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**Physics.** — “*On the Theory of the Friction of Liquids*”. By Prof. J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS).

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§ 1. *Introduction.* The theory of the friction of gases has been made the subject of numerous researches, the theory of friction of liquids on the other hand has met with but scant attention. Yet it is clear that the explanation given to account for the friction of gases — viz. that it is brought about in consequence of this that molecules diffusing from one gas layer to another, at the same time transport an amount of momentum from one layer to another — cannot equally apply to the friction of liquids. For the friction of gases increases at higher temperature. For liquids on the other hand the viscosity becomes slighter at higher temperature. Such a behaviour cannot be accounted for with “friction by means of transport.”

Maxwell calculated that on the supposition of “friction by means of transport” the coefficient of friction  $\eta$  should be proportional to  $\sqrt{T}$  if we assume that the molecules are perfectly rigid spheres, which do not attract each other. Other assumptions concerning the nature of the molecules (repulsion in inverse ratio with the fifth power of the distance, MAXWELL, or mutually attracting rigid spheres, SUTHERLAND and REINGANUM) lead to a still more rapid increase of  $\eta$  with  $T$ . Nor can the thermal expansion of the liquids explain the sign of the coefficient of temperature of  $\eta$ . For gases  $\eta$  appears to be independent of the volume. For liquids the expansion will promote an increase of  $\eta$  with  $T$ , and not a decrease. This has been shown experimentally (except for water, where the reverse takes place), and it is also easy to understand that this is to be expected for friction by means of transport, at least for not associating or dissociating liquids. The expression derived by MAXWELL:

$$\eta = \frac{1}{3} \rho l s = \frac{1}{3} \frac{m s}{\pi \sigma^2 \sqrt{2}} \quad \dots \dots \dots (1)$$

in which  $\rho$  represents the density,  $l$  the mean length of path,  $s$  the mean velocity,  $m$  the mass, and  $\sigma$  the diameter of a molecule, will namely have to be corrected for liquids, to:

$$\eta = \frac{1}{3} \frac{ms}{\pi \sigma^2 \sqrt{2}} \frac{v-b}{v} \dots \dots \dots (1a)$$

which quantity increases with  $v$ . Other well-known corrections have been left out of consideration.

Accordingly for liquids we shall not principally have to think of transport of momentum by the diffusing molecules, but we shall have to explain the friction by forces which the molecules exert on each other. If at an arbitrary moment we could suddenly check the motion of the molecules, and if we could arrest them in the position which they occupied at that moment, the friction by means of transport would at the same moment be destroyed, so that we should not have any means to study the friction in those resting molecules.

The case is different for "friction through molecular forces". At least when we think the molecular forces independent of the velocity, the frictional forces would continue to exist also after the immobilisation of the molecules. They would be a consequence of the grouping of the molecules in space. It is now the question: of what nature are the molecular forces and what is the grouping of the molecules, which gives rise to the existence of the tensor of tension as we meet with it for the friction of liquids. The following three answers might be given to this question:

1. *Friction through impact forces or through an instantaneous transfer of momentum.* We might assume that the forces that the molecules exert on each other at an impact would furnish the explanation of viscosity. Let us consider the simple case of a liquid in which the current only moves in a single direction, which has been chosen as  $x$ -direction of a cartesian system of coordinates, this velocity ( $u$ ) being a linear function of  $z$ , hence:

$$u = az, \text{ (with } a > 0\text{).} \dots \dots \dots (2)$$

Then the layers with greater  $z$  will move towards the righthand side with regard to the underlying layers, if the system of axes is orientated in space in the usual way. A consequence will be that the line connecting the centres of two colliding molecules, which I shall call the central line, will be found more often in the second quadrant of the  $xz$ -surface than in the first. When the system of coordinates is turned over an angle of  $45^\circ$ , so that the  $+x$ -axis moves towards the  $+z$ -axis, and when the new axes are called  $x'$  and  $z'$ , the pressure that the molecules exert on each other will be greater in the  $z'$  direction than in the  $x'$  direction. It is evident that this agrees with the value of the tensor of tension in this case.

