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J. W. POWELL, DIRECTOR

SUBSIDENCE

OF

FINE SOLID PARTICLES IN LIQUIDS

BY

CARL BARUS

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CONTENTS.

CHAPTER I.

CHAPTER II.

ILLUSTRATIONS.

LETTER OF TRANSMITTAL.

DEPARTMENT OF THE INTERIOR,
UNITED STATES GEOLOGICAL SURVEY,
DIVISION OF CHEMISTRY AND PHYSICS,
Washington, D. C., January 18, 1886.

SIR: I have the honor to transmit, through Prof. F. W. Clarke, Chief Chemist, the accompanying paper on the subsidence of fine particles of insoluble solid in liquids for publication as a bulletin of the Survey.

Very respectfully,

CARL BARUS.

Hon. J. W. POWELL,
Director U. S. Geological Survey, Washington, D. C.

SUBSIDENCE OF FINE SOLID PARTICLES IN LIQUIDS.

By Carl Barus.

CHAPTER I.

GENERAL RELATIONS OF THE PHENOMENON OF SUBSIDENCE.

INTRODUCTORY.

The remarks in this paper were suggested by Prof. W. H. Brewer's memoir on sedimentation, to a condensed account of which I had the honor of listening at the New Haven meeting of the National Academy of Sciences, November, 1883.

It is my endeavor in Chapter I to analyze the phenomenon of subsidence into parts such that the conditions under which subsidence is to be explained from a chemical or from a physical point of view may be better discernible. As an attempt is made to cover as much ground as possible, the chapter is largely qualitative in character. With these data in hand I then begin the quantitative study of but one of the more important features of subsidence. The results of this work are given in Chapter II.

I may add that the present interruption of the work, at a very interesting stage of progress, is unavoidable. Whether or not the work will be resumed at an early day, I cannot tell; I have therefore carried it as far as I can without special apparatus for very constant temperatures. Without these facilities the nice discrimination between the arbitrary thermal effects (convection, viscosity) and what I believe is an important subsidence phenomenon (stratification), is not satisfactorily feasible.

If thoroughly triturated insoluble material (clay, rock) is shaken up with distilled water and then allowed to subside, the solid particles will descend gradually and at a rate depending on their respective degrees of comminution. Particles may readily be obtained so fine that their rate of subsidence is practically infinite. These, therefore, remain suspended in the water indefinitely, giving rise to permanent opalescent turbidity.[1] In endeavoring to account for this occurrence some of the gentlemen present at the meeting were inclined to refer it to a case of hydration. The ultimate particles are supposed to combine with water, forming colloidal hydrates in a way analogous to the known behavior of silica. I accepted this hypothesis in the above simple form with great hesitation. It is, I believe, without *direct* proof, and probably does not admit of it; and my original purpose in writing this paper was so to exhibit the phenomena that I could dispense with the auxiliary chemical assumption. When viewed in the light given by the details of physical experiment the hypothesis is also incomplete. It does not even account for the observed suspension, inasmuch as it gives no sufficient reason why hydrated particles should be more readily suspended than particles which are not so affected. At least, if we regard the rate of descent as a function of the dimensions of the subsiding particles, then the chemical view assumes that the very fine particles descend under conditions essentially different from the coarser ones—a complication for which I saw no real necessity. Dust is suspended permanently in air under circumstances where hydration is impossible. Furthermore, what is the effect of hydration upon the particles? Are they disintegrated into molecules?—then the liquid should not be turbid, but clear. Or is the effect merely superficial?—then fine and coarse particles present *surfaces of like nature* to the liquid in which they are suspended: their rate of descent, varying solely with the frictional resistance in their progress through the given liquid, must be expressible by a general and purely physical law in terms of their dimensions, figure, and density. From this law, moreover, must the effects to be anticipated be deducible when the particles are so small as to be comparable in size with the molecules of the liquid.

The application of this good working hypothesis showed, contrary to my expectations, that any theory which is based exclusively on physical causes is untenable.[2] If, in the case of gases, internal friction is a kinetic phenomenon, it is certainly no longer wholly so in the case of liquids. It appears from my results, I think, that the chemical relation of the suspended solid to the liquid very materially influences the frictional resistance encountered by the particles. For given pairs of solid and liquid, however, this effect remains constant; it is thus seen that the auxiliary supposition of a chemical influence is neither essential to the physical explanations to be attempted nor incompatible with them, and that the whole discussion may be expediently subdivided into physical and chemical parts.

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[1] Professor Brewer found that even after five or six years this turbidity still continued. In studying these phenomena quantitatively particles of some convenient finite size must of course be dealt with. I shall use the term "descend" throughout. A particle which is "stationary" has an infinite rate of descent.

[2] Hydration or similar action might have been assumed as an immediate datum of the theory of mass-action.

When a liquid is forced through capillary tubes the outer layers adhere to the walls of the tubes, and the friction encountered is that between the layers of the liquid; and hence this friction, or, in other words, the viscosity of the respective liquids, is, cæteris paribus, proportional to the times of efflux of given fixed quantities. The same fact is observed in various ways—indeed, wherever liquids flow over solids. But the rates of descent of given very fine solid particles suspended in liquids bear no obvious relation to the respective viscosities of the liquids. At least, so far as the evidence from my experiments goes, where unusually large ranges of viscosity are excluded, this is the unavoidable result. In the earlier portions of the present paper it will for this reason often be *temporarily* convenient to speak as though in the case of subsidence the solid particle itself actually falls through the liquid; that it is not surrounded by an adhering layer of liquid in a way to necessitate a descent of solid particle and liquid envelope, as a system.[1]

It may still be added that the comminuted material is not to be introduced into the liquid in such a quantity that the particles in their descent would interfere with one another. All remarks, therefore, apply as it were to dilute mixtures.

Mr. Durham[2] was the first to make experiments on the phenomenon of suspension, and our knowledge of the effect of precipitants is largely due to him. Similar experiments were made at about the same time by Hunt.[3] To Professor Brewer's paper reference has been made. I am aware that Prof. C. R. Stuntz, of Cincinnati, has made similar experiments. But the general trend of the researches of these gentlemen is not such, I believe, as to be intersected by my work. My thanks are due to Prof. M. C. White, of New Haven, by whose large experience in microscopic research I have profited.

GENERAL INFERENCES.

Analogies.—The problem immediately suggests an inquiry into the general cause for the suspension of finely comminuted material. If a solid particle is so small that the force of the efficient gravity-component acting upon it is less than the frictional resistance which would be encountered during a downward motion through the molecules of the liquid, then the particle must remain fixed in position relative to the walls of the liquid which inclose it. The degree of comminution necessary for apparent suspension is readily obtainable, even in the

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[1] In the cases both of gases and of liquids the friction (external) of the fluid on the solid is enormously large in comparison with the friction (internal) of the fluid on itself. The external friction of gases is measurable only when the gas is in a state of great tenuity. (Kundt and Warburg, Pogg. Ann., CLV, pp. 337 and 525, 1875.) Successful experiments on the external friction of liquids were made by Helmholtz and Piotrowski. (Wiener Sitzungsber., XL, p. 607, 1860.)

[2] Durham, Chem. News, XXX, p. 57, 1874; ibid., XXXVII, pp. 47, 48, 1878.

[3] Hunt, Proc. Bost. Soc. Nat. Hist., p. 302, Feb., 1874.

case of gases. Maxwell,[1] using Stokes's formulæ and his own value for the viscosity of air, shows that a drop of water whose diameter (0.0025 cm.) is about one-half that of a human hair would descend in air one thousand times rarer than itself at a rate of only 2 cm. per second. The rate of descent of particles of like figure and density varies as the square of their linear dimensions. It follows that if we diminish the diameter of the particle a hundred fold we diminish its rate of descent ten thousand fold; hence a drop the dimensions of which lie near the limit of microscopic vision[2] (say, 0.000025 cm.) is practically stationary, its rate being 0.0002 cm. per second.

Returning from this digression to water, which is comparatively so much more viscous than air, we find the conditions for suspension proportionately favorable. We reasonably infer that the dimensions of the particle which will just descend are correspondingly increased. We conclude that the suspension of solid dust in a fluid is to be referred to the occurrence of molecular friction.

The physical variables.—Problems connected with the motion of solids in an incompressible fluid frequently present formidable difficulties or lead to involved results. But for the comparatively simple case in hand—i. e., the conditions of uniform motion of a small spherule of radius R falling through a liquid by its own weight—the final result is fortunately simple. Let P be the resistance encountered by a spherule moving through a liquid whose frictional constant is k at a given rate x. Then[3]

$$P=6\pi kRx \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

on the other hand, the effective part of the force of gravity is expressible by

$$P'=\frac{4\pi}{3}R^3(\rho-\rho')g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where P' is the actuating force, g the acceleration of gravity, and ρ and ρ' the densities of the solid particle and the liquid, respectively. Under conditions of uniform motion $P = P'$, and hence

$$x=\frac{2}{9k}R^2(\rho-\rho')g=AR^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A is a constant.

If there be no chemical relation between the solid and the liquid, then the constants in equation (3), or values proportional to them, are all experimentally determinable. The equation yields the mean value of R. If, however, the liquid acts chemically on the suspended solid (as would

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[1] Theory of Heat. (Appleton & Co., 1883, pp. 299, 300.)

[2] Theoretically, according to Helmholtz, $\frac{1}{36360}$ cm. and $\frac{1}{48480}$ cm. for the ordinary and immersion systems, respectively. The limit of visibility, as experimentally found by Harting, is $\frac{1}{33130}$ cm., and by Dippel, $\frac{1}{35000}$ cm. On the other hand, strong coloring matter may be diluted as much as 100,000,000 times (Muschenbrœck, Achard, Hoffmann) without fading beyond recognition.

[3] Kirchhoff (Math. Physik, p. 381, Leipzig, 1876) deduces this equation.

be the case, for instance, in hydration), then equation (3) is but a single relation for three unknown quantities, k, R, ρ. We may add that the relation between R, ρ, and mass of particle, leads us no further, since we know nothing of the change of mass involved.

Here, I think, we strike the keynote of one of the main difficulties which these phenomena present. Our assurance that the particle is not in some way acted on by the liquid is never perfect, nor have we to guide us any clew as to the effect of "mass-action," the amount of superficial change, or the depth of penetration of water, for instance. Water shows a striking selective power in discriminating between degrees of comminution. At ordinary temperatures the particles remain granular. The impression received in the case of subsidence in ether is almost that of particles falling in vacuo; barring flotation, small and large particles seem to fall equally fast; the precipitate is flocculent. Let water and ether be mixed, so that there shall be equal bulks of etherized water below and aqueous ether above, and then let the dust be added. If now this mixture is violently shaken and thereupon allowed to subside, the ether is washed clean of particles in a few minutes, whereas the sediment remains suspended in the water for weeks or even months. Another experiment, very nearly the converse of this, may be added. If a turbid solution of shellac in alcohol be shaken with naphtha, the opaque material is washed out, gradually ascending to float in the naphtha on the shellac. Subsidence then takes place in the naphtha. Eventually the two liquids (naphtha above and the clear alcoholic solution of shellac below) are separated by a layer of compacted sediment.

Whatever the surface change may be, it necessarily becomes more and more effective in proportion as the particle decreases in size. That the radius of many particles is smaller than the depth of surface penetration is quite probable. And hence, in equation (3), ρ and R must be regarded as variable—the former very largely so; whereas k may a priori be assumed as constant.[1] When liquids are forced through capillary tubes none of these difficulties are encountered, and hence their observed friction is the true viscosity of the transpiring liquid.

STRATIFICATION.

