STUDIES OF PARTICLE SIZE CHARACTERISTICS OF AQUEOUS DISPERSIONS OF POLYACRYLIC ESTERS, AND OBSERVATIONS ON THE MECHANISM OF THEIR FORMATION.

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Studies of Particle Size Characteristics of Aqueous Dispersions of Polyacrylic Esters, and Observations of the Mechanism of Their Formation

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SUMMARY

The history and the development of aqueous dispersions of the polyacrylic esters are reviewed. Their properties and principal uses are described.

Methods of measuring particle sizes are discussed. A detailed description is given of a rapid optical method, based on the ability of these systems to scatter light quantitatively according to Rayleigh's law. The validity of the method is confirmed by independent centrifugal sedimentation studies.

The significance of this work as an experimental confirmation of Rayleigh's law is discussed.

The effects on particle size of variations in polymerization conditions are investigated experimentally. Results are given and discussed.

A modification of the apparatus, enabling it to be used to study growth of particles during the polymerization reaction, is described. Experiments, in which the growth of particles is followed, are recorded. Results are given, and their significance discussed.

The mechanism of "Emulsion Polymerization" is discussed. Experiments designed to elucidate this mechanism are described, and the results are summarized and evaluated.

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STUDIES OF PARTICLE SIZE CHARACTERISTICS OF AQUEOUS DISPERSIONS OF POLYACRYLIC ESTERS, AND OBSERVATIONS ON THE MECHANISM OF THEIR FORMATION.

I INTRODUCTION

During the past ten to fifteen years, many new plastic materials have been developed in laboratories all over the world, and several have undergone considerable commercial development. Most of these products have been produced by polymerization processes, as distinct from those of the preceding period, which were mostly end products of condensation reactions. Polymers of vinyl acetate, vinyl chloride, the acrylic and methacrylic esters, together with the various synthetic "rubbers" made from butadiene, butylene or chloroprene, with various additaments, have all attained practical prominence, and represent some of the most creative work of the organic chemist, in that they have made possible the production of products with properties, or combinations of properties, unattainable in any known combination of natural or modified natural products.

In the early stages of the development of many of these polymers, the polymerizations were carried out on solutions of the monomeric compounds in liquids which were solvents for both monomer and polymer. In the case of the acrylic ester polymers, with which this discussion is particularly concerned, the required amount of monomeric ester was dissolved in some suitable solvent - such as ethylene dichloride, or ethyl acetate - a soluble catalyst such as benzoyl peroxide was added, and the whole heated under a reflux condenser with stirring until analysis of the solution for nonvolatile matter indicated that polymerization was substantially complete.

The drawbacks of this method were many. The reaction was slow, involving times up to, and even exceeding, three full days. The end products were very viscous at any but low concentrations, and residual monomeric, or low polymeric, material could not be removed in a satisfactory way, so that when these materials were used as cements or coatings a very pungent and disagreeable odour, produced by these residues, resulted. This odour is most persistent.

Approximately twelve years ago, the so-called emulsion polymerization process was announced. In this method, described first in the patent literature, and later in articles and textbooks, the means of accomplishing the polymerization, and the nature of the end product, are markedly different from those of earlier methods. On the surface, and according to the descriptions, the procedure is to emulsify the monomer, with the help of suitable emulsifying agents, in a liquid which is not a solvent for the monomer, (water being the liquid most commonly used) to add small amounts of certain oxidizing agents as catalysts, and to subject the resulting emulsions to heating or irradiation. This emulsion then (apparently) polymerizes with the formation of a dispersion of fine polymer particles stabilized by the emulsifying agent present.

The final products are latex-like liquids with quite remarkable properties. They are frequently - and erroneously - described in the literature as emulsions, but it is, of course, obvious that, although before polymerization such systems are emulsions, after polymerization they are dispersions of plastic (i.e. pseudo solid) particles. They behave as lyophobe dispersoid sols, exhibiting stability of an order which leaves them literally unaffected by years of normal storage.

Descriptions, in more or less detail, of the formation and properties of these polymerized emulsions, including formulae for preparing them, are given in the patents, articles and textbooks listed below. Their preparation may be typified by the following example taken from British Patent No. 358,534, dated February 6, 1931.

"Example 1.

100 parts of pure acrylic methyl ester are emulsified in 200 parts of water containing 0.3 percent of Marseilles soap, 0.5 percent of propyl naphthalene sulphonic sodium salt and 2 percent of 30 percent aqueous hydrogen peroxide,

and the emulsion is heated for 3 hours at from 80° to 90° Centigrade in a stirring vessel provided with a reflux condenser. The emulsion is then freed from the last traces of non-polymerized ester by blowing with steam until it is odourless . . . . ."

(The remainder of the description in this example covers the coagulation of the resulting latex and processing of the coagulum, with which we are not here concerned.)

Other examples from the literature disclose the use of other emulsifying agents such as sulphated castor oil (Turkey red oil) ammonium and sodium oleates, sodium alpha-oxy octadecane sulphonate, and other catalysts such as ammonium persulphate, benzoyl peroxide, ozone, and the like. In order to simplify procedure as much as possible, most of the experiments carried through in the investigations here described were run with the same highly sulphated castor oil as sole emulsifying and stabilizing agent, and hydrogen peroxide as catalyst. Both are very effective.

Below is given a general bibliography of patents, articles, and textbooks in which the emulsion polymerization of acrylic esters is described and discussed. The listing of patents is confined to the early ones in the field, as the number covering modifications and improvements in procedure is now quite large.

1. Patents

   a. U. S. pat. 2,086,093, July 6, 1937, to Hermann Plauson
      (Germany, Feb. 1, 1930)
   b. U. S. pat. 2,123,599, July 12, 1938, to Hans Fikentscher and Claus Heuck
      (Germany, Jan. 28, 1930)
   c. British pat. 358,534, I. G. Farbenindustrie - - - 1931
   d. British pat. 374,436, Röhm & Haas Co. - - - 1931
   e. British pat. 456,442, I. G. Farbenindustrie - - - 1937

f. British pat. 466,898, I. G. Farbenindustrie - - - 1936

g. British pat. 467,084, I. G. Farbenindustrie - - - 1934

2. Articles

a. "Emulsion Polymerization" - Harry Barron
British Plastics and Moulded Products Trader
Vol. XI, pp. 464-467 (April, 1940)

b. "Emulsionspolymerisation und Technische Auswertung" - Hans Fikentscher

Paper read before the 51st meeting of the German Chemical Society, at Bayreuth, June 7-11, 1938. Reported in Angewandte Chemie, 51, 433 (July, 1938)

c. "Latexähnliche Emulsionen auf Basis nicht vulkanisierbarer Polymerisations produkte" - C. Creamer

Paper read before the 11th meeting of the German Rubber Society, in Hamburg. Reported in "Gummi-Zeitung" 52, 1099 (1938)

d. "On Some Latex-type Synthetic Emulsions" - Anonymous
Rubber Age (London) 20, 89 (1939)

e. "Industrial Progress in Synthetic Rubberlike Polymers" - H. I. Cramer
J. Ind. Eng. Chem. 34, 243 (Feb., 1942)

f. "Emulsion Polymerization" - Fryling and Harrington
J. Ind. Eng. Chem. 36, 114 (Feb., 1944)

3. Textbooks

a. "Polymerization" - Burk, Thompson, Weith, and Williams
Reinhold Publishing Corp., N. Y. 1937
pp. 175-176, Emulsion polymerization of dienes

b. "Chemie und Technologie der Kunststoffe" - R. Houwink
Akademische Verlagsgesellschaft M.B.H. - Leipzig 1939
Chapter 8, by E. Trommsdorff

c. "High Polymeric Reactions, Their Theory and Practice" - H. Mark and R. Raff
Interscience Publishers, N. Y. 1941
pp. 81-83 - Polymerization of Emulsions
pp. 269-270 - Emulsion polymerization of butadiene

The author has been continuously associated with the development in the U. S. A. of polymer dispersions of the acrylates and similar compounds, since 1933, when the first experimental quantities were prepared in his laboratory. To the limit of his knowledge, these were the first preparations of these products in the United States. His particular interest has been in the development of these synthetic latices as coatings for leather, which is by far the largest use for them in this country to date. The growth of their use as leather coating materials is indicated by the following table, giving in pounds the amounts used by the American leather industry from 1933 to 1941.

Year	Pounds
1933	1,500
1934	48,000
1935	106,500
1936	307,000
1937	355,000
1938	511,000
1939	866,500
1940	1,127,000
1941	2,371,000

The advantages and drawbacks of these materials as leather coatings, or as components of leather coatings, have been described by the author in the following:

a. U. S. Patent #2,204,520 - Issued to Henry B. Walker and Paul W. McWherter, and assigned to Rohm & Haas Company.

b. An article "Synthetic Resins and Their Uses in the Leather Industry," presented as a paper before the 37th Annual Meeting of the American Leather Chemists Association, and published in the Journal of that Association in January 1941 (Vol. 36, p. 12).

c. "Modern Practice in Leather Manufacture" (Reinhold, N. Y., 1941) by John Arthur Wilson. The section in Chapter seventeen of this book (pp. 594-598) describing the development of lacquer and synthetic resin coatings on leather was written by the author at the late Dr. Wilson's request.

It is not necessary, therefore, to describe here in detail the properties of these materials as leather coatings. Suffice it to say they produce films of extraordinary adhesion, flexibility, and water resistance, with the additional advantage that the flexibility - inherent as it is in the polymer itself, and not conferred by the addition of mobile plasticizers - is of a very permanent order. Because the application to the leather surface is in the form of a relatively concentrated latex of high fluidity, the composition is taken up by the tanned skin according to the absorptive quality of each part. The more open and absorbent parts get all the material they need to form a satisfactory coating, while the surplus is removed from the more compact portions. This results in a pronounced "levelling" effect which is most desirable in overcoming the natural differences in texture between different parts of the tanned animal hide.

In addition to their use in the leather industry, aqueous dispersions of polymerized acrylic esters find employment as textile finishing materials, imparting a desirable "hand" to cotton and rayon goods which, unlike the firmness produced by starch, is not readily washed out when the goods are laundered. They also find limited use for coating fabrics, but, in such applications, where much coating material is used on a cheap backing, the cost is generally too high to make feasible any extensive commercial application. They have also been used as coatings for paper.

The emulsion polymerization of acrylates and methacrylates also finds application in the preparation of moulding powders. Here, however, the objectives are different. Instead of a stable dispersion, the requirement is to produce, by polymerization under controlled conditions, a dispersion which will precipitate in granular form when the desired granule size has been attained. The granule size may be varied at will by varying the conditions. Thus, in this type of preparation the aqueous dispersion is only a transition stage in the production of solid polymer, and falls outside the scope of the present discussion.

Many of the elastomers commonly called "synthetic rubber" are also produced by polymerization of aqueous emulsions of the monomeric materials. In this case also, the resulting latex is usually treated to form a coagulum of the polymer, which is then ready for further processing. Some aspects of the preparation of these materials, and some of the assertions which have been made regarding the process, are discussed and criticized below in the section dealing with the probable mechanism of emulsion polymerizations. (See pages 11 and 12)

II OBJECTS OF WORK

The studies described in this thesis were undertaken for two main purposes. Of these, the first was the measurement of particle size, and the growth of particle size during polymerization, while the second was to attempt to throw light on the real mechanism of the reaction. The work under these two heads is not sharply divided, some parts of it contributing information on one aspect only, others providing data on both.

Particle size, particle size distribution, and the course of particle growth during polymerization, are of obvious importance in products of this type.

Their significance will be discussed in detail later, but at this point a word of explanation on the reasons for attempting elucidate the mechanism is in order.

a. Mechanism of Process - Discussion

The mechanism of "Emulsion Polymerization" is not as simple as it appears on casual examination. The usual statement of the patent literature and the descriptive articles is that an emulsion of monomer is prepared with the aid of a suitable emulsifying agent, and that this emulsion is polymerized to obtain a latex-like dispersion. The implication of these descriptions - and indeed of the very name "Emulsion Polymerization" - is that the droplets of emulsion polymerize individually to form the particles of the dispersion, and this apparently straightforward view of the process is commonly accepted by many of those familiar with it.

In the early stages of the work with these compositions, however, a number of purely qualitative observations were made which were not in accord with this view of the mechanism of formation. Even casual examination in the dark field microscope of the size of the emulsion droplets before polymerization and the disperse particles after polymerization shows that the latter are so much smaller than the former that their size is of an entirely different order of magnitude. It is, in fact, unnecessary to have a preliminary emulsion at all. Dispersions can be prepared by adding monomeric ester to a solution of dispersing agent plus catalyst with only the gentlest kind of agitation. Such dispersions exhibit a particle size as fine as - or even finer than - a dispersion prepared from a true emulsion of the identical materials under identical conditions.

The statement is usually made, in describing this process, that the monomer is emulsified in a liquid with which it is immiscible, or in which it is "substantially" or "practically" insoluble, without defining these terms. Barron, in an article in "British Plastics and Molded Products Trader" for April 1940 (p. 464) refers to the case where the monomer is soluble - presumably completely soluble - in water, and the polymer insoluble. He quotes vinyl alcohol as a case in point. This statement is, of course, in error, as monomeric vinyl alcohol is unknown, being tautomeric with acetaldehyde. The polyvinyl alcohol of commerce is obtained by polymerization of vinyl acetate and hydrolysis of the resultant polymer. Polyvinyl alcohol is water soluble, producing viscous solutions of value as sizings, thickening agents, and stabilizers for pigment dispersions, emulsions, and other dispersed systems.

General observation of the process led to the idea that at least part of the essential mechanism depended on the solubility of the monomer in the water. It seemed possible that the soluble portion polymerized, separating from the solution as fine precipitated globules of insoluble polymers, which were prevented by the emulsifying agent from flocculating and settling. The removal of monomer from solution in this way produced an unsaturated condition so that more monomer dissolved, more polymerized from solution, and so on, establishing a cycle which continued until all the available monomer was used up.

Fikentscher, one of the pioneers in the study and development of this process, in a paper before the fifty-first meeting of the German Chemical Society at Bayreuth in June 1938, reported in Angewandte Chemie, 51, p. 433, states that (translation) "The results of experiments incline us to the view that, in Emulsion polymerization, it is not, as often assumed, that portion of the vinyl compound emulsified into droplets which polymerizes, but the part which is actually dissolved in the water phase. This portion replenishes itself continually from the emulsified drops of liquid, and in this way remains constant during the whole polymerization, as long as such droplets exist.

"The solubility in water of the vinyl compounds varies; in some cases it is considerable. Polymerization of a water clear saturated solution of a monomeric vinyl compound in water containing emulsifying agent, promoted if necessary by heating and the addition of an accelerator, gives rise to a milky emulsion of water-insoluble polymer."

The views here expressed are in accord with those developed by this author and his colleagues on the basis of qualitative observation, with the exception, however, that the solution of vinyl compound in water need not be saturated, as Fikentscher states. Solutions of the lower acrylic esters far below the saturation point show the behaviour he describes.

In a chapter on "Kunststoffe aus Polymerisation von Aethylenderivaten" in Houwink's "Chemie und Technologie der Kunststoffe," Trommsdorff points out (p. 320) that the superiority of water soluble catalysts in emulsion polymerization leads to the belief that the soluble portions of the monomer, rather than the droplets of emulsified material, undergo polymerization. He describes an experiment in which a quantity of dilute solution of an emulsifying agent, containing a small amount of water soluble catalyst, is covered with a layer of monomeric acrylic or methacrylic ester and the whole heated to about 60°C. without agitation. After a short time the water layer becomes more and more milky, while the monomer layer becomes smaller and eventually disappears.

This observation may be readily verified for a number of compounds, as will be shown in the experimental section below - it will also be shown that there are some compounds which do not form a water dispersion under these conditions - but while it demonstrates that polymerization can and does occur by this mechanism, it offers no evidence that formation of polymer dispersions occurs exclusively in this way where there exists a considerable excess of monomer over the amount required to saturate the water phase. Quantitative data are required for this.

In their recently published book "High Polymeric Reactions, Their Theory and Practice," Mark and Raff discuss emulsion polymerization in a general way (pp. 81-83). All of the statements made are obviously predicated on the assumption that the actual emulsion droplets polymerize to form a dispersion, and several of them are, in this writer's opinion, open to question.

Thus, for example, it is stated in point #4, page 81, that a colloidal dispersion of the monomer(s) is required. It has been pointed out above that this is, for most vinyl derivatives, unnecessary, and this will be shown in the experimental sections which follow. The need for a stabilizer, in the sense defined in point 5, for a regulator of surface tension as described in point 6, for a "regulator" (point 8) or for a buffer (point 9) may also be doubted. These considerations are obviously based on experience in the emulsion polymerization of the butadiene-styrene or butadiene-acrylonitrile systems employed in preparation of the Buna type rubbers, and are certainly not generally applicable to all polymerizations in emulsified systems.

It seems probable that these additive materials, many of which are disclosed and claimed in the patent literature, have been added by various investigations from time to time to overcome sundry practical difficulties, and that they are incidental, but not necessarily fundamental (as stated by Mark and Raff) to the process.

In a later section of this book, (p. 270) these authors, discussing emulsion polymerization of butadiene, state that "it is not known exactly how emulsion polymerizations proceed" and then refer to Fikentscher's view of the process as already described above.

H. I. Cramer, in an article on Synthetic Rubberlike Polymers (J.I.E. Chem. 34, 243 (1942)) discusses emulsion polymerization of dienes along the same lines as Mark and Raff. Here again it seems legitimate to raise a question on how real is the necessity for the various "modifying agents" and "directive agents" mentioned as appearing in the patent literature. Further critical research on these points appears to be indicated.

b. Particle Size - Significance

In the preparation of the stable type of polyacrylic ester dispersion used for coatings, the particle size and the particle size distribution of the end product are of profound importance, affecting the stability of the material on storage, and its properties as a coating. Preparations made under adverse conditions may give relatively coarse dispersions - or dispersions containing a considerable coarse fraction - which sediment rapidly on short storage. The sediment in such preparations may coagulate on the bottom of the container in the course of a few days to a solid mass of resin which cannot be redispersed, thus rendering the material quite worthless, while other preparations, made under adverse conditions of a different sort, may contain particles so fine that they are difficult to identify as discrete particles. Materials of this sort show great stability but penetrate excessively into the substratum to which they are applied, producing results markedly inferior to those with similar material where the particle sizes are within the optimum range.

The manifest importance of particle size, and particle size distribution, led to consideration of methods of measuring these properties, so that commercial production could be evaluated quantitatively and controlled as to conditions producing optimum results. It was also recognized that a proved and accurate method of measurement would open up the possibility of experimental study of factors affecting particle size, as a guide to successful control of commercial production through knowledge of the influence of these factors and the understanding of the mechanism of the reaction developed by such study.

III METHODS OF MEASURING PARTICLE SIZE - DISCUSSION

For measuring the particle size of these dispersions, there appeared to be several possible methods, which are listed and discussed below:

1. Direct microscopic observation, using a quartz cell of about 2 microns thickness of liquid layer, illuminated with critical dark field illumination by a cardioid condenser, and employing a ruled micrometer in the eyepiece.

In this technique, the eyepiece micrometer, ruled in squares of suitable size, is first calibrated with a stage micrometer. The cell is carefully cleaned with boiling concentrated sulphuric and chromic acids and ignited to burn off residual material so that optically clean surfaces are obtained. The dispersion is diluted with water, distilled in vacuo, to such concentration as gives a field of workable density. The liquid layer in the cell is observed by the use of a special 2 mm. glycerine immersion objective and the diameters of the particles are evaluated by comparison with the calibrated rulings on the eyepiece micrometer. The condenser, quartz cell and the glycerine immersion objective for this work are made by Messrs. Bausch and Lomb, of Rochester, N. Y.[1]

This method has been used in the author's laboratory to determine droplet sizes in emulsions of various types. It is rapid and reasonably accurate and estimates of the relative numbers of particles in various size ranges may be made by counting.

Attempts were made to apply this method to determination of particle sizes in aqueous polyacrylic ester dispersions. It was quickly found to be quite unsuitable.

The particles present in these dispersions - even the relatively coarse ones - are so small that they appear in the microscope field as minute points, or

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[1] Bausch & Lomb Optical Co. Catalogue No. 31-58-60

diffraction rings, of light, in most vigorous Brownian motion, similar to that shown by colloidal sols of metals. No evaluation of particle diameter in comparison with the rulings of the eyepiece is possible, nor any differentiation between particles of different sizes.

As a result of the nonabsorbing nature of these resin particles, the illumination of the particles is particularly brilliant, and it may be pointed out, as an aside to this discussion, that these dispersions provide quite the most beautiful and striking demonstration of Brownian motion that has come to the attention of this author.

2. Projection, at known magnification, of particles precipitated as a thin film on a glass surface, either on a screen or on a photographic plate.

This technique, developed by Green and his co-workers at the research laboratories of the New Jersey Zinc Company, and others[2,3] has been used in this author's laboratory to determine particle sizes of pigments. Using dark field illumination, and a narrow spectral band of light filtered from the blue-green region of the visible spectrum, it is capable of determining particle sizes with fair certainty down to a diameter of approximately 0.5 microns.

This method requires the fixation of the particles to be measured, on the surface of a microscope slide. All efforts to accomplish this with the particles from a polyacrylic ester dispersion were unsuccessful. The particles, when dried on the surface of a slide, were quite indistinguishable, either by direct or dark field illumination. This may be accounted for on the basis of the closeness of the refractive indices of polymethyl acrylate and glass (1.472 and 1.517 respectively) and the very small sizes of the particles.

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[2] Henry Green. J. Frank. Inst. 192, 637 (1921)

[3] E. J. Dunn. J. I. E. Chem. An. Ed. 2, 59 (1930)

When this work was started, (early 1939) the electron microscope was in the infancy of its development as a practical research tool. Its apparent applicability to the problems involved here is obvious, and it has been reported to the author recently (communication from Dr. R. J. Myers, 1944) that the electron microscope has now been used successfully in the study of particle sizes and particle size distributions in synthetic latices of the type here considered. The number of these instruments now available is still very limited, however, and their use is not a practical answer to the problems encountered in most laboratories.

3. Ultramicroscopic counts of particles

This well-known method of colloid chemistry, using a cardioid condenser and a quartz cell of the same type as described under Method 1, above, was attempted. Dilution with very pure glycerol instead of water, was used in order to minimize the Brownian movement of the particles. This was fairly effective insofar as the Brownian motion alone was concerned, but other difficulties presented themselves. To obtain entire freedom from dust particles - many of which under dark field illumination are indistinguishable from the particles in the acrylate dispersions - is very troublesome and time consuming, and the method itself is laborious and subject to errors which have been discussed in detail by others*.

This method was abandoned, after a number of trials, in favour of other methods described below.

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* Thomas. "Colloid Chemistry" McGraw Hill Book Co. (1934)

4. Sedimentation Methods

a. Gravitational Sedimentation

Methods using change of density of a suspension as disperse particles separate under the influence of gravity[5,6,7], sedimentation on a balance pan [8,9,10,11], or analysis of samples withdrawn from a settling system[12,13,14,15,16], such as have been extensively used with pigments, clays, and hydrated lime are inapplicable because of the very small difference in density between the acrylic ester polymers and the water in which they are dispersed, and also the very small particle sizes involved. Sedimentation does not occur, except with preparations of abnormally large particle size.

b. Centrifugal Sedimentation

Centrifugal sedimentation methods are effective with forces of the order of 25,000 times gravity, and were used in the investigations herein described. A special centrifuge head was designed by the author for this work,

[5] Kelly. J. I. E. Chem. 16, 928 (1924)

[6] Duncombe & Withrow. J. Phys. Chem. 36, 31 (1932)

[7] Knapp. J. I. E. Chem. An. Ed. 6, 66 (1934)

[8] Svedberg and Rinde. J. A. C. S. 45, 943 (1923)

[9] S. Odén in J. Alexander's "Colloid Chemistry" Vol. 1, p. 861
(Chem. Catalog Co. 1926)

[10] Calbeck & Harner, J. I. E. Chem. 19, 58 (1927)

[11] Bishop. Bur. Stds. J. Res. 12, 173 (1934)

[12] Andreasen. Kolloid Beihefte 27, 349 (1928)

[13] Andreasen. Kolloid Zeit. 48, 179 (1929)

[14] Andreasen. Angew. Chem. 20, 283 (1935)

[15] Andreasen. Kolloid Zeit. 82, 37 (1938)

[16] Loomis. J. Amer. Ceramic Soc. 21, 393 (1938)

and was manufactured by the International Equipment Company as an accessory to one of their centrifuges. This centrifuge, and its operation, are described in the experimental section below.

Centrifugal sedimentation in this centrifuge was used to determine particle sizes and also particle size distributions by an extension of Odén's graphical method[9,10].

As the principal use of the centrifugal sedimentation method was to check the validity of the light-scattering method, discussion of the applicable theory is not given here, but is postponed to the experimental section, following the discussion and verification of the light-scattering method.

The results of the centrifugal sedimentation experiments are also given in the experimental section, and the extent to which they confirm the determinations by the light-scattering method is also discussed.

5. Optical Methods - Scattering of radiant energy.

a. Discussion of Theory

It was observed very early in handling these dispersions that many of them, in dilute form, showed a pronounced chromatic effect, being quite red when viewed by transmitted daylight, and very blue against a dark background. This is, of course, the well-known Tyndall effect, discussed and analyzed with delightful elegance, and precision of language, by Lord Rayleigh (then J. W. Strutt) in a series of articles in the Philosophical Magazine[17,18,19], from 1871 to 1899. His findings are summarized in a paper entitled "On the Transmission of Light Through an Atmosphere Containing Small Particles in Suspension and on the Origin of the Blue of the Sky."[19].

[17] Phil. Mag. (4) 41, 107, 274, 447 (1871)

[18] " " (5) 12, 81 (1881)

[19] " " (5) 47, 375 (1899)

From the considerations given in this series of papers, Rayleigh concludes that, when a beam of radiation of energy E_0 and wave length λ is partly scattered by passage through a thickness x of a suspension of particles, each of volume T, present in a concentration of n particles per unit volume of suspension, the energy of the transmitted, or unscattered beam, E, is given by

$$E = E_0 e^{-\left[\frac{8 \pi^3 n}{3} \quad \frac{(D' - D)^2}{D^2} \quad \frac{T^2 x}{\lambda^4} \right]}$$

where D' is the optical density of the material constituting the particles and D is the optical density of the surrounding medium.

Richard Gans, of Koenigsberg, writing in a section entitled "Lichtzerstreuung," in Wien and Harms' Handbuch der Experimentalphysik[20] considers scattering on the basis of the electromagnetic theory of light, using optical dielectric constants (ε) equal to the squares of the refractive indices, and arrives at the relationship:

$$R = NR_1 = \frac{8 \pi^3}{3} \left(\frac{\varepsilon - \varepsilon_0}{\varepsilon_0} \right)^2 \left(\frac{3 \varepsilon_0}{\varepsilon + 2 \varepsilon_0} \right)^2 \frac{NV^2}{\lambda^4} J_0 = h J_0$$

where R_1 = total radiation from 1 particle

N = number of particles per unit volume

V = volume of scattering particle

J_0 = intensity of incident radiation (energy per unit area)

ε $(= n^2)$ = optical dielectric constant of particle

$\varepsilon_0 (= n_0^2)$ = optical dielectric constant of suspension medium

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[20] "Handbuch der Experimentalphysik" Wien and Harms
Akademische Verlagsgesellschaft, Leipzig, 1928.

Now, if we consider a beam of radiation of intensity J_0, entering a cylindrical volume dT of cross section q and depth dx, at distance x, then at x + dx the intensity will be $J_0 + d\,J_0$ and

$$\left[J_0 - (J_0 + d\,J_0)\right]\ q = R\ dT$$

i.e. the decrease in energy of the beam in passing through dT is equal to the amount of light scattered.

$$\therefore -\frac{d\,J_0}{dx}\ q\ dx = R\ dT$$

since $q\ dx = dT$

$$-\frac{d\,J_0}{dx} = R = h\ J_0$$

i.e. h is, by definition, the extinction coefficient.

Using the more familiar I for radiation intensity we have

$$\frac{d\,I}{dx} = -\,h\ I$$

or $\dfrac{d\,I}{I} = -\,h\ dx$

$$\therefore \log_e \frac{I}{I_0} = -\,h\ (\Delta x)$$

where I_0 = incident radiation per sq. cm.

I = transmitted radiation per sq. cm.

Δx = thickness in cms. scattering material

$$\therefore I = I_0 e^{-h\ (\Delta x)}$$

or, since $h = \dfrac{8\ \pi^3}{3} \left(\dfrac{n^2 - n_0^2}{n_0^2}\right)^2 \left(\dfrac{3\ n_0^2}{n^2 + 2\ n_0^2}\right)^2 \dfrac{NV^2}{\lambda^4}$

$$I = I_0 e^{-\left[\frac{8\ \pi^3}{3} \left(\frac{n^2 - n_0^2}{n_0^2}\right)^2 \left(\frac{3\ n_0^2}{n^2 + 2\ n_0^2}\right)^2 \frac{NV^2(\Delta x)}{\lambda^4}\right]} \qquad (1)$$

This is the same expression as that derived by Lord Rayleigh with the inclusion of the factor

$$\left(\frac{3\,n_0^2}{n^2 + 2\,n_0^2}\right)^2$$

which is close to unity if one assumes, as did Rayleigh, that the refractive indices of the particle and the suspension medium are nearly equal.

Now, if the refractive index terms are constant, which they are if we confine our attention to any one material, and ρ represents the density of the particles, then:

because $c = NV\rho$

(c being concentration in weight per unit volume)

$$NV = \frac{c}{\rho}$$

Substituting in equation (1), expressing the refractive index terms by K, and considering a layer of unit thickness, we have:

$$I = I_0 e^{-K\frac{cV}{\rho\lambda^4}} \qquad (2)$$

Taking the logarithm of both sides of this equation, and transposing, we obtain

$$\log_e \frac{I_0}{I} = K\frac{cV}{\rho\lambda^4} \qquad (3)$$

or $$\log_{10} \frac{I_0}{I} = D = K'\frac{cV}{\lambda^4}$$

where D represents the optical density of the dispersion of scattering particles.

thus $$\log_{10} \frac{I_0}{I} \times \frac{\lambda^4}{c} = K'\,V \qquad (4)$$

which means that the optical density of a unit layer of the dispersion, multiplied by the fourth power of the wave length of the incident radiation and divided by the concentration, is proportional to the "particle volume" of the dispersion.

Consideration is necessary here of what is meant by "particle volume" of a dispersion in which the particles are of non-uniform size. Two methods of designating the "average" or "effective" particle size in non-uniform systems have come into common use. These are the "number average" and the "weight average" particle size. The former is, as its name implies, the effective particle size in cases where the number of particles falling within any designated size range is determined (as in counting methods) and is represented by the location of the centre of gravity of a particle size distribution curve constructed by plotting particle size ranges as abscissae and number of particles in each range as ordinates. The "weight average" particle size, on the other hand, is represented by the location of the centre of gravity of a distribution curve obtained by plotting particle size ranges against weight (or volume) of material within each range. Sedimentation methods yield such curves.

As the light scattering method here discussed involves particle volume to the first power when reduced to the form actually used, it will evidently record weight (or volume) average particle sizes. Thus "average particle volume" as used throughout the following discussion is actually "effective particle volume," and is considered to be identical with the term "weight average" particle volume as commonly used.

The limiting conditions under which the assumptions involved in the derivation of the Rayleigh-Gans relationship are valid are:

1. That the scattering particles are small in comparison with the wave length of the radiation, spherical, and of material which is a good dielectric, and that neither the particles nor the suspension medium absorb the radiation selectively. This means that, in the particular, and limited, case where the radiation falls within the visible spectrum, both must be colourless.

2. That the incident radiation be monochromatic or nearly so. This is important because, as the amount of scattering is inversely proportional to the

fourth power of the wave length, the departure from the relationship expressed by equation (3), above, becomes quite marked with increasing width of the spectral band used.

3. That the apparatus be arranged so that the scattered radiation is absorbed, and only the unscattered radiation is measured.

Some investigators, notably Gamble & Barnett, of the New Jersey Zinc Company, have used the degree of departure from this relationship to measure particle size and particle size distribution in a purely relative way.[21] They describe experiments designed to show the relative particle sizes and size distributions of pigment dispersions by measuring the amount of radiation scattered by the samples at a number of different wave lengths. Because of the relatively large size of the pigment particles, they were compelled, in order to get wave lengths sufficiently greater than the particle diameters, to use radiation up to 4000 $m\mu$. A rock salt spectrometer was employed to separate the desired wave length bands and the unscattered radiation was measured with a vacuum thermopile and a galvanometer.

Their results show fairly good concordance between calculated and observed values. The relationship between the intensities of the incident and transmitted beams, and the other parameters involved (equation 1, above) is incorrectly stated in this article. The refractive index terms are shown as the first, instead of the second power; no term involving the thickness of the layer is included, and the statement that "the intensity of the transmitted radiation varies directly as the fourth power of the wave length and inversely as the third power of the particle diameter" is in error. It is the negative logarithm of the transmitted radiation which varies as indicated with wave length and particle diameter. Since the results are relative only - the apparatus being standardized

[21] Gamble & Barnett. J.I.E. Chem. An. Ed. 9, 310 (1937)

by a pigment dispersion of known particle size - these errors do not affect the experimental results. Their statement that they assumed the scattered radiation was all lost calls for some amplification. In work of this kind it is necessary to make certain that all the scattered radiation is absorbed, and only the unscattered radiation is measured.

In a later article by one of these authors[22], in which a correlation of the wave lengths of maximum selectivity with the refractive indices of the pigments used is derived, the error in the statement of the Rayleigh-Gans relationship is corrected, but the thickness of the layer on which measurements are made is still left unmentioned.

Pfund, in an article[23] on scattering in the infrared, says (page 144) "The complete Rayleigh formula for transmission of radiation through a scattering medium is:

$$I = I_0 \exp \left[4 \pi^2 \quad \frac{(n^2 - n_0{}^2)^2}{(n^2 + 2\, n_0{}^2)^2} \quad \frac{NV^2}{\lambda^4} \right] \qquad "$$

It is not clear how this is derived.

Several authors[24,25,26,] discussing scattering of light by colloidal sols, do so on the basis of Rayleigh's earlier papers,[17,18,] where he considered

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[22] Barnett. J. Phys. Chem., 46, 69 (1942)

[23] Pfund. J. Opt. Soc. Amer. 24, 143 (1934)

[24] Wells. Chem. Rev. 3, 343 (1927)

[25] Thomas. Colloid Chemistry, McGraw Hill, 1934. p. 35

[26] Freundlich. Capillary & Colloid Chemistry

Methuen, London. 1926. p. 381.

the intensity of the scattered light at a definite distance from the particle, and at a definite angle with the direction of the incident beam. These considerations have been used by Mie[27] in his classic discussions on scattering by gold sols, but present a very difficult practical problem when an effort is made to verify or use these relationships experimentally.

b. Possibility of Making Absolute Measurements

Consideration shows that water dispersions of acrylic ester polymers fulfill the conditions demanded by the Rayleigh-Gans relationship almost ideally. From the marked Tyndall effect they show, it is clear that their diameters must be small in comparison with the wave lengths of the visible spectrum, and it is hard to conceive, knowing how they are formed, and considering the numbers of polymer "molecules" present in even the smallest particles (this is brought out and discussed in the experimental sections which follow) that their shape can be other than spherical. Electron microscope studies on similar synthetic latices[27a] and recent work reported to the author*, have actually shown the particles to have a spherical shape. The particles in the polyacrylic ester dispersions are of a material well known as a good dielectric, and both they and the suspension medium, water, are colourless.

In addition, the refractive indices of the suspension medium, and of the polyacrylic ester, are known or can be measured; the density of the particles, and their concentration, can also be measured, so that all terms, except V, in equation (1) are measurable. Thus a direct determination of V becomes possible.

This is, to the limits of this author's knowledge, the first time a direct experimental verification of the Rayleigh-Gans relationship has been

[27] Mie. Annalen der Physik 25, 377 (1908)

[27a] Ardenne and Beischer. Kautschuk 16, 55 (1940)

* Communication from Dr. R. J. Myers, 1944.

possible or attempted. The actual calculations, and a comparison of the values obtained with those indicated by centrifugal sedimentation, are given below in the experimental part. (Section V.)

All considerations emphasized the apparent suitability of light-scattering and centrifugal sedimentation methods for determining particle sizes in these dispersions, and such methods were worked out, verified, and used, as described in the experimental sections which follow.

IV METHODS OF MEASURING PARTICLE SIZE - EXPERIMENTAL

1. LIGHT-SCATTERING METHOD

a. Apparatus - Design

The apparatus consists essentially of a light source, a collimator, a light filtering system, an absorption cell, an arrangement for absorbing the scattered radiation, and a device for measuring the intensity of the unscattered radiation. In the form it finally assumed after a number of changes during its development, it is shown diagramatically in Figure I. Figure I-A is a photograph of the apparatus, opened up to show the internal arrangement.

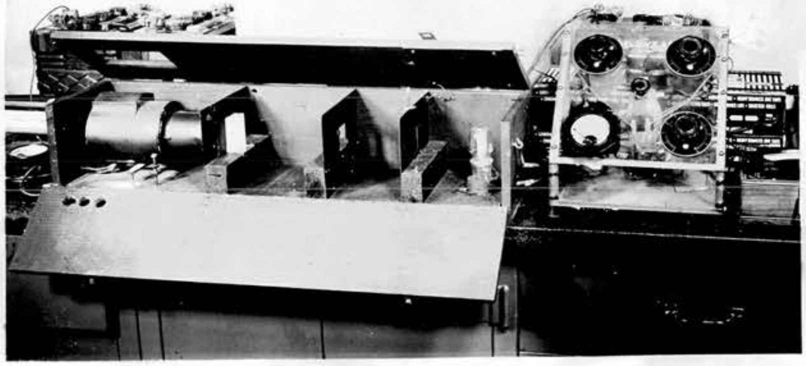
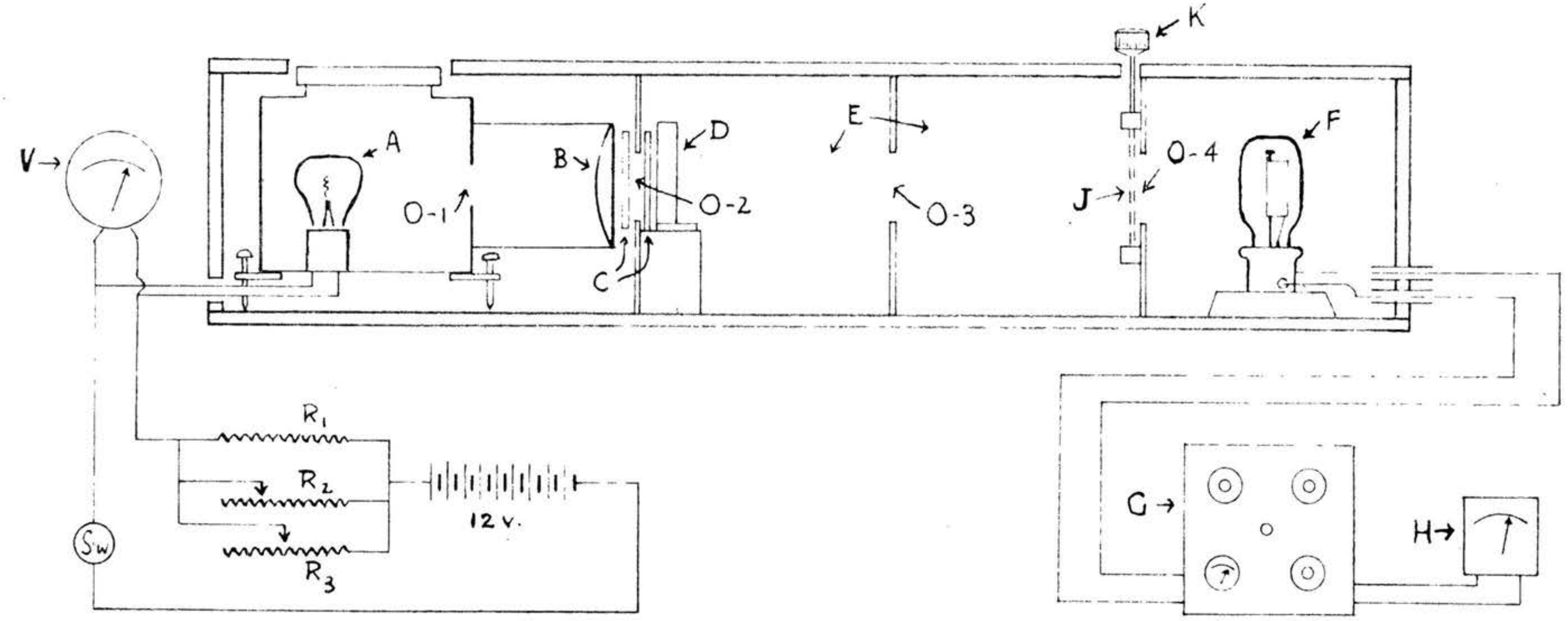


Figure I-A

— DIAGRAM OF APPARATUS USED TO MEASURE
LIGHT SCATTERING OF POLYACRYLIC ESTER DISPERSIONS —



— FIGURE I —

In Figure I, A is the light source, B the collimator, C the light-filtering system, D the absorption cell, E the absorbing system for the scattered radiation, F the photoelectric cell leading to the amplifier G and the microammeter H, this system being used to measure the intensity of the unscattered radiation. The shutter J, actuated by knob K, is used when necessary to shut off all radiation from the photoelectric cell.

