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Theory, Production and Mechanism of Formation of Monodispersed Hydrosols

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Introduction

The preparation of a colloidal dispersion by condensation from initially supersaturated solution is a well-known procedure. This method is being reinvestigated[1] in This Laboratory in conjunction with modern theories of phase transitions[2,3] to develop a theory which will account for the production of monodispersed colloids.

The preparation of a colloid which was sufficiently monodispersed to exhibit higher order Tyndall spectra was achieved in 1941 in This Laboratory[4] for various oil aerosols by the use of foreign nuclei. The method was extended in 1943 to sulfur hydrols[5] by the careful control of the concentration of hydrochloric acid and sodium thiosulfate but without the addition of nuclei.

The addition of sulfur, dissolved in an organic solvent such as ethanol or acetone, to a large volume of a miscible non-solvent like water has always resulted in a polydispersed preparation, commonly called "milk of sulfur."[6] The process is again one of self-nucleation. It is the purpose of this paper to summarize the unpublished theory[1] for the reaction of acid and thiosulfate; to show by an appropriate application of this theory how monodispersed sols can also be prepared by a dilution method; to present a mechanism for their formation involving the relationship between the initial concentration of sulfur and the amount of water added; and to establish the growth rates and the monodispersity of the preparations.

Theory of Nucleation.—Consider the principles involved[1] in the preparation of a monodispersed sulfur hydrosol by the slow decomposition of dilute sodium thiosulfate in dilute hydrochloric acid. The reaction $2HS_2O_3^- = 2HSO_3^- + S_2$ produces molecularly dissolved sulfur, bisulfite ion and also a certain amount of polythionate depending upon the initial concentrations.[7,8,9,10,11,12]

Schematically Fig. 1 shows that the concentration of sulfur builds up during stage I at a rate which varies as $(Na_2S_2O_3)^{3/2}$ and $(HCl)^{1/2}$ until a critical concentration is reached.[8] On reaching this reproducible metastable condition the system becomes heterogeneous by a process of self-nucleation yielding droplets of supercooled liquid lambda sulfur. The rate of nucleation, as judged by the reproducibility of the timing and the concentration of sulfur at which the system becomes heterogeneous, is so exceedingly sensitive to an increase in the concentration of dissolved sulfur that the rate becomes effectively infinite. For practical purposes it may be considered a critical phenomenon.[1,2] This critical concentration consequently

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[1] V. K. LaMer, Paper read before the Division of Physical and Inorganic Chemistry, American Chemical Society, New York, N. Y., September, 1947. V. K. LaMer and R. H. Dinegar, Paper read before the Division of Colloid Chemistry of the American Chemical Society, Atlantic City, N. J., September, 1949.

[2] M. Volmer, "Kinetik der Phasenbildung," Edwards Bros., Ann Arbor, Michigan, 1945.

[3] J. J. Frenkel, "Kinetic Theory of Liquids," Oxford University Press, 1946, Chapter 7.

[4] V. K. LaMer and D. Sinclair, N. D. R. C.-O. S. R. D. Report 57, July 1, 1941—see Sinclair and LaMer, *Chemical Reviews*, **44**, 245 (1949).

[5] V. K. LaMer and M. D. Barnes, *J. Colloid Science*, **1**, 71–79 (1946); I. Johnson and V. K. LaMer, THIS JOURNAL, **69**, 1184 (1947).

[6] A. W. Thomas, "Colloid Chemistry," McGraw-Hill Co., 1934, p. 135; R. Audubert, in Alexander, "Colloid Chemistry," Chemical Catalog Co., New York, N. Y., 1926, Vol. I, p. 354, mentions a thesis by Boutaric (Paris, 1918) in which it is pointed out that large spheres transmit blue light better than red and on p. 361 discusses the problem of particle growth in a preliminary way which proves to be in accord with the treatment we present.

[7] LaMer and Kenyon, *J. Colloid Science*, **2**, 257 (1947).

[8] E. M. Zaiser and V. K. LaMer, *ibid.*, **3**, 571 (1948).

[9] H. Bassett and R. G. Durant, *J. Chem. Soc.*, 1401 (1927).

[10] C. K. Jablcynski and Z. Warszawska-Rytel, *Bull. Soc. Chim. France*, **39**, 409 (1926).

[11] A. F. Holleman, *Rec. trav. chim.*, **14**, 71 (189).

[12] F. Prakke and E. Stiasny, *ibid.*, **52**, 615 (1933).

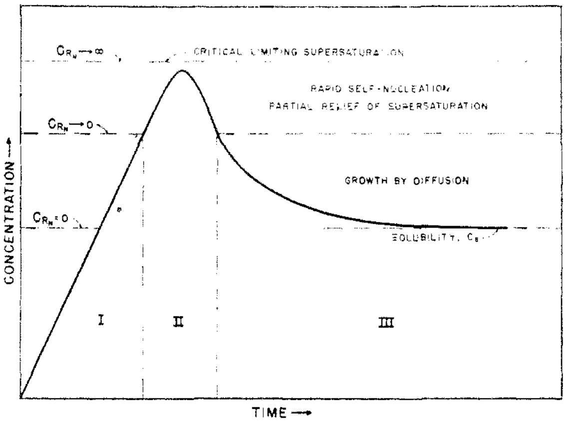

Fig. 1.—Schematic representation of the concentration of molecularly dissolved sulfur before and after nucleation as a function of time.

represents a limiting state of supersaturation and is labelled C_{ss} on the figures. The appearance of nuclei in stage II partially relieves the supersaturation, at least rapidly enough that the rate of nucleation falls almost immediately to zero, when the initial concentrations are in the range $C_{Na_2S_2O_3}$ and $C_{HCl} = 0.002\ M$. Consequently, by controlling the initial concentrations of acid and thiosulfate, the period in which repetitive nucleation can occur is made so short that a monodispersed colloid results by the subsequent uniform growth on the existing nuclei. The supersaturation level at which the rate of formation of nuclei, R_n, becomes practically zero is shown at a small but at present indeterminate concentration below the point where R_n is effectively infinite.

