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THE APPARENT FORCES BETWEEN FINE SOLID
PARTICLES TOTALLY IMMERSED IN LIQUIDS. I.

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THIS investigation was undertaken at the suggestion of Professor Milton Whitney, of the United States Agricultural Department, in order to throw light on the physical bearings of certain points in his theory of the effect of fertilizers upon the retentiveness of soils for moisture. I desire to express my obligations to him for his continual interest and valuable suggestions, and for much information and many references upon the subject of flocculation.

I would also acknowledge my indebtedness to Professor Rowland for his courtesy and assistance at all times; and to Dr. Joseph S. Ames for his continual guidance and suggestions in both theory and experiment.

§ 1. The experiments described in the first part of this paper were made in order to reproduce, if possible, some of the phenomena of flocculation under more definite and controllable conditions, while in the second part (to be published in a subsequent number of the PHYSICAL REVIEW) an attempt is made to give a fuller theory of these phenomena than has hitherto appeared. The facts of flocculation are well known and may be summarized as follows:—

When a few drops of various solutions are added to a jar of pure water, in which clay or finely divided sand is suspended, certain marked effects occur : —

(1) If acids, lime, common salt, or almost any acid or neutral salt are added, the clay particles gather themselves into groups, — they become flocculated.

(2) When a very small trace of ammonia, caustic potash or soda, carbonate of potash or soda, or borax is added, the particles seem to attain a more finely subdivided condition than in pure water and may thus be held in suspension much longer.

(3) When an excess of these last substances is added, the same effect is produced as by the addition of acids, — flocculation is caused.

PART I. EXPERIMENTS.

§ 2. Observations on flocculation have, for the most part, been made only incidentally in experimenting upon the rate of settling of sediments in water and solutions. Professor Whitney has, however, placed a little clay-water under a powerful microscope, and upon adding a drop of very dilute hydrochloric acid has seen the particles form into closer groups. Violent currents are, of course, set up by the entry of the drop, so that individual grains can hardly be watched and little can be told of the process which has taken place except that, after the currents cease, the grains are in groups instead of separate.

§ 3. It therefore seemed interesting to try with larger bodies, whose movements could be more closely watched, whether the film of liquid, which we must suppose to be adherent to each of their surfaces — even when in so-called contact under water — could be made to change its thickness considerably by adding a slight trace of salt, and whether a sufficient force could be so called into play to move the bodies. This is, of course, a totally distinct phenomenon from the well-known interactions of floating solids, such as corks, though both are due to the same molecular forces. Experiments were accordingly begun in November, 1892, by a method suggested by Dr. Ames. A pair of large lenses, used for projecting Newton's rings in lecture experiments, were

placed one on top of the other in a vessel of pure water, and the reflected system of rings obtained. Several grams of 20 per cent salt solution were then put in. A simultaneous expansion of the rings would have meant that the glasses had moved nearer than in pure water, a contraction the reverse, but the lenses were far too heavy, and no motion could be observed even with a microscope. After several months of trial of more and more delicate modifications of this apparatus, the following method was found to answer :—

Method.

§ 4. *ABC* (Fig. 1) is a large evaporating crystal which was filled with pure water and placed under the microscope. *L* is an ordinary spectacle lens and *F* a very small fragment of a microscope cover-glass, the thinnest obtainable. A mirror reflected a

Fig. 1.

beam of sodium light *RF* on this fragment, and the Newton's rings formed between its lower surface and the lens were observed in a microscope *M*. The latter was fitted with a three-inch objective and a micrometer, whose scale was 1 mm. = 675 divisions. An average size of the fragment of cover-glass used was 400×600 divisions, or about one-half a square millimeter in area, weighing $\frac{1}{4}$ mg. The appearance of the rings was now carefully noted,

and their position determined with the micrometer cross-hairs. After watching carefully for half an hour or more to make sure that no accidental change was taking place in the rings, a little solution of the salt to be tried was introduced, the manner varying as the experiments gave more experience. Whether the light fragment had been attracted closer to the surface of the lens or repelled from it was now shown by the way the rings changed. The amount even of motion away from the lens could be roughly determined by the number of times the central spot changed color, the surrounding rings meanwhile shrinking. On the other hand, an expansion of the rings denoted a drawing down of the fragment, and the distance could be approximated in the same way. Further details will be found in §§ 7 to 10 below, and a consideration of the effect of change in the index of refraction and other sources of error in § 11 and § 12.

