Physics. — "*A Viscosimeter for volatile liquids*". By Prof. J. P. KUENEN and S. W. VISSER.

In determining the viscosity of a volatile liquid it is necessary to take the measurements in a closed viscosimeter. It is moreover desirable that the apparatus should be small, so that it can be easily handled and the temperature can be easily kept constant in all parts and that the liquid does not come in contact with mercury; the use of mercury at temperatures below its freezing point is in any case excluded.

In designing an apparatus that should fulfil these requirements, we based ourselves upon OSTWALD's viscosimeter [1]). His viscosimeter consists of a glass *U*-tube with one wide and one capillary arm; the wide tube has a bulb at the bottom and the capillary tube one at the top. The capillary tube opens at the bottom into a wider tube, which curves into the lower bulb. The time which the liquid takes to pass from the bulb through the capillary tube into the bottom bulb is observed. The experiment begins, when the liquid surface passes a contraction above the bulb, and ends, when it reaches the capillary tube. Before each determination the liquid is drawn up through the capillary or pressed up from the other side.

The first thing that we tried to do was to make this viscosimeter into a closed apparatus by joining the two branches of the *U*-tube above into an *O*; our intention was to collect the liquid every time in the upper bulb by simply turning the apparatus upside down.

This was not successful, as the liquid would not join in this position, some of it remaining in the wide tube above the capillary.

On this account the bottom reservoir was blown directly on to the capillary tube and the wide tube was then sealed to it in the immediate vicinity of the capillary tube. By this means the apparatus became more compact, as the curved portion of the wide tube disappeared.

Still liquid remained above the capillary tube, which prevented it readily flowing back. Moreover the time which the liquid took to pass through appeared to depend upon the way in which the liquid flowed out of the capillary tube along the walls of the bulb.

Finally, the capillary tube was provided with a continuation reaching nearly to the bottom of the bulb. When the apparatus is tur-

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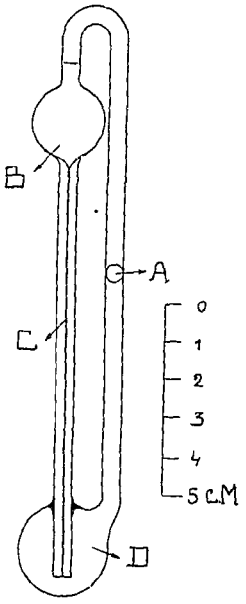
[1]) W. OSTWALD, Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen, p. 195, 1893.

ned upside down the extremity of the capillary tube projects above the liquid, and the liquid runs back without any difficulty. During the determination the liquid now flows out continually under the liquid surface. As the figure shows, in making this apparatus a hole is blown in the bulb; through this the capillary tube is introduced and the two are then sealed together. The final form of the apparatus is sufficiently clear from the figure. The liquid is introduced by the side tube A; after filling this is sealed off. In the inverted position the liquid fills the bulb B and part of the wide tube. If the viscosimeter is then turned up the liquid flows partly out of the wide tube to the bulb in which the capillary tube ends; the flow through the capillary tube begins at the same time and the meniscus passes along the upper curve; at the moment that the liquid passes a mark above the bulb B, a chronometer is set going. This mark takes the place of the contraction in OSTWALD's viscosimeter, where a drop of liquid is apt to collect. Through the capillary tube B is now emptied and the chronometer is stopped when the liquid dips into the capillary; when the apparatus is turned upside down, the bulb quickly empties itself.



The viscosimeter is placed in a wider tube, in which a bath of constant temperature is maintained; this tube is put up in such a way, that it can easily be turned upside down.

The whole apparatus is not more than 15 cm. long and by taking a finer capillary tube, or a larger bulb, it can be made even a little shorter.

No absolute determinations were made: the times of flow for various liquids were compared to that of water.