When the concentration falls below $R_n \sim 0$ the system is still supersaturated, consequently the process of growth of stable nuclei to form discrete particles can proceed by diffusion of molecularly dissolved sulfur to the nuclei. The concentration of molecularly dissolved sulfur, in this region (III), represents a balance between the rate of production by the chemical reaction and the removal by diffusion to the nuclear sinks. The final rate of growth is accordingly controlled by the rate of the chemical reaction.

If the initial concentrations are not dilute (> *ca.* 0.01 M) the rate of production of sulfur by the chemical reaction will become so rapid that the concentration of dissolved sulfur will continually exceed the concentration at which $R_n \sim 0$. A continual cascading of nuclei in addition to growth then ensues. Obviously, then, the size of any given particle will depend upon when it was formed. Non-uniform growth and a polydispersed sol is the final result in this case.

There is nothing in the foregoing treatment that limits the mechanism by which the value of C_{ss} is reached. Supersaturation can be achieved not only by building up the concentration of dissolved sulfur in a medium of constant solubility—but also starting with a certain concentration of sulfur and then decreasing the solubility (increasing the chemical potential) either by lowering the temperature or by adding a miscible non-solvent for sulfur, for example, the addition of water to sulfur dissolved in an organic solvent such as acetone or alcohol.

If one starts with a given concentration of sulfur in alcohol or acetone and adds water, the system remains homogeneous until the critical addition is reached. By adjusting the initial concentration of sulfur and the amount of water added one should be able to produce a supersaturation of sulfur that will meet the conditions described above, *i. e.*, produce just one brief outburst of nuclei, leaving enough dissolved sulfur to produce diffusional growth. A monodispersed preparation should result. Schematically, but not to scale, this is shown in Fig. 2. The relationship between initial concentration and the amount of water necessary to start rapid nucleation is labelled the "critical curve."

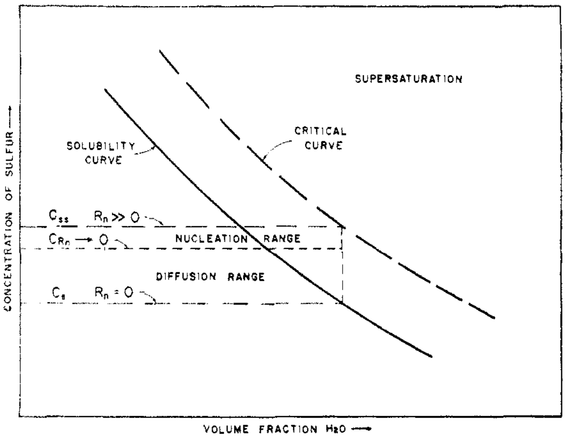

Fig. 2.—Schematic representation of the critical supersaturation and equilibrium saturation concentration of dissolved sulfur in an organic solvent–water mixture as a function of the volume fraction of water.

Experimental Results.—The experimentally determined critical curve for sulfur dissolved in 100% ethanol is shown in Fig. 3, where the log of the final concentration is plotted as a function of the partial molal volume fraction of water. The sulfur used was purified by the method of Bacon and Fanelli[13] and dissolved in 100% C. P. ethyl alcohol (n^{25}_D 1.3600).

Two methods of noting the phase transition or critical point were employed in the construction of this curve—a visual method and a turbidimetric analysis. In the first the diluted sulfur–ethanol solutions were titrated dropwise with distilled water with continuous stirring at room temperature (~25°). The end-point in the titration was taken to be that point at which the further addition of one drop of water produced an immediate large increase in the turbidity of the solution. The end-point was observed visually, the solution being illuminated by approximately parallel white light, oriented 90 degrees to the observer.

When the sulfur solution was titrated *rapidly* with water three regions of different optical properties were noted depending on the initial concentration of sulfur. If the initial concentration of sulfur in alcohol was less than 1×10^{-4} g. at. S/l. no sharp end-point was observed—only a

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(13) Bacon and Fanelli, *Ind. Eng. Chem.*, **34**, 1043 (1942).

slowly increasing turbidity was noted. If the initial concentrations were between 2.5×10^{-4} and 2.9×10^{-3} g. at. S/l. the appearance of a sharp end-point with a rapidly increasing turbidity was observed. In this case, however, the Tyndall beam, initially of a bluish white color, transformed in a few minutes into the higher order Tyndall spectra of angular red and green colors characteristic of a monodispersed system.[4,5] The number of red spectral bands observed was 1 to 2 in the lower concentrations and as many as 6 in the upper concentration range. The particle radii produced were, accordingly, 0.2 to 0.45 micron.

With initial concentrations of sulfur greater than 3×10^{-3} g. at. S/l. the end-point of the titrations was sharp and a rapid increase in turbidity occurred but the color change was from a bluish white Tyndall beam to a white opalescent solution indicating polydispersity. No higher order Tyndall spectra were observed. The opalescent color was soon followed by the formation of large particles that scintillated in the illuminating beam indicating the appearance of a crystalline precipitate. The amount of crystalline material was very large when the initial concentration of sulfur was 5.79 and 9.37×10^{-3} g. at. S/l. Back titration with alcohol showed that the sulfur appearing in the colloidal form could be easily redissolved by the subsequent addition of one or two milliliters of ethanol.