Results.

§ 5. The substances tested were:—

- (1) NaCl and HCl (chiefly the former), as types of substances which tend to produce flocculation.
- (2) KOH and NH_4OH , as types of those which tend to prevent it.

§ 6. The results are briefly:—

1. KOH. (a) The first effect of the change from pure water to very dilute KOH is to raise the fragment, off the lens, very roughly a distance of 7×10^{-5} cm. on the average.

(b) As the solution around the fragment grows in strength, the direction of motion is reversed, and the fragment settles back partly. This return motion did not always take place, and when it did, was usually less than the direct, so that the fragment was left further from the lens than in pure water.

(c) By increasing considerably the amount of KOH by further additions, the fragment was sometimes brought back to its position in pure water, and, more rarely, seemed to be drawn closer to the lens.

(d) By Method I., which allowed the solution about the particle of cover-glass to decrease in density as the salt first added settled

to the bottom, the fragment would be drawn down when a second drop was added, would rise again as this in turn settled, and could be made to repeat this process several times, approaching, however, a position closer to the lens as the repeated drops began to affect the strength of the solution throughout the vessel.

(*e*) By Method II., which allowed solution of definite density gradually to replace pure water, .0007 gr. per cubic centimeter was shown to be too much KOH to produce the greatest separation of lens and fragment. .0024 seems to be enough to bring them closer together than in pure water, though this limit is more uncertain.

To sum up: A trace of KOH—less than .0007 gr. per cubic centimeter—added to pure water tends to increase the thickness of the glass-liquid surface film and so separate two glass surfaces immersed in the liquid. An excess beyond this trace tends to reverse this phenomenon. (Compare effects of excess of alkali on suspended clay or sand particles § 1.)

2. NH_4OH . Few experiments were tried with this substance on account of the fumes. Of four experiments, one gave no result, one a drawing down of the fragment (flocculation), two (one of them very accurate) a result precisely like KOH.

3. NaCl . A large number of trials were made with this, most of which showed absolutely no motion of the rings. A few of the earlier experiments gave contradictory motions one way or the other. The later, more careful ones showed either no change whatever or, in one or two instances, a motion of as much as 1×10^{-5} cm. towards the lens, so small a distance that it may easily have been imagined or due to accident.

4. HCl . Tried only a very few times, usually without effect. Once there seemed to be undoubted raising of the fragment, once a slight drawing down, and once a raising followed, with increasing strength of solution, by a greater drawing down.

In a number of experiments after repeated failure with drops of NaCl and HCl , a drop of KOH on being added at once produced its characteristic effect. This indicates conclusively that the effects of KOH are not due to currents in the liquid, since the solutions were all dropped in in the same way and were, moreover, very closely of the same density and index of refraction.

Borax was tried once without result.

Details.

§ 7. The chief difficulty to be overcome was in making the change from pure water to dilute solution. At first a much larger vessel than that described in § 4 was used, and the salt was added by pouring in a few grams of 20 per cent solution at a distance from the fragment. The time taken for the solution to reach any given strength around the fragment was indeterminate, and therefore the position of the rings had to be observed with great care from the moment the salt was put in until all possibility of effect was past. This was done by making, during this time, repeated settings of the cross-hairs upon the middles of three or four successive bands, which could be done to within $\frac{1}{20}$ of the width of a band. In the course of from five minutes to an hour or more from the time of putting in the salt, there were at times considerable changes in the positions of the rings, *i.e.* a shifting in or out of $\frac{1}{4}$ or $\frac{1}{2}$ the width of a ring. There was, however, never any certainty that the changes were coincident with the arrival of the salt in the neighborhood of the fragment, and the results could never be repeated with any certainty by trying to reproduce the same conditions. It may, however, be said that observations kept up for an hour before any salt was put in rarely showed a small fraction of the change which followed its addition. The results as a whole were, however, contradictory and showed nothing.

