

*The Measurement of the Viscosity of Gases at High Pressures.—The Viscosity of Nitrogen to 1000 Atms.*

By A. MICHELS and R. O. GIBSON.

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According to the classical kinetic theory the viscosity of a gas is independent of the density and increases with increasing temperature. The experimental verification of this at ordinary pressures provided "one of the most striking triumphs of the theory."\* The viscosity of liquids, however, has been shown to be very sensitive to small changes in density and to decrease with increasing temperature.†

It is thus of interest to measure the viscosity of gases under increasing pressures in order to follow its change as the density becomes comparable with that of liquids. But little experimental work has as yet been done along these lines. Warburg and Von Babo‡ and P. Phillips§ have determined the viscosity of carbon dioxide between 20° and 40° C. up to 120 atmospheres. Wildhagen|| made some measurements with air at room temperature up to 200 atmospheres, and Boyd¶ has worked with nitrogen, hydrogen and their mixtures at 30°, 50° and 70° C., up to 200 atmospheres.

With carbon dioxide the viscosity increases continuously with density to the higher viscosities typical of the liquid state. Below the critical temperature the viscosity-density curves for the liquid and the gaseous states are apparently continuous. The viscosities of the other gases also show a tendency to increase with increasing pressure.

A method is described in the present paper for the measurement of the viscosity of gases at high pressures and the results are given for nitrogen up to 1000 atmospheres. The measurements have not been carried to higher pressures owing to the lack of reliable compressibility data needed in the calculation of the results.

\* Jeans, "The Dynamical Theory of Gases," chap. 11, p. 294 (2nd ed., 1916).

† Cf. Hatschek, "The Viscosity of Liquids," chaps. 5 and 6 (1928).

‡ E. Warburg and L. von Babo, 'Wied. Ann.,' vol. 17, p. 390 (1882).

§ P. Phillips, 'Proc. Roy. Soc., A,' vol. 87, p. 48 (1912).

|| Max Wildhagen, 'Z. Angew. Math. Mechanik,' vol. 3, p. 181 (1923).

¶ J. H. Boyd, 'Phys. Rev.,' vol. 35, p. 1284 (1930).

*The Method.*

A method based on the transpiration of gas through a narrow capillary was chosen as the most suitable for adaptation to high pressures. Methods involving the damping of oscillations, measurement of torque, etc., would necessitate a knowledge of the change of the elastic constants of the suspensions with pressure before the absolute viscosities could be calculated.

The theory of the transpiration method, which is fully treated in the textbooks,\* leads to Poisseuille's relationship for a fluid

$$I = -\frac{\pi}{8\eta} r^4 \rho \frac{dp}{dl},$$

where  $I$  is the mass of fluid, of density  $\rho$  and viscosity  $\eta$  flowing in unit time through a capillary of radius  $r$  under a pressure gradient  $dp/dl$ .

Before integrating in the case of a gas, where  $\rho$  is not constant over the length of the capillary, this expression must be rearranged to give

$$-\frac{\pi}{8\eta} \rho dp = I \frac{dl}{r^4}.$$

If it is assumed that  $\eta$  and  $I$  are constant over the length of the capillary, then

$$-\frac{\pi}{8\eta} \int_{p_1}^{p_2} \rho dp = I \int_0^l \frac{dl}{r^4}.$$

This expression, which may be rewritten

$$I = -\frac{\pi}{8\eta} \frac{\int_{p_1}^{p_2} \rho dp}{\int_0^l \frac{dl}{r^4}} \quad (1)$$

shows what quantities must be considered in designing the apparatus.

According to the theory of Reynolds,† the pressure difference  $p_1 - p_2$  to avoid turbulent flow in the capillary must be comparatively small. A preliminary calculation showed that, for nitrogen, with a tube 80 cm. long and with a diameter of the order of 0.1 mm. pressure differences up to about 1 atmosphere could be used.

To obtain an accurate evaluation of  $\int_0^l \frac{dl}{r^4}$  it was advisable to use a glass capillary so that the variation of the diameter over the whole length could be measured. The use of a glass capillary necessitated the application of an

\* *E.g.*, Barr, "A Monograph on Viscometry," chap. 7 (1931).

† Barr, *loc. cit.*, p. 5, etc.



internal and an external pressure of the same order. This at the same time simplified the calculation of the effect of the pressure on the dimensions of the capillary.

The chief problem in designing the apparatus was to find a means of measuring accurately pressure differences of the order of  $\frac{1}{2}$  atmosphere at a high total pressure. In order that the method adopted may be readily understood, a description will be given in terms of the diagrammatic sketch (fig. 1).

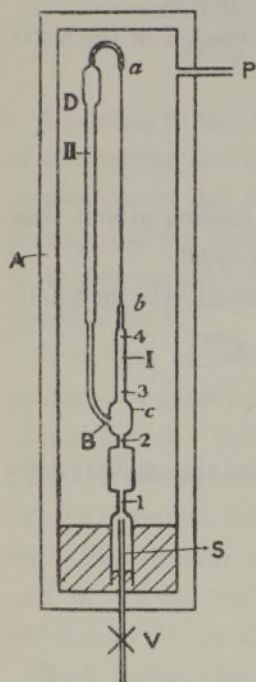


FIG. 1.

The viscometer consists of a glass apparatus with a capillary (*ab*). This is placed in a steel vessel (*A*) containing mercury at the bottom, the remainder being afterwards filled with oil. The glass apparatus is filled with the gas under investigation through the narrow steel tube (*S*).

A known pressure is applied to the oil at *P* causing the mercury to rise inside the glass. The height of the mercury can be indicated at four points (1, 2, 3, 4) where it makes contact with platinum wires sealed through the glass. The total mass of gas in the apparatus is first found from measurements of the pressure at each of the contacts 1 and 2 and from a knowledge of the volume between them, or that of the whole apparatus.

The pressure is then increased. When the mercury passes the glass junction (*B*) it compresses the gas in the two portions (*I* and *II*) independently, so long as the rate of increase of pressure is large compared with the rate of transpiration of the gas through the capillary. Under these conditions the mercury may rise to the positions *C* and *D* and, if the pressure is then maintained constant, the gas transpires through the capillary under this head of mercury.

