CAPILLARY VISCOMETRY*

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1. Introduction

This paper reviews some principles and applications which are pertinent in attempts to solve rheological problems by capillary viscometry in many material fields including that of cosmetics. Rather than an exhaustive review of capillary viscometry the paper emphasizes those aspects of the field which are especially pertinent to rheological investigations conducted in the light of current rheological understanding. Some aspects of the field having primarily historical interest may be ignored. References to the literature are not cited in many cases of facts of sufficiently long standing to be considered classical. Much of the unreferenced material is thoroughly discussed in several excellent general references (1–3) which may be consulted for further details. For the convenience of the reader the literature references cited in other cases are not always the original references, but rather those likely to be most conveniently available.

2. Fundamental Rheological Quantities

It is helpful at the outset to review the definition of the fundamental rheological quantities involved in capillary and other types of viscometry. These quantities are two in number: (1) a kinematic quantity, the rate of shear, which concerns the state of motion of the experimental material and (2) a dynamical quantity, the shearing stress, which concerns the associated forces on the material. These quantities are defined microscopically as well as macroscopically only for laminar as distinct from turbulent flow. Laminar flow is defined as flow in which all the flow lines are parallel. It is only to laminar flow that the following discussion applies.

The above quantities are illustrated through the cube shown in Fig. 1. A (tangential) shearing force F acting on the top surface of the cube results in a continuous deformation of the cube into the rhomboid indicated by the dashed lines. The top surface moves to the right with a velocity

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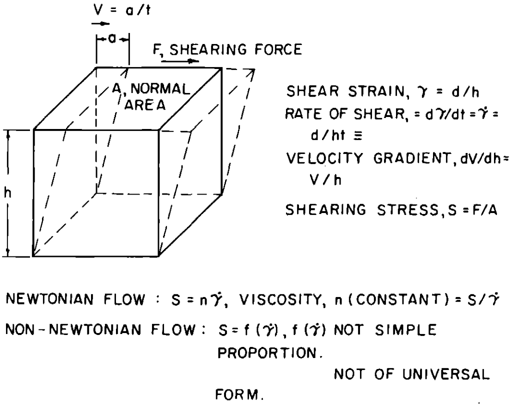

Figure 1.—Diagrammatic representation of simple shear.

$$v = a/t \tag{1}$$

where a is the distance moved in time t. The shear strain γ to which the cube is subject at time t is

$$\gamma = a/h \tag{2}$$

where h is the separation between the top and bottom surfaces of the cube. The rate $\dot{\gamma}$ of this shear (where shear is understood to mean shear strain) is

$$\dot{\gamma} = d\gamma/dt = a/ht \tag{3}$$

This quantity is the second derivative of deformation with respect to separation and time. If the order of the differentiation is reversed this identical quantity can be viewed as the velocity gradient

$$\dot{\gamma} = d\gamma/dt = d^2a/dtdh = d^2a/dhdt = dv/dh = v/h \tag{4}$$

The shearing stress s throughout the cube is

$$s = F/A \tag{5}$$

where A is the normal area of the top surface of the cube.

For Newtonian flow

$$s = \eta\dot{\gamma}; \qquad \eta = s/\dot{\gamma} \tag{6}$$

the constant of proportionality being the viscosity η. For non-Newtonian flow

$$s = f(\dot{\gamma}) \tag{7}$$

but $f(\dot{\gamma})$ is not a simple proportionality and it does not have a universal form.

3. SIMPLE RHEOLOGICAL THEORY OF CAPILLARY VISCOMETRY

In capillary viscometry the dynamical quantity (associated with shear

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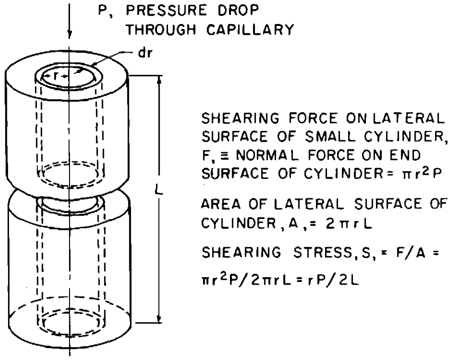

Figure 2.—Diagrammatic representation for deriving shearing stress in a right circular cylindrical capillary tube.

stress) actually measured or calculated directly is the pressure, P, forcing the fluid through the capillary, i.e., the pressure drop between the entrance and the exit ends of the capillary. The corresponding kinematic quantity (associated with rate of shear) is the volume rate of flow, $\mathcal{Q}$, of fluid through the capillary. To be rheologically useful, these observed quantities must be reduced to the corresponding fundamental rheological quantities, shearing stress and rate of shear.

The possibility of such reduction by reasonably simple treatment is based on the assumption that, as fluid flows through a capillary, that material immediately adjacent to the capillary wall remains stationary in the macroscopic sense. The material at effectively finite distances from the wall must move in the macroscopic sense however, or there would be no over-all flow. Therefore a velocity gradient is established according to which the farther an element of fluid is from the wall, the faster it moves through the capillary. There then exists a shear field essentially like that pictured in the preceding section. The calculations discussed there can be applied to the right circular cylindrical geometry of a capillary.

To calculate the shearing stress at any radial distance, r, in a capillary one considers the cylinder described by all points at that distance, illustrated in Fig. 2. The shearing force acting on the lateral surface of that cylinder is $\pi r^2 P$, which is the product of P and the area of an end surface of the cylinder (πr^2). The area of the lateral surface of the cylinder is $2\pi r L$, where L is the length of the capillary. The shearing stress is

$$s = \pi r^2 P / 2\pi r L = rP/2L \tag{8}$$

In making this calculation nothing has been said about whether the flow is Newtonian or non-Newtonian. The result is valid for either case.

Mathematically the rate of shear at any radial position is obtained

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through a calculation of the volume rate of flow through that cylinder described by all points at that radial position. In practice this volume rate of flow can be experimentally measured only for the entire cross section of the capillary. Therefore the only radial position where the rate of shear can be experimentally determined is that at the capillary wall. Since one can always experimentally determine s also at this radial position, and therewith determine the relation between shearing stress and rate of shear, this limitation is no handicap.

If the velocity of flow at a radial position is v, the volume rate of flow, $d\mathcal{Q}$, through an incremental cylindrical shell at that position, as illustrated in Fig. 2, is $2\pi rvdr$ since $2\pi rdr$ is the cross-sectional area of the shell. $\mathcal{Q}$ is obtained by integrating $d\mathcal{Q}$ above between the limits $r = 0$ and $r = R$, the radius of the capillary. Performance of this integration by parts using the velocity boundary condition $v = 0$ at $r = R$ eliminates v itself from the integral and introduces its gradient dv/dr, yielding

$$\mathcal{Q} = -\pi\int_0^R r^2 \frac{dv}{dr}\,dr \tag{9}$$

So far this development is again independent of whether the flow is Newtonian or non-Newtonian. If we now specify to Newtonian flow, substituting s/η for dv/dr above and expressing s in terms of r by *egn.* 8, there results after integration $\mathcal{Q} = \pi R^4 P/8\eta L$. Extracting s_w, the shearing stress at the capillary wall, *via. egn.* 8 gives

$$\mathcal{Q} = \frac{\pi R^3}{4}\cdot\frac{s_w}{\eta} \tag{10}$$

Since for Newtonian flow s_w/η is equal to the rate of shear at the capillary wall, $\dot{\gamma}_w$, we have now related this quantity with $\mathcal{Q}$ by

$$\dot{\gamma}_w = 4\mathcal{Q}/\pi R^3 \tag{11}$$

The viscosity is then

$$\eta = s_w/\dot{\gamma}_w = \frac{RP/2L}{4\mathcal{Q}/\pi R^3} = \frac{\pi R^4 P}{8\mathcal{Q}L} \tag{12}$$

For non-Newtonian flow the procedure beyond equation 9 is similar to the above. The functional relation between dv/dr and s will be something other than that expressed in equation 6. If some specific functional relation, such as, e.g., a power law, is applicable it is used to substitute for dv/dr in equation 9 in terms of s and therefore of r in view of equation 8. If the function substituted is such as to give an integrable expression, an explicit expression for $\dot{\gamma}_w$ in terms of $\mathcal{Q}$ will be obtained—otherwise, not.