The shallow crystal shown in Fig. 1 was now substituted for the larger vessel used before, so that a drop of solution could be put in with a rod or dropper, as in that figure, and settling to the surface of the lens, pass over the spot occupied by the fragment. It was then easy to ensure the presence of salt in the surface films between the two within a few minutes after the drop was put in by giving the lens a very slight slope and dropping in the solution a little higher up than where the small fragment *F* lay. The whole process was now as follows:—

METHOD I.—The lens, dish, and a number of fragments were soaked for a day in strong bichromate solution. They were then carefully washed in running water and left to soak in it over night. With a final rinsing in the morning in water filtered to

remove grit, the fragments were picked up on a glass rod and placed on the lens, care being taken to touch the latter only on the edges. The lens was then put in the dish and a final rinse given. This was sure to wash the light fragments off the lens if the surfaces were not so clean as to make very good contact, and therefore furnished a very useful though often most provoking test of the efficiency of the cleaning process. Enough filtered tap-water was now put in to cover the lens entirely, and the whole put under the microscope. The reflector was then placed so as to make the angle RFM as small as possible. All the fragments were then brought into the field in turn, and the one which gave the most perfect rings chosen. The position of one or more of the edges of this were then fixed with the micrometer as a check upon motion of the fragment as a whole along the lens. A rough sketch of the fragment and a few of the central rings being made, and also a note descriptive of the general appearance of the whole system of rings, the latter were carefully watched for a half hour, and, if any change occurred in their position or in the point of closest contact between the fragment and lens, the former was discarded as not trustworthy, and others successively were tried until one was found that stood the test. A drop of solution—20 per cent in the earlier and 5 per cent in the later experiments—was now put in, as described above, and in the course of a few minutes the changes in the rings took place, whenever there were any at all. These were carefully noted, together with the time at which they took place, and were afterwards tabulated, so that the whole evidence could be seen together. Extracts from these tables are given herewith.

TABLE I.

METHOD I.

(+ means motion of rings *out*, or glass *down*.)

No.	Solution and number of drops.	Motion.		Remarks.
		Rings (number of changes).	Fragment (10^{-3} cm., up and down).	
XXIII.	KOH 20 % few drops	-10 then reversed +2	-30 +6	Rings very good and complete. Size of fragment, 3 sq. mm. Both same in XXV. and XXVI.
	NaCl 20 % repeated drops	No effect at all		Nos. XXIII.-XXVIII. contrast the effect of acid and alkali, no change whatever being made between the two parts of the experiment.
XXV.	HCl several	No effect		See No. XXIII.
	KOH 20 % 1 or 2	Marked contraction		
XXVI.	several each of NaCl & HCl	No effect with either		See No. XXIII.
	KOH 20 % 1 or 2	Marked contraction		
XXVIII.	NaCl 20 % several	+ $\frac{1}{2}$ -5	+1.5 -20	Very small fragment, .2 mm. in area, triangular in shape, with point of contact in one corner. About 60 of rings showing. See, also, XXIII.
	KOH 20 % 3 or 4	-5	-15	
XXXV.	KOH Very dilute few drops	-1 followed by	-3 <i>greater +</i>	Washed in HCl instead of bichromate. One of very few experiments where reverse motion was greater than the original.

TABLE I. (*continued*).

METHOD I.

(+ means motion of the rings *out*, or glass *down*.)

