SEDIMENTATION EQUILIBRIA
OF
COLLOIDAL PARTICLES

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I. Summary and Conclusions

The recent work of Burton, Porter, Barkas and others on the equilibrium distribution of colloids sedimenting in large vessels shows a substantially uniform concentration throughout the body of the cell. This result is in marked disagreement with the Laplace-Einstein law of such distribution, based on the kinetic theory. The purpose of the present work was to throw further light on the causes of this departure from molecular kinetic law, if such departure should prove real, or to extend to deeper regions the scope of the earlier work on colloidal sedimentation equilibrium if the departure were not to be substantiated.

Gold colloidal suspensions made by the Zsigmondy nuclear process were allowed to settle in water in fused quartz cells about 8 mm. deep, and 8 mm. in diameter. The distribution was observed by ultramicroscopic count at intervals until a steady state was reached. To avoid those causes of disturbance which might have been responsible for the non-Laplacian results of the recent work mentioned, great care was observed in the purity of the materials, the inertness of the cell walls, the monodispersity of the colloid, the positive and exact thermostating of the sedimentation cells continuously during the entire settling period, the mechanical stability of the cells, and the method of making the observations so as not to interfere with the steady settling.

The results of this work show that the Laplacian distribution is applicable without qualification for the deepest regions observed, or about 1 cm., just as it was for the shallow regions studied by such early workers as Perrin, Westgren, Constantin, Svedberg and others. The "critical radius" as postulated by Burton is not substantiated. The "limiting concentrations" mentioned by Burton are not found. The recent work of Burton, Porter, et al., and the present work are discussed in the light of the earlier work, the Laplacian law and the theoretical studies of Mason and Weaver, Weaver, and Fürth on the duration of the transient state. Appended tables and calculations are included to substantiate the conclusions.

II. Introduction

The immediate problem was to test the equilibrium distribution of particles in a colloidal suspension in a relatively large vessel, to find further experimental evidence in connection with the validity of the molecular-kinetic laws for this case.

The early work on the distribution in the steady state of colloidal sedimentation showed agreement with the Laplacian law:

$$\log n/n_0 = - Nvgh(d_1-d_2)/RT.$$

In this equation, n is the concentration of particles at a height h above a reference point where the concentration is n_0; v is the volume of a particle, g is the gravitational acceleration constant, d_1 and d_2 are the densities of the particle and of the medium respectively, and N, R and T have their usual significance. The well known experiments of Perrin, (5) Westgren, (6) Constantin (10) and others, have shown very little significant departure from molecular kinetic behavior in colloidal suspensions.

Common experience however has often led to the supposition that in larger volumes than those studied by the early workers, the logarithmic equilibrium distribution may not exist. This possibility led Burton (1) (2) and Porter (3) and their co-workers, and Barkas (4) and later Laird (11) to carry out sedimentation experiments in larger vessels. Their results would call for the existence of a special law governing colloidal settling in deep vessels, as in each case the final state examined, and thought to be the equilibrium state, showed an essentially uniform distribution. In the work of Porter (3) and of Barkas (4), the upper very thin layer of the suspension was observed to follow Perrin's type of distribution, which, however, soon shaded off into uniformity throughout the body of the cell.

To explain the departure of these results from those to be expected on the basis of molecular kinetic theory, and from those consistently obtained by the early workers in this field, Burton and Porter advanced theories of internal behavior of the suspensions which are contradictory to the assumptions and results of the kinetic theory. Burton contends that for a given type of suspension there is a "critical radius" of the particles, such that for any particle of smaller radius the force of gravity is ineffective against the extreme activity of Brownian motion. Again, he speaks of a "limiting concentration" beyond which colloidal suspensions resist further concentration, even by evaporation. Finally he postulates electrical forces of repulsion between the particles to help account for the uniformity of the suspensions in his work. The idea of electrical forces is the most reasonable of the three suggestions, although it would cause a lateral as well as a vertical repulsion, with consequently higher concentration at the walls than in the body of a sedimentation cell. None of the logical consequences of these three suggestions is supported by experiments other than those of Burton, Porter, Barkas and Laird. Porter does not accept Burton's electrical repulsion theory, but postulates a van der Waal's equation of state for the colloidal suspension, using a co-volume term but no internal pressure term. The calculations of the effective collisional volumes of the particles show absurdly large ratios of collisional to "true" volume. Further study of the work of Porter (3) and of Barkas (4) shows unexpectedly low values of the limiting concentration and surprisingly small depths at which the surface layer shades off into the uniform concentration of the body of the cell. In short, experimental substantiation for the various elements of behavior suggested by Burton and Porter to explain their data is singularly lacking in other work on sedimentation, and the application of these suggestions to other phases of colloidal behavior such as diffusion, Brownian motion and spontaneous fluctuations would lead in almost all cases to direct conflict with experiment.

It was the aim of the present work to obtain sedimentation data in suspensions deep enough to show this uniform concentration, yet shallow enough to allow the final state to be reached in a reasonable time, and also to allow the use of the method of ultramicroscopic count. The particles were to be distinctly below the "critical radius" of Burton, and the maximum concentration was to be in excess of his "limiting concentration". Thus the experiments were carefully planned to show the uniform distribution if it existed, with the intention of allowing a study of its causes. One of the most important phases of the work was the extreme care to be used in the technique of making and handling the suspensions, to eliminate the spurious effects which may have been present in the work of Burton, Porter, Barkas and Laird. The fact that the results of this present work are entirely in accord with the molecular-kinetic laws seems good evidence that the deviations from this law as found in the recent work mentioned must be ascribed to such external causes as faulty manipulation and insufficient attention to the theoretical calculations of the duration of the transient state.

III. Experimental Methods

In order to obtain significant data on the equilibrium state of colloidal sedimentation which may be checked with theoretical calculations, it is necessary that the suspension be monodisperse, free from all contamination, mechanical disturbance, appreciable thermal gradients, and strong light, and that the manner of obtaining data be such as to have the minimum effect on the steady approach to the equilibrium condition. It is also advisable to compare the time at which such equilibrium has been reached with the best theoretical calculations of the duration of the transient state. To comply with these requirements, the suspensions were made by the Zsigmondy nuclear process in water supplied by a specially constructed still which produced "conductivity" water low in inert suspended matter. The suspension was allowed to settle in a fused quartz cell solidly mounted in a heavy and closely thermostated observation trough bolted to a large concrete pier on a sub-basement floor. Ultramicroscopic counts were taken with the aid of a cored carbon arc and an adjustable optical system mounted separately from the concrete pier. The room was thermostated.

To produce the water for the suspensions, a special still was built as shown in Figure 1. It comprises a 5 liter Pyrex distilling flask(A) with an elongated exit tube extending to the bottom of a tinned copper settling chamber (B), heavily lagged with soft pressed felt. The dry steam from the extreme upper end of this chamber passed into a solid tin tube (C) of 1/4" bore with its intake end flared obliquely and curved downward to cause any possible unintended condensation to drop back into the settling chamber, and go to waste. This solid tin tube (C) passed obliquely downward without a break through a condenser jacket (D), through which air was circulated at such a rate that only part of the steam was condensed, and the resulting water left hot as it passed into a Jena glass collecting bottle (E). The uncondensed steam carrying practically all the foreign gases was taken through a second condenser (F) and collected in a common bottle (G).

The charging stock for the Pyrex distilling flask was commercial distilled water, of resistivity at 22°C. of 1500 to 4000 ohms per cc., and containing a fair concentration of suspended matter. With this was added about 0.2 g/l. of $KMnO_4$ crystals and 0.2 g/l. of K_2CO_3. The heat from a Bunsen flame was distributed over the bottom of the flask by an asbestos filled wire gauze. Very severe "bumping" was the cause of poor results for a long time in spite of the use of glass beads, broken glass, broken porcelain, porous porcelain, sharp cornered metallic blocks, etc. Finally small aluminum cubes and cylinders with 1/16" holes drilled in them from all sides were used for two weeks at a stretch with excellent results over a wide range of heating rates. The holes in these blocks simply provided a vapor phase at all times, causing smooth boiling. These aluminum blocks required cleaning periodically, as they ceased to function when clogged with MnO_2 from the reduced permanganate. The normal distillation rate was 300 cc. per hour, so that overnight distillation could be used. At this rate the air and water circulation through jackets (D) and

(F) respectively was so controlled that a little steam issued with the good water at (E), and the water at (G) was collected hot. This water was nearly as good as that at (E), and was consequently used as part of the recharging stock in the Pyrex flask. The resulting water at (E) was tested for conductivity and for suspended matter. It was not used if the resistivity fell below 800,000 ohms/cc. at 25°C. This test frequently gave figures up to 1,800,000 ohms/cc. The optical test caused rejection if the water showed more than 5,000 particles/cc. In general, these particles were much larger than the colloids, and simply caused stray light. Most of the optical tests showed no Tyndall beam whatsoever, and less than 1000 particles/cc.