In cases where no specific functional relation is known between dv/dr and s, equation 9 can also be developed to a usable result. For this purpose both sides of equation 9 are multiplied by $4/\pi r^3$ to give on the

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left hand side the quantity $4Q/\pi R^3$ which equation 11 equates to $\dot{\gamma}_w$ for Newtonian flow. For non-Newtonian flow this quantity is no longer $\dot{\gamma}_w$, but will be shown below to have useful properties. To avoid confusion, we shall designate it by the symbol D. Transformation of the argument of equation 9 from r to s via equation 8 and formal substitution for dv/dr by $f(s)$ yields as a counterpart to equation 9

$$D = (4/s_w^3)\int_0^{s_w} s^2 f(s)ds \qquad (13)$$

The form of $f(s)$ need not be specified here. All that is required of the function is that some such function exist for the fluid concerned, and that it be mathematically well behaved. If D is differentiated with respect to s_w, the differentiation can be formally carried under the integral sign so that the integration and the differentiation cancel each other, yielding the explicit result

$$dD/ds_w = -3D/s_w + (4/s_w)f(s_w) \qquad (14)$$

The function $f(s_w)$, which is equal to $\dot{\gamma}_w$, can be extracted from this result to give, after convenient rearrangement,

$$\dot{\gamma}_w = (D/4)\left(3 + \frac{d \log D}{d \log s_w}\right) \qquad (15)$$

The derivative $d \log D/d \log s_w$ can be obtained graphically from the experimental data if it is measured over a range of these quantities, and from equation 15 the value of $\dot{\gamma}_w$ corresponding to a given value of s_w can be calculated. For Newtonian flow $d \log D/d \log s_w$ is unity and the above required identity between $\dot{\gamma}_w$ and D for this case is confirmed.

The foregoing is the complete simple rheological theory of capillary viscometry. The rest of this paper will be devoted to the experimental application of this theory, complications of it, and comparison of the results with those from other types of viscometry.

A by-product of the simple theory is the usefulness of the quantity D in analyzing non-Newtonian flow, as mentioned incidentally above. In equation 13 s is only a dummy variable. Therefore D depends only on s_w. Especially important is the fact that the relation between these two qualities is entirely independent of the dimensions of the capillary used to determine it. This means that for any non-Newtonian material for which a functional relation exists between $\dot{\gamma}$ and s, there also exists a corresponding, but different, functional relation between D and s_w. This latter relation appears to have only mathematical rather than physical significance.

Nevertheless, measurements made at the same value of s_w in capillary viscometers having different geometries should yield the same values of D, and results obtained from viscometers of different geometries in dif-

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ferent regions of the variables can be combined to form an extended curve characteristic of the flow of the experimental material. Since D is obviously much easier to calculate than is $\dot{\gamma}$, the use of D is a great convenience and is perfectly satisfactory when one desires only a mathematical characterization of the flow.

4. COMPLICATIONS

The simple rheological theory of capillary viscometry just presented is based on several physical assumptions, requires the elimination of several extraneous factors from the observed data, and is subject to distortion by several foreign experimental effects. The following of these complications will be discussed here.

1. Uniqueness of Relation Between Shearing Stress and Rate of Shear.
2. Laminar Versus Turbulent Flow.
3. Slippage at Capillary Wall.
4. Kinetic Energy Contribution.
5. End Contributions.
6. Surface Tension Contribution.
7. Drainage from Reservoir Walls.
8. Dissipation of Heat.

4.1 Uniqueness of Relation Between Shearing Stress and Rate of Shear

The principal goal of all types of viscometry is to determine the relation between shearing stress and rate of shear for a material. Obviously this cannot be done unless a unique functional relation exists between these two quantities for the material concerned under the experimental conditions prevailing. Numerous cases have occurred where the results of arduous investigations have been rendered meaningless by the fact that no such relation existed for the material under investigation.

The criterion to be applied is whether at the same temperature and pressure a material always exhibits the same rate of shear at a given shearing stress. Examples for which this is not so are materials exhibiting, e.g., thixotropy, work-hardening or any type of permanent degradation. In these cases a unique relation involving shearing stress and rate of shear can be obtained only if the variable of time is also included in the relation.

This is only one type of situation in which no unique relation exists between the two variables concerned. In general the complete mechanical behavior of a substance will be described by a function including time, stress, strain and all the time derivatives of the latter two. Two familiar classes of materials exist for which this general function is greatly simplified by the fact that all but a few of these variables can be neglected.

One class is elastic materials, for which all the variables except stress and strain can be neglected. The other class is viscous materials, with

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which we are now concerned. For these all the variables except stress and rate of strain can be neglected. However, many materials exist on which viscometric investigations may be desirable, but which do not exhibit a unique relation between the two appropriate variables. The well-known viscoelastic materials are examples of materials that can be adequately described by the inclusion of only a few additional variables. Under properly selected experimental conditions these may sometimes be adequately treated as viscous materials.

The cases of thixotropy, work-hardening and degradation cited above are different from simple viscoelasticity. The only additional variable which need be included is time, and this can never be neglected in these cases. There may be a philosophical point of whether one is dealing with a single material in these cases, or whether as the shearing proceeds one deals with a continuously changing material. Whichever position is adopted the fact remains that the complete description of the rheological behavior requires only shearing stress, rate of shear and time.

The above discussion does not mean that viscometry investigations are useless on materials for which the subject unique function does not exist. On the contrary, such investigations may in fact give valuable information about the complicating processes in the flow. What is difficult or impossible for these materials is to reduce the experimentally observed data to fundamental rheological quantities. If the goal of an investigation is to give qualitative information about disturbing effects, it can be highly useful.

4.2. Laminar Versus Turbulent Flow

Laminar flow as defined in an earlier section is only one kind of flow which can occur in a capillary. It is the only type by which viscosity can be measured. The principal other type of flow in a capillary is turbulent flow. This occurs when the orderly parallel paths of elements of the material flowing through the capillary become disturbed. These paths may become irregular and vortices eventually appear. Under these conditions no comprehensive relation is known between the experimentally observed data and the fundamental rheological and other quantities. Therefore the flow data cannot be analyzed to yield viscosity data.