Instead, however, of the calculation of the forces appearing in case of collision, the friction through this cause can also be calculated by means of the momentum that at impact is momentarily conveyed from the centre of one of the colliding molecules to that of the other. This method of calculation seems simpler and will be carried out in § 2.

II. *Friction for double points. Formation of streaks.* We might also assume the molecules to be electrical or magnetical double points. When they were orientated with regard to each other quite arbitrarily, they would equally frequently repel as attract each other, so that the mean force would be zero. Through the couples which they exert on each other, they will, however, turn so that attraction prevails. When we now assume that molecules that approach each other, are still little orientated, whereas this is the case to a higher degree with molecules that have moved past each other, and recede again from each other, the molecules whose central line lies in the  $x'$ -direction will be more orientated on an average than those for which it lies in the  $z'$  direction, so that a traction in the  $x'$  direction will result, greater than in the  $z'$ -direction, which can again account for the tensor of tension.

When we consider more than two molecules whose centres lie on the same line in the  $x$ -direction, the couples they exert on each other, will strengthen each other, which can give rise to the formation of a kind of streaks, which still more promotes the friction.

It is difficult to compute the accurate amount of this orientation of the molecule axes; it will be different according as one thinks the rotations of the molecules determined by classical mechanics or by the laws of the theory of quanta. Besides there is no occasion in the experimental data to assume that this case actually presents itself. I shall, therefore, not attempt to calculate the friction according to this hypothesis, though possibly it plays a decisive part in the friction of exceedingly viscous liquids, which present themselves as bi-refringent in case of friction, as likewise in the glassy state.

III. *Friction in consequence of formation of groups.* Finally we can assume the molecules to combine to groups in consequence of their mutual attraction. In liquids at rest these groups will possess spherical symmetry on an average. When, however, a liquid is in a motion for which  $u = az$ , these spherical groups will be elongated to ellipsoids. This variation of shape will now again give rise to a greater traction in the  $x'$ -direction. This cause of friction will probably chiefly make itself felt in the neighbourhood of the critical point. In § 4 and following paragraphs I will make an attempt

to calculate the amount of the friction which is to be ascribed to this cause.

§ 2. *Friction in consequence of impact forces.* For an accurate calculation of the friction through this cause the accurate knowledge of the distribution of the velocities would be required. I shall, however, confine myself here to an approximate method of calculation of about the same nature as the method of calculation of the "friction by means of transport" for gases by MAXWELL in his papers in the *Phil. Mag.* in 1860. I shall, namely, assume that the distribution of the velocities of the molecules the centres of which lie in a definite layer  $z = z_1$  is found by compounding the velocity of the current of the liquid in that layer with a thermal motion for which the unmodified partition of velocities of MAXWELL is thought to hold.

The error that we make on this supposition will probably be smaller for liquids than for gases. The free length of path is namely very small here, and the supposition departs little from MAXWELL'S supposition that the molecules have the velocity of current of the layer in which they have collided last. Even when JEANS' correction is taken into account for the persistence of the velocities, we shall have to assign a velocity to the molecules corresponding with the velocity of current of a layer which is only a small fraction of  $\sigma$  removed from the layer in which their centre is situated. I shall disregard this small fraction.

When we now consider a definite horizontal layer, for which we choose  $z = 0$ , an instantaneous transfer of momentum through this layer takes place at every collision for which the centres of the colliding molecules lie on different sides of this layer. At every impact an instantaneous transfer from above downwards takes place and one in opposite direction. These two quantities are equal and of opposite signs. Hence we may also take into account double the amount of the transfer from above downwards. We shall now first consider the collisions for which the 'centre of molecule I lies between the planes  $z = z_1$  and  $z = z_1 + dz_1$  ( $0 > z_1 > -\sigma \cos \gamma$ ), the central line<sup>1)</sup> forming an angle between  $\gamma$  and  $\gamma + d\gamma$  with the  $z$ -axis, and lying in a plane forming an angle between  $\beta$  and  $\beta + d\beta$  with the  $xz$ -plane. Further the components of velocity of molecule I. will lie between  $u_1$  and  $u_1 + du_1$ ,  $v_1$  and  $v_1 + dv_1$  and  $w_1$  and  $w_1 + dw_1$ , those of molecule II lying between  $u_2$  and  $u_2 + du_2$  etc. The chance that such components of velocity occur is represented for the two molecules respectively by

