STABILITY OF MONODISPERSED SULFUR HYDROSOLS

Robert H. Dinegar[1] **and Robert H. Smellie**[2]

The Departments of Chemistry, Columbia University, New York City,
and Trinity College, Hartford, Connecticut

Received February 18, 1952

INTRODUCTION

The production of a colloid whose particles do not differ in radii by an appreciable amount makes possible a precise study of several colloidal properties that heretofore either could not be measured at all or at best only approximated. These properties include coagulation, electrophoresis, and the stability of the particles to changes in the ionic environment. In addition, the applicability of such absorption equations as Beer's law to the scattering of light, may be investigated.

It is our purpose to report and discuss the results of the investigation of these colloidal properties in a series of three papers. Part I will consist of the applicability of Beer's law to light scattering by colloidal sulfur particles and the stability of dilute sodium thiosulfate–hydrochloric acid sulfur hydrosols. Part II will deal with the electrokinetic phenomena associated with the stability of colloidal sulfur. Part III will comprise the results of coagulation and particle-interaction studies.

PART I

APPLICABILITY OF BEER'S LAW TO THE SCATTERING OF LIGHT BY MONODISPERSED COLLOIDAL SULFUR

When monochromatic light enters an absorbing medium its intensity decreases exponentially in accordance with the law of Lambert, i.e., $I = I_0e^{-kl}$ where k is a constant for a given wavelength, l is the thickness of the absorbing medium, and I_0 and I refer to the original and transmitted intensities at a given wavelength.

If, in addition to the above, the absorbing medium is a solution, the intensity decreases exponentially in accordance with the Beer-Lambert law, $I = I_0e^{-kcl}$, where c is the concentration of absorbing solute. Thus for a given tube length, Beer's law predicts a linear dependence of the optical density ($\log I_0/I$) of an absorbing solution on the concentration of the solute.

---

[1] Present address: Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

[2] Present address: Department of Chemistry, Trinity College, Hartford, Conn.

The Beer-Lambert law is found to apply in all cases where no alteration of the solute molecules has occurred, but does not hold if the molecules dissociate, ionize, associate, or in any way change their absorbing properties.

If the absorbing particles increase in size until they are no longer of molecular dimensions, the total amount of light abstracted from the incident beam will no longer depend only on the concentration but also on the size since now an appreciable amount of light is scattered as well as absorbed.

This is the situation for spherical particles of colloidal sulfur in aqueous solution, subjected to illumination of wavelength less than 3900 A. (in the air) (1). For wavelengths greater than 3900 A. the total dissipation of light is that due to scattering only, for sulfur is transparent to wavelengths above this value.

The equation relating the intensity of the incident and transmitted light to the area of the particles of radius r and number n is: $\log I_0/I = Kr^2nl/2.3$, where K is a constant describing the total dissipation of radiant energy/unit area/particle.

If no change in the size and shape of the particles occurs and if there is a negligible amount of secondary scattering of light, Beer's law of absorption should apply to the scattering and to the scattering plus absorption of light by colloidal particles.

EXPERIMENTAL

Monodispersed sulfur sols were made with minor variations according to the method of La Mer and Barnes (2) using 0.0015 M $Na_2S_2O_3$ and 0.0020 M HCl.

At the desired time the growth of the sol was arrested by the addition of I_2 in KI. The optical density of the sol was measured for two selected wavelengths with a Beckman quartz spectrophotometer (model DU) in 10-cm. quartz cells. Aliquots of the same sol were diluted with varying amounts of solution and the optical density of these portions measured. The diluting solutions chosen were: (*a*) 0.0015 M $Na_2S_2O_3$; (*b*) 0.002 M HCl; (*c*) 0.002 M HCl and 0.0015 M $Na_2S_2O_3$, plus the same concentration of I_2 in KI used to arrest sol growth; and (*c*) distilled water.