The time taken for the mercury to rise between the contacts 3 and 4 is measured. As the volume between these contacts had been calibrated and the pressure is known, the mass of gas passing through the capillary in a known time is measured. The pressure difference is calculated from a knowledge of the dimensions of *I* and *II*, and of the total quantity of gas present in the apparatus. In this connection a knowledge of the compressibility isotherms of the gas is essential.

Any measurement can be repeated by lowering the pressure till the mercury

is below the junction B and then increasing it again rapidly. In order to work at higher or lower pressures, the pressure is decreased till the mercury is below the top of the tube (S), when gas can be added to or removed from the apparatus through the valve (V).

The dimensions of the glass work are so chosen that the mercury level in I after the rapid compression is some distance below the first time contact 3, so that there is sufficient time for the heat of compression to be dissipated before the run begins.

### *The Apparatus.*

*Dimensions of the Viscometer.*—A scale drawing of the viscometer in detail is given in fig. 2. The steel mantle is shown in 2A, the glass work in 2C, and the mounting for it in 2D.

In order to simplify the calculations, it was desirable that the tubes (I *b* and II *b*), in which the mercury rises and falls respectively during the viscosity run, should have as nearly the same diameter as possible. As tubes of 1 sq. cm. area guaranteed uniform better than 1 in 1000 could be obtained from Schott and Genosse of Jena, made of their standard 16 III glass, these were used for the two parts in question. Care was taken in sealing the contacts 3 and 4 to cause as little deformation as possible. In such tubes the correction for the capillary depression of the two mercury surfaces is less than 0.03 cm., so that the pressure difference must be of the order of 30 cm. to ensure an accuracy of 1 in 1000.

In order to obtain the same accuracy in the volume measurements, it was unnecessary for I *b* to have a volume greater than 16 c.c. as the mercury surface rises steadily to both contacts. It was found during the calibration that a reproducibility of at least 1 in 2000 could be obtained for this volume.

The greatest length of capillary that could conveniently be used was 80 cm. As has already been mentioned, the desirable diameter of this tube must be of the order of 0.1 mm., in the case of nitrogen, for the range of pressure differences to be used.

*The Calibration.*—The following dimensions of the apparatus were measured before assembling :

- (1)  $\int_0^l \frac{dl}{r^4}$  for the capillary.
- (2) The volumes I *b* between the platinum contacts and I *c* between the top contact and the entrance of the capillary.
- (3) The volume II from the end of the capillary (*a*) as a function of the distance from a fixed point on II *b*.
- (4) The volume between the contacts 1 and 2.



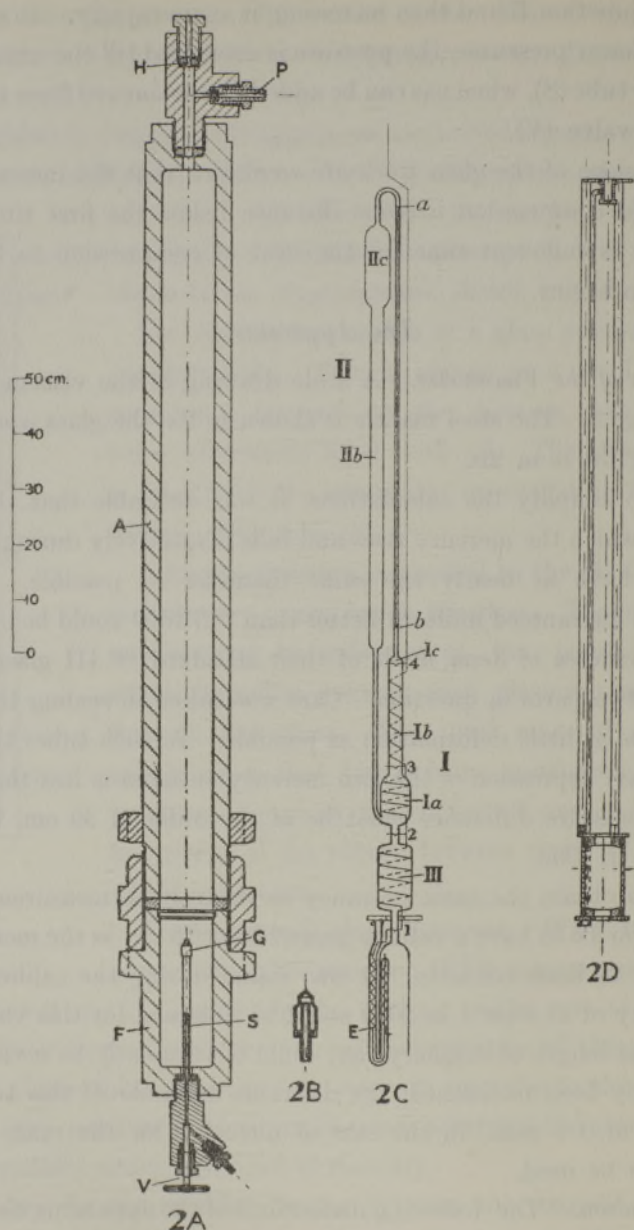


FIG. 2.

(1) A number of capillary tubes of Jena 16 III glass were examined for uniformity and roundness of bore and for freedom from subsidiary capillaries, and one of the required diameter was chosen. The ellipticity was less than 2 per cent., in which case it can be shown that the error in the viscosity by assuming the tube round is less than 0.1 per cent.\*

\* Barr, *loc. cit.*, p. 65.

The tube was calibrated by a procedure similar to that described by Schultze\* and by Fisher,† although the method of computation was somewhat different. The mean area was determined from the weight of a measured thread of mercury filling the length  $l$  of the tube to be used. In this way the mean square of the radius  $R^2$  was obtained, whilst the mean of  $r^4$  is required. The length of a small pellet of mercury was therefore measured in different positions in the tube.

As is shown by Fisher

$$\int_0^l \frac{dl}{r^4} = \frac{\pi^2}{V^2} \left[ \int_0^l \lambda^2 dl \right] \left[ \int_0^l \frac{dl}{\lambda} \right]^2$$

where  $\lambda$  is the length of the pellet and  $V$  is the volume of the length  $l$ .