<sup>1)</sup> Counted in the direction of molecule I towards II.

$$\frac{1}{\pi\sqrt{\pi}} e^{-\frac{1}{\alpha^2} \{(u_1 - uz_1)^2 + v_1^2 + w_1^2\}} d\frac{u_1}{\alpha} d\frac{v_1}{\alpha} d\frac{w_1}{\alpha}$$

and

$$\frac{1}{\pi\sqrt{\pi}} e^{-\frac{1}{\alpha^2} \{(u_2 - az_2)^2 + v_2^2 + w_2^2\}} d\frac{u_2}{\alpha} d\frac{v_2}{\alpha} d\frac{w_2}{\alpha}$$

in which  $z_2 = z_1 + \sigma \cos \gamma$ .

Hence the number of the collisions in question per second and per surface unity of the layer is

$$\frac{n^2}{\pi^3} e^{-\frac{1}{\alpha^2} \{(u_1 - az_1)^2 + v_1^2 + w_1^2 + (u_2 - az_1 - \alpha \cos \gamma)^2 + v_2^2 + w_2^2\}} v_1 \cos \mu \sigma^2 \sin \gamma d\gamma d\beta dz. \quad (3)$$

in which  $n$  denotes the number of molecules per  $\text{cm}^3$ ,  $v$ , the relative velocity of molecule II with respect to molecule I, and  $\mu$  the angle between the direction of  $v$ , and the central line, so that:

$$v_1 \cos \mu = (u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma$$

At each of these collisions the  $x$ -component of the quantity of motion, which is instantaneously transferred from above downwards is:

$$m v_1 \cos \mu \sin \gamma \cos \beta. \quad (4)$$

The condition that really transfer of momentum through the chosen plane is to take place is.

$$z_2 > 0 \text{ or } \gamma < Bg \cos \frac{-z_1}{\sigma}$$

Hence  $\eta$  is found by multiplication of (3) by (4), and then by integration with respect to

$$\begin{array}{llll} \gamma & \text{between } 0 & \text{and } Bg \cos \frac{-z_1}{\sigma} \\ \beta & \text{,, } 0 & \text{,, } 2\pi \\ u_1 \dots w_2 & \text{,, } -\infty & \text{,, } +\infty \\ z_1 & \text{,, } -\sigma & \text{,, } 0 \end{array}$$

We have then still to multiply the expression by 2 for the transfer from below upwards. We must, however, still pay attention to something else. In the limits set above collisions have been taken into account which are impossible in reality. Only those combinations of values of the independent variables can occur, for which  $\mu$  is obtuse, hence  $\cos \mu < 0$ . It is simpler to introduce the condition that  $v_1 \cos \mu < 0$ . This condition can be introduced in the way of DIRICHLET

by multiplication by  $\frac{1}{\pi} \int_{-\infty}^{+\infty} e^{q\eta} \frac{\sin p\eta}{\eta} d\eta$ .

Which integral is 1 for  $-\rho < q < \rho$

and 0 for  $q < -\rho$  and for  $q > +\rho$ .

Now if we put  $p = s$  and  $q = v, \cos \mu + s$ , and if we make  $s$  to increase indefinitely, the integral appears to become 1 for  $v, \cos \mu < 0$  and 0 for  $v, \cos \mu > 0$ .