All measurements were made as rapidly as possible ($< \frac{1}{2}$ hr.) so as to eliminate any effects of settling, coagulation, and general instability due to the change in medium.

DISCUSSION OF RESULTS

The results are shown in Figs. 1 and 2 where the optical density is plotted as a function of the fraction of the diluting medium. It is seen that the sols follow Beer's law of dilution and that no large discrepancies are noted.

Since Beer's law holds and secondary scattering is absent, the optical density of a mixture of hydrosols of various sizes and number, should be the sum of that fraction taken of the individual components. Experiments run on mixtures of hydrosols showed this to be true (3). A complete treatment of the analysis of mixtures of hydrosols by this method has been given by Kerker and La Mer (3).

STABILITY OF MONODISPERSED SULFUR HYDROSOLS WITH RELATION TO CHANGES IN IONIC ENVIRONMENT

The stability of colloidal systems is usually considered only from the standpoint of their resistance to coagulation and the effect of ionic environment on the rate of flocculation. This aspect will be discussed more fully in Part III of this series of papers. Dilute sulfur sols prepared by the dilute acid decomposition of dilute sodium thiosulfate show instability in an entirely different manner. In these sols the reaction products are capable of reacting together and forming not only the original reactants, but also higher polythionates; i.e.:

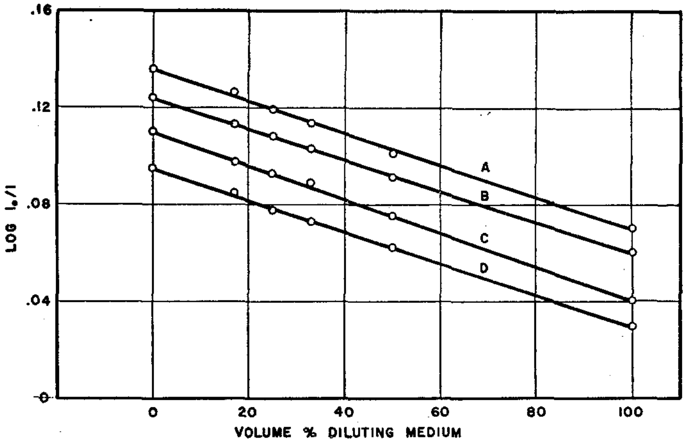

FIG. 1. Curve *A:* Sol diluted with equivalent concentration of hydrogen ion. Plotting increment = +.07; λ = 4500 A.

Curve *B:* Sol diluted with equivalent concentration of hydrogen ion, thiosulfate ion, and iodine in potassium iodide. Plotting increment = +.06; λ = 4500 A.

Curve *C:* Sol diluted with equivalent concentration of thiosulfate ion. Plotting increment = +.04; λ = 4500 A.

Curve *D:* Sol diluted with distilled water. Plotting increment = +.03; λ = 4500 A.

Curve *E:* Sol diluted with distilled water. Plotting increment = + .05; λ = 4500 A.

Curve *F:* Sol diluted with distilled water. λ = 3500 A.

(Curves *E*, *F* see page 373.)

forward reaction:

$$HS_2O_3^- + S_2O_3^{--} \rightleftarrows S_2 + HSO_3^- + SO_3^{--} \qquad [1]$$

reverse reaction:

$$SO_3^{--} + S \rightarrow S_2O_3^{--} \qquad [2]$$

$$SO_3^{--} + (x-1)S \rightarrow S_xO_3^{--}. \qquad [3]$$

For bulk sulfur, reaction [2] is quite slow (4). This need not hold, however, when the sulfur is in the finely divided or colloidal state. In fact, it will be demonstrated that the reverse reaction is much faster than the forward reaction. Stable products, formed by reaction [3], with $x > 2$ are quite unlikely. In addition, higher polythionates ($S_4O_6^{--}$, $S_5O_6^{--}$) have been tested for (5) and were found either to be completely absent or in concentrations very much smaller than SO_3^{--}. Consequently, Eq. [2] will be considered as the complete reverse reaction. In moderate to strong acid solutions, the concentration of SO_3^{--} is so low that reaction [2] is negligible with respect to reaction [1]. Under these conditions, the production of sulfur goes practically to completion.

