LaMer’s 1950 Model for Particle Formation of Instantaneous Nucleation and Diffusion-Controlled Growth: A Historical Look at the Model’s Origins, Assumptions, Equations and Underlying Sulfur Sol Formation Kinetics Data

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Figure S1. (Figure on page 412 from SI ref 1.) Plots of extent of reaction, x (as determined by turbidity) versus time for the formation of sulfur sol. The data were obtained by optical spectroscopy from the reaction performed starting with 5 mL of 0.1 M Na$_2$S$_2$O$_3$, 10 mL water, and 5 mL of 0.5 M HCl (Curve #1), 5 mL of 1.0 M HCl (Curve #2), 5 mL of 5.0 M HCl (Curve #3), 5 mL of 0.25 M HCl (Curve #4), 2.5 mL of 0.5 M HCl plus 2.5 mL of 0.5 M NaCl (Curve #5), 10 mL water saturated with SO$_2$ plus 5 mL of 1.0 M HCl (Curve #6). Solid curves over the data points have been drawn arbitrarily without using any fitting function. Reprinted with permission from SI ref 1. Copyright 1926 Wiley-VCH Verlag GmbH & Co. KGaA.
Figure S2. (Figure 7 from SI reference 2.) Growth rates of sulfur particles in terms of radius (microns) vs. time (minutes) prepared by adding water to a sulfur solution in ethanol or acetone. The circles represent experiment points, the solid line representing the theoretical calculation using diffusion coefficients calculated for the solution having viscosity of 1 centipoise:\[^2\] \( D = 3.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \) for ethanol solutions (A); \( D = 5.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1} \) for acetone solution (B). Reprinted with permission from SI ref 2. Copyright 1950 American Chemical Society.
## Table S1 Summary of the literature on sulfur sols citing the LaMer model.

<table>
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<th>Entry</th>
<th>Title</th>
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<th>Comments and/or Relevance to the LaMer Model</th>
<th>Ref.</th>
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<td>1</td>
<td>La Decomposition Autocatalytique de l’acide hyposulfureux</td>
<td>Formation of sulfur particles from the autocatalytic decomposition of &quot;hyposulfuric acid&quot; was studied. The reaction was followed by measuring the turbidity of the reaction solution.</td>
<td>The formation of sulfur sols was observed using turbidity (light scattering) techniques. Data was plotted as extent of reaction versus time (in minutes). The data exhibit clear sigmoidal curves. The authors claim that the growth of the sulfur sols is autocatalytic.</td>
<td>This paper was published 24 years prior to LaMer’s classic 1950 <em>JACS</em> paper. It demonstrates that sulfur sol formation has an autocatalytic growth phase. The sigmoidal data has solid curves drawn over them, but unfortunately, there no associated fitting equation is provided. The presence of sigmoidal curves in the formation of sulfur sols is disproof of “instantaneous” nucleation.</td>
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<td>2</td>
<td>Autocatalytic decomposition of thiosulfuric acid</td>
<td>Solutions of Na₂S₂O₃ were acidified in order to monitor the decomposition of H₂S₂O₃ into H₂SO₃ and S. The decomposition reaction was monitored by spectrophotometric measurements.</td>
<td>Again, turbidity (opalescent) was used to monitor the formation of sulfur sols. Opalescence is only observed after relatively large, polyatomic aggregates of sulfur are formed.</td>
<td>This paper was, again, published 24 years prior to the LaMer model. The authors assert the autocatalytic growth of sulfur aggregates. As with entry 1, this paper serves as a disproof of “instantaneous” nucleation.</td>
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<td>Observations on the angular scattering of light by sulfur sols</td>
<td>Dilute aqueous solutions of sodium thiosulfate and sulfuric acid (~0.001 M) were studied by the angular scattering of light.</td>
<td>The authors find that “very dilute (about 0.001 M)²⁴ solutions of starting material solutions produce sharper, more defined colors in light scattering. The light scattering data suggests the sulfur sols have grown to 0.4 and 0.6 microns after five and nineteen hours, respectively. Also, the authors report that growth of the sulfur sols can be stopped by the addition of iodine.</td>
<td>This paper primarily serves as an initial proof-of-concept that LaMer was able to observe the formation of sulfur sols and calculate their sizes by light scattering techniques. This paper highlights their ability to replicate the results of Bidhubhusan Ray from 1921.</td>
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<td>4</td>
<td>Monodispersed Hydrophobic Colloidal Dispersions and Light Scattering Properties. I. Preparation and Light Scattering Properties of Monodispersed Colloidal Sulfur</td>
<td>Monodispersed sulfur sols were prepared from the decomposition of sodium thiosulfate and sulfuric acid in water and monitored by light scattering.</td>
<td>The authors present their simple and direct method for producing sulfur sols. They claim these colloidal dispersions can be grown to different sizes and then growth quenched by the addition of iodine. They empirically demonstrate that the small sols “exhibit the optical properties predicted by the Rayleigh equation”, but for larger sols, they “observed the higher order effects that can be predicted from the general electromagnetic theory of light scattering.”¹⁵</td>
<td>As was noted by the authors in their text, their approach is “purely empirical.” As it is the first paper in a series, this paper serves as a proof-of-concept for the formation of sulfur sols and their ability to be monitored by light-scattering techniques.</td>
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<td>Kinetics of the Formation of Monodispersed Sulfur Sols from Thiosulfate and Acid</td>
<td>Sulfur sols were prepared from aqueous solutions of dilute sodium thiosulfate and hydrosulfuric acid. The decomposition reaction and subsequent sulfur sol formation was monitored using a Beckman quartz spectrophotometer.</td>
<td>The transmittance of the species in solution was measured. Primarily, transmission measurements were carried out at 300 nm to measure the appearance of what was thought to be molecular sulfur. The optical density of sulfur was calculated and converted to concentration of sulfur and plotted against time. The authors claim that “sulfur is being continuously formed during the homogeneous period of this reaction.”</td>
<td>The data provide evidence for continuous formation of (S), during the induction period. Further explanations of their data assume supersaturation, yet no measurement of supersaturation is reported.</td>
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The Determination of the Particle Size of Monodispersed Systems by the Scattering of Light

