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LIGHT SCATTERING METHODS AND THEIR APPLICATION TO THE STUDY OF THE PRECIPITATION OF AMMONIUM DIURANATE USING A SIMPLE AND NOVEL APPARATUS

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ABSTRACT

Light scattering theory and practice, especially as it applies to the precipitation of alkaline U-VI products, is critically reviewed. A simple and novel apparatus is described and some possibilities for further applications and some improvements are discussed.

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1. INTRODUCTION

The physical and chemical characteristics of ammonium diuranate (ADU), the product precipitated from hexavalent uranium solutions by means of ammonia containing reagents, are of importance in determining the quality of resulting UO_2 powders used in fuel manufacture. Knowledge of these characteristics also helps continuity and efficiency of production. The consistent production of even an arbitrary product is still entirely empirical and somewhat uncertain, while the chemical composition of the product is subject to varied interpretation (Woolfrey 1968).

Kinetic factors are known to influence the characteristics of any precipitate, and the present investigation has shown pronounced kinetic effects in this ADU system. Precipitation kinetics are being investigated and light scattering methods are the best tool for this. This report outlines available light scattering methods and delineates their usefulness in the investigation of this system.

A novel light scattering instrument is described, and potential industrial applications of the method are discussed.

2. THEORETICAL

2.1 Light Scattering as a Means of Particle Size Monitoring

The use of light scattering methods for both molecular weights and particle size determination is now well established, particularly for organic macromolecules. The literature was reviewed by Kratohvil (1964, 1966) and the theory by Van de Hulst (1957). These and other reports show very few applications to inorganic precipitation reactions, and work reported in that area covers only crystals of high symmetry. Since the present investigation seeks to extend the application to more anisotropic systems and also to apply measurements in situ to a loop-system, the relevant theory is presented in a condensed form. This is the more desirable since some errors have crept into the literature, as pointed out by Sinclair (1947). The multiplicity of symbols used and the unavailability of reliable text books also make a brief critical review useful. Stacey's book (1956) on "Light Scattering in Physical Chemistry" is out of print. The most comprehensive description of inorganic applications was given by Beattie (1958) and more briefly by Meehan and Beattie (1960). These latter references should be referred to where greater detail is required.

The main advantage of light scattering measurements is that they involve a minimum of interference either to the reaction being examined or the sample taken, if any. Samples are usually taken, and, indeed, some methods depend on various solutions of such samples. While continuous monitoring is not entirely new, it is considered in some detail here, mainly because of its very limited use in the past. Such continuous monitoring is one of the best methods for observing a precipitation reaction, and it may be supplemented by auxiliary methods which are discussed in Section 4.2.

The light scattering method has been most useful for particles of approximately 10-10,000 nm but this range will probably be extended, mainly downward, due to the increased use of gas lasers. The interpretation of results is often difficult in a new system but, once the initial work has been performed, the method should prove a valuable aid to rapid and reliable observation. Initial interpretation can be greatly assisted by use of the electron microscope, the ultracentrifuge, centrifugal settling, the Coulter counter or the ultramicroscope.

2.2 Light Scattering Theories

Two models of the light scattering process are currently used. The first is based on Rayleigh's concept (1871) of independent oscillating dipoles, the second on Einstein's treatment of density fluctuations, as adapted by Debye to concentration fluctuations. Both methods are useful approximations, for a limited range, to the rigorous solution of Maxwell's equations which are the basis of all present-day scattering theory.

Experimentally, we can use the intensity of the light scattered in a particular direction or the attenuation of the incident beam itself. The attenuation may be measured either directly or by integration of the scattered intensity over all angles. Finally, we may use the ratio of intensities in two suitably chosen directions. Each of these methods has theoretical and practical limitations which will be discussed. However, in each case an average particle size of the solid phase in a suspension can be obtained with the help of certain assumptions or auxiliary data.

2.3 Rayleigh's Concept

Rayleigh's theory is based on secondary radiation emitted in all directions perpendicular to the light induced oscillations of dipoles. Other effects which involve interactions with the scatterer, such as the Raman effect, are not considered here. A general form of the Rayleigh equation defines the intensity of light scattered at an angle θ (measured from the forward direction) by a unit volume of a suspension of uniformly dispersed spheres having a refractive index n_p in a 'solvent' whose refractive index is n_o, with $n_p \neq n_o$

$$R_\theta = \frac{I_\theta d^2}{I_o} = \frac{9\pi^2 NV^2}{2\lambda^4} \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 (1 + \cos^2 \theta) \quad \ldots(1)$$

where R_θ is the reduced intensity (or Rayleigh ratio),

I_θ is the intensity of the scattered light at a distance d,

I_o is the 'intensity' (or flux) of parallel incident unpolarised light,

N is the number of particles of volume V per unit volume of suspension, and

λ is the wavelength of the incident light in the medium, which equals the wavelength in vacuo divided by n_o.

The factor containing m where $m = n_p/n_o$ is proportional to the polarisability of the particle. The last factor relates to the two mutually perpendicular components of the oscillations of the electric vector, the first term being perpendicular to the plane of observation and the second one parallel to it. Figure 1 shows some of these relationships schematically.

Before discussing the geometrical representation and the limits of validity of the equation, let us see what results can be obtained from it. For any static system the volume fraction of the 'solute' can be determined independently, or is known a priori. It is NV. If we measure R_θ and m is known, then the product NV^2 can be calculated readily from Equation (1), so V can be found. It can be seen that for identical NV values the Rayleigh ratio varies as the third power of the particle diameter, provided that the particle shape remains unchanged. This is an important fact to bear in mind when discussing a much less tractable dynamic system, in which N or V, or both, may vary.

In a system in which particles are created, the meaning of the volume fraction must be critically examined. While the total content of solute may be known by virtue of the initial composition or by analysis, it is quite clearly not practically equal to NV, as long as N is the number of particles in a practical sense (i.e. particles sufficiently large to cause readily detectable dipole oscillations). Strictly speaking, of course, V can still be obtained by using the total volume fraction instead of NV but it will be an average over a range wide enough to render it quite meaningless (i.e., a range of 8-9 orders of magnitude).

In a dynamic system therefore an absolute determination of particle size depends on an independent determination of NV in terms of the solid phase only. Theoretically, there are three ways in which the volume concentration of the solid phase can be found. These are:

(i) direct measurement after phase separation,

(ii) monitoring the activity of the fraction remaining in solution,

(iii) measuring a physical property depending on the concentration in solution (e.g. conductance).

There exists one set of circumstances in our precipitation reaction in which an absolute measurement is possible, since NV is accurately known. This occurs when precipitation is complete. However, it remains to be shown that the range of validity of the Rayleigh treatment can be extended to cover the sizes involved at that stage, and that the anisotropy of our particles can be accommodated in this treatment.

Also, it must be mentioned that Equation 1 does give an approximation of the rate of growth of V, but only when based on general principles derived from theories of nucleation and crystal growth. From these theories it follows that immediately after a single addition of a precipitant to a system, dN/dt reaches a peak and then rapidly decreases. Then $N \approx$ const., and from Equation (1) $R_\theta \propto V^2$. Later when NV approaches its maximum, $dN/dt < 0$ and $NV \approx$ const. It follows that $R_\theta \propto V$. These relationships are very valuable guides, limited only by the lack of an inherent indication of when the transition occurs.

An even simpler relationship applies when Equation 1 is used for randomly oriented particles not larger than λ. Then if $V_1 < V_2$, $R_{\theta 1} < R_{\theta 2}$. Simple as this is, one can easily lose sight of it when all the complicating factors are considered, and this relationship remains valid well beyond the range of validity of Equation (1). However, for non-uniform particle sizes the distribution must remain substantially unaltered. The usefulness of this relationship is greatest for qualitative interpretations of the influence of individual factors on the rate of crystal growth.

2.3.1 Limits of the validity of the Rayleigh equations

In the form given here, Equation (1) is valid for dilute suspensions of small isotropic spheres. Approximate limits of the validity are often quoted. An attempt is made here to give more definite figures as a guide for experimental work. Such figures must be treated with some reserve, as they are based on arbitrary requirements of accuracy.

Firstly the concentration. This should be as low as possible consistent with reproducibility. If the scattered light is measured, the concentration must be high enough to give an adequate signal for detection from a sufficiently low scattering volume to allow determination of the scattering angle. It is a good rule of thumb that the total attenuation of the incident beam should not greatly exceed 10 per cent of its intensity (Van de Hulst 1957, p.6). This will ensure low incidence of multiple scatter.

Secondly, particle size. The usual reference to an upper limit is $r < \lambda/20$ where r is the radius of the sphere. In fact, however, r_{max} strongly depends on m. Heller (1959, 1965) made a detailed examination of limits from which it appears that in our case the limit is approximately $r < \lambda/14$. This means that, with red light, size can be monitored up to ~ 75 nm diameter based on the Rayleigh equation, but if this diameter is exceeded, the extensions discussed in section 2.3.2 must be used.

Finally, anisotropy must be taken into account. This may be due to either shape or internal structure of the particles or both. Since in our case the particle shape may be assumed to be governed by the unit cell, a single polarisability tensor can be postulated even if the shape is not strictly similar to the unit cell itself. It may be assumed that most of the anisotropy is due to the particle shape rather than to structural anisotropy, since the three refractive indices only differ by 5.6 per cent for $UO_3.2H_2O$. The structure of the product containing NH_4^+ ions is not very different, as evidenced by the similar main lines of the X-ray diffraction pattern. The product crystallises in thin hexagonal platelets.

Corrections required for anisotropy were investigated by Cabannes (1929). Two correction factors (f and f') are usually quoted but the correct use of the factor for scattered light $f = (6 + 6\rho)/(6 - 7\rho)$ is not very clear. It seems confined to scatter at 90°. For Equation (2) for turbidity, the factor $f' = (6 + 3\rho)/(6 - 7\rho)$ is used and seems to be universally accepted. However, the published literature gives no indication which one of the three refractive indices should be used, or rather how their values should be averaged when used in conjunction with a Cabannes factor. This point may be of minor importantance in our case because of the relatively small range of the indices.

It can be concluded that the Rayleigh equation can only be used for the early stages of crystal growth in our case, and then only in the form for specific turbidity. This form is:

$$\frac{\tau}{NV} = 24\pi^3 \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \frac{V}{\lambda^4} \left(\frac{6 + 3\rho}{6 - 7\rho}\right) \qquad \ldots(2)$$

where τ is the turbidity defined as the natural logarithm of the fractional decrease in intensity per unit light path and ρ, the 'depolarisation ratio', is the ratio of the horizontal component of light scattered at 90° to the vertical component when an unpolarised light source is used. N or NV must be known or found independently. Measurements for use with this equation may involve either the measurement of the transmitted intensity or the intensity of scattered light at 90° (I_{90}). The latter is related to τ by:

$$\tau = \frac{I_{(90)} d^2}{I_o} \; \frac{16\pi}{3} \qquad \ldots(3)$$

This relationship (Heller 1959) must be used when τ is very small, i.e. when the attenuation cannot be reliably measured. However, care must be taken to use the appropriate Cabannes factor.

