The effect of an electric field on the viscosity of liquids

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An apparatus for measuring the effect of an electric field on the viscosity of liquids has been developed, in which the liquid runs in a narrow channel between plane metal boundaries which can be used as electrodes. The apparatus allows the use of fields up to an average strength of 35 kV/cm, and gives a high degree of accuracy. With non-polar liquids, either dry or contaminated with water so as to conduct, and with non-conducting polar liquids an electric field transverse to the line of flow has no marked effect on the viscosity. With polar liquids that conduct relatively well, either normally or when contaminated with water, the electric field causes a considerable increase in apparent viscosity. This effect increases with increasing strength of field, but reaches a limiting value for very high fields. With polar liquids whose conductivity can be diminished by successive purifications the magnitude of this limiting effect is proportional to the conductivity of the specimen.

With an alternating field the effect on viscosity remains constant, as frequency is increased, until a certain critical frequency is reached, and thereafter decreases with frequency, until it becomes too small to be detected. The critical frequency decreases as the distance between the electrodes increases and increases as the temperature is raised.

There is no effect on viscosity with a field parallel to the lines of flow.

All these experimental facts can be explained on the theory that the effect is due to the accumulation of ions that takes place in the neighbourhood of the electrodes when the liquid conducts. The ions act as centres round which polar molecules cluster. Thus for an effect to appear it is necessary to have a liquid which conducts and which is made up of polar molecules. The limiting increase of apparent viscosity which takes place at high fields is due to the fact that the increase of viscosity of the liquid near the electrodes slows down the ions, and thus tends to diminish the number of excess ions. The variation of the effect of an alternating field with frequency also finds a ready explanation in this theory. The theory has been made to account for various other observed facts.
PART I. EXPERIMENTAL METHODS AND RESULTS

INTRODUCTION

It is now generally accepted that the variation of viscosity of normal non-associated liquids with temperature is closely expressed by the formula\(^*\)

\[ \eta = Ae^{b/T}, \]

where \(kb\) is a factor which measures the particular energy involved in the interchange which gives rise to the viscous forces, \(k\) being Boltzmann’s constant. This energy may depend upon the volume: Andrade has attempted to allow for this by taking \(b\) as inversely proportional to the atomic volume, deriving the formula

\[ \eta v^b = Ae^{b/vT}, \]

which further takes account of the effect of the thermal expansion on molecular distances. Andrade (1934, 1940) has suggested that the activation energy in question can be represented as an energy of orientation in the local electric field. Later, Eyring (1936), applying the theory of reaction rates to the viscosity problem, took \(b\) as being the activation energy necessary if a molecule is to pass over a barrier from one potential minimum to another. Whatever view be taken, it is clearly of interest to see if this energy factor can be influenced by an external electric field.

We may write

\[ \eta = Ae^{E/kT} \]

or

\[ \frac{d\eta}{\eta} = \frac{E}{kT} \frac{dE}{E}. \]

The value of \(E/kT\) is for most organic liquids somewhere about 3, \(E/k\) being about 800, or \(E = 10^{-13}\) ergs approximately. Taking the external field as 30 kV/cm. = 100 e.s.u./cm., and considering a dipole moment of the order \(10^{-18}\) e.s.u., then the change of energy is of the order \(10^{-16}\) erg and \(d\eta/\eta = 3 \times 10^{-3}\) which is easily measurable. By choosing a liquid of large dipole moment it should be possible, if fields of 100 e.s.u./cm. and more are practicable, to get something approaching a 1 % effect.

Turning to a non-polar molecule, the polarizability is given by

\[ \frac{4\pi}{3} N \gamma = \frac{n^2 - 1}{n^2 + 2d} M, \]

where \(N\) is Avogadro’s number, \(M\) is the molecular weight, \(d\) the density, \(n\) the refractive index and \(\gamma\) the polarizability. The value of \(\frac{n^2 - 1}{n^2 + 2d}\) is round about 0.3.