For the preparation of the gold suspensions, the Zsigmondy nuclear method was selected as most reliable for giving monodisperse suspensions. The results of measurements by Rinde (12) were relied upon in this respect, and his adaptation of the nuclear method was followed. The chlorauric acid was first made from pure gold sheet, but better results were later obtained with Merck's Purified Gold Chloride. The glass capsule from Merck was washed in hot cleaning solution, then in distilled, and finally in conductivity water. The 15 grains of $HAuCl_4$ were dissolved in 167 cc. of water, making a stock gold solution of 0.0175 mols/l. Solutions of red phosphorous in ethyl alcohol (50% saturated) and of c.p. K_2CO_3(0.1 molal) were made. A 33% hydrogen peroxide (Merck's Perhydrol) was obtained. The method of making the gold colloidal suspension consisted in first producing muclei by reduction of the chlorauric acid with phosphorous, and then "gilding" or building up these nuclei to any desired size by further additions of chlorauric acid, with hydrogen peroxide as the reducing agent. A typical instance of this procedure, using the solutions described above, is outlined as follows:

Sol 1: 1 cc. $HAuCl_4$
100 cc. H_2O
8 drops K_2CO_3
10 drops P
Boiled for 1 minute. Color, violet pink changing to wine red.

Sol 2: 10 cc. Sol 1.
0.6 cc. $HAuCl_4$
30 cc. H_2O
4 drops K_2CO_3
3 drops H_2O_2
Color, deep red by transmitted light.

Sol 3: 5 cc. Sol 2
.5 cc. $HAuCl_4$
30 cc. H_2O
4 drops K_2CO_3
4 drops H_2O_2
Color, violet red by transmitted light.

Sol 3 diluted with from 50 to 200 volumes of water was used to fill the quartz cells which were immediately closed with sealing wax. The deviations from the practise above outlined were insignificant. Three steps were required to obtain particles large enough to sediment to their final steady state in a few days, as the precaution must be taken not to build up the particles more than about 3 diameters per step. More rapid gilding than this results in a polydisperse system. The colors of the sol varied from a hazy pink through deeper shades of red and purple to a deep violet blue. Occasionally an orange would appear in the scattered light, and frequently the general appearance was murky rather than clear. This entire process was carried through rapidly in carefully cleaned Pyrex.

Sedimentation Methods

The cells used for the sedimentation (Figure 4) were made entirely of clear fused quartz. The body of the cell was of 8 mm. clear quartz tubing. Its ends were ground flat and parallel to allow optically flat thin plates of quartz to be fused in place for the observation window and floor respectively. It was thought advisable to have as flat and horizontal a floor as possible, as the most important measurements were expected in its vicinity. The internal height of the most satisfactory cell was 8.3 mm. Two 1 mm. side arms were fused in for filling and cleaning. The cell was filled so the liquid in the side arms stood at the height of the top window of the cell, so that disturbing lateral diffusion would be cut to a minimum. Immediately after filling, the top of each side arm was well closed with sealing wax, to prevent any lateral flow in the cell.

The fundamental parts of the observation apparatus were an optical system (Figures 2 and 3), a thermostated observation trough (Figure 3), and a temperature control tank (Figure 2). After preliminary tests had shown the type and intensity of illumination necessary, and the kind of mechanical control that was advisable, an adjustable optical system was built. This comprised a rectangular frame (A) which could be raised or lowered by four corner screws (B) with 4" graduated heads. This frame was supported on a heavy wooden stand (C) on the floor. On the rectangular frame was placed a sliding cross member (D) to act as the optical bench. This member was moved laterally by a long screw operated by a crank (E). On this optical bench were mounted an enclosed, hand-fed carbon arc assembly (F), a rectangular cuprous chloride absorption cell (G), a 6 cm.

aspheric condenser lens (H) and a 16 mm. Bausch and Lomb objective (I). The light beam from this optical system passed through a thin plate glass window directly into the sedimentation trough (J). A light shield (K) protected the observer's eyes from all direct arc light.

The sedimentation trough was bolted directly to a heavy pyramidal concrete pier (P) standing on the sub-basement floor of Room 061 in the West Bridge Laboratory. It comprised a heavy-walled space (J) about 3" on a side, with the plate glass window in front, and opening on both sides into large chambers. In the center of the thick-walled part was a heavy brass pedestal (L) on which the quartz cell (M) was solidly clamped. Directly above the cell pedestal was an opening to admit the objective of the observation microscope (N). Water was circulated from a main control tank into one end chamber, through the trough and thus around the cell on all sides, into the other chamber and back to the tank. This slow but steady circulation of water was found necessary to remove the heat of the illumination beam. The equalization of temperature was aided by the high conductivity of the pedestal and thick wall of the trough. The end chambers were used to remove any turbulence of flow, as well as to form large even-temperatured bodies of water near the cell. The whole trough assembly was painted with optical black wherever light might strike, and was very heavily lagged with soft pressed felt (O).

The main control tank, of 38 gallon capacity, was in the form of a rectangular sheet metal tank in a wooden box, insulated with a double layer of corrugated paper, and having a removable cover. On one end was mounted a vertical section of 1 1/2" brass tubing connected to the tank at the lower end and to the trough at the upper end. A double propeller in this vertical tube furnished circulation from the trough to the tank. The return circuit was direct, both connections with the trough being made through 6" sections of 1" thin walled rubber tube, to minimize vibrations reaching the trough from the tank. A small motor, separately mounted, was used to drive a stirring propeller as well as the circulation propeller. The tank was further equipped with a copper cooling coil, a heater coil of #26 chromel wire enclosed in a copper tube, a blackened, carbon filament lamp of 100 watt capacity, in series with an external 150 ohm rheostat, a thermal regulator and a two-stage relay controlling the carbon lamp. The regulator was of thin walled Pyrex, filled with CCl_4, with a mercury manometer and platinum contact wire with micrometer adjustment. The design was such as to spread the 210 cc. of liquid capacity over a large region in the tank and also give it the large contact area of 650 sq. cm., so that its thermal reaction should be quick. Carbon tetrachloride was used because its thermal expansion coefficient is the largest available in a commercial, non-corrosive liquid. The capillary first tried was about 0.1 mm. in diameter, but this arrangement was so sensitive that changes in atmospheric pressure caused unstable action. Later a capillary of about 0.5 mm. diameter was used successfully. The regulator contact was used to ground the grid of a vacuum tube whose resulting plate current operated a telegraph relay to control the heater currents. The copper-jacketed heater coil was used only in bringing the bath to the desired temperature after a period of disuse, the 100 watt lamp being sufficient for maintaining the constant temperature. A steady, small stream of cooling water was used on warm days. The 150 watt rheostat was adjusted from time to time to give equal periods of heating and cooling, as the closest thermal control results from this type of operation.

After the sedimentation cell had been filled and sealed, it was clamped in the trough. The circulation and thermal control being continuously operative over a period of several months, the cell soon came to thermal equilibrium, and the light and observing microscope were adjusted for a reading of initial concentration. The observation microscope, mounted rigidly with the rest of the optical system, was finally composed of the mechanics of a Bausch and Lomb instrument, a Leitz 20x Hyperplane eyepiece, a Bakelite tube, and a 16 mm. objective. The eyepiece was equipped with a ruled plate in its focal plane, carrying 36 large ruled squares, one of which was subdivided into 25 small squares. The original brass tube had to be removed because the heat transferred from the observer's eye started serious drifting of the colloids in a few seconds. The objective was immersed in the trough water, so that after it had been adjusted to focus in the Tyndall beam of illumination for a given cell, vertical motion of the entire optical system for obtaining the concentration at different depths would not require resetting the microscope. There were reasons for this arrangement other than mere convenience. By this means, the microscope's focal plane was always in the same part of the Tyndall beam, even on successive days so as to provide a constant intensity of illumination. Also, measurements of the level of a given reading were always made on the scale of the optical system, rather than partly on the microscope's fine adjustment, and partly on another arbitrary scale. Also, mechanical disturbance was lessened by having the microscope objective moved slowly with the heavy optical system, rather than directly by hand. The fine movements of the optical system were measured to 0.028 mm. by a stationary cathetometer (P) (Figure 3) adjusted once for all to read on a diamond scratch on a glass slide clamped near the microscope. The coarse motions were measured on the large divided heads of the 4 levelling screws. The two types of scales were needed because great accuracy was required near the floor of the cell, where the rate of change of concentration was greatest, yet the entire 8.3 mm. height of the cell must be under observation, necessitating a greater range than that of the cathetometer.