Equation (1) in its unextended form does not seem useful for quantitative work in our case, except perhaps for the early stages of the reaction in highly diluted systems.

2.3.2 Extensions of the range of validity of the Rayleigh equations

Since deviation from the Rayleigh equation is the result of interference of the scattered radiation from individual dipoles, any extension of validity has to allow for, or calculate the extent of, such interference.

The general correction for anisotropy given by Cabannes (1929) has already been mentioned. No detailed description of its practical application is given in either the recent literature or in the original work. The use of a general correction factor for angular scatter other than at right angles requires some study. There is no particular reason to doubt the applicability of this factor up to $r \approx 75$ nm, but, in the absence of experimental confirmation, care is indicated.

With regard to size limitation, several extensions have been suggested. The best-known of these is the 'Rayleigh-Gans' treatment. This is not confined to spheres but has other limitations discussed below. Another extension is given briefly only because no detailed report about it has been studied. This is the Stevenson equation:

$$\frac{\tau}{NV} = \frac{24\pi^3 V}{\lambda^4}\left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \cdot \left(1 + \frac{12\pi r}{5\lambda}\ \frac{m^2 - 2}{m^2 + 2}\right) \qquad \ldots(4)$$

This equation is quoted by Heller (1959) as valid for spherical particles for a range which in our case is approximately $r \leq 150$ nm. It may be compared with Equation (2) to which it reduces as $\frac{r}{\lambda} \rightarrow 0$. When the last factor in Equation (2) is applicable, in other words whether Equation (4) may be used for non-spherical particles or not, will need further study. Heller implies that it can.

Equation (4) seems to be very useful, but confirmation of it is desirable. According to it, values of m below $\sqrt{2}$ will give a negative deviation from the Rayleigh equation and those above it a positive one, irrespective of the magnitude of r/λ. This is not what one would expect from the experimentally found universal scattering curve shown in Figure 2, (Sinclair 1950).

The Rayleigh-Gans treatment allows for interference by using a multiplication factor appropriate to the shape of the scattering particles. This factor, which is a distribution function for the scattered intensity, is obtained by integration over all angles of particle orientation for each scattering angle. The function is usually normalised to unity at $\theta = 0$. The integration has been carried out for a few geometrical forms. Probably the most useful for our purposes is the model of randomly oriented discs calculated by Kratky and Porod (1949). Some data for oblate spheroids are also available, but these will require much more calculation and are expected to fit our hexagonal platelets less accurately.

The basis for these calculations are modified Bessel functions of various orders. Some of the most useful are given by Van de Hulst, who also gives the factor for randomly oriented discs as:

$$R^2 = \frac{2}{Z^2} \left[1 - F(2z)\right] \qquad \ldots(5)$$

where $z = (4\pi r/\lambda) \sin 1/2\ \theta$ and $F(2z)$ is a Bessel function of the first kind and of 3/2 order, divided by the first term of its expansion (Van de Hulst 1957, pp. 98-9).

The factor may be used with Equation (1) at several angles. The deviation of the experimental intensity distribution from the theoretical one is then a measure of the width of size distribution, and also of the fit of the model. If this approach proved promising, additional information might be gained by artificially narrowing the distribution, e.g. by ageing, gel filtration, selective dissolution, etc. Typical distribution functions for various particle shapes are shown in Figure 3 (Billmeyer 1964).

Other extensions of the validity of the Rayleigh approximation have been suggested, but at their present stage of development they do not appear to be appropriate to our system.

2.4 Debye's method

Based on Einstein's (1910) thermodynamic treatment of density flunctuations for turbidity, Debye (1944) derived an equation linking the turbidity at high dilutions to the number of suspended or dissolved particles (N) per unit volume of solution. He used Van Hoff's equation for osmotic pressure $P = NkT$.

$$\tau = \frac{32\pi^3 n_o^2 (n_s - n_o)^2}{3\lambda^4 N} \qquad \ldots(6)$$

where n_s and n_o are the refractive indices of the solution (or suspension) and of the solvent respectively. This very simple relationship holds for ideal solutions only.

A practically more useful form of this equation introduces the concentration of the solution (c), on which the Van de Waals forces depend, and the molecular weight (M), the quantity usually measured by this method (Debye 1947);

$$Hc/\tau = 1/M + 2Bc \qquad \ldots(7)$$

where $$H = \frac{32\pi^3 n_o^2 (dn_s/dc)^2}{3\lambda^4 N_A}$$

B is a constant for any given particle shape or molecular structure, and N_A is Avogadro's number.

The equation is evaluated graphically by plotting Hc/τ aginst c, when the intercept at $c = 0$ gives $1/M$ and the slope is 2B. For the determination of particle volume, V may be substituted for M, and NV for c. According to Zimm and Doty (1944) the extrapolation gives a weight-average molecular weight (or particle volume) for a polydispersed system.

At very low concentrations Equation (7) reduces to Equation (6) when 2Bc vanishes and $(n_s-n_o)^2/c^2 \approx (dn_s/dc)^2$. Since M/N_A is the weight of one molecule, and N is their number per litre, $MN/N_A = c$ is the weight of the solute per litre. Thus both equations become $\tau = MHc$ as $c \rightarrow 0$.

Instead of τ one can use R_θ at either $\theta = \frac{\pi}{2}$ or $\theta = 0$ (denoted as R_{90} and R_0 respectively hereafter). Suitable modifications of Equation (7) can be made by use of Equation (3) and by using the relationship $R_0 = 2R_{90}$. The fact that these substitutions are strictly valid only for $V \rightarrow 0$ and $NV \rightarrow 0$ does not invalidate the general treatment. For organic macromolecules Debye has used R_{90} and a considerable number of workers have used this method successfully. Zimm (1948) found R_0 by a double extrapolation method in which $c \rightarrow 0$ and $\theta \rightarrow 0$, using a plotting method named after him. This has also found wide application and approval. It seems that the Zimm plot is less sensitive to anisotropy and can also indicate other effects when subjected to detailed analysis. Multiple scatter, change of shape, or change of aggregation can be detected by curvature of the lines.

These methods are valid for a rather large, although not well defined, range of particle sizes. However, the refractive index of the solute (a quantity which does not directly appear here) must not be too different from n_o, so that the incident beam is not appreciably changed during passage through a particle.

2.4.1 Extensions of validity of Debye's method

Two useful extrapolation methods for correction of secondary effects may be mentioned here. The Zimm-Dandliker (1954) equation involves both reduced intensity measurements at angle θ with vertically polarised light $(R_{\theta,v})$ and specific turbidity. It is:

$$(2K_1 + K_2) \left(\frac{c}{R_{\theta,v}}\right)_{\substack{c \rightarrow 0 \\ \theta \rightarrow 0}} = \frac{1}{M} \qquad \ldots(8)$$

where

$$K_1 = \frac{2\pi^2 n_o^2}{N_A \lambda^4} \left(\frac{\partial n_s}{\partial c} \right)^2 \quad \text{and} \quad K_2 = \frac{n_o^2}{4\lambda^2 N_A} \left(\frac{\tau}{c} \right)^2_{c \to o}$$

This equation is in a form quoted by Meehan and Beattie (1960) who state that it is not restricted to spherical particles. They used it successfully for m values of 1.7, considerably higher than our m = 1.30.

The other method due to Billmeyer (1954) also quoted by Meehan and Beattie (1960) is used for specific turbidity data and relies on extrapolation to zero concentration and to infinite wave length. Beattie (1958) has quoted the shape factor applicable to discs, not given in the original paper. However, between these three references there are several discrepancies,particularly regarding the range of validity which seems to be below our requirements. How Beattie (1958) could use this method, or why it should be valid for high m values well beyond the stipulated range, is not apparent from any of these references. The use of the extrapolation $\lambda \to \infty$ is not recommended for our system.

2.5 Larger Particles

2.5.1 Mie theory

Above the range of validity of the Rayleigh concept, the light scattered by a particle no longer depends on the scattering angle in the fixed way governed by the factor $1 + \cos^2\theta$. The mutual interference of the fields generated by different multipoles in the same particle becomes paramount in determining the shape of the scattering envelope. This envelope may be visualised as a geometrical shape whose distance from the scattering particle is proprtional to the scattered intensity in any given direction. For Rayleigh particles the shape is that of a coaxial dumb-bell, whose length is twice its width at 90°, irrespective of particle size within the range of validity, as long as the scatterers are spheres.

Figure 4 shows the scattering envelopes calculated for larger spheres by Blumer (1925). They are strongly displaced in a forward direction and curve b cannot even show the very large forward part. The dotted lines represent the horizontal component of the scattered light. These shapes are characteristic of size for isotropic spheres, and can form the basis of particle size determination irrespective of the scattered intensity, and thus independent of the concentration. When the particles are not spherical or isotropic in structure then this departure from central symmetry is no longer a uniquely determined function of size. Particle shape must then be taken into account as well. This is difficult, and very often so-called 'equivalent dimensions' are used to correlate experimental data for non-spherical shapes with calculations for spheres.

The basis of such calculations is the theory of Mie (1908) for spherical scatterers. Two intensity functions are calculated, one pertaining to the vertical component, the other to the horizontal component with regard to the scattering plane. (Numerical values have been tabulated: e.g. Lowan 1948; Gumprecht 1951). Each function is based on the same pair of intermediate functions which vary with the size (r) and relative refractive index (m). These are converted to the intensity functions by means of Legendre polynomials (in terms of cos θ). They can also be used for computing the scattering coefficient (K), a factor by which the geometrical cross section must be multiplied to give the scattering cross section. A plot of K v. $(m^2 - 1)\ 2r/\lambda\ (m^2 + 2)$ as shown in Figure 2 approximately holds for most colloidal suspensions and is therefore very helpful in understanding the uses and limitations of many methods discussed in this report.

Further details of the Mie theory, can be found in texts such as Stratton (1941).

2.5.2 Angular dependence and dissymmetry

Both these methods have partly been discussed above as modifications of the simpler approximate treatment for small particles. Dissymmetry is a special case of angular dependence which compares measurements at angles $\theta < \frac{\pi}{2}$ and $\pi - \theta$. The accuracy of these methods could be expected to increase as the particle size increases, that is as it moves away from the Rayleigh range.

