THE GENERAL THEORY OF VISCOSITY OF TWO-PHASE SYSTEMS.

Mr. Emil Hatschek read a Paper on "The General Theory of Viscosity of Two-Phase Systems."

Notwithstanding the importance of this physical constant, and the fact that the literature of the subject contains many records of viscosity determinations, and of attempts to explain changes in heterogeneous systems on the basis of such measurements, the author is not, with one exception, aware of any attempt to treat the internal friction of such systems mathematically beyond two papers (1) published by him in 1910–11. The reader is referred to these for full details, only the main features and the results being reproduced in the present paper.

The first paper deals with the viscosity of a liquid, in which are suspended undeformable spheres of small diameter, which occupy in the aggregate only the smaller part of the total volume of the system, say not more than 40 per cent. of it. Fig. 1 shows such a system diagrammatically, the layer of liquid being contained between two parallel plates, one of which is stationary, while the other is moved in itself with a constant velocity. It is obvious that the liquid at the upper pole of each spherical particle moves with a somewhat greater velocity than at the lower pole, which is equivalent to a translatory movement of the particles with a velocity equal to half the difference of the two velocities prevailing at the two poles. By carrying through the calculation on the basis of this reasoning, an expression is obtained for the viscosity of the whole system. If we call—

η viscosity coefficient of liquid (or continuous phase),

f the ratio $\dfrac{\text{Total volume of particles (or disperse phase),}}{\text{Total volume of system}}$

η^1 viscosity of system,

the latter is given by the formula—

$$\eta^1 = \eta\,(1 + 4{\cdot}5 f) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

The radius and the distance of the particles do not appear, and the formula accordingly states that *the viscosity of a system of undeformable particles suspended in a liquid is independent of the size of the particles and is a linear function of the volume of disperse phase only.* The only qualification necessary is the following: Stokes's formula is employed in the calculation, and the formula (1) accordingly holds good only between those limits between which Stokes's formula holds good.

An almost identical result had been obtained by A. Einstein (2) in 1906. This paper deals with the determination of Avogadro's number by thermodynamical methods, and incidentally Einstein obtains the following expression (using the same symbols as before) for the viscosity of a liquid with small spherical particles suspended in it—

$$\eta^1 = \eta\,(1 + f) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The formula is therefore functionally identical with the author's formula (1), and only differs in the numerical constant, which is 1 instead of 4·5.

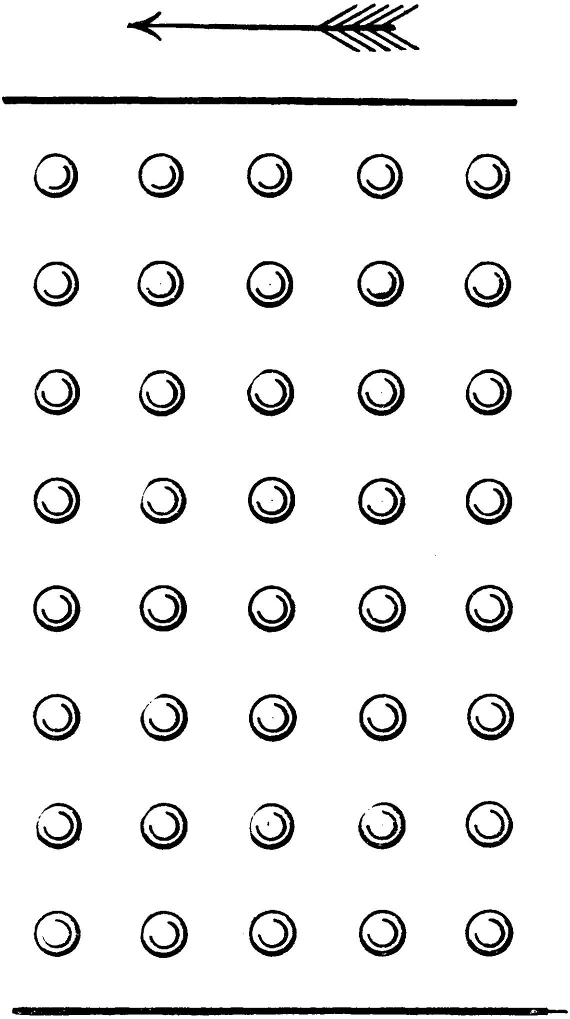

FIG. 1.