The position of equilibrium and the rate of the reverse reaction may be determined in the following manner. After the same length of time of growth, all solutions of the same initial concentration of reactants have the same value of total sulfite and unreacted thiosulfate. By adjustment of the pH of the solution the position of equilibrium may be found. If the pH is too high, the particles will dissolve; if it is too low, the particles will grow. The rate of change of particle size is then a measure of the rates of the two processes. Since the rate of growth has been previously measured (6), it will not be discussed here, and attention will be focused on the rate of dissolving at high pH and the position of equilibrium.

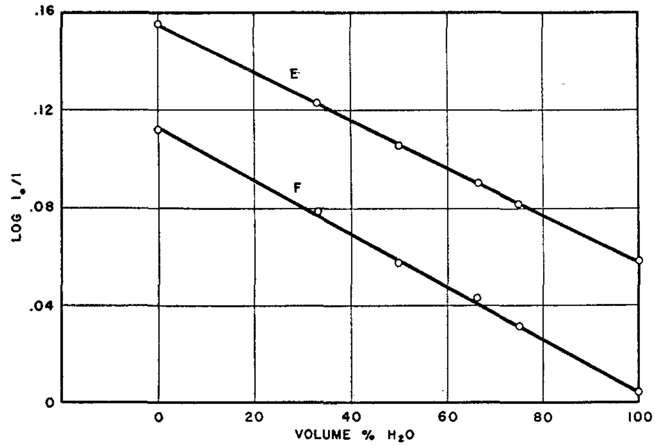

FIG. 2. See Fig. 1 for details.

EXPERIMENTAL

Monodispersed sulfur sols were made by mixing 0.0020 *M* $Na_2S_2O_3$ and 0.0020 *M* HCl and allowing the reaction to proceed for a period of 8 hr. at 25°C. At this time the value of the hydrogen ion was adjusted by neutralization with NaOH and addition of small (<0.001 *M*) amounts of phosphate or acetic acid–acetate buffers. The pH of the

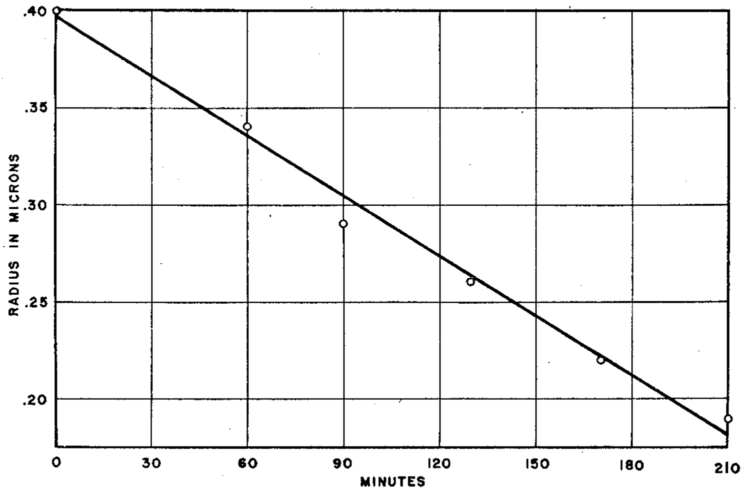

FIG. 3. Radius of sulfur particle in microns as a function of time in minutes.

solution was then measured by a glass-electrode pH meter, standardized against Clark and Lubs' buffer at pH 7.00 and 6.00, periodically, and was constant to ±.02 pH units. The amount of thiosulfate unreacted and the amount of total sulfite generated up to this point was determined by titration of an aliquot with standard I_2 in KI, the molarity of which was approximately $\frac{1}{2}$ that of the original thiosulfate. One ml. of a 1% starch solution was the indicator.