Some preliminary measurements were made with a larger experimental tube. In the final apparatus the dimensions used were such, that in determining the viscosity of normal butane a period of flow of at least three minutes could be reckoned upon. In the preliminary determinations a difficulty showed itself; in turning the apparatus over, the small bulb did not easily fill itself, on account of the great capillarity of water. With liquids such as ether and alcohol no difficulty was experienced. It seemed probable that determinations with water would be impossible with a much narrower tube. The apparatus was therefore standardized with water before the U-tube

was closed, while the apparatus was still used like OSTWALD's viscosimeter.

Influence of the quantity of liquid.

The time of flow depends upon the total amount of liquid in the apparatus. The more liquid there is, the higher the surface is in the lower bulb and the smaller is the pressure under which the liquid flows.

In OSTWALD's viscosimeter the same volume is taken of the various liquids: in this way the influence of the filling of the viscosimeter is eliminated. When the apparatus is filled with a liquid of high vapour-pressure or liquid gas, it is difficult to fulfil accurately the condition of equal volumes and it becomes necessary to investigate experimentally the influence of the volume of liquid. This can be done by measuring the time of flow of the same liquid, e.g. water, with various fillings. If we then know the weight of another liquid used and its specific gravity, we know the total volume. From the measurements previously made with water we can then find the time of flow for the same amount of water. From the ratio of the times of flow (t and t_w) the viscosity (η) is then calculated by the equation

$$\eta : \eta_w = dt : d_w t_w.$$

Influence of capillarity on the time of flow.

In consequence of the capillary action the pressure is not that of the mean difference of height, but is smaller. It is sufficient to make an estimation of this correction.

The capillary rise in a tube which is placed inside a second tube is given by the formula

$$h = \frac{2\sigma}{dg}\left(\frac{1}{r} - \frac{1}{R - r_1}\right),$$

in which σ represents the capillary constant, d the density, r the internal and r_2 the external radius of the first tube, R the internal radius of the second tube. By this formula the capillary rise was calculated for a series of positions of the liquid surface during the flow; further the volumes between the chosen positions were estimated and by means of these the times elapsing between the moments at which the positions were reached. The capillary ascension was then represented graphically as a function of the time and by means of the curve the mean rise was determined. This divided by the mean height of the liquid gives the correction for the capillarity in percentages.

For water at 0° with $\sigma = 75.5$ we found: mean capillary rise

0.034 cM.; the mean height of pressure is 11.6 cm., which gives for the correction 0.3%. For water at 30° with $\sigma = 71.0$ it is also 0.3%.

The capillary rise of water in the capillary at 0° was 8.0 cm., that of butane at the same temperature 2.4 cm.; the correction for the time of flow was therefore for butane 0.09 %: this may be regarded as constant in the field of temperature used.

REYNOLDS'S *critical velocity.*

To make sure that the velocity of the liquid remained below REYNOLDS'S critical value, an estimation was made. The volume of the upper bulb was about 3.5 ccm.; the capillary tube was fully 11 cm. long, the diameter of the capillary tube D was 0.038 cm., the viscosity η is about 0.002, the density d at 0° is 0.60, and the time of flow 300 seconds. With these data we find for $\frac{Ddv}{\eta}$ the value 117, which is far below REYNOLDS'S critical value (2000).

Determinations with water. Influence of the temperature.

The water used was doubly distilled. Great care was taken to keep it free from dust. It was renewed from time to time, which had however very little influence upon the results.

The viscosimeter was placed in a water-bath, which was kept in circulation by a rotating screw and at constant temperature by means of an adjustable number of platinum spirals through which an electric current was passed. Everything was bound round with cotton wool, which was partially removed at the beginning and end of the time determinations. The temperature was read every minute. The greatest difference during one observation was 0.07°, in the second series during 54 minutes it was 0.

During the measurements at 0° the viscosimeter stood in ice.

The two ends of the U-tube were covered by glass caps. After each determination the liquid was sucked up by a water pump.

I	temp.	time	II	temp.	time
31 Oct. '12	26.05	12 m. 11.4 s.	1 Nov.	26.48	12 m. 6.8 s.
	25.99	11.4		26.48	6.7
	26.03	11.6		26.48	6.2
	26.03	11.7		26.48	6.6
	26.05	11.2			
mean	26.03	731.5 s.		26.48	726.6 s.
Corrected for capillarity		729.3 sec.			724.4 sec.