Analogies.—If very finely comminuted material be suspended in distilled water, the subsidence usually takes place in such a way that while the very slow descent of particles is in progress the liquid presents a stratified appearance. A single surface or plane of demarkation is readily observable, or indeed a number of planes, oftentimes sharply

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[1] Unfortunately mere variation of ρ and R in plausible amounts for constant k does not satisfactorily account for the observed enormous changes of rate. An attempt to reconcile this discrepancy is made in the sequel. It is difficult to retain a fixed value of k throughout. If the viscosity of water is studied with particles of graded size the large corpuscles may exhibit distinct relations to the viscosity of the liquid, such as gradually vanish when we approach the extremely fine particles.

defined. This phenomenon is quite puzzling. At first sight we call to mind that air rendered densely turbid by suspended particles of water behaves practically like a distinct liquid, possessing determinate hydrostatic properties. A heavy fog will fall through pure air and subside in the valleys. Fogs of less specific gravity than air rise as clouds. Hence it would appear that in the case of subsidence of solid particles in liquids cognizance must be taken of two kinds of motion: a gradual descent of the whole mass of particles in virtue of gravity in the first place and a rearrangement of the various parts of the liquid in a way consistent with their respective specific gravities in the second. It follows that, to allow the second process or redistribution to come fully into effect, the rate of subsidence must be sufficiently small. Now, the experiments given below (p. 27) seem to show that this is often the case. If, for instance, we so adjust the consistency of the liquids in a number of sedimentation glasses that the rate of subsidence increases from tube to tube in some regular order—a condition of things which we may easily effect in a way to be indicated in the next paragraph—we shall find that surfaces are obtainable only when the rate of subsidence falls below a certain value. After this the liquid clarifies in such a manner that surfaces of demarkation are nowhere visible, passing from opaque turbidity through translucency to clearness sooner at the top than at the bottom of the tube.

Descriptive equation.—The serious objection to this plausible view is that it presupposes a degree of imperfect mixture of the parts of the turbid liquid which *at the outset* of the actual experiment is hardly met with.[1] Indeed I believe that the occurrence of sharply defined surfaces singly is rather to be regarded as the result of accident, for the particles with which our experiments are most usually conducted (clayey material, tripoli) have already undergone subsidence in nature. They have passed through a selective process which has thrown particles of like rates of subsidence together. These particles need not be of a size; but their figures, dimensions, densities must be such as in each case to correspond to the observed rate. I will suppose, therefore, that in a general case of triturated material the particles vary in size from a very small to a relatively large value, but that by far the greater number approach a certain mean figure and dimension.

There is a distributive equation of frequent occurrence in mathematical physics which contains a characteristic maximum. In the kinetic theory of gases it expresses Maxwell's well known law, and may then be reduced to the very elegant form

$$y = \frac{4}{\sqrt{\pi}} x^2 e^{-x^2}$$

where y is the probability of occurrence of the molecular velocity, x, expressed in terms of the most probable velocity. This law of distribu-

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[1] See p. 20.

tion may advantageously be adopted here, granting of course that the selection made is wholly empiric. I therefore postulate

$$y = \frac{4}{\sqrt{\pi}} x^2 e^{-x^2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

where y is the probability of the rate of subsidence x expressed in terms of the most probable rate. Hence ydx denotes the number of particles, relative to the total number, whose velocity in terms of the unit[1] specified lies between x and $x + dx$. The maximum of equation (4) is well adapted to illustrate the consequences of subsidence, when the particles vary in size as much as in an ordinary case of trituration.

Suppose the turbid liquid characterized by the function y to be inclosed between vertical parallel plates, then the degree of opacity observed on looking through the trough in the direction of a normally impinging beam of light is due partially to absorption and partially to diffuse reflection at the surfaces of the particles. As regards their effect on the transmitted beam, these two phenomena are here not essentially dissimilar and may be described by a common equation. I assume therefore the law of absorption

$$i = i_0 e^{-O\vartheta} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

where i_0 is the original intensity, i the reduced intensity of transmitted light in consequence of the thickness of turbid liquid ϑ, through which the beam has passed. e^{-O} is the coefficient of absorption, with the understanding that O is to refer both to the phenomena of absorption and of reflection; or, perhaps more logically, that i be the sum of two expressions each of which has the character of (5), one however referring to absorption and the other to diffuse reflection.

The signification of this constant is very clear in the differential equation

$$di = -Oi_0 d\vartheta,$$

and the problem now reduces to a consideration of the variation of O consequent upon a change in the number and position of the suspended particles. Moreover, since O varies from zero to infinity as the liquid passes continuously from clear to opaque, the constant O may conveniently be termed the opacity of the turbid liquid.

The degree of opacity, dO, which ydx particles add to the liquid is dependent on

$$ydx\,(c'\tfrac{4}{3}\pi R^3) \text{ and } (c4\pi R^2)\,ydx \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

where R is the radius of the particle whose rate of subsidence is x, and c' and c are constants. In the expressions (6), c' and its coefficient refer

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[1] If the unit of time be 1 s. then the unit of length involved is the distance passed over, per second, by the particle whose velocity is the most probable velocity. These units give compactness to Maxwell's equation. To secure similar facility of expression rates of subsidence and not radii of particles are distributed.

solely to light absorbed, c and its coefficient to light reflected;[1] but it is a fact of observation that all the phenomena under consideration appear with equal clearness when the particles illuminated by a vertical beam of light are viewed in a horizontal direction. Hence the first of the terms within the parenthesis is made negligible in comparison with the second. It follows, in view of equations (3) and (4), that the total opacity at the inception of the experiment is

$$O_0 = \frac{16c\sqrt{\pi}}{A}\int_0^\infty x^3 e^{-x^2}dx = \frac{8c\sqrt{\pi}}{A} \quad . \; . \; . \; . \; . \; . \; . \quad (7)$$

From the elementary equations the opacity O apparent at a depth d after a time t dated from the moment at which sedimentation commenced is deducible. In view of the simplifying condition of uniformity of motion, the particle, whose rate is $x=\frac{d}{t}$ (expressed in terms of the unit above), will just have passed through the section. Hence the residual opacity is

$$O = \frac{8c\sqrt{\pi}}{A}\int_0^{\frac{d}{t}} x^3 e^{-x^2}dx \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

an integrable form readily reduced to

$$O = \frac{8c\sqrt{\pi}}{A}\left[1-\left(1+\frac{d^2}{t^2}\right)e^{-\frac{d^2}{t^2}}\right] \quad . \; . \; . \; . \; . \; . \; . \quad (9)$$

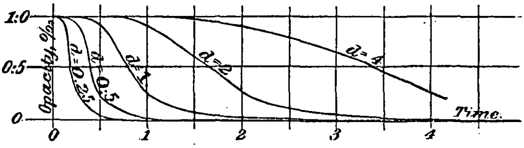

FIG. 1.—Relation of opacity to time of subsidence at different depths.

A clear view of the character of O is exhibited in Fig. 1, which contains the second factor of the second member of equation (9), time (t) as abscissa, relative opacity $\frac{O}{O_0}$ as ordinate.

The function O as given by equation (9), taken conjointly with equation (5), reproduces the march of the actual phenomenon pretty well, so long as very slow rates of descent and particles very nearly alike in size are excluded. The plane of demarkation has more fully vanished in proportion as the depth at which an observation is made is greater. An inspection of equation (9), moreover, shows that if, in place of y, we had selected a function containing a more striking and abrupt max-

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[1] The optical properties of a beam of light reflected from particles small in comparison with the wave length of light are discussed by Stokes (Phil. Trans., p. 530, 1852).

imum[1], the function O would be characterized by steep declivity throughout greater depths or that the plane of demarkation would be more persistent. The reverse of this takes place where y is replaced by a function of flat maximum. But the important deduction is this, that if the rate of all particles is increased in like ratio the character of the phenomenon will not be changed.

Effect of density[2] of mixture.—When the particles under experiment are practically identical in size and exceedingly small, a second phenomenon having an immediate bearing on clearness of stratification may be discerned. Indeed this new fact seems to show that for the circumstances under consideration, at least, it is not permissible to treat the particles individually; that an analysis based upon the conditions of motion of descending integrant systems of particles alone leads to the observed results. In other words, in addition to the size of the particles themselves, the dimensions of the interstitial canals separating the particles show pronounced relations to the rate of subsidence. I regard this observation sufficiently important to deserve special investigation and discussion, and shall therefore in this paper only advert to a few pertinent data.

Three test tubes, 2 cm. in diameter and 15 cm. long, were filled with distilled water to which very different quantities of tripoli had been added. The first of these, after shaking, was densely opaque; the second much less so; the third only just translucent. After the coarser material had subsided, the following results were obtained with the very fine particles. d is the distance between surface of liquid and surface of demarkation after the lapse of time h (expressed in hours); d, therefore, is the length of the clear column:

Date.	h	Very opaque. d	Opaque. d	Translucent. d
		mm.	*mm.*	*mm.*
October 9, 1885	234	12	35	50
October 13, 1885	331	20	50	77
October 15, 1885	385	29	60	90
October 16, 1885	408	33	65	96
Rate of subsidence $\frac{mm}{h}$		0.12	0.17	0.28
Sediment deposited		20	4	1

The amount of substance originally in suspension is fairly indicated by the height of the column of sediment after subsidence is complete.

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[1] The actual work usually leads to imperfect gamma-functions and involved results. This is quite unnecessary here, since the essential points are illustrated with sufficient clearness by the above. I may add that it would probably have been simpler, and at the same time more in keeping with the point of departure taken in Chapter II, to have avoided optical considerations altogether—to have simply defined turbidity as mass of sediment of a given kind per unit of volume of liquid and then to have discussed turbidity essentially in the manner pursued in the text.

[2] Measured by the number of particles per unit of volume, for instance.

The deduction from these precursory experiments of immediate interest here is this: Since the rate of descent decreases with the density of the mixture turbid liquids manifest a marked tendency toward maintaining their surfaces of demarkation clearly defined, so long at least as the particles are very nearly of a size and descend very slowly. For it is difficult to remove material out of such a surface without diluting it, but in virtue of this dilution the transported system again descends at greater rates, finally to merge into the surface out of which it was taken. Furthermore, if within a turbid liquid there exist a region of low density, these particles must subside at greater rates and eventually merge into an interior surface.

Sharp demarkation.—The presence of surfaces of separation furnishes the best available means for the investigation of rates of subsidence. When the experiment is made under satisfactory conditions the surfaces descend uniformly, and the observation may be made with some accuracy by projecting them upon a scale read off at a distance with a telescope. I have found it advantageous to place the tubes behind a black screen and illuminate the particles from above. The number and position of the surfaces is then clearly discernible, until the turbidity fades beyond recognition. With fine particles distinct surfaces appear gradually after two hundred hours—for instance, in the example discussed in the last paragraph. But they appear more rapidly on second and subsequent subsidences. We infer a time-effect due to continued contact with water.

An essential requisite for the production of sharp stratification is constancy of temperature. When temperature fluctuates convective currents arise in the liquid, transporting above its normal level and diluting some of the finer material. This in turn rearranges itself, forming a *second* (false) surface, as soon as the parts of the liquid are again at rest. Here, therefore, is an example of a fog subsiding in the liquid in the way explained in the first part of this section. But, supposing the order of occurrences reversible, this new surface would not show a depth $d=0$ for $t=0$, nor could the old surface, after this interference, be brought back to $d=0$ for $t=0$. Hence the effect of convection is virtually a change of the co-ordinates to which O, d, and t are referred. This change is irregular, and may, therefore, seriously confuse the results, since the corrective effect due to differences of density is not always sufficient, or sufficiently prolonged, to annul this discrepancy. It increases with the width of the glass; but in very narrow tubes surfaces are not discernible at all. The diameter 2.3 cm. is perhaps a good mean.

TEMPERATURE.

Chemical effect.—The subsidence of fine earthy dust suspended in distilled water is enormously more rapid at 100° than at 0°. This is easily accounted for by the hydration theory, for it is merely necessary to assume that hypothetical hydrates, which occur and are formed spontaneously at ordinary temperatures, are no longer possible at 100°. When we call to mind the augmented thermal activity of the water molecule at 100° this explanation gains much in plausibility.

