[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Determination of the Particle Size of Monodispersed Systems by the Scattering of Light[1]

BY IRVING JOHNSON[1a] AND VICTOR K. LA MER

When a beam of white light is passed through a monodispersed colloid, in which the radius of the dispersed particles is roughly comparable in magnitude to the wave length of the light and the indices of refraction of the dispersed and continuous phases differ appreciably, it is possible to demonstrate a beautiful optical effect which is most appropriately designated as the higher order Tyndall Spectra. It is the purpose of this paper to show how the particle radius and the degree of homogeneity of a colloidal dispersion of sulfur in water may be determined in a relatively simple way by visual observations of these spectra.

B. Ray[2] in 1921 observed that the light scattered by a sulfur hydrosol, produced by mixing dilute aqueous solutions of sodium thiosulfate and sulfuric acid and allowing the mixture to stand for at least thirty minutes, exhibited "axial colors" depending on the angle of observation of the scattered light. Ray interpreted these colors as due to the assymmetrical distribution of the light scattered by the sulfur particles and to the strong dependence of the shape of the scattering patterns on the wave length of the incident light. He made some calculations using Love's[2a] extension of the Rayleigh theory to support this interpretation, but as the computations were very tedious he did not pursue the matter further.

La Mer and Barnes[3] found that when, among other factors, the initial concentrations of the thiosulfate and acid were selected within a narrow range of concentration, of the order of 0.0015 N, the monodisperse character of the sol could be greatly improved. By a careful control of conditions they found that as many as nine distinct orders could be detected in the spectra of the scattered light, whereas Ray's statements could be interpreted at best as representing a maximum of three rather diffuse bands. La Mer and Barnes recognized that the angular positions of the colors of the scattered light paralleled the growth in droplet size of monodisperse particles. By simply stopping the growth of the droplets of sulfur by the addition of iodine at a predetermined time a strictly monodisperse colloid, of a given particle size which remained perceptibly unchanged for several days, could be produced at will. The range of particle size which could be produced was from 0.1 to 1.0 micron.

Although many bands of colors of varying shades and intensities are exhibited in these scattering spectra, the sols can be characterized most simply and easily by observing visually the number and angular positions of the bands of reddish hue. We shall refer to these bands as "red spectral scattering orders" or more simply "orders."

In a preliminary note[4] data were presented showing that the increase in number and the change in angular position of these orders as a function of time could be reproduced quantitatively. The development of the higher order Tyndall spectra therefore offers a simple, ready and convenient method of determining particle size, provided one calibrates the angular positions of the orders either from theory or from an independent experimental method or both.

As will be demonstrated in detail later, the existence of distinct orders requires that the particles be very homogeneous in respect to size. Concurrently with this research, studies were made by Barnes and La Mer[5] on the dependence of the optical transmission of these sols upon the wave length of the incident light. They demonstrated that transmittance could be utilized for the determination of an average particle size, and that this method is not restricted to strictly monodispersed sols. They interpreted their data in terms of the Mie[6] theory of the scattering of light by transparent dielectric spheres.

The higher order Tyndall Spectra were observed by La Mer and Sinclair in 1940 while searching for a method for the preparation of monodisperse aerosols. They employed (1941) certain of the procedures outlined above for the determination of particle size in such systems. To that end the extensive tables of the scattering functions of the Mie theory which are referred to in the present paper were computed by Dr. Arnold Lowan and his staff of the Applied Mathematics Panel, and appear in the O. S. R. D. Report of La Mer and Sinclair[7] entitled Verification of the Mie Theory.

Although the optics of hydrosols and aerosols are essentially identical the method of preparation

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[2] B. Ray, *Indian Assoc. Cultivation Sci.*, **7**, 1 (1921).

[2a] A. E. H. Love, *Proc. London Math. Soc.*, **30**, 308 (1899); **31**, 489 (1899).

[3] V. K. La Mer and M. D. Barnes, *J. Colloid Sci.*, **1**, 77 (1946).

[4] V. K. La Mer and I. Johnson, THIS JOURNAL, **67**, 2055 (1945).

[5] M. D. Barnes and V. K. La Mer, *J. Colloid Sci.*, 1, 79 (1946).

[6] Gustav Mie, *Ann. Physik*, [4] **25**, 377 (1908).

[7] V. K. La Mer and D. Sinclair, O. S. R. D. Report #1857 (1943) (Div. 10 N. D. R. C.). Available through Department of Commerce Office of Publications, Report no. 944. The mathematical tables are being republished (See National Research Council, Mathematical Tables II, Number 15, July, 1946). Report #1857 treats an important theoretical pitfall in the quantitative application of the theory best designated as the "Geometric shadow effect." The reader must refer to the report for details, and to a forthcoming paper in the J. Optical Society.

and the laws of growth are different. To understand and interpret the observations of present research it is necessary to present the salient features of the Mie theory.