The entire system is enclosed as shown in a wooden case 28 x 7 x 5 1/2 inches (71 x 18 x 14 cm.) interior dimensions. Both front and top of the case are hinged, and all surfaces are sprayed with flat black lacquer to minimize light reflection. The discussion below of each individual part of the system, under its appropriate heading, gives the considerations that led to its selection, and in some cases covers arrangements which did not work, as well as those which were satisfactory.

In the design of this instrument, much valuable guidance was obtained from the excellent review, "Photoelectric Methods in Analytical Chemistry," by R. H. Müller of New York University[28] which was published just prior to the start of this work. This article summarizes thoroughly all the significant previous work, and its two hundred sixty-three references form a complete bibliography of the field to that date. Due and grateful acknowledgment is made to this article and its author. Assistance and advice were obtained also from Mr. F. E. Eldredge of the Westinghouse Electric & Manufacturing Company, and Dr. Francis J. Norton of the Research Laboratories of the General Electric Company, whose work on the optical properties of suspensions of Bentonite Clays is well known.

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[28] J. I. E. Chem. An. Ed. 31, 1 (1939)

A and C: Light source and filter system

These are considered together because of their interdependence. Together they generate the band of radiation used for the measurement.

The light source used is a 6 volt, 50 candle power coiled filament motor car headlight bulb, mounted vertically, and operated at approximately 5.6 volts. This voltage is chosen for two reasons. The first is that accurate data on the spectral distribution of the radiant energy of a 50 c.p. tungsten filament lamp have been determined by the General Electric Company. This data, given in Figure II, below, was used in determining the effective mean wave lengths of the spectral bands used. The second is that this voltage is well within the operating range of the bulb used, so that it does not become blackened prematurely, and has a long operating life.

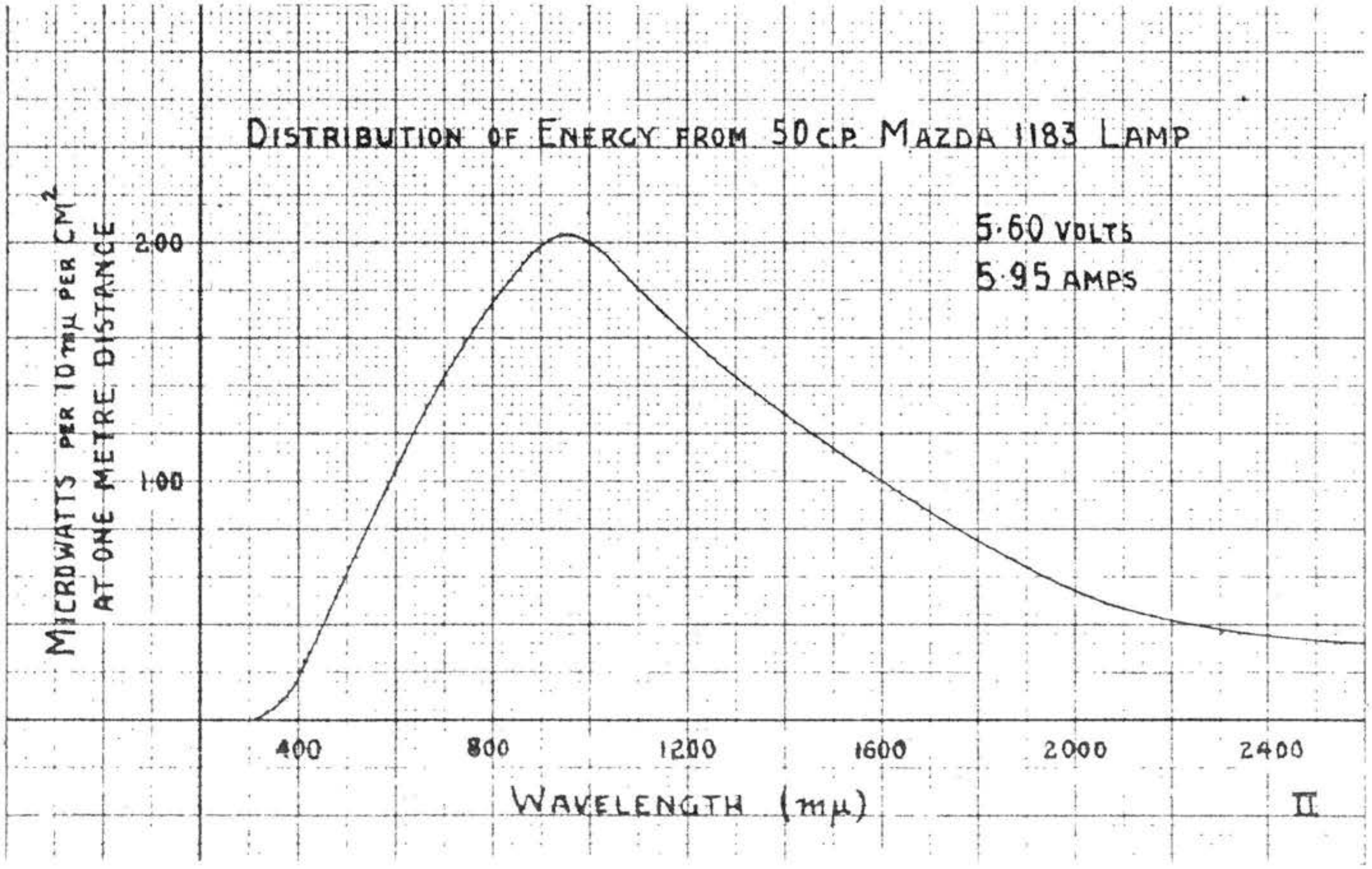

Figure II

In any photometric instrument, one of the major problems is to obtain a constant source of light. It has been shown[29] that, for the unfiltered radiation from a lamp of the type used here, the relationship

$$I = kV^n$$

holds over a wide range. In this equation

V = lamp voltage

I = photocurrent produced by radiation from lamp

k is a constant and n a number between 3 and 4.

Consideration of this relationship shows that control of the photocurrent to any suitable degree of precision would involve a control of voltage so precise as to be very difficult to attain. Storage batteries of reasonable size, even when operating on the optimum portion of their discharge curve cannot maintain a sufficiently exact voltage across the filament of a lamp like this to ensure practical constancy of photocurrent for more than a few seconds.

It would be much more reasonable to use photocurrent to control lamp voltage, and this is, in effect, what is done in this instrument. The voltmeter V, connected across the lamp terminals is used simply as an indicator to show that the voltage is approximately 5.6, and the exact voltage is regulated by the controlling rheostats to produce a standard response from the photoelectric cell. As the bulb is used it blackens on the inside from volatilization of the filament, and when the voltage necessary to give standard light intensity rises above 5.8, it is replaced.

In order to obtain the full required voltage across the lamp terminals during the full discharge period of the batteries, six lead accumulator cells and three resistances, R_1, R_2, and R_3 are employed. Six cells are used rather than four - which would be adequate - because motor car batteries are manufactured in banks of three cells and commercially available chargers are designed to operate on three or six cells.

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[29] Müller. Mikrochemie, 11, 353 (1932)

R_1 is a fixed resistance of heavy nichrome wire wound on a porcelain tube. Its resistance is 6 ohms and it carries most of the load. R_2 is a spiral wound, slide contact rheostat, total resistance 8 ohms and current capacity 8.5 amps. It serves as a coarse adjustment for lamp voltage. R_3 is a rheostat of type similar to R_2, but with a total resistance of 115 ohms and a current capacity of 2 amps. It is situated in the apparatus beside the microammeter H, and serves as the fine adjustent for lamp voltage to set the photocell response to standard value.

With this arrangement it is possible to keep the photocell response constant over a period of hours, from full charge to almost complete discharge of the batteries.

The filter system, as finally worked out, consists of two or three filters for each spectral band. In all cases the first filter is a 2 mm. thickness of Jena BG 18 glass[30]. The main function of this glass is to remove all wave lengths above 700 mμ, in which the radiation from the filament is rich, and to which the dyed gelatine filters used to isolate specific portions of the visible spectrum are all very transparent.

The dyed gelatine filters used are the Wratten Filters made by the Eastman Kodak Company[31] and either one or two of these are used to isolate rather narrow spectral bands. The transmission characteristics of the filters used, and the method of determining the mean effective wave length of any combination of them, is described below in the section covering the experiments run to establish the validity of the method.

B Collimator

This is a simple crown glass, plano convex lens[32] diameter 61.5 mm. focal length 150.2 mm. It is mounted in the barrel protruding from the front

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[30] Jena Glass Works, Jena, Germany. Bull. 4892-E.

[31] Eastman Kodak Co. "Wratten Light Filters"

[32] Bausch & Lomb Optical Co. Catalog D-10. Lens #41-53-20-012
Rochester, N. Y.

of the lamp housing at a distance from the filament approximately equal to the focal length. Final adjustment for parallelism of the emergent beam is made by sliding the lamp socket in the guides provided until an image of the filament is focussed on a wall about 40 feet away. With the lamp housing in place in the apparatus, the lamp is then moved slightly towards the collimator until the beam just fills apertures O-3 and O-4.

Aperture O-1 is a circular aperture 30 mm. in diameter and placed 95 mm. from the filament. It allows the direct radiation from the filament to fill the full aperture of collimator B, but cuts off stray light from any other part of the inside of the lamp housing. The entire inside of the lamp housing is coated with matt black lacquer, to reduce light reflection to a minimum. The lamp housing is ventilated to permit escape of the very considerable amount of heat generated.

The socket for lamp A is adjustable in all directions so that, in addition to being focussed, the filament may be centered accurately with aperture O-1 and collimator B. The lamp housing assembly is also adjustable within the casing so that its optic axis may be lined up accurately with that of apertures O-2, O-3 and O-4. O-3 is adjustable so that it can be lined up with O-2 and O-4.

D Absorption cell

The cell used for all ordinary measurements is an optical glass cell of rectangular cross section, 55 mm. high, 35 mm. wide and 10 mm. thick, interior dimensions. The edges are fused together so that the cell is impervious to chemical attack[33]. The base of the cell extends 10 mm. beyond the face of the cell on one side, to give greater stability. The cell rests on a wooden block equipped with brass guides so that it may be slid into place in contact with the face of aperture O-2.

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[33] Arthur H. Thomas Co., Philadelphia, Pa. General Catalogue, Item 9173.

In order to utilize to the maximum the area of the absorption cell, the area of the square glass filters, and the rectangular cathode of the photoelectric cell, apertures O-2 to O-4 were made rectangular, 30 mm. wide and 40 mm. high.

The special cell, used in the experiments to determine growth of particle size during polymerization, is described in the section dealing with these experiments.

E Absorption System for Scattered Light

This consists simply of the boxes formed by the partitions carrying O-2, O-3 and O-4, and the walls of the case. The entire interiors of these spaces are sprayed with matt black lacquer to absorb the scattered light, and only the unscattered radiation (plus the very small amount of the scattered radiation that is contained within the solid angle from any point on the illuminated part of the cell D to the edges of aperture O-4) passes through the apertures and is recorded by the measuring system.

Tests were made during the development of the apparatus, using several additional apertures, and no additional aperture, between apertures O-2 and O-4. With no aperture at O-3, a barely detectable increase in recorded radiation was observed at high illumination levels. The use of more than one aperture between O-2 and O-4 had no effect.

F, G, H Measuring system

This is, fundamentally, the most important part of the entire instrument. Collectively, it must possess the following characteristics:

1. Linearity of response. The readings given by the meter must have a definite functional relationship (preferably direct proportionality) to the intensity of the radiant energy falling on the photoelectric cell.

2. Stability. The response must be stable.

3. Sensitivity. The system must record small changes in intensity accurately and reproducibly. It must have reasonably uniform response to radiation of different wave lengths within the range used.

4. Flexibility. The system must be adjustable to record intensities over a wide range.

The attainment of these characteristics is achieved by proper selection, design and construction of photocell, amplifier, and meter.

The simplest photoelectric measuring device is, of course, the "barrier layer" or "self energizing" cell, of the Weston "Photronic" or Westinghouse "Photox" type[34] connected directly to a microammeter or galvanometer. This arrangement possesses serious limitations. The current output at any given illumination level varies with the resistance of the external circuit, as shown in Figure III, being nearly directly proportional to the illumination intensity when the external resistance is low.

An arrangement of this kind was used in the first exploratory experiments. The resistance of the external circuit was held down by using a low resistance, multirange microammeter (manufactured by the Sensitive Research Instrument Corp., of Brooklyn, N. Y., their Model S). This instrument had a uniform resistance of 100 ohms on all ranges from 50 to 1000 microamperes full scale reading. As the level of illumination was low (of the order of 20 foot candles maximum) the proportionality between current output and illumination was fairly exact. The microammeter, however, proved unsatisfactory because of the low operating torque, and failed to give reproducible readings.

[34] "Die Photoelemente und ihre Anwendung"
J. A. Barth, Leipzig (1936) 2 vol.

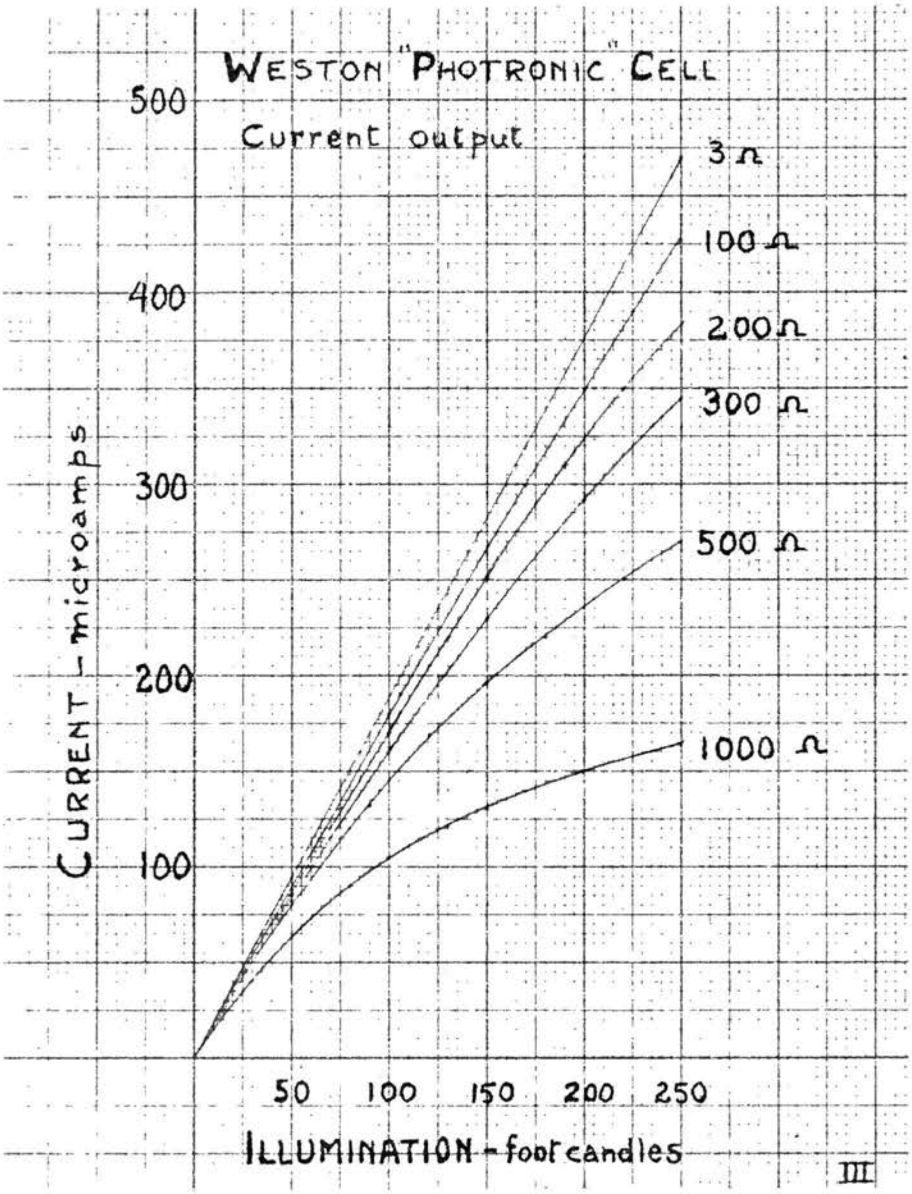

Figure III

These difficulties were overcome by the use of a barrier layer cell in a "zero-resistance" circuit. This circuit has been described by Fogle[35] and Wood[36] and its essentials are summarized in Technical Service Bulletin B-18A of the Weston Instrument Co. The actual circuit used in this work is shown in Figure IV. The microammeter was rebuilt by the manufacturers to have

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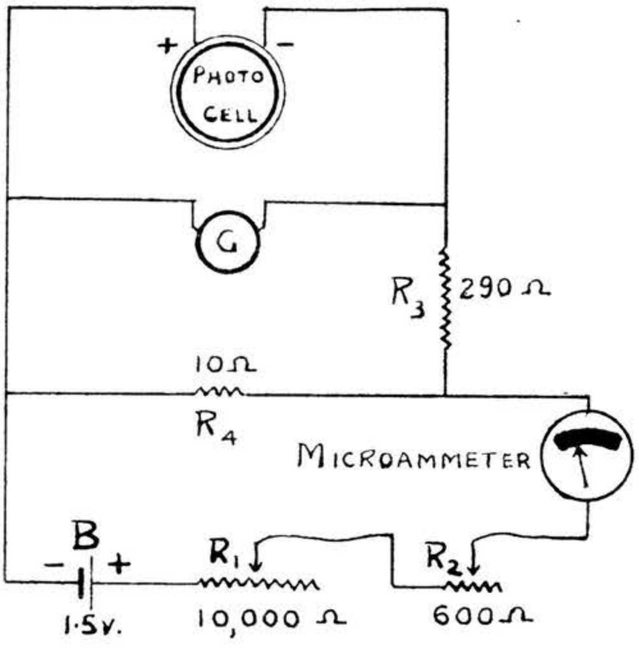
[35] Trans. Elect. Chem. Soc. 66, 271 (1934)

[36] Rev. Sci. Instr. 7, 3 157 (1936)

a uniform resistance on all ranges of 500 ohms. This increased the torque, and gave the instrument satisfactory operating characteristics.



"ZERO-RESISTANCE" CIRCUIT WITH BARRIER LAYER PHOTOCELL

IV

Figure IV

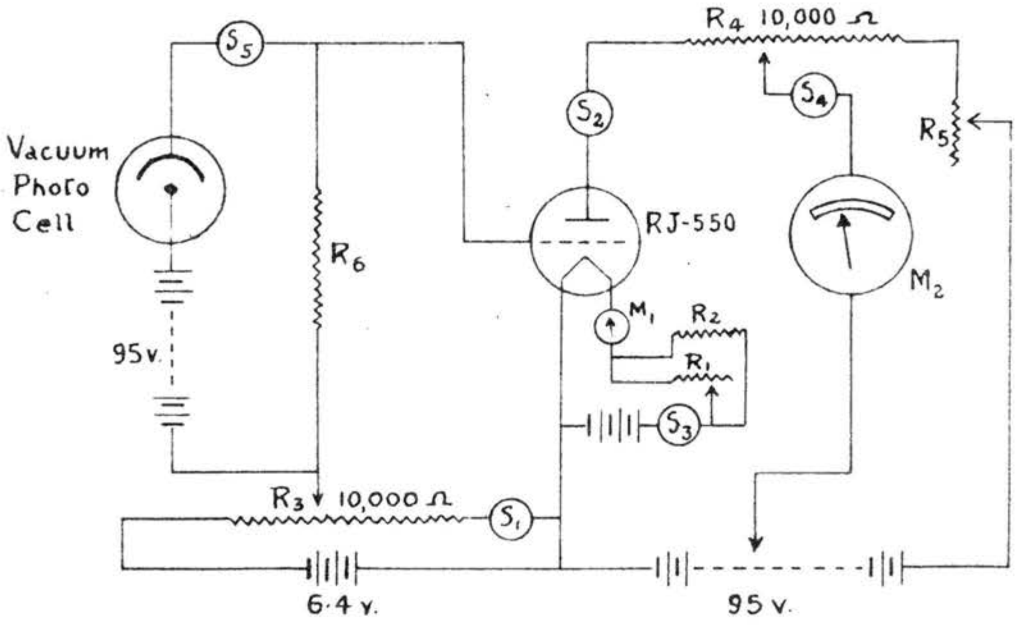
In this circuit, when the cell is illuminated with the radiation to be measured, rheostats R_1 and R_2 are adjusted (R_2 being the fine adjustment) until galvanometer G shows a balance. In this condition, battery B is supplying just enough E.M.F. to overcome the external resistance of the circuit, so that the external voltage drop across the photoelectric cell is zero, which means that, from the standpoint of the cell, the condition is equivalent to no external resistance. Thus, the relationship between light intensity and current output is truly linear. The current flowing through the meter is related to that flowing through the cell by

$$I_{\text{meter}} = I_{\text{cell}} \times \frac{R_3 + R_4}{R_4}$$

which in this case is 30:1.

This arrangement works very well for measuring the transmission of a material in a stationary cell. It proved unsatisfactory, however, in the experiments described later in which the growth of particle size was studied. In these experiments the transmission of the liquid is continually changing, sometimes quite rapidly, and the need for balancing the galvanometer before taking a reading on the microammeter makes the whole proceeding very cumbersome. When the transmission is changing rapidly, the galvanometer goes off balance before a reading can be obtained.

The most satisfactory arrangement, and the one in use today, is a combination of a potassium oxide vacuum phototube, a straight line amplifier, and a high resistance microammeter. The circuit diagram is indicated in Figure V.



AMPLIFIER CIRCUIT

V

Figure V

In this arrangement, the voltage drop of the photocell current through the grid resistor of the amplifier tube changes the grid potential, and therefore the plate current, in direct ratio to the illumination intensity. The meter is installed in the crossarm of the bridge arrangement shown, so that the steady plate current may be balanced out, and only an amount proportional to the change in plate current is read on the meter.

Photoelectric cells (tubes) - Discussion

A vacuum phototube is used because of the exactness, over a wide range of conditions, of the relationship between its conductivity and the intensity of the radiation falling on it. The gas filled tube, while showing greater conductivity per lumen, is suited for exact measurements only at voltage and illumination levels well below the point where glow discharge appears.

The common caesium oxide tube was first employed but was found to be quite unsuitable because of its high response in the infrared. While this characteristic is desirable in securing maximum response to the unfiltered radiation from a tungsten lamp, it is a decided drawback when it is necessary to measure exactly the energy of a filtered band of radiation within the visible spectrum. The dyed gelatine filters are all very transparent to infrared radiation, and none of the heat absorbing glass filters (Jena BG 19, Jena BG 18, Corning, Aklo 398) cut off the infrared radiation entirely. As the scattering varies inversely with the fourth power of the wave length, and the measurement is made on the unscattered radiation, it may be seen very readily that the presence of a small component of long wave length radiation may, with a cell very sensitive to such radiation, produce marked departure from the expected relationships. This was actually found to be the case with a cell of which the cathode was coated with caesium oxide. Increasing concentrations of a selected polymethyl acrylate dispersion were prepared, and transmission measurements made in the apparatus described, using a caesium oxide tube. These measurements were made with spectral bands of various mean effective wave lengths (determined by the procedure given below) and plots made of optical density versus concentration. The resulting curves (Figure VI) show marked departure from the expected straight lines.

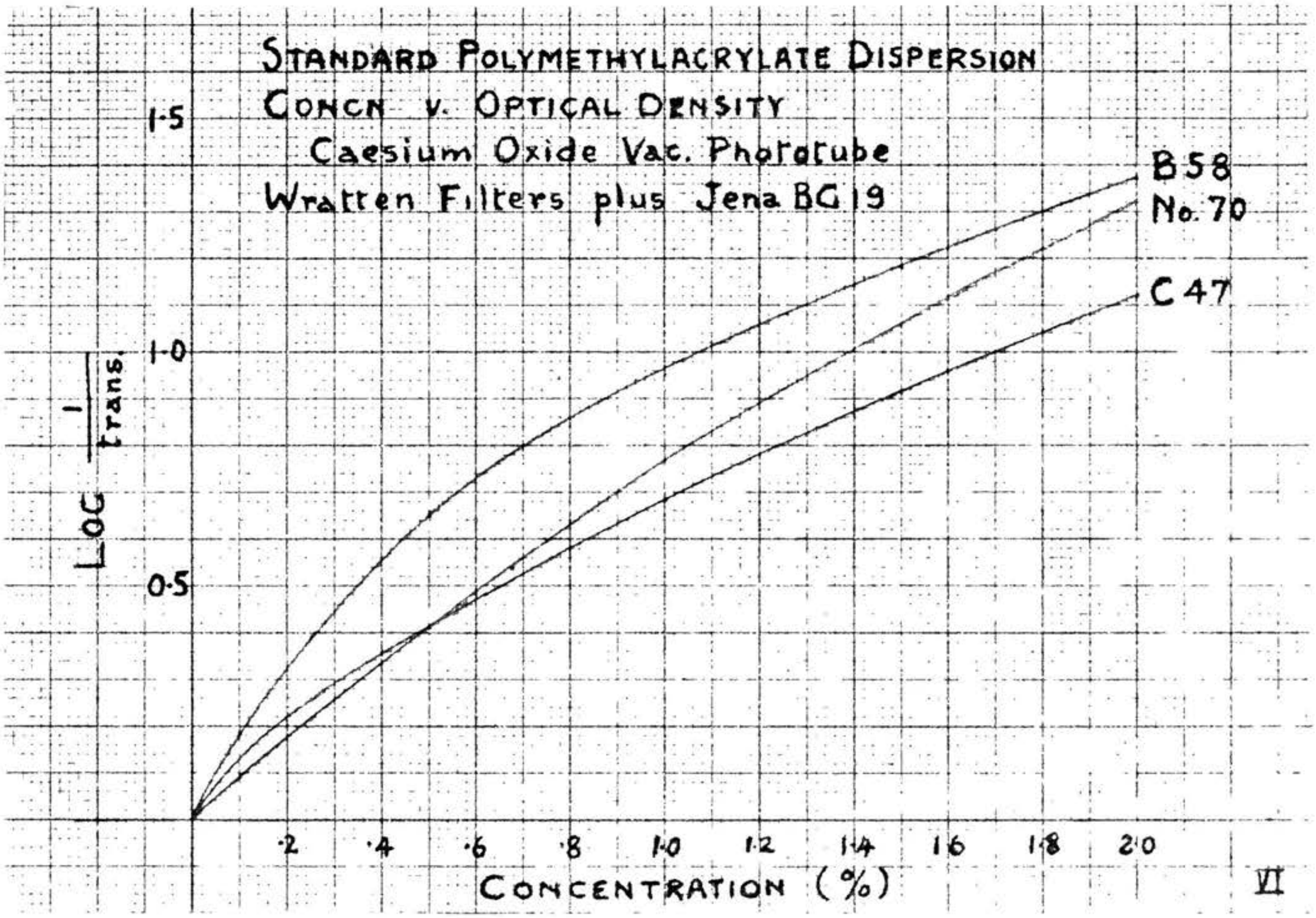


Figure VI

The fact that the departure from linearity increased with reduction in wave length indicated that a long wave length component, beyond the range of the visible spectrum, was present. The caesium oxide tube was replaced by a potassium oxide tube. This type of tube has a sharp cutoff at 800 mμ , so that any long wave length component passing through the filter combination is not recorded.

The relative responses of the potassium oxide and caesium oxide tubes to radiation of equal energy at different wave lengths is shown in Figure VII.

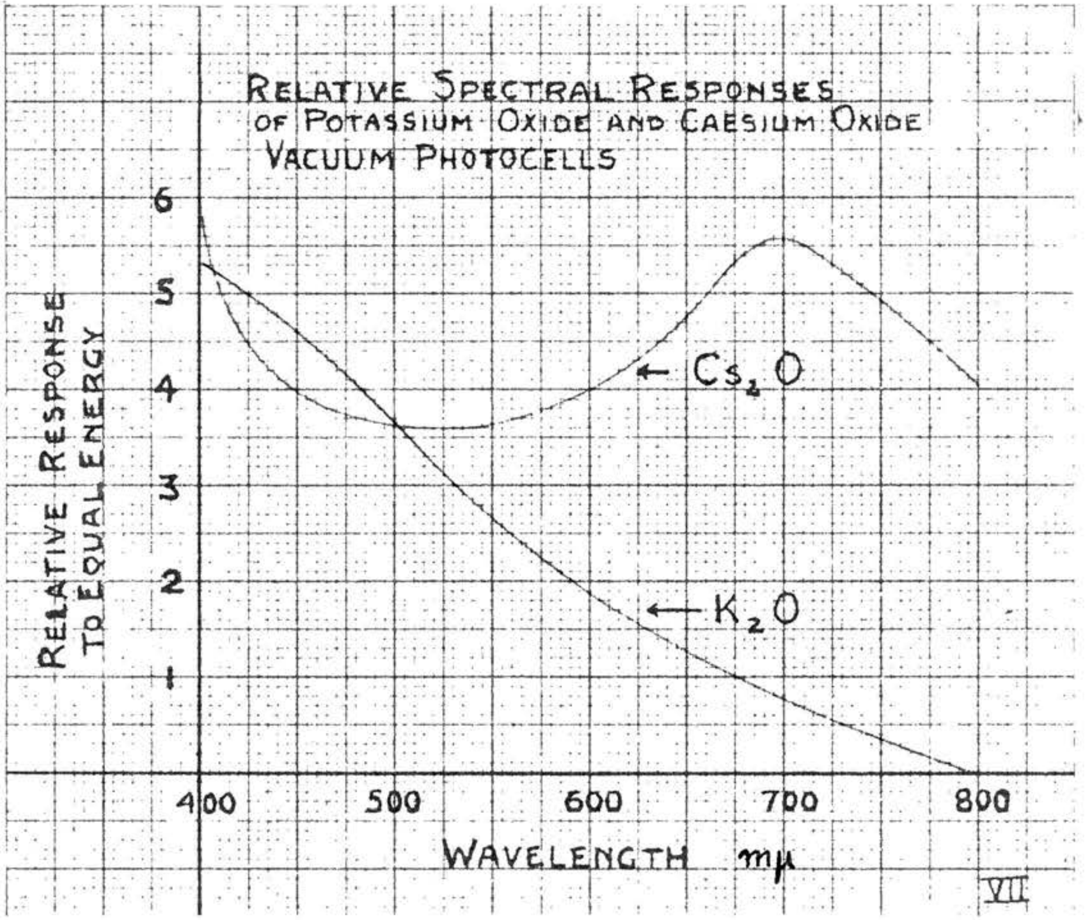


Figure VII

Potassium oxide cells are manufactured by G-M Laboratories of Chicago, Illinois, from whose data sheets[37] the above curves are taken. They are known as Type D, and are usually produced as gas-filled cells. For this work a special vacuum cell, No. 71-DV was obtained. This cell has a central vertical anode and a curved cathode of 1 1/4" height and 1" effective width. In order to avoid leakage currents, the Bakelite base was removed and replaced with a glass base made from the neck of a broken pyrex flask. This base was mounted in a

[37] Tech. Bulls. Nos. 119-C and 587, G.M. Laboratories, Chicago.

cork, the cell cemented to it with a polyacrylate cement, and the lead wires carried through small holes pierced in the glass base. Figure VIII is a photograph of the completed cell assembly.

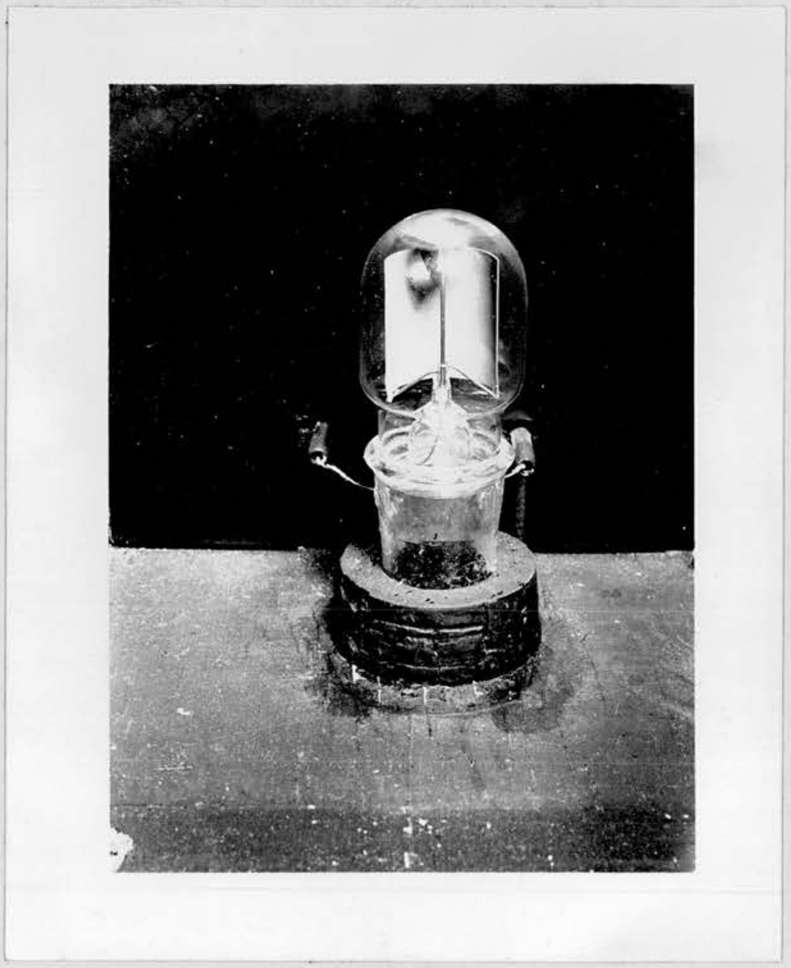


Figure VIII

With this photocell, very exact proportionality between concentration and optical density of a polyacrylate dispersion was obtained. This will be shown in the experimental work described below (Table 4 and Figure XIII).

Amplifier design

The amplifier circuit is shown in Figure V above, and a brief description is there given. The basic design was suggested by the Engineering Department of the Lamp Division of the Westinghouse Electric & Manufacturing Company, and is a modification of that given in their Technical Bulletin TD-76, p. 7, (circuit "b"). It is based on their semi-electrometer tube RJ-550 which is characterized by a very low grid current.[38] The actual tube used was found to correspond closely to the average values given in the Westinghouse literature, with the exception of the voltage-current characteristics of the filament. To maintain the required 0.92 amps. recommended filament operating current, the filament voltage had to be 3.0 v. instead of the 2.5 v. stated. The mutual characteristics of this tube, as determined experimentally with a grid resistance of 0.49 megohms and a plate circuit resistance of 400 ohms is shown in Figure IX.

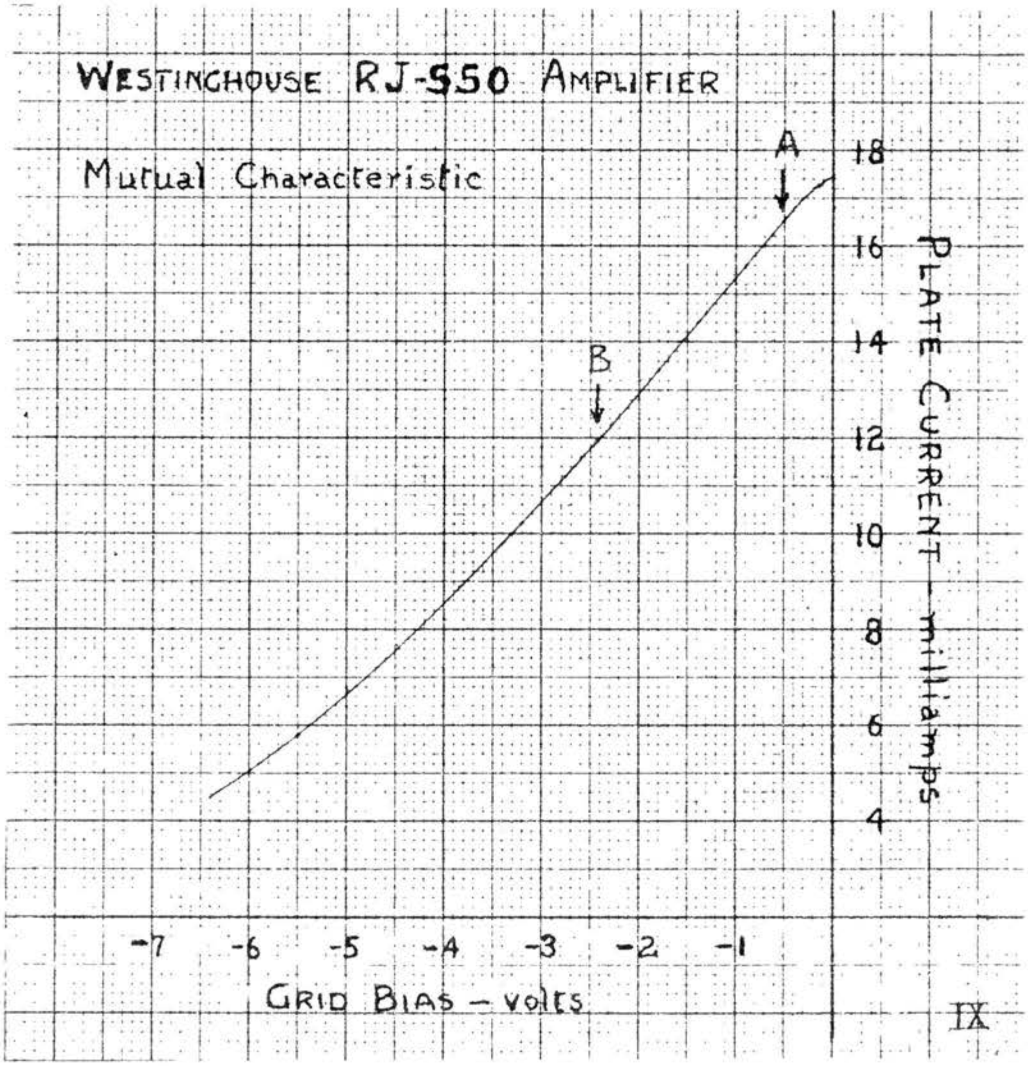


Figure IX

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[38] Tech. Bull. F-3025-A. Westinghouse Electric Co.