Einstein's formula was checked experimentally by M. Bancelin in 1911 (3). Certain discrepancies led Bancelin to correspond with Einstein, and the latter revised his calculations and altered the numerical constant from 1 to 2·5. Bancelin used spheres of gamboge made according to Perrin's method (precipitation of an alcoholic solution and fractionation by centrifuging) and found that the *viscosity of a suspension of such particles in water* *was independent of the diameter of the particles and increased in linear ratio with the volume of disperse phase,* up to 3 per cent. of the latter. The constant however was found to be *2·9*. The volume of disperse phase was determined by weighing, a method open to certain objections to be dealt with further on.

The author's formula was tested by Wm. Harrison (4) with suspensions of starch granules of very different origin, and therefore diameter, in water. This investigator found *an increase in viscosity independent of the size of the particles* (*i.e.*, the same increase with all starches used) *and in linear ratio to the* volume of disperse phase present, with a numerical constant of *4·75 instead of 4·5*. He also determined the *true volume* of disperse phase; weighing being out of the question, in view of the swelling of the starch, he centrifuged the suspensions in graduated tubes, and read the volume of disperse phase directly. The volume thus determined is no doubt somewhat too large, on account of the probable voids between the grains, but is certainly directly proportional to the true volume. Harrison found the formula to hold good up to 30 per cent. of disperse phase.

The systems just referred to are of course suspensions with a disperse phase consisting of particles very much larger than those which occur in colloidal solutions of the suspensoid class. A number of viscosity determinations on such sols are also to be found in the literature. In many cases these have been made on systems of the low degree of concentration which is generally characteristic of such sols, so that the variations in viscosity which have been measured are frequently very little in excess of the errors of experiment. A series of determinations free from objections —except certain difficulties in dealing with ultra-microscopic particles which are inherent—has recently been published by Sven Oden (5). The sols used were sulphur sols, made by Svedberg and Oden's method of fractionated coagulation, which permits the preparation of sols having particles of uniform size, and of considerable concentration, up to 50 per cent. by weight or about 25 per cent. by volume. The measurements show two important divergencies from the theoretical result: (1) the viscosity above a certain concentration grows more rapidly than in linear ratio, and (2) the viscosity of sols containing smaller particles is, for equal weights, higher throughout than that of sols with larger particles.

At the present moment there appears to be no satisfactory explanation of the first discrepancy. It is at least possible that it may be in part due to the use of the ordinary capillary viscometer, and measurements at much lower rates of shear in a different apparatus are therefore required to settle this point. Such measurements and the apparatus used will be referred to further on. As regards the higher viscosity of more highly disperse systems, *i.e.*, such containing smaller particles, the case is different, and several points of high theoretical interest are raised by it. It must be remembered that all that is definitely known is the *weight of disperse phase*, whereas the formula, or any conceivable mathematical expression, contains the *volume*. As regards this, certain well-known assumptions are always made in ultra-microscopic determinations, viz., that the particles are of a simple geometrical shape, necessarily assumed to be the same for large and small particles, and that the density of ultra-microscopic particles is the same as that of substances in bulk. The further assumption that, for equal weights, disperse systems of different degrees of dispersity also contain equal volumes, is a necessary corollary of the previous ones.

As is well known, neither of the two assumptions is capable of proof. The examination of microscopic—as compared with ultra-microscopic—

precipitates shows, however, that particles of different sizes may, and very generally do, have very different shapes, and therefore very different coefficients of friction or resistance when moving in a liquid.

This question, which may well arise in the case of many sols, is however practically eliminated in that of the sulphur sols examined by Sven Oden, as a spherical shape is reasonably certain in these sols. Nevertheless, there are extremely strong grounds for the view that the *effective volume* is not constant, *i.e.*, simply proportional to the weight, for different degrees of dispersity. It is quite generally supposed that such particles as are here considered are surrounded with an adsorption envelope, which moves with them, so that the effective volume of the particle is the sum of two factors: volume of actual disperse phase (probably, but not necessarily proportional to the weight) plus volume of adsorption envelope.