Theory

The electric field associated with a light wave incident upon a particle produces a periodic oscillation of the electrons in the particle. These oscillating electrons produce a radiation field outside of the particle, *i. e.*, a field that falls off inversely with the distance from the particle. When the particle is very small compared to the wave length of the incident light, a single periodically varying dipole may be substituted for the oscillating electrons. The frequency of oscillation of this dipole will be the same as the incident light while the amplitude will be determined by the optical properties of the particle. The fields around the particle and hence the intensity of the scattered light may be calculated. If the particle is an isotropic sphere, the intensities of the scattered light may be written in the form first given by Rayleigh[8]

$$J_1 = \frac{\lambda^2\alpha^6}{8\pi^2R^2}\left(\frac{m^2-1}{m^2+1}\right)^2$$
$$J_2 = \frac{\lambda^2\alpha^6}{8\pi^2R^2}\left(\frac{m^2-1}{m^2+1}\right)^2\cos^2\vartheta \qquad (1)$$

Here J_1 is the intensity of the component of the scattered light whose electric vector is perpendicular to the plane determined by the light source, particle and observer, J_2 is the component whose electric vector is parallel to the same plane, λ is the wave length of the incident (and scattered) light in the medium surrounding the particle, R is the distance from the particle to observer, $\alpha = 2\pi r/\lambda$, r is the radius of the particle. Here m is the ratio of the refractive index of the sphere to that of the surrounding medium and ϑ is the angle of observation measured from the backward direction of incident light propagation. Equation (1) is for *unpolarized* incident light of *unit* intensity. (See ref. 7 for an error prevalent in the application of the Rayleigh Theory.)

When the particle is comparable in size to the wave length of the incident light, it is no longer justifiable to replace the array of oscillating electrons by a single vibrating electric dipole. Mie[6] solved the problem of the scattering of light by a sphere of any size as a boundary value problem in electromagnetic theory. His solution may be discussed in terms of superposition of the radiation from electric and magnetic multipoles. In solving this problem, the scattered field around a sphere is constructed from an infinite series of spherical harmonics with arbitrary coefficients. This scattered field and the field due to the incident light wave are combined at the surface of the sphere to determine the arbitrary coefficients. The intensity of the scattered light is computed from the uniquely determined scattered field. The result of this long and involved calculation[9] may be put in the form

$$J_1 = \frac{\lambda^2}{8\pi^2R^2}\left|\sum_{n=1}^{\infty}\left[\frac{a_n}{n(n+1)}\,\pi_n + \frac{p_n}{n(n+1)}\,\{v\pi_n - (1-v^2)\,\pi_n'\}\right]\right|^2$$
$$J_2 = \frac{\lambda^2}{8\pi^2R^2}\left|\sum_{n=1}^{\infty}\left[\frac{a_n}{n(n+1)}\,\{v\pi_n - (1-v^2)\,\pi_n'\} + \frac{p_n}{n(n+1)}\,\pi_n\right]\right|^2 \qquad (2)$$

where a_n and p_n are complex functions of α and m, $\pi_n = \alpha P_n(v)/\alpha v$, $P_n(v)$ is a Legendre function, $v = \cos\vartheta$ and the other symbols have the same meaning as in equation (1). In general m is complex and of the form $m'(1 - ki)$ where m' is the ordinary relative refractive index and k the absorption index, proportional to the electrical conductivity. In the case of perfect dielectrics, *i. e.*, for transparent particles, m will be real. In case of conducting particles, *i. e.*, for optically absorbing particles (for example a gold sol or a sol containing a colored pigment), m will be complex.

The number of terms which must be included in the sums of equations (2) for practical calculation depends upon the values of α and m. Since the values of m normally used are small—in the present paper $m = 1.44$—these equations may be discussed in terms of α alone, however, keeping in mind that the exact limits of any approximation will depend also on the value of m. When α is so small that only the term involving a_1 is significant, it is found that $a_1 = 2\alpha^3(m^2 - 1)/(m^2 + 2)$ and hence equations (2) reduce to the Rayleigh equations (1). This approximation is valid for values of α less than about 0.3. For larger values of α it is necessary to take more terms, but to gain insight into the nature of the deviations from the Rayleigh law, it is sufficient to consider only the next two terms which involve p_1 and a_2. These correspond to a magnetic dipole and electric quadripole, respectively. To this order of approximation we may write equations (2) in the form

$$J_1 = \frac{\lambda^2}{8\pi^2R^2}\left|\frac{a_1}{2} + \left(\frac{a_2}{2} + \frac{p_1}{2}\right)\cos\vartheta\right|^2$$
$$J_2 = \frac{\lambda^2}{8\pi^2R^2}\left|\frac{a_1}{2}\cos\vartheta + a_2\cos^2\vartheta - \frac{a_2}{2} + \frac{p_1}{2}\right|^2 \qquad (3)$$

p_1 and a_2 are both negative and hence these added terms will produce an asymmetry in the intensity of the scattered light with more light scattered into the forward than into the backward directions. The parallel polarized component J_2 is not zero for $\vartheta = 90°$ as in the case of Rayleigh scattering, and hence the light is no longer completely polarized in this direction.[10] However, the

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8) Rayleigh, *Phil. Mag.*, **12**, 81 (1881).

(9) We are greatly indebted to Dr. Arnold Lowan and his staff of the Applied Mathematics Panel who made the tedious numerical computations of the quantity in bars$|\;|^2$ as a function of both α and m. His values for these functions have been used to compute the "order" positions as described in detail on page 8.

(10) Since both a_2 and p_1 are proportional to α^5 the intensity of the light scattered at 90° will vary inversely as the eighth power of the wave length giving rise to a very beautiful deep blue color in this direction when the light is viewed with a Nicol oriented so as to pass only light polarized parallelly.

position of complete polarization is not lost but moves back to a smaller angle ϑ' which is given approximately by the expression

$$\vartheta' = \cos^{-1}\left(\frac{a_2 - p_1}{a_1}\right) \qquad (4)$$

This angle is very close to 90° for values of α for which the above (eq. 3) approximation is valid, for example, for a value of $\alpha = 0.5$, $\vartheta' = 89° 13'$.

