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A Nephelometric Study of Silver Bromide Sols

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"A NEPHELOMETRIC STUDY

OF SILVER BROMIDE SOLS"

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Colorimetry measures the quantity of absorbed light; nephelometry measures the quantity of reflected light.

Nephelometry possesses certain advantages not to be found in other quantitative methods. The average worker is accustomed in most cases to estimating relatively large amounts of substances by gravimetric means, the limitations of which are well known. Insolubility, knowledge of composition, purity, rapid filtration, accurate weighing, constancy of ignition—many of these are sometimes difficult in practice to attain. Nephelometric determinations often may be carried out without the necessity of accomplishing the above.

The main advantages of nephelometry may be classified:

1. The small amounts of reagents used seldom makes the cost a factor.

2. The diluteness often eliminates interfering substances and color; it insures a more complete control of the media of precipitation.

3. The nature and composition of the precipitant and precipitate need not be known.

4. Occlusion and adsorption in many cases do not influence the accuracy.

5. The ability to use organic reagents unsuited for ordinary gravimetric procedures means almost unlimited methods available.

6. Whereas protective colloids are a hindrance to many procedures, in nephelometry they become beneficial.

7. The extreme sensitivity of the nephelometer will detect substances not easily determined by other methods.

Kober's and Egerer's[3] reagent for phosphorus will detect 1.0 part in 333 million parts of water.

The earliest real nephelometer was introduced in 1894 by Richards[4] to compare opalescent precipitates. The instrument consisted essentially of two test tubes covered by sliding jackets to regulate the quantity of incident light. The tubes were inclined slightly to permit the observer to look into both. When the opalescence was equal, the precipitate was taken as inversely proportional to the lengths exposed to the light.

In 1904, Richards and Wells[5] modified the first nephelometer by introducing a light-tight box and a set of measuring prisms, increasing the accuracy to within a few per cent. Although the apparatus was excellent for the correction of certain atomic weight determinations, Richards believed nephelometry was not suitable for general analytical work, due to his unfortunate experiences with silver chloride suspensions, which later were shown to be very difficult to obtain in a suitable condition for such measurements.

Kober[6], in 1912, introduced the first nephelometer giving reliable results with but a few readings. A Duboscq colorimeter was converted to a nephelometer by painting the plungers black

(3) Kober and Egerer, J. Am. Chem. Soc., **37**, 2375 (1915).

(4) Richards, Proc. Am. Acad. Arts Sci., **30**, 385 (1894).

(5) Richards and Wells, Am. Chem. J., **51**, 235 (1904).

(6) Kober, J. Biol. Chem., **13**, 485 (1912-13).

and introducing a special receptacle cup. Most modern instruments are quite similar. They consist primarily of a constant source of lateral illumination, a cup for holding the suspensions, plungers for measuring the height of the illuminated column, prisms for accurate split-field viewing, and an easily read scale and vernier[7].

Theory of Nephelometry

The theory of nephelometry involves the explanation of the scattered visible light coming at right angles from an illuminated suspension. The concentration of the suspension is related to the intensity of the reflected light. Although part of the visible light may be due to refraction, it is included in the term "reflected light". According to Kleinman[8]: "The light coming from a turbidity at right angles to the incident light consists of refracted light, pure light of reflection, or a mixture of these, depending upon the size of the particles composing the suspension. The total amount of scattered light certainly depends upon the size and the number of the particles"

If all the reflected light from a suspension were to reach the surface unaltered, the formation of an expression to show the relationship of incident and reflected light in various concentrations would be relatively simple. But it must be seen that some of the light from the lower layers in a column of suspension will be absorbed by the supernatant layers. The index of refraction of the particles and the solvent, and the varying indices of refraction and absorption of each wave length of light will also influence the character of the scattered light. Any law including all these factors would be extremely difficult to develop and as yet remains unsolved. Fortunate

(7) For a complete description of various types of nephelometers, see Yoe, "Photometric Analysis", Vol. II, John Wiley and Sons Inc., New York, 1929.

(8) Yoe, loc. cit., page 68.

the average nephelometric determinations are usually made by comparison and within certain well-defined limits, so that many of the influences are eliminated.

Ignoring the refractive indices of the dispersed phase and dispersion medium (alike for the same substance in suspension), we may write from Rayleigh's Law[9]:

$$I_s = kI_0 \frac{mv^2}{\lambda_4} \qquad (1)$$

Where I_s is the scattered light; I_0, the incident light; m, the number of particles; v, the average volume of particles; and λ, the wave length of the scattered light. Since the concentration $c = mvd$, where m = number, v = volume, and d = density of the particles, then

$$I_s = kI_0 \frac{cv}{d\lambda_4}$$

Hence, if the size of the particles is constant, the reflected light is proportional to the concentration. This is fundamental to nephelometry. This direct proportionality, however, only holds for definite conditions of turbidity involving a single point of pure Tyndall light. Consideration of the total Tyndall light will not necessarily yield a direct proportion between scattered light and concentration. P. V. Wells[10] hasinddicated that for large thicknesses of suspension and considering the total Tyndall light, the scattered light is an exponential function of the concentration.

The relation between the intensity of scattered light and the depth of suspension may be expressed as follows: If l is the length of the column, and I_0 is the intensity per unit thickness of column,

(9) Thomas, "Colloid Chemistry", McGraw-Hill Book Co.,

New York, 1934, page 40.

(10) Wells, Chem. Reviews, 3, 331 (1927).

then the illumination due to a section of thickness $\underline{dx}$ and a distance $\underline{x}$ from the top of the column will be $dI = I_o dx$. All of this light does not reach the top because of absorption and reflection. If we can apply Lambert's Law [11] to this suspension, the fraction of transmission will be e^{-kx}, so that:

$$dI = e^{-kx} I_o dx$$

Integrating:

$$I = \int_0^L e^{-kx} I_o dx \qquad (2)$$

$$= \frac{I_o}{k} (1 - e^{-kL})$$

For small values of kL we have approximately:

$$e^{-kL} \cong 1 - kL$$

Substituting in equation (2) we find:

$$I = \frac{I_o}{k} kL = I_o L \qquad (3)$$

$$I_o = \frac{I}{L}$$

In this work, the transmitted light is set equal to a fixed standard. I is a constant, hence the intensity of the reflected light will be proportional to the reciprocal of the column measured. Therefore, in experiments involving intensity as a function of the time, the reciprocal of the nephelometric reading may be plotted against the time.

Protective Colloids

In certain nephelometric determinations, the prepared

(11) Taylor, "A Treatise on Physical Chemistry", Vol. II, D. Van Nostrand, New York (1931), page 1461.

dispersions are not stable long enough to permit a series of readings to be taken at the maximum intensity. The use of gelatin, gum arabic, albumen, starches, and other such substances has been found to stabilize such suspensions at least for a convenient period.

Three possibilities arise in the use of such protective colloids[12]: (1) if the particles of the protective colloid such as gelatin are smaller than the particles of the suspension, the mutual adsorption will result in the formation of a protecting film of gelatin around the particles; (2) if the particles of gelatin are of the same size as the suspension, an arrangement similar to that in (1) is possible, but a lower protection prevails; (3) if the gelatin particles are much larger, then the dispersed particles are adsorbed on the surface of the protecting colloid.

In this treatise the first possibility assumes primary importance since the dilute solutions of gelatin used will no doubt give particles of gelatin approaching molecular size. Sheppard, Lambert and Keenan[13] have shown that gelatin is adsorbed on silver bromide and even after water digestion a monomolecular layer of gelatin is present on the grain.

The instability of "lyophobic" colloids is due to the natural repulsion between the suspended particles and the medium. In "lyophilic" colloids such as gelatin, these repulsive processes are absent. On the introduction of a lyophilic colloid to a lyophobic colloidal suspension, the former is adsorbed to the

(12) Weiser, "Colloid Chemistry", John Wiley and Sons, New York (1939), page 250.

(13) Sheppard, Lambert and Keenan, J. Phys. Chem., 36, 174-84, (1932).

lyophobic particles, giving their exterior the properties of a lyophilic colloid. This accounts for their greater stability.

The stabilization of salt colloidal solutions will be discussed in greater detail later. Gelatin and other lyophilic colloids stabilize suspensions of insoluble salts, such as the silver halides. The great sensitivity of photographic emulsions depends on this effect. The effect discussed in this paper, however, is due to a decrease in diffusion of ions rather than the prevention of coalescence of particles.

In this investigation we shall study the effect of time on the intensity of light reflection from dilute silver bromide dispersions, and the change of this time-turbidity curve affected by various concentrations of gelatin. We shall attempt to explain these effects by proposing a theory for the precipitation of silver bromide and for the effect of gelatin on this precipitating process.

THEORY OF SILVER BROMIDE PRECIPITATION

Dispersions may be classified into three general groups, namely: true solutions, colloidal solutions, and suspensions. True solutions of electrolytes consist of extremely small ions, their sizes being of the order of a few Ångstrom units and of the same order of magnitude as those of the molecules of the solvent. Such a solution does not scatter light; i.e., not Tyndall effect is observable. The particles are not resolvable by the ultramicroscope.

If a solution contains particles larger than about 100 Å, a distinct Tyndall effect may be observed[14]. Those particles larger than ten millimicrons are visible in the ultra-microscope. Such a suspension is ordinarily called colloidal.

Particles larger than one micron usually do not remain suspended over long periods of time[15]. Ordinary gravitational effect overcomes the Brownian Movement and repulsion of the particles, hence coagulation and precipitationmay take place from a suspension.

This paper deals with the formation of the intermediate colloidal state of suspended particles of silver bromide; i.e., those silver bromide particles which have the ability to reflect light, but which form fairly stable suspensions.

According to the present concepts of precipitation, the first particles formed are extremely small nuclei. By one means or another these nuclei grow larger until finally precipitation

(14) Kolthoff and Sandell, "Textbook of Quantitative
     Inorganic Analysis", The MacMillan Co., New York,
     1936, page 87.

takes place. It must be apparent then that in all precipitations, at some time the particles must be of colloidal dimensions. Harry Jones[16] concludes that "the colloidal solution, or at most the colloidal suspension is the natural condition of solid matter when first formed as the result of a reaction".