Fisher evaluated this expression graphically, but if the lengths of the pellet have been measured end to end along the tube, then substitution of

$$V = \pi R^2 l$$

and

$$\lambda = \lambda_m + \Delta$$

(where  $\lambda_m$  is the mean length of the pellet and  $\Delta$  is the deviation from it) leads to

$$\frac{l}{R^4} \left\{ 1 + \frac{1}{\lambda_m^2 l} \int_0^l \Delta^2 dl \right\}^3.$$

Instead of obtaining the value of the integral  $\int_0^l \Delta^2 dl$  graphically, it is possible to replace it by the sum  $\Sigma \Delta^2 \lambda_m$ , assuming that the tube is homogeneous over the length of the small pellet. In this case the expression becomes

$$\frac{l}{R^4} \left( 1 + \frac{\Sigma \Delta^2}{\lambda_m l} \right)^3$$

or, on expanding and neglecting all terms of higher order than  $\Delta^2$

$$\frac{l}{R^4} \left( 1 + 3 \frac{\Sigma \Delta^2}{\lambda_m l} \right).$$

In order to be able to use this method, an arrangement was made by which the pellet could be adjusted in any position in the tube.

At the ends, where the capillary widens rapidly, the values of  $l/r^4$  were calculated for overlapping lengths and added to the value of  $\int_0^l \frac{dl}{r^4}$  obtained as above to give the final value to be used in equation (1) to calculate the viscosity.

\* H. Schultze, 'Ann. Physik,' vol. 5, p. 140 (1901).

† W. J. Fisher, 'Phys. Rev.,' vol. 28, p. 73 (1909).



(2) For the calibration of the volume I *c*, a length of glass tube, about 2 mm. in diameter, was etched with divisions at every  $\frac{1}{2}$  cm. and calibrated by weighing with mercury. Part of this tube was sealed on to the top of I *c* and part to the end of the capillary (*b*).

The volumes between the contacts and from the top contact to the divisions of the narrow tube, were obtained by the method already described by the authors in connection with the calibration of piezometers for isotherm measurements.\*

The volume from the divisions to the entrance of the capillary was measured in a similar way. The 2 mm. tubes were joined together amongst the divisions, so that the volume from the top contact to the entrance of the capillary could be calculated, the uncertainty due to the fuse being less than the required accuracy.

(3) The tube II *b* was supplied etched at every centimetre and the cross section of this tube was controlled by weighing with mercury. The volume II *c* from a fixed mark on II *b* to the entrance of the capillary was calibrated by a similar process to I *c*, using a length of 2 mm. tube.

(4) Volume III between the contacts 1 and 2 was obtained by the same method as I *b*.

*Further Details of the Apparatus.*—Two precautionary details of the apparatus may be particularly mentioned. During the working of the apparatus the mercury was, of course, above the top of the steel tube (S). In this case there was a chance of gas, trapped in the tube and valve, being displaced by mercury when the pressure was raised and so altering the amount present during the measurements. To avoid this a steel hood (G), shown on a larger scale in fig. 2B, was fitted to the top of the tube. The volume of the hood was such that, whatever the position of the mercury, none could enter the tube.

It has already been mentioned that when the apparatus was filled with gas the mercury level must be brought below the top of the tube (S). In order to ensure that the mercury was in the correct position, and not too high or too low, the safety device shown at (E), fig. 2c, was fitted. This consisted of a glass U-tube containing a resistance wire with two platinum points sealed through it in such positions that the mercury level was correct if it lay between them.

All the platinum contacts in the apparatus were linked together with resistances to form one arm of a Wheatstone's bridge in a manner similar to that

\* A. Michels and R. O. Gibson, 'Ann. Physik,' vol. 87, p. 850 (1928).

already described by the authors.\* When the mercury reached a contact the bridge was disturbed and the fact indicated by the deflection of a galvanometer.

*Assembling of the Apparatus.*—The first stage was carried out as follows: the lower part of the steel vessel (F) was fitted with the valve (V), the tube (S) and hood (G), and filled with the required amount of mercury. The cleaned and dried glass work fitted with the safety contact tube and mounted in the brass frame (fig. 2D) was then placed in the lower vessel (F).

In order to appreciate the next stage it may be remembered that, as has already been mentioned in the description of the method, during the measurements the pressure was applied at (P). This pressure was measured and kept constant by means of a pressure balance similar to that described by one of the authors.†

The whole system from the piston of the balance to the surface of the mercury was filled with oil, of which the density was known as a function of pressure and temperature. It was therefore possible to calculate the pressure at any point in the oil from a knowledge of the pressure at the balance and the height of the point with reference to the piston. As, however, the pressure on the gas was required, the correction for the mercury head inside the viscometer had to be determined.

For this purpose a wide glass tube was fitted over the viscometer, mounted as described above, and a gas-tight joint made to the vessel (F). Connections were made from the glass tube, and the valve (V) to the two sides of a differential mercury manometer and to vacuum pumps. The inside and outside of the viscometer were then evacuated at the same time. The valve (V) was then shut and air admitted to the outer tube, forcing the mercury up inside the viscometer. When the mercury touched any of the contacts the pressure difference on the manometer was read with a cathetometer. This gave the desired mercury head. The relative heights of the different parts of the apparatus needed in the calculations were measured at the same time with the cathetometer.

The outside tube was then again evacuated until the mercury level inside the viscometer was below the hood (G). The apparatus was filled with nitrogen through the valve (V) until the pressure was about 90 cm. of mercury, air being admitted to the outer tube at the same rate. The outer glass tube was then removed and the steel jacket (A) placed in position. The insulated electrical lead at (H) was fitted and the system filled with oil.

\* *Loc. cit.*

† A. Michels, 'Ann. Physik,' vol. 72, p. 285 (1923); vol. 73, p. 579 (1924).



The completely assembled pressure vessel was placed in a closed thermostat and the connections made to the press. The thermostat was double-walled and in it the temperature could be maintained constant to  $\pm 0.001^\circ \text{C}$ . for considerable periods of time.

The temperatures were measured with mercury thermometers divided in  $0.01^\circ$ , which were completely immersed in the thermostat and read by means of a periscopic device. This arrangement avoided the stem correction and made it possible to control the temperature equilibrium between different points in the thermostat.

#### *Experimental Procedure.*

With the mercury level between the two safety contacts, pure nitrogen from a cylinder was admitted to the apparatus by the valve V which could be controlled through the bottom of the thermostat. The gas was passed through a copper helix cooled in solid  $\text{CO}_2$  and alcohol before entering the apparatus.