The aggregate volume of these adsorption envelopes is the product of their thickness into the total surface of the disperse phase. If the thickness is constant for a given system, *it follows at once that the aggregate volume of adsorption envelopes and therefore the effective volume of disperse phase increases with increasing dispersity*, as found by Oden. The two sols investigated by the latter were a sol with submicroscopic particles of 100 $\mu\mu$ diameter, determined ultra-microscopically in the usual way, and an amicroscopic sol with particles estimated at 10 $\mu\mu$ diameter. It is of course possible to calculate from these data and the observed ratio of the two viscosities the thickness of the adsorption envelope. This has been done by the author (6), and the figure found is 0·87 $\mu\mu$. The value has nothing inherently improbable, and the only striking feature is that so slight an envelope is sufficient to increase the effective volume so considerably.

The adsorption envelope, while it accounts perfectly for the greater viscosity—given equal weights of disperse phase—hardly explains the other discrepancy between the theoretical conclusions and the observed results in sols, viz., the more than linear increase of the viscosity with growing concentration. Several explanations, all tentative, suggest themselves. One is the possibility of particles impeding one another at much lower concentrations than those assumed, while the formula disregards mutual disturbances. Another is the assumption that a mere translatory motion of the particles in the direction of shear does not fully represent conditions, as an additional rotary motion of the former is quite conceivable: this would call for further energy, which would increase with decreasing distances between particles and accordingly with increasing concentration.

It finally appears possible, as already mentioned, that the capillary viscometer may give rise to disturbances, and it appears at least eminently desirable to determine the viscosity of heterogeneous systems by some alternative method—even if this should lack the convenience of the transpiration method. For this purpose the author has adapted the apparatus used by Couette (7) for determining the viscosity of water at low rates of shear. Owing to the very great difficulties experienced in bringing the apparatus to its present convenient form, and to pressure of other work, only a few results are available at the time of writing, which will be given later. The method appears even more essential for obtaining an insight into the mechanism of the processes in a system of two liquid phases, such as we shall have to consider next, and the description of the apparatus therefore follows the theoretical consideration of this class, the emulsions and emulsoids.

The systems considered so far all contain a disperse phase which is not deformable, and which amounts to considerably less than half the total volume of the system. It is by no means necessary that the disperse phase should be, in bulk, a solid substance: small globules of liquid widely separated would undergo no appreciable deformation during shearing, and the whole reasoning would apply to them equally.

If we are therefore to account for the peculiarities, and more especially the high viscosities, of systems like emulsions, which are known, and emulsoids, which for many cogent reasons are considered, to be systems of two liquid phases, we have to make a further assumption, namely that *the disperse phase occupies a considerable part, say at least one half and generally very much more,* of the total volume. It is obvious that such phase ratios are possible with two liquid phases, and equally obvious that the system must have a perfectly definite geometrical structure.

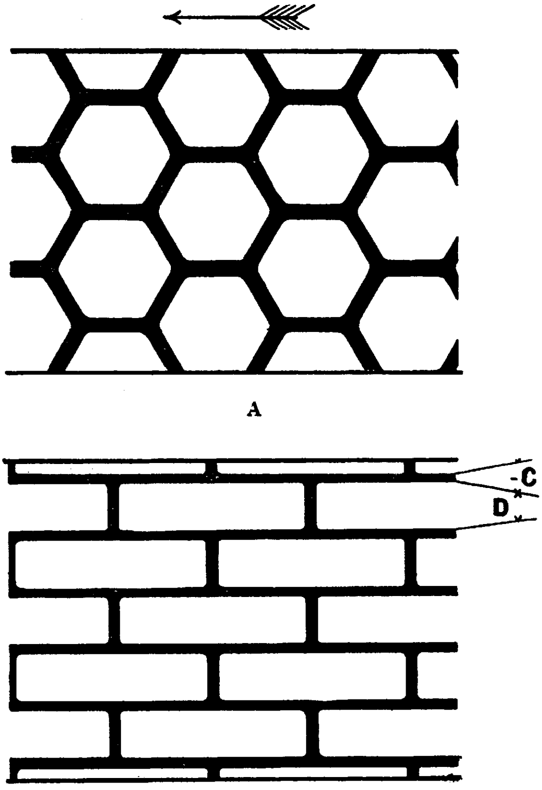

FIG. 2.