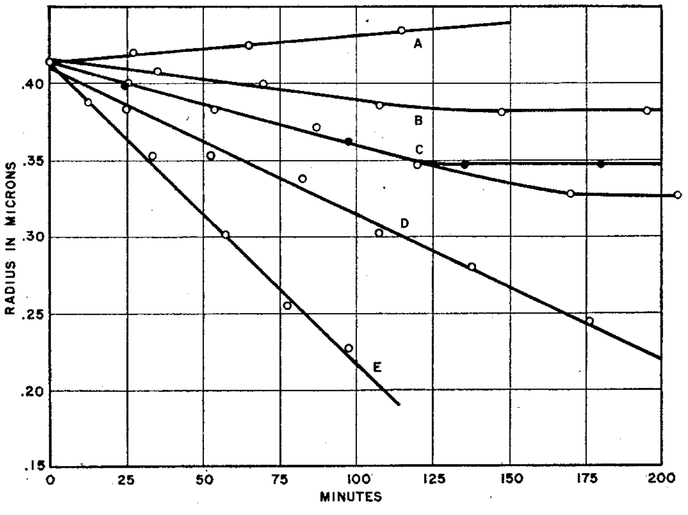

FIG. 4. Variation of radius of particle with time for various values of the pH.

Curve A: pH = 3.08; curve B: pH = 4.88; curve C: pH = 5.50 open circles, pH = 5.49 plus ~0.002 M $S_2O_3^{--}$ solid circles; curve D: pH = 5.92; curve E: pH = 5.92 plus ~ 7×10^{-6} M SO_3^{--} added.

The particle size was determined according to the method of angular scattering described by Johnson and La Mer (7). The particle number was determined by the transmission method of La Mer and Barnes (2).

DISCUSSION OF RESULTS

The rate of change of particle size with time at constant pH involves a linear relationship between the radius of the particle and time. A representative run is shown in Fig. 3, where the radius in microns is plotted against time in minutes over the extent of the reaction observed.

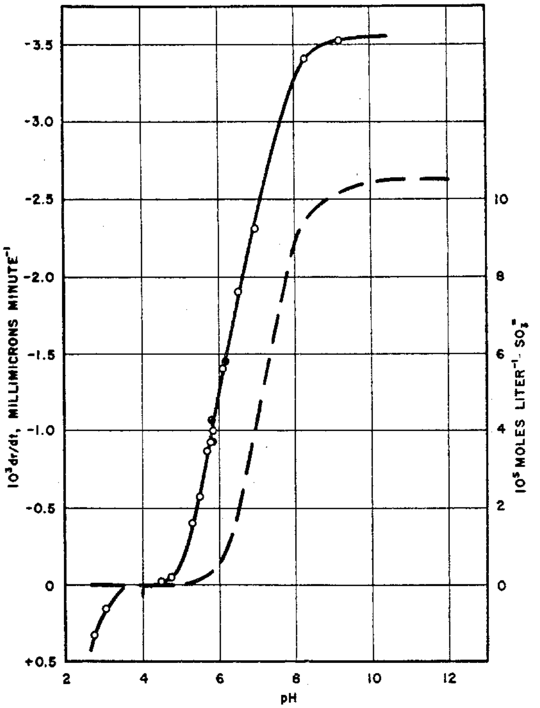

FIG. 5. Variation of dr/dt with pH (solid curve).

Solid circles = all solutions purged with N_2, before and during runs. Variation of SO_3^{--} concentration with pH (dashed curve).

The rate of change of radius is plotted in Fig. 4 for various values of the pH. For values of hydrogen ion greater than the equilibrium value (curve *A*), the particle size increases with time. For pH values close to equilibrium, only a small decrease in size occurs, with the resulting radius being constant (curve *B*).

