THE KINETICS OF THE FORMATION AND GROWTH OF MONODISPERSED SULFUR HYDROSOLS

Ethel M. Zaiser and Victor K. La Mer

Contribution from the Department of Chemistry, Columbia University, New York 27, N. Y.
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INTRODUCTION

Colloidal dispersions which are formed by condensation from an initially homogeneous phase pass very rapidly through an early stage of growth and coagulation. The processes that occur in this stage cannot be studied satisfactorily by present techniques until the rate decreases. By that time a polydispersed colloid has formed. If, however, the substance which is to constitute the dispersed phase is slowly and continuously produced in the system, for example by a chemical reaction, repetitive nucleation is obviated and the growth on the first nuclei proceeds uniformly. The product is a monodispersed colloid which can be characterized precisely as to particle size and number by optical methods.

Aerosols which were so monodispersed in respect to particle size that they exhibited higher order Tyndall spectra were prepared for the first time by La Mer and Sinclair by regulating the cooling of vapors in the presence of controlled numbers of nuclei. These monodispersed preparations were used in the experimental verification of the Mie theory for the scattering of light (1,2). These findings were extended by La Mer and Barnes to monodispersed sulfur hydrosols (3,4). When the homogeneous solution of sulfur produced by the reaction of very dilute thiosulfate and acid becomes sufficiently supersaturated, droplets of supercooled liquid sulfur suddenly appear (5). These droplets grow slowly and so uniformly that monodispersed systems of different particle sizes are readily obtainable for study, after stabilization by the addition of iodine. The sphericity of the micelles and their monodispersed character simplifies the application of the Mie theory as a means of determining the size and number of particles (4,6,7,8).

It is the purpose of this paper to investigate the factors which influence the formation and growth of the particles in these sols, which are easy to reproduce and measure quantitatively. This study may be divided into 3 stages.

I. The homogeneous reaction. The reaction begins as soon as the acid and thiosulfate are mixed, and produces molecularly dispersed sulfur. This stage is terminated when the sulfur solution becomes sufficiently supersaturated for stable nuclei to form.

II. The condensation stage. Here the rapid condensation of molecularly dispersed sulfur upon the nuclei relieves the supersaturation with the result that the rate of subsequent nucleation is greatly decreased.

III. The heterogeneous stage. The sulfur droplets slowly increase in size by diffusion of dissolved sulfur to the particle surfaces. The preservation of a high degree of monodispersity in this stage depends upon a low rate of formation of dissolved sulfur and the absence of repetitive nucleation and of secondary coagulation.

I. The Homogeneous Reaction

A. *Historical Summary*

Landolt (9) reported that an acidified solution of sodium thiosulfate remains clear for a time interval which depends on temperature and concentration, following which colloidal sulfur appears. This "induction period" was investigated by Foussereau (10). He reported a steady decrease in conductivity from the time the reactants were mixed. Biltz and Gahl (11) improved Landolt's method for detecting the Tyndall beam by using an ultramicroscope. A comprehensive review is given by Sheffer and Böhm (12). Ostwald (13) expressed the view that the sudden appearance of colloidal sulfur marks the end, not of an induction period, but of a state of supersaturation with respect to dissolved sulfur. In the absence of foreign nuclei a high degree of supersaturation would be expected. Since the reaction does not go to completion the removal of sulfur by the formation of a second phase should favor the forward progress of the reaction. Jablczynski and Warszawska-Rytel (14) reported transmission curves in the visible range using a Koenig-Martens spectrophotometer for $0.025 \ M \ Na_2S_2O_3$ and 0.125–$1.25 \ M$ HCl. At these high concentrations stage I is complete in less than 1 min. and a polydispersed colloidal system is formed. They interpreted their results as revealing an autocatalytic effect attributable to the formation of colloidal sulfur.

The products of the reaction have been studied extensively (12,14,15, 16,17). It has been shown that near pH = 3 about 80% of the reaction yields sulfur and sulfite, while side reactions produce polythionates. The results of different kinetic investigations (12,14,16,18) are not in harmony as to the mechanism of the reaction or even the identity of the reacting species, although it now seems certain that $HS_2O_3^-$ is involved (18,19).

La Mer and Kenyon (5) demonstrated experimentally the formation of dissolved sulfur by transmittance studies in the ultraviolet region, where sulfur absorbs. Their results indicate that, under ordinary condi-

tions, a definite concentration of molecularly dispersed (*i.e.*, dissolved) sulfur must be produced before sulfur micelles appear. Experiments designed to test the order of the reaction and the effects of added salts should yield information about the nature of the homogeneous reaction and the identity of the reacting species.

B. Experimental

Materials. Sodium thiosulfate, C. P., was recrystallized according to the method of La Mer and Tomlinson (20). The wet crystals were dissolved immediately in water and the solutions were standardized against $K_2Cr_2O_7$, then diluted and restandardized to give stock solutions whose concentration was $1.000 \pm .001$ M. Stock solutions of 1.5 M H_2SO_4 and 3 M HCl were made from reagent grade acids and standardized against Bureau of Standards potassium acid phthalate. Lanthanum sulfate was made from the nitrate by the action of sulfuric acid. The other salts used were C. P. grade and were not purified further.
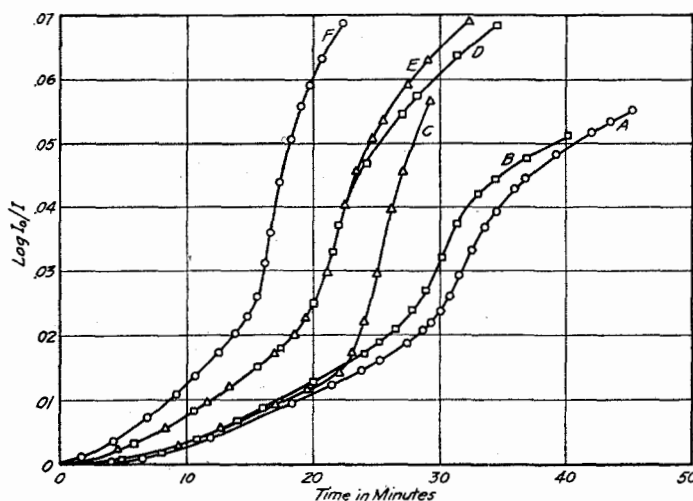

FIG. 1. Effect of salts on optical density as a function of time after mixing at $\lambda = 3000$ Å. $Na_2S_2O_3 = 0.002$ M, HCl $= 0.002$ M. A. No added salt, B. 0.0118 M $NaNO_3$, C. 0.2 M KCl, D. 0.0014 M $La_2(SO_4)_3$, E. 0.0005 M $La(NO_3)_3$, F. 0.0028 M $La(NO_3)_3$.

Method. Suitable aliquots of thiosulfate stock solution were delivered from a 2 ml. hypodermic syringe and mixed in nearly 1 l. of distilled water or a specified salt solution. The addition of acid from a syringe, mixing, and making up to volume occupied 20 ± 3 sec. The temperature was maintained at $25 \pm 0.05°C$. The ranges covered were from 0.001 to 0.003 M in thiosulfate, from 0.001 to 0.006 M in H^+, and from 0.007 to 0.03 in ionic strength.

The formation of molecularly dispersed sulfur (5) can be followed by transmittance measurements at $\lambda = 3000$ Å. The increase in optical density as a function of time was accordingly measured at this wavelength in 10 cm. quartz cells with a Beckman quartz spectrophotometer (model DU), using a solution of appropriate thiosulfate concentration as the blank. The absorption cells were refilled every few minutes from the reaction mixture which was kept at 25°C. The optical density readings were reproducible to within ±0.0005. Typical curves for log (I_0/I) vs time are shown in Fig 1.

