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Phil. Trans. R. Soc. Lond. A 1950 **243**, 37-66
doi: 10.1098/rsta.1950.0013

THERMODYNAMICS AND RHEOLOGICAL BEHAVIOUR OF ELASTO-VISCOUS SYSTEMS UNDER STRESS

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(*Communicated by E. K. Rideal, F.R.S.—Received* 3 *October* 1949—*Revised* 4 *March* 1950)

CONTENTS

The systems discussed were obtained from dissolving aluminium and calcium soaps of fatty and naphthenic acids in hydrocarbons with the aid of peptizers like water, xylenols, alcohols, 'Cellosolve' or cresols. They behave similarly to solutions of rubber in benzene. Rheologically they exhibit certain peculiarities associated with secondary flow phenomena.

It was observed that when such systems were subjected to stress, their free energies increased. The first series of experiments dealt with the behaviour of jets in the form of expanding conical sheets. Newtonian liquids broke up when the kinetic energy of the jet exceeded a certain function of the surface energy which tended to stabilize the sheets. With these elasto-viscous systems, the kinetic energy required to break up the expanding conical sheets was much greater than this function and thus it was concluded that the stressed sheets had a higher free energy than the unstressed relaxed body of the same liquid.

The second series of experiments dealt with the quantitative evaluation of the free energy on subjecting the systems to stress at different temperatures. A rod was rotated inside a stationary sleeve, the space between being full of the liquid under consideration. From the drop in the level of the liquid, it was deduced that the internal energy and the entropy were both raised by shearing the system. The increase in internal energy was greater than the rise in entropy, and hence the free energy, as a whole, increased on shearing. These effects became less noticeable as the temperature was raised.

Next a series of experiments was conducted on the behaviour of these systems when subjected to different states of shear between discs, cones or cylinders in which one member was rotated and the other held stationary. In all experiments secondary spontaneous flow from regions of high shear to regions of low shear confirmed the hypothesis that the increase in free energy on

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straining (or stressing) the system resulted in local instability. Surfaces of uniform shear acted as if they were semi-permeable membranes with a concentration gradient across them due to the structural units moving from regions of high to those of low shear values. Thus a species of osmotic pressure was generated which could be measured. These peculiar phenomena only occurred when there was a marked difference in the rate of shear between different points in the system; under uniform rates of shear they did not arise.

Finally, experiments with pipes showed that these systems possessed two peculiarities: (1) the inlet end effects were far greater than those encountered with Newtonian systems under similar conditions; and (2) there appeared to be a retarding layer effect in the pipe.

It is concluded that for these systems studies of the balance between input energy and the portions which are lost and stored would be better approaches to the study of the structure of the systems than a study of the viscosity of the liquids as such.

General introduction

The systems under consideration are those obtained from dissolving aluminium and calcium soaps of fatty and naphthenic acids in hydrocarbons, with the aid of peptizers like water, xylenols, alcohols, Cellosolve, or cresols. In general, they behave in an analogous manner to solutions of rubber in benzene. Solutions of glue in water or of Perspex in benzole also resemble them in behaviour.

When subject to continuous shearing, as in flowing through pipes or in rotational viscometers, they exhibit certain characteristics of viscosity and elasticity which have been reported already (Wood, Nissan & Garner 1947). However, certain other behaviours appear to be peculiar to these systems and are not so readily explicable in terms of ordinary concepts of viscosity and elasticity. As these characteristics have afforded an insight into the structure of these colloidal systems, and as they are novel* in several respects, they exclusively will be treated in this paper.

Qualitatively, several of these characteristics are readily demonstrated by simple experiments.

The first peculiarity that is observed appears when the soap or rubber is being dissolved in the hydrocarbon by means of a stirrer in a container. When the stirrer rod is rotated in a beaker containing soap or rubber in, say, benzene, at first the vortex normally observed with ordinary liquids appears around the shaft. As the solute dissolves and the viscosity increases, the vortex disappears. However, when a certain amount is dissolved it is observed that the liquid begins to climb the rotating shaft against the action of gravity, and builds up a layer rotating with the shaft, i.e. stationary relatively to the shaft. This layer is flung off the shaft eventually by centrifugal forces.

A similar peculiarity of secondary flow appears when a circular disk is held stationary in a rotating cylindrical container containing a solution of rubber or aluminium soap in hydrocarbon. Small coloured particles reveal a secondary flow from the periphery of the disk towards its centre; counter-flow takes place in the relatively unsheared material above or below the disk.

Again, when these liquids issue from a pipe or a nozzle, it is observed that the material 'swells' beyond the exit, i.e. material flows at right angles to the main direction of flow in

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* The work reported here was done between 1942 and 1946; most of it was finished in 1944. The work was for the Petroleum Warfare Department and was released for publication in 1949.

a similar manner to rubber being extruded from a tube. This phenomenon has been independently observed and reported by Merrington (1943).

Other observations are not so direct and will be discussed later in their appropriate sections. However, the above three peculiarities appear to reveal an instability of the system in regions of relatively high state of shear compared with regions of low shear, resulting in a spontaneous movement of the liquids down the space gradients of the shear. As the ordinary laws of hydrodynamics based on the flow of continua did not appear to afford an explanation of the phenomenon it was concluded that it was due to the internal structure and energetics of the colloidal system built up and broken by the shear. In thermodynamical terms it appeared that the free energy—or the work function, if constant volume is assumed—of the system must be increasing with shear. An increase in the free energy in one part of the system relative to another would create a tendency for the liquid to migrate to regions of low free energy. As this simple hypothesis appeared to explain the phenomena observed—and also others, e.g. the apparent strain-hardening of threads drawn from the liquid—it became necessary to investigate:

(1) whether free energy increases measurably with shear;

(2) if it does, whether it is due to changes in internal energy or in entropy (or in both) of the structure when sheared; and

(3) whether it is possible to correlate changes in these thermodynamic parameters of the system with the experimental conditions of shear, distances, etc.

Although the work was not carried out in this order—indeed, the theoretical treatment of the subject came as a secondary development to the main and pressing requirements of the evaluation of the properties of these liquids for warfare purposes—the order enumerated will be followed here as it renders the treatment simple to present.

Increase of free energy on straining

Introduction

If a sheet of liquid is projected downwards from a nozzle in the form of a hollow cone, the kinetic energy of the liquid urges the cone to grow. The effect of the viscosity of the liquid is to slow the rate of growth without changing its shape. The surface tension, however, by exerting a hoop tension tends to contract the sheet to ever-decreasing dimensions. Thus at low speeds the conical sheet will expand at first to a maximum diameter and then contract. The general shape of the bubble is two cones joined smoothly at their bases. At high speed another property of liquids comes into play. This is the property of a liquid to break up into smaller fragments possessing minimum total surface when the original shape of the jet is stretched out beyond some limiting dimension. Thus, if a cylinder of liquid is elongated it will break up into fragmentary cylinders when its length to its diameter reaches certain limiting ratios. The important point here is that whilst this peculiarity is due to the surface tension, the ratio of the length to the diameter at which rupture occurs is the same for all ordinary liquids, independently of the value of the surface tension.

Thus, if the conical jet is projected from a nozzle at high speed the kinetic energy of the jet will force it to expand, and when the expansion reaches a certain value, characteristic of the geometry of the apparatus, the jet will shatter. As all ordinary liquids will have the same value of total surface area at the moment of shatter for any one apparatus operated under standardized conditions, the kinetic energy per unit volume of the jet will be a measure of the dynamic surface tension of the jet.

Thus, the critical kinetic energy per unit volume of the jet or any standard multiple of this quantity at which the conical sheet is observed to break up may be termed the 'rupture strength' of the jet. This was taken as equal to ρv^2, where ρ is the density of the material in g./cm.^{3} and v is the mean velocity at the nozzle in cm./sec., and is therefore given in ergs/cm.^{3}. Rupture strength will be a characteristic of the liquid in any one apparatus. If the degree to which the sheet is stretched is the same for all liquids, then rupture strength so measured will be proportional to the dynamic surface tension of the liquid. If the apparatus is calibrated with liquids which are known to possess a dynamic surface tension which is the same as the static surface tension, then the apparatus can be used to measure the dynamic surface tension of other liquids.

Finally, if the rupture strength for any particular liquid is found to be higher than that determined by its static surface tension then this fact shows that either the dynamic surface tension is greater than the static value or that the liquid, unlike ordinary liquids, can be stretched beyond the limits of ordinary liquids or that both conditions are obtaining. By any of these three mechanisms a higher rupture strength than that determined by the static surface tension indicates that more energy is being stored in the material under the stressed condition of flow than under the unstrained static condition.

Hence an apparatus was designed on these principles to investigate the characteristics of these special colloidal systems.

The apparatus, which was called a 'cohesimeter', is illustrated diagrammatically in figure 1 and a photograph is given in figure 2. Figures 3 and 4 illustrate the shapes of the jet below and above the critical velocity of rupture. Essentially, the cohesimeter consists of a diverging annulus, through which the fluid is forced under pressure from a reservoir. The annulus is formed between a cone-shaped needle, A, and a co-axial conical aperture with the same angle of divergence as the needle. The total angle of the cone is 20°, i.e. each side has a slope of 10°. The width of the annular opening can be varied by moving the needle up and down along its axis by means of a micrometer screw, B. The needle is kept in an exactly central position by means of three adjusting screws, C, set at intervals of 120° round the chamber above the orifice. A fine gauze on the support, D, serves to streamline the fluid before entry to the aperture, and also acts as a filter. E is a trigger valve, connected to an electrically started stop-watch, reading to 0·1 sec. so that the time for a given quantity to flow (and hence the velocity of flow) can be determined accurately. The capacity of the reservoir is about 300 ml., and the diameter of the large end of the diverging aperture was 0·200 in. (0·508 cm.). The smallest opening which gave a well-formed jet was one with a cross-sectional area (taken perpendicular to the direction of flow) of 0·0296 cm.^{2}. This was adopted as a standard opening. (The photograph shows the jet flowing whilst the trigger valve is closed. This was specially arranged for the photograph; normally the trigger valve fully controls the flow.) In using the apparatus the pressure at which the jet just shattered was determined by a 'bracketing' procedure, i.e. the pressure was alternately maintained just below and just above the critical value. Then the velocity of the jet at the critical pressure was determined by timing a quantity of the liquid through the jet nozzle. This was the critical velocity v and ρv^2 was called the rupture strength.

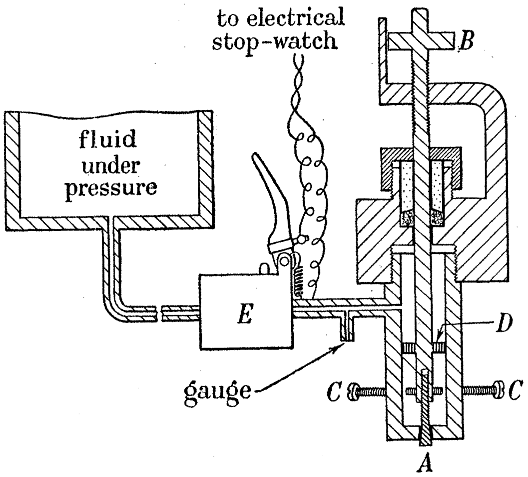


FIGURE 1. Sectional drawing of cohesimeter.

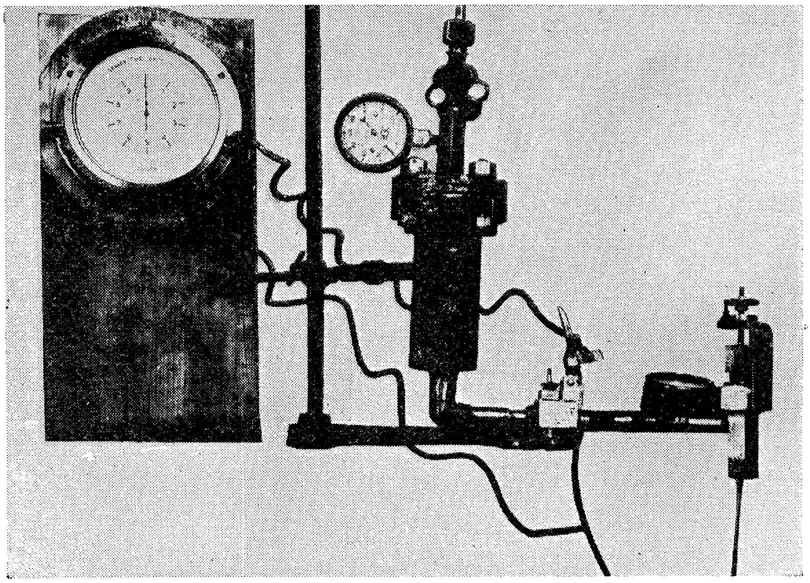


FIGURE 2. Photograph of cohesimeter.

Use of the apparatus

Before the apparatus could be used on the special systems under study, the following points had to be ascertained:

(1) that the rupture strengths of liquids were reproducible;

(2) that the rupture strength was not a function of other properties, e.g. the viscosity of the fluid, or (more fundamentally) was not a function of the Reynolds number *Re*.