After the microscope and light had been adjusted, and after the colloidal suspension had come to rest, the readings were started. Visual counts of colloidal concentrations in large volumes of liquid must be governed by a convention as to the limits of the focal volume. Particles above the focal volume appear as blurred spots with a bright kernel, and those below as a series of diffraction rings. For the reason of the uncertainty necessarily attendant on the interpretation of such appearances, all the successive readings on a given cell were made by the same observer. Differences in interpretation between successive cells are meaningless, as only the relative values of concentration in a given cell are of importance. If the concentration were low, numerical counts were made in the large squares; if high, in the small squares, and sometimes for medium values, strips of 5 small squares were used to define an area. Successive visual counts were made at regular intervals as rapidly as feasible, to lessen eye fatigue, and consequent change in interpretation of the number of colloids in focus in a given field. These readings were written down by the other experimenter or by an assistant, who controlled the arc and all other adjustments on the apparatus. Sets of readings at a given level were never fewer than 25 in number, were most often 50, though frequently 100. At the extreme low levels near the floor of the cell only 25 readings were taken because of the strong stray light, the large numbers involved and the fact that when the particles were so close together as they generally were for these readings, the Brownian motion took them from one square to another or behind each other so rapidly that counts of fairly large numbers must be made with great rapidity. Only rarely were counts taken greater than 8 per square, however. It is to be noted that in high concentrations the same statistical accuracy follows from a smaller total number of counts. For an example of the data taken see Appendix A. With the record of the visual counts, were taken the level, frequent readings of trough temperature, and remarks about the counting conditions, drift, etc., allowing a subsequent estimate of the reliability of the data.

Two types of auxiliary data were taken. As a check on the particle size as calculated from the final sedimentation curve, long Pyrex tubes of about 6 mm. diameter were filled with the colloid, sealed at both ends, and set in a vertical position. Cathetometer observations of the falling boundary were used with Stokes Law for particle size determinations.

The concentration of particles near the floor of the cell was extremely high and difficult to observe. However, the lower levels are the most important for detecting any departure from the molecular-kinetic behavior due to proximity of the particles. The highest concentration observed in the work in quartz cells was $6.2 \cdot 10^{8}$ per cc., which is still so dilute that the particles ($3.61 \cdot 10^{-6}$ cm. in diameter) are 162 diameters apart. It was thought advisable to try to obtain sedimentation data in sols in which the particles were closer than 20 diameters, which would make the concentrations about $3.3 \cdot 10^{11}$ per cc. This is beyond the range which can be counted visually without an immersion objective, but it was hoped that some approach to the critical concentration could be reached, so that a distinct departure from the linear logarithmic curve could be detected. This led to an attempt to secure particle counts near the floor in a different type of cell, where a higher power objective could be used. A thin cell, similar to that used by Perrin and others, but set in a vertical plane, was used with a 4 mm. objective. The cell was clamped to the mechanical stage of a Spencer microscope, and illumination was provided variously by a dark field illuminator, oblique light beneath the stage, and oblique light above the stage. The difficulties with this work were mostly in obtaining a dark enough field illumination near the lower edge of the cell. In general, the data from these thin cells were no better at the higher concentrations than those from the quartz cells, and the experimental conditions were certainly not as good for securing entirely undisturbed sedimentation equilibria.

For data from the settling tubes see Table 2.

IV. Experimental Results

In the preliminary work, observations were made on dispersed oils, and on Bredig sols of copper, silver, aluminum, lead and tin. An attempt was made to produce monodisperse suspensions from the Bredig sols by means of a Sharples Super Centrifuge, but it was found impracticable to so remodel the centrifuge bowl as to obtain continuous fractionation within the range of particle size desired. In adapting a centrifuge bowl to the sharp separation of colloidal particles within a narrow range of sizes, the density differences to be dealt with are extremely minute. Inasmuch as the nuclear method had been shown by several observers (12) (13) (14) to give good monodispersity in the case of gold, and inasmuch as the sedimentation equilibrium would be attained in less time the greater the density of particles, it was decided to use the nuclear method with gold. In all, 32 batches of colloids were made up and observed in 51,750 counts. In the case of almost all of the first 25 sols, trouble was experienced with poor thermal conditions which caused convection currents. The results of only three of these runs will be presented, as being of import. Numerical data concerning all the useful runs will be found in Table 1.

Run 7 never reached the equilibrium state, and is representative of a number of the early runs. Its curves are shown in Figure 5. Curve A was taken with insufficient copper chloride in the heat absorption cell, so that bad drifting resulted. Curve B, taken after 4.6 days shows the typical result of convection disturbances, namely a high concentration near the bottom, fairly uniform concentration throughout the body of the cell and a falling off near the top. This is the same type of distribution as found by Porter and Hedges (3) and also agrees with the curves for certain stages of the transient state as given by Mason and Weaver (7) and Fürth (9). The parameter used by Mason and Weaver to characterize a suspension is α = RT/NXl, where X is the gravitational force on a particle, l is the depth of the settling chamber, and the other letters have their usual significance. As the value of α for the suspension of Run 7 is 0.0093, a direct comparison may be made with the curves of Mason and Weaver (7), P. 418, Fig. 1, and also with those of Fürth (9), P. 359, Fig. 3.

The chief interest in Run 7 lies in the fact that it is not only an experimental equivalent of part of the work (3) which caused this undertaking, but that it is also in agreement with the best theoretical work (7) (8) (9) on the transient state, thus indicating that in the recent work (3), true equilibrium was never reached. Curves C and D are taken at 5.6 days and 6.8 days respectively and are representative of a later transient stage, but are fundamentally different from the true equilibrium state, as shown in Figure 13.

Figure 6 shows in logarithmic form the result of the first successful attempt to secure an uninterrupted, steady settling, as accomplished in Run 22. An oil layer was put over the exposed water in the observation trough to prevent evaporation, but the benefit of this layer alone could not be regularly relied on to prevent troublesome thermal changes in the trough. Curves A, B, and C were taken after 1.9, 2.4, and 3.1 days respectively. That equilibrium was apparently reached as well after 1.9

days as after the theoretical time of 3.6 days, may be explained by the assertion of Weaver (8c) that his theoretical considerations lead to an upper limit for the duration of the transient state, and not an exact limit. The argument that the data of Run 22 represent only an approach to equilibrium cannot be sustained because the data agree altogether too closely with the linear logarithmic relationship for the same particle size as found by the settling tube method (Table 2).

The results of Run 23, given in Figure 7, show strikingly the effect of coagulation. This run was one of very few in which this trouble was encountered, and is shown in contrast with those which follow, in which the slight variations of radius do not indicate coagulation.

In Figure 8 are shown the curves of Run 28, the first taken successfully with the finally improved thermostat system. The thermal regulation is seen to be much closer than that of previous runs. The change of slope and position of Curve B relative to Curve A in this run is to be explained by the fact that the first curve was taken just as the sedimentation was approaching the steady state, and the second one after that state had been fully reached. It will be noted that in Curve A there is a tendency for the curve to be convex upwards, which is the condition found in the last stages of the transient state. As the sedimentation becomes more complete, the center of gravity of the colloid moves downward, as in Curve B, and the convexity of the curve straightens out.

In Figure 9 are given the results of Run 29. Here the same tendency to convexity is noted in Curve A (dots), while after 31 hours more settling, Curve B (circles) is seen to have lost this transient characteristic without having moved the center of gravity of the colloid. Curves C and D show the colloid moving towards its final steady state. The decrease in slope and apparent radius are probably due to experimental error; part of the displacement of the latter curves may be due to slight errors in locating the exact floor of the cell.

Curves A and B in Run 30, Figure 10, are as nearly identical as were ever found by the methods used in this work. Their transposition, Curve A being below Curve B, is due to experimental error, as is also their difference in slope. It will be noted from Table 1 that the particle size determinations from these curves differ by less than 1%. All experimental conditions for this run were better than for most others. The complete set of data for this run is reproduced in Appendix A.

Figure 11 shows the data from the longest run made during this investigation. As will be seen from the curves, no coagulation was apparent, and no settling of the center of gravity of the colloid occurred. The first set of data was taken after the end of the transient state, as was also the case in Run 30. The maximum variation from the mean of particle size calculated from these data is 3.3%, and the mean variation only 1.55%. The run was terminated arbitrarily after two weeks.