Conditions of operation of the amplifier are so chosen that the tube functions only on the straight part (A-B) of the characteristic. The filament current is controlled by a rheostat R_1 (Figure V) General Radio Company, Type 214-A, 7 ohms[39] in parallel with a fixed resistance R_2 of nichrome wire (6 ohms). An ammeter M_1 records the filament current. Potential dividers R_3 and R_4 are each of 10,000 ohms, General Radio Company, Type 471-A[39], while R_5 is a tubular slide wire rheostat of 610 ohms total resistance and is used as a fine adjustment in setting the zero reading of the instrument.

The grid resistor R_6 is mounted between two binding posts. Any grid resistor of the type commonly used in assembling radio sets may be inserted, depending on the over-all intensity of the spectral band used. A value for the grid resistor is selected which gives full scale, or nearly full scale reading on microammeter M_2 with the uninterrupted beam and a voltage of 5.6 on the lamp A.

Switches S_1, S_2, S_3 and S_4 are all embodied in a single unit, multiple contact switch, General Radio Company, Type 339-A[39]. By using a unit of this type the entire amplifier may be turned on or off with one knob. Switch S_5 is a small porcelain base knife switch, and is used only to protect the photocell batteries if, for any reason, the case has to be opened to daylight for a considerable time.

The whole assembly is mounted on a base and inclined front panel of 1/4" sheet Plexiglas supported by a strip brass frame and resting on rubber feet. The complete amplifier assembly is shown in Figure X.

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[39] General Radio Co., Cambridge, Mass. Catalog K (1939)

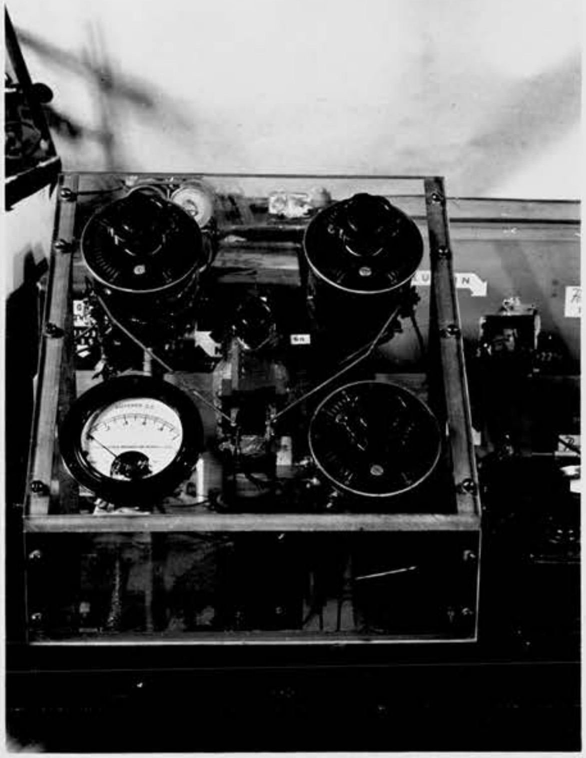

Figure X

The batteries used are commercial radio "B" batteries. At the low current drain here experienced, they exhibit "shelf life."

The entire box surrounding the photocell is shielded with sheet brass. The photocell and grid resistor leads are run through glass tubes shielded with tinfoil. The amplifier tube and potentiometer R_3 are also shielded with tinfoil. All shielding is interconnected and grounded.

Meter M_2 is the same rebuilt meter as described on page 34 above. It has five ranges for full scale reading 50, 100, 200, 500 and 1000 microamperes, with a uniform resistance of 500 ohms for each range.

b. Apparatus - Use of Instrument

In making actual determinations with this instrument, the following procedure is employed:

1. The grid bias of the amplifier is set at -2.3 v. and a grid resistor is inserted which will give full scale deflection of the microammeter on either the 500 or 1000 microampere range with the uninterrupted beam when the lamp voltage is approximately 5.6.

2. Shutter J is closed. Lamp A and amplifier G are turned on and allowed to warm up for ten or fifteen minutes.

3. With shutter J in the closed position, the microammeter reading is adjusted to zero by means of potential divider R_4 and rheostat R_5 (Figure V).

4. Shutter J is opened, and the intensity of the uninterrupted beam is adjusted by rheostats R_2 and R_3 (Figure I) until the reading on the microammeter is 100, i.e. full scale, or some convenient value close to full scale reading.

5. The absorption cell, carefully cleaned and filled with distilled water, is placed in position against aperture O-2, and the microammeter reading is recorded.

6. The cell is rinsed out three times with the dispersion on which a measurement is desired, and then filled with the dispersion. The zero and full scale readings of the instrument are checked to insure against drift, and reset if necessary. The cell is reinserted and the microammeter reading is recorded.

This procedure is a "rapid substitution" method of determining transmission. In all cases determinations are made immediately after the zero and full scale readings have been set, and these are always rechecked after each determination. In actual practice, the zero reading remains very constant after the amplifier is warmed up, and the only drift of the full scale reading is that produced by the gradual discharge of the batteries supplying the lamp.

c. Establishment of Validity of Light Scattering Method of Measuring Particle Size

Equation (4) above, derived from Rayleigh's Law, states that

$$\log \frac{I_o}{I} \times \frac{\lambda^4}{C} = K'V$$

i.e. the optical density of a finite thickness of dispersion multiplied by the fourth power of the wave length of the radiation and divided by the concentration is proportional to the average particle volume.

The validity of the wave length and concentration relationships for aqueous dispersions of polyacrylic esters may be checked by making measurements of optical density, under conditions where all the scattered light is absorbed, of one selected dispersion at different wave lengths and concentrations. When one such preparation is used, the average particle volume is, of course, constant. One such polymethyl acrylate dispersion, made in commercial production, of average fine particle size and free from sediment, was selected and used for this work. This material is referred to in subsequent work as "Standard Polymethyl Acrylate Dispersion."

A number of combinations of light filters were worked out to produce fairly narrow bands of radiation, all lying within the visible spectrum. The effective mean wave length of each was determined by the method described below, and measurements were made on the standard polymethyl acrylate dispersion.

Method of Determining Mean Effective Wave Lengths of Radiation Bands

The mean effective wave length of any spectral band filtered from the continuous spectrum of a tungsten lamp, and measured with a vacuum phototube, depends on three factors. These are:

1. The spectral distribution of the radiation emitted by the lamp, under specified operating conditions.

2. The spectral transmission of each of the filters used in the combination.

3. The spectral distribution of the response of the photoelectric cell.

From the data specifying each of these factors, a resultant spectral distribution curve is calculated. This is plotted, and a pattern made from light cardboard of uniform weight. The centre of gravity of this pattern is determined, by balancing it on a needle point, and projected on the wave length axis. The wave length so indicated is the mean effective wave length of the combination.

The following examples typify the procedure:

Example I. Determination of Effective Mean Wave length of Wratten C & H Filters. Lamp voltage 5.2. Filament temp. 2700°K.

TABLE 1.

Wave length mμ	Transmission of C filter (31)	Transmission of H filter (31)	Relative emission of filament (Fig. II)	Relative sensitivity of phototube (Fig. VII)	Product
420	40.7	.00	13.8	5.01	0
430	47.7	.31	16.1	4.88	1,162
440	48.8	8.85	19.2	4.72	39,150
450	46.2	22.5	22.4	4.60	107,100
460	41.3	33.1	26.0	4.37	155,300
470	34.7	39.9	29.5	4.17	170,200
480	27.0	40.9	33.7	4.00	148,700
490	18.6	38.0	38.1	3.81	102,600
500	11.1	30.2	42.9	3.63	52,200
510	8.0	20.8	48.6	3.43	17,350
520	1.58	11.5	54.3	3.22	3,179
530	.32	3.99	60.5	3.02	233
540	.10	.50	66.6	2.84	9.5
550	.00	.00	72.8	2.65	0

The curve, wave length v. product is shown in Figure XI. The curve used in the actual E.M.W. determination was plotted on a scale twice that of Figure XI.

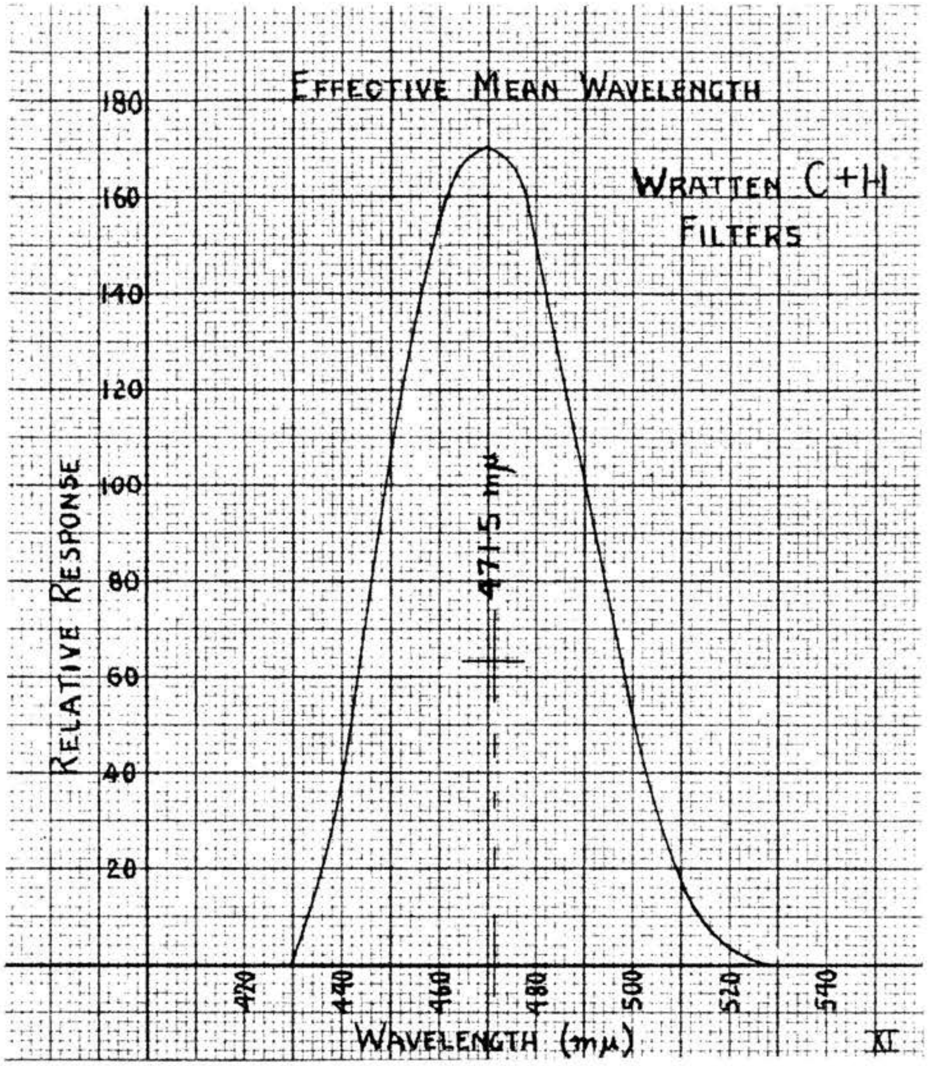

Figure XI

Experimental determination of the centre of gravity of this curve, and projection of the centre of gravity on the wave length axis, gives the effective mean wave length as 471.5 mμ .

Example II

Determination of Effective Mean Wave length of Wratten Filter #62 plus Jena Filter BG 18.

Lamp voltage 5.6 v. Filament temp. 3100°K.

Table 2.

Wave length mμ	Transmission of No. 62 filter (31)	Transmission of BG 18 filter (30)	Relative emission of filament (Fig. II)	Relative response of phototube (Fig. VII)	Product
500	.00	.81	53.0	3.63	0
510	.26	.81	57.4	3.43	41.48
520	8.00	.82	61.9	3.24	1316
530	14.7	.81	66.4	3.06	2419
540	10.9	.80	71.0	2.84	1758
550	5.00	.73	75.2	2.65	727.3
560	1.46	.70	80.0	2.48	202.7
570	.16	.50	85.0	2.32	15.77
580	.00	.32	91.9	2.18	0

A half scale replica of the curve, wave length v. product, is shown in Figure XII. From this, the effective mean wave length of the combination is found to be 533.6 mμ .

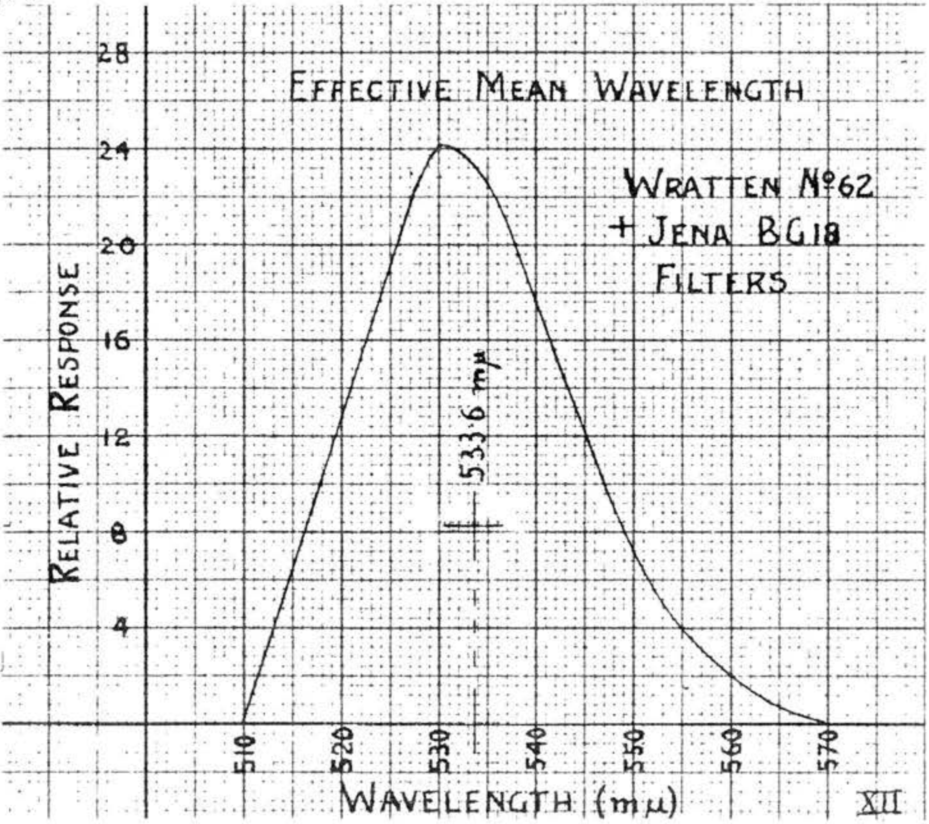

Figure XII

Following this same procedure, effective mean wave lengths were determined for a number of filter combinations, as follows:

Table 3.

Filter combination	Color	Effective mean wave length (millimicrons)
Wratten C + H	Blue	471.5
Wratten 62 + Jena BG 18	Green	533.6
Wratten 62 + Jena BG 19	Green	534.3
Wratten B-58 + Jena BG 19	Green	536.0
Wratten B-58 + E	Yellow	575.8
Wratten No. 70	Red	658.6

Establishment of Validity of Concentration and Wave Length Relationships

Measurements were made, using each of the filter combinations of Table 3, on a series of dilutions of the standard polymethyl acrylate dispersion. The data are given in Table 4 and plotted in Figure XIII.

Table 4.

	Filter Combinations					
	C + H		62 + BG 18		62 + BG 19	
	E.M.W. = 471.5		E.M.W. = 533.6		E.M.W. = 534.3	
	5.2 v.	40 megs.	5.6 v.	60 megs.	5.4 v.	60 megs.
Conc'n	rdg.	$\frac{1}{\text{trans.}}$	rdg.	$\frac{1}{\text{trans.}}$	rdg.	$\frac{1}{\text{trans.}}$
blank	800		600		600	
water	747		560		560	
0.001	272	2.74	294	1.90	298	1.88
0.0025	62.5	11.95	118	4.74	120	4.6
0.005	6.9	108	26.5	21.1	28.8	19.4
0.0075	-		6.5	86.3	7.9	71.0

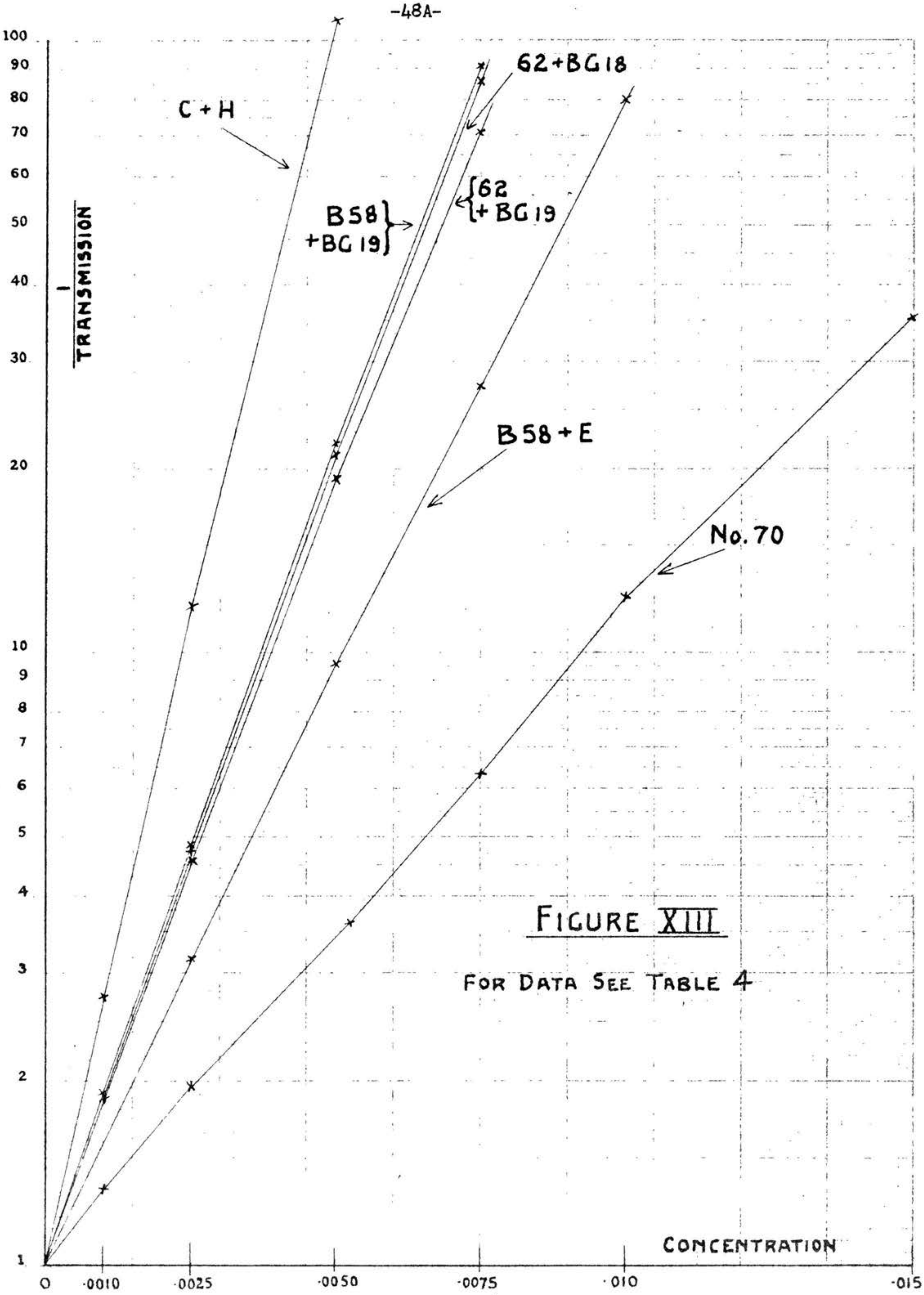

FIGURE XIII

FOR DATA SEE TABLE 4

Table 4 - continued -

	Filter Combinations					
	B-58 + BG 19 E.M.W. = 536.0		B-58 + E E.M.W. = 575.8		No. 70 E.M.W. = 658.6	
	5.4 v.	10 megs.	5.4 v.	110 megs.	5.2 v.	110 megs.
Conc'n	rdg.	$\frac{1}{\text{trans.}}$	rdg.	$\frac{1}{\text{trans.}}$	rdg.	$\frac{1}{\text{trans.}}$
blank	700		700		700	
water	655		655		648	
.001	342	1.92	410	1.60	482	1.34
.0025	135	4.85	206	3.18	328	1.97
.005	31.5	20.8	68.1	9.62	182	3.56
.0075	7.2	91.0	24.1	27.2	102	6.35
.010	-	-	8.2	80.0	52.4	12.4
.015	-	-	-	-	18.5	35.1

E.M.W. = Effective Mean Wavelength in millimicrons.

Voltages refer to lamp filament voltages.

Resistances in megohms refer to grid resistors used.

The data show good proportionality between concentration and $\log \frac{1}{\text{transmission}}$ for all wavelength bands.

In Table 5 are given the data checking the degree of concordance with " λ^4" law. If the relationship expressed by Equation (4), above, is valid then the expression

$$\log \frac{1}{\text{transmission}} \times \frac{\lambda^4}{c}$$

should be constant for all wavelengths.

TABLE 5

Filter Combination	Effective Mean Wavelength (in mμ)	λ^4	$\frac{1}{\text{trans.}}$ at c=.0025	$\log \frac{1}{\text{trans.}}$	$\log \frac{1}{\text{trans.}} \times \frac{\lambda^4}{c}$
C + H	471.5	4.942×10^{10}	11.95	1.0774	2.129×10^{13}
62 + BG 18	533.6	8.107×10^{10}	4.74	.6758	2.192×10^{13}
62 + BG 19	534.3	8.150×10^{10}	4.60	.6628	2.161×10^{13}
B 58 + BG 19	536.0	8.254×10^{10}	4.85	.6857	2.264×10^{13}
B 58 + E	575.8	10.99×10^{10}	3.18	.5024	2.209×10^{13}
#70	658.6	18.81×10^{10}	1.97	.2945	2.217×10^{13}

The mean value of the "constant" in the last column of this table is 2.195×10^{13}. The percentage deviation from this mean, in the case of each filter combination, is given below.

TABLE 6

Filter combination	% deviation from mean
C + H	- 3.01
62 + BG 18	- 0.137
62 + BG 19	- 1.55
B 58 + BG 19	+ 3.14
B 58 + E	+ 0.638
No. 70	+ 1.003

This is a good degree of constancy, especially when it is considered that much of the data - transmissions taken from manufacturers catalogues, for example - is of only an approximate nature, and that the wavelengths derived from this data are involved to the fourth power.

The experiments described above establish the validity of the concentration and wavelength relationships, as expressed in Equation (4) above, for measurements made in this apparatus on a single polymethyl acrylate dispersion in which the particle volume, V, is constant.

It is reasonable to suppose that the method would therefore give accurate relative values of the average particle volumes when optical density measurements were made at known wavelength and concentration, on dispersions of different average particle volumes. This, however, can be checked only by measurements using a totally independent method.

2. Determination of Particle Sizes by Centrifugal Sedimentation

a. Preliminary Investigation

In the discussion above (pp. 13-25) on possible methods of determining particle sizes, it has been shown that, apart from the light-scattering method already described, the most practical way to determine particle size in water dispersions of polyacrylic esters is by centrifugal sedimentation. This was done by the use of the "multispeed" attachment to the Type SB reinforced centrifuge of the International Equipment Company, together with a special centrifuge head, designed by the author, and manufactured by the International Equipment Company.

The regular "multispeed" attachment to this centrifuge[40] consists of a Duralumin conical head, six inches in diameter, carrying six glass tubes, each 7 ml. capacity, held in rubber cushions at approximately 30° from the horizontal. The head revolves on a vertical spindle running on roller and needle bearings immersed in oil. It is driven by a belt from the motor shaft, the ratio of speeds being 4.6 to 1. This head can be operated, therefore, at speeds up to 20,000 r.p.m., developing a relative centrifugal force at the bottoms of the tubes of approximately 30,000 times gravity.

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[40] Bulletin C-1, 1940, p. 7. International Equipment Company

Boston, Massachusetts, U. S. A.

Preliminary trials with this apparatus indicated that the force exerted was capable of throwing down completely the polymer from a fine polymethyl acrylate dispersion in approximately one hour at top speed.

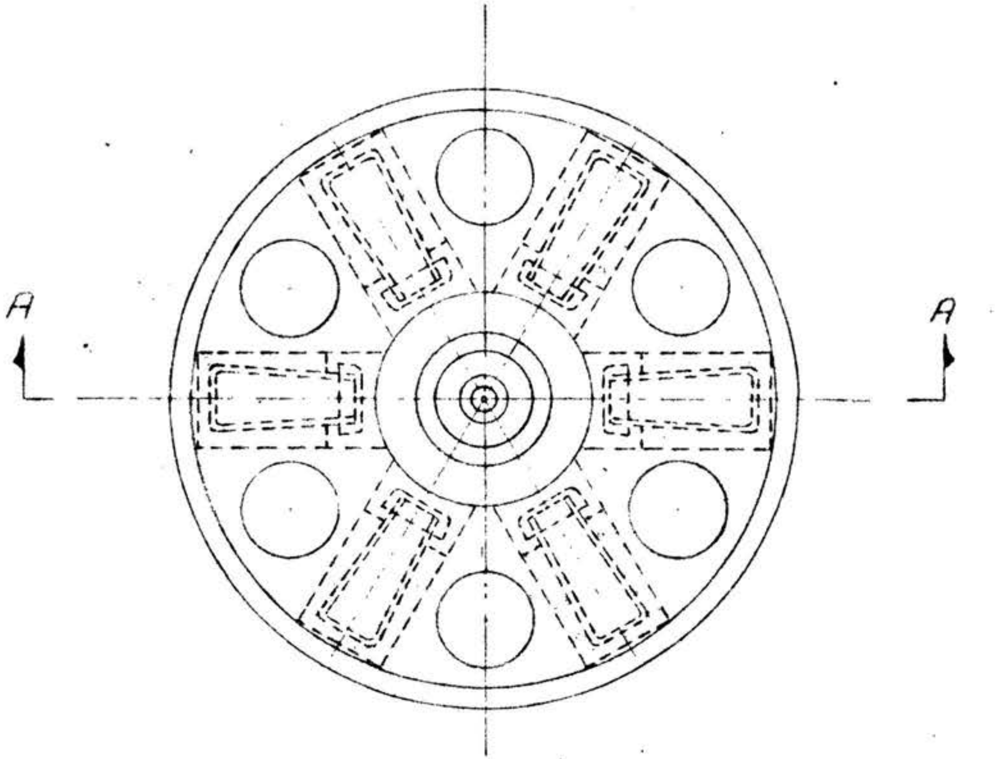
When particles are sedimented in a conical type head with its inclined tubes, it is not possible to calculate particle sizes from the sedimentation data. This is because most of the particles are first thrown against the outer wall of the tube and then slide down the tube in contact with the wall. The path is indefinite, and the friction against the wall is unknown.

b. Description of Special Centrifuge

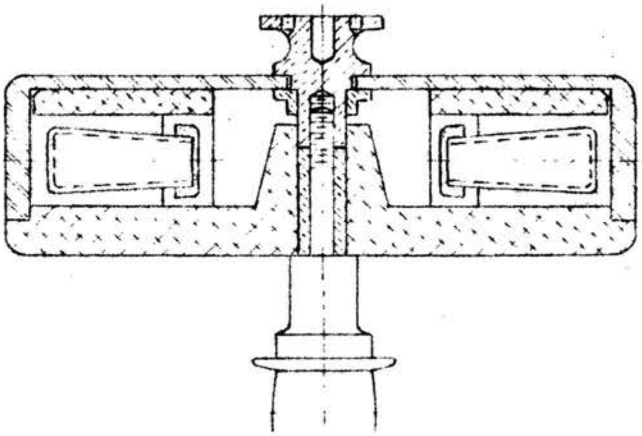
To overcome this drawback, a centrifuge head was designed especially for particle sedimentation studies. This special head was manufactured to order by International Equipment Company. The design is shown in Figure XIV and the actual head, together with the tubes and rubber cushions, in Figure XV.

Figure XV

FIG. XIV



PLAN VIEW WITHOUT COVER



CROSS SECTION A-A

SPECIAL CENTRIFUGE HEAD FOR PARTICLE SIZE DETERMINATIONS

SCALE - HALF SIZE 2-15-44

The salient features incorporated in this design are:

1. The axis of the tubes is perpendicular to the axis of rotation of the head, so that sedimentation occurs along the tube axis.

2. The tubes are sector shaped, being wider at the bottom than at the top, so that the walls do not interfere with the fall of the particles.

3. The tubes are flat on the bottom. Thus the sedimentation distance may be determined accurately.

4. The tubes are completely filled with liquid, and capped with rubber caps, so that no displacement of liquid with air occurs when the tubes are handled, or when the centrifuge is started and stopped.

5. The tubes are short, and are placed as far as possible from the centre of the head, so that the "centrifugal gradient" along the tube is minimized, and the relative centrifugal force at the bottoms of the tubes is at a maximum.

Temperature Regulation

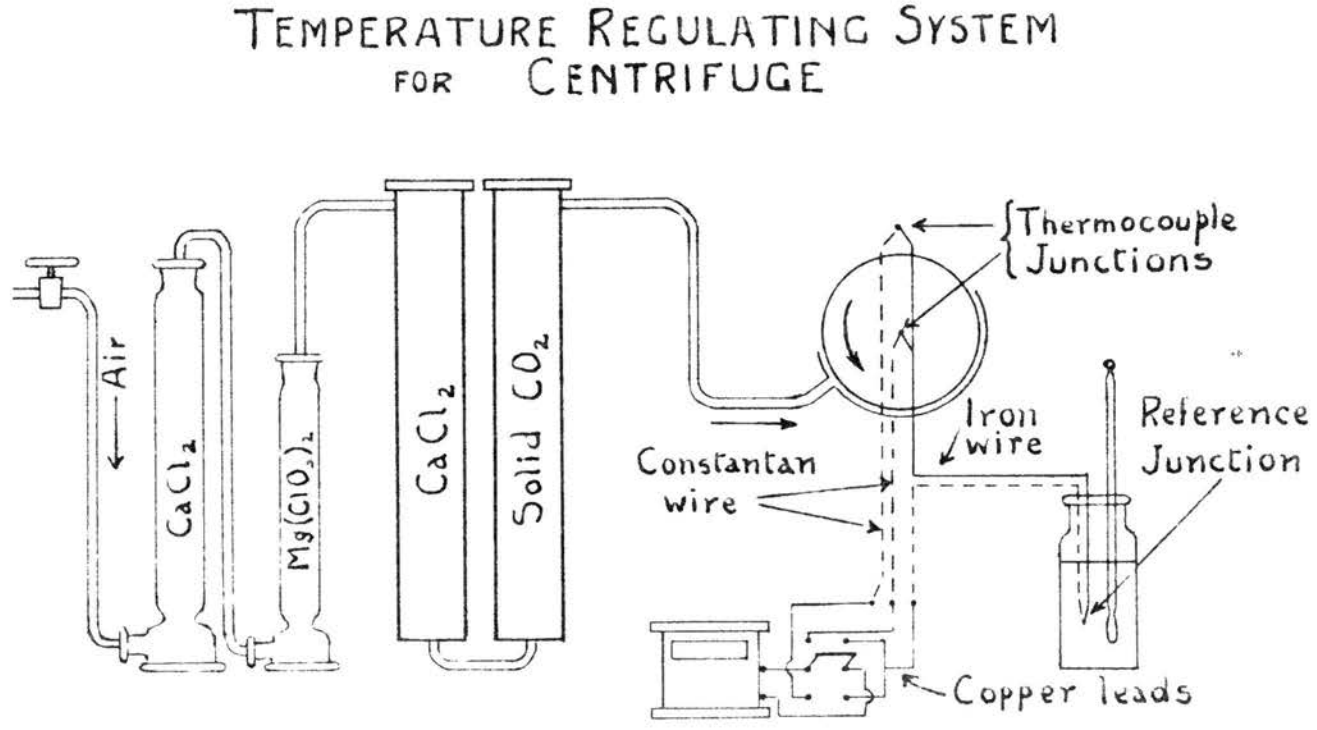
One of the major problems in operating a centrifuge of this type is to keep the temperature of the head constant. In spite of the fact that the Duralumin head and the stainless steel cover are both highly polished, skin friction is considerable. At the top speed used - 16,000 r.p.m. - the peripheral velocity is of the order of 490~~0~~ ft. per second or 335 miles per hour, and the head, if not cooled artificially, becomes so hot in a few minutes that it cannot be handled. Any such change of temperature during centrifuging invalidates completely any data obtained, first because the viscosity of the dispersion medium changes with change in temperature, and second and more important, convection currents are set up which create sufficient disturbance to nullify the sedimentation so that no accurate classification can be made. This is particularly true of a system, such as those considered here, where the particles are small and where the difference in density between dispersed and dispersion media is also small.

A number of schemes were tried to keep the temperature of the head constant while a run was being made. One which proved eminently satisfactory was worked out, and is in use today. It is described below.

A "shield" is mounted on the multispeed attachment of the centrifuge. This is made from heavy sheet brass and extends approximately half way around the head so that when the head is running the clearance between shield and head is approximately 3/16 inches (4.5 mm.). To the "leading edge" of this shield is attached a copper pipe terminating in a slot cut through the shield. Through this pipe and slot is forced a current of air, taken at 20 pounds per square inch from the laboratory air supply, dried, and passed through a heavily insulated metal cylinder containing broken pieces of solid carbon dioxide. A needle valve attached to the air supply enables the stream of air to be regulated with precision.

In the centre of the knob which holds the cover on the centrifuge head is drilled a small well approximately 1/4 inch in diameter and 1/2 inch deep. In the centre of this well is suspended one junction of an iron-constantan thermocouple. The reference junction for this thermocouple is held, together with a thermometer, outside the apparatus in a bath of castor oil. A second thermocouple is suspended just beyond the periphery of the head, and away from the blast of cold gas emerging from the shield. This second thermocouple serves as a check on the temperature of the atmosphere in the main body of the centrifuge. Either of the thermocouples may be connected at will with the reference junction by means of a double throw, double pole knife switch. The current generated by difference in temperature between either of the thermocouples and the reference junction is recorded by a reflecting galvanometer with an internal resistance of 24 ohms, and an external critical damping resistance of 95 ohms. This instrument is made by Leeds and Northrup Company, their number 2420-b[41]. The sensitivity of the whole arrangement is eight scale divisions per Centigrade degree.

The apparatus is shown diagrammatically in Figure XVI.



XVI

Figure XVI

This diagram is self-explanatory. Two cylinders carrying the supply of solid CO_2 are incorporated in the apparatus, in parallel, so that the contents of one may be replaced while the other is in use. This provides for continuous operation of the apparatus. The centrifuge head, with thermocouple arrangement is shown in Figure XVII and the centrifuge cooling arrangement in Figure XVIII.

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[41] Catalogue ED, 1939, p. 11.

Leeds & Northrup Company, Philadelphia, Pa., U. S. A.

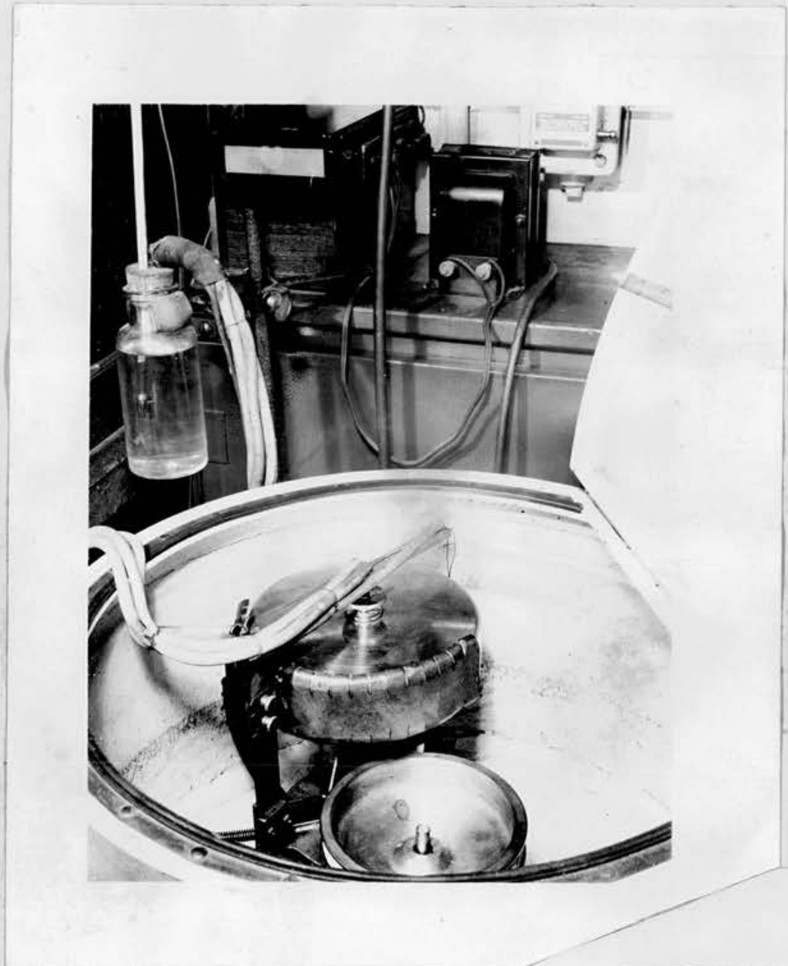
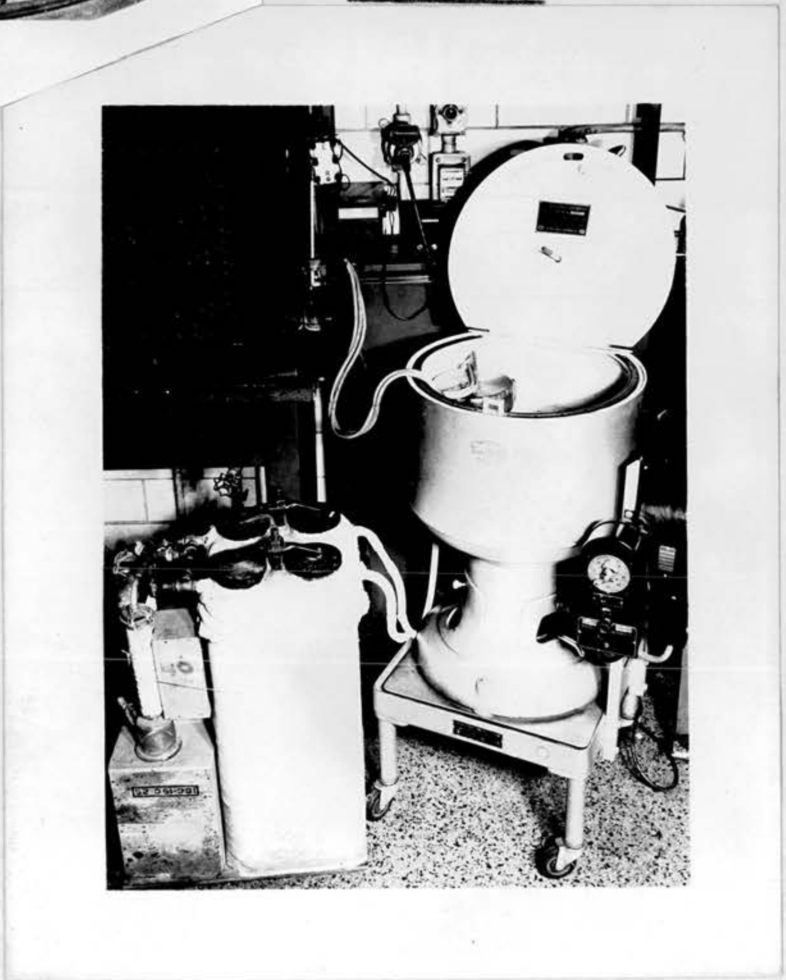


Figure XVII

Figure XVIII



Technique of Operation of Centrifuge

Tubes, head, centrifuge and dispersion to be analysed are allowed to stand in close proximity until all have attained the prevailing room temperature. Six tubes are then filled to the brim with the dispersion and capped so as to exclude all air. They are placed in the rubber cushions and balanced in pairs on a scale sensitive to 0.01 gm. Small differences in the weights of the tubes themselves, and of the cushions, enable this to be done without difficulty.