By experimenting on both Newtonian and non-Newtonian fluids, it was found that the rupture strength could be reproduced independently of how many times the apparatus was dismantled and reassembled. A point of interest is that there are two types of jet, one smooth and round, the other irregular, with apparently plane surfaces intersecting in curved sides. The second type is not merely 'turbulent regime' jet, as it can be formed and maintained at will at low velocities. Only the first type was used to determine the critical velocity. The repeatability of the critical velocity was established before any further work was carried out.

To determine the influence of Reynolds number, viscosity, etc., experiments were made with the liquids tabulated in table 1 (see also figure 5).

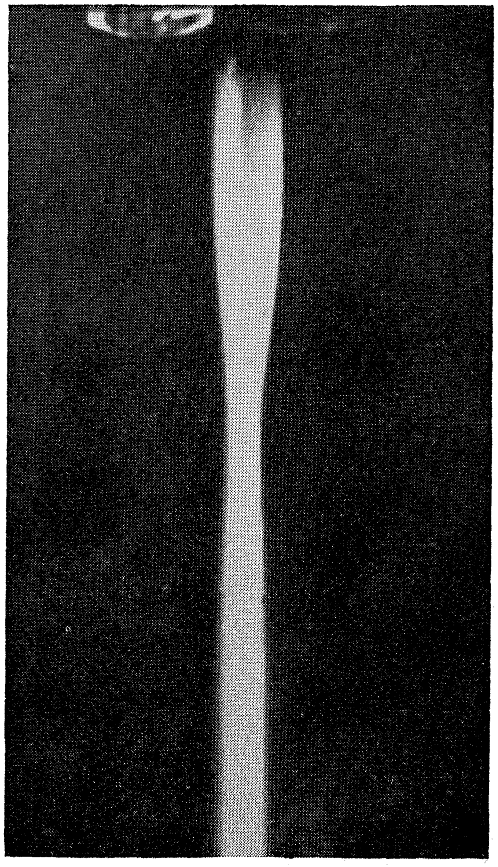


FIGURE 3. Appearance of jet below critical speed.

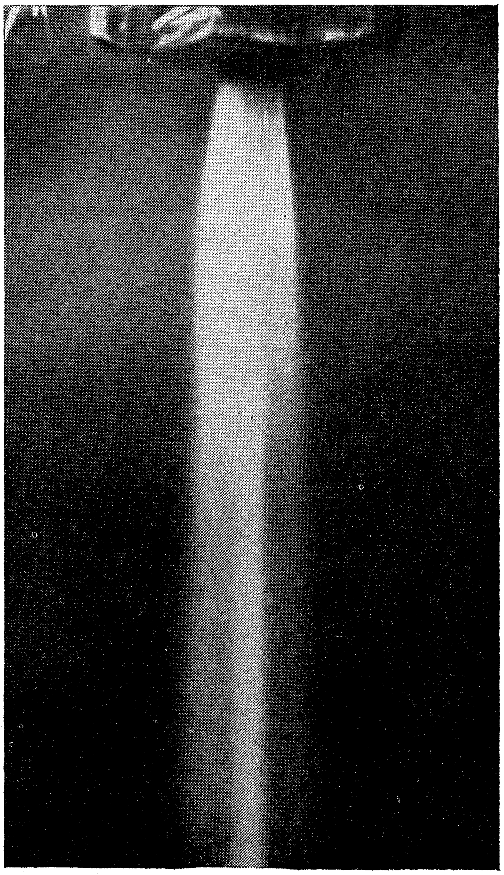


FIGURE 4. Appearance of jet above critical speed.

TABLE 1

liquid	critical velocity (cm./sec.)	rupture strength ($10^{-6}\rho\bar{v}^2$)	surface tension (dynes/cm.)	viscosity (*cP*)	Reynolds number *Re*
kerosine	1860	2·79	25	1·90	3160
gas oil	1830	2·90	27	2·55	2470
spindle oil	1830	2·87	28	7·33	860
glycerol in water	2330	6·41	68*	20·70	530
sucrose in water	2090	5·15	55*	5·73	1720

* Surface tension measured after use in apparatus, liquid contaminated.

The influence of viscosity was only on the coefficient of discharge of the apparatus. Thus kerosine, gas oil and spindle oil, with similar cohesive properties but different viscosities, gave similar values for rupture strengths.

The Reynolds number was calculated as the product of velocity by (density/viscosity) and 4 times the hydraulic mean depth of the conical nozzle. The break-up velocity occurs at values of *Re*, ranging from 530 to 3160, and so it is concluded that the critical velocity is independent of *Re* within the viscous regime. The critical velocity of water should be about 2·8 times that of kerosine; *Re* for kerosine was 3160 and water would give a value of 11,200 at the critical momentum. Hence it was anticipated that long before break-up owing to the instability of the system under cohesive properties sets in, break-up by turbulence should occur. Nevertheless, a divergent-convergent water jet was obtained up to a Reynolds number of 9520. Stability of the viscous regime up to this high value is probably brought about by the influence of the central rod. Although this breaking velocity is lower than that giving cohesional instability, it is in the right direction to emphasize the lack of influence of viscosity and Reynolds number on the critical velocity, provided that the regime is viscous.

Having established the validity of the assumptions on which the apparatus was built and the reproducibility and general technique of the apparatus, several solutions in organic liquids, of rubber, soaps, cellulose acetate and Perspex, were tested. Table 2 gives the results obtained under the standard conditions used in obtaining table 1.

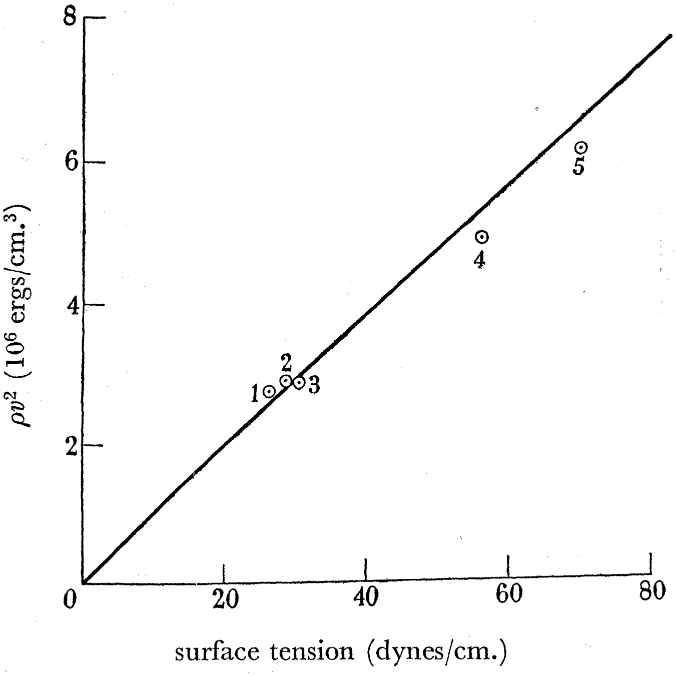
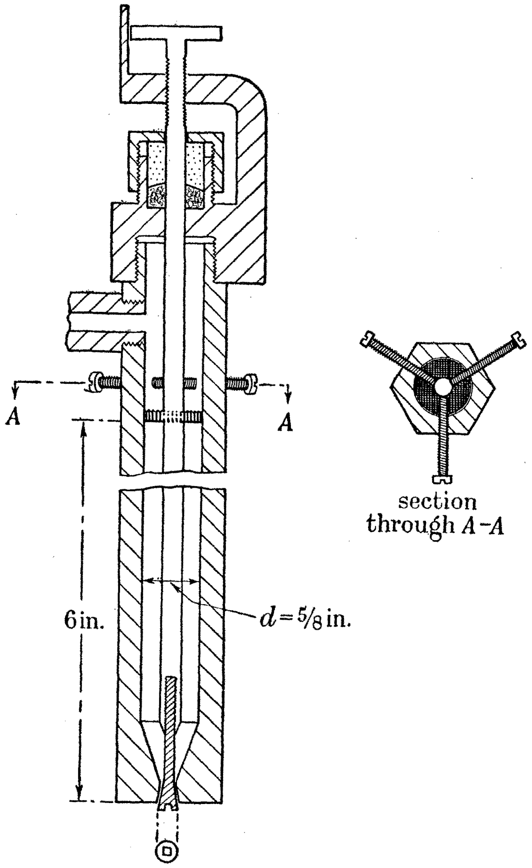


Figure 5. Calibration curve of cohesimeter. 1, kerosine; 2, gas oil; 3, spindle oil; 4, sugar solution in water; 5, glycerol solution in water.

Table 2 illustrates the very high rupture strength that these solutions possess compared with the simple liquids of table 1. These results were the first indication that straining the materials was producing peculiar conditions internally, because the static surface tensions of the liquids differed only a little from that of the liquids without the solutes.

It may be of interest to note here that a better design for the instrument would be one like that given in figure 6. However, a much simpler apparatus for measuring rupture strength was evolved and is given in figure 7. This apparatus was lent to Dr A. E. Clarke, and he obtained rupture strength figures for several liquids similar to those shown in table 2. The method of use of the apparatus was as follows:

A pressure reservoir, which was fed by a nitrogen cylinder, was attached through a quick-release valve to the top of the apparatus. The piston was placed at the top of the cylinder



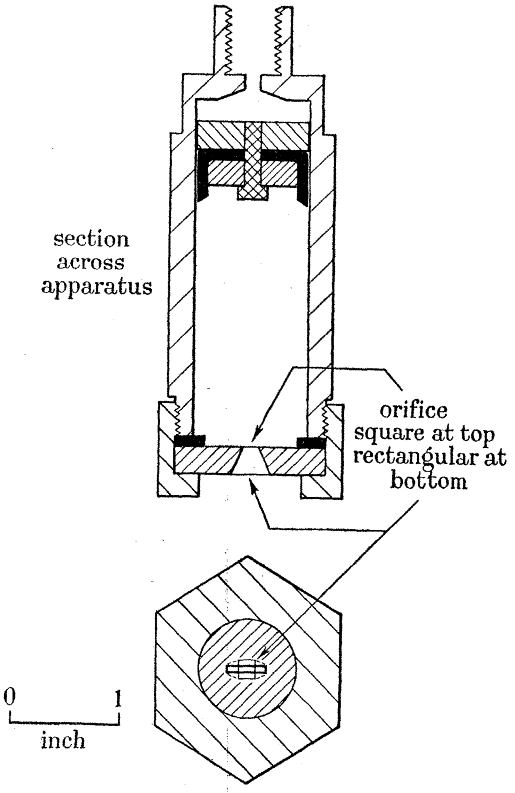


FIGURE 6. Improved design of cohesimeter. FIGURE 7. Miniature rupture strength apparatus.

TABLE 2

liquid no.	solutes	solvent	density	rupture strength (10^6 ergs/cm.^{3})
1	4·5 % aluminium stearate + 2·7 % mixed xylenols	pool petrol	0·780	7·62
2	6·0 % aluminium stearate + 3·6 % mixed xylenols		0·785	6·68
3	2·5 % rubber		0·759	14·6
4	2·0 % rubber	redistilled petrol	0·777	5·25
5	1·5 % rubber		0·737	5·39
6	4 % aluminium stearate + 4 % mixed xylenols	pool petrol	0·779	6·92
7	5 % aluminium stearate + 5 % mixed xylenols		0·781	6·90
8	6 % aluminium stearate + 6 % mixed xylenols		0·792	9·58
9	4 % Napalm*		0·760	9·48
10	5 % Napalm*		0·768	12·0
11	5 % Perspex	benzole	0·880	6·31
12	2·5 % Perspex		0·874	5·80
13	3·0 % cellulose acetate + 15·5 % cresol		0·913	11·8
14	2·5 % cellulose acetate + 15·5 % cresol		0·912	12·3
15	1·5 % cellulose acetate + 15·5 % cresol		0·910	9·97
16	12·5 % cellulose acetate	acetone	0·854	27·0
17	6 % aluminium laurate	pool petrol	0·763	6·23
18	5 % aluminium laurate		0·769	6·68
19	2·5 % aluminium laurate + 1 % Cellosolve		0·768	21·0
20	3 % aluminium laurate + 0·9 % Cellosolve + 0·3 % oleic acid		0·748	12·9

* 'Napalm' designates American soaps of aluminium and mixed acids.

which was then filled with the liquid under test. Then, having built up a known pressure in the reservoir, the valve was opened and the piston forced the liquid downwards through the orifice which was square (3 × 3 mm.) at the top and rectangular (9 × 1 mm.) at the bottom.

A sheet of liquid was thus formed which was being stretched along its length. The forces tending to stretch the sheet were provided by the kinetic energy of the sheet, which depended upon the applied pressure, while those forces which make up rupture strength acted in opposition. Thus, for a particular applied pressure, if the rupture strength were high then the amount of stretching of the sheet was low.

The liquid fell on to a horizontal plane, 1 m. below, where the length of spread was measured. The experiment was repeated for different values of applied pressure, and the length of spread was plotted against this pressure, giving the curves shown in figure 8. It is apparent that, with increasing applied pressure, a maximum length of spread, indicating the break-up of the sheet, was reached for each liquid. The minimum pressure to give this maximum spread and the maximum spread itself were used as measures of rupture strength. Thus a liquid having a small spread at a high pressure has a high rupture strength, while a large spread at a low pressure shows a low rupture strength. A summary of the results obtained is shown in table 3.