Physical effect.—At this stage of the investigation it seemed to me necessary to call to mind that we are frequently operating with particles smaller than any physically measurable quantity; with particles, in other words, small even in comparison with the wave length of light and at once commensurable with molecular dimensions. It behooves us, therefore, to inquire what the anticipative conditions of subsidence will be when the dimensions of the particles decrease from some estimable mean value indefinitely. Obviously these conditions for very small particles include those for larger particles, and the special considerations to be made in the former case vanish when the dimensions increase. Hence in the sequel I shall interpret all results, with special reference to small particles, with the proviso that if the degree of comminution under experiment be insufficiently small the considerations simplify and revert to views which have already been expressed for relatively coarse particles.

In the first section I compared the effective weight of a suspended particle with the frictional resistance of the liquid. It is to be remembered, however, that the molecules of water are in a state of incessant vibration. The atoms oscillate in virtue of the internal molecular energy, and the molecule itself continually changes place and position. For very small particles, and during very small intervals of time, it is evident that this state of motion is not compatible with absolute constancy of the frictional force. We rather infer that its value varies within relatively wide limits, and the early remarks in reference to permanent opalescence have therefore tacitly assumed that the times during which gravity acts sensibly on any suspended particle are negligible in comparison with the times during which its action is without effect.

But even particles of relatively large rates of descent in water are still quite invisible microscopically (see page 35). Their linear dimensions must therefore be estimated as considerably smaller than 0.00003 cm. Hence it is safe to accept 0.000005 cm. as a fair mean expression for the diameter of the subsiding solid spherules. On the other hand the distance between the centers of two adjacent water molecules is probably not smaller than 0.00000005 cm., or about one one-hundredth of the mean diameter of the solid corpuscles.[1] It follows that the num-

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[1] O. E. Meyer (following Maxwell and Van der Waals), Kinet. Theorie der Gase, p. 226, Breslau, 1877. The value given above, which is taken directly from the kinetic theory of gases, is usually conceded to be a better estimate than the other values derived by Thomson, Maxwell, and Lorenz from capillary or electrical phenomena. Cf. Am. Journ. (2), L, pp. 38 and 258; Phil. Mag. (4), XLVI, p. 453, 1873; Pogg. Ann., CXL, p. 644, 1870.

ber of liquid molecules surrounding and impinging upon a suspended particle of average size varies between 10,000 and 50,000; that if, for instance, the distance between centers of two adjacent water molecules be magnified to the diameter of a pea, the subsiding solid may be typified by a bomb between a foot and a yard in diameter. The distance between the centers of two adjacent molecules is not to be confounded, however, with the diameters of the molecules themselves, and a better statement of the mean conditions involved is that of a spherical shell 0.000005 cm. in diameter and 0.00000005 cm. thick, within which, say, 30,000 molecules are free to oscillate. This number again decreases with the square of the linear dimensions of the particle. The number of molecules producing the pressure in any observable case of Boyle's law is measured in trillions. It seems to me, therefore, that where we are observing effects due to particles whose dimensions frequently fall below these mean values indefinitely, we have to take frictional forces into consideration, which, as regards all feasible measurements, are constant, but are no longer so when viewed minutely, i. e., in their variation from the beginning of any small interval of time to the next consecutive. It follows that it is possible for such a particle to descend in a liquid in virtue of the action of gravity alone, although its weight is *below* the mean or *measurable* value of the friction encountered.

Whatever the difference between the greatest and least values of frictional resistance during the unit of time may be (it is difficult to form a satisfactory estimate, since we know but little about the liquid molecule and its rate and manner of motion or the variation of molecular forces), we may argue fairly, I think, that the interval between the limits in question will increase with the degree of molecular activity of the liquid.[1] The particles, under conditions of intense agitation of the surrounding molecules, are more liable to be shaken through the liquid, as it were (as powders are shaken or jarred through a series of sieves, to use a common but apt comparison), than when the molecule is comparatively quiet. Hence any means which may tend decidedly to increase this molecular disturbance, even though it slightly increase viscosity (as in the case of salt solutions), may effect an increment in the rate of subsidence. These views are to be examined with some detail.

The most direct means of increasing the molecular agitation of a liquid is temperature. It is to be anticipated that the rate of subsidence of suspended particles of a given degree of comminution will be greater when the liquid is at 100°, for instance, than when it is at ordinary temperatures. I made this experiment:

Two identical glass tubes, closed at one end and drawn to a fine aperture at the other, were half filled with distilled water rendered

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[1] The mean velocity of particles of air, at 0° C., for instance, is much over 400 meters per second. The velocity of the molecules of liquids is not known, but must be of like order.

densely turbid by dust of white bolus. Both were kept at 100° for some time, for the purpose of expelling air, then hermetically sealed with a blast lamp. The tubes measured about 0.8 cm. in diameter and 15 cm. in length. One of these was left in the room, without interference, at ordinary temperatures; the other, shaken up simultaneously with the first, was exposed to the constant temperature 100°, by suspending it in a boiling point apparatus, as shown in the annexed diagram.[1] (Fig. 2.)

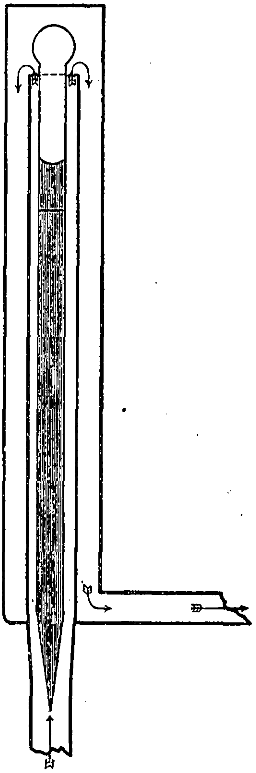

FIG. 2.—Apparatus for subsidence at 100°.

The following results were obtained: The third and fourth columns of Table 1 give the depth d (in millimeters) of the plane of demarkation below the bottom of the meniscus, after a lapse of time h (in hours) given in the second column.

TABLE 1.—*Subsidence at 15° and at 100° compared.*

	h	d 15°.	d 100°.
First experiment	3	0	3
Rate $\left(\frac{mm}{h}\right)$	....	(0.1)	1.0
Second experiment	24	3	*clear*
Rate $\left(\frac{mm}{h}\right)$	....	0.1	(2.0)

After three hours a difference in rate is already clearly perceptible. Within 24 hours (experiment prolonged overnight) the sediment in the hot tube has completely subsided in the form of a flocculent precipitate somewhat like alumina. The cold tube is almost free from precipitate,[2] while the surface of demarkation is down only 2 to 3 mm. below the bottom of the meniscus.

The rate of subsidence proves, therefore, to be very much greater at 100° than at 15°. A result of this general character was to be anticipated, but the enormous difference of rate in the two cases is exceedingly striking. The effect of the diminished viscosity[3] at 100° would not have sunk the dust in the hot tube more than 15mm. below the meniscus.

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[1] The diagram is readily intelligible. The direction of the currents of steam is shown by the arrows. The sedimentation tube occupies a central position and is thus doubly jacketed with steam.

[2] The large amount of precipitate in the hot tube is good evidence in favor of the views on the coherence of particles, as discussed on page 37.

[3] The viscosity of water at different temperatures has been measured by Poiseuille, Rosencranz, and Slotte. (See digest of the latter, in the Ann. der Physik, XX, pp. 266, 267, 1883.) At 100° the viscosity of water is about one-sixth of its value at zero. But the corresponding rates of subsidence are in a ratio which, although qualitatively in accordance, is quantitatively out of all proportion herewith.

I will waive further discussion of this result here in consequence of quantitative comparisons which I have in view, comparisons made at different temperatures, varying between 0° and 100°. Below 100° we experiment with solid particles of a given mean size, descending or subsiding in a given liquid at determinable rates. Regarded from this standpoint the experiment is of sufficient importance to demand careful measurements.

RECIPITANTS.

Chemical effect.—Acids, salts, alkalies, indeed foreign material in general,[1] when added to distilled water permanently turbid with some finely comminuted insoluble solid in quantities not too large, increase the rate of subsidence in a marked degree, in numerous cases even many hundred fold.

The chemical theory appears very readily to suggest these phenomena. The addition of the substances enumerated interferes with or prevents the formation of the hypothetical hydrates; but the force of this explanation is apparently weakened when we pass from purely qualitative to quantitative data. By reducing some of the results below to a molecular basis, I find that a single molecule of acid or salt, in molecules of water varying in number from 10,000 to 50,000, is sufficient to produce very marked changes in the rate of subsidence. It is conceivable that this amount of dissolved material may in some instances be commensurable with the amount of suspended material, and therefore act appreciably on it. In such a case there should be a difference of rate due to a difference in the degree of turbidity of otherwise identical turbid solutions. I have failed thus far to bring satisfactory quantitative evidence to bear upon this point. I am pursuing these experiments with considerable care and therefore need merely indicate the nature of the difficulties encountered here. Instead of considering the particles individually, as has been done above (p. 14), all the particles in the unit of volume may be taken collectively. *A priori*, the only available force is gravity, and we must regard the weight of the particles in unit of volume to be the measure of the influence in virtue of which water is forced through the capillary interstices of the descending system. The analysis shows that the rate of descent of this system must decrease rapidly with the number of particles per unit of volume. Hence, the purely mechanical effect has the same sense as the hypothetical chemical effect to be investigated, and it is therefore exceedingly difficult to discriminate between the two.

Physical effect.—On the other hand, the examination into the molecular conditions of subsidence, commenced in the last section, here suggests so many analogies that further discussion is at once demanded. We have reasons for inferring that in the case of water, or perhaps any other simple liquid, there is presented to us a comparatively quiet mole-

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[1] The definite organic compounds (alcohols, ethers) are frequently exceptions.

cule; by which I mean that dissociations and recombinations of the molecule H_2O, akin to those premised by Williamson[1] in his views on the process of etherification, and by Clausius[2] in his theory of electrolysis, are, at ordinary temperatures at least, of rare occurrence. The electrical conductivity of pure water[3] is at most one ten-billionth of that of pure mercury. It needs but very trifling admixture of acid or salt or alkali to increase this minimum value enormously. If it be remembered that as small an addition as 18 per cent. by weight of hydrochloric acid increases the conductivity of water more than a million times, it may easily be estimated how insignificant is the amount of HCl which would suffice to increase the conductivity by a fraction of itself. Even very perfect liquid insulators, like alcohol and turpentine, when added to water, produce incremental electrolytic effects. Indeed HCl, in the pure state, is an insulator of the same order as water.[4] According to Clausius, no electrolytic effect will be produced by electromotive forces of practicable magnitude, in a space where temporary dissociation[5] does not occur and partial molecules are therefore absent. Hence at ordinary temperatures the solution of one substance in another ("electrolytic system") is the essential condition of good electrolytic conductivity. It is on the basis of these facts that the assumption of a "quiet" molecule of water, in the above sense, was made. The result of mixture is molecular kinetic energy permanently gained in large amount.

Now, I believe that the dissociations which Clausius and Williamson premise present a more plausible occurrence if the separation is superinduced by an intermediate substance of known affinity for one or the other partial molecule. If a solid particle is introduced into an electrolytic system its effect upon the meandering partial molecules may be regarded as somewhat similar to electromotive force, inasmuch as in a general case different parts of the suspended solid attract partial molecules of different kinds. Furthermore, in view of the occurrence of mass-action, in view of the continually recurring dissociations and recombinations between solid and liquid, I see no avoidance of the

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[1] Williamson: Ann. der Chem. und Pharm., LXXVII, p. 37, 1857.

[2] Clausius: Mech. Wärmetheorie, 2d ed., Vol. II, p. 155–169, 1879.

[3] Measured by a number of observers, among them by F. Kohlrausch, Pogg. Ann., Erg. VIII, p. 1, 1876. Kohlrausch's last value is 30×10^{12} (Berl. Sitzb., XL, p. 3, 1884).

[4] Gore: Proc. Roy. Soc. London, p. 256, Vol. XVII, 1868–1869, and others.