The tubes are placed in the holes in the head, the members of each balanced pair being placed opposite each other. The head is assembled and the thermocouples placed in position with the central thermocouple connected. The drying towers are filled with fresh desiccants and the cooling towers with solid CO_2 broken into small lumps. At this stage the galvanometer is in balance and the temperature at the reference junction is recorded by the thermometer.

The centrifuge is started, and accelerated as rapidly as possible to the desired speed. As soon as the galvanometer moves away from the centre, air is turned on through the cooler and adjusted to keep the galvanometer in balance. This can be done with ease and precision. The temperature at either of the thermocouples may be checked by throwing the knife switch. The speed is checked on the central motor shaft by the tachometer attached to the centrifuge.

When the centrifuge has run the required time it is shut off and decelerated by the brake as rapidly as possible, the cold air blast being reduced as the speed decreases so as to keep the temperature constant.

The head is dismounted and the tubes removed, being handled with care so as not to disturb their contents. The rubber cushions and caps are removed and the tubes placed on an eye-level platform in front of an illuminated ground glass screen. In this way it is possible to see clearly the boundary between the sedimented and unsedimented material. The unsedimented portion is removed by withdrawing it carefully with a small, specially constructed pipette having an inverted tip, as shown in Figure XIX.

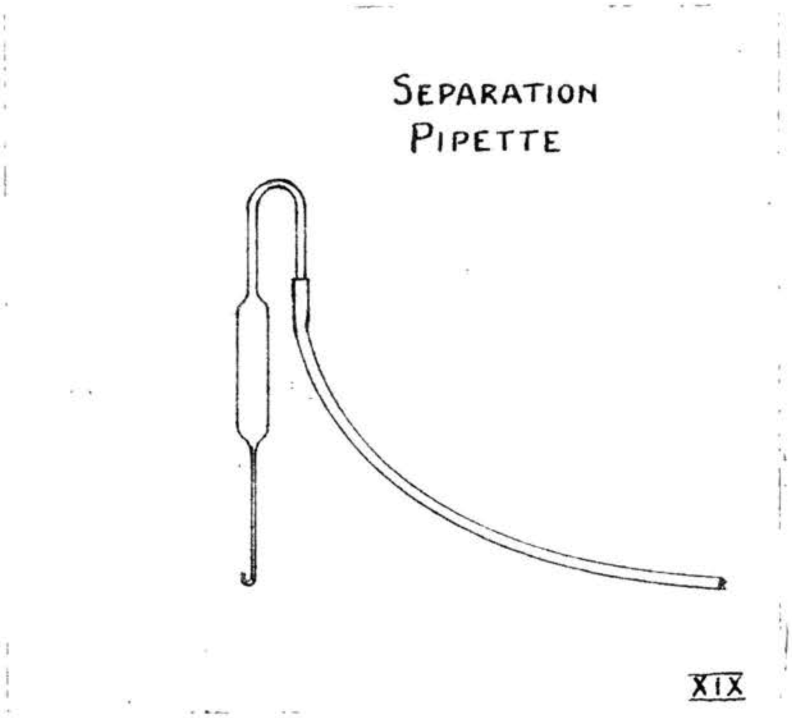


Figure XIX

The unsedimented fraction is analysed for polymer by drying to constant weight at 100°C.

Any desired number of runs may be made on one material, increasing the length of time for each fraction. If it is desired to remove only a relatively coarse fraction, and the time calculated to throw this down fall below approximately fifteen minutes, the speed of the head is reduced, and the time increased. This is done because, in order to minimize starting and stopping errors, fifteen minutes is about the shortest practical running time for the centrifuge.

c. Theory of Sedimentation[42]

If, in a polydisperse system of spherical particles in a liquid where:

(1) the particles are uniformly distributed when settling begins,

(2) the concentration is lower than that at which interference between the particles occurs during settling,

it is postulated that any particle of a given diameter has a characteristic constant rate of fall through the liquid at a definite temperature, then

$$S = s' + t\frac{dS}{dt} \qquad (5)$$

where S is the total weight of sediment deposited in time t.

This equation (5) postulates that the sediment S separated from a polydisperse system in time t is composed of two parts, the portion s' comprising particles of such diameter as settle the full length of the liquid column h in time t or less, and the portion $t\frac{dS}{dt}$ consisting of particles smaller than this but which settled to the bottom in time t because they fell through a distance less than h; i.e. they started from points below the surface of the liquid.

Odén[43] has shown how the relative amounts of these fractions present at any time may be computed from a sedimentation curve by drawing tangents to the curve at times corresponding to the settling times, through the full height h, of particles of various sizes. These times are determined by applying the proper values for the measurable physical properties to Stokes' equation as given below.

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[42] A most excellent and complete discussion of determination of particle size distributions by sedimentation methods, published after much of this work was completed, is given in a paper on this subject by S. W. Martin in "Symposium on New Methods for Particle Size Determination in the Subsieve Range," American Society for Testing Materials, March 4, 1941. This paper, which is notable for the clarity and logic of its presentation, should be studied by anyone interested in this field of research. In this discussion, I have borrowed freely from Dr. Martin's terminology, and acknowledge gratefully the assistance derived from this paper in setting forth the basic ideas involved.

[43] S. Odén in "Colloid Chemistry," Jerome Alexander
Vol. 1, p. 861. Chemical Catalog Company - New York, 1926.

Figure XX shows a typical sedimentation curve, and indicates its use in obtaining the values of s' and $t\frac{dS}{dt}$ in equation (5) above.

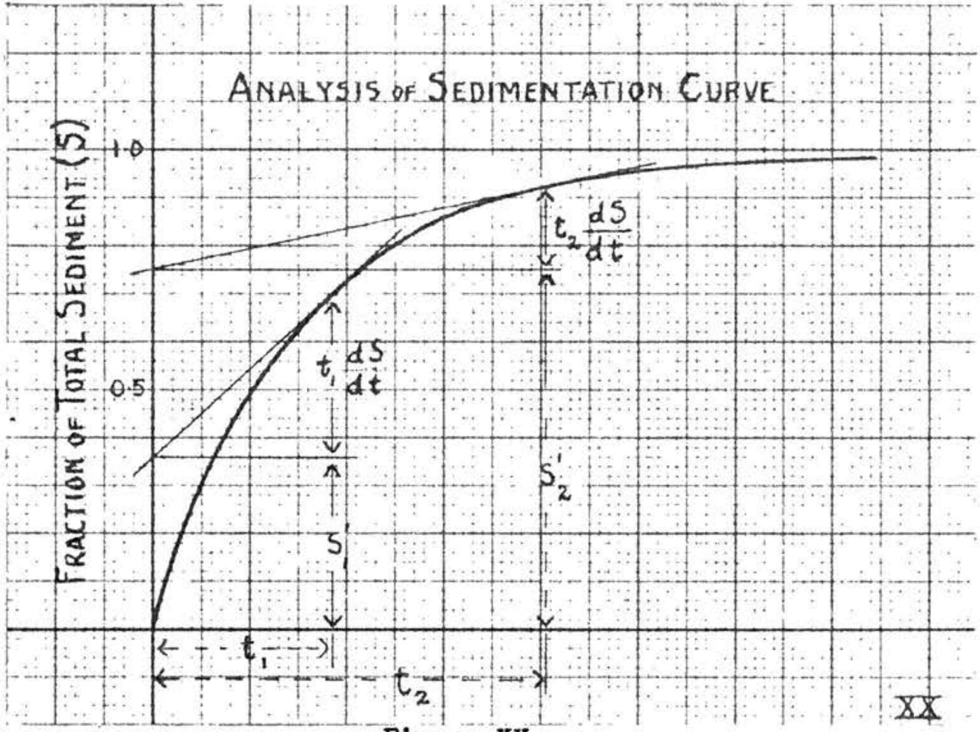

Figure XX

In Figure XX intercept s'_1 represents the weight fraction of the total sedimentable material which consists of particles equal to or greater in diameter than those which would fall through a liquid column of height h in time t_1; s'_2 the fraction equal to or greater in diameter than those falling through height h in time t_2.

To calculate the diameters of the particles falling the full length of column h in times t_1, t_2, t_3, .. etc. we require a functional relationship between particle diameter, D, and time, t. For gravitational sedimentation this is provided by Stokes' well known equation for the terminal velocity of a particle falling through a liquid medium.

$$V = \frac{2\,r^2\,\Delta p\,g}{9\eta}$$

from which we derive that the diameter D of a spherical particle falling through height h in time t is

$$D = \sqrt{\frac{18\eta\,h}{\Delta p\,g\,t}} \qquad (6)$$

where η = the viscosity in poises of the suspension medium

Δp = the difference in density between the particle and the suspension medium

g = the acceleration due to gravity.

When centrifugal sedimentation is considered, the gravitational acceleration is replaced by the centrifugal acceleration, which is equal to

$$\omega^2 X$$

where ω is the angular velocity of rotation, in radians per second, and X is the distance of the particle from the axis of rotation of the centrifuge. From this it is seen that the sedimenting force increases as the particle passes down the tube, being proportional to the distance from the axis of rotation.

It has been shown[44] that the velocity component of a sedimenting particle, perpendicular to the axis of rotation is

$$\frac{dX}{dt} = \frac{D^2 \omega^2 X \Delta p}{18 \eta}$$

where the symbols have the definitions given above.

Now if we consider a particle of diameter D falling by centrifugal sedimentation through a tube containing a liquid column of height h, so placed in the centrifuge head that

X_0 = the distance from the axis of rotation to the top of the tube

X_1 = the distance from the axis of rotation to the bottom of the tube

(thus $X_1 - X_0 = h$)

then

$$\int_{X_0}^{X_1} \frac{dX}{X} = \int_{t_0}^{t} \frac{D^2 \omega^2 \Delta p \, dt}{18 \eta}$$

$$\therefore \log_e \frac{X_1}{X_0} = \frac{D^2 \omega^2 \Delta p (t - t_0)}{18 \eta}$$

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[44] Hauser and Lynn. J.I.E. Chem. 32 (659) 1940.

Now if $t_0 = 0$ which is approximately the case when the centrifuge is accelerated rapidly from rest to the desired speed

$$t = \frac{18\eta}{\Delta p \, D^2 \omega^2} \log_e \frac{X_1}{X_0} \qquad (7)$$

or

$$D = \frac{6}{\omega} \sqrt{\frac{\eta \log_e \frac{X_1}{X_0}}{2 \, \Delta p \, t}} \qquad (8)$$

which is the "centrifugal analogue" of the equation (6) given above for gravitational sedimentation[45].

d. Determination of Particle Sizes and Particle Size Distributions from Centrifugal Sedimentation Data

It has been shown by Romwalter and Vendl[46] that Oden's tangential intercept method of evaluating particle sizes from a sedimentation curve is valid when applied to the curve obtained when polydisperse material is sedimented in a centrifuge of the type here described.

According to Romwalter and Vendl

$$S = s' + \frac{X_1^2 - X_0^2}{4.60 \, X_0^2 \log \frac{X_1}{X_0}} \cdot t \, \frac{dS}{dt}$$

where the symbols have the same meanings as in the preceding section.

Since in any one centrifuge, X_0 and X_1 are constant, this equation reduces to

$$S = s' + K t \frac{dS}{dt} \qquad (9)$$

which is the same as equation (5), above, with the addition of the constant K.

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[45] See also: T. Svedberg "Colloid Chemistry" pp. 179 - Chemical Catalog Company, New York, 1928.

[46] Romwalter, A and Vendl, M. "Die Ermitlung die Kornungskurve und Schleuderversuchen" Kolloid - Zeitschrift, 72, 1. (1935)

As $X_1 - X_0 = h$ (the height of the sedimenting column) the factor K approaches unity as h becomes small. Thus in any short sedimenting tube, Oden's tangential intercept method may be applied to analysis of the data obtained from a sediment v. time curve obtained under any prescribed set of conditions.

Romwalter and Vendl, in their derivation of this relationship postulated a centrifuge free from vibration and particle sizes such that interference due to diffusion could be neglected. von Buzágh[47] indicates that this is significant only with particles below about 1 mμ in diameter. As the centrifuge used here is free from vibration, and the particles exceed by at least thirtyfold the limiting diameter, Romwalter's and Vendl's relationships are applicable to the experimental data.

In analysing a dispersion by this method, the procedure is simply to determine a centrifugal sedimentation curve by the method described above under "Technique of Operation of Centrifuge." On the basis of experience a selection is made of the most suitable operating speed, and a number of runs are made for different lengths of time. The amount of material sedimented at each time interval is determined by analysis of the supernatant liquid and all time intervals are corrected to a common temperature by applying the correction indicated by the change in viscosity with temperature.

From equation (7) above, it is seen that the time of fall of a particle is directly proportional to the viscosity of the suspension medium. In the cases here considered the suspension medium is a dilute solution of sulphated castor oil in water. Determinations have shown that the measurable difference in viscosity between water and these solutions is of a magnitude much below the order of precision of the other measurements involved, so that all calculations,

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[47] A. von Buzágh "Colloid Systems" p. 35
Technical Press, London (1937).

and temperature corrections have been based on the viscosity of water. The viscosity of water at different temperatures is shown in Table 7, from Bingham and Jackson's determinations[48].

Table 7

Temp. °C.	Viscosity centipoises	Temp. °C.	Viscosity centipoises	Temp. °C.	Viscosity centipoises
10	1.3077	20	1.0050	30	.8007
11	1.2713	21	.9810	31	.7840
12	1.2363	22	.9579	32	.7679
13	1.2028	23	.9358	33	.7523
14	1.1709	24	.9142	34	.7371
15	1.1404	25	.8937	35	.7225
16	1.1111	26	.8737	36	.7085
17	1.0828	27	.8545	37	.6947
18	1.0559	28	.8360	38	.6814
19	1.0299	29	.8180	39	.6685

Thus, for example, if all values were being corrected to a temperature of 28°C., a run of 40 minutes at 26°C. would be equivalent to a run under the same conditions of

$$40 \times \frac{\text{Viscosity of water at } 28^\circ\text{C.}}{\text{Viscosity of water at } 26^\circ\text{C.}}$$

$$\text{or} \quad \frac{40 \times .8360}{.8737} = \underline{38.3} \text{ minutes}$$

When all the running times have been calculated to a common temperature basis, a sedimentation curve using these corrected times as abscissae and the amounts sedimented as ordinates, is plotted on a large scale. From equation (7) above, the times corresponding to any selected particle diameters (or volumes)

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[48] Bull. Bur. Stds. (now Bur. Stds. J. Res.) 14, 75 (1918).

are calculated, and tangents to the curve are drawn at the points represented by these times. The intercepts made by these tangents on the vertical axis through the origin of the curve represent the fraction of the total weight lying between the limits selected.

From these intercepts a particle size distribution curve of the dispersion may be obtained. The weight average particle size may then be obtained for comparison with the value determined by the light-scattering method.

V COMPARISON OF LIGHT SCATTERING AND CENTRIFUGAL SEDIMENTATION METHODS OF DETERMINING PARTICLE SIZE

It has been shown above that the light scattering method yields relationships between concentration and wavelength which are in accord with theory (Section IV, 1, c); that it is possible, with the systems here considered, to calculate weight average particle sizes directly from the light scattering data (Section III, 5, b) and that weight average particle sizes may also be obtained from analysis of centrifugal sedimentation data (Section IV, 2, d).

Thus it becomes possible to check the validity of the light scattering method by making determinations of the weight average particle size on the same material by both methods. This was done. The procedure and results are discussed below.

1. Selection of Material

The dispersion used for this part of the work was selected at random from a number of experimental preparations made during the study of the rate of growth of particle size during polymerization.

It was prepared by polymerization at a temperature of 90°C. of a 2% solution of very pure (99.5%) methyl acrylate in water using as dispersing agent 2% highly sulphated castor oil and as catalyst 0.3% hydrogen peroxide. The amount of dispersing agent and catalyst are based on the weight of monomeric methyl acrylate. The time of polymerization was 28.5 hours. The details of the technique used in making these polymerizations is given below in the section in which these studies are described and discussed (Section VIII).

The dispersion showed a fine particle size (although not extremely fine) and great stability. When used for the first series of these determinations, it had been stored on the laboratory shelf for a period of ten months, and showed a very slight amount of sedimentation. It was used again for a complete recheck six months later, and showed again a trace of sedimentation.

It is identified by the number 5221-D1.

2. Determination of Average Particle Size by Light Scattering

a. Experimental

The light scattering apparatus was set up and determinations were made in accordance with the procedure given in Section IV, 1, b, above. The apparatus arrangement was:

Filters:	Wratten #62 plus Jena BG 18
Effective Mean) Wavelength)	533.6 m (Section IV, 1, c, above)
Grid resistor:	60 megohms
Lamp Filament Voltage:	5.6 volts

The "water phase" used in the preparation of the emulsion, i.e., the water plus dispersing agent, plus catalyst, was prepared and used as the standard of comparison in determining the amount of light scattering given by the dispersion. It was also analysed for solids by the same procedure as used for determination of polymer, and the amount of dispersing agent was subtracted from the total solids to give the amount of actual polymer present.

These corrections are of minor consequence when measurements are being made on original or diluted dispersions, but become significant when working with fractions from which most of the polymer has been removed by centrifuging.

The following readings of the microammeter were obtained:

Without absorption cell (Standard)		600 μ amps.
With absorption cell filled with distilled water		543 "
With cell filled with "water phase" of dispersion		536 "
With cell filled with dispersion 5221-D1		31 "
Solids concentration of dispersion gms./gm.	.01922	
" " " water phase "	.00037	
∴ Concentration of polymer "	.01885	

b. Calculation

From this data the following calculations were made.

The Rayleigh-Gans equation (eqn. (1), p. 19) is

$$I = I_0 e^{-\left[\frac{8\pi^3}{3}\left(\frac{n^2 - n_0^2}{n_0^2}\right)^2\left(\frac{3\,n_0^2}{n^2 + 2\,n_0^2}\right)^2\frac{NV^2\Delta x}{\lambda^4}\right]}$$

where N = number of particles per cubic centimetre of dispersion

V = average particle volume, in c.c.

λ = wavelength of radiation in cm.

n = refractive index of particle

n_0 = refractive index of dispersion medium

I_0 = intensity of incident radiation per unit area

I = intensity of transmitted radiation per unit area

Δx = thickness of layer of scattering medium in cm.

whence $\log_{10}\frac{I_o}{I} = \frac{K'\ cV\ \Delta x\ (10^7)}{(2.303)\ \lambda^4\rho}$ (Compare Equation (4) p. 20)

where ρ = density of particles in gms. per c.c.

c = concentration of dispersion in gms. per c.c.

and V is expressed in cubic millimicrons ($m\mu^3$)

λ is " " millimicrons ($m\mu$)

$$\text{let } K = \frac{K'\,(\Delta x)(10^7)}{(2.303)\,\lambda^4 \rho}$$

$$\text{then } K = \frac{8\pi^3}{3}\left(\frac{n^2 - n_0^2}{n_0^2}\right)^2 \left(\frac{3\,n_0^2}{n^2 + 2\,n_0^2}\right)^2 \frac{\Delta x\,(10^7)}{(2.303)\,\lambda^4 \rho}$$

for polymethyl acrylate

ρ = 1.21 at 30°C. (See Appendix "A")

$n = 1.472$ $n^2 = 2.167$

for "water phase"

$n_0 = 1.333$ (See Appendix "B") $n_0^2 = 1.776$

$$K = \frac{8\ (3.14)^3}{3 \times 1.21} \cdot \left(\frac{0.392}{1.776}\right)^2 \left(\frac{5.322}{5.715}\right)^2 \frac{\Delta x\ (10^7)}{(2.303)\,\lambda^4}$$

$$= 1.260 \times 10^7 \times \frac{\Delta x}{\lambda^4}$$

For the apparatus, as used in this experiment

Δx = 1 cm.

λ = 533.6 mμ

$\lambda^4 = 8.107 \times 10^{10}$ mμ^4

$\therefore K = 1.555 \times 10^{-4}$

$$\therefore \log_{10} \frac{I_0}{I} = 1.555 \times 10^{-4}\ cV$$

where c is in gm./ml., V in mμ^3

With the dilute solutions here used the density of the solution is 1.00, so that c is also in gms./gm.

$$V = \frac{1}{1.555 \times 10^{-4}\ c} \cdot \log_{10} \frac{I_0}{I}\ \text{m}\mu^3$$

$$= \frac{6.43 \times 10^3}{c} \log_{10} \frac{I_0}{I}\ \text{m}\mu^3 \qquad (10)$$

In this experiment

$\frac{I_0}{I} = \frac{536}{31} = 17.29$ $\log_{10} \frac{I_0}{I} = 1.238$

c = 0.01885

$$V = \frac{6.43 \times 10^3}{0.01885} \times 1.238$$

$$= \underline{\underline{42.3 \times 10^4}}\ m\mu^3$$

3. Determination of Average Particle Size by Centrifugal Sedimentation

a. Experimental

The centrifuge was set up and run according to the procedure given in Section IV, 2, b, above.

Using dispersion 5221-D1, six runs were made, as follows, at 16,100 r.p.m.

Table 8 (Experiment 3112)

Fraction	Time at 16,100 r.p.m.	Temp. °C.	Visc. water phase at ind. temp. (poises)	Volume of largest particle left in suspension
1	18 mins.	28.5	.00827	$108 \times 10^4\ m\mu^3$
2	22 "	27.0	.00854	83×10^4 "
3	26 "	27.0	.00854	65×10^4 "
4	34 "	27.5	.00845	43×10^4 "
5	54 "	27.5	.00845	22×10^4 "
6	90 "	27.0	.00854	10×10^4 "

The values in the last column of Table 8 were obtained by calculating, from Equation (8) above, the size of particle which would just fall the full length of the tube on centrifuging for the prescribed time under the indicated conditions.

This equation is:

$$D = \frac{6}{\omega} \sqrt{\frac{\eta \log_e \frac{X_1}{X_0}}{2 \Delta p\ t}}$$

for this centrifuge

$$X_1 = 7.075 \text{ cm.}$$

$$X_0 = 3.525 \text{ cm.}$$

$$\omega = \frac{\text{r.p.m.} \times 2\pi}{60} = \frac{16,100 \times 6.283}{60} = 1685 \text{ radians/sec.}$$

and, for polymethyl acrylate dispersion at 30°C.

$\Delta p = 0.21$ (See Appendix "A")

The particle diameters obtained as values of D are calculated to particle volumes in cubic millimicrons.

The fractions obtained from the centrifuge runs were analysed for polymer, and examined in the light scattering apparatus, with the results shown in Table 9.

"Fraction 0" in this table represents the original material before centrifuging.

Table 9

Mean Effective Wavelength 533.6 mμ
Full Beam reading 600 microamps
Water Phase reading 536 microamps

Fraction	Reading in micro-amps	Optical density (reference water phase)	Concn. polymer	Average particle volume (mμ³)
0	31	1.238	.01885	42.3×10^4
1	84	.806	.01263	41.1×10^4
2	103	.717	.01134	40.7×10^4
3	133	.605	.00961	40.5×10^4
4	206	.416	.00690	38.8×10^4
5	407	.120	.00301	25.6×10^4
6	504	.0273	.00150	11.7×10^4

The values for the average particle volumes, as would be expected, show little change until we reach centrifuging conditions which will throw down, completely, particles approximating the average size present in the original material. This begins to show in fraction No. 4. From that point on, a fair correspondence is shown between the average particle volumes determined by light scattering, and the maximum particle volumes calculated from centrifuge data. (Compare last column of Table 9 with last column of Table 8.)

b. Analysis of Data

A centrifugal sedimentation curve was plotted from the data in Tables 8 and 9, as shown in Table 10.

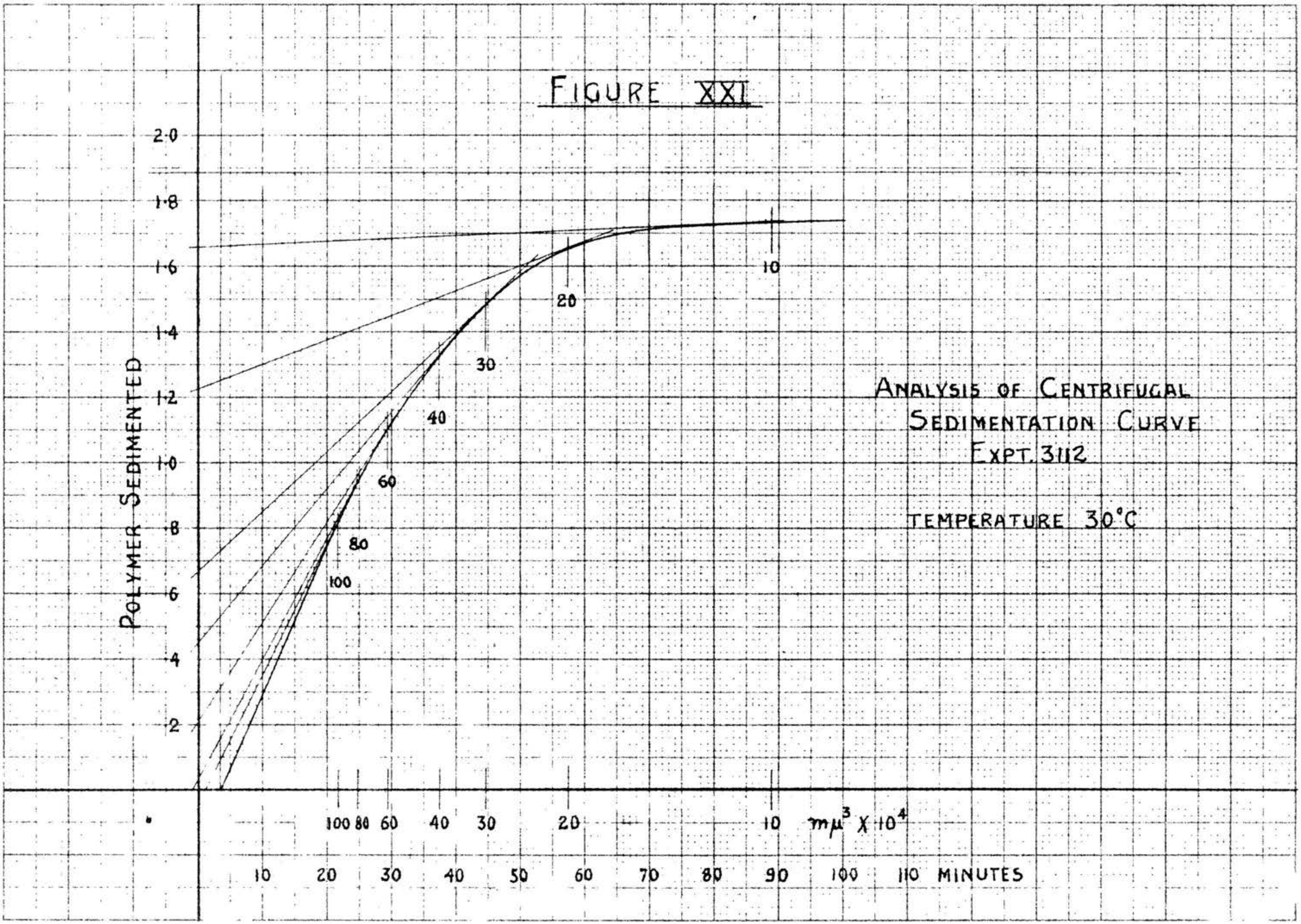
Table 10

1 Fraction	2 Time (mins.)	3 Temp. (°C.)	4 Equiv. time at 30°C. (mins.)	5 Concn. polymer (%)	6 Amount sedimented (%)
0	-	-	-	1.885	-
1	18	28.5	17.3	1.263	0.622
2	22	27.0	20.0	1.134	0.751
3	26	27.0	24.25	0.961	0.924
4	34	27.5	32.25	0.690	1.195
5	54	27.5	51.0	0.301	1.584
6	90	27.0	85.0	0.150	1.735

The sedimentation curve of Figure XXI is obtained by plotting column 4 of Table 10 against column 6. Figure XXI is a half-scale reproduction of the actual sedimentation curve used to obtain the data which follow.

It will be noted that the sedimentation curve crosses the time axis at a low positive value, in this case, + 3.5 minutes, instead of at zero minutes, as would be expected. This was found in the case of all sedimentation curves run

FIGURE XXI



ANALYSIS OF CENTRIFUGAL
SEDIMENTATION CURVE
EXPT. 3112

TEMPERATURE 30°C

with the centrifuge operating at maximum speed, and varied in value from +3 to +5 minutes. The centrifuge head is belt driven, and tachometer measurements to determine speed are made on the driving, not the driven, pulley. Belt slippage occurs, particularly near the upper speed limit, for an attempt is always made to accelerate the head as rapidly as possible. Thus, although the tachometer may read the desired speed, the time at which the head actually attains this speed lags to about the degree here indicated.

The particle size distribution obtained graphically from these curves has in each case been determined by moving the vertical axis to coincide with this point. It will be seen from inspection of Figure XXI that the effect of this on the actual distribution is small, except in the case of the largest fraction, which is, in turn, small in amount. Making this correction for the belt slippage gives an intelligible physical meaning to the value of the intercept for the largest fraction.

Times of centrifuging corresponding to different particle volumes were calculated from Equation 8, as shown in Table 11.

Table 11

Temp. 30°C. Viscosity of water phase, .00800 poises

1 Particle volume ($m\mu^3$)	2 Corresponding diameter ($m\mu$)	3 Time of fall t (mins.)	4 Corrected time (t plus 3.5 mins.)
120×10^4	131.2	16.28	19.78
100×10^4	123.4	18.41	21.91
80×10^4	114.6	21.33	24.83
70×10^4	109.5	23.36	26.86
60×10^4	104.1	25.86	29.36
50×10^4	97.9	29.22	32.72
40×10^4	90.9	33.90	37.40
30×10^4	82.6	41.08	44.58
20×10^4	72.1	53.84	57.34
10×10^4	57.3	85.45	88.95

Tangents were drawn to the sedimentation curve of Figure XXI at the times shown in column 4 of Table 11. From the intercepts of these tangents on the vertical through the origin of the curve, the data shown in Table 12 were obtained.

Table 12

1 Particle Volume cubic mμ x 10^4	2 Point of intersection of upper limit	3 Intercept	4 Percent of total
0	1.885	-	
0-10	1.660	.225	11.9
10-20	1.255	.405	21.5
20-30	0.730	.525	27.8
30-40	0.530	.200	10.6
40-50	0.400	.130	6.9
50-60	0.315	.085	4.5
60-70	0.225	.090	4.8
70-80	0.160	.065	3.5
80-100	0.100	.060	3.2
100-120	0.000	.100	5.3

From Table 12, the particle volume distribution curve was plotted. Figure XXII is a half scale replica of the actual curve used. The ordinates of the last two fractions, where the spread is 20 x 10^4 cubic millimicrons, are plotted as one half the values shown in column 4 of the table.

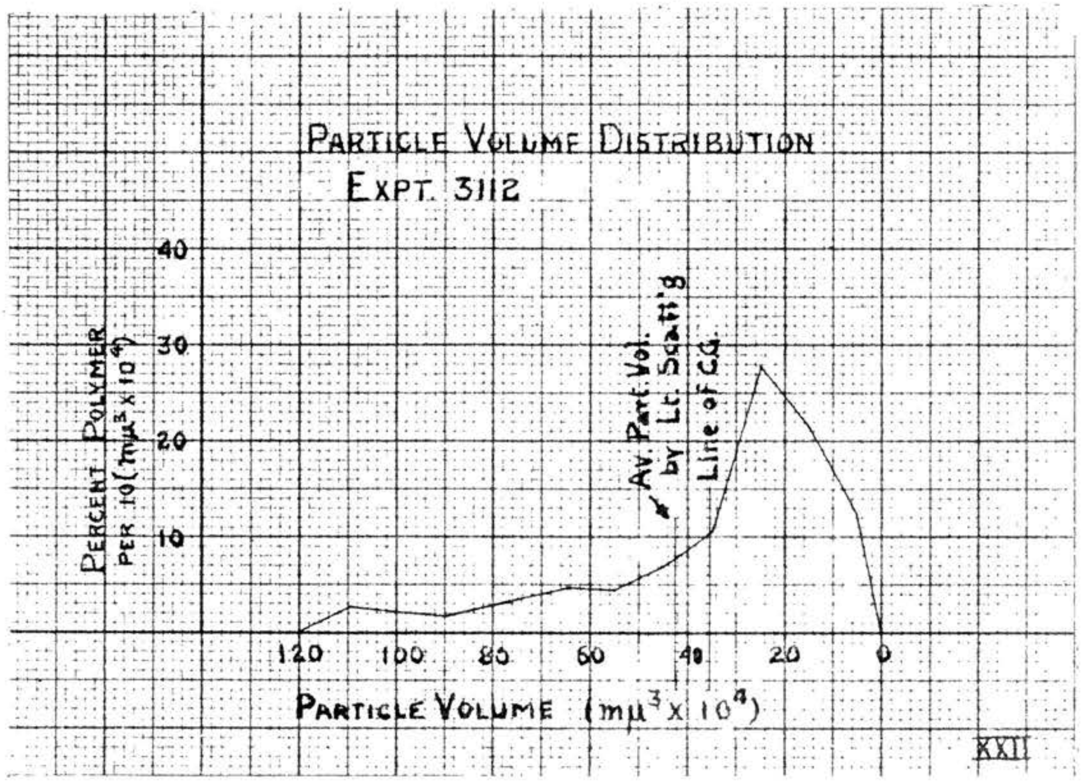


Figure XXII

The centre of gravity of the distribution curve was determined by the same method as used for determining the centres of gravity of the energy distribution curves (Section IV, 1, c, above). The centre of gravity projected on the particle volume axis gives the average particle volume as

$\underline{35.6 \times 10^4}$ $m\mu^3$

as compared to

$\underline{42.3 \times 10^4}$ $m\mu^3$

obtained from light scattering data.

4. Repeat Determination

This entire determination was repeated six months later, using the same material, 5221-D1. By that time the technique of determining particle size distribution had been more nearly perfected, and the data obtained are regarded as being more precise.

This second determination yielded the following data.

Table 13 (Experiment 9302)

Fraction	Time at 16,100 r.p.m. (minutes)	Temp. °C.	Visc. water phase at ind. temp. (poises)	Volume of largest particle left in suspension
1	16	28.0	.00836	140 x 10^4 $m\mu^3$
2	20	29.5	.00810	89 x 10^4 "
3	30	26.5	.00863	53 x 10^4 "
4	45	27.0	.00854	29 x 10^4 "
5	60	28.0	.00836	18 x 10^4 "
6	90	26.0	.00874	11 x 10^4 "

The fractions from these runs in the centrifuge were analysed for polymer, and their average particle volumes determined from the light scattering data, as shown in Table 14.

Table 14

Mean Effective Wavelength	533.6 $m\mu$
Full Beam Reading	750 microamps
Water Phase Reading (except fraction 6)	679 microamps
Water Phase Reading, Fraction 6.	669 microamps

Fraction	Reading in micro-amps	Optical density (reference water phase)	Concn. polymer	Average particle volume ($m\mu^3$)
0	38	1.252	.01873	43.1 x 10^4
1	99	.836	.01310	41.1 x 10^4
2	160	.627	.00995	40.5 x 10^4
3	251	.432	.00683	40.7 x 10^4
4	428	.200	.00347	37.0 x 10^4
5	581	.0671	.00145	29.8 x 10^4
6	643	.0169	.00088	12.4 x 10^4

If the value for the average particle volume of "fraction 0," the uncentrifuged material, is compared with that for the same "fraction" in Table 9, above, it will be noted that in the six months which elapsed between the two experiments, the average particle size, as determined by light scattering, showed a slight increase.

A centrifugal sedimentation curve was plotted, using the data from columns 4 and 6 of Table 15.

Table 15

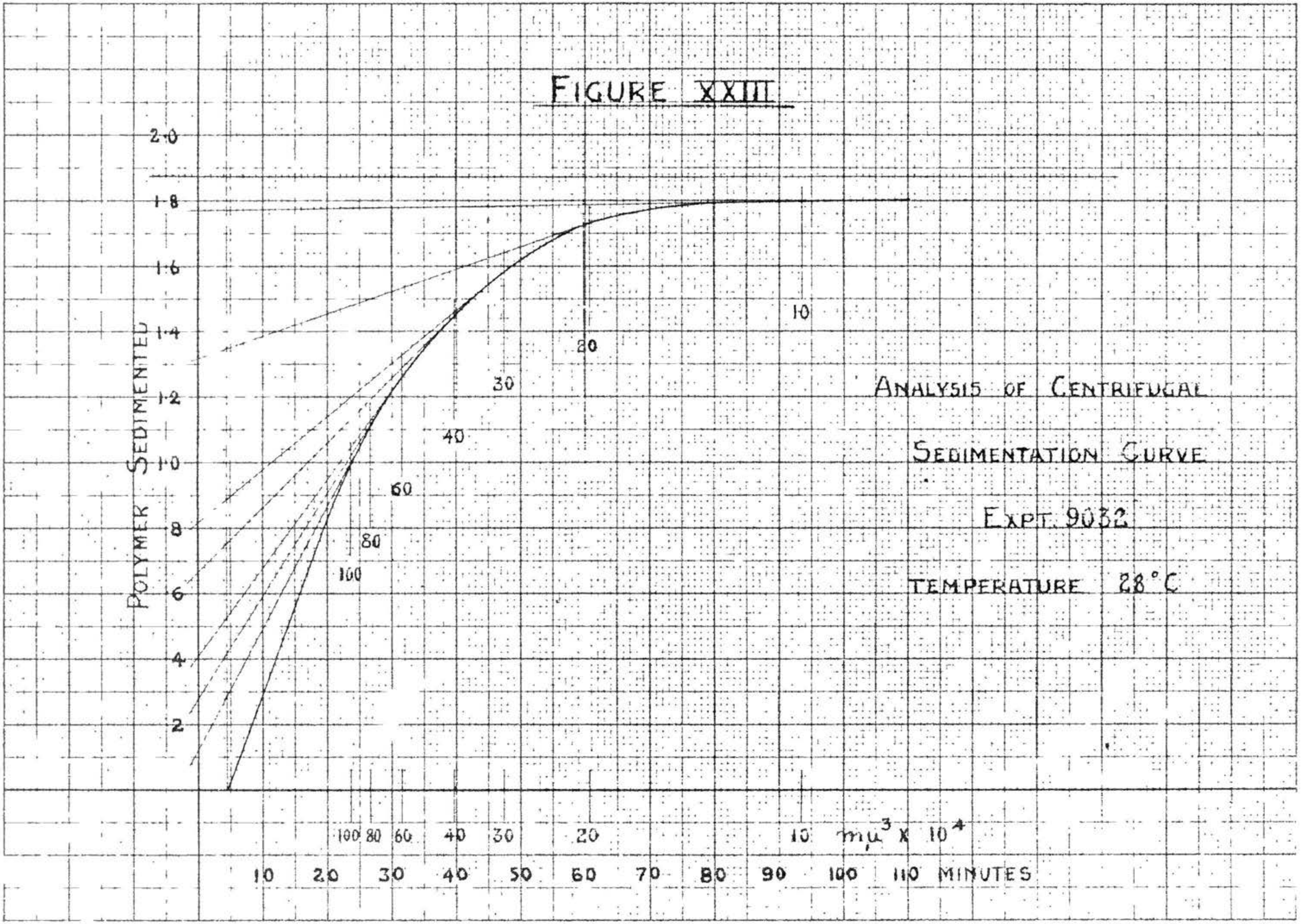
1 Fraction	2 Time (mins.)	3 Temp. (°C.)	4 Equiv. time at 28°C. (mins.)	5 Concn. polymer (%)	6 Amount sedimented (%)
0	-	-	-	1.873	-
1	16	28.0	15.0	1.310	0.563
2	20	29.5	20.6	0.995	0.878
3	30	26.5	29.0	0.683	1.190
4	45	27.0	44.0	0.347	1.526
5	60	28.0	60.0	0.145	1.728
6	90	26.0	86.1	0.088	1.785

A half scale replica of the curve obtained is shown in Figure XXIII.