III	temp.	time	IV	temp.	time
5 Nov.	0.00	24 min. 59.7 s.	7 Jan. '13	0.00	24 min. 57.2 s.
		59.7			57.2
		59.6			56.9
					57.0
					56.7
mean	0.00	1499.7 s.		0.00	1497.0 s.

Mean time of flow at 0° 1498.5 sec.

Corrected for capillarity 1494.0 sec.

Specific gravity of water at 0° 0.9999; at 26.48° 0.9967; at 26.03° 0.9968.

$$\eta_0 : \eta_{26.48} = 1493{,}9 \times 0.9999 : 724{,}4 \times 0.9967 = 2.069$$

$$\eta_0 : \eta_{26.03} = 1494.0 \times 0.9999 : 729.3 \times 0.9968 = 2.055$$

THORPE and RODGER [1]) give for the viscosity of water at

0°	0.01778
25°	0.00891
30°	0.007975

BINGHAM [2]) assumes the reciprocal of η as a linear function of the temperature. From THORPE and RODGER's figures follows:

at 0° $\frac{1}{\eta}$	= 56.2
„ 25°	112.0
„ 30°	125.4

From this follows:

at 26.48° $\frac{1}{\eta} = 115.97$ at 26.03 114.76

For the ratio of the viscosities at 26.48° and 0° we find from this:

$$\frac{\eta_0}{\eta_{26.48}} = \frac{115.96}{56.2} = 2.063$$

and

$$\frac{\eta_0}{\eta_{26.03}} = \frac{114.76}{56.2} = 2.042.$$

Our result at 26.48, 2.069, agrees with this to less than $^1/_3$ %, which may be regarded as sufficient. The agreement of the other figures is a little less satisfactory (about 0.7 %), which is probably the consequence of the less perfect equilibrium of temperature.

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[1]) THORPE and RODGER, On the relations between the viscosity of liquids and their chemical nature. Phil. Trans. 185 A, p. 449, 1894.

[2]) EUGENE C. BINGHAM and Miss J. PEACHY HARRISON, Viskosität und Fluidität. Z. f. Physik. Ch. 66, p. 1, 1909.

EUGENE C. BINGHAM Viscosity and Fluidity, A Summary of Results. Phys. Rev. XXXV, p. 407, 1912; Phys. Rev. (2) I, p. 96, 1913.

Influence of the total quantity of water.

All the determinations were made at 0°.

Small quantities of water were added or drawn off. After each series of determinations the viscosimeter was weighed with water and at the end the empty viscosimeter. From this follows the volume of water at each determination. Usually two measurements were made in each series. The greatest difference between them was 1.4 sec. in a total time of 25 minutes, a difference of less than 0.1 %.

The results were the following:

	weight of water.	time of flow.
10 Jan. 1913	3,24 gr.	1470,3 sec.
10 „ 1913	3,53 „	1480,2 „
7 and 8 Jan.	4,06 „	1497,0 „
8 „	4,41 „	1516,3 „
11 „	4,42 „	1517,2 „
9 „	4,88 „	1528,3 „
9 „	5.24 „	1544,4 „

Graphically represented these figures give a curve with two points of inflexion. If the bottom reservoir were cylindrical, the curve would be a hyperbola, as the product of pressure and time of flow is constant. The deviation from the hyperbola which the curve shows can be explained in every particular by the irregular form of the bottom reservoir (bulb with a tube sealed in at the side).

Determinations with Normal Butane.

The side tube A was connected to the reservoir which contained the butane prepared according to GRIGNARD's method [1]). After the viscosimeter had been pumped out, the butane was distilled over. For this purpose the lower bulb was cooled in a mixture of ice and salt. After cooling the side tube was sealed off.