[5] According to Clausius the substance (acid, salt, alkali, &c.) after solution may be regarded as an aggregate of partial molecules, such that opposite electrical properties are equally represented. Electromotive force produces a moving effect whenever the other conditions which influence a partial molecule are favorable, i. e., temporarily at a minimum. If any imaginary interface be described between the positive and the negative electrode, then more positive than negative partial molecules will pass in the direction from the positive to the negative side and more negative than positive partial molecules in the contrary direction. The result is practically this: During the action of the electromotive force a certain number of positive partial molecules pass through the interface in a positive direction and the same number of negative partial molecules in the negative direction.

hypothesis that the surface of the suspended particle must, in particular, be a locus of violent molecular agitation.

Returning from this digression to the subject in hand, I infer that, just as in the above instance a marked increment of the rate of subsidence of extremely small particles suspended in water was obtained in consequence of the augmented thermal energy of the water molecules (heating to 100°), so must also an analogously increased rate result at ordinary temperatures from the intensified molecular agitation due to the solution of foreign material in water. I offer the following experiments on this point:

Experimental results.—In Table 2 the results obtained with finely comminuted white bolus, red bolus, and tripoli, respectively, each suspended in distilled water, are given. Stand-glasses, about 3 cm. in diameter and 30 cm. high, hold these mixtures. The fourth, fifth, and sixth columns of the table show the depth, *d*, of the respective surface or surfaces of demarkation below the level of the liquids at the times given in the second column. The surfaces were distinct for tripoli, less so for white bolus, washed in the case of red bolus; *d* is given in arbitrary units;[1] *h* in hours. Where two sets of figures are given, two surfaces were apparent.

TABLE 2.—*Subsidence in distilled water.*

Date.	Time of day.	*h*	*d*		
			White bolus.	Red bolus.	Tripoli.
December 24	12 p. m.	0	0	0	0
December 25	12 p. m.	24	6	3	28
December 26	2 p. m.	38	11	5	58
December 26	5 p. m.	41	12	4	61
December 27	1 a. m.	49	14	5	71
December 27	9 a. m.	57	16	5	81
December 27	8 p. m.	68	20	6	93
December 28	1 a. m.	73	20 22	6	100 104
December 28	11 a. m.	83	22	7	108 120
December 29	2 a. m.	98	24 30	7	121
December 29	11 a. m.	107	26 32	8	131
December 30	1 a. m.	121	34 29	9	140
December 30	12 m	132	30 36	10	148
December 31	3 a. m.	147	....	....	156 165 180
December 31	12 m	156	....	....	160 170
Rate $\left(\frac{d}{h}\right)$	....	....	0.28	0.09	1.3

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[1] About 2 mm. each.

If we regard d as a function of h we find it linear in the case of white and of red bolus and quadratically retarded in the case of tripoli, but to the latter fact I would attach no significance. It may be due to the unavoidable fluctuations of temperature.[1] So long as the descent is uniform (d proportional to h) the force acting on the particle is nil. The effect of gravity is exhausted in doing work against the frictional resistance.

In Table 3 are given the results obtained with fine tripoli suspended in distilled water to which various percentages (by weight) of common salt (NaCl) have been added. The precipitation tubes in this series of experiments were 3 cm. in diameter and 15 cm. long. Values for d are given only when planes of demarkation were observable. In other respects the table is like the preceding one, except that d is here expressed in millimeters. Where two sets of figures are given, two surfaces were apparent.

TABLE 3.—*Subsidence in salt solutions.*

Date.	Time of day.	h	d								
			0.1 per cent.	0.25 per cent.	0.5 per cent.	1.0 per cent.	2 per cent.	5 per cent.	7 per cent.	10 per cent.	15 per cent.
December 27, 1883	10 a. m..	0	0	0	0	0	0	0	0	0	0
December 27, 1883	2 p. m..	4	5	9	13	Largely down.	Sediment falls rapidly in all the tubes; rate not observable, from absence of stratification.				
December 27, 1883	6 p. m..	8	7	14	16 30	No demarkation surface.					
December 28, 1883	1 a. m..	15	11 14	29	45						
December 28, 1883	4 p. m..	30	17 26	58	87.						
December 29, 1883	2 a. m..	40	42 62	85	128						
December 20, 1883	12 m	50	30 53	104	Bottom.						
December 30, 1883	1 a. m..	63	41 69	135	....						
December 30, 1883	12 m	74	47 80	Bottom.	....						
December 31, 1883	3 a. m..	89	56 95	....	....						
December 31, 1883	12 m	98	63 105	....	....						
Rate $\left(\frac{mm}{h}\right)$	....	....	1	2	3	(20)					

The experiments show that the rate of sedimentation increases rapidly with the quantity of salt in solution; that even small quantities of salt produce very marked effects; d varies linearly with h. The absence of stratification in cases of greater rates of subsidence (solutions 1 to 15 per cent.) is confirmatory of the remarks made in an earlier paragraph (p. 16) on the rearrangement of particles according to the density of different parts of the liquid and accords well with the other views there given. The remarkably accelerated increase of rate observed on passing from fractional to integral per cents. (composition) is to be noticed.

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[1] See p. 20 as to convective currents and the change of co-ordinates resulting.

Table 4 gives the results obtained with red bolus, white bolus, tripoli, talc, and bone ash, respectively, all finely comminuted and suspended in weak brine. The percentage of salt dissolved is shown at the head of each column. The solutions are held in test tubes about 1 cm. in diameter and 13 cm. long. They were mixed in a way to be indicated at the head of Table 5. In most cases surfaces of demarkation were either absent or not clearly observable; *d*, therefore, shows the depth of tints or turbidities of like density or degree below the level of the liquid measured on an arbitrary scale; *cl.* denotes clear; *tr.* translucent.

TABLE 4.—*Subsidence in salt solutions.*

Date.	Time of day.	*h*	*d*									
			Red bolus.					White bolus.				
			0.05 per cent.	0.1 per cent.	0.2 per cent.	0.4 per cent.	0.8 per cent.	0.05 per cent.	0.1 per cent.	0.2 per cent.	0.4 per cent.	0.8 per cent.
January 7, 1884	2 p.m.	0	0	0	0	0	0	0	0	0	0	0
January 7, 1884	3 p.m.	1	0	0	0	0	0	1	1	0	3	40
January 7, 1884	5 p.m.	3	0	0	0	0	0	1	2	0	6	*cl.*
January 7, 1884	6 p.m.	4	0	0	0	0	0	1	1	0	*tr.*	......
January 7, 1884	9 p.m.	7	1	1	1	2	5	1	2	3	*cl.*	.....
January 7, 1884	12 p.m.	10	1	1	1	4	30	2	2	4	......	......
January 8, 1884	3 a.m.	13	2	2	2	5	*tr.*	3	3	20	......	......
January 8, 1884	11 a.m.	21	2	2	2	4	......	3	3	*tr.*	......	......
January 8, 1884	7 p.m.	29	3	3	3	7	*cl.*	8	7	......	......	......
January 8, 1884	12 p.m.	34	4	5	6	10	......	9	10	*cl.*	......	......
January 9, 1884	10 a.m.	44	5	4	5	9	......	6	7	......	......	......
January 12, 1884	1 p.m.	119	12	13	15	25	......	21	33	......	......	......
January 13, 1884	3 p.m.	145	12	13	15	30	......	28	38	......	......	......
Rate $\left(\frac{d}{h}\right)$	....	......	0.09	0.10	0.12	0.25	2	0.2	0.3	0.8	2	5

Date.	Time of day.	*h*	*d*														
			Tripoli.					Talc.					Bone ash.				
			0.05 per cent.	0.1 per cent.	0.2 per cent.	0.4 per cent.	0.8 per cent.	0.05 per cent.	0.1 per cent.	0.2 per cent.	0.4 per cent.	0.8 per cent.	0.05 per cent.	0.1 per cent.	0.2 per cent.	0.4 per cent.	0.8 per cent.
January 7, 1884	2 p.m.	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
January 7, 1884	3 p.m.	1	2	2	2	1	2	2	2	3	3	4	Clarifies rapidly, at rates increasing with the quantity of salt dissolved.				
January 7, 1884	5 p.m.	3	2	3	3	3	3	23	....	....	*cl.*	*cl.*					
January 7, 1884	6 p.m.	4	3	6	3	4	7	....	*cl.*	*cl.*							
January 7, 1884	9 p.m.	7	4	7	5	9	7	*cl.*	...	....	....	....					
January 7, 1884	12 p.m.	10	7	12	7	14	*tr.*	....	....	...	....	....					
January 8, 1884	3 a.m.	13	8	14	10	30	*l.*	....	....	....	....	...					
January 8, 1884	11 a.m.	21	8	16	9	*tr.*	...	...	....	....	....	....					
January 8, 1884	7 p.m.	29	12	22	24	...	....	....	....	....	....	....					
January 8, 1884	12 p.m.	34	13	22	*tr.*	*cl.*	..	....	....	....	....	....					
January 9, 1884	10 a.m.	44	13	25	..	...	...	...	....	....	....	....					
January 12, 1884	1 p.m.	119	*tr.*	*tr.*	*cl.*	..	....	...	....	....	....	....					
January 13, 1884	3 p.m.	145	..	....	..	..	....	...	....	....	....	....					
Rate $\left(\frac{d}{h}\right)$	....	....	0.4	0.6	0.7	1.5	2	2	2	3	3	4					

The absence of stratification which frequently occurs for thin walled tubes of small diameter I refer to convection due to fluctuations of temperature. The results of this table have a smaller claim to accuracy.[1] The difference in the rates of subsidence in case of solutions of the same percentage quantity of salt is probably wholly due to differences of comminution in the various cases. An accelerated increase of rate with the strength of the brine is again generally apparent.

In Tables 5 and 6 various stages of subsidence of tripoli, in solutions of different chemical composition, are given, Table 5 showing the results obtained with 0.01 per cent. solutions, Table 6 the results for 0.05 per cent. solutions, of the anhydrous compounds HCl, H_2SO_4, $CuSO_4$, $ZnSO_4$, $MgSO_4$, KI, NaCl. In addition to the mean rates the electrical conductivities[2] of the divers solutions are added. The tables are readily intelligible. The particles subsided in tubes 3 cm. in diameter and 20 cm. long. In order to warrant the assumption that the contents of the tubes are identical, except in the respects mentioned, the following plan of mixture was pursued: One per cent. solutions of each of the substances enumerated were first prepared, after which 1 cubic centimeter and 5 cubic centimeters of each were diluted to 100 cubic centimeters with distilled water permanently turbid with tripoli. In the case of Table 4 above, equal volumes of turbid water were added to each of the tubes and the contents then diluted to the desired amount with clear distilled water. This general method gives assurance that both the number and the mean dimensions of the solid particles in each cubic centimeter of the different solutions were originally identical—a condition of essential importance.

TABLE 5.—*Subsidence in* 0.01 *per cent. solutions.*

Date.	Time of day.	h	d					
			$CuSO_4$.	KI.	NaCl.	H_2SO_4.	HCl.	H_2O.
January 6, 1884	8 p. m.	0	0	0	0	0	0	0
January 7, 1884	9 a. m.	13	......	......	......	*tr.*	*cl.* (*a*)	......
January 7, 1884	6 p. m.	22	11	5	5	......	......	......
January 7, 1884	12 p. m.	28	5 25	......	......	*cl.*	......	......
January 8, 1884	12 m ...	40	36	10	10	......	......	......
January 8, 1884	7 p. m.	47	50	......	......	......	......	......
January 9, 1884	10 a. m.	62	*tr.*	20	20	......	......	18
Rate $\left(\frac{mm}{h}\right)$	......	......	1.0	0.3	0.3	(10)	(100)	0.3
Conductivity ($\times 10^9$)	......	......	4	6	13	40	75	......

a Translucent in 1 hour and 30 minutes.

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[1] Measurements of this kind, unless we resort to special optical apparatus, are always unsatisfactory. To the eye, however, the evidence furnished by these experiments was quite conclusive. After the expiration of a month the tubes with red bolus, for instance, were still distinctly colored, the mean tint varying in height and in degree inversely as the quantity of salt contained in the liquid.

[2] Interms of mercury.