A comparison of the curves of Figures XXI and XXIII shows that they correspond closely in general form, but it is evident that an increase in particle size has occurred between the two determinations.

In this case, the point of intersection of the sedimentation curve with the time axis occurs at a value of + 4.5 minutes. This is attributed to belt slippage during acceleration of the centrifuge head (see discussion under Experiment 3112, above) and correction has been made for it in the data which follow.

FIGURE XXIII



ANALYSIS OF CENTRIFUGAL SEDIMENTATION CURVE

EXPT. 9032

TEMPERATURE 28°C

Tangents were drawn to the curve at points corresponding to the times of fall of different sized particles, as shown in Table 16.

Table 16

Temperature 28°C. Viscosity of water phase .00836 poises

1	2	3	4
Particle volume $(m\mu^3)$	Corresponding diameter $(m\mu)$	Time of fall t (mins.)	Corrected time (t plus 4.5 mins.)
130 x 10^4	134.7	16.17	20.67
120 x 10^4	131.2	17.01	21.51
100 x 10^4	123.4	19.25	23.75
80 x 10^4	114.6	22.29	26.79
70 x 10^4	109.5	24.39	28.89
60 x 10^4	104.1	27.06	31.56
50 x 10^4	97.9	30.58	35.08
40 x 10^4	90.9	35.41	39.91
30 x 10^4	82.6	42.94	47.44
20 x 10^4	72.1	56.30	60.75
10 x 10^4	57.3	88.90	93.40

From the intercepts of the tangents, drawn to the curve at these points, with the ordinate passing through the origin of the curve a particle volume distribution curve was plotted. The data are given in Table 17 and the curve in Figure XXIV. The actual curve used for centre-of-gravity determination was drawn on a scale twice as large as that of Figure XXIV.

Table 17

Particle volume cubic mμ x 10^4	Point of intersection of upper limit	Intercept	Percent of total
0	1.873	-	-
0-10	1.775	.118	6.3
10-20	1.357	.398	21.3
20-30	0.891	.466	24.9
30-40	0.753	.138	7.4
40-50	0.646	.107	5.7
50-60	0.522	.124	6.6
60-70	0.471	.051	2.7
70-80	0.408	.063	3.4
80-100	0.284	.124	6.6*
100-120	0.060	.224	11.9*
120-130	0.000	.060	3.2

*** The figures marked with an asterisk are plotted in Figure XXIV at one half the values given, since they cover a range of 20 x 10^4 mμ ^{3} instead of 10 x 10^4 mμ ^{3}.**

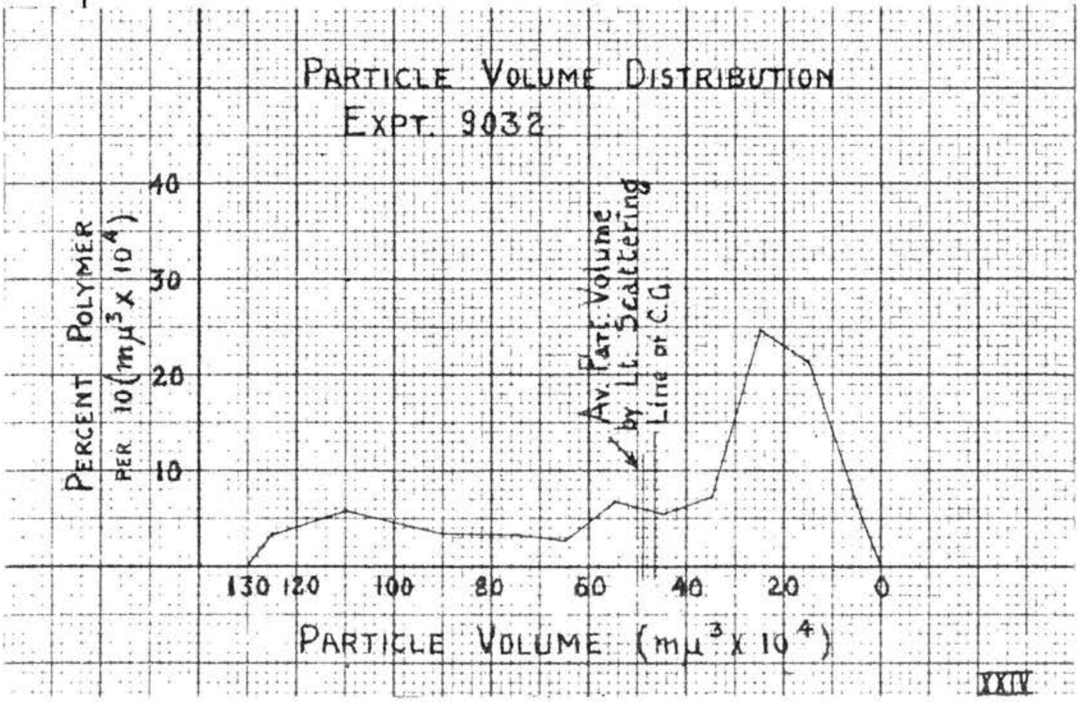


Figure XXIV

The centre of gravity of this distribution curve was found to lie at a point corresponding to:

$$\underline{44.5 \times 10^4\ m\mu^3}$$

which checks very closely with the value of:

$$\underline{43.1 \times 10^4\ m\mu^3}$$

obtained from light scattering data on the same dispersion at the same time.

5. Conclusions

It was considered that these data established the validity of the light scattering method as an absolute basis for determining the weight average particle size of water dispersions of polyacrylic esters.

It was also considered that a direct experimental verification of the Rayleigh-Gans relationship had been obtained.

In the work which is reported in the following parts, the light scattering method is used to determine particle sizes.

VI METHOD OF RECORDING PARTICLE SIZE - DISCUSSION

It has become customary, in dealing with, and discussing, particle sizes and particle size distributions in suspensoids, to refer to them in terms of radii or diameters - most frequently the latter.

It will have been observed that in this discussion, particle sizes have been described and compared always in terms of particle volumes. This has been done by deliberate choice after careful consideration.

It seems probable that the custom of referring to particle sizes in terms of diameters has arisen from the practice of measuring them by sedimentation, or diffusion, which methods depend on the cross-sectional area of the particle, or by microscopic observation, where diameter is measured directly. This may be appropriate in some circumstances, but to refer in other cases to particle sizes in terms of diameters may be misleading, yielding a distorted concept of "size" in the sense in which the term is most appropriate.

In considering dispersoids of the type described and discussed in this thesis, we are concerned mainly with the question of the degree of subdivision of the dispersed phase. This being the case, the most important attribute of the individual particle is the amount of this dispersed phase contained within it. In a comparative way, this is expressed directly by the weight, or volume, of the particle, and not by its diameter.

The optical method of determining particle sizes as here employed yields values expressed directly as particle volumes. The centrifugal method yields values expressed as particle diameters, which have in all cases been converted to particle volumes for comparison with the values obtained from the optical method.

The reason for regarding comparison of particle sizes on the basis of volume as more desirable, may be seen clearly by reference to Figure XXIV-A, in which diameter in millimicrons has been plotted against volume in cubic millimicrons x 10^4. This is simply calculated from the relationship

$$V = \frac{\pi D^3}{6}$$

and has the familiar form of any $y = ax^3$ curve.

Within the range 10 x 10^4 and 100 x 10^4 cubic millimicrons - a tenfold spread in which most of the particles here considered are found - particle diameter increases from 56 mμ to 124, a spread of only a little over twofold. This compression of the scale which results from considering size in terms of diameter leads us to say, for example, that a particle 100 mμ in diameter is twice as large as one 50 mμ in diameter, whereas it actually contains seven times as much dispersed polymer.

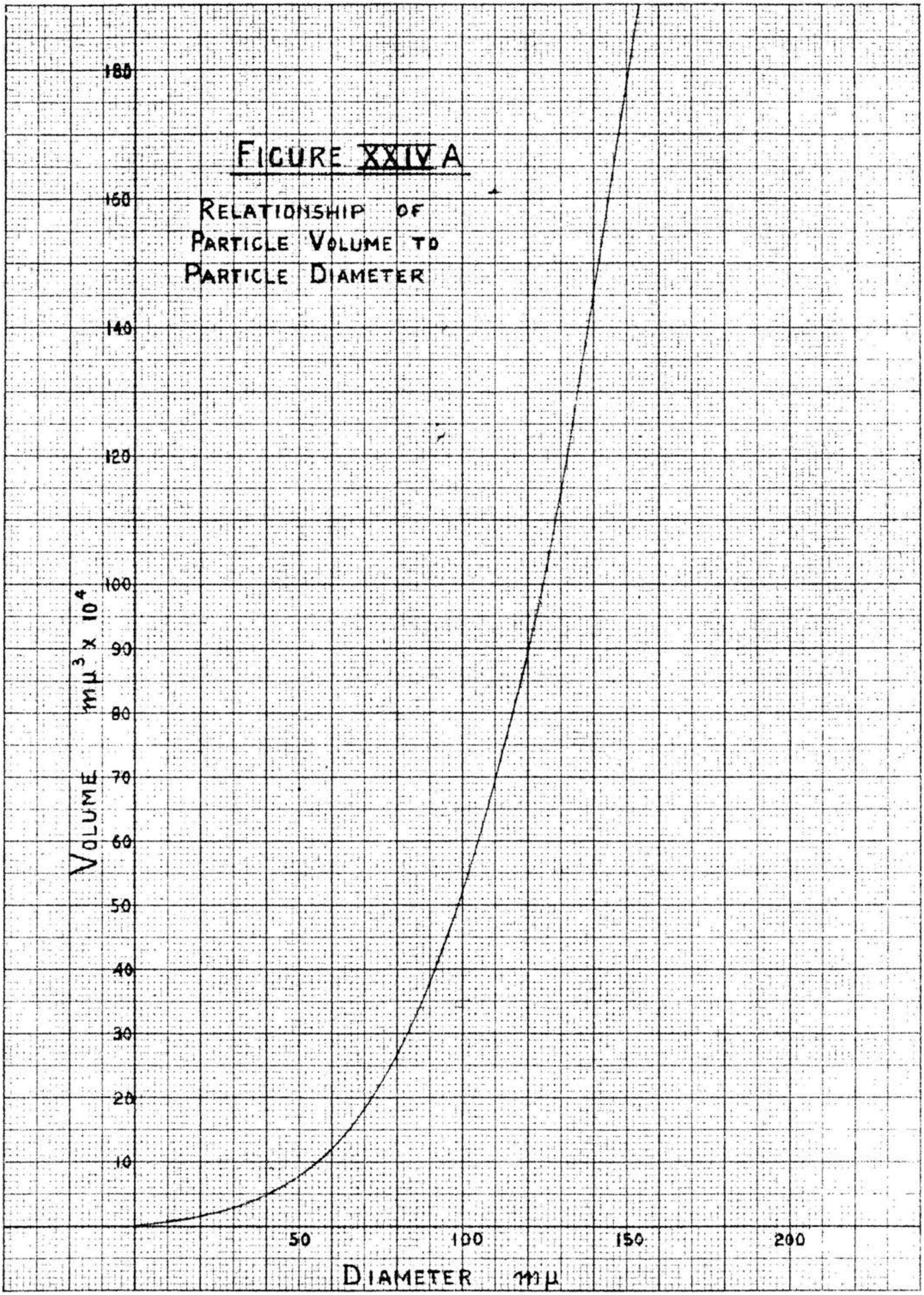


FIGURE XXIV A

RELATIONSHIP OF PARTICLE VOLUME TO PARTICLE DIAMETER

For these reasons, and because the light-scattering method yields particle volumes directly, the system of measuring and comparing particle sizes in terms of volume has been adopted. The curve shown in Figure XXIV-A may be used at any time as a means of converting rapidly from one system of units to the other.

VII EFFECTS OF VARIOUS FACTORS IN POLYMERIZATION ON AVERAGE PARTICLE SIZE (VOLUME)

Since previous work, described in the foregoing parts of this thesis, had provided a rapid and reliable method of measuring average particle volumes in dispersions of aqueous polyacrylic esters, an investigation was made of the effects on particle size of varying one by one the different controllable factors in the polymerization of methyl acrylate.

1. Apparatus and Method

The apparatus used in this part of the work consisted of four 1 litre three-neck round bottom Pyrex flasks mounted in an electrically heated, continuously stirred, thermostatically controlled, oil bath. Each flask was equipped with reflux condenser, stirrer, and calibrated dropping funnel. The four stirrers, carrying pulleys of the same size, were driven by a single electric motor with a variable voltage speed control. A revolutions counter was used to check stirring speed.

Figure XXV is a photograph of the assembled apparatus.

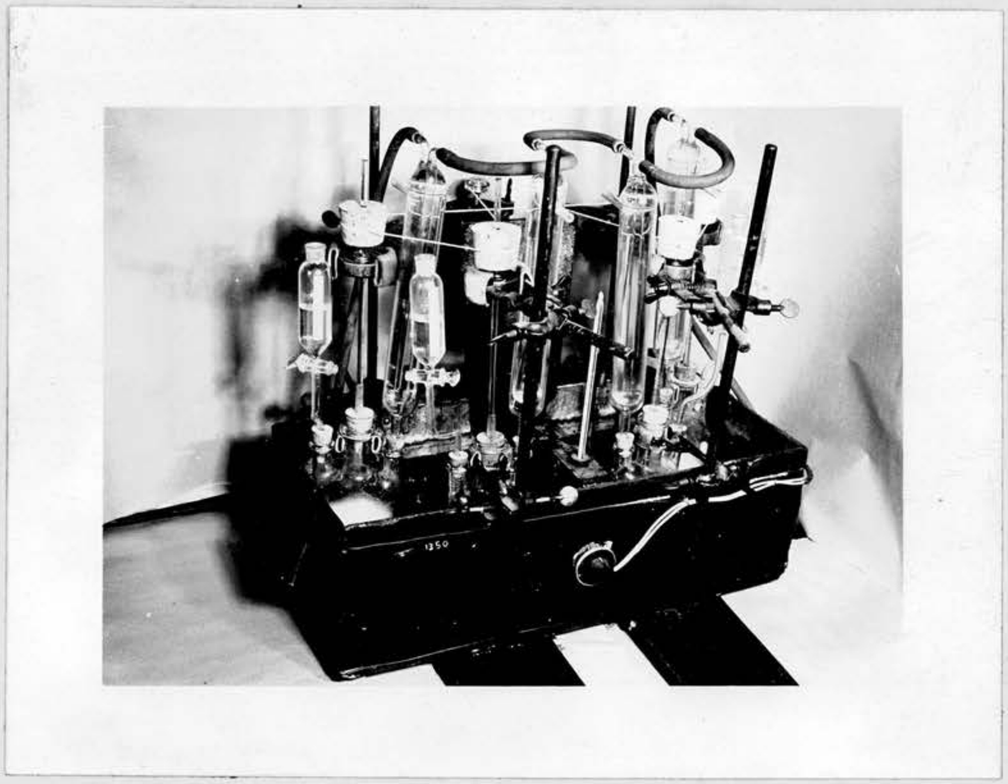


Figure XXV

With this apparatus it is possible to run up to four polymerizations simultaneously under identical conditions. The water phase, with or without part of the monomeric acrylic ester, is placed in the flasks, the oil bath is heated to the desired temperature, and the monomer, or balance of the monomer, is added at any desired rate through the calibrated dropping funnel. Rate of stirring is the same in the four flasks, and, if straight condensers are used, thermometers may be placed in the liquid in the flasks by attaching cords and lowering them through the condensers.

When polymerization is complete, as indicated by cessation of reflux, the flasks are removed and the polymerized dispersions poured into labelled bottles to cool. Polymer analyses are made by determining nonvolatile matter, and transmission measurements are made on the light-scattering apparatus on any convenient dilution. From these data the average particle volume of each preparation is calculated.

2. Reproducibility of Results

The first thing done was to check the reproducibility of the average particle size under an arbitrary set of conditions taken as "standard." These were chosen in accord with earlier experience to represent the conditions most suitable for the polymerization of methyl acrylate.

"Standard" charge in the flasks was:

Water Phase:

Distilled Water	134 gm.
Sulphated Castor Oil (70.5% solids)	0.42 gm.
Hydrogen Peroxide (30%)	0.5 ml.

This was heated to 83-85°C. (by raising oil bath temperature to 90°C.) with stirring at 900 r.p.m., and "Pure" freshly distilled methyl acrylate, (see Appendix "C") 14.9 gm. was added dropwise through the funnel at any desired rate.

The rate of addition of the monomeric acrylate was regulated by timing the fall between calibrations on the funnel. "Standard" rate was that required to maintain a reasonable amount of reflux in the condensers, approximately 1.5 ml. per min.

Reflux was found to subside completely within five minutes of the addition of the last of the monomer, and heating was continued for ten more minutes before stopping the stirrers and removing the polymer dispersion from the flasks.

Eight polymerizations, run on this formula, yielded the following average particle volumes, shown in Table 18.

Table 18

Prepn.	Solids Content %	Rdg. with Water	Rdg. with prepn. (7 in 1000)	Average particle volume
1-A	8.10	543	513	25.5×10^4
2-A	8.40	543	516	22.1×10^4
3-A	8.20	543	513	25.2×10^4
4-A	8.25	543	515	23.3×10^4
1-B	7.60	540	511	26.4×10^4
2-B	7.66	540	513	23.4×10^4
3-B	7.65	540	512	25.2×10^4
4-B	7.40	540	515	23.2×10^4

These preparations showed that a good degree of reproducibility could be maintained among preparations made at the same time under comparable conditions.

3. Influence of Various Factors - Experimental

The influence on particle size was studied for a number of the factors in the preparation. These were:

a. The amount of catalyst.
b. The amount of dispersing agent.
c. The type of dispersing agent.
d. Temperature.
e. Rate of addition of monomer.
f. Amount of monomer added to water phase before polymerization.

The experiments run and the results obtained are given below.

a. Variations in Amount of Catalyst

Water phase:	670 gms.	distilled water
	210 "	Sulphated Castor Oil #565 (70.5% solids)

Placed 134.4 gms. this solution in each flask. Added 14.9 gms. methyl acrylate.

Catalyst: 30% Hydrogen peroxide, amounts as indicated in Table 19.

Table 19

Amount 30% H_2O_2 used (ml.)	% Catal. on monomer	Solids in prepn. (%)	Rdg. with dist. water	Rdg. with prepn. (7 in 1000)	Average particle volume ($m\mu^3$)
1.50	3.0	8.75	543	512	23.9×10^4
1.00	2.0	8.60	543	510	26.8×10^4
0.75	1.5	8.45	543	512	24.7×10^4
0.50	1.0	8.20	540	509	25.9×10^4
0.50	1.0	7.70	543	510	26.0×10^4
0.375	0.75	8.55	543	510	26.3×10^4
0.25	0.50	7.15	538	510	26.9×10^4
0.125	0.25	6.41	543	514	31.3×10^4
0.10	0.2	6.70	540	507	33.8×10^4
0.05	0.1	7.0	540	500	39.4×10^4
0.025	0.05	5.9	540	492	57.0×10^4

These results are shown graphically in Figure XXVI, on the page following. In this figure, the continuous line represents the relationship

$$V = \frac{c}{x} + K \qquad (10)$$

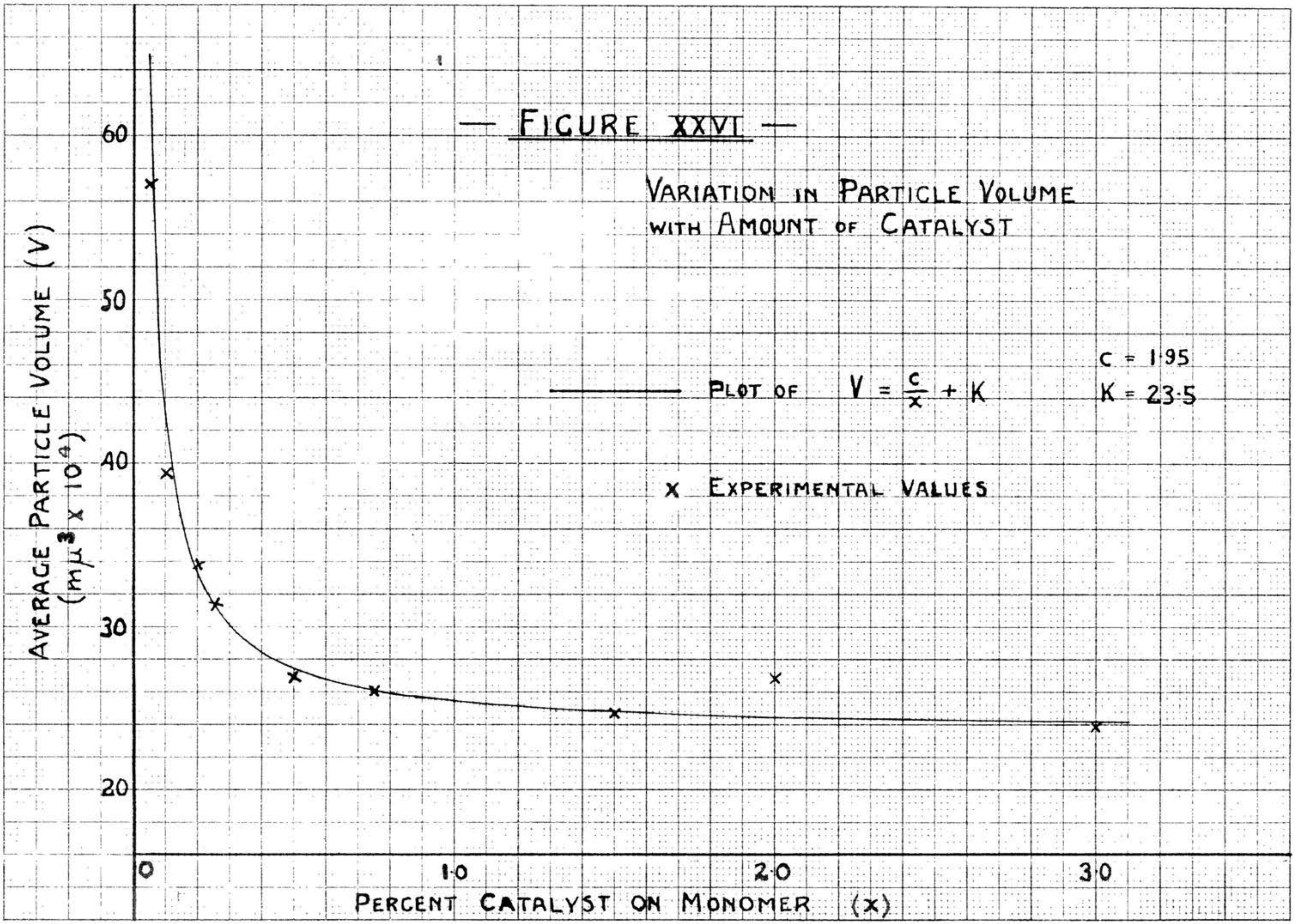
where x = percentage of catalyst on monomer

V = average particle volume

c = constant = 1.95

K = constant = 23.5

while the crosses represent the experimental values from Table 19. It will be seen that the experimental values follow the curve closely, well within the limits of the experimental errors involved in the method.



— FIGURE XXVI —

VARIATION IN PARTICLE VOLUME WITH AMOUNT OF CATALYST

In equation 10, above, as x increases $\frac{c}{x}$ tends to become zero. Thus the value of K represents the smallest value the average particle volume can attain with increasing amounts of catalyst. In this case it is a value of 23.5 x 10^4 cubic millimicrons.

In any one series of experiments, the value of c in equation 10 is determined by the conditions of the experiment, and the scales of values selected to represent x and V.

b. Variations in the Amount of Dispersing Agent

Placed in each flask 134 gms. water.

Added Sulphated Castor Oil #565 as indicated in Table 20.

To each flask then added

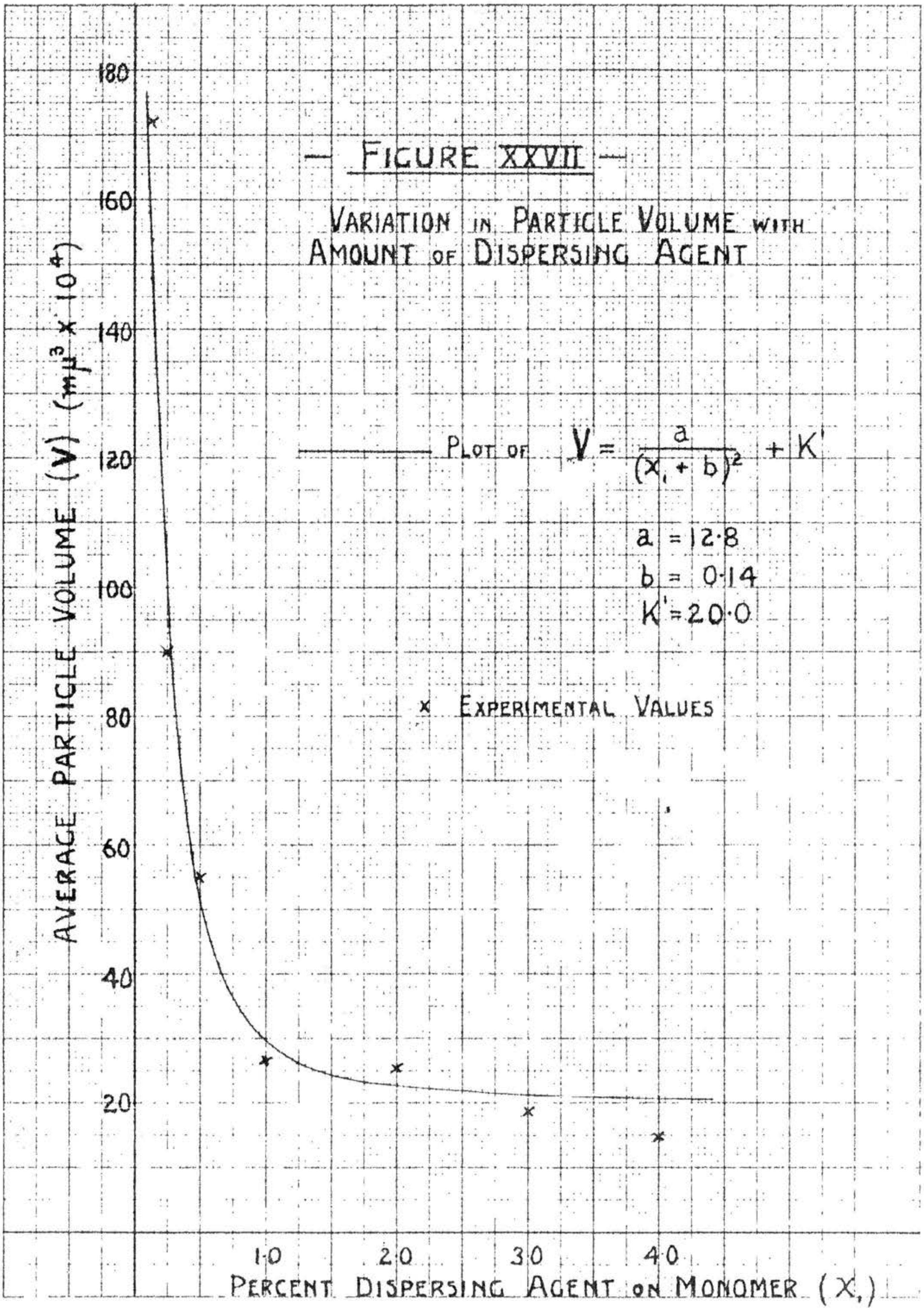
14.9 gms. "Pure" redistilled Methyl Acrylate

0.5 ml. 30% H_2O_2

Table 20

Amt. disp. agt. used (gm.)	% Disp. agent on monomer	Solids content of prepn. (%)	Reading with distilled water	Reading with prepn. (7 in 1000)	Average particle volume ($m\mu^3$)
0.84	4%	8.0	541	523	14.9 x 10^4
0.63	3%	8.4	541	518	18.7 x 10^4
0.42	2%	8.4	541	510	25.3 x 10^4
0.21	1%	7.1	541	513	26.8 x 10^4
0.10	0.5%	7.75	539	479	55.0 x 10^4
0.05	0.25%	7.95	539	442	90.0 x 10^4
0.025	0.125%	8.24	539	421	174 x 10^4

These results are shown graphically in Figure XXVII, on the following page.



— FIGURE XXVII —

VARIATION IN PARTICLE VOLUME WITH AMOUNT OF DISPERSING AGENT

In Figure XXVII, the continuous curve represents the relationship:

$$V = \frac{a}{(x_1 + b)^2} + K' \qquad (11)$$

where x_1 = percentage dispersing agent on monomer

V = average particle volume

a = constant = 12.8

b = constant = 0.14

K' = constant = 20.0

The points indicated by the crosses are the experimental values given in Table 20. The agreement here is not as close as in the experiments where the relationship of particle volume to amount of catalyst is studied, but it is reasonably good, and is probably within the limits of the errors of the experiment.

In equation 11, above, the value of K' is the limiting value to which the average particle volume tends, as the amount of dispersing agent is increased, while "a" is a constant determined by the conditions of the experiment, and the units employed. "b" is a constant which yields the value of V corresponding to the case where the amount of dispersing agent is zero. In such a case the particle size does not become infinite although the particles do not remain dispersed and their average size cannot be measured. According to equation 11, when x becomes zero $V = 674 \times 10^4$ cubic millimicrons.

This is a reasonable value.

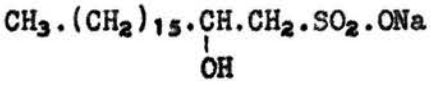
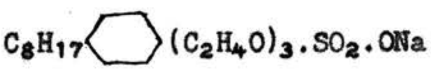
c. Use of Dispersing Agents of Different Types

It became very obvious, in the course of the early experimental work on this project, that the type of dispersing agent used had a decided effect on the particle size of the ultimate dispersion. It was also evident that the particular dispersing agent was very specific to the system in which it was being used. Therefore, it must be noted that the following observations are applicable strictly only to the system, methyl acrylate in water, generally to the lower acrylic esters in water, and not at all to systems involving copolymers of acrylic esters with other unsaturated compounds.

Table 21, below, shows the effect of four different dispersing agents on the particle size of polymethyl acrylate under the "standard" conditions of this series of experiments.

In each flask
134 gm. Distilled Water
0.5 ml. 30% H_2O_2
0.3 gm. Dispersing agent solids (nature as shown in table)
14.9 gm. "Pure" redistilled methyl acrylate

Table 21

Nature of disp. agt.	Concn. disp. agt.	Amt. used	% Solids of prepn.	Rdg. with dist. H_2O	Reading with prepn. (7 in 1000)	Average particle vol. $(m\mu)^3$
Sulphated castor oil	70.5%	0.42 gm.	8.4	539	512	21.9×10^4
Sulphated castor oil (repeat expt.)	70.5%	0.42 gm.	6.9	540	518	21.6×10^4
Sodium salt of α-oxy octadecane sulphonic acid  $CH_3.(CH_2)_{15}.\underset{OH}{CH}.CH_2.SO_2.ONa$	74.76%	0.40 gm.	8.55	539	510	23.3×10^4
Diisobutyl phenoxy ethoxy ethoxy ethoxy sodium sulphonate 	28.0%	1.06 gm.	7.6	539	432	105.6×10^4
Sodium oleate. Lab. prepn. from sodium hydroxide & oleic acid	5.0%	5.95 gm.	0.17 (much pptn. of polymer)	539	500	$1580^* \times 10^4$
Sodium oleate C.P. purchased from Merck & Co.	100%	0.30 gm.	5.22 (consid. pptn. of polymer)	540	(2 in 1000) 294	$1480^* \times 10^4$

* These values, corresponding to a particle diameter of approximately 300 mμ are probably inaccurate, as this diameter is very close to the wavelength of the light employed. The particle volume is, however, very large.

From this it is evident that sodium oleate, frequently recommended in the patent literature, and currently used as dispersing agent in Buna rubber polymerization, is unsatisfactory in the polymerization of methyl acrylate in concentrations comparable to that at which other dispersing agents are satisfactory.

d. Effect of Temperature

In discussing the effect of temperature on polymerizations of this type, it is necessary to note the limitations imposed by the system itself on the variations in temperature which can be made. With any specific acrylic ester the temperature during the reaction is controlled by the nature of the ester. Any attempt to raise the temperature results only in an increase in the reflux; any attempt to reduce the temperature produces a diminution in the rate of reflux, and a reduction in the rate of polymer formation. Towards the end of the reaction, when reflux has almost ceased, it is possible to raise the temperature.

The following table, Table 21, shows the effect of low, normal, and high temperature, insofar as it is possible to control it, on the average particle volume of polymethyl acrylate.

Water phase: 938 gms. Distilled Water
2.95 gms. Sulphated Castor Oil #565 (70.5% solids)

In each flask: 134.4 gms. Water phase
14.9 gms. "Pure" redistilled Methyl Acrylate
0.5 ml. 30% H_2O_2

A thermometer was placed in each flask to record temperature.

Table 21

Temp. of oil bath °C.	Initial temp. of water phase °C.	Temperature during polymerization °C.	Solids content of preparation %	Reading with dist. water	Reading with preparation (7 in 1000)	Average particle volume ($m\mu^3$)	Mean value (2 expts.)
80	75	74-79	7.25	540	511	27.2×10^4	27.0×10^4
80	75	74-79	5.05 (gum formation)	540	520	26.7×10^4	
90	85	76-85	7.65	540	511	25.8×10^4	24.9×10^4
90	85	76-85	7.66	540	513	24.0×10^4	
100	94	76-94	7.72	540	514	22.0×10^4	21.1×10^4
100	94	76-94	7.70	540	516	20.2×10^4	

Note: In spite of differences in initial temperature, the temperature during the main part of the reaction is about the same (74° to 76°C.).

e. Effect of Rate of Addition of Monomer

In this series of experiments, addition of the total amount of monomer to the reaction flask was made at different rates, both faster and slower than the "standard" rate. The data are recorded in Table 22.

Water phase:	670 gms.	Distilled Water
	2.10 gms.	Sulphated Castor Oil #565 (70.5% solids)
In each flask:	134.4 gms.	Water phase
	0.5 ml.	30% H_2O_2
Monomer:	14.9 gms.	"Pure" redistilled Methyl Acrylate.

Table 22

Start of addn. (a.m.)	End of addn. (a.m.)	Time of addn.	% Solids in prepn.	Rdg. with dist. water	Reading with prepn. (7 in 1000)	Average particle volume $m\mu^3$
10:42	10:47	5 mins.	7.25	539	507	23.3 x 10^4
10:48	11:01	13 mins.	6.45	539	522	17.9 x 10^4
11:00	11:25	25 mins.	7.0	539	519	19.2 x 10^4
11:12	11:43	31 mins.	7.35	539	517	20.4 x 10^4

f. Effect of Pre-emulsification of Part of the Monomer in the Water Phase

In this series of experiments, different sized portions of the total monomer were pre-emulsified in the water phase before adding the catalyst and beginning the polymerization, the balance of the monomer being then added in the usual way.

Water phase:	670 gms.	Distilled Water
	2.10 "	Sulphated Castor Oil #565 (70.5% solids)

In each flask: 134.4 gms. Water phase
"Pure" redistilled Methyl Acrylate in the amount indicated in Table 23
0.5 ml. 30% H_2O_2

The balance of the monomer, to make a total of 14.9 gms. in each flask, was then added dropwise at a rate of about 1 ml. per minute.

The stirring rate in these experiments was raised to 1500 r.p.m. to ensure thorough emulsification.

Table 23

Amount monomer in prelim. emulsion	Percent of total monomer in prelim. emulsion	Percent solids in preparation	Reading with dist. water	Reading with preparation (7 in 1000)	Average particle volume $(m\mu^3)$
0 gms.	0	7.9	539	513	22.2×10^4
4 gms.	26.8	6.26	539	512	29.4×10^4
8 gms.	53.6	7.20	539	512	25.5×10^4
10 gms.	67.0	6.82	539	512	26.9×10^4

4. Conclusions

The experiments described in this section lead to the following conclusions for the system where methyl acrylate is polymerized in an aqueous system using hydrogen peroxide as catalyst, and a highly sulphated castor oil as dispersing agent.

a. The average particle volume, V, varies inversely as the amount of catalyst used, x. The relationship is

$$V = \frac{c}{x} + K$$

where c and K are constants depending on conditions of preparation.

b. The average particle volume varies inversely as the square of the amount of dispersing agent used, x_1, plus a constant. The relationship is

$$V = \frac{a}{(x_1 + b)^2} + K'$$

where a, b and K' are constants depending on conditions of preparation.

c. The average particle volume is influenced enormously by the type of dispersing agent used.

d. Variations in temperature, within the limits imposed by the conditions of polymerization, have a slight influence on average particle volume. Increase in temperature tends to produce a smaller average particle volume. The evidence on this point cannot be considered conclusive, but a fairly definite trend is apparent.

e. Variations in rate of addition of the monomeric acrylate to the water phase produce only small changes in average particle volume.

f. The average particle volume is not affected by pre-emulsification of part of the monomer in the aqueous phase. The significance of this observation is discussed later, in Section IX, dealing with the mechanism of the polymerization.

VIII GROWTH OF PARTICLES DURING POLYMERIZATION

1. Principle

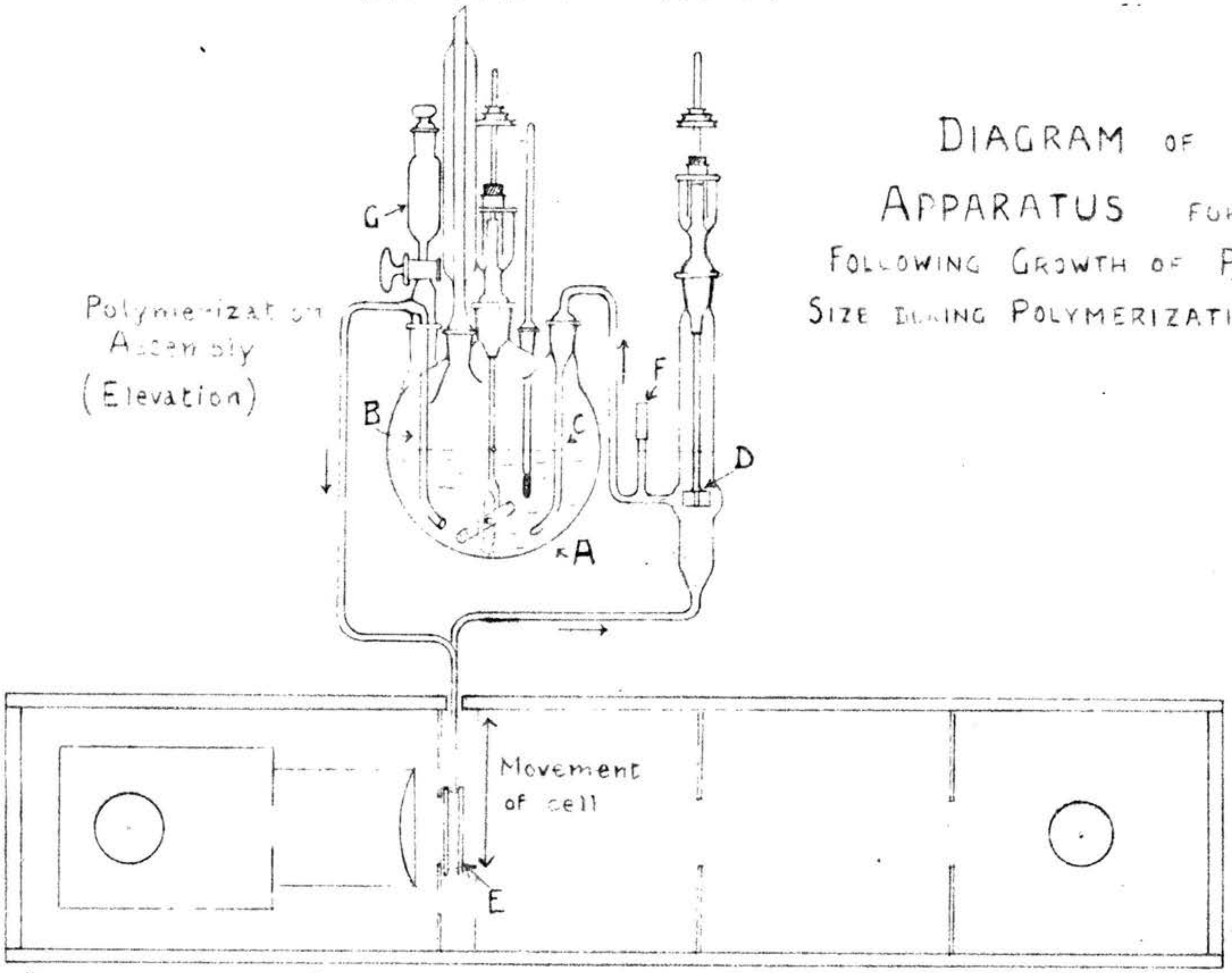
It has been pointed out, in the foregoing discussion, that water dispersions of the acrylic esters may be obtained by heating water solutions of the monomers in presence of catalyst and enough dispersing agent to prevent flocculation. Such solutions, at concentrations up to and including saturation, are clear and transparent, except for a slight haze from the small amount of dispersing agent. On heating these solutions to the refluxing temperature, they develop increased haziness, and soon become quite milky. The milkiness continues to increase until the appearance is characteristic of polyacrylic ester dispersions which have been prepared by the usual "emulsion" polymerization, and diluted to the same solids content.