Figure 5 shows the variation of the rate of change of radius, dr/dt, as a function of pH. The parallel dotted curve represents the concentration of SO_3^{--} as a function of pH. The rate of dissolving is seen to reach a constant value as the concentration of SO_3^{--} reaches its maximum value, indicating a direct proportionality between SO_3^{--} and the rate.

Figure 4 shows the effect of added Na_2SO_3 at constant pH (curve *E*). Curve *D* is for no added sulfite. Curve *C* shows the effect of added $S_2O_3^{--}$ over the normal curve (0). The large increase in rate with added sulfite further identifies sulfite as the reacting species of ion. Addition of $S_2O_3^{--}$ made no change in the rate of dissolving but caused the extent of reaction to be lessened.

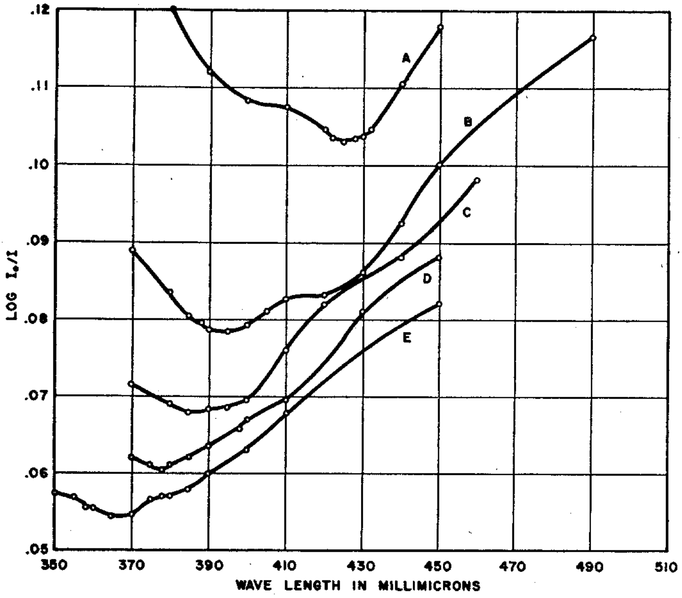

FIG. 6. Transmission curve of monodispersed hydrosol process; pH far from equilibrium value.

Figure 6 shows several typical transmission curves during the dissolving process. The "minimum" is preserved as additional evidence of the monodispersed character of the reverse reaction. The lack of a large variation of particle number with time is shown by three measurements giving the particle number ($\times 10^6/\text{cm.}^3$) over 4 hr. of dissolving as 3.4 ± .2; 2.4 ± .1; 2.8 ± .03. A transmission curve near the equilibrium is shown in Fig. 7. The average initial radius of 20 runs was 0.41 ± .004 μ measured by angular scattering methods and a sol prepared under the same conditions gave a radius of 0.41 ± .02 μ by transmission methods. The concentration of total sulfite was measured as 10.5×10^{-5} moles/l. of sol for seven runs which checked with the value obtained by Zaiser and La Mer (10.2×10^{-5} moles/l.) (5).

KINETICS OF THE REVERSE REACTION

The reaction between sulfur and SO_3^{--} in the system under discussion might be thought of as occurring in several different ways. The first is essentially a homogeneous reaction between sulfite ion and molecularly dissolved sulfur throughout the entire body of the solution—the removal of which causes sulfur atoms to leave the surface of the particle and go into solution thereby maintaining the S (dissolved) $\rightleftarrows$ S (solid) equilibrium. Depending upon whether the rate of reaction of SO_3^{--} with S or the rate of detachment of sulfur atoms is the slower, the rate-controlling step will differ. Attempts to formulate the problem along these lines gave no significant correlation between theory and experiment.