Taking again the field to be 100 e.s.u./cm.

\[ \gamma = \frac{100}{4 \times 6 \times 10^{23}} 0.3 = 1.25 \times 10^{-23}, \]

\(^*\) This formula was put forward independently by Andrade (Nature, 1 March 1930) and S. E. Sheppard (Nature, 29 March 1930). For its history see E. N. da C. Andrade, Phil. Mag. 1934, 17, 703.
and energy due to field \( f \) is

\[
\gamma f^2 = 1.25 \times 10^{-19} = dE = \text{change of energy in field.}
\]

Then

\[
\frac{d\eta}{\eta} = \frac{E \, dE}{kT \, E} = \frac{1.25 \times 10^{-19}}{1.37 \times 10^{-16} \times 300} = 3 \times 10^{-6}.
\]

There is little hope of detecting an effect of this magnitude without great refinement of any technique at present in use, and it may be noted that such a change corresponds to a temperature variation of a few ten thousandths °C.

Many previous workers, in papers to be discussed later, have attacked the problem of the effect of an electric field on viscosity, but, in the case of polar liquids, there have been wide divergencies in the results obtained. In the experiments to be described we have made an extended series of careful measurements on the effect, with both polar and non-polar liquids. We have used much higher fields than previous workers and, in addition to steady fields, have made systematic measurements with alternating fields of various frequencies, which have thrown light on the phenomena. In particular, we have in all cases measured the small current carried by liquids under the different steady applied potentials, which has usually been neglected. Both the transverse and the longitudinal effects have been investigated, although the measurements on the latter are comparatively few, since the results, negative in all cases, showed that it had a more restricted interest, at any rate in these preliminary investigations.

In the case of polar liquids our work leads us to believe that the large effects found by many previous workers, including changes of many tens of per cent, sometimes of over a hundred per cent, in viscosity, are spurious, being caused, in the case of liquids which conduct, by an accumulation of ions in the neighbourhood of the electrodes, which leads to a modification of the state of aggregation of the polar molecules and a consequent increased viscosity in this region. This effectively reduces the channel. The local accumulation of ions also modifies the distribution of the electric field.

Our experiments further throw light on the conduction of electricity by certain classes of polar liquids. We believe that we have established the conditions under which a true effect of electric field on viscosity can be sought with polar liquids, but circumstances which need hardly be specified* have prevented us from embarking on determinations under these conditions. We hope that an opportunity to do this will occur in the future.

**Experimental method**

After certain preliminary experiments in which the liquid flowed longitudinally between concentric cylinders, separated by a small gap, it was decided to use a long gap of rectangular cross-section. The width of the cross-section of the gap was large

* The work here described was essentially completed in 1939. A preliminary announcement of certain results was made in *Nature* (Andrade & Dodd 1939a,b).
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compared to the height, and the potential difference was applied between the larger opposite faces, giving a field transverse to the direction of flow.

A serious difficulty in the way of constructing an apparatus of this kind, in which metal surfaces have to be fixed in liquid-tight contact to insulating strips, is to find a cement which is a good insulator and is not attacked by the various organic solvents with which it is desired to make measurements. Another difficulty is to make the gap, which should only be a fraction of a millimetre across, sufficiently uniform. In the final form of our apparatus we utilized, for one side of the gap, three high-precision steel gauges, made by Messrs Pitter, 14 cm. long, 1 cm. wide, and 3 cm. deep, bolted together with the $14 \times 3$ faces in contact so that the $14 \times 1$ cm. surface of the central one projected 3 mm. beyond the like surfaces to either side, all these surfaces being made accurately parallel. The projecting plate was tapered away at each end and holes were drilled in it normal to the $14 \times 1$ face, to provide admission for the liquid. For the other side of the gap a steel base-plate $14 \times 6 \times 2$ cm. was used. To separate the stepped face from the flat plate two quartz slips $14 \times 1.5 \times 0.32$ cm., optically worked by Messrs Hilger, were employed. The gap was then formed by assembling the gauges and quartz strips as shown in figure 1a, which represents a central transverse section, the depth of the gap being 0.20 mm. Figure 1b shows the general arrangement of the apparatus in longitudinal section.