When α is larger than 0.3, a_1 is no longer proportional to α^3 but approaches a maximum value and then decreases rapidly. On the other hand, the other coefficients become large compared to a_1 and consequently predominate in determining the angular dependence of the intensity of the scattered light. Since the angular functional factors of these higher terms are more complicated than the a_1 factors, the resulting scattering patterns have many more maxima and minima. An example is shown in Fig. 1 where a magnitude proportional to the J_1 component has been plotted for an α value of 6 and an m value of 1.44.

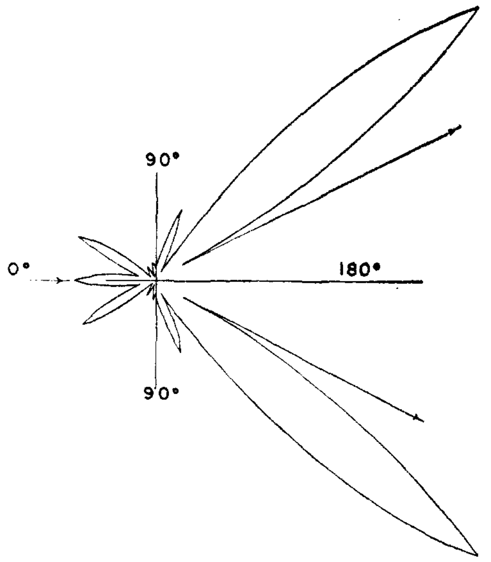

Fig. 1.—Angular variation of the intensity of the J_1 component of the light scattered by a spherical particle: calculated using the Mie theory, $\alpha = 6$ and $m = 1.44$.

The many maxima and minima of intensity in these scattering patterns are responsible for the higher order Tyndall spectra exhibited by the light scattered by sulfur sols. At those angles for which the intensity of the red scattered light is greater than the green, the scattered light will appear red in color. The angular position and number of orders depends upon r, the particle size; m, the refractive index of the particles relative to the medium; and also upon m_0, the refractive index of the medium. If the values of those three parameters are known, the number and position of the orders may be calculated using equation (2). It has been found that more numerous and more distinct orders are shown by observing the scattered light whose electric vector is perpendicular, *i. e.*, the J_1 component.

Calculation of the Position of Orders.—To calculate the positions of the orders, it is sufficient to compute the ratio of the intensity of the red scattered light to the green scattered light and determine the angles at which this ratio is a maximum. Since the wave length dependence of equation (2) enters through α, the intensities must be calculated for two different α values whose ratio is the same as the ratio of the wave lengths of red to green light. The absolute values of α used will depend on the radius of the particle r and the refractive index m_0 of the medium surrounding the particle, since λ the wave length in the medium is related to λ' the wave length *in vacuo* by $\lambda' = m_0\lambda$. The α value used to compute the red intensity is given by

$$\alpha_{\text{red}} = 2\pi r m_0/\lambda'_{\text{red}} \qquad (5)$$

The value of α used to compute the green intensity is given by $\alpha_{\text{green}} = \alpha_{\text{red}}\ \lambda'_{\text{red}}/\lambda'_{\text{green}}$. A red-green wave length ratio of 1.2 is used, corresponding to a red wave length of 6290 Å. (*in vacuo*) and a green wave length of 5240 Å.

In using equation (2) for calculating the intensities it is necessary to know the value of m the relative refractive index of the particle. For sulfur sols a value of m equal to 1.44 is used. Orders will occur at those angles where the red-green intensity ratio has a maximum. Figure 2 shows an example of such a calculation made for an α_{red} value of 5 (and hence an α_{green} value of 6). It is seen that orders should be observed at angles of $45^1/_2$, $73^1/_2$, 95, 121 and $151^1/_2$°. For sulfur sols in water ($m_0 = 1.333$) and for a red wave length of 3690 Å. α equal to 5 corresponds to a radius of 0.376 micron.

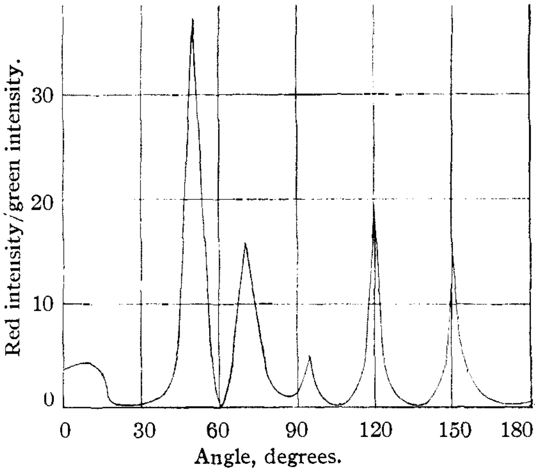

Fig. 2.—Ratio of intensities of red to green light scattered by a sphere, calculated using the Mie theory: $\alpha_{\text{red}} = 5$, $\lambda_{\text{red}}/\lambda_{\text{green}} = 1.2$, $m = 1.44$.

This calculation has been made for absolutely monodispersed spherical particles and two exactly defined wave lengths. Since these conditions can be only approximated in practical experiments, some deviations from the calculated positions should be expected. This question will be taken up in greater detail later.