TABLE 6.—*Subsidence in 0.05 per cent. solutions.*

Date.	Time of day.	*h*	*d*					
			$CuSO_4$.	KI.	NaCl.	H_2SO_4.	$MgSO_4$.	$ZnSO_4$.
January 13, 1884	5 p. m.	0	0	0	0	0	0	0
January 14, 1884	10 a. m.	17	*cl.*	22	20	*cl.*	*tr.*	*cl.*
January 21, 1884	5 p. m	192		60	60			
Rate $\left(\frac{mm}{h}\right)$				0 5	0.5			
Conductivity ($\times 10^9$)			8	12	26	80	10	8

In Table 5 surfaces of separation were apparent except in the case of HCl and H_2SO_4; in Table 6, however, they were apparent only in the case of KI and NaCl. I avoid greater length of detail in the present data, since all other desirable relations are sufficiently indicated in the earlier results.[1]

Table 7 contains the results obtained with tripoli falling through concentrated ether, absolute alcohol, water, and glycerine, respectively. Subsidence takes place in tubes like those described on page 23; *h* is in hours, *d* in millimeters.

TABLE 7.—*Subsidence in divers liquids.*

Date.	Time of day.	*h*	*d*			
			Ether.	Alcohol.	Water.	Glycerine.
January 21, 1884	10 p. m.	0.00	0	0	0	0
		0.03	9			
		0.07	16			
		0.10	21	5		
		0.13	26			
		0.17	30			
		0.20	32	10		
		0.25	36			
		0.48	43	23		
		0.75	45	34		
		1.00		44		
		1.25		53		
January 22, 1884	2 p. m.	16			2	
After 40 days						6
After 61 days						13
After 180 days						25
After 290 days						35
After 600 days						52
Rate $\left(\frac{mm}{h}\right)$			250	45	0.1	0.02

From these tables it appears that the descent is much more rapid in ether than in alcohol and enormously more so in these liquids than in water. In the case of ether the rate of subsidence decreases rapidly as time increases; but the tube is not long enough for the study of sedimentation occurring at such phenomenally large rates. Particles reach their lowest positions and pack before a normal rate is fully obvious.

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[1] The effect of HNO_3 is analogous to that of the other acids.

The supernatant liquid is clear. In case of alcohol and water it remains slightly opalescent. Surfaces of demarkation are in all cases sharp.

Values for rate of subsidence, such as are obtainable from Table 7, cannot be immediately compared. To arrive at data of this kind, the liquids (ether, alcohol, water) should be examined when in similar molecular conditions. This would, for instance, be the case when each is at its boiling point. Differences of rate, in these cases, will be much less pronounced. (See Table 1.)

An interesting feature of this experiment may be noticed here. After subsidence has taken place, in the case where about equal amounts of tripoli are originally suspended (the liquids being in tubes of like caliber), the permanent column[1] of sediment was found to be longest for ether, shortest for water, of intermediate length for alcohol: directly, therefore, as the respective rates of subsidence. But further experiments show that this is not always the rule. In the following Tables 8 and 9 the results obtained by suspending 1 gram of tripoli in various liquids are contained. l denotes the length (mm.) of a column of sediment, of a given diameter and weighing 1 gram, after complete subsidence has taken place.

TABLE 8.—*Bulk of sediment after subsidence.*

	Methyl alcohol.	Ethyl alcohol.	Ether.	Water.
After 40 days, $l =$	45	66	134	58

TABLE 9.—*Subsidence in divers liquids—bulk.*

	h	Methyl alcohol.	Ethyl alcohol.	Ether.	Water.
	0.0	0	0	....	....
	0.7	34	21	....	....
	1.1	38	38	....	....
	2.7	44	55	....	....
	12.7	48	67	....	....
	23.7	49	70	....	....
	45.7	49	72	....	....
Rate $\left(\frac{mm}{h}\right)$	....	70	40	....	....
After 21 days, $l =$	....	55	59	118	49

Methyl alcohol shows an exceptional value. In all cases the rate materially decreases as time increases and finally reaches zero asymptotically. As the particles descend they interfere with one another, and this in proportion as the quantity of sediment in the unit of volume increases. The friction of particles on themselves complicates the phenomena[2] and is without interest in the present discussion.

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[1] Bulk here varies linearly with length.

[2] "Packing" is probably due to slow descent of smaller particles between the interstices of the larger, on the hour-glass principle, until the equilibrium of position of larger masses or corpuscles is undermined.

A final exhibit of the divers rates of sedimentation encountered in the above tables, reduced to $\frac{mm}{h}$ and to $\frac{cm}{sec}$ is desirable.

TABLE 10.—*Rates of subsidence—final digest.*

1. *Subsidence in distilled water,* 15° *and* 100°, *respectively—bolus.*

15°		100°	
$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$
0.1	3	1.0	30
0.1	3	2.0	60

2. *Subsidence in distilled water.*

White bole.		Red bole.		Tripoli.	
$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$
0.6	20	0.2	6	2.6	80

3. *Subsidence in weak brine—tripoli.*

0.1 per cent.		0.2 per cent.		0.5 per cent.		1 per cent.	
$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$
1	30	2	60	3	90	(20)	(600)

4. *Subsidence in weak brine—bole, tripoli, talc.*

	0.05 per cent.		0.1 per cent.		0.2 per cent.		0.4 per cent.		0.8 per cent.	
	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$
Red bolus....	0.2	6	0.2	7	0.3	9	0.6	18	5	150
White bolus .	0.5	1.5	0.7	20	2.0	60	5	150	13	390
Tripoli	1.0	30	1.5	45	1.8	54	3.7	110	5	150
Talc	5	150	5	150	7	210	8	240	10	300

5. *Subsidence in* 0.01 *per cent. solutions of divers substances—tripoli.*

$CuSO_4$		KI		NaCl		H_2SO_4		HCl		H_2O	
$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$
1.0	30	0.3	9	0.3	9	(10)	(300)	(100)	(3000)	0.3	9

TABLE 10.—*Rates of subsidence—final digest*—Continued.

6. *Subsidence in 0.05 per cent. solutions of divers substances—tripoli.*

$CuSO_4$		KI		NaCl		H_2SO_4		$MgSO_4$		$ZnSO_4$	
$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$
......	....	0.5	1.5	0.5	1.5	......	....	......	....	......	....

7. *Subsidence in divers liquids—tripoli.*

Ether.		Alcohol.		Water.		Glycerine.	
$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$
250	7500	45	1300	0.1	3	0.02	0.6

9. *Subsidence in divers liquids—tripoli.*

Methyl alcohol.		Alcohol.	
$\frac{mm}{h}$	$\frac{cm}{sec}10^6$	$\frac{mm}{h}$	$\frac{cm}{sec}10^6$
70	2000	40	1200

Facilities for obtaining absolutely constant temperatures would have much improved these crude results; but they are the best available under the circumstances. I may add that the sedimentation effect of the addition of ether and of alcohol to distilled water seems to be a decided retardation of rate,[1] and that the rate is not independent of the amount of sediment in suspension but decreases with the turbidity of the mixture. Hence even in the above experiments different rates occur in different series of experiments for this reason alone; but to these results I attach crucial importance, and shall therefore treat them specially in another paper.

DISCUSSION.

Mechanical relations.—In the equation by which I endeavored to describe the appearance of the tube at different times (p. 18), it was convenient to express depth, d, in terms of the distance traveled per second by a particle whose rate, δ, is the most probable rate. If D be the actual depth in centimeters, then $d = \frac{D}{\delta}$; and hence equation (9) takes the form

$$C = \frac{8c\sqrt{\pi}}{A}\left\{1 - \left(1 + \frac{D^2}{(\delta t)^2}\right)e^{-\frac{D2}{(\delta t)^2}}\right\}$$

Inasmuch as δ and t enter this equation symmetrically it is evident at once that if the rate of all particles be increased n-fold the column

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[1] It is well to desiccate the particles intended for subsidence in ether.

of turbid liquid will present a given appearance or stage of subsidence in $\frac{1}{n}$ of the original time; the character of the phenomenon is not essentially changed. If, however, the increase of velocities is produced by solution of precipitants, we find experimentally that the column which presents surfaces of demarkation for the class of very weak solutions clarifies without exhibiting this characteristic feature during any stage of subsidence for the class of stronger solutions, and, furthermore, that the transition from stratified subsidence to unstratified subsidence is apparently abrupt. I infer that in the case of subsidence superinduced by precipitants the equation for the original distribution of rates, $y=f(x)$, is radically changed, and this in proportion as the amount of precipitant dissolved is greater. Furthermore, that this change is equivalent to a flattening of the maximum in the direction of greater rates; or that the difference of rate between consecutive particles is largely incremented, although not in uniform measure for all the particles. Again, surfaces of demarkation remain distinct until the (long) column as a whole fades beyond recognition. This is the essential difference between subsidence of fine particles in water, as actually observed, and simple viscous subsidence as described by equation (9), for instance.

If we accept Slotte's[1] value for the viscosity of water at 20°, $k=0.0101$ (g cm^{-1} sec^{-1}), Poiseuille's[2] value for the viscosity of ether, $0.3\ k$, and Graham's[3] values for the viscosity of methyl alcohol and of ethyl alcohol, $0.63\ k$ and $1.20\ k$, respectively; if, furthermore, we assume as the density of the subsiding substance (quartz, clay) the value $\rho=2.5$ whence $\rho'-\rho=1.5$ in round numbers; if, finally, $g=980$ (cm. sec^{-2}), then Table 10 (7 and 9) supplies the remaining data a (cm. sec^{-1}) for estimating the mean linear dimensions of the subsiding particles. We obtain

	Centimeters.
Water	$R=0.00001$
Ethyl alcohol	$R=0.00019$
Methyl alcohol	$R=0.00020$
Ether	$R=0.00024$

These results point out in a striking way the essential difference between subsidence in distilled water and subsidence in liquids (alcohols, ethers) whose affinities for silica and silicates are demonstrably feeble. The value of R is smallest in the case of water; certainly too large in the case of the remaining liquids. The dimensions found are therefore just in the inverse order of the values, which hydration would compel us to infer. The discrepancy is due in part to the value of density entering into the arguments; but the large error is more simply ex-

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[1] Slotte, Wied. Ann., XX, p. 262, 1883.

[2] Poiseuille, Ann. de Chim. et de Phys. (3), VII, p. 50, 1843; ibid., p. 76, 1847.

[3] Graham, Phil. Mag. (4), XXIV, p. 238, 1861.

plained by the fact that in the two classes of experiment, even though made upon the same material, we have *different particles* under observation. I have adverted to the coagulated appearance of the sediment when submerged in ether or in alcohol. The particles cohere closely, and the coarser material sweeps the finer material down, particularly in the case of dense mixtures; hence the poor selective power, the bulky sediment, and hence we fail to arrive at values for the rates of subsidence of the thoroughly comminuted dust at all. In the tripoli employed I indeed measured particles microscopically[1] as large as 0.00005 centimeter to 0.0007 centimeter, but these are at once ejected by water as well as by ether, are found at the bottom before the surface of demarkation has fallen 0.05 centimeter, and have no bearing on the phenomenon in hand.

Electrical relations.—If we compare the results for rate of precipitation taken from Tables 5 and 6, or from Table 10, with the known values of electrical conductivity of the respective solutions, we fail to find any detailed similarity in the two sets of data. In a general way, perhaps, the strong mineral acids show marked power to increase both rate of subsidence and electrical conductivity. But the salts of copper, of magnesium, and of zinc increase the rate of precipitation to a much larger degree than can be inferred from their electrical constants. Much of the discordance is no doubt to be referred to the coarseness even of the best available methods for measuring rates of subsidence. Chemical affinity produces a distortion; in the case of acids, for instance, effecting actual solution of particles of extreme fineness. But with due allowance for all these sources of error, I feel convinced that more elaborate experiments will not substantially change the results. Regarding this question from a theoretical point of view, greater accordance of results than has here been obtained is not at all to be anticipated. The electrical conductivity in case of dilute solutions is dependent on the friction against which the ion moves in its passage through water—a quantity which has not an immediate bearing on the subsidence of a small solid particle.

