP to potassium bromide produced an unstable sol (Table I). However, when from 10^{-5} to $10^{-2}\%$ PVP was added at various times from 0.5 min to 3 hr after silver nitrate, the particle size became constant immediately and changed less

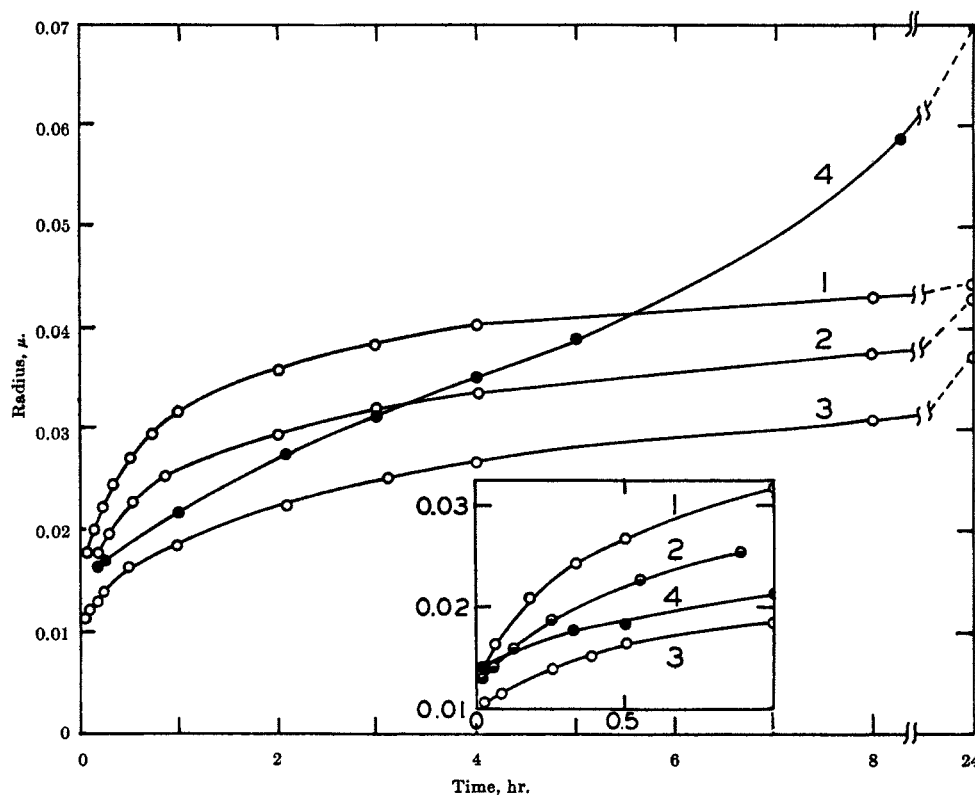


Figure 3. Particle radius vs. time: silver nitrate added to 10% excess of potassium bromide. Concentration of sol, $10^{-3} M$. Ethanol (vol %): 1, 0; 2, 10; 3, 50; and 4, 90.

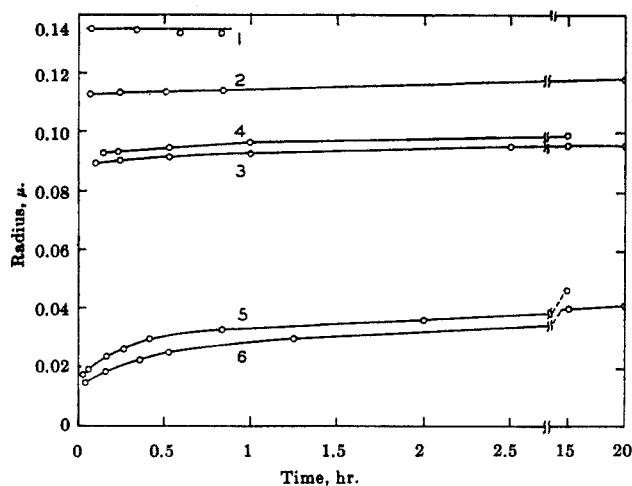


Figure 4. Particle radius vs. time. Potassium bromide (10% excess) added to silver nitrate. Concentration of sol, $10^{-3} M$. Concentration of ammonia: 1, 0.1 M ; 2, 0.05 M ; 3, 0.025 M ; 4, 0.005 M ; 5, 0.0005 M ; and 6, 0.

than 20% in the next 20 hr. Results at varied concentrations of reactants and PVP are summarized in Table II.