The time at which a sharp break occurs in the log (I_0/I) curve, marking the beginning of light scattering by colloidal sulfur, is desig-
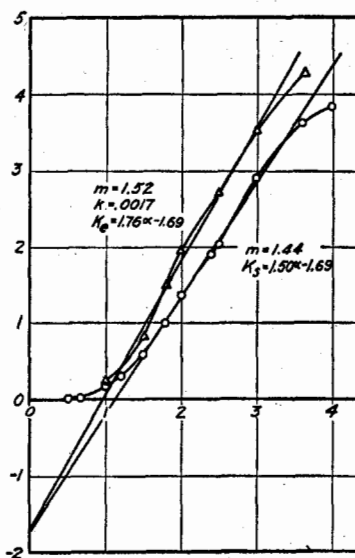

FIG. 2. Theoretical scattering area coefficient K_s as a function of $\alpha = 2\pi r/\lambda'$.

nated as "t_B." The uncertainty in the estimation of t_B is decreased to ±½ min. if the slope of the log (I_0/I) vs. time curve for $\lambda = 3000$ Å is examined and t_B taken as the point at which the slope increases rapidly. The application of this criterion to the data of La Mer and Kenyon (5) gives t_B values of 61 min. for 0.0010 M thiosulfate and 0.0015 M H_2SO_4, and 30 min. for 0.0015 M thiosulfate and 0.003 M HCl, instead of their values of 70 and 35 min., respectively. It also changes their estimate of the sulfur concentration at t_B from 5.5×10^{-6} to between 3 and 4×10^{-6} g.-atom/l.

C. Results

Constancy of Log (I_0/I) at t_B. Table I shows some results of experiments designed to test the reproducibility of t_B data. The average devia-

tion is ± 1 min. In Table II are indicated the values of $\log (I_0/I)$ observed at t_B for sols representing the entire range of reactant concentrations and ionic strengths studied. The constancy of $\log (I_0/I)$ at t_B $(0.020 \pm 5\%)$ makes it possible to use t_B as a measure of the rate of the formation of dissolved sulfur. The value 0.020 could be used to determine the sulfur concentration in the supersaturated solution just before condensation occurs if the extinction coefficient of sulfur in water were known. Using La Mer and Kenyon's (5) averaged value of 1460 cm^2./g.-atom for the extinction coefficient of sulfur in organic solvents, the sulfur concentration at t_B is 3.2×10^{-6} g.-atom/l. The order of magnitude of this figure is correct and is a qualitative indication of how very small the solubility of sulfur in water must be.

TABLE I

Reproducibility of t_B at $\lambda = 3000$ Å

Thiosulfate	H$^+$	t_B, min.	Average t_B
0.002 M	0.002 M	31, 29, 27.5, 30.5, 29, 28, 28, 28, 30	29$\pm$1
0.002	0.003	25, 21, 24, 25, 22, 24	23.5$\pm$1

Dependence of Rate on Reactant Concentrations. Since the amount of sulfur formed at t_B is constant, and the extent of reaction is very small, the following relationship is valid:

$$(S)_B/t_B = k(T)^a(H)^b,$$

where $(S)_B$ = sulfur concentration at t_B, and (T) and (H) = concentrations of total thiosulfate and acid, respectively. A comparison of the reaction rates at constant ionic strength for different thiosulfate and acid concentrations shows that $a = \frac{3}{2}$ and $b = \frac{1}{2}$. Table II shows the results of the calculation of a constant $k_S = k/(S)_B = [t_B(T)^{\frac{3}{2}}(H)^{\frac{1}{2}}]^{-1}$, from which it is seen that $k_S = 8700 \pm 5\%$ liter^2 mol^{-2} min.$^{-1}$.

Salt Effect. From an examination of the data in Table II it is evident that the effect on t_B of small amounts of univalent salt such as were used to adjust the ionic strength of some reaction mixtures is hardly differentiated from the usual variations in t_B that are due to failure of exact reproduction of a given set of condensation conditions, or merely to uncertainties in estimating t_B. The slight trend toward a positive salt effect indicated that further experimentation designed to prove or disprove the existence of such an effect might prove fruitful. The effect of adding a larger amount of KCl (0.2 M) is shown in Fig. 1, curve C. Here the rate of sulfur formation increases only slightly, but condensation begins at a

TABLE II

Constancy of log (I_0/I) at t_B and Dependence of Homogeneous Reaction Rate on Molar Concentrations of Reactants

10^3 (T)	10^3 (H)	10^3 KCl	μ	log (I_0/I) at t_B	t_B min.	10^{-3} k_S
1	3 x	—	0.0075	0.0200, 0.0190	66	8.8
	x	6.0	.0135	.0205	66	8.8
	x	9.9	.0174	.0185, .0195	63	9.2
	x	10.4	.0179	.0200, .0195	61	9.5
1	4	0.4	.0074	.0205	62	8.1
1	6 x	6.0	.0180	.0200	46	8.9
2	1	—	.0070	.0190, .0215	43	8.2
		0.3	.0073	.0225, .0205	45	7.9
		3.2	.0102	.0195	43	8.2
2	2	—	.0080	.0185,. .0200	29	8.6
		5.4	.0134	.0190, .0185	29	8.6
		10.0	.0180	.0190, .0205	26	9.6
2	3 x	—	.0105	.0205, .0225	24	8.5
	x	—	.0105	.0195, .0210	25	8.2
	x	3.0	.0135	.0210, .0215	24	8.5
	x	7.5	.0180	.0180, .0190	22	9.3
	x	20.0	.0305	.0195, .0180	21	9.7
3	1	8.0	.0180	.0185	24	8.0
3	1.5	7.5	.0180	.0185	17	9.2
3	2	7.0	.0180	.0185	15	9.1

x = H_2SO_4 was used; HCl used in all other runs.

Average log (I_0/I) at t_B = 0.020 $\pm$ .001.

Average 10^{-3} k_S = 8.7 $\pm$ 0.4 liter^2 mol^{-2} min.$^{-1}$.

TABLE III

Effect of Salts on the Rate of the Homogeneous Reaction of 0.002 M $Na_2S_2O_3$ and HCl

Salt	Log (I_0/I) at t_B	t_B	10^{-3} k_S
None	0.0210	28.5	8.8
0.0118 M $NaNO_3$	.0205	26.5	9.4
.0028 M $La(NO_3)_3$	.0205	14	17.8
.0010 M $La(NO_3)_3$	.0215	16	15.6
.0005 M $La(NO_3)_3$	.0210	19	13.2
.0014 M $La_2(SO_4)_3$	.0195	18.5	13.5

value of optical density lower than usual, indicating that salting out or perhaps some effect on nucleus formation may have occurred. The positive catalytic salt effect is demonstrated more clearly by the experiments with La^{+++} salts (Table III and Fig. 1), in which increasing quantities of $La(NO_3)_3$ produce correspondingly increasing catalytic effects. The nitrate ion has no specific effect on the reaction, as shown by the very small catalysis by 0.01 M $NaNO_3$. When $La_2(SO_4)_3$ is used, however, the catalysis is much less efficient, 0.0028 M La^{+++} in that form being only as effective as 0.0005 M La^{+++} in the form of the nitrate. This can be explained in the same manner as was Tomlinson's kinetic data on the bromacetate-thiosulfate reaction (21). The La^{+++} ions set up very large local deviations from the average bulk concentration of reactant ions, thus making it easier for the negative ions which are attracted to their vicinity to react. This interpretation is further supported by the opposing effect of sulfate ion to the La^{+++} catalysis, since these doubly charged anions offer the reacting species serious competition for places near La^{+++} ions.

II. THE CONDENSATION STAGE

A. Theory

The onset of the condensation stage under constant conditions of medium and temperature has been used in the preceding section as a criterion of the rate of the homogeneous reaction. We now examine some of the factors other than the rate of formation of dissolved sulfur that affect the beginning of the phase transition and the early stages of growth of the particles (22,23).

Thermodynamic Equilibrium between Phases. It was first shown by J. Willard Gibbs (24) that a spherical mass of phase II of radius r^* can remain in equilibrium with a surrounding mass of phase I which is supersaturated with respect to a droplet of II having an infinite radius. When the influence of the surface of contact between the two phases is taken into account, the equality $P_I = P_{II}$ is replaced by

$$P_{II} - P_I = 2\sigma/r^*,$$

where σ = surface tension, P_{II} = the pressure of the interior mass of the droplet of phase II, and P_I = the pressure of the exterior mass, phase I. The reversible work required to form such a mass in the interior of an infinite mass of the other phase is given by the general equation

$$W = \sigma s - V_{II}(P_{II} - P_I), \tag{1}$$

where σs = the work spent in forming the surface s, and $V_{II}(P_{II} - P_I)$ = the work gained in forming the interior mass of volume V_{II}. Gibbs further pointed out that W is always positive and equal to $\sigma s/3$—*i.e.*, the second term in Eq. 1 is $\frac{2}{3}$ of the first for a spherical droplet.