The determinations above 0° were made in a water-bath, like the determinations with water. The glass jacket, which consisted of two coaxial tubes fastened by an india-rubber ring, was turned round with the viscosimeter. The latter was clamped between two corks in which a number of holes were bored. No determinations were made above 35°, as then the internal pressure may exercise a very uncertain influence upon the volume. The vapour-pressure of butane at 35° is 3.5 atmospheres.

At 0° the viscosimeter was placed in a wide test-tube which was closed by a cork. Two glass tubes, fastened with sealing wax into

[1]) J. P. KUENEN Comm. Phys. Lab Leiden, No. 125, p. 4. 1911.

a strip of cork, made two openings in the ice for the observation of the beginning and end points. The test-tube stood vertically in ice, in which also two tubes left room for the observations. After one determination the test-tube was lifted out of the ice, turned upside down and put back in its place again after the upper bulb was filled.

Finally a determination was made in a bath of boiling methyl chloride.

At the suggestion of Prof. KAMERLINGH ONNES a vessel of german silver was constructed for this, in which the viscosimeter was suspended in methyl chloride in such a manner that it could be turned round while inside and that the position of the liquid in the upper bulb could be observed. In the construction connections with substances like sealing wax which come into contact with the cold liquids have to be avoided. By this means we avoid contamination of the liquid and cracking or giving way of the connections which the cold might cause. All connections are therefore made in the lid of the vessel. The three projections are represented in fig. 1, 2 and 3 at $^1/_5$ of the actual size. The details in fig. 4—6 are actual size. The vessel consists of a neck H of circular section, a wide part, of elliptical section, E, and the bottom, which consists of a semicircularly bent strip R, the diameter of which is equal to the large axis of the ellipse and two curved sideplates P_1 and P_2 which complete the vessel. The vessel is provided with a number of strengthening rings v (necessary for working at low internal pressure) and stands in a box filled with cotton wool.

The viscosimeter hangs in the lower part of the vessel in a frame, BG, which is attached to a german silver tube TS, which projects above the vessel through an opening. This opening is made air-tight by a stuffing box PB (fig. 4). The tube has a bend by which the opening in the lid comes just outside the middle, which is necessary in view of the available space. This tube can be moved up and down in the stuffing box.

The viscosimeter can be turned round an axle. (fig. 5). The two tubes of the viscosimeter wound round with silk are clamped between two blocks B_1 and B_2 by two screws S_1 and S_2. B_1 is soldered to the axle. The axle is provided with a pulley K_1, which is worked by means of an endless spiral spring SV (fig. 1 and 2) by a second pulley K_2 in an air-tight box above the lid of the vessel; the axle projects outside through a stuffing box (see fig. 6). This pulley is raised up out of the way of the other parts on two tubes B_1 and B_2 soldered on to the cover, and through which the spiral spring runs.