Sulfur sols were prepared from aqueous solutions of dilute sodium thiosulfate and hydrochloric acid. Using higher order Tyndall Spectra, the authors applied Mie Theory to determine the radius of the sulfur sols and system homogeneity as a function of time. In addition, concentration, temperature, and viscosity were determined to be the major factor influencing the growth rate.

The technique only allows for particles >0.2 microns to be quantified. While their method for determining polydispersity was novel for the time, it does not offer compelling evidence that the system produces truly monodisperse—one sized—particle product.

Monodispersed Sulfur Sols. IV. Comparison of the Particle Radius Determined by Transmittance and by the Angular Positions of Higher Order Tyndall Spectra from Mie Theory

Sulfur sols were prepared from aqueous solutions of dilute sodium thiosulfate and hydrosulfuric acid. The decomposition reaction and subsequent sulfur sol formation were monitored using a Beckman quartz spectrophotometer to obtain higher-order Tyndall spectra. The authors verify the use of Mie Theory for the dependence of the scattering coefficient ($K_s$) on the angular dependence, $\alpha = \frac{2\pi r}{\lambda}$, when $\alpha \leq 6$. Particle radii were analyzed for sulfur sols between 0.3 – 0.5 microns. The authors claim their results confirm what can be calculated theoretically at the time.

The authors have shown there is agreement between theory and experiment for $\alpha \leq 6$. However, for $\alpha > 6$, theory and experiment are not in good agreement.

A Note on the Symbols and Definitions Involved in Light Scattering Equations

No specific chemical system is discussed in this paper. The authors have provided a description of the symbols and units used in light scattering. The majority of the theory and symbols are based on Mie Theory, the scattering coefficients of Stratton, the Rayleigh equation, and Lowan’s scattering functions.

Papers like these are very important to their field, because it is necessary for every field to have an established “ground truth” in regards to the system under study, the investigative tools being used, and the analysis being conducted. Here, the authors are working to establish a uniform set of symbols and definitions for all working with light scattering equations.

