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

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Leningrad, Mar. 8.

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 assumptions 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, ρ the density. The formula 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.
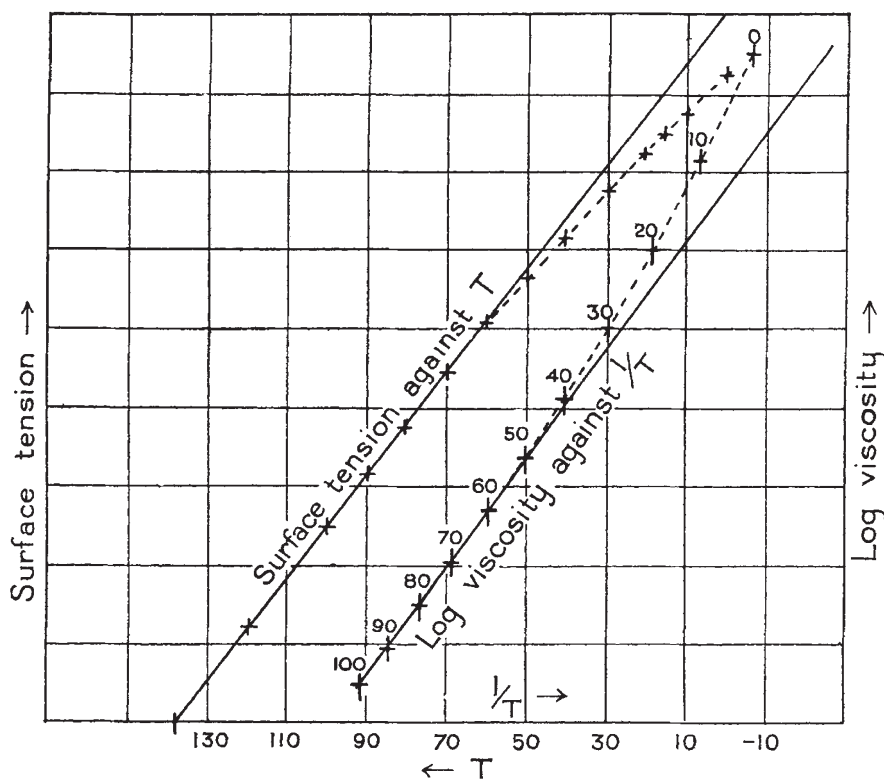

FIG. 1.

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

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

melting point I suppose that practically every collision leads to a sharing of momentum, so that the number obtained should be of the order of the total number of collisions. In the case of mercury this number comes out to be $3 \cdot 7 \times 10^{12}$ per sec., which is reasonable, being of the same order as the vibration frequency of the solid. I have also obtained a rough value for the internal pressures of one or two organic liquids, which come out to be of the right order, but the assumptions made in this case are of a tentative nature, and I am now devoting further attention to this problem.

I distinguish between true association, as occurring in liquids ordinarily called associated, and the brief union needed for the sharing of momentum which I postulate for all liquids. True association, in which molecules are bound together in clusters of two or more for a time large compared to the intervals between collisions, leads, with the mechanism postulated, to an increase of viscosity. The application of the formula to many associated liquids leads to some very interesting results. It is found to hold accurately at higher temperatures, but as the temperature falls the actual viscosity becomes increasingly greater, compared to that predicted by the formula. This I take to mean that at the higher temperatures the liquids are either not associated at all, or else that such association as may exist is of a stable kind, unaffected by the temperature. In the case of water the formula $\eta = Ae^{b/T}$ expresses the viscosity within 0·5 per cent from 100° to 60°, when the deviation begins to set in and rapidly increases. It is striking that the surface tension of water is a linear function of the absolute temperature above 60°, but that below 60° the deviation from linearity rapidly increases, as shown by Fig. 1, in which surface tension plotted against T, and the logarithm of viscosity plotted against $1/T$, are exhibited in the same diagram. As an inverse temperature scale would make it troublesome to trace the point at which the viscosity law changes, the actual temperature values of the different points are indicated on the curve itself. Water and many other associating liquids can be fitted by the formula $\eta = A'e^{b'/T-\theta}$ as an approximation, the formula having no detailed theoretical basis, but being derived by an obvious analogy from other branches of physics. For water the fit is within about 1 per cent throughout the range. It seems more reasonable, however, to use a formula of the type $\eta = A(1 + ae^{-\beta T})e^{b/T}$, the term $1 + ae^{-\beta T}$ expressing the decrease of association with temperature. This formula, it is true, has four constants, but four constants are commonly used in empirical formulæ designed to fit water.[1] It gives the viscosity over the range $T = 263 \cdot 7$ (supercooling of 9° C.) to $T = 363$ within 0·25 per cent (the viscosity at 100° seems experimentally doubtful). The variations in the viscosity of water, as measured by different observers of high repute, markedly exceed this at many temperatures. There is no indication of a systematic deviation. For fitting the formula I have taken the mean of the results of Hosking, and of Bingham and White, as given in Landolt-Bornstein, 1923 edition, for which the greatest variation at any one temperature is 0·9 per cent, while at most temperatures the agreement is good. For supercooled water the values of White and Twining, quoted in Landolt-Bornstein, are taken.