Precipitation increases in a marked degree with the amount of salt of a given kind in solution. This is equally true of electrical conductivity. Nevertheless, here again there is probably not perfect parallelism in the march of the two phenomena. The increase of conductivity

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[1] The diffraction method applies, of course, only to much larger particles; at least the exceptionally large corpuscles which are just within reach of violet light fall too rapidly for uniformity of distribution. In connection with the values of R it is interesting to note that the dimensions of the vesicles of mist in the air as obtained by Fraunhofer, (Schumacher, Astr. Nachr., III, p. 62) and later by Kaemtz (Meteorologie, III, p. 111, Mousson, Phys., II, 1872), are 0.0017 centimeter and 0.0033 centimeter, respectively, the numbers varying with climatic conditions. It is well known that lycopodium spores (0.003 centimeter) and Bowista spores (0.0004 centimeter) come nicely within the range of the diffraction method.

for such (small) quantities of dissolved salt as are enumerated in the tables is regular and uniform. The rate of subsidence appears to increase very slowly, almost imperceptibly at first, until a certain amount of solid is dissolved; further additions are accompanied by rapid acceleration in the rates of subsidence. But this inference is liable to error, inasmuch as at the critical stage in question, surfaces of demarkation are no longer available.

My results on the relation of conductivity and sedimentation, when considered in the aggregate, may therefore be summarized thus: A similarity between corresponding data for electrical conductivity and rate of subsidence is roughly apparent when the change of internal energy of water is produced either by heat alone or by solution of different quantities of one and the same salt. Between the values of these variables obtained by dissolving different salts no relation is observable, except perhaps of a very general kind. In the case where precipitation takes place in different simple liquids (water, alcohol, ether) the respective rates differ enormously from the values which the conductivity of these substances would lead us to infer.[1]

In view of the fact that the degree of comminution of the particles under consideration is much smaller than the limit of microscopic visibility it is permissible to make this inference: The frictional resistance experienced by the solid particle in its passage through the liquid, although apparently constant, is no longer so when regarded with reference to its value during a number of consecutive indefinitely small times. If, furthermore, we admit that the limits within which this frictional force is comprehended increase with the degree of molecular agitation of the liquid, then the analogy between the phenomenon of electrical conductivity, as explained by Clausius, and the phenomenon of subsidence of extremely fine particles in liquids is very nearly complete: in one case the ion is sensibly acted on by an electromotive force during the times when it is relatively in a state of freedom as regards the powerful chemical attraction of surrounding molecules; in the other, the tendency of gravity to urge the particle downward produces an effect when its weight is temporarily greater than the variable friction encountered during its motion through agitated molecules. The ultimate result in the electrical experiment is the appearance of free ions at the electrodes; in the other experiment a sediment collects at the bottom of the tube.

Particles of larger dimensions.—I will introduce this paragraph by the following random selection from a large number of data. The table

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[1] Remarks of an analogous kind are made by those who have endeavored to express the electrical conductivity, k, in terms of the quantity, p, of salt dissolved and the viscosity, η, of the solution. Grotrian (Pogg. Ann., CLVII, p. 250, 1876) obtains good agreement (at 18° and 15°, respectively) by using the formula $k=c\frac{p}{\eta^n}$, where c and n are constants.

contains a comparison of the rates of subsidence in brine of 0 per cent., 0.5 per cent., and 1 per cent. strength, respectively, when in one case the original mixtures are densely turbid and opaque, in the other only just opaque fading into translucent; tubes, 3 cm. in diameter and 20 cm. long. In both sets of experiments I observe three different degrees of turbidity, in which the suspended material varies as 4 : 2 : 1 for each of the stated percentages of salt solution. *o.* denotes opaque, *tr.* translucent, *cl.* clear, as above. The depth of the opaque stratum is determined by noting the point of the tube at which a beam of the light of the sky reflected from a distant plane mirror and passing through the tube is extinguished. Depth is always given in millimeters below the meniscus as a datum; time, in hours (*h*).

TABLE 11.—*Subsidence of opaque and of translucent mixtures in brine.*

Date.	*h*	Strength of brine =	NaCl, 0 per cent.			NaCl, 0. 5 per cent.			NaCl, 1 per cent.		
		Relative turbidity =	4	2	1	4	2	1	4	2	1
Oct. 3, 1885 ...	0	Densely opaque mixtures.	*o.*	*o.*	*o.*	*o.*	*o.*	*o.*	*o.*	*o.*	*o.*
	5. 3		*o.*	*o.*	*o.*	*tr.*	*tr.*	*tr.*	*cl.*	*cl.*	*cl.*
Oct. 4, 1885 ...	21		*o.* 15	*o.* 25	*o.* 50	*cl.*	*cl.*	*cl.*	......	......	......
Oct. 6, 1885 ...	69		*o.* 50	*o.* 90	*o.* 160						
			Demarkation indistinct.			Particles fall in the ratio of turbidity and concentration, leaving a filmy opalescence behind; sediment, bulky and flocculent, collects at the same rate. Precipitation is complete in fractions of an hour.					
Oct. 1, 1885 ...	0	Dilute semi-translucent mixture.	*o.*	*o.*	*o.*	*o.*	*o.*	*o.*	*o.*	*o.*	*o.*
Oct. 3, 1885 ...	38		No demarkation. Tubes approach translucency in the exact order of concentration and turbidity, being turbid still, although 1 per cent. is nearly clear. Effect of quantity of salt not very readily obvious.								
	48		*o.*	*o.* *tr.*	*tr.* *cl.*	*o.*	*tr.*	*tr.* *cl.*	*cl.*	*cl.*	......
Oct. 4, 1885 ...	63		*o.* *tr.*	*tr.*	*tr.* *cl.*	*o.* *tr.*	*tr.*	*tr.* *cl.*	*cl.*	*cl.*	......

This table reproduces an exceedingly striking observation in an unavoidably coarse and imperfect way. The action of the precipitant is marked and instantaneous when the solutions are densely turbid, I may add, in such a way as to contain relatively large corpuscles in suspension. When the turbidity is slight and the particles are fine, the tendency of salts to produce precipitation, however pronounced, is no longer quite so obvious.

Many of the particles here subsiding are probably too large to fall within the scope of the hypothesis enunciated in the preceding paragraph. But causes for the observed coherence of particles, the bulky and flocculent precipitates and the rapid subsidence seem to me not far to seek. The view which I advance provisionally is based on a principle similar to that by which Lesage, of Geneva, endeavored to explain the mechanism of gravitation. Suppose for a moment that the particles are without weight. If we regard any one of them individually, the effect of the molecular agitation would in general be nil so far as motion of the particle is concerned, inasmuch as this action is symmetrically distributed over the whole surface. If, however, there be given two particles, and if these be placed in sufficient proximity, then this symmetry of action is destroyed; the two particles will mutually screen or shield each other from impact on the parts of their surfaces which face each other, whereas the external parts of the surfaces are left exposed in full. The result is a force tending to move the particles together in a line joining their centers. In some such way, I believe, the larger particles in the presence of precipitants, or at higher temperatures (i. e., under conditions of intensified molecular disturbance at the surfaces of the particles), attract the finer particles, sweeping the greater number of them to the bottom of the tube at relatively large rates.

Subsidence and viscosity.—In this place the results in Tables 7 and 9, referring to ether, alcohol, and water, throw new light on the discussion. For the viscosities of these substances Poiseuille[1] found the relative data 0.3, 2.2, 1, respectively—where, however, the alcohol is not absolute, but an 80° (alcoholometer) spirit. Graham[2] finds the viscosities of water and alcohol in the ratio of 1 to 1.2. These values are proportional to the times occupied by the liquids in passing through identical capillary tubes under identical circumstances (transpiration). Now it would appear that in the case of subsidence we have quite an analogous experiment. In the first instance, a fine thread of liquid moves through a fixed solid; in the second, a fine particle of solid moves through a stationary liquid. In both cases the two substances move relatively to each other under conditions by which eddies are excluded, and the whole kinetic energy is at once converted into molecular kinetic energy or heat. Table 7, however, in connection with the results of Poiseuille and of Graham, shows conclusively that a relation between the rates of subsidence and the rates of transpiration is by no means apparent. The necessary inference is either that the frictions encountered in the two cases are radically different, or that the dimensions and the density of the particles change with the properties of the liquid in which they are submerged, or both. Above (p. 15) I accepted the last as the most probable conclusion; but it is nevertheless difficult and unsatisfactory to endeavor to make allowance for the observed enormous variations of rate of subsidence by simple variations of density and dimensions of the subsiding particles. These remarks are further exemplified by the results obtained with saline solutions.

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[1] Poiseuille, Ann. de Chim. et de Phys. (3), XXI, p. 104, 1847.

[2] Graham, Phil. Mag. (4), XXIV, p. 239, 1862.

The effect of the solution of the salts $CuSO_4$, $MgSO_4$, $ZnSO_4$, $NaCl$, and of the acids HCl, H_2,SO_4 in water, at ordinary temperatures, is an increase of the viscosity of the liquid nearly proportional (where, as in the above tables, only fractions of a per cent. are dissolved) to the quantity of salt or acid in solution.[1]

There are some salts,[2] notably among them KI, the viscosity of whose weak solutions at low temperatures is less than the viscosity of water. But the value of the decrement produced by addition of quantities as small as 0. 1 per cent. is in no case phenomenal or even large. Table 6, moreover, shows no marked difference between the respective rates of subsidence in solutions of KI and of NaCl, whereas in the first instance the viscosity of water has been increased, in the second diminished, by the solution of like quantities of the two salts. To me it appears impossible that additions of small fractions of a per cent. of acid or of salt to water should be able to affect the mean or measurable viscosity of this liquid in any marked degree; certainly not to such an extent as increases the rate of subsidence even many hundred fold.[3]

CONCLUSION.

In the above pages I have endeavored to throw light on the phenomenon of subsidence from three points of view. I adverted in the first place to the mechanical conditions of subsidence, i. e., to the dependence of rate of descent upon the figure and physical constants of a single particle or upon the constants of a stated group of particles. I then attempted to point out certain possible analogies in the sedimentation of very fine material with Clausius's interpretation of electrolysis—to find some expression for the dependence of subsidence on the molecular conditions of the liquid. Finally, I called to mind the probability of certain permanent chemical effects of the liquid on the subsiding solid. The last of these subjects of inquiry is more nearly open to investigation, independently of the others, than either the first or second. This, therefore, seems to be the proper point of departure for

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[1] The literature of the viscosity of liquids since the original memoirs of Girard (Mém. de l'Acad. Roy. de l'Inst. de France, 1816) and by Poiseuille (Ann. de Chim. et de Phys. (3), VII, p. 50, 1843; ibid., p. 76, 1847) has been steadily increasing, though the more important additions are of recent date. The reader desiring further information is referred to the papers of Sprung, Pogg. Ann., CLIX, p. 1, 1876; Grotrian, Pogg. Ann., CLII, p. 1, 1876; ibid., CLX, p. 1, 1877; Wagner, Wied. Ann., XVIII, p. 259, 1883, and others. Grotrian studies the vibration about a vertical axis of a very large horizontal disk suspended in a liquid, the theory of which experiment is fully known. In other researches, however, Grotrian, in common with the remaining physicists, adopts the more accurate method of transpiration. See Graham, "On liquid transpiration, etc.," Phil. Mag. (4), XXIV, p. 238, 1861.

[2] NH_4Cl, NH_4NO_3, NH_4Br, KI, KBr, KNO_3, KCl (Sprung, l. c.), $BaNO_3$ (Wagner, l. c.).

[3] Similar remarks may be made with reference to the capillary and cohesion constants of liquids, those of Gay Lussac, for instance. Cf. Mousson, Physik, I, pp. 263, 267, 1871.

further research; and I believe, if the relations in question are systematically studied, that the quantitative results will not only elucidate many obscure points of the chemical behavior of solids,[1] but that they will even furnish data bearing directly upon the phenomenon of solution. Solution is here the limit of turbidity.[2] Indeed, I know not whether the degree of extreme divisibility of subsiding particles, or even the mean size of the particles of an ordinary precipitate, has ever been *systematically* put into relation with the conditions, physical and chemical, under which subsidence takes place.