The Kinetics of the Formation and Growth of Monodispersed Sulfur Hydrosols

Sulfur sols were prepared from aqueous solutions of thiosulfate and acid, which was either hydrosulfuric acid or hydrochloric acid. Again, measurements were conducted on a Beckman quartz spectrophotometer. The authors claim the sulfur sols go through three stages: the homogeneous reaction, the condensation stage, and the heterogeneous stage. The effects of several salts on the reaction were measured. The first stage (homogeneous reaction) was determined to be autocatalytic in nature. At later times, the authors claim growth is diffusion-controlled.

The observable particle formation (by their spectroscopic method) is claimed to be autocatalytic, yet the authors ascribe a different kinetic “rate” equation to this process. As the results of this paper lead directly to the development of the LaMer Model, it is noteworthy that the authors (LaMer among them) claim in the early stages of the reaction there is “continued formation of new particles while older ones are growing.” This experimental evidence directly supports the hypothesis that nucleation and growth occur simultaneously during the formation of sulfur sols—that is, that nucleation is not a “burst” phenomena. As such, this work disproves applicability of the LaMer model to the formation of sulfur sols.
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<th>Light scattering properties of monodispersed sulfur sols; monochromatic ultraviolet angular scattering; effect of the complex index of refraction upon transmittance</th>
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| Sulfur sols were prepared from aqueous solutions of thiosulfate and sulfuric acid. For the use of ultraviolet spectra, an apparatus was constructed, as “an electronic means of measuring the intensity of the scattered bands.”

The most important result from this paper, was the development, by LaMer and coworkers, of a method for measuring particle size using ultraviolet light scattering. The transmittance provided the authors an easy method to determine the size and quantity of particles, given that the $k$ (coefficient of absorption) was < 0.1.

This paper represents one of the first papers to overlap previous research by LaMer on aerosols with his newer research on sulfur sols.

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<th>Light Scattering As A Measure of Particle Size in Aerosols</th>
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| This paper focuses on light scattering on aerosol materials such as oil-based fogs that are of similar sizes to sulfur sols.

The authors present 4 types of measurements: transmitted light as a function of wavelength, intensity of (scattered) light at a given wavelength, color of the scattered light, and polarization of (scattered) light at a given wavelength. They primarily were analyzing aerosol data from oil-based fogs.

The authors focused on equations and theory for perfectly spherical particles made of transparent material whose radii < 1 micron, as one can understand and rationalize for the times in which the research was performed.

One of the assumptions in the LaMer model is the constant number of nuclei present after the ‘instantaneous nucleation event’. In this paper, the authors state that “it is possible and, in fact, probably, that there is some error in the nuclear concentrations quoted by Zaiser and La Mer, since these authors point out that the number of nuclei was not observed to be strictly constant during the period of growth.”

We contend that this observation is not an error, but that Zaiser and La Mer were correct in their observation of a changing number of nuclei. This example teaches the “grip” on the field then—and since—of the Classical Nucleation Theory based, LaMer-model postulate of “burst” nucleation.

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<th>Diffusional Boundary Value Problems Involving Moving Boundaries, Connected with the Growth of Colloidal Particles</th>
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| The paper analyzes different mathematical methods for treating diffusion issues in systems with moving boundaries, such as aerosol and sulfur sol formation.

To address the issue of the moving boundary in the formation of sulfur sols, the authors assume a spherically symmetric model and a growing particle with a rigid boundary. Furthermore, the values for the diffusional coefficient of sulfur and the supersaturation of sulfur in water were estimated.