The valve V was then shut and pressure applied at P until the mercury reached the first contact where the pressure was measured with the balance. The pressure was increased again and the measurement repeated at the second contact. Sufficient data were thus obtained to calculate the total amount of gas in the apparatus. It may be noted that the volume between the contacts was about half of the total volume and, therefore, that the accuracy of the measurement was only about half that of the available isotherm data.

After the normal volume had been measured, the pressure was rapidly increased to give about the desired pressure difference and then kept constant with the help of the pressure balance whilst the gas transpired through the capillary. After a lapse of 30 to 60 minutes the mercury reached contact 3, causing a Weston galvanometer relay, placed in the Wheatstone's bridge circuit, to start a stop-clock. When the mercury reached contact 4 the same relay stopped the clock. The time was thus measured for the mercury to drive a known amount of gas through the capillary.

The clock could be read to one-fifth second, and, when not in use for measurements, was checked against the time signal broadcast from Nauen. The clock lost about 6 seconds in 24 hours, a correction which could be neglected.

The nitrogen used in these measurements was the purest obtainable from Hoek & Son, of Schiedam. The makers guaranteed it free from oxygen and to contain less than 0.01 per cent. of impurities.

*Calculation.*

In order to calculate the viscosity from the experimental data by means of the expression

$$I = - \frac{\pi}{8\eta} \frac{\int_{p_1}^{p_2} \rho \, dp}{\int_0^l \frac{dl}{r^4}} \quad (1)$$

given in the introduction, it is necessary to integrate to give

$$M = \int_0^T I \, dt = \int_0^T \frac{\pi}{8\eta} \frac{- \int_{p_1}^{p_2} \rho \, dp}{\int_0^l \frac{dl}{r^4}} \quad (2)$$

where  $M$  is the total mass of gas passing through the capillary in time  $T$ .

This, however, involves a knowledge of the pressures on the gas in both parts of the apparatus and therefore, also, the densities as a function of time. This function is so far unknown. The total mass of gas  $M$  transpiring through the capillary is also difficult to calculate as the pressure in volume (I) varies with time.

As the total pressure is kept constant during a run by means of the pressure balance, the pressure at a given level in the mercury remains constant. Under these conditions the pressure on the gas, and therefore the density on both sides of the apparatus, will be a simple function of the heights of the mercury above this level. The right-hand side of expression (2) may therefore be expressed in terms of these two heights, or in terms of the height of the mercury on one side above a fixed level and the pressure difference ( $\Delta p$ ) corresponding to the mercury head. There is a connection between these two variables from the fact that the total quantity of gas in the system remains constant.

In the present calculation the level of contact (4) has been taken as the fixed level and the distance,  $n$ , an unknown function of time, measured down from it. Equation (1) then has the form

$$I = \frac{1}{\eta} f_1(n). \quad (3)$$

Now

$$I = - \frac{dQ}{dt} = - \frac{dQ}{dn} \cdot \frac{dn}{dt}, \quad (4)$$



where  $Q$  is the mass of gas in volume (I) which may be expressed as a function of  $n$  giving

$$I = f_2 \left( n, \frac{dn}{dt} \right). \quad (5)$$

The elimination of  $I$  between (3) and (5) gives

$$f_3 \left( n, \frac{dn}{dt}, \eta \right) = 0. \quad (6)$$

This on integration gives an expression in terms of  $\eta$ ,  $\lambda$  and  $T$ , from which  $\eta$  may be calculated from the experimental data,  $\lambda$  being the distance between the contacts 3 and 4, and  $T$  the total time of flow.

The following relationships between the pressures and volumes which are needed in the calculation may first be written:—

$$(\alpha) \quad p_1 = p + n\kappa,$$

where  $p_1$  is the pressure in the gas in (I) and  $p$  the constant pressure in the mercury at the level of contact (4).  $\kappa$  is a factor introduced to change a pressure unit of 1 cm. of mercury into atmospheres.

$$(\beta) \quad p_2 = p_1 - \Delta p,$$

where  $p_2$  is the pressure in the gas in volume II and  $\Delta p$  the pressure difference corresponding with the mercury head.

$$(\gamma) \quad V_1 = V_{(Ic)} + an,$$

where  $V_1$  is the volume from the mercury level in (I) to the entrance of the capillary,  $V_{(Ic)}$  the volume from the top contact (4) to the entrance of the capillary and  $a$  the cross section of the tube (I  $b$ ).

$$(\delta) \quad V_2 = V_{(IIc)} + b \left( H + n - \frac{1}{\kappa} \Delta p \right),$$

where  $V_2$  is the volume above the mercury in (II),  $V_{(IIc)}$  the volume from the fixed mark at the top of the tube (II  $b$ ) to the capillary,  $H$  the distance from contact (4) to this mark on (II  $b$ ) and  $b$  the cross section of the tube.

$$(\epsilon) \quad \rho = \rho_0 \frac{p}{f(p)},$$

where  $\rho$  is the density and  $f(p)$  the experimental value of  $pv$  of the gas expressed in Amagat units (*i.e.*,  $p$  in international atmospheres and  $v$  in volumes of gas at  $0^\circ$  C. and 1 atmosphere).

The accuracy of the method is limited by the knowledge of these isotherms as is mentioned on p. 303.

$$(\zeta) \quad Q = \rho_1 V_1 = \rho_0 \frac{p_1}{f(p_1)} V_1 = \rho_0 \frac{1}{f(p_1)} (p + n\kappa) (V_{(c)} + an).$$

It is now possible to substitute in equation (1) and, by using relation ( $\varepsilon$ ) to obtain

$$I = -\frac{\pi}{8\eta} \rho_0 \frac{\int_{p_1}^{p_2} \frac{p \, dp}{f(p)}}{\int_0^l \frac{dl}{r^4}}. \quad (7)$$

If it can be assumed that, within the desired limits of accuracy,  $f(p)$  is constant over the pressure range ( $p_1 - p_2$ ) this may be written

$$I = -\frac{\pi}{8\eta} \frac{\rho_0}{f(p)} \int_0^l \frac{dl}{r^4} \cdot \frac{1}{2} (p_2^2 - p_1^2), \quad (8)$$

or, with the help of the results given in the note (p. 300)

$$I = \frac{\pi \rho_0}{16\eta f(p)} \int_0^l \frac{dl}{r^4} \cdot (K + Ln + Mn^2). \quad (3^*)$$

