

for viscosity and temperature will prove to be the most satisfactory. In this connexion a comparison of the derivations of J. S. Dunn's equation (*Trans.*

(*NATURE*, Mar. 1, p. 309) have been calculated for a somewhat viscous oil from the viscosity values at 35° C. and 80° C., and the agreement between the observed results and those calculated from the two formulae shown in the accompanying table.

Temp.	Water, $A = 1.522$ , $\beta = -0.003822$ , $b = 243$		Octane, $A = 1.128$ , $\beta = -0.002399$ , $b = 190$	
	$\eta$ obs.	$\eta$ calc.	$\eta$ obs.	$\eta$ calc.
0° C.	0.01792	0.01787	0.007060	0.007060
10	01308	01289	006159	006152
20	01005	00996	005419	005423
30	00801	00797	004828	004826
40	00656	00657	004328	004328
50	00549	00554	003907	003908
60	00469	00474	003551	003548
70	00406	00410	003241	003238
80	00357	00359	002971	002967
90	00317	00317	002730	002730
100	00284	00281	002520	002519
110	—	—	002335	002332
120	—	—	002160	002165

The values for  $\eta$  obs. for water are those of Bingham and Jackson, for octane those of Thorpe and Rodger.

*Farad. Soc.*, 22, pp. 401-405; 1926)  $1/\eta = Ae^{-Q/RT}$  based on kinetic theory considerations and  $\eta = Ae^{b/T}$  put forward by Prof. Andrade should be of great interest.

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One naturally expects to be able to obtain closer agreement between observed and calculated results with a formula containing three constants than with one containing two, but in this connexion a further interesting fact was observed. It was found that the value of  $C$  obtained from eight oils of widely varying viscosities could be expressed with considerable accuracy by the formula

$$C = ad^n$$

where  $a$  and  $d$  are constants which are independent of the nature of the oil and the approximate values of which were  $1.5 \times 10^{-3}$  and 400 respectively. Thus Slotte's formula also becomes one in which there are only two constants the values of which are dependent on the nature of the liquid. On examining the values of  $C$  and  $n$  obtained for other liquids it was found that, with the exception of the alcohols, they were connected by a similar relationship, the values of  $a$  and  $d$  differing but slightly from those obtained for the mineral oils. This empirical relationship was not published, and it was thought that the results might be of some interest when considering the theoretical aspects of the problem.

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A SATISFACTORY explanation of the decrease of liquid viscosity with temperature has long been required, and Prof. Andrade's theoretical treatment of the subject will be awaited with interest. His simple formula connecting viscosity and temperature appears to give good agreement for certain liquids, but I should like to point out that it does not give such good agreement when applied to measurements on some mineral oils, as does a formula due to Slotte. The measurements were taken several years ago and in attempting to find an empirical relationship between the viscosity and the temperature, I obtained, quite independently, a formula which was identical

Temp.	$\eta$ calc. (Andr.)	$\eta$ obs.	$\eta$ calc. (Slotte).
20	12.36	15.20	15.46
25	9.03	10.15	10.19
30	6.67	7.04	6.99
35	4.97	4.97	4.93
40	3.75	3.58	3.58
45	2.85	2.67	2.66
50	2.18	2.00	2.01
55	1.685	1.550	1.558
60	1.313	1.232	1.217
65	1.028	0.965	0.966
70	0.813	0.780	0.777
75	0.646	0.633	0.636
80	0.517	0.517	0.522
85	0.417	0.432	0.435
90	0.337	0.362	0.363
95	0.275	0.306	0.305

with that due to Slotte and adopted by Thorpe and Rodger as best representing their experimental results. This formula is usually written in the form

$$\eta = \frac{c}{t+a} n$$

where  $\eta$  is the viscosity,  $t$  the temperature in °C., and  $C$ ,  $a$  and  $n$  constants depending on the liquid used. The constants  $A$  and  $b$  in Prof. Andrade's formula