No.	Solution and number of drops.	Motion.		Remarks.
		Rings (number of changes).	Fragment (10 ⁻⁶ cm. up and down).	
XXXI.	NH ₄ OH dilute	-1	-3	Showing effect of excess of alkali, as do also XXXVII. and XXXVIII. Rings clear and complete. Fragment large, about 4 sq. mm. Each time a drop of KOH entered, it drew down the fragment, which rose as the salt settled or became diffused, but not to so great a distance from the lens as before. Hence, as the solution throughout the vessel strengthened, the change each time became less, and the fragment drew continually nearer to the lens.
	1 or 2	followed by + $\frac{1}{2}$	+1.5	
	more	-1 $\frac{1}{4}$	-3.7	
		(no reverse motion)		
	KOH 20 %	+6	+18	
	1 or 2	followed by -5	-15	
	1 or 2 more repeated	smaller + smaller -	followed by each time	
XXXVII.	KOH 20 %	-1 $\frac{1}{2}$	-4.5	Washed in very strong bichromate solution for 3 hours and then in running water for 2, and obtained very clear and steady rings.
	1 drop			
	several more	no effect		
	more yet	+1.5 followed by - $\frac{1}{4}$	+4.5 -3.8	
	twice again	each time same as the last growing less		
XXXVIII.	KOH 5 %	-2.5	-7.5	First experiment after four months' absence. Very much like the last, except that the fragment does not seem to have risen between the last drops.
	1 drop	followed by +1.7	+5.0	
	more	+ $\frac{1}{2}$	+1.5	
	more	no effect		

§ 8. After the preliminary methods had been given up, all the experiments, except six with KOH, were made substantially as above. Not one single instance of a contraction of the rings following the addition of NaCl was observed by this method, and most of these experiments were never even tabulated. Of six that are included in the table, three show no motion whatever, and three a very slight spreading of the rings, the greatest amount being one-half the width of the central spot, *i.e.* corresponding to an approximation of the two surfaces by 1.5×10^{-5} cm. This lack of effect is easily explained on the theory that NaCl would, if possible, produce a drawing together of the surfaces, as it flocculates clay; but they could actually move closer only in a few accidental cases, since the weight of the fragment, of itself, pressed it into contact with the lens, owing to the care which was taken to have the surfaces perfectly clean. With KOH, on the other hand, within a very few minutes after the drop went in, the rings would almost invariably draw in towards the center, the latter changing color about four times on the average. This change occupied about one-half minute, and was then often followed by an immediate reversal of the motion of the rings. This reverse motion was sometimes rapid, at times quite gradual, but very rarely did it indicate a motion beyond the point from which the fragment originally started. Sometimes it took a dozen drops to bring the fragment as close to the lens as it would go, and in the meanwhile each drop, as it entered, would draw it down, and in five or ten minutes it would commence to rise once more as the drop flowed past and solution around the fragment weakened, only to be again drawn down a little further by the entry of the next drop, thus indicating that for each degree of the strength of solution there was a tendency to a film of liquid of definite thickness between the glasses.

The trials with HCl and NH_4OH need not be dwelt upon, as, where any results followed, they were like those with NaCl and KOH. The most interesting experiments by this method were those where a number of drops of NaCl (or in two experiments HCl) were added and produced no effect, or, in a few instances, a slight approximation of the glasses; and then, without in any

manner changing the position of the little fragment or any other condition of the experiment, a drop of KOH was put in, and found at once to produce its characteristic separation of the glasses. It was thus shown very conclusively that the effects with this salt were in no way accidental, but depended on a specific difference between it and the two others, since the drops were all put in in the same manner, and were carefully made of very nearly the same refractive index. Moreover, by reversing the process and adding the alkali first, the same difference was shown.

