257. *Rhythmic Turbidity in the Precipitation of Barium Sulphate.*

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The instruments used in this investigation were the turbidimeter of the disappearing-filament type, called D.F., and the photoelectric densitometer, called P.E. We prefer to term the latter an opacimeter.

The theory of the D.F. instrument is treated fully in a paper by Toy, Davies, Crawford, and Farrow (Report on Turbidity, *Proc. 7th Internat. Cong. on Photography*, 1922). A lamp filament is viewed through a layer of suspension the thickness of which may be varied. The extinction depth is reached when the apparent brightness of the filament and that of the adjacent background are not to be distinguished one from the other. The sensation excited by the apparent brightness of the filament decreases as the thickness d of the obscuring layer increases from zero. The apparent brightness of the adjacent background at first increases, and then decreases, with increase in d. At the extinction depth d_e the eye cannot distinguish between the two adjacent brightnesses. The sensitivity of the eye for contrasts in brightness varies with the total light intensity in the field. There is, however, a range of total intensity of illumination over which the contrast sensitivity of the eye is constant, and this constant value is found to be a minimum. Toy, Davies, Crawford, and Farrow (*loc. cit.*) define visual turbidity as follows: If the total retinal brightness of the filament image is f', then this is also equal to $f + s$, where f is the brightness due to undeviated light, and s that due to scattered light. Let s' be the brightness of the field immediately adjacent to the filament, and further, let δB be the least difference of brightness perceptible at brightness B; $\delta B/B$ is the contrast sensitivity or Fechner's fraction, which may be written as K. By plotting $\log f'$ and $\log s'$ against thickness of obscuring layer, two curves are obtained, which approach one another until their distance apart has been reduced to K, when

$$\log(f + s) - \log s' = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The thickness at this point is the obscuring thickness d_e. If the total intensity range has been chosen so that $\delta B/B$ is a minimum, then K is a constant, which is independent of variation of f' within the chosen range, as verified by Walsh (" Photometry," 1927, p. 52).

Equation (1) may then be put into the form

$$f/s = e^{k-1} = \text{const. (where const.} = K) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The definition of turbidity then follows : "A turbid medium is one that scatters light, and its visual turbidity for a given observer, apparatus, and wave-length of light is the inverse of the mass of the disperse phase per sq. cm. at the obscuring thickness when measured under conditions such that the least sensation difference which the eye can detect is a minimum."

When the brightness is of the correct order, the highest and lowest values for total intensity which occur in using the instrument will lie within the region where $\delta B/B$ is constant, and Renwick's dilution law (*Roy. Photograph. J.*, 1927, **67**, 185) will hold, *i.e.*, $d_e c$ = constant (where c = concentration of obscuring substance).

The instrument used in this work was a modified Donnan-type colorimeter. A filament lamp working from 220 volts D.C. mains was fixed below the cup, which was painted black outside, except for the window at the bottom. The lens was removed from the eye-piece, which was replaced, and the path of the light, which would normally pass through the standard cell and the remainder of the field, was blocked. The image of part of the filament could be observed by applying the eye to the pin-hole in the eye-piece.

The Photoelectric Opacimeter, P.E.—As the thickness of a layer of a turbid medium is increased from zero, the rate of loss of brightness of the undeviated light is at first greater than that of increase of brightness from emergent scattered light; hence, for a thin layer, densitometric measurements may bear a definite relationship to turbidimetric. If the scattering power of the obscuring substance is small, this relationship may hold for an appreciable thickness of layer. In the experimental densitometer or opacimeter a beam of light from an opal lamp of 100 watts run from 220-volts D.C. mains passed vertically downward through two apertures in alinement and 7 cm. apart (to secure approximate parallelism), then impinged upon a Petri dish which stood upon the flat surface of a planoconvex condenser lens. An aperture in a piece of black paper between the dish and the flat surface of the lens corresponded in size, shape, and alinement with the other apertures. At the focus of the lens was placed the window of the photoelectric cell, which was of the cuprous oxide type, having a resistance of several thousand ohms. The window was only partly covered by the beam of light. The *E.M.F.* was registered by a sensitive mirror galvanometer (an Onwood by Gambrell) having a resistance of 860 ohms at 20°. Deflections were reduced in a definite proportion by addition of suspensions from a burette. The depths of these suspensions were accurately controlled on account of the large surface of the dish.

Registration marks were made upon the dish, and upon its support, as the dish was not optically worked, and variable results might be obtained from different orientations.