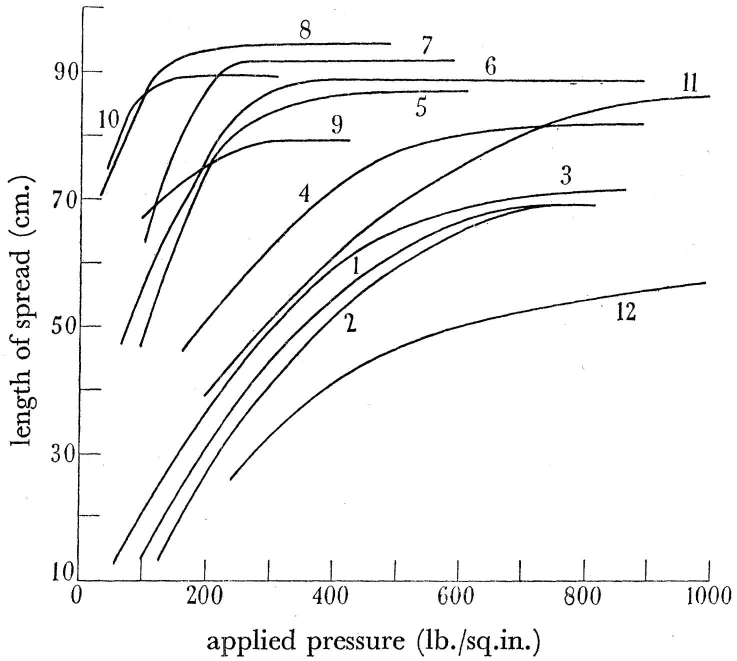


FIGURE 8. Spread of jets under varying pressures from miniature rupture strength apparatus.

With this apparatus it is seen that the degree of stretching these liquids can withstand is not the same for all but specific to each one.

Having been satisfied that stressing the material increases the free energy of the colloidal structure, we were interested in measuring the free energy and analyzing it into its two components, the internal energy and the entropy of the system. The apparatus described was not suitable for such purposes. Therefore other and simpler apparatus and technique were developed. These will be discussed next.

Table 3. Measurements with the miniature rupture strength apparatus

liquid	no. on graph	minimum pressure for maximum spread (lb./in.^{2})	maximum spread (cm.)
S.B.P. no. 1, 5 % aluminium laurate, 2·0 % Cellosolve	1, 2	700	68·5
S.B.P. no. 1, 4 % aluminium laurate, 1·6 % Cellosolve	3	750	71·5
S.B.P. no. 1, 3 % aluminium laurate, 1·2 % Cellosolve	4	750	82·0
S.B.P. no. 1, 2 % aluminium laurate, 0·8 % Cellosolve	5	400	86·5
S.B.P. no. 1, 5 % aluminium laurate, 2·0 % xylenols	6	350	88·5
S.B.P. no. 1, 4 % aluminium laurate, 1·6 % xylenols	7	250	91·5
S.B.P. no. 1, 3 % aluminium laurate, 1·2 % xylenols	8	200	93·5
S.B.P. no. 1, 5 % aluminium laurate, 0·5 % xylenols	9	250	78·0
S.B.P. no. 1, 6 % calcium naphthenate	10	150	89·0
L.A. 7	11	1000	86·0
A.B.X.	12	1000	58·0*

* At 1000 lb./in.^{2} pressure the spread was increasing at the rate of approximately 2 cm. per 100 lb./in.^{2} increase in pressure.

The internal energy and entropy changes on straining

Introduction

If there is no change in the specific volume of the material on straining in shear, then the free-energy increase is identical with Helmholtz's work function increase, ΔA, where A is the work function of the system. As all these materials are liquids, the change in the specific volume on shearing is negligible. Thus the free energy or the work function change can be expressed by the equation

$$\Delta A^T = \Delta E^T - T\Delta S^T,$$

where $\Delta A^T =$ the change in the Gibbs free energy (or Helmholtz's work function) at temperature T° K, due to straining; ΔE^T and $\Delta S^T =$ the corresponding changes in the internal energy and the entropy of the system at constant volume and the same temperature T° K.

Owing to the urgency of the work, it was not possible for a long time to evaluate the two components which go to make up ΔA^T. Therefore an analogy was sought and this was found in the behaviour of rubber in many respects. With rubber there is an increase in the free energy of the system on straining. It has always been assumed in the literature on rubber that ΔE^T was zero at constant volume. A paper by Elliott & Lipmann (1945) appeared to give theoretical proof to this point of view. Accordingly, we assumed for a long time that ΔE^T was zero and therefore that the increase in the free energy was entirely owing to the decrease in entropy on changing the mean length of the kinetic units comprising the colloidal structure. Thus the explanation we gave for the various behaviours of the systems was based on this assumption up to the latter part of 1946. However, in attempting to derive quantitatively certain parameters and formulae, it was always found impossible to fit this hypothesis to the observed phenomena with congruence at all points. Experiments were therefore performed in the end to determine whether the change in A^T was due to a single change in S^T or to changes in both E^T and S^T. These experiments have shown that the analogy with rubber was correct only in part: in both rubber and in solutions of rubber in benzene or of aluminium soap in hydrocarbons A^T increases with shear strain; whilst with rubber only S^T decreases, in solutions both E^T and S^T *increase*, giving a net increase in A^T. With this experimental observation, it became possible to correlate theory with observation.

The cohesimeter and the miniature rupture strength apparatus were not easily adaptable, nor could they be readily interpreted for the purpose of analyzing A^T. Therefore another form of apparatus was used.

It will be recalled that in 1942 it was observed that a stirrer rotating in these liquids will have a climbing layer of liquid on it continuously moving upward until centrifugal forces throw the liquid out. The explanation advanced on the basis of the present hypothesis is that at the line of contact between rotating stirrer and liquid there is an increase in the free energy of the system over that portion of the liquid which is attached to the stirrer and rotating with it in air as the latter portion of the liquid is relatively unstrained. Hence the liquid climbs the shaft of the stirrer to regions of low free energy. It was decided that if this explanation was true, then on putting a sleeve around the shaft and holding the sleeve stationary and off the bottom of the container, the liquid should move downwards. The liquid between the stirrer and the sleeve will be highly sheared, whereas outside the sleeve the liquid is unstrained; hence the liquid in the sleeve will be possessed of higher free energy and will move downwards and into the unstrained region. This prediction was confirmed experimentally. Hence, if the sleeve is short, the level of the liquid inside it will reach the bottom of the sleeve—and this was observed—but if the sleeve is sufficiently long then the level inside it will drop until the hydrostatic head (i.e. potential due to position) opposing flow equals the free-energy head producing this flow. This was also confirmed. An apparatus embodying this principle was built. However, as no figures were available for the best values for the diameter of the shaft, the annular width between shaft and sleeve, etc., it was decided to use a conical shaft in a cylindrical sleeve and choose by experiment the best position at which to maintain the level of the fluid inside the sleeve.

Figure 9 illustrates the apparatus. The aluminium shaft was gripped at the top by a chuck and rotated up to 1600 r.p.m. in ball bearings. Both inner and outer cylinders were made of glass; the liquid was in communication in both chambers through large holes and passages in the centring cork pieces and brass bushing. (In later forms of the apparatus the holes were enlarged and the bottom portion slightly modified to render easy flow of fluid between the two compartments.) The top of the apparatus was open to the atmosphere both inside and outside the glass cylinder. A hole was bored in the cork bottom of the apparatus, and a U-tube was inserted with one limb rising externally to the top level of the apparatus; more or less fluid could thus be admitted into the apparatus at will. The whole apparatus was immersed in a water-bath up to the level of the top cork centralizer.

To take observations the apparatus was partly filled with the liquid to be studied and brought up to temperature. On rotating the shaft at constant speed the level inside and outside the inner cylinder changed from equality. More fluid was admitted to the apparatus, or some sucked away, through the bottom, until the level inside the inner glass tube came to a standard mark, measured downward from the top of the conical shaft, say 15 cm., and the speed, temperature, centricity, etc., checked and maintained. When equilibrium was established, the difference in level between the inner and outer free surfaces was measured on a vertical scale and the other data recorded. On changing the speed or other variables, the level of the inner annulus was always brought to the same mark, so that the separation between the conical shaft and the cylinder was maintained constant. Of course, the surface here was not *level*, but the mean level of this surface was maintained at the standard mark. The theory of the apparatus was tested on Newtonian oils, and then the apparatus was used with the special liquids using the standard level and speed range which were found to give the most reproducible and steady results on the oils.

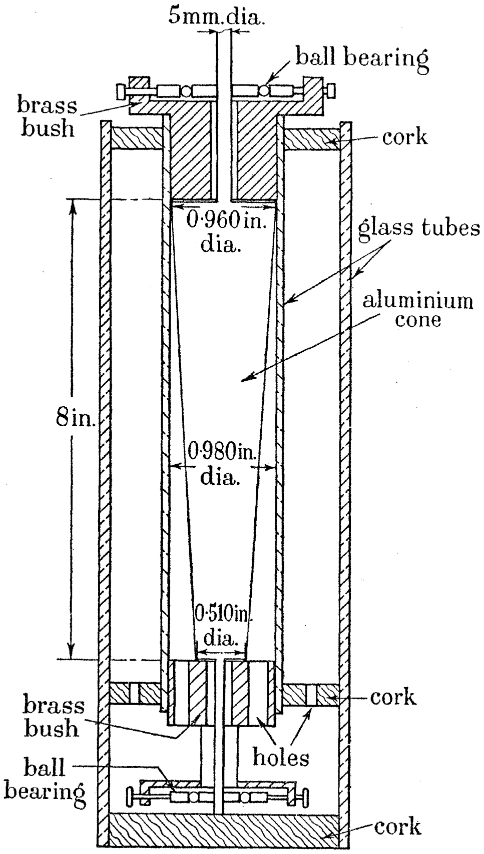


FIGURE 9. Sectional drawing of rotary apparatus for measurements of free energy increase with straining.

Theory of the apparatus

Consider the shaft rotating in a liquid and the liquid is in hydraulic contact with a stationary portion of itself. Let the suffix 'rot.' refer to the variables in the rotating region, and the suffix 'stat.' refer to those in the stationary portion. The energy of the particles at the rotating surface will vary with the distance, as v, the velocity of the particles at this surface, varies with the radial distance from the shaft. Therefore, a mean of the square of the velocity, $\overline{v^2}$, will be taken. Similarly, the height of the surface is not a constant and a mean height $\bar{Z}$, above a datum line, will be taken. Equating the energies of the system when equilibrium is established in this type of flow, we get

$$(E_{\text{stat.}}-T_{\text{stat.}}S_{\text{stat.}})+\bar{Z}_{\text{stat.}}+P_{\text{stat.}}=(E_{\text{rot}}-T_{\text{rot.}}S_{\text{rot.}})+\bar{Z}_{\text{rot.}}+P_{\text{rot.}}-\frac{1}{2}\frac{\overline{v^2_{\text{rot.}}}}{g}+H_f,$$

where E = internal energy head in cm. of liquid;
T = temperature, ° K;
S = entropy in cm. head/° K;
P = hydrostatic pressure head, cm.;
$\bar{Z}$ = mean potential energy head due to position in cm.;
$\overline{v^2}$ = mean of the square of the velocity, cm.^{2}/sec.^{2};
g = gravitational constant, cm./sec.^{2};
H_f = frictional head in cm. of liquid.

Working under isothermal conditions at T° K will be denoted by the index T. Thus as $P_{\text{stat.}} = P_{\text{rot.}}$

$$(E^T_{\text{rot.}} - E^T_{\text{stat.}}) - (T_{\text{rot.}}\, S^T_{\text{rot.}} - T_{\text{stat.}}\, S^T_{\text{stat.}}) = (\bar{Z}_{\text{stat.}} - \bar{Z}_{\text{rot.}}) + \left(\frac{1}{2}\frac{\overline{v^2_{\text{rot.}}}}{g} - H_f\right)$$

or

$$\Delta E^T - T\Delta S^T = -\Delta\bar{Z} + \left(\frac{1}{2}\frac{\overline{v^2_{\text{rot.}}}}{g} - H_f\right),$$

since

$$T_{\text{rot.}} = T_{\text{stat.}} = T.$$

As

$$\Delta E^T - T\Delta S^T = \Delta A^T,$$

where A = Helmholtz's work function (or Gibbs's free energy as the process is at constant volume) in cm. liquid, therefore

$$\Delta A^T = -\Delta\bar{Z} + \left(\frac{1}{2}\frac{\overline{v^2_{\text{rot.}}}}{g} - H_f\right).$$

To obtain ΔE^T and $T\Delta S^T$ from ΔA^T we can use

$$\Delta E^T = \Delta A^T - T\left[\frac{\partial(\Delta A)}{\partial^T}\right]^T_V$$

and

$$\Delta S^T = \left[\frac{\partial(\Delta A)}{\partial T}\right]^T_V,$$

where the suffix V represents the constant specific volume. Thus it is necessary to evaluate three quantities, $\bar{Z}$, $\overline{v^2}$ and H_f at different temperatures T in order that ΔA, ΔE and ΔS may be calculated. $\bar{Z}$ is measured directly, $\overline{v^2}$ is evaluated from the rate of rotation of the shaft, H_f will be discussed below.