In Figures 12 and 13 are given the logarithmic and actual concentration curves for Run 32. The actual curve in Figure 13 is given to show why most of the curves are terminated at relatively low levels in the cell, rather than extended to the top, as are the actual counts. The concentrations become so extremely low in the first 0.05 cm. that not only do the counts taken above this level fail to have good statistical value, but the curve becomes practically identical with the h axis. Frequently at the higher levels only a few particles were visible in an otherwise black field of view, so the squares laid out in the eyepiece of the microscope were no longer visible, making the counts impossible. Further, several thousand counts would be required to give statistically correct concentrations. And since at all the levels above 0.05 cm. the counts show a fraction of one particle per square, the curve of Figure 13 may be said accurately to approach the h axis asymptotically, as required by the Laplacian law.

Settling tubes were used in obtaining check values of particle radius to compare with those obtained from the quartz cell sedimentation equilibrium. These were of Pyrex, about 6 mm. in diameter, sealed off at the bottom and drawn down to a tip closed with sealing wax at the top. These tubes were partly filled with the concentrated sol, part of which was diluted in a 100:1 ratio for use in the quartz cell. Observations of the falling boundary of this concentrated sol were made by means of a cathetometer. As the meniscus of the liquid had a height of well over 1 mm., readings of the position of the boundary were in general not taken until a fall of at least 2 mm. had occurred, because in changing from a curved meniscus to a horizontal plane, the boundary did not fall linearly with the time at first. The use of the settling tube was discontinued after Run 22, as the tubes were not very closely thermostated, so the data were thought not to be very significant and there were at that time no data on particle size from the quartz cells with which to compare the results. The entire effort was concentrated on the quartz cell thermostating after Run 22.

V. Discussion of Results

Several specific conclusions are to be drawn from the experimental results here shown:

1. The true equilibrium state of colloidal sedimentation is in good agreement with the Laplacian distribution law for vessels up to at least 1 cm. in depth as well as for the shallower vessels used by earlier workers. This is in direct contradiction to the results of recent work (1) (2) (3) (4) (11). The validity of the results of the recent work quoted is seriously in question due to the use of distinctly polydisperse sols in (1) (2) and (3); the probable failure to allow the proper period of time before making determinations of the distribution, in all cases; the failure to provide the requisite thermostating during the entire period of sedimentation, in all cases; and the failure of the authors to publish the significant data to demonstrate their conclusions contradicting the kinetic theory.

2. The transient state of colloidal sedimentation shows distributions which agree well with the theoretical calculations (7) (8) (9). The form of these distributions is very similar to that found by several of the recent workers (3) (4), which leads to the conclusion that the recent data quoted is for a disturbed or transient distribution rather than for the true equilibrium.

3. The postulate of a "critical radius" is definitely shown to be contrary to fact. The smallest radius of gold particles used in the present work was $3.61 \cdot 10^{-6}$ cm., or 1/8 of the "critical radius" of $30.0 \cdot 10^{-6}$ cm. as calculated by Burton (15) for gold suspended in water. The idea of a "critical radius" is not only disproved by experiment, but is theoretically

unsound. The behavior of the smallest particles mentioned above was in exactly as good agreement with ideal kinetic law as was that of larger particles; the experimental limit of size of sedimenting particles is thus very certainly much smaller than 1/8 of Burton's "critical radius", if such a limit should exist at all. As no reliable work points to the existence of such a limit, the authors prefer to consider that all sizes of particles sediment, even in deep vessels.

4. The "limiting concentration", or constant concentration found in the body of the vessels used in recent investigations (1) (2) (3) (4) is also disproved. The maximum concentration measured in the present work was $6.2 \cdot 10^8$ particles/cc., which is 21 times as great as Barkas' maximum value (4) for silver particles of about the same size, and 62 to 620 times as great as Porter and Hedges' maximum value (1) for gamboge and paraffin oil respectively. Early work (6) (10) went to concentrations slightly less than 8 times the maximum of the present work, with no trace of departure from ideal behavior. Above 9 times this maximum value, Constantin found a gradually increasing deviation from the Laplacian law. The effective "collisional volumes" which were required by Porter (1) and Barkas (4) to account for their limiting concentrations are from $2 \cdot 10^4$ to $4 \cdot 10^8$ times the "true" volume, in contrast with the results of Westgren's work (6) which shows that this volume ratio cannot be greater than 2900 in the extreme case. Westgren arrives at this figure from the maximum discrepancy between experimental and ideal behavior in the case of diffusion, and at figures of 1600 in the case of sedimentation equilibrium, and 225

in the case of spontaneous fluctuations. These various phenomena of colloidal behavior must all be satisfied by a new law devised for any one phenomenon before that law may be accepted.

5. No concentration studied was high enough to show any effect of interaction of the particles on the distribution at equilibrium. It was with the hope of studying the behavior of such interaction that the work was originally undertaken. As shown in Appendix B, Part 4, the maximum concentrations that can be determined by the ultramicroscope are probably not high enough to show such interaction, and consequent departure from ideal kinetic behavior.

Some of the details of the present experimental technique should be mentioned briefly. The thermal control is indicated by the figures of Table 1, but some analysis should be made for comparison with figures of other recent work. The thermal regulator described on page 13 was sensitive to a fraction of 0.001°C. The main control tank remained within a maximum range of 0.005°C. for the entire period of any one run, and the sedimentation trough itself remained constant generally within 0.005°C. and sometimes within less than 0.001°C. for several days at a time. The changes which did occur were most rapid during the counts, when the trough temperature rose at a maximum rate of 0.004°C/hr. The mean rate of change of sedimentation temperature over a period of more than two months was 0.000688°C. per hour, and over the two weeks of Run 31, only 0.00044°C. per hour. The actual changes were in both senses, as shown by the fact that the maximum range is much lower than it would be if the mean rate were that of a constant drift.

The effect of a gradual temperature drift on the steadiness of colloidal settling is much greater than the effect of changes of short duration in both senses, because slow but steady convection currents would be set up in the cell by a constant thermal gradient, whereas small positive and negative gradients of short duration would be relatively ineffective in counteracting the inertia of the suspension, and would in any case tend to nullify each other's effects.

The only data on thermal control given in the recent literature is in the work of Burton and Currie (2). Here the temperature changed 7°C. in 4 months, the largest single change being caused by the starting of the heating plant for the winter months. From this scant data, it is apparent that the changes were mostly in the same sense, that one relatively sudden change was an appreciable number of degrees in itself, and that the minimum possible rate of change would have been 0.00243°C. per hour, if the drift had been uniform over the entire period. When this thermal gradient is considered as acting on a volume of polydisperse colloidal suspension 3 cm. by 145 cm. in height, it is not difficult to locate the cause of the apparent departure from ideal kinetic behavior.

The matter of the duration of the transient state deserves brief comment. The rule of Mason and Weaver (7) that the final equilibrium will be effectively reached at most in the length of time required for a given particle to fall twice the height of the cell, is based on sound assumptions, and is universally accepted as being substantially correct. The duration of the transient state has no meaning for a polydisperse system, unless there is a known and definite minimum particle size. The only monodisperse systems dealt with in the recent work are those of Porter and Hedges (3) on gamboge, and of Barkas (4) on copper particles. No mention is made of the required periods of 10 to 28.5 days being allowed for the passage of the transient state. In Burton's work (1) (2) for example, a conservative estimate of the time would be of the order of 50 years, with a reasonable assumption as to the sizes of the particles. As will be seen from Table 1 of the present work, the theoretical time was observed in all cases, except in Run 22.

The recent work (3) (4) in which a non-uniform distribution was found near the top surface of the suspension unfortunately does not mention the bottom layer where the chief effect would naturally exist. The present work was devoted chiefly to a study of the bottom layer, although as shown in Appendix A, the upper region was always examined carefully.

A list of prospective experimental studies in this field might include:

1. A study of the range of concentrations in which the Laplacian law of distribution breaks down, with a view to finding the nature of the deviations, and their possible causes;

2. A study of sedimentation in still deeper cells, although the prospect of finding any real variation in behavior with increasing cell height is very poor, and the experimental difficulties are great;

3. A continued study of the same field with special attention to exact determinations during the transient state, which might test the

reliability of the theoretical work and also throw some light on the actual equilibrium states to be expected in the cases of very deep cells, and of very small particles, both of which present great experimental difficulty if the settling time must be continued to the final steady state;

4. Amplification of the present work to include non-metals, and possibly substances lighter than the settling medium;

5. A study of sedimentation, the observations to be so taken that they may also be used for calculations of spontaneous fluctuations;

6. A study of the two methods of approach to equilibrium, by settling and by diffusion, in the deep cells of the present work, to extend the admirable results of Westgren (6);

7. An attempt to study the actual ionic charge of colloidal particles by means of rapid observations of cataphoretic velocities, with a view to repeating the "oil drop experiment" in a liquid instead of a gas, and to correlate these results with those of the first problem in high concentrations to find whether the deviations from ideal behavior are due to electrical repulsion.

