

OPACITY CHANGES IN GEL-FORMING MIXTURES DURING SETTING

Part I. Thorium Molybdate, Stannic Arsenate and Silicic Acid Gels

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THE transparency or opacity measurements of colloidal solutions were first made by Mukherjee and co-workers during their study of the kinetics of the coagulation of sols by electrolytes. In their earlier studies they measured¹ the intensity of light transmitted through the coagulating system in various spectral regions by means of a spectrophotometer. Later on, Mukherjee and Majumdar² measured the transparency of the coagulating sol by allowing the transmitted light to fall on a thermopile connected to a sensitive galvanometer. The use of this method was extended by Prasad and Hattiangadi³ for the study of the kinetics of the setting of silicic acid gels.

Desai⁴ modified Mukherjee and Majumdar's method by substituting a photo-cell in place of thermopile. According to him a photo-cell is decidedly more sensitive and reliable than the thermopile as it is easier to eliminate stray light than stray heat. Desai's photo-cell method was modified by Prasad and Modak⁵ who magnified the current generated in the photo-cell by a single stage amplification unit.

The photo-cell methods of Desai and co-workers and Prasad and Modak require that the current feeding the source of light should be kept constant throughout the investigation. These co-workers used the current from the main supply and corrected it for any fluctuation by means of a potentiometric arrangement. A second necessary requirement of their apparatus arising out of the photo-cell arrangement is that the potential applied to excite the cell should be kept constant throughout. This was achieved by using storage cells giving constant voltage. Any change in the constancy of these two factors will introduce large errors and would lead to wrong conclusions.

An apparatus described in the following pages was assembled with a view to get over all the possible errors mentioned above by an auto-controlled device and it was employed to measure the changes in opacity taking place during the setting of mixtures giving rise to gels of thorium molybdate, stannic arsenate and silicic acid.

*Experimental**Description of the apparatus—*

The apparatus mainly consists of three parts:

- (a) Rectifying circuit.
- (b) Arrangements for maintaining the source of light and photo-cells under constant conditions.
- (c) Arrangement for measuring the current.

(a) *Rectifying circuit.*—This is the usual rectifying arrangement which converts 230 A.C. into D.C. at about 400 volts and 180 milliamps. It was provided with the filter system to smoothen the current output. The D.C. current thus obtained was used in the arrangements described under the heading (b).

(b) *Source of light.*—The circuit diagram of this part of the apparatus is shown in Fig. 1. In this diagram

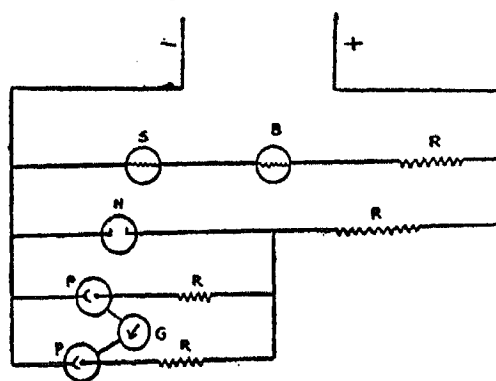


FIG. 1

S = Source of light (lamp).

B = Regulating valve (Barreter's filament lamp).

N = Neon stabilizer.

P = Photo-cell.

G = Galvanometer.

R = High resistances.

The source of light is supplied with constant amperage by means of the regulating valve B which is put in series with it and which controls automatically the small fluctuations occurring in the mains. The voltage applied to the photo-cells is autocontrolled by the neon-stabiliser N which is put in parallel with the photo-cells as shown in the figure. It was found that a change in the main A.C. current by about 10% causes no appreciable changes in (1) the current feeding the source of light and (2) the voltage applied to the photo-cells.

In order to make this arrangement direct reading, the source of light *S* was placed between the two photo-cells (*P*) of the same type. They were connected in parallel as shown in Fig. 2. The neon-stabiliser, the source