Sloan (1955) describes a detailed method based on angular dependence derived from earlier papers (Sloan et al. 1954) and claims an effective range of 0.1 to 100 μ radius. The lower limit is close to the upper limit of our particles as originally formed, but the method could well be of interest in observing ageing processes. Sloan also refers to discs which are found to differ only slightly from spheres in scattering behaviour. He has used the method for the ageing of barium sulphate precipitates. Although the method is an absolute one, it has not found wide acceptance over the past 15 years, probably because of the high lower limit of validity and to its incomplete description in the journal literature. A recent review of this method by Livesey and Billmeyer (1969) may revive interest in it.

The same remarks apply to dissymmetry. Beattie (1958) has successfully applied this method to silver bromide sols, but used the Mie functions for spheres to evaluate the results. In our case this would probably be very inaccurate. Riley and Oster (1952) give an approximate dissymmetry equation for thin discs:

$$I_\theta / I_{(\theta-\pi)} = 1 + \frac{2}{3} \left(\frac{2\pi\tau}{\lambda} \right)^2 \cos\theta \qquad \ldots(9)$$

but the range of validity is not well defined. Note the dependence on λ^2, not λ^4. Details of evaluation and an expansion for I_θ are given by Debye and Anacker (1951).

2.5.3 Depolarisation

When the size of isotropic spheres approaches and passes the upper limit of Rayleigh scatter, the ratio of the two scattered intensity components $i_{1\theta}$ and $i_{2\theta}$ no longer equals $1/\cos^2\theta$. This can be seen from Figure 4. While this deviation may be used to compute the size of the spheres, it offers no advantage over dissymmetry. On the other hand, deviation from perfect symmetry of shape affects this so-called depolarisation to a greater extent than it affects the dissymmetry, especially at low angles.

It follows that this method is very cumbersome for particle size measurement. It does give a very pronounced response to changes in shape or anisotropy of internal structure. The greater the departure from sphericity, the greater the depolarisation effect. The random orientation of individual shapes decreases the depolarisation, but does not eliminate it. The greatest effect can be observed at $\theta = \frac{\pi}{2}$ where the depolarisation ratio for unpolarised light (a somewhat incongruous term) ρ may be measured. Its use for corrections was discussed in section 2.3.1.

2.6 Some Generalisations and Opinions

Very generally, the size limitations of the Rayleigh and the Debye approximations are due to the particles no longer conforming to the single dipole model assumed. Mutual interference inside the particle gives rise to more complicated patterns. Similarly, high concentrations and high relative refractive indices cause strong secondary fields. The action of such fields cannot be completely disregarded as is done when using these approximations.

In regard to the limitations of shape, especially for larger particles, two important aspects should be considered. Cauchy (1841) has shown that irregular shapes, randomly oriented, will project an area approximately equal to a quarter of their total surface. The other consideration is that the lower a body's symmetry, the more data required to define its shape and size. Taken together these statements show the relative merit of an empirical approach to the measurement of the size of non-spherical particles.

A further argument in favour of an empirical treatment is the difficulty of complete segregation of the transmitted light beam. The extinction paradox discussed by Van de Hulst (1957) shows that the total radiative energy removed from a light beam by a particle equals twice that intercepted by it. The excess caused by diffraction (Babinet's principle) is only partly detected by instruments of finite length. For a narrow size range the proportion detected is constant for an instrument. Thus results calculated by a empirical treatment are justified.

The universal scattering curve Figure 2., being itself of empirical origin, cannot justify the validity of empirical evaluation but does give strong support to it. A brief discussion of this very important curve is in order.

The universal scattering curve shows a smooth, but not monotonic, decrease of the power-dependence between the scattering cross section of a particle and its diameter. The value of this power is six for Rayleigh particles and two for large particles (e.g. $2r^2\pi$ for spheres). The corresponding powers of the scattering coefficient (K) are four and zero. The independence of K from particle size in the higher ranges is the result of polydispersity and of random orientation, both of which tend to obscure the theoretically expected oscillations around the value of 2.

The value of K=2 itself shows the effect of diffraction as discussed before (extinction paradox). The importance of a well-collimated light-beam is again demonstrated. It is also of interest to note that the maximum value of K is around 4 and that K decreases rapidly on both sides of the maximum. This rapid decrease suggests that the cross section of a particle can actually decrease as the particle grows. This however is not usually detected in polydispersed suspensions, since it happens only over a narrow range. Even so, the range around K_{max} is not easy to use for accurate determinations. To avoid it, one should change λ or m by suitable means. If the Rayleigh equation is used beyond the range of validity, the particle size obtained will be underestimated.

To sum up, the best chances of obtaining useful information in light scattering work seem to be through an empirical or semi-empirical evaluation of the results. For narrow particle size distributions such an approach should be sufficiently accurate. After all, the very definition of particle size for irregular shapes is not possible with any great accuracy. The valuable help which the method can give to the understanding of precipitation reactions should not be discarded, nor should it be discredited because of unreasonable demands on its performance.

3. APPARATUS

3.1 Commercial Light Scattering Apparatus

It can be seen from the preceding discussion that an apparatus for experimental investigationof precipitation kinetics should have the following properties:-

(i) It must separate scattered light from transmitted light as completely as possible.

(ii) It should measure small changes in transmitted light accurately, expressed in terms of the intensity of the incident beam.

(iii) It should reproducibly measure the intensity of scattered light relative to the incident light at chosen specific angles.

(iv) It must use reasonably monochromatic light, preferably variable through a wide range and equipped with polarising facilities.

(v) It should take cells of variable optical path lengths, and preferably of a flow-through type.

(vi) The sample should be kept at a selected constant temperature while measurements are made.

(vii) The range of measurement should be as wide as possible.

No standard commercial equipment satisfies these requirements completely at present. However both the most widely known instruments, Bryce-Phoenix and Sofica (or Aminco), have most of these features. They are built for measurements predominantly on polymers, but have been used for inorganic colloids as well. Fitted with a flow cell, either of these instruments could give the necessary data.

The interpretation of these data does not seem to be covered by the maker's operating instructions which refer to organic polymers. The high precision obtainable would largely be wasted on a polydispersed system of anisotropic particles of unknown optical constants.

Manuals for these instruments are not readily available. It would appear that the main difference between them is a more elaborate control of temperature and stray reflections in the Sofica, achieved by immersing the scattering cell into a suitable liquid, while the Bryce-Phoenix is of a more modular construction suitable for easy modification. The former is based on a design described by Oster (1953) and the latter on a paper by Brice et al. (1950). Both follow the principles laid down by Zimm (1948). Some of the differences have recently been discussed by Tomimatsu et al. (1968).

An apparatus used for kinetic measurements on barium sulphate is very sketchily described by Nielsen (1958). An interesting way of producing inorganic sols in the scattering cell is suggested by Ottewill and Parreira (1958) who describe their apparatus in some detail. However, the lack of reported work suggests that this apparatus has not found wide application. This apparatus permitted measurements of reaction times of a few seconds, but very fast reaction kinetics can be studied by a laser-probe described by Berne and Frisch (1967). Reactions with rate constants up to 10^{10} can be followed. Blum and Salsburg (1968, 1969) discuss the theory and Yeh and Keeler (1969) report an experimental application in which the broadening of the depolarised scattered light frequency is measured by interferometry.

While considering the adaptation of such instruments for this purpose, it was decided to construct the novel apparatus described in the next section. It was expected that the many changes required during early experimental work would be easier to make and would be cheaper than buying and modifying a commercial instrument.

3.2 A Novel Simple Apparatus

The light scattering apparatus which was developed is less elaborate in construction than the commercial instruments. It requires less precision and no elaborate electronic circuitry. The main novel feature is the provision of co-axially aligned annular detectors for the scattered light. Their use is justified by the axial symmetry of the scattering envelope around the incident beam for unpolarised light. It also permits the separation of the depolarised component of scatter originating from polarised incident light. In both cases the signal is integrated over an azimuthal angle of 2π and over a narrow range of the scattering angle θ.

This range is set by the size of the detector and its distance from the scatterer. The width of the range depends on the width of the annulus of the exposed part of the detecting cell.

As a result of this construction the total signal received is much stronger than usual, and less sophisticated detectors can be used successfully. In the apparatus in present use ordinary selenium photo-electric cells are provided and their output is fed into a 'Keithley 149' nanovoltmeter. The cells, with suitable holes drilled at their centre, are mounted on an optical bench (200 cm long) so that they are all in an optical line with the scatterer.

One limitation of this detecting system is the loss of angular definition, resulting in the loss of fine structure of the intensity pattern. This system also restricts the construction of the scattering cells to an axial symmetry about the incident light beam. Optical flats used as end windows fulfil this requirement. These must be accurately parallel and the incident light beam should also be fairly well collimated. Corrections are required for reflection, for the scattered light, and also for refraction. Total reflection sets an upper limit to scattering angles observable by the detectors. Neither of these limitations is very important for dilute aqueous inorganic sols of non-uniform particle size. However, suitable corrections must be made, especially when non-aqueous standards are used for comparisons.

A diagram of the assembly is shown in Figure 5 and a photograph in Figure 6 shows the light-proof shield removed and a flow-through cell of 1 mm optical path in position.

3.2.1 The light source

The light source is a 24V 250W quartz iodine lamp supplied from a transformer fed by a 500W 'Stabilac' voltage stabiliser through a 'Variac' transformer to regulate the intensity. The lamp is cooled by a fan and the light is collimated by two quartz lenses and two diaphragms of 3 mm diameter, which can be replaced by larger diaphragms. Iris diaphragms did not provide sufficiently reproducible intensity of illumination.

Grubb-Parsons narrow-band interference filters were used to obtain monochromatic beams. Reflected diffused light was cut down by tubular light traps and baffle plates, not shown in the photograph. Provision was also made for variable angles of polarisation.

Considerable effort was made to obtain a well-collimated source, but the result has not been very satisfactory. This may be due to lack of expertise, or it may not be possible without considerable loss of intensity. At present a divergence of 0.5° has been achieved at considerable cost in intensity.

3.2.2 Sample cell and loop

Several types of flow cells have been used and quartz cells (Heraeus) were found satisfactory. The one in use at present has an optical path length of 1 mm. It is suitable for suspensions containing concentrations of U down to 0.001M. For more dilute solutions cylindrical cells with optical paths of 20 to 100 mm have been used. They are not suitable for concentrated sols because they cause multiple scattering and because the particles tend to settle out due to reduced circulation velocities.

When back-scattered light is measured, it is important to place the cell exactly perpendicular to the incident beam to prevent part of the reflected light from the entry window falsifying the readings.