Figure 1a

Figure 1b
The steel and quartz surfaces were so well worked that good optical contact was secured along the whole quartz-steel surface, the adhesion being such that it was extremely difficult to produce relative movement between the parts. As a precaution against displacement a cement of glue and black treacle was applied along the external re-entrant angle, but this cement played no part in retaining the liquid or in the insulation. It was clear in subsequent experiment that no liquid ever penetrated between the surfaces in optical contact. To close each end of the gap a mica plate was placed over the small rectangular hole, and held in position by a stout bakelite plate, secured by screws to the metal plates. This gave perfect insulation and the whole assembly was free from leak. A liquid left in the apparatus for several days maintained its original resistance, and other tests also showed that it was unchanged.

Stainless steel tubes were fastened with bakelite cement into the bottom of glass viscometer bulbs, of the form shown in figure 1b, and these tubes were screwed into the holes in the central gauge block. The viscometer bulbs were provided at their upper ends with conical ground joints, to enable them to be connected to a hand suction pump through a two-way tap. The liquid could thus be drawn to the desired height in either bulb, and flow then initiated by turning the tap so as to connect the air above the two bulbs. Two similar viscometers were constructed on these lines, so that one could be used without field while the other was used with field: the lower plates of these two viscometers were in contact with a thick metal plate, and the effect of any small, slow temperature fluctuations was thus minimized. The glass-walled tank containing the two viscometers was totally immersed in a thermostatically controlled water-bath. The variations of temperature were so small that the time of flow of a typical liquid was constant in successive runs to within 0.2 sec. for a total time of 500 sec. The lower plates of the viscometers were earthed, and the upper plate of either could be connected to a source of high potential.

The time taken for the liquid to fall between the marks on the 50 cm.³ viscometer bulbs was measured with a $\frac{1}{10}$ sec. stop watch and taken as a measure of the viscosity. This time was never less than 4 min. and generally much longer. Several runs were always taken and the average adopted.

The source of potential for the steady field was a number of ordinary wireless high-tension batteries. The difference of potential was measured by a Wulff bifilar electrostatic voltmeter up to 300 V, and above that by a Leybold unifilar instrument. For the alternating field a large Sullivan oscillator was used.

The current carried by the liquid, which has been neglected by most previous workers, was measured by means of a sensitive galvanometer or, when larger, by a microammeter.

For the longitudinal field, a viscometer was constructed which consisted of ten channels in series, as shown in figure 2, arranged normally to metal electrodes separated by a distance of 6 cm. The channels were 1 cm. wide and 0.03 cm. deep, cut centrally in bakelite strips which were cemented together at the edges with bakelite cement. The liquid passed up one channel and down the next, through a
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comparatively open space joining the adjacent ends of each pair of adjacent channels. To apply the field two large circular brass plates were cemented one to each opposite end of the channel block, so that the field ran parallel to the flow. The distance between these plates was 6 cm. Exit and entrance ports were provided at the ends of the channel system. The viscometer bulbs attached to the entry and exit tubes were of the same type as used in the transverse apparatus. The whole was immersed in transformer oil. A p.d. of 100,000 V or so was furnished by a powerful Wommersdorf influence machine.

![Diagram of an electrode](image)

**Figure 2**

**Measurement of the conductivity**

In the course of the work the conductivity of certain organic liquids was often taken as an index of the purity and special measurements were therefore made in a conductivity cell. This was of glass, holding about 1 cm.³, with platinum plate electrodes of area 2 cm.², 3 mm. apart. The cell was closed by a glass stopper with a mercury seal. The cell constant in the equation

$$\text{conductivity} = \frac{\text{cell constant}}{\text{resistance}}$$

was found to be 0.085 by measuring the resistance when filled with n/1000 potassium chloride solution, allowance being made for the conductivity of the water used. All measurements were made at 0° C. The resistance was measured by means of an a.c. bridge incorporating a Wagner earthing device, as described in the standard books.
Preliminary experiments were carried out with transformer oil in an earlier version of the apparatus described, made with brass plates cemented with sealing wax to quartz separating strips. The gap was about 0.8 mm deep. There were two exactly similar viscometers, one used as a control to eliminate the effect of small temperature variations during the run. Readings of the rate of flow were taken with both viscometers simultaneously, first with the field applied to one apparatus and later with it applied to the other. The average time of flow with field was compared with the average time of flow without field.