APPENDIX A

Complete data of Run 30, quartz cell sedimentation:

July 3, 1929 - Water resistivity 1 megohm/cc.

Nuclear sol made with $HAuCl_4$ from solution of 15 grains Merck's Purified Gold Chloride in 155 cc. water.

Sol 1: 1 cc. Au solution
100 cc. H_2O
8 drops K_2CO_3
10 drops P
Boiled 2 minutes - color: light, hazy pink.

Sol 2: 10 cc. Sol 1.
30 cc. H_2O
0.5 cc. Au solution
5 drops K_2CO_3
3 drops H_2O_2 Deep violet blue color.

Sol 3: 5 cc. Sol 2
30 cc. H_2O
0.5 cc. Au solution
4 drops K_2CO_3
3 drops H_2O_2 Sol turned orange by scattered and violet by transmitted light. Appearance is quite murky.

Quartz cell set up at 3:30 P.M. Initial count at 4:30 P.M.

Large squares:

12110	10231	10100	13120	11210	22011	32	
02110	21011	03120	12212	21222	03101	37	Av. <u>1.15</u>

First count - July 6, 1929 - 2:20 to 3:30 P.M.

Optical system level: Cathetometer:

Small squares: 8.35 - 3.50

23021	21221	10110	23211	02211	34	
20210	01212	21021	12210	21020	28	Av. <u>31</u>.

Small squares: 8.37 - 3.62

00212	32232	42423	34322	44211	58	
43311	22232	34133	12512	23112	57	Av. <u>58</u>.

Small squares: 8.39 - 3.75

21220	32224	43342	43243	23444	69	
44234	53335	42522	32323	34342	80	Av. <u>75</u>.

Small squares: 8.41 - 3.87
11231 22212 11214 23213 13211 45
21334 10311 33222 31213 20312 49 Av. 47.

Small squares: 8.43 - 4.00
11201 10010 11011 10211 00000 16
20211 01002 21100 10101 01001 18 Av. 17.

Small squares: 8.45 - 4.12
01001 01000 02100 00110 11010 11
10001 01021 02101 01000 00101 13 Av. 12.

Strips of 5: 8.48 - 4.33
01010 10011 01011 00010 00121 13
00111 00112 11010 10000 20001 14 Av. 2.7

Large squares: 8.51 - 4.55
21112 20234 21272 21311 11012 45
13222 42231 10113 12022 10212 41 Av. 1.7

Large squares: 8.55 - 4.81
10111 00100 10110 10101 11110 15
00112 10110 11100 21111 00111 19 Av. 0.68

Large squares: 8.60 ------
Very few in field. Av. -

Large squares: 9.00
20100 11000 10001 01001 11001 12
20111 00110 01100 00120 10010 14 Av. 0.52

Large squares: 10.00
12011 00000 21202 01111 01202 21 Av. 0.84

Large squares: 11.00
20121 01110 01012 11010 31101 22 Av. 0.88

Large squares: 12.00
10000 20011 00100 11001 00110 11 Av. 0.44

Large squares: 12.30
11010 00010 10100 11020 01101 13 Av. 0.52

Top of cell 12.63

Bottom of cell 8.34 and 3.50

Second Count - July 7, 1929 10:30 A.M. to 11:40 A.M.

Room temperature 23.7°C. Sedimentation trough 26.600°C.

Bottom of cell at: Cathetometer 4.26

Optical system level: Cathometer:

Small squares:			8.35 - 4.32			
10111	01000	10100	00100	00101	10	
12010	21000	11110	01100	10000	14	Av. 12.
Small squares:			8.37 - 4.45			
12412	20222	11220	22010	23230	39	
12121	22012	11221	01220	10130	31	Av. 35.
Small squares:			8.39 - 4.56			
34323	44444	12431	13345	41234	76	
44312	32330	13140	33233	21433	61	Av. 69.
Small squares:			8.41 - 4.68			
40130	22231	12211	21424	02322	47	
32312	23330	32230	21232	31223	53	Av. 50.
Small squares:			8.43 - 4.82			
23110	11102	13101	02111	01011	26	
11012	12110	12110	31010	10101	23	Av. 25.
Strips of 5:			8.45 - 4.95			
21322	22211	11321	23421	12213	47	
10222	22120	23213	20423	12223	46	Av. 9.3
Strips of 5:			8.47 - 5.07			
12120	30022	21021	21131	11321	35	
40212	31012	21201	00201	21011	30	Av. 6.5
Large squares:			8.49 - 5.23			
12253	12424	31122	32633	21311	60	
33324	13442	23321	22333	34345	72	Av. 2.65
Large squares:			8.55 - 5.63			
20111	11110	21101	12021	12111	26	
11021	00211	10111	10100	10101	18	Av. 0.88
Large squares:			9.00			
00001	00211	01021	00111	00011	14	Av. 0.56
Large squares:			10.00			
20102	11011	01101	11001	11011	19	Av. 0.76

Large squares: 11.00
10001 20211 00111 11000 01000 14 Av. <u>0.56</u>

Large squares: 12.00
10001 00001 10010 00010 01001 8 Av. <u>0.32</u>

12.30
3 or 4 in whole field.

Top of cell at 12.63, as before.

Room temperature 23.7°C. Sedimentation trough 26.604°C.

The optical system levels are measured on the large divided heads of the 4 levelling screws, (B) in Figure 3. One revolution is equivalent to 1.953 mm. The cathetometer divisions are also arbitrary, one division being equal to 0.290 mm. Thus two check measurements were always obtained on the lowest, most important levels, and one measurement on the upper levels.

It will be noted that the two lowest levels apparently had smaller concentrations than those immediately above. This is an experimental error due to generally poorer dark field illumination near the floor of the cell, and also due to the focal volume actually extending into the floor of the cell at the lowest reading.

The plot of these data will be found in Figure 10. The temperature log for Run 30 follows:

July 3

4:00	P.M.	26.600°C.
5:55		26.600
10:00		26.600
10:40		26.599

July 4

10:10	A.M.	26.599
1:35	P.M.	26.599
2:25		26.600
6:05		26.600
10:45		26.600

July 5

9:10	A.M.	26.599
11:00		26.597
11:40		26.598
1:00	P.M.	26.599
1:45		26.598
2:50		26.598
3:35		26.598
4:00		26.599
11:05		26.598

July 6

8:55	A.M.	26.600
10:25		26.600
12:05	P.M.	26.600
1:40		26.600
3:25		26.604+
10:30		26.600

July 7

9:30	A.M.	26.600
1:00	P.M.	26.603+
4:50		26.600
5:25		26.601

July 8

11:45	A.M.	26.599

+ Asterisks mark time of counts.

APPENDIX B

1. Calculation of Particle Size from Sedimentation Data.

From the Laplace equation:

$$\log n/n_o = - Nvgh(d_1-d_2)/RT,$$

in a monodisperse sol, at constant temperature, the only variables are n and h. The graph of log n vs. h is a straight line, whose slope is:

$$\log (n/n_o)/h = - Nvg(d_1-d_2)/RT$$

For the case of Run 22, for example:

Slope of curve A $= - 86 = - Nvg(d_1-d_2)/RT$.