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<td>13</td>
<td>Transitions</td>
<td>Sulfur sols were prepared from solutions of dilute sulfur in organic solvent (ethanol or acetone). Water was titrated in to induce supersaturation of sulfur and the subsequent formation of sulfur sols. The authors used a model DU Beckman spectrophotometer to conduct their optical experiments. The author reports the formation of “monodispersed colloids exhibiting higher order Tyndall spectra.” They found the sulfur sols formed from this supersaturation method (by titrating water into organic-sulfur solutions) were approximately the same size as sols formed from the acid decomposition method reported in previous papers. Next, the authors claim to have derived a differential equation to describe the growth process, which then can be integrated “to obtain the analytical expression between x and t^2” (where x = sulfur sol radius and t = reaction time). The authors have developed their growth model with the following assumptions: (i) instantaneous nucleation; (ii) the number of nuclei remains constant throughout the entire growth period; (iii) the growth of each nuclei is independent of each other with no competition for nearby diffusible sulfur; and (iv) the product, D*C0, is independent of temperature (where D = diffusion coefficient of sulfur and C0 = total amount of diffusible sulfur). As stated in the main text of this paper, we have found several inconsistencies with this paper in light of the ca. 70 years of additional literature and hindsight.</td>
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<td>14</td>
<td>Kinetics of the Acid Decomposition of Sodium Thiosulfate in Dilute Solutions</td>
<td>Sulfur sols were prepared from aqueous solutions of dilute sodium thiosulfate and acid. Specifically, the acid decomposition of sodium thiosulfate was monitored. The fractional rate law LaMer previously provided was updated and the time of formation of colloidal sulfur is expressed as ( \frac{1}{t} = (H^+)^{\frac{1}{3}}(S_2O_3^-)^{\frac{1}{3}} ). Further, the authors report that “the thiosulfuric acid is not completely dissociated with respect to its second ionization.” Finally, the decomposition of sodium thiosulfate shows a positive primary salt effect. While more data has been provided, the kinetics of the decomposition of thiosulfate in acid still do not appear to be well understood. There are questions remaining regarding the decomposition products and whether the production of polythionates in dilute solutions can be completely neglected or not. Overall, this paper supports and adds improvements to the LaMer model. However, this is done by applying the assumption of being under steady-state conditions. An important conclusion the author states is “that a sufficiently large growth will narrow the relative distribution on any nth power of the radius.” This point merits further investigation in modern nanoparticle formation research.</td>
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<td>15</td>
<td>The Growth of Uniform Colloidal Dispersions</td>
<td>An exact chemical system is not addressed. The author is presenting a mathematical treatment for “growth of uniform colloidal dispersions” using the “growth by diffusion process.” Reiss presents a new mathematical method for explaining “growth by diffusion.” He shows that the concept of the impermeable shell is unnecessary. In addition, he introduced the concept of competing growth to the model using a steady-state assumption. Overall, this paper supports and adds improvements to the LaMer model. However, this is done by applying the assumption of being under steady-state conditions. An important conclusion the author states is “that a sufficiently large growth will narrow the relative distribution on any nth power of the radius.” This point merits further investigation in modern nanoparticle formation research.</td>
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<td>Nucleation in Phase Transitions</td>
<td>This review covers an array of contributions to nucleation starting from Gibbs (1874) and spanning to Ostwald (1897), Volmer (1926), Farkas (1927), Becker and Doering (1935), Frenkel (1939) and finally LaMer’s work (1940–1950). Examples of homogeneous and heterogeneous nucleation in gaseous, liquid, and metallic systems are mentioned. It reviews the contributions to the field of nucleation and growth by Gibbs, Ostwald, Farkas, Frenkel, Volmer, Becker, Doering, and LaMer. LaMer’s review entitled “Nucleation in Phase Transitions” is well crafted and presents a nice summary of the history of Classical Nucleation Theory (CNT) (1838 – 1950). While we (the authors of this review) still have reservations concerning the reversibility of nucleation in CNT and how it has been applied, Prof. LaMer’s concise summary of the literature and theories known and broadly used at the time, in 1952, is both notable and</td>