It therefore became evident that, if a suitable apparatus could be devised, it would be possible to follow the growth of the particles in such a solution by circulating it through an optical cell during polymerization and making readings of the amount of unscattered radiation as the polymerization proceeded. Analysis of samples withdrawn at suitable intervals would enable a time vs. concentration curve to be drawn. From this, and the curve showing time vs. optical density a curve showing average particle volume at any time could be derived.

2. Apparatus and Method

The apparatus finally worked out, after several unsuccessful attempts, is shown diagrammatically in Figure XXVIII, and in Figure XXIX as a photograph of the completed assembly.

DIAGRAM OF
APPARATUS FOR
FOLLOWING GROWTH OF PARTICLE
SIZE DURING POLYMERIZATION



"Light-Scattering" Apparatus (Plan)
For details see Figure I

— FIGURE XXVIII —

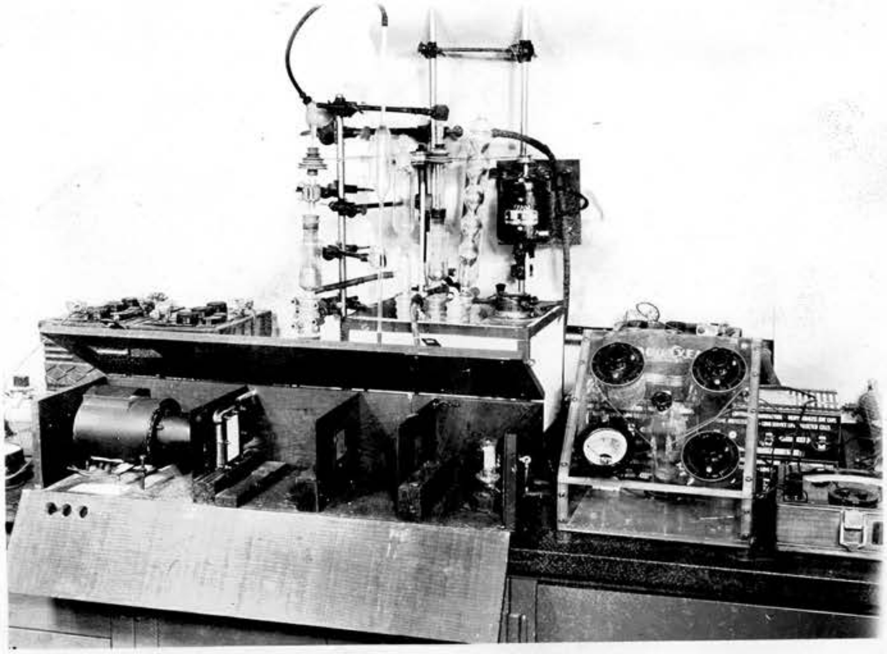


Figure XXIX

In Figure XXVIII, A is a pyrex flask, of two litres capacity, immersed in an electrically heated, thermostatically controlled oil bath. This flask is provided with five necks, each of them a standard taper, ground glass joint. The centre opening carries a glass stirrer equipped with a mercury seal. This stirrer may be omitted, and replaced with a plain stopper if desired. The reason for this will appear later (Section VIII, 3, d). The other openings carry, respectively, a reflux condenser, a thermometer dipping below the surface of the liquid, an outlet tube B, and a return tube C. The liquid is circulated in the direction indicated, by a four-bladed glass impeller, D, mounted in a vertical tube equipped with a ground glass, standard taper joint, and a mercury seal. This tube is so proportioned and so placed that the level of liquid in it may accommodate itself to any liquid level in the flask.

Within the "light-scattering" apparatus described in Section IV, 1, a, above (Figure I) is placed a special optical cell, E. This is constructed from two 2 in. by 3 in. microscope slides, crown glass, optical "flats," clamped in a frame of 18-8 stainless steel. The surfaces of the frame and the spacer adjacent to the glass are ground flat, and gaskets of fine white bond paper are used on each side of the glass slides. Inlet and outlet tubes, also of 18-8 stainless steel, are provided so that liquid may be circulated through the cell. The component parts of this cell are shown in the photograph, Figure XXX, and the whole assembly, in place in the light scattering apparatus, is shown in Figure XXXI. The assembled cell slides in grooves cut in the supporting block, so that it can be instantly placed in the beam of light coming through aperture O-2 (Figure I), or slid back to leave this aperture unobstructed.

The thickness of the liquid layer in this cell is 0.619 cm.

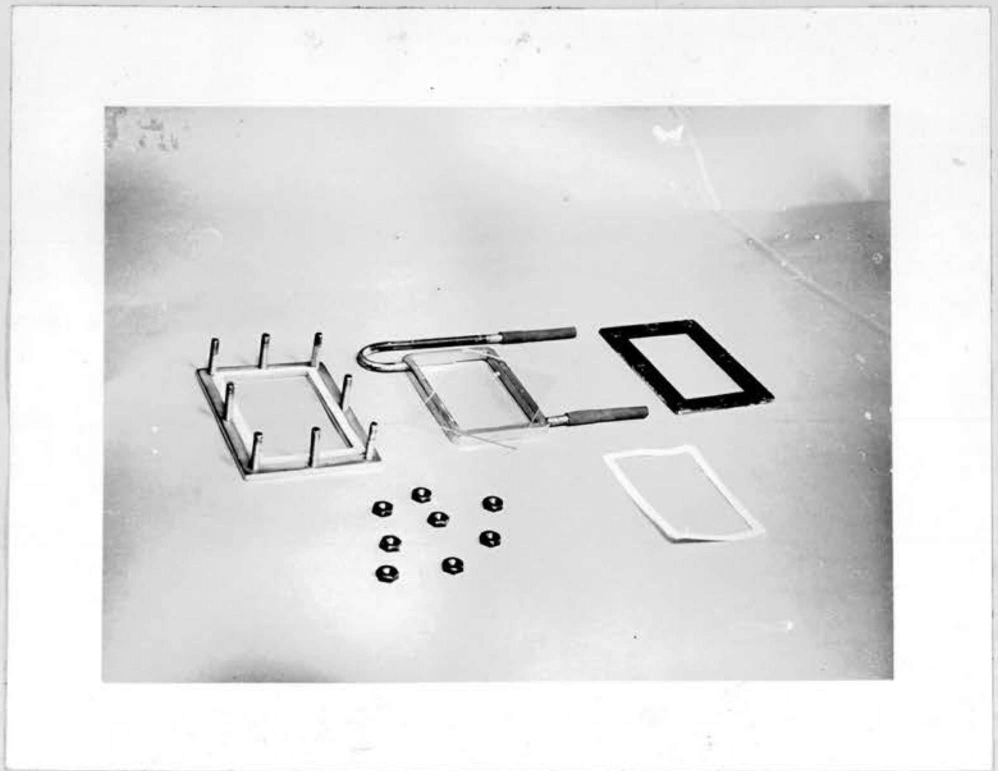


Figure XXX

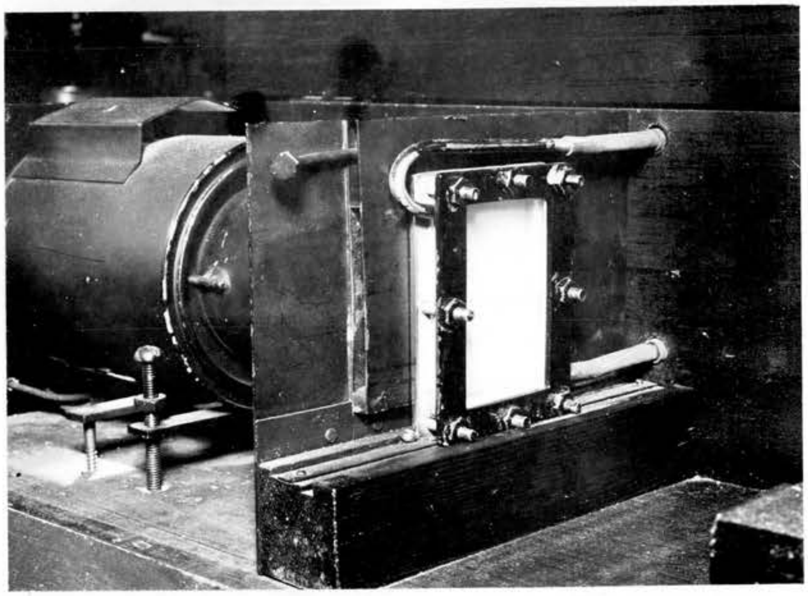


Figure XXXI

The tubes connecting the polymerization flask, the circulating pump, and the optical cell are glass, wrapped to reduce heat losses, and so arranged that the movement required to allow the cell to slide into and out of the light beam, is taken up by rotation of glass butt joints, held together with gum rubber tubing. This arrangement insures that the liquid in the system is in contact almost entirely with glass and with stainless steel, rather than rubber.

In using this apparatus to study growth of particle size during polymerization of solutions of the acrylic esters, the solution is made up to the desired concentration, of monomer and dispersing agent, and placed in the polymerization flask. It is then brought into the circulating system by withdrawing air from the tube F, which carries a rubber tip into which a pipette may be inserted to withdraw samples. Care is taken to see that all air bubbles are removed from the system.

The temperature of the oil bath is raised, to heat the solution in the flask to the desired temperature. When this is reached, the light-transmission of the solution is determined by sliding the absorption cell into the standardized light beam, and reading the microammeter. The calculated amount of catalyst is added through the funnel G, and after a lapse of about two minutes, a sample is withdrawn, through tube F, and immediately refrigerated to check polymerization. From this point, the temperature is held constant, circulation of the solution is continued, frequent readings of the light-transmission are made, and samples are withdrawn periodically for analysis.

From the data obtained, the curves representing optical density (relative to the initial light-transmission of the solution) versus time, and concentration versus time, are plotted. From these the curve representing average particle volume versus time is calculated from the relationship:

$$\log_{10} \frac{I_0}{I} \times \frac{\lambda^4}{c} = K' V$$

(This is equation (4), Section III, 5, a, above.)

which, in the apparatus here employed, at an effective mean wavelength of 533.6 mμ, and using an absorption cell 0.619 cm. thick, reduces to

$$V = \frac{1.039 \times 10^4}{c} \times \log_{10} \frac{I_0}{I}$$

where V is in cubic millimicrons

and c is in gms. polymer per gm. liquid.

(The calculation of the value of K', and the reduction of the relationship to numerical values, are given in Section III, 5, b, above. The difference here in the numerical value of the collected constants is due to the difference in the thickness of the absorption cell.)

The number of these "average particles" per unit weight (or volume) of the dispersion is also a significant value, and a study of its course during the polymerization helps in visualizing what occurs. It is, of course, readily calculable at any point when we know the concentration of the dispersion and the average, or "effective," particle volume. The relationship is:

$$N = \frac{c}{V \times \rho}$$

where N = number of "average particles" per gram

c = polymer concentration in gms./gm.

V = average particle volume in cc.

ρ = density of polymer in gms./cc.

3. Experimental

a. Solutions of Methyl Acrylate up to Saturation Point in Water

Because of the great bulk of data involved in the record of each of these experiments, only a few typical examples are given here in full. In the others, graphs plotted from the original record are given.

As the first typical example, to illustrate the technique, we have taken the polymerization of a two percent solution of methyl acrylate. This particular experiment was run four times, with very good agreement between runs.

Experiment 8111 - L1

Polymerization of 2% solution of Methyl Acrylate in water at 85°C.

Charge: 980 gms. Distilled Water

0.56 gms. Sulphated Castor Oil #565

(≡ 0.4 gms. disp'g agt. solids 2% on monomer)

heated to 75°C. and added,

20 gms. Monomeric Methyl Acrylate

(B.p. 80.6°C. at 758 mm.

Saponification number 651 ≡ 99.8%)

Catalyst 2 ml. 30% H_2O_2

The actual observations made are shown in Table 24.

Table 24

Time August 11 1941	Elapsed time (hours)	Temp. in flask (°C.)	Temp. of oil bath (°C.)	Meter reading (microamps)	log $\frac{I_o}{I}$
10:52		84.6	95	568)	
10:57		84.6	96	568) I_o	
11:00	0.00	Added catalyst		)	
11:02	0.03	85.0	96	568)	0.000
11:04	0.07	Sample #0			
11:06	0.10	85.0	96	562 (I)	0.0045
11:11	0.18	85.1	96	555 ↓	0.010
11:17	0.28	85.3	96	549	0.014
11:19	0.32	85.3	96	548	0.015
11:20	0.33	85.3	96	545	0.018
11:25	0.42	85.3	96	539	0.023
11:26	0.43	85.3	96	533	0.0275
11:28	0.47	85.3	95	528	0.031
11:30	0.50	85.2	95	523	0.036
11:32	0.53	85.2	95	518	0.040
11:35	0.58	Sample #1			
11:37	0.62	86.0	95	505	0.051
11:39	0.65	86.0	95	500	0.055
11:41	0.68	86.0	95	493	0.061
11:44	0.73	85.7	95	491	0.063
11:49	0.82	85.3	95	484	0.069
11:53	0.88	85.1	94	478	0.075
11:57	0.95	85.0	94	472	0.080
12:01	1.02	85.1	94.5	468	0.084
12:04	1.07	85.1	95	467	0.085
12:08	1.13	85.1	95	462	0.090
12:11	1.18	85.2	95	460	0.091
12:14	1.23	Sample #2			
12:16	1.27	85.4	95	457	0.094
12:19	1.32	85.3	95	453	0.098
12:24	1.40	85.2	95	452	0.099
12:28	1.47	85.0	94.5	449	0.102
12:35	1.58	85.0	94.5	447	0.104
12:41	1.68	85.0	94.5	443	0.108
12:50	1.83	Lamp burned out. Replaced			
15:08	4.13	85.0	94	420	0.132
15:30	4.50	85.0	94	418	0.134
16:08	5.13	85.0	94	413	0.138
16:14	5.23	85.0	94	413	0.138
16:20	5.33	85.0	94	412	0.139
16:24	5.40	85.0	94	412	0.139
16:26	5.43	Sample #3			
16:30	5.50	85.0	94.5	412	0.139
16:37	5.62	84.8	94	412	0.139
16:45	5.75	84.7	94	412	0.139
16:49	5.82	85.1	95	412	0.139
19:50	8.83	84.0	94.5	395	0.158
20:02	9.03	84.0	94.5	395	0.158
20:24	9.40	84.8	95	394	0.159
20:29	9.48	84.5	95	394	0.159

Table 24 - continued -

Time August 11 1941	Elapsed time (hours)	Temp. in flask (°C.)	Temp. of oil bath (°C.)	Meter reading (microamps)	$\log \frac{I_0}{I}$
20:31	9.52	Sample #4			
20:45	9.75	84.0	95	393	0.160
20:55	9.92	84.5	94.5	392	0.161
21:05	10.08	85.0	95	391	0.162
21:30	10.50	85.0	95	389	0.164
August 12					
8:15	21.25	85.5	95.5	348	0.213
8:30	21.50	85.5	95.5	348	0.213
8:36	21.60	Sample #5			
8:40	21.67	85.5	95	348	0.213
9:30	22.50	85.0	95	338	0.225
10:17	23.28	84.2	95	330	0.235
10:40	23.67	85.0	95	327	0.239
11:02	24.03	85.0	95	323	0.245
12:56	25.93	85.0	95	307	0.267
13:00	26.00	Sample #6			
13:04	26.07	85.1	95	307	0.267
14:44	27.73	85.0	95	289	0.293
15:05	28.08	84.5	95	281	0.305
15:07	28.17	Sample #7			
15:12	28.20	85.0	95	281	0.305
15:12	Stopped run.				

Analyses of Samples 0 to 7 gave the values recorded in Table 25.

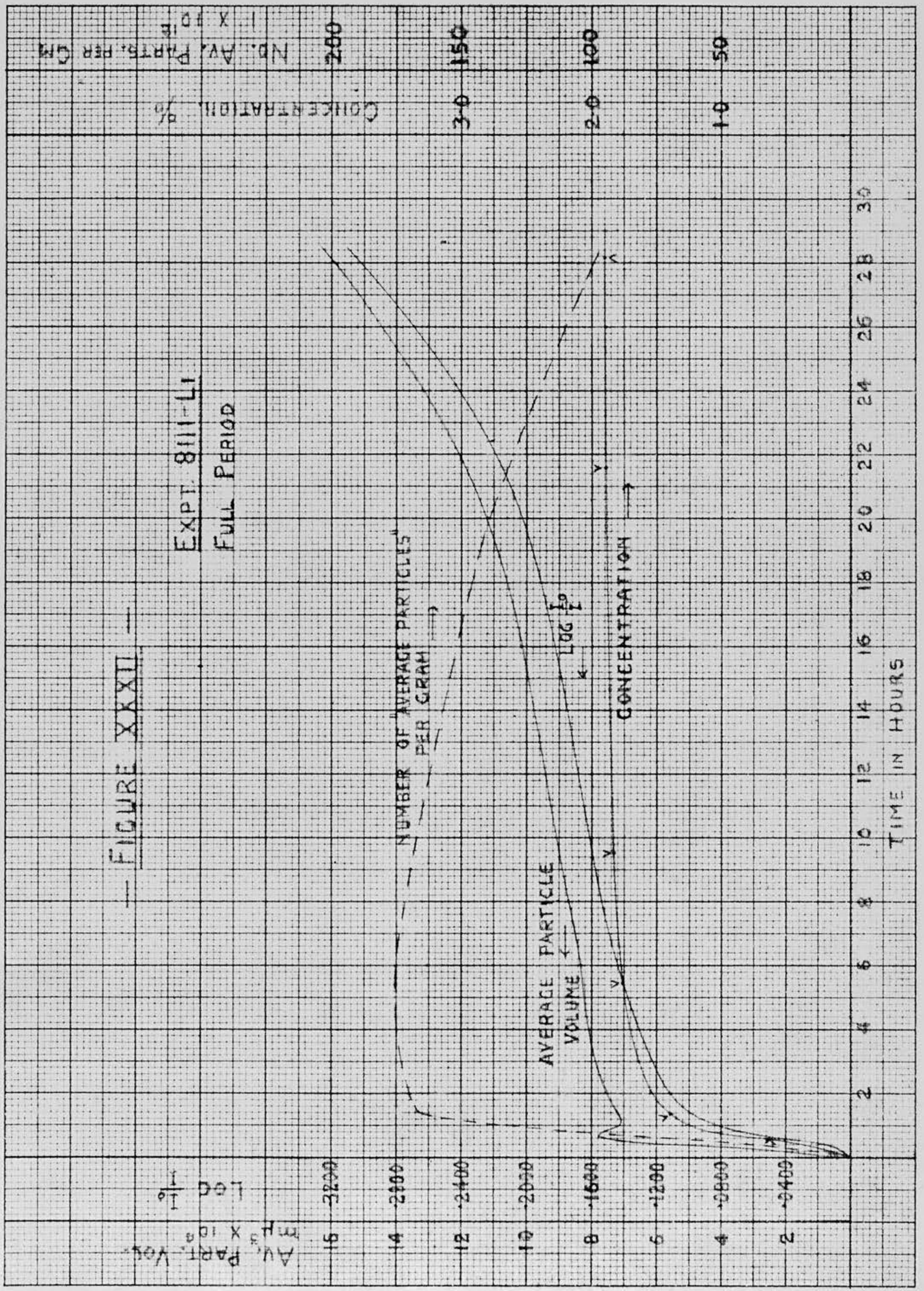
Table 25

Sample number	Elapsed time (hours)	Percent solids	Percent polymer (solids corrected for solids in sample 0)
0	0.07	0.076	0.000
1	0.58	0.720	0.644
2	1.23	1.426	1.350
3	5.43	1.831	1.755
4	9.52	1.891	1.815
5	21.60	1.968	1.892
6	26.00	1.973	1.897
7	28.17	1.968	1.892

Curves showing change with time of

1. Optical density
2. Concentration of polymer
3. Average particle volume
4. Number of "average particles" per gram

are shown for the whole course of the reaction in Figure XXXII, and, on a larger scale, for the first three hours in Figure XXXIII. The data from which Figure XXXIII is constructed are shown in Table 26. In this table, the interpolated values of the optical density and the concentration for any specific time are obtained from the experimental curves, and the corresponding particle volume is calculated. This is considered a legitimate procedure because the inflections of the optical density curve are known precisely, while the concentration curve is smooth and any reasonable variations that can be made in its shape within the limits allowed by the experimental values do not change the general shape of the particle volume curve. The significance of the course taken by the particle volume curve is discussed below, following the presentation of the experimental data.



— FIGURE XXXII —

EXPT. 811-Li
FULL PERIOD

Table 26

<u>Experiment 8111-L1</u> "Optical density" and Concentration for early stages. Values taken from experimental curves.

Elapsed time (hours)	Concn. %	log $\frac{I_0}{I}$	Average particle volume (cubic mμ)
.30	.25	.0140	5.82×10^4
.40	.37	.0220	6.18×10^4
.50	.52	.0350	7.00×10^4
.60	.66	.049	7.71×10^4
.70	.82	.061	7.74×10^4
.80	.95	.069	7.56×10^4
.90	1.08	.076	7.31×10^4
1.00	1.19	.082	7.16×10^4
1.10	1.27	.087	7.11×10^4
1.2	1.33	.091	7.10×10^4
1.3	1.38	.096	7.22×10^4
1.4	1.42	.099	7.24×10^4
1.5	1.46	.102	7.27×10^4
1.6	1.48	.105	7.32×10^4
1.7	1.51	.107	7.37×10^4
1.8	1.52	.109	7.45×10^4
1.9	1.54	.111	7.48×10^4
2.0	1.55	.113	7.57×10^4
2.5	1.59	.120	7.84×10^4
3.0	1.63	.124	7.90×10^4
4.0	1.69	.131	8.05×10^4

As a second typical example, we have taken the polymerization of a saturated solution of methyl acrylate in water. This experiment was run three times with very good agreement between runs.

The solubility of methyl acrylate in water at various temperatures was determined. Details of the method used are given in Appendix D. It was found that the solubility increased only slightly with increasing temperature, and that it was very close to 5.4%. This knowledge is required to permit calculation of the necessary amounts of dispersing agent and catalyst so that they may be kept proportional to the amount of monomer.

Experiment 7102-D1

1 litre distilled water was shaken with an excess (75 gms. in all) of "pure" methyl acrylate, b.p. 80.6°C. at 758 mm. Sap. No. 651, purity 99.8%, in a 2 litre separating funnel, and allowed to separate. The mixture was reshaken vigorously at half hour intervals for a period of three hours, and then allowed to separate overnight. The following morning, exactly one litre of the lower layer of saturated solution was separated and placed in the polymerization flask together with

1.53 gms. Sulphated Castor Oil #565

(= 1.08 gms. dispersing agent solids, or 2% on monomer)

Heated to 77°C. (gentle reflux) and added 5.4 ml. 30% H_2O_2 as catalyst. Complete data given in Table 27.

Table 27

Time July 10 1942	Elapsed time (hours)	Temp. in flask (°C.)	Temp. of oil bath (°C.)	Meter reading (microamps/5)	"100" scale	log $\frac{I_0}{I}$
11:42		76.0	92.0	96.0	I_0	
11:49		76.8	94.0	96.0		
11:50	.000	Added catalyst				
11:55	.083	Sample #0				
11:58	.13	76.5	95.1	96.0		
12:01	.18	77.0	95.1	96.0		
12:10	.33	77.3	93.5	96.0		
12:16	.43	76.9	92.0	95.1		.00389
12:22	.53	77.0	93.1	95.0	I	.00475
12:26	.60	77.8	92.2	92.6		.016
12:32	.70	77.9	91.0	91.1		.023
12:38	.80	77.9	91.0	89.5		.030
12:43	.88	Sample #1				
12:49	0.98	77.8	86.0	83.4		.061
12:55	1.08	77.0	85.0	80.8		.075
13:00	1.17	77.0	84.0	77.9		.091
13:04	1.23	77.0	84.0	76.7		.097
13:07	1.28	77.0	84.0	73.9		.114
13:12	1.37	77.0	83.5	71.7		.127
13:17	1.45	77.0	84.0	69.5		.130
13:19	1.48	Sample #2				
13:23	1.55	77.1	83.5	66.7		.158
13:27	1.62	77.0	83.4	64.6		.172
13:34	1.73	77.0	84.1	62.8		.184
13:39	1.82	77.0	84.0	59.6		.207
13:46	1.93	77.0	84.5	57.3		.224

Table 27 - continued -

Time July 10 1942	Elapsed time (hours)	Temp. in flask (°C.)	Temp. of oil bath (°C.)	Meter reading (microamps/5) "100" scale	log $\frac{I_o}{I}$
13:47	1.95	Sample #3			
13:49	1.98	77.1	85.0	56.2	.232
14.08	2.30	77.0	84.7	51.3	.272
14.25	2.58	77.0	85.2	48.0	.301
14:50	3.00	77.0	87.0	44.2	.337
14:53	3.05	Sample #4			
14:55	3.08	77.4	86.0	43.9	.340
15:55	4.08	77.0	85.7	35.6	.431
15:59	4.15	Sample #5			
16:01	4.18	77.0	86.2	35.2	.436
16:31	4.68	77.1	85.8	32.9	.465
16:48	4.97	76.8	84.5	31.2	.488
17:05	5.25	Sample #6			
17:08	5.30	77.8	86.0	30.5	.498
20:00	8.17	76.8	85.0	24.2	.599
20:05	8.25	Sample #7			
20:10	8.33	77.0	85.5	24.1	.600
July 11					
0:00	12.17	77.1	85.6	20.8	.664
0:05	12.25	Sample #8			
0:09	12.37	77.4	86.0	20.8	.664
4:04	16.23	77.	86.0	18.8	.708
4:08	16.30	Sample #9			
4:14	16.40	77.1	86.2	18.9	.706
9:15	21.42	76.1	87.0	17.4	.742
9:17	21.45	Sample #10			
9:19	21.48	77.3	89.0	17.4	.742
10:26	22.60	77.0	86.5	17.2	.747
11:58	24.13	77.2	86.5	17.1	.749
12:00	24.17	Sample #11			
12:02	24.20			17.1	.749

Analyses of Samples 0 to 11 gave the values recorded in Table 28.

Table 28

Sample number	Elapsed time (hours)	Percent solids	Percent polymer (solids corrected for solids in sample 0)
0	.083	.1095	.000
1	.88	.4170	.3075
2	1.48	1.324	1.215
3	1.95	1.935	1.826
4	3.05	2.745	2.636
5	4.15	3.344	3.234
6	5.25	3.730	3.620
7	8.25	4.330	4.220
8	12.25	4.700	4.590
9	16.30	4.820	4.710
10	21.45	4.910	4.800
11	24.17	4.940	4.830

The curves showing the course of the optical density, the concentration, the average particle volume, and the average number of particles per gram are shown in Figure XXXIV for the entire course of the experiment, and for the first three hours in Figure XXXV. Table 29 records the data, interpolated from the curves, from which Figure XXXV was constructed.

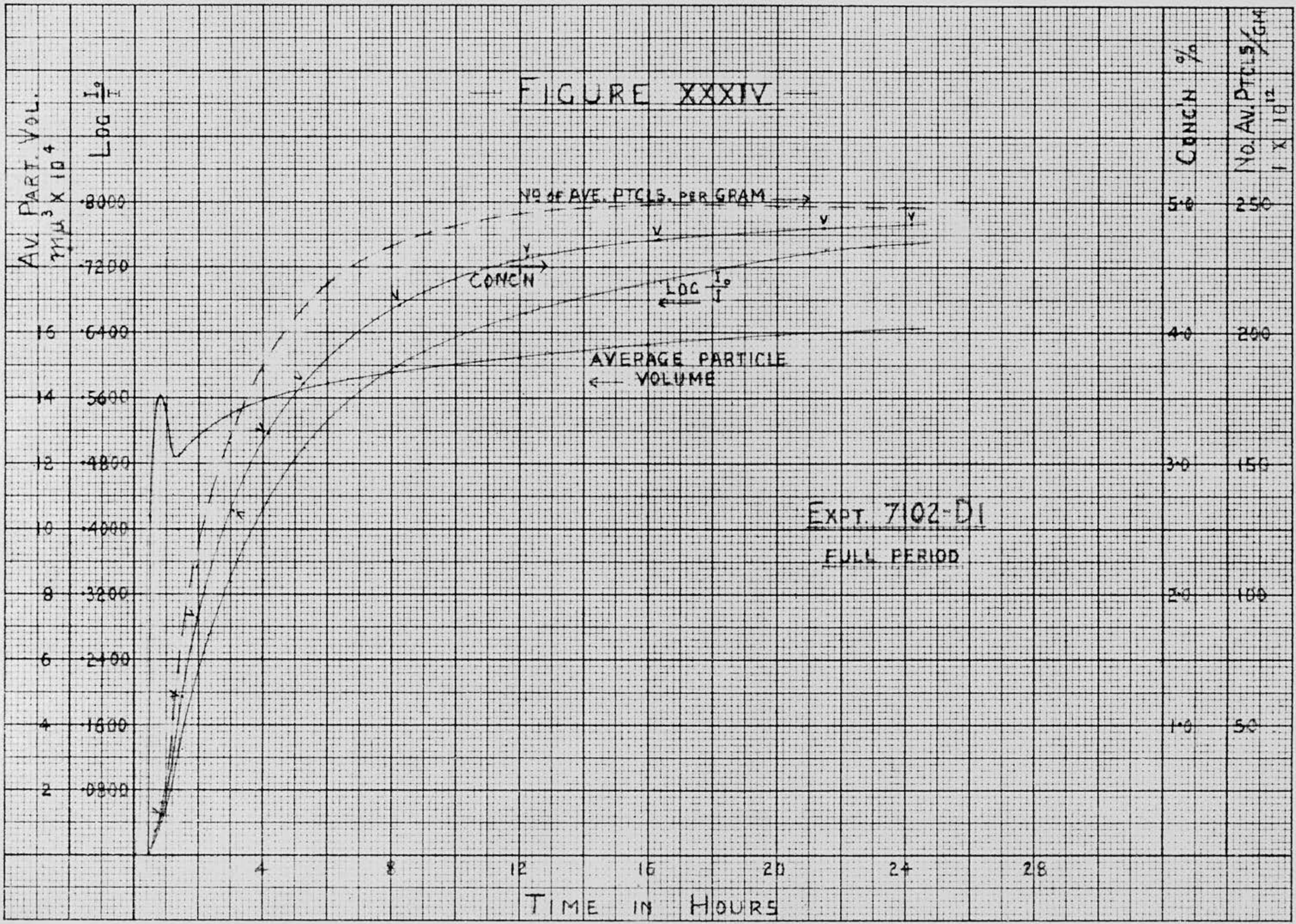


FIGURE XXXIV

Table 29

Experiment 7102-D1 "Optical density" and concentration for early stages. Values taken from experimental curves.

Elapsed time (hours)	Concn. %	$\log \frac{I_0}{I}$	Average particle volume (cubic mμ)	Elapsed time (hours)	Concn. %	$\log \frac{I_0}{I}$	Average particle volume (cubic mμ)
0.50	.05	.005	10.4×10^4	1.40	1.10	.130	12.3×10^4
0.60	.10	.0120	12.5×10^4	1.50	1.26	.150	12.4×10^4
0.70	.15	.0200	13.9×10^4	1.75	1.60	.195	12.7×10^4
0.80	.23	.032	14.5×10^4	2.00	1.88	.234	12.9×10^4
0.90	.34	.045	13.8×10^4	2.25	2.10	.266	13.15×10^4
1.00	.47	.060	13.2×10^4	2.50	2.30	.293	13.25×10^4
1.10	.61	.077	12.6×10^4	3.00	2.61	.338	13.45×10^4
1.20	.77	.094	12.2×10^4	3.50	2.87	.380	13.75×10^4
1.30	.94	.112	12.25×10^4	4.00	3.14	.422	13.95×10^4

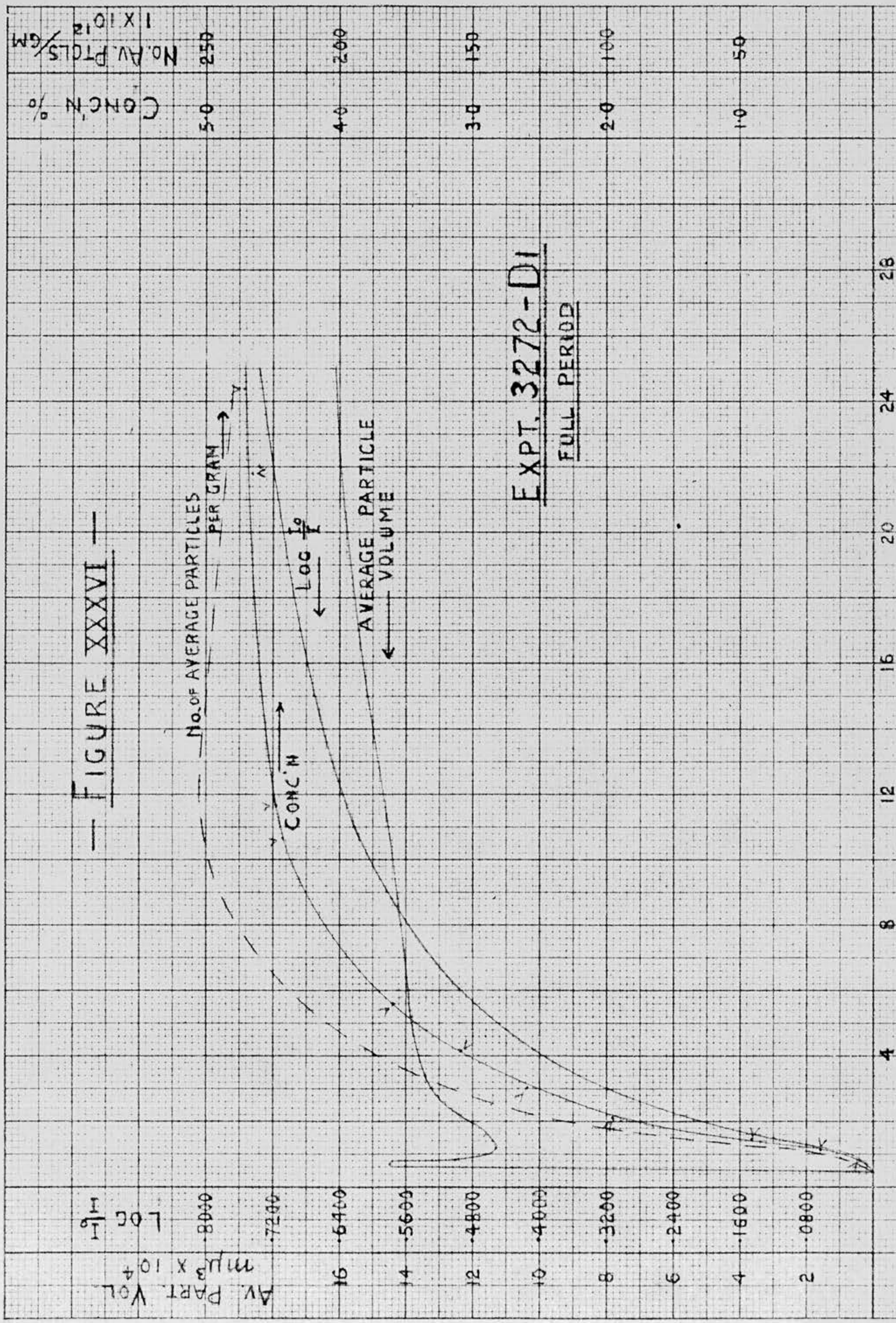
b. Reproducibility

To indicate the degree of duplicability attainable by this method, Figures XXXVI and XXXVII show the results obtained on an exact duplicate (Experiment 3272-D1) of Experiment 7102-D1. Figure XXXVI corresponds to Figure XXXIV and Figure XXXVII to Figure XXXV. It will be noted that the agreement is good.

Experiments studying the growth of particle size at 1% concentration and 3% concentration of methyl acrylate showed the same behavior pattern as illustrated above for a 2% solution.

c. Summary of Results

Examination of the courses followed by the curves in Figures XXXII to XXXVII, inclusive, shows a number of significant characteristics, some of them quite unexpected.


— FIGURE XXXVI —
EXPT. 3272-D1
FULL PERIOD
No. of AVERAGE PARTICLES PER GRAM →
CONC'N →
LOG $\frac{I_0}{I}$ ←
AVERAGE PARTICLE VOLUME ←
CONC'N %
5.0
4.0
3.0
2.0
1.0
No. AV. PTCLS/GM
1 x 10^{12}
250
200
150
100
50
LOG $\frac{I_0}{I}$
.8000
.7200
.6400
.5600
.4800
.4000
.3200
.2400
.1600
.0800
AV. PART. VOL.
mμ^3 x 10^4
16
14
12
10
8
6
4
2
4
8
12
16
20
24
28
TIME IN HOURS

The course of the reaction may, in all cases, be divided into five phases, as follows:

Phase 1. A period, following the addition of the catalyst, when no detectable reaction occurs. No change in the light transmission of the starting solution is observed, and study of the concentration curves (see particularly Figure XXXVII) indicates no polymer formation during this period. This initial "no reaction" period varies from four to twenty-five minutes, and is regarded, without more detailed investigation, as being somewhat fortuitous, depending, perhaps, on the presence, or absence, of trace impurities acting as inhibitors.

Phase 2. The period of twenty to thirty-five minutes immediately following the first detectable change in light transmission of the starting solution, characterized by formation of small amounts of polymer of relatively large particle size. This particle size, established in the very early stages of the reaction, appears to be characteristic of the conditions of the experiment, because the final particle size, apart from the changes attributable to agglomeration, is always of the same order of magnitude.

The observation that the first particles formed were of the same average volume as those formed in the later stages of the reaction was unexpected. Prior to this it had been believed that the volume of the particles grew as the concentration of polymer increased, and that the growth paralleled - more or less closely - the increase in concentration. Instead, it is seen that it is the number of particles in the dispersion which parallels the increase in polymer concentration.