Application of Light Scattering Methods to Particle Size Determination.—The feasibility of using light scattering methods for the determination of particle size depends upon the relative refractive index, shape, size and concentration of the dispersed phase. Exact theory has been completed for only a few of the many types of possible systems. Thus, the simple theory of Rayleigh is competent to treat only the case of very dilute systems of small isotropic spherical particles where $r \leqq \lambda/20$. The theory of Gans[11] extends this treatment to dilute systems of *non*-spherical particles of almost any regular shape, but still carries the restriction $r \leqq \lambda/20$.

The treatment of dilute systems of spherical isotropic particles of any size requires the more general Mie theory as presented in this paper. In the limit $r >> \lambda$, the Mie theory approaches the classical theory of geometric optics.

A theory of less dilute dispersions, based on the fluctuation treatment of Smoluchowski[12] and of Einstein,[13] has been applied by Debye[14] recently to the determination of the molecular weights of high polymers. This theory is restricted to the small particles of the Rayleigh region. Zimm[15] has also treated the same problem.

The present paper treats dilute dispersions of larger spherical isotropic particles, *i. e.*, where the radius is comparable to the wave length of the incident light. To exhibit orders the system must also have a narrow size distribution. "Orders" become distinct in the scattered light when the values of $\alpha \geq 2$ (approximately).

Consequently the lower limit of the radii which may be measured using the "order" method is determined by the wave length observed. For visual observation this wave length is fixed by the color sensitivity of the eye. However, there is nothing in the theory which fixes this wave length or prohibits the use of other detectors. Thus by observing in the ultraviolet it is possible to determine smaller sizes. For example, when α equals 5 (m = 1.44), five spectral scattering orders are predicted by theory. When the wave length observed is equal to 6290 Å. (red), this corresponds to the radius of 0.376 micron; whereas, if λ equals 3000 Å. (ultraviolet), the corresponding radius is 0.18 micron. On the other hand, by observing in the infrared, one should be able to use the method for larger sizes than we are reporting for visible light.

When the radius is too small for the sol to exhibit orders, yet too large to be treated by the simple equation of Rayleigh (1), the radius may be determined by measuring the degree of polarization of the scattered light at some convenient angle, such as 90°. This procedure has been applied by LaMer and Sinclair[16] to determine the particle radius of aerosols. The degree of polarization, defined as $(J_1 - J_2)/(J_1 + J_2)$, may be calculated as a function of α and m from the Mie equations (2).

Experimental

Observations on the Number and Positions of Orders.—The apparatus necessary for the observation of the position and number of orders is simple and is shown diagrammatically in Fig. 3.

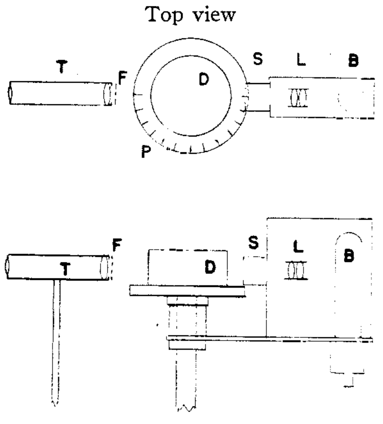

Fig. 3.—Diagram of apparatus used to observe order positions.

It consists of four essential elements: (1) an intense *parallel* beam of light, (2) a transparent dish to hold the sol, (3) a telescope to observe the scattered light, and (4) a protractor (P) to measure the angle between the incident beam and the telescope. A parallel beam of light was obtained by using a G.E. 108 watt projection bulb (b), a pair of lenses (L) and slits (S) $^1/_{32}''$ by $^1/_2''$. The dish (d) was a Pyrex, 8-cm. crystallizing dish. The telsecope (T) was made by mounting the lens elements from a small hand magnifier in a brass tube and placing a cross-hair at the focal plane of the eye lens. A piece of Polaroid J film (F) was cemented in front of the objective lens oriented so as to pass only the light with the electric vector perpendicular. The light source could be rotated around the axis of the dish. With this apparatus the position of an order can be determined to within 1° of angle.

Preparation of Sulfur Sols.—The sulfur sols were prepared by adding 10 ml. of 0.1 M sodium thiosulfate and 10 ml. of 0.2 M hydrochloric acid solutions to about 980 ml. of distilled water which had been brought to 25° in a thermostat. The volume was made up to one liter, thoroughly mixed, and returned to the thermostat. All glass-

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(11) R. Gans, *Ann. Physik*, [4] **37**, 881 (1912).

(12) Smoluchowski, *Ann. Physik*, **25**, 205 (1908).

(13) A. Einstein, *ibid.*, **33**, 1275 (1910).

(14) P. Debye, *J. Applied Physics*, **15**, 338 (1944).

(15) B. Zimm, *J. Chem. Physics*, **13**, 141 (1945).

(16) LaMer and Sinclair, Div. 10 N. D. R. C., O. S. R. D. Report No. 1857, 1943, declassified to open.

TABLE I

DATA OF TYPICAL EXPERIMENTS ON ORDER POSITIONS AND TIME OF GROWTH

Time, hr.	Radius, microns[a]	Angular degrees								
		Expt. 47								
13.33	0.501	30	45	60½	75	93	111	134	155	
14.20	.512	28	44	58	75	94	115	138	157	
15.25	.529	28	43	57	73	90	117	137	159½	
16.67	.540	26	42	56	71	86	99	120	140	161
18.95	.566	25	41	53	67	83	102	121	142	162
		Expt. 48								
1.55	.220	121								
1.85	.243	66	134							
3.25	.324	53½	85	111½	147					
5.08	.384	44	66	95	128	155				
6.30	.414	41	62	85	110	136	162			
7.17	.430	37½	57	79	114	139	166½			
7.83	.438	36½	55	76	94	118	142	170		
8.92	.450	34½	53	73	94	121	145			
10.44	.468	34	50	69	85	103	125	150		
11.20	.477	34	48	65	83½	106	127	152		
13.26	.500	28	46	62	78	93	112	133	159	

[a] Found by the use of Fig. 6, see below.

ware was cleaned with acid chromate cleaning solution and carefully rinsed. No difficulty was experienced in reproducing the sols. The growth rates of a series of sols were studied in 1943, and the results were duplicated[4] almost exactly in 1945 using reagents of different origin.