The conditions under which turbulence may arise are partially described by the Reynolds number. This criterion indicates the relative magnitudes of the acceleration effects which tend to promote disturbances and the viscous effects which tend to damp them out. The Reynolds number R for capillary flow is calculated by the equation

$$R = \frac{vd\rho}{\eta} \tag{16}$$

where v is the average linear velocity of the material flowing through

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the capillary, d is the diameter of the capillary and ρ and η are, respectively, the density and viscosity of the experimental material.

In capillary flow, turbulence never occurs under conditions where the Reynolds number is below the so-called critical value of 2300. At Reynolds numbers above the critical value turbulence may occur and eventually should if a given volume of fluid remained in a shear field an infinite length of time. In practice a volume of fluid does not remain in a shear field an infinite length of time so turbulence does not necessarily always occur above the critical Reynolds number depending on the condition of the capillary wall, the shape of the entrance end of the capillary, the disturbance present in the fluid before it enters the capillary, and possibly other factors. The exact conditions under which laminar flow does transform to turbulent flow in practice are not at all understood and are the subject of much current investigation by hydrodynamicists. Reynolds numbers as high as 50,000 have been reached in the flow of simple liquids without the onset of turbulence (4). The important fact for viscometry is that if one maintains conditions below the critical Reynolds number the results will not be complicated by turbulence.

There have been suggestions (5) that in some viscoelastic and colloidal materials a special kind of turbulence called "structure turbulence" can occur at Reynolds numbers much lower than 2300, possibly as low as 10. However this suggestion is subject to much doubt (6) and it is highly likely that approximately the same critical number applies for viscoelastic fluids as for simple liquids.

Certain hydrodynamical investigations (7) have suggested that turbulence is much more likely to occur at Reynolds numbers only slightly higher than 2300 in polymer solutions than in simple liquids. This suggestion is inconclusive and does not propose any special kind of turbulence below the usual critical Reynolds number.

Although turbulent flow is not useful for the determination of fundamental rheological quantities it is sometimes of great importance in practical deformation processes. For example, in many cases mixing and the maintenance of suspensions are dependent on turbulence. Its rejection here is limited to the pursuit of fundamental rheological quantities.

4.3. Slippage at Capillary Wall

The assumption that in capillary flow the material immediately adjacent to the capillary wall sticks to the wall is not always justified. A method of detecting and correcting for such deviation was developed by Mooney (8). Measurements are made in several capillaries of a common length to diameter ratio (to eliminate end effects, as will be mentioned later), but having different diameters. All other factors behaving properly, if the material sticks to the wall the calculated viscosity should be independent

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of capillary diameter. However if the material slips along the wall, there will be a dependence on diameter.

Since the perimeter of the capillary cross section increases as the radius while its area increases as the square of the radius, if there is slippage it will become relatively less important as the capillary diameter is increased. Therefore the calculated viscosity will increase with increasing capillary diameter; eventually reaching a correct asymptotic value when the wall effect becomes relatively insignificant. If it is assumed that the disturbing effect is a clean slippage at the wall and does not extend any distance into the capillary, the velocity of this slippage can be calculated from the increase of calculated viscosity with capillary radius. Using this velocity the calculated viscosity may be corrected for the slippage to yield a correct value. A modification of the above procedure has been designed by Oldroyd (9) to deal with slippage at the capillary wall in turbulent flow.

Cases have been known (10) where, in the above test, the calculated viscosity decreased instead of increased with increasing capillary diameter. This effect might be interpreted as something the opposite of slippage, but is more likely a compositional than a rheological effect.

4.4. Kinetic Energy Contributions

So far in this paper it has been implicitly assumed that in capillary viscometry the pressure drop through the capillary is associated entirely with overcoming viscous resistance to flow. This is not always true. Other effects can contribute to this pressure drop. Under some circumstances these other contributions are significant and cannot be disregarded.

One sometimes important other contribution is associated with the kinetic energy which must be imparted to the liquid to make it flow through the capillary. When a unit volume of liquid of density ρ is accelerated from rest to a uniform velocity v an amount of kinetic energy equal $(^1/_2)\rho v^2$ must be supplied. Furthermore if the liquid is accelerated to a nonuniform velocity averaging to the value v, there will be an additional requirement proportional to ρv^2 because the kinetic energy is a quadratic rather than a linear function of the velocity.

When the liquid decelerates to rest after emerging from the capillary, it gives up the kinetic energy originally imparted to it. If this kinetic energy were all dissipated at the exit end of the capillary in such a way as to raise the pressure there, it would serve only to raise the pressure at both ends of the capillary by an equal amount and make no contribution to the difference. However an undetermined amount of this kinetic energy, depending partly on the shape of the capillary exit, is instead dissipated immediately as heat at the exit end of the capillary, in which case it does not raise the pressure at the exit end but does make a contribution to the pressure drop through the capillary.

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This contribution can be evaluated as follows. Transposition of equation 12 gives as the pressure drop due to viscous resistance

$$P_v = 8\mathcal{Q}L\eta/\pi R^4 \tag{17}$$

If kinetic energy effects are also included in the total pressure drop through the capillary this total drop will be

$$P = 8\mathcal{Q}L\eta/\pi R^4 + m\rho v^2 \tag{18}$$

where m is an unknown coefficient. Now $v = \mathcal{Q}/\pi R^2$ and $\mathcal{Q} = V/t$ where V is the volume of fluid which flows through the capillary in time t. Using these relations, equation 18 transforms to

$$Pt = \frac{8LV_4\eta}{\pi R^4} + \frac{m\rho V^2}{\pi^2 R^4}\frac{1}{t} \tag{19}$$

If measurements are made in a capillary over a range of values of P, then a plot of Pt versus $1/t$ at fixed V will give as its intercept $8LV\eta/\pi R^4$. Since everything is this quantity except η is known, the correct value of η, free of kinetic energy effects, can be extracted from it. If the value of the coefficient m is desired, it can be obtained from the slope of the above plot, which is $m\rho V^2/\pi^2 R^4$ in which everything but m is known.

If none of the kinetic energy imparted to the fluid at the capillary entrance is reconverted to hydrostatic pressure at the capillary exit, the value of m to be expected theoretically is unity. In practice at very low rates of capillary flow, apparently all the kinetic energy imparted at the entrance is reconverted to hydrostatic pressure at the exit and the experimental value of m is zero. At higher rates of flow the kinetic energy is not reconverted and as the rate increases m approaches an asymptotic experimental value in the neighborhood of 1.1. Why this value is greater than unity is not exactly understood.

The importance of the kinetic energy contribution in any case is easily evaluated from the relative magnitude of the two terms of the right hand side of equation 19, and is readily subject to the control of the investigator through the proper choice of the experimental conditions.

4.5. End Contributions

Another contribution besides that expressed in equation 17 to the observed pressure drop arises just inside the entrance and just outside the entrance and exit ends of the capillary. The flow laminae in these regions are, respectively, converging to and diverging from the right circular cylindrical shells which prevail within the capillary. These processes require extra energy which is reflected in a contribution to the observed pressure drop. This contribution is often referred to as the Couette effect.