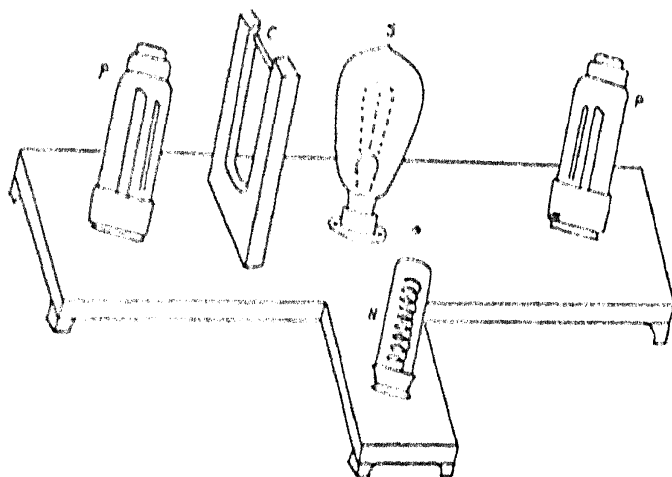


FIG. 2

of light and the photo-cells were mounted on a suitable board and their positions were fixed in order to avoid any discrepancies creeping in the results on account of the shifts in their respective positions. *C* is a glass cell mounted on a wooden base, employed to contain the gel-forming system. The glass cell exactly fits in the base and can be removed easily from it for cleaning purposes. The regulating valve *B* becomes very hot when the current is put on and it was found to interfere with the results when mounted on the same board. Consequently it was mounted on a separate base and was kept in a distant corner.

The distances between the source of light and the photo-cells were so adjusted that when the glass cell is empty there is practically no initial current flowing through the galvanometer. Any changes noted by the galvanometer after introducing a gel-forming mixture in the glass cell are therefore exclusively due to the changes taking place in the system with time.

(c) *The measuring instrument.* This part of the apparatus consists of a sensitive moving coil galvanometer of deat-beat type. The deflections of the galvanometer were measured on a scale placed at a suitable distance from it.

The apparatus described above was kept in an air thermostat maintained at a constant temperature, since the rate of gelation has been found to alter with a change in temperature. The galvanometer took nearly one hour to reach a steady state, after switching on the current; hence all observations were taken after this interval.

The source of light is constantly kept on during the period of observations and thus photo-cells always remain in a steady state.

The current produced by the photo-cell is very small and hence extreme care was taken to avoid any possible leakage.

All the apparatus was set up in a dark room and extreme care was taken to keep all stray light away from the thermostat.

The deflection of the galvanometer when one of the photo-cells was completely covered was 11.1 cms. This is a measure of the total light falling on the photo-cell.

Experimental Procedure

Varying amounts of the solution of one of the constituents of the gel-forming mixture were taken in one test-tube and in other test-tube were taken varying amounts of the other constituents and the volumes in each test-tube were made up to 4 c.c. by the addition of the required amount of distilled water. The test-tubes were properly corked and kept in the thermostat for half an hour. The contents of one test-tube were then poured into the other and back again and this was repeated five times. A stopwatch was started just at the time of mixing. The gel-forming mixture was then poured in the glass cell which was covered with a glass slide and placed in its socket. The glass door and the black curtain of the thermostat were then put on and the position of the spot of light on the scale was noted. All this process took one minute since the commencement of the mixing of the constituents of the gel-forming mixture. The reading taken after the first minute has been taken as the zero reading. No error is involved in this process as it has been observed that during the first few minutes the changes in opacity are extremely small. The deflections of the galvanometer were then noted at various intervals of time till they reached a constant value.

White light was employed throughout. The constancy of the initial reading of the galvanometer with the empty cell and the repeatability of the results were tested from time to time.

After each set of readings the glass cell was thoroughly washed and completely dried. It was then kept in the thermostat for about 20 minutes so that it may attain the temperature of the thermostat.

1. Thorium Molybdate Gels

These gels were prepared by the method of Prasad and Desai.⁶ The following solutions were used:

(A) Solution of thorium nitrate containing 48.14 g. per litre.