To evaluate $\overline{v^2}$ consider the shaft rotating at Ω radians/sec., and suppose that the level of the rotating fluid cuts the shaft at a point h cm. from the top. Let the radius of the shaft at this point be a and the inside radius of the cylindrical glass sleeve be b cm. The radius b is 1·245 cm., and the value of a can be calculated from the dimensions of the shaft, thus $a = 0{\cdot}785$ cm. when $h = 15$ cm., and $a = 0{\cdot}945$ cm. when $h = 10$ cm.; the velocity v in cm./sec. at any point will vary from $v = \Omega a$ at the shaft to $v = 0$ at the sleeve.

Assuming viscous flow in a manner similar to that in a rotating cylinder viscometer of the Couette type $(v_{\text{rot.}})_r$ at point r cm. radial distance from the axis is given by

$$(v_{\text{rot.}})_r = \frac{\Omega a^2(b^2 - r^2)}{(b^2 - a^2)\, r}$$

and

$$(v_{\text{rot.}})^2_r = \frac{\Omega^2 a^4}{(b^2 - a^2)^2}\left(\frac{b^2 - r^2}{r}\right)^2 = K^2\left(\frac{b^2 - r^2}{r}\right)^2,$$

then
$$\overline{v^2_{\text{rot.}}} = \frac{2\pi \int_a^b r(v_{\text{rot.}})^2_r\,dr}{2\pi \int_a^b r\,dr}$$

$$= \frac{2K^2}{(b^2-a^2)}\left\{b^4\left[2{\cdot}303\log\left(\frac{b}{a}\right)-0{\cdot}75\right]+b^2a^2-\tfrac{1}{4}a^4\right\},$$

where
$$K^2 = \frac{\Omega^2 a^4}{(b^2-a^2)^2} = \frac{4\pi^2\,(\text{r.p.m.})^2\,a^4}{(3600)\,(b^2-a^2)^2}.$$

Then
$$\frac{\overline{v^2_{\text{rot.}}}}{2g} = \frac{1{\cdot}11\times 10^{-5}a^4}{(b^2-a^2)^3}\left[b^4\left(2{\cdot}303\log\left(\frac{b}{a}\right)-0{\cdot}75\right)+b^2a^2-\tfrac{1}{4}a^4\right]\text{r.p.m.}^2.$$

Two values for a were used, i.e. $a_{15} = 0{\cdot}785$ cm. and $a_{10} = 0{\cdot}945$ cm. Thus

$$\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}\right)_{15} = 8{\cdot}511\times 10^{-7}\,(\text{r.p.m.})^2$$

and
$$\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}\right)_{10} = 1{\cdot}354\times 10^{-6}\,(\text{r.p.m.})^2.$$

Use of the apparatus

It was seen that the free-energy change on shearing at temperature T was given by

$$\Delta A^T = -\Delta\overline{Z}+\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}-H_f\right).$$

Further, of the quantities involved, $\Delta\overline{Z}$ can be directly read on a scale. The quantity in brackets had to be evaluated. It was felt that a practical advantage would ensue if the quantities in the brackets could be reduced, in an empirical manner if necessary, into a single quantity. To investigate this possibility a series of tests were performed with Newtonian oils where $\Delta A^T = 0$ and accordingly

$$\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}-H_f\right) = \Delta\overline{Z}.$$

An attempt was therefore made for evaluating k in the following expressions:

$$H_f = \frac{\overline{v^2_{\text{rot.}}}}{2g} - \Delta\overline{Z} = \frac{\overline{v^2_{\text{rot.}}}}{2g}\,(1-k), \quad \text{i.e.} \quad k = \frac{\Delta\overline{Z}}{(\overline{v^2_{\text{rot.}}}/2g)};$$

thus
$$\Delta A^T = -\Delta\overline{Z}+\frac{\overline{v^2_{\text{rot.}}}}{2g}\,(1-1+k) = -\Delta\overline{Z}+k\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}\right).$$

Table 4 gives the results obtained. It will be noted that when $k = \dfrac{\Delta\overline{Z}}{(\overline{v^2_{\text{rot.}}}/2g)}$ was plotted against the quantity $[\Omega a\nu(b-a)]$, where ν is the kinematic viscosity, *cS.*, a family of curves was obtained converging to a single asymptotic line at $k = 0{\cdot}2$ for values of $[\Omega a\nu(b-a)]$ exceeding 800 (see figure 10). It should be stated that attempts to correlate k with the Reynolds number of the system proved unsuccessful. The expression $[\Omega a\nu(b-a)]$ is not dimensionless and has only the practical use of ensuring that the frictional head is a small easily calculated quantity.

TABLE 4

oil		viscosity ν	density ρ	a		$\Delta\bar{Z}$	$\dfrac{\bar{v}^2_{\text{rot.}}}{2g}$	$\dfrac{\Delta Z}{(\bar{v}^2_{\text{rot.}}/2g)}=k$	
no.	symbol	(*cS.*)	(g./cm.^{3})	(cm.)	r.p.m.	(cm.)	(cm.)		$\Omega av(b-a)$
1	△	1·464	0·900	0·785	800	0·31	0·62	0·500	45·0
					1000	0·37	0·85	0·435	56·2
					1200	0·55	1·22	0·450	67·2
					1400	0·65	1·65	0·394	78·5
					1500	0·75	1·92	0·392	84·0
2	×	2·12	0·910	0·785	800	0·27	0·62	0·435	65·0
					1000	0·30	0·85	0·352	81·2
					1200	0·35	1·22	0·288	97·5
					1400	0·40	1·65	0·243	112·0
					1500	0·43	1·92	0·224	122·0
2	⊙	2·12	0·910	0·945	800	0·37	0·87	0·424	50·5
					1000	0·50	1·36	0·368	63·0
					1200	0·70	1·95	0·359	75·6
					1400	0·90	2·65	0·339	88·5
					1500	1·00	3·05	0·326	94·5
3	⊡	26·0	0·945	0·945	800	0·30	0·87	0·345	620
					1000	0·35	1·36	0·256	770
					1200	0·42	1·95	0·215	928
					1400	0·59	2·65	0·222	1080
					1500	0·65	3·05	0·212	1160
4	⬭	4·80	—	0·945	800	0·33	0·87	0·380	114
					1000	0·40	1·36	0·294	142
					1200	0·53	1·95	0·272	172
					1400	0·65	2·65	0·245	200
					1500	0·80	3·05	0·262	214
5	⊕	13·90	0·924	0·945	1000	0·37	0·36	0·272	412
					1200	0·50	1·95	0·258	495
					1400	0·65	2·65	0·245	582
					1500	0·75	3·05	0·246	619

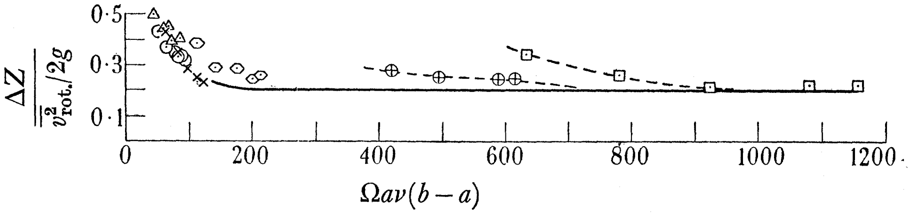


FIGURE 10. Correlational graph for the estimation of frictional losses with rotating apparatus of figure 9.

It will be noted that for Newtonian oils $\Delta\bar{Z}$ is always positive. Further, provided the level is chosen for $a = 0{\cdot}945$ cm. and speeds exceeding 800 r.p.m. are used, then for viscous oils $\Delta\bar{Z}$ may be represented by $0{\cdot}2\left(\dfrac{\bar{v}^2_{\text{rot.}}}{2g}\right)$ fairly accurately. For the solution of aluminium soap in hydrocarbon to be tested there is no *a priori* derivation of either $\bar{v}^2_{\text{rot.}}$ or of H_f. But by choosing a viscous solution (initial—i.e. Newtonian regime—viscosity at 20° C of order of 850 poises, i.e. nearly 10^5 *cS.*), standardizing at $a = 0{\cdot}945$ cm. and speeds in excess of 800 r.p.m., it was reasonable to assume that similar frictional losses would occur. As this is only of the nature of a correction, it was deemed that differences in the frictional losses between oils and the aluminium soap solution would only introduce small quantities of second order in the final results. Thus a solution of about 7 % of aluminium stearate (weight soap/vol. solvent) in petrol peptized by mixed xylenols was subjected to the test. The values of $\Delta\bar{Z}$ were always negative as expected. Thus ΔA^T was always positive, since

$$\Delta A^T = -\Delta\bar{Z} + k\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}\right) = -\Delta\bar{Z} + 0\cdot 2\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}\right)$$

for the conditions of the apparatus. Table 5 gives the results.

TABLE 5

temp. (°C)	...	8·0			20·0			30·0	
r.p.m.	$\Delta\bar{Z}$ (cm.)	$0\cdot 2\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}\right)$ (cm.)	$\Delta A^{281\cdot 1}$ (cm.)	$\Delta\bar{Z}$ (cm.)	$0\cdot 2\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}\right)$ (cm.)	$\Delta A^{293\cdot 1}$ (cm.)	$\Delta\bar{Z}$ (cm.)	$0\cdot 2\left(\frac{\overline{v^2_{\text{rot.}}}}{2g}\right)$ (cm.)	$\Delta A^{303\cdot 1}$ (cm.)
1000	−5·9	0·17	6·1	−4·7	0·17	4·9	−2·6	0·17	2·8
1200	−6·2	0·24	6·4	−5·4	0·24	5·6	−3·0	0·24	3·2

Graphical differentiation of ΔA^T with temperature was performed and the results are shown in table 6.

TABLE 6

r.p.m.	$\left[\frac{\partial(\Delta A)}{\partial T}\right]^{281\cdot 1}$	$\Delta E^{281\cdot 1}$ (cm.)	$\Delta S^{281\cdot 1}$	$\left[\frac{T\Delta S}{\Delta E}\right]^{281\cdot 1}$
1000	−0·075	+27·2	+0·075	0·78
1200	−0·075	+27·5	+0·075	0·78
average	—	—	—	0·78
r.p.m.	$\left[\frac{\partial(\Delta A)}{\partial T}\right]^{293\cdot 1}$	$\Delta E^{293\cdot 1}$ (cm.)	$\Delta S^{293\cdot 1}$	$\left[\frac{T\Delta S}{\Delta E}\right]^{293\cdot 1}$
1000	−0·15	+48·8	+0·15	0·90
1200	−0·10	+34·9	+0·10	0·84
average	—	—	—	0·87
r.p.m.	$\left[\frac{\partial(\Delta A)}{\partial T}\right]^{303\cdot 1}$	$\Delta E^{303\cdot 1}$ (cm.)	$\Delta S^{303\cdot 1}$	$\left[\frac{T\Delta S}{\Delta E}\right]^{303\cdot 1}$
1000	−0·28	+ 87·7	+0·28	0·97
1200	−0·48	+148·4	+0·48	0·98
average	—	—	—	0·98

Discussion

Before moving to the next series of experiments it would be well to summarize the observed and derived results. It was observed in these experiments with the rotating shaft that there is a fundamental difference in behaviour between Newtonian liquids and liquids composed of solutions of aluminium soap in hydrocarbons. With Newtonian liquids, the behaviour was in accord with the ordinary hydrodynamical theory of centrifugal pumps; the rotating portion of the liquid occupied a higher positional level than the stationary portion outside the sleeve. As the frictional head increased, the increase in height of the rotating liquid was less; it was never zero, but always positive. With the special solutions under study the rotating liquid was at a *lower* level than the stationary portion of the liquid. The pumping action was reversed and fluid moved from the rotating portion into the stationary portion.

These were the observed factors. The derived quantities were ΔA^T, ΔE^T and ΔS^T. It was seen that the free energy of the system A^T increased on straining the liquid. This would explain the motion of the liquid from the rotating to the stationary compartments. Further, it was found that both E^T and S^T increased, but $\frac{T\Delta S^T}{\Delta E^T}$ was a constant ratio at any one temperature for two rates of revolutions of the shaft. To check the constancy of this ratio at constant temperature, other preliminary experiments which were performed previously to those reported above (but which were not confirmed by several repetitions as were those in table 6) were analyzed, and it was found that this ratio of $\frac{T\Delta S^T}{\Delta E^T}$ was approximately constant and independent of the rate of revolution of the shaft.

Thus it appears that when the colloidal system is sheared, a certain amount of energy ΔE^T is imparted to and stored in the system as a recoverable energy. At the same time a certain portion of this energy equal to $T\Delta S^T$ is lost, i.e. becomes non-recoverable, and this portion is a constant fraction, say f, of ΔE^T, where

$$f = \frac{T\Delta S^T}{\Delta E^T}.$$

These remarks imply no mechanisms whereby the energy is stored or lost. The simplest assumptions to make regarding the mechanism appear to be the following: The colloidal structure appears to be due to weak bonds between the aluminium soaps and between these and the peptizers. There are several possible points on the aluminium soap whereon a weak bond may be localized. All the soaps tested had, on average, two acid radicals and one hydroxyl radical. Thus on taking a molecule of soap out of the structure one or more bonds of varying strengths would be broken. Energy would be required for this process. However, not the full energy is required because of the possibilities that: (i) the process of shearing may break units larger than one soap molecule, and thus many of these bonds will be satisfied within the fragment leaving only a fraction of the full value of the bonds unsatisfied per soap molecule; (ii) even if the structure were broken into single molecules the weak bonds would be able to satisfy each other by bending towards each other and only the energy due to strain would be necessary. In either event happening an energy increment will be stored in the fragments and the mean value of this increment per cm.^{3} of the strained solution is ΔE^T. Thus ΔE^T represents the energy stored in the solution on straining and is available originally as these broken fragments can travel against pressure gradients towards other fragments to give up their energy, or owing to their abundance in the sheared portion relative to their paucity in the unsheared portion, they tend to move towards the unsheared portion and set up a species of osmotic pressure.