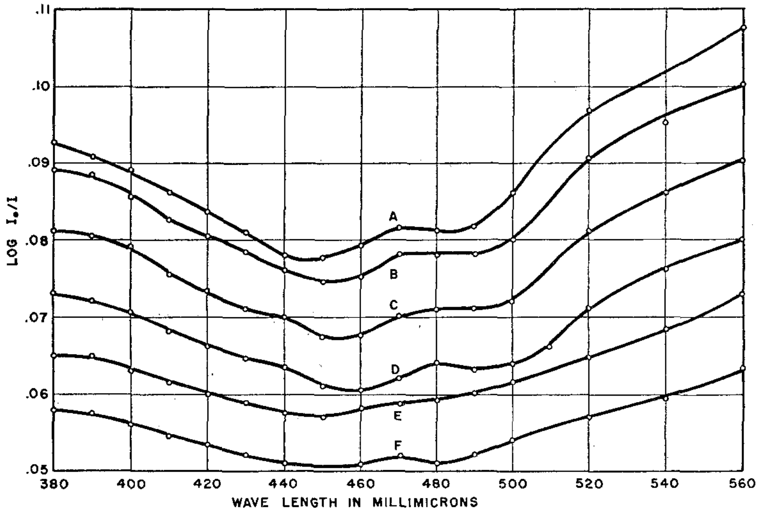

FIG. 7. Same as Fig. 6 except pH is near the equilibrium value.

A second possible mechanism involves the reaction of SO_3^{--} with S either directly attached to the sulfur particle or in a thin layer of sulfur-saturated solution around each particle. Again two possible rate-controlling steps arise in each case, depending upon the relative rates of diffusion of SO_3^{--} to the particle surface and rate of $SO_3^{--} + S$ reaction. The following development will assume that the rate-controlling step is the diffusion process. Although this assumption is sufficient to derive equations that predict the experimental results quite well, it will not be possible to say precisely whether the reaction occurs at the particle surface or in a thin saturated film around the micelle; the latter, however, is quite probably more nearly correct.

The total flux onto a spherical particle of radius r is given by Collins (8)

$$\Phi = 4\pi D C_0 r \frac{(\alpha r)}{\rho}, \qquad [1]$$

where D = diffusion coefficient,
α = probability factor,
ρ = jump length ratio, and
C_0 = initial concentration of diffusing species.

The rate of transport of (SO_3^{--}) to the particle surface is then given by Φ, and if the rate of reaction of (SO_3^{--}) with the sulfur is more rapid than Φ, the flux of (SO_3^{--}) to the surface then measures the rate of disappearance of (SO_3^{--}), i.e.:

$$k\Phi = \frac{-d(SO_3^{--})}{dt} \qquad [2]$$

and

$$\frac{-d(SO_3^{--})}{dt} = k4\pi D C_0 r^2(\alpha/\rho). \qquad [3]$$

Since the total sulfite $(SO_3^{--} + HSO_3^{-})$ concentration, T, is proportional to the volume of sulfur suspended in the colloidal form, we may write

$$Br^3 = T = B'v, \qquad [4]$$

where: B and B' are constants of proportionality, with v being the volume of colloidal sulfur.

To calculate the concentration of SO_3^{--}, given a total sulfite ion concentration T, and acidity (H^+), we may proceed as follows:

First dissociation equilibrium,

$$\frac{(H^+)(HSO_3^-)}{(H_2SO_3)} = K_1.$$

Second dissociation equilibrium,

$$\frac{(H^+)(SO_3^{--})}{(HSO_3^-)} = K_2 = 6.2 \times 10^{-8}.$$

For $H^+ < 10^{-4}M$, the first equilibrium is insignificant.

