

For reference, the following equation for the vapor pressure of sulfur versus temperature is given here:  $t_p = 444.6 + 0.221_5 (t_p + 273.1) \log (p/760)$ . This equation was deduced from the observations of Mueller and Burgess.

### Summary

Data are presented on the variation with pressure of the boiling points of naphthalene and benzophenone within the pressure range of 700 to 800 mm. of mercury. The data are primarily intended for use in thermometry. The pressure-temperature relation for anthracene is also given but the normal boiling point of the pure material has not been determined with sufficient accuracy to establish it as a fixed point in precise thermometry.

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[CONTRIBUTION FROM THE LABORATORY OF COLLOID CHEMISTRY, UNIVERSITY OF WISCONSIN]

## THE USE OF SCATTERED LIGHT IN THE DETERMINATION OF THE DISTRIBUTION OF SIZE OF PARTICLES IN EMULSIONS<sup>1</sup>

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RECEIVED MARCH 9, 1925

PUBLISHED JUNE 5, 1925

The determination of the distribution of size of particles in a disperse system has been made with the application of Stokes' law by two general methods. One consists in following the rate of sedimentation of the disperse phase of a system passing a definite boundary, or settling onto a balance pan.<sup>2</sup> The other consists in determining the variation in the concentration of the disperse phase with height, after a definite interval of time has elapsed for sedimentation. In this method the concentrations at different heights may be determined photometrically by the variation with height in the light absorption,<sup>2e,3</sup> or by the intensity of the scattered light at right angles to the source. In this investigation the use of scattered light has been developed.

Inasmuch as the disperse phases used were all lighter than the dispersion medium, the direction of sedimentation of the particles was upwards. After a period of sedimentation both the concentration and the size of the particles increased progressively from the bottom to the top of the system.

<sup>1</sup> A portion of a thesis submitted by Alfred J. Stamm in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

<sup>2</sup> (a) Odén, *Proc. Roy. Soc. Edinburgh*, **36**, 219 (1916). (b) Fisher and Odén, *ibid.*, **44**, 98 (1923). (c) Odén, *Bull. Geol. Inst. Upsala*, **16** (1916). (d) Wiegner, *Landw. Vers. Sta.*, **91**, 41 (1919). (e) Svedberg and Rinde, *THIS JOURNAL*, **45**, 943 (1923). (f) Kraemer and Stamm, *ibid.*, **46**, 2709 (1924). (g) Kelly, *Ind. Eng. Chem.*, **16**, 928 (1924).

<sup>3</sup> (a) Svedberg and Nichols, *THIS JOURNAL*, **45**, 1910 (1923). (b) Svedberg and Rinde, *ibid.*, **46**, 2677 (1924).

Upon illuminating such a system from the two sides in a narrow cell with a dark opaque background, the intensity of the light scattered to the front also increased from bottom to top. This intensity variation was recorded photographically, and the densities on the photographic plate were determined with a photometer.

In obtaining the distribution of the size of the particles from this density-height relationship, two questions arise for consideration. First, does the variation of the photographic density with height accurately record the "unimpaired" intensity-height relationship, and if not how can it be corrected? (The term "unimpaired" intensity is used to denote the light intensity that would result if there were no boundaries such as the bottom of the cell or upper meniscus to interfere with the normal scattering.) Second, how can this intensity-height relationship be converted to a concentration-height relationship? After solving these two problems the determination of the distribution of the size of the particles depends merely upon the application of Stokes' law of settling.

$$r = \sqrt{\frac{9 \eta x}{2 (\rho_p - \rho_e) g t}} \quad (1)$$

where  $r$  is the radius of the particles,  $\eta$  the viscosity of the dispersion medium,  $x$  the height,  $(\rho_p - \rho_e)$  the difference between the densities of the dispersed phase and dispersion medium,  $g$  the acceleration of gravity and  $t$  the time in seconds. For the systems studied this simplifies to

$$r = 0.000307 \sqrt{\frac{x}{t_1}} \quad (2)$$

where  $t_1$  is the time in hours. The value of  $r$  calculated from this relationship corresponds to the size of the particles that have just completely passed above the height  $x$  in the time  $t_1$ . In accordance with the precedent set in earlier papers<sup>4</sup>  $dS/dr$  has been chosen as the distribution function. Thus any element of area under a  $dS/dr$  versus  $r$  curve represents the mass of particles dispersed between the sizes represented by the bounding abscissas. The value of the function  $dS/dr$  cannot be determined directly, but must be expressed in terms of  $dI/dx$  or  $dD/dx$ , where  $I$  is the intensity at the front of the cell, and  $D$  is the corresponding photographic density.