Phase 3. A period of approximately twenty-five minutes, immediately following that in which the "characteristic" particle size is established, during which the average particle volume decreases measurably, while the concentration of polymer is increasing sharply. It is, in fact, during the latter part of this period that the rate of polymer formation reaches its maximum, together with the rate of increase in number of particles per unit volume (see particularly Figure XXXIII).

This decrease in average particle volume, following the rapid establishment of the "characteristic" volume, was most unexpected. When first observed in an experiment run in November, 1940, it was regarded with extreme skepticism, but it has been confirmed so frequently and consistently that its occurrence seems to be beyond all reasonable doubt.

The possibility was considered that this decrease in average particle volume was only apparent, and that it might result from the change in refractive index of the continuous phase produced by removal of the monomer from solution. Examination of this possibility shows that the effect of removal of monomer from solution can result only in a very slight apparent decrease in particle volume. Thus, denoting refractive index, as usual, by n, we have:

n_m, for monomeric methyl acrylate = 1.4025. $n_m^2 = 1.9671$
n, for polymethyl acrylate = 1.4720. $n^2 = 2.1668$
n_o, for water = 1.3329. $n_o^2 = 1.7766$
n_s, for sat'd soln. of monomeric methyl acrylate in water = 1.3362. $n_s^2 = 1.7854$

The refractive index terms of Equation 1, (Section III, 5, a, above) in the case where the dispersion medium is a saturated solution of methyl acrylate in water, have a value of 0.039776. When the dispersion medium is water, they have a value of 0.041881. Equation 3 (Section III, 5, a) shows that, under the conditions of these experiments, the average particle volume is inversely proportional to the refractive index terms (K), so the effect of removing all the monomeric methyl acrylate from the solution at the point of maximum particle volume would be to reduce the apparent volume by the fraction $\frac{.002105}{.039776}$ or 5.3%.

The actual amount of monomer removed between the maximum and minimum particle volumes is, of course, much less than this, being about ten percent of the total amount present. This means that the greatest apparent reduction of particle volume from this effect would be from the value shown of 14.5×10^4 $m\mu^3$ to 14.3×10^4 $m\mu^3$. The measured drop is much greater than this.

The possibility that the removal of the dispersing agent from solution by adsorption on the surface of the polymer particles was influencing the readings was also considered, but careful measurements of the refractive indices of the dilute solutions used, failed to distinguish between them and distilled water alone.

The significance of this decrease in average particle volume will be discussed later, when the mechanism of the reaction is considered.

Phase 4. The period of several hours during which the average particle volume increases again to a value close to, or slightly greater than, that established in the first stages of the reaction, while the polymer formation increases to 80-90% of the initial amount of monomer present, and the rate of polymer formation falls off to a low level. (See Figures XXXII, XXXIV, and XXXVI.)

Phase 5. The final period, when from 85% to 90% of the monomer has been converted into polymer, the average particle volume again increases, and the number of "average particles" per gram decreases. This phase is evidently the result of agglomeration of particles already formed, as this is the only way to explain a decrease in the number of particles while the concentration of polymer is either stationary, or increasing very slowly.

The occurrence of agglomeration of particles in the last stages is more evident in the polymerization of the 2% solution of methyl acrylate (Figure XXXII) than in the polymerization of the saturated waste solution of methyl acrylate. (Figures XXXIV and XXXVI) This is attributed to the fact that, in these experiments, the amount of dispersing agent was kept proportional to the amount of monomer, so that in the water phase the concentration of dispersing agent was almost three times as great in the case of the saturated solution as in the case of the 2% solution. In polymerizing 1% and 3% solutions it was observed that agglomeration was greater at 1% and less at 3% than at 2%.

The interpretation of these results is discussed later, following presentation of the results of experiments on polymerizing saturated solutions of methyl acrylate in presence of excess monomer.

d. Saturated Solutions with Monomer in Excess

From the construction and arrangement of the apparatus used in this part of the work, (Figures XXVIII and XXIX) it is evident that, if the stirrer in the centre of the flask is removed, it will be possible to follow the polymerization of a saturated water solution of an acrylic ester with an excess of monomer present in the form of a layer floating on the surface of the water phase. The resulting dispersion, as it forms, will be continuously "sampled" via outlet tube "B," pumped through cell "E," and returned to the flask via return tube "C." Agitation of the water layer will be provided by the inflow and outflow of the circulating liquid, and by the thermal agitation resulting from reheating the returning liquid to a temperature but a few degrees below the boiling point of the monomer. It seems reasonable to suppose that this will suffice to maintain the saturation of the aqueous phase, and the evidence indicates that it does in fact do so.

By using this technique, it should therefore be possible to follow the growth of particle size in a saturated solution which is maintained at saturation. A number of experiments were run in this way. The following experiment on the polymerization of a 10% dispersion of methyl acrylate by this method, serves as a typical example.

Experiment 3192-D1

In the polymerization flask, A, (Figure XXVIII) were shaken together several times:

850 gms.	Dist. water
100 gms.	Methyl Acrylate (b.p. 80.6°C. at 760 mm. Sap. No. 650)

The flask was then placed in the oil bath and the mixture permitted to separate into two layers. The amount of methyl acrylate here used is a little more than double the amount soluble in the amount of water present (see Appendix D).

The lower layer was then brought into the circulating system by sucking air from the sampling tube, F, and to the lower (aqueous) layer, via tube F, was added:

2.80 gms. Sulphated Castor Oil #565 (= 2.0 gms. solids)

dissolved in 50 gms. water.

The contents of the flask were then heated, while keeping the circulating pump running briskly, to refluxing temperature, 77°C.

Catalyst 10 ml. 30% H_2O_2.

Table 30, below, is a transcript of the record of this experiment.

Table 30

Time March 19 1942	Elapsed time (hours)	Temp. in flask (°C.)	Temp. of oil bath (°C.)	Meter reading (microamps x 2)	$\log \frac{I_0}{I}$
11:10		76.5	85.0	938 } I_0	
11:15		77.0	87.0	938	
11:18	Added catalyst				
11:20	.03	77.0	86.0	932 I	.000
11:22	.07	77.5	86.0	928	.002
11:25	.12	77.2		924	.004
11:30	.17	Sample #0			
11:33	.25	77.0	83.0	915	.008
11:37	.32	77.4	83.0	915	.008
11:44	.43	77.7	79.0	914	.009
11:52	.57	76.0	78.0	868	.031
11:54	.60	Sample #1			
11:58	.67	76.2	84.0	825	.053
12:00	.70	76.7	84.0	801	.066
12:02	.73	77.0	84.0	775	.080
12:03	.75	Sample #2			
12:05	.78	77.4	82.0	732	.105
12:07	.82	77.5	81.0	716	.115
12:09	.85	77.3	80.0	703	.123
12:10	.87	77.1	81.0	686	.133
12:11	.88	Sample #3			
12:14	.93	76.8	80.0	643	.161
12:16	.97	76.7	84.0	619	.178

Table 30 - continued -

Time March 19 1942	Elapsed time (hours)	Temp. in flask (°C.)	Temp. of oil bath (°C.)	Meter reading (microamps x 2)	$\log \frac{I_o}{I}$
12:20	1.03	77.0	83.5	590	.199
12:21	1.05	77.1	83.0	564	.218
12:24	1.10	Sample #4			
12:25	1.17	77.5	83.3	525	.249
12:30	1.20	77.3	81.0	473	.295
12:34	1.27	77.0	81.0	445	.321
12:40	1.37	77.0	81.0	390	.378
12:41	1.38	Sample #5			
12:45	1.45	77.0	81.5	350	.425
12:50	1.53	76.9	82.0	300	.493
12:55	1.62	77.0	82.5	269	.540
12:59	1.68	77.0	82.0	247	.577
13:09	1.85	77.2	82.0	192	.686
13:10	1.87	Sample #6			
13:13	1.92	77.4	81.5	166	.750
13:20	2.10	77.0	80.2	95	1.005
13:33	2.25	77.0	83.0	45	1.316
13:35	2.28	Sample #7			
13:40	2.37	77.2	83.5	34	1.438
14:16	2.97	Sample #8			
14:17	2.98	77.0	82.5	6	2.192
15:00	3.70	Sample #9			
15:01	3.72	77.0	83.0		
16:09	4.85	Sample #10			
16:10	4.87	77.9	86.0		
16:57	5.65	Sample #11			
16:59	5.68	77.2	84.0		
March 20, 1942					
14:20	27.03	Sample #12			
14:21	27.05	78.0	81.0		

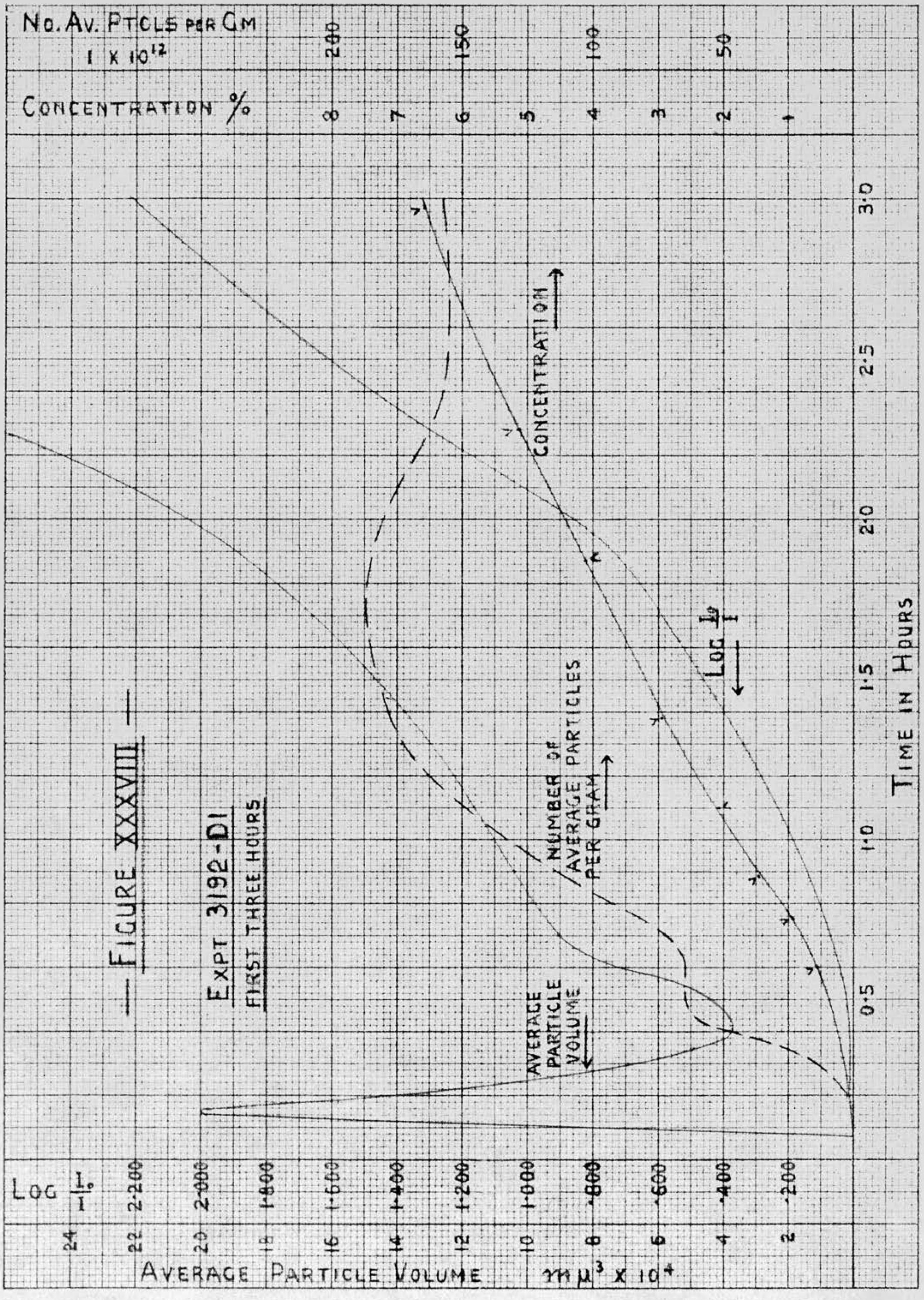
Table 31, below, gives the results of the analyses, for polymer concentration, of Samples 0 to 12.

Table 31

Sample number	Elapsed time (hours)	Percent solids	Percent polymer (solids corrected for solids in sample 0)
0	0.17	0.190	
1	0.60	0.733	0.543
2	0.75	1.108	0.918
3	0.88	1.629	1.439
4	1.10	2.255	2.065
5	1.38	3.149	2.959
6	1.87	4.292	4.102
7	2.28	5.315	5.125
8	2.97	6.75	6.560
9	3.70	8.025	7.835
10	4.85	8.915	8.725
11	5.65	9.233	9.043
12	27.03	10.36	10.170

Figure XXXVIII shows the course of the optical density, polymer concentration, average particle volume, and "number of average particles per gram" curves for the first three hours of this experiment. Beyond this point, direct particle volume measurements could not be made, because of the opacity of the dispersion, which had by then attained a polymer concentration of over six percent.

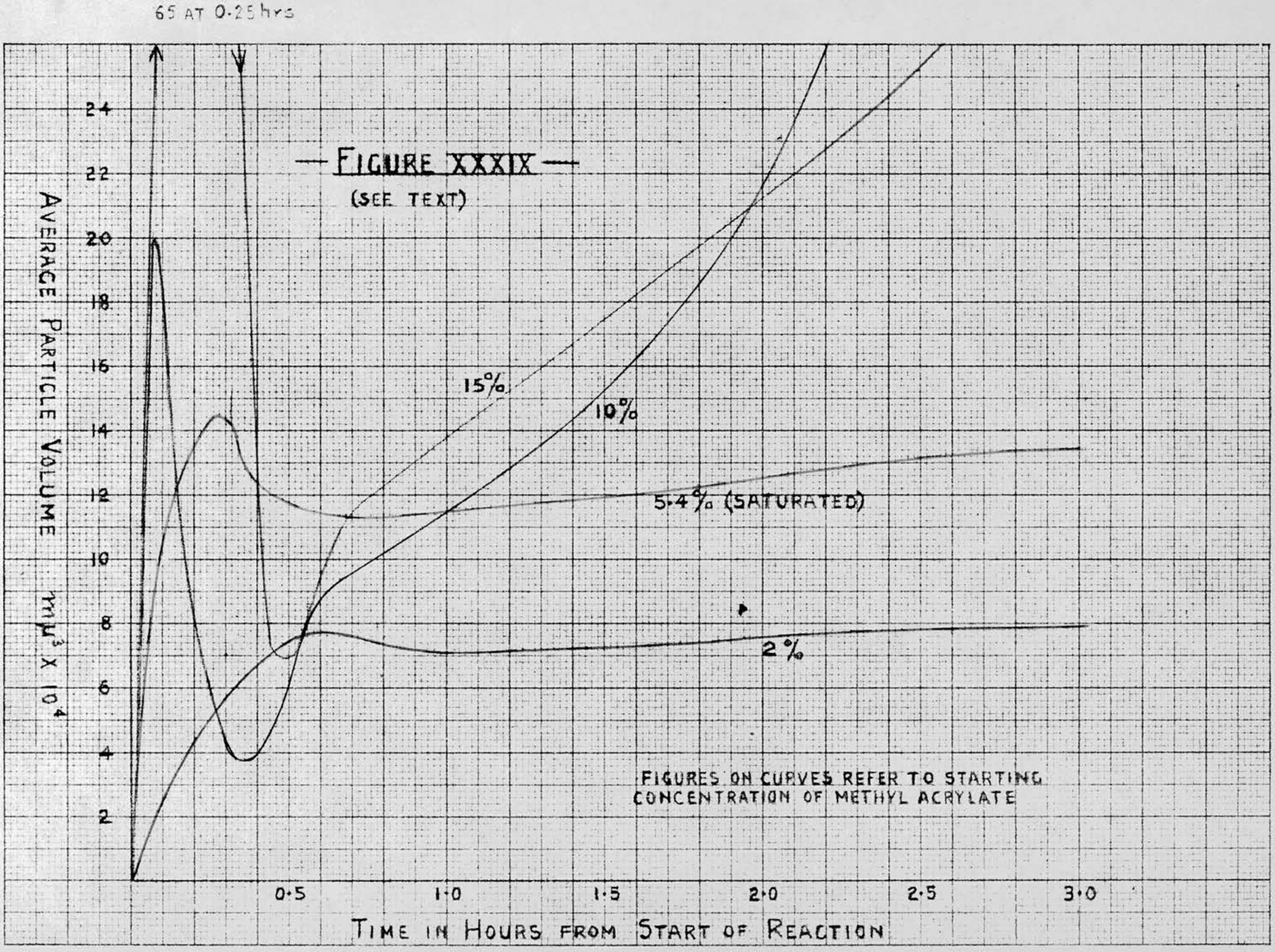
Other experiments run with various amounts of excess monomer beyond that required to saturate the water phase showed the same behaviour pattern as that illustrated in the experiment detailed above. The curve showing particle volume growth for a dispersion of 15% methyl acrylate in water is shown in Figure XXXIX, together with the curves for 10%, a saturated solution, and a 2%



— FIGURE XXXVIII —

EXPT 3192-DI

FIRST THREE HOURS



— FIGURE XXXIX —

(SEE TEXT)

solution, replotted from Figures XXXVIII, XXXVII, and XXXIII, respectively. In order to put these curves on a comparable basis, the time is taken, not as the time from addition of the catalyst, but as the time from the start of the reaction as evidenced by the first detectable change in light transmission. This merely has the effect of moving the curves bodily along the time axis, so that all of them are brought to a common origin.

e. Summary of Results

The growth of particle size when excess monomer is present is seen to follow the same pattern as shown by solutions of monomer up to the saturation point, i.e. the reaction exhibits five distinct phases:

1. An initial "no reaction" period.
2. Rapid development of large particles.
3. Decrease in average particle size.
4. Growth of particle size to approximately the initial value.
5. Increase of particle size due to agglomeration.

The comparison brought out in Figure XXXIX shows that when excess monomer is used, these phases, particularly numbers 2, 3 and 4, are emphasized in degree, and are accelerated. The particle size first developed is larger, and appears to increase with increase in concentration, the drop in particle size is more pronounced, and more rapid, and the subsequent "re-growth" is also great and rapid.

It is interesting to note that at the time of writing (October, 1944) a recent report[49] by Dr. P. P. Debye (a son of Professor P. J. W. Debye) published in June, 1944, and given limited circulation by the Office of the Assistant Rubber

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[49] War Production Board (U.S.A.)

Office of Assistant Rubber Director for Research and Development of Synthetics. General Report No. 12.

"Analysis of GR-S Latex by Light Scattering" by P. P. Debye

Director in the U. S. A., has just come to the author's attention. This report describes studies of particle sizes of GR-S latex (butadiene-styrene copolymer) by observations of the angular distribution of radiation scattered by the latex. Samples withdrawn from both plant and laboratory runs at periods up to fourteen hours, were evaluated. The following conclusion is quoted directly from the summary on page 56 of the report:

"The results can be expressed qualitatively in saying that in the first hour or two of the polymerization particle diameters increase rapidly until they reach a maximum, then gradually decrease to a minimum at about 2/3 polymerization time and then show possibly a slight rise towards the end of the polymerization period."

The general agreement between the results reported in this thesis, and those reported by Doctor Debye, working with a different system, and evaluating results by a different method, is striking.

4. Discussion of Results

It must, we believe, be considered reasonable to postulate that each "particle" in these dispersions is the result of the generation of a nucleus, and that growth around the centre so created yields ultimately the stable discreet sphere of polymer to which we apply the term "particle."

Consideration of the courses followed by the volume of the "average" particle, and the number of these particles, during the polymerization, then leads us to the following views.

a. The first detectable reaction (phase 2) is the result of the generation of a (relatively) few nucleii, followed by rapid growth to the size characteristic of the system.

b. The next part (phase 3), during which the average particle volume decreases, must result from generation of nucleii at a rate greater than the rate of growth. It should be noted again that during this period the rate of polymer formation is high, reaching its maximum near, or immediately following, the end of this phase. This means that the ratio of the rate of nucleus formation to the rate of propagation is not constant, as is so frequently assumed in discussion of the kinetics of chain reactions, but that this ratio increases, either by increase of the rate of nucleus formation, or by decrease in the rate of propagation, or both. Since the rate of polymer formation does not fall off during this period, it seems probable that the rate of propagation remains constant, or nearly so, and that the rate of generation of nucleii increases.

There is also the possibility that more than one type of nucleus formation may be involved. In discussing different possible processes of nucleus formation, Mark and Raff[50] point out that nucleii of (a) short (about 10^{-2} secs.) and (b) long (up to several days) average lifetimes have been recognized, and that both may be formed in a single reaction system. Concerning this last possibility, they say, "It seems that this case occurs more frequently than was previously assumed, and is responsible for the complicated course of many of the polyreactions in the form in which they are carried out in practice."

It is evident that one can readily explain the observed course of particle size growth on this basis. One need only postulate that the first particles formed are the result of production of the (a) type of nucleii, and that those formed later are from the (b) type, of relatively long average lifetime. This is, however, at our present stage of knowledge, pure speculation, and no matter how interesting or plausible such an idea may be, further quantitative experimental evidence is required to decide whether this mechanism, or that based on the view that nucleus formation is auto-catalytic or self accelerating, is closer to reality. For the time being, we shall adhere to the simpler idea that acceleration of the rate of nucleus formation is responsible for the observed phenomena.

[50] Reference 53, below. Page 214.

c. In the next phase (phase 4) the rate of generation of nucleii falls off rapidly, to become once more slower than the rate of propagation. From this point on, the polymer produced (note that most of the polymer is still to be formed) is in particles of the same size range.

This drop in the rate of formation of nucleii must be the result of either (1) tying up all available catalyst

(2) exhaustion of monomer in the unactivated state, i.e. most of the monomer present (note again that only a small part has polymerized at this stage) is in an activated condition, or

(3) both (1) and (2) have occurred.

At this stage we have insufficient evidence to say which of the above possibilities is closest to fact, but it may be observed, by reference to the work described in Section VII, 3, a, above, that the amounts of catalyst used in the experiments now under discussion are well above the range where amount of catalyst has any influence on particle size. This lends support to the idea that the bulk of the methyl acrylate is brought into an activated state quite early in the reaction period, this period being regarded as the time taken for most of the polymer (say 80 to 90%) to be formed.

In this connection, an incidental observation made repeatedly during these experiments seems pertinent. When the system water - dispersing agent - monomer has been assembled in the reaction vessel and heated to refluxing temperature, the amount of reflux depends on the temperature at which the mixture is maintained, and remains constant as long as heat is supplied to maintain this temperature. Within a very few minutes after the addition of the catalyst, however, the reflux dies down to almost nothing, although there may be no evidence that the polymerization has begun, and an increase in temperature of several degrees is required to restore the reflux to its original amount.

This would seem to indicate than an initial reaction between monomer and catalyst occurs, not leading directly to polymer formation, but converting the monomer to a state in which its volatility is decreased. It has been pointed out by R. E. Burk[51] that germ formation may, in the case where a catalyst is present, consist first of addition of catalyst to monomer,

$$H + K \longrightarrow HK$$

and that this would, presumably, be a fast process, occurring practically without activation energy, and with a steric factor approaching unity. If HK can act as a nucleus, the result is a first order nucleus formation with regard to H, but if HK is incapable of acting as a nucleus by itself, a second step

$$HK + H \longrightarrow H_2$$

which would be a second order reaction with regard to H, must follow, and that this is the reaction which actually leads to the formation of a polymerizable nucleus.

There is an obvious analogy between this point of view and the observation that reflux drops sharply when catalyst is added to the system.

d. Increase in particle size in the stage of the reaction beyond the point where the "number of average particles per gram" reaches a maximum, is the result of agglomeration of particles already formed.

It should be pointed out that, although it has been postulated that each "particle" in these aqueous dispersions results from generation of a nucleus, it has <u>not</u> been stated that each particle is the result of the generation of only one nucleus, in the sense in which that term is generally used in discussing the

[51] Reference 54, below. Pages 165-166.

kinetics of chain polyreactions.[52,53,54,55,56]. In this sense each nucleus is regarded as leading to the development of one macromolecule, of "average" molecular weight. Were it true that each particle in the aqueous dispersions resulted from the generation of but one nucleus, this would be equivalent to saying that the "molecule" and the "particle" are one and the same. At one time in the course of this work it was considered that the very small particles might be identical with the usual macromolecules, with molecular weights of the orders assigned them by the customary determinations of intrinsic viscosity, according to the procedure of Staudinger[57] and others[58]. Calculation quickly showed, however, that particles with a volume of 6×10^4 $m\mu^3$ - among the smallest final particles identified in these experiments - must contain about 600,000 methyl acrylate molecules, and have a molecular weight of about 5,000,000. By the usual concepts of high polymer chemistry, such a polymer would be quite insoluble in any solvent, whereas the polymers from these experiments are all readily soluble in acetone, benzene, ethyl acetate, and a number of other solvents, so that it must be considered certain that each such particle contains many - about five hundred - macromolecules. The larger particles obtained in the experiments described in this section, and in Section VII, above, must consist of numbers of macromolecules ranging from one thousand to four or five thousand, while the number of macromolecules per particle in methyl acrylate dispersions of commercial

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[52] Burk, Thompson, Weith, and Williams - "Polymerization" - N. Y. 1937.

[53] Mark. "Physical Chemistry of High Polymeric Systems" - N. Y. 1940.

[54] Mark & Raff. "High Polymeric Reactions" - N. Y. 1941.

[55] E. P. Irany. J.A.C.S. 62, 2690 (1940)

[56] "Chemistry of Large Molecules." Edited by Burk and Grummit. N. Y. 1943.

[57] Staudinger. "Die Hochmolekularen Organischen Verbindungen" - Berlin. 1932.

[58] For a particularly thorough review and discussion of viscosity data and their interpretation, see Reference 53, above, p. 258 et seq., and the references therein cited. Also Reference 56, pages 125 to 189.

production must be of the order of ten thousand. These estimates are based on a value of about 1000 for the degree of polymerization of the methyl acrylate, which is a reasonable average value on the basis of current knowledge.

There is nothing basically incompatible in the statements that each particle results from the initial formation of one nucleus, and that each particle ultimately contains many macromolecules, each of which is initiated by formation of a nucleus. It is conceivable, and even probable, that newly generated nucleii may attach themselves to the growing particle, or may be formed at or on its surface. It seems likely, from other evidence which will be discussed in the following Section, that the inter-phase boundaries in these systems are the seat of much of the reactivity, and the view that nucleii may form at or on the surface of the growing particle is entirely consistent with this.

This review of the growth of particle size during polymerization is necessarily rather qualitative in nature. The author believes that the conclusions drawn, and the discussion given, go as far as is reasonable on the basis of the experimental evidence. To draw more precise, or more nearly quantitative conclusions would be, in his opinion, unjustified, and the reader is cautioned against so doing.

Further work of a more precisely quantitative nature is required to answer the questions raised by the observations which have been made. Some of these questions are indicated in the discussion above, and others will be discussed in Section XI, below, which summarizes the conclusions and outlines future work.

IX MECHANISM OF "EMULSION POLYMERIZATION"

1. General Review

It has been shown, by other investigators, and by the work described in the preceding sections, that methyl acrylate may be polymerized in the form of an aqueous dispersion by heating solutions of the ester in the presence of small amounts of hydrogen peroxide. These solutions may be far below the concentration necessary to saturate the water, and, if a small amount of a suitable dispersing agent is present to prevent precipitation of the polymer as it forms, the resulting dispersions are identical in properties with those made by the customary "emulsion polymerization" technique. The same observations have been made for ethyl, n-propyl and n-butyl acrylates. (The solubilities of these esters in water are given in Appendix D.)

We have thus established beyond reasonable doubt that polymerization can and does occur in water solutions of the lower acrylic esters, with generation of dispersed polymer particles which separate from the solution as they are formed. We know, therefore, that the so-called "emulsion polymers" may be formed without having an emulsion present at all, and that the mechanism discussed in the introductory part of this thesis (Section II, a), does occur.

Additional evidence may be cited on this point. Reference has been made (page 10) to the experiments described by Trommsdorff where he floated a layer of monomeric acrylic ester on a solution of small amounts of catalyst and dispersing agent in water, and kept the system at a temperature of about 60°C. for several days. The monomer layer dwindled slowly away while the water phase became milky, and finally all the ester was found to be polymerized and dispersed in the water.

2. Qualitative Experiments

The present author has used Trommsdorff's technique on a number of compounds, to determine whether or not the mechanism proposed may be considered applicable. All the lower acrylates and methacrylates, up to and including octyl, show the behaviour described, but when the higher members of the series are tested, they are found not to be polymerizable in this way. The precise borderline has not been established, because of the difficulty of preparing all the compounds in the series, but it is evident that the effect disappears at the point where water solubility also disappears. Cetyl methacrylate, for example, will not polymerize under these conditions, and all efforts to polymerize it under the usual "emulsion polymerization" conditions have been unsuccessful, in the sense that a stable dispersion, of fine particle size, has not been produced.

In the cases where the polymerization does proceed in this way, the rate of disappearance of the monomer layer is observed to be roughly proportional to the solubility of the monomer in water.

Styrene, a hydrocarbon, ordinarily listed in literature and handbooks as "insoluble" in water, polymerizes quite readily under the conditions described. The author has found, by bromine absorption methods, a very definite and measurable water solubility for styrene, of the order of 0.02%.

An experiment* recently reported by Dr. Hermann Mark in a lecture on High Polymers at Brooklyn Polytechnic Institute, and credited to Mark and Hohenstein, goes even further than this. Styrene was suspended in a small cup over a solution of catalyst and dispersing agent in an evacuated vessel. Polymer was formed in the water phase by transfer of vapor, and the rate of formation was found to increase as the temperature was raised. When inhibitor was added to the styrene, the reaction proceeded as before, but when inhibitor was added to the water, a marked delay was produced.

3. Discussion of Experiments on Particle Growth

In the work described in Section VII of this thesis, it has been shown that rate of addition of monomeric methyl acrylate to the water phase does not affect particle size, and that pre-emulsification of part of the monomer in the water phase is likewise without effect. Both these observations tend to support the view that the reaction occurs in the aqueous phase, and further evidence of a quantitative nature may be obtained by consideration of some of the experiments recorded in Section VIII.

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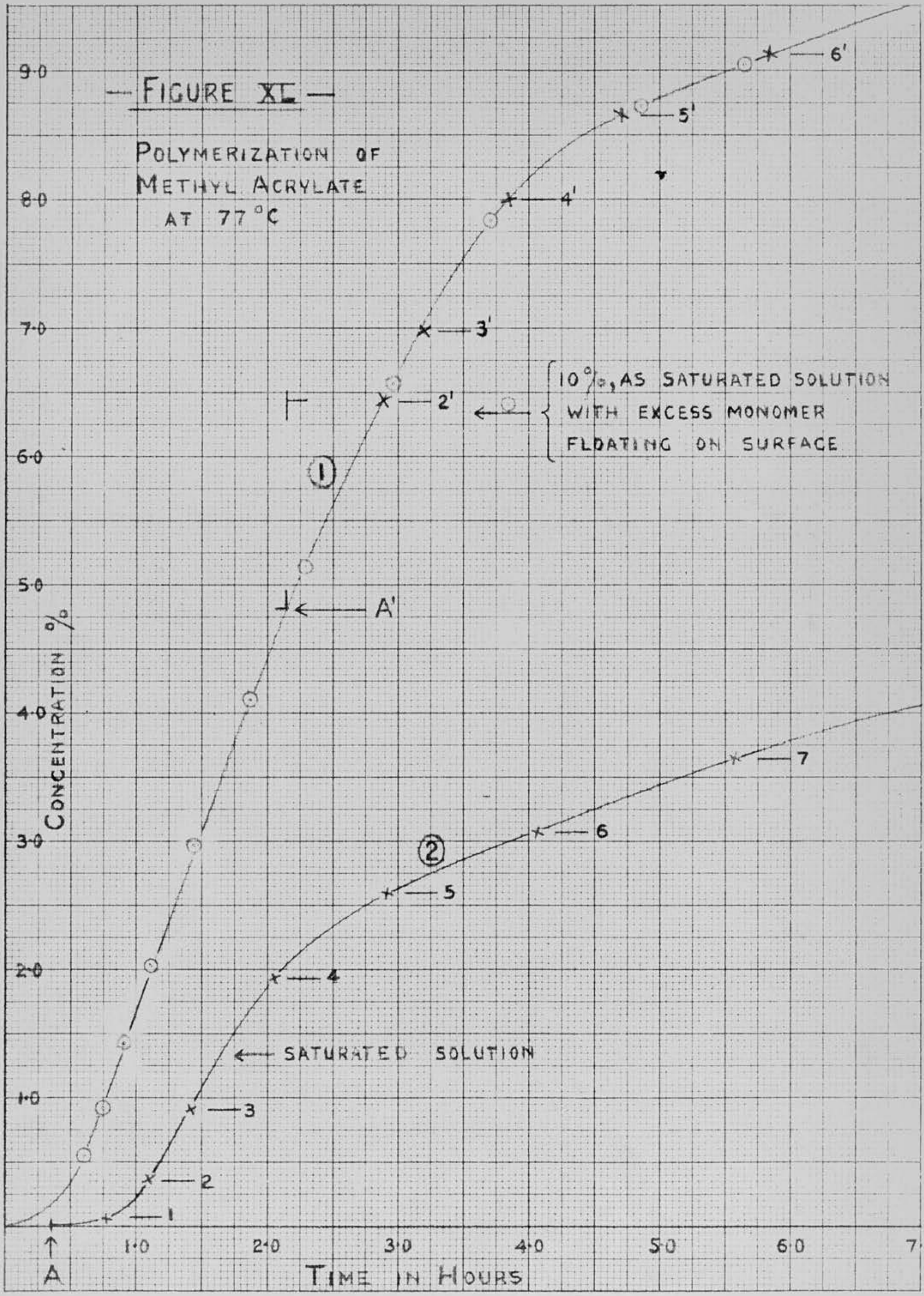
* Communication from Dr. C. L. Levesque - November, 1944.

If the idea that the polymerization occurs in the aqueous phase is correct, then it is to be expected that the rate of polymer formation will remain constant as long as monomer is present in an amount greater than that required to saturate the aqueous phase. From the point where the excess disappears, the rate of polymer formation should be characteristic of a saturated solution of monomer.

Figure XXXVI records the progress of the polymerization of a saturated solution of methyl acrylate, in the apparatus illustrated in Figures XXVIII to XXXI. Figure XXXVIII records the progress of the polymerization of a saturated solution, in the same apparatus, with a layer of excess monomer present on the surface to replenish the solution as monomer is converted to polymer and removed from the reaction. In Table 32 and Figure XL the rates of polymer formation in these two experiments are compared.

Table 32

Experiment 3272-D1. Saturated solution - no excess (Curve 2)		Experiment 3192-D1. Saturated solution, with excess monomer. (Total, 10%) (Curve 1)	
Elapsed time (hours)	Polymer concentration (percent)	Elapsed time (hours)	Polymer concentration (percent)
0.766	0.093	0.60	0.543
1.083	0.392	0.75	0.918
1.417	0.927	0.88	1.439
2.050	1.964	1.10	2.065
2.917	2.622	1.38	2.959
4.067	3.091	1.87	4.102
5.567	3.657	2.28	5.125
10.62	4.442	2.97	6.560
11.63	4.479	3.70	7.835
21.77	4.662	4.85	8.725
24.35	4.721	5.65	9.043
-	-	27.03	10.170



— FIGURE XI —

POLYMERIZATION OF METHYL ACRYLATE AT 77°C

The saturated solution, Curve 2, after it has passed through the usual induction period, shows a falling rate corresponding approximately to that of a bimolecular reaction. The system with the excess monomer, however, after it has passed through its induction period, exhibits a constant rate up to a polymer concentration of about 4.5%, and then the rate falls off in much the same way as that of the saturated solution.

Now it is found that if Curve 2 is compared with the upper part of Curve 1, it corresponds very exactly. Curve 1 is given by the circles; Curve 2 by the crosses. When Curve 2 is superposed on the upper part of Curve 1, points 2 to 6 fall as indicated by points 2', 3', 4', 5' and 6'. This shows that the upper part of Curve 1 depicts the polymerization of a saturated solution, and that the lower portion of this curve, represents also the polymerization of a saturated solution in which the saturation is maintained by the presence of excess monomer. This is regarded as good evidence that the solution remains saturated under the conditions of these experiments.

It has been noted that the lower portion of Curve 1, after passing through the induction period, becomes substantially a straight line, and remains so up to a concentration somewhere between 4.5 and 5.0%. This has been confirmed repeatedly, and typifies the so-called "zero-order" reaction, where the concentration of reactants is maintained constant by some external regulating factor, so that the rate does not change.

There is one difference between the polymerization of the saturated solution represented by Curve 2, and that represented by the upper part of Curve 1. In the former case, the reaction is started with a saturated solution, and has to pass through an induction period, whereas in the latter case, the reaction is already under way when the excess is used up, and the polymerization of the saturated solution (without excess monomer present) begins. For this reason, point 1 on Curve 2 is omitted in superposing the two curves.

In these experiments, particle size determinations were made, so that we know, in the case of Curve 2, just when the reaction started, as shown by the first appearance of turbidity. This is indicated by point A. If now we take the time interval of 0.75 hours between point A and point 2, and measure of this same time interval from point 2' on Curve 1, we arrive at point A' as the point where the excess monomer must have disappeared. While the legitimacy of this procedure may be questioned, it is most interesting to note that point A' gives the concentration of the saturated solution as (10.0 - 4.8) or 5.2%. The best value obtainable for the solubility of methyl acrylate in water by determinations of saponification numbers (see Appendix D) is 5.3%.

4. Study of Rate of Polymerization of Ethyl Acrylate

On the basis of the theory that the polymerization goes on in the aqueous phase, it was reasoned that, when excess monomer was present, the rate of polymer formation should remain constant until the excess disappeared, and then should follow a course characteristic of a saturated solution. It has been shown, in the part immediately preceding (this Section, Part 3; Figure XL) that this behaviour is actually found for methyl acrylate.

Because methyl acrylate has a fairly high solubility in water, the straight portion of the polymer formation curve is rather short unless we work at relatively high concentrations, of the order of 15 to 20%. This introduces the complication of a greater amount of precipitation of polymer on the walls of the flask and in the circulating system, so it is more appropriate to conduct these experiments with an ester less soluble in water than methyl acrylate. Such an ester is the next higher member of the series, ethyl acrylate, of which the solubility in water (see Appendix D) is 1.82%.

Polymerization rate studies of ethyl acrylate were made, and the same type of behaviour was found as with methyl acrylate, except that, at the ten percent level, the straight portion of the curve is much prolonged, and the rate of polymer formation begins to fall off when a concentration above eight percent is reached. This is exemplified in Figure XLI, in which the rate of polymer formation in a saturated solution of ethyl acrylate (Curve 2) is compared with that in a saturated solution of ethyl acrylate with excess monomer present so that the final concentration of polymer should be ten percent (Curve 1). Both reactions were run in the apparatus shown in Figure XXVIII, with the optical cell omitted from the circulating system. The record of these experiments is given below.

Experiment 12163-G1. Polymerization of saturated solution of ethyl acrylate with excess monomer (total concentration 10%)

1300 grams freshly distilled water were shaken repeatedly in the reaction flask with

150 grams freshly distilled Ethyl acrylate

(b.p. 98.8°C. at 756 mm. Sap. No. 557. "purity" 99.9%)

and allowed to separate

To the lower layer, via the circulating system, was added

4.2 grams Sulphated Castor Oil #565, 71.4% (2% solids on monomer) dissolved in 50 gms. water.

The whole mixture was then heated to refluxing temperature (83°C.) while the circulating pump was kept running briskly. Added, as catalyst, 15 ml. 30% H_2O_2 to start reaction.

The data obtained are recorded in Table 33.