Substitution of relation ( $\zeta$ ) in equation (4) gives

$$I = -\frac{\rho_0}{f(p)} (ap + \kappa V_{(c)} + 2a\kappa n) \frac{dn}{dt}. \quad (5^*)$$

Elimination of  $I$  between ( $3^*$ ) and ( $5^*$ ) gives

$$\frac{\pi}{16\eta} \int_0^l \frac{dl}{r^4} \cdot (K + Ln + Mn^2) + (ap + \kappa V_{(c)} + 2a\kappa n) \frac{dn}{dt} = 0, \quad (6^*)$$

which may be written

$$\frac{\pi}{16\eta} \int_0^l \frac{dl}{r^4} \, dt = -\frac{ap + \kappa V_{(c)} + 2a\kappa n}{K + Ln + Mn^2} \, dn. \quad (9)$$

Integration of (9) gives

$$\eta = \frac{\pi}{16} \frac{\int_0^l \frac{dl}{r^4}}{\int_0^A \frac{ap + \kappa V_{(c)} + 2a\kappa n}{K + Ln + Mn^2} \, dn} \quad (10)$$

which can be evaluated.



*Corrections.*

The corrections for calculating the pressure from the experimental data of the pressure balance are applied in the manner described in the paper previously quoted.\* These include the corrections for the thermal expansion and com-

\* *Loc. cit.*

*Note.*—The required relationship between  $\Delta p$  and  $n$  and therefore the expression of  $-(p_2^2 - p_1^2)$  in terms of  $n$  for substitution in equation (6) may be obtained in the following way:—

The normal volume,  $N$  (*i.e.*, the volume at N.T.P.) of the gas in the apparatus can be expressed as the sum of the normal volumes in the two parts I and II

$$N = \frac{p_1 V_1}{f(p_1)} + \frac{p_2 V_2}{f(p_2)}.$$

As it is assumed that  $f(p_1) = f(p_2)$ , then substitution of the expressions  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  for  $p_1$ ,  $V_1$ ,  $p_2$  and  $V_2$  gives

$$Nf(p) = (p + \kappa n)(V_{(Ic)} + an) + (p + \kappa n - \Delta p) \left\{ V_{(IIc)} + \frac{b}{\kappa} (\kappa H + \kappa n - \Delta p) \right\}$$

or

$$(\kappa n - \Delta p)^2 + A(\kappa n - \Delta p) + X + Yn + Zn^2 = 0,$$

where

$$X = \frac{\kappa}{b} [p(V_{(Ic)} + V_{(IIc)} + bH) - Nf(p)],$$

$$Y = \frac{\kappa}{b} [\kappa V_{(Ic)} + ap],$$

$$Z = \kappa^2 \frac{a}{b},$$

$$A = \frac{\kappa}{b} \left[ \frac{b}{\kappa} p + V_{(IIc)} + bH \right].$$

Solution of the quadratic gives

$$\Delta p - \kappa n = \frac{A}{2} \pm \frac{1}{2} \sqrt{A^2 - 4(X + Yn + Zn^2)},$$

which may be expressed in a form more adaptable to numerical calculation by first expanding to give

$$\Delta p - \kappa n = \frac{A}{2} - \frac{1}{2} \sqrt{A^2 - 4X} + \frac{Yn + Zn^2}{\sqrt{A^2 - 4X}} + \frac{Y^2 n^2}{(\sqrt{A^2 - 4X})^3} + \dots,$$

which on further expansion gives

$$\begin{aligned} \Delta p - \kappa n = & A \left\{ \left( \frac{X}{A^2} \right) + \left( \frac{X}{A^2} \right)^2 + 2 \left( \frac{X}{A^2} \right)^3 + \dots \right\} \\ & + \frac{Y}{A} \left\{ 1 + 2 \left( \frac{X}{A^2} \right) + 6 \left( \frac{X}{A^2} \right)^2 + \dots \right\} n \\ & + \left[ \frac{Z}{A} \left\{ 1 + 2 \left( \frac{X}{A^2} \right) + 6 \left( \frac{X}{A^2} \right)^2 + \dots \right\} + \frac{Y^2}{A^3} \left\{ 1 + 6 \left( \frac{X}{A^2} \right) + 30 \left( \frac{X}{A^2} \right)^2 + \dots \right\} \right] n^2. \end{aligned}$$

Now

$$-(p_2^2 - p_1^2) = \Delta p (2p + 2\kappa n - \Delta p),$$

pressibility of the oil and mercury columns. There are, however, two corrections to which special attention must be drawn.

- (1) *Hydrostatic Head of Gas*.—At high pressures the density of the gas is no longer negligible compared with that of mercury. The effective driving force  $\Delta p_{eff}$  on the gas passing through the capillary will be correctly given by an expression which calculation shows to be

$$\Delta p_{eff} = \left( \frac{d - \rho}{d} \right) \cdot \Delta p,$$

where  $\Delta p$  is the head of mercury and  $\rho$  and  $d$  the densities of the gas and mercury respectively. The density of the gas  $\rho$  may be assumed constant throughout the apparatus. Therefore the only correction for gas density is the factor  $(d - \rho)/d$  which is constant for any given measurement and can be introduced into equation (8).

- (2) *The Hagenback-Couette Corrections*.—It is generally accepted that the slip of the gas along the wall of the capillary can be neglected except for very low pressures. Part of the effective pressure difference, however, is used to accelerate the gas on entering the capillary and along its length on account of the expansion, and, also, to overcome the extra friction in the first part of the capillary before the flow has become laminar.