In a recent issue of *NATURE* (Mar. 1, p. 309) Prof. Andrade publishes the following formula,  $\eta = Ae^{b/T}$ , for the coefficient of viscosity of liquids as a function of the temperature  $T$ , which he shows to be in excellent agreement with the experimental data. Now I wish to point out that a practically equivalent formula, namely,  $\eta = CT e^{U/kT}$ , was given by me more than four years ago in a paper on the heat motion of solid and liquid bodies (*Zeit. f. Phys.*, 35, p. 664-667; 1926). Since this has obviously remained unnoticed, it may be well to state briefly the fundamental conception on the heat motion of liquids upon which the above formula is based.

The 'crawling' of the particles of the liquid is considered as a combination of oscillations about a (temporary) position of equilibrium and of a jerky displacement of this position from time to time. The average number of oscillations performed about the same equilibrium position is equal to  $e^{U/kT}$ , where  $u$  is the energy required to tear the particle out of it. An elementary displacement of the equilibrium position is consequently achieved in a time  $\tau = \tau_0 e^{U/kT}$ ,  $\tau_0$  being the period of the oscillations, which corresponds to a 'crawling' velocity  $v = \frac{\delta}{\tau} = \frac{\delta}{\tau_0} e^{-U/kT}$ , where  $\delta$ , the average range of this displacement, is of the order of the mean distance between neighbouring particles, and to a diffusion coefficient  $D = \frac{1}{3} \delta v = \frac{\delta^2}{3\tau_0} e^{-U/kT}$ . Now

the latter is connected with the friction coefficient  $f$  (=ratio of force to the mean velocity which is due to it) by Einstein's formula  $Df = kT$ . If, on the other hand, we regard the particle as a small sphere of radius  $a \cong \delta$  then we have by Stokes's formula  $f = 6\pi a \eta$ .

Hence  $\eta = \frac{\tau_0 k T}{2\pi a \delta^2} e^{U/kT}$  which is the above formula with

$$C = \frac{\tau_0 k}{2\pi a \delta^2}$$

Putting here  $\tau_0 \approx 10^{-13}$  sec. and  $a \approx \delta \approx 10^{-8}$  cm. : one gets for  $C$  or Andrade's coefficient  $A = CT$  values of the correct order of magnitude.

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I AM naturally gratified at the interest which my brief letter on liquid viscosity, published in NATURE of Mar. 1, seems to have aroused. In view of the correspondence which has ensued I should like first to indicate briefly the theoretical considerations, mentioned in passing in my former letter, which lead me to the formula  $\eta = Ae^{b/T}$ ; secondly, to refer to the general directions in which I look for experimental confirma-

the action of the residual field of the molecules, which suffices to bind them permanently in the solid state, but is overcome by the energy of motion in the liquid state. General considerations suffice to show that the greater the temperature agitation the smaller the probability that the residual field of fixed average strength will result in temporary union for a given molecule. The viscosity of a liquid, therefore, decreases with rise in temperature until finally the energy of motion overcomes the molecular field and the liquid boils. The general picture is one of the liquid 'crystallising' temporarily in minute patches: at the temperature of solidification the crystallisation becomes general and permanent, at the boiling point it must be very small.

To obtain the quantitative law more precise as-

sumptions are necessary. We can suppose that the temporary combination represents the position of minimum potential energy of the molecule with respect to the local field. Just as in Langevin's theory of magnetism the tendency of the molecules to set, with respect to an external field, in the position of minimum potential energy, with axes parallel to the field, is opposed by the thermal agitation, so here too the tendency of two molecules to combine is opposed by the thermal agitation. The simplest application of Boltzmann's formula leads to the viscosity formula given in my former letter. In this formula the constant  $b$  is, of course, of the form  $-E/k$ , where  $E$  is the energy, numerically negative, of juxtaposition,  $k$  the Boltzmann constant. The constant  $A$  contains as factors  $M^{3/2}\rho^{-1/3}$ , where  $M$  is the molecular weight,  $\rho$  the density. The formula