§ 9. METHOD II.—To show more conclusively that the effect of KOH was not due to disturbance on account of currents in the liquid, and to gain, if possible, a more definite idea of the density of the solution which accompanied the phenomena, the following more elaborate method was used a few times, only with KOH:—

The lens was supported near the top of a much deeper vessel, into the bottom of which liquid could be introduced by a siphon from a glass reservoir. The latter was supported on a stand of variable height, so that the rapidity of the flow through the siphon could be regulated or even reversed if necessary. The vessel containing the lens being placed under the microscope, the siphon was started and the vessel filled. The flow was then stopped, and the best fragment, as to rings and stability, was selected by trial as before, and the flow of water being again started, was watched for half an hour or more to test the effect of the mere current upwards due to the siphon, which was run at a considerably greater rate than that afterwards used. If, as was usually the case, the fragment was found to be so stable that the rings were in no degree affected by this much more rapid flow, the reservoir was filled with water to a known mark and a measured quantity of the KOH solution stirred into it. Now starting the flow at a very slow rate, the salt solution of known concentration very gradually rose in the vessel under the microscope, the pure water flowing off at the top. The fragment was always so placed that it would be directly under the point of overflow, so that the alkalinity of the liquid in which it lay could be easily determined by touching test paper to this overflow. In this manner the

moment when the liquid at the point in question changed from pure water to solution of known strength could be ascertained very closely. Its very remarkable coincidence with the time of the changes in the rings in the few trials made by this method, served to preclude any doubt that one was the cause of the other, while the almost imperceptible strength of current prevented the phenomena from being ascribed to such mechanical disturbance. These experiments gave, further, the rough values of the respective strengths of solution which caused the greatest separation of the two surfaces and a closer approximation than in pure water. These were given in § 6.

TABLE II.

METHOD II. (By SIPHON.)

(+ means motion of the rings *out*, or fragment *down*.)

No.	Grams KOH per cu. cm. siphon- ed in.	Motion.		Remarks.
		Rings (number of changes).	Fragment (10 ⁻⁶ cm. up and down).	
XLII.	.0024	+2.5	+7.5	No contraction at all; fragment seems suddenly to have passed from the pure water into solution dense enough to show effects of excess of alkali. See section 10 and Fig. 2.
XLVI.	.0008	-2 followed by +1.5	-6 +4.5	Washed in fresh bichromate. Center of rings shifted a very little, otherwise experiment was very good. After the first part of the experiment the .0008 solution was run off and siphon filled with the stronger solution.
	.0015	slight further +		
XLVII.	.0007	-1.5 followed by +5	-4.5 +1.5	Made to test the effect of acidity or alkalinity of surface before experiment. Everything precisely the same as in XLII. except that between the two the lens and fragments were soaked in strong KOH and then in running water.

§ 10. The way in which observations of changes in the rings were usually noted is shown by the sketches in Fig. 2, which are copied from my note-book, Experiment No. XLII. The shape of the fragment was a trifle more irregular, but roughly a triangle in which $AB = .89$ mm., $AC = 1.42$, $BC = 1.54$. The same ring is made heavy throughout and serves to fix the amount and direction of the change in the whole system. The siphon ran at varying

Fig. 2.

rates with pure water (Method II. was used) from 2.45 P.M. to 3.25, and was then started with KOH solution whose strength was .0024 grams per cubic centimeter. The change noted in sketch 2 began at 4.25. An expansion from the center of two rings is shown, as also that the stability of the fragment was not very good, since it tilted over a very little towards AC during the experiment.

In the earlier experiments distilled water was used, but it was found that that available was a little greasy, and in all the later trials filtered tap-water was used for the final washing and the experiment itself.

Sources of Error.