These corrections, known as the Hagenback and Couette corrections, have recently been discussed by Erk.\* He has shown that it is necessary to add to the viscosity a correcting term

$$- \frac{\rho_1 V}{8\pi T l} \left( m + \ln \frac{p_1}{p_2} \right),$$

where  $m$  is a constant of value 1.12 and  $V$  the volume of gas of density  $\rho_1$  passing through the capillary in time  $T$ .

which on substitution for  $(\Delta p - \kappa n)$  gives

$$- (p_2^2 - p_1^2) = K + Ln + Mn^2,$$

where

$$K = (2p - A) A \left\{ \left( \frac{X}{A^2} \right) + \left( \frac{X}{A^2} \right)^2 + 2 \left( \frac{X}{A^2} \right)^3 + \dots \right\} + X,$$

$$L = 2p\kappa + (2p - A) \frac{Y}{A} \left\{ 1 + 2 \left( \frac{X}{A^2} \right) + 6 \left( \frac{X}{A^2} \right)^2 + \dots \right\} + Y,$$

$$M = \kappa + (2p - A) \left[ \frac{Z}{A} \left\{ 1 + 2 \left( \frac{X}{A^2} \right) + 6 \left( \frac{X}{A^2} \right)^2 + \dots \right\} + \frac{Y^2}{A^3} \left\{ 1 + 6 \left( \frac{X}{A^2} \right) + 30 \left( \frac{X}{A^2} \right)^2 + \dots \right\} \right] + Z.$$

\* S. Erk, 'Z. Tech. Phys.,' vol. 10, p. 453 (1929).



This expression is deduced on the assumption that the pressures  $p_1$  and  $p_2$  and, therefore, the rate of flow remain constant. In the present case where this assumption is not true, it is justifiable to replace the constant rate of flow by the average value, as the correction is never larger than 0.5 per cent. The term  $\ln p_1/p_2$  involves a very small correction with the present apparatus, as at low pressures  $\rho_1 V$  is very small and the whole expression negligible, and at high pressures, when it can be written as approximately  $\Delta p/p$ , it is small with respect to  $m$ .

### Results.

The results of the measurements made with nitrogen at 25°, 50° and 75° C. up to 1000 atmospheres, are given in Tables I to III. The pressures are given in international atmospheres, the densities in Amagat units ( $D_A$ ) and in grams per cubic centimetres ( $\rho$ ) and the viscosities in c.g.s. units.

Table I.—Viscosity of Nitrogen at 25° C.

Filling and run.		$p_{\text{atm.}}$	$D_A$	$\rho$	$\eta \cdot 10^6$	$\eta/\rho$
1	II	10.95	10.05	0.01257	179.4	0.01427
	V	12.71	11.67	0.01460	179.6	0.01231
	III	13.57	12.46	0.01558	179.9	0.01154
	IV	14.44	13.27	0.01659	180.0	0.01085
	I	15.33	14.08	0.01760	180.2	0.01024
13	III	15.36	14.11	0.01764	180.5	0.01023
2	III	48.22	44.37	0.05549	186.4	0.003360
	II	57.59	52.97	0.06624	188.4	0.002844
	I	66.98	61.55	0.07700	190.8	0.002479
3	I	92.31	84.46	0.1056	198.1	0.001876
	II	104.5	95.19	0.1190	200.5	0.001685
	III	118.6	107.5	0.1345	204.9	0.001524
	IV	132.7	119.6	0.1496	209.4	0.001400
	III	165.5	146.7	0.1834	219.9	0.001199
4	IV	174.9	154.1	0.1927	223.1	0.001158
	II	189.0	164.9	0.2063	228.2	0.001106
	I	212.4	182.3	0.2300	236.7	0.001038
6	IV	277.7	226.0	0.2826	258.3	0.000914
	III	320.4	251.2	0.3141	276.4	0.000880
7	I	364.6	274.8	0.3436	294.1	0.000856
6	VI	364.6	274.7	0.3436	294.8	0.000858
	I	387.6	286.1	0.3578	304.0	0.000850
	V	430.2	305.5	0.3821	319.4	0.000836
7	II	430.2	305.6	0.3821	320.9	0.000840
6	IIb	473.1	323.1	0.4041	337.4	0.000835
7	III	476.1	324.3	0.4055	338.5	0.000835
	IV	541.7	348.2	0.4354	363.4	0.000834
8	I	541.7	348.2	0.4354	365.4	0.000839
7	V	587.7	363.6	0.4548	382.0	0.000840
	VI	630.3	376.6	0.4710	397.4	0.000844
8	II	630.4	376.7	0.4711	399.7	0.000848
	III	742.0	406.5	0.5084	440.4	0.000866
	IV	854.1	432.4	0.5408	480.2	0.000888
	V	965.7	454.5	0.5684	520.5	0.000916

Table II.—Viscosity of Nitrogen at 50° C.

Filling and run.		$p_{\text{atm.}}$	$D_A$	$\rho$	$\eta \cdot 10^6$	$\eta/\rho$
13	I	15.37	12.98	0.01623	191.3	0.01179
12	I	57.60	48.37	0.06049	198.1	0.003274
11	II	104.5	86.59	0.1083	208.8	0.001928
10	I	212.4	165.3	0.2067	237.3	0.001148
9	VI	320.4	229.9	0.2875	273.7	0.000952
	IV	430.2	282.1	0.3528	312.9	0.000887
	V	541.7	324.1	0.4053	350.9	0.000866
8	IX	630.4	352.6	0.4409	378.6	0.000859
	VI	742.1	382.7	0.4786	416.5	0.000870
	VIII	854.1	409.2	0.5117	455.0	0.000889
	VII	965.8	432.1	0.5404	491.3	0.000909

Table III.—Viscosity of Nitrogen at 75° C.

Filling and run.		$p_{\text{atm.}}$	$D_A$	$\rho$	$\eta \cdot 10^6$	$\eta/\rho$
13	II	15.37	12.03	0.01505	202.2	0.01344
12	II	57.61	44.71	0.05591	208.8	0.003734
11	I	104.5	79.72	0.09970	217.5	0.002181
10	III	212.4	152.1	0.1902	240.8	0.001266
	II	320.3	212.6	0.2659	274.6	0.001033
9	III	430.2	262.8	0.3287	307.9	0.000937
	II	541.7	304.3	0.3806	342.6	0.000900
	I	630.3	332.5	0.4158	370.1	0.000890
8	XII	742.0	362.8	0.4537	401.6	0.000885
	XI	854.1	389.2	0.4867	436.2	0.000896
	X	965.7	412.1	0.5153	470.3	0.000913

In the calculations use was made of the compressibility isotherms given by Bartlett\* in his critical survey and estimated by him to have an accuracy not greater than 0.1 per cent. Calculation shows that this figure involves an accuracy of 0.15–0.50 per cent. in the viscosity, according to the size of the mercury head in different runs with any filling. In the experiments it was found that the maximum variations between measurements with different fillings and the same pressure, and therefore with different mercury heads, was 0.50 per cent. On the other hand, with the same filling and the same mercury head the reproducibility was never worse than 1 in 5000.