Since $T = (SO_3^{--}) + (HSO_3^-)$,

$$T = (SO_3^{--}) + \frac{(H^+)(SO_3^{--})}{K_2},$$

from which it follows that:

$$(\mathrm{SO_3}^{--}) = \frac{T}{1 + \frac{(\mathrm{H}^+)}{K_2}};$$

$$\therefore \quad (\mathrm{SO_3}^{--}) = \frac{T}{K}, \text{ where } K = \frac{1}{1 + \frac{(\mathrm{H}^+)}{K_2}}; \qquad [5]$$

$$\therefore \quad (\mathrm{SO_3}^{--}) = \frac{Br^3}{K} \qquad [6]$$

and

$$(\mathrm{SO_3}^{--})^{\frac{2}{3}} = \frac{B^{\frac{2}{3}}r^2}{K^{\frac{2}{3}}}. \qquad [7]$$

Substituting [7] in [3]:

$$\frac{-d(\mathrm{SO_3}^{--})}{dt} = k4\pi DC_0(\alpha/\rho)\left[\frac{K^{\frac{2}{3}}(\mathrm{SO_3}^{--})^{\frac{2}{3}}}{B^{\frac{2}{3}}}\right]. \qquad [8]$$

Defining C_0, the initial concentration of $\mathrm{SO_3}^{--}$ as $\frac{T_0}{K}$, Eq. [8] becomes:

$$\frac{-d(\mathrm{SO_3}^{--})}{dt} = 4\pi Dk\alpha/\rho T_0 B^{-\frac{2}{3}}K^{-\frac{1}{3}}(\mathrm{SO_3}^{--})^{\frac{2}{3}}, \qquad [9]$$

or

$$\frac{-d(\mathrm{SO_3}^{--})}{(\mathrm{SO_3}^{--})^{\frac{2}{3}}} = GK^{-\frac{1}{3}}dt, \text{ where } G = 4\pi DK\alpha/\rho T_0 B^{-\frac{2}{3}}, \qquad [10]$$

which, when integrated becomes:

$$-3(\mathrm{SO_3}^{--})^{\frac{1}{3}} = GK^{-\frac{1}{3}}t - 3(\mathrm{SO_3}^{--})_0^{\frac{1}{3}}. \qquad [11]$$

The concentration of sulfur (S), given in terms of the individual particle radius (r) and their number (n) is $4/3\pi r^3\rho n/m$, with ρ and m being the density and molecular weight of sulfur, respectively.

Since

$$r = \left[\frac{(\mathrm{S})m}{4/3\pi\rho n}\right]^{\frac{1}{3}}$$

or

$$r = A(\mathrm{S})^{\frac{1}{3}}, \qquad \text{where} \qquad A = \left(\frac{m}{4/3\pi\rho n}\right)^{\frac{1}{3}} \qquad [12]$$

$$\therefore \frac{dr}{dt} = \frac{A\,d\,(\mathrm{S})^{\frac{1}{3}}}{dt}. \qquad [13]$$

Assuming that the product formed by the reverse reaction is $S_2O_3^{--}$, one concentration unit of sulfur is equal to one concentration unit of SO_3^{--}. Substitution in Eq. [13] gives

$$\frac{1}{A}\frac{dr}{dt} = \frac{d(SO_3^{--})^{\frac{1}{3}}}{dt}. \qquad [14]$$

Equating the time derivative of Eq. [11] with the left-hand side of Eq. [14] gives:

$$\frac{dr}{dt} = G^1K^{-\frac{1}{3}}. \qquad [15]$$

Thus a plot of dr/dt vs. $K^{-\frac{1}{3}}$ should be a straight line with a slope of G^1. The result of such a plot using our experimental data is shown in Fig. 8. An excellent straight line is obtained over the entire range of concentrations studied.