§ 11. CHANGE IN THE INDEX OF REFRACTION. — Let the point P (Fig. 3), in a plane tangent at O to a sphere of radius R , be at a distance $MP = e$, from the sphere, measured perpendicular

to the plane; and let $OP = \rho$. Then if P' is a point in a parallel plane at a distance p above the tangent one, $t = p + e = MP'$.

$$\text{Hence } \rho^2 = 2Re = 2R(t - p) = \left(\frac{n}{2\mu} \sec r - 2m\right)\lambda R, \quad (1)$$

where λ is the wave-length in air; r the angle of refraction through the film of liquid, and μ the index of refraction of the latter; and where $m = \frac{p}{\lambda}$, *i.e.* m is the distance p expressed in wave-lengths in air. n is the number of the ring of radius ρ from the center and is, of course, even for a dark band and odd for a light one.

The point observed in the experiments was the number of times the central spot ($\rho = 0$ approximately) changed through a complete

cycle, *i.e.* from n to $n - 2$, n being always counted from the ultimate black spot which would occupy the center were the lens and fragment in perfect contact. If, then, n changes from n to $n + \delta$ when salt is put in and the index of the dilute

solution thus formed is μ_1 , then the condition that it is the central spot which is being observed gives

$$\frac{n}{2\mu} \sec r - 2m = \frac{n + \delta}{2\mu_1} \sec r - 2m_1 = 0,$$

or

$$m_1 = \frac{\mu}{\mu_1} m + \frac{\sec r \cdot \delta}{4\mu_1}.$$

Therefore, if

$$\frac{\mu}{\mu_1} m + \frac{\sec r \cdot \delta}{4\mu_1} > m; \text{ i.e. } \frac{\sec r \cdot \delta}{4} > m(\mu_1 - \mu),$$

m_1 is greater than m , *i.e.* the particle has moved away from the lens. In order, then, that the change δ shall be wholly accounted for by the change in the index of refraction, m , the distance of the fragment from the lens at starting must be at least as great as

$$m = \frac{\sec r \cdot \delta}{4(\mu_1 - \mu)}.$$

I give below the requisite values of m for various values of δ , the number of times the center changed color. The data are for 5 per cent and 20 per cent solutions, the strength of the *drops* put in, which was very much diluted before reaching the fragment, and for $r = 0$, which makes m a minimum.

	μ_1	$\mu_1 - \mu$	m		
			$\delta = 1.$	$\delta = 2.$	$\delta = 4.$
NaCl 5 %	1.340	0.006	41	83	167
20 %	1.369	0.035	7	14	29
KOH 5 %	1.341	0.007	35	71	142
20 %	1.360	0.026	9	19	39
NH ₄ OH	—	negative	∞	∞	∞

The average change in the experiments due to a few drops of 5 per cent KOH was a contraction of two rings ($\delta = 4$), and to account for it wholly we should have to suppose a distance of 142 wave-lengths or $\frac{1}{10}$ mm. to separate the two glass surfaces supposed to be in contact at starting. Further, the change in the rings with NaCl should have been greater than with KOH; and NH₄OH should have produced the opposite change to what it did. The indices for such dilute solutions are not given in Landolt and Börnstein's tables, but were calculated from refraction equivalents. They are at 18° and μ for water is taken as 1.334.

§ 12. OSMOTIC PRESSURE. — A more important source of error was suggested by Dr. Ames, who thought there might be a very strong force tending to lift the fragment due to imperfect diffusion of the salt into the interstice between the two glasses. A method of attacking the question was found in an extension of an equation given by J. J. Thomson.¹ The Lagrangian function of the molecules of salt (supposed to behave like those of a perfect gas) in the volume of a solution and also in the surface films bounding it, is there given. Here two similar terms were added for the volume of liquid between the glasses and the two glass surfaces bounding thereon, the density of the salt being supposed to differ there from

¹ Application of Dynamics to Physics and Chemistry, pp. 190, ff.

its value in the open liquid immediately around. The glass surfaces are for simplicity assumed plane and parallel and separated by a distance x . If, then, H is the Lagrangian function of the salt molecules in the interstice and the liquid immediately around the fragment, $\frac{\delta H}{\delta x} = F$ is the force tending to separate the two. To determine F completely would require a knowledge of the rate at which the solutions become equalized in strength as x increases under the action of the force. A minimum value, not far from the true one, may be found by assuming that the only change is that due to the flow into the interstice, as the particle rises, of enough strong solution from without to fill the increase of volume.