If we imagine a system of spheres in a given space, and let their radius or their number increase until they are in closest contact, *i.e.*, until each sphere touches twelve others, the aggregate volume of the spheres is 74·04 per cent. of the total space occupied. The twelve points of contact are the centres of the faces of a dodecahedron (two different dodecahedra are possible, into which question it is not necessary to go), and, if the volume of the spheres is increased further, flattening must take place and the faces of the dodecahedron be developed more and more.

While the author has found a general treatment of the viscosity of a system of two liquid phases impossible, it is comparatively easy to proceed synthetically from the stereometric considerations just developed. Fig. 2 A shows diagrammatically a film of such a two-phase system, the disperse phase being shown white and the films of continuous phase black. As explained, the former assumes necessarily the shape of dodecahedra, the hexagons being sections through these. If the system is now sheared, the polyhedra must slide over one another, and in a certain position the system must assume the altered shape shown in Fig. 2 B. A simple calculation, for which the reader is referred to the original paper, will show that such rectangular prisms fill space again continuously and are therefore possible.

If shearing is continued, the system has of course a tendency to assume its original shape. The factor tending to bring about this return is the interfacial tension between the two phases, which would reduce the interface to the minimum possible in the circumstances, *i.e.*, to the polyhedral shape. This tendency, however, is counteracted by the viscosity of both phases, principally by that of the disperse phase, and it is therefore quite possible to conceive that, *above a given velocity of shear, there may not be time for this return to the polyhedral shape and that the system would remain as shown in Fig.* 2 B.

In that event it is obvious that *shearing only takes place in the horizontal films of continuous phase*, and it is a simple matter to calculate the work done on this assumption. It is also obvious that neither the interfacial tension (which has not time to act) nor the viscosity of the disperse phase enter into the calculation, which is given *in extenso* in the original paper. The formula finally obtained, if the viscosity of the continuous phase is taken as unity, is the following—

$$\eta = \frac{\sqrt[3]{A}}{\sqrt[3]{A} - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which the symbols mean :—

η = co-efficient of viscosity of system,

$$A = \text{ratio} : \frac{\text{Volume of system}}{\text{Volume of disperse phase}}.$$

The curve corresponding to the above equation is shown in Fig. 3, and the similarity to the concentration-viscosity curves obtained with a number of sols, such as caseinogen, rubber, nitrocellulose, etc., is striking without detailed comparison.

The question naturally arises at once, whether the assumption of a minimum or critical velocity of shear is tenable, *i.e.*, whether shearing under ordinary conditions does proceed with such a velocity that the conditions on which the formula is based arise. On the basis of the material available this question can unhesitatingly be answered in the affirmative. The rate of shear in the usual method, transpiration through a capillary, appears far in excess of the minimum, *i.e.*, no anomalies can be observed. Even the very low rates of shear used in the Couette apparatus appear sufficient to bring about the stable condition of stress postulated in many cases.

As regards the application of the formula, a distinction has to be made. In emulsions, in the strict sense of the word, it is of course possible to determine the volumes of both phases, either by using known amounts of them in preparing the emulsion, or by breaking up an emulsion of unknown composition and measuring the resulting two phases. Experiments have been made with coarse emulsions of ordinary paraffin oil in ¾ per cent. soap solution, prepared by the author's method. The phase ratio was determined from the finished emulsion by breaking up with dilute hydrochloric acid. A 50 c.c. burette is filled up to the fifty mark with dilute acid, and then to the zero