Many factors determine the particle size of the precipitate formed. The predominating influence has been qualitatively generalized by Van Weimarn[17] who formulated relative supersaturation with respect to the slightly soluble substance thus:

$$\frac{Q - S}{S}$$

where Q is the total concentration and S is the solubility of coarse crystals. Although the expression is not quantitative, it is possible by changing $\frac{Q - S}{S}$ of a given precipitate to change the size of the particles between wide limits. When the supersaturation is small, relatively few nuclei form. These particles grow slowly to form fairly large and perfect crystals.

Since the speed of nuclei formation is proportional to the degree of supersaturation, an increase in supersaturation increases the number of nuclei or primary particles formed. Kolthoff and Sandell[18] state that: "In the most extreme case all the material present is precipitated in the form of primary particles which cannot grow at the cost of the dissolved material, since the solution is no longer supersaturated. The size of such a primary precipitate can change by secondary processes only". This type of

(16) Jones, "New Era of Chemistry", D. Van Nostrand Co., New York (1913)

(17) Van Weimarn, Die Allgemeinheit des kolloiden zustandes, Th. Steinkopff, Dresden (1925).

(18) Loc. cit., page 93.

change in particle size is known as "aging" and is the most
important influence in silver halide precipitation since the
solutions are very supersaturated.

It has been proven that the solubility of particles decreases
with increasing size. Hulett[19] found a saturated solution of
ordinary gypsum to contain 2.080 grams of calcium sulfate per liter.
Upon shaking with very finely divided gypsum the content was
increased to 2.542 grams per liter.

When mixtures of large crystals and very small ones stand in
contact with each other, the small ones disappear and the large ones
increase in size. When a precipitate first forms there will be some
variation in particle size. In time, due to the above effect, the
larger crystals grow at the expense of the smaller. This will
continue until all of the particles are of fairly large size. This
phenomenon is known as "Ostwald Aging".

A more recent concept of aging has been given by Kolthoff[20]
and co-workers. Since recrystallization takes place very slowly as a
rule in solutions of extremely low solubility, Ostwald aging can not
account for the rapid growth of crystals in such precipitates as the
silver halides. Most inorganic precipitates have an ionic lattice.
Particles containing positive surface ions will attract those having
negative surface ions. Thus there will be a cementing together of
smaller particles to form larger aggregates. In the case of silver
halides this tendency to decrease in external surface is very pronounced

(19) Hulett, J. Amer. Chem. Soc., 27, 49 (1905).

(20) Kolthoff and Sandell, loc. cit., page 100. Also Kolthoff
and O'Brien, J. Chem. Phys., 7, 401 (1939).

Regardless of the mechanism used, when any precipitate stands, the smaller particles disappear and the larger particles increase in size. Aging then is always accompanied by a decrease in total external surface. Any method of determining this change in surface is a method of following the aging of a precipitate.

Exhaustive study of the changein optical properties of silver chloride suspensions with time by Wells[21], Kober[22], Kleinmann[23], and others has shown the reflected light from the suspension to increase for a time, pass through a maximum, and then decrease. This indicates an increase in total external surface to a maximum, and finally a decrease.

Many explanations have been offered for this phenomenon. Kober[24] suggests a soluble complex between silver chloride and silver nitrate which slowly hydrolyzes to precipitate silver chloride. Lamb, Carleton and Meldrum[25] give two influences at work. The first, a precipitation of dissolved silver chloride causing an increase in surface, proceeds with decreasing velocity. The second, a coalescence or growth of particles causing a decrease in surface, continues until actual settling takes place. Therefore, the opalescence will first increase and then decrease.

The same general curve has been noted in the work of the writer

(21) Wells, Am. Chem. J., 35, 99 (1906).

(22) Kober, J. Ind. Eng. Chem., 10, 556 (1918).

(23) Kleinmann, Biochem. Zeit., 99, 141 (1919).

(24) Loc. cit.

(25) Lamb, Carleton and Meldrum, J. Am. Chem. Soc. 42, 251 (1920).

on silver bromide. An explanation similar to that of Lamb, et. al., appears to be satisfactory. Since the relative supersaturation of the solution is large, a large number of silver bromide nuclei form. These particles increase in size in the presence of the supersaturated solution by the "plating out" of silver ions and bromide ions on the crystal lattice. Since we can expect a more or less homogeneous distribution of these nuclei, their increase in size will be quite uniform and will continue until the point of saturation is reached.

For particles whose size is infinitesimal compared with that of light, Rayleigh[26] derived the relation that is applicable. For a given system in a nephelometer column, with a constant light source,

$$I = knv^2$$

This has fair applicability up to a diameter of several hundred millimicrons. In the first part of the preliminary particle formation, this is probably valid. As the particles increase in size, however, they begin to act as macroscopic reflectors, where the intensity of scattered light becomes proportional to the surface exposed.

There will be, therefore, a very great increase in intensity of reflected light as long as Rayleigh's relation holds. A small increase will occur when the second condition exists, since here the reflection will be proportional to $v^{2/3}$. Assuming that this condition exists at the equilibrium point that is reached, then the following derivation is valid:

(26) Rayleigh, Phil. Mag., 41, 107 (1871).

Since, in the dilute suspensions used in this investigation we can expect considerable homogeneity, the primary particles will remain about the same size. They will be formed instantly on the formation of the silver bromide, and will grow at the expense of the excess silver bromide in the vicinity of the particle. The rate of growth of these primary particles will depend on three factors, to which they will be proportional. They are: (a) the total surface available on the particles, (b) the concentration of silver bromide in the surrounding solution in excess of the saturated solution, and (c) inversely as the solubility of the precipitated silver bromide.

The first effect is equal to $4\pi nr^2$ where n is the number of particles of radius r. The excess concentration of silver bromide in the surrounding solution will be given by:

$$V - 4/3 \pi nr^3$$

where V represents the total volume of silver bromide that finally precipitates out in this solution.

The third effect is more difficult to estimate. It has been shown that the solubility of a substance is related to the size of the particles by the relation[27]:

$$\frac{RT}{M} \ln \frac{Sr}{S} = \frac{2\sigma}{dr} \tag{4}$$

where Sr is the solubility of particles with radius r, S the normal solubility for macroscopic particles, σ the surface tension, and d the density. All of the quantities are constant in this case, except Sr and r, which are related by:

$$\ln Sr = k/r$$

which may also be written:

$$Sr = e^{kr} \tag{5}$$

Hence, the rate of growth of primary particles will be given by:

$$\frac{dv}{dt} = 4\pi nr^2 \frac{dr}{dt}$$

$$= k^{11} \cdot 4\pi nr^2 \cdot (V - 4/3 \pi nr^3) e^{-k/r}$$

Then

$$\frac{dr}{dt} = k^{11} (V - 4/3 \pi nr^3) e^{-k/r}$$

Introducing our assumption of light refelction, we find:

$$\frac{dI}{dt} = \frac{d}{dt} k^{111} \cdot 4\pi nr^2$$

$$= 8k^{111} \pi nr \frac{dr}{dt}$$

$$= k_1 nr(V - 4/3 \pi nr^3) e^{-k/r} \tag{6}$$

combining all constants.

It is apparent from this that the intensity increases very rapidly at first, but finally arrives at a maximum when the solution becomes saturated. There is no further growth at this point when

$$V = 4/3 \pi nr^3$$

It should be pointed out that this relation has limited applicability, since in the early formation of the primary particles, Rayleigh's Law applies, so that the increaseof intensity with time will be much greater here. It is difficult to estimate at what point Rayleigh's Law ceases to apply and where the laws of macroscopic reflection set in. The actual mechanism of this

(27) Kolthoff and Sandell, loc. cit., page 97.

transition is not known and will probably be quite complicated[28]. At any rate a theory based on these principles of nuclei formation will account for the change of intensity with time.

It is interesting to note that equation (6) would require that dI/dt pass through a maximum in this process as the radius r of the particles increases. The experimental procedure followed here would not permit the investigation of this point.

At the point at which this primary formation of particles is completed, we have a state of equilibrium, in which particles of silver bromide are suspended in a medium saturated with respect to it. If all particles were of the same size and the same state of perfection, a permanent equilibrium would result. However, the smaller and less perfect particles are more soluble than the others, so they tend to go into solution. As they do, the solution becomes supersaturated with respect to the larger crystals and silver bromide precipitates out on them. This becomes a cumulative process for, as solution continues, the smaller particles decrease in size, thus increasing their solubility.

By making a simplifying assumption, this process can be subjected to mathematical treatment. Let n_1 represent the number of larger particles of radius r_1 while n_2 represents the number of smaller particles and r_2 the radius of a smaller particle. The assumption that all the n_1 particles are about the same size and all the n_2 particles are about the same size is approximate, and our results cannot be subjected to too vigorousinvestigation.

If V represents the total amount of precipitate, then:

$$V = 4/3 \; \pi \; (n_1 r_1^3 + n_2 r_2^3)$$

(28) Wells, Chem. Reviews, 3, 331 (1927).

On integration we find:

$$n_1 r_1^2 \frac{dr_1}{dt} + n_2 r_2^2 \frac{dr_2}{dt} = 0 \qquad (7)$$

The rate of growth of the larger particles will depend on two factors: (a) the total surface exhibited by the particles upon which silver and bromide ions may crystallize, and (b) the rate with which the silver bromide dissolves from the smaller particles. This latter effect will be proportional to the solubility of the smaller particles, given by equation (5). Hence, we may write:

$$\frac{dv_1}{dt} = 4\pi n_1 r_1^2 \frac{dr_1}{dt} = k^1 (4\pi n_1 r_1^2) \, e^{k/r_2}$$

Then

$$\frac{dr_1}{dt} = k^1 e^{k/r_2} \qquad (8)$$

A   Again assuming that the intensity is proportional to the total surface:

$$\frac{dI}{dt} = \frac{d}{dt} k^{11} (n_1 r_1^2 + n_2 r_2^2)$$

$$= k^{11}(n_1 r_1 \frac{dr_1}{dt} + n_2 r_2 \frac{dr_2}{dt})$$

From equation (7) and (8) this leads to:

$$\frac{dI}{dt} = k^{11} n_1 r_1 (1 - \frac{r_1}{r_2}) \frac{dr_1}{dt}$$

$$= k_2 n_1 r_1 (1 - \frac{r_1}{r_2}) \, e^{k/r_2} \qquad (9)$$

We notice that at the beginning of this process, where all particles have about the same radius, the intensity remains constant. However, as soon as the smaller particles begin to dissolve and crystallization takes place on the larger particles (i.e., r_1 increases and r_2 decreases), the quantity in parenthesis begins to take on increasingly large negative values. Hence, the intensity will decrease.