Calibration of Instruments.—The suspensions used in calibrating the D.F. instrument were prepared as follows. 10 C.c. each of $N/10$-solutions of pure barium chloride and potassium sulphate were well mixed by pouring, allowed to stand, heated, made up to 250 c.c., and kept over-night. The variations between successive readings upon this suspension carried out in the manner to be described were not more than 2—3%, which is the average error of these determinations. A known dilution of the well-mixed suspension was placed in the cup; the plunger was lowered to $d = 0$ on the scale at the side, and was then raised until the filament just disappeared. These observations are fatiguing, and much practice is needed to obtain satisfactory results. The optimum brightness defined above was first obtained. A screen consisting of a photographic plate, exposed in sections for various times, and then developed and fixed, was interposed between the lamp and the cup, and the concentrations c (in millimols./l.) of the suspensions were varied. Values of $d_e c$ were plotted against d_e as shown in Fig. 1. It will be observed that all the graphs are approximately linear, but that the product $d_e c$ increases or decreases with reduction in d_e, except at a certain illumination controlled by screen 3, which gave the required relation with two separately prepared suspensions. After much practice in measuring the solution, mixing, and reading the extinction depth, the whole operation could be completed and recorded in 4 minutes, allowing such rest to the eye that observations could be continued for as long as 40 minutes.

Under the standard conditions, turbidities, T, are expressed as $1000/d_e c$. This has the dimensions of an area, *e.g.*, cm.^{2}/g. Suppose that c is expressed in g./1000 c.c., then $T = 10/d_e \times c$ = turbidity or obscuring power in dcm.^{2}/g., is a convenient unit. When concentrations are constant in a series of suspensions, $10/d_e$ may be used to compare turbidities.

In the case of the photoelectric instrument, variations in the supply voltage, and hence in the intensity of the illumination, were almost eliminated by taking extinction coefficients. The intensity of the light source, determined at intervals during 20 minutes, varied as shown in Fig. 1 by about ± 2% between extreme values. A ground-glass plate was placed over the trough, and the resulting intensity was measured alternately with that of the light source, I_0. The mean values of log I_0/I showed maximum deviations ± 0·95 on the mean value. The extinction coefficient was taken as a measure of the opacity, O. Although no exact proportionality between O and T was to be expected over a wide range, yet an approximate proportionality over a limited range could be obtained as follows. The total net effect measured as extinction depth d_e varies directly as the light transmitted forward, and inversely as that scattered forward, whilst the intensity of illumination I, measured on the P.E. instrument, includes both transmitted and scattered light. If, however, the intensity I after absorption includes only a small proportion of scattered light, which is further reduced by selecting a narrow beam parallel to the direction of incidence, then O should be nearly proportional to T. This was confirmed experimentally.

FIG. 1.

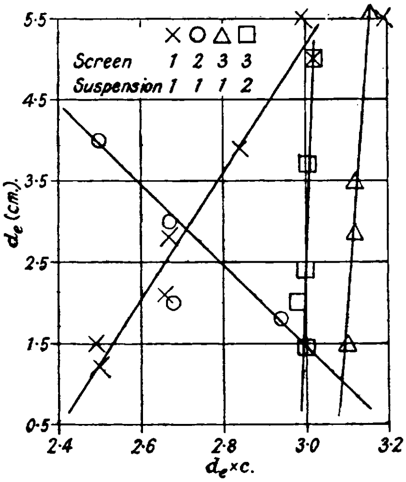
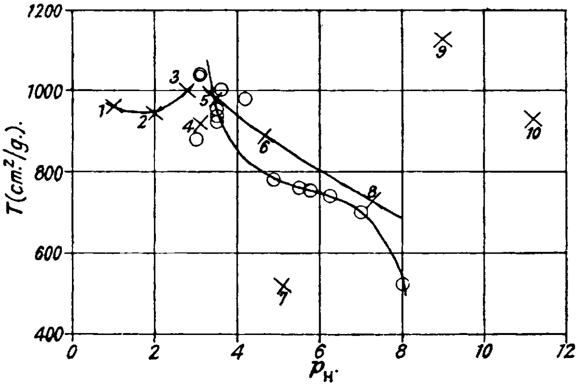


FIG. 2.