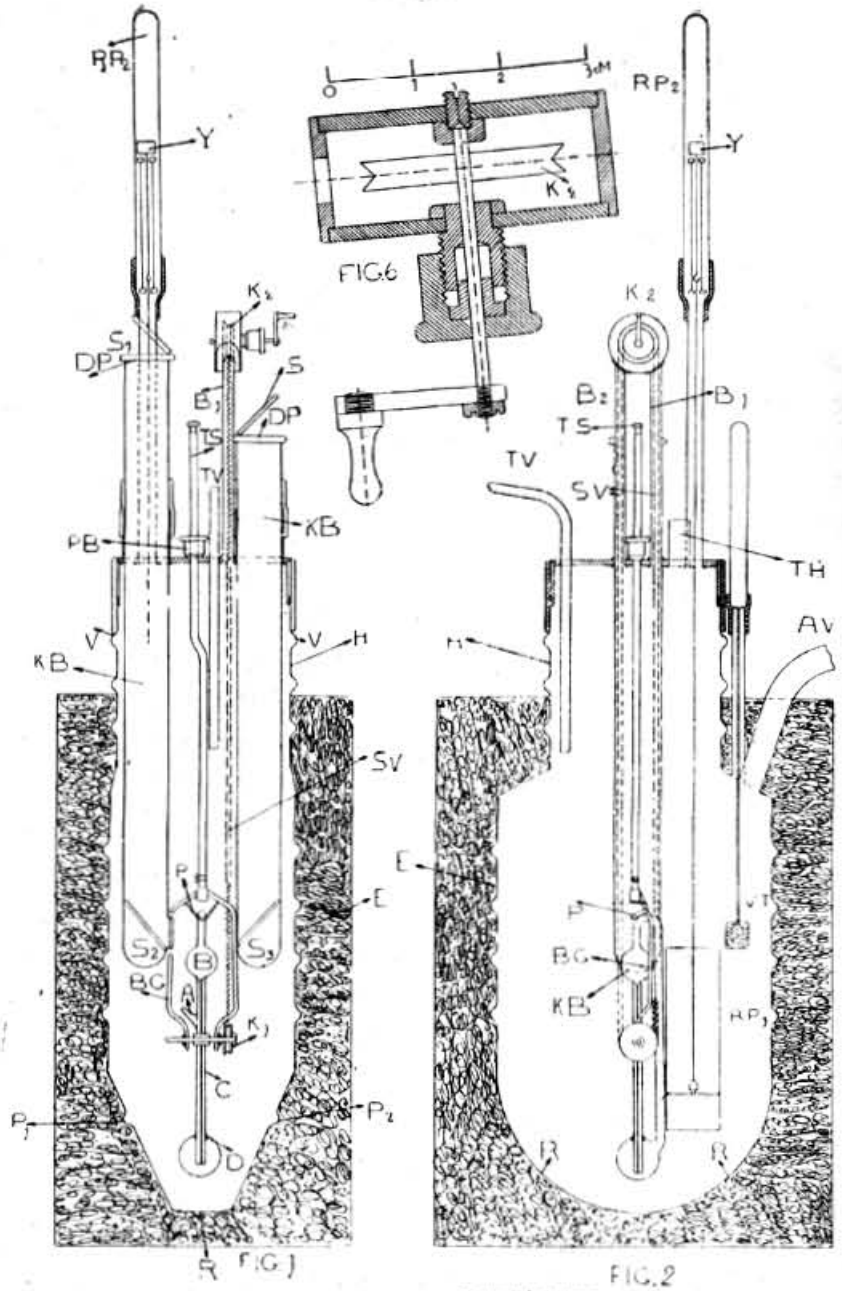

FIG.6

FIG.1

FIG.2

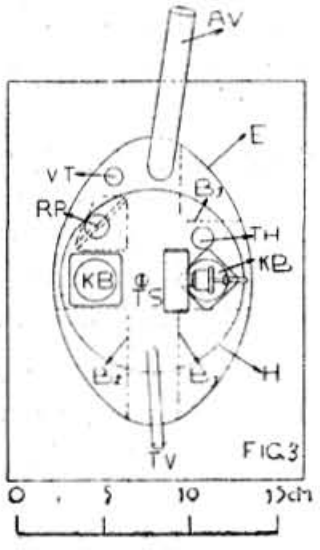

FIG.3

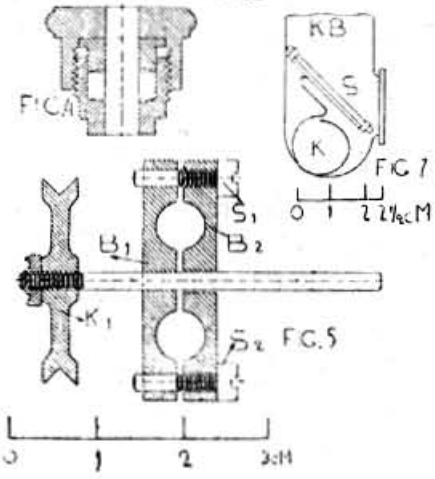

FIG.7

FIG.5

The frame BG is provided with a pall bound with silk, which prevents the viscosimeter going beyond the vertical position. The turning takes place in a plane parallel to the long axis of the ellipse.