For the case of the systems investigated, two reasonable assumptions may be made as to the nature of the scattering of light. First, as the concentrations of the systems are small, the manner in which one particle scatters light is independent of the manner in which adjacent particles scatter the light. From this it follows that the amount of light scattered towards the front of the cell depends directly on the number of particles scattering the light. Second, the particles are of such a size (diameters from 5-20 times the wave length of light) that the scattering may be con-

<sup>4</sup> "Colloid Chemistry," by The Svedberg, American Chemical Society Monograph, Chemical Catalog Company, 1924, p. 136.

sidered to be that of ordinary reflection. From this it follows that the amount of light scattered by a particle depends directly upon its surface, or the square of its radius.<sup>5</sup> From these two assumptions the following relationship may be formulated,

$$I = hr^2n \quad (3)$$

where  $I$  is the intensity of the light scattered to the front of the cell,  $n$  the number of particles scattering the light and  $r$  their radius. The constant of proportionality  $h$  is dependent on the inherent characteristics of the scattering system. If  $r$  and  $n$  varied independently the expression

$$dI = hn \cdot 2rdr + hr^2dn \quad (4)$$

would give the change  $dI$  resulting from, first, an increase  $dr$  in radius of the  $n$  particles, and, second, a change  $dn$  in the number of particles of radius  $r$ . Consider, however, the amount  $dI$  by which the light scattered from level  $x + dx$  above the bottom of the cell exceeds that which is scattered from a level  $x$  in a system in which a steady state of sedimentation exists. Since all particles of the same radius move upwards at the same velocity, the concentration of a given size of particle is uniform above that level which has just been reached by those particles of the given size which were initially at the bottom of the cell; while below that critical level the concentration of this given size of particle is zero. Thus, those sizes of particles which are present at level  $x$  are also present, and at the same concentrations, at level  $x + dx$ . Hence there is no change,  $dr$ , in the radius for particles present both at level  $x$  and level  $x + dx$ , and the first term of (4) is zero. It follows that

$$dI = hr^2dn \quad (5)$$

It will be shown later by experiment that the two assumptions on which Equation 5 is based are valid, and hence the equation may be used in determining the value of the distribution function.

Let the distribution of the size of the particles in a system be characterized by the above-mentioned function  $dS/dr$ , whose integral, between  $r_1$  and  $r_2$ , gives the weight of those particles whose radii are between  $r_1$  and  $r_2$ . At time  $t$  there are, below a plane at height  $x$ , no particles of radius greater than  $r$ , and below a plane at height  $x + \Delta x$  no particles of radius greater than  $r + \Delta r$ , the values of  $r$  being calculated from Equation 2. The intensity at  $x + \Delta x$  exceeds that at  $x$  by an amount  $\Delta I$  due to the number  $\Delta n$  of particles whose radii are contained between  $r$  and  $r + \Delta r$ . From the relationship between  $\Delta S$  and  $\Delta n$

$$\frac{dS}{dr} = \frac{4}{3} \pi \rho_p r^3 \frac{dn}{dr} \text{ it follows that; } dn = \left( \frac{dS}{dr} \right) \frac{3 dr}{4 \pi \rho_p r^3}$$

From (2)

$$dr = \frac{K dx}{2 \sqrt{kx}}$$

<sup>5</sup> For particles smaller than the wave length of light Rayleigh's law of scattering ( $I = Kr^6n$  for each particle, or  $I = Kr^3$  for a constant mass-concentration) has been verified by Mecklenburg using small sulfur particles. *Kolloid-Z.*, 16, 97 (1915).

so that

$$dn = \frac{3t \, dx \left( \frac{dS}{dr} \right)}{8 \pi \rho_p K^2 x^2} \quad (6)$$

This number of particles contributes, according to Equations 5 and 6 an increment to the intensity given by

$$\begin{aligned} dI &= \frac{hr^2 \cdot 3t \, dx \left( \frac{dS}{dr} \right)}{8 \pi \rho_p K^2 x^2} \\ &= \frac{3h dx \left( \frac{dS}{dr} \right)}{8 \pi \rho_p x} \end{aligned}$$

Thus

$$\frac{dI}{dx} x = \frac{3h}{8 \pi \rho_p} \left( \frac{dS}{dr} \right) \quad (7)$$

The exact distribution function could hence be obtained from the experimental values of  $dI/dx$  if the value of the constant  $h$  were determinable.<sup>6</sup> Without the value of  $h$  the actual values of  $dS/dr$  cannot be determined, but merely values proportional to  $dS/dr$ . The areas under the distribution curves obtained in this investigation do not give the actual mass of particles, but merely numbers proportional to the mass. The value of  $h$  might be calculated by comparing the experimentally determined area under the complete distribution curve with the known mass of dispersed material. This, however, could not be done very accurately in this investigation, due to the instability of the systems, and the fact that the distribution curves cannot be determined with any great accuracy near either end, and hence extrapolating them to cut the axis of abscissa would be uncertain.

### Apparatus

The apparatus consisted of a glass cell, C (Fig. 1),  $10 \times 10 \times 1$  cm. containing the dispersed system. A black opaque plate of bakelite was placed in the bottom of the cell to cut down surface reflection, and another, fitted into the cell to serve as a background, was so adjustable that its distance from the front could be varied. The cell was placed in a fixed position in a larger cell, A, which in turn was cemented in place in a water thermostat, T, in such a way that water could circulate on all sides except front and top. The front of the cell, A, was flush with the thermostat, and contained an open slot through which the cell C could be photographed. On either side of the thermostat were two illumination boxes, B, containing 100-watt Mazda lamps. The windows, X, in both A and B were masked to  $3 \times 9$  cm. openings. The inside and outside of A were painted dull black, as was also the inside of T. The water in the thermostat was stirred by bubbling air through glass tubes containing several fine orifices. The thermostat was provided with an insulated top. The temperature was held at  $25^\circ \pm 0.02^\circ$ .