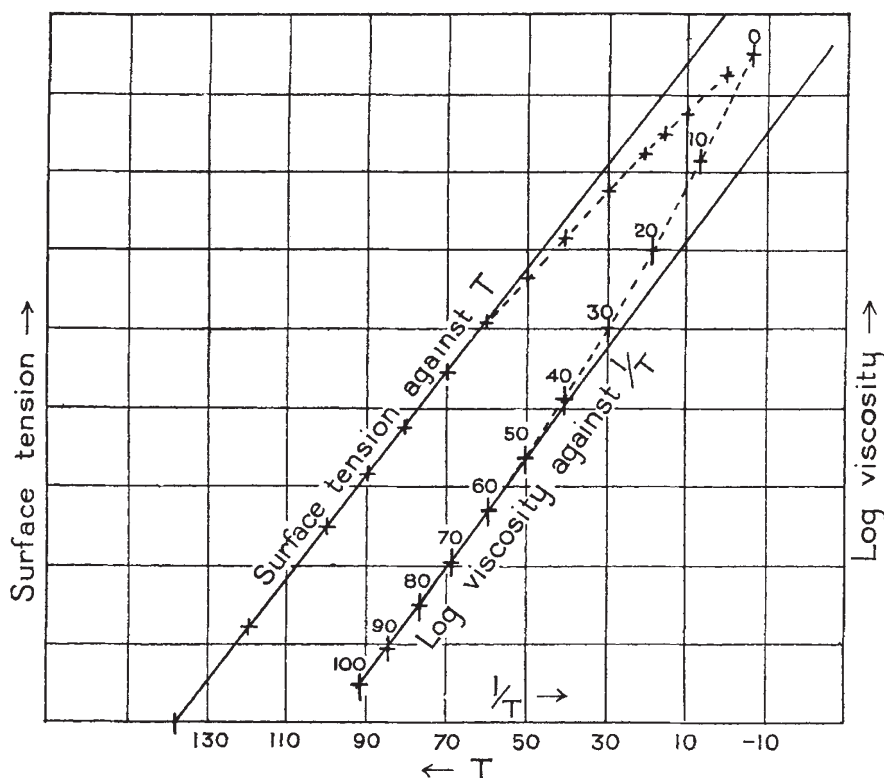


FIG. 1.

tion; and thirdly, to discuss some of the points raised by the correspondence.

The method by which I arrive at the formula is by taking two layers of molecules, parallel to the direction of motion of the liquid and considering the transfer of momentum between them. In the case of a gas, Maxwell showed how the viscosity can be derived by considering this momentum as being communicated by molecules transferring themselves bodily through a distance large compared to their own sizes, from one layer to the other. But both the non-fulfilment of the conditions postulated in Maxwell's treatment, and the fact that while gas viscosity goes up with temperature liquid viscosity goes down, show that some radically different picture is needed for liquids. I suppose that momentum is transferred from layer to layer by a temporary union of molecules in contiguous layers, the duration of this union not exceeding the very brief time required for the molecules to acquire a common velocity of translation. The union takes place under

virtually assumes that the number of impacts is independent of the temperature, the effect of the increased velocity being opposed by certain factors, such as the expansion. It is probable that  $A$  depends slightly on the temperature, and I am now trying to elaborate this point, but comparison with the recorded data shows that  $A$  may be taken as a constant to a first approximation.

It is my belief that the constant  $b$ , expressing in some way the strength of the intermolecular field, will prove of great importance for the theory of liquids, and will take its place alongside the surface tension. The constant  $b$  can be accurately determined from the variation of viscosity with temperature, the constant  $A$  less so, it being very insensitive, like the constant  $A$  in O. W. Richardson's thermionic formula.

One way in which to check the reasonableness of the hypothesis on which the theory is based is to calculate the number of momentary combinations which it requires to give the observed viscosity. Just above the