J. J. Thomson arrived at an equivalent and more often quoted expression for r^* in terms of

$$(\mu_r^* - \mu_\infty) = 2\sigma v_{II}/r^*,$$

where μ_r^* and μ_∞ = chemical potentials of the molecules in droplets of phase II of radius r^* and of infinite radius, respectively, and v_{II} = molecular volume in the droplet. For the case of equilibrium in a supersaturated vapor the J. J. Thomson equation takes on the familiar form

$$\ln (p_r^*/p_\infty) = 2\sigma v_{II}/kTr^*,$$

where k = Boltzmann gas constant, T = absolute temperature, p_r^* = vapor pressure of a liquid droplet of radius r^*, and p_∞ = vapor pressure over a flat surface of the liquid. Droplets smaller than the critical size are unstable because phase I is unsaturated with respect to them, while for $r > r^*$ phase I is supersaturated and again instability results. For $r = r^*$, a metastable equilibrium exists. Since the work required to form the surface of a droplet is of considerable magnitude, a comparable degree of supersaturation is necessary before the formation of droplets of the critical size can proceed at a measurable rate (22).

Nucleus Formation. The probability of the formation of the smallest mass of a new phase which can grow in the mother phase through further acquisition of molecules depends on $e^{\Delta S/k}$, where ΔS is the increase in entropy associated with a variation from the normal state of the system large enough to produce a nucleus. If the minimum work required to bring about such a change by an isothermal reversible process is $W = \sigma s/3$, the probability of forming Z droplets of phase II of the critical size in a large mass of phase I is

$$w = Ze^{-W/kT}.$$

If τ = the average lifetime and J' = the frequency of formation of the droplets,

$$J' = w/\tau = (Z/\tau)e^{-W/kT}.$$

In reality, a nucleus once formed has an equal chance of decreasing in size or of growing. However, only the latter course produces a change of state of the original phase I. If we imagine a process by which each nucleus on which any additional growth has taken place is removed from the system, so that the state of phase I remains substantially unchanged, the frequency J of formation of nuclei effective in the phase transition will be $J = J'/2 = (Z/2\tau)e^{-W/kT}$.

The factor Z/τ can be evaluated for some special cases by a kinetic treatment (22). The order of magnitude of the exponent W/kT, however, is all that is really important in determining the sharp limit of supersaturation at which J becomes so large that a spontaneous phase transition occurs. For water vapor at 300°C. in the absence of foreign nuclei

this limit lies between $p_r/p_\infty = 4.1$ and 4.2. The very rapid increase of J with supersaturation is shown by the fact that for $p_r/p_\infty = 3$ it would take 1000 years to form a droplet in 1 cm.[3] of vapor, while the process would require only 10^{-8} seconds if $p_r/p_\infty = 5$.

The work W required for nucleus formation is the analog of the free energy of activation for a chemical process, and the path followed has been assumed to be the one of lowest activation energy or highest probability. The theory as sketched here does not assume any mechanism for the nucleus formation, although it is believed that the fluctuations in the density of the molecular population of a phase produce "embryos" of a new phase. The fluctuations required are of the heterophase type, i.e., they exceed the limits of the normal homophase fluctuations which are insufficient to lead to a macroscopic change of state.

Growth of Particles. After nucleus formation, growth proceeds by the diffusion of molecules from the original phase to the nucleus. This can be expressed in a simple mathematical form by making the following assumptions (25): (a) the particle is spherically symmetrical, and (b) a stationary state is reached soon. In terms of the number of molecules dn diffusing in time dt through each spherical surface about the particle one gets:

$$dn/dt = 4\pi R^2 D(dc/dR), \qquad (2)$$

where c = molecular concentration at the distance R from the nucleus, and D = diffusion coefficient. The following expression can be differentiated to find dc/dR:

$$(c - c_s)/(c_o - c_s) = 1 - r/R,$$

where c_s = concentration of the saturated solution at the particle surface where $R = r$, and c_o = original concentration at the distance $R = \infty$. Substitution for dc/dR in Eq. 2 and expression of n in terms of the particle radius r and the molecular volume v_{II} in the new phase, followed by integration, yields the final equation:

$$r^2 = r_o^2 + kt,$$

where $k = 2Dv_{II}(c_o - c_s)$, and r_o = radius of particle when growth begins (at $t = 0$). Consequently, when a stationary state is set up, a spherical particle of phase II should exhibit a constant rate of increase of the area of the surface it presents to the surrounding phase I, provided the rate is diffusion controlled.

B. Some Qualitative Observations

Any change in the medium that affects the solubility of sulfur will produce a corresponding change in the concentration of sulfur that can exist before condensation starts. Examples are furnished by the salting-

out effect of 0.2 M KCl (see Fig. 1), and reports by earlier workers (26) of the greater "stability" of thiosulfuric acid in alcoholic solution. The addition of small amounts of alcohol, dioxane, or similar solvents to the reaction mixture increases the concentration of sulfur (or the optical density) that is reached before condensation sets in. An extreme example is the solvent 50% dioxane-water, in which colloidal sulfur does not appear after 2 days. The addition of water brings about an immediate precipitation of sulfur.

Since neither the solubility nor the extinction coefficient of sulfur in water is known, it is impossible at present to determine the degree of supersaturation at the phase transition. "Self-nucleation" of the sort described above would be indicated if the limiting degree of supersaturation were consistent with that predicted from theory. If the degree of supersaturation at t_B were much less than the theoretical, the presence of foreign nuclei favoring condensation at a lower degree of supersaturation would be suspected. There are several ways in which this could occur: a charged nucleus decreases the critical radius r^*, a surface-active substance would lower the energy required for the formation of the surface of the nucleus, or minute particles of another phase might provide small surfaces on which condensation could proceed. If the phase transition is not initiated by self-nucleation, the foreign nuclei must be present in ordinary distilled water in fairly constant amounts, and must be unaffected by ordinary methods of purification. Attempts to modify the behavior of the usual solvent, distilled water, by redistillation or treatment with nitrogen to remove dissolved oxygen produced no noticeable effects. The "artificial" nuclei tried thus far have not proven attractive to the dissolved sulfur, e.g., sulfur particles from an older sol of the same type, polysulfides, and sulfur precipitated from acetone by water were tried. The nucleation process is currently under investigation by Mr. James Yates of this laboratory (27).

C. Particle Size and Growth Rate Immediately after the Phase Transition

Method. La Mer and Kenyon (5) noted that, when condensation begins, scattering of light without the added complication of absorption can be detected at wavelengths to which sulfur is transparent. It was hoped that the growth rate of particles in this stage could be determined by measuring the time of initiation of scattering (t_B) at different wavelengths. When such measurements were made, however, no simple dependence of wavelength on time was found. An attempt was then made to calculate particle sizes from optical density *vs.* time curves obtained at different wavelengths. When Rayleigh's law was applied to such data the radii corresponding to the smallest increase in optical density that is

detectable as scattering starts were calculated to be of the order of $\frac{1}{3}$ to $\frac{1}{2}$ the wavelength of the light used, *i.e.*, above the range of sizes for which Rayleigh's law is valid. The more general Mie theory for the scattering of light must be used.

An examination of the theoretical scattering area (2,28,29) coefficient K_s as a function of $\alpha = 2\pi r/\lambda'$ (Fig. 2) shows that, for α values between 1.2 and 3.0, K can be expressed approximately by the empirical linear relations

$$K_s = 1.50\alpha - 1.69 \text{ for } m = 1.44,$$
$$K_e = 1.76\alpha - 1.69 \text{ for } m = 1.52 \text{ and } k = 0.0017,$$

where m = relative refractive index of sulfur and water,
  λ = wavelength in air,
  λ' = wavelength in water,
  k = extinction coefficient of sulfur,
  K_e = extinction area coefficient (for scattering plus absorption).