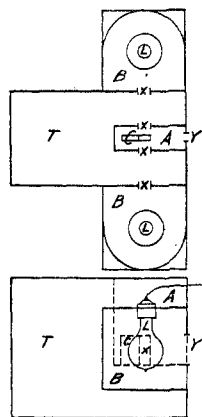


Fig. 1.

<sup>6</sup> Professor Warren Weaver of the Mathematics Department of the University of Wisconsin, derived this relationship.

The camera lens was a rapid rectilinear portrait lens with 39cm. (16-inch) focal length. Stop f 22 was used for this work. A sector wheel geared down from an electric motor was used to control the exposures. A variable slot in the wheel made it possible to make exposures from 0.5 to 2 seconds long. Pictures were taken full size. The plates were Eastman D-C (double coated) 10 × 12.5 cm. (4 × 5 inches). The plate holder was arranged so that four exposures could be taken on each plate. The plates were developed for three minutes in a hydroquinone-potassium metabisulfite contrast developer at 8–12°.

The photometer used was a König-Martens instrument adapted for the purpose by the authors and J. B. Nichols of this department. Brass carriages operated by micrometer screws and carrying a neutral wedge No. 25, density 4.0, and compensating wedge No. 25C made by the Eastman Kodak Company were fastened to the front of the photometer so that each of the wedges covered one of the photometer slits. The instrument was used as a zero instrument. With the eyepiece nicol set at 45°, equality of transmissions through the photographic plate and compensating wedge on the one side and the neutral wedge on the other was obtained by appropriate adjustment of the neutral wedge. The densities were thus determined in terms of the neutral wedge. The green mercury line (5461 Å.) was used as a source of light in the photometric work.

As a check on the calibration of the neutral wedge, the densities of two photographic strips were determined separately and superimposed upon each other.

Let  $T$  be the transmission of strips and  $D$  the corresponding density.

$$\begin{array}{l} \text{Then} \\ \log \frac{1}{T_A} = D_A \\ \\ \log \frac{1}{T_B} = D_B \\ \text{Sum} \end{array} \quad \frac{\log \frac{1}{T_A T_B} = D_A + D_B}{}$$

$T_C$  (the transmission when  $T_B$  is superimposed on  $T_A$ ) =  $T_A T_B$

$$\log \frac{1}{T_C} = D_C = \log \frac{1}{T_A T_B} = D_A + D_B$$

This relationship was checked for both high and low densities, showing that no correction of the neutral wedge calibration was necessary.

The dispersed systems used were all benzene-in-water emulsions prepared according to the arbitrary standard method given by Kraemer and Stamm.<sup>2†</sup> All samples were homogenized twice in a Briggs homogenizer with a pressure in the receiver of 14 cm. of mercury. The soaps were prepared according to the method given by White and Marden<sup>7</sup> from pure palmitic acid and alkali carbonates.

### Photographic Density Corrections

It was pointed out above that one of the two essentials for determining the distribution of the size of particles by this method is the accurate knowledge of the true density-height relationship on the photographic plate resulting from the unimpaired intensity at the front of the cell. Hence, it became necessary to find whether the photographic plate recorded the intensities in their proper ratios under the conditions of the experiments. For this reason the characteristic curve of the photographic plate was determined by exposing plate strips through the neutral wedge long enough to give the same range of density that was obtained from the

<sup>7</sup> White and Marden, *J. Phys. Chem.*, **24**, 618 (1920).

emulsions exposures. Fig 2 gives the results from such exposures. The curves are all linear between densities two and beyond seven. The part below a density of two corresponds to the under-exposed zone. Though the time of development was exactly the same for all of the exposures, the slope of the straight line portion, or "contrast" of the plate varied from plate to plate (from 1.60-2.00 with an average of 1.90). As the plates were from different boxes purchased at different times, this deviation is to be expected. The fact that these plates differ slightly in "contrast" requires that all of the photographs for a single determination be made on the same plate. It will be shown later that practically no error will result in the determination by neglecting the deviations from the linear relationship below a density of two, as these low density values correspond only to the initial part of the final distribution curves.

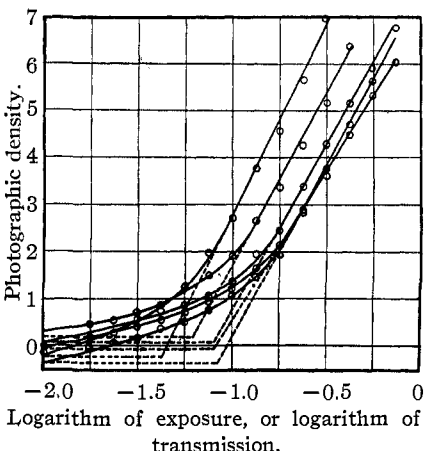


Fig. 2.—Characteristic curve of photographic plates.