Numerous experiments in which the number and size of colloidal particles were measured before and after

Table II: Stability of Sols (Excess of Bromide): PVP Added 1 Min after Silver Nitrate

[AgBr], M	[KBr], M	PVP, %	Change in radius from 2 min to 24 hr, %
10^{-4}	10^{-5}	0	200
		10^{-2}	110
		10^{-4} - 10^{-1}	4-7
10^{-3}	10^{-4}	0	200
		10^{-4}	200
		10^{-2} - 10^{-1}	17-24
10^{-2}	10^{-3}	0	180
		10^{-2} - 10^{-1}	1-3
		10^{-3} - 10^{-1}	5

the addition of PVP showed that the addition of PVP did not change either number or size.

Previous work showed that upon dilution of fresh sols with water or with potassium bromide solution, a pronounced and almost discontinuous increase in radius occurred.² The dilution effects were observed also in the presence of gelatin, but the peculiar effects were completely eliminated when the sol was diluted with PVP solution.

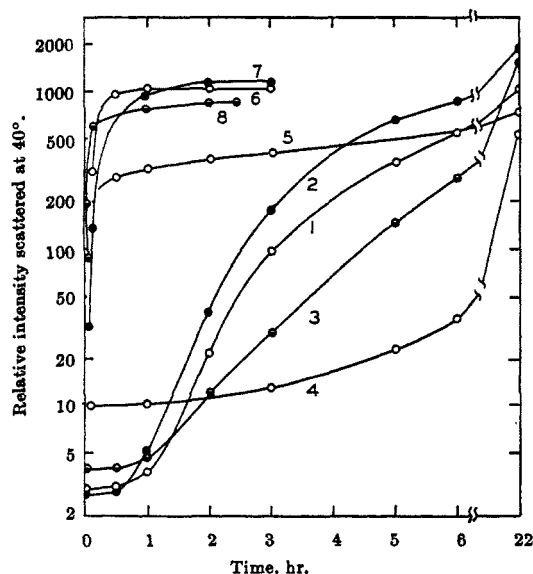


Figure 5. Relative i_{40} vs. time for 100% excess of silver nitrate added to potassium bromide containing PVP. Concentration of sol, $1.2 \times 10^{-3} M$. Concentration of PVP (wt %): 1, 10^{-2} ; 2, 10^{-3} ; 3, 10^{-4} ; 4, 10^{-5} ; 5, 10^{-6} ; 6, 10^{-7} ; 7, 10^{-8} ; and 8, 0.

Discussion

The growth curves for times greater than 2 min belong to two classes. In one class the radius is relatively small at 2 min and attains a limiting value only after some hours or days. In the other class the limiting radius is practically attained at 2 min and no further growth occurs. How the size, number, and growth patterns are related to concentration and supersaturation is discussed below.

Since the formation of colloidal silver bromide (as shown by conductance) is complete well within 2 min,^{2,9} the total number of colloidal particles can be calculated from the concentration of suspension and the average radius. The calculation is not exact because the sols are not homogeneous. However, the distribution of sizes in such sols is not broad.⁴ Assuming that the particles are spherical and have the bulk density 6.473 g ml^{-1} , the value of n , the number of particles per milliliter of suspension, is given by the relation

$$\log n = 9.84 + \log c - 3 \log r \quad (1)$$

where c is molar concentration of colloidal material and r is radius in microns. The relation between n and supersaturation is considered next.

In this paper supersaturation σ is defined as the concentration of silver bromide at the instant of mixing, divided by the solubility at equilibrium, s . Other workers have defined the supersaturation of the

slightly soluble ionic substance AB as the square root of the ratio of the ion activity products in the supersaturated state to the saturated state.^{10,11} (In the experiments of the present paper, ionic strengths are low and no activity corrections are required.) When equimolar amounts of A^+ and B^- are mixed, and if AB is completely dissociated, the two definitions of supersaturation are identical. The definitions are not the same, however, when the amounts of A^+ and B^- are unequal. For example, if the solubility product $S_{AB} = 10^{-10}$ and the initial concentrations of A^+ and B^- are 2×10^{-3} and $1 \times 10^{-3} M$, respectively, the equilibrium solubility is $10^{-7} M$. Since the sol concentration is $10^{-3} M$, supersaturation as defined in this paper is 10^4 , whereas according to the definition of La Mer, *et al.*,^{10,11} it is $\sqrt{(2 \times 10^{-3})(1 \times 10^{-3})/10^{-10}} = 140$. Moreover, the latter definition does not take into account the possibility of incomplete dissociation of AB or, even more important, the formation of complexes either with A^+ or with B^- . For example, consider a suspension made by mixing equal volumes of $0.01 M$ silver nitrate and $0.02 M$ potassium bromide. S_{AgBr} is 5.0×10^{-13} .¹² At the instant of mixing, $[Ag^+] = 5 \times 10^{-3} M$ and $[Br^-] = 1 \times 10^{-2} M$. The second definition of supersaturation^{10,11} yields $\sigma = \sqrt{5 \times 10^{-3} \times 10^{-2}/5 \times 10^{-13}} = 1 \times 10^4$. Since $[Br^-]$ at equilibrium = $5 \times 10^{-3} M$, $[Ag^+]$ at equilibrium = $1 \times 10^{-10} M$, but this does not correspond at all to the solubility. The concentration of undissociated silver bromide is $1 \times 10^{-8} M$ and that of $AgBr_2^-$ is $5 \times 10^{-8} M$.¹³ Hence the actual solubility is $6 \times 10^{-8} M$ and the supersaturation as defined in this paper is $5 \times 10^{-3}/6 \times 10^{-8} = 8.3 \times 10^4$.