Observation of Order Positions.—Sols were prepared in the manner outlined above, samples removed after known time intervals, and the number and position of the orders observed. The results of two typical runs are tabulated in Table I and shown by the open circles of Fig. 4. To avoid the use of two figures the data have been plotted as a function of particle size instead of time. The relation between time of growth and particle size can be found in Fig. 6.

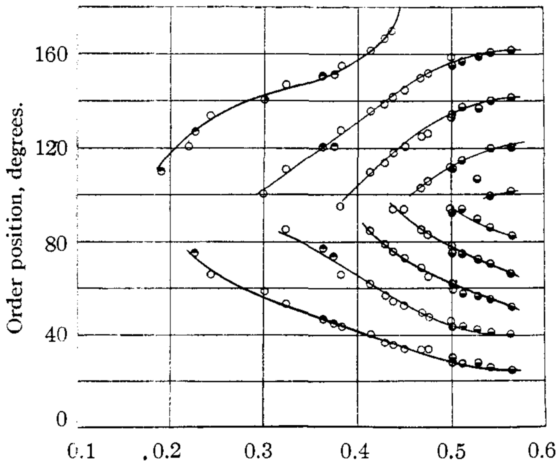

Fig. 4.—Order positions for sulfur sols: ◒, experimental run no. 47; O, experimental run no. 48; ◓, theoretical, calculated using the Mie theory with $m = 1.44$.

Numerical Computation of Order Positions from Mie Theory.—As explained above the computation of the order positions from the Mie theory requires knowledge of the refractive index of the particle and the medium. When this is known, the intensity of the light scattered for a particular sized particle can be computed at various angles and different wave lengths using equation 2. These computations were made for two different wave lengths, one in the red (λ = 6290 Å.) and the other in the green (λ = 5240 Å.). In making these computations the ratio of the refractive indices of the particle and the medium is needed and should correspond to the value for the particular wave length (*in vacuo*) for which the computation is being made. The value to be used in the present case will depend on the physical form of the sulfur.

Microscopic examination of the larger sulfur particles produced by this method reveals that they are liquid spheres, presumably of supercooled sulfur. The existence of small supercooled sulfur particles at room temperature is not unreasonable in view of Fanelli's[16a] observation that droplets, 3 mm. in diameter, remained liquid for one to two weeks. Using the data reported by Mellor[17] for the refractive index of molten sulfur, the relative refractive indices are found to be 1.4274 at λ = 6290 Å. and 1.4602 at λ = 5240 Å. The average of these two values, 1.44, was used for both the red and green intensities. Using the tabular values now available[9] for the Mie functions, computations of the order positions for five different particle sizes were made. The results are shown by the triangles of Fig. 4 and given in Table II.

(16a) R. Fanelli, THIS JOURNAL, **67**, 1832 (1945).

(17) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, Green and Co., London 1930, p. 70.

TABLE II

Order positions for super-cooled liquid sulfur droplets in water computed using the Mie theory and a relative refractive index of 1.44, with $\lambda_{\text{red}} = 6290$ Å. and $\lambda_{\text{green}} = 5240$ Å.

Radius, microns	Angular positions, degrees				
0.179	110				
.227	75	127			
.301	59	100	141		
.363	47	77	120	151	
.376	$45^1/_2$	$73^1/_2$	95	121	$151^1/_2$

Tabular values of the complicated functions needed to evaluate equation 2 were not available for larger values of α; hence it became necessary to calibrate the method beyond this range by actually measuring the particle size using an independent experimental method.

Determination of the Size by Rate of Deposition.—This method depends upon measuring the rate of deposition of the particles on a horizontal surface from a "stirred" system.

The rate of deposition dn/dt per unit area is equal to the velocity of settling v times the number concentration $N(t)$

$$dn/dt = v \cdot N(t) \qquad (6)$$

Since the system undergoing settling is being mixed constantly by thermal gradients, etc., it is not permissible to integrate equation (6) treating $N(t)$ as a constant in time. It is assumed that as soon as a few particles have settled out the remaining solution is mixed again to give a uniform concentration. Consequently, the rate of change in concentration will be equal to the rate at which particles are depositing (per unit area) divided by the height h of the system

$$\frac{dN(t)}{dt} = -\frac{v}{h}\,N(t) \qquad (7)$$

whose solution is simply

$$N(t) = N_0e^{-vt/h} \qquad (8)$$

Here N_0 is the initial concentration. When equation (8) is substituted into equation (6) and the integration carried out there results

$$n = hN_0\,(1 - e^{-vt/h}) \qquad (9)$$

The average force acting on any particular spherical particle over a sufficiently long time interval results from the addition of the viscous, buoyant and gravitational forces. Since the particles are electrically charged, there will be an additional force due to cataphoresis. This electric force has been neglected[18] since it is small in comparison with the other forces. Consequently, Stokes' law may be used to compute v, *i. e.*, $v = 2r^2g(d - d_0)/9\eta$, where r is the radius, g the acceleration due to gravity, $d - d_0$ is the effective density of the particle, and η is the viscosity.

