about —87°. The ammoniate, $2NH_4SCN.13HN_3$, would probably melt in the vicinity of —80°.

5. The lowest eutectic point lies in the vicinity of —96°.

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A METHOD OF MEASURING ABSOLUTE VISCOSITY.

By Harold P. Gurney.

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The desirability of expressing the viscosity of liquids in absolute units cannot be too strongly urged. Unfortunately, most methods employed to this end are either not adapted to rapid commercial work, or are not capable of giving absolutely accurate results. The advantages that may be claimed for the following method are: (1) it can be made extremely accurate, (2) the manipulation is simple and rapid, (3) opaque liquids can be tested, (4) the apparatus can be set up in any chemical laboratory at short notice, taking but little time to calibrate, and (5) only a very small quantity of liquid is required.

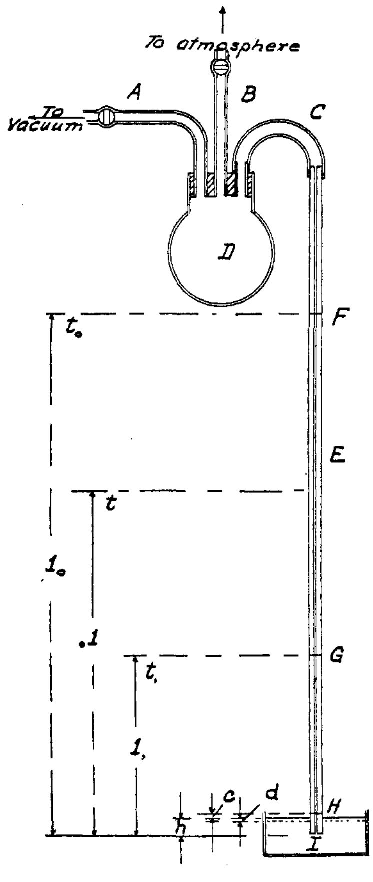

Fig. 1.

The apparatus is outlined in Fig. 1. The flask *D* is connected by a stopcock, *A*, to a vacuum pump and by rubber tubing, *C*, to a vertical glass tube, *E*, of capillary bore. A stopcock, *B*, connects with the atmosphere. A cup with vertical walls contains the liquid where viscosity is to be tested. There are three marks or etched rings around the glass tube at *F*, *G*, and *H*. In Fig. 2, the apparatus is shown with a jacket for temperatures other than room temperature.

The method of operation is simple. The cup *I* is filled with liquid until it just rizes inside the capillary to the line *H*. The stopcock *A* is opened and *B* is shut until the liquid has been sucked up above the line *F*. *A* is closed and *B* opened, thereby admitting atmospheric pressure above the liquid in the capillary tube. The level of the liquid in the capillary descends with but slightly diminishing velocity, and the time required to pass from F to G is measured by stop watch. Increased accuracy may be attained by repeating and averaging results. The distances of F, G, and H from both the bottom and top of the tube are carefully measured; the density of the liquid may be obtained by any suitable method, and the radius of the capillary may be determined from the length and weight of a thread of mercury. The tube should be placed parallel to a plumb-line to insure accurate perpendicularity. In case the water or steam jacket is used, the liquid should first be sucked up, then lowered to atmospheric pressure and the liquid adjusted to H. Then it should be raised to the top of the jacket above F until the temperature is the same as that of the jacket, waiting say a minute or two, and then allowed to descend as before. When the level of the liquid passes F, practically all of the liquid which was not exposed to the jacket will be out of the capillary. In this way, the amount of liquid to be heated up is extremely small, hence saving in time of operation.