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<td>17</td>
<td>The electrokinetic properties of dilute monodisperse sulfur hydrosols. Sulfur hydrosols were prepared from dilute aqueous solutions of sodium thiosulfate and hydrochloric acid. Spectroscopic measurements were conducted on a Beckman spectrophotometer. Electrophoresis was carried out on a microelectrophoretic device detailed in the main text of the paper. The authors observe differing surface charge depending on three different starting concentrations of starting material: (i) 2.0 mM Na₂S₂O₃ and 2.0 mM HCl exhibit only positively charged particles over 24 hours; (ii) 2.0 mM Na₂S₂O₃ and 3.0 mM HCl also exhibit only positively charged particles over 24 hours; and (iii) 3.0 mM Na₂S₂O₃ and 2.0 mM HCl initially exhibit positively charged particles, but after ~5 hours measurements show negatively charged particles. The authors attribute the negatively charged particles in (iii) to the attachment of pentathionate ions to the surface of the sulfur particles. Control experiments spiking the reaction solution with pentathionate were conducted and show a negative mobility shift.</td>
<td>The authors claim one of the most important observations from this study is that pentathionate (or a similar species) is much more effective at reversing the positive charge on the sulfur particles than the starting material thiosulfate. It is important to note an observation by the authors that “after a period of 20 hours, mobilities of particles in samples taken from the top of the flask differed considerably from the mobilities in samples taken from the bottom.” It is intriguing that a charge gradient forms in the undisturbed reaction solution. This is something not presently addressed in the LaMer model or any adaptation that relates to sulfur sols.</td>
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<td>18</td>
<td>Particle size distribution in monodisperse sulfur hydrosols Sulfur hydrosols were prepared from the decomposition of dilute aqueous solutions of sodium thiosulfate and hydrochloric acid. The particle-size distributions were investigated by two independent methods: The Coulter Counter and Higher Order Tyndall Scattering (HOTS). The results between the two techniques produce broad, but single-peaked distributions of particle sizes. It was found that the average diameter by the Coulter Counter was ca. 0.15 microns greater than the diameter found by the HOTS method. The author states “that the HOTS is not completely indicative of a sharp distribution of particles sizes but is due to an unbalance in the number of particles scattering a given color at a given angle. If this unbalance exceeds a critical value, which is as yet undetermined, (then) HOTS results and the corresponding particle size is (are) a measure of the most populated size value.”</td>
<td>This paper and its results demonstrate the limitations of the HOTS technique that was extensively employed by LaMer and coworkers. The conclusions from this paper point out that LaMer’s sulfur sols should not be considered monodisperse. Furthermore, this paper strongly suggests that nucleation is not an ‘instantaneous’ event. This paper is, then, an important, classic and at least somewhat overlooked contribution.</td>
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<td>19</td>
<td>Particle Size Distribution in LaMer Sulfur Sols Sulfur sols were prepared in dilute aqueous solution from sodium thiosulfate and hydrochloric acid. Careful attention was paid to remove dust from the solutions with 0.22 micron filters. The authors found that they were able to reproduce the previous results done by LaMer and by Petro. Overall, the authors experimentally reproduced LaMer sols and verified computationally the results. The removal of dust was shown to narrow the size-distribution considerably, an important, overlooked contribution!</td>
<td>The removal of dust and its effect on the narrow of the size-distributions is an important and impactful discovery for the field of nucleation and growth. We find the authors disprooof-based approach to their science commendable. One of the alternative hypotheses they present is “that the sharpening of the distribution up to 3 hr. is a consequence of the growth of the hydrosol by diffusion of the continuously generated sulfur to the existing particles.” This alternative hypothesis is consistent with modern Ockham’s razor-obeying</td>
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### Time Dependence of Particle Size Distribution and Number Concentration in LaMer Sulfur Sols
Sulfur hydrosols were prepared in the same method as in Entry 19 (ref. 28) from dilute aqueous solutions of thiosulfate and acid. Hydrolysols were experimentally measured by light scattering at 18 angles of observation using absolute intensity measurements. Theoretical measurements were done using Mie formulas and distribution functions (zero order logarithmic and Khrgian-Mazin).