Simultaneously with these events, there are entropy changes. Each fragment or molecule so freed from the colloidal structure gains in degrees of freedom in which to orientate itself or move. Thus the entropy of the system increases. Due to this increase in degrees of freedom many of these fragments will reunite locally with each other, thus in effect decreasing the total free energy available for doing work. This loss in recoverable energy is represented by $T\Delta S^T$. The net result of the simultaneous events is a residual free energy ΔA^T. As the temperature increases the loss of energy by reunion of fragments increases, i.e. $\frac{T\Delta S^T}{\Delta E^T}$ increases.

Apparently at 32° C for the solution tested, every fragment broken finds, on an average, an outlet for its energy and loses it 'immediately'. Thus, above 32° C there should be purely viscous loss of energy on continuously shearing the material.

Ever since Maxwell invented a model of elastic and viscous elements to represent liquids, several workers have followed his lead—adding to and elaborating the models by putting several elements in series and parallel. It appears, therefore, from this work that ΔE^T represents the elastic energy and $T\Delta S^T$ the viscous energy loss. It should be noted, however, that it is not a matter of 'elements' in series and parallel but it is simultaneous *processes* which the structure undergoes that gives these liquids their peculiarities. Whilst mathematically the behaviour of the liquid may be adequately represented by models of elastic springs and viscous dashpots, it is believed that a physical insight can be obtained into the structure of these materials more readily and certainly by studying it as a whole structure being broken down under shear and being rebuilt spontaneously and by thus studying the processes themselves.

Having determined ΔE^T and $T\Delta S^T$ it should be interesting to correlate the thermodynamics of the shearing of these liquids with the energy input and hydrodynamics of the experiments. This will be treated next.

Correlating the free energy with the mechanical shearing of the system

Introduction

Consider 1 cm.^{3} of a solution of aluminium soap or rubber in benzene being uniformly sheared throughout at a rate equal to $\dot{\sigma}$, where σ represents the shear and $\dot{\sigma}$ the time rate of shearing. The colloidal structure before shearing will be assumed to be in its whole stable state. At the end of 1 sec., the energy imparted to the cm.^{3} considered will be equal to $(F\dot{\sigma})$, where F is the shearing stress operating corresponding to $\dot{\sigma}$. Thus some of the structure will be broken up. It was seen that some of the fragments will be reunited, thus the energy $(F\dot{\sigma})$ input will go into a portion which is dissipated and a portion which is stored, which will be called ϕ. With time ϕ will increase until it becomes large. When this happens the system becomes unstable and fragments will therefore tend to move into regions where the energy input per second per unit volume $(F\dot{\sigma})$ is smaller than in the cm.^{3} under observation. Secondary flow will take place. Thus ϕ will be stabilized at a value equal to ΔA^T by secondary flow. It follows then that ΔA^T will be affected by two parameters:

(1) the energy input $(F\dot{\sigma})$ per unit volume per second, and

(2) the energy dissipation by flow down the spatial gradient of $(F\dot{\sigma})$ to regions of low-energy input.

Thus, a first approximation to correlating ΔA^T with the hydrodynamical parameter is that it should increase with $(F\dot{\sigma})$. Further, F is a single-valued function of $\dot{\sigma}$ which can be given very nearly by $F=\mu_A\dot{\sigma}$, where $\mu_A=$ apparent viscosity and is approximately equal to $B\dot{\sigma}^{-c}$, where B and c are constants. Therefore ΔA^T should increase with $\Delta(\dot{\sigma}^{2-c})$ or with $\Delta(\dot{\sigma}^d)$, where $d=2-c$, a constant. (Note that the *difference* in $\dot{\sigma}$ is significant in these secondary flow phenomena and not $\dot{\sigma}$.) In the experiments with the rotating shaft $\Delta\dot{\sigma}$ is proportional to the rate of revolution, r.p.m., under standard conditions of radii, separation, etc. It follows then that ΔA^T should increase with (r.p.m.)^d or a plot of log (ΔA^T) against log (r.p.m.) should give straight lines (only approximately as c is not truly constant) with a slope of d. This slope should be capable of correlation with the viscosity rate of shear curve for the same fluid, in that $d = 2-c$. A series of measurements were therefore made varying the rate of rotating the shaft, the position of the rotating level and the temperature and these simple predictions were confirmed. This apparatus, however, suffers from certain disadvantages for the purpose of the present correlation. At the free level, the climbing liquid rotates at the same speed as the shaft and interferes with the remaining liquid. Also, as will be seen in the derivation in the theoretical section below, certain distances are required for the correlation and are ambiguous in this apparatus.

For the purposes of correlating ΔA^T with the hydrodynamical parameters of the experiment, certain experiments performed with a rotating cylindrical container having a stationary disk inside it are of value, as here there is no free liquid/air/solid line of intersection. Dr K. Weissenberg discovered that when a disk was maintained in a stationary horizontal position parallel to, and within a short distance from, the flat bottom of a rotating cylindrical container, the space being filled with a solution of aluminium stearate in hydrocarbon, a vertical force acted on the stationary disk. In the Department of Chemical Engineering of the University of Birmingham it was discovered that holes drilled in the stationary disk and connected to manometric tubes showed that the pressure on the stationary disk was not a maximum at the rim where the rate of shear was a maximum but increased from zero at the rim to a maximum at the centre of the disk—the 'pressure' so measured was the excess in pressure over the free surface of the liquid in the rotating beaker. The following solutions showed this peculiar pressure effect: solutions of aluminium stearate in hydrocarbon peptized with xylenols, with Cellosolve, or with 'gold size', of aluminium laurate in petrol with oleic acid and xylenols, of calcium naphthenate in petrol, of rubber in petrol, of Perspex in benzol and of glue in water. The following did *not* show the phenomenon: water, lubricating oils, bentonite in water and aqueous solutions of starch and of gelatine. Indefinite results were obtained with cellulose acetate in acetone, and in benzol peptized with cresol, with corn-starch in water and with 'smalts' in water. All the liquids that showed the pressure phenomenon also exhibited secondary flow from the rim of the stationary disk to the centre, both above and below the disk. Although Dr Weissenberg propounded a theory based on the tensor analysis of continua under stress to explain the pressure under the disk, we felt that the hypothesis we developed with the cohesimeter based on increase of free energy of the colloidal structure explained the behaviour of the fluid under the disk and connected it with the other phenomena of secondary flow which we observed previously. Hence our results and hypothesis were communicated to Dr Weissenberg and his colleagues and the connexions of the peculiar pressure phenomena with secondary flow and rod-climbing pointed out.

Theory of the apparatus

Consider a horizontal flat disk being maintained stationary and parallel to a rotating disk h cm. apart, the speed of rotation of the disk being Ω radians/sec. The same analysis as was used for the rotating shaft may be employed here. Taking two points on the disk with radial distances r_1 and r_2, and using the suffixes 1 and 2 for all other corresponding variables,

$$E_1 - TS_1 + Z_1 + P_1 - \frac{1}{2}\frac{\Omega_1^2 r_1^2}{g} + H_{f1} = E_2 - TS_2 + Z_2 + P_2 - \frac{1}{2}\frac{\Omega_2^2 r_2^2}{g} + H_{f2},$$

and all terms are in cm. liquid. At the face of the stationary disk $\Omega_1 = \Omega_2 = 0$, and $Z_1 = Z_2$. Therefore

$$(E_2 - E_1) - T(S_2 - S_1) = (P_1 - P_2) + (H_{f1} - H_{f2})$$

or

$$\Delta E - T\Delta S = \Delta A = -\Delta P + \Delta H_f.$$

With Newtonian liquids and certain non-Newtonian systems the equation is found to be equal to zero. However, with the systems under study, it is found that if ΔH_f is neglected then ΔA is a positive quantity as ΔP is negative. However, it was found with the rotating cylinder experiments that

$$H_f = \frac{\Delta \overline{v^2}}{2g}(1-k) = \frac{\Delta \overline{v^2}}{2g} k_1$$

and also

$$\Delta Z = k\left(\frac{\Delta \overline{v^2}}{2g}\right),$$

where $\overline{v^2}$ is the mean square velocity across the fluid at the points considered. Here it was assumed that similarly, if in those experiments ΔZ were made zero by superimposing a pressure differential ΔP, then $\Delta Z = \Delta P$ and

$$\Delta H_f = k_2 \Delta P$$

or

$$\Delta A = -\Delta P(1-k_2) = -k_3 \Delta P,$$

where k_1, k_2 and k_3 are constants of proportionality between the terms of the equations. Thus the negative of the difference in pressures at the disk face may be taken to represent the free-energy difference between the two points.

To correlate ΔA or $(-\Delta P)$ with the hydrodynamical parameter of the system consider what happens at the two points. For simplifying the analysis let $r_1 = 0$, i.e. the centre of the stationary disk. Then for another point radial distance r from the centre let there be shearing at the rate $\dot{\sigma}$ with corresponding stress F dynes/sq.cm. The energy input in ergs/cm.^{3}/sec. at the two points will be zero and $(F\dot{\sigma})$ respectively, i.e.

$$(\text{energy-input/cm.}^3\text{/sec.}) = \Delta(F\dot{\sigma}) = (F\dot{\sigma}).$$

Let each fragment of the structure require, on average, ϵ ergs to break. Hence a number n_1 of fragments per cm.^{3} will break per second at point r cm. radial distance where

$$n_1 \propto \frac{\Delta(F\dot{\sigma})}{\epsilon} \propto \frac{(F\dot{\sigma})}{\epsilon}$$

and

$$n_1 \epsilon \propto \Delta E \propto (F\dot{\sigma}).$$

[A proportionality is used and not an equation because $(F\dot{\sigma})$ is used not only in breaking up the colloidal structure but also to provide the energy of activation for the molecules of the solvent and induce ordinary viscous flow. This latter requirement must be small for solutions having a very high relative viscosity, as is the case with the solutions under discussion. Thus an equation could be used for these proportionalities with only small errors, i.e. $n_1 \epsilon = (F\dot{\sigma})$.] A certain number n_2 of these will relax locally by reunion. It is postulated that

$$\frac{n_2}{n_1} = \frac{T\Delta S}{\Delta E}.$$

Thus, there are produced every second $n_3 = n_1 - n_2$ fragments per unit volume containing excess energy to the total amount of $n_3 \epsilon = \Delta A$. These fragments possess excess energy, and will migrate to the regions of lower shear energy by diffusion where they have greater chances of relaxation by union amongst themselves, union with peptizers, or with loose points on the colloidal structure. However, some of them relax on the way through these several mechanisms. Thus let one mode of relaxation be through two fragments uniting in their travel through the distance Δr. The net effective number n_4 reaching the region of low shear energy will be reasonably proportional to $n_3/\Delta r$. Another mode would be union of the fragment with a loose point on the structure with further decrease in n_4, i.e. n_5 becomes proportional to $n_3/\Delta r^2$, and in general if there are n ways in which n_3 decreases by relaxation in its travel along a distance Δr, then the survivors n_n will be proportional to $n_3/\Delta r^n$. Thus the act of shearing at point r cm. from the centre results in pumping n_3/r^n fragments into the centre per second. These are free fragments and they will set up an osmotic pressure at the centre which is in excess to the pressure at point r, the surfaces of equal $\dot{\sigma}$ acting as semipermeable membranes. Taking the pressure at the rim as zero, the pressure at point r will be P_r and at the centre P_0. The excess pressure $(P_0 - P_r)$ will, therefore, be proportional to $n_3/\Delta r^n$ or n_3/r^n as $\Delta r = r$. Hence

$$(P_0 - P_r) \propto \frac{n_3}{r^n}$$

$$\propto \frac{n_1 - n_2}{r^n}$$

$$\propto n_1\left(1 - \frac{T\Delta S}{\Delta E}\right)\Big/ r^n$$

$$\propto F\dot{\sigma}(1-f)/r^n,$$

where f is constant at constant temperature. Therefore

$$(P_0 - P_r) \propto \frac{(F\dot{\sigma})}{r^n}.$$

However, F is a single-valued function of $(\dot{\sigma})$ and can be approximated to for these materials by $F = B\dot{\sigma}^{(1-c)}$, where B and c are constants. Thus for the solution of aluminium stearate in petrol which was tested, experiments with a capillary viscometer have established that the apparent viscosity $(F/\dot{\sigma})$ at different values of $\dot{\sigma}$ was at first constant, then above $\dot{\sigma}$ of the order of unity it began to decrease, reaching another approximately constant value at very high values of $\dot{\sigma}$. Over the major portion of the curve of $(F/\dot{\sigma})$ against $\dot{\sigma}$ an approximation was possible as follows:

$$\frac{F}{\dot{\sigma}} = B\dot{\sigma}^{-0\cdot 6},$$

i.e. the log of the apparent viscosity gave a nearly straight line with a slope of $(-0\cdot 6)$ when plotted against log $\dot{\sigma}$. Hence

$$(P_0 - P_r) \propto \frac{\dot{\sigma}^{2-0\cdot 6}}{r^n} \propto \frac{\dot{\sigma}^{1\cdot 4}}{r^n},$$

as the particular case of the general formula

$$\Delta(P_r) \propto \frac{\Delta(F_r \dot{\sigma}_r)}{\Delta(r)^n}.$$

Thus in this derivation it is possible to derive the variation of the pressure at the disk face with quantities measurable by independent means except for the variable n.