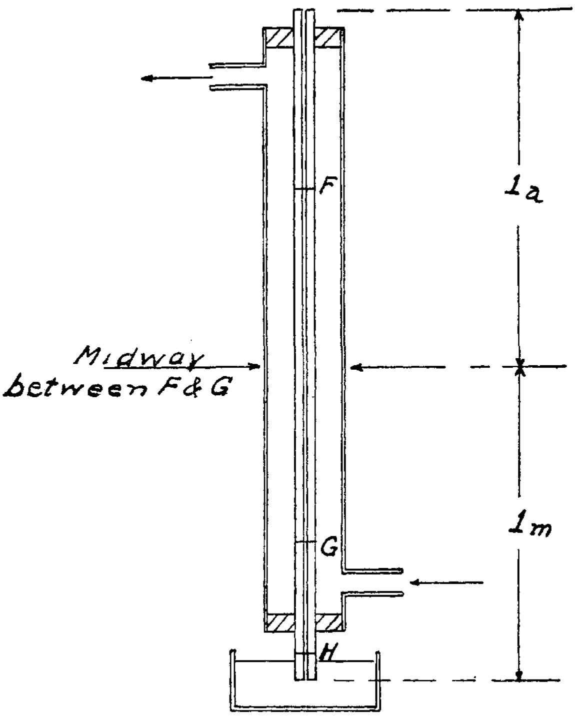

Fig. 2.

In the following mathematical discussion, all reasonable corrections will be taken into account and some of these will later be shown to be negligible. The following notation will be employed:

l = the distance of the level of the liquid in the capillary to the bottom of the tube at any time t.
l_0 = the distance of F from the bottom of the tube or the level at time t_0.
l_1 = the distance of G from the bottom of the tube or the level at time t_1.
r = the radius of the capillary.
R = the radius of the dish.
q = the cross-section of the capillary.
Q = the surface of the liquid in the dish.

$\beta = q/Q$.
h = the distance between the original surface of the liquid in the dish and the bottom of the tube.
c = the capillary head.
d = the variable depression of the surface of the liquid in the dish at time t from that of the original adjustment.
γ = the density of the liquid.
μ = the viscosity of the liquid.
g = the acceleration of gravity.
P = the pressure tending to change the velocity of the column of liquid.
a = the pressure due to the resistance of the air in the capillary tube.
v = the velocity of the capillary liquid level.

All quantities should preferably be expressed in gram-centimeter-second units. At any time t, the pressure P tending to change the velocity of the capillary column of liquid is given by the following equation:

$$\mathrm{P} = -\frac{8\mu l\,dl^{[1]}}{r^2dt} + \frac{0.005\,\gamma l v^2}{r} + \frac{\gamma v}{l} + c\gamma g + h\gamma g - (l+d)\gamma g + a.$$

Of these quantities $\frac{8\mu l\,dl}{r^2dt}$ and $l\gamma g$ are the largest, by far. Equating these alone we would obtain:

$$-\frac{8\mu l\,dl}{r^2dt} = l\gamma g$$

$$v = -\frac{dl}{dt} = -\frac{r^2\gamma g}{8\mu}.$$

Since $\frac{r^2\gamma g}{8\mu}$ is made up of constant quantities, v would be constant under this assumption. However, certain other factors cause v to vary slightly. The change in velocity of the column of liquid is small and since $\mathrm{P} = \mu l\,dv/dt$ the value of P will be entirely neglected.
Also,

$$Qd = q(l - h - c),$$
$$d = \beta(l - h - c),$$

where

$$\beta = \frac{q}{Q} = \frac{\pi r^2}{\pi \mathrm{R}^2} = \left(\frac{r}{\mathrm{R}}\right)^2$$

and

$$\gamma g\,[l - h - c][1 + \beta] - \frac{\gamma v^2}{2} - \frac{0.005\,\gamma l v^2}{r} - a = -\frac{8\mu l\,dl}{r^2dt}.$$

Both β and the quantity $\left(\frac{\gamma v^2}{2} + \frac{0.005\gamma l v^2}{r} + a\right)$ are small, and if $\left(h + c + \frac{v^2}{2g} + \frac{0.005\gamma l v^2}{gr} + \frac{a}{\gamma g}\right)$ be designated by z a variable, the equation may be simplified to the form

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[1] dl is itself negative since l diminishes.

$$\frac{\gamma g r^2(1+\beta)dt}{8\mu} = -\frac{l\,dl}{l-z}.$$

Integrating between the limits of t_0 and t_1, and l_0 and l_1, respectively,

$$\frac{\gamma g r^2(1+\beta)(t_1-t_0)}{8\mu} = l_0 - l_1 + z\ln\frac{l_0-z}{l_1-z};$$

let

$$t_1 - t_0 = \mathrm{T} \text{ and } l_0 - l_1 = \mathrm{L};$$

then,

$$\mu = \frac{\gamma g r^2 \mathrm{T}(1+\beta)}{8\left(\mathrm{L} + z\ln\frac{l_0-z}{l_1-z}\right)}$$

and

$$z = h + c + \frac{0.005\, l_m v_m^2}{gr} + \frac{v_m^2}{2g} + \frac{a}{g\gamma}$$

where

$$v_m = \mathrm{L}/\mathrm{T} \text{ and } l_m = {}^1/{}_2(l_0 + l_1).$$

It will be shown later, in a numerical example, that, with all other quantities given, the value of μ may be expressed as a linear function of z instead of a complex logarithmic function; $h + c$ is the larger part of z, but for accurate work other values should be taken into account.