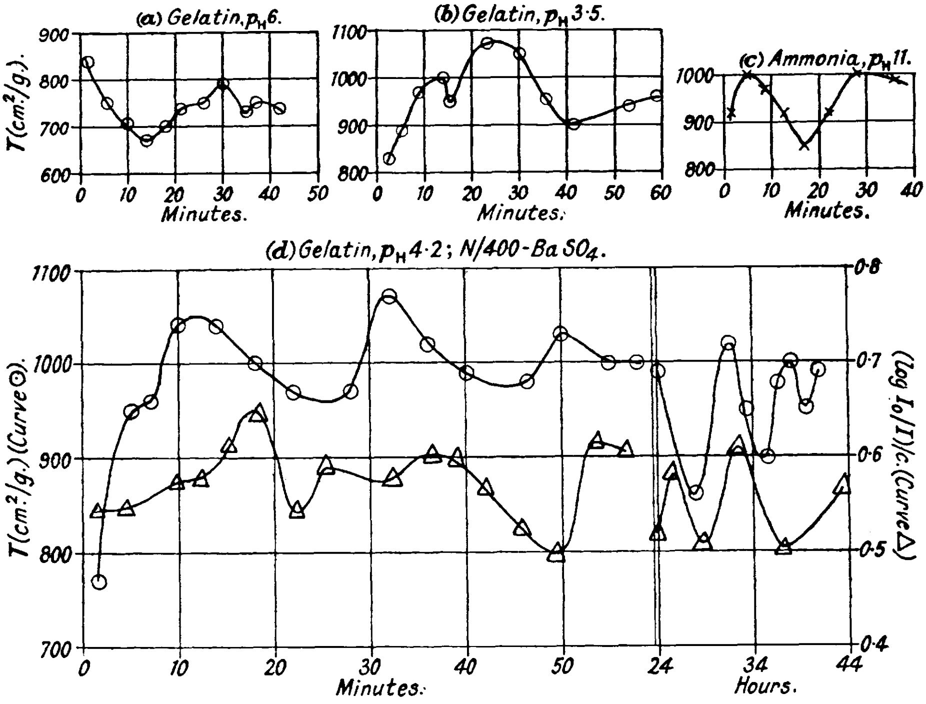
O, *Gelatin, acid or alkali.*
X, 1, 2, 3, *Hydrochloric acid.*
X, 4, 7, *Phthalate.*
X, 5, 6, *Acetate.*
X, 8, 9, *Phosphate.*
X, 10, *Ammonia.*

Preparation of the Experimental and Standard Suspensions.—The suspensions under investigation were prepared by mixing in a uniform manner, which was designed to ensure that precipitation should take place on existing nuclei. 100 C.c. of N/100-potassium sulphate were well mixed with 10 c.c. of N/100-barium chloride, and kept for 5 minutes; 200 c.c. of water, buffer solution, or dilute gelatin were added, the mixture was stirred and kept for 2 minutes, the remainder of the barium chloride then added, and the whole well mixed by pouring to and fro. The suspensions were then investigated in the D.F. and sometimes in the P.E. instrument.

Effects of Variations in the Concentrations of the Hydrogen and Other Ions.—On account of one of the original objects of the work, many of the solutions contained up to 0·02% of gelatin, but this apparently had no effect on turbidities. Results obtained for N/400-barium sulphate in various buffered or unbuffered solutions are shown in Fig. 2. The more acid solutions, of p_H 1—3, were obtained with hydrochloric acid, those of p_H 3—4 with acetic acid, p_H 4—6 with gelatin and acid or alkali, or with acetate buffers, and of p_H 7 with phosphate. On account of the variability referred to below, results were represented as maximum, or more usually as average, turbidities. These were calculated by a graphical method. Squares under the curves were counted, and the area was converted into a rectangle, the base of which was the time axis. The p_H values were sometimes calculated, sometimes determined with the aid of indicators.

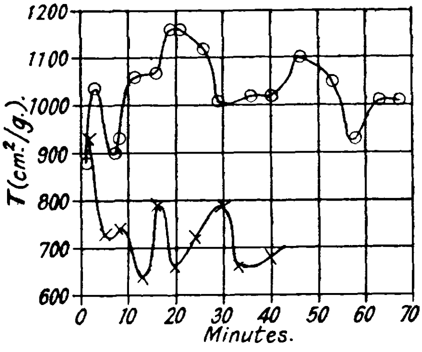
It is evident that the mean (and also the maximum) turbidities increase with diminution of p_H for constant concentrations of suspensions. The highest maximum is at p_H 3 in the presence of gelatin. The few values which fall far off the curves can usually be explained. The abrupt drop in the presence of higher concentrations of hydrochloric acid is probably due to incomplete precipitation. An acid phthalate solution at p_H 3 gave a normal T = 9·18, while an alkali phthalate at p_H 5·1 gave only 5·2, the normal value in acetate at p_H 4·7 being 9·6. The precipitate in the alkali phthalate was in an unusually coagulated condition. Also, the observations with the D.F. instrument lay nearly on a straight line, so that no rhythmic effect was present. Phosphate buffer at p_H 7·3 gave $T = 7{\cdot}24$, but at p_H 9 gave a high value, 11·34, probably due to the presence of barium phosphate.