Since $K = 2.3 \log (I_0/I)/\pi r^2 nl$ and $\alpha = 2\pi r/\lambda'$, the above equations will give relations of the form

$$A \log (I_0/I)/n = Br^3/\lambda' - r^2, \qquad (3)$$

where A and B are constants depending on m, the absorption path length l, *etc.* For optical density measurements at $\lambda = 8000$ Å (for which $m = 1.44$), $A = 4.34 \times 10^6$ and $B/\lambda' = 9.24$, while at 4000 Å (for which $m = 1.52$ and $k = 0.0017$) A is unchanged and $B/\lambda' = 21.9$. If it is assumed that the particle number n is nearly constant during the short period of rapid condensation and is approximately equal to the number found to be present shortly after the initial condensation rate has fallen off somewhat, r can be calculated from optical density data. It can be understood from inspection of Eq. 3 why no simple relationship was found for the time of appearance of scattering (*i.e.*, the time when $\log (I_0/I)$ reaches the just measurable magnitude of 0.0005 corresponding to a decrease in transmittance of 0.1%) and the wavelength used for its detection.

Experimental. In order to utilize linear relationships between K and α it was necessary to work at wavelengths for whose m values computations of K were available, *i.e.*, at 4000 Å and 8000 Å. The procedure followed in the preparation of the sols, and the measurement of their optical density as a function of time, was the same as that used in the study of the homogeneous reaction. The most convenient procedure was to prepare tables of optical densities calculated for arbitrary values of radii, of λ', and values of n corresponding to the condensation stage. The times corresponding to the given sizes were then read off the experimental curves for $\log (I_0/I)$ as a function of time. The method for finding n will

be described later when the heterogeneous stage is discussed. The values of the radius determined by these experiments are in error by not more than $\pm.01\mu$.

Results. The smallest particle radius found was 0.07μ, calculated from optical density data at $\lambda = 4000$ Å just after scattering was perceptible in a sol which had 2.7×10^6 particles/cm.^{3} This particle number is larger than that of most of the monodispersed sols studied previously in this laboratory. In more dilute sols the particle size would have to be larger than 0.07μ before a decrease in transmittance could be observed. Since
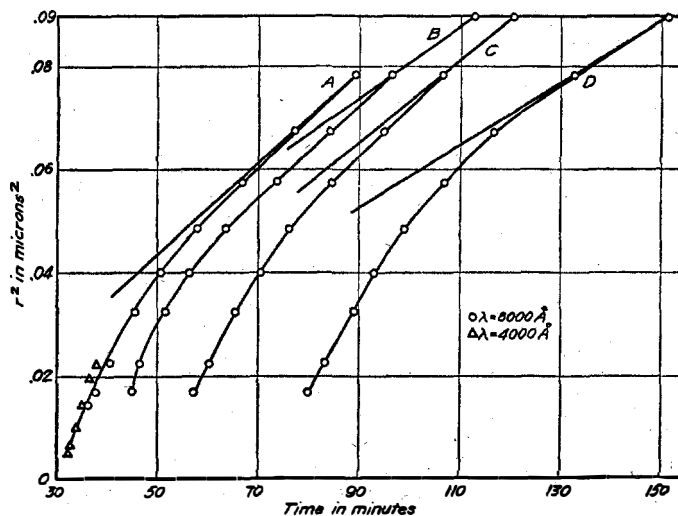

FIG. 3. Variation of r^2 with time in the condensation stage.

	Thiosulfate	HCl	$10^{-6}n$/cm.^{3}
A.	0.002 M	0.002 M	2.7
B.	.002	.0015	2.1
C.	.001	.006	1.8
D.	.001	.003	1.0

a Tyndall beam usually cannot be detected visually until 2 or 3 min. after the scattering of light of wavelength 4000 Å is detected spectrophotometrically, it is safe to say that true Rayleigh scattering (proportional to r^6/λ^4) has never been observed in any of the monodispersed sulfur sols because the number of particles (10^6/cm.^{3}) is too small. The particle number which is necessary to give perceptible scattering in the Rayleigh region ($r < \lambda/10$) is so large that rapid coagulation would occur according to Smoluchowski's theory (as will be discussed later). These sulfur sols are quite different from dispersions of high polymers where stability is possible with particle numbers of the order of 10^{15}/cm.^{3} No

data have been obtained, therefore, to describe the growth of particles from the time of nucleation until the time when $r = 0.07\mu$. This time interval is no greater than 2 min., and it seems fairly certain that, at its conclusion, the supersaturation of sulfur has been sufficiently relieved that further nucleus formation occurs only slowly.

By assuming that the particle number is constant for about an hour (*i.e.*, that formation of nuclei has virtually ceased) the growth of particles between $r = 0.07\mu$ and 0.30μ can be followed. Fig. 3 shows the variation of r^2 with time for 4 different sols in the early stage of growth. It would be expected that these systems should reach a steady state in which the generation of sulfur by the chemical reaction balances the loss of sulfur from solution by deposition on the colloidal particles. It will be noted, however, that dr^2/dt is not constant, indicating that a steady state has not been reached. The decrease in dr^2/dt could be interpreted as a lowering of the concentration gradient about each particle. This may be due to the gradual relief of the initial supersaturation, or to a decrease in the rate of formation of dissolved sulfur, or to both. The relief of supersaturation is the dominant factor here, since the system eventually reaches a steady state in which the variation of r^2 with time is linear (*cf.* Fig. 6). This will be shown when the heterogeneous stage of the reaction is discussed.

III. The Heterogeneous Stage

A. Discussion of Methods to Be Applied

Chemical Analyses. The sols exhibit an increase in iodine titer and a decrease in NaOH titer with time, caused by the following stoichiometric reactions (17):

$$H^+ + S_2O_3^= = S + HSO_3^-,$$
$$6H^+ + 5S_2O_3^= = 2S_5O_6^= + 3H_2O.$$
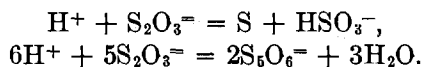
Thus, titrations should reveal the total extent of reaction, and through that, the total amount of sulfur formed. Iodine can be consumed in these systems only by thiosulfate and sulfite, and one mol of iodine is equivalent to two mols of thiosulfate or one mol of sulfite. Polythionates are not affected by iodine in neutral or acid solutions (30), and influence the iodine titer only because they require thiosulfate for their formation. If $\Delta(I_2)$ denotes the increase in iodine titer (in mols iodine/liter of sol), $\Delta(I_2)$ = mols sulfite formed

$-\frac{1}{2}$ mols thiosulfate consumed in sulfite formation
$-\frac{1}{2}$ mols thiosulfate used to form polythionate.   (4)
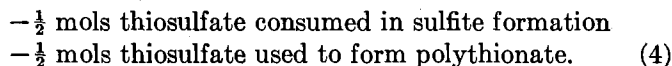
The decrease in NaOH titer will depend on the extent of polythionate formation and on the amount of sulfite present. One may choose as the endpoint in the titration a pH at which the first dissociation of H_2SO_3

is complete, *e.g.*, at pH $= 5.8$, since $K_1 = 1.7 \times 10^{-2}$, $(HSO_3^-)/(H_2SO_3)$ $\sim 10^4$. Since $K_2 = 5 \times 10^{-6}$, $(SO_3^=)/(HSO_3^-) = 3.1$, so that the total sulfite concentration is given by

$$(SO_3^=) + (HSO_3^-) = 4.1(HSO_3^-).$$

If $-\Delta(H^+)$ denotes the decrease in hydrogen ion concentration,

$-\Delta(H^+) = $ mols H^+ bound as HSO_3^-
$+ $ mols H^+ used in polythionate formation,

or $-\Delta(H^+) = (1/4.1)$ mols total sulfite
$+ 6/5$ mols thiosulfate used in polythionate formation. (5)