Use of the apparatus

There are several points in the derivation of this formula which can be used as a critical check for the whole theory.

(1) P_0 and P_r are found here to be isotropic pressures and are not affected by the direction in which they are measured. Experiments were therefore performed with the disks shown in figure 11.

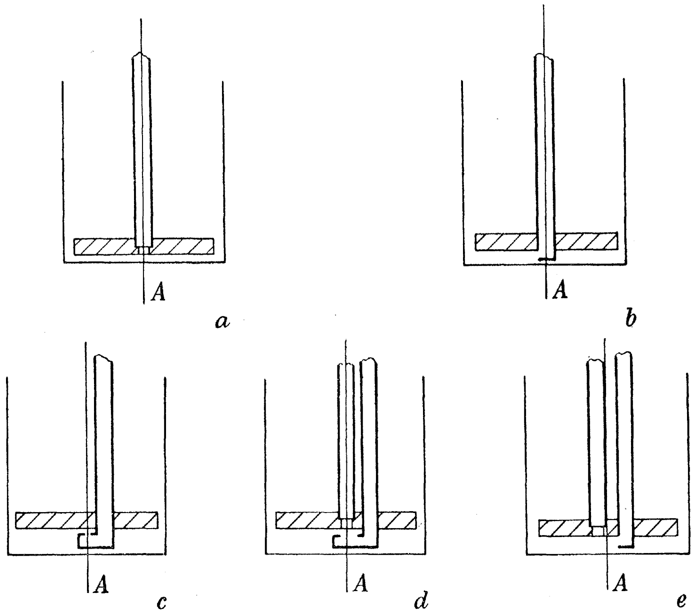


FIGURE 11. Various dispositions of manometric tubes for measuring the pressure in different directions in the rotating beaker apparatus. A is the axis of rotation of the beaker.

It was found that for the same conditions of radial distance of the holes and separation of disk from beaker the pressures measured in the solutions were independent of the direction of measurement. The pressures were therefore as envisaged—isotropic pressures.

(2) The theory is based on the hypothesis that the pressure generated is due to the *difference* in the shear-energy input at two points and not to the mere fact that there is shear. Thus if a surface has uniform shear on it there should be no excess pressure generated at any point compared with any other. This can be tested in several ways: (*a*) In a Couette-type viscometer the inner static cylinder when *totally immersed* experiences uniform shear at all points sufficiently removed from the edges. Further, for small separations the shear is almost uniform in the strained fluid. A hole was therefore drilled in the inner cylinder of such an apparatus and the pressure tested as in *a* of figure 12. No pressure was generated.* (*b*) When an inner double cone was substituted as in figure 12*b*, thus varying the rate of shear at the surface, the excess pressure phenomenon was observed. (*c*) A condition of uniform shear can also be produced on the conical face of a stator, as in figure 12*c*, provided that the cone

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* There is an apparent paradox here: the liquid inside the manometric chamber is stationary and, on the present hypothesis, it should act as a sink for the broken fragments of the colloidal structure and show a pressure head. However, the head here is compared with the level of the liquid in the beaker which has very low rates of shear throughout and is therefore also a sink. In other words fragments would concentrate both in the manometer chamber and the free volume above the cylinder. The net result is a *small* pressure after a long time, which in fact was observed in some experiments.

touches the rotating beaker at its centre and is symmetrically placed as shown. Again, a negative result at all speeds should prove that the derivation was correct. Actually, it is very difficult to produce the ideal conditions, required by this experiment, of coincidence between the centre of the beaker and the apex of the cone and of the axes of the cone and beaker. If such coincidences take place, then at any point radial distance r from the axis located on the stationary cone with half apex angle α, for a beaker rotating with Ω radians/sec.

$$h = r\tan(90^\circ - \alpha)$$

and for large angles α

$$\dot{\sigma}_r = \left(\frac{dv}{dh}\right)_r = \frac{\Omega r}{r\tan(90^\circ - \alpha)} = \text{constant}.$$

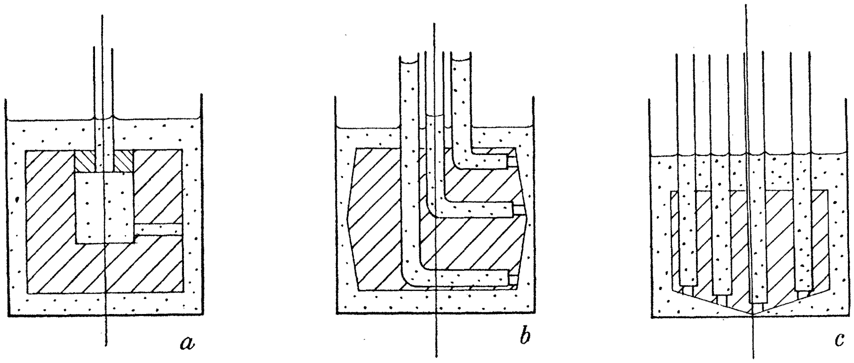

FIGURE 12. Demonstrating the necessity of variable rates of shear at the surface for the rise of pressure effect.

Thus $\dot{\sigma}_r$ is independent of r. However, let a small accidental displacement in the vertical direction amounting to δ take place between apex of cone and bottom of beaker, then

$$\dot{\sigma}_r = \left(\frac{dv}{dh}\right)_r = \frac{\Omega r}{\delta + r\tan(90^\circ - \alpha)} = \frac{\Omega}{\dot{\sigma}/r + \tan(90^\circ - \alpha)}.$$

Thus $\dot{\sigma}$ increases slightly with radius and small excess pressures should be noted near the centre. Since such pressures tend to increase δ further, the system is unstable at coincidence. Accordingly, in the experiments performed, three holes were drilled at equal distance from the centre and with 120° angular displacements and manometric tubes were attached. These were used to centralize and level the apparatus, as they read the same value of pressure when perfect symmetry is attained around the axis. It was found that only small equal heads were generated in the central and the three 120° tubes. By imparting small displacements between the apex of the cone and the bottom of the cylinder or by slightly tilting the cone very low excess pressures were observed. It appears that in the limit when centralization and coincidence of the axes and of the apex with the flat bottom is reached the pressures generated are, as in the case of the concentric cylinders, negligibly different from zero (see footnote to p. 58, however).

(3) In deriving the formula only n is an arbitrary constant. As this constant affects only r, then the variation of the pressure with the angular speed and the displacement of the flat surfaces should be obtainable from independent experiments. Thus, for two flat disks at a *small* distance h apart and one of the disks rotating with Ω radians/sec., then

$$\dot{\sigma}_r = \frac{\Omega r}{h}.$$

Hence $$(P_0-P_r) \propto \frac{\dot{\sigma}^{2-c}}{r^n} \propto \left(\frac{\Omega}{h}\right)^{2-c} r^{2-c-n}.$$

For the liquid under test c was measured from capillary viscometry to be 0·6 to 0·7. Hence

$$(P_0-P_r) \propto \left(\frac{\Omega}{h}\right)^{1\cdot 4} r^{1\cdot 4-n}.$$

The index 1·4 is not exact and 1·3 is probably equally valid. Thus it should be possible to correlate (P_0-P_r) with the rate of rotation of the beaker and the distance of separation directly, so long as the rotation is not too high to affect the value of c and h is not too large to render the simple formula $\dot{\sigma}_r = \Omega r/h$ inapplicable.

The value of P_0 is not measurable. The flow inwards at the stationary surface reverses near the centre and changes to an outward flow along the rotating surface. Thus the conditions assumed in the derivation are not realizable in practice at the centre. However, P_0 must be assumed as a hypothetical pressure that would have been realized if secondary flow did not interfere with the experimental conditions—for example, if the gap between the disks were made extremely narrow. Under any one set of constant experimental conditions P_0 would be constant and

$$P_r = P_0 - K\left(\frac{\Omega}{h}\right)^{1\cdot 4} r^{1\cdot 4-n},$$

where K = constant. Hence, a plot of $|P_r|$ against $|(\Omega/h)^{1\cdot 4} r^{1\cdot 4-n}|$ should give a straight line, if the analysis and interpretation of the phenomena observed are correct.

Experiments with this end in view were performed. The beaker used was of aluminium with a flat bottom, and the stationary disk was of steel, to which glass tubes were cemented with plaster of Paris. The following procedure was used to obtain parallelism between the disk and the beaker bottom. The disk was allowed to rest on the beaker bottom under its own weight, and clamps were fitted to the central tubes, care being taken not to disturb the position of the disk. The clamps were then loosened slightly, the disk and tubes were slid vertically upwards through the clamps to the required position and the clamps were tightened. The vertical movement, i.e. the clearance between disk and beaker bottom, was measured with a Brinell microscope. The speed of rotation of the beaker was measured by counting the number of revolutions in a given time. Precautions were taken to minimize evaporation of petrol from the solution, but since this could not be prevented entirely a fresh sample of solution was used each day, the samples being taken from a 40-gallon drum.

Despite these precautions, the accuracy of the experiments is poor owing to the following causes:

(1) As was shown in the previous qualitative experiments, the shape of the gap has a pronounced effect on the position of maximum pressure and the shape of the pressure effect. Owing to the vibrations, it was almost impossible to ensure with this simple apparatus that the disk remains exactly parallel to the beaker bottom, and differences of a small fraction of a millimetre may have a considerable effect on the results obtained.

(2) Owing to voltage fluctuations, the speed of the electric motor driving the turn-table varied slightly. Although the mean speed was kept constant by repeated checkings, it is not known that the pressure effect obtained for a varying speed of rotation will be the same as that obtaining at a constant speed of rotation equal to the mean of the varying speed.

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Before measuring the heights of the solution in the tubes, the system was left for at least 3 hr., in order to ensure that a true equilibrium had been reached. In this connexion an interesting phenomenon was observed. To cut down the experimental time, the solution was sucked up the tubes to the approximate equilibrium position. The solution could be sucked to a certain height, H, at which the level was falling, i.e. the head H is greater than the pressure at the disk. However, when left for a sufficient time, the level would stop falling, begin to rise and eventually attain a position higher than H. Thus it appears that the pressure generated at the disk increases gradually with time to a maximum value. Whilst this may possibly be owing to the effect of position noted above, the disk changing its position slightly in a horizontal direction till the position for maximum rise is attained, it is nevertheless in line with the mechanism outlined above where fragments of the colloidal structure tend to accumulate with time at the sinks of shear-energy input. That there is no vertical movement can be checked by observations with the Brinell microscope. This phenomenon is not due to concentration changes in the gel caused by evaporation, since it can be observed with the same sample of gel on two consecutive days. Further, very special precautions were taken to avoid vaporization and ensure uniformity of material in obtaining table 8, which gives the equilibrium values obtained.

TABLE 8

clearance h (mm.)	P_r = height of liquid in cm., above free surface of liquid in beaker at radius in cm. of					speed (r.p.m.)
	0	1·0	1·4	1·85	2·35	
4·4	13·2	6·8	1·2	—	—	118
3·7	17·9	8·0	1·8	1·4	—	
1·5	24·5	18·3	12·0	8·0	5·9	
0·4	79·1	58·0	40·1	27·2	15·3	
5·6	7·7	5·0	0·6	—	—	155
3·6	17·2	11·6	7·4	2·8	—	
1·4	55·6	38·3	18·1	13·3	11·0	
0·8	87·8	56·5	47·9	31·4	16·0	
0·7	54·5	36·8	8·2	1·4	12·1	
8·6	8·8	6·0	—	—	—	225
5·0	18·8	10·4	0·4	—	—	
3·6	20·3	37·4	1·5	—	2·9	
1·6	47·9	38·4	15·2	5·9	6·7	
0·5	86·5	—	25·0	30·3	20·9	

The points are plotted in figure 13. In figure 14 a plot of P_r in cm. of solution against $(\varpi/h)^{1\cdot4}r^{-1\cdot6}$ is given where ϖ = rate of rotation in r.p.m., h is distance of separation (range of values was between 0·8 and 8·6 mm.) and r the radial distance (range from 0·8 to 2·0 cm.).

The equation

$$P_r = P_0 - K\left(\frac{\varpi}{h}\right)^{1\cdot4} r^{-1\cdot6}$$

fails at high speeds, when c is not expected to be 0·6 and when, probably, turbulence, etc. may set in; at extremely low values of h, i.e. $h = 0\cdot4$ and 0·7 mm. where our method of measurements and alinement were not reliable, and for radial distances which are less than 0·8 cm. where there is reversal of flow under the disk from inwardly under the stationary disk to outwardly over the rotating surface. Typical examples of the failures are also shown. Thus the formula is proved with the value of $n = 3$.