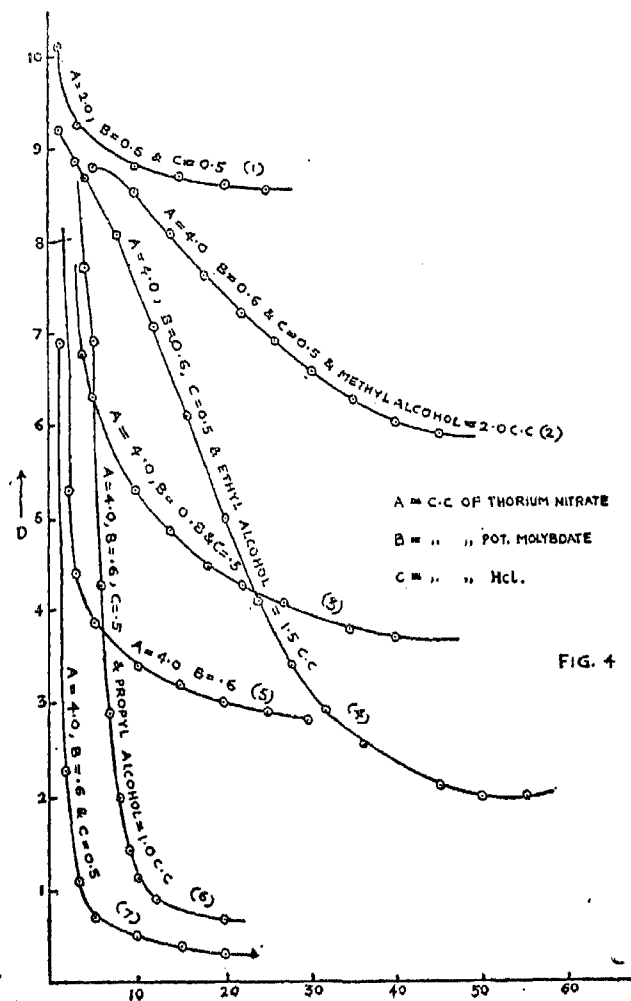
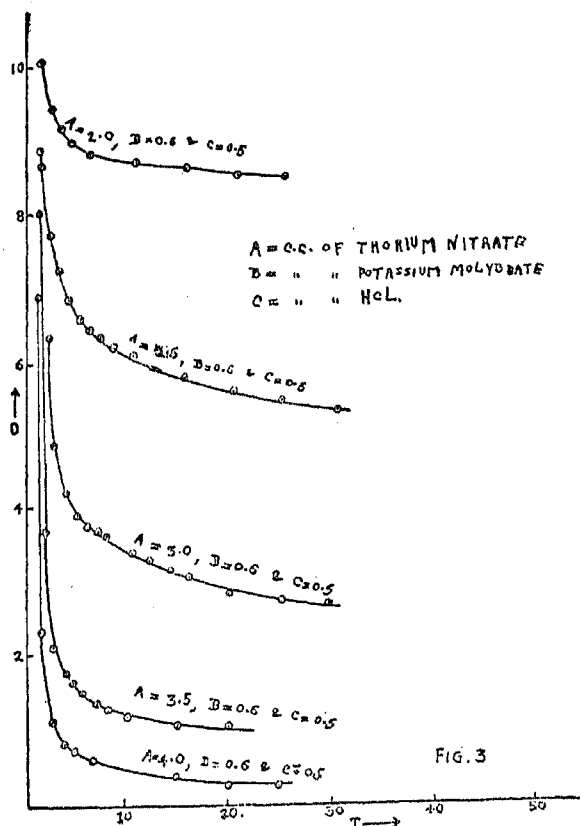
(B) Solution of potassium molybdate containing 100 g. per litre.

(C) 0.2 N HCl.

The effects of the addition of different amounts of (A), (B), (C) and of non-electrolytes on the opacity changes during the course of gel-formation were investigated. The results are shown by means of curves obtained by plotting observed deflections in cms. against time in minutes.

The effect of thorium nitrate was studied by adding 1.5 to 3.5 c.c. of (A) to the solution containing 0.6 c.c. of (B) and 0.5 c.c. of (C). The effect of potassium molybdate was studied by adding 0.4 to 1.0 c.c. of (B) to 0.5 c.c. of (C) before it was added to 4.0 c.c. of (A). The effect of HCl was studied by adding 0 to 0.25 c.c. of (C) to 0.6 c.c. of (B) before it was added to 4.0 c.c. of (A). The effect of methyl, ethyl and propyl alcohols were studied by adding 0 to 2 c.c., 0 to 1.5 c.c., 0 to 2.0 c.c. of the respective alcohols to a mixture of 0.6 c.c. of (B) and 0.5 c.c. of (C) before it was added to 4 c.c. of (A).

Some of the results obtained are shown in Figs. 3 and 4.



2. Stannic Arsenate Gels

These gels were prepared by the method of Prasad and Desai (*loc. cit.*) by mixing different amounts of the following solutions:—

(A) Stannic chloride solution containing 195.28 g. of the salt (Merck) and 4.0 c. c. of nitric acid per litre. (Nitric acid is added to prevent hydrolysis.)

(B) 10% of solution of pyro-arsenic acid (Merck).