Since the end-point in the titration was chosen to be that of rapidly increasing turbidity it is not surprising that only in certain ranges of concentration was this criterion of a sharp end-point met. The time rate of increase of turbidity is dependent not only on the increase of particle number but particularly upon the scattering coefficient which varies from the +4 to −2.2 power of the radius of the particle.[14] Hence, one would expect in those regions where both nucleation and appreciable growth occur, that a more rapid increase in turbidity will occur than in the regions where nuclei production only is taking place. Diffuse end-points correspond to those regions where only nucleation and little growth occurs, since the formation of nuclei has exhausted the necessary supersaturation. In the monodispersed region nucleation followed by slow growth occurs with the added restriction that *no* secondary nucleations take place. At high concentrations of sulfur, both nucleation and growth occur rapidly but here there is such a high degree of supersaturation at the endpoint that R_n does not fall to zero rapidly enough to avoid repetitive nucleation. This is the customary situation leading to the production of "white milk of sulfur."

The appearance of increasing amounts of crystalline sulfur in the same solutions which initially showed a white opalescent colloid (polydispersed amorphous particles) is attributable to the relatively high concentration of dissolved sulfur. These concentrations not only produced large numbers of amorphous droplets along with repetitive nucleation, but also an appreciable number of crystalline nuclei. The crystalline nuclei and supercooled liquid particles then collide by a mechanism similar to that of coagulation, the crystal nuclei crystallizing the supercooled liquid droplets upon contact. The higher the initial concentration of sulfur the greater are all these effects until it becomes impossible to prepare a sol that is stable for any appreciable length of time. At concentrations in the range $> 10^{-2}$ g. at. S/l., stable sols could not be prepared—the dispersed droplets of any sol so prepared crystallized in a very few minutes.

If the titration was carried out by a *slow* addition of water, a different result was obtained. The first additions produced no visible effect but with increasing amounts the solution slowly became turbid. The turbidity of the solution then seemed to remain almost constant on further addition of water until the volume fraction of water in the mixture corresponded to that obtained when the water was added rapidly. A few milliliters beyond this point the whole solution became very turbid and opaque even to indirect light. The amounts of water necessary to cause these initial and secondary increases in turbidity are shown below for the run starting with 20 ml. of ethanol sulfur concentration equal to 5.88×10^{-4} g. at. S/l. $\bar{V}_{H_2O}$ is the partial molal volume fraction of water; $\bar{V}_{H_2O}$ (initial) = 0.41; $\bar{V}_{H_2O}$ (secondary) = 0.59.

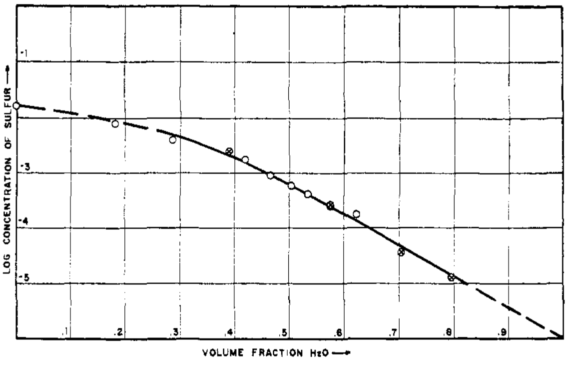

Fig. 3.—Experimental critical supersaturation concentration of sulfur in ethanol–water mixtures as a function of the volume fraction of water: ○, visual; ⊗, spectrophotometer.

The end-points accompanying slow addition were not particularly sharp and no monodispersed sol was produced in this manner.

The slow increase in turbidity before the point of maximum condensation is predictable theoretically. It exhibits analogies to the light scattering observed on concentrating cationic detergent solutions as reported by Debye.[15,16]

Debye has shown that it is a natural consequence of the law of mass action for equilibrium between simple molecules and their aggregates that a critical concentration exists—above which the predominant form is the aggregate or nucleus and below which the system is composed *mainly*, but *not entirely*, of the molecular species. If one recognizes that the addition of water releases sulfur by decreasing the solubility in the medium and that the formation of the nucleus is the aggregation of such molecules for which the over-all equilibrium $n(\mathrm{S}) \rightleftarrows (\mathrm{S})_n$ holds, it can be shown that small numbers of small particles, capable of scattering light should appear at volume fractions of water below that for which the given amount of sulfur is at a critical concentration $R_n \sim \infty$. The rate of increase of the number of particles with increasing amounts of water is small below the critical point leading to a corresponding small rate of increase of turbidity. At the critical particle formation point, however, the rate of increase of number becomes exceedingly large and the additional growth of the particles by diffusion leads to a very rapid increase in turbidity.

Solutions prepared in a similar manner were subjected to a turbidimetric analysis. This consisted of adding known amounts of water to sulfur alcohol solutions and after several hours in a thermostat at 25° (±0.02°) the resulting mixtures were examined in a Beckman spectrophotometer, model DU, using 10-cm. quartz cells. The

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[14] V. K. LaMer, *J. Phys. Colloid Chem.*, **52**, 65 (1948), and ref. 4, *Chem. Revs.* (fig. 5).

[15] Debye, *Annals of N. Y. Acad. of Sciences*, **51**, 575 (1949).

[16] Debye, *J. Coll. Sci.*, **3**, 407 (1948).

optical density of each sample was measured as a function of wave length at 250 Å. intervals between 4000 and 6000 Å. The optical density as a function of the volume fraction of water in the alcohol–water solution for three runs is shown in Fig. 4, for wave length 5000 Å.