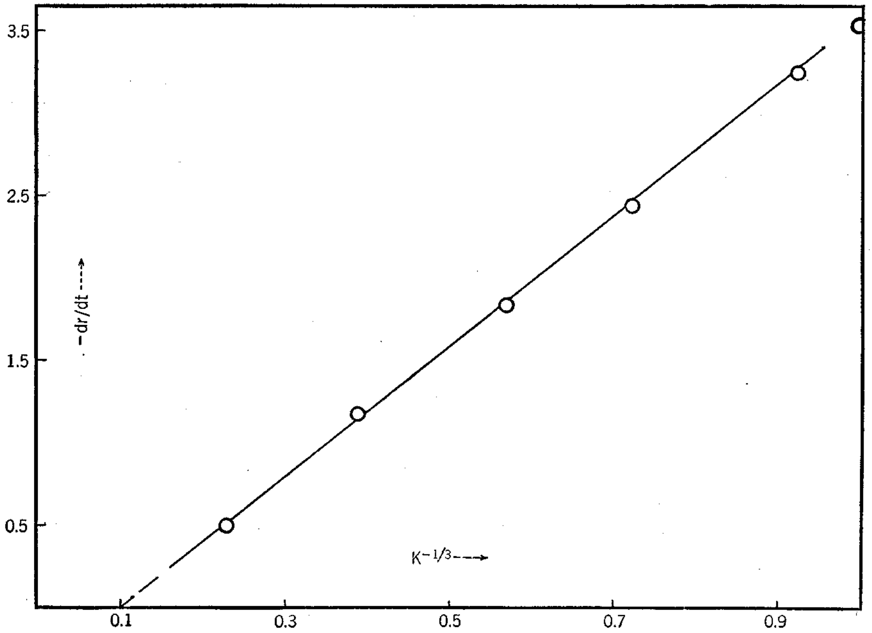

FIG. 8. Plot of $-10^3(dr/dt)$ versus $K^{-\frac{1}{3}}$.

The point of intersection of the straight line with the $K^{-\frac{1}{3}}$ axis is the value of $K^{-\frac{1}{3}}$ at equilibrium, $dr/dt = 0$. This value corresponds to a pH of 4.2 in excellent agreement with Fig. 5 which showed no growth or shrinkage of the particles when the pH was initially made 4.2.

ACKNOWLEDGMENTS

This paper has been constructed in part from a dissertation by R. H. Dinegar submitted in December, 1950, in partial fulfillment for the Ph.D. degree to the Faculty of Pure Science of Columbia University. We wish to acknowledge the encouragement of and frequent discussions with Professor V. K. La Mer on this problem during the development of our individual dissertations under his direction.

SUMMARY AND CONCLUSIONS

1. Monodispersed dilute acid–thiosulfate sulfur hydrosols obey Beer's law with respect to the scattering and scattering plus absorption of light.
2. Sulfur particles prepared by this chemical reaction method are unstable with respect to a change in ionic environment, the instability being due to a reversal of the decomposition reaction in neutral or alkaline solution.
3. The reversal of the decomposition reaction has been found to be due to reaction of sulfur with SO_3^{--}, forming $S_2O_3^{--}$. The rate of this reaction is strongly dependent upon the pH of the solution, occurring predominantly in alkaline solution.
4. The kinetics of the $SO_3^{--} + S$ reaction is adequately described theoretically by the assumption of a diffusion mechanism whereby the rate-controlling step is the diffusion of SO_3^{--} to the sulfur particle with subsequent chemical reaction taking place.

REFERENCES

1. La Mer, V. K., and Kenyon, A. S., *J. Colloid Sci.* **2**, 258 (1947).
2. La Mer, V. K., and Barnes, M. D., *J. Colloid Sci.* **1**, 71 (1946).
3. Kerker, M., and La Mer, V. K., *J. Am. Chem. Soc.* **72**, 3516 (1950).
4. Bichowsky, F. R., *J. Am. Chem. Soc.* **45**, 2225 (1923).
5. Dinegar, R. H., Smellie, R. H., and La Mer, V. K., *J. Am. Chem. Soc.* **73**, 2050 (1951).
6. Zaiser, E. M., and La Mer, V. K., *J. Colloid Sci.* **3**, 571 (1948).
7. Johnson, I., and La Mer, V. K., *J. Am. Chem. Soc.* **69**, 1184 (1947).
8. Collins, F. C., *J. Colloid Sci.* **5**, 504 (1950).