The relationship will have limitedapplication, when it is kept in mind that as the small particles become infinitesimal in size,

they no longer obey the laws of macroscopic reflection. For the portions of the curves not too far displaced from the maximum, it should be fairly valid. We have also assumed the particles to be spherical. This is far from the truth in the case of the smaller particles, especially those in a poor state of perfection.

Effect of Gelatin

On the addition of gelatin to a suspension of silver bromide particles, the gelatin immediately is adsorbed to the surface of the particles. In case the gelatin is fairly dilute, then the surface of the silver bromide will be incompletely covered with a layer of gelatin molecules one molecule deep. With larger gelatin concentrations, all of the particles will become covered, and the layer will then become greater than one molecule thick. We shall discuss the effect of gelatin then, under two headings:

(A). The surface of the particles is largely bare: Let f be the fraction of the surface which is covered with gelatin. Since the diffusion of ions in gelatin will be much less than in the solution, practically all of the solution or crystallization will take place from the uncovered surface. Hence, we have for the first process:

$$\frac{dv}{dt} = (1 - f) \left(\frac{dv}{dt}\right)_o$$

Since $v = 4/3 \pi nr^3$, we see that $\frac{dr}{dt} = (1 - f) \left(\frac{dr}{dt}\right)_o$, hence, on substitution:

$$\frac{dI}{dt} = k^1 nr \frac{dr}{dt} = k^1(1-f)nr\left(\frac{dr}{dt}\right)_o$$

$$= (1 - f) \left(\frac{dI}{dt}\right)_o$$

The fraction of the surface covered, under these conditions, will be proportional to the concentration of gelatin, c, and inversely as the amount of surface available, $4 \pi n r^2$. Hence, we have

$$\frac{dI}{dt} = (1 - \frac{k_3 c}{n r^2}) (\frac{dI}{dt})_o \tag{10}$$

We see that the presence of gelatin slows up the initial increase of intensity with time. The effect is greater with higher gelatin concentrations and small particles. Therefore, the effect should be more pronounced at the beginning of the process.

During the second part of the process, the effect of gelatin has a double effect. The rate of solution of smaller particles is now $(1 - f)$ of the rate assuming no gelatin, while the rate of crystallization on the larger particles is only $(1 - f)$ as great as before. Hence, we have:

$$\frac{dv_1}{dt} = k^1 (1 - f) (4 \pi n_1 r_1^2) e^{k/r_2} (1 - f)$$

This leads to the relation:

$$\frac{dI}{dt} = (1 - f)^2 (\frac{dI}{dt})_o$$

If we let S stand for the total surface of the particles, we find as before:

$$\frac{dI}{dt} = (1 - \frac{k_4 c}{S})^2 (\frac{dI}{dt})_o \tag{11}$$

Notice that the gelatin has a similar "slowing-up" effect asbefore, but that the quantities enter as squared terms. Hence, for a given change in surface, there will be a greater change. However,

the change of surface in the second phase is much less than the first, but the effect is exaggerated in our intensity measurements.

(B). The surface of the particles is completely covered: In this case, the concentration of gelatin is sufficiently great that all particles will be covered with a layer of gelatin. The effect of increasing the concentration of gelatin will be to merely increase the thickness of the film. Since the viscosity of the gelatin layer is very high, the ions will be greatly retarded in passing through the film. The processes of solution and recrystallization will be diminished, resulting in a slowing-up of the intensity change.

If the particles are sufficiently large, the thickness of the film will be inversely proportional to the surface of the particles, and directly as the concentration of gelatin. We see, therefore, that the proportionality is the same as in the case of partially covered surfaces, hence equations (10) and (11) will apply here.

We can expect, however, a much greater effect in these cases, due to the slow diffusion of silver and bromide ions through the protective film.

It should be pointed out that these relations are all approximate. Only with particles which are large compared with the size of the gelatin molecules, is the surface covered or the thickness of the film proportional inversely to the concentration of gelatin. Further, the extent of coverage will vary with the particles. Small or imperfect particles should adsorb a greater amount of gelatin. One would expect considerable variation in the amount of coverage on imperfect particles. Hence, when we reach the first equilibrium point, there will be a greater diversity in size of particles. The second effect of solution and crystallization will set in sooner. All processes are, of course, greatly diminished by the presence of the protective colloid.

Use of Nephelometer

The use of a precision instrument such as the nephelometer requires a special technique of its own. Extreme accuracy is obtainable only after long periods of practice. The instrument must be used in a dark room, and the observer should remain in the dark for a short period before taking readings in order for the eyes to attain maximum sensitivity.

Some factors influencing the readings are: (a) stray light; (b) lint on the cups; (c) dust in the atmosphere; (d) variations in the position of the receptacle cups; (e) bubbles collecting under the plungers. One serious error not noted by other authors but observed by the writer was the adherence of a film of silver halide to the cup which was not removed by ordinary washing. This film had to be removed frequently with ammonia.

The instrument used was of the Kober stationary plunger, movable cup type, made by the Klett Manufacturing Company. The cup on the left side was removed. A permanent color standard was made by passing the light from the lamp house through gray paper, reflecting it from light blue paper and passing it into the left plunger. This gave a bluish gray color very similar to the suspensions of silver bromide studied.

It would be difficult to match the standard against the suspension at all times since the first formation of silver bromide gives a very blue color, in a few minutes becoming grayish-blue and in a few hours quite gray. Consequently, the very earliest and latest readings were not as accurate as the intermediate ones. Of thirty shades of blue tried, only the one used compared favorably over the longest period of time. Other shades, of course, must be

used in examining the very earliest or latest periods during the precipitation process.

T. W. Richards [29] insisted that both unknown and standard be treated in the same way and protested against the use of permanent standards for any other purpose than for investigating the change in the light reflecting power of a suspension with time. Since in these determinations the major consideration was that of time, the use of a permanent standard was considered permissable.

A serious error was noted in the earliest readings due to the effect of light on the suspensions. If the nephelometer light is left on constantly during a series of readings, the same general curve of increase and decrease in opalescence will be noted but the maximum is reached much sooner and visible coagulation takes place earlier. Reproducible results could be obtained only by making approximately the same number of readings and over the same period of time.

The question of reproducibility is of major importance. Richards[30] believed nephelometry was not suitable for general analytical work owing to its inaccuracy. Kober[31] stated that the greatest source of error in nephelometry was an instrumental one. On the other hand Wells[32] and Kolthoff and Yutzy[33] strongly indicate that the limiting factor is the reproducibility of the dispersion. The writer agrees entirely with the latter statement since after a

(29) Richards, Am. Chem. J., 35, 510 (1906).

(30) Richards, Orig. Com. 8th Inter. Cougr. Appl. Chem., 1, 426, (1912)

(31) Kober, J. Biol. Chem., 13, 490 (1915).

(32) Wells, Chem. Rev., 3, 331 (1927).

(33) Kolthoff and Yutzy, J. Am. Chem. Soc., 55, 1916 (1933).

carefully standardized procedure was adopted the results could be reproduced with little error. Without extreme care and regularity, however, in preparation of the dispersions, reproducibility becomes very poor.

Materials

Silver nitrate—C.P. grade recrystallized once from conductivity water and dried twelve hours at 106°C.

Potassium bromide—Reagent grade recrystallized once from conductivity water and dried twelve hours at 106°C.

Nitric acid—Redistilled once over silver nitrate.

Ethanol—Synthetic absolute alcohol distilled once over silver nitrate and calcium oxide.

Gelatin—Granulated Walker brand dried in vacuo at 50°C for twelve hours. Gave no turbidity with silver nitrate.

Conductivity water—Distilled water redistilled over silver nitrate, potassium permanganate and sodium hydroxide. Gave no turbidity with silver nitrate.

Method of Procedure

The suspensions were made up in 50 cc volumetric flasks. They contained 25 cc of ethanol; 5 cc of 0.2 N nitric acid; varying amounts of silver nitrate, potassium bromide, and sometimes gelatin; and water to make 50 cc. The potassium bromide was added last unless otherwise indicated.

It was found that solutions containing no alcohol were very unstable and practically impossible to reproduce. Approximately fifty per cent ethanol was used[34]. Preliminary examination also showed

[34] Concentration used by Lamb, Carlteon and Meldrum in the determination of chloride as AgCl; J. Am. Chem. Soc., 42, 251 (1920).

the necessity of some nitric acid in producing maximum opalescence.

In most cases the potassium bromide was added to an excess of silver nitrate. This prevented a change in lattice charge from positive to negative; hence, the danger of precipitating the colloid at the neutral point was lessened.

The rate of mixing was kept constant since excessive shaking caused settling out in ten or fifteen minutes. The flasks were inverted five times and each time shaken gently. The rate of addition of reagents was also kept constant. A difference in turbidity was produced if the addition was varied from drop to pour method. The reagents were run in freely from pipettes.

The results of the determinations are given in the following tables. Each determination represents two or more runs. Representative data are plotted on corresponding graphs.