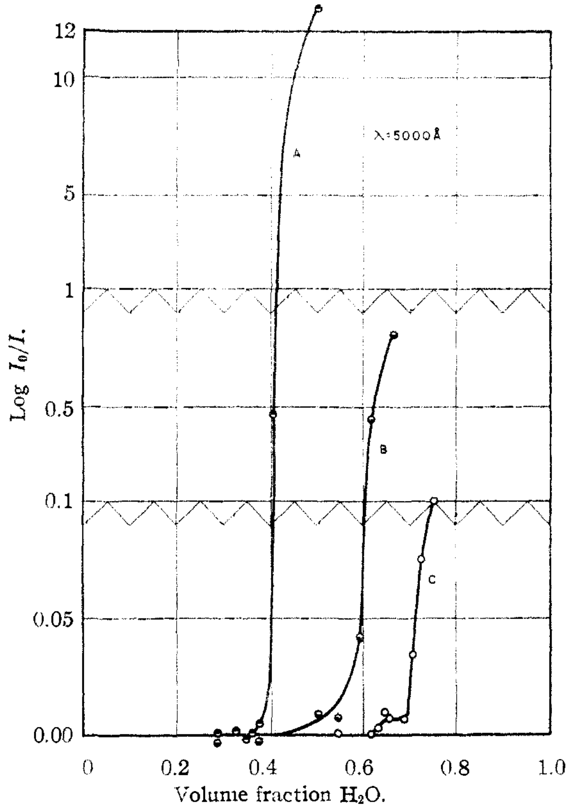

Fig. 4.—Optical density (log I_0/I) of sulfur dissolved in ethanol–water mixtures as a function of the volume fraction of water. Initial concentration of sulfur gr. at./l.: A, 37.5 $(10)^{-4}$; B, 5.88 $(10)^{-4}$; C, 1.18 $(10)^{-4}$.

Log I_0/I *vs.* volume fraction of water showed a region in which a few small particles were produced followed by another region in which the optical density increased tremendously on addition of a small increment of water (see Initial C = 5.88×10^{-4} g. at. S/l.). In this region rapid particle formation is accompanied by rapid growth.

The critical points obtained by this method fell on the same curve as those obtained by the visual method and are shown by appropriate symbols in Fig. 3. The curve could not be extended by using this method to volume fractions of water greater than 0.8. Initial sulfur concentrations as low as 1.5×10^{-5} g. at. S/l., were tried and no change in turbidity was noticed even on tenfold additions of water volume fractions. This corresponds to a final sulfur concentration of less than 1.5×10^{-6} g. at. S/l. Since it has been reported previously[8] that a sulfur concentration of 3.2×10^{-6} g. at. S/l. must be generated by the reaction of acid and thiosulfate in water for light scattering to be observed, it is to be expected on this basis that a sulfur concentration of less than 1.5×10^{-6} g. at. S/l. could not result in any perceptible turbidity at any volume fraction of water attainable. Extrapolation of the critical curve obtained by the present method gives 1×10^{-6} g. at. S/l. for the critical concentration of sulfur in pure water. This figure is in satisfactory agreement with the value given by Zaiser[16] when it is recognized that her determination was made spectrophotometrically assuming the extinction coefficient of sulfur in pure water to be the average of those of a number of organic solvents.

Rate of Growth and the Diffusion Coefficient of S_8: (1) Experimental.—In order to study the rate of growth of monodispersed sols produced by dilution with non-solvent of sulfur in ethanol and acetone, another method of preparing the sols was devised. It consisted of adding to the sulfur–ethanol or sulfur–acetone solution by an hypodermic syringe the amount of water needed to cause nucleation. This technique afforded more instantaneous and homogeneous mixing. The heat of mixing, however, raised the temperature to about 31°—enough to prevent immediate nucleation. The mixture was chilled in 90 seconds with continuous stirring to approximately 29°. Nucleation took place between these temperatures and the particles grew uniformly producing monodisperse preparations. The slight rise in initial temperature prevented nucleation until all the water had been added thus insuring homogeneity and the liberation of sulfur in equivalent amounts at all points in the solution. The solution was then put in a constant temperature room at 25°. The maximum particle size was reached in about 25 minutes during which time the temperature of the mixture had decreased only about 2°. Very little, if any, change in size occurred as the sol reached equilibrium at 25° some 70 minutes later, indicating that the temperature coefficient of the solubility of sulfur is too small to be noted by the accuracy of the method used, for particles of size greater than 0.4 μ radius.

The method used for determining the size of the particles was developed by LaMer and Sinclair for aerosols[4] and applied to hydrosols by Johnson and LaMer.[17] It utilizes the change in angular position, θ, of the red bands of the higher order Tyndall spectra with particle size. The angular positions of the red bands were determined as a function of time by viewing the sol illuminated by approximately parallel white light through a telescope on which was mounted a Polaroid H filter No. 330, oriented so as to pass only the scattered light whose electric vector is perpendicular to the plane determined by the light source, particle, and observer. θ is the angle of observation measured from the backward direction of incident light propagation. The calibration[17] has been determined by transmission methods, theoretical calculation, the rate of deposition of sulfur hydrosols in aqueous solution and rechecked by Kerker and LaMer[18] for dependence of radius upon time of reaction.

The number of particles was determined from the wave length and intensity value of the minimum in the optical density *vs.* wave length transmission curve measured by a model DU Beckman spectrophotometer, using 10-cm. quartz cells. The value of the optical density at the minimum in the transmission curve is related to the number of particles, n, having a radius, r, by the relationship[19,20]

$$2.3 \log (I_0/I) \text{ min.} = (\pi r^2 n l)^{-1} K_s = 2.08$$

where $2\pi r/\lambda'$ min. = 6.8 for $\lambda' > 3200$ Å., λ' = wave length of the light in the medium, l = cell length = 10 cm.

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[17] I. Johnson and V. K. LaMer, This Journal, **69**, 1184 (1947);

[18] M. Kerker and V. K. LaMer, *ibid.*, **72**, 3516 (1950).

[19] M. D. Barnes, A. S. Kenyon, E. M. Zaiser and V. K. LaMer, *J. Colloid Science*, **2**, 349 (1947).

[20] Kenyon and LaMer, *ibid.*, **3**, 163 (1949).