Microscope slides were placed upon a $^3/_8''$ layer of mercury on the bottom of a trough (1″ × 4″ × 13″). The sulfur sol was poured into a depth of about 0.7 cm., accurately determined with a screw micrometer. To prevent the size changing during this sedimentation, the reaction was arrested by titrating almost to equivalence the unreacted thiosulfate with iodine. Every twenty minutes a slide was removed and the number of particles deposited per sq. cm. determined by microscopic count. The microscope was fitted with an ocular micrometer in the form of a square of 7.24×10^{-4} sq. cm. total area subdivided into 100 equal smaller squares. The thin layer of liquid (0.7 cm.) assured a turbulent condition in the solution, and the removal of the slides every twenty minutes contributed to making this condition more certain by the stirring accompanying such removal.

The data of a typical experiment are shown in Fig. 5. The curve shown was calculated using equation 9 with a value of v equal to 6.34×10^{-5} cm./sec., and N_0 equal to 6.9×10^5 no./cc. This value of N_0 was found by extrapolating the straight line obtained when log n is plotted against $1/t$ to infinite time. The value of v was obtained from the slope of the experimental curve of n *vs.* t at zero time. This value of v corresponds to a radius of 0.508 micron. If a cubic equation is fitted to the experimental data, both the radius and the number concentration may be calculated from the coefficient. It is easily seen, on expanding the exponential of equation 9, that the coefficient of the term in the first power of t is N_0v, and the coefficient of the term in the second power of t is $-N_0v^2/2h$. The ratio of the first two coefficients is, therefore, equal to $-v/2h$. Knowing v, the radius is calculated from Stokes' law. The ratio of the first two coefficients of the cubic equation fitted by least squares to the data shown in Fig. 5 gave a value for the radius of 0.486 micron.

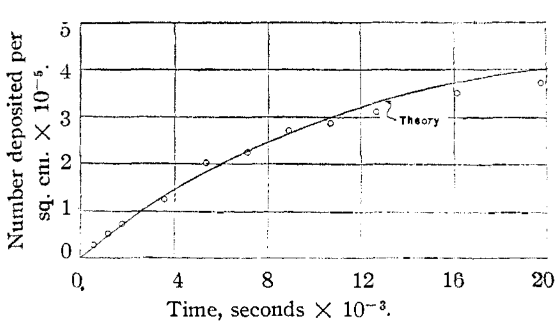

Fig. 5.—Test of deposition equation $n = hN_0(1 - e^{-vt/h})$: ○ experimental points. Full line computed using $h = 0.70$ cm., $v = 6.34 \times 10^{-5}$ cm./sec. and $N_0 = 6.9 \times 10^5$ particle/cc.

Using this method, the radii of the particles of eight sols of different ages were determined. The

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[18] Smoluchowski (*Kolloid-Z.*, **18**, 194 (1916)) has shown that the ordinary viscous force must be increased by a small quantity when the particle is charged. This quantity differs from unity by a factor which varies inversely with the square of the radius and hence is very small for particles as large as being considered here, being of the order of 10^{-6}; see also Tiselius, *Kolloid-Z.*, **59**, 306 (1932).

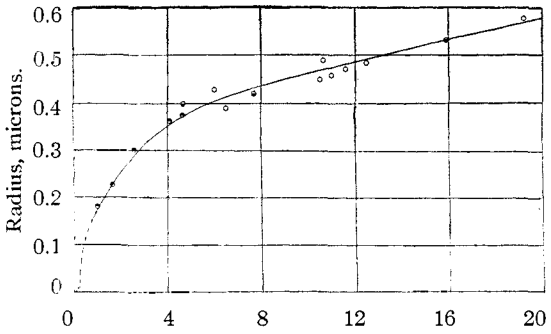

Fig. 6.—Rate of growth of the sulfur particles in a sulfur sol: (initial solutions 0.001 *M* $Na_2S_2O_3$ and 0.002 *M* HCl, temperature 25°) ◓, from comparison of observed order positions and positions computed using the Mie theory (m = 1.44); O, from rate of deposition measurements; ◒, from optical transmission data obtained by Barnes and LaMer[5] (the data of Barnes and LaMer is for 0.0015 *M* solution of $Na_2S_2O_3$ and 0.00075 *M* H_2SO_4 which accounts for the slightly faster rate of growth).

data have been plotted in Fig. 6 and are given in Table III.

TABLE III

SIZE OF DROPLETS IN SULFUR SOLS DETERMINED BY RATE OF DEPOSITION

Age of sol, hours	Radius, microns
6.0	0.43
6.5	.39
10.5	.45
10.7	.49
11.0	.46
11.6	.47
12.5	.485
19.2	.575

The radii were also determined by comparing the observed order positions with those calculated using the Mie theory and are plotted in Fig. 6. It is seen that both sets of data give a reasonably continuous curve. Also on this figure are shown the data obtained by Barnes and La Mer[4] for the size of similarly aged sols. Their results were determined by fitting the observed total transmission (optical) curve to the theoretical curve calculated from the Mie theory. The solutions used by Barnes and La Mer were 0.0015 *M* in sodium thiosulfate and 0.00075 *M* in sulfuric acid and, therefore, not exactly the same as those used in this research. However, the difference is small and accounts for the slightly larger sizes obtained by them.