The flow-cell can be replaced by standard 10 mm cells for use with static samples. A 100 mm cylindrical quartz cell serves for both attenuation measurements (turbidimetry) and the detection of 90° scattered light (nephelometry) for very dilute suspensions. It can be used for either flowing or static samples.

The test solution is fed into the measuring loop by a metering pump from the stirred and thermostated reaction vessel into the bottom of the scattering cell and expelled through the top back to the vessel via sensors for conductance and potentiometric measurements. It is important to keep the loop free of air bubbles and at a constant temperature. The Watson-Marlow flow inducer generates some heat by friction, and the stirrer must not be allowed to create a vortex.

The interior of the light scattering apparatus is thermostated by means of vaned copper sheets with copper tubing soldered on. This helps reduce temperature fluctuations which would otherwise greatly influence the output voltage from the selenium cells and affect the conductance measurements.

Conductance measurements are also affected by slow bleeding into the circuit of the electrolyte from the salt bridge in the pH reference electrode. This is minimised by the use of an EIL combined glass electrode Type SHD33C, and by the use of 0.01M KCl instead of a saturated solution. This introduced only a small error, easily adjusted during standardisation by comparison with an external cell. The leakage of KCl into the reaction system was negligible, an important consideration for the more dilute solutions.

3.2.3 The detecting system

The intensities of both the scattered light and the transmitted light are measured by 'Megatron B' selenium cells. For the former, 45 mm diameter discs were provided with a central hole of 21 mm diameter which was carefully machined to avoid contact across the layers. The transmitted light detector is a standard 25mm mounted cell, placed at an angle sufficiently different from 90° to avoid interception of the reflected light from it by the scattering cell, or by any of the detectors facing it. This is best ascertained by trial and error.

The cells were sandwiched between a suitably cut sheet of copper (front) and a perspex sheet (back) with a hole approximately 25 mm in diameter. The perspex sheet presses a copper contactor against the cell. All connections were made with copper wire and low-thermal solder. Each cell for the scattered light has a 2200 Ω resistor across its terminals. These are connected to the input lead of a Keithley 'Milli-microvoltmeter 149' via a 12 point 'Ledex' solenoid switch. The switch is driven by a synchronised signal from a 12 point Kent recorder. Six cells can be connected, and the other points are used for ancillary data and for the transmitted light. The transmitted light detector is connected direct to the recorder without amplification and has a 56K Ω resistor across its terminals.

For very low intensity scattered light at 90° a photomultiplier tube (HTV-R136) can be placed in position and the output recorded on a Heath single-channel recorder. The angle of acceptance need not be narrow and the sensitivity of commercial instruments should be equalled or exceeded.

For the independent detection of the horizontal and vertical components of scattered light, annular 'Polaroid' sheets were cut and adapted to fit over the individual annular detectors. These two components are not the ones usually referred to by these terms, since they usually refer to orientation with regard to the scattering plane. On this instrument we can only measure either component as integrated over 2π azimuthally.

Depolarisation of the transmitted light can be measured with a standard P.T.I. 'Polaroid' analyser. No analyser has been used for the 90° scatter observed by the photomultiplier, but it can be provided should the need arise.

3.2.4 Calibration

Theoretically, no calibration should be needed to express the scattered intensity in terms of the intensity of the incident light, since the Se-cells can be made from matched sets. Thus, simple geometric calculations should give the necessary correlation. In practice, however, it is preferable to make the comparison. When the photomultiplier is used as the detector such a procedure is absolutely essential. The calibration should be done at the wavelength used, otherwise the difference in spectral response can introduce substantial errors.

The efficiency of the Se-cells can be compared by means of a low-turbidity standard diffuser working in the Rayleigh range. If such a standard is not available, an opaque white sheet can be placed in the position normally occupied by the scattering cell. In this case illumination must be from the reverse side, i.e. the side where the detectors are situated. We then assume the 'cosine law' to be valid, that is that the intensity of the reflected light is identical in all directions from the illuminated spot. Relative sensitivities can then be calculated from the geometry, better still, the actual geometry of the annular system may be reproduced, but illumination must be provided by a carefully shielded non-axial source.

Calibration of the photomultiplier tube is somewhat more involved. Figure 5 shows the schematic arrangement of this detector when used at 90° with the slits in position. (When the slits are not used, only relative changes in intensity can be measured and precise correlation with I_o is not required.) The following calibration method relates to measurements at 90° only.

If we call the total light intercepted by the P.M.-tube L_{90} then this must be related to $I_{90}d^2$, the quantity we are usually interested in measuring. As long as the geometry is constant, these two quantities are proportional:

$$I_{90}d^2 = k\, L_{90} \qquad \ldots(10)$$

where k is a constant for any single frequency.

If the diameter of the incident beam is not negligible or if it is not located exactly in the centre of a cylindrical cell, then the geometry will be affected by any change in the refractive index of the sample under observation (Hermans and Levinson, 1951). It is therefore best to determine k by using a medium of closely similar n_o to the experimental sample, i.e. usually an aqueous medium such as 'Ludox' silica suspension (Alexander and Iler 1953).

The exact nature of the constant k need not be defined, but the following relationship exists when only relative values are considered:

$$k = \frac{S_{Se} \times d^2}{V_{90} \times A \times S_{PM}}$$

where S_{Se} is the sensitivity of the selenium cell, S_{PM} that of the photomultiplier, V_{90} is the volume 'seen' by the detector, and A is the area of the cathode 'seen' by the scatterer. Neither V_{90} nor A is readily measured.

For practical purposes it is sufficient to find k so that $I_{90}\, d^2$ can be expressed in terms of I_o. This can be done by using equation (3), if we remember that $\ln\,(I_o/I) = \tau\ell$ by definition, where ℓ = length of the optical path in the sample. When using Equation (3) it is essential to bear in mind that I_o as used there is the incident light intensity at the location of the scattering volume and not at the entrance window of the cell (I'_o). This value will always lie between I'_o and I as usually defined. The two definitions of I_o become identical as $I_o \rightarrow I$. In practice this is achieved by a decrease in τ brought about by extrapolation to infinite dilution. Alternatively I_o may be calculated from the known geometry, for example if the observation is at the half-length point of the cell then I_o is the geometric mean of I_o and I.

We have then the following two simple equations for use with our instrument, where the measured quantities L_{90} and I_o can be given in mutually independent arbitrary units, provided only that k has been determined by the use of the same arbitrary units.

$$R_{90} = k\left(L_{90}/I_o\right) \qquad \ldots(11)$$

$$\tau = \left(16\pi k/3\right)\left(L_{90}/I_o\right) \qquad \ldots(12)$$

Either equation can be used to determine k if we have a standard sample of known R_{90} or τ. However, there is no need for such a standard when using Equation (12), since our apparatus can determine τ independently of k. Care must be exercised, however, to make sure that the calibrating solution is a pure Rayleigh scatterer. The easiest way to check this is by the absence of any dissymmetry.

The subject of calibration is not often described in the literature, probably because it is covered by makers of the instruments. For this reason it has been treated here in some detail. Further information can be found in the papers of Ottewill and Parreira (1958) and Beattie (1958). References given there cover the subject reasonably well. Corrections for reflection are discussed by Tomimatsu et al. (1968).

4. APPLICATION TO PRECIPITATION REACTIONS

4.1 Precipitation Kinetics

In every precipitation process nucleation and crystal growth occur. In addition one or more chemical reactions are usually involved, and in all but the most dilute solutions agglomeration of the primary particles to aggregates of macroscopic size also occurs.

A few remarks about each of these stages are given, but it must be borne in mind that the stages overlap to a considerable degree both in time and in dimensions. In fact even the definitions can often merge. General theoretical information can be found in Nielsen (1964), Walton (1967), Vol. 5 of the 'Discussions of the Faraday Society' (1949), and a number of general texts on crystal growth (e.g., Strickland-Constable 1968).

The main condition for any precipitation reaction is a saturation ratio S = c/s greater than unity. Here c = concentration at a given time and s = concentration at equilibrium. The energy change involved in crystallisation is proportional to $\ln S$. The energy used in forming an interface is proportional to the interfacial tension and must be deducted. The former varies as r^3, the latter as r^2. Thus for any 'equilibrium' condition there is only one stable value for r. Smaller particles tend to dissolve, larger ones to grow. It follows that true equilibrium only exists for very narrow size distributions with S close to unity.

Homogeneous nucleation rates vary exponentially with the second power of S and generally have a very large pre-exponential factor. It is therefore very difficult to observe such nucleation directly. In usual experimental work S is too low for it to occur at all. When it does occur, it is very fast and usually concurrent with heterogeneous nucleation which is often the sole nucleation process even at the higher values of S encountered in technical precipitations. Nucleation rates are usually estimated from indirect evidence.

Crystal growth rates also depend exponentially on S, but only to the first power. Furthermore, the pre-exponential factor is about two orders of magnitude lower. Thus it is possible to measure growth rates directly, provided S is kept sufficiently low. Towards the end of the growth process, where S approaches unity, the dissolution of small particles and concurrent growth of large ones prevails. This stage is called Ostwald ripening. Modern theories (Frisch and Collins 1952, 1953; Turnbull 1953) predict (for constant S) a linear dependence on time of the particle radius for small radii, while larger radii vary faster in proportion to the square root of time. The change occurs when the surface-controlled mechanism is replaced by diffusion control.

Agglomeration of primary particles to macroscopic aggregates usually occurs and interferes with experimental work. It is, however, of great technical importance and deserves attention as a distinct process. Generally suspensions containing less than 10^7 colloidal particles per ml are not subject to appreciable agglomeration (Overbeek 1952). Charged particles or stabilising agents can raise the stability by many orders of magnitude. Kay and Boardman (1962) in another context, and referring probably to larger particles, give an upper limit of 0.05 per cent solids for non-aggregation.

4.2 Light Scattering Methods for Precipitation Kinetics

Most of the methods outlined in this incomplete list have been used for the investigation of kinetics of particle growth. Most past applications refer to polymerisation studies in organic systems. In comparison very little work has been done on a small number of inorganic systems. Of these, most have been investigated several times.

The earliest work (apart from Tyndall's original discovery) on inorganic systems was probably on sulphur sols, (La Mer et al. 1946) and extended to selenium by Watillon and Dauchot (1968). Silver bromide was investigated by Tezak et al. (1950), Beattie (1958), and

Napper and Ottewill (1963), the iodide by Jaycock and Parfitt (1965), and the chloride by Mailliet and Pouradier (1961). Silicic acid is described by Alexander (1953) and Audsley and Aveston (1962). The precipitation of barium sulphate was reported by Collins and Leineweber (1956), Nielsen (1958, 1961) and Doremus (1970). Among the hydroxyl compounds, those of aluminium were reported by Bontoux et al. (1965), and thorium and uranium hydrolysis products were subjected to repeated studies including some turbidity work by Tomazic et al. (1968) and Bilinski et al. (1963).