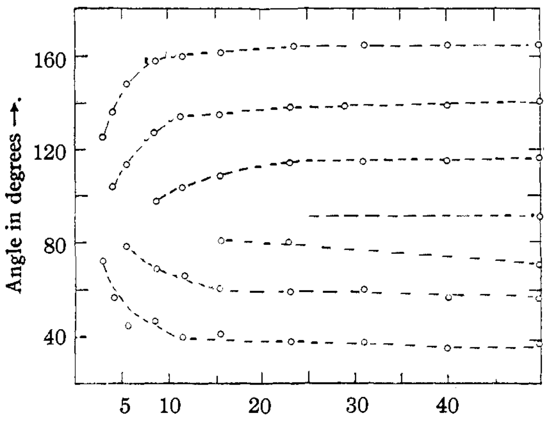

Fig. 5.—Angular position of maximum red orders as a function of time for a monodispersed sol prepared by the addition of water to sulfur dissolved in ethanol.

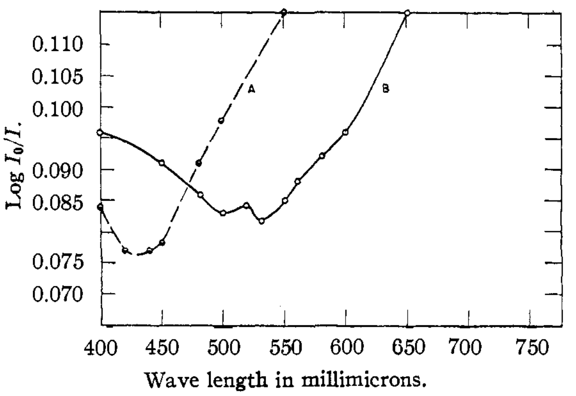

Fig. 6.—Optical density (log I_0/I) *vs.* wave length for two monodispersed sulfur–organic solvent–water sols: ●, alcohol sol, plotting increment = +0.01; r = 0.36 micron, n = $1.9_3(10)^6$ cc.$^{-1}$; ○, acetone sol; r, 0.43 micron; n, $1.5_6(10)^6$ cc.$^{-1}$.

The graph of theta *vs.* time in Fig. 5 is very similar to those obtained previously for sols made by the acid decomposition of thiosulfate, except that the number and position of the red orders reaches a constant value signifying the exhaustion of the liberated sulfur. The optical density *vs.* wave length curve shows the characteristic "minimum" (Fig. 6). The numbers of particles per ml. calculated from these sols are in the same range as those obtained by acid decomposition, *i. e.*, 1 to 4 × 10^6 per ml. The final radius, number of particles per ml., along with the initial concentration of sulfur and volume of water added for fifteen runs for the solvents ethanol and acetone are shown in Table I.

The sigu of the electric charge on the particles of sols prepared by dilution methods is either positive or negative depending upon the *p*H of the solution. For alcohol–water sols the iso-electric point is at *p*H 5.8 and for acetone–water sols, at *p*H 6.0, both sols being positive at a *p*H lower than the isoelectric point. The sign of the charge is reversible to titration with either HCl or NaOH. The electrophoretic mobility of an alcohol–water sol at *p*H 6.9 of radius 0.5 μ was -1.3 ± 0.3 μ/sec./volt/cm. This corresponds to a charge of 1500 electrons per particle, or a surface density of charge equal to 23 abs. e. s. u. cm.$^{-2}$. These electrophoretic experiments were performed jointly with Robert H. Smellie, using apparatus he developed. He finds that traces of acetic acid produced by oxidation of the alcohol are responsible for the positive charges on the sols below *p*H 5.8.

Theory of Growth.—The growth rates of sols produced by the dilution method represent the diffusion of a substance in a thermodynamically unstable state onto the surface of a nucleus. The diffusing species are almost certainly S_8 rings,[21,22] uncontaminated in the case of the dilution method by any other substances such as polythionates. It is possible to gain information concerning the diffusion coefficient of S_8 from such measurements. The results will be approximate, since the theory used is not exact. In addition, certain approximations and assumptions concerning the experimental data are necessary.

The mathematical formulation of the diffusion problem has been treated by Reiss.[23,24] Specializing this treatment to the case at hand, one may derive on theoretical grounds alone, an equation giving the radius of the particles as a function of the time after formation of nuclei.

Consider the situation within a very short interval of time after mixing the solutions. Stable particles of super-cooled liquid sulfur have formed in the midst of a mixture of organic solvent and water that is supersaturated with respect to dissolved sulfur. Further deposition of sulfur on the particles is a natural process and occurs spontaneously. The final size to which the particles will grow and the rate at which they will grow depends upon three variables.

The first is the number of nuclei which are to grow. This number is assumed constant throughout the growth and equal to the number of particles present at any time. Since the total amount of sulfur to be deposited is distributed homogeneously throughout the solution one must proportion $1/n$ times this amount to each nucleus, where n equals the number of particles per ml. Then each particle is influenced only as to growth by an amount of sulfur contained in a volume, spherically symmetric about the origin, of radius equal to h and volume $4/3\pi h^3$. This "particulate volume" associated with each nucleus equals $1/n$. Since no material outside of this volume influences the growth of any one given particle, h is the radius of an impermeable shell.

The second variable influencing the growth of the particles is the total amount of diffusible sulfur. Provided there are no other sources of diffusable sulfur, this value is given by the difference between the amount of sulfur originally in the mixture and the solubility of supercooled liquid sulfur in the medium, *e. g.*, $(C_{ss} - C_s)$. Unfortunately C_s is not known independently. The dif-

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(21) W. H. Latimer and J. Hildebrand, "Reference Book of Inorganic Chemistry," The Macmillan Co., New York, N. Y., Chapter XII.

(22) L. Pauling, *Proc. Nat. Acad. Sciences*, **35**, no. 9 (1949).