Thus: $v = 86\ RT/Ng(d_1-d_2)$

$$= \frac{86 \cdot 8.31 \text{ exp}7 \cdot 299.6}{60.6 \text{ exp}22 \cdot 981.6\ (19.32 - 1.00)} = 1.972 \text{ exp}{-16}$$

Then: $r^3 = \frac{3 \cdot 1.972 \text{ exp}{-16}}{4\pi}$, or: $\underline{r = 3.61 \cdot 10^{-6} \text{ cm.}}$

APPENDIX B (CONTINUED)

2. Calculation of Particle Size from Settling Tube Data.

The settling tubes were deep enough to allow the use of Stokes' law of free fall in a viscous medium:

$$V = 2g(d_1 - d_2)r^2/9\eta$$

Solving for the particle radius:

$$r = \sqrt{\frac{9\eta V}{2g(d_1 - d_2)}}$$

Substituting the actual values of Run 22, c:

$$r = \sqrt{\frac{9 \cdot 0.00981 \cdot 5.57 \cdot \exp{-6}}{2 \cdot 981.6 \cdot (19.32 - 1.00)}} = \underline{3.66 \cdot 10^{-6} \text{ cm.}}$$

APPENDIX B (CONTINUED)

3. Calculation of Theoretical Settling Time from Particle Size.

Reversing the process of the above calculation, if r is given from settling tube or sedimentation data, then the Stokes velocity, and time for falling twice the height of a given cell is calculated as follows:

$$V = 2g(d_1 - d_2)r^2/9\eta$$

For Run 22, C: $r = 3.61 \cdot 10^{-6}$ cm.

$$V = \frac{2 \cdot 981\ (19.32 - 1.00) \cdot (3.61)^2 \cdot 10^{-12}}{9 \cdot 0.00981} = 5.40 \cdot 10^{-6} \text{ cm/sec.}$$

Then for $h = 0.83$ cm., $2h = 1.66$ cm.

$$t = 2h/V = 1.66/5.40 \cdot 10^{-6} = 3.26 \cdot 10^5 \text{ sec.}$$

$$= \frac{3.26 \cdot 10^5}{86{,}400} = \underline{3.82 \text{ days}}.$$

APPENDIX B (CONTINUED)

4. Calculations of Concentration Limit for the Ultramicroscopic Method.

The maximum concentration measured in this work was $6.2 \cdot 10^{8}$ particles per cc. These counts were made with a magnification of approximately 200 and a focal volume per small eyepiece square of $4.8 \cdot 10^{-9}$ cc., making the average number of particles per count about 3. The counting square in the microscope image plane appeared about 3 mm. on a side at 25 cm. from the eye. In a square of this size 8 particles are difficult to count with certainty when in violent Brownian motion. Moreover, the maximum number of particles that can be counted quickly in a square of any size is about 10. Thus the practical limit of visual counts may be expected at an average of about 5 particles in a 3 mm. square at 25 cm. from the eye. With good dark field illumination, a magnification of 1200 diameters would be possible, with a working distance of 1.9 mm. in water. This objective (Primary magnification 40, N.A. 0.75, water immersion) will have a focal depth about $0.30/0.75 = 0.4$ that of the objective (Primary magnification 10, N.A. 0.30, dry) used in the present work. Thus the focal volume of the proposed microscope would be smaller in the ratio of $1:(1200/200)^{2}/0.4$ or 1:90. This would allow concentrations up to $90 \cdot 6.2 \cdot 10^{8} \cdot 5/3 = 9.3 \cdot 10^{10}$ particles per cc., if it be assumed that an average of 5 particles per square can be counted.

The average spacing of particles at this concentration is $1/\sqrt[3]{9.3 \cdot 10^{10}} = 2.21 \cdot 10^{-4}$, or $2.21 \cdot 10^{-4}/2 \cdot 3.61 \cdot 10^{-6} = 30.6$ diameters for the above mentioned particle size. It is not known definitely at what spacing the departures from ideal behavior become appreciable, even in definite cases. But it is apparent that unless a very considerable interaction had been manifested at a larger spacing than 30.6 diameters, an attempt at ultramicroscopic study of the behavior of such forces would be futile.

If larger particles were used, a limit would soon be reached at which the extremely small differences in level would become difficult to measure. If particles of $10 \cdot 10^{-6}$ cm. radius were used, the slope of the distribution curve would be 1835, and the concentration reached at 0.05 cm. in Run 22 would be reached with these larger particles at a height of only 0.00093 cm. which would make it extremely difficult to measure the microscope levels. In even this extreme case, the particle spacing would be reduced to only 11 diameters. The other alternative, the use of lighter and larger particles is the obvious means to avoid the difficulties mentioned in making the physical measurements. Here, however, two other bad features are encountered, in the difficulty of producing monodisperse sols of materials other than gold, and the long periods that must be allowed for equilibrium to be attained, if a lighter substance than gold is used.

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TABLE 1

QUARTZ CELL DATA.

Fig. No.	Run No.	Slope $\frac{\ln n/n_0}{h}$	Radius calc., cm·10^6	Temperature, °C.			Settling Time		Remarks
				Max. Range	Max. Rate °C./hr.	Mean Rate °C./hr.	Actual Days	Calc. Days	
5	7 B	-	-	-	0.100	-	4.6	-	Accurate temperature log not kept throughout day, but only during readings.
	C	-	-	-	0.126	-	5.6	-	
	D	-	-	-	0.082	-	6.8	-	
6	22 A	86	3.61	0.363	-	0.0074	1.9	3.6	Oil layer on exposed water in sedimentation trough.
	B	86	3.61	0.363	0.023	-	2.4	3.6	
	C	86	3.61	0.363	0.064	-	3.1	3.6	
7	23 A	140	4.24	0.470	0.096	0.0094	3.8	2.6	Coagulation noted in unused portion of this colloid.
	B	345	5.73	0.549	0.014	-	5.1	1.5	
8	28 A	111	3.93	0.109	0.0065	0.00127	2.1	3.0	New thermal regulation.
	B	141	4.24	0.109	0.0000	-	3.0	2.6	Note maximum thermal rate.
9	29 A	149	4.33	0.005	0.0020	0.00039	2.2	2.5	
	B	149	4.33	0.005	0.0025	-	3.5	2.5	
	C	122	4.05	0.007	0.0037	-	4.0	2.8	
	D	112	3.94	0.008	0.0012	-	4.2	2.9	
10	30 A	190	4.70	0.003	0.0013	0.00029	3.0	2.1	This complete run shown in Appendix A.
	B	185	4.66	0.007	0.0023	-	3.8	2.0	
11	31 A	96	3.74	0.004	0.0012	0.00044	3.1	3.3	The longest run of the series, with no serious thermal disturbances.
	C	91	3.68	0.008	0.0033	-	4.9	3.4	
	D	93	3.70	0.014	0.0060	-	6.0	3.4	
	E	85	3.59	0.017	0.0036	-	7.8	3.6	
	F	89	3.65	0.017	0.0049	-	9.0	3.5	
	G	99	3.78	0.017	0.0030	-	10.1	3.3	
	H	102	3.82	0.017	0.0040	-	13.1	3.2	
	I	96	3.74	0.017	0.0014	-	13.8	3.3	
12	32 A	89	3.65	0.011	0.0072	0.00156	3.2	3.5	
	B	89	3.65	0.053	0.0147	-	5.2	3.5	

TABLE 2

SETTLING TUBE DATA.

Run No.	Distance cm.	Time Hours	Rate of Fall cm/sec $\cdot 10^6$	Radius cm $\cdot 10^7$
7 A	0.34	13.0	7.25	41.7
B	0.51	25.2	5.66	36.9
C	0.91	36.0	7.00	41.0
D	1.00	40.5	6.85	40.6
9 A	0.56	39.5	3.94	30.8
B	0.93	62.0	4.17	31.6
C	1.29	86.5	4.14	31.5
D	1.93	110.2	4.86	34.1
E	2.60	138.0	5.22	35.0
F	3.16	158.0	5.55	36.5
G	3.72	188.0	5.50	36.3
10 A	1.00	48.0	5.78	37.3
B	2.45	120.5	5.65	36.8
18 A	0.27	18.2	4.12	31.4
B	0.84	47.4	4.92	34.4
C	1.54	67.7	6.32	39.0
19 A	0.07	4.0	4.86	34.2
B	0.29	9.0	8.95	46.4
C	0.32	12.0	7.40	42.2
D	0.54	17.0	8.81	46.0
20 A	0.10	21.0	1.32	17.8
B	0.23	34.7	1.84	21.0
C	0.24	39.0	1.71	20.3
D	0.38	46.0	2.29	23.4
E	0.44	58.7	2.08	22.4
F	0.75	95.0	2.19	23.0
21 A	0.63	4.0	43.7	102.5
B	3.47	18.5	52.1	111.9
22 A	0.06	8.0	2.08	22.4
B	0.15	10.5	3.97	30.9
C	0.45	22.4	5.57	36.6
D	2.30	76.3	8.42	45.0