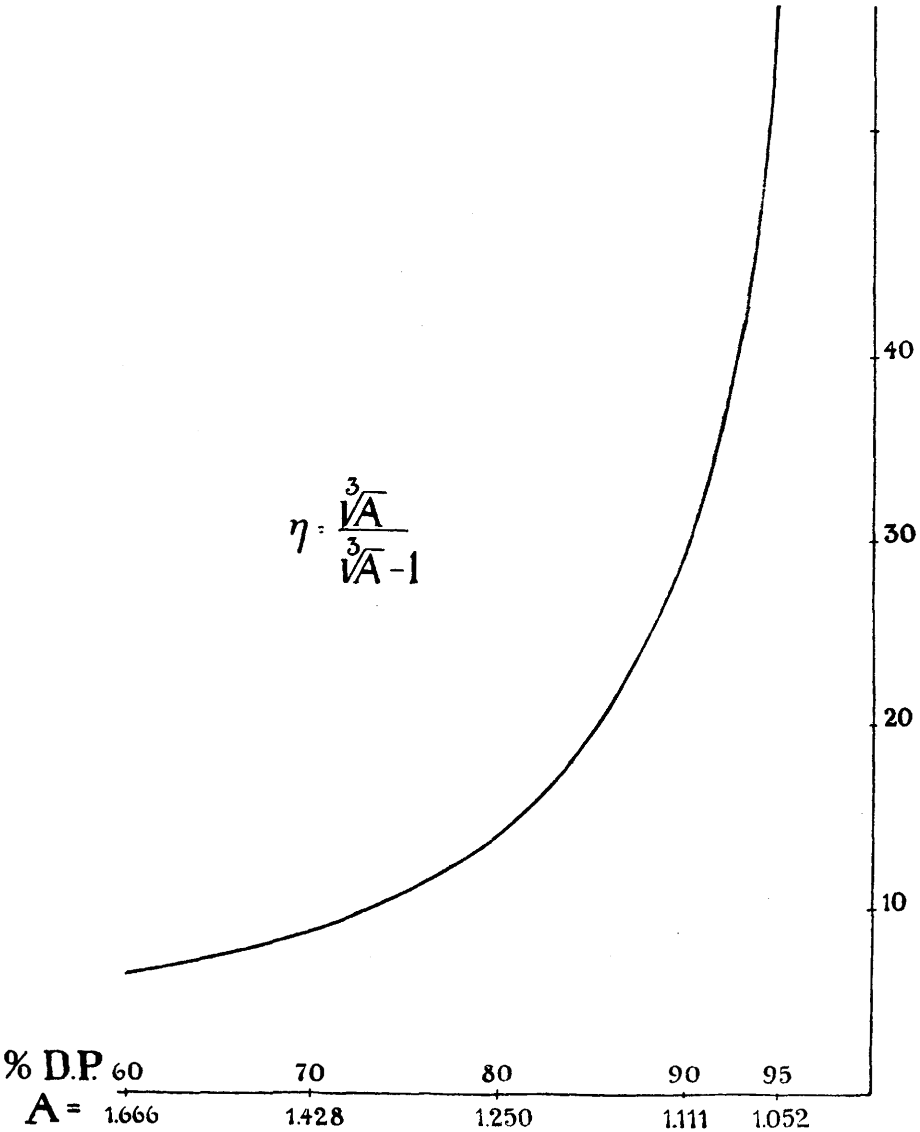

FIG. 3.

mark with 50 c.c. of emulsion. Mixing at once causes breaking up, and after separation the volume of oil can be read off directly. The results are given in Table II and show a very satisfactory agreement.

With emulsoids the case is somewhat more complicated. As is well known, the sol of an emulsoid, say gelatine or silicic acid, must be assumed to consist of two liquid phases, the disperse phase consisting of droplets of what may roughly be called a hydrate or solvate of the dissolved substance, *i.e.*, composed of the latter and a certain amount of the solvent definitely associated with it. This amount is unknown, and the volume of the disperse phase is obviously equally so. There is accordingly no possibility of applying the formula to such systems unless we make some assumption with regard to the volume of disperse phase, or rather with regard to *the relation of this volume to the weight of substance dissolved*, the latter being the factor usually known.

The simplest assumption, and one, moreover, in entire accord with what we know of the closely related phenomenon of "swelling," is that, at any given temperature, a definite weight of substance takes up a constant amount of solvent to form together with it the disperse phase, or, in other words, that at any given temperature *the volume of disperse phase is a constant multiple of the volume—or weight—of the dissolved substance.* Thus, 1·4 gr. of gelatine, *i.e.*, 1 c.c., might conceivably at a certain temperature take into the disperse phase say 10 or 15 c.c. of water, *i.e.*, 1·4 gr. would form 11 or 16 c.c. of disperse phase.