Photographs of uniformly dispersed emulsions do not give a uniform density across the whole length of the picture, but show a certain amount of end shadowing at the bottom surface of the cell and at the upper meniscus (Fig. 3). By changing the masking of the source of illumination and the camera angle, this

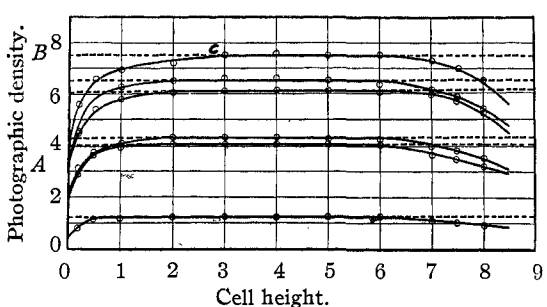


Fig. 3.—End-shadowing correction.

may be modified but not removed. As the emulsion is diluted, and the corresponding photographic density decreased, the extent of the end shadowing is decreased proportionately. Both the degree of shadowing at the bottom of the cell and the height to which it extends upwards are proportional to the photographic density at the center of the cell. At the top of the cell only the degree of shadowing seems to be pro-

portional to the density at the center of the cell. This difference has not been explained, and for this reason readings near the meniscus have been avoided. The difficulty might have been partially avoided by masking the illumination source so that the meniscus would not have been illuminated or, better yet, by using an improved source of illumination that would give more nearly parallel light. As will be shown later, readings near the top were not required, so no attempt was made to make corrections at this end. Table I shows the relationship of the end shadowing at the bottom of the cell to the density at the center of the cell for the curves of Fig. 3.

TABLE I  
END SHADOWING CORRECTION

Density $\frac{OB}{AB}$	Deviation at zero height $\frac{AB}{AB}$	Deviation	Extent inward of shadowing $\frac{BC}{BC}$	Extent inward
		density $\frac{AB}{OB}$		density $\frac{BC}{OB}$
1.25	0.75	0.60	0.55	0.44
4.05	2.20	.54	1.60	.39
4.30	2.30	.53	1.80	.42
6.15	3.25	.53	2.50	.41
6.60	3.60	.55	2.60	.39
7.55	4.15	.55	3.00	.40

As the density deviations are roughly proportional to the true densities, all of the curves may be approximately corrected for this end shadowing. For any definite cell height the ratio of the observed density, in the case of a uniformly dispersed emulsion, to the correction necessary to make the straight horizontal line is equal to the ratio of the observed density at the same height for any emulsion to its unknown density correction. To obviate any error from this approximate correction, measurements were made under conditions where this correction was small (in Fig. 7 by increasing the time of sedimentation). For the purpose of this investigation it is, hence, merely necessary to correct the photographic densities for end shadowing at the bottom of the cell to obtain the corrected density corresponding to the unimpaired intensity resulting from the scattering of the light.

#### Conversion of Intensities to Concentrations

The second consideration in the determination of the distribution of size of particles is that of transposing the intensity-height relationship  $dI/dr$  to that of  $dS/dr$ . This has been done in the first part of the paper from a theoretical standpoint. It remains merely to justify this theoretical development experimentally. A study of the effect of emulsion concentration on the scattering of light was therefore investigated. The black, opaque background was fixed in a vertical position 3 cm. from the front of the cell *C*. A freshly prepared 1% emulsion 0.0005 *N* in potassium palmitate was placed in the cell and photographed, and three other ex-

posures were made on the same plate at fractional concentrations of this value. The densities were determined with the photometer near the center of the plate so as to avoid the end-shadowing correction. A subtractive correction was applied for the slight fog on the unexposed part of the plate. The photographic densities were converted to cell intensities by dividing the absolute density by the average contrast slope obtained from the characteristic curves of the photographic plate (Fig. 2) and then taking the antilog, as  $D\alpha = \gamma \log I$ . A linear relationship between the intensities  $I$  and concentration  $C$  was obtained. Fig. 4 gives the results of such measurements. The three lower curves, B, C and D, represent check results with slopes 1.15, 1.07 and 1.02, respectively. The vertical displacement is due to a slight difference in the inertia period of the plates, and has no significance here. The particles in these systems are not of a uniform size, but may be represented by a definite distribution of size. It is reasonable to conclude, however, that if but one size of particle were present, the intensity  $I$  would still be directly proportional to the concentration. In fact, this conclusion must hold unless the linear relation for the aggregate of sizes is caused by a complicated sort of compensation between the effects produced by the different sizes, a possibility which does not seem physically reasonable. Fig. 4A represents the intensity-concentration relationship for an emulsion similar to the others except that it was homogenized four times in a colloid mill instead of twice in the Briggs homogenizer. The mill gave a considerably smaller average size of particles. Distribution curves were determined by the method of Kraemer and Stamm<sup>2f</sup> for emulsions homogenized in the two ways given above. The Briggs homogenizer gave an emulsion with the maximum of its distribution curve corresponding to a radius 1.35 times as great as that obtained with the mill. This ratio represents approximately that of the average radii for the particles in the two emulsions. Now if the intensity of the scattered light varies as the total surface of the particles, the average surface of the particles times the number =  $4 \pi r^2 \times \frac{3C}{4 \pi r^3} = \frac{3C}{r}$ . As  $C$  is the same for the two emulsions, it is obvious that the ratio of the total surface of the emulsion with the smaller particles to that with the larger is 1.35. This should be the ratio of the slopes of the two curves. This is the case, for A has a slope of 1.51, which is 1.40 times the average of the