In the first experiments, with the oil as supplied by the manufacturer, small increases of viscosity, sometimes as great as 1%, were noted. The oil was then degassed by maintaining it at 46° for an hour in a flask continuously evacuated by means of a rotary oil pump. Dry air was then admitted from phosphorus pentoxide drying tubes, and the oil was filtered through a fritted glass filter to remove any particles. The oil treated in this way showed no change in viscosity as great as 1 part in 2000, even when the apparatus was subjected to a potential difference of 4000 V, corresponding to a field of 50 kV/cm. The slight increases previously obtained were probably due to the presence of dissolved gas and particles.

The dipole moment of the oil was determined by finding the dielectric constant and density at four temperatures over a range of 40° C. The molar polarization was found to have the constant value of 95.5 cm. Since this method is not strictly applicable to liquids, Debye's method of measuring the polarization of different concentrations of the liquid dissolved in a non-polar solvent was used. Benzene was taken as the non-polar solvent and the polarizations of four solutions of oil of different concentrations were found from dielectric constant and density measurements carried out at constant temperature. We have to thank Dr H. R. Sarna for putting at our disposal for these measurements a special condenser and bridge circuit which he was using in his own research. The molar polarization is

\[ P_{12} = \frac{k - 1}{k + 2} \frac{M_1 f_1 + M_2 f_2}{d}, \]

where \( M_1 \) and \( M_2 \) are molecular weight of benzene and oil respectively, \( k \) and \( d \) are the dielectric constant and density of the solution, and \( f_1 \) and \( f_2 \) are the molar concentrations of benzene and oil respectively. By plotting \( P_{12} \) against the concentration \( f_2 \), the values of \( P_2 \), the molar polarization of the oil, were deduced for various values of \( f_2 \). From a second graph of \( P_2 \) against \( f_2 \) the value at infinite dilution was found.

The refractive index of the oil was determined with a Zeiss-Pulfrich refractometer, and from this a value of the distortion polarization \( P_D \) of the oil found by use of the Lorentz-Lorenz equation. The dipole moment = 0.0127 \times 10^{-18}(P - P_D) T. Our values for \( P \) and \( P_D \) were 84.9 and 85.2 c.c. respectively, from which it appeared that the oil had no measurable dipole moment. Thus for this particular non-polar oil the change of viscosity with field must be less than 1 part in 10^5 per kV/cm.
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Measurements with non-polar liquids

Carbon disulphide

Carbon disulphide, a non-polar liquid which can be readily obtained in a fairly pure state, was the first definite chemical compound tried. The liquid was carefully distilled and then filtered through a fritted glass funnel. Both viscometers, of the construction described under ‘Experimental method’, were dried out, filled with the liquid and placed in the thermostat. After 4 hr. all times of flow had become constant.

About 100 V were applied to the first apparatus and the difference of the times of flow again found. The applied voltage was gradually increased by increments of about 50 V, and although voltages up to 635 V were applied, the difference in the two times of flow remained the same to within 0·2 sec.

The results obtained for carbon disulphide are given in full, as being typical of the method used for all liquids (table 1). Rough statistical treatment of the results indicates that the viscosity does not change by more than 1 part in 20,000 for an average field of 5 kV/cm, supposing the effect to be proportional to the field, while the four last determinations, made at an average field of 26 kV/cm., give a most probable variation of 1 part in 5000. It may be concluded generally that the effect of an electric field on the apparent viscosity* of carbon disulphide certainly does not exceed 1 part in 5000 for a field of 26 kV/cm., and is probably much less.