The effect of stannic chloride was studied by adding 2.5 to 3.75 c.c. of (A) to 0.3 c.c. of (B). The effect of pyro-arsenic acid was studied by adding 0.2 to 1 c.c. of (B) to 4.0 c.c. of (A). The effects of methyl, ethyl, propyl alcohols, glycerine and pyridine were studied by adding 0 to 1.0 c.c. of the various alcohols and glycerine and 0 to 0.2 c.c. of pyridine to 1.0 c.c. of (B) before it was added to 4.0 c.c. of (A). The effect of HCl was

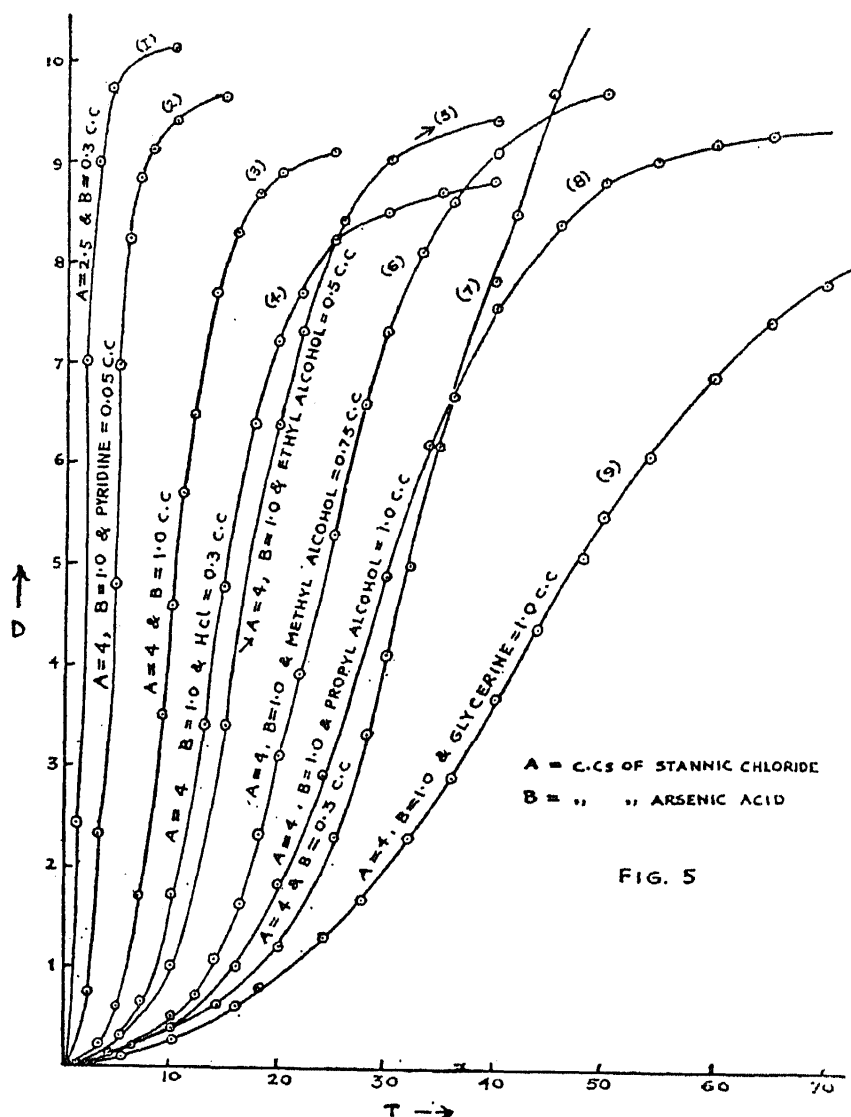


FIG. 5

studied by adding to 0 to 0.5 c.c. of 0.2 N HCl to 1.0 c.c. of (B) before it was added to 4.0 c.c. of (A).

Some of the results obtained are shown in Fig. 5.

3. Silicic Acid

These gels were prepared by mixing solutions of sodium silicate (A) (25%) and 20% ammonium acetate (B).