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[1] The tendency to hydration under varying conditions of mass per unit volume of liquid, for instance.

[2] See above, page 12, and chapter II, p. 42.

CHAPTER II.

THE DEPENDENCE OF RATE OF SUBSIDENCE ON ORDER OF SURFACE, CONCENTRATION, AND TURBIDITY.

EXPERIMENTAL RESULTS.

Introductory.—In this chapter it is my object to begin a minute study of the conditions subject to which a column of turbid liquid must present a stratified appearance. The turbidity is assumed to be due to very finely comminuted insoluble matter which the liquid holds in suspension.

The strata in question are usually characterized by sharp upper surfaces, below which opacity decreases until a depth is reached at which another surface juts out, as it were; from this point, downward, turbidity decreases again as far as the next consecutive surface, and so on for the remaining surfaces. Particles are thus aggregated on every surface and near it from below. If we suppose depth to be laid off vertically downward and opacity horizontally to the right, the appearance of the tube would be well given by a saw placed so that the cutting edges of the teeth may be upward on the right and nearly horizontal; in other words, the serrated outline of the diagram passes from left to right downward, indicating a general increase of opacity from top to bottom of the column. I need only add that the continuous decrease of opacity for parts of the column between the first and second, second and third surfaces, &c., is not so marked as between consecutive lower surfaces.

It has been stated above (p. 20) that in the case of fresh material the surfaces in question do not seem to appear until after the lapse of a large interval of time, say one to two hundred hours; but when the particles have just undergone subsidence, strata may be obtained sooner. Again, the occurrence of pronounced stratification is observable sooner with semitranslucent than with very opaque mixtures; in the latter case they eventually appear in greater number than in the former. Finally, after the strata have come into distinct definition, they retain their individuality until they ultimately vanish, or, at least, become too faint for measurement. Fluctuation of temperature interferes with sharpness of outline. In the present paper, however, some of the experiments have extended over 1,200 hours, so that the aggregated effect of temperature is probably nil.

The general method by which I hope to arrive at definite results on the ultimate cause of stratification consists in a minute study of the rate at which subsidence takes place considered in its dependence upon the order of the surface, the concentration, and the turbidity of the solution. It will be convenient to number the surfaces from the top downward, and distinguish them as surfaces of the first, second, third ...... order. Under concentration is to be understood the number of grams of dissolved precipitant per cubic centimeter of solution; under turbidity, similarly, the number of grams of insoluble dust of a given kind per cubic centimeter of solution. In the present experiments, however, it has been expedient to express turbidity arbitrarily.

Data.—Tripoli suspended in distilled water or in weak brine subsides at rates of practically convenient magnitude. This mixture has therefore been used in the present work.

The first series of results refers to diluted, i. e., to semitranslucent mixtures. The degrees of concentration vary from 0 to 1 per cent. of salt. For each strength of brine, moreover, three degrees of turbidity in the ratio of 4:2:1 are observed. The following Table 12 is a clear exhibit of the contents of the several tubes, the data indicating the number of cubic centimeters of turbid water, brine, and clear water mixed in each case.

TABLE 12.—*Semitranslucent mixtures—contents of tubes.*

Ingredients.	0 per cent.			0.1 per cent.			0.2 per cent.		
	4	2	1	4	2	1	4	2	1
Tripoli water.............cubic centimeters.	40	20	10	40	20	10	40	20	10
Brine.............................do	0	0	0	1	1	1	2	2	2
Distilled water ....do	10	30	40	9	29	39	8	28	38

Ingredients.	0.4 per cent.			0.6 per cent.			0.8 per cent			1 per cent.		
	4	2	1	4	2	1	4	2	1	4	2	1
Tripoli water ....cubic centimeters.	40	20	10	40	20	10	40	20	10	40	20	....
Brine.................................do	4	4	4	6	6	6	8	8	8	10	10	....
Distilled water ....do	6	26	36	4	24	34	2	22	32	0	20	....

Tripoli water used after standing three days.
Brine: 10 grams in 200 cubic centimeters.
Tubes (diameter, 25mm.; length, 200mm.) shaken up simultaneously October 1, 1885, 6 p. m.

Table 13 gives the results obtained with these mixtures; column first contains the date; column second, the time in hours elapsed since the beginning of the experiment; the remaining columns indicate the depth in millimeters of the surfaces of demarkation, for the condition of concentration and turbidity given at the column heading, below the surface of the liquid as a datum. Whenever the column shows a number of surfaces (surfaces of different orders), the depth of each is noted, the data being placed vertically above one another, in proper sequence; *c.* denotes clear.

TABLE 13.—*Semitranslucent mixtures — consecutive positions of the surfaces of demarkation.*

Date.	Time of day.	h	0 per cent.			0.1 per cent.			0.2 per cent.		
			4	2	1	4	2	1	4	2	1
October 1, 1885	6 p. m	0	0	0	0	0	0	0	0	0	0
October 6, 1885	7 p. m	121	20	40	70	23	52	80	25	42	72
October 8, 1885	10 a. m	160	26	45	85	27	65	97	32	53	92
			50	90	....	45	100	....	45	90	....
			70	......	....	70	......	......	61	......	....
			90	......	....	100	......	......	90	......	....
October 9, 1885	10 a. m	184	32	54	90	35	74	112	35	60	105
			58	100	....	58	120	......	55	......	....
			80	......	....	82	......	......	74	......	....
			100	.....	....	115	.....	......	105	.....	...
October 10, 1885	10 a. m	208	35	59	*c.*	38	82	*c.*	44	70	*c.*
			65	110	....	59	......	......	84	......	....
			90	......	..	92	......	......	......	......	....
			115	......	....	......	......	......	.....	......	....
October 11, 1885	10 a. m	232	40	65	*c.*	42	95	*c.*	50	82	*c.*
			75	......	...	67	......	......	98	......	....
						102					
October 12, 1885	12 m	258	44	72	*c.*	45	102	*c.*	57	89	*c.*
			80	......	..	75	......	......	105	......	....
October 13, 1885	1 p. m	283	49	77	*c.*	50	110	*c.*	64	98	*c.*
			89	......	..	82	......	......	......	......	....

Date.	Time of day.	h	0.4 per cent.			0.6 per cent.			0.8 per cent.			1 per cent.		
			4	2	1	4	2	1	4	2	1	4	2	1
October 1, 1885	6 p. m	0	0	0	0	0	0	0	0	0	0	0	0	....
October 6, 1885	7 p. m	121	40	60	*c.*	65	90	*c.*	100	*c.*	*c.*	*c.*	*c.*	....
October 8, 1885	10 a. m	160	50	75	*c.*	85	110	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	....
			89	....	....	....	....	....	....	....	....	....	....	....
October 9, 1885	10 a. m	184	60	83	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	....
October 10, 1885	10 a. m	208	72	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	*c.*	....
October 11, 1885	10 a. m	232	85	....	....	....	....	....	....	....	....	....	....	....
October 12, 1885	12 m	258	95	....	....	....	....	....	....	....	....	....	....	....
October 13, 1885	1 p. m	283	105	....	....	....	....	....	....	....	....	....	....	....

Table 14, finally, contains data for the rates of subsidence of each of the divers orders of surfaces, degrees of concentration and degrees of turbidity given in Table 13. Rates are expressed in $\frac{mm}{h}$. To derive these results I used graphic methods. The accuracy thus obtainable is fully in keeping with the accuracy of the other work.

TABLE 14.—*Semitranslucent mixtures—rates of subsidence.*

Order of surface.	0 per cent.			0.1 per cent.			0.2 per cent.		
	4	2	1	4	2	1	4	2	1
1	0.16	0.28	0.54	0.18	0.40	0.63	0.23	0.35	0.57
2	0.32	0.54	......	0.28	0.64	......	0.30	0.56	......
3	0.44	......	......	0.44	......	......	0.40	......	......
4	0.56	......	......	0.62	......	......	0.57	......	......

Order of surface.	0.4 per cent.			0.6 per cent.			0.8 per cent.		
	4	2	1	4	2	1	4	2	1
1	0.35	0.46	......	0.54	0.71	......	0.82	......	......
2	0.56	......	......	......	......	......	......	......	......
3	......	......	......	......	......	......	......	......	......
4	......	......	......	......	......	......	......	......	......

The next three tables are constructed on a plan identical with that pursued in the cases of Tables 12, 13, and 14. Time, h, is given in hours, depth in millimeters, rate of subsidence in $\frac{mm}{h}$. In addition to the experiments with water, it was found convenient to compare the rates of subsidence in pure water and in water charged with alcohol and with ether, respectively, in the proportions specified in the last four columns of Table 15.

TABLE 15.—*Opaque mixtures—contents of tubes.*

Ingredients.	0 per cent.			0.5 per cent.			1 per cent.			Alcohol.		Ether.	
	4	2	1	4	2	1	4	2	1	W.	A.	W.	E.
Tripoli water....cubic centimeters..	60	30	15	60	30	15	60	30	15	60	60	70	70
Brine.......................do......	0	0	0	8	8	8	16	16	16	......	....	......	......
Distilled water...............do......	16	46	61	8	38	53	0	30	45	20	......	10	......
Alcohol......................do......	....	....	....	...	....	....	....	....	....	......	20	......	......
Ether.......................do......	....	....	....	...	...	....	..	....	....	......	.....	......	10

Tripoli water, densely opaque.
Brine, 10 grains in 200 cubic centimeters.
Tubes (diameter, 25 mm.; length, 200 mm.) shaken up simultaneously October 3, 1885, 12 m.

TABLE 16.—*Opaque mixtures — consecutive positions of the surfaces of demarkation.*

Date.	Time of day.	*h*	0 per cent.			0.5 per cent.			1 per cent.			Alcohol.		Ether.	
			4	2	1	4	2	1	4	2	1	W.	A.	W.	E.
October 3, 1885	12 m	0	0	0	0	0	0	0	0	0	0	0	0	0	0
						Subsidence takes place in the ratio of concentration and turbidity, and is almost complete in fractions of an hour. No demarkation.									
October 10, 1885	10 a. m.	166	10	17	25										
			....	(*a*)	65										
			....	....	90										
			....	....	110										
October 11, 1885	10 a. m.	190	13	22	30										
			....	60	67										
			....	75	100										
			....	95	120										
October 12, 1885	12 m.	216	15	27	34	....	....	....	....	....	....	...	(*b*)	....	(*b*)
			....	70	80										
			....	85	110										
			....	104	145										
October 13, 1885	1 p. m.	241	19	30	40										
			....	52	87										
			(*a*)	65	120										
			....	80											
			....	100											
			....	125											
October 14, 1885	5 p. m.	269	22	35	45										
			....	55	97										
			....	70	140										
			...	90											
			....	110											
			....	140											
October 16, 1885	9 a. m.	309	25	38	52	....	....	....	....	....	....	36	60	23	(*b*)
			38	65	111	....	....	....	....	....	....	50	(*b*)	34	
			50	78	....	....	....	....	....	....	....	63			
			63	100	....	....	....	...	....	....	....	77			
			73	125											
			85												
			105												
October 17, 1885	2 p. m.	338	29	42	60	....	....	...	..	....	....	41	....	25	
			44	70	123	....	....	...	..	...	..	56	....	37	
			56	85	....	....	....	...	..	....	..	74			
			69	110	....	....	....	...	....	....	...	88			
			81	138											
			95												
			112												
October 19, 1885	9 a. m.	381	33	49	68	....	.	..	...	....	....	45	72	31	
			53	80	135	....	...	.	....	....	....	65	....	44	
			66	96	....	....	....	....	..	....	....	84			
			80	124											
			90												
			107												
			126												

a Incipient stratification. *b* Column turbid.

TABLE 16.—*Opaque mixtures—consecutive positions of the surfaces, &c.*—Continued.