<table>
<thead>
<tr>
<th>Voltage on app. no. 1 (kV)</th>
<th>Galvonometer deflexion (cm.)</th>
<th>Time of flow $t_1$ in sec.</th>
<th>Time of flow $t_2$ in sec.</th>
<th>Galvonometer deflexion (cm.)</th>
<th>Voltage on app. no. 2 (kV)</th>
<th>$t_1 - t_2$ (sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>105</td>
<td>0·7</td>
<td>269·9</td>
<td>249·4</td>
<td></td>
<td>20·4</td>
<td></td>
</tr>
<tr>
<td>116</td>
<td>0·9</td>
<td>269·9</td>
<td>249·3</td>
<td></td>
<td>20·5</td>
<td></td>
</tr>
<tr>
<td>155</td>
<td>1·1</td>
<td>269·9</td>
<td>249·4</td>
<td>0·9</td>
<td>20·4</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>1·7</td>
<td>269·9</td>
<td>249·3</td>
<td></td>
<td>20·3</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>2·9</td>
<td>269·9</td>
<td>249·4</td>
<td></td>
<td>20·5</td>
<td></td>
</tr>
<tr>
<td>385</td>
<td>3·2</td>
<td>269·9</td>
<td>249·2</td>
<td>2·8</td>
<td>20·4</td>
<td></td>
</tr>
<tr>
<td>480</td>
<td>7·6</td>
<td>269·8</td>
<td>249·4</td>
<td></td>
<td>20·4</td>
<td></td>
</tr>
<tr>
<td>635</td>
<td>14·4</td>
<td>269·8</td>
<td>249·3</td>
<td>7·6</td>
<td>20·5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>269·8</td>
<td>249·3</td>
<td></td>
<td>20·4</td>
<td></td>
</tr>
</tbody>
</table>

Gap across which voltage is applied = 0·2 mm.
Galvonometer constant = 8·3 x 10$^{-9}$ amp./mm.

* By ‘apparent viscosity’ we denote the viscosity needed to give the observed time of flow on the assumption that the viscosity of the liquid is uniform throughout the gap. The reason for this term will become apparent in the discussion at the end of the paper.
Carbon tetrachloride

A pure dry specimen of carbon tetrachloride showed no change in time of flow for applied fields up to 40 kV/cm. The current passed was very small, never exceeding 0.5 μA. When the carbon tetrachloride was saturated with water there was likewise no change of time of flow with electric field, but the current was of the order of 1 mA.

Benzene

With a pure dry specimen of benzene no change of apparent viscosity was obtained even when fields of over 40 kV/cm. were applied. The current never exceeded 0.5 μA. With wet benzene, as with wet carbon tetrachloride, there was likewise no viscosity effect, but the current was once more of the order of 1 mA.

\[ K = 2.58 \times 10^{-6} \, \Omega^{-1} \, \text{cm}^{-1} \]

**Figure 3a**

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Measurements with polar liquids

Acetonitrile

As the first example of a polar liquid with a large permanent dipole moment, we chose acetonitrile, using the pure Kahlbaum product. The two viscometers were used, and runs made as before. An increase of time of flow with field was obtained. Interpreting this as due to rise of viscosity, the variation of viscosity with mean field \* was as shown in figure 3a. It will be seen that very large increases were obtained, rising to a limiting value of some 115% with the highest fields. The current for various fields is shown by the broken line, the scale being given on the right. The $K$ given in the diagram indicates the conductivity in reciprocal ohm cm., obtained from independent measurement made as described.

The relatively large value of the current might, it was held, be due to impurity. The Kahlbaum product was therefore shaken for one hour with phosphorus pentoxide and distilled. The distillate was again shaken with pentoxide and redistilled, and this distillate again distilled four times. With this product the results recorded in figure 3b were obtained. The form of the curve of viscosity increase and of the current curve were similar to those obtained with the original liquid, but the effects were reduced.

Further purifications were then effected, the measurements being repeated after each process. The results are shown in figures 3c, d and e, \dagger from which it is seen that the limiting value of apparent viscosity increases was finally reduced to about 27%, and the cell conductivity, which is recorded on each diagram, from its original value of $25.8 \times 10^{-7}$ to $5.78 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$.

The limiting values of the increase of apparent viscosity, as indicated by times of flow, taken from the curves of figure 3, were then plotted against the conductivity, as shown in figure 4, the figures being

\[
\begin{array}{cccccc}
K \times 10^7 & 25.8 & 22.3 & 18.4 & 15.1 & 5.78 \\
At/t & 1.15 & 0.92 & 0.78 & 0.64 & 0.27 \\
\end{array}
\]

$At$ here denotes the excess of the time of flow $t$ above the normal field-free value for the high fields at which it reaches a limiting value. From figure 4 it appears that this excess is proportional to the conductivity and, within the accuracy that the measurements permit, that there would be very small or no increase of apparent viscosity in a liquid so pure that it did not conduct, if such a specimen could be prepared.