Thus we finally find for the force which the liquid above the plane  $z = 0$  exerts per surface unity on that below it:

$$\begin{aligned} \eta a = & -\frac{2n^2 \sigma^3 m}{\pi^4} \int \{(u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma\}^2 \times \\ & \times e^{-\frac{1}{z^2} \{(u_1 - az_1)^2 + v_1^2 + w_1^2 + (u_2 - az_1 - a\sigma \cos \gamma)^2 + v_2^2 + w_2^2\}} \times \\ & \times e^{+\varphi \{(u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma + s\}} \times \frac{\sin s \rho}{\rho} \times \\ & \times \sin^2 \gamma \cos \beta \, d\gamma \, d\beta \, d\alpha \, \frac{u_1}{\alpha} \dots d \frac{w_2}{\alpha} \, dz_1 \end{aligned} \quad (5a)^1$$

As  $az_1$  and  $az_2$  will be in general very small compared with  $u_1$  and  $u_2$ , we may write for the first exponential factor under the integral sign:

$$\left\{ 1 + \frac{1}{\alpha^2} 2a (u_1 z_1 + u_2 z_1 + u_2 \sigma \cos \gamma) \right\} e^{-\frac{1}{z^2} (u_1^2 + w_1^2 + u_2^2 + w_2^2)}$$

When we substitute this in the integral, the term 1 between the accolades in (6) will furnish 0 after integration: it is the value of the force of friction for  $\alpha = 0$ . The integrals with  $\frac{2a}{\alpha^2} z_1 u_1$  and  $\frac{2a}{\alpha^2} z_1 u_2$  will become equal, but of opposite sign, so that they cancel each other, and the integral with  $\frac{2a}{\alpha^2} u_2 \sigma \cos \gamma$  only remains.

When we now divide by  $a$ , and when we still put  $\frac{z_1}{\sigma} = z'_1$  and  $\frac{u_1}{\alpha} = u'_1 \dots \dots \frac{w_2}{\alpha} = w'_2$ ,  $a\rho = \rho$  and  $\frac{s}{\alpha} = s'$ , and when we then again omit the accents, we get:

<sup>1)</sup> The minus sign has been written for this, because  $v \cos \mu$  is negative, while the number of collisions are naturally positive, and the sign of expression (3) should properly speaking be reversed.

$$\eta = \frac{-4n^2 \sigma^4 m \alpha}{\pi^4} \int \left\{ (u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma \right\}^2 \times u_2 \times \left. \begin{aligned} &\times e^{-(u_1^2 + \dots + w_2^2) + i\varphi \{ (u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma + s \}} \times \\ &\times \frac{\sin s \varphi}{\varphi} \sin^2 \gamma \cos \gamma \cos \beta \, d\gamma \, d\beta \, d\varphi \, du_1 \dots dw_2 \, dz_1 \end{aligned} \right\} \quad (5b)$$

If we substitute in this

$$\left. \begin{aligned} u_1 + \frac{1}{2} \nu \rho \sin \gamma \cos \beta &= \xi_1 & u_2 - \frac{1}{2} \nu \rho \sin \gamma \cos \beta &= \xi_2 \\ v_1 + \frac{1}{2} \nu \rho \sin \gamma \sin \beta &= \eta_1 & v_2 - \frac{1}{2} \nu \rho \sin \gamma \sin \beta &= \eta_2 \\ w_1 + \frac{1}{2} \nu \rho \cos \gamma &= \zeta_1 & w_2 - \frac{1}{2} \nu \rho \cos \gamma &= \zeta_2 \end{aligned} \right\} \quad (6)$$

we get:

$$\eta = \frac{-4n^2 \sigma^4 m \alpha}{\pi^4} \int \left\{ (\xi_2 - \xi_1) \sin \gamma \cos \beta + (\eta_2 - \eta_1) \sin \gamma \sin \beta + (\zeta_2 - \zeta_1) \cos \gamma + \nu \rho \right\}^2 \times \left. \begin{aligned} &\times (\xi_2 + \frac{1}{2} \nu \rho \sin \gamma \cos \beta) \times e^{-(\xi_1^2 + \dots + \zeta_2^2) - \frac{1}{2} \nu^2 \rho^2 + \varphi s} \times \frac{\sin s \varphi}{\varphi} \times \\ &\times \sin^2 \gamma \cos \gamma \cos \beta \, d\varphi \, d\gamma \, d\beta \, d\xi_1 \dots d\zeta_2 \, dz_1 \end{aligned} \right\} \quad (5c)$$