Table 33

Time Dec. 16 1943	Elapsed time (hours)	Temp. in flask (°C.)	Sample number	Percent solids	Percent polymer
16:07	0	84	0	0.195	-
17:07	1.00	83	1	0.720	0.525
18:25	2.33	82	2	1.816	1.62
20:20	4.25	83	3	2.60	2.41
Dec. 17					
0:10	8.08	84	4	4.19	4.00
2:00	9.92	83	5	4.96	4.77
4:15	12.17	83	6	5.96	5.77
6:07	14.00	83	7	6.75	6.56
9:00	17.92	83	8	8.48	8.29
12:00	19.92	83	9	9.34	9.15
14:10	22.08	83	10	9.61	9.42
16:00	23.92	83	11	9.77	9.58

Experiment 3034-G1. Polymerization of saturated solution of ethyl acrylate.

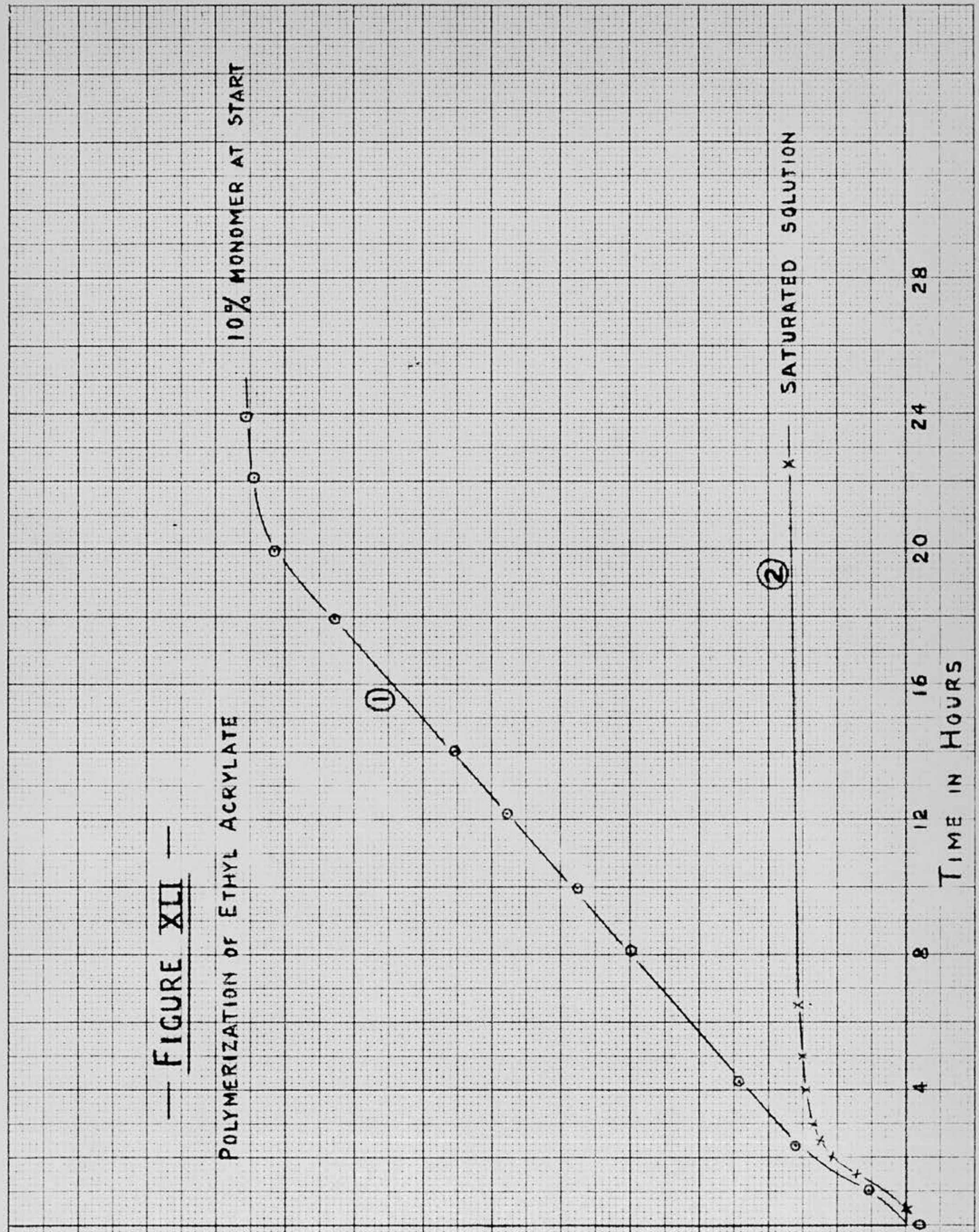
1560 grams freshly distilled water were shaken with 75 grams of "pure" ethyl acrylate, b.p. 98.8°C., Sap. No. 556, in a 2 litre separating funnel. The shaking was repeated several times, and the mixture allowed to separate overnight. The following morning, 1500 grams of the lower layer of saturated solution was separated and placed in the polymerization flask with

0.78 grams Sulphated Castor Oil #565 (2% solids on monomer in soln.)

Flask contents heated to 83°C. (gentle reflux) with circulating pump running, and added, as catalyst

15 ml. 30% H_2O_2

Table 34 records the data obtained.



— FIGURE XII —

POLYMERIZATION OF ETHYL ACRYLATE

Table 34

Time March 3 1944	Elapsed time (hours)	Temp. in flask (°C.)	Sample number	Percent solids	Percent polymer
10:04	0	82	0	0.0251	-
10:34	0.5	83	1	0.0270	.002
11:34	1.5	83.5	2	0.747	0.722
12:04	2.0	83	3	1.118	1.093
12:34	2.5	83	4	1.283	1.258
13:04	3.0	83	5	1.358	1.333
14:04	4.0	83	6	1.461	1.436
15:04	5.0	83	7	1.533	1.508
16:34	6.5	83	8	1.588	1.563
March 4					
8:35	22.5	83	9	1.720	1.695

Figure XLI shows the course of the polymerization in these two experiments. It will be observed that the general relationship between them is the same as that between the analogous experiments on methyl acrylate, graphed in Figure XL, with the differences already noted. There is some evidence, in the slope of the straight portion of Curve 1 in comparison with the slope at the beginning, that the solution was not quite saturated, but this is not certain, and does not change the general aspects of the discussion which follows.

While an impressive weight of evidence has been accumulated, from the work reported in this thesis and from the work of others which has been cited, to show that in the "emulsion polymerization" process, the actual polymerization goes on in the aqueous phase, with the organic phase acting as a reservoir of reactant, there is one important characteristic of the process which is still unexplained. In the introductory discussion (page 1) it was pointed out that one of the great drawbacks of solution polymerization is the long time required. One of the greatest advantages of "emulsion polymerization" is the rapidity with which the reaction proceeds to practical completion. If the mechanism is merely that of the polymerization of a saturated solution of monomer in the water phase, then the rate of polymerization of this saturated solution must govern the rate of polymer formation in the whole system. When we consider the rates of polymerization which have been found for saturated solutions of methyl and ethyl acrylates (Figures XL and XLI) we find that - even if we assume that the solutions were not quite saturated, and take the most optimistic value for the possible rate - the polymerization of an emulsion containing 30% monomer should require at least 24 hours. We know, however, that such an emulsion can be polymerized to practical completion in either laboratory or plant in about an hour. Any comprehensive theory of the mechanism of the process must explain this fact.

A very obvious difference in the experiments run in the apparatus of Figure XXVIII with a layer of monomer floating on a saturated solution, in comparison with the usual technique, is the absence of mechanical agitation. Now, if the process is dependent only on the polymerization of the saturated solution, the presence or absence of mechanical agitation should have no effect on the course of polymerization of either a saturated solution or a saturated solution with excess monomer. A series of carefully controlled experiments was set up to test this.

In these experiments, much care was taken to ensure comparable conditions among all the members of the series. The same monomer, redistilled in the same way before each experiment, the same distilled water supply, the same bottle of dispersing agent, and the same bottle of catalyst, were used. The temperature was carefully regulated and any experiment which went out of control in any way was repeated. Duplicability was found to be good, and the results are regarded as being of a "better-than-average" degree of significance.

The first group consisted of four experiments as follows:

1. Saturated solution of ethyl acrylate. No stirrer.
2. Saturated solution of ethyl acrylate, with stirrer.
3. 9% ethyl acrylate. No stirrer.
4. 9% ethyl acrylate, with stirrer.

The record of these experiments is given below.

Experiment IX-1. Saturated solution. No stirrer.

1500 gms. distilled water

75 gms. Ethyl acrylate (B.p. 99.2 - 99.8°C.)

Shaken in separating funnel and allowed to stand overnight.

1492 gms. saturated solution

4.37 gms. Sulphated Castor Oil #565 (68.7% solids)

Placed in reaction flask, heated to 83°C.

Catalyst 3 ml. 30% H_2O_2

Data in Table 35.

Table 35

Time of day	Elapsed time (hours)	Temp. in flask (°C.)	Sample number	Percent solids	Percent polymer
9:44	0	83	0	0.210	0.00
10:04	0.33	83	1	0.2145	0.0045
10:24	0.67	83	2	0.60	0.39
10:44	1.00	83	3	1.18	0.97
11:04	1.33	83	4	1.51	1.30
11:24	1.67	83	5	1.66	1.45
11:44	2.00	83	6	Sample accidentally lost	
12:24	2.67	83	7	1.83	1.62
13:44	4.00	83	8	1.88	1.67
16:14	6.50	83	9	1.93	1.72

Percent polymer v. time plotted in Figure XLII, Curve 1.

Experiment IX-2. Saturated solution, with stirrer.

1492 gms. Saturated Ethyl acrylate solution

4.37 gms. Sulphated Castor Oil #565 (68.7% solids)

Heated to 83°C. in reaction flask with rapid stirring.

Catalyst 3 ml. 30% H_2O_2

Data in Table 36.

Table 36

Time of day	Elapsed time (hours)	Temp. in flask (°C.)	Sample number	Percent solids	Percent polymer
10:28	0	83	0	0.214	0.00
10:48	0.33	83	1	0.313	0.099
11:08	0.67	83	2	0.814	0.60
11:28	1.00	83	3	1.27	1.06
11:58	1.50	83	4	1.42	1.21
12:58	2.50	83	5	1.53	1.32
13:58	3.50	83	6	1.56	1.35
15:58	5.50	83	7	1.63	1.42
17:13	6.75	83	8	1.72	1.51

Percent polymer v. time plotted in Figure XLII, Curve 2.

Experiment IX-3. Saturated solution plus excess monomer (Total 9%). No stirrer in flask.

1350 gms. distilled water

140 gms. Ethyl acrylate (B.p. 99.2 - 99.8°C.)

Shaken several times and allowed to separate overnight.

Next morning added to lower layer

4.37 gms. Sulphated Castor Oil #565 (68.7% solids)

dissolved in 30 gms. saturated ethyl acrylate solution.

Heated to 83°C.

Catalyst 3 ml. 30% H_2O_2, washed through funnel with 20 gms. saturated ethyl acrylate solution.

Data in Table 37.

Table 37

Time of day	Elapsed time (hours)	Temp. in flask (°C.)	Sample number	Percent solids	Percent polymer
9:45	0	82	0	0.160	0.00
10:00	0.25	82.5	1	0.175	0.015
10:15	0.5	83	2	0.174	0.014
10:25	0.67	83.5	3	0.385	0.225
10:35	0.83	83.5	4	0.850	0.690
10:45	1.00	83	5	1.22	1.06
11:00	1.25	83	6	1.62	1.46
11:15	1.50	83	7	1.93	1.77
11:45	2.00	83	8	2.33	2.17
13:00	3.25	83	9	3.36	3.20
14:15	4.50	83	10	4.30	4.14
16:00	6.25	83	11	5.69	5.53

Percent polymer v. time plotted in Figure XLII, Curve 3.

Experiment IX-4. Saturated solution plus excess monomer (Total 9%). With stirrer.

1400 gms. distilled water

140 gms. Ethyl acrylate (B.p. 99.2 - 99.8°C.)

4.37 gms. Sulphated Castor Oil #565 (68.7% solids)

Heated to 83°C. with rapid stirring.

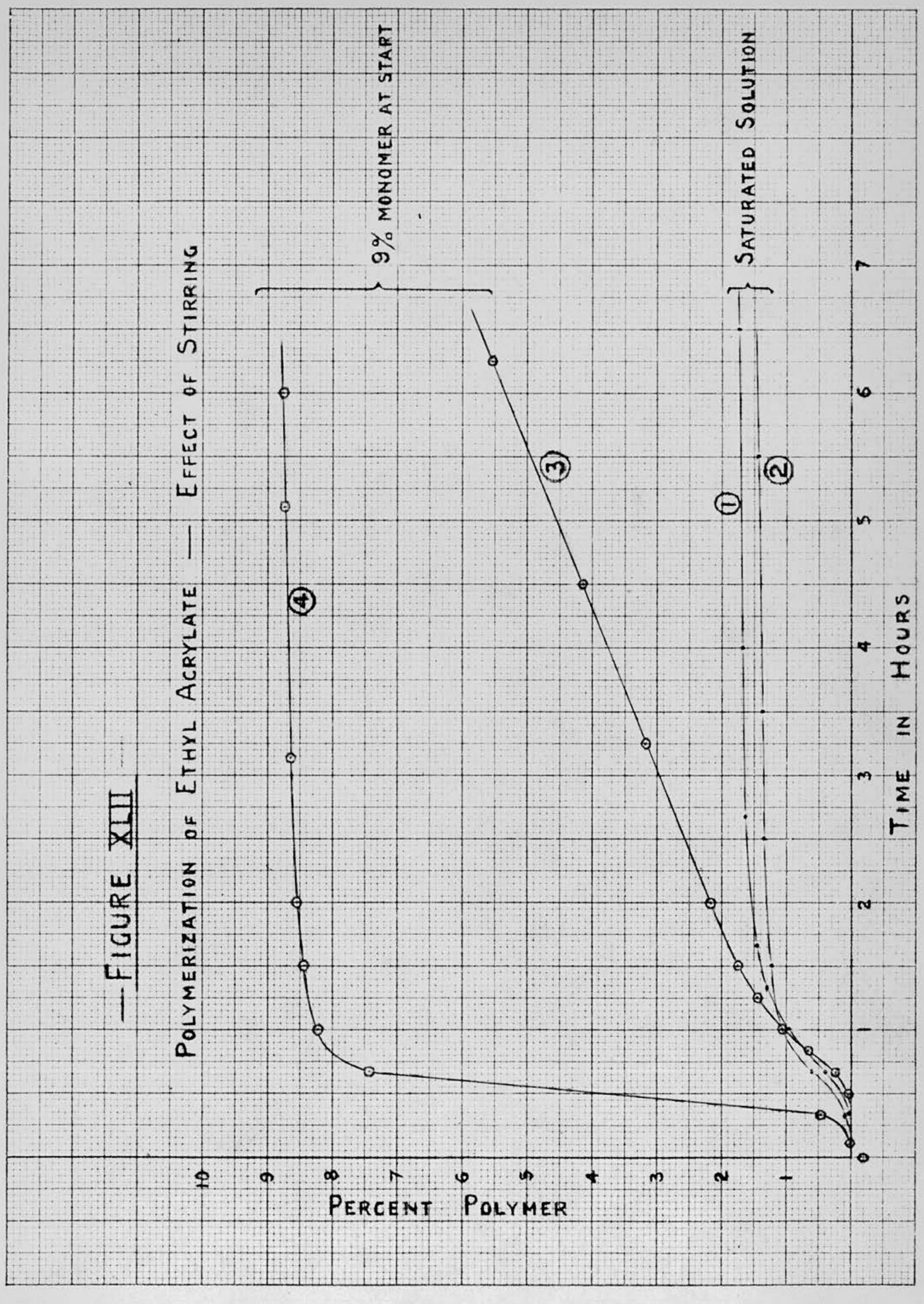
Catalyst 3 ml. 30% H_2O_2

Data in Table 38.

Table 38

Time of day	Elapsed time (hours)	Temp. in flask (°C.)	Sample number	Percent solids	Percent polymer
9:59	0	83	0	0.210	0.00
10:19	0.33	84	1	0.680	0.470
10:39	0.67	85	2	7.63	7.42
10:59	1.00	83	3	8.42	8.21
11:29	1.50	83	4	8.65	8.44
11:59	2.00	83	5	8.74	8.53
13:07	3.13	83	6	8.86	8.65
13:59	4.00	83	7	8.90	8.69
15:05	5.10	83	8	8.96	8.75
15:59	6.00	83	9	8.99	8.78

Percent polymer v. time plotted in Figure XLII, Curve 4.



—FIGURE XLII

POLYMERIZATION OF ETHYL ACRYLATE — EFFECT OF STIRRING

Comparison of the data, and of the four curves of Figure XLII, shows that the mechanical stirring has almost no effect on the rate of polymerization of the saturated solution. The reaction starts earlier, which is reasonable, because it must be remembered that it is set off by adding the catalyst, and the effect of stirring must be to distribute the catalyst more quickly throughout the solution.

The same effect of the stirring in making the reaction start earlier is evident in comparing the experiments in which 9% ethyl acrylate is polymerized, but in addition, it produces a startling increase in the rate of polymer formation so that, at the end of an hour, the reaction with stirring is 91% complete, while that without stirring is but 12% complete. The ratio of the rates of polymer formation represented by the straight portions of the two curves is 28 to 1, and the maximum rate attained at any point by the system without stirring is one twelfth of the rate in the system which is stirred.

This increase in rate of polymer formation produced by mechanical agitation of the system when excess monomer is present over the amount required to saturate the water phase has been confirmed repeatedly, and it seems clear that such agitation is necessary to have the reaction proceed at the high rate we have come to regard as characteristic.

In seeking an explanation for this phenomenon, we must consider what the effects of rapid agitation may be on such a system as this. The most evident effect is the creation of a large interface between the phases. The interface in the flask when the phases are separate is 187 sq. cm., and is, of course, the same regardless of the amount of excess monomer. In the experiments described above, with a total of 9% ethyl acrylate, if we assume that the average diameter of the monomer droplets is 4 microns - a reasonable value - calculation shows that the interface between the phases becomes one and a half million sq. cm.

When we consider an interface, we immediately think of adsorption phenomena, and we have considered it possible, purely as a working hypothesis, that adsorption of the catalyst at the interface may occur, or that the reactants may be concentrated or oriented at the interface in such a way that, although the reaction proceeds within the aqueous phase, a great acceleration occurs at or near the phase boundary.

If this is so, then it is reasonable to expect that variations in the size of the interface will affect the reaction rate. One of the most practical ways to vary the interface progressively is to start with a saturated solution (where no interface exists) and add progressively increasing amounts of excess monomer, keeping the degree of agitation constant. It is also reasonable to expect that, as the amount of excess monomer is increased, a point will be reached beyond which further increase will produce no corresponding increase in reaction rate, for it is evident that with a constant degree of agitation, the interface per unit volume of the system must approach a limiting value. It cannot become infinite.

To test this idea, additional experiments on the polymerization of ethyl acrylate were run at concentrations of 2%, 3%, and 5% of monomer on the water phase, equivalent to 1.95%, 2.9%, and 4.75% potential polymer concentration respectively. The reaction conditions were kept identical with those of the experiments of Tables 35 to 38, the composition of the water phase was the same, and all the components were drawn from the same supplies, and handled in the same way as in the other experiments. The actual conditions are noted below, and the data summarized in Table 39.

Experiments 6, 7 and 8 (IX-6, IX-7, IX-8)

Composition of water phase

1500 gms. distilled water

4.37 gms. Sulphated Castor Oil #565, 68.7%.

(0.2% disp. agt. solids on water)

3 ml. 30% H_2O_2

(0.2% by volume on water)

Temperature of reaction 83°C.

All three experiments run with stirrer in reaction flask.

Table 39

Experiment IX-6 30 gms. Ethyl Acrylate (1.95%)		Experiment IX-7 46.6 gms. Ethyl Acrylate (2.90%)		Experiment IX-8 71.5 gms. Ethyl Acrylate (4.75%)	
Elapsed time (hours)	Percent polymer	Elapsed time (hours)	Percent polymer	Elapsed time (hours)	Percent polymer
0.167	0.00	0.167	0.00	0.25	0.41
0.33	0.16	0.33	0.77	0.50	3.80
0.50	0.55	0.50	1.47	0.75	4.12
0.67	0.87	0.67	1.85	1.00	4.22
0.83	1.09	0.83	2.04	1.50	4.35
1.00	1.19	1.00	2.14	2.00	4.39
1.50	1.40	1.50	2.33	3.00	4.43
2.00	1.47	2.00	2.46		
3.25	1.58	3.25	2.52		

These data are plotted in Figure XLIII together with the data from Experiments IX-2 and IX-4, so that we see there the effect on polymerization rate of 0%, 10%, 70%, 165%, and 420% excess monomer over the amount required to saturate the water phase. It will be observed that the predicted behaviour is actually found, as the rate of polymer formation during the main part of the reaction exhibits an increase with excess monomer up to (very approximately) about 100% excess, after which it shows no further increase.

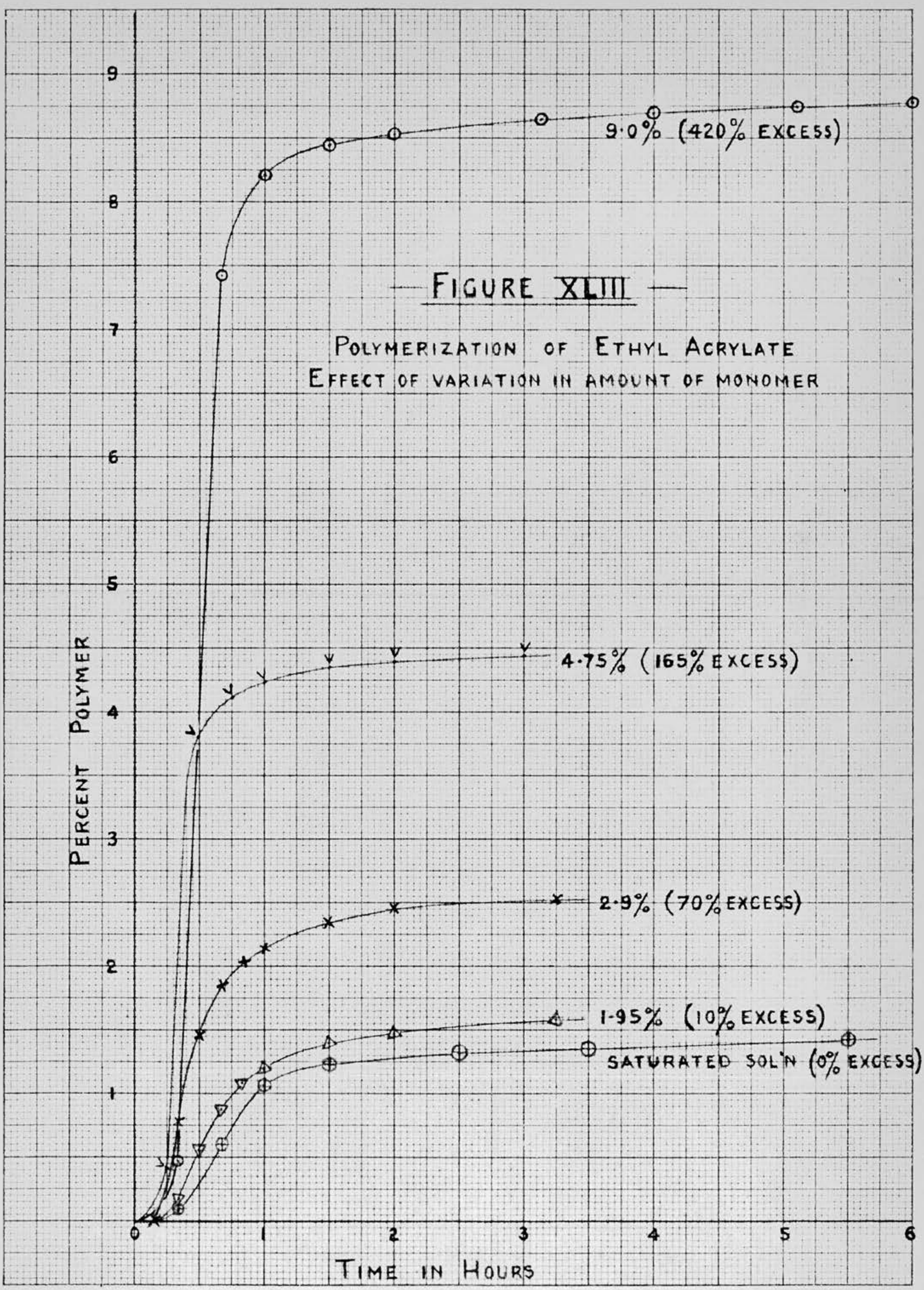


FIGURE XLIII
POLYMERIZATION OF ETHYL ACRYLATE
EFFECT OF VARIATION IN AMOUNT OF MONOMER
9·0% (420% EXCESS)
4·75% (165% EXCESS)
2·9% (70% EXCESS)
1·95% (10% EXCESS)
SATURATED SOL'N (0% EXCESS)
PERCENT POLYMER
TIME IN HOURS
0
1
2
3
4
5
6
7
8
9

This seems to confirm to some degree the validity of the hypothesis advanced to explain the observed phenomena, so, for the time being, and until further evidence can be brought to bear, we regard it as probable that the mechanism of "Emulsion Polymerization" includes a catalysis, or acceleration, of the reaction at or near the interface between the phases.

X SUMMARY OF RESULTS

The following list summarizes the principal results from the work described in this thesis.

1. A rapid optical method of determining volume (or weight) average particle sizes in polyacrylic ester dispersions has been worked out, and its validity confirmed. (Sections IV and V.)

2. An experimental confirmation of the theoretical realationship between light scattering and particle volume, as derived by Rayleigh, and amplified by Gans, has been obtained. (Section V.)

3. In the "emulsion polymerization" of methyl acrylate, the effects of variations in amount of catalyst, and amount of dispersing agent, have been determined, and found to be very marked. Approximate quantitative expressions of these effects have been derived. (Section VII, 3, a and b.)

4. It has been shown that the nature of the dispersing agent used has a great influence on particle size. (Section VII, 3, c.)

5. Evidence has been presented to show that particle size in these systems tends to decrease with increase in polymerization temperature. (Section VII, 3, d.)

6. Variations in rate of addition of monomer to the system, and preemulsification of part of the monomer in the water phase, are without effect on particle size. (Section VII, 3, e and f.)

7. The method of measuring particle volume has been extended to measure average particle size, and change in average particle size during polymerization, thus enabling growth to be studied. Growth studies have been made. (Section VIII.)

8. The most striking features of the particle growth are that

(a) A "characteristic" size is established very rapidly.

(b) This is followed by a marked and rapid drop in average particle size, succeeded by

(c) A return to the "characteristic" particle size, and then

(d) Agglomeration of particles already formed. (Section VIII.)

9. Evidence has been presented to show that, in "emulsion polymerization" of the lower acrylates the reaction depends on the water-solubility of the ester, and occurs in the portion dissolved in the water phase. As long as the water phase remains saturated with monomer, the rate of polymer formation is constant.

It has also been shown, however, that, when excess monomer beyond that required to saturate the water is present, stirring the system to emulsify this excess monomer produces a many-fold increase in the rate of polymer formation. A small excess produces a moderate increase in rate, which increases with increase in the amount of excess monomer, up to a point beyond which further increase does not affect the rate of polymer formation. (Section IX.)

XI SUMMARY OF CONCLUSIONS

The results of the work reported in this thesis are summarized in Section X, above. They lead to the following tentative conclusions, in addition to the conclusions implicit in the statement of results in Section X.

1. In "emulsion polymerization" of the lower acrylic esters, the formation of polymer occurs in that portion of the monomer which is dissolved in the aqueous phase, but is greatly accelerated at the interface between the phases. This effect is attributed to "interface catalysis" resulting perhaps from adsorption of catalyst at the interface.

2. The formation of nucleii - the first step in the chain reaction leading to the formation of the polymer - is a reaction starting at a low rate

and accelerating rapidly until much of the available monomer is in the form of activated material. Following this, the formation of nucleii falls off again to a rate lower than that of the propagation of nucleii into completed polymer molecules.

3. The particles in aqueous dispersions of polyacrylic esters contain several hundred to several thousand macromolecules.

XII OUTLINE OF FUTURE WORK

The results of, and conclusions from, the work described in this thesis, suggest a program for future work according to the following outline. It is, of course, obviously inadvisable to consider tackling such a program all at once. It would be reasonable to go ahead with Parts 1 and 2, about as outlined, modifying the approach as further information was acquired. Periodic reevaluations of the program would have to be made at intervals of from six to twelve months, depending on the number of people engaged in the work, and the amount of progress recorded.

1. Effect of Variables in Polymerization on Course of Particle Size Growth

Further light would probably be thrown on the nature and mechanism of the reaction by study of the effects on the course of particle size growth of:

a. Use of different types of catalysts

b. Variation in amounts of catalysts

c. Use of different types of dispersing agents

d. Variation in amounts of dispersing agents

e. Variations in temperature, within the limits imposed by the system itself.

f. Variation of pH of the system

g. Presence of different electrolytes in various amounts.

When the work described in Section VII, covering the effects of various controllable factors on ultimate particle size, was planned, consideration was given to the possibility of including the effect of pH. As the system can be buffered to a designated pH only by the use of electrolytes, and since these aqueous dispersions are very sensitive to electrolytes, it is difficult to divorce the two effects. For this reason, it was decided at that time not to attempt to investigate the effect of pH, but the attempt should be made in connection with further studies of particle growth.

2. Experiments on Rate of Polymer Formation

It is believed that further elucidation of the mechanism of "emulsion polymerization," and further data tending to support or refute the "interface catalysis" theory would be obtained by studying the effects on rate of polymer formation of

a. Degree (or rate) of agitation

b. Variation in the factors listed above under 1, a to g.

3. Particle Size Distribution

Determination of particle size distribution, and changes in particle size distribution during polymerization would probably be most informative. It has been shown that such distributions may be obtained by centrifugal fractionation, but such experiments are tedious and time consuming. It should be possible to work out an extension of the light-scattering method, determining scattering at different wavelengths, similar to the method used by Gamble and Barnett in their study of pigments, to indicate particle size distribution at least in an approximate and relative way. For this, a spectrometer type of instrument, selecting wavelengths by a prism or grating would be preferable to the present light-filter type.

The present instrument could well be redesigned and rebuilt in more compact form. Since it was built, a number of constant wattage transformers and other current regulating devices have appeared on the market, so that it would now be possible to design a null type photometer to operate directly from the power line, and so dispense with batteries. The present instrument suffers from the common defect of all "firsts" in research appliances; that it was built in as flexible a form as possible to permit changes in any point found to be unsatisfactory. It could readily be rebuilt to occupy less than half the space it does now.

4. Correlation of Particle Sizes and Molecular Weights

The polymer in an aqueous polyacrylic ester dispersion may be coagulated readily by freezing and then thawing. The precipitated polymer may then be filtered off, washed, dried, and dissolved in a suitable solvent. The viscosity of the solution may then be determined, and the molecular weight estimated.

The author has used this technique to evaluate relative molecular weights of acrylic ester polymers, but no systematic study of molecular weights in relation to particle sizes has been made.

In a very general way, the indications are that molecular weight and particle size run parallel, but this is by no means established. A study to determine the relationships would be, in the author's opinion, a worth-while enterprise in shedding light on the mechanism of the polymerization process. An extension into an effort to correlate molecular weight distribution with particle size distribution would probably be most informative.

For determination of molecular weights, the recently developed method of measuring refractive index and turbidity of solutions, developed by Professor P. J. W. Debye[59,60] at Cornell University should be considered, as being simpler, and more fundamentally sound, than the "intrinsic viscosity" method.

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[59] Journal of Applied Physics, 15, 338 (April, 1944)

[60] Lecture by P. J. W. Debye, Brooklyn Polytechnic Institute, November 25, 1944, heard by the author and recorded in Report #22, (1944) H. B. Walker.

5. Extension to Other Compounds and to Copolymerization Processes

It is obvious that the techniques used are applicable to polymerizable compounds other than the acrylates. Studies of the effects of copolymerization with other compounds, particularly bifunctional compounds capable of forming cross linked (three dimensional) polymers would, in all probability, be especially fruitful. The recent striking results of Mayo and Lewis[61] in studying the copolymerization of styrene and methyl methacrylate are evidence of the potentialities of copolymerization studies in providing insight into the mechanism of these reactions.

From this outline it will be seen that the field of research opened up by this work is very broad. The work done so far, and described in this thesis, is merely a beginning, and poses many more questions than it answers. It is the author's firm conviction that one of the criteria of research is that it must always point the way to further investigation and lead ultimately to deeper understanding of those natural phenomena which our science seeks to unravel. Along that way lies progress, but no ending.

XIII ACKNOWLEDGMENTS

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HB Walker.

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[61] F. R. Mayo and F. M. Lewis. J. Am. Chem. Soc. 66, 1594 (Sept., 1944).

XIV APPENDIX

A. Determination of Relative Density of Polymethyl Acrylate Particles in Water Dispersion

The standard polymethyl acrylate dispersion was analyzed for non-volatile solids by drying at 100°C. to constant weight. A dilution of this material, containing 2.00 grams solids per hundred grams was prepared.

A pycnometer was filled with this diluted dispersion at 30°C. and allowed to come to temperature equilibrium in a water bath at this temperature. It was then capped, washed off with distilled water, dried in a desiccator and weighed. The same operation was repeated with distilled water in the pycnometer.

This was repeated at temperatures of 35°, 40°, 45°, 50°, and 55°C. The actual weights obtained were plotted and found to lie on smooth curves. The data follow.

Temp. (°C.)	Weight of water in pycnometer (gms.)	Weight of 2% dispersion in pycnometer (gms.)
30	54.7055	54.9014
35	54.6171	54.8111
40	54.5269	54.7244
45	54.4292	54.6303
50	54.3233	54.5275
55	54.2048	54.4115

The density of the dispersed particles, relative to that of water at the same temperature, was then calculated from the following considerations.

Weight of dispersion in pycnometer x concentration (0.02)
= weight of dispersed solids
Weight of dispersion in pycnometer - weight of dispersed solids
= weight of water in dispersion
Weight of water in pycnometer - weight of water in dispersion
= wt. of vol. of water equal to volume of dispersed solids
Density of dispersed solids rel. to water at same temp. (ρ)
$= \frac{\text{wt. of dispersed solids}}{\text{wt. of equal vol. water}}$

The calculations gave the following values.

Temp.	30°C.	35°C.	40°C.	45°C.	50°C.	55°C.
ρ	1.21(7)	1.215	1.220	1.225	1.230	1.234

B. Determination of Refractive Index of "Water Phase"

Instrument used was an Abbė direct reading refractometer, Valentine Improved Precision Model, Serial No. 470, Industrial Scientific Company, Colemar, Pennsylvania. Temperature is regulated by circulating water from a thermostatically controlled water bath through the instrument.

Appendix. (Continued)

The instrument is standardized by the use of monobromnaphthalene. Determinations were made on a solution of 1.08 gms. Sulphated Castor Oil (#565) solids per litre, and on distilled water, with the following results.

R.I., sodium D line, 20°C., water 1.3329
R.I., " " " " , solution 1.3329

C. Preparation of "Pure" Acrylic Esters

General procedure. Methyl and Ethyl Acrylates.

Commercial production, ranging from 97% to 99% "purity," as determined by saponification number, was used as starting material. 500 ml. of this ester was placed in a 1 litre, round-bottomed flask with 10 gms. dibetanaphthol and 2 gms. anhydrous potassium carbonate. The flask and contents were attached to an insulated glass column 75 cm. long and 2.2 cm. diameter, (30 ins. x 7/8 in.) packed with 3/16 in. glass Raschig rings. A 2% solution of dibetanaphthol, prepared with the previous batch of distilled ester, was dripped slowly down the column to inhibit polymerization. Ratio of take-off to reflux was regulated by a stopcock, and reflux ratios between 1:4 and 1:6 were maintained. Temperature was measured at the point of take-off, and heating was done by immersing the flask in an oil bath placed on a circular electric heater regulated by a variable transformer.

"Heads" and "tails" were discarded, and the middle fraction, coming over within a temperature range of 0.2 centigrade degrees, or less, was used.

Typical analyses were.

Methyl acrylate

Boiling point, 760 mm.	80.4 to 80.6°C.
Saponification number	648 to 651
(Theoretical	651)
Acid number	0.0 to 0.1
Refractive index 20°C.	1.4022 to 1.4026

Ethyl acrylate

Boiling point, 760 mm.	99.6 to 99.8°C.
Saponification number	555 to 558
(Theoretical	558)
Acid number	0.0 to 0.1
Refractive index 20°C.	1.4067 to 1.4069

Immediately before use in polymerization experiments these esters were redistilled with addition of 2% dibetanaphthol, from a Claisen flask with a glass wool plug in the side arm to prevent entrainment and carry-over of the inhibitor.

Appendix. (Continued)

n-Propyl acrylate

This was prepared in the laboratory, by trans-esterification from methyl acrylate, and fractionated in the same way as the ethyl and methyl acrylates.

Boiling point, 760 mm.	123.5 to 123.6°C.
Saponification number	492
(Theoretical	492)
Acid number	0.1

n-Butyl acrylate

Prepared in laboratory by trans-esterification from methyl acrylate. Fractionated through a vacuum fractionating column similar to that used for the fractionations at atmospheric pressure.

Boiling point, 45 mm.	65°C.
Saponification number	435
(Theoretical	435)
Refractive index 20°C.	1.4186

D. Determination of Solubilities of Methyl Ethyl, n-Propyl, and n-Butyl Acrylates in Water

Solubility of methyl acrylate in water at various temperatures

Method: A 2-litre, 3-neck flask was equipped with a stirrer, a reflux condenser, and a thermometer, and mounted in an electrically heated oil bath controlled by an adjustable thermostat. In this flask were placed 1 kg. water, 100 gms. methyl acrylate, B.p. 80.6°C., Sap. No. 648, and 2 gms. hydroquinone.

A 25 ml. pipette was jacketed with a length of glass tube extending from two inches above the tip to just below the graduation mark. The jacket was packed with glass wool and contained a thermometer and a nichrome wire heating coil attached by a flexible lead to a variable transformer.

The contents of the flask were stirred vigorously at the desired temperature (see table below). When temperature equilibrium had been maintained for at least five minutes, the stirrer was stopped and the excess methyl acrylate allowed to separate as a layer on the surface. Separation was rapid and complete. The pipette was preheated to the same temperature by adjusting the variable transformer, the end inserted into the water layer, and a sample withdrawn, transferred to a tared flask, stoppered and chilled. Two such samples were withdrawn at each temperature.

Saponification numbers were run on the samples, using the entire sample, weighed in the tared flask. The values recorded represent, as usual, the number of milligrams of potassium hydroxide required to saponify one gram of the sample.

Appendix. (Continued)

Results

Temp. (°C.)	Sap. No. first sample	Sap. No. second sample	Sap. No. average	Solubility (percent)
29	35.1	35.1	35.1	5.42
36	34.4	33.8	34.1	5.27
41	33.1	34.9	33.5	5.18
48	33.7	32.4	33.1	5.12
54	34.4	33.5	34.0	5.26
60	34.0	33.6	33.8	5.23
68	34.1	35.0	34.6	5.34
75	33.4	32.7	33.1	5.12

These figures indicate that the solubility of methyl acrylate in water shows little change with temperature, within the range 30° to 75°C. As the errors in the method all tend to give low results, a solubility of 5.3% is considered to be the most probable value.

Solubility of ethyl acrylate in water at 30°C.

Sap. No. of ester	555
Sap. No. of solution saturated at 30°C.	10.1
Solubility 1.82%	

Solubility of n-propyl acrylate in water at 30°C.

Sap. No. of ester	492
Sap. No. of solution saturated at 30°C.	2.87
Solubility 0.58%	

Solubility of n-butyl acrylate in water at 30°C.

Sap. No. of ester	435
Sap. No. of solution saturated at 30°C.	0.7
Solubility 0.16%	

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