Eqs. 4 and 5 can be solved simultaneously to give Eqs. 6 and 7, by means of which the extent of sulfite and polythionate formation can be calculated from experimentally determinable quantities:

$$\text{Total sulfite} = [2\Delta(I_2) - (5/6)\Delta(H^+)]/1.20. \tag{6}$$

$$\text{Polythionate} = (2/5)[\text{total sulfite} - 2\Delta(I_2)]. \tag{7}$$

Optical Measurements. By methods developed in this laboratory (4,7,8), the radius and number of particles can be calculated from transmittance data on a monodispersed colloid. In practice, it is necessary only to find the wavelength and optical density corresponding to the principal maximum in the curve for transmittance *vs.* wavelength of a sol. Values of the scattering coefficient K_s as a function of α as calculated from the Mie theory can be used to relate transmittance data to the radius and number of particles, since $\alpha = 2\pi r/\lambda'$ and $K_s = 2.3 \log (I_0/I)/\pi r^2 nl$. At wavelengths at which sulfur absorbs, the calculations of the extinction area coefficient K_e, based on the complex index of refraction, must be used (8). The number of mols of sulfur in colloidal suspension at any time can be calculated as $1000 \times 4\pi r^3 n\rho/3M = 261.8 nr^3$ mols/l., where $n = $ number of particles/cm.^{3}, $r = $ radius in cm., $\rho = $ density of sulfur, and $M = 32 = $ atomic weight of sulfur.

Coagulation and Settling Corrections. Only the colloidal sulfur in suspension is measured by this optical method. To find the total amount of colloidal sulfur formed, the number of particles settling out and/or coagulating must be considered. The following equation gives the fractional decrease in number per unit time due to coagulation (first term) and stirred settling (second term) (6):

$$- dn/n = \kappa n + v/h,$$

where $\kappa = 4kT/3\eta$ as in the Smoluchowski coagulation theory, and v/h comes from $n = n_0 e^{-vt/h}$, in which $v = $ velocity of fall as predicted from Stokes' law, $h = $ height of the system, and $t = $ time. The coagulation term is independent of the radius of the particles, while the settling term

depends upon $v = 2r^2g(\rho - \rho_0)/9\eta$, where r = radius of particle, g = acceleration due to gravity, $(\rho - \rho_0)$ = effective density of the particle, and η = viscosity. The proposed corrections are, of course, only approximate, since stirring is certainly not complete and no account is taken of the effect of micellar electric charges on the coagulation rate (31). It should be of interest, nevertheless, to obtain an estimate of the extent of decrease in number and of the relative importance of coagulation and settling in that decrease.

B. Experimental

The technique for preparation of the sols was the same as that described in Section I on the homogeneous reaction. The sols were prepared in 2-liter quantities and held at 25°C. Two separate aliquots of each solution were prepared, one of which was studied from time = 0 to 12 hr. and the other from time = 12 to 24 hr. after mixing. The concentrations ranged from 0.0005 to 0.003 M in thiosulfate and 0.00075 to 0.006 M in HCl. Preliminary experiments showed that small amounts of added KCl made no perceptible difference in any of the quantities measured, and the use of KCl in adjusting the ionic strength of the reaction mixtures to equality was omitted. In the experiments reported here, the only case in which a salt was added was in the demonstration of a positive kinetic salt effect by La^{+++} ion.

Titration Experiments. At approximately 2-hr. intervals, 25 ml. aliquots were removed from the reaction mixture for titration with iodine and NaOH. The iodine solution for each run was made by diluting a stock solution of 0.1 M I_2 in 0.25 M KI so that its molarity was half that of the thiosulfate in the sol. The iodine was standardized against a $Na_2S_2O_3$ solution for which $K_2Cr_2O_7$ had been used as the primary standard. In each titration 1 ml. of 1% starch solution served as an indicator, and a blank was run on 1 ml. of indicator in a volume of distilled water equal to the total volume present at the endpoint of the titration of the sample. The NaOH reagent was carbonate-free. The molarity of the NaOH used in each run was approximately equal to that of the HCl in the sol. Methyl red was the indicator, and the titration was concluded at pH = 5.8. When the endpoint was very near, the volume of the solution was adjusted to 60 ml. and the titration was completed by further addition of NaOH and comparison with Clark and Lubs buffers of pH values 5.6, 5.7, 5.8, and 5.9 to which indicator had been added. The blanks consisted of indicator and distilled water.

Optical Density Measurements. Measurements of transmittance were made on aliquots of sol, in which the progress of the reaction was arrested by the addition of 50% of the stoichiometrically equivalent amount of 0.1 M I_2, in quartz cells, 10 cm. length, in a Beckman spectrophotometer

(model DU). In most cases the minimum in the curve for optical density as a function of wavelength could be located in 15 min. The particle radius was calculated from the wavelength of this minimum transmittance from the relation $\alpha_{min.} = 2\pi r/\lambda'_{min.} = 6.8$ for $\lambda' > 3200$ Å. For lower wavelengths, where absorption occurs, Kenyon's (8) values for $\alpha_{min.}$ were used. The particle number was calculated from the optical density (7,8):

$$(K_s)_{min.} = 2.3 \log (I_0/I)_{min.}/\pi r^2 nl = 2.08.$$

Errors. The accuracy and reproducibility of the quantities of reactants delivered by the hypodermic syringes used in the preparation of the sols was within 1%, as determined by titration. The pH (5.8) at the endpoint of the NaOH titrations was estimated to within 0.05 pH unit. An error of 0.05 pH unit causes a 1.5% error in the calculated amount of total sulfite. The latter quantity exhibits an average total error of $\pm 3\%$, since it also depends on the iodine titration.

The optical method used has been shown (7) to yield values of the radius that are accurate to within $\pm 0.01\mu$, while the numbers of particles are correct to within 5%. A total error as large as 10% in the quantity nr^3, from which the number of mols of colloidal sulfur in suspension is calculated, is small in comparison with the change in that quantity produced by varying the concentration of one of the reactants.

C. Results

Chemical Analyses. To obtain values of $-\Delta(H^+)$ and $\Delta(I_2)$ for the same time, the experimentally determined curves for $-\Delta(H^+)$ and $\Delta(I_2)$ as a function of time were plotted. Values at arbitrarily chosen time intervals were read from them and used, as shown in Table IV, to calculate the concentrations of sulfite and polythionate. The concentrations of sulfite and polythionate as a function of time from Table IV are plotted in Fig. 4. Both runs shown are 0.002 M in $Na_2S_2O_3$ and HCl. In run 83, 0.0005 M La(NO$_3$)$_3$ was added. As in the homogeneous reaction, a positive salt effect indicates that the rate-controlling step in the formation of sulfite is a reaction between ions of like (and therefore negative) charge. The rate of formation of sulfite in the heterogeneous stage of the reaction is expressed by:

$$d(\text{sulfite})/dt = k(T)^2(H).$$

Table V shows the effect of the concentrations of the reactants on the rate of sulfite formation. The k values are calculated for times at which 10% of the original thiosulfate had decomposed. In most cases, formation of polythionate accounts for $\frac{1}{4}$ to $\frac{1}{3}$ of the consumption of thiosulfate. This means that polythionate determined by the decrease in H$^+$ concentration represents only about 8 mol-% of the sulfur-containing products of the reaction.

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TABLE IV

Sulfite and Polythionate Calculated from Titration Data for 0.002 M $Na_2S_2O_3$ and HCl
(Units of concentration = 10^{-5} mols/l.)

</div>

Run	Time	$-\Delta(H^+)$	$\Delta(I_2)$	Sulfite	Polythionate	Thiosulfate decomposed
	hrs.					
83[a]	4	6.5	3.8	10.6	1.2	13.6
	8	11.9	6.1	18.6	2.5	24.8
	12	17.3	7.5	24.5	3.8	34.0
	16	21.3	8.6	29.2	4.8	41.1
	20	24.0	9.7	32.8	5.4	46.2
	24	25.6	10.7	35.6	5.7	49.8
84	4	5.8	2.8	8.7	1.2	11.8
	8	10.8	4.8	15.6	2.4	21.5
	12	14.8	6.1	20.4	3.3	28.6
	16	18.4	7.1	24.6	4.2	35.0
	20	21.0	8.2	28.2	4.7	40.0
	24	23.2	9.2	31.4	5.2	44.8

[a] La(NO$_3$)$_3$ added = 0.0005 *M*.