This additional pressure drop can be taken into account in the calcula-

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tions by substituting for the actual capillary length the sum of this length plus an increment of length equivalent to the additional pressure drop. The value of the equivalent increment of length to be used in any case can be evaluated by making measurements in capillaries of a given radius but several different lengths, with identically shaped ends. If the observed pressure drop for these capillaries for a given rate of flow is plotted versus their actual lengths, there will be a negative intercept indicating the pressure drop due to the end contributions. From this can be calculated the increment to be added to the actual length in calculations.

Theory indicates that the equivalent increment of length for this end effect should be proportional to the capillary diameter and that the constant of proportionality, n, should be about 1.14 when the flow is laminar just outside both the entrance and exit ends of the capillary. This is the case at very low rates of flow. At higher rates the flow becomes turbulent outside the exit end and the theoretical value of n is reduced by half to 0.57. Experimental values of n generally fall in the broad neighborhood of unity.

Another, often much larger, type of end effect sometimes appears in the viscometry of viscoelastic materials (11). This is due to elastic adjustment which are required in the region of the capillary entrance and exit. Such effects have not been theoretically analyzed to any appreciable extent, but it does not appear that they are always proportional to the capillary diameter. If their magnitudes are expressed empirically in terms of an equivalent increment of capillary length, values of n as high as 100 are not uncommon for this contribution. However, since it has not been analyzed systematically it is difficult to correct for the effect.

4.6. Surface Tension Contributions

The entrance and exit ends of a capillary viscometer are usually connected with reservoirs having free surfaces of the experimental material. If the forces exerted by these two surfaces because of surface tension are not equal and opposite, there will be a corresponding contribution to the experimentally observed pressure drop. The forces exerted by the two surfaces will be equal only if their geometries are maintained identical during the entire course of a measurement. Such an arrangement is possible, but is complicated and is not often used.

If the two surfaces have different geometries at any time during a measurement, the surface tension contribution to the pressure drop can be evaluated and corrected for only by calculating and if necessary integrating the appropriate components of surface tension for the surfaces concerned. Since a wide variety of surface geometries are used in capillary viscometry, no systematic correction scheme has been devised. Swindells (12) gives

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a comprehensive discussion of the calculation of surface tension corrections for several surface geometries based on Bashforth and Adams' tables (13) for the components of surface tension of curved surfaces.

Fortunately conditions can usually be found where surface tension corrections are negligible.

4.7. Drainage from Reservoir Walls

The rate of flow of experimental fluid through a capillary is most often determined by observing the fall of the meniscus in the reservoir from which the fluid enters the capillary. This observation must be combined with the geometry of the reservoir to give the rate of flow. In this procedure an error can arise if the fluid drains down off the capillary wall slowly enough in comparison with the rate of fall of the meniscus so that an appreciable film of fluid temporarily adheres to the wall during the time the fall of the meniscus is under observation. This film decreases the effective cross-sectional dimension of the reservoir by twice the film thickness. The result is that less fluid flows through the capillary in an observed interval of time than is calculated from the cross section of the reservoir. Correspondingly the uncorrected derived rate of flow is higher than the true rate, and too low a viscosity is obtained. This effect is usually taken into account by a procedure using the results of measurements including both directions of flow through the capillary; thus measuring rates of both falling and rising meniscii in the reservoir. The procedure is sometimes complicated by the concomitant interchange of entrance and exit ends of the capillary. The end effects discussed in subsections 4.4 through 4.6 of this paper are altered by this interchange. Drainage corrections are discussed more thoroughly by Swindells, *et al.* (12).

4.8. Dissipation of Heat

During the course of any viscous process, by its very nature, mechanical energy is necessarily converted to heat. The rate of heat dissipation per unit volume is given by the product of the shearing stress and the rate of shear. Under gentle shearing conditions, which are often used in viscometry, this heating is not sufficient to cause any detectable temperature rise in the experimental material. However, if measurements are made at high rates of shear, especially on materials of high viscosity, it is easy to reach shearing conditions where the heat dissipation in the flow process does cause a noticeable temperature rise in the flowing material. This temperature rise must then of course be taken into account in analyzing the results of the measurement.

Taking this temperature rise into account is not as simple as measuring a single temperature for the flowing material. Since according to equation 8 the shearing stress and accordingly the rate of shear vary from zero at

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the capillary's axis to maxima at its wall, so does the rate of heat dissipation vary. Therefore elements of fluid at different radial positions in the capillary are heated to different temperatures when viscous heat dissipation is not negligible. No means is known for measuring the temperature at each radial position in the capillary. Even methods for measuring the temperature at a single radial position are crude at best. Furthermore under these conditions there is not a unique relation between shearing stress and rate of shear, since varying temperature must be included, so it is difficult, if not impossible, to analyze the experimental results of the viscosity measurement.

Attempts have been made to calculate theoretically (14–16) the temperature rise as a function of radial position in a capillary with detectable viscous heat dissipation. Calculations are made only for two ideal conditions neither of which are closely realized in practice. One is the so-called isothermal condition according to which the capillary wall remains always at the ambient temperature and conducts away all excess heat which reaches it. The other is the so-called adiabatic condition according to which the capillary wall conducts no heat so that all heat dissipated in the flowing fluid remains in the fluid. The most exact treatment of the problem in either case becomes an eigenvalue problem, and the solutions are difficult to use in analyzing experimental data though they have been applied in some special cases.

A particularly troublesome confusion arising in connection with viscous heating effects is their confusion with non-Newtonian effects. If a measured viscosity decreases with increasing rate of shear, the experimental material is non-Newtonian if there is no temperature rise. If there is a temperature rise, however, it alone can account for the decrease in viscosity in the complete absence of any non-Newtonian behavior whatever. Before concluding that a material is non-Newtonian, therefore, it is necessary to demonstrate that increasing rate of shear is not accompanied by an increase in temperature. Reputable investigators have erroneously concluded that a material was non-Newtonian when the observed decrease in viscosity with increasing shear rate was later discovered to originate in a heating effect. All investigators should stand warned in this matter.

With regard to viscous heating effects in capillary viscometry, an investigator should examine his needs carefully to ascertain whether he cannot avoid conditions where they are detectable before he undertakes the difficult task of dealing with them.

5. SPECIFIC CAPILLARY VISCOMETERS

This section attempts to indicate the scope of applications in which capillary viscometers are useful. This scope is illustrated by discussion of specific capillary viscometers designed to meet various experimental

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requirements. No attempt is made to mention all capillary viscometers which have been used, or even all those which are in current use. Many interesting instruments are not mentioned. Those mentioned are selected to illustrate a variety of types of applications. It is believed that they provide at least an approach to complete coverage of the applications range of this type of viscometer.