On integration with respect to  $\xi_1 \dots \zeta_2$  terms containing odd powers of  $\xi_1 \dots \zeta_2$  vanish, so that the only terms left are those with  $+ \{ [(\xi_2^2 + \xi_1^2) \sin^2 \gamma \cos^2 \beta + (\eta_2^2 + \eta_1^2) \sin^2 \gamma \sin^2 \beta + (\zeta_2^2 + \zeta_1^2) \cos^2 \gamma] \frac{1}{2} \nu \rho \sin \gamma \cos \beta + 2 \xi_2^2 \nu \rho \sin \gamma \cos \beta - \frac{1}{2} \nu \rho^3 \sin \gamma \cos \beta \}$ .

These terms do not change when  $\xi_2^2$  is substituted for  $\xi_1^2, \eta_1^2, \eta_2^2, \zeta_1^2$ , and  $\zeta_2^2$ , so that  $+ (3\xi_2^2 \nu \rho - \frac{1}{2} \nu \rho^3) \sin \gamma \cos \beta$  may be written for the sum of the remaining terms. After execution of the integrations we find:

$$\eta = -\frac{2}{\pi} n^2 \sigma^4 m \alpha i \int (3 - \varphi^2) \times e^{-\frac{1}{2} \nu^2 \rho^2 + \varphi s} \times \sin s \varphi \times \left. \begin{aligned} &\times \sin^2 \gamma \cos \gamma \cos^2 \beta \, d\varphi \, d\gamma \, d\beta \, dz_1 \dots \dots \dots \end{aligned} \right\} \quad (5d)$$

Let us now replace  $e^{i\varphi s}$  by  $\cos \varphi s + i \sin \varphi s$ , and execute the integration with respect to  $\varphi$ , bearing in mind that we seek the value of the integral for  $\lim. s = \infty$ . Then the term with  $\sin s \varphi \cos s \varphi$  vanishes, and in the term with  $\sin^2 s \varphi$  we may replace this expression by its mean value  $\frac{1}{2}$ . Thus we find:

$$-i \int_{-\infty}^{+\infty} e^{-\frac{1}{2} \nu^2 \rho^2 + \varphi s} \times \sin s \varphi \times (3 - \varphi^2) \, d\varphi = \sqrt{2\pi}$$

$$\int_0^{2\pi} \cos^2 \beta \, d\beta = \pi$$



$$\begin{aligned}
 & \int_0^{B\eta \cos(-z_1)} \sin^2 \gamma \cos \gamma \, d\gamma = \frac{1}{4} [\sin^4 \gamma]_0^{B\eta \cos(-z_1)} = \frac{1}{4} (1 - z_1^2)^2 \\
 & \int_{-1}^0 (1 - z_1^2)^2 \, dz_1 = \frac{8}{15} \\
 & \eta = \frac{4\sqrt{2\pi}}{15} n^2 \sigma^4 m a \dots \dots \dots (5e)
 \end{aligned}$$

In the calculation of the number of collisions we have, however, up to now disregarded the influence of the mutual attraction of the molecules and of their dimension in the direction of the velocity. If for this we introduce the usual corrections, we find:

$$\eta = \frac{4\sqrt{2\pi}}{15} n^2 \sigma^4 m a \frac{v}{v-b} e^{-\frac{\epsilon}{RT}} \dots \dots \dots (5)$$

in which  $\epsilon$  represents the difference between the amount of potential energy that the molecules in the liquid possess on an average, and the amount which they possess at the moment of a collision.