The narrow range and marked repetitiveness evident in this list shows the tentative nature of the results, and of their interpretation. It also shows an increasing confidence in tackling the problems involved, which is based on recent advances in light scattering theory and techniques.

A precise interpretation of light scattering data has never been achieved, even for the most simple precipitation reactions. Quite apart from experimental limitations, the theories of light scattering and of precipitation are not sufficiently advanced to determine the width of the particle size distribution accurately. A suitable distribution is usually assumed and often the results are consistent with the assumed function.

The question whether this approach is then worthwhile or not, must be answered in the affirmative, despite any shortcomings. A general statement by Walton (1967) may be quoted: "The two main techniques used for following precipitation processes have been conductivity and light scattering. Considerable difficulties have been encountered with both methods, though they may be used semi-quantitatively". Similar views are held by Doremus (1970). Accuracy is therefore only required where it helps to define the magnitude or validity of the approximation which is to be used in any particular case.

Auxiliary methods can help in two different ways. Some are needed to make interpretation of the measurements possible, for example, optical data for the components of the suspension, and analytical data to determine the composition of the phases. It is worth noting that changes in these data occur during the precipitation process and that such changes and their influence on results have often been disregarded without even a discussion.

Other auxiliary methods may not be directly relevant to the calculation of light scattering results, but may help in the interpretation generally. These include size classifying methods and any physical or chemical measurement (e.g. potentiometry, conductance) that is preferentially sensitive to the material in either phase. The centrifuge, the ultracentrifuge, and the gel filtration technique can all provide such help, while the Coulter counter, the ultramicroscope, and particularly the electron microscope, belong to both categories. The electron microscope provides an independent alternative to light scattering methods and could be superior to them if a true and rapid sampling method were available. It is a very effective means of confirmation and calibration.

4.2.1 Continuous monitoring

Earlier studies listed above have used light scattering data for particle size determination, but not for continuous monitoring in situ. While the examination of samples outside the reaction system may permit more accurate measurements, their relevance to the reaction mechanism is probably inferior to that of less accurate data more closely correlated with time.

The work in progress uses a closed loop as a sampling device, details of which are given in Section 3.2.2. While the use of flow cells is certainly not novel, apparently their use in precipitation kinetics is new. It must be remembered that the availability of a loop sampling system in no way precludes the taking of other samples independently whenever this may be of advantage (e.g. for tests at greater dilution). However, the use of continuous monitoring favours a semi-quantitative treatment.

The aim of a semi-quantitative approach is to examine the influence of well chosen parameters on the rate of precipitation and to distinguish as far as possible between the various stages of the precipitation. In favourable cases one should be able to discuss critically a postulated mechanism for the precipitation reaction. The ultimate objective is the prediction of properties of the precipitation product under varying conditions.

4.2.2 Anisotropic systems

Once the approximate nature of the light scattering data has been recognised, the method need not be confined to highly symmetrical crystal structures. Although the inaccuracies can be much greater, anisotropy should also be capable of helping interpretation as will be shown.

When considering a complicated anisotropic system, the simple principles set out at the end of Section 2.3.1 can be helpful. Quite generally, precipitation experiments show, and theories mentioned in Section 4.1 explain, that we must expect a rather prolonged delay before a light scattering effect becomes evident. This so-called induction period is followed by a very sudden rise in light scattering effects, due to the larger particles present. The time elapsing before this sudden rise occurs is a very important indicator of the growth rate.

The shape of the intensity v. time curve would give detailed information, if the size distribution were either known, or very narrow. Unfortunately this is not to be expected, and assumptions about the nature of the distribution must be made. The effect of the small particles is swamped by the large ones and, since the large ones grow much quicker, the observed slope of the curve represents the fate of the larger particles almost entirely. Early growth rates, which are unobserved during the induction period, are determining factors in creating the observable excursion of growth. Therefore one should attempt to refine the methods of observation sufficiently to follow the very slow increase of scattered light during the 'induction period'. A knowledge of absolute sizes would be desirable, but not essential. The distribution at this stage ($N \approx$ const. $\approx$ max; $S \approx$ const.) must be assumed to be extremely narrow.

During this period the Rayleigh equation is fully valid. The anisotropy would be measured by polarisation ratios at, say, 90°, but would not appreciably influence results for R_θ at $\theta \to 0$.

The rate of growth during the 'excursion' stage may be followed by Rayleigh-Gans treatment on the lines described for randomly oriented discs. The Stevenson Equation (4) may be used as a check. Towards the end of growth the range of validity may be exceeded even for red light, but since this is the most uncertain stage (due to a wide size distribution) this will not mean a great disadvantage versus more accurate models for quasi-spherical crystals.

During the Ostwald ripening (S = const = min., NV = const. = max.) light scattering in situ is expected to give qualitative assistance only. On the other hand it may be possible to get more quantitative data by dilution techniques or with additives on independent samples using, for example, the Zimm-Dandliker equation. Results here must be carefully checked, especially when agglomeration occurs concurrently.

A particularly interesting possibility seems to be the detection of agglomeration based on the anisotropy of the primary particles. Unless they preferentially attach themselves in the direction of the longest dimension one would expect a considerable decrease in anisotropy and depolarisation for the same NV values.

Provided the particle shape remains unchanged during the precipitation process, only a marginal disadvantage appears to be involved when light scattering methods are used for anisotropic precipitates, and most of this disadvantage relates to absolute particle sizes, which have been of limited use for rate determinations in inorganic precipitation reactions.

4.2.3 The ammonium hydroxide-uranyl nitrate system

Woolfrey (1968) gave a comprehensive review of this system. This showed that little reliable knowledge exists about the reaction involved in the precipitation process. Although unable to define the exact nature of the reaction or its products, Szego and Marshall (1971) have shown that $UO_2(OH)_2.H_2O$ is not obtained, and that the NH_4^+ ion takes part in the precipitation reaction.

This precipitation reaction differs from those previously investigated by light scattering in that it is not a simple reaction between two ionic species, mixed in the form of their soluble salts. Another difference is the strong hydrolysis and generally high co-ordinating power of the uranyl ion. These conditions do not favour the use of supporting electrolytes and also give rise to early polymerisation.

Optical data for $UO_2(OH)_2.H_2O$ are given by Landoldt-Börnstein (1962), but no data are given for light dispersion. The effect of NH_4^+ ions on the refractive indices either must be disregarded, or new data must be obtained for the actual precipitate. In view of the similarity in shape and structure as evidenced by X-ray diffraction (Stuart and Whateley 1968) it seems justifiable to assume very similar values. A small error here would only slightly affect the Rayleigh or Rayleigh-Gans treatment, and only when used for absolute values. The lack of dispersion data is probably more serious anyway.

The Debye method on the other hand is quite unsuitable for a system in which the concentration changes are outside the control, or even the knowledge, of the experimenter, and accurate optical data are required. It is indeed surprising that Meehan and Beattie (1960) were able to get reasonably consistent results based on widely differing $\partial n/\partial c$ values. Perhaps a clear re-definition of these values in a precipitation system could overcome some confusion.

Although the re-determination of optical data for this precipitate is not contemplated at present, such an investigation may well be worth while. The same also holds for UO_2 powders.

4.3 Effect of Particle Size Distribution

We have seen that light scattering methods in general are strongly biased towards the larger particles in a polydispersed system. This is always true for particles smaller than those corresponding to the maximum scattering coefficient K_{max} shown in Figure 2. If we are interested in the growth rate of particles at the lower end of the particle size distribution, then light scattering methods will be of direct use only if we have independent evidence of, or good theoretical grounds to assume, a constant and preferably narrow particle size distribution. Otherwise light scattering data will only supply indirect evidence of earlier growth rates. Of course, classifying methods can partly overcome this difficulty, but such methods are outside the scope of this report.

The type of distribution obtained in any precipitation reaction strongly depends on the conditions of the reaction. From the principles outlined in Section 4.1 it follows that the distribution will be relatively narrow if S is kept low and will also become narrower with age. It seems to be a widely held view that in precipitation reactions the prevalent type of distribution is a log normal one, as defined by Galton and MacAlister (1879). Such a distribution was shown to apply to silver halides (Loveland and Trivelli 1927) and was used for light scattering calculations by Beattie (1958) and by Mailliet and Pouradier (1961). The log normal distribution can be represented by a straight line on semi-logarithmic probability paper when the cumulative number of particles smaller than the variable r is plotted v. r, the latter taken on a logarithmic scale. A simple form of this distribution is given by Meehan and Beattie (1960):

$$f(r)dr = C \exp\left[-\frac{1}{2}\left(\frac{\log r/r_g}{\log \sigma_g}\right)^2\right] dr \qquad \ldots(13)$$

where $f(r)dr$ = number of particles larger than r, but smaller than $r + dr$,

r = the variable particle radius,

r_g = geometrical mean radius,

σ_g = geometric standard deviation,

$C = [f(r)]_{max}$ = const.

For a more detailed discussion of distributions the reader is referred to "Small Particle Statistics" by Herdan (1960) particularly chapter 4, "The Distributions of Particle Size and Their Averages" and chapter 6, "Some Standard Forms of the Distribution Function". Irani and Callis (1963) also discuss these aspects, and some remarks which are particularly relevant to kinetic treatments are given (p.39-47). They conclude that when the initial radius is very small then a log normal distribution is very likely to apply. In the writer's opinion this is the case when a single dose of precipitant is rapidly added to highly diluted solutions.

Very briefly, the smaller the particles, the higher the order of average required for a good approximation of the true distribution. Stacey (1956) states: "it is the Z-average of the principal dimension which is determined" (p.2). The Z-average is defined as the summation of the cubes of the particle weights divided by the summation of their squares. For a weight average we take powers one unit lower. According to Billmeyer (1964) a rectilinear Zimm plot (c.f. 2.4.1) gives accurate weight average particle weights.

The best average is not easy to choose, but careful analysis of the methods used usually gives strong pointers for a judgement. It is important to realise that both averages mentioned are heavily weighted for the larger particles and are therefore usually close to the right answer for particle sizes less than

$$r \approx \frac{\lambda(m^2 + 2)}{10(m^2 - 1)} \quad ,$$

a size corresponding to the maximum scattering coefficient in the universal scattering curve (Sinclair 1950). The difference can be significant, especially for wide distributions. But for randomly-oriented non-spherical particles the inherently low accuracy will usually not be greatly reduced by this type of error.