A logical classification of capillary viscometers is according to the treatment of the quantities, one kinematic (rate of flow) and one dynamical (driving force), which in general are measured in the instrument. Perhaps the most common class is (a) that special case in which the driving force is that of gravity and the resulting rate of flow is measured. Two other classifications used here are the logical ones in which (b) some sort of controlled positive pressure is used as driving force and the resulting rate of flow is measured and (c) a controlled rate of flow is maintained and the required driving force is measured. The viscometers considered here, classified as above, are listed below:

Gravity Drive
  Ostwald viscometer
  Fenske viscometer
  Multiple-bulb viscometer
  Ubbelohde viscometer
Positive Pressure
  Bingham viscometer
  Tsuda viscometer
  Rising column viscometer
  Willenberg and Fritz viscometer
Controlled Flow Rate
  Swindells', Coe's and Godfrey's injection viscometer
  Maron and Kreiger viscometer
  McKee viscometer

5.1. Gravity Drive Viscometers

In this type of viscometer the experimental fluid is forced through the capillary by the force of gravity acting on a column of the fluid in one arm of the viscometer which is filled to a higher level than is another arm. If the difference in the levels of the two arms is h and the density of the fluid is ρ, the driving force is, of course, $h\rho g$, where g is the acceleration of gravity. As the fluid flows through the capillary the difference between the fluid levels in the two viscometer arms decreases. Therefore the force driving the fluid through the capillary is continually decreasing during the course of a measurement. If one measures the time of flow for a given volume of liquid, it is therefore necessary to use some kind of integrated average pressure in the subsequent calculation of viscosity.

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The variation from this average pressure can be minimized by arranging for most of the fluid in each arm to be contained in bulbs of large cross section which also contain the fluid surfaces so that a relatively large volume of fluid can flow through the capillary with only a relatively small change in the hydrostatic head. If this procedure is not practicable or adequate, the average head can be corrected for these variations. Swindells (12) has discussed these corrections.

5.1(a). Ostwald Viscometer. Probably the most classical capillary viscometer is that of Ostwald (17), illustrated in Fig. 3. The time is observed for the level of the experimental fluid to fall from *A* to *B* as a result of the fluid's flowing through the capillary. Viscosity is calculated from the observed data by the use of equation 19, usually after calibration with several calibrating fluids of different known viscosities. Many modifications of this viscometer have been designed to achieve various special advantages. Cannon and Fenske (18) describe two with small capillary radius and bulbs, respectively, for measuring low viscosities and for use with small samples. Cannon (19) describes one with a bulb of large radius to reduce the change in hydrostatic head during the course of the measurement.

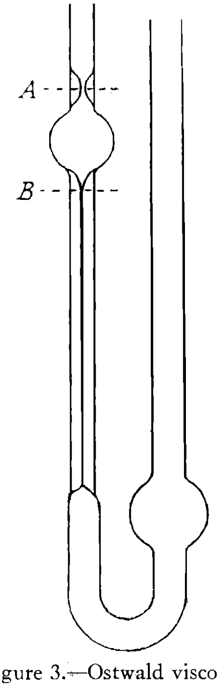

Figure 3.—Ostwald viscometer (Courtesy) *Edward Arnold & Co.*).

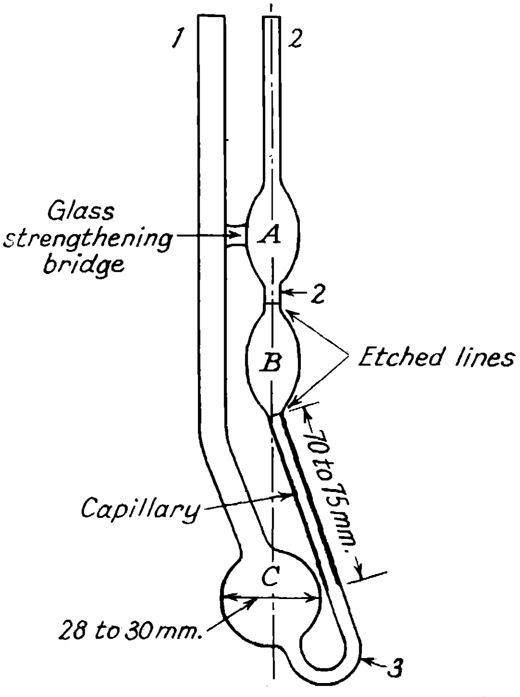

Figure 4.—Fenske-modified Ostwald viscometer (Courtesy *Edward Arnold & Co.*).

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5.1(b). Fenske Viscometer. Figure 4 illustrates a Fenske-modified Ostwald viscometer (20) in which the capillary is positioned obliquely to reduce errors introduced by deviations from perfectly vertical mounting.

5.1(c). Multiple-Bulb Viscometer. Ostwald viscometers have been modified by the introduction of several bulbs. Such a viscometer used by Fox, Fox and Flory (21) is illustrated in Fig. 5. During a single run the different bulbs are used for measurements at different rates of shear according to the pressure head to which each corresponds. One modification by Stabin (22) uses a coiled capillary to achieve an unusually low pressure head and therefore rate of shear when a measurement is made with the lowest bulb.

5.1(d). Ubbelohde Viscometer. In a more extreme modification of the Ostwald viscometer Ubbelohde (23) has eliminated one of the bulbs to eliminate its contribution to the change of pressure head during the course of a measurement. The Ubbelohde suspended-level viscometer is illustrated in Fig. 6. After filling, Arm *3* is closed at the top and air pressure applied to Arm *1* or vacuum to Arm *2* raises the sample liquid into Bulb *B*. When Arm *3* is opened at its top the liquid drops away from

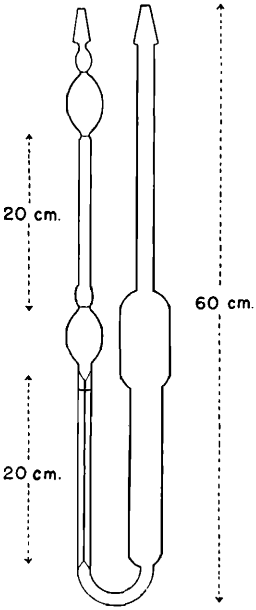

Figure 5.—Fox and Flory multiple-bulb viscometer (Courtesy *American Chemical Society*).

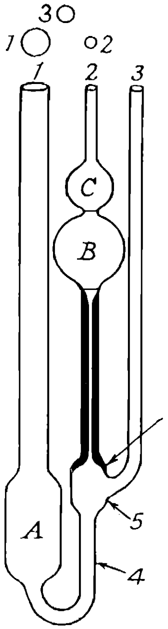

Figure 6.—Ubbelohde suspended level viscometer (Courtesy *Edward Arnold & Co.*).

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the bottom end of the capillary leaving a suspended level of liquid there. In some further modifications bulb *A* has been enlarged to form a mixing chamber which is convenient for measurements on successively diluted solutions; the dilution being performed in this chamber.

5.2. Positive Pressure Viscometers

In this type of viscometer the force driving the fluid through the capillary is controlled at a fixed value and the resulting rate of flow is measured. The force of gravity is of course superposed on the controlled force. If the effective head due to gravity is not zero it must be corrected for in high precision work, whether it results from a difference in the shape of two bulbs or from different average vertical levels of the bulbs.

5.2(a). Bingham Viscometer. A widely used positive pressure viscometer is that of Bingham (24), illustrated in Fig. 7. The trap *A* is used to ensure a uniform filling of the viscometer. Measured, controlled gas pressure applied to the left arm forces the experimental fluid through the capillary. The time required for the fluid level to move from B to D is measured.

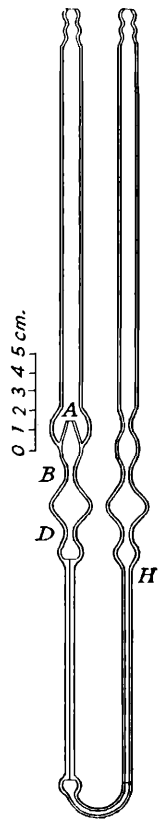

Figure 7.—Bingham viscometer (courtesy *Edward Arnold & Co.*).