The accompanying table exhibits the fit.

If b measures the strength of the molecular field, as defined by the conditions specified, it should be connected on one hand with the boiling point, and on the other hand with the dielectric polarisation due to deformation of the molecule. In all homologous series

for which measurements are accessible to me, b increases regularly with the boiling point and with the polarisation. This is an aspect of the subject at which I am now working with some promise of result. Among other results obtained by considering the variation of b throughout homologous series, I may mention that, plotted against numbers of carbon atoms for the fatty acids, b lies on one curve for the odd numbers of carbons, and another for the even numbers. The data are

VISCOSITY OF WATER.

$$\eta_{\mathrm{calc.}} = 4\cdot328e^{1554/T}(1 + e^{12\cdot097 - \cdot0477T}) \times 10^{-5}$$

Temperature °C.	$\eta_{\mathrm{obs.}} \times 10^5$.	$\eta_{\mathrm{calc.}} \times 10^5$.	$\dfrac{\eta_{\mathrm{obs.}} - \eta_{\mathrm{calc.}}}{100\,\eta}$. (Percentage error.)
− 9·3	2545	2539	+ ·2
− 8·48	2454	2456	− ·1
− 7·23	2337	2338	− ·05
− 6·2	2246	2246	0
− 4·7	2118	2122	− ·2
− 2·1	1927	1930	− ·2
0	1795	1792	+ ·2
5	1523	1521	+ ·1
10	1306	1308	− ·15
15	1140	1139	+ ·1
20	1003	1003	0
25	894	892	+ ·2
30	800	800	0
35	723	722	+ ·15
40	657	657	0
45	600	600	0
50	550	551	− ·2
55	508	508	0
60	471	471	0
65	436	437	− ·2
70	407	407	0
75	380	381	− ·3
80	356	356	0
85	335	335	0
90	315	315	0
95	(297)	296	− ·3
100	(281)	280	− ·35

In the experimental values for 95° and 100° Hosking's values, which are markedly higher than those of other observers, are omitted. The values given are averages for Slotte, Thorpe and Rodger, and Bingham and White. Accurate determinations in the neighbourhood of the boiling point are badly needed.

very scanty, but this conclusion seems justified, and extends to the liquid state conclusions based on the behaviour of the solid state to X-rays.

The variation of viscosity with pressure is another part of the subject which is yielding promising results. The general nature of the increase is clearly represented by the theory, log η being a linear function of P as a first approximation, but even in cases such as water something of a more quantitative nature has already been obtained. The viscosity of solutions is another field to which the general formula is being applied.

One of the greatest troubles which I have met with in trying to check the theory is the lack of precise data. Organic chemists tell me that it is doubtful, for example, if the fatty acids used for the recorded determinations were pure. Again, the variations between the results obtained by different observers with certain of the most ordinary substances, for example, ethyl ether or mercury, are very large : for ether they amount to as much as 9 per cent in the neighbourhood of 20° C., and for mercury to 3 per cent at temperatures above 140° C. (see Erk, "Unsere Kenntnis der Zähigkeit von Quecksilber," *Zeitschrift für Physik*, **47**, 886 ; 1928). The range of measurements

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[1] The purely empirical four-constant formula which Bingham and Jackson (Bureau of Standards, No. 298) give for fitting water from 0° to 100° shows an error of 1·4 per cent when extrapolated to − 9° C.

is, in general, extraordinarily limited compared to, say, that available for surface tension : there are, in general, no measurements above the boiling point at atmospheric pressure, and for low boiling liquids scarcely any at all below 0° C., which is in many cases, for example, pentane, the most important part of the range. I am planning a series of investigations to be carried out in this laboratory, in the hope of adding to the reliable data for viscosity, more especially the temperature variation required to give b.