(23) H. Reiss, *Trans. N. Y. Acad. of Sciences*, Series II, Vol 11, No. 7 (1949).

(24) H. Reiss and V. K. LaMer, *J. Chem. Physics*, **18**, 1 (1950).

ference $(C_{ss} - C_s) = C_0$ is, however, obtainable from the size and number of particles after diffusional growth has ceased. Only C_0 will enter into the growth equation and its value may be estimated.

Actually, C_0 is a function of the temperature since C_s is dependent on the temperature. The temperature coefficient of solution of sulfur in the medium has been estimated theoretically (calculations based on the change of mole fraction with temperature as related to the heat of fusion) as 1.9% per degree. Experiments substantiate this value approximately. This change of solubility with temperature requires that the final C_0 be corrected for the small temperature drop during growth, by writing $C_0(t) = C'_0(0) + f(t)$. The value of $C_0(t)$ at any time is obtained by constructing an average cooling curve and adding to $C'_0(0)$ the correction $f(t)$ for the sulfur liberated by the drop in temperature up to the time t. The effect of the temperature drop is the same as if there were a reaction generating sulfur in addition to the amount originally set free by the addition of water. The equation taking into account C_s as a function of time (temperature) is identical in form with the equation considering C_s as a constant but with a source function k present in the system (*cf.* ref. 24).

The third variable is the diffusion coefficient, D, of sulfur in the medium. D in turn depends inversely on the viscosity and directly on the temperature. These temperature coefficients must also be neglected. In addition their direction of change is opposite to that of $(C_{ss} - C_s) = C_0$ and since the product DC_0 will always be dealt with, the variations will tend to cancel one another.

Consider the flux, Q, through any spherical shell of radius, r, concentric with spheres of radii x and h (x equals radius of the nucleus). Assuming Fick's law; this flux is given by

$$Q(t) = -4\pi r^2 D \, \mathrm{d}c/\mathrm{d}r \qquad (1)$$

subject to the boundary conditions: (1) at the surface of the particle the value of the concentration of sulfur is the saturation value; *i. e.*, $C(x,t)$ equals $C_s(t)$; (2) at any point in the system, initially, the concentration of sulfur is the supersaturation value, *i. e.*, $C(r,0)$ equals C_{ss}; (3) at the impermeable shell at h: $(\partial c/\partial t)_{r=h} = 3Q(t)/4\pi h^3$. Integrating (1) with respect to r gives

$$C(r, t) = Q(t)/4\pi rD + f(t) \qquad (2)$$

At time t equals 0, equation (2) becomes

$$C(r,0) = Q(0)/4\pi rD + f(0)$$

but, since $(\partial c/\partial r)_{t=0} = 0$, $Q(0) = 0$, and $C(r,o)$ equals $f(0)$ equals C_{ss} by condition (2).

Boundary condition (3) demands that the time derivative of equation 2 specialized to r equal h be given by $3Q(t)/4\pi h^3$

$$(\partial c/\partial t)_{r=h} = \frac{1}{4\pi hD} \, \mathrm{d}Q/\mathrm{d}t + \mathrm{d}f/\mathrm{d}t$$

or

$$\mathrm{d}f/\mathrm{d}t = 3Q(t)/4\pi h^3 - {}^1/_4\pi hD \, \mathrm{d}Q/\mathrm{d}t \qquad (3)$$

Integration of equation 3 gives

$$f(t)\Big[_0^t = -\frac{1}{4\pi hD} Q(t)\Big]_0^t + \frac{3}{4\pi h^3}\int_0^t Q(t)\mathrm{d}t$$

From condition (2), f(0) equals C_{ss}. From equation (1), $Q(0)$ equals 0

$$\therefore f(t) = C_{ss} - \frac{1}{4\pi hD} Q(t) + \frac{3}{4\pi h^2}\int_0^t Q(t)\mathrm{d}t$$

or from equation (2)

$$C(r,t) = C_{ss} + \frac{Q(t)}{4\pi Dr}\left[\frac{1}{r} - \frac{1}{h}\right] + \frac{3}{4\pi h^3}\int_0^t Q(t)\mathrm{d}t$$

since $h >> r$, $\frac{1}{h} << \frac{1}{r}$

$$\therefore C(r,t) = C_{ss} + \frac{Qt}{4\pi Dr} + \frac{3}{4\pi h^3}\int_0^t Q(t)\mathrm{d}t \qquad (4)$$

Since the particle is increasing with size as material is deposited on its surface, $-Q(t)$ must be proportional to the rate of increase of volume, *i. e.*

$$-Q(t) \propto \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{4}{3}\pi x^3\right)$$

Depending on the units used the proportionality constant varies. For $Q(t)$ in g. sec.$^{-1}$ and x in cm., x = radius of the particle

$$-Q(t) = 4\pi\rho x^2 \, \mathrm{d}x/\mathrm{d}t \qquad (5)$$

ρ = density of diffusing sulfur. Equation (4) and (5) then give

$$C(r,t) = C_{ss} - \frac{P}{D} x^2 \, \mathrm{d}x/\mathrm{d}t(1/r) - {}^3/_4\pi h^3 \int_0^t 4\pi\rho x^2 \frac{\mathrm{d}x}{\mathrm{d}t}\,\mathrm{d}t \qquad (6)$$

Evaluating

$$\int_0^t \frac{3\rho}{h^3} x^2 \frac{\mathrm{d}x}{\mathrm{d}t}\,\mathrm{d}t$$

with $x(0) = 0$, and for $r = x$ we obtain

$$\mathrm{C}(x, t) = C_{ss} - \frac{\rho x}{D}\frac{\mathrm{d}x}{\mathrm{d}t} - \frac{\rho x^3}{h^3} \qquad (7)$$