5.2(b). Tsuda Viscometer. This viscometer (25) is illustrated in Fig. 8. The horizontal placement of the capillary, shown at the left of the figure, eliminates any gravity head and permits measurements at extremely low shearing stresses.

5.2(c). Rising Column Viscometer. This is an extremely simple and versatile type of viscometer. A version by Stow, Horowitz and Elliott (26) is illustrated in Fig. 9. A tube is immersed in the experimental material. Vacuum applied to the tube or gas pressure applied to the experimental material forces the material to rise in the tube at a rate which is measured. By varying the internal diameter of the tube an extremely wide range of viscosities can be covered with this type of instrument.

5.2(d). Willenberg and Fritz Viscometer. This rugged viscometer was originally designed for measurements on highly viscous materials such as lubricating greases (27). It is illustrated in Fig. 10. The capillary connects the bottoms of the two vertical cylinders which contain the experimental material. Weights on pans supported by pistons in these cylinders force the material through the capillary at a rate indicated by the measured rate of descent of the pan. Since the

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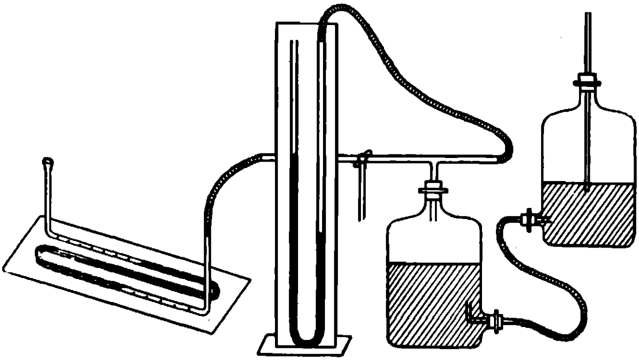

Figure 8.—Tsuda horizontal capillary viscometer (Courtesy *U. S. Department of Justice, Office of Alien Property*).

material can repeatedly be forced back and forth between the two cylinders an indefinite number of measurements can be made on a given sample without recharging the instrument. This feature provides an advantage over many other capillary viscometers in which such repeated measurements cannot be made.

5.3 Controlled Flow Rate Viscometers

This type of viscometer provides certain advantages to be mentioned in connection with the specific examples considered. Measurement is made of the driving force required to maintain a given rate of flow through the capillary.

5.3(a). Swindells', Coe's and Godfrey's Injection Viscometer. In the most recent determination of the absolute viscosity of water (28) adopted internationally as the standard for all viscosity values Swindells used an injection viscometer of this type. His viscometer is illustrated in Fig. 11. A special pump piston injector (not shown) forces liquid through the capillary at a precisely controlled rate. The associated pressure difference between the two ends of the capillary is then read on the two manometer arms which are connected outside the figure.

5.3(b). Maron and Kreiger Viscometer. Maron, Kreiger and Sisko (29) describe the versatile general purpose injection viscometer illustrated in Fig. 12. Fluid is forced through the capillary *A* at a fixed rate by use of the Syringe *G* with an auxiliary drive. The pressure developed is measured on either the mercury or the oil manometers, *w* and *m*, respectively. During the course of a single run the rate of flow can repeatedly be varied as soon as the corresponding pressure is established, and thus measurements over a range of rates of shear are conveniently made. A recent variation of

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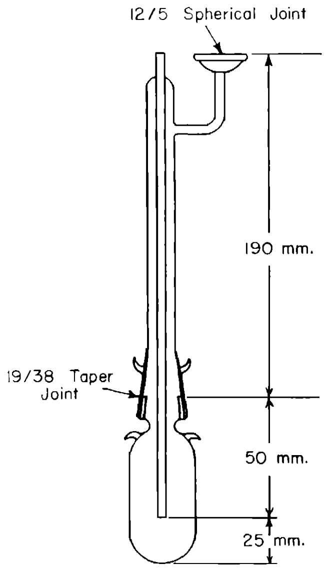

Figure 9.—Stow, Horowitz and Elliott rising column viscometer (Courtesy *Academic Press, Inc.*).

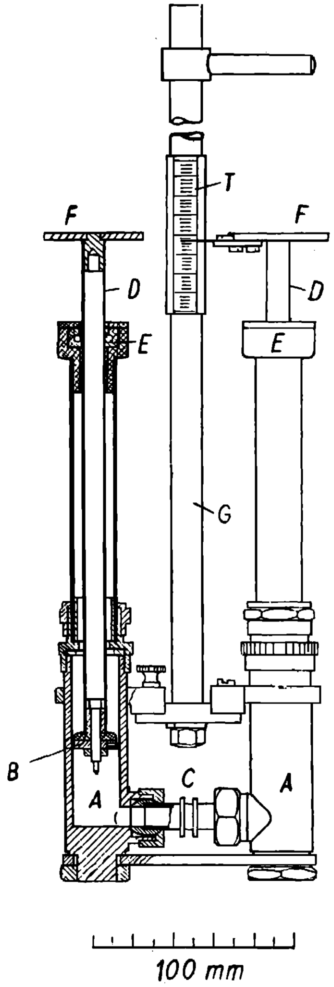

Figure 10.—Willenberg and Fritz viscometer (Courtesy *Verlag Chemie GmbH*).

this instrument by Maron and Belner (30) operates on the positive pressure principle and is capable of measurements at very low shearing stresses.

5.3(c). McKee Viscometer. This viscometer is illustrated in Fig. 13 (31, 32). Cam *H* motivates Yoke *E* which through driving pins *K* drives opposed pistons within cylinders which contain the experimental material and are separated by a disk penetrated by the measuring capillary. As the pistons force the fluid through the capillary at a controlled rate the cylinder in its housing is held stationary by a scale which measures the driving force. The reciprocating feature of this instrument gives it the