The effect of sodium silicate was studied by adding 2.2 to 3.0 c.c. of (A) to 4.0 c.c. of (B). The effect of ammonium acetate was studied by adding 3.0 to 4.0 c.c. of (B) to 2.2 c.c. of (A). The effect of HCl was studied by adding 0 to 0.2 c.c. of 0.2 N HCl to 2.2 c.c. of sodium silicate before it was added to 3.25 c.c. of ammonium acetate. The effect of methyl, ethyl, propyl alcohols, glycerine were studied by adding 0 to 0.4 c.c., 0 to 0.3 c.c., 0 to 0.4 c.c. and 0 to 0.2 c.c., respectively, of the alcohols and glycerine to 2.2 c.c. of (A) before it was added to 3.0 c.c. of

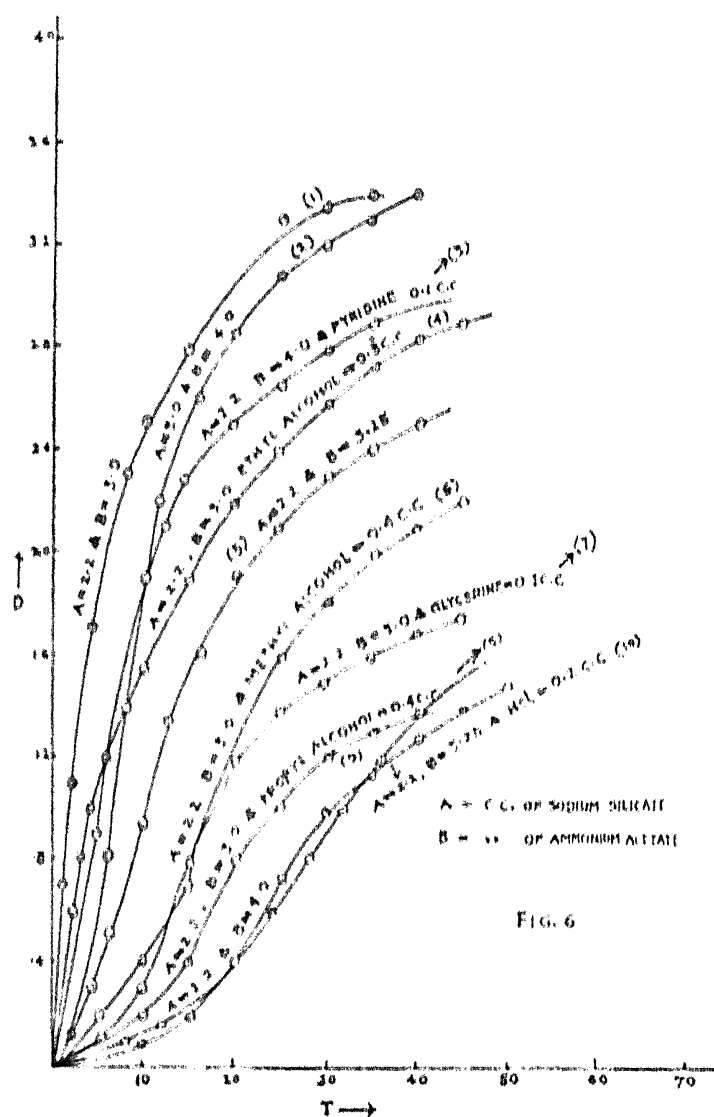


FIG. 6

(B). The effect of pyridine was studied by adding 0 to 0.15 c.c. of the same to 2.2 c.c. of (A) before it was added to 4.0 c.c. of (B).

Some of the results indicating the various effects are shown in Fig. 6.

Discussion of Results

It was observed that all the results given in the foregoing pages are fairly reproducible; several observations taken with the same gel-forming mixture under identical conditions did not differ by more than $\pm 2\%$. These results are therefore important as they represent fairly accurately the changes in opacity taking place in the gel-forming mixtures during setting.

It will be seen that all the opacity-time curves shown in various figures are smooth and continuous. This shows that the process of gel-formation, as revealed by opacity changes, is a continuous one.

The several curves in various figures show that the opacity values of a gel-forming mixture at different intervals of time change with a change in the amounts of the constituents of the gel-forming system and by the addition of alcohols and hydrochloric acid. These effects have been discussed severally in the following for each gel.

1. Thorium Molybdate Gels

It will be seen from the curves in Figs. 3 and 4 that thorium molybdate gels are very opaque in the beginning and their opacity decreases during the course of setting at first rapidly and then slowly until after sometime it tends to reach a constant value. This constant value has been called as the final value of opacity in the following discussion.