5. PRESENT AND POTENTIAL APPLICATIONS IN INDUSTRY

5.1 Present Industrial Applications

A complete review of industrial applications of light scattering methods is beyond the scope of the present report, but a few references are given below. Many references made in the industrial literature are of a very general and vague nature e.g. Orr and Dallavalle (1959) list the following materials under the heading 'Uses': Viruses, bentonite, halloysite, ferric oxide solutions, gold and other solutions, screening smokes, insecticidal dusts, fogs, mists, fumes, catalysts, coal, coke, oil-water emulsions, haemoglobin, albumin, soaps, metallic films, bacteria, gels, glasses, kaolin, alloys and "many other substances". No further details are given. Of course, specific details of routine quality control work are not usually published, except when established standards have been defined.

Quite a number of industrial research laboratories have published work on light scattering, thus showing their interest in this field. Gledhill (1962) describes AgBr solutions for Kodak Research Laboratories. The DuPont Corporation engaged in early work on minerals, e.g. sphalerite, cerussite, cryolite and barytes (Bailey 1946). This later served as the foundation for the universal scattering curve of Sinclair (1950). The same company also sponsored the development of an early light scattering instrument by Aughey and Baum (1954) a forerunner of a popular current commercial instrument. Angular dependence data was evaluated at the same firm by Sloan and co-workers (1954, 1955) and applied to monodisperse and polydisperse suspensions, e.g. of titanium dioxide and various barium sulphates.

Billmeyer (1964) (also from the Dupont Corporation) describes the usefulness of light scattering in the polymer industry. The range of molecular weight is from 10,000 to 10,000,000 but both limits can be exceeded under favourable conditions. He names sucrose at the lower end and proteins at the upper end of the range. There is little doubt that to date plastics and elastomers have been the most fruitful areas for this technique.

Some institutes for applied research have also taken an active interest, e.g. the Centre de Recherches sur les Macro-molecules, Strasbourg, with a number of papers by H. Benoit and others in the 1950's. Some interest in pigments was taken by C.S.I.R.O. (Blevin and Brown 1961), but they do not appear to be active in this field at present.

Evidence of the widespread use of light scattering in industry is indirectly available from the pamphlets of the instruments makers. Bulletin BP-2000B of the Phoenix Precision Instrument Co. lists approx. 70 industrial organisations in the U.S.A. using their instruments. Among foreign organisations, the C.S.I.R.O., Sydney, and the Wool Research Division, Melbourne, are quoted.

5.2 In-Line Monitoring

A loop system of measurement has considerable potential for application in technology when properly adapted to a specific problem. Application to relatively concentrated solutions will require continuous dilution of the sample by means of proportionating pumps.

ADU studies involve very small particles (of the order of $<0.1\mu$) in very dilute solutions, not often encountered in industrial processes. However, the reliability of a loop system for use in light scattering work has already been amply demonstrated by the data collected. Rayleigh ratios in the range of 10^{-6} to 10^{-4} have been determined to a precision of ± 10 per cent, a very satisfactory result in view of the fact that the quantity of interest (the particle length) determines this ratio by a sixth power relationship. The accuracy has not yet been determined fully.

For the larger particles involved in industrial processes (up to $\sim 100\mu$) the methods described in 2.5.2 are particularly suited. In addition an empirical treatment (Rose 1952) based on transmittance was said to give good agreement with more elaborate methods of particle size analysis such as complete photosedimentation analysis (Rose and Lloyd, 1946) which can be performed on a commercially available instrument (Irani and Callis 1963). Further information on particle size determination can be found in textbooks such as Orr and Dallavalle (1959), Cadle (1965) and others previously mentioned.

In evaluating the reliability of measurements of this type, important facts reported by Sinclair (1947, 1950) should be considered. Diffraction results in a scattering coefficient of 2.0 for particles larger than $\sim 2\mu$. This means that a particle will intercept and deflect light corresponding to twice its geometrical cross section. However, the practical detection of this effect strongly depends on the distance of the detecting device from the particle in relation to the particle size itself. A very long light path will completely eliminate this difficulty.

Secondly, as can be seen from Figure 2, the universal light scattering curve shows that when $k>2$, two different particle sizes may cause the same scattering effect.

Usually, this relates to particles whose longest dimension is around 2μ. Since this broad range is of considerable practical importance it is necessary to establish on which part of the curve the average value is located. Heller (1955) suggested the simple expedient of making a second determination at a different frequency of the incident light. This makes the result unambiguous.

5.3 Characterisation of Ceramic Powders

Once set up, very rapid and simple methods can give valuable information on the size of powdered materials. Ceramic powders in particular are mentioned because these are of interest not only to the nuclear industry, but also in many other industries. The use of light scattering is suggested to complement, not to replace, slower but more precise methods. The review given in the preceding sections will convey a general picture of the prospective use of light scattering methods for this purpose. However, because many industrial powders, and particularly nuclear fuel powders, are rather dark in colour, the effect of light absorption and opacity in general is discussed below.

A recent paper by Meehan (1968) discusses the work on lead sulphide suspensions by A.E. Gyberg (to be published). He states that generally the same considerations apply to opaque powders as to transparent ones, as long as one uses the complex refractive index ratio $\hat{m} = m\,(1 - ik)$, where $i = \sqrt{-1}$. If these data are not available, they can be calculated from the known particle size by using transmittance and forward scattering data jointly. This suggests that an instrument could be standardised comparatively easily for this purpose.

In the writer's opinion it is not yet possible to get reliable size data for strongly absorbing particles in suspension by simple light scattering methods. Nevertheless it is quite possible that rapid determination of the identity or the lack of identity of two samples can be made, and possibly also some useful correlation can be established between routinely-obtained data and the performance, or the particle -

size distribution, of a powder.

6. LIMITATIONS OF THE METHOD AND POSSIBLE IMPROVEMENTS

Many of the limitations of the light scattering method generally have been discussed in this report in their appropriate context. It remains to briefly summarise them, and to discuss the shortcomings of our instrument in particular, with suggestions for improvements.

Perhaps the main limitation of light scattering methods is their inability to deal adequately with polydispersity when this is considerable and when it does not follow a known pattern. Secondly we have the adverse influence of absorbance when it is strong and spread over the whole spectrum. Thirdly, there is an absence of tractable mathematical treatment for irregular shapes suitable for rigorous calculations. Finally the required optical data are not always readily available.

On the positive side it can be said that most of these difficulties become of reduced significance as the particle size increases and the angle of observance decreases. When only relative data are required or when empirical formulae are used, significant data can usually be obtained. This is especially the case when two or more methods of observation are used simultaneously. When such data are of high accuracy then a close approximation to the true measurements should generally be obtainable.

To obtain high accuracy, two improvements to our apparatus are essential. The collimation of the light source must be made as good as possible, and the sensitivity of the detectors must be made better without significant increase in noise. Both of these objectives can be readily achieved by the use of a low power helium-neon gas laser source (Livesey and Billmeyer 1969).

A further improvement would be the continuous recording of the angular dependence of the scattered intensity. This could be achieved by a simple eccentric drive to move an annular Se-cell to and fro in the direction of the incident light beam. Driven by a small synchronous motor this would provide a harmonic motion suitable for computer treatment of the intensity data.

With a single detector, calibration is much easier and the number of observations is not restricted by geometry as at present. The data so obtained can be interpreted rapidly by the method of Sloan et al. (1954) or Livesey and Billmeyer (1969).

7. SUMMARY

Light scattering theory and practice, especially as it applies to the precipitation of alkaline U-VI products, has been critically reviewed. The most essential features of a rather wide field have been presented mainly for the scientist not specially interested in the theory of light scattering, but rather in the uses to which it can be put. These, in the authors opinion, are in research work and in the optimisation and control of the production of a wide variety of solid products from solutions.

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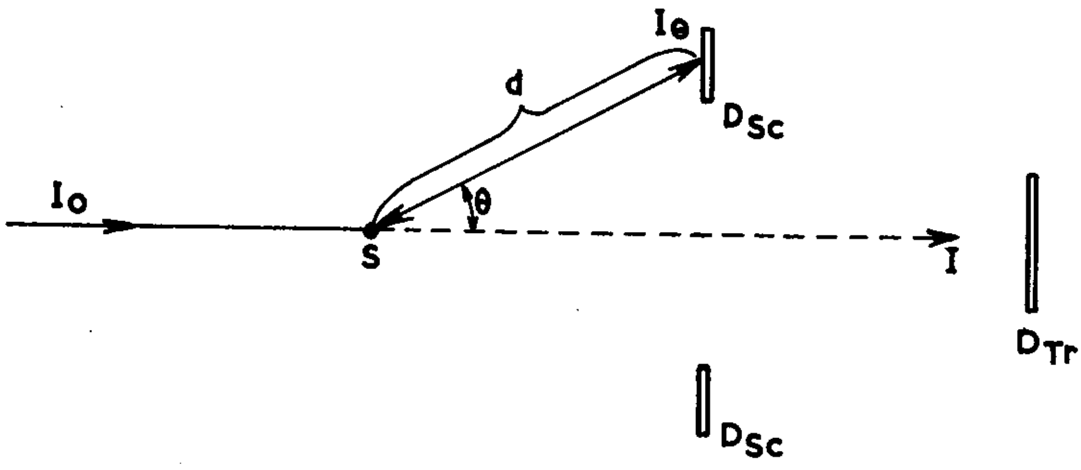


FIGURE 1 (a) Schematic arrangement for light scattering measurements.
I_o = intensity of incident light beam, I_θ intensity of scattered light at distance d from the test sample S, as measured (by e.g. an annular detector D_{Sc}). The intensity of the transmitted light I is measured by the detector D_{Tr}. The same detector measures I_o when S is removed from the light path.