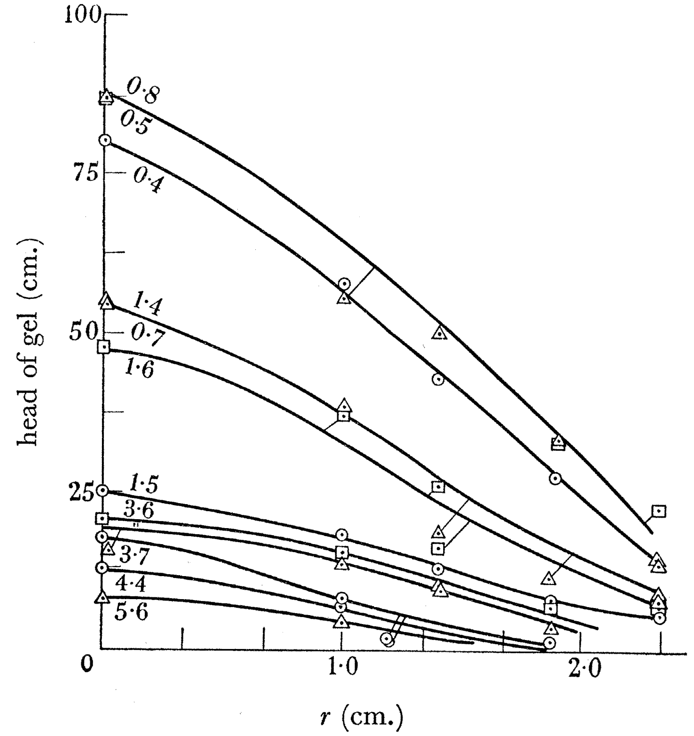

FIGURE 13. Variation of pressure on stationary disk with radius in rotary beaker apparatus. Speeds (r.p.m.): ⊙, 118; △, 155; □, 225. The numbers on the curves are the clearances in mm.

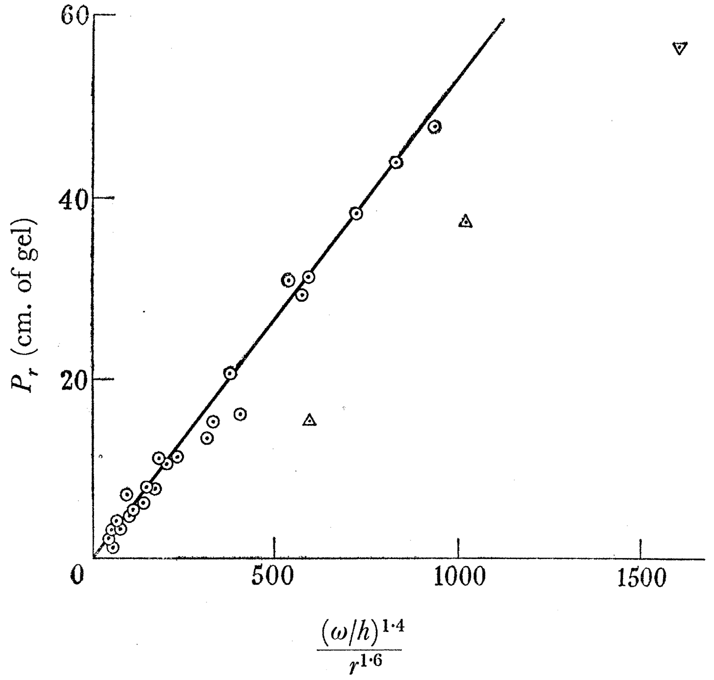

FIGURE 14. Variation of pressure on stationary disk with speed, displacement and radius of the point. Range of variables for plotted points: ω, 118 to 225 r.p.m.; h, 0·8 to 8·6 mm.; r, 0·8 to 2·0 cm. The points △ are for $\omega = 225$ r.p.m. and the top one is for a point too near the centre of the disk.

Thus, it appears that the theories described account for the observed facts in several experiments.

Flow in pipes

On the basis of the theories propounded in the previous sections, the flow of these liquids in pipes should show certain peculiarities. The first is to be observed at the inlet. As the liquid converges into the pipe it is moving from regions of low free energy to regions of high free energy. Therefore the structural units of flow should tend to oppose this flow either by establishing a secondary back flow or by secondary helicoidal flow. By any mechanism envisaged the pressure loss at the inlet should be abnormally high.

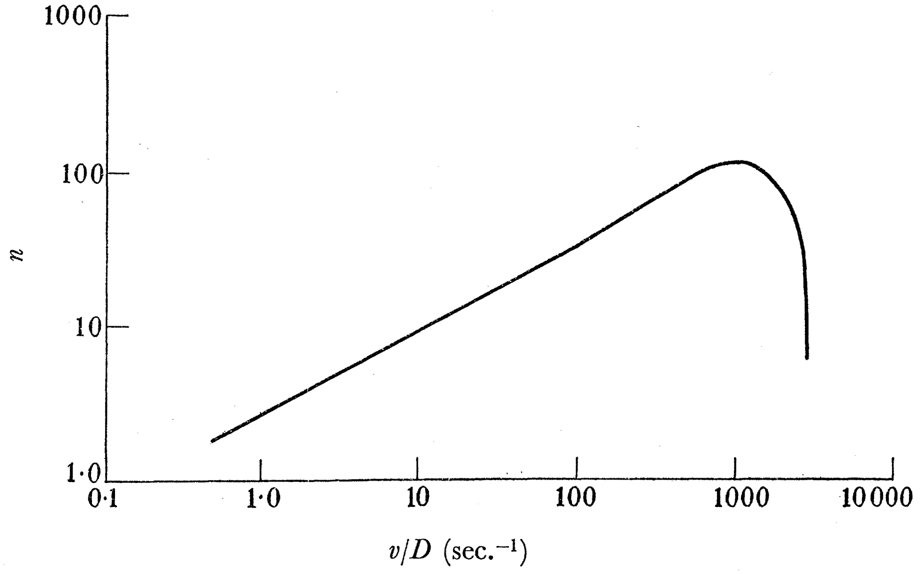

Figure 15. The Couette loss in terms of number of diameters of pipe against function of rate of shear for aluminium soap in hydrocarbon systems.

With ordinary liquids the inlet losses are due to a kinetic energy loss equal to approximately $1\cdot4\rho v^2$, where ρ = density and v is the mean velocity, and a so-called Couette loss equal to the pressure lost in a length of the pipe of the order of one diameter. In experiments we performed with a great number of these liquids in a variety of pipes ranging from capillaries up to 2 in. iron pipes, the inlet loss was always found to be far greater than that encountered with ordinary liquids of similar viscosities (see Wood, Nissan & Garner 1947). The kinetic energy loss was found to be the same as for ordinary liquids, viz. $1\cdot14\rho v^2$. However, the Couette loss was as high as that encountered in a length of pipe equal to 100 diameters. See figure 15, where n denotes the length of a pipe, in terms of its diameter, which would have caused the same pressure loss as that lost at the inlet of the pipe at the same value of v/D. For ordinary liquids n is of the order of unity.

The second abnormality arises from the fact that inside the pipe ordinary liquids flow in concentric laminae of increasing rates of shear. These liquids, on the present theories, would tend to migrate across the stream tubes. As the migration is a function of $\dot{\sigma}^{2-c}$, approximately, with $c<1$ the abnormal effects will show more in the outer layers than in the inner layers. Thus the liquid will appear to flow with a layer next to the pipe of higher viscosity than the bulk viscosity. This, mathematically, is equivalent to the well-known slip phenomenon with flow of suspension in pipes but with the slip having a *negative* sign with these special liquids. In other words, for the same average shearing stress wider pipes will show higher rates of shear than narrow pipes of the same L/D ratio, where L = length of pipe, and D = diameter of pipe. Figure 16, taken from the same paper (1947), illustrates this point. (Liquids with the ordinary slip phenomenon have higher mean rates of shear in narrow pipes than in wide pipes. For full discussion, see our 1947 paper.)

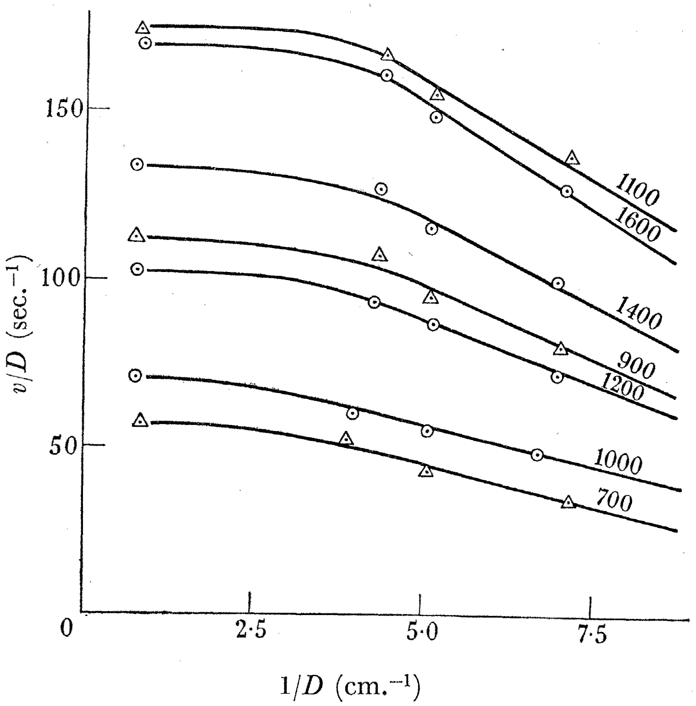

FIGURE 16. Demonstrating the negative slip phenomenon in flow of aluminium soap in hydrocarbon system in pipes. Values of L/D: ⊙, 40; △, 100. The numbers on the curves are values of F (dynes/cm.^{2}).

CONCLUSIONS AND IMPLICATIONS

1. *Observed phenomena*

When solutions of rubber, of calcium or aluminium soaps, of Perspex or of certain cellulose acetates in hydrocarbons or solutions of glue in water are subjected to non-uniform shear, there appears to ensue secondary flow from regions of high to regions of low shear which is not readily explicable by hydrodynamics of ordinary fluid systems. This secondary flow is also accompanied by certain anomalous pressure distributions as when a shaft rotates within a sleeve in hydraulic contact with a stationary portion of these liquids, or when a disk is maintained stationary in a rotating container full of these liquids.

2. *Theoretical explanation*

It appears that when these liquids are sheared a certain amount of the shear energy is stored in the liquids with a resulting increase in the free energy of the system. This increase in the free energy renders secondary flow from regions of high to regions of low shear probable. On reaching the regions of lower shear energy the liquids relax yielding their energy in the form of an excess isotropic pressure similar in characteristic to an osmotic pressure in regions of high concentration of solute.

3. *Derived parameters*

The excess free energy appears to be the result of an increase in the internal energy accompanied by a smaller increase in the entropy of the system on shearing. As the temperature rises the increase in entropy approaches equality with the increase in internal energy. When these two factors equal each other, the peculiar phenomena disappear.

4. *Implications*

(i) *Surface energy*

The increase in free energy renders these liquids capable of storing greater amount of surface energy before rupture than their static surface energy would allow them. Thus they have higher 'rupture strength' and are amenable to formation of threads, sheets, etc., when they are under high rates of shear, i.e. a longer thread can be drawn when the action is quick than when slow.

(ii) *Shear elasticity*

Of a total energy input ΔE ergs/cm.^{3}/sec., equal very nearly to $F\dot{\sigma}$, to the system, these liquids appear to dissipate locally a portion equal to $T\Delta S$ and store a portion equal to ΔA which is again finally dissipated by moving towards energy sinks. It seems that to a first approximation this sharing of energy between recoverable and irrecoverable portions is a temperature function only, but other experience with the systems makes us believe that it is also influenced by the state and rate of shear.

(iii) *Viscosity*

The most significant implications of these findings are in the domain of viscosity and viscometry. These findings render the conventional terminology and concepts inapplicable to these systems. Thus, in experiments in which shearing is rapid and intense a yield value is obtained. However, when the liquids are left to stand they will always reveal a flat mirror surface denoting absence of yield values. It is this fact that modified the conclusion drawn in the section on shear elasticity to the effect that besides the temperature the rate of shearing influences the partition of the energy input into shear elastic, recoverable portion and an irrecoverable portion. Whilst a model of elastic and viscous elements in series would represent this behaviour mathematically (a model of spring with *variable* elasticity and a non-Newtonian liquid dash-pot in parallel is really necessary to represent it) it is felt that the use of such models should be purely for calculation purposes; the systems are not made up of several elements in series or parallel, but they undergo several processes in parallel.

In viscometry, viscosity is defined as the ratio of F to $\dot{\sigma}$, the shearing stress to the rate of shear acting at a small element of area. In practice, however, it is almost impossible to obtain a system in which $\dot{\sigma}$ is uniform throughout the liquid. Hence, according to these findings, there is rarely a case of simple shear; secondary flow down the space gradients of $\dot{\sigma}$ either on a microscopic or colloidal scale will always take place. Hence this ratio of F to $\dot{\sigma}$ need not be a characteristic of the system but will be affected by the conditions of the experiments. However, if the 'viscosity' of a liquid were related to the fraction of the energy input which becomes irrecoverable, the evidence of this work tends to show that this fraction is to a first approximation a characteristic of the liquid influenced by the temperature only, being the ratio of $T\Delta S$ to ΔE. Thus it appears as if the fraction dissipated of the product $(F\dot{\sigma})$ is of greater value in understanding these colloidal systems than the ratio $(F/\dot{\sigma})$.