Table I

EFFECT OF TIME ON AgBr DISPERSIONS

25 cc ethanol   KBr
10 cc 0.005 N $AgNO_3$ H_2O to make 50 cc
5 cc 0.2 N HNO_3

L = Nephelometer reading

| Minutes	0.0002 N AgBr 1		2		0.00025 N AgBr 1		2	
	L	100/L	L	100/L	L	100/L	L	100/L
3	25.0	4.0	22.0	4.5				
6	13.2	7.6	12.5	8.0				
10	8.3	12.0	8.12	12.3				
15	6.6	15.2	6.5	15.4				
20	6.1	16.4	6.1	16.4				
25	5.7	17.5	5.8	17.2				
30	5.7	17.5	5.6	17.9				
40	5.7	17.5	5.6	17.9	5.1	19.6	5.1	19.6
50	5.7	17.5	5.6	17.9	5.1	19.6	5.1	19.6
60	5.7	17.5	5.6	17.9	5.1	19.6	5.2	19.2
70	6.0	16.7	5.7	17.5	5.3	18.9	5.3	18.9
80	6.2	16.1	6.0	16.7	5.5	18.2	5.5	18.2
90	6.4	15.6	6.3	15.9	5.7	17.5	5.8	17.2
100	6.6	15.2	6.5	15.4	5.9	16.9	6.0	16.7
110	7.0	14.3	7.0	14.3	6.1	16.4	6.2	16.1
120	7.4	13.5	7.3	13.7	6.4	15.6	6.4	15.6
130	7.7	13.0	7.6	13.2	6.7	14.9	6.7	14.9
140	8.1	12.3	8.1	12.3	7.0	14.3	6.9	14.5
150	8.8	11.4	8.6	11.6	7.2	13.9	7.2	13.9
160	9.4	10.6	9.2	10.9	7.5	13.3	7.6	13.2
170	10.0	10.0	9.9	10.1	8.0	12.5	8.0	12.5
180	10.7	9.3	10.5	9.5	8.4	11.9	8.5	11.8
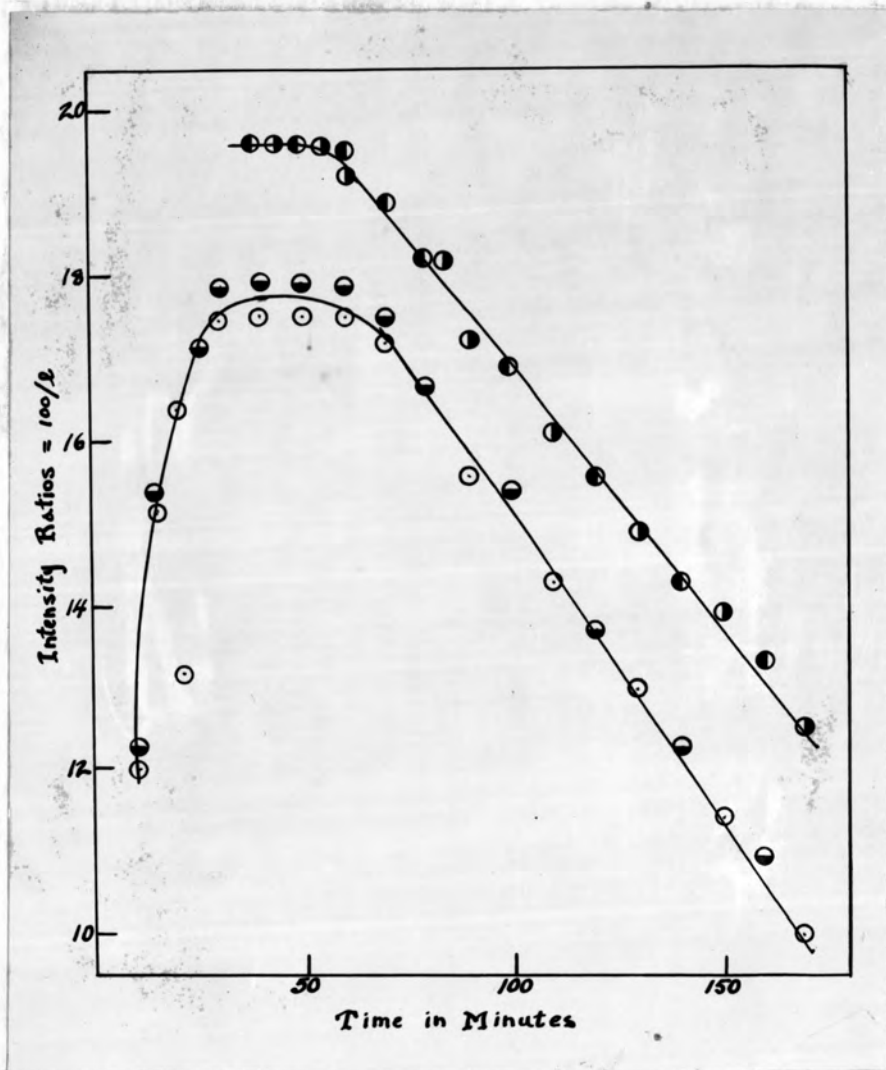
Fig. 1. Effect of time on AgBr dispersions.

Data from Table I. ⊙ ◐ 0.0002 N AgBr; ◑ ◐ 0.00025 N AgBr.

Table II

EFFECT OF VARIOUS CONCENTRATIONS OF GELATIN IN
PRODUCING MAXIMUM OPALESCENCE. (GELATIN ADDED
BEFORE PRECIPITATION).

25 cc ethanol   Gelatin
10 cc 0.005 N AgNO$_3$ 5.0 cc 0.0025 N KBr
5 cc 0.2 N HNO$_3$ H$_2$O to make 50 cc

L = Nephelometer reading

Minutes	o/o GELATIN									
	0.0 o/o		0.00001 o/o		0.00004 o/o		0.0001 o/o		0.0002 o/o	
	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L
15	8.8	11.4	10.0	10.0	16.1	6.2	25.5	3.9	50.0	2.0
30	6.9	14.5	7.5	13.3	11.5	8.7	18.3	5.5	45.0	2.2
45	6.0	16.7	6.6	15.2	9.7	10.3	15.5	6.5		
60	5.5	18.2	6.1	16.4	8.7	11.5	14.4	6.9	37.0	2.7
90	5.5	18.2	5.9	16.9	7.5	13.3	13.4	7.5	34.0	2.9
120	5.5	18.2	5.7	17.5	7.2	13.9	----	--	----	---
150	5.5	18.2	5.7	17.5	6.8	14.7	11.6	8.6	30.5	3.3
180	5.8	17.2	5.8	17.2	6.8	14.7	10.8	9.3	----	---
240	6.0	16.7	6.0	16.7	6.5	15.4	10.5	9.5	25.0	4.0
300	7.0	14.3	6.5	15.4	6.5	15.4	10.0	10.0	23.0	4.3
375	9.0	11.1	7.4	13.5	6.9	14.5	9.3	10.8	----	---
480	11.2	8.9	10.2	9.8	7.3	13.7	9.5	10.5	17.0	5.9
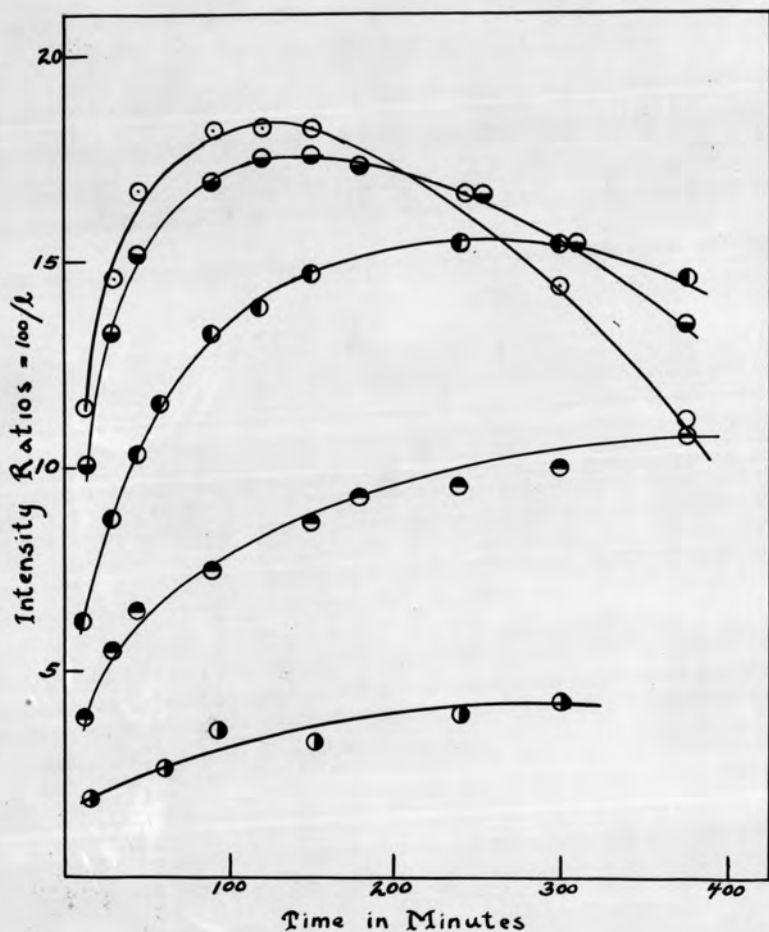
Fig. 2. Effect of various concentrations of
gelatin in producing maximum opalescence.
(Gelatin added before precipitation). Data from
Table II. o/o Gelatin = ⊙ 0.0 o/o; ⬤ 0.00001 o/o;
◐ 0.00004 o/o; ⬤ 0.0001 o/o; ◑ 0.0002 o/o.

Table III

EFFECT OF VARIOUS CONCENTRATIONS OF GELATIN IN
PRODUCING MAXIMUM OPALESCENCE.(GELATIN ADDED
BEFORE PRECIPITATION).