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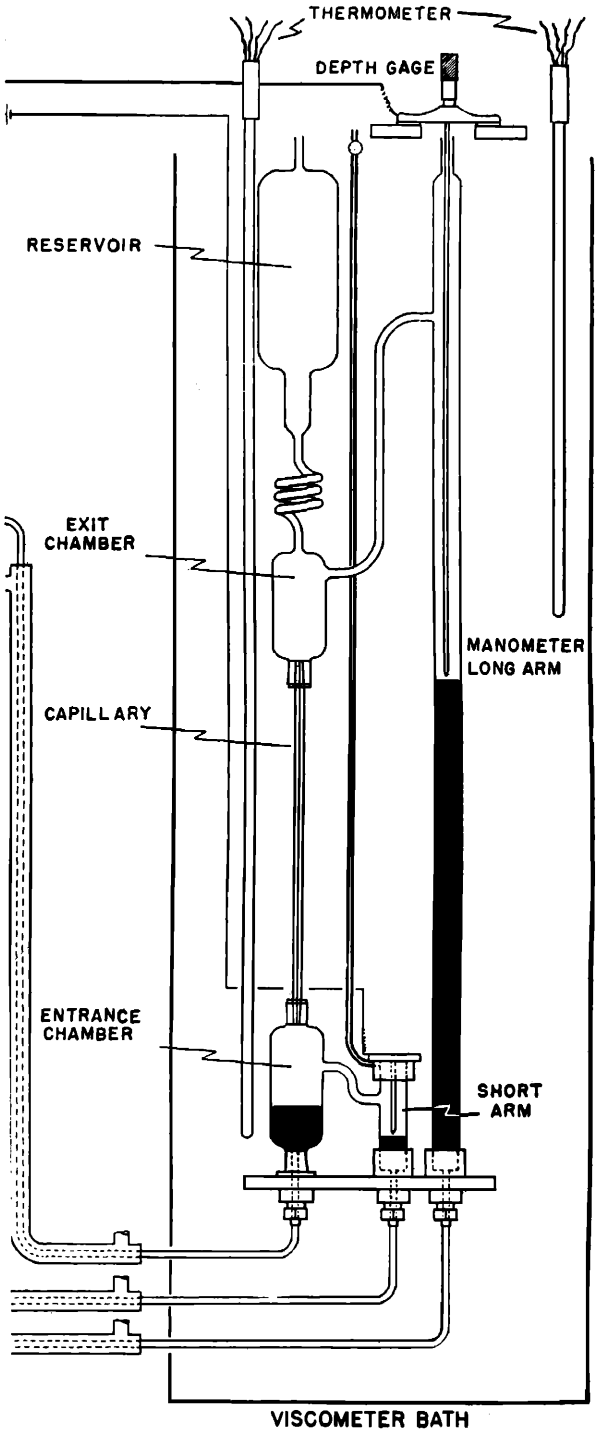

Figure 11.—Swindells, Coe and Godfrey injection viscometer (Courtesy *National Bureau of Standards*).

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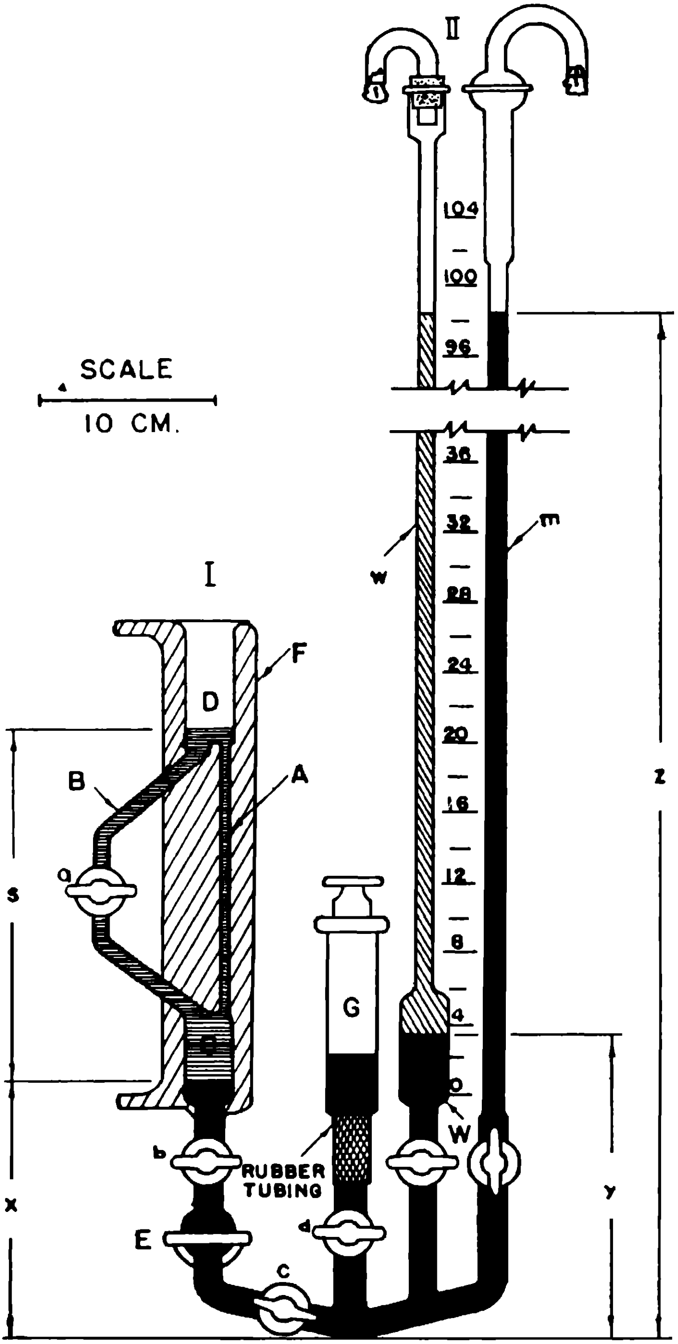

Figure 12.—Maron, Kreiger and Sisko viscometer (Courtesy *American Institute of Physics*).

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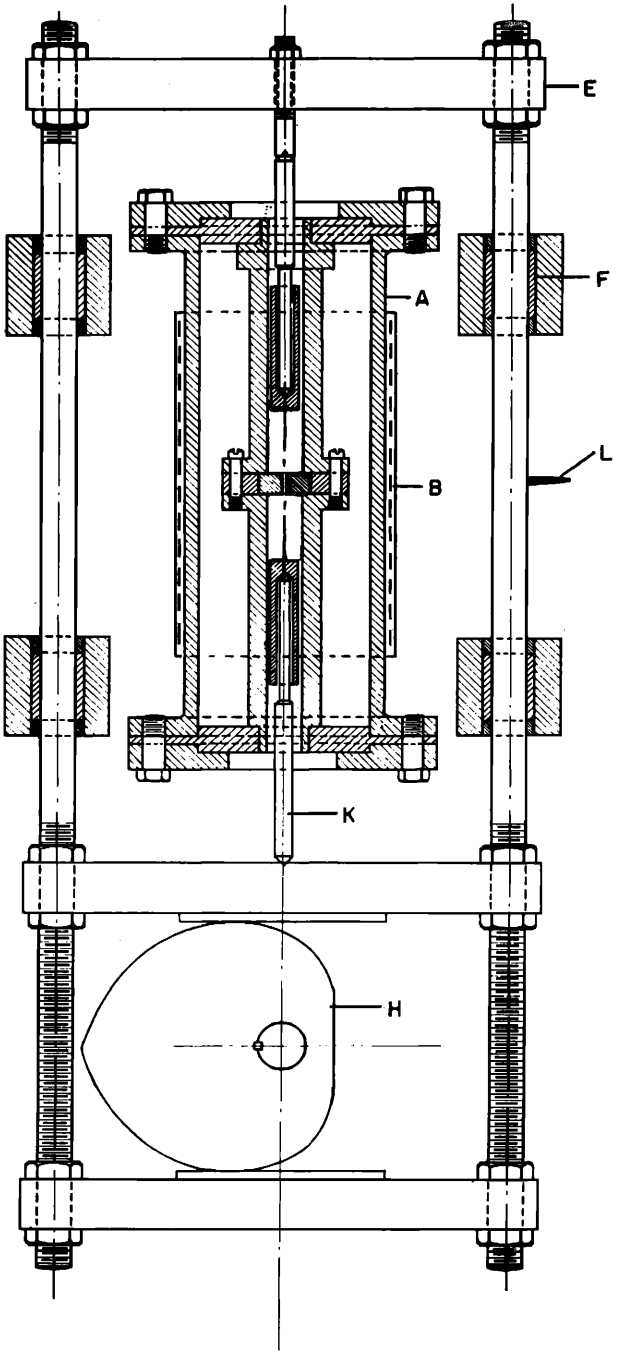

Figure 13.—McKee and White reciprocating viscometer (Courtesy *National Bureau of Standards*).