Variation of the current with the field. A curve of current against field for acetonitrile shows that for this very polar liquid ($\mu = 3.4 \times 10^{-18}$ e.s.u.) Ohm's law breaks down at fields in the region 2500 V/cm., and that the current after tending towards a

\* By 'mean field' we denote the applied potential difference divided by the distance between the electrodes. It will appear later that the potential fall is not uniform in a conducting liquid.

\dagger The curves of figure 3 do not lie as regularly as might be wished, those of $b$ and $c$ crossing other curves. We intended to repeat the measurements, but were prevented by the war. These were the earliest of the systematic measurements on polar liquids: later results, such as those on acetone, are perfectly regular.
acetonitrile

\[ K = 2.23 \times 10^{-6} \ \Omega^{-1} \ \text{cm}^{-1} \]

\[ \frac{\Delta \eta}{\eta} \]

field (kV/cm.)

Figure 3b

acetonitrile

\[ K = 1.84 \times 10^{-6} \ \Omega^{-1} \ \text{cm}^{-1} \]

\[ \frac{\Delta \eta}{\eta} \]

field (kV/cm.)

Figure 3c
The effect of an electric field on the viscosity of liquids

**Figure 3d**

Acetonitrile

\[ K = 1.5 \times 10^{-6} \Omega^{-1} \text{cm}^{-1} \]

\[ \frac{\Delta \eta}{\eta} \]

Field (kV/cm.)

\[ \text{Current (mA)} \]

**Figure 3e**

Acetonitrile

\[ K = 5.78 \times 10^{-7} \Omega^{-1} \text{cm}^{-1} \]

\[ \frac{\Delta \eta}{\eta} \]

Field (kV/cm.)

\[ \text{Current (mA)} \]
saturation effect begins to increase rapidly and, of course, would become very large when a spark passed if the voltage were still further increased. Indeed, the whole curve is reminiscent of that for an ionized gas.

A very tentative estimate of the coefficient of recombination of the ions in acetonitrile can be made from these curves showing the relation between current and applied field.

![Graph showing limiting value of \( \frac{dI}{dt} \) vs. conductivity.](http://example.com)

**Figure 4**

It may be shown that for an ionized gas

\[
\frac{\alpha}{e} = \frac{I}{i^2} \frac{4k^2X^2}{l}, \quad \text{provided } i \ll I,
\]

where \( \alpha \) is the coefficient of recombination of the ions whose charge is \( e \),

\( I \) is the saturation current density,

\( l \) is the distance between the electrodes,

\( i \) is the current density with an applied field \( X \),

\( k \) is the mobility of positive and negative ions, assumed the same.

From figure 3e

\[
I = 0.1 \mu A/cm.2 = 3 \times 10^5 \text{ e.s.u./cm.}^2, \\
i = 1.2 \times 10^4 \text{ e.s.u./cm.}^2, \\
X = 250 \text{ V/cm.}, \\
k = 2 \times 10^{-8} \text{ cm.} \text{sec.}^{-1}/\text{V cm.}^{-1}, \\
l = 2 \times 10^{-2} \text{ cm.}
\]

Therefore

\[
\frac{\alpha}{e} = \frac{3 \times 10^5}{1.44 \times 10^8} \frac{4 \times 4 \times 10^{-6} \times 2.5^2 \times 10^4}{2 \times 10^{-2}} = 0.105.
\]
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A value for $\alpha/e$ for the ions produced in liquids by rays from radium has been determined by Jaffé (1910) and van der Bijl (1912). For liquid hexane van der Bijl finds $\alpha/e = 2.26$, which is not unreasonably different from that for the ions in acetonitrile calculated by the above method, when all the different circumstances are considered.

**Heating due to the current.** There must be a small heating effect due to the current, and this will in turn influence the viscosity. An estimate was made of the size of this effect. With 100 V (5 kV/cm.) the current with acetonitrile in the apparatus did not exceed 1 mA, corresponding to a generation of heat of 0.025 cal./sec. If all this heat were used to raise the temperature of the liquid, none being communicated to the metal—an extreme supposition—then for 30 cm.³ of a liquid of specific heat 0.5 flowing through in 300 sec., the rise of temperature would be 0.5° C. This is very much an upper limit.