Fig. 3.



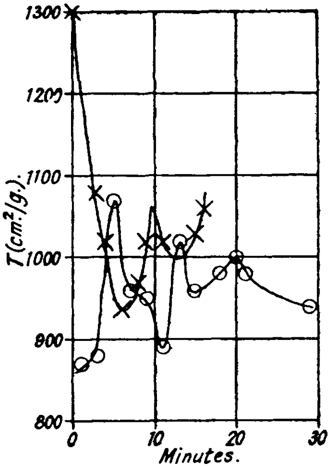
O, *Suspension* E 1(1). △, *Suspension* E 1(2).

Fig. 4.
N/400-BaSO$_4$.



O, *Gelatin*, p_H 3; *constant stirring.*
X, *Phosphate*, p_H 7·3.

Fig. 5.
Conductivity water; N/400-BaSO$_4$.



The Rhythmic Effect.—It soon became evident that the turbidities of suspensions prepared as already described were not constant but varied in a more or less regular manner. Some of the curves are shown in Figs. 3 and 4. Similar curves (Fig. 5) were obtained in solutions free from gelatin. The character is very well marked in a solution, *e.g.*, at p_H 3—4, in which the waves had an amplitude of 22% of the mean value and a period of 45 minutes. The waves may begin in opposite phases, either with an increase or with a decrease in turbidity.

In order to test a possible criticism that the effect might be due to "rhythmic fatigue," a similar experiment was carried out with the P.E. instrument. The results are shown in Fig. 3 The two curves refer to the same suspension : although the wave systems are not identical, the general effect is confirmed. It has been repeated in solutions of various p_H and this does not appear to be a determining factor. It appears to be initiated by mechanical stirring. Suspensions which had settled down after 30—40 minutes were kept for several hours or a week, and then again mixed by pouring to and fro. The results are shown in Fig. 4. The whole process, starting from a point near that of mean or equilibrium turbidity, was repeated with the same amplitude but a shorter period, the same mean turbidity being reached in each case. Rhythmic variations in the concentration of sodium chloride and other diffusible salts when in contact with gelatin, hæmoglobin, membranes, and particles of barium sulphate have been observed by Waelsch, Kettel, and Busztin (*Kolloid-Z.*, 1936, **74**, 29). Although these cannot in themselves affect turbidity, they may yet play a part in the interconversion of more or less turbid forms.

Examination of Possible Causes.—Variations in the turbidities of suspensions having the same concentration can be explained in several ways, *e.g.*, by change in (1) the amount, (2) the size, or (3) the form of the particles.

(1) *Incompleteness of precipitation.* The stock solutions of potassium sulphate and barium chloride were exactly equivalent, as was proved by precipitation according to the method of Hahn (*Z. anorg. Chem.*, 1923, **126**, 257) and testing the filtrate, which did not show the slightest turbidity with either reagent. Selective adsorption of ions must also be considered. Information on this, and on the general solubility of barium sulphate, is summarised by Friend and Wheat (*Analyst*, 1932, **57**, 559). When the nuclei are formed in the presence of an excess of potassium sulphate as described above, it might be expected that this salt would be adsorbed on the precipitate, leaving a slight excess of barium chloride in the final solution. Some of this was found to give a slight turbidity on standing, showing a slight supersaturation, and after a further filtration, a faint turbidity on treatment with potassium sulphate, indicating the adsorption of this on the original nuclei. All these turbidities are so slight that they could not possibly account for the variations observed.

(2) *Variations in size.* The sizes of the two kinds of particle, under a magnification of 335 diameters, or as seen in photographs, appeared to be of the same order, the ratio of the linear dimensions of (*b*) to those of (*a*) being about 1·6. This is insufficient to account for the observed variations in *T* and *O*, since it appears from Dunn's results (*Ind. Eng. Chem.*, 1932, **24**, 181) * that variations in the size of such large particles as we had under observation do not produce proportionately great changes in extinction depth. Also, in the present case the larger particles showed the larger turbidity, whereas the effect to be expected from mere change of size is in the contrary direction.