Since it has been demonstrated that the optical characteristics and, therefore, the size of the sulfur particles, are the same for all sulfur sols prepared in the same way and grown for the same length of time, this curve, Fig. 6, allows the size corresponding to a particular time of growth to be determined. This has been done in preparing Fig. 4. In Table IV the order positions corresponding to rounded values are tabulated.

TABLE IV

ORDER POSITIONS FOR VALUES OF THE RADIUS OF SULFUR SOLS

Radius, microns	Angular positions								
0.20	115								
.25	64	136							
.30	56	84	107	145					
.35	48½	79	118	149½					
.40	41½	64½	89½	105	132	158			
.45	35½	53½	73½	90	121½	146	(177)		
.50	30½	46	61	77	95	112½	134	156½	
.55	26	41½	54½	69	85½	101	120½	141	161

Observations on the Orders in Mixtures of Different Sized Sols.—La Mer and Barnes[3] have presented several qualitative observations which support the assertion that these sulfur sols are "mono-dispersed." It would be highly desirable to give this statement precision by estimating the half-width of the distribution curve of the radii of these particles. It has not been possible to detect the small differences which presumably must exist in the particle sizes of these "monodispersed" sols by any method at our disposal. Particles large enough to be resolved under a light microscope all appear to have the same size, but since it is not possible to measure differences of less than 0.2 micron under the very best of conditions, this is certainly not adequate evidence to establish uniformity in the size range in question. This microscopic evidence does, however, limit the spread to be expected to about 20% in either direction.

The existence of distinct orders in the scattered light, however, is very much better evidence that the sol is monodisperse. To give this statement greater precision, it would be necessary to define the term "distinct order." While this term is capable of exact mathematical definition, namely, in terms of the height and half-widths of the bands of Fig. 2, there do not exist at present experimental data sufficiently precise to warrant such a definition. On the other hand, a distinct order may be defined qualitatively as one whose position may be fixed easily to within one degree of angle. When the eye is used as a detecting device, this will set a lower limit to the ratio of red to green intensities that may be distinguished from the background colors. Quantitative measurements indicate that a ratio of red to green intensities of less than 1.2 is detected with extreme difficulty.

If sufficient numerical computations of the intensity functions using the Mie equations (2) were available, the exact shape of the maxima (as shown in Fig. 2) could be determined and compared with experimental curves. With the limited tabular data available, it can be shown that the red-green ratio at the maxima depends on the position of the maxima (*i. e.*, on the particular order being considered) and on the particle size for which the computation is made. From these computations it is also apparent that if the particles have different sizes, the height will be reduced and the band will be widened. In addition the height and breadth of a given band depend on the value of the relative refractive index *m*—the larger the value of *m* the sharper and more numerous the bands.

In most practical experiments in which the red-green ratio is measured, two important experimental errors must be considered. The first is that measurements of the intensity are necessarily made over a small angular increment, and the second that light of a small range of wave lengths is used. Both errors will have the same effect on the ratio of red to green intensity as a mixture of different sized particles. Both errors could be reduced greatly, however, by adopting a procedure similar to that used in determining the exact shapes of infrared absorption peaks.

To obtain quantitative data on the red-green intensity ratio the telescope on the apparatus, Fig. 3, was replaced by a Luckiesch brightness meter. A sheet of Polaroid J Film was placed in front of the brightness meter in order to observe only the light with the electric vector perpendicular to the horizontal plane. Readings were taken with the instrument at various angles using a no. 29 (red) Wratten gelatine filter and then a no. 58 (green) Wratten gelatine filter. These light filters have, when corrected for the visibility curve of the eye, maximum transmissions at 6760 (no. 29) and 5600 Å. (No. 58), with half-widths of 350 and 565 Å., respectively.

Using this apparatus, measurements of the red-green intensity ratio were made on several sols. A typical example is shown in Fig. 7. This curve was constructed from data obtained on a 6.33 hour sol (*i. e.*, about 0.41 radius). The positions of the maxima are very close to those expected for such a sol.

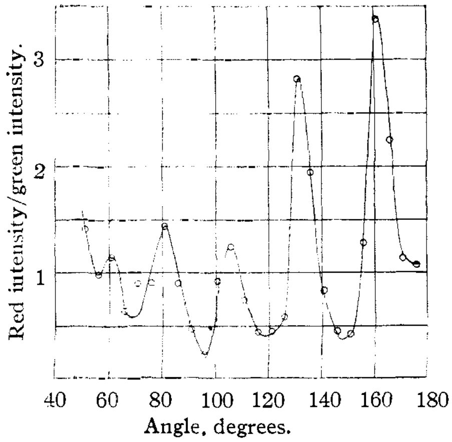

Fig. 7.—Ratio of intensity of red to green scattered light. The sulfur sol was 6.3 hours old with particles of 0.41 micron radius.

Synthetic Mixtures.—Observations were taken on synthetic mixtures of two sols designated as A and B whose radii (determined by the positions of the orders in Fig. 3) were 0.467 micron (A) and 0.476 micron (B). The sol containing smaller sized particles had an order at 136° while the sol with the larger sized particles exhibited a green color in that region. The total number of orders were A equals $6^1/_2$ and B equals 7.