Variation in Number of Suspended Particles. Table VI shows data obtained from optical measurements in a typical run, the calculated particle radii and numbers, and the corresponding molar concentrations
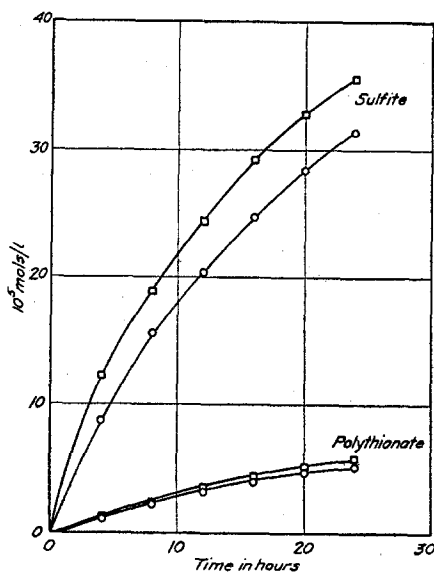

FIG. 4. Formation of sulfite and polythionate as a function of time from 0.002 *M* Na$_2$S$_2$O$_3$ and 0.002 *M* HCl. ○ no added salt. □ 0.0005 *M* La(NO$_3$)$_3$ added.

TABLE V

Dependence of Rate of Sulfite Formation on Reactant Concentrations

$(T)_0$, $(H)_0$ = initial conc. of $Na_2S_2O_3$ and HCl in mols/l.

$(H)_t$ = conc. of HCl at time t when 10% of thiosulfate has decomposed.

10^5 $(T)_0$	10^3 $(H)_0$	t	10^3 $(H)_t$	10^5 (sulfite)	$10^5 \frac{\text{(sulfite)}}{t(H)}$	10^{-3} k
		hr.				
0.5	3	14.4	2.98	3.16	73.2	3.2
	6	7.1	5.98	3.09	72.8	3.2
1	1.5	15.3	1.47	7.20	308	3.4
	3	10.2	2.97	7.34	241	2.7
	4.5	6.8	4.47	7.08	232	2.6
	6	4.0	5.97	7.30	304	3.4
2	0.75	18.0	0.69	15.3	1180	3.3
	1.5	9.0	1.42	14.9	1130	3.1
	2	7.4	1.90	14.5	1010	2.8
	3	4.5	2.92	13.4	1010	2.8
	4.5	2.8	4.43	14.4	1150	3.2
3	0.75	18.0	0.66	22.4	1770	2.2
	1.5	6.6	1.40	21.5	2250	2.8
	3	3.5	2.89	21.0	2040	2.5
2^a	2	6.3	1.90	15.2	1240	(3.4)

[a] $La(NO_3)_3$ added = 0.0005 M.

Average $10^{-3} k = 2.9 \pm 0.3$.

of the sulfur in colloidal suspension—*i.e.*, the sulfur capable of scattering light. When the variation of particle number with time was examined, it was noted that in every sol studied the particle number increased in

TABLE VI

Typical Transmittance Data and Results for 0.001 M $Na_2S_2O_3$ and 0.0015 M HCl

Time	λ' min. Å	Log (I_0/I) min.	r, μ	$10^{-8} n/cm.^3$	$10^5 (S)^a$ mols/l.
hr.					
2.5	2750	0.0093	0.26	0.47	0.22
4.8	3510	.0222	.38	.54	.78
6.7	3670	.0263	.40	.59	.96
11.6	3900	.0300	.42	.59	1.17
14.0	4700	.0370	.51	.50	1.74
15.8	4810	.0347	.52	.45	1.66
19.2	5130	.0314	.56	.36	1.61
24.1	5650	.0272	.61	.26	1.53

[a] (S) = colloidal sulfur *in suspension* in the solution.

the early stages of growth, then decreased later. This is illustrated by the uncorrected curves for number *vs.* time in Fig. 5. It was also observed (see Table VII) that the maximum reached by the number of suspended particles in a sol was dependent on $(T)^2(H)$, or the rate of the chemical reaction, and that n began to fall off when r was approximately 0.4μ, a size at which the rate of settling of the particles becomes appreciable (32). These facts can be explained if it is assumed that increases in particle
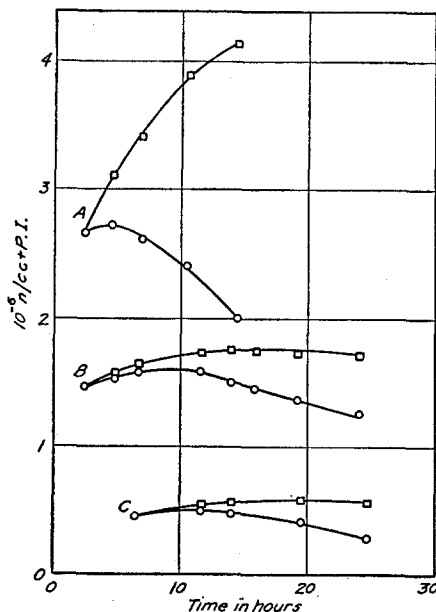

FIG. 5. Particle number *vs.* time, ◯ uncorrected and ☐ corrected for losses due to coagulation and settling.

	Thiosulfate	HCl	P.I.
A.	0.002 M	0.002 M	0
B.	.001	.0015	1
C.	.0005	.006	0

number are caused by the generation of sulfur at a greater rate than it can be deposited on the growing particles already available. If N = total number of sulfur droplets, and n = number in suspension,

$$dn/dt = dN/dt - \kappa n^2 - vn/h.$$

When $n = n_{\text{maximum}}$, $dn/dt = 0$, and $dN/dt = \kappa n^2_{\text{max.}} + vn_{\text{max.}}/h$. In the sols with which we are dealing, appropriate values for the quantities in the above equation are $n_{\text{max.}} = 10^6/\text{cm.}^3$, $\kappa = 6 \times 10^{-12}$ cm.^{3}/sec., $v = 4 \times 10^{-5}$ cm./sec. (for $r = 0.4\mu$), and $h = 10$ cm. Thus, the coagulation term is only 6×10^{-24} cm.$^{-3}$ sec.$^{-1}$, while the settling term is 4×10^{-12}

cm.$^{-3}$ sec.$^{-1}$ Since r, when $n = n_{max.}$, is nearly constant (as shown in Table VII), v is nearly constant also. Therefore, $n_{max.}$ is proportional to dN/dt. If dN/dt is proportional to the rate of the sulfur-producing reaction, $n_{max.}$ becomes proportional to $(T)^2(H)$. This confirms the experimental results in Table VII.

Growth of Particles in the Heterogeneous Stage. The curves in Fig. 6 show the variation of r^2 with time. After an initial rapid rise, r^2 becomes linear in time, showing that a steady state has been reached in the diffusion process that is responsible for particle growth. This steady state

TABLE VII

Particle Radii when $n = n_{maximum}$ and Effect of Reactant Concentrations on $n_{maximum}$

$$k_n = n_{max.}/(H)_0(T)_0{}^2$$

10^3 $(T)_0$	10^3 $(H)_0$	Time when $n = n_{max.}$	r when $n = n_{max.}$	10^{-6} $n_{max.}/cm.^3$	10^{-9} $n_{max.}/(H)_0$	10^{-14} k_n
0.5	3	12.0 hr.	0.44 μ	0.26	0.087	3.5
	4.5	12.0	.45	.38	.084	3.4
	6	11.5	.45	.50	.083	3.3
1	1.5	9.5	.41	.62	.413	4.1
	3	4.5	.38	1.19	.397	4.0
	4.5	12.0	.44	1.52	.338	3.4
	6	6.5	.38	2.06	.343	3.4
2	0.75	11.0	.46	1.24	1.65	4.1
	1.5	11.0	.44	2.45	1.63	4.1
	3	8.0	.38	5.44	1.81	4.5
	4.5	4.0	.35	7.84	1.74	4.3
3	0.75	6.0	.36	3.04	4.05	4.5
	1.5	5.0	.35	5.84	3.89	4.3
	3	<0.2	—	11.3	3.76	4.2

Average r when $n = n_{max.}$ is $0.41 \pm .04\mu$.