The results may be extrapolated to 1 atmosphere and reduced to 0° C. by

\* E. P. Bartlett, 'J. Amer. Chem. Soc.,' vol. 49, pp. 694, 1956 (1927); vol. 50, p. 1284 (1928); vol. 52, p. 1363 (1930).



means of Sutherland's relationship, using the value of the constant = 118 given by C. J. Smith\*

$$\begin{array}{lll} 25^{\circ} & \eta_{1 \text{ atm.}} = 177.5 \times 10^{-6} & \eta_0 = 165.6 \times 10^{-6} \\ 50^{\circ} & \eta_{1 \text{ atm.}} = 189.6 & \eta_0 = 166.2, \\ 75^{\circ} & \eta_{1 \text{ atm.}} = 200.0 & \eta_0 = 165.6 \end{array}$$

The values reduced to  $0^{\circ}$  compare favourably with that given by Smith,  $\eta_0 = 166.5 \times 10^{-6}$ , and those by other observers.

### Discussion.

The values of the viscosity are plotted against the pressure in fig. 3. It will be seen that at low pressures the viscosity has a positive temperature coefficient  $(\partial\eta/\partial T)_p > 0$ , whilst at higher pressures, as is the case for liquids  $(\partial\eta/\partial T)_p < 0$ .

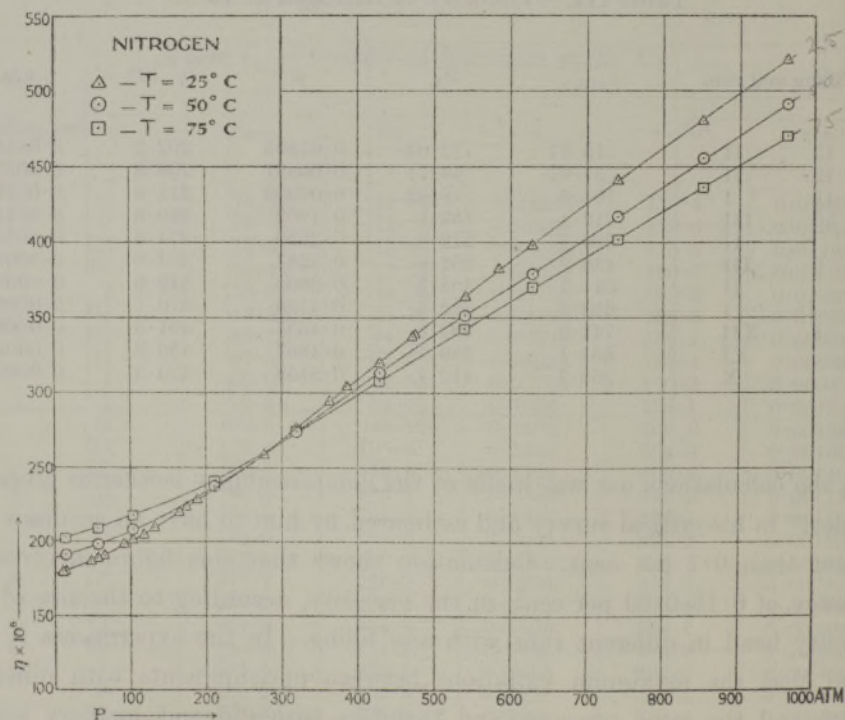


FIG. 3.—Viscosity pressure curves.

If, however, the value of  $(\partial\eta/\partial T)_p$  for liquids is calculated from the compressibility data and the temperature and pressure coefficients of viscosity, it appears that this is approximately zero, whilst for a gas it should be positive according to the classical kinetic theory. In fig. 4 the viscosity has been plotted

\* C. J. Smith, 'Proc. Phys. Soc.', vol. 34, p. 155 (1922).

against density. It is seen that  $(\partial\eta/\partial T)_\rho$  is positive and that within the limits of the experimental accuracy, it remains constant over the whole density range,

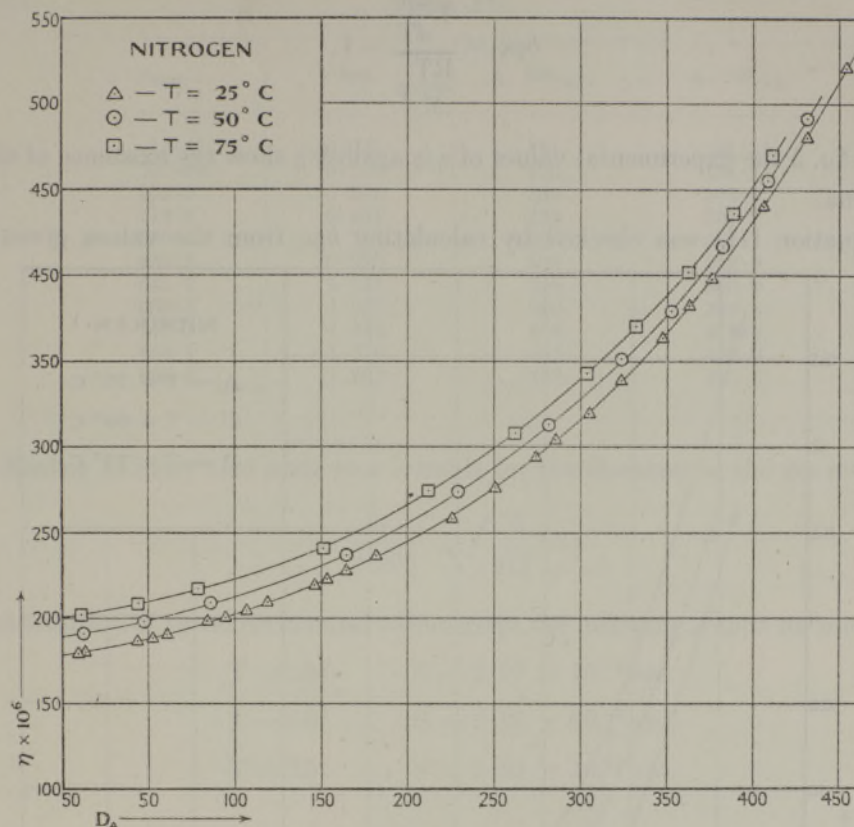


FIG. 4.—Viscosity density curves.

although, of course, the specific temperature coefficient  $1/\eta (\partial\eta/\partial T)_\rho$  becomes progressively smaller as the viscosity increases.