G. JÄGER <sup>1)</sup> and M. BRILLOUIN <sup>2)</sup> had already derived expressions for the friction of liquids; JÄGER considers exclusively "friction in consequence of impact forces", whereas BRILLOUIN takes besides these also the friction by means of transport into consideration. The method of calculation differs somewhat from that followed above. The results at which they arrive, are in somewhat modified notation:

$$\begin{aligned}
 \text{JÄGER} \quad \eta &= \frac{\sigma v s}{6 \left( 1 - \sqrt{\frac{b}{v}} \right)} \\
 \text{BRILLOUIN} \quad \eta &= \frac{1}{3} \rho s \left\{ \alpha D + \beta \frac{\sigma}{2(D-\sigma)} \right\}
 \end{aligned}$$

In this  $\rho$  represents the density,  $s$  the mean velocity of the molecules, and  $D$  the mean distance of a pair of adjacent molecules.  $\alpha$  and  $\beta$  are two unknown constants, which will not differ much from 1, and which have been introduced, because all kinds of approximations have been introduced into the calculation, which renders the numerical coefficients not entirely certain. The first term of BRILLOUIN's formula refers to transport, the second to impact forces. It seems to me that BRILLOUIN should also have corrected the first term for the "thickness" of the molecules. In his train of

<sup>1)</sup> G. JÄGER, Wiener Sitzungsber. CII, p. 253, Anno 1893.

<sup>2)</sup> M. BRILLOUIN, Leçons sur la Viscosité des Liquides et des Gaz. Paris. GAUTHIER-VILLARS 1907.

thought this might have been done by multiplication by a factor  $\frac{D-\sigma}{D}$ . That he failed to do so deprives his test of the experimental data of much of its value, in my opinion.

§ 3. *Test of the formulae for liquids not too near the critical point.* Let us call the "coefficient of friction by means of transport"  $\eta_1$ , that through forces of collision  $\eta_2$ , and that in consequence of formation of groups  $\eta_3$ . For liquids not too near the critical point we shall disregard  $\eta_3$ . We have further:

$$\frac{\eta_2}{\eta_1} = c \frac{b^2}{(v-b)^2}$$

in which  $c$  is a numerical coefficient of moderate value. We may no doubt consider this quantity as large compared with 1, so that we shall also neglect  $\eta_1$ .

When we do so we notice first of all that for constant volume  $\eta$  according to the formula must increase with  $T$  proportional to  $\sqrt{T}$ . There are only few substances for which the experimental data are available, required to verify whether the sign of  $\frac{\partial \eta}{\partial T_v}$  is really positive. It is clear that always  $\frac{\partial \eta}{\partial T_p}$  has been measured, and not  $\frac{\partial \eta}{\partial T_v}$ . Ether and Benzene are the only substances for which I have found records for  $\frac{\partial \eta}{\partial T_p}$  <sup>1)</sup>, so that  $\frac{\partial \eta}{\partial T_v}$  can be found according to the formula

$$\frac{1}{\eta} \frac{\partial \eta}{\partial T_v} = \frac{1}{\eta} \frac{\partial \eta}{\partial T_p} + \frac{1}{\eta} \frac{\partial \eta}{\partial p_T} \frac{\partial p}{\partial T_v} = \frac{1}{\eta} \frac{\partial \eta}{\partial T_p} - \frac{1}{\eta} \frac{\partial \eta}{\partial p_T} \frac{1}{v} \frac{\partial v}{\partial p_T}$$

We find:

for ether	for benzene
$\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_p} = -0,01075$ <sup>2)</sup>	$-0,01853$ <sup>2)</sup>

<sup>1)</sup> Except for water, which will most likely also behave abnormally in this respect, and for  $CO_2$  in the neighbourhood of the critical point, which observations will be discussed later on.