Average $10^{-14} k_n = 3.9 \pm 0.4$.

is reached when r is between 0.35 and 0.40μ. The data for $r \leq 0.3\mu$ agrees with that obtained in the study of the condensation stage. The slopes of the r^2 *vs.* time curves in all the cases studied were between 0.007 and $0.012\mu^2$/hr. The average slope for 15 sols, all having different concentrations of reactants, was $0.010\mu^2$/hr. $\pm 20\%$. It has been shown that the rate of sulfur formation has a very marked effect on the number of particles formed. This seems to be the chief effect produced, since the rate of increase of r^2 with time is relatively constant. It is this constancy that accounts for the ease of reproduction of the sols when particle radius is the sole criterion, since a 20% variation in r^2 causes only a 10% vari-

ation in r. This is the basis for the hitherto unexplained fact that the radius *vs.* time data of both Johnson (6) and Barnes (4) (see Fig. 6) fall on the same curve, although each experimenter used different concentrations of thiosulfate and acid.
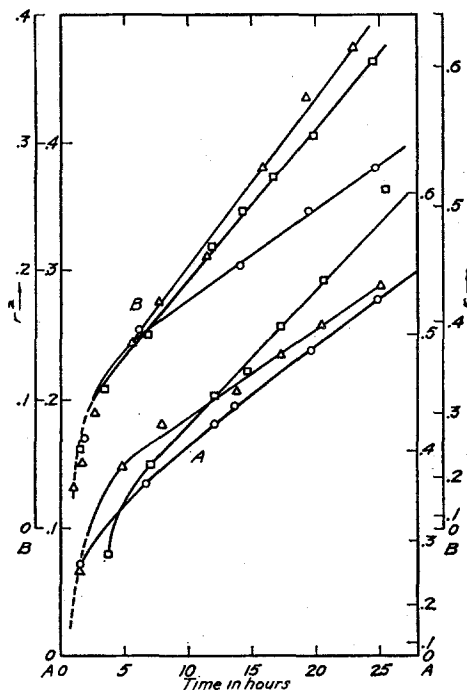

FIG. 6. Growth of droplets by diffusion process (r^2 and r in μ *vs.* time). Dotted lines represent data obtained during the condensation stage (*cf.* Fig. 3). Points were obtained as described under the heterogeneous stage.

		Thiosulfate	HCl	Slope (μ^2/hr.)
A.	○	0.003 M	0.0015 M	0.0076
	□	.0005	.0045	.0104
	△	.002	.00075	.0070
B.	○	.001	.0045	.0070
	□	.001	.006	.0119
	△	.001[a]	.002	.0130
		.0015[b]	.003	.0130

[a] Johnson and La Mer.
[b] Barnes and La Mer.

Correction of n for Coagulation and Settling. Fig. 5 shows some results of correcting n for decreases due to coagulation and settling. Since κ for water at 25°C. = 6.08×10^{-12} cm.^{3}/sec., the percentage decrease in particle number/hr. is equal to $(6.08 \times 10^{-12} n + v/h) \times 3.6 \times 10^5$ or

$(2.19 \times 10^{-6}n + 3.6 \times 10^5 v/h)$. Corrections were made on each n value observed by adding the number of particles that had disappeared due to coagulation and settling. The calculation of each correction was based on the average number and radius of the suspended particles during the time interval between the measurement to be corrected and the one before it. At any time, then, the total number of particles that had been formed was taken to be the measured number plus the sum of all the corrections calculated for each measurement up to that time. This method is illustrated in Table VIII which shows some typical corrections applied to n. It should be noted that in Table VIII the particle number is fairly large for this type of sol, so that, until the particles reach a size of about 0.5μ, the hourly decrease in number due to coagulation far exceeds the decrease due to settling. In more dilute sols this is not the case—e.g., when $Na_2S_2O_3 = 0.0005\ M$ and $HCl = 0.003$, 0.0045, or $0.006\ M$, the

TABLE VIII

Correction of n for Coagulation and Settling, 0.002 M Na$_2$S$_2$O$_3$, 0.002 M HCl
$- \Delta n' =$ decrease in n between a given measurement and the one immediately preceding it.

Time, hr.	2.5	4.6	6.9	10.5	14.4
r, μ	0.31	0.36	0.40	0.46	0.50
$10^5\ v$, cm./sec.	2.29	3.19	3.99	5.13	6.08
h, cm.	11.8	10.2	9.1	7.7	6.7
$10^{-6}n/cm^3$.	2.65	2.73	2.59	2.40	2.01
$\%(-\Delta n)$/hr. due to settling	0.70	1.12	1.58	2.40	3.27
$\%(-\Delta n)$/hr. due to coagulation	5.80	5.98	5.67	5.26	4.40
$10^{-6}(-\Delta n)/cm^3./hr.$	0.17	0.19	0.19	0.18	0.15
$10^{-6}(-\Delta n')/cm^3.$	—	0.38	0.44	0.67	0.66
Corrected $10^{-6}n/cm^3$.	(2.65)	3.11	3.41	3.89	4.16

particle number is in the range 0.2–$0.5 \times 10^6/cm^3$. This means that the rate of disappearance of particles due to settling will be from 2 to 4 times greater than that attributable to coagulation. Such sols are more nearly monodispersed than the ones in which the coagulation rate is greater. Polydispersity caused by coagulation increases rapidly with increasing concentrations of thiosulfate and acid. If both reagents are 0.004 M, the $n_{max.}$ predicted by using the average k_n from Table VII is $2.5 \times 10^7/cm.^3$, and such a number will have an initial rate of decrease of 55%/hr. due to coagulation.

These corrections are only approximate because of the following sources of error: incomplete stirring (settling correction should be larger), electric charge on micelles (coagulation correction should be smaller), and decrease in monodispersed character as the sol ages (coagulation correction assumes a monodispersed system exists). A further error may

be present in the case where La^{+++} is added, since coagulation there is probably faster than in other sols. The corrections serve, however, to give a better estimate of the total amount of colloidal sulfur formed in these sols than can be obtained from the uncorrected data. A comparison of the relative importance of coagulation and settling in sols of different particle size and number also furnishes an explanation for the dependence of monodispersed character on low reactant concentrations (as already shown), and for the instability of the sols as they "age." From a comparison of the corrected and uncorrected curves for n $vs.$ time, it will be noted that a few new particles are continually being formed. As the sol ages, the original monodispersed set of particles first formed when
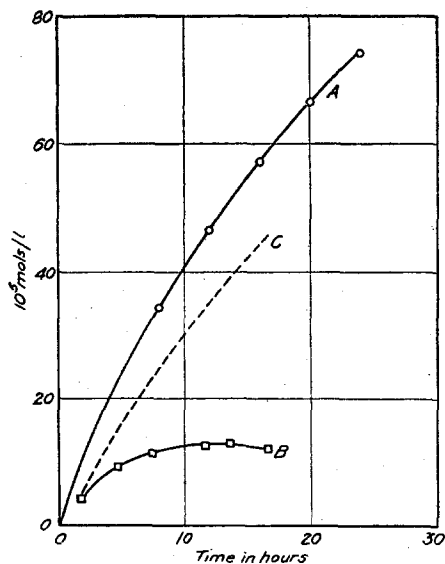

FIG. 7. Sulfite (A), suspended colloidal sulfur (B), and estimated total colloidal sulfur (C) as a function of time for 0.002 M Na$_2$S$_2$O$_3$ and 0.0045 M HCl.

the supersaturation built up in the homogeneous stage was relieved, and which comprised the majority of the suspended particle population, gradually settles out. Both these factors, in addition to coagulation, make for polydispersity when the sol ages. At higher dilutions, where the rate of generation of sulfur has decreased after 15–20 hr., the formation of new particles at that time is slow and settling has taken such a toll that the solutions are almost clear.