A comprehensive theory of the viscosity of compressed gases has been put forward by Enskog.\*† He concludes that  $\eta/\rho$  plotted against  $\rho$  must give a minimum and that the curve must satisfy the equation

$$\frac{\eta}{\rho} = \frac{1}{2.545} \left( \frac{\eta}{\rho} \right)_{\min.} \left[ \frac{1}{b\rho\kappa} + 0.800 + 0.7614 b\rho\kappa \right], \quad (11)$$

where  $b\rho\kappa$  is obtained from his equation of state for compressed gases

$$p + a\rho^2 = \frac{RT}{M} \rho (1 + b\rho\kappa),$$

\* D. Enskog, "K. Svenska Vetén. Hand.," vol. 63, No. 4 (1922). See also J. D. van der Waals, Jr., "Versl. Akad. Wet.," Amsterdam, vol. 27, p. 744 (1918).

† The authors are indebted to Professor Lennard Jones for drawing their attention to the importance of Enskog's work in relation to their own.



and can be calculated from isotherm data on the assumption that  $a$ ,  $b$  and  $\kappa$  are all independent of temperature. In this case

$$b\rho\kappa = \frac{T \frac{dp}{dT}}{\frac{RT}{M} \rho} - 1.$$

In fig. 5 the experimental values of  $\eta/\rho$  against  $\rho$  show the existence of these minima.

Equation (11) was checked by calculating  $b\rho\kappa$  from the values given by

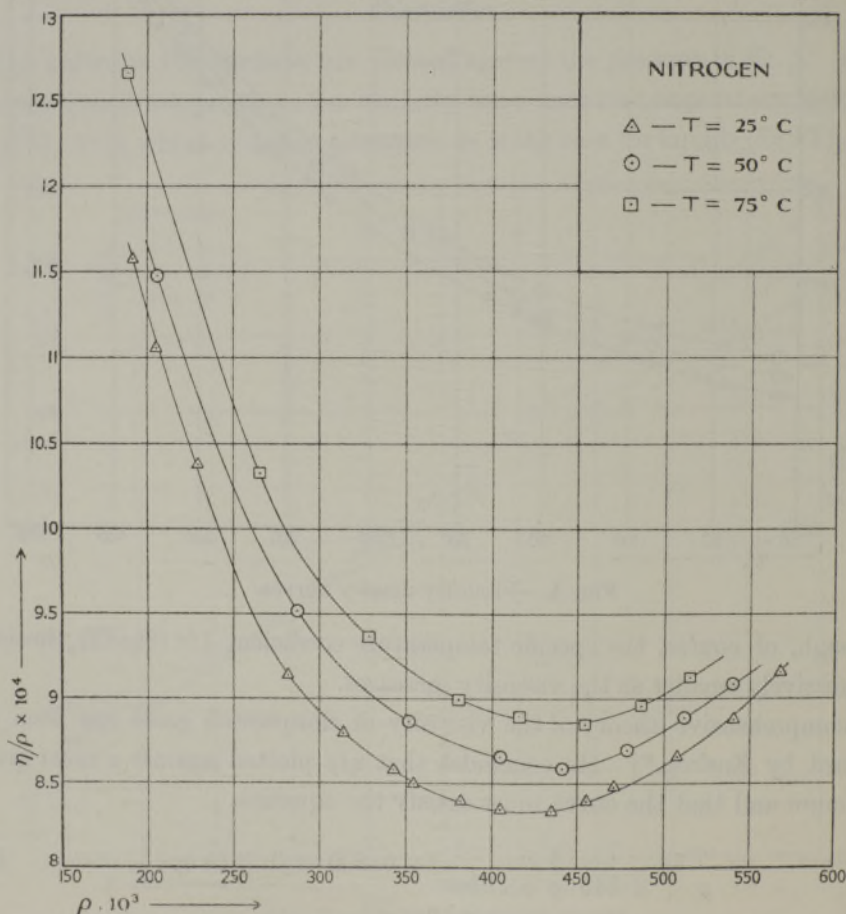


FIG 5.

Deming and Shupe\* based on Bartlett's results, and by using the values of  $(\eta/\rho)_{\min.}$  obtained from the above curves.†

\* W. E. Deming and Lola E. Shupe, 'Phys. Rev.', vol. 37, p. 638 (1931).

† It was possible to put a smooth curve through all the values calculated from Deming and Shupe's figures except that at 700 atmospheres. This point was neglected and the value from the curve was used.

The calculated and experimental values of  $\eta$  for 50° C. are given in Table IV.

Table IV.

$P_{\text{atm.}}$	$bp\kappa.$	$\eta \cdot 10^6_{\text{calc.}}$	$\eta \cdot 10^6_{\text{exp.}}$
15.37	0.031	181	191.3
57.60	0.119	190	198.1
104.5	0.215	205	208.8
212.4	0.491	224	237.3
320.4	0.717	266	273.7
430.2	0.920	308	312.9
541.7	1.111	348	350.9
630.4	1.247	380	378.6
742.1	1.413	418	416.3
854.1	1.576	455	455.0
965.8	1.732	492	491.3

Enskog's theory also leads to a formula for the diameter of the gas molecule

$$s = \frac{1}{0.955} \sqrt{\frac{M}{RT}} \left( \frac{\eta}{\rho} \right)_{\text{min.}}$$

Substitution of the experimental values gives the following results for nitrogen :

$$T = 25^\circ \quad S = 2.97 \times 10^{-8} \text{ cm.}$$

$$T = 50^\circ \quad S = 2.94 \times 10^{-8} \text{ cm.}$$

$$T = 75^\circ \quad S = 2.92 \times 10^{-8} \text{ cm.}$$

### *Summary.*

In the present paper a description is given of a method for measuring the viscosities of gases at high pressures. The method depends on the transpiration of gas through a capillary. A detailed account is given of the apparatus and of the method of calculating the viscosity from the experimental data.

Results are given for the viscosity of nitrogen at 25°, 50° and 75° C. up to 1000 atmospheres.

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