Dispersions prepared as in Table II

L = Nephelometer reading

| Minutes	o/o GELATIN							
	0.0 o/o		0.00000 4 o/o		0.00003 o/o		0.00006 o/o	
	L	L/100	L	L/100	L	L/100	L	L/100
15	6.8	14.7	10.7	9.3	13.3	7.5	17.0	5.9
30	6.0	16.7	7.5	13.3	10.0	10.0	13.5	7.4
45	5.9	16.9	6.8	14.7	9.2	10.9	12.0	8.3
60	5.5	18.2	6.3	15.9	7.6	13.2	9.8	10.2
90	5.5	18.2	5.8	17.2	6.8	14.7	8.2	12.2
120	5.5	18.2	5.6	17.9	6.4	15.6	7.8	12.8
210	6.0	16.7	5.6	17.9	6.2	16.1	7.3	13.7
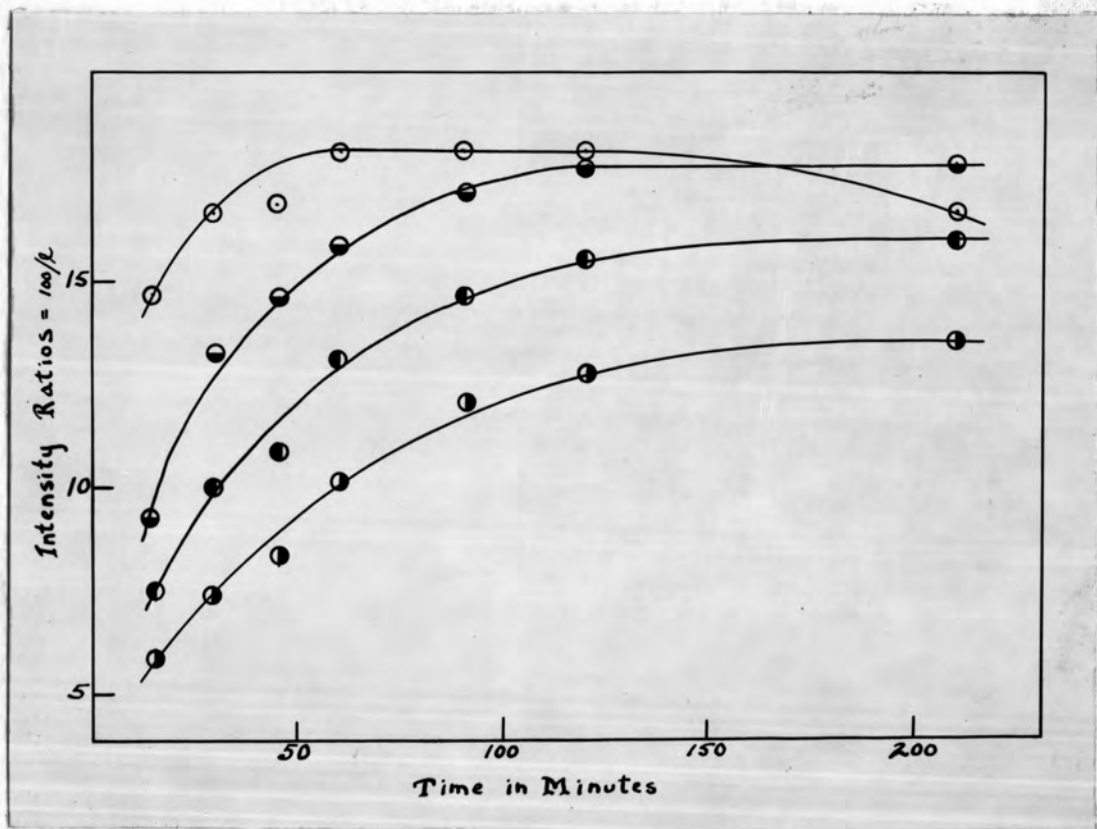
Fig. 5. Effect of various concentrations of gelatin in
producing maximum opalescence. (Gelatin added before
precipitation). Data from Table III. o/o Gelatin =
⊙ 0.0 o/o; ◒ 0.000004 o/o; ◑ 0.00003 o/o; ◐ 0.00006 o/o.

Table IV

EFFECT OF VARIOUS CONCENTRATIONS OF GELATIN IN PRODUCING MAXIMUM OPALESCENCE. (Gelatin added before precipitation).

Dispersions prepared as in Table II

L = Nephelometer reading

| Minutes	o/o GELATIN											
	0.00002		0.00004		0.00006		0.00008		0.00010		0.00012	
	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L
15	10.7	9.3	14.0	7.1	15.5	6.4	29.0	3.5	33.0	3.0	45.0	2.2
30	8.0	12.5	11.0	9.1	11.5	8.7	20.5	4.9				
60	6.5	15.4	8.2	12.2	9.0	11.1	14.0	7.1	17.0	5.9	20.0	5.0
120	5.5	18.2	6.6	15.2	7.4	13.5	10.4	9.6	13.0	7.7	14.0	7.1
180	5.4	18.5	5.9	16.9	6.6	15.2	8.7	11.5	10.3	9.7	11.3	8.8
240	5.4	18.5	5.7	17.5	6.1	16.4	8.0	12.5	9.7	10.3	10.0	10.0
420	6.5	15.4	5.7	17.5	5.9	16.9	7.0	14.3	8.0	12.5	8.5	11.7
1020	17.5	5.7	13.5	7.4	7.5	13.3	6.5	15.4	6.7	14.9	7.8	12.8
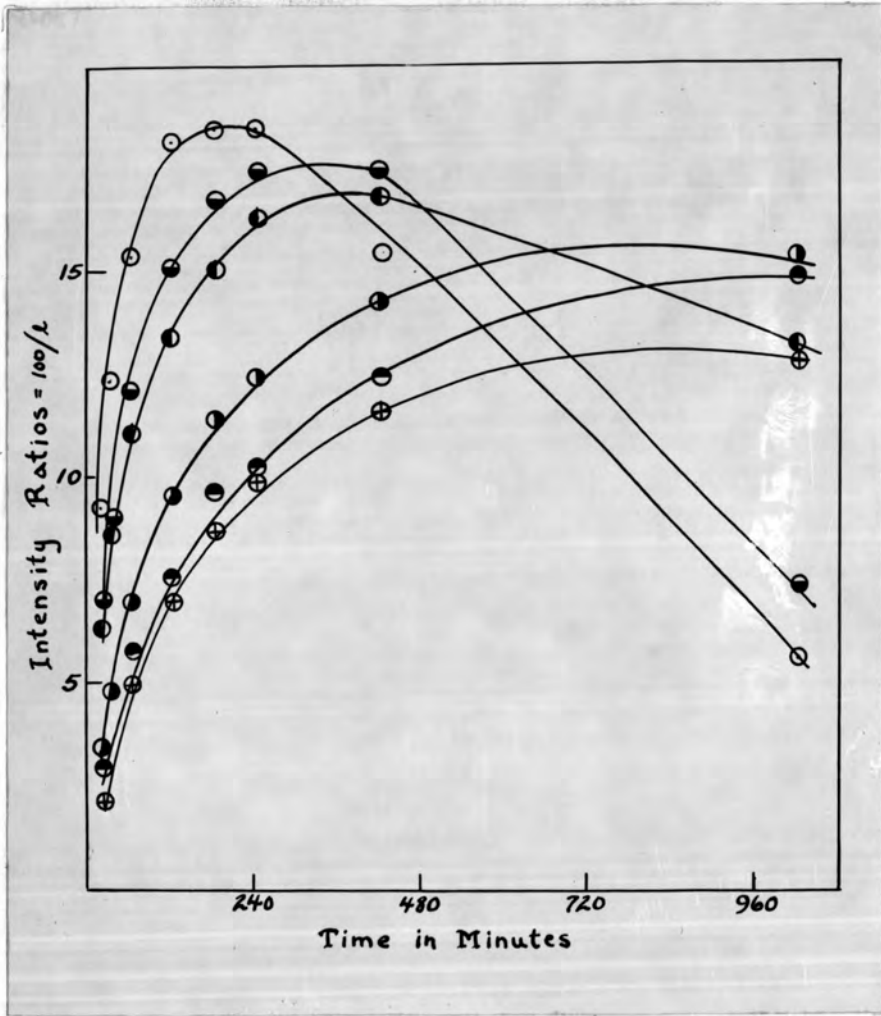
Fig. 4. Effect of various concentrations of gelatin in producing maximum opalescence (Gelatin added before precipitation). Data from Table IV. o/o Gelatin = ⊙ 0.00002 o/o; ◒ 0.00004 o/o; ◑ 0.00006 o/o; ◐ 0.00008 o/o; ◓ 0.00010 o/o; ⊕ 0.00012 o/o

Table V

EFFECT OF GELATIN IN DECREASING OPALESCENCE WITH TIME.
(Gelatin added after precipitation)

25 cc ethanol   5 cc 0.0025 N KBr
10 cc 0.005 N AgNO$_3$ Stand 30 minutes
5 cc 0.2N HNO$_3$ Add gelatin and H$_2$O to 50 cc

(Nephelometer light left on)

L = Nephelometer Reading

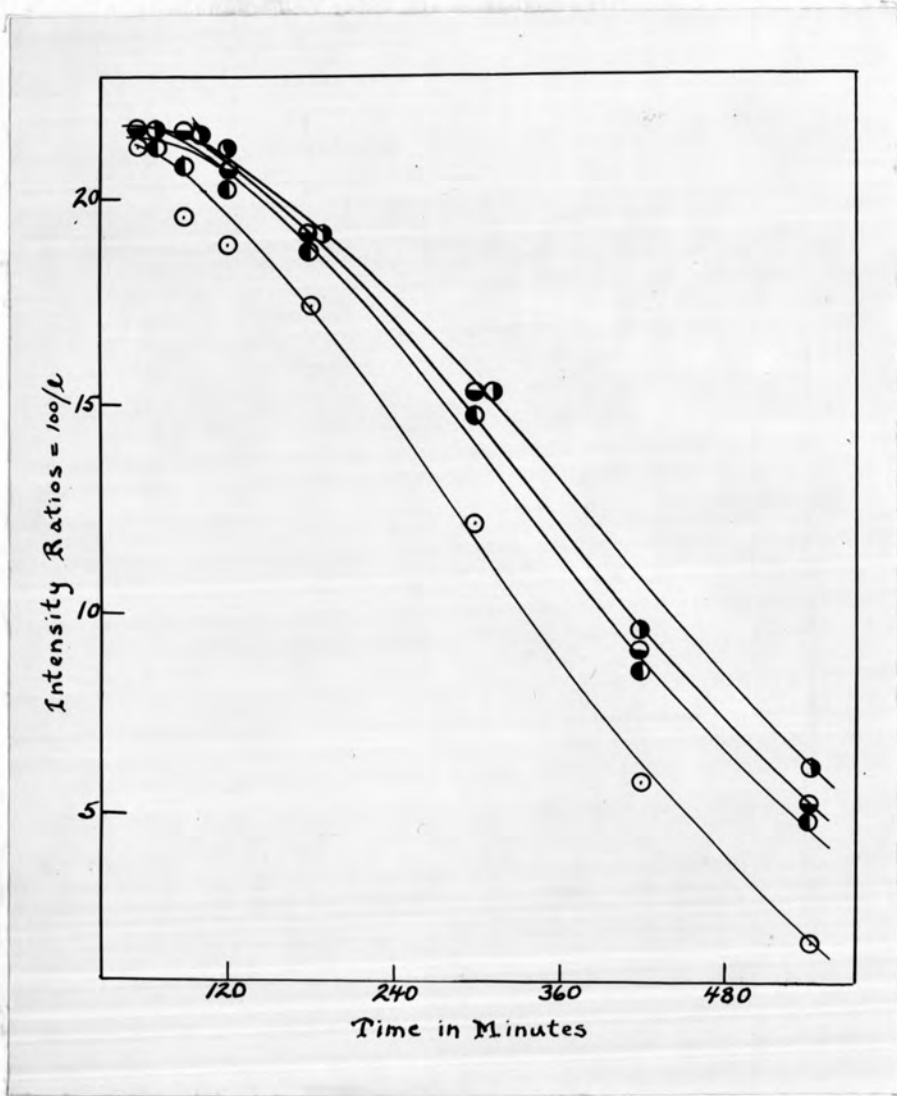| Minutes | o/o GELATIN | | | | | | | |
| | 0.0002 o/o | | 0.0004 o/o | | 0.0006 o/o | | 0.0008 o/o | |
	L	100/L	L	100/L	L	100/L	L	100/L
40	4.6	21.7	4.7	21.3	4.8	20.8	4.6	21.7
60	4.7	21.3	4.7	21.3	4.6	21.7	4.6	21.7
90	5.1	19.6	4.8	20.8	4.6	21.7	4.6	21.7
120	5.3	10.9	4.9	20.4	4.8	20.8	4.7	21.3
180	5.7	17.5	5.3	18.9	5.2	19.2	5.2	19.2
300	8.2	12.2	6.7	14.9	6.5	15.4	6.5	15.4
420	17.0	5.9	11.5	8.7	11.0	9.1	10.5	9.5
540	50.0	2.0	20.0	5.0	19.0	5.3	16.0	6.3