Particles which have settled out or which have coagulated and then settled out are still in contact with the solution in which they grew. It is, therefore, not unreasonable to suppose that further growth will take place on them. If it is assumed that growth occurs on all particles, whether

still in suspension or not, curves for total colloidal sulfur such as the one in Fig. 7 are obtained. Such curves parallel the formation of sulfite as measured in titration experiments somewhat better than would curves based on the assumption that growth ceases after settling. The total colloidal sulfur which is calculated if the growth of the particles is assumed to continue, even after settling occurs, is certainly an overestimate of the total colloidal sulfur in the system, not only because of this latest assumption but because of the assumptions made in correcting n for settling and coagulation. Despite this, the difference between the number of mols of sulfite and the estimated number of mols of colloidal sulfur is too large to be interpreted as the number of mols of dissolved sulfur present. The application of such an interpretation to the data on the heterogeneous stage would lead to the conclusion that the concentration of dissolved sulfur increases very greatly with time. This is not the case, as was seen above when the growth rate of particles in this stage was discussed. It is well known, however, that polythionates in acid solution form higher polythionates by reacting with free sulfur or by taking up sulfur directly from thiosulfate (33,34):

$$S_5O_6^= + S \rightleftarrows S_6O_6^=$$

or

$$H^+ + S_5O_6^= + S_2O_3^= \rightleftarrows S_6O_6^= + HSO_3^-.$$
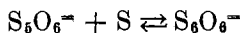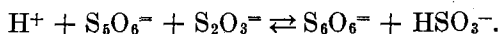
Either reaction would account for the fact that the quantity of sulfur is less than that of the sulfite found in the heterogeneous stage. The number of mols of sulfite and polythionate computed from titration data are correct since the reactions above do not alter the stoichiometric relations used in the calculation of those quantities.

IV. SUMMARY

An investigation has been made of the kinetics of the formation and growth of monodispersed sulfur sols prepared by the action of dilute HCl (0.00075–0.006 M) on Na$_2$S$_2$O$_3$ (0.0005–0.003 M). The study has been divided into three parts.

I. The Homogeneous Reaction. The formation of molecularly dispersed sulfur begins as soon as the reactants are mixed. Ultraviolet absorption measurements with a Beckman quartz spectrophotometer at $\lambda = 3000$ Å show that the concentration of dissolved sulfur reaches a constant value representing a limiting state of supersaturation, after which further formation of sulfur leads to condensation. Within the limits of experimental error the concentration of sulfur at the time, t_B, when the phase change occurs is unaffected by changing the concentrations of

the reactants or by adding small amounts of salts. Furthermore, this time is reproducible and varies with the rate of formation of sulfur. It depends also upon the degree of supersaturation of sulfur, the solubility of sulfur in the medium, the nature of the nucleation process that occurs at the phase transition, and the wavelength of light used to detect the initiation of scattering. Since these variables were eliminated by using the same solvent and wavelength for all experiments, t_B is a valid measure of the rate of the homogeneous reaction.

The effect of changing the concentrations of the reactants showed that the rate of formation of sulfur is proportional to $(T)^{\frac{1}{2}}(H)^{\frac{1}{2}}$, where (T) and (H) are the total molar concentrations of thiosulfate and hydrogen ion. The fractional order and the shape of the curves for optical density as a function of time indicate an autocatalytic reaction, probably of the chain type. The reaction exhibits a positive Brønsted primary salt effect —e.g., the addition of lanthanum salts produces a marked acceleration. The rate-controlling step is, therefore, a reaction between negatively charged ionic species, either ($S_2O_3^= + HS_2O_3^-$) or ($2HS_2O_3^-$).

II. The Condensation Stage. This stage begins with the formation of nuclei capable of further growth, less than 2 min. before the appearance of colloidal sulfur is detected experimentally. The existence of a limiting state of supersaturation is in accord with the accepted theory for phase transitions. The degree of supersaturation that must be reached before condensation occurs is dependent to a critical extent on the rate of nucleus formation.

Although, when the Tyndall beam first appears, the scattered light is bluish, its intensity is not proportional to r^6/λ^4 and Rayleigh's limiting law (for $r < \lambda/10$) cannot be applied to the determination of the sizes of particles because their radii are already $\frac{1}{3}$ the wavelength of light. Attempts to detect the scattering at smaller radii failed because the number of particles is so small ($10^6/cm.^3$). The particle number which is necessary to give perceptible scattering in this region is so large that rapid coagulation would occur according to Smoluchowski's law. Values of the radius were determined by applying the Mie theory to measurements of optical density as a function of time at $\lambda = 4000$ and 8000 Å. At these wavelengths sulfur is transparent and has refractive indices for which calculated values of the scattering area coefficient $K_s = 2.3 \log (I_0/I)/\pi r^2 nl$ as a function of $\alpha = 2\pi r/\lambda'$ are available. In the range $\alpha = 1.2$–3.0 the variation of K_s with α can be expressed by empirical linear relationships, thus permitting the determination of radii from 0.07 to 0.30μ. Since the variation of r^2 with time is non-linear, a steady state in the diffusion process by which dissolved sulfur is deposited on the surfaces of the particles is not set up in the early stage of growth.

III. The Heterogeneous Stage. The overall rate of the chemical changes that occur during the growth of a sol has been found by titrations with iodine and alkali to be proportional to $(T)^2(H)$. The variation with time of the number and radii of the particles in suspension was determined by an application of the Mie theory to transmittance measurements. The occurrence of a maximum in the number *vs.* time curves is explained by ascribing increases in number to the formation of molecularly dispersed sulfur at a greater rate than it can diffuse to the growing particles already present. Decreases in number result from coagulation and settling. From the asymptotic linear variation of r^2 with time it is suggested that a steady state has been reached in which the rate of diffusion of dissolved sulfur to the particle surfaces remains constant.

The monodispersity of a sol is strongly influenced by the rate of sulfur formation. Polydispersity in the early stages of particle growth is caused by the continued formation of new particles while older ones are growing, and by coagulation, and is, therefore, favored by high reactant concentrations. The deterioration of a monodispersed sol on aging is largely due to the settling out of the particles.

An overestimate of the total amount of colloidal sulfur in these systems has been made by correcting the particle number for decreases due to coagulation and settling, and by assuming that growth continues on all particles whether they are in suspension or not. In spite of this, the difference between the amount of sulfite found and the estimated total colloidal sulfur is too great to be interpreted as the quantity of dissolved sulfur present. This indicates that the pentathionate which is the product of a side reaction takes up sulfur to give higher polythionates.

V. Conclusions

1. The homogeneous reaction proceeds in an autocatalytic manner with a rate dependence on $(T)^{\frac{3}{2}}(H)^{\frac{1}{2}}$ to a constant concentration of dissolved sulfur at which condensation occurs.

2. Positive salt catalysis by La^{+++} ion shows that the rate controlling step in the homogeneous reaction and in the overall chemical reaction that continues as the colloidal particles grow is a reaction between negatively charged ionic species, either $(2HS_2O_3^-)$ or $(S_2O_3^= + HS_2O_3^-)$.

3. An empirical linear relationship expressing the variation of the scattering area coefficient K_s with $\alpha = 2\pi r/\lambda'$ as calculated from the Mie theory has been used to determine particle sizes in the range $r = 0.07$–0.30μ.

4. Studies of the growth rate of particles show that growth proceeds by a diffusion process in which a steady state is reached after a pre-

liminary stage in which rapid condensation partially relieves the super-saturation existing at the time of nucleation.

5. The rate of sulfite formation is proportional to the rate of the overall chemical reaction which titration measurements show depends on $(T)^2(H)$ in the heterogeneous stage. Optical measurements show that this rate determines the number of colloidal particles that form.

6. Increases in the number of particles in suspension with time are due to the production of dissolved sulfur more rapidly than it can diffuse to the growing particles, while decreases in number are caused by coagu-lation and settling. The characteristics of sols on aging are ascribable to these effects.

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Erratum

On page 334 of this volume, the sentence ending on the last line should read " . . . . is here invalid," instead of " . . . . is herein valid."