Turning to the letters which have been sent to NATURE since my first letter was printed, the letter from my old friend Dr. S. E. Sheppard, published on Mar. 29, gives what is practically my formula and states one of my first results, namely, that for a large number of liquids the formula represents the observed data, within experimental error, over a wide range of temperature. The complete independence of our work— our letters were written within a few days of one another, his in America, mine in England—may serve to emphasise the point that I wish to stress, namely, that this formula has a fundamental significance, and the constant b—Sheppard's k—has an intimate relation to the various properties connected with the internal energy of liquids. The other points of interest which Sheppard raises are not the same as mine. Sheppard has not made it quite clear how he obtains his a for associating liquids, for $\eta = Ae^{b/T}$ will not fit, for example, water. Presumably, he has found the value of b by fitting one or two of the low temperature values. I note that he has found that the formula has been already given by Senor J. de Guzman in the *Anales de la Sociedad Española de Fisica y Quimica*, 1913. Prof. Kendall has pointed out to me that he mentions it, in the form $\log \eta^{1/3} = a/T + b$, in a footnote to a paper in the *Journal of the American Chemical Society*, **39**, 1799 ; 1917. I have also, since deriving it, found that J. S. Dunn has given it in a short paper in the *Transactions of the Faraday Society*, **22**, 401; 1926, as quoted in Mr. E. W. Madge's letter. Mr. Dunn's paper had escaped my attention just as it has that of Dr. Sheppard and his collaborators. No particular attention ever seems to have been paid to the formula before, and it is not quoted in the standard books, for example, Hatschek's " Viscosity of Liquids ". It is

always distressing to find that one has been anticipated, in whatever degree, but it certainly does not seem to have been previously realised that the formula $\eta = Ae^{b/T}$ is fundamentally characteristic of normal liquids.

As regards Mr. E. W. Madge's formula, $\eta = \dfrac{A}{T-b}e^{\beta T}$, it does not seem to fit octane sensibly better than my formula with two constants, and it does not fit water so well as the formula $\eta = Ae^{b/T-\theta}$, with the same number of constants, which I quote earlier in this letter, variations as large as 1·5 per cent occurring in Mr. Madge's table, as against 0·9 per cent over the same range with my simpler three-constant formula. If Mr. Madge had computed the value for supercooled water at $-9\cdot3°$ C., he would have found a discrepancy of nearly 5 per cent, as against 1·3 per cent given by $\eta = Ae^{b/T-\theta}$!

Dr. Frenkel's formula is scarcely, as he claims, " practically equivalent " to mine, for it is $ATe^{b/T}$, instead of $Ae^{b/T}$, and the multiplication by T renders it unable to fit the variation of viscosity with temperature, interesting as is its derivation.

I am afraid I can attach but little importance to the fact, cited by Dr. Black, that the formula does not fit commercial mineral oils, of no definite composition, in view of my success, confirmed by Dr. Sheppard, in fitting a great variety of pure chemical substances. I have investigated the type of variation from the formula shown by Dr. Black's oils, and it is of a nature quite different from that shown by pure substances which do not fit, namely, such as associate strongly. So far as I can learn, oils of this type often change their viscosity permanently on heating.

Sir Ambrose Fleming's very interesting letter deals with the points which lie somewhat off the main current of my argument.

I feel that some apology for the length of this letter is needed, but, even in this space, I have only been able to refer in the briefest possible manner to points connected with the subject which I have under immediate investigation.

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Catalytic Reactions at High Pressures.

THE technical synthesis of ammonia by high pressure catalysis has given a great impetus to the development of high pressure reactions. At the present time reaction pressures are confined to a few hundred atmospheres, at which pressures the technical problems in so far as material and construction are concerned may be fairly claimed to be solved. Work in the high pressure laboratory at Amsterdam envisages operating pressures above ten thousand atmospheres and a few determinations of physical constants have already been made at pressures as high as 35,000 atmospheres. At these pressures, again, especially at high temperatures, new problems of material, construction, and design will confront the engineer hoping to industrialise a process operating under these conditions. Technical interest in catalysis at high pressures is at present focused on the numerous reactions involving the use of water gas as raw material and on hydrogenation of coal, including products derived from coal. Many others involving processes of amination and oxidation are doubtless capable of development.

Whilst the difficulties involved in the hydrogenation of coal are partly economic in character and lie partly in the variability of the raw material, these factors are not so important in many of the reactions involving

water gas, and in that field it is clear that a whole series of careful physical chemical investigations are necessary before the state of affairs may be considered to be at all satisfactory.

In developing the synthesis of ammonia, preliminary work involved the determination of the data necessary to establish the conditions of equilibrium of the system

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

over a wide range of pressure and of temperature. This phase of the problem was in part simplified by the absence of other reactions in the combination of the two gases and by a knowledge, with fairly accurate data available, of the specific heats of hydrogen and nitrogen and approximate values for the heat of formation of ammonia, its specific heat and compressibility. More accurate data have only recently been obtained, but the approximate data available before development of the industrial processes were sufficiently accurate.

In the case of reactions involving water gas, the state of affairs is much more complex because there is a whole series of reactions which are possible with the gases carbon monoxide and hydrogen. The initial