For the observation of the viscosimeter there are two view tubes KB fastened into the cover in the direction of the short axis of the ellipse, which reach below the upper bulb, (fig. 1 and 3). (In fig. 2, part of one of the tubes is shown). These tubes are closed air-tight above the cover by thick glass covering plates DP. The light of a glowlamp is thrown upon the viscosimeter by the mirrors S_1 and S_2, it can be viewed by the mirrors S_3 and S (fig. 1). The mirrors S_2 and S_3 (fig. 7) are attached to a copper cross which is soldered on to a hoop of copper wire K, resting upon the bottom of the view-tube, and by which the mirrors can be easily adjusted. When they are in the right position the wire is fastened with paraffine. Opposite to the mirror the view-tubes have a side opening ground flat, on to which a covering glass is fastened with fish-glue. This connection remains firm even in liquid air. By this means the light falls through a plan-parallel layer of liquid, so that the bulb does not appear distorted. To avoid the glue being exposed to pressure, there are openings higher up in the view-tubes (fig. 1). By moving the viscosimeter a short distance up and down with the handle TS the mark above the bulb or the beginning of the capillary tube can be brought into view. The spiral spring remains tight the whole time.

In addition the vessel contains:

1°. an electro-magnetic stirring pump RP (fig. 2 and fig. 3; in fig. 1 a part of it). The iron core Y is moved up and down by an electro-magnet round the tube RP_2. The bottom of the cylinder RP_1 and the piston are provided with suitable valves, turning on an axis represented in fig. 3 by a double dotted line. The shape of the cylinder is here shown also.

2°. a floater which indicates the height of the boiling liquid.

3°. a platinum resistance-thermometer, of which only the tube sealed into the cover is shown: TH (fig. 2 and 3).

4°. a supply tube for the liquid TV, which is closed after filling.

5°. a tube AV to lead off the vapour, when working at low pressure.

6°. three tubes B_1, B_2 and B_3 (fig. 3) which fill up the superfluous space, to save liquid and trouble.

When tested this cryostat appeared to be in every way satisfactory, the distinctness of the readings left nothing to be desired. At the same time the volume of the butane was so much diminished by contraction that it was difficult to get sufficient pressure, when

the viscosimeter was turned round, to drive the remaining liquid out of the capillary. Only one determination was successful. We hope later on to be able to publish more extensive determinations at low temperatures.

Our results are given in the table.

The liquid-densities were measured by a dilatometer.

temp.	time	corrected	density	η
34.5°	235.5	235.2	0.556	0.00163
18.5°	258.5	258.2	0.577	176
0.0	291.8	291.5	0.601	207
—23.6	352.6	352.3	0.631	265

The method of calculation of η from the data is made clear by the following example.

The viscosimeter when filled weighed 16.78 gr. and empty 14.26 gr.

The weight of the butane was therefore 2.52 gr. with a volume of 4.20 ccm.

The time of flow of 4.20 ccm. water at 0° is 1504.0 sec. (according to table on page 80; of the butane 291.8 sec.

Corrected for capillarity these times become 1499.8 and 291.5.

$\eta_w = 0.01778$ [1]) therefore $\eta_b = 0.01778 \frac{0.601 \times 291\,5}{1498.9 \times 0.9999} = 0.00207$.

THORPE and RODGER (p. 590) give for the viscosity at the boiling point for

normal	pentane	$\eta \times 10^5$	200	isopentane	203
„	hexane		204	isohexane	205
„	heptane		199	isoheptane	198
„	octane		198		

As the boiling point of butane is just below 0°, the value we find for η corresponds well with that for the other hydrocarbons.

Physics. — *"On the law of the partition of energy."* III. By Prof. J. D. VAN DER WAALS Jr. (Communicated by Prof. J. D. VAN DER WAALS Sr.).

§ 9. *The distribution in configuration.*

In § 7 of my preceding note on this subject I have called attention to the deviations of BOLTZMANN's law for the distribution in configuration, but then I did not give a possible formula for it. Nor can I give a formula for the general case now. I will however try for

[1]) THORPE and RODGER l. c. p. 449.