<sup>2)</sup> These values, like those of  $\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_p}$  for other substances given below have

$$\begin{aligned} \frac{1}{\eta_v} \frac{\partial \eta}{\partial p_T} &= 0,00073 \text{ } ^1) & 0,00093 \text{ } ^1) \\ \frac{1}{v} \frac{\partial v}{\partial T_p} &= 0,001585 \text{ } ^2) & 0,0011763 \text{ } ^3) \\ \frac{1}{v} \frac{\partial v}{\partial p_T} &= -0,000139 \text{ } ^4) & -0,0000783 \text{ } ^5) \end{aligned}$$

This yields for ether

$$\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v} = -0,01075 + 0,0088 = -0,00195$$

and for benzene

$$\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v} = -0,01853 + 0,01462 = -0,00391$$

Theoretically we should find according to equation (5):

$$\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v} = \frac{1}{2T} = +0,00183.$$

Accordingly there is not even agreement in the sign of  $\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v}$ . When we, however, take into consideration that the value found is the difference of two values which are each about five times the value of the amount sought, and that they are very inaccurately known, it is not excluded that  $\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v}$  is in reality negative. Even in the value of  $\frac{1}{v} \frac{\partial v}{\partial p_T}$  an error of 4% is by no means excluded, and the error in the determination of  $\frac{1}{\eta} \frac{\partial \eta}{\partial p_T}$  will without doubt be many times larger than that in  $\frac{1}{v} \frac{\partial v}{\partial p_T}$ . On the other hand it is of course

been found by differentiation of the empirical formulae of the form:  $\eta = \frac{a}{(b+t)^c}$ , in which THORPE and RODGER, Phil. Trans. Royal Soc. of London 185 p. 397, A. 1894 comprise their observations.

<sup>1)</sup> According to WARBURG and SACHS, Ann. d. Phys. u Chem. 22 p. 521. A 1884. The pressure is expressed in kg. per cm<sup>2</sup>.

<sup>2)</sup> According to AMAGAT 1893, extrapolated for 0° and 1 atm. from the values given in the Recueil de constantes physiques.

<sup>3)</sup> According to KOPF, 1847. Borrowed from the "Recueil etc."

<sup>4)</sup> According to SUCHODSKI 1910, extrapolated for 0° and 1 atm. from the values given in the "Recueil etc."

<sup>5)</sup> According to RÖNTGEN 1891, extrapolated for 0° and 1 atm. from the values given in the "Recueil etc."

also possible that even if formula (5) is valid, the value of  $\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_p}$  must

be negative, in consequence of the factor  $e^{-\frac{\epsilon}{RT}}$ , or because  $\sigma$ , hence also  $b$  depend on the temperature. The experimental data are not sufficiently accurate to decide this question.

More satisfactory results are furnished by another test, which can be applied on a more extensive scale. It consists in this that we compare the experimental values of  $\left(\frac{1}{\eta} \frac{\partial \eta}{\partial T_p}\right)^1$  with the values following from equation (5).

For this purpose we write:

$$\frac{1}{\eta} \frac{\partial \eta}{\partial T_p} = \frac{1}{\eta} \left( \frac{\partial \eta}{\partial T_v} + \frac{\partial \eta}{\partial v} \frac{\partial v}{\partial T_p} \right)$$

and in this we put:

$$\frac{1}{\eta} \frac{\partial \eta}{\partial T_v} = \frac{1}{2T} \quad \frac{1}{\eta} \frac{\partial \eta}{\partial v} = \frac{1}{v} - \frac{1}{v-b} = \frac{-b}{v(v-b)} = -\frac{b\left(p + \frac{a}{v^2}\right)}{v \cdot RT}.$$

We shall neglect  $p$  by the side of  $\frac{a}{v^2}$  and roughly assume

$RT_k = \frac{8a}{27b}$  and  $p_k = \frac{1a}{27b^2}$ : we then get:

$$\frac{1}{\eta} \frac{\partial \eta}{\partial v} = -\frac{1}{RTv^3} \left(\frac{3}{8}\right)^2 \frac{R^3 T_k^3}{p^2 k}.$$