The two computational methods with distribution functions produced approximately the same time dependence on $N$ (number concentration). The zero-order logarithmic distribution (ZOLD) function is skewed toward larger particle sizes, while the modified Khrgian-Mazin function (KMF) is skewed toward smaller particle sizes. The computation results compared to the experimental results suggest that, as the authors state, there is “a small variation in particle concentration with different sols and a smaller variation in concentration with time for a given sol.”

Two conclusions can be extracted from this paper. First, this was one of the earliest reports of computational studies directly compared to experimental studies on sulfur hydrosols. Second, the observed time variation of particle number concentration is evidence against the assumption of constant particle number during the ‘growth phase’ of the LaMer model.

### The Reaction of Colloidal Sulfur with Sulfite
Colloidal sulfur sols were prepared from dilute aqueous solutions of thiosulfate and hydrochloric acid. Desired particle size was reached by quenching the reaction with I$_2$ and pH was adjusted and held constant by using acetic acid-acetate buffer. Light scattering measurements were made using a Brice-Phoenix light-scattering photometer.

The authors observed the reaction of colloidal sulfur + SO$_3$$_2^-$ $\rightarrow$ S$_2$O$_3^{2-},$ where the “average particle size in a suspension of colloidal sulfur is measure by light-scattering techniques as a function of pH, total sulfite concentration, and particle number.” Addition of sulfite results in the decreased sulfur colloid size until the colloid radius reaches 0.15-0.20 microns.

The results by the authors suggest the colloidal sulfur sols are a mixture of solid elemental sulfur with sulfite and thiosulfite ions adsorbed on the surface. This suggests the growth of the sulfur sol is a result of (autocatalytic) surface growth. In addition, all authors surmise that the effect of temperature upon the reaction rate, if accurate, would then “rule out a diffusion-controlled process.” Furthermore, the authors postulate a surface ‘adsorption mechanism’.

### Time Dependence of the Size Distribution, Number Concentration and Surface Area in LaMer Sulfur Sols
Sulfur sols are formed from dilute solutions of sodium thiosulfate and hydrochloric acid in water. A 2000 series Brice-Phoenix Universal Light Scattering Photometer was used to make light scattering measurements.

The four primary results are as followed: (i) the particle growth rate rapidly decreases for 40 minutes after the onset of nucleation, where the authors claim diffusion-controlled-growth commences; (ii) the particle number reaches a maximum 17 minutes after nucleation begins and then decreases with time; (iii) an inverse relationship is reported between the maximum particle number and the particle size; and (iv) as the particle size increases, the breadth parameter (size distribution) decreases.

The observation that the number of nuclei changes (both increase and then decrease) throughout the growth process is a direct refutal of the LaMer model. It provides experimental evidence (on LaMer’s exact system) of the particle number not remaining constant during the ‘growth phase’. Furthermore, it is implied in the text the nucleation is not a burst or instantaneous event, but rather that it is occurring over a period of time and overlapping with growth. Again, this is direct disproof in 1975 of the LaMer model.

### Monodisperse Sulfur Sols from the Air Oxidation of Hydrogen Sulfide Solutions
Sulfur sols are produced by the reaction of acidic aqueous hydrogen sulfide solution with dissolved oxygen. Further measurements are done with the addition of various trace metals and electrolytes. Measurements of size Induction periods (of varying length depending on exact experimental conditions) are observed for the formation of sulfur sols. No particle sizes are observed below 0.1 microns. The induction period was decreased by the following: increased HS$^-$ concentration, increased partial pressure of oxygen, and increased temperature.

The authors relate their study to the work of LaMer$^{2,4,6,10}$ as it pertains to HOTS. They claim, “the growth of the sulfur particles [to be] diffusion controlled.” The most important point we wish to