This assumption can obviously be tested by experimental data. From the known viscosity of a system we can immediately calculate the phase ratio, by the following formula, which is a transformation of (3) :—

$$A = \left(\frac{\eta}{\eta - 1}\right)^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

A is the ratio $\frac{\text{Total volume}}{\text{Volume of disperse phase}}$. If the amount of dissolved substance is, as is usually the case, given in per cent., this is also a ratio with the same numerator, viz.: $\frac{\text{Total volume}}{\text{Dissolved weight}}$, and, if our assumption is correct, there must accordingly be *a constant ratio between the two*, *i.e.*, the phase ratio must be a constant multiple of the percentage contents.

Various experimental data have been examined in this sense, and the results are shown in Table I. Column I shows the weight dissolved in per cent.; II, the measured coefficient of viscosity; III, the ratio A calculated from the latter by formula (4); IV, the corresponding ratio: total volume : weight of dissolved substance, and finally, V, the ratio of III and IV, which, according to the assumption, should be constant.

It will be seen that this constancy shows itself satisfactorily between fairly wide limits of concentration. With caseinogen, for instance, 1 gr. of dissolved substance produces approximately 9·5 c.c. of disperse phase, or 1 c.c. (density about 1·3) 12·3 c.c. of disperse phase. The reason why there are discrepancies at lower concentrations is also obvious. 4·35 gr. of caseinogen would only make about 41 per cent. of disperse phase, that is, less than one-half of the total volume. The structure on which the formula is based cannot yet arise at this ratio, and the system cannot therefore conform to it. As a general conclusion, thoroughly confirmed by experience, the emulsoid character, *i.e.*, the very rapid rise of viscosity with concentration, can, even with typically emulsoid substances, *show itself above certain concentrations only*: the dissolved substance plus the solvent associated with it must occupy more than about 50 per cent. of the total volume. Until this happens, the ratio between viscosity and amount of dissolved substance is approximately linear. This shows itself strikingly in all published viscosity curves, but the percentage at which the characteristic rapid rise of viscosity sets in varies enormously in different substances, and is a measure of their "emulsoid" or "lyophilic" properties. With caseinogen it begins at about 5 per cent., with glycogen about 25 per cent., while indiarubber solutions show extremely rapid rises at concentrations above the low limit of 0·4 or 0·5 per cent. From figures given by Schidrowitz and Goldsborough the author calculates that, in forming the disperse phase, rubber takes up 70 to 100 times its own volume of solvent—a figure which is not surprising to those familiar with the preliminary swelling of rubber in its solvents.

Even more than in the case of suspensions, it appears desirable to study the viscosity of emulsions in some way which permits variations *in the rate of shear*. The latter cannot be altered in the capillary viscometer, as the velocity of flow is settled by the dimensions of the capillary, which are in turn fairly strictly defined by the necessity of avoiding turbulent flow. Such experiments have been made by Garrett (8) on sols of silicic acid, albumen and gelatine: the method employed was the determination of the decrement of the oscillations of a disc submerged in the liquid. Apart from the complicated mathematical treatment necessary, this procedure possesses the grave drawback that the velocity of shear is different at every radius of the disc. While this is no objection in the case of homogeneous liquids, it tends to obscure still further the questions which arise in the investigations of heterogeneous systems, which may conceivably have viscosities either constant

TABLE I.

Percentage by Weight of Dissolved Substance.	η — Coefficient of Viscosity; Water at same Temperature being taken at Unity.	$A - \frac{\text{Total Volume}}{\text{Volume of Disperse Phase}}$ calculated from Formula 4.	$A' - \frac{\text{Total Volume}}{\text{Weight of Dissolved Substance}}$ (100 : Percentage).	Ratio $\frac{A'}{A}$ which should be constant.
Glycogen Sol (F. Botazzi and G. d'Errico.) (10)				
20	3·548	2·685	5·00	1·862
25	4·548	2·108	4·00	1·897
30	7·370	1·525	3·33	2·184
35	12·220	1·292	2·85	2·212
40	20·550	1·161	2·50	2·155
45	62·000	1·050	2·11	2·010
Casein (Sodium caseinogenate) Sol (H. Chick and C. J. Martin.) (11)				
4·35	3·37	2·860	22·99	8·040
6·05	6·12	1·715	16·53	9·638
7·06	8·48	1·457	14·17	9·722
8·49	13·66	1·256	11·78	9·377
9·39	23·72	1·138	10·56	9·358