$v$  is the volume per gram-molecule, hence  $v = m \frac{1}{\rho}$ , so that we finally find to test:

$$\left(\frac{1}{\eta} \frac{\partial \eta}{\partial T_p}\right)_{exp} = \frac{1}{2T} - \frac{3^3 R^3 \rho^2 T_k^3}{8^2 T m^2 p k^2} \left(\frac{1}{v} \frac{\partial v}{\partial T_p}\right) \dots \dots (7)$$

Borrowing the values of  $\rho$ ,  $p_k$ ,  $T_k$  and  $\frac{1}{v} \frac{\partial v}{\partial T_p}$  from the "Recueil etc.", we find: (See Table p. 754).

The agreement is on the whole as satisfactory as could be expected in view of the many approximations. Generally the experimental value is somewhat smaller than the theoretical one, for ether more than for other substances, benzene and orthoxylyene deviating in the opposite sense. For acetic acid and for the alcohols the agreement is much less than for the normal substances.

<sup>1)</sup> See note 1 on pag. 751.

	$\left(\frac{1}{\eta} \frac{\partial \eta}{\partial T_p}\right)_{exp}$	$\left(\frac{1}{\eta} \frac{\partial \eta}{\partial T_p}\right)_{theor.}$	$\sigma \times 10^8$	$\sigma' \times 10^8$
Pentane	0.01019	0.01269	5.486	4.863
Isopentane	1081	1171	5.774	4.838
Hexane	1123	1354	6.716	5.166
Heptane	1214	1353	7.779	5.456
Octane	1394	1574	9.808	5.714
Chloroform	1149	1066	6.515	4.317
Ether	1075	1463	6.578	4.731
Benzolene	1853	1382	9.770	4.559
Toluolene	1462	1524	8.451	4.867
Orthoxylene	1700	1385	10.871	5.170
Metaxylene	1418	1478	7.973	5.223
Paraxylene <sup>1)</sup>	1472	1414	6.716	5.187
Acetic acid <sup>1)</sup>	1826	2607	4.713	4.382
Methyl alcohol	1634	1988	4.527	3.749
Ethyl "	2086	1250	10.273	4.046
Propyl "	2887	0970	36.103	4.421

So far we have tested the temperature-coefficients of  $\eta$ . We can also test equation (5) directly, namely by for instance calculating  $\sigma$  from it, and by comparing the values obtained thus with the values of  $\sigma$  calculated in another way. When we again omit the factor  $e^{-\frac{\epsilon}{RT}}$  and when we put  $\frac{2}{3}\pi\sigma^3 N = b = \frac{RT_k}{8pk}$  ( $N =$  number of molecules per gram-molecule), substituting again  $\frac{RT}{p + \frac{a}{v^2}}$  for  $v - b$ , and neglecting  $p$  by the side of  $\frac{a}{v^2}$ , we find:

<sup>1)</sup> For these substances the values for  $\frac{1}{\eta} \frac{\partial \eta}{\partial T_p}$  also for 0° C. have been calculated from the empirical formula of RODGER and THORPE, though they are solid at this temperature.

$$\sigma = \frac{640}{27} \left( \frac{\pi T}{R^3} \right)^{1/2} \frac{\eta^{5/2} p k^3}{\rho^3 T_k^3} \eta \dots \dots \dots (8)$$

The values thus calculated for  $\sigma$  are recorded in the table on p. 754. With these the values calculated from the critical quantities:

$$\sigma' = \left( \frac{3RT_k}{16\pi N p k} \right)^{1/3} \dots \dots \dots (9)$$

have been compared.  $N = 6,08 \times 10^{-23}$  (SOMMERFELD).

They are represented by  $\sigma'$  and recorded in the last column of the table. It appears that equation (8) gives values that are in perfect concordance with those of equation (9) as far as order of magnitude is concerned. It is noteworthy that the values for  $\sigma'$  differ little inter se, those for  $\sigma$  presenting much greater differences between each other. The alcohols show again great deviations.