That the rise was much less was indicated by the fact that the time of flow before and after the application of the field was unchanged. To investigate the matter more closely a thermodn junction, protected by a very thin quartz tube, was placed both at the entrance and exit from the gap. With the field applied no temperature difference amounting to 0.01° C could be detected. A further test was made by holding the liquid steady and applying the field for 10 min. On allowing flow to start a rise of temperature at the exit of 0.3° C was observed, which rapidly fell to 0.02° C and then to zero. The first rise was due to the liquid which had been warmed in the gap for 10 min., and had communicated heat to the metal in contact with it. The entry of the cold liquid from the viscometer bulb soon cooled the metal and reduced the effect to an unobservable value.

Thus, when the liquid is flowing, even with a current of 1 mA passing, the heat exchange with the metal is so good that the rise in temperature of the liquid is less than 0.01° C. For the majority of the liquids used the current was only a fraction of a milliampere, even with 800 V between the plates. The rise of temperature is, therefore, negligible.

**Acetone**

With acetone, curves showing the variation of the time of flow with applied voltage were obtained for three samples of varying purity obtained by repeated distillations. These curves showed very pronounced limiting values, the increase of viscosity effect increasing by only 1 % when the voltage was increased from 240 to 360 V (see figure 5).

The conductivity of each sample was obtained by measuring the resistance in the same conductivity cell as was used for acetonitrile:

$$K \times 10^6 \quad 3.42 \quad 1.96 \quad 0.87$$

$$At/t \text{ (limiting)} \quad 29.8\% \quad 17.0\% \quad 7.7\%$$

The limiting values of viscosity increase were much smaller than those obtained for acetonitrile. The graph of limiting increases of viscosity against conductivity

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acetone

$K = 3.42 \times 10^{-6} \, \Omega^{-1} \, \text{cm}^{-1}$

$K = 1.96 \times 10^{-6} \, \Omega^{-1} \, \text{cm}^{-1}$

$K = 6.87 \times 10^{-6} \, \Omega^{-1} \, \text{cm}^{-1}$

Figure 5
The effect of an electric field on the viscosity of liquids

was again a straight line passing through the origin (see figure 6), indicating that there would be very small or no change of viscosity with field in a specimen of acetone which passed no current.

![Diagram of acetone viscosity change](image)

**Figure 6**

**Diethylamine**

A pure specimen of diethylamine was tested and was found to give a large increase in apparent viscosity. The curve representing the variation of this increase with the applied field was of the usual form, showing a well-defined limiting increase of 41.6 % as represented in figure 7. The current obeyed Ohm's law for fields up to 33 kV/cm., for which field the current was 250 μA.

**Ethylene dichloride**

The pure dried liquid showed an increase in apparent viscosity with applied field, the curve expressing the relation between this increase and the field producing it being of the usual form. The limiting value of the increase in apparent viscosity was 28.8 % (figure 8).

The current passing through the liquid was strictly proportional to the applied voltage, having a value of about 70 μA when the field was 33 kV/cm.
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The alkyl acetates

Pure specimens of the first five members of the homologous series of acetates were in turn distilled directly into the apparatus and their apparent viscosity measured under various electric fields. The curves of increase in apparent viscosity against field were of the same general shape, a limiting value for the increase being obtained for a field of about 25 kV/cm. (see figure 9). This value, however, decreased steadily
as the specimen moved higher up the series, being 47·5 % for methyl and only 7·5 %
for \( n \)-amyl acetate. The current was much greater for the former than for the latter
(table 2).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Current for 600 V (µA)</th>
<th>( \Delta t/t ) (limiting) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl acetate</td>
<td>1050</td>
<td>47·5</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>670</td>
<td>41·5</td>
</tr>
<tr>
<td>( n )-propyl acetate</td>
<td>300</td>
<td>29·0</td>
</tr>
<tr>
<td>( n )-butyl acetate</td>
<td>175</td>
<td>14·0</td>
</tr>
<tr>
<td>( n )-amyl acetate</td>
<td>85</td>
<td>7·5</td>
</tr>
<tr>
<td>isobutyl acetate</td>
<td>65</td>
<td>12·6</td>
</tr>
</tbody>
</table>

For the three members, normal propyl, butyl and amyl, the current obeyed
Ohm’s law, but for the other two members, methyl and ethyl, the current ceased
to be proportional to the applied voltage for fields greater than about 10 kV/cm.
This agrees with the general observations that Ohm’s law breaks down when the
currents are high.

