

XCIH.—*The Viscosity of Ether at Low Temperatures.*

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AS explained in a former paper (J., 1924, 125, 726), we wished to know the rate of change of viscosity with temperature of certain organic liquids at low temperatures. The viscosity of acetone has been investigated (*loc. cit.*). The present experiments deal with the viscosity of ethyl ether over a temperature range of 0° to -110°, the measurements being made at 10° intervals.

\* These are the values of  $dE/dT$  at 25° determined graphically from the *E.M.F.*-temperature curve.

*Materials and Apparatus.*—"Anhydrous ether distilled over sodium" was treated with three successive portions of water to remove alcohol, dried over calcium chloride, then over sodium and distilled.

The Ostwald type of viscometer was used and the apparatus was set up as shown in Fig. 1. To prevent atmospheric moisture from condensing in the viscometer both ends were connected to calcium chloride drying tubes. Careful observation convinced us that no difference in the time of flow was caused by inserting these tubes. The required volume of ether was transferred from a supply flask by means of a syphon, one end of which passed into

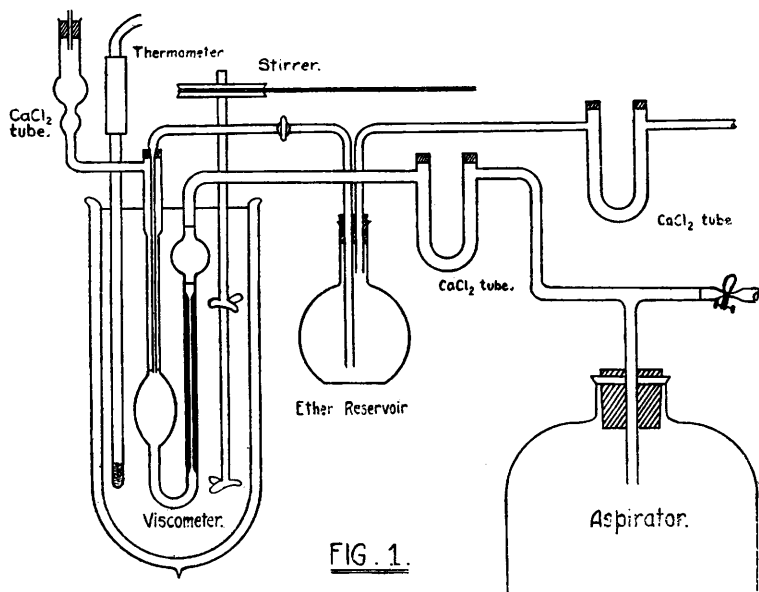


FIG. 1.

the larger end of the viscometer. The liquid was drawn up to the graduation above the bulb by means of an aspirator.

The cryostat consisted of a large unsilvered Dewar tube of about 10 cm. internal diameter which was almost filled with dry ether. For measurements from  $0^{\circ}$  to  $-75^{\circ}$  carbon dioxide snow was used to regulate the temperature, small amounts being added at intervals. Below  $-75^{\circ}$ , liquid air was used, and was handled after the manner devised by Henning (*Z. Instrument.*, 1913, 33, 33).

The temperatures were indicated by a platinum resistance thermometer of the bridge type, Leeds and Northrop Meter Bridge, No. 4201, being used, reading to 0.0001 ohm, corresponding to about  $0.01^{\circ}$ . The resistance element was contained in a quartz

tube which also contained gold compensating leads. The galvanometer was observed with lamp and scale. The resistance of the leads was eliminated by taking the mean of two readings at opposite positions of the commutator switch.

The thermometer was standardised by the Bureau of Standards in September 1923, and  $\delta$  in the Callendar equation was found to be 1.50. On installation in this laboratory, the thermometer was checked at 0°, and observations were made at the temperatures of the ether and solid carbon dioxide mixture (−78.34° at atmospheric pressure) and of boiling oxygen (−182.95°) to determine the deviation from the parabolic formula. At −78.34°, the thermometer read 0.04° low and at −182.95°, 1.77° low. These values correspond to Henning's corrections to the parabolic formula (*Ann. Physik*, 1913, **40**, 735), and these corrections were accordingly used. A resistance-temperature chart was plotted and used to obtain the temperatures at which the viscosity measurements were made.

At the higher temperatures, the cryostat could be controlled within 0.1°, and below −30° within 0.2°.