It will be noticed from the various curves in Fig. 3, that with an increase in the amount of thorium nitrate in a gel-forming mixture the rate of change of opacity systematically increases and the final value of the opacity systematically decreases to such an extent that the gel formed in the presence of 4.0 c.c. of thorium nitrate are practically water clear. The observed behaviour is attributed to the peptising action of the thorium ions. The reverse effect takes place by the addition of increasing amounts of potassium molybdate (*cf.* curves 7 and 3, Fig. 4).

The addition of increasing amounts of HCl causes the same effects (*cf.* curves 7 and 5, Fig. 4) as the increase of thorium ions (*cf.* curves 7 and 1, Fig. 4), that is, increases the rate of change of opacity and decreases the final value of the opacity to a large extent. The addition of methyl, ethyl and propyl alcohols, however, decreases the rate of change of opacity and makes the gels more opaque (*cf.* curves 7 and 2, 7 and 4, 7 and 6, respectively, Fig. 4).

2. Stannic Arsenate Gels

It will be noticed from the curves in Fig. 5, that stannic arsenate gels, unlike thorium molybdate gels, are transparent in the beginning and become

opaque during setting. The opacity increases at first rapidly and then slowly until it tends to reach a constant value, the opacity-time curves being S-shaped. Further it will be noticed that the rate of change of opacity decreases on increasing the amounts of stannic chloride (*cf.* curves 1 and 7), decreasing the amounts of arsenic acid (*cf.* curves 3 and 7) and by the addition of HCl (*cf.* curves 3 and 4) and methyl (*cf.* curves 3 and 6), ethyl (*cf.* curves 3 and 5), and propyl (*cf.* curves 3 and 8), alcohols and glycerine (*cf.* curves 3 and 9). However, the addition of increasing amounts of pyridine increases the rate of change of opacity (*cf.* curves 3 and 2).

3. Silicic Acid Gels

It will be seen from the curves in Fig. 6 that like stannic arsenate gels, the gels of silicic acid are transparent in the beginning and become opaque during setting. Some of the opacity-time curves first rise rapidly and then slow down and tend to reach a constant value while others are S-shaped. These results are in conformity with those obtained by Prasad and Hattiangadi.⁷ The different curves in Fig. 6 show that the rate of change of opacity is decreased and the gel becomes more transparent as the amount of ammonium acetate in the gel-forming mixture is increased (*cf.* curves 1, 5 and 8) and HCl (*cf.* curves 5 and 10) and methyl (*cf.* curves 1 and 6), ethyl (*cf.* curves 1 and 4) and propyl (*cf.* curves 1 and 9) alcohols and glycerine (*cf.* curves 1 and 7) are added. However, the rate of change of opacity increases and the gel becomes more and more opaque as the amounts of sodium silicate (*cf.* curves 2 and 8) and pyridine (*cf.* curves 3 and 8) in the gel-forming mixture are increased.

The observed change in opacity may be attributed to the changes in the intensity of light scattered and absorbed by the micelles in the gel-forming mixtures during setting. The intensity of light scattered by colloidal particles is given by the mathematical expression developed by Lord Rayleigh

$$I = \frac{9 N \pi^2 V^2 A^2}{\lambda^4 X^2} \left(\frac{n_1^2 - n_2^2}{n_1^2 + 2 n_2^2} \right)^2 \sin^2 \theta,$$

in which the terms involved have the usual meaning.

This equation reduces to $I = K N V^2$ where N and V are the number and volume of the particles. So the changes in opacity that take place during gelation are due to the changes in the values of N and V .

The changes in the intensity of scattered light may also be due to the changes in the anisotropy, distribution, and arrangement of the micelles in the gel. D. S. Subba Ramiah's measurement of depolarisation factors (ρ_w , ρ_v and ρ_h) have shown⁸ that the particles in gold sols are anisotropic.

K. Subba Ramiah has shown that changes in the anisotropy of the micelles of silicic acid gels take place during setting.⁹ It is probable that changes in the anisotropy, distribution and arrangement of the micelles in the gels studied in this investigation may be taking place during setting and on changing the constituents of the gel-forming mixtures and these changes may also contribute to the rate of change and final values of opacity observed, in addition to changes in the values of N and V during gel-formation, mentioned above.

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Summary

The opacity changes during the setting of thorium molybdate, stannic arsenate and silicic acid gels have been investigated by an improved apparatus assembled by the authors. The effects of the addition of different amounts of the gel-forming constituents, HCl and non-electrolytes on the gels, have been investigated and the results discussed. It has been suggested that changes in the number, size, distribution, arrangement, etc., of the micelles of the gel contribute to the observed changes in opacity.

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