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same capability for repeated measurements mentioned for the Willenberg and Fritz viscometer. By using various capillaries and drives viscosities of one to several million poises may be measured with this instrument over a wide range of shearing stresses and rates of shear depending on the viscosity. Materials as viscous as raw synthetic rubbers are easily investigated in this viscometer.

6. RELATIVE MERITS OF CAPILLARY VISCOMETRY TECHNIQUES

The initial advantage of capillary viscometers over other types lies in their potential extreme simplicity of construction and operation, as exemplified by the rising column viscometer. As is often the case this advantage is detracted from by the attendant lack of simplicity of interpretation of the observed results.

The complications stem partly from the several corrections which must be applied as mentioned in a preceding section. These cannot always all be made reliably and in any case an undesirably large number of opportunities for the entrance of error is thereby furnished. In comparison, however, most other types of viscometry are also subject to an objectionably large number of errors. Therefore capillary viscometry is not in a relatively bad position in this respect. When the precision desired in measurements is low the above disadvantages are correspondingly less critical.

A second source of complication is the fact that the rate of shear in a capillary varies with the radial position. The raw experimental results therefore are governed by the rheological behavior of the fluid over a significant range of rate of shear. These results can therefore not be used directly to characterize the behavior of a rheologically complex material at any one rate of shear.

In compensation, if a non-Newtonian material does have some functional relation between shearing stress and rate of shear, though it may be unknown and complicated, the rheological behavior of the material at the maximum rate of shear in the capillary (that adjacent to the capillary wall) can be extracted relatively simply by analysis using the differentiation method of reduction, for which equation 15 is the working relation. The use of this method is appreciably simpler for capillary viscometry than for many other types of viscometry (33) and especially for Couette rotational viscometry (34) in which it requires either the use of rotors of different sizes or analysis by series.

The above advantage is sometimes of considerable importance. The claim is sometimes made for rotational viscometry that if the separation between the inner and the outer rotor is minimized the variation of shear rate within the instrument can be neglected. Although this claim is valid in many cases it is not always so. If the experimental material is

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extremely non-Newtonian (extremely non-linear) even small deviations from a uniform shearing field can have significant effects on the observed results, and if they are neglected fallacious conclusions can result. In such cases it is more satisfactory to use the differentiation method where it is applicable and obtain a reliable characterization of the behavior at a single rate of shear. When this is done capillary viscometry is more convenient than rotational.

For materials for which no unique functional relation exists between shearing stress and rate of shear the differentiation method of reducing observed experimental data is not valid. Examples of such materials are those exhibiting thixotropy, work hardening, permanent degradation or certain other types of viscoelastic behavior under certain experimental conditions. Important information about these complicating factors can be obtained by capillary viscometry. However, if one desires to measure the basic rheological quantities for such materials, methods other than capillary may be preferable.

For the satisfactory characterization of non-Newtonian materials it is usually necessary to measure viscosities over a wide range of rates of shear. In connection with this requirement capillary viscometry has a decided advantage over most other types. Capillary techniques can be used for measurements over significantly larger ranges than can other techniques. The range available to capillary viscometers extends to values as low as those available to most other types of viscometers. Capillary viscometers are especially advantageous at high rates of shear, being capable of reaching much higher values than possible in most other types of viscometers.

A specific advantage of capillary viscometers over many rotational instruments lies in their avoiding certain manifestations of the normal stress or Weissenberg effect. Materials exhibiting this effect to an appreciable extent will often rise on the rotor of a rotational viscometer. This behavior removes part of the material from the shearing field thus complicating the geometry of the field and yielding fallacious results. For instance a false indication of thixotropy or hysteresis can be obtained. Such a manifestation cannot occur with capillary viscometers.

7. CONCLUSION

Capillary viscometry is perhaps the oldest, experimentally simplest and most versatile type of quantitative viscometry. The experimental simplicity is in some cases accompanied by numerous and uncertain corrections and by complicated reduction of observed results for rheologically complex fluids. Subsequent types of viscometry have been developed which eliminate some of these difficulties. Possibly because of its versatility, however, capillary viscometry has not been and probably will not

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be completely supplanted by any other type or combination of types of viscometry. Other types of viscometry are sometimes accompanied by special complications of their own which do not apply to capillary viscometry. For capillary viscometry the reduction of observed results for rheologically complex fluids, though complicated, is explicit and of a closed nature which is not the case for some other types of viscometry.

The most serious inadequacies of capillary viscometry probably arise for materials which do not have a unique relation between shearing stress and rate of shear. For such materials the cited method of reduction of observed results is not valid, and no successful modification or replacement for it has been developed. The types of materials referred to are illustrated by those exhibiting such effects as thixotropy, work hardening or permanent degradation, and certain types of viscoelastic materials in certain ranges of experimental conditions.

For viscometric pursuits which are of an exploratory nature, which do not require high precision, in which great effort is expendable to achieve high precision, or in which interest is centered on complicating processes rather than on fundamental rheological quantities, capillary viscometry is likely to continue indefinitely as an important experimental technique.

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EXPERIMENTS ON MITOTIC FLARE-UP AND ACANTHOSIS*

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L'examen de la poussée mitotique est fait sur la tétine de cobaye mâle. On applique une goutte de la solution à tester, puis on injecte au cobaye de la colchicine. Cet alcaloïde est un révélateur des cellules en division. On évalue ensuite le nombre des mitoses sur la coupe histologique. Les oestrogènes et les produits ayant un effet toxique primaire entre autre provoquent une telle poussée mitotique. Parmi 8 dérivés du dinitrochlorobenzène examinés de cette mamière, les 4 produits connus comme eczématogènes provoquèrent une forte poussée mitotique tandis que les 4 autres n'en donnèrent pas. D'autres produits tels que térébenthine, chrysarobine, cignoline, certains alcools et hydrocarbures, le géraniol et le farnésol, etc., provoquent également une poussée mitotique.

L'examen du pouvoir acanthogène d'un produit est fait sur le flanc du cobaye. Après avoir appliqué la substance, soit pure, soit diluée dans un excipient, pendant plusieurs jours, on prélève un échantillon du flanc traité et du flanc non traité. On mesure l'epaisseur de l'épiderme sur les coupes histologiques. On voit ainsi si l'épiderme s'est épaissi ou non sous l'influence du produit appliqué.

Nous avons examiné de cette manière différents onguents ainsi que toute une série d'alcools et d'acides aliphatiques saturés et non saturés. Tandis que pour les alcools saturés (de C_2 à C_{18}) on ne remarque pas d'effet acanthogène, les alcools avec une double liaison (C_{11} et C_{18}) montrent une forte action. Parmi les acides saturés on remarque un maximum avec l'acide laurique; quant aux acides avec une double liaison, ils sont nettement acanthogènes à partir de C_{10} et cet effet augmente jusqu'à l'acide érucique (C_{22}).

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