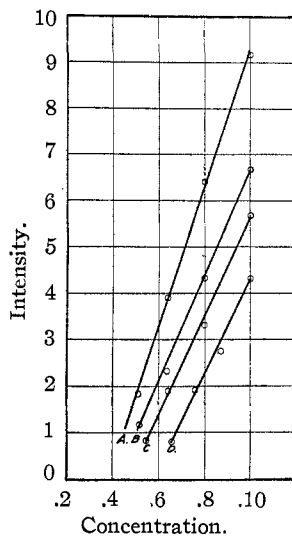


Fig. 4.

The Briggs homogenizer gave an emulsion with the maximum of its distribution curve corresponding to a radius 1.35 times as great as that obtained with the mill. This ratio represents approximately that of the average radii for the particles in the two emulsions. Now if the intensity of the scattered light varies as the total surface of the particles, the average surface of the particles times the number =  $4 \pi r^2 \times \frac{3C}{4 \pi r^3} = \frac{3C}{r}$ . As  $C$  is the same for the two emulsions, it is obvious that the ratio of the total surface of the emulsion with the smaller particles to that with the larger is 1.35. This should be the ratio of the slopes of the two curves. This is the case, for A has a slope of 1.51, which is 1.40 times the average of the



other three. Hence, it seems that for the sizes of particles studied, the assumption that the intensity of the scattered light is proportional to the square of the radius may be accepted. Such a comparison of the slopes of the intensity-concentration curves would serve as a means of obtaining the ratios of the average sizes of the particles in a disperse system, the average diameter of whose particles is at least two to three times the wave length of light. It would serve for systems in which the difference of density between the dispersed phase and the dispersion medium is so small that sedimentation methods cannot be resorted to.

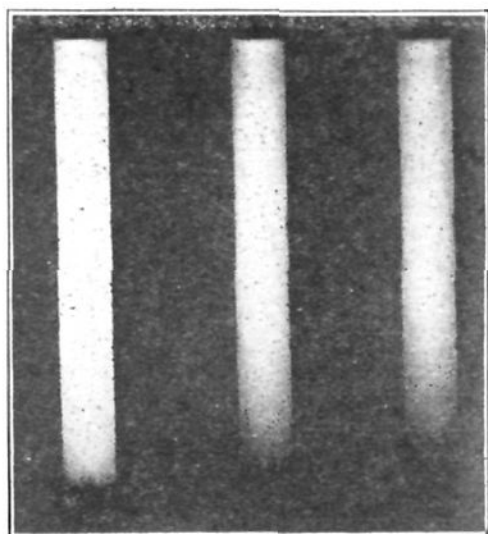
It is of interest to know the effect of absorption of light within the emulsion itself. Hence, photographs were taken with the emulsion concentration held constant, 1% of benzene and the distances of the opaque plate from the front of the cell varied. This also gave a straight line relationship. Evidently there is no effective absorption of the light by a system such as this which is illuminated from the sides. It does not follow from this that the absorption constant for the emulsions used is zero, for entirely different results might be obtained under transmission conditions.

Another factor worthy of consideration is that of the self illumination of the particles. In the case of a uniformly dispersed system, after several multiple scatterings of light have taken place, the particles in an element of volume near the center of the cell illuminate the particles in elements of volume just above and just below to the same extent. This is not necessarily true after sedimentation has taken place, as there is then a concentration and particle size gradient. However, if the concentration and particle size gradient contains no abrupt change, the error in neglecting this correction for unbalanced self illumination may be small. In the density-height curves given in Fig. 6 it is evident that the only sharp break in the curves occurs where the density suddenly changes from zero to an appreciable value. At these points the unbalanced self illumination might be quite pronounced. Fortunately, these points correspond only to the initial part of the distribution curves, and hence have but a slight effect on the nature of the curve. Disregarding this self illumination factor seems, further, perfectly justifiable in that the distribution results by this method check very well with those obtained by microscopic count.

### Distribution Determinations

Photographs were taken with the opaque plate 2 cm. from the front of the cell for fresh 1% benzene emulsions 0.0005 *N* in potassium palmitate. Exposures were made immediately and after sedimentation for 0.5, 1.0 and 1.5 hours. (Fig. 5 shows a print of a similar plate.) Fig. 6 gives the curves for the variation in density with cell height, and Table II the corresponding data. It was shown under the heading of "Photographic Density Corrections" that the true density corresponding to the unimpaired

intensity can be obtained over the range required merely by correcting for the end shadowing at the bottom of the cell. The dotted lines in Fig. 6 show this correction and indicate that it decreases in value as the sedimentation period increases. It was shown under the heading of "Conversion of Intensities to Concentrations" that the theoretically derived equation expressing the relationship between  $dS/dr$  and  $dI/dx$  is valid. Having made the measurements and corrections in terms of photographic



A. B. C.

Fig. 5.—Sedimentation photograph for a 1% benzene emulsion, 0.0005 *N* in potassium palmitate. *A*, Before sedimentation; *B*, After 30 minutes; *C*, After 45 minutes.