Let v_1 represent the volume of liquid between the fragment and the lens; $\frac{1}{2} S_1$, the area of the lower face of the fragment, *i.e.* S_1 the total area of glass surface bounding the volume v_1 ; t_1 the thickness of the film on this surface and T_1 its surface tension, ρ_1 and σ_1 the densities of salt in v_1 and S_1 respectively; and $\eta_1 = v_1 \rho_1$ and $\xi_1 = \sigma_1 S_1 t_1$ the total weights of salt in each. Let the same characters without subscripts denote similar quantities in the liquid immediately around. J. J. Thomson's equation for H is (adding two necessary terms in the subscript quantities):—

$$\begin{aligned}
 (1) \quad H = & \eta R \theta \log \frac{v \rho_0}{\eta} + \eta \{f(\theta) - \omega_1\} - S T \\
 & + \eta_1 R \theta \log \frac{v_1 \rho_0}{\eta_1} + \eta_1 \{f(\theta) - \omega_1\} - S_1 T_1 \\
 & + \xi R \theta \log \frac{S t \rho_0}{\xi} + \xi \{f(\theta) - \omega_1\} \\
 & + \xi_1 R \theta \log \frac{S_1 t_1 \rho_0}{\xi_1} + \xi_1 \{f(\theta) - \omega_1\};
 \end{aligned}$$

where θ is the temperature and R an analogous quantity to the same symbol in Thermodynamics, *i.e.* $R \theta \rho = p$, the osmotic pressure; ω_1 and ρ_0 are constants of integration not depending on x . Remembering that

$$(2) \quad \frac{\delta \eta}{\delta x} + \frac{\delta \eta_1}{\delta x} + \frac{\delta \xi}{\delta x} + \frac{\delta \xi_1}{\delta x} = 0;$$

since the total quantity of salt is not a function of x , we get

$$F = \frac{\delta H}{\delta x} = R\theta \left[\left\{ \frac{\delta \eta_1}{\delta x} + \frac{\delta \xi_1}{\delta x} \right\} \log \frac{\rho}{\rho_1} - \frac{1}{2} S_1 (\rho - \rho_1) \right].$$

For complete solution we need an equation giving

$$\frac{\delta \eta_1}{\delta x} + \frac{\delta \xi_1}{\delta x},$$

the rate of inflow of salt as the fragment rises, but we can find a minimum by assuming that no diffusion takes place during the very short time occupied by the change in the rings, and no weak solution flows out to be replaced by stronger. Then

$$\frac{\delta \eta_1}{\delta x} + \frac{\delta \xi_1}{\delta x} = \rho \frac{\delta v_1}{\delta x} = \frac{1}{2} \rho S_1,$$

since $\frac{1}{2} S_1$ is the area and x the height of the space v_1 . Substituting we get the minimum value of the force,

$$F = \frac{R\theta}{2} \left[S_1 \left\{ \rho \left(\log \frac{\rho}{\rho_1} - 1 \right) + \rho_1 \right\} \right].$$