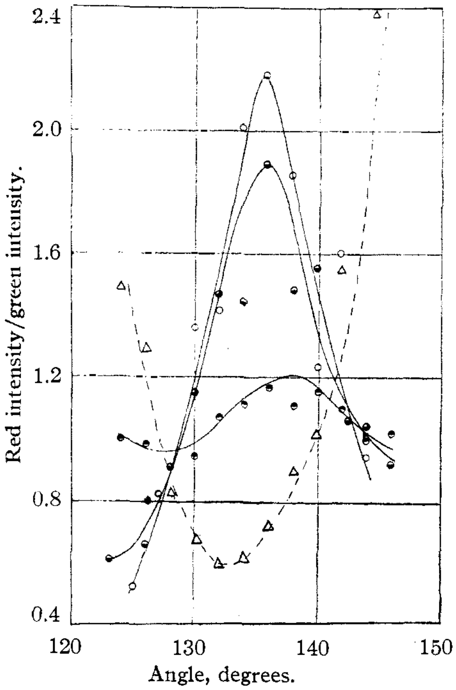

Fig. 8.—Experimentally determined red-green intensity ratio for the light scattered by homogeneous sulfur sols and mixtures: Sol A, 0.467 microns radius; Sol B, 0.476 microns radius; ○ 100% A; ◒ 90% A, 10% B; ◓ 50% A, 50% B; △ 100% B.

It is seen in Fig. 8 that the presence of only 10% of the larger particles makes a measurable difference in the sharpness coefficient of the order, while in a 50% mixture the order is practically obliterated. The size difference in these two sols is only 2%. Therefore, a 10% impurity of a 2% larger particle can be easily detected. It cannot be asserted without gathering further evidence that in general this method is always as sensitive to the presence of small amounts of slightly larger (or smaller) particles. It is clear, however, from this synthetic mixing experiment why the phenomenon of distinct spectral scattering orders has not been observed previously in colloidal systems. Apparently colloidal dispersions having the required high degree of monodispersity have not been prepared previously.

Factors Influencing the Rate of Growth of Sulfur Sols.—In order to be certain of reproducing the size of a given sol, a preliminary survey was made of some of the factors which influence the rate of growth of the sulfur sols. Concentration is by far the most important single factor in determining the rate of growth and the monodisperse character. Concentrations of about 0.001 M in thiosulfate and 0.002 *M* in hydrochloric acid seem to be small enough to give uniformly sized particles and still furnish a large enough concentration of particles to be observed easily. A 15° rise in temperature just about doubles the rate of attaining a given size. Several experiments using an 8.8% glycerol solution showed that glycerol affected the time of initial appearance of the Tyndall beam. In the absence of glycerol the solution remains crystal clear for about one-half hour following mixing after which time fine sulfur particles form rapidly giving a Rayleigh type blue Tyndall beam. The first order appears in about one hour. With a solution containing 8.8% glycerol the first orders did not become distinct until about three or four hours had elapsed after mixing the reagents. The viscosity of the glycerol solution is only about twice that of water. Hence it is difficult to ascribe the increased induction period solely to a viscosity effect. It is more likely that the decrease in dielectric constant through its affect on the activities of the reacting species and the solubility of the products affects the important initial steps in the reaction. The effects of these factors, as well as those of neutral salts upon the kinetics of sol formation and growth are being studied.

Summary

The light scattered by sulfur sols which have been prepared by mixing dilute (0.001 *M*) solutions of sodium thiosulfate and hydrochloric acid exhibits different colors depending on the angle of observation. Especially significant are the red bands, called "orders," which increase in number from zero to nine as the radii of the sulfur droplets increase. The number and positions of these orders have been measured as a function of the time after mixing. A special apparatus was designed and constructed consisting of a parallel beam of light, a dish to hold the sol, and a photometer to observe the scattered light.

Using the electromagnetic theory of the scattering of light by spheres, it is possible to compute the ratio of the red to green scattered light intensity. At those angles where the red–green intensity ratio is a maximum, the scattered light will appear red. Therefore, it is possible to compute the angular positions at which orders should be observed as a function of the radius and relative refractive index of the sphere and the refractive index of the medium surrounding the sphere.

By comparing the observed and theoretically calculated positions, assuming the refractive index of the liquid sulfur droplets to be 1.92, the radii of the sulfur droplets have been determined. Since theoretical computations are available only for values of the radii up to about 0.4 microns, the order positions were related empirically to the size beyond this range. The size was determined using a method based on the rate of deposition of the spherical droplets from a stirred system. The results obtained using this rate of deposition method for the radii fit smoothly with the results obtained using the theoretical calculations from the light scattering theory.

Measurements were made with a visual photometer of the intensities of the light scattered at different angles using two narrow wave length bands centered in the red and green, respectively. The ratio of the "red" and "green" intensities when plotted against the angle had maxima at the same angles where orders were observed using the simple visual method.

Similar measurements, on synthetic mixtures of sols of different sized droplets, demonstrated that the distinctness of the orders of a sol is very sensitive to small amounts of droplets differing slightly in size. These observations on synthetic mixtures are convincing evidence to support the assertion that these sols are highly monodisperse

Conclusions

1. The existence of higher order Tyndall spectra in the visible light scattered by monodisperse sulfur sols may be explained quantitatively on the basis of the general electromagnetic theory of the scattering of light by a single transparent dielectric sphere developed by Mie.
2. The position and number of orders observed visually may be used as a convenient method of measuring the radii of the dispersed particles of a colloidal system provided the particles are sufficiently monodisperse.
3. A quantitative measure of the degree of monodispersity of a system may be obtained by examining in detail the magnitude of the ratio of the intensity of red to green scattered light.

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