Date.	Time of day.	*h*	0 per cent.			0.5 per cent.			1 per cent.			Alcohol.		Ether.	
			4	2	1	4	2	1	4	2	1	W.	A.	W.	E.
October 20, 1885	8 a. m.	404	34	50	74	....	....	....	....	....	....	50	75	32	
			55	84	....	....	....	....	....	....	....	70	....	45	
			70	100	....	....	....	....	....	....	....	90			
			85	130											
			98												
			117												
			138												
October 21, 1885	8 a. m.	428	38	55	75	....	....	....	....	....	....	51	....	38	
			59	90	....	....	....	....	....	....	....	71			
			75	111	....	....	....	....	....	....	....	92			
			90	136											
			103												
			122												
			145												
October 22, 1885	8 a. m.	452	39	59	80	....	....	....	....	....	....	54	82	39	
			62	95	....	....	....	....	....	....	....	75	....	54	
			80	....	....	....	....	....	....	....	....	100			
			95												
			108												
			128												
			152												
October 23, 1885	12 m.	480	40	60	85	....	....	....	....	....	....	57	87	40	
			65	100	....	....	....	....	....	....	....	84	....	60	
			85												
			104												
			117												
			137												
October 24, 1885	2 p. m.	506	45	66	90	....	....	....	....	....	....	64	91	44	
			70	107	....	....	....	....	....	....	....	90	....	65	
			89												
			109												
			122												
			145												
October 25, 1885	9 a. m.	525	45	68	93	....	....	....	....	....	....	65	95	45	
			72	110	....	....	....	....	....	....	....	92			
			92												
			113												
			125												
			147												
October 26, 1885	8 a. m.	548	46	70	99	....	....	....	....	....	....	65	96	47	
			74	118	...	....	....	....	....	....	....	95			
			95												
			119												
			130												
October 27, 1885	8 a. m.	572	50	74	101	....	....	....	....	....	....	70	100	50	(*a*)
			78	120	....	....	....	....	....	....	....	98			
			100												
			125												
			135												

a Column turbid.

TABLE 16.—*Opaque mixtures—consecutive positions of the surfaces, &c.*—Continued.

Date.	Time of day.	*h*	0 per cent.			0.5 per cent.			1 per cent.			Alcohol.		Ether.	
			4	2	1	4	2	1	4	2	1	W.	A.	W.	E.
October 28, 1885	8 a. m.	596	51 80 102 128 141	75 125	110 ...	....	....	....	... .	... .	....	72 102	103	51	
October 29, 1885	1 p. m.	625	55 85 108 134 149	80 131	112	....	....	....	....	....	....	74 106	107	54	
October 31, 1885	9 p. m.	681	59 91 118 141	85 140	118	....	....	....	....	....	....	80	113	56	
November 2, 1885	10 a. m.	718	62 97 125	91 149	124	....	....	....	....	....	...	83	118	59	
November 3, 1885	8 a. m.	740	63 99 126	91	126	....	....	....	....	....	....	86	120		
November 5, 1885	7 a. m.	787	103 133 67	99	133	....	....	....	....	....	....	90	124		
November 9, 1885	12 m	888	79 118 149	110	147										
November 13, 1885	9 p. m.	993	87 129	127	(*a*)										
November 23, 1885	6 p. m.	1,230	104 150	145	(*a*)	....	...	...	....	....	....	...	(*b*)	...	(*b*)

a Clear. *b* Column turbid.

TABLE 17.—*Opaque mixtures—rates of subsidence.*

Order of surface.	0 per cent.			Water.		Ether.	
	4	2	1	W.	A.	W.	E.
1	0.08	0.12	0.17	0.12	0.17	0.08	......
2	0.13	0.20	0.36	0.17	.....	0.12	......
3	0.17	0.25	0.51	0.22	......	......	......
4	0.21	0.32	0.65	0.25	....	......	......
5	0.24	0.40	......	.....	......	......	......
6	0.28	0.51	......	......	......	......	......
7	0.33	... ..	......	......	......	.....	......

A few remarks on these tables are in place here. The observation that distinct stratification is an earlier occurrence in translucent solutions than in very opaque solutions is well shown by the data in Table 16. The alcohol and the ether solutions remain turbid during the whole of the 1,230 hours within which subsidence is in progress. The descending surface in alcohol (very dense) must therefore be of an order higher than the first. Possibly the persistent turbidity may be connected with slow evaporation of alcohol or of ether out of the solvent water. Where subsidence takes place too rapidly for the formation of surfaces, no data are given, since these results would not be comparable with the other data, and the qualitative character of the phenomena has already been fully given in Chapter I.

The term translucent solution is used interchangeably with diluted mixture, opaque solution interchangeably with dense mixture. The extreme members of the dilute and of the opaque series differ largely in turbidity; but the degrees of turbidity of the intermediate members (i. e., high degrees for translucent solutions and low degrees for opaque solutions) probably overlap.

DEDUCTIONS.

The discussion may expediently be made to conform with the general plan pursued in the experiments. Rate of subsidence is therefore to be studied with regard to its dependence on order of surface, on concentration, and on turbidity.

Surfaces of different orders.—Turning first to the data for diluted mixtures, Table 14, I find three series of results available for comparison. In these there appears a distinct tendency of rate of subsidence to augment by nearly the same increment on passing each of the consecutive surfaces of demarkation. In the case of one and the same column, therefore, like differences of order correspond approximately to like differences of rate. This deduction is nearly true for the 0 per cent. solutions, and true to a smaller extent for the 0.1 per cent. and 0.2 per cent. solutions.

It is remarkable that as far as the 0.6 per cent. brines, the lowest surfaces for all turbidities and concentrations have like rates. This, however, may be merely accidental, so that if the tubes had been of greater length the result would no longer hold. Any rate in turbidity 1 is, as a rule, repeated in turbidity 2; rates in turbidity 2 are repeated in turbidity 4. When turbidity decreases, greater rates are more frequently repeated than smaller rates. We are thus inclined to infer that for continued dilution the column of finer material eventually becomes so nearly transparent that the surfaces escape detection; but this explanation is not valid, as will be shown presently in the case of opaque mixtures. For brine of greater strength than 0.6 per cent. the observations lose in accuracy, and we begin to encounter marked evidences of the effect of salt. Finally the increment of rate from surface to surface is augmented in marked degree in proportion as the turbid column approaches translucency.

With these suggestive results in hand it is well to turn for further corroboration to the experiments upon opaque solutions given in Table 17. The three degrees of turbidity of the 0 per cent. solutions, as well as the water of the alcohol and the ether series, are here available for comparison. The evidence given by all of these corroborates the deductions made above in a very satisfactory manner, viz: for one and the same turbid column the rate of subsidence tends to increase, step by step, in regular order, downwards. If mere dilution were of moment here, the upper layers would subside fastest. The column, which at the outset is continuously opaque, splits up into periods of nearly the same value. Again, the increment of rate of subsidence corresponding to two consecutive surfaces is manifestly smaller for opaque than for translucent solutions, and varies quite regularly with the degree of turbidity. This result is fully confirmed by the data for dilute solutions.

The very satisfactory accordance of all data in hand may be shown graphically by regarding rate of subsidence as a function of order of surface and constructing the linear loci on which the isolated points of observation approximately lie. This has been done in the annexed Fig. 3. If these lines taken as a whole be prolonged in the direction of order decreasing, we infer from the positions of the divers points of intersection with the axis X, that probably only one or at most two surfaces of very slow rate have escaped detection. Whether or not such prolongation be permissible remains to be seen, but the particles belonging to one of these surfaces are probably the cause of the permanent opalescent turbidity which frequently remains after measurable subsidence is complete.

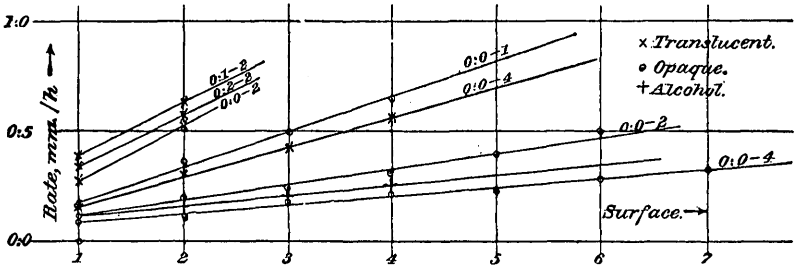

FIG. 3.—Relation of rate of subsidence to order of surface for different degrees of turbidity.

Concentration.—In the case of dilute mixtures turbidity 4, surfaces 1 and 2, and turbidity 2, surfaces 1, are available. It appears that rate of subsidence as a function of concentration varies at a gradually accelerated rate, almost imperceptibly between 0 per cent. and 0.2 per cent.; more rapidly from 0.2 per cent. on. Surfaces are obtainable even as far as 1 per cent. In the case of very opaque solutions surfaces are no longer obtainable even for brine of a few tenths per cent. of strength. Here, therefore, rate of subsidence increases with concentration much more rapidly than holds for dilute mixtures.

Turbidity.—In the case of opaque solutions the six consecutive surfaces of the 0 per cent. series are available. The data show that velocity of subsidence diminishes at a gradually decreasing rate as turbidity increases. This diminution is more pronounced for the upper rapidly-falling surfaces than for the lower surfaces of slower descent. Regarded as a whole, therefore, the curves converge more and more nearly in proportion as the original column is more opaque (Fig. 4). Hence for very opaque solutions, cæteris paribus, the curves probably converge in the rate of subsidence zero. In other words, the tendency is toward permanent opacity without stratification.

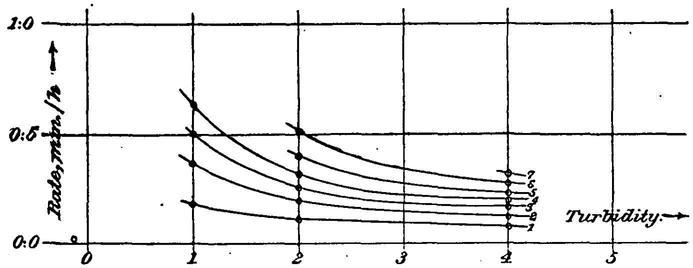

FIG. 4.—Relation of rate of subsidence to turbidity for consecutive orders of surfaces.

All these inferences are sustained by the data in hand for translucent solutions, where first surfaces of the 0.0, 0.1, 0.2, 0.4 per cent. solutions, and second surfaces of the 0.0, 0.1, and 0.2 per cent. solutions have been compared. Unfortunately, the results for opaque and for dilute solutions are on a different scale of turbidity. It is a question, moreover, whether surfaces of like order can be at once co-ordinated, so that further inquiry into this subject will be desirable and fruitful.

Temperature.—It has already been pointed out, as a result of the error introduced by temperature, that the actual locus does not necessarily pass through the origin. This assumption, therefore, is only partially correct. It is, however, the only method of representation which may be consistently applied throughout. I may add, that, columns of liquid placed side by side, show parallel variations of temperature discrepancy. If the surfaces observed above were due to temperature only, then we ought to find traces of a daily effect. In the 1,230 hours of examination, therefore, fully fifty such surfaces should be anticipated. The phenomenon observed is essentially different from this.

Sedimentation battery.—The experiments made suggest the following scheme for researches of a final kind: The tubes for subsidence should be 50 cm. long and about 3 cm. wide. This will give assurance not only that all surfaces have been detected, but will enable the observer to follow each one through a large interval of descent. These tubes (36 to

100) are to be conveniently arranged in tiers of say 6 to 10 in each horizontal row and the same number in each vertical row. Where brine and tripoli, for instance, are the ingredients, the degrees of concentration 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1 per cent. (horizontal row) and the degrees of turbidity 1, 2, 4, 6, 8, 10 (vertical row) will probably suffice to enable the observer to follow all the essential phenomena closely. It is highly desirable that each tube be provided with a millimeter scale (etched). It is necessary that the battery be placed in a room whose temperature is constant. Great pains must be taken to detect and observe all surfaces, and even to seek for such as are apparently invisible, by some such method as that described in the text, page 49. The experiments must, of course, be extended to a variety of subsiding solids. They must frequently be repeated to exhibit the time effect of the action of the liquid on the suspended solids.

INDEX.

Pres
Issue