Remembering that $p = R\theta\rho$, we have

$$F' = \frac{S_1}{2} \left\{ p \left(\log \frac{\rho}{\rho_1} - 1 \right) + p_1 \right\},$$

where S_1 is the area of glass bounding on the interstice, *i.e.* twice the area of the lower surface of the little piece of cover-slip; ρ_1 is the density of salt in the interstice and ρ in the liquid outside; and p_1 and p are the pressures of a number of hydrogen molecules per unit volume equal to the number of salt molecules in densities given. The assumption that the salt in dilute solution follows Avogadro's law is to be noted. From data in Everett's "C. G. S. System of Units," $p = 4 \times 10^8 \rho$ and $p_1 = 4 \times 10^8 \rho_1$. Hence

$$F' = 2 \times 10^8 S_1 \left\{ \rho \left(\log \frac{\rho}{\rho_1} - 1 \right) + p_1 \right\} \text{ dynes,}$$

or
$$4 \times 10^6 \rho \left\{ \frac{\rho_1}{\rho} - \left(1 + \log \frac{\rho_1}{\rho} \right) \right\}$$

dynes per square millimeter of the under surface of the glass fragment. In the following table F' is given for various ratios of

the density in the interstice to that in the liquid around. ρ is taken as .00075, an average value in the experiments by Method II., where alone the density was definitely known.

F' FOR KOH.

$\frac{\rho_1}{\rho}$	F'	$\frac{\rho_1}{\rho}$	F'	$\frac{\rho_1}{\rho}$	F'
0.00	∞	0.10	4200	0.70	180
0.01	10830	0.30	1500	0.90	15.7
0.05	6150	0.50	520	1.00	00

In order to compare this with the force downward due to the weight of the fragment, a whole cover-slip was weighed and its diameter measured, and was found to weigh .46 mg. per square millimeter, or to be subject to a downward force of 2.94 dynes per square millimeter in water, which is insignificant compared to F' .

Considering the first effect with KOH alone, *i.e.* the rise of the fragment as the drop of solution reaches it, this force would abundantly explain the action, since the fragment ought to rise until the densities above and below it became equal, and then, the force having ceased to exist, drop back. The explanation is insufficient because:—

(1) Were this force alone acting, a second drop should again cause the fragment to rise, since the solution beneath it would again be more dilute than that outside, but in the majority of cases the reverse was the case and a second drop, if it produced any effect, usually caused a fall of the fragment, which is quite in accord with the fact that excess of alkali flocculates.

(2) So far as could be found,¹ NaCl, in ordinary cases, diffuses less rapidly than KOH, and if this holds for very dilute solutions and capillary openings, we should expect a greater disparity in the strength inside the interstice and without in the case of NaCl, and consequently a greater lifting force, whereas no lifting at all was observed. The lifting force for equal ratio of the strength inside and out is with NaCl 95 per cent of that with KOH.

¹ Ostwald's Solutions, trans. by Muir, p. 134.

While, in the absence of sufficient data with regard to diffusion in capillary spaces, some may prefer to consider the experiments as largely explained by the osmotic force, it seems to the writer more natural to suppose, considering both (1) and (2), that the effects are the result of two sets of forces both tending to raise the fragment in the case of dilute KOH, and, on the other hand, almost exactly counterbalancing each other in the case of NaCl and stronger KOH, the first set being the molecular forces which act in flocculation, and the other those which bring about diffusion.

§ 13. To sum up: The effects summarized in § 6 are a reproduction of those observed in the flocculation of clay particles, as may be seen from the following comparison:—

Results of the Experiments.

1. The effect of very dilute alkalis, represented by KOH, is to raise the glass fragment away from the lens.
2. As the KOH solution became stronger the fragment returned to its original position, and at times seemed drawn closer to the lens.
3. If the glass surfaces were closely in contact at starting, very little effect should have been expected from substances tending to draw them closer. They could only act by bending the fragment. This lack of effect was found with NaCl, in marked contrast with the strong effect of KOH.

Flocculation.

1. Fine solid particles are held further apart in very dilute alkaline solutions than in pure water.
2. More concentrated alkaline solutions reverse this effect and cause flocculation.
3. The effect of NaCl and the other substances of its class is to produce a closer grouping of the particles of clay than in pure water.

The writer hopes to extend these qualitative results to a wider range of substances and, if possible, obtain quantitative observations connecting the thickness of the adherent films separating the glasses with the density of the solution.

Fig. 2.