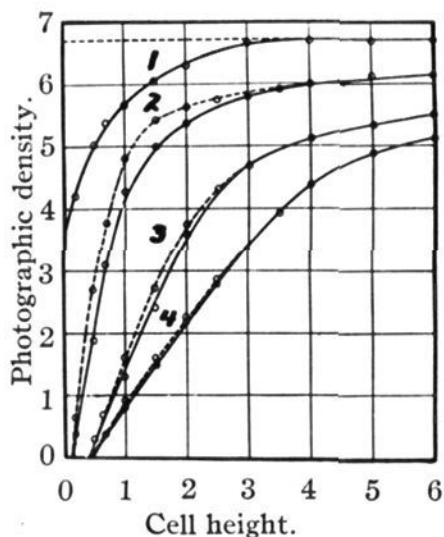


Fig. 6.—Sedimentation curves for a 1% benzene emulsion, 0.0005 *N* in potassium palmitate. 1, before sedimentation; 2, after 30 minutes; 3, after 60 minutes; 4, after 90 minutes.

densities, rather than in terms of cell intensities, Equation 7 may be expressed as follows.

$$\frac{dD}{dx} = \frac{d \log I}{dx} = \frac{1}{I} \log e \frac{dI}{dx}$$

$$\frac{dD}{dx} Ix = \frac{3h \log e}{8 \pi \rho_p} \cdot \frac{dS}{dr} \quad (8)$$

Hence, by taking the slope of the corrected density-height curve and multiplying it by the corresponding height and intensity, a term proportional to  $dS/dr$  is obtained. This is plotted against the corresponding value of  $r$  obtained from Equation 2. Table III gives the calculations for the data of Table II. From this the curves of Fig. 7*B* were drawn. Figs. 7*A* and *C* give the corresponding results with 0.0005 *N* cesium palmitate and sodium palmitate. Runs were made using 0.0005 *N* palmitic acid as emulsifier, and with 0.0005 *N* potassium palmitate and various benzene concentrations. The positions of the maxima are given in Table IV.

The distribution curves represent the distribution of particles of all sizes that have not settled out completely up to the time of photographing.

TABLE II  
PHOTOGRAPHIC DENSITY-HEIGHT RELATIONSHIP FOR A 1% BENZENE EMULSION, 0.0005  
N IN POTASSIUM PALMITATE

Height Cm.	Densities for initial exposure	Densities for exposures after sedimentation of		
		0.5 hr.	1.0 hr.	1.5 hrs.
0.2	5.90	2.10	..	..
.5	6.75	3.60	2.00	1.80
.7	7.10	4.80	2.40	2.10
1.0	7.35	6.00	3.00	2.50
1.5	7.75	6.70	4.10	3.20
2.0	8.00	7.05	5.30	3.90
2.5	..	..	..	4.50
3.0	8.40	7.50	6.40	..
3.5	..	..	..	5.60
4.0	8.40	7.70	6.85	6.10
5.0	8.40	7.85	7.05	6.60
6.0	8.35	7.85	7.20	6.85

1.70 density of unexposed portion of plate to be subtracted.

These densities are expressed in terms of centimeters along the neutral wedge and must be multiplied by 0.247 to obtain the absolute densities.

TABLE III  
DISTRIBUTION CALCULATIONS FOR A 1% BENZENE EMULSION, 0.0005 N IN POTASSIUM  
PALMITATE

x	0.5 hr.					1.0 hr.					1.5 hrs.				
	in $\mu$	r	I	dD/dx	dS/dr	in $\mu$	r	I	dD/dx	dS/dr	in $\mu$	r	I	dD/dx	dS/dr
0.2	1.94	1.22	6.95	1.69	..	..	..	..	..	..	..	..	..	..	..
.5	3.07	2.25	5.23	5.88	2.17	1.09	2.67	1.46	1.77	1.03	1.46	1.752	..	..	..
.7	3.64	3.12	3.82	8.35	..	..	..	..	..	..	..	..	..	..	..
1.0	4.34	4.27	2.04	8.70	3.07	1.64	2.54	4.17	2.50	1.31	1.40	1.83	..	..	..
1.5	5.32	5.11	.743	5.70	3.76	2.28	2.20	7.53	3.07	1.61	1.35	3.26	..	..	..
2.0	6.14	5.43	.357	3.88	4.34	3.08	1.52	9.37	3.55	1.92	1.31	5.03	..	..	..
2.5	..	..	..	..	..	..	..	..	3.96	2.34	1.25	7.32	..	..	..
3.0	7.52	5.76	.157	2.72	5.32	4.09	0.635	7.80	4.34	2.80	1.15	9.66	..	..	..
4.0	8.68	6.03	.086	2.07	6.14	4.68	.293	5.48	5.02	3.73	0.643	9.60	..	..	..
5.0	..	..	..	..	6.86	4.96	.180	4.47	5.61	4.34	.343	7.45	..	..	..
6.0	..	..	..	..	7.52	5.19	.128	3.99	6.14	4.68	.214	6.00	..	..	..