From condition (1) $C(x,t) = C_s(t)$; therefore the final equation becomes

$$\frac{\mathrm{d}(x^2)}{\mathrm{d}t} = [C_{ss} - C_s(t)]\frac{2D}{\rho} - \frac{2D}{h^3}x^3 \qquad (8)$$

This equation may now be integrated[25] in closed form to obtain the analytical expression between x and t only if C_s is considered independent of t Thus the final result for this special case is

$$t = \frac{h^2}{3D}\left(\frac{P}{C_0}\right)^{1/3}\left\{{}^1/_2 \ln \frac{\left[\left(\frac{C_0}{\rho}\right)^{2/3} h^2 + \left(\frac{C_0}{P}\right)^{1/3} hx + x^2\right]}{\left(x - \left|\frac{C_0}{P}\right|^{1/3} h\right)^2} + \sqrt{3}\left[\tan\frac{-1\sqrt{3}}{3} - \tan^{-1}\left(\frac{2x + \left|\frac{C_0}{P}\right|^{1/3} h}{\left|\frac{C_0}{P}\right|^{1/3} h\sqrt{3}}\right)\right]\right\} \qquad (9)$$

Since it is possible to use equation (9) only for a calculation of x *versus* t when C_0 is constant and it

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(25) Pierce, "Short Tables of Integrals," 3rd Edition, Eqn. 61.

was desired to take into account the small dependence of C_0 on t as previously described, equation (8) was integrated numerically by the method of Cauchy and Lipschitz.[26]

All quantities in this equation are experimentally measurable except one—the diffusion coefficient, D. One may then choose values of D and see if any value will give a theoretical curve of x *vs.* t that reproduces the experimental curve. The equation also depends upon the number of particles, n. If one varies n experimentally and then finds that the same D must be used in each case to reproduce the experimental curve, the value of D so obtained takes on added significance. In addition, since D varies with the viscosity, it is important to see if sols prepared in media of different viscosities would give growth curves that predict the same value of D when referred to a standard viscosity.

The rate of growth curves are shown in Fig. 7 for sols prepared by the previous method from 100% ethanol and acetone—the viscosities of these two media being significantly different. It was found that the experimental curves could be reproduced by equation (8).

The values of the diffusion coefficient necessary are shown in Tables I and II. The time, t_0, is the time of formation of nuclei as predicted by the theoretical equation. It is seen at the bottom of the tables that the starting times are within the quenching periods with the majority of them being zero. The number of particles varies over a sixfold range and the viscosity by a factor of 50%. When referred to a standard viscosity of 1 centipoise, the calculated value of D_0 is 7.2×10^{-6} cm.^{2} sec.$^{-1}$ for the alcohol–water sols and 7.7×10^{-6} cm.^{2} sec.$^{-1}$ for the acetone–water sols in good agreement with D_0 for substances of comparable molecular weight, which lie in the range 4 to 7×10^{-6} cm.^{2} sec.$^{-1}$.[27]

TABLE I

SULFUR IN ETHANOL, 25-ML. SAMPLES USED

No.	10^4 C'_{ss} gr. at. S/l.	H_2O added, cc.	Radius (max.), microns	10^6 n/cc.	10^5 C_0 gr. at. 2/l.	% Sulfur in colloidal form	$C_{ss}/(C_{ss} - C_0)$
1	3.00	46.5	0.39	1.55	2.4	22	1.22
2	3.00	46.5	.30	3.18	2.2	21	1.21
3	3.00	46.5	.39	1.60	2.5	23	1.23
4	3.00	46.5	.36	1.93	2.3	22	1.22
5	5.88	36.0	.40	1.40	2.4	11	1.11
6	6.00	34.0	.37	3.05	4.0	16	1.16
7	6.00	35.0	.47	1.00	2.7	12	1.12
8	6.00	38.0	.41	1.97	3.6	18	1.18
9	6.12	37.5	.37	4.40	5.8	24	1.24
						Av.	1.19

No.	1	3		4	6	9
Viscosity, c. p.			2.1			
$10^6 D$, sq. cm./sec.			3.5			
$10^6 D_0$, sq. cm./sec.			7.2			
t_0, min.	1.5	0		0	2	1

$C_{ss} = C'_{ss}(1 - \bar{V}_{H_2O})$

TABLE II

SULFUR IN ACETONE, 25-CC. SAMPLES USED

No.	10^4 C'_{ss} gr. at. S/l.	H_2O added, cc.	Radius (max.), microns	10^6 n/cc.	10^5 C_0 gr. at. S/l.	% sulfur in colloidal form	$C_{ss}/(C_{ss} - C_0)$
10	5.00	42.0	0.47	0.83	2.2	12	1.12
11	5.00	42.5	.43	1.15	2.4	13	1.13
12	5.00	42.5	.49	0.85	2.6	14	1.14
13	5.00	42.5	.56	.70	3.2	17	1.17
14	5.00	43.0	.48	1.17	3.4	18	1.18
15	5.00	44.0	.45	1.56	3.7	20	1.20
						Av.	1.16

No.	9	11		12	13	14
Viscosity, c. p.			1.3			
$10^6 D$, sq. cm./sec.			5.9			
$10^6 D_0$, sq. cm./sec.			7.7			
t_0, min.			all zero			

$C_{ss} = C'_{ss}(1 - \bar{V}_{H_2O})$

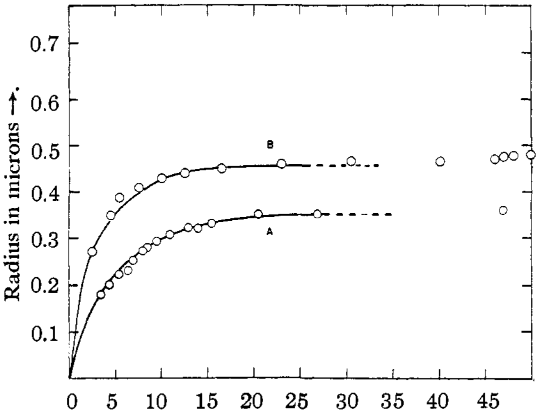

Fig. 7.—Growth rates of sulfur particles in terms of radius (microns) *vs.* time (minutes) prepared by adding water to ethanol or acetone sulfur solutions. The circles represent experiment points, the solid line representing the theoretical calculation using diffusion coefficients: $D = 3.5(10)^{-6}$ cm.^{2} sec.$^{-1}$ for ethanol solutions (A); $D = 5.9(10)^{-6}$ cm.^{2} sec.$^{-1}$ for acetone solution (B); *cf.* Tables I and II.