For measurements between 0° and −30°, a viscometer having a very fine capillary was used. The water rate at +20° was 385.2 sec., and the maximum time of flow of ether was 211.2 sec. at −32.1°. At the lower temperatures, a tube of somewhat larger bore was employed. The water rate in this case was 207.6 sec. at 0° and the maximum time of flow for the ether 341.2 sec. at −109.8°.

By means of a stop watch, the time of flow could be measured to within 0.2 sec.

*Results.*—The viscosities were calculated from the observed times of flow in the same manner as in the previous paper (*loc. cit.*) using the equation

$$\eta = \frac{dt}{d_w t_w} \left( \eta_w + \frac{m d_w V}{8 \pi l t_w} \right) \{ 1 - 0.000008(0 - t) \} - \frac{m d V}{8 \pi l t}$$

where  $\eta$  is the coefficient of viscosity of the liquid,  $V$  the volume of liquid which flows through the capillary in the time  $t$ ,  $d$  the density of the liquid,  $l$  the length of capillary, and  $m$  a constant = 1.12 (Boussinesq, *Compt. rend.*, 1891, **112**, 1099); those symbols with subscript  $w$  relate to water.

This expression includes corrections for kinetic energy and for the change in the dimensions of the instrument with temperature. The density values were taken from the work of Taylor and Smith (*J. Amer. Chem. Soc.*, 1922, **44**, 2456).

The results are given in Table I, in which the viscosities are

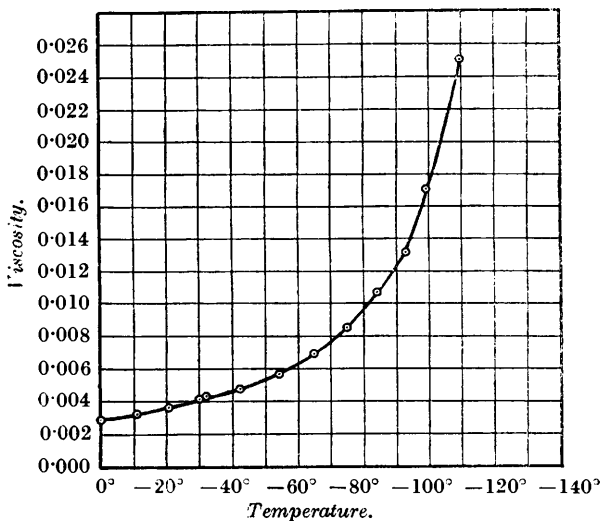
expressed in absolute units, that of water at 0° being taken as 0.01792. In most cases, they are given to four significant figures, which is the accuracy warranted by the time measurement and temperature control. Where the time of flow was relatively short or the agreement in a series of measurements not close, the results are given to only three significant figures. For completeness, the densities at the various temperatures are included in the table.

TABLE I.

Temp.	<i>d.</i>	$\eta$ .	Temp.	<i>d.</i>	$\eta$ .
0.0°	0.73629	0.002903	- 64.5°	0.80554	0.00693
-10.2	0.74750	0.003239	- 75.4	0.81695	0.008664
-20.2	0.75842	0.003636	- 84.4	0.82621	0.010747
-30.1	0.76906	0.004109	- 92.2	0.83426	0.01334
-32.1	0.77121	0.00420	- 99.8	0.84180	0.01708
-43.0	0.78289	0.00485	-109.8	0.85210	0.02514
-53.9	0.79443	0.00574			

Fig. 2 shows a plot of viscosity against temperature. As in the case of acetone, the curve rises very steeply at the lower tem-

FIG. 2.



peratures. To illustrate further this rapid rate of increase of viscosity, some values of the temperature coefficient have been calculated at each end of the temperature range. These are expressed in Table II as percentage values of the viscosity value at the end of each 10°-interval, *i.e.*,  $\alpha = 100(\eta_2 - \eta_1)/\eta_2(T_1 - T_2)$ .

TABLE II.

*Temperature Coefficients of Viscosity of Ether.* $\eta_1$  = viscosity at temp.  $T_1$ ;  $\eta_2$  = viscosity at temp.  $T_2$ .

$T_1$ .	$T_2$ .	$a$ .	$T_1$ .	$T_2$ .	$a$ .	$T_1$ .	$T_2$ .	$a$ .
0°	-10°	0.99	-40°	-50°	1.33	-80°	-90°	2.26
-10	-20	1.10	-50	-60	1.49	-90	-100	2.72
-20	-30	1.17	-60	-70	1.86	-100	-110	3.24
-30	-40	1.24	-70	-80	1.89			

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