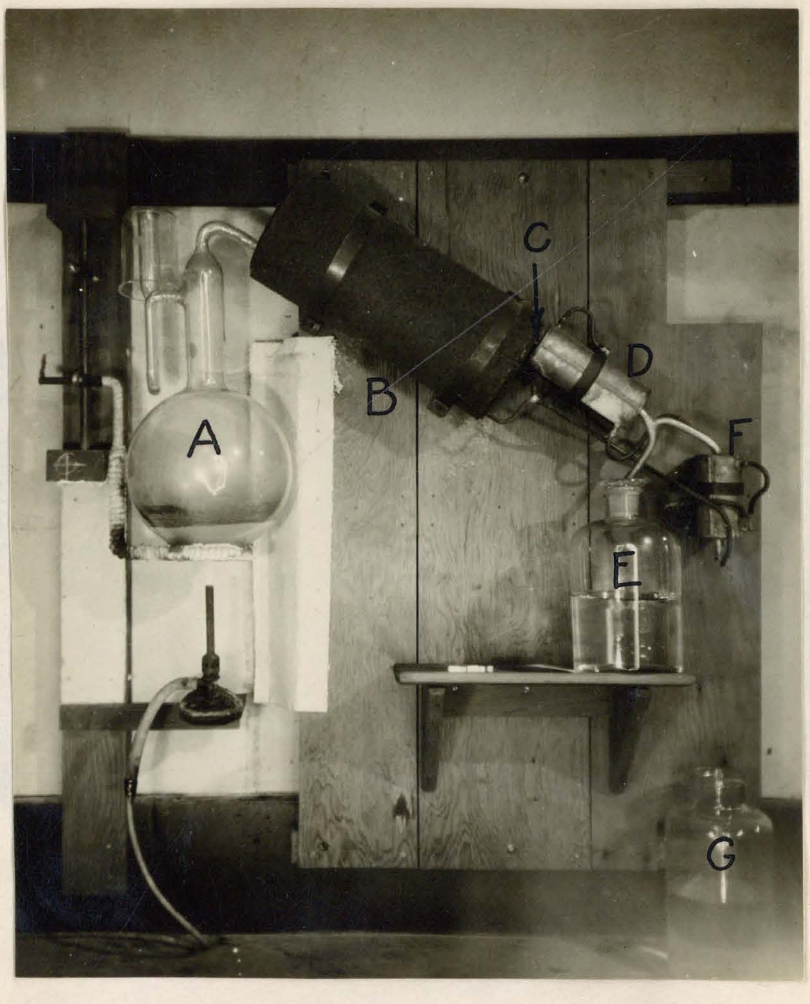

FIGURE 1

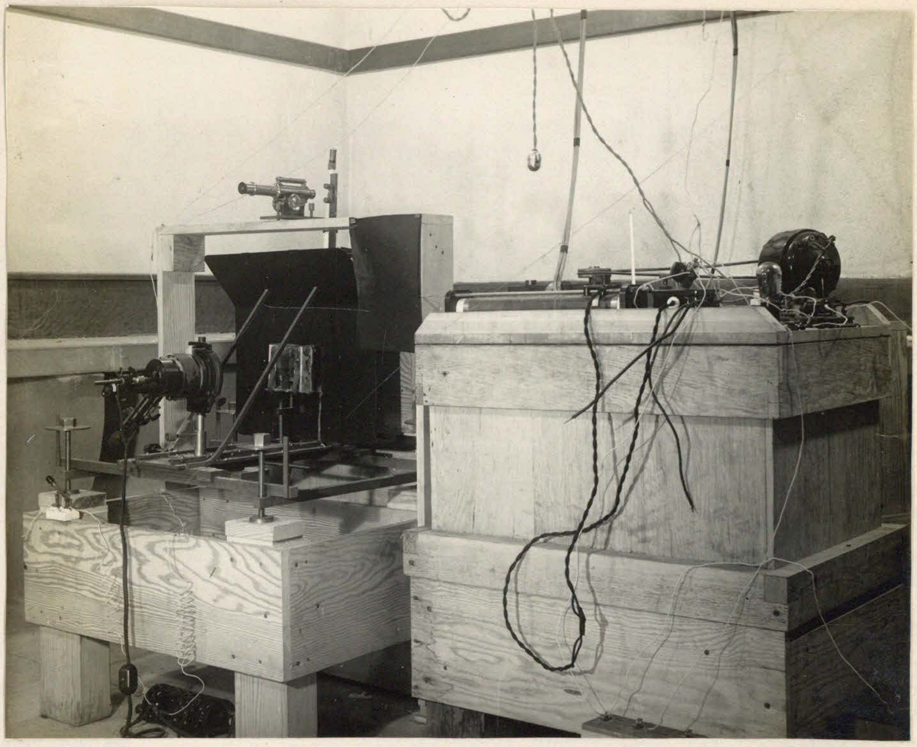

FIGURE 2

FIGURE 3

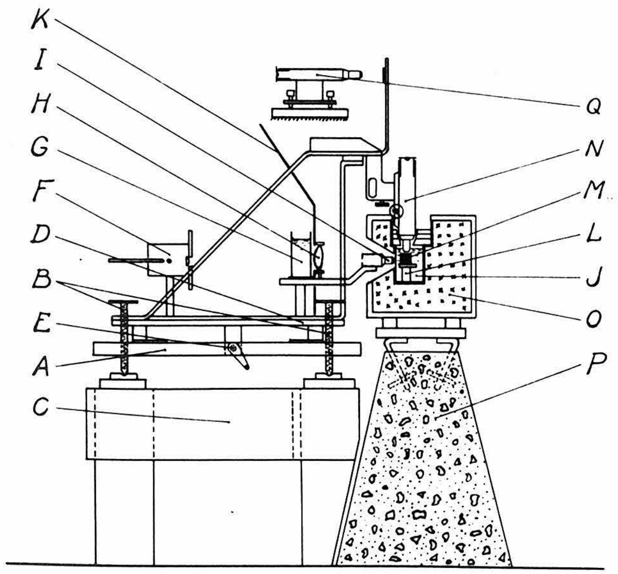

FIGURE 4

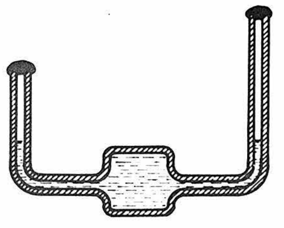

FIGURE 5

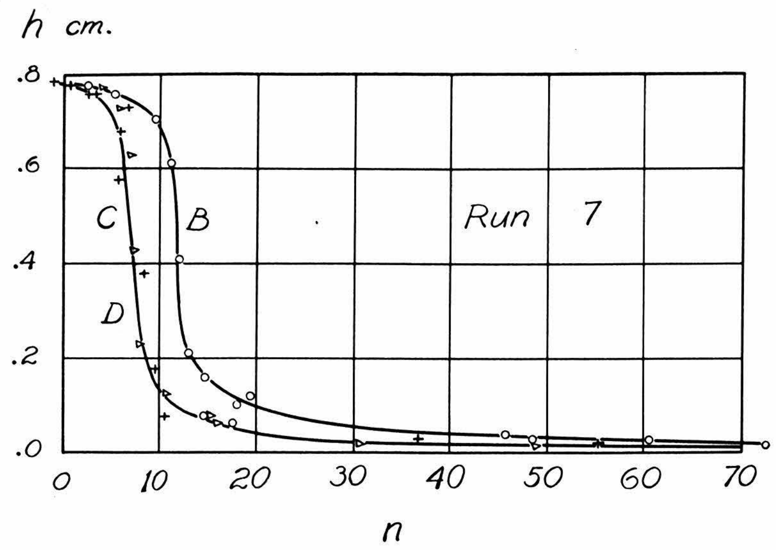

FIGURE 6

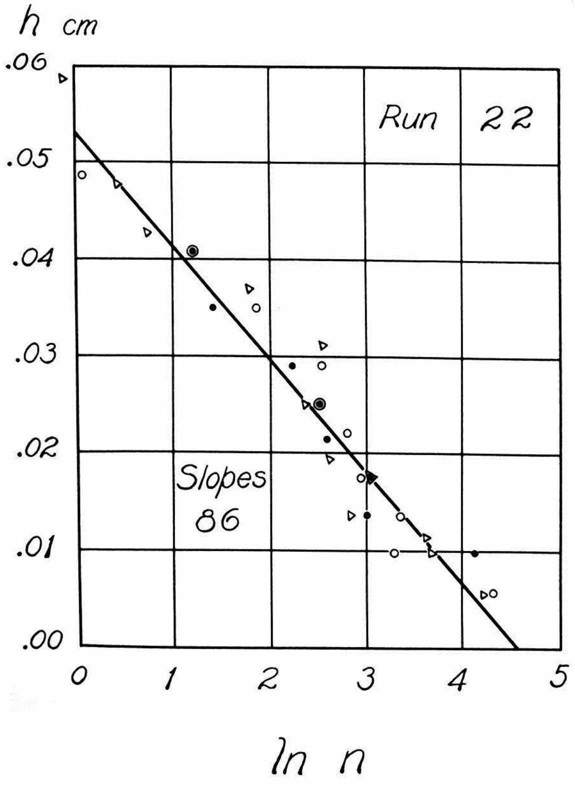

FIGURE 7

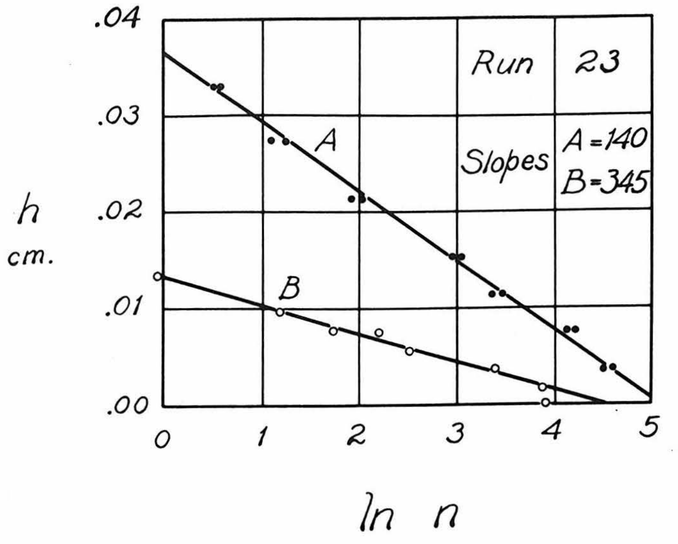

FIGURE 8