Fig. 5. Effect of gelatin in decreasing opalescence with
time (Gelatin added after precipitation). o/o Gelatin =
⊙ 0.0002 o/o; ◐ 0.0006 o/o; ◖ 0.0008 o/o; ◑ 0.0004 o/o;
⊕ 0.0010 o/o.

Table VI

EFFECT OF GELATIN IN DECREASING OPALESCENCE WITH TIME
(GELATIN ADDED AFTER PRECIPITATION).

Dispersions prepared as in Table V except
to stand 40 minutes before adding genatin.

L = Nephelometer reading

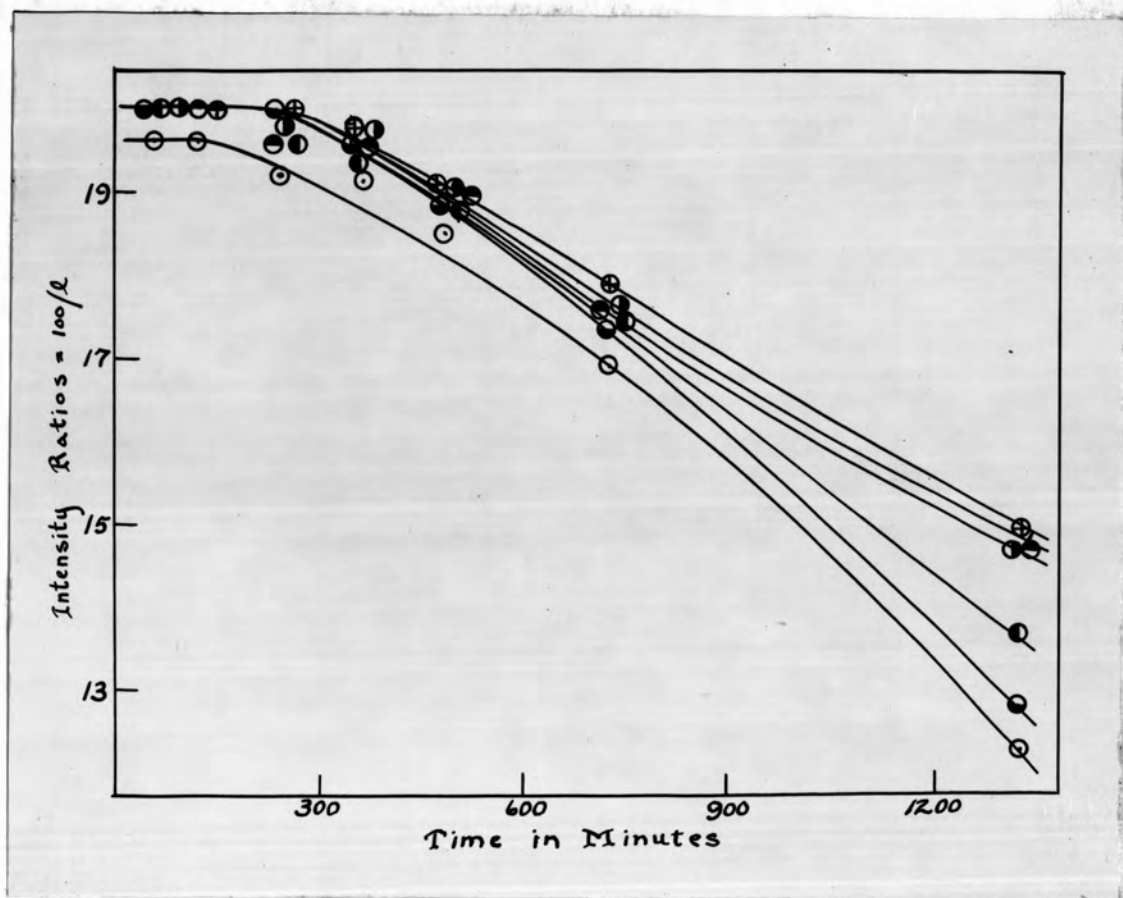|	o/o GELATIN											
Minutes	0.0002 o/o		0.0004 o/o		0.0006 o/o		0.0008 o/o		0.0010 o/o		0.0012 o/	
	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L
60	5.1	19.6	5.0	20.0	5.0	20.0	5.0	20.0	5.0	20.0	5.0	20.0
120	5.1	19.6	5.0	20.0	5.0	20.0	5.0	20.0	5.0	20.0	5.0	20.0
240	5.2	19.2	5.1	19.6	5.1	19.6	5.1	19.6	5.0	20.0	5.0	20.0
360	5.2	19.2	5.1	19.6	5.1	19.6	5.1	19.6	5.1	19.6	5.1	19.6
480	5.4	18.5	5.3	18.9	5.3	18.9	5.3	18.9	5.3	18.9	5.3	18.9
720	5.9	16.9	5.7	17.5	5.7	17.5	5.7	17.5	5.7	17.5	5.6	17.9
1320	8.1	12.3	7.8	12.8	7.3	13.7	6.8	14.7	6.8	14.7	6.7	14.9

Fig. 6. Effect of gelatin in decreasing opalescence
with time (Gelatin added after precipitation).

o/o Gelatin = ⊙ 0.0002 o/o; ◒ 0.0004 o/o; ◗ 0.0006 o/o;
◖ 0.0008 o/o; ⊖ 0.0010 o/o; ⊕ 0.0012 o/o.

Table VII

EFFECT OF GELATIN IN DECREASING OPALESCENCE WITH TIME (GELATIN ADDED AFTER PRECIPITATION).

Dispersions prepared as in Table V with
new solutions of gelatin.

L = Nephelometer reading.

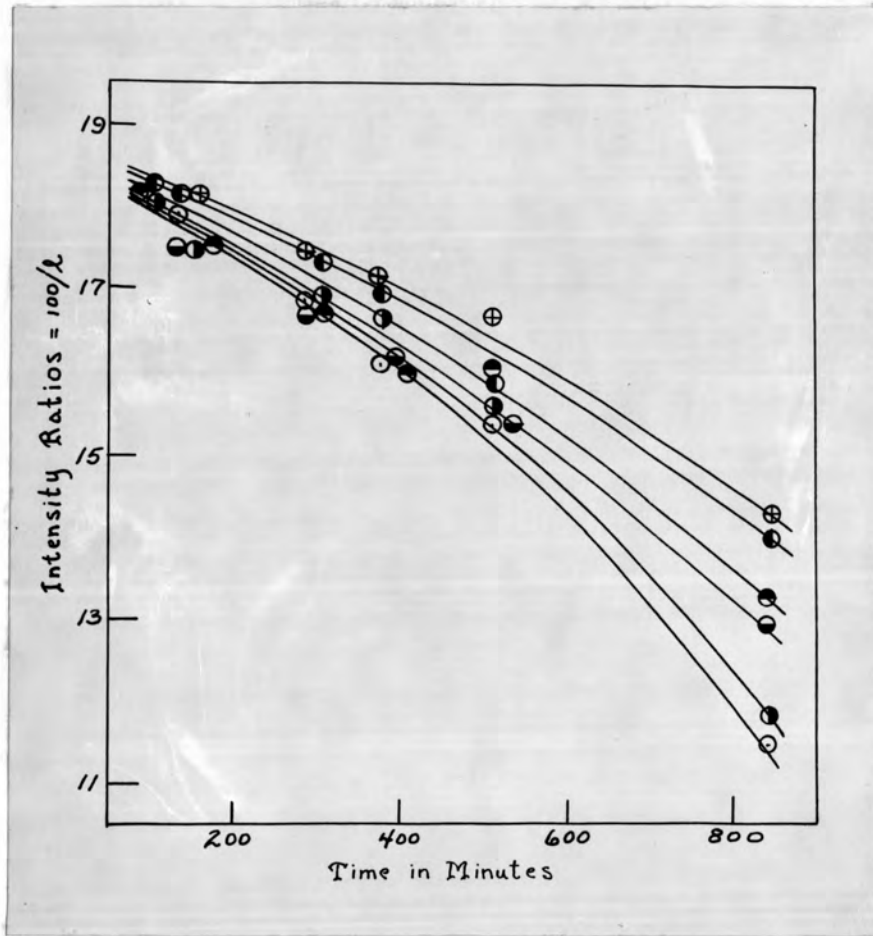| Minutes	o/o GELATIN											
	0.0004 o/o		0.0008 o/o		0.0012 o/o		0.0016 o/o		0.0020 o/o		0.0024 o/o	
	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L
85	5.5	18.2	5.5	18.2	5.5	18.2	5.5	18.2	5.5	18.2	5.3	18.9
130	5.6	17.9	5.7	17.5	5.7	17.5	5.7	17.5	5.5	18.2	5.5	18.2
280	5.9	16.9	6.0	16.7	5.9	16.9	5.9	16.9	5.6	17.9	5.7	17.5
370	6.2	16.1	6.2	16.1	6.0	16.7	6.2	16.1	5.7	17.5	5.8	17.2
505	6.5	15.4	6.5	15.4	6.4	15.6	6.2	16.1	6.1	16.4	6.0	16.7
840	8.7	11.5	7.7	13.0	8.5	11.8	7.5	13.3	7.1	14.1	7.0	14.3

Fig. 7. Effect of gelatin in decreasing opalescence
with time (Gelatin added after precipitation).   o/o Gelatin
= ⊙ 0.0004 o/o; ◐ 0.0008 o/o; ◑ 0.0012 o/o; ⊖ 0.0016 o/o;
◑ 0.0020 o/o; ⊕ 0.0024 o/o.