(3) *Variations in form.* It is known that barium sulphate is precipitated in at least two forms : (*a*) Simple prismatic crystals from hot dilute solutions, especially those containing free hydrochloric acid ; (*b*) branching crystals, mostly cruciform, from neutral solutions and those containing free acetic acid. Sketches of these two types have been furnished by Kolthoff and van Cittert (*Z. anal. Chem.*, 1923, **63**, 392) and by Balarew (*Z. anorg. Chem.*, 1922, **123**, 69), who has also described cruciform structures with a fern-like character which are precipitated from weakly acid solutions containing ammonium chloride. Various complex formulæ have been assigned, *e.g.*, $K[Ba_5(SO_4)_6]$, $Ba[Ba_5(SO_4)_6]$. Complexes such as $BaClKSO_4$ and $Ba(KSO_4)_2$ are said to be almost as insoluble as barium sulphate (Kolthoff and Vogelsang, *Z. anal. Chem.*, 1919, **58**, 49). Small proportions of such adsorption complexes, which may be present in precipitates of almost theoretical composition, appear to have a considerable effect in determining the form of the crystals. Microphotographs of some forms have been given by Ardagh, Richardson, Richardson, and Humber (*J. Soc. Chem. Ind.*, 1934, **53**, 1035). Their precipitations were made in much higher concentrations of salts, in the presence of free hydrochloric acid, and often of ammonium chloride, which seems to favour the formation of simple prisms. When potassium sulphate was run into barium chloride with ammonium chloride and 0·33*N*-hydrochloric acid, " bow-tie " crystals were obtained with an abundance of simple prisms from about 70° upwards. The latter were stained selectively, at the edges and in patterns, the former completely, by crocein-scarlet 3BX, an acid azo-dye with sulphonic groups. This possibly shows positively charged areas or surface, due to adsorption of barium ions. If the acid con-

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* These suspensions, however, were much more concentrated than ours.

centration were 0·041—0·15*N*, many clusters were formed at 100°. When barium chloride was run into potassium sulphate, without ammonium chloride, but with 0·6*N*-acid, perfect orthorhombic crystals were not obtained, but many branching forms even up to 100°. None of these crystals stained with crocein-scarlet.

Our methods gave different results : (*a*) Alternate addition of the salts to excess of hot water gave a few clusters, with a large proportion of simple prisms ; (*b*) precipitation in the cold, in the presence of an initial excess of potassium sulphate, gave few large clusters, but chiefly simple aggregates of a cruciform type. Form (*b*) has the higher turbidity, and shows the rhythmic effect. Type (*a*) may be prepared by Hahn's method (*loc. cit.*), which gives theoretical weights of barium sulphate in water or dilute acetic acid, but low results (0·4%) in *N*-hydrochloric acid. Solutions of *N*/100-barium chloride and potassium sulphate were added alternately, 5 c.c. at a time, from two burettes to 100 c.c. of hot water. After the addition of 50 c.c. of each, the suspension was cooled and made up to 200 c.c. The D.F. instrument indicated an extinction depth beyond its range. On the P.E. instrument the opacity was 0·108—5%. Another precipitation in the hot by Hahn and Kolthoff's method in neutral solution, with 50 c.c. each of *N*/50-reagents, gave an *N*/200-suspension, the values of d_e being 32·6 and 31·8 mm. Therefore $T = 10/(3{\cdot}22 \times 0{\cdot}584) = 5{\cdot}32$, and as O was 0·284 and 0·288, $T/O = 18{\cdot}6$. (*b*) A suspension of *N*/400-barium sulphate was prepared by precipitation on nuclei in acetate buffer having p_H 3·5. The mean turbidity was constant in time, and after 2 months d_e was 32 mm. ; therefore $T = 10{\cdot}7$. The mean value of O was 0·458 (0·455 and 0·462), therefore $T/O = 23{\cdot}4$.

The two preparations were examined microscopically. A drop of the liquid was placed over a trace of Mayer's albumin-water on a slide, and dried over the embedding oven. The slide was heated so as to fix the albumin, and was rinsed, covered, etc., according to the usual technique. The appearance of the photographs has been described above.

From the results mentioned above it will be observed that T has been increased in a higher ratio than O. It would be expected that the forms present in (*b*) would possess a greater scattering power, since the surfaces contain re-entrant angles, and are altogether more complex than the simple reflecting planes of the prismatic crystals. The difference between the T values of the two forms would be sufficient to account for the rhythmic changes, which may be due, therefore, to periodic transformations of the cruciform aggregates into the simple prismatic crystals and *vice versa*. This, of course, does not explain the rhythmic character. It seems, however, that the free energies of the two forms must be rather evenly balanced in order that such slight disturbances should initiate what appear to be oscillations about a position of minimum energy.

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