Symbols used

A^T	free energy at T° K
A (suffix)	apparent
a	radius of shaft
B	constant $=\mu_A/\dot{\sigma}^{-c}$
b	radius of glass sleeve
C	constant; $F=C\dot{\sigma}^{(1-c)}$
c	constant
d	$d=2-c$
D	diameter of pipe
E	energy
F	shear stress
f (suffix)	frictional
f	$f=T\Delta S^T/\Delta E^T$
g	acceleration due to gravity
H	head of liquid
h	height
K	constant
k, k_1, k_2, etc.	constant
l	length
L	length of pipe
n	number
P	pressure
R	radius
r	radius
r (suffix)	at radius r
rot. (suffix)	in rotating region
Re	Reynolds number
R.S.	rupture strength
S	entropy
stat. (suffix)	in stationary region
T	temperature (° K)
T (suffix)	at temperature T° K
V	specific volume
v	velocity
x	distance
Z	height
α	angle
Δ	increment of
δ	displacement
ϵ	free energy (small) of molecule
ϕ	stored part of $(F\dot{\sigma})$
ν	kinematic viscosity
θ	angle
μ	absolute viscosity
ρ	density
$\dot{\sigma}$	rate of shear strain
Ω	angular velocity (constant)
ϖ	angular velocity (variable) and r.p.m.

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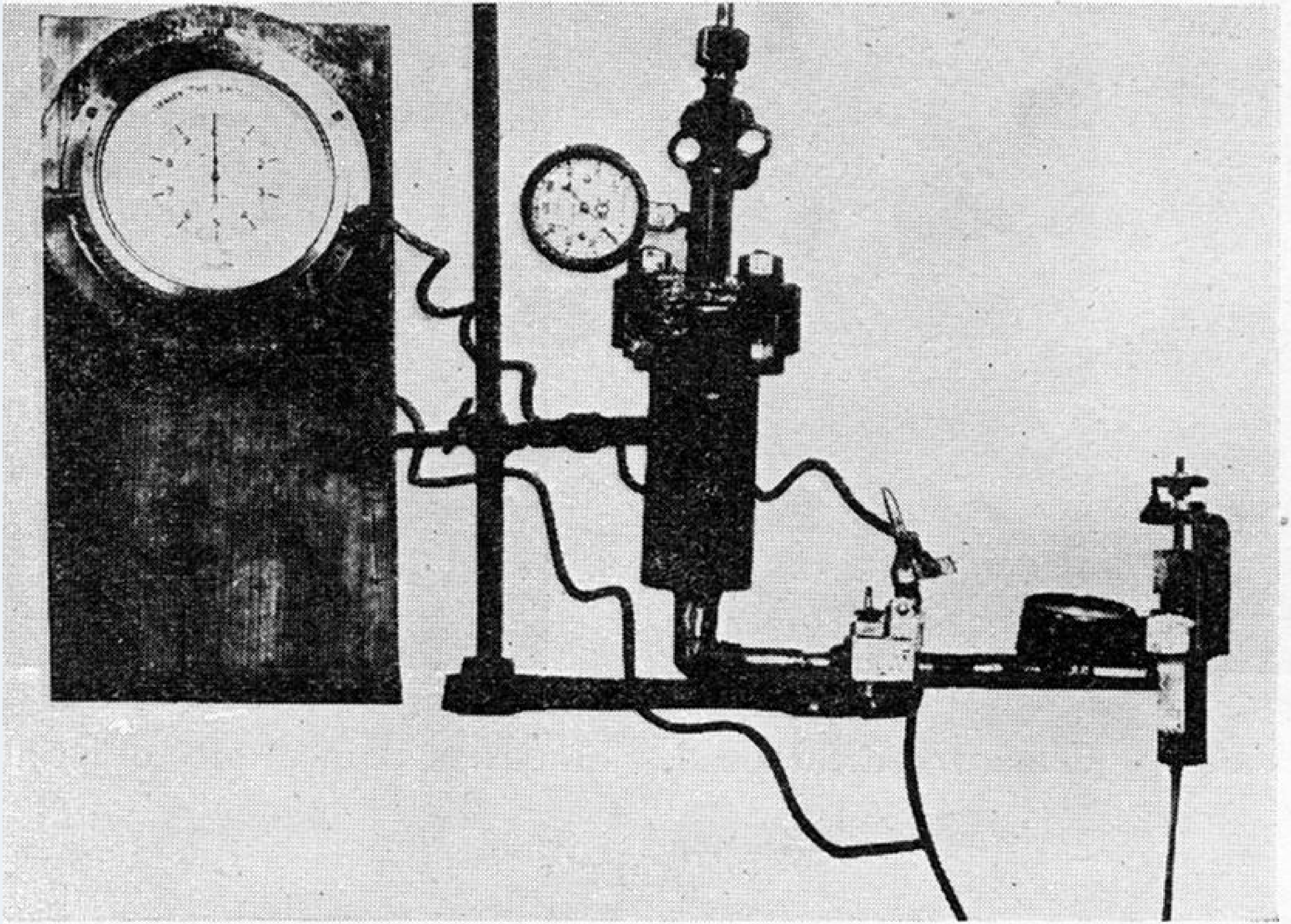
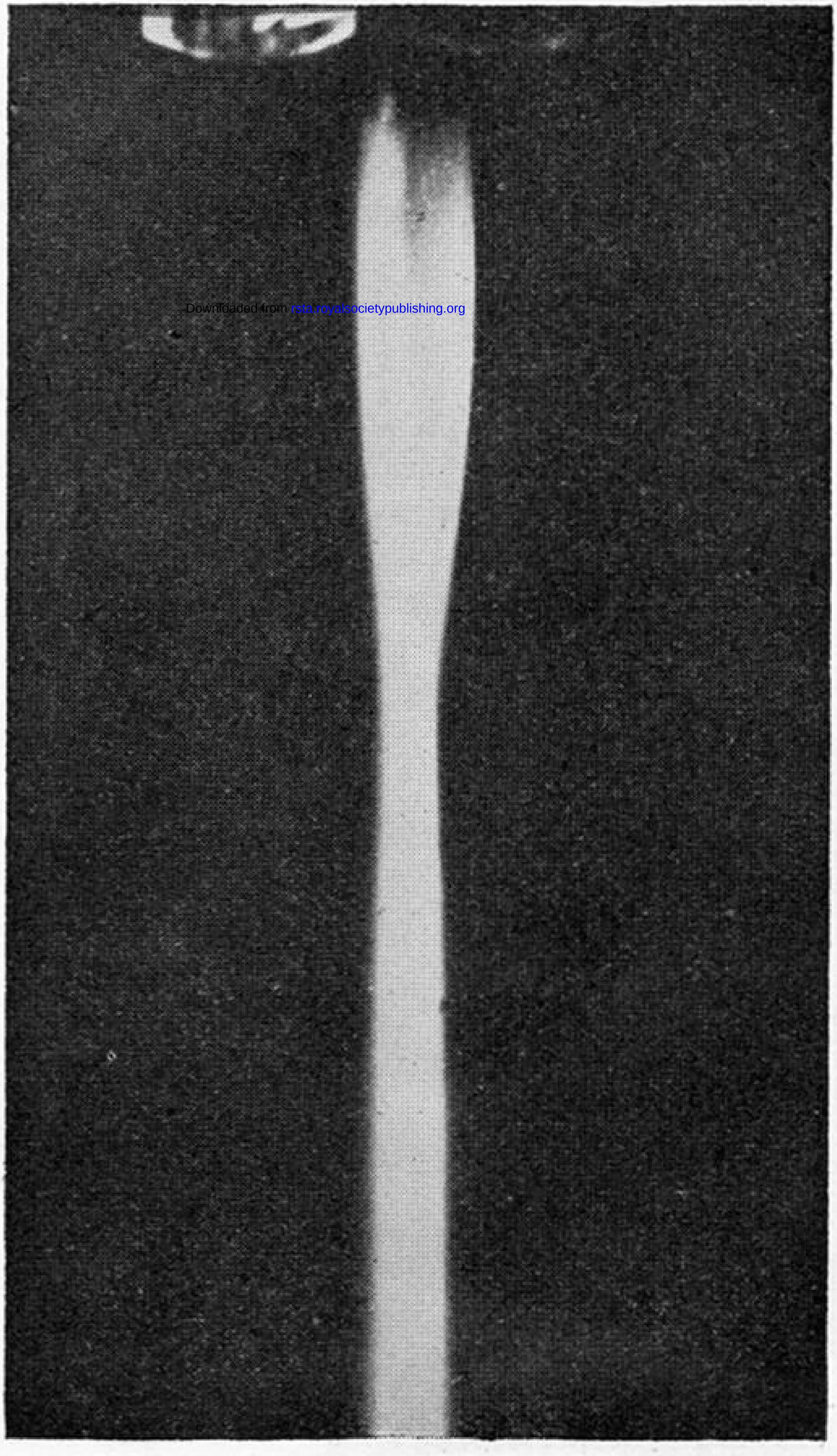
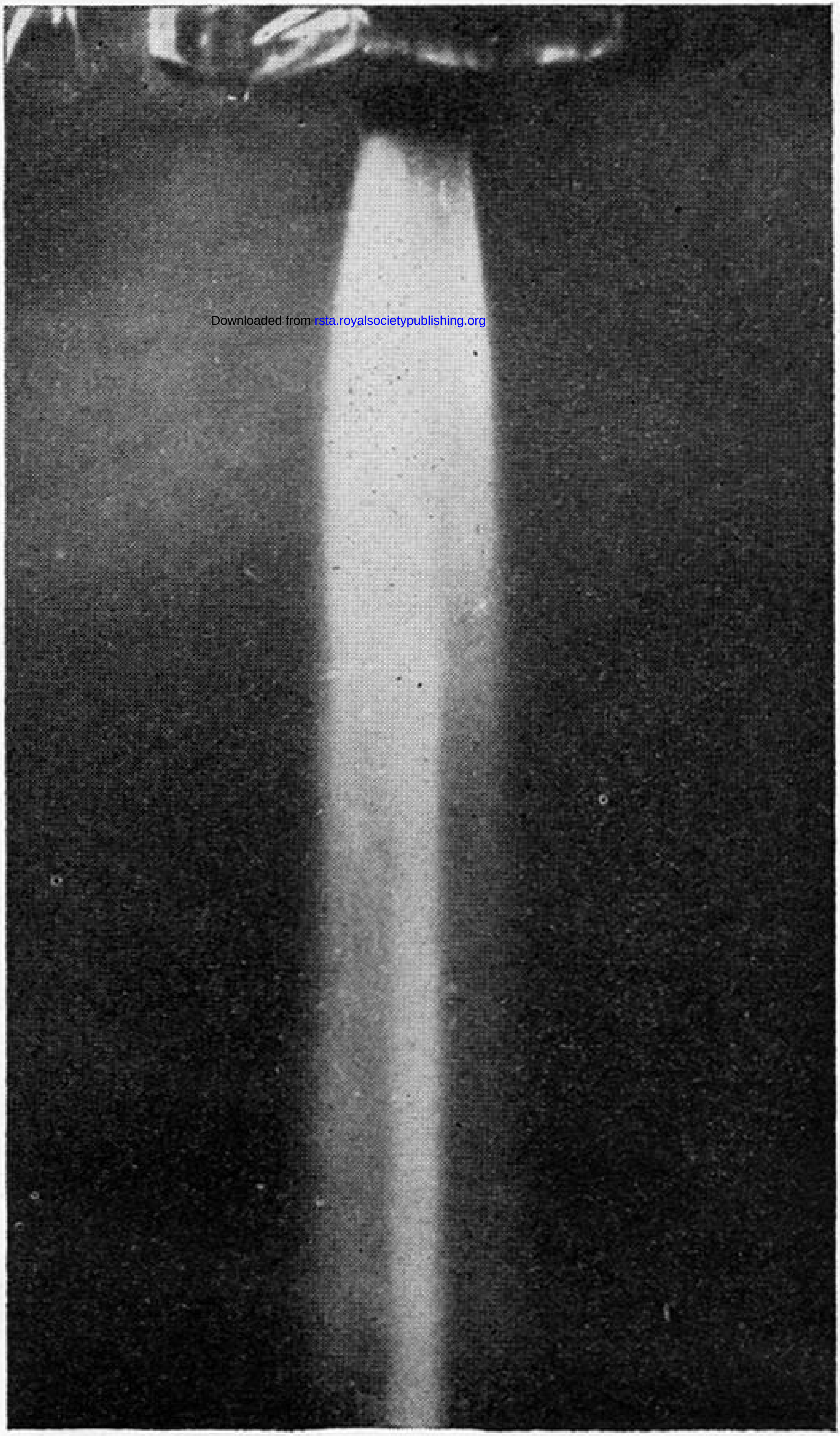


FIGURE 2. Photograph of cohesimeter.



IGURE 3. Appearance of jet below critical speed.



IGURE 4. Appearance of jet above critical speed.