Table VIII

EFFECT OF GELATIN IN DECREASING OPALESCENCE WITH TIME.
(GELATIN ADDED AFTER PRECIPITATION).

Dispersions prepared as in Table V.

L = Nephelometer reading.

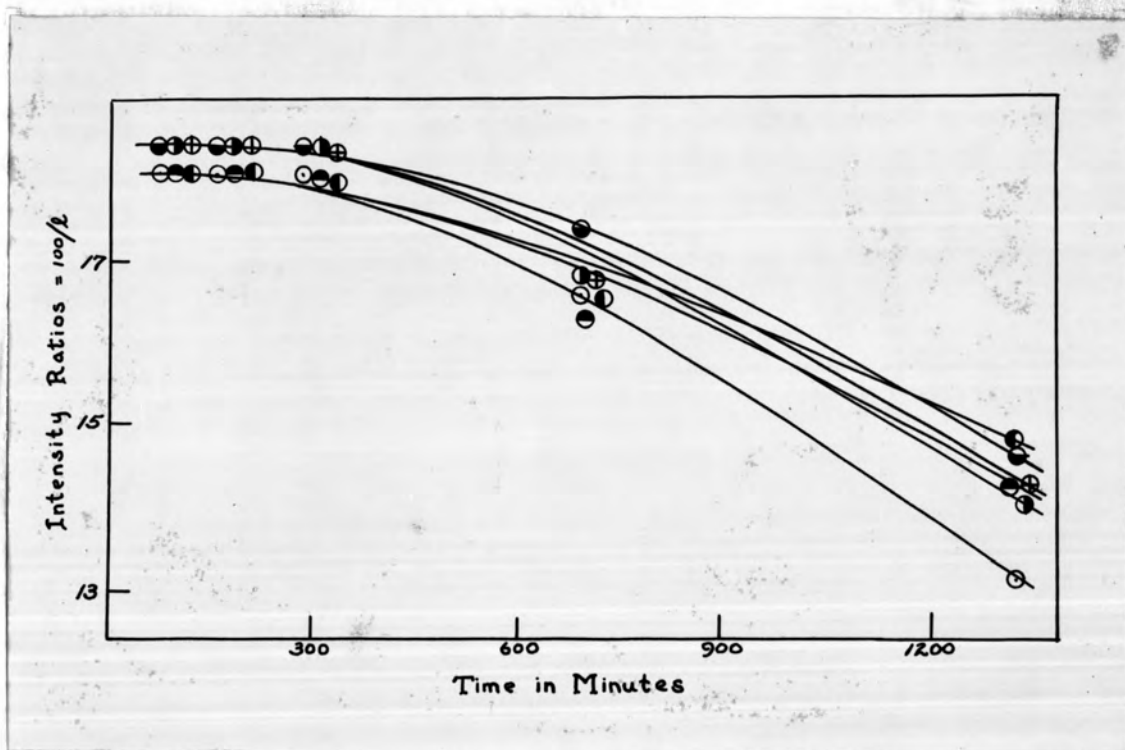|	o/o GELATIN											
Minutes	0.002 o/o		0.004 o/o		0.006 o/o		0.008 o/o		0.010 o/o		0.012 o/o	
	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L
90	5.5	18.2	5.4	18.5	5.4	18.5	5.5	18.2	5.5	18.2	5.4	18.5
180	5.5	18.2	5.4	18.5	5.4	18.5	5.5	18.2	5.5	18.2	5.4	18.5
300	5.5	18.2	5.4	18.5	5.4	18.5	5.5	18.2	5.5	18.2	5.4	16.7
690	6.0	16.7	5.7	17.5	5.9	16.9	6.1	16.4	6.0	16.7	6.0	16.7
1320	7.5	13.3	6.8	14.7	7.0	14.3	7.0	14.3	6.7	14.9	7.0	14.3

Fig. 8. Effect of gelatin in decreasing opalescence with
time (Gelatin added after precipitation). o/o Gelatin =
⊙ 0.002 o/o; ◕ 0.004 o/o; ◐ 0.006 o/o; ◓ 0.008 o/o;
◑ 0.010 o/o; ⊕ 0.012 o/o.

Table IX

EFFECT OF GELATIN IN DECREASING OPALESCENCE WITH TIME
(GELATIN ADDED AFTER PRECIPITATION).

Dispersions prepared as in Table V.

L = Nephelometer reading.

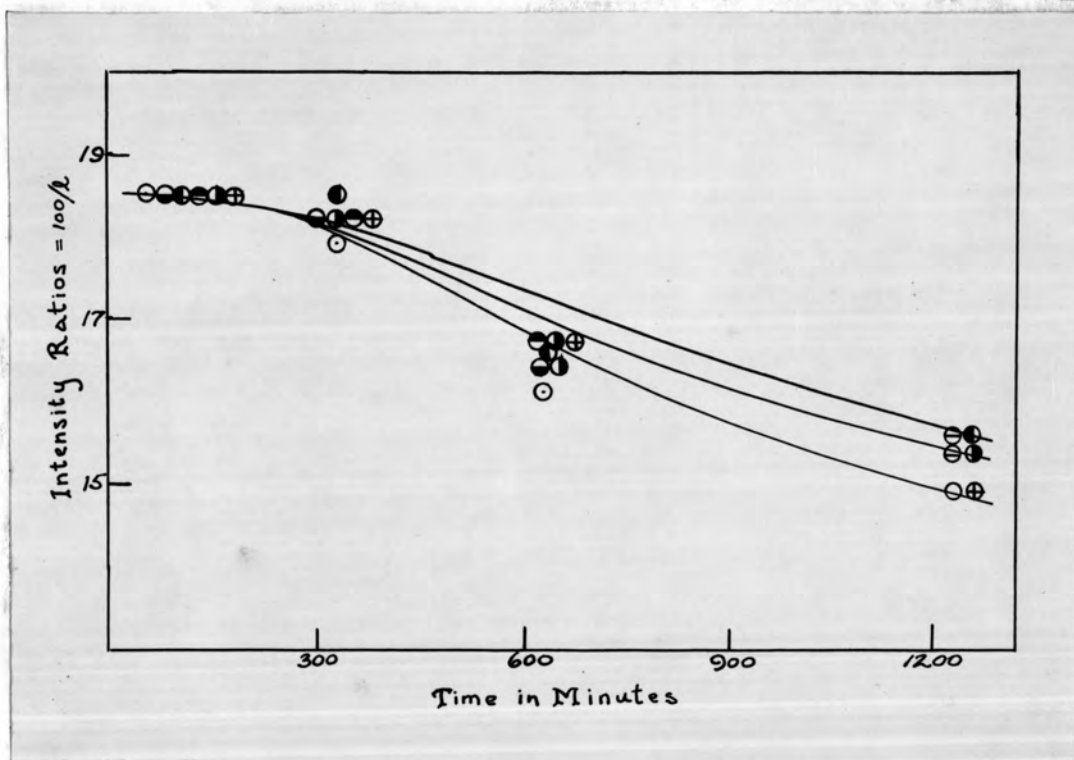| Minutes	o/o GELATIN											
	0.02 o/o		0.04 o/o		0.06 o/o		0.08 o/o		0.10 o/o		0.12 o/o	
	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L	L	100/L
90	5.4	18.5	5.4	18.5	5.4	18.5	5.4	18.5	5.4	18.5	5.4	18.5
330	5.6	17.9	5.5	18.2	5.5	18.2	5.5	18.2	5.4	18.5	5.5	18.2
630	6.2	16.1	6.1	16.4	6.1	16.4	6.0	16.7	6.0	16.7	6.0	16.7
1230	6.7	14.9	6.4	15.6	6.4	15.6	6.5	15.4	6.5	15.4	6.5	15.4
1440	7.0	14.3	6.5	15.4	6.7	14.9	6.8	14.7	6.5	15.4	7.1	14.1

Fig. 9. Effect of gelatin in decreasing opalescence with time. (Gelatin added after precipitation). o/o Gelatin = ⊙ 0.02 o/o; ◐ 0.04 o/o; ◑ 0.06 o/o; ● 0.08 o/o; ◑ 0.10 o/o; ⊕ 0.12 o/o.

Table X

EFFECT OF TIME ON PRODUCING MAXIMUM OPALESCENCE WITH VARYING CONCENTRATIONS OF AgBr.