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<td>24</td>
<td>The Molecular Composition of Hydrophilic Sulfur Sols Prepared by Acid Decomposition of Thiosulfate</td>
<td>Hydrophilic sulfur sols were prepared from combining sodium thiosulfate and concentrated sulfuric acid solutions. Purification was done by centrifugation, precipitation in 200 mL H₂O followed by precipitation by NaCl 10 times. Characterization was done using chemical analysis, FT-IR, ion-pair chromatography, and reversed-phase HPLC. The authors report, “the composition of the sol is Na₁₋₆₆₇S₈₋₁₀O₉ • 5.9n Sₙ • 1.0 NaCl. The elemental sulfur Sₙ (n = 6-14; mainly S₈) accounts for 17% the total sulfur; 83% of the S are present as long-chain polythionates which form micelles in which the Sₙ molecules are dissolved.” This study reports the compositional characterization of sulfur sols. It gives the correct stoichiometry and equations for the chemical reactions taking place during the formation and decomposition of the sols.</td>
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<td>25</td>
<td>Colloidal Properties of a Microbiologically Produced Sulfur Suspension in Comparison to a LaMer Sulfur Sol</td>
<td>Two types of sulfur sols were prepared and compared. First, LaMer sulfur sols were prepared according the procedure by Weitz &amp; coworkers. Second, sulfur sols were extracted from mixed cultures of Thiobacillus-like bacteria. The following experiments were conducted: electrophoretic mobility, flocculation, dynamic light scattering, and electrolyte concentration effects. The microbiologically produced sulfur sols are assumed by the authors to have negatively charged biopolymers attached to an orthorhombic sulfur nucleus. Meanwhile, the LaMer sulfur sols are assumed to have a vesicle structure composed of long-chain polythionates. High electrolyte concentrations result in a decreased particle size of the biologically-produced sols. The LaMer sulfur sols are compositionally different than sulfur sols produced in nature. Furthermore, it appears the primary difference is in the ligands or ions bound to the surface of the elemental sulfur core of the sulfur sol.</td>
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<td>26</td>
<td>Mechanism for the Formation of Elemental Sulfur from Aqueous Sulfide in Chemical and Microbiological Desulfurization Processes</td>
<td>Various sulfur systems are addressed in this paper. The author presents elemental sulfur forming reactions starting from sulfides, disulfides, and thiosulfates. Primarily, the author presents results for the formation of elemental sulfur from aqueous sulfide. The majority of this paper is devoted to the presentation of a mechanism of elemental sulfur formation from aqueous sulfide and hydroxysulfide radicals. However, he also presents evidence for the rapid agglomeration of hydrophobic S₈ molecules when in aqueous mediums. The rapid formation of the hydrophobic S₈ molecules in water from hydrophilic precursors is important to note. This is the same process that occurs in LaMer’s sulfur systems where, once S₈ is formed, it will quickly agglomerate into a (S₈) colloid.</td>
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<td>27</td>
<td>Model of Nanocrystal Formation in Solution by Burst Nucleation and Diffusional Growth</td>
<td>The authors report a computational model that parallels the LaMer model. It retains many of the important assumptions used in Classical Nucleation Theory (CNT), in particular “instantaneous rethermalization below the critical nucleus size and irreversible diffusive growth above the critical size.” The authors use numerical integration in their calculations. They also discuss the physical effects that may highlight from this paper is the observation of “induction periods of sulfur formation.” The observation of such an induction period is, by itself, not consistent with ‘instantaneous’ or ‘burst’ nucleation. Instead, it is evidence consistent with and strongly supportive of continuous nucleation. Some of the results stated by the authors are as followed: “the average cluster size, as measured by the number of atoms, grows proportionally with time, while the width of the cluster distributions grow proportionally to the square root of time”; they “derived asymptotic predictions for the behavior of the average size and width of the particle distribution”; and they “identified the assumption of instantaneous rethermalization as the main source of the expected growth above the critical size.”</td>
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<td>28</td>
<td>Aqueous Sulfur Sols</td>
<td>This review covers the formation of hydrophobic or hydrophilic sulfur sols produced directly from starting materials, by oxidation of hydrogen sulfide, or biologically from bacteria.</td>
<td>Elemental sulfur (S₈) is a largely hydrophobic species, but through the functionalization with organic groups (like sulfonates) it can be made to be hydrophilic. The primary species formed from the decomposition of thiosulfate and acid is thiosulfuric acid, “which disproportionates in a series of complex redox reactions producing elemental sulfur, hydrogen sulfide, sulfur dioxide, and polythionic acids.” In addition, the author notes “the reversible coagulation of Raffo [LaMer-like] sols is strongly temperature dependent. The higher the temperature the more ‘soluble’ the particles are.” The proposed mechanism is, if correct, evidence against the proposed n = 2 that LaMer and coworkers' proposed 53 years earlier.</td>
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REFERENCES