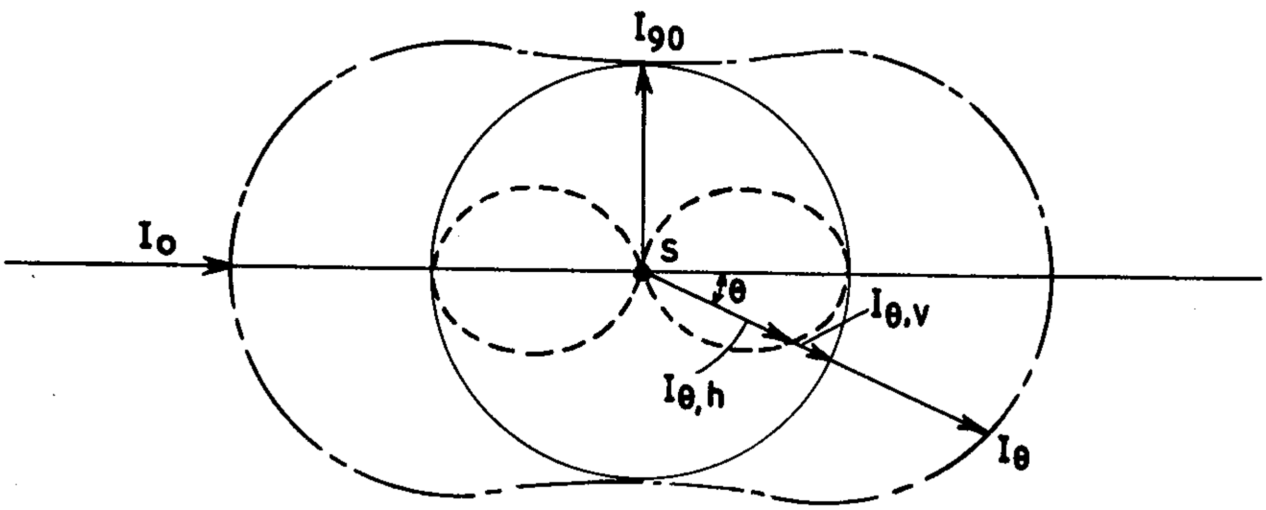


FIGURE 1 (b) Angular variation of pure Rayleigh scatter.
$I_{\theta,h}$ represents the horizontal component (in the plane of the paper) – – – and $I_{\theta,v}$ the vertical component ——— of the total scattered light of intensity I_θ — — — — . The intensities are indicated by the respective distances from S.

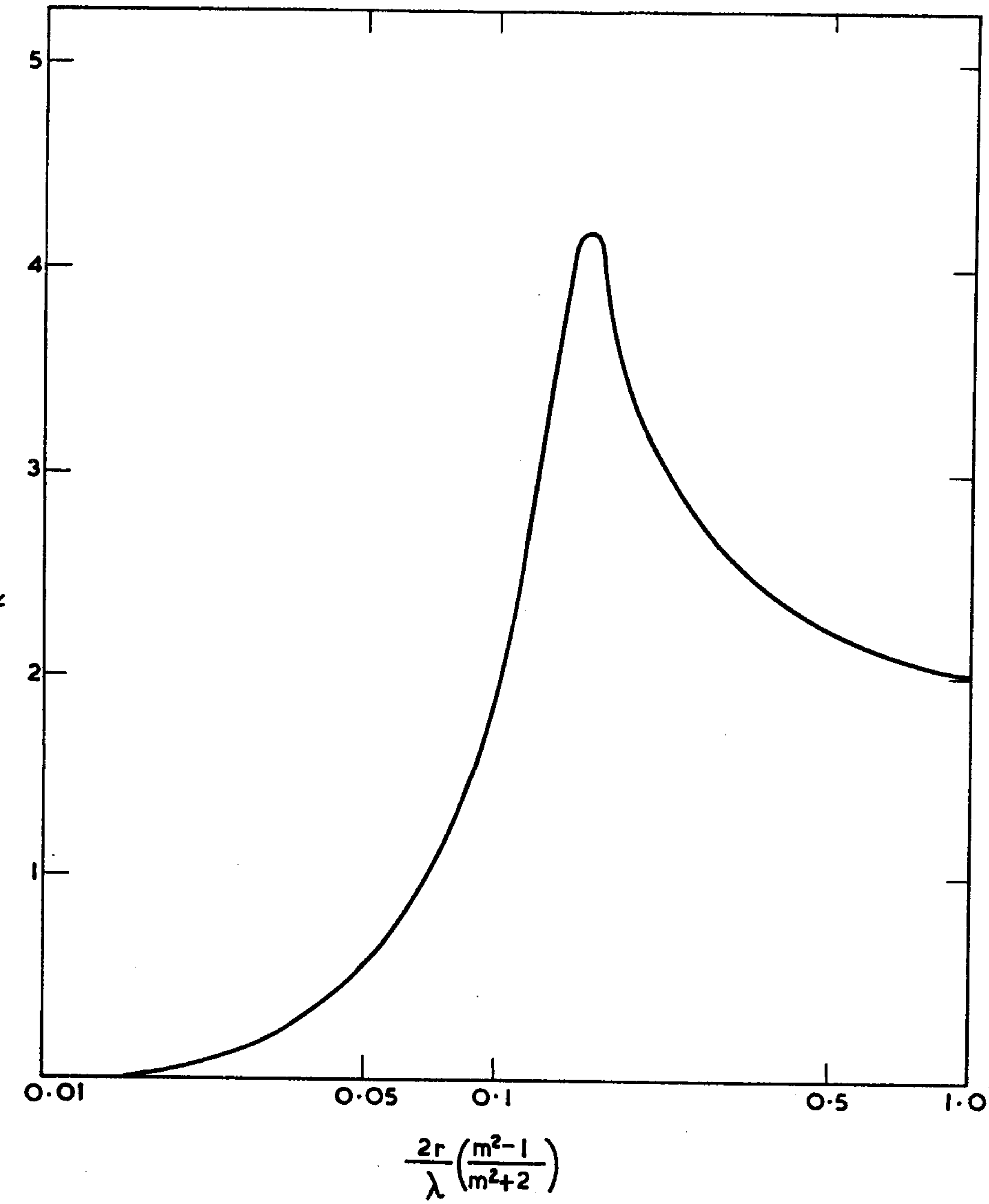


FIGURE 2 The 'universal scattering curve' for spheres (after Sinclair, 1950) plots the scattering coefficient (K) versus the size parameter $\frac{2r}{\lambda}\left(\frac{m^2-1}{m^2+2}\right)$. r is the radius of the sphere, and the other symbols are as defined for equation 1.

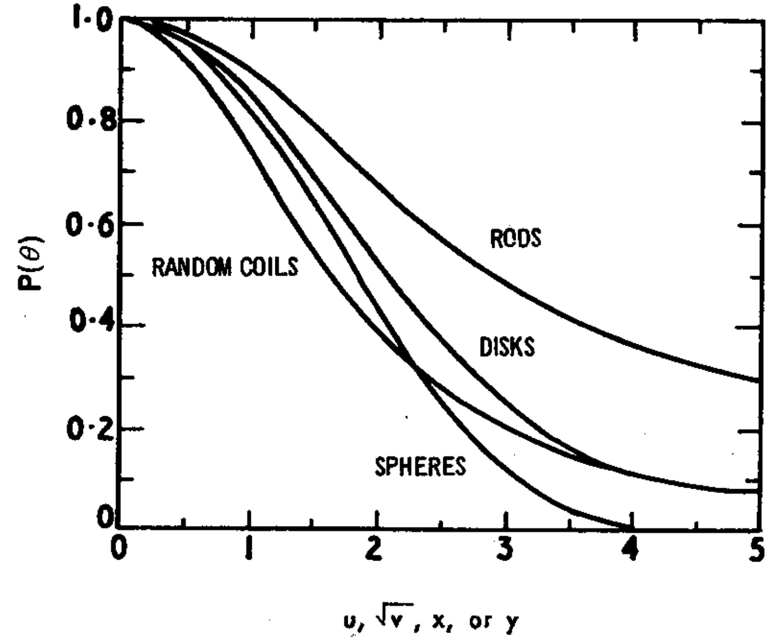


FIGURE 3 (a) Variation of the particle scattering function $P(\theta)$ with the size parameter u (spheres), $\sqrt{v}$ (monodisperse random coils), x (rods), or y (disks). (After Billmeyer 1964).

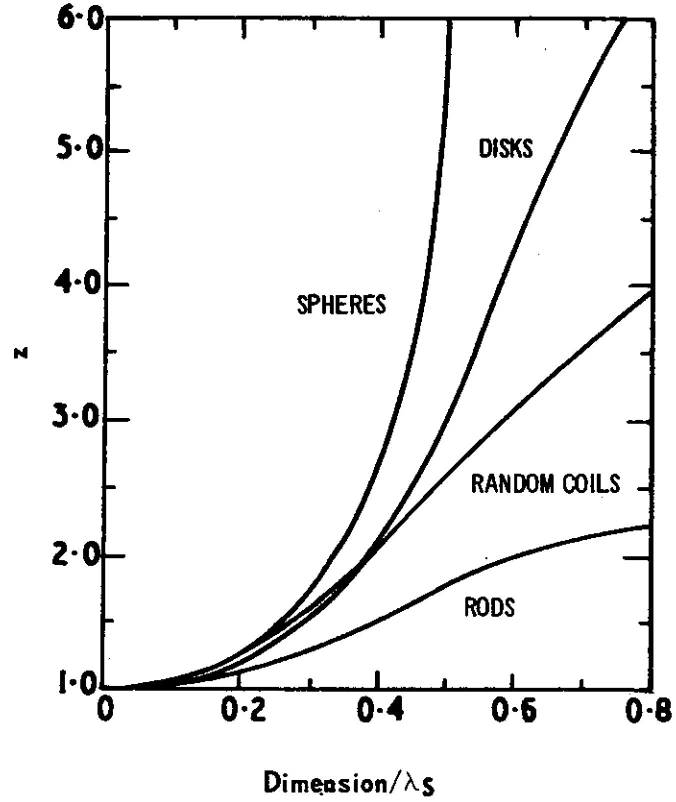


FIGURE 3 (b) Variation of dissymmetry with ratio (size parameter) /λs for spheres, monodisperse random coils, rods and disks. (After Billmeyer 1964).

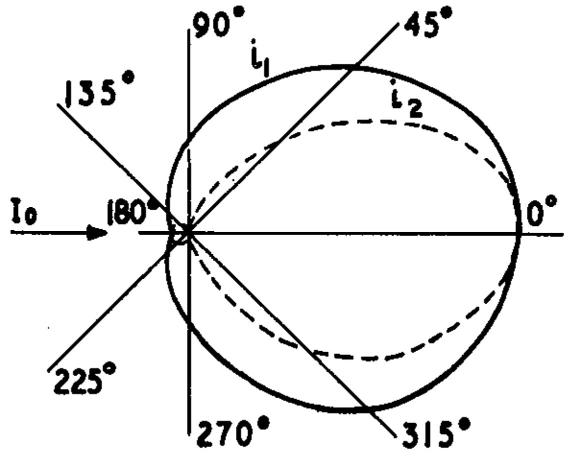


FIGURE 4 (a) Relative intensity of scattering about isotropic particle of radius ~ 0.13 λ. (After Bender 1952).