Supersaturations were calculated as described above. Equilibrium constants for the formation of $AgNH_3^+$, $Ag(NH_3)_2^+$, and AgY^{3-} were taken from the IUPAC tables.⁶ Solubilities in the presence of ethanol and acetone were calculated from the data of Krahtovil and Tezak.¹⁴ In the mixed solvents the complex bromides are much more stable than they are in water. Therefore, when bromide is present in excess, the solubility in the mixed solvents is larger than it is in aque-

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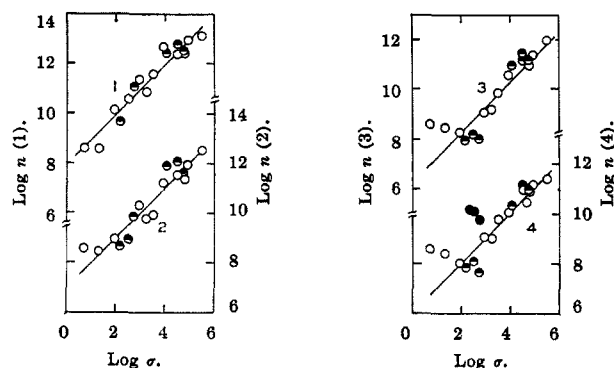


Figure 6. $\log n$ vs. $\log \sigma$ for silver nitrate added to potassium bromide: \circ , aqueous; \bullet , with ethanol or acetone; \bullet , with EDTA. Time: 1, 2 min; 2, 1 hr; 3, 6 hr; and 4, 1 day.

ous solution, despite the fact that S_{AgBr} in the mixed solvents is much smaller than it is in water.

In sols prepared by addition of silver nitrate to an excess of potassium bromide, in the absence or presence of ethanol or acetone, n is directly proportional to σ over wide limits (Figure 6). At a given time t , the data (silver added to bromide, above a certain minimum σ , *vide infra*) are represented by

$$\log n = a(t) + \log \sigma \quad (2)$$

which applies up to $\log \sigma = 5.5$. The values of $a(t)$ and the approximate lower limit of validity of eq 2 are

	2 min	1 hr	6 hr	1 day
$a(t)$	7.96	6.98	6.31	6.06
Lower limit of $\log \sigma$	0.7	1.0	1.5	2.0

The dependence of $a(t)$ upon t is represented well within experimental error by

$$a(t) = 6.38 - 0.684 \log t(\text{sec}) \quad (3)$$

Combining eq 1-3 there is obtained

$$\log r(\mu) = 1.15 + \frac{1}{3} \log s + 0.23 \log t \quad (4)$$

where s is the molar solubility at equilibrium, equal as stated above to total dissolved silver in all forms. Equation 4 may be written in the equivalent form

$$r(\text{cm}) = (1.4 \times 10^{-3}) s^{1/3} t^{0.23} \quad (5)$$

The effects of temperature upon growth rates in a $5 \times 10^{-3} M$ silver bromide sol in $5 \times 10^{-4} M$ bromide have shown that the slow growth (at times greater than 37 min) is due to Ostwald ripening, while the initial rapid growth (at 32 sec) is a fast flocculation.² The present results indicate that for similar sols the slow growth process is dominant at times as short as 2 min.

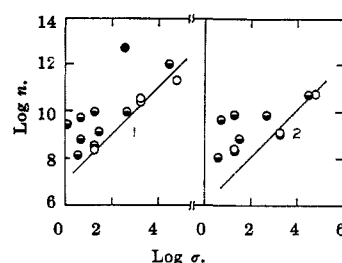


Figure 7. $\log n$ vs. $\log \sigma$ for potassium bromide added to silver nitrate: \circ , aqueous; \bullet , with ammonia; \bullet , with EDTA. Time: 1, 4 min; and 2, 1 day.