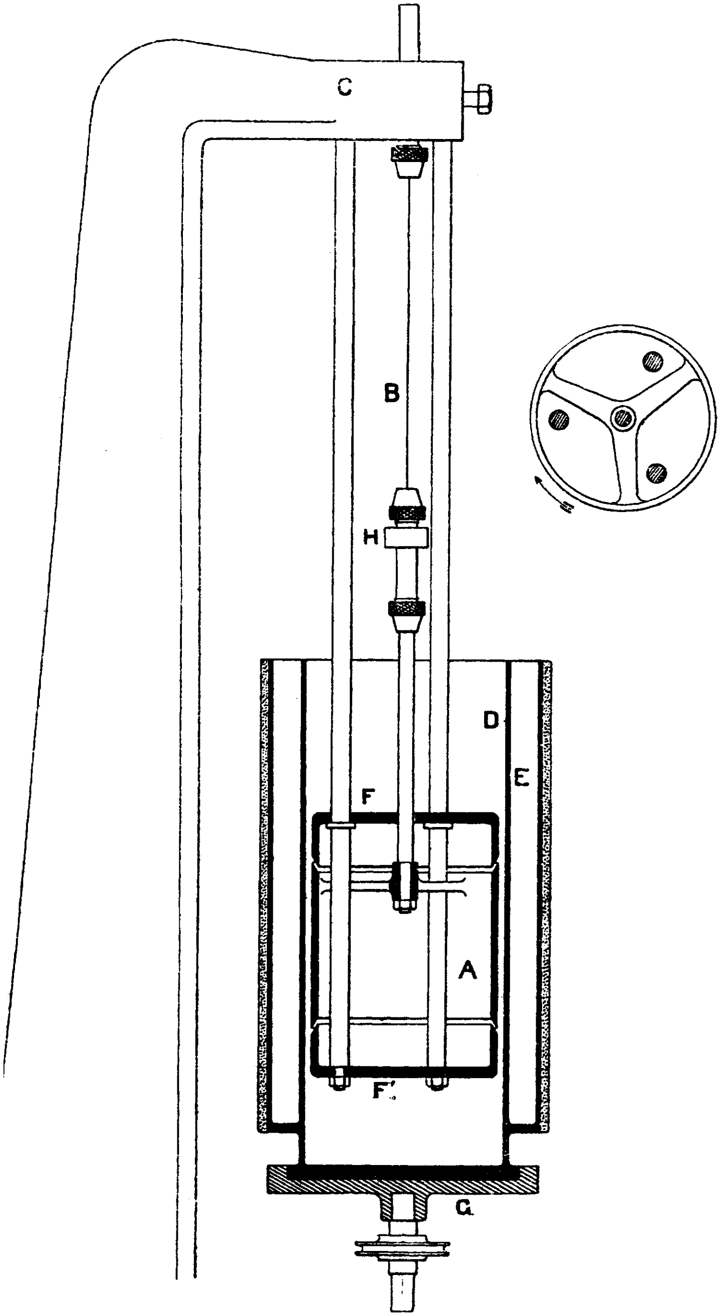

FIG. 4.

only above certain critical velocities, or altogether inconstant, *i.e.*, the viscosity might even be a function of the velocity of shear throughout.

These objections are avoided in Couette's apparatus, the form of which finally adopted by the author is shown in Fig. 4. A hollow cylinder A, which is open and bevelled at the ends, is suspended by a wire B from a heavy bracket C, provided with levelling screws (not shown). This cylinder A is coaxial with an outer cylinder D, which is provided with a water jacket E covered with insulating material. Two short guard cylinders, F and F^1—closed at one end—are placed opposite the open ends of the cylinder, leaving a clearance of about 2 mm. between the bevelled surfaces. The outer cylinder D rests on a table G, which can be rotated by suitable gearing. The suspended cylinder A is provided with a mirror H, and its deflection read by scale and telescope.

TABLE II.

VISCOSITY DETERMINATION BY MEANS OF COUETTE'S APPARATUS.

System: Emulsion of Paraffin in Soap Solution.