In regard to $a/g\gamma$, the resistance head of the air in the capillary tube, this may be expressed in terms of γ_a, the density of the air; μ_a, the viscosity of the air; and l_a, the mean length of the air column in the capillary tube:

$$a = \frac{8\mu_a l_a v_m}{r^2} + \frac{0.005\gamma_a l_a v_m^2}{r} + \frac{\gamma_a v_m^2}{2} + \frac{0.5\,\gamma_a v_m^2}{2}$$

Of this expression, the three last quantities are small compared with the first, and μ_a may be expressed in terms of the absolute temperature Θ degrees centigrade by the simple relation $\mu_a = c\,\Theta$ where c is a constant and equal to 6.2×10^{-7} approximately,

$$\frac{a}{g\gamma} = \frac{8c\Theta l_a v_m}{g\gamma r^2}.$$

It is directed to place the tube perpendicularly. Should, however, the tube deviate by an angle α degrees, the measured value of μ would be too large by an amount which is a fraction of its true value $\times\ 0.00015\alpha^2$. If the value of g is only carried to three places, it is obviously inconsistent to take into account a deviation of one or two degrees.

Let us now take up a specific numerical example. A capillary tube of one meter in length has the following dimensions: $r = 0.03475$ cm., $r^2 = 0.001207$ sq. cm., $l_0 = 78.45$ cm., $l_1 = 21.37$ cm., $l_a = 50.09$ cm., $l_m = 49.91$ cm., and $\mathrm{L} = 57.08$ cm. Also $\mathrm{R} = 4.4$ cm.

$$\mu = \frac{gr^2(1 + \beta)\gamma T}{8\left(L + z\,ln\,\frac{l_0 - z}{l_1 - z}\right)},$$

wherein

$$\beta = \left(\frac{r}{R}\right)^2 = \left(\frac{0.03475}{4.4}\right)^2 = 0.0000624.$$

The effect of β can obviously be neglected. As γ and T will differ with different liquids, we will simply endeavor to express the coefficient of γT as a linear function of z. Δ are the differences in the coefficient per unit difference in z.

z.	$\frac{gr^2}{8\left[L + z\,ln\,\frac{l_0 - z}{l_1 - z}\right]}$.	Δ.
0	0.002593	0.000060
1	0.002533	0.000059
2	0.002474	0.000060
3	0.002414	0.000061
4	0.002353	0.000061
5	0.002292	....

Then within reasonable limits:

$$\frac{gr^2}{8\left[L + ln\,z\,\frac{l_0 - z}{l_1 - z}\right]} = 0.002593 - 0.000060\,z = 0.002593(1 - 0.0231z).$$

Now,

$$z = h + c + \frac{8c\Theta l_a v_m}{g\gamma r^2} + \frac{v_m^2}{2g}\left[1 + \frac{0.005(l_1 + l_0)}{r}\right].$$

If the temperature is 20° C., $\Theta = 293.7$. Also $g = 981$; then,

$$z = h + c + 0.062\,\frac{v_m}{\gamma} + 0.008\,v\ ^2.$$

When v_m is small, it can be neglected in commercial work, and if $h + c$ be made equal to 2.00 cm., then,

$$\mu = 0.00247\gamma T.$$

VISCOSITY OF SOLUTIONS OF THE METAL AMMONIA SALTS.

By Arthur A. Blanchard and Harold B. Pushee.

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In a previous article by one of the authors[1] it has been pointed out that in series of homologous liquid organic compounds, the viscosity is greater, the greater the molecular weight, and smaller, the greater the symmetry of the molecule. From this it has been assumed to be a general principle that an increase in viscosity is due to an increase in the size

[1] This Journal, 26, 1315 (1904).