Nielsen¹⁵ has given an approximate theoretical treatment of the growth rate due to Ostwald ripening. When the rate is determined by dissolution and reprecipitation, and the rates of surface reactions are of no consequence, Nielsen has found that the radius r should be given approximately by the expression

$$r^3 \cong \frac{\gamma v^2 D s t}{kT} \quad (6)$$

where s is the equilibrium solubility in molecules per cubic centimeter, γ is the surface energy, ergs per square centimeter, v the mean ionic volume, D the diffusion coefficient, k the Boltzmann constant, and T the temperature. The present work (eq 5) confirms the predicted dependence upon s . Using the numerical estimates: $\gamma = 40$ ergs cm^{-2} , $v = 10^{-22}$ cm^3 , $D = 10^{-5}$ $\text{cm}^2 \text{sec}^{-1}$, $s = 10^{-16}$ molecule $\text{cm}^{-3} = 1.6 \times 10^{-8} M$, and $kT = 4 \times 10^{-14}$ erg, Nielsen's eq 6 yields $r \cong 10^{-6} t^{1/3}$. For the same value of s , the experimental eq 5 becomes $r = 3.5 \times 10^{-6} t^{0.23}$.

As stated already, eq 2-5 apply above a certain minimum σ . At very small σ , practically all the particle growth occurs within 2 min or less, which accounts for the deviations at low σ from the straight lines of Figure 6. It is of interest also to note that 1-day-old sols prepared in the presence of EDTA have a particle number larger by 10-20-fold than sols of the same σ prepared without EDTA.

Sols prepared by the addition of excess of potassium bromide to silver nitrate have somewhat fewer particles initially than those prepared by the reverse order (Figure 7). At a given σ , the value of n at 4 min in the former case is about the same as at 1 hr in the latter. However, after 1 day of growth the n - σ relation is practically the same for both modes of addition. Sols prepared in the presence of ammonia (Figure 7) appear to deviate from the n - σ relation observed in the absence of ammonia. In general, the number of

(15) A. E. Nielsen, "Kinetics of Precipitation," Pergamon Press Inc., New York, N. Y., 1964, pp 108-115.

particles at a given σ is larger in the presence than in the absence of ammonia.

Nothing can be concluded from these experiments about the rate of nucleation. The experimental fact² that fast flocculation is occurring at 35 sec means that the number of particles observed at 2 min is determined not only by the number of primary nuclei formed

during mixing but also by the rate of fast flocculation. The fact that the observed value of n varies linearly with σ , whereas according to generally accepted nucleation theory the number of primary nuclei should vary exponentially with σ , indicates that the rate of fast flocculation also must vary exponentially with the supersaturation.

Electron Spin Resonance Studies of γ -Irradiated High Surface Area

Silica. I. Identification of Defects

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Electron spin resonance (esr) studies have been made of the defects introduced in a high surface area silica by γ -irradiation. The esr spectrum has been analyzed in terms of contributions from four distinct types of defects in the glass structure. Two of these defects are thought to be formed in the silica network by the trapping of an electron in an oxygen vacancy. There is some evidence that $\sim 10\%$ of the oxygen vacancies have nearby hydroxyl groups. The remaining two defects are thought to consist of holes trapped in silicon-oxygen and boron-oxygen bonds. The evidence for the former assignment is not conclusive. The boron in the latter case occurs as an impurity in the silica. It is found to be trigonally coordinated in contrast to the tetrahedral coordination observed in other glasses. This result is explained in terms of the low concentration of network modifier present. The spectrum arising from the B-O defect is described by an axially symmetric spin Hamiltonian with $g_{||} = 2.0100$, $g_{\perp} = 2.0023$, $A_{||} = 1.40 \times 10^{-3} \text{ cm}^{-1}$, and $A_{\perp} = 1.25 \times 10^{-3} \text{ cm}^{-1}$. The relationship between this B-O defect and the Al-O defect found in irradiated smoky quartz is briefly considered.

I. Introduction

Electron spin resonance (esr) techniques have been used in a number of cases to study the nature of the paramagnetic defects introduced in glasses by ionizing radiation. For example, spectra have been reported for fused silica,¹⁻³ alkali borate,⁴⁻⁶ aluminosilicate,^{7,8} and phosphate^{9,10} glasses. Quite often hyperfine effects are observed. In these cases, the interpretation of the spectrum is usually based on concepts de-

veloped in the study of defects in alkali halide crystals, viz., electrons or holes trapped at vacancies in the lattice.

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