The fact that the curves for the shorter sedimentation periods give a larger amount of the smaller particles than those for a greater period is due to the fact that convection currents at the beginning of the run prevent the immediate attainment of a steady state of sedimentation. The particles move a shorter distance in a given time than Stokes' law requires, and hence appear to be smaller than they actually are. As the sedimentation period increases, this time for the attainment of the steady state becomes a smaller and smaller part of the total time, and the sedimentation results approach their true value. Fisher and Odén<sup>2b</sup> found that such convection currents in the systems they studied persisted for fully an hour.

As another check on the accuracy of the assumption in regard to the effect of the particle size on scattering of light, a number of microscopic

determinations were made; 300 to 1000 particles were measured per run, and placed into size classes. The smallest class measured was of the order of  $0.5 \mu$  in radius. Multiplication of the cube of the class size by the number of particles of that size gave a number proportional to the mass of particles of that size  $\Delta S/\Delta r$  (where  $S$  is taken for 100 particles). These values were plotted against the corresponding values of  $r$  to give the curves in Figs. 8 and 9. The values of the maxima in Fig. 8, as well as the general shape of the curves, check very nicely with those of Fig. 7, and those of Fig. 9 with values in Table IV. Hence it is evident that the assumption regarding the effect of the number and the size of the particles upon their scattering power is valid for the sizes of particles studied.

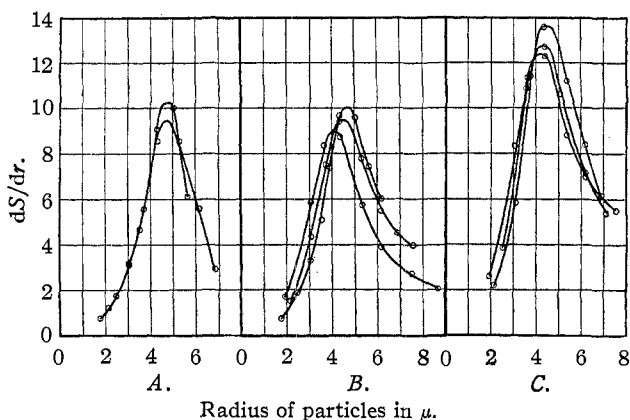


Fig. 7.—Distribution curves for 1% benzene emulsions, by photographic means. A, 0.0005  $N$  in cesium palmitate; B, 0.0005  $N$  in potassium palmitate; C, 0.0005  $N$  in sodium palmitate.

The positions of the maxima obtained for the different soaps, cesium, potassium and sodium (Figs. 7 and 8) are the same. This shows that the positions of the mass maxima are not dependent on the nature of the emulsifying agent as are the maxima on the number basis obtained by Finkle, Draper and Hildebrand<sup>8</sup> and Harkins.<sup>9</sup> The data from the microscopic count gave no number maxima. Cesium, however, showed a considerably larger number of the small particles, potassium less and sodium still less. It is possible that if measurements could have been carried to smaller sizes, a shift in the number maxima, as obtained by these other workers, might have resulted. The reason for the differences in the results on the two bases is not obvious, and it is hoped that by further study a substantial theory of emulsification covering this may be evolved.

<sup>8</sup> Finkle, Draper and Hildebrand, *THIS JOURNAL*, **45**, 2780 (1923).

<sup>9</sup> Harkins, *Science*, **59**, 463 (1924).

It is of special interest to note the shift in the maxima with changes in the benzene concentration, and constant soap content (0.0005 *N* in po-

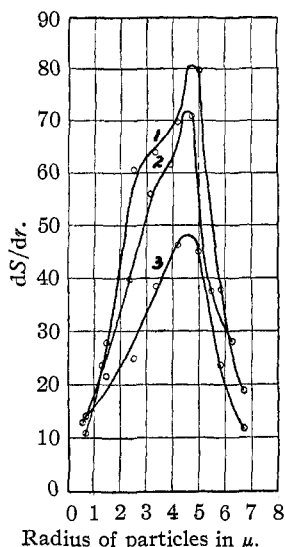


Fig. 8.—Distribution curves for 1% benzene emulsions, by microscopic means. 1, 0.0005 *N* in sodium palmitate; 2, 0.0005 *N* in potassium palmitate; 3, 0.0005 *N* in cesium palmitate.

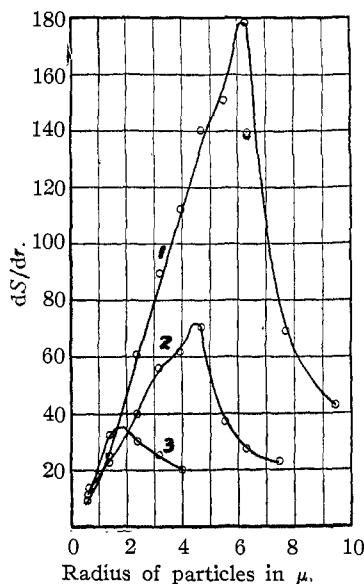


Fig. 9.—Distribution curves for benzene emulsion, 0.0005 *N* in potassium palmitate, by microscopic means. 1, 2% benzene; 2, 1% benzene; 3, 0.5% benzene.