A. *Viscosity of Continuous Phase:* 0·75 *per cent. Soap Solution.*

Zero.	Reading.	Deflection (Reading minus Zero).	Time per Revolution in Secs.	Product of Time and Deflection, *i.e.*, Rel. Viscosity.
230	266	36	3·8	136·8
,,	271·5	41·5	3·2	132·8
,,	282	52	2·65	137·8
				Mean 135·8

B. *Viscosity of Emulsion.*

Zero.	Reading.	Deflection (Reading minus Zero).	Time per Revolution in Secs.	Product of Time and Deflection, *i.e.*, Rel. Viscosity.
29	46	17	96	1632
,,	48	19	83	1577
,,	53	24	67·5	1620
				Mean 1609

When the outer cylinder is filled with a liquid and rotated, the inner cylinder A is deflected, owing to the viscosity of the cylindrical layer of liquid between A and D. The two guards F and F^1 keep the liquid in the interior of A entirely at rest and eliminate the very complicated effect of the ends, which arises where a closed suspended cylinder is used, as has been done by some observers. It has been shown by Couette and others (9) that the rate of shear is practically uniform in the cylindrical layer of liquid, and that the couple tending to deflect the cylinder A is: viscosity × velocity × an apparatus constant. For a given wire, therefore, assuming the viscosity (as has been shown to hold good for water) to be independent of the rate of shear, the deflection divided by the angular velocity is a constant. It is more convenient, especially for the low velocities to which the apparatus particularly lends itself, to use the product: deflection × reciprocal of velocity, *i.e.*, time taken for one revolution. For relative determinations the apparatus can be gauged with water at a definite temperature exactly like the capillary viscometer, *i.e.*, the above product is determined. For the same wire, these products for two different liquids are in the ratio of the viscosities, and the specific gravity does not, as in the capillary apparatus, enter into the calculation.

The sensitiveness of the apparatus may be pushed to any desired degree, by using thin wire and a distant scale. The time per revolution is determined by stop watch, by observing the passage of a mark on the cylinder through some non-parallactic sight, of course counting an appropriate number of revolutions. The lowest angular velocity used by the writer so far has been about 3° 38′ per second, viz., one revolution in 99 seconds.

As a first instance of measurements by this apparatus may be mentioned the determination of the viscosity of an emulsion referred to above. This was an emulsion of ordinary lamp paraffin in a $\frac{3}{4}$ per cent. soap solution, prepared by the author's method (12). This emulsion is fairly coarse, and contains even macroscopic oil globules, so that the use of the capillary viscometer is impossible. (N.B. This has been tried, but with a great range of instruments it was impossible to obtain concordant readings.) The full data are given in the Table I already referred to above.

If the viscosity of the continuous phase is taken as unity, the viscosity η of the emulsion is $1609 : 135{\cdot}8 = 11{\cdot}85$.

The ratio $A = \frac{\text{Total volume}}{\text{Volume of disperse phase}}$ calculated from formula (4) is accordingly $A = \frac{11{\cdot}85}{10{\cdot}85} = 1{\cdot}302$.

The volume percentage of disperse phase is therefore $100 : 1{\cdot}302 = 76{\cdot}7$ per cent.

Fifty c.c. of the emulsion was broken up by hydrochloric acid and gave 10·1 c.c. of water and 39·9 c.c. of oil, or 79·8 per cent. of the latter, a satisfactory agreement with the calculated value of 76·7 per cent.

Further work on emulsoid sols is in progress, but the results must be reserved for a future communication. It is however possible to state already that investigation, particularly on gum arabic and gelatine sols, shows that these possess different viscosities at different rates of shear below certain limits. The need of *kinetic methods*, so strongly emphasized by Dr. Ostwald, is equally pronounced in this particular direction. The capillary viscometer only furnishes points, *i.e.*, the viscosity of a given system at given temperatures, and at *those velocities of shear which establish themselves automatically in conformity with the dimensions of the apparatus* and the gravity of the liquid. To gain an insight into the *mechanism* of the viscosity of heterogeneous systems, something more is wanted, viz., investigation at different rates of shear to be altered at will.

In conclusion, the author may perhaps be permitted to express the hope that the theoretical and experimental study of the viscosity of heterogeneous systems may ultimately furnish a starting-point for a general theory of the viscosity of homogeneous systems. The term "homogeneous" is after all only relative, and a solution containing hydrates with many molecules of water may quite probably be treated by the same mathematical methods as similar systems containing microscopic or ultra-microscopic aggregates.

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