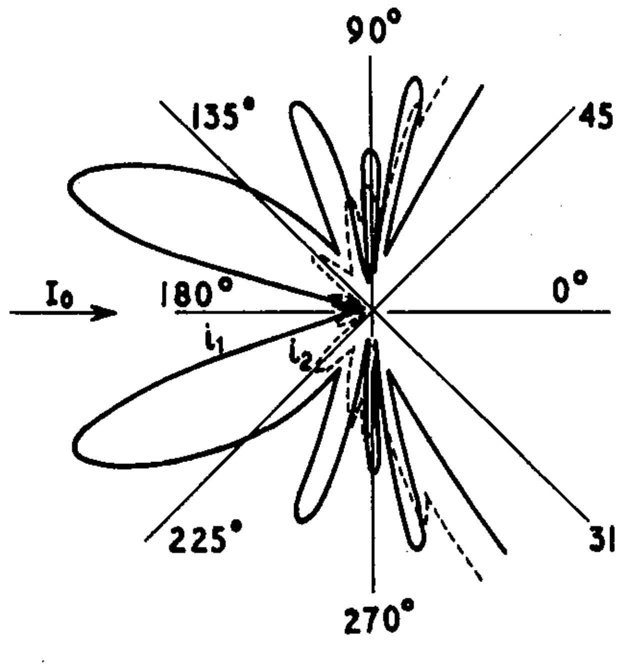


FIGURE 4 (b) Relative intensity of scattering about isotropic particle of radius ~ 0.65 λ. (After Bender 1952).

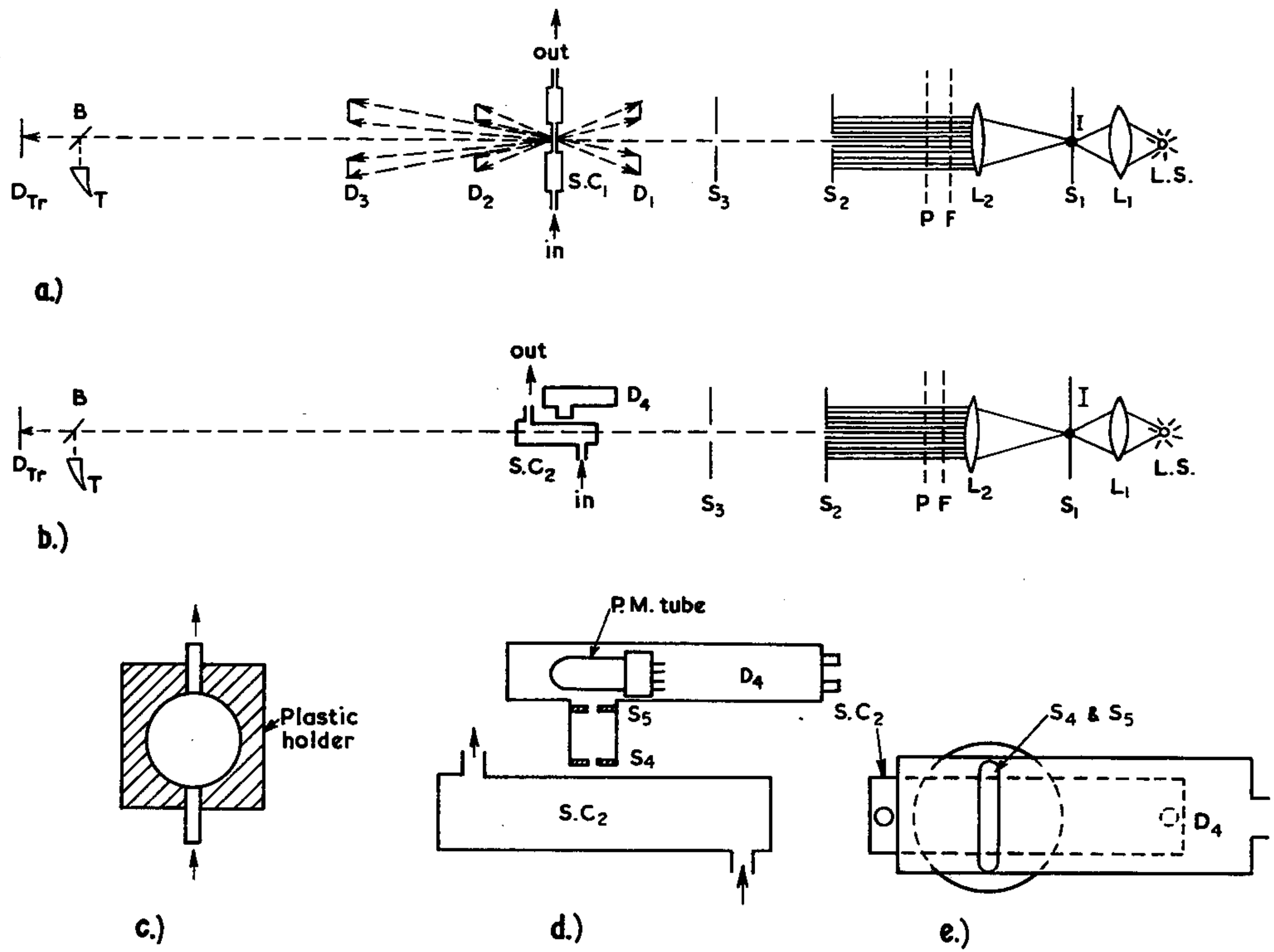
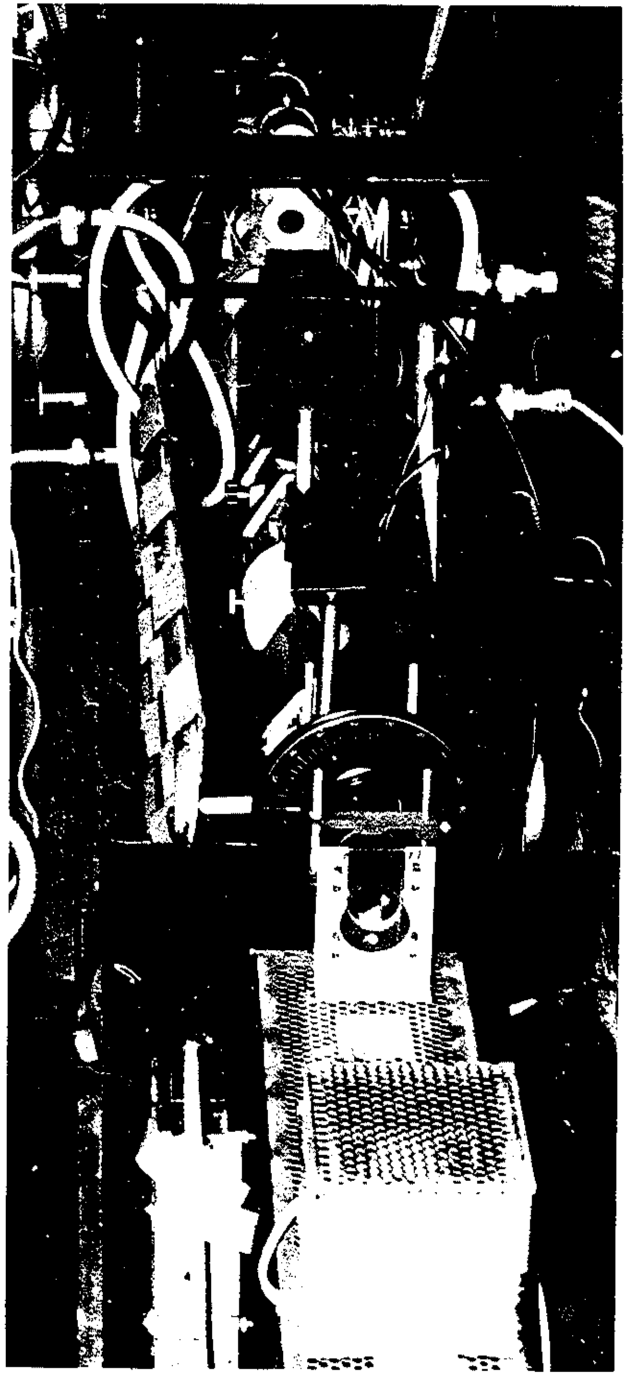


FIGURE 5 Schematic outline of light path and detector arrangement a) for angular scatter b) for nephelometry (90° scatter) c) front view of sample cell $S.C_1$ d) Side view of $S.C_2$ and detector arrangement e) Top view of slits for photomultiplier detector D_4.
L.S. light source; L_1, L_2 collimating lenses; I point image of source in hole of S_1; F filter; P polariser; S_2, S_3 collimating slits; D_1, D_2, D_3 annular selenium photoelectric cells; D_{Tr} disc Se-cell; $S.C_1$ flat circular sample cell; $S.C_2$ round cylindrical sample cell; D_4 photomultiplier housing; P.M. photomultiplier tube; S_4, S_5 collimating slits for 90° scattered light.



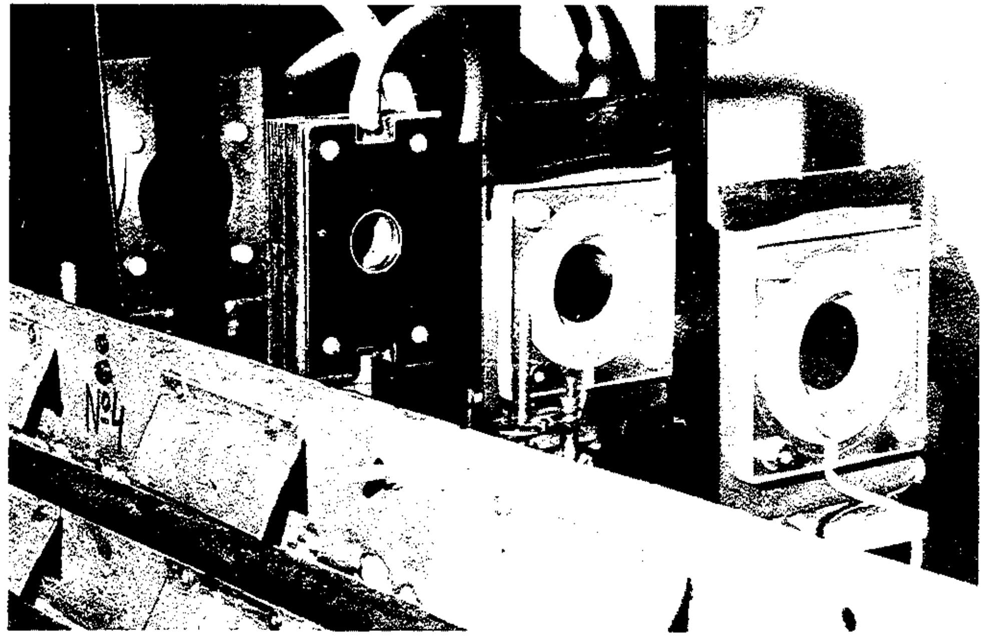


FIGURE 6 The light scattering apparatus