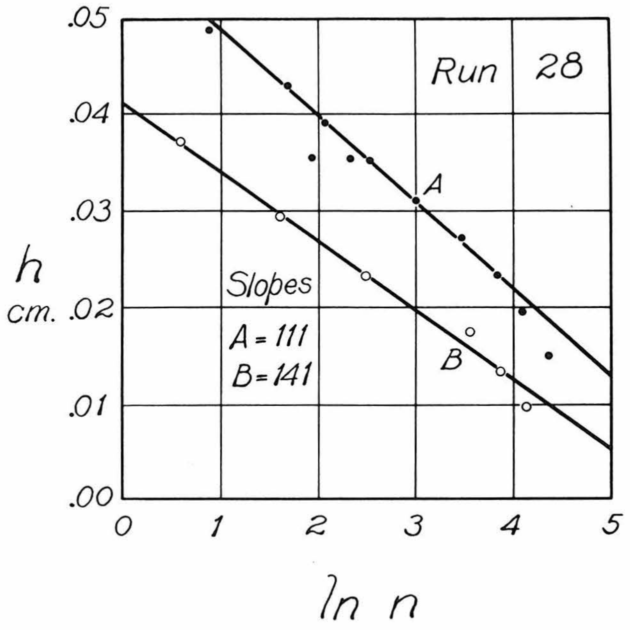

FIGURE 9

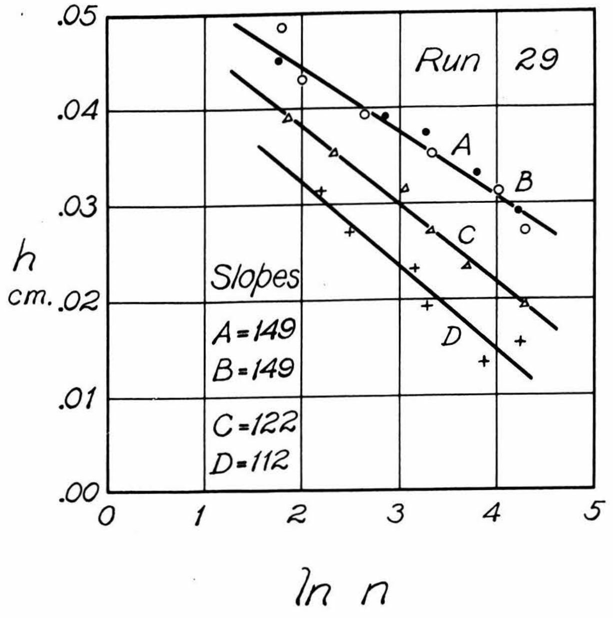

FIGURE 10

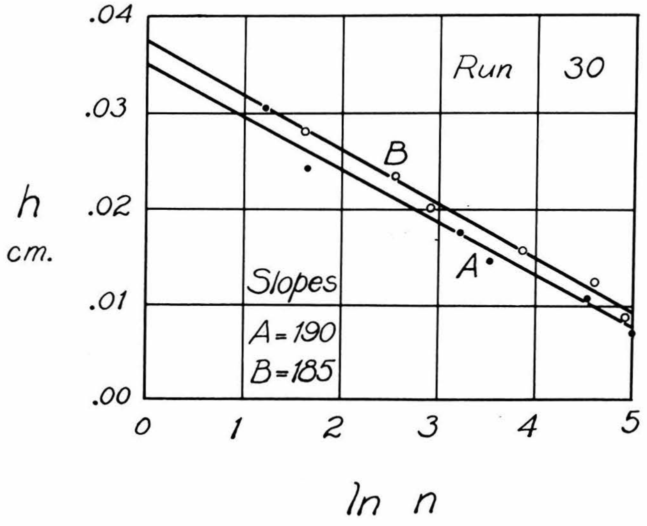

FIGURE 11

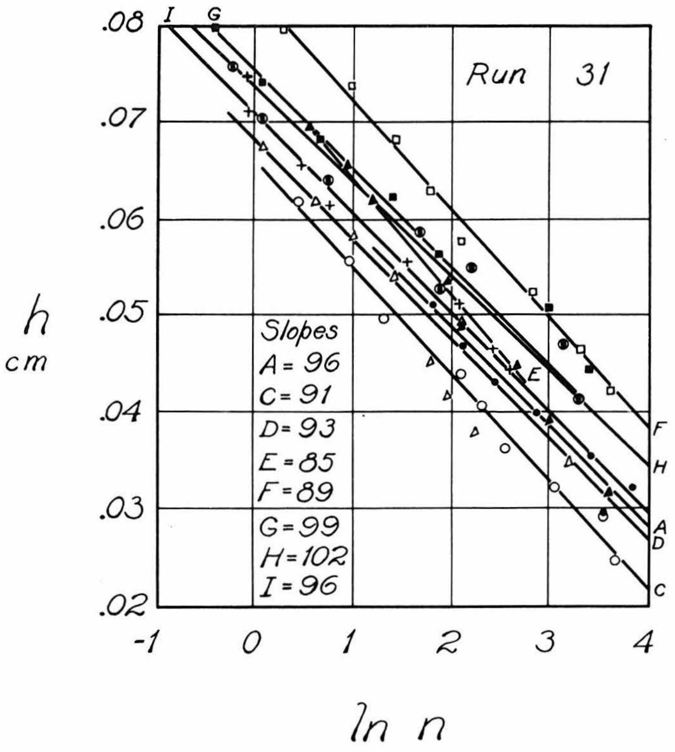
Run 31
h
cm
.08
.07
.06
.05
.04
.03
.02
-1
0
1
2
3
4
ln n
I
G
E
F
H
A
D
C
Slopes
A = 96
C = 91
D = 93
E = 85
F = 89
G = 99
H = 102
I = 96

FIGURE 12

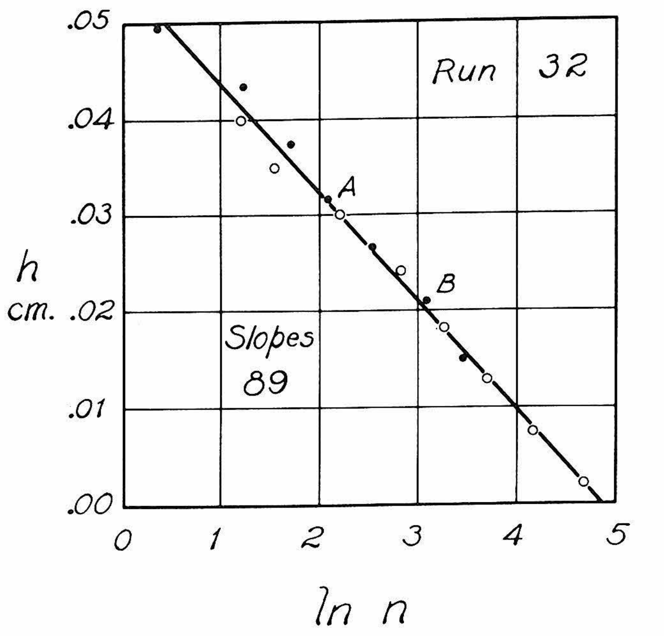

FIGURE 13