25 cc ethanol   KBr
5 cc 0.2 N HNO_3 H_2O to make 50 cc
10 cc 0.005 N $AgNO_3$

Solution 1 contains 2.0 cc 0.0025 N KBr
Solution 2 contains 4.0 cc 0.0025 N KBr
Solution 3 contains 7.0 cc 0.0025 N KBr
Solution 4 contains 10.0 cc 0.0025 N KBr

L = Nephelometer readings

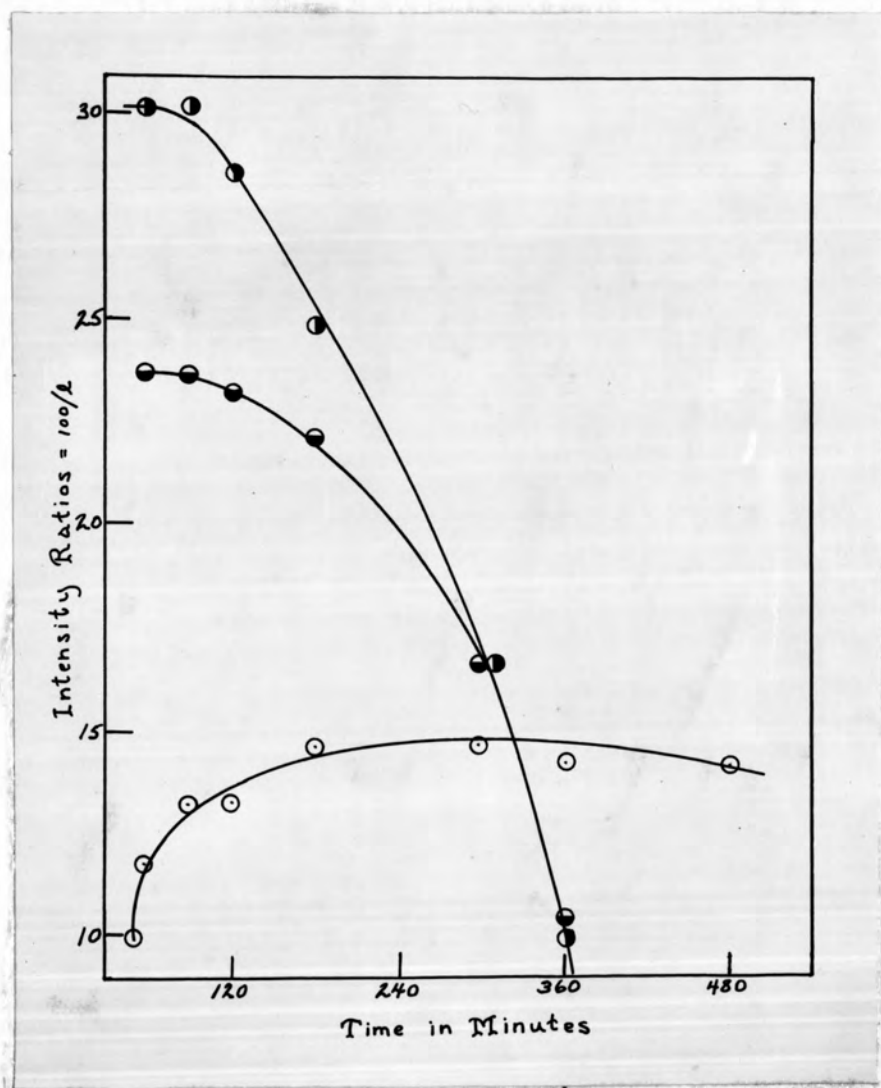| Minutes | Concentration of AgBr | | | | | | | |
| | 1 0.00010 N | | 2 0.00020 N | | 3 0.00035 N | | 4 0.0005 N | |
	L	100/L	L	100/L	L	100/L	L	100/L
20	40.0	2.5	10.7	9.3	4.5	22.2	3.3	30.3
40	32.0	3.1	9.5	10.5	4.3	23.3	3.3	30.3
60	29.0	3.4	8.5	11.8	4.2	23.8	3.3	30.3
90	---	---	7.5	13.3	4.2	23.8	3.3	30.3
120	24.0	4.2	7.5	13.3	4.3	23.3	3.5	28.6
180	---	---	6.8	14.7	4.5	22.2	4.0	25.0
300	21.5	4.7	6.8	14.7	6.0	16.7	6.0	16.7
360	20.0	5.0	7.0	14.3	9.5	10.5	10.0	10.0
480	20.0	5.0	7.0	14.3	---	---	---	---

Fig. 10. Effect of time on producing maximum opalescence
with varying concentrations of AgBr. Concentration of AgBr
⊙ 0.00020 N;   ◑ .00035 N;   ◐ .0005 N.

DISCUSSION OF RESULTS

Considerable comment has been made in the literature as to the difficulty in obtaining reproducibility in nephelometric determinations, especially when a fixed standard is used. While this is generally true, when compared with ordinary colorimetric determinations, it is quite evident in this work that the results were quite reliable. As an example, in table I (figure 1) is given the data of two sets of duplicate determinations. The sets of data are in complete agreement within experimental error. These determinations were made on independent suspensions, made up by identical methods. Care must be taken to observe the precautions enumerated on page 21 of this thesis.

As pointed out before, a source of error was encountered that has not been mentioned in the literature. The particles of silver bromide seem to adhere to the plunger and cups of the nephelometer. This layer is very tenacious and must be removed with ammonia between each determination.

The general change of opalescence with time is illustrated in figure 1. Immediately on making up the solutions, there is a sudden increase in intensity of scattered light. In the absence of a protective colloid, a maximum is reached in one-half to one hour. This maximum lasts for about another half-hour, then a decrease sets in as observed.

The first portion of the curve is due to the building up of primary particles from the supersaturated solution. In general, great difficulty is encountered in the study of this. The color of

the suspension changes very rapidly from a deep blue to gray-blue of the maximum range. It is impossible to follow this change with a given fixed standard with any degree of accuracy. Theoretically, the treatment of such data would be very involved. With the formation of infinitesimal particles, Rayleigh's law applies, with the increase of intensity proportional to the square of the volume of the particles and inversely as the fourth power of the wave length. This accounts for the deep blue of the suspension.

At the stationary maximum, the solution has become saturated, with particles of about the same state of size and perfection. Little change takes place, then, until solution and recrystallization sets in, resulting in a decrease in surface and the corresponding diminution of reflected light. Normally, this process should continue until all particles are of macroscopic dimensions. Since the latter part would result in a heterogeneous system, it would be meaningless to study the suspensions in this range.

The data of table X demonstrates the reaction between intensity of light and the concentration of the suspension. The height of the maximum is a function of the concentration, but is not proportional to it, as would be expected. We can also see that the maximum is more slowly forming with the more dilute solutions. Since in the latter case, the supersaturation is less, there will be fewer nuclei formed. Hence, a greater time of diffusion is required for the migration of ions to the nuclei. Therefore the maximum will be displaced to the right as observed.

The effect of gelatin has been derived previously (page 18). In general, it will decrease both the first and second effects.

In tables II, III, and IV are listed data of results
obtained when the gelatin was added before the precipitating agent.
It is at once apparent that the initial increase in opalesence is
diminished. This is in agreement with the theory described on
page 18, since the primary particles are now covered with a film
of gelatin. Diffusion of ions through this film is much less
than through the solution, so that the increase in growth of primary
particles is decreased. As the concentration of gelatin is increased,
this becomes more evident. As the fraction of the surface of the
silver bromide particles which is bare is decreased, an increasing
amount of crystallization on the particles must take place through
the viscous gelatin layer. A definite difference seems to occur
around a concentration of 0.00005 per cent gelatin. This
probably corresponds to the point at which the entire surface of the
primary particles becomes covered. This point should be considered
more carefully, in further experimentation.

We also observe a lower maximum in the presence of gelatin.
This is also in accord with our theory. During this process of
primary particle growth, any difference in size which might exist
will be exaggerated by the presence of gelatin. Normally, a
smaller, inperfect particle might give rise to a faster growth, due
to the fact that the imperfection itself will permit a more rapid
crystallization. However, such smaller particles will now show an
abnormal tendency to adsorb gelatin. Hence, it will acquire a
larger film of gelatin and, hence, its rate of growth will be
retarded still more. We will, therefore, reach the point of
saturation with respect to these particles in a shorter time, and

the second process of solution of these particles will begin
sooner, thus preventing the establishment of the equilibrium
that we would obtain if the particles were all of the same size.
If this is the case, we would expect a less definite maximum than
in the case of curves in the absence of gelatin. It would be
difficult to observe this because of the fact that gelatin slows
up all the processes.

In tables V to IX, gelatin was not added until the
suspension had attained its maximum opalescence. In tables V and
VI, it was demonstrated that it did not matter just when the gelatin
was added, as long as the solution had attained this maximum.

It is to be noted in these cases that there is, in general,
a decrease in the change in opalescence. It is very marked at first,
with small concentrations of gelatin, then it seems to reach a
fairly steady state, beyond which the addition of further gelatin
results in little change in the opalescence. This is to be expected
from the theory developed on page 20. With incompletely covered
surfaces, the effect of gelatin is very great, since most of the
aging now takes place on the "bare spots". As soon as the surface
becomes completely covered, then the further addition of gelatin
has relatively little effect.

In general, then, we can conclude that the theory of
coagulation of dilute silver bromide sols developed in the first
part of this thesis, affords a satisfactory explanation for the
change of opalescence of these sols when studied nephelometrically.
In the time available for this study, many factors had to be
overlooked, which would well afford furtherinvestigation. The
following are some of the problems which should be studied:

(1) The initial rate of nuclei formation. This would require a more careful consideration of the applicability of Rayleigh's law. A study of the presence of gelatin in this range seems especially promising.

(2) The size of the silver bromide particles in these concentrations studied. An investigation by means of an ultramicroscope would probably solve this problem. Unfortunately, such an instrument was not available during this study.

(3) A large number of determinations should be carried out in determining the effect of varying gelatin concentrations on the change in opalescence. We should be able to locate concentrations beyond which the particles are apparently completely covered. From a study of these concentrations, one should be able to learn something of the size of the silver bromide particles during the course of the study.

The field is, therefore, a promising one. It opens up a new method of attack on colloidal solutionsof analytically important compounds. The results obtained should make a very definite contribution in our study of theoretical colloidal and analytical chemistry.

SUMMARY

1. A theory is developed to account for the changes taking place during the formation of dilute silver bromide sols. The theory is examined by means of nephelometric study of such suspensions. The results obtained are in agreement with the theory.

2. A study is made of the effect of gelatin on these suspensions. A similar examination of such suspensions with the nephelometer also confirms the theory of this action.

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