tassium palmitate), Fig. 10. The size of the particles corresponding to the maximum in the mass-distribution curves is decreased exponentially as the relative amount of stabilizing agent is increased. The values were

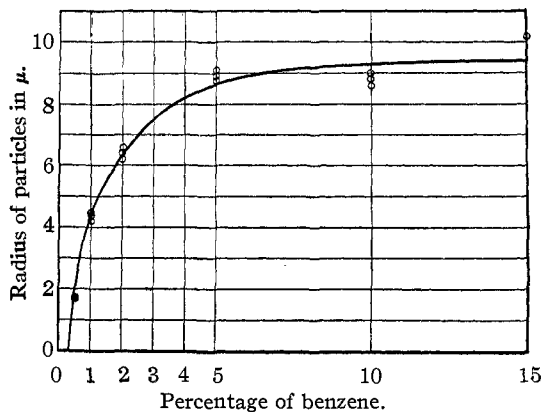


Fig. 10.—Shift in mass maxima with concentration.

obtained by three different methods as indicated in Table IV. The last result for potassium palmitate in Table IV (5% of benzene 0.0025 *N* in potassium palmitate) gives a maximum at a larger radius than that for 1% of benzene 0.0005 *N* in potassium palmitate, in which the benzene and soap are present in the same ratio. This indicates that the efficiency of homogenization increases with dilution, and accounts for the fact that

TABLE IV  
RADIUS CORRESPONDING TO MASS MAXIMUM FOR VARIOUS EMULSIONS DETERMINED BY DIFFERENT MEANS

Soap	Conc. of soap <i>N</i>	Vol. % of benzene	Radius at maximum $\mu$	Method	Remarks
Potassium palmitate	0.0005	15.0	10.2	S <sup>a</sup>	Data from paper of Kraemer and Stamm
		10.0	8.8	S	
		10.0	9.0	S	
		10.0	8.6	S	
		5.0	8.9	S	
		5.0	8.8	S	
		5.0	9.1	M	1067 particles meas.
		2.0	6.3	P	0.5 hr. sedimentation
		2.0	6.5	P	0.75 hr. sedimentation
		2.0	6.2	M	507 particles meas.
		1.0	4.1	P	0.5 hr. sedimentation
		1.0	4.5	P	1.0 hr. sedimentation
		1.0	4.7	P	1.5 hrs. sedimentation
		1.0	4.5	M	456 particles meas.
		1.0	4.5	M	489 particles meas.
		0.5	1.7	P	2.0 hrs. sedimentation
		Palmitic acid	0.0025	5.0	6.5
0.0005	5.0		12.1	S	
	5.0		12.5	S	
	5.0		12.0	M	771 particles meas.
	1.0		6.9	P	0.267 hr. sedimentation
	1.0		6.6	P	0.50 hr. sedimentation
	1.0		6.6	P	0.75 hr. sedimentation
	1.0		6.7	P	0.267 hr. sedimentation
	1.0		6.5	P	0.517 hr. sedimentation
	1.0		6.5	P	0.75 hr. sedimentation
Sodium palmitate	0.0005	1.0	4.2	P	0.50 hr. sedimentation
		1.0	4.3	P	0.75 hr. sedimentation
		1.0	4.5	P	1.00 hr. sedimentation
		1.0	4.7	M	676 particles meas.
Cesium palmitate	0.0005	5.0	8.8	M	307 particles meas.
		1.0	4.7	P	1 hr. sedimentation
		1.0	4.8	P	1.5 hrs. sedimentation
		1.0	4.5	M	1076 particles meas.

<sup>a</sup> Sedimentation method of Kraemer and Stamm (Ref. 2 f), following the rate of sedimentation of the dispersed phase passing a definite boundary. M. Microscopic method. P. Photographic method.

the smaller particles are smaller than those obtained by Harkins, who used 50% benzene emulsions 0.1 *N* in soaps.

A further study of the theory of emulsification is now in progress, using this method of determining the distribution of size of particles, as well as that of Kraemer and Stamm.<sup>2f</sup>

The authors are especially indebted to Dr. E. O. Kraemer, National Research Council Fellow, for his aid during the senior author's absence, in evolving the theoretical aspects of the paper, and for making innumerable suggestions in carrying out the work.

### Summary

A new method has been developed for the determination of the distribution of the size of particles using scattered light.

In the case of the emulsions studied, the scattering of light varies as the surface or square of the radius of the particles, indicating that true reflection is taking place.

It has been shown that the ratio of the average sizes of the particles in dispersed systems whose diameters are at least two to three times the wave length of light may be determined directly from the ratio of the slopes of the intensity-concentration curves.

Mass-distribution curves have been obtained which agree very well with those calculated from microscopic measurements.

Different alkali soaps do not shift the mass maxima, although microscopic measurements indicate an increase in the number of small particles in going from sodium to potassium to cesium soaps.

An increase in the benzene concentrations, with the amount of stabilizer constant, causes an exponential increase in the radius corresponding to the mass maxima.

An increase in the benzene concentration, with the ratio of benzene to stabilizer constant, gives maxima corresponding to a larger size of particles.