The sensitivity of the theoretical equation to the value of D chosen is seen in Fig. 8. In this case the value of D giving the best agreement between experiment and theory is 6×10^{-6} cm.^{2} sec.$^{-1}$. Using a value of $D = 3 \times 10^{-6}$ cm.^{2} sec.$^{-1}$ and 12×10^{-6} cm.^{2} sec.$^{-1}$ give theoretical curves corresponding to the broken lines. It is seen that variation by a factor of only 2 or $^1/_2$ in D gives theoretical curves that are markedly different not only in shape, but in the region of the most rapid change in slope.

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[26] Ford, "Differential Equations," McGraw-Hill Book Co., New York, N. Y., 1933, p. 161.

[27] "International Critical Tables," Vol. V, pp. 63-76.

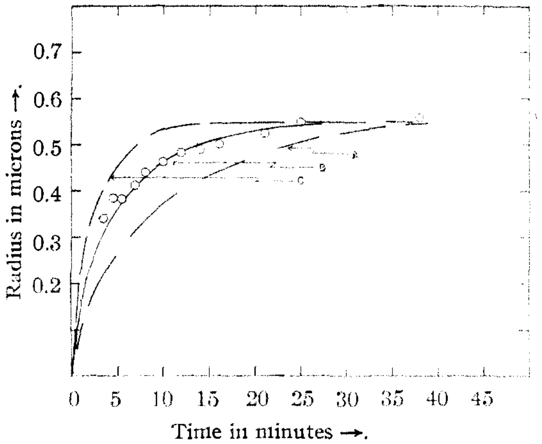

Fig. 8.—Effect of varying the value of D in 10^6 cm.^{2} sec.$^{-1}$ units employed in theoretical calculation for the growth of the sulfur sol in acetone–water solution: A = 12; B = 6; C = 3; O = experimental values.

General Considerations.—From the amount of sulfur dissolved initially in the organic solvent and the amount appearing in the colloidal form, one can estimate the extent to which the initial solution was supersaturated and calculate the supersaturation ratio C_{ss}/C_s even though C_s is not known independently. Where $C_0 = (4\pi r^3 \rho n)/96 = 0.262\, nr^3$ gr. at./cm.^{3}, $C_s = (C_{ss} - C_0)$ and $C_{ss}/C_s = C_{ss}/(C_{ss} - C_0)$. It is seen in Tables I and II that approximately 10 to 20% supersaturation is needed to produce a monodispersed preparation. Nucleation at this small degree of supersaturation is undoubtedly aided by the formation of the minute cavities during the syringing and mixing of the solutions, but it is also a direct consequence of the relatively high concentration of dissolved sulfur at the phase transition ($\sim 10^{-4}$ g. at. S/l.) in organic solvent–water as compared to the concentration ($\sim 10^{-6}$ g. at S/l.) in water in the acid–thiosulfate decomposition method where the supersaturation value is higher. It is because nucleation can be accomplished at this small degree of supersaturation that a monodispersed system does result. Obviously, the older method, namely, that of pouring a small amount of sulfur concentrated in an organic solvent into a large volume of H_2O, should not, and never does, produce a monodispersed colloidal dispersion.

The degree of supersaturation necessary for a phase transition to occur should depend not only on the total concentration of material present but also on the surface tension and orientation requirements of the particle to be formed—the ratio increasing with an increase in both these effects.

To test these ideas and to obtain an estimate of the importance of each, the supersaturation requirements for the sparingly soluble sulfates of barium, strontium and lead have been measured. A comparison of barium sulfate with sulfur gives an idea of the dependence of the supersaturation ratio upon the surface tension and the effects of crystal orientation whereas a comparison of strontium and lead with barium gives the magnitude of the effects caused by solubility alone, since the other effects should be approximately equal. The results are discussed in a following paper.

We should like to acknowledge the suggestion and help of Professor Howard Reiss of Boston University in calculating the diffusion coefficient from our data.

Summary and Conclusions

1. Monodispersed colloids exhibiting higher order Tyndall spectra have been prepared by precipitation of sulfur from ethanol and acetone solutions by the careful addition of water.
2. The relationship between the concentration of sulfur and the volume fraction of water at the critical point of sulfur–ethanol–water solutions has been investigated.
3. Sols prepared by this dilution method have been investigated as to dispersion of wave length in their angular scattering of visible light and their transmission as a function of wave length.
4. The size, number and charge of the particles of such sols are in the same range as those prepared by the acid decomposition of sodium thiosulfate.
5. The rates of growth of sols prepared by such a dilution method have been investigated. The growth rates obtained have been reproduced from previous theoretical considerations which allow the estimation of the value of the diffusion coefficient of S_8 in alcohol–water and acetone–water mixtures. The value of this diffusion coefficient lies in the range 7–8 × 10^{-6} cm.^{2}/sec. for both media. The application of this method for estimating diffusion coefficients is valid for any colloidal system that is characterized by a small particle size distribution at all stages of its growth.
6. A qualitative explanation is offered for the necessary conditions under which monodispersed colloids may be prepared for both the dilution and acid decomposition of sodium thiosulfate methods.

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