Determinations were made on an isomeric form of one member of the series, with
interesting results. The liquid selected was isobutyl acetate, and its limiting value
for the increase was almost the same as that for the normal acetate, although the
current was almost three times as great for the latter.

**Diethyl ether**

The ether used in the first place was especially pure and had been dried over
sodium and redistilled. This liquid conducted hardly at all, the current never ex-
ceeding 1 µA, although voltages up to 700 V were applied. No increase in the apparent
viscosity was found, even when a field of 35 kV/cm. was applied. Since an increase
of only 0·2 sec. in the time of flow (400 sec.) could have been detected if present, this
means that any increase in apparent viscosity must be less than one part in 2000.

The above sample was mixed with a little water, shaken up in a separating funnel
and allowed to stand, with frequent shakings, for 2 weeks, by which time the ether
could be assumed to be saturated with water. This fraction was poured from the
funnel into the apparatus, care being taken to see that none of the excess water
entered.

On applying a low field, a current of several microamperes was observed, which
obeyed Ohm’s law well. An increase in apparent viscosity was obtained which
increased with the applied field, as shown in figure 10, but it was found that the
liquid would not stand more than 9 kV/cm. With this voltage the current would
become momentarily very large, resume its previous value, and then leap up again,
the whole process giving indication that a spark was imminent at any moment. For
fields up to 8 kV/cm., the increase in apparent viscosity was proportional to the
square of the applied field, but for higher fields the effect fell off slightly, suggesting
that if the field could be increased sufficiently, a limiting value for the increase would
be reached, as usual. In figure 11 the fractional increase in apparent viscosity for
The effect of an electric field on the viscosity of liquids

increases up to 18 % is plotted against the square of the field. Except for the largest field applied, the current was strictly proportional to the potential difference between the two plates of the apparatus.

\[\text{moist ether}\]

\[\begin{array}{c|c|c|c|c|c|c|c|c}
\text{field (kV/cm.)} & 0 & 2.5 & 5.0 & 7.5 & 10.0 \\
\hline
\text{\(\Delta W/\eta\)} & 0.0 & 0.1 & 0.2 & 0.3 & 0.4 \\
\hline
\text{current (\(\mu\)A)} & 0 & 10 & 20 & 30 & 40 \\
\end{array}\]

\textbf{Figure 10}

\textit{Monochlorobenzene}

An exceptionally pure specimen of monochlorobenzene was obtained which passed a current of less than 0.1 \(\mu\)A even when the applied field was as large as 40 kV/cm. The time of flow without the field was about 600 sec., and no change in the time was observed even when the largest field was applied. Since the electrical conductivity of this specimen was almost zero, from the work on acetone and acetonitrile described earlier in this paper, no increase in viscosity would be expected even though the molecules were of a dipolar nature.

This specimen was shaken with a little water and allowed to stand in contact with it for over a month, by which time the chlorbenzene should have become saturated with water. This liquid, when placed in the apparatus, now passed a finite current when a strong electric field was applied to the apparatus. An increase in apparent viscosity of several per cent was obtained when the field was applied, a limiting effect of 8.7 % being observed under a field of 30 kV/cm., the current being about
10μA. The curve showing the variation of this increase with the applied field is given in figure 12. Up to 20 kV/cm, the increase is roughly proportional to the square of the field.

![Graph showing the variation of increase with square of field](image)

**Figure 11**

**Influence of size of channel on limiting values**

To investigate the effect of the distance between the electrodes two fresh sets of quartz separating plates were used, giving depths of channel of 0.22 and 0.28 mm. With a pure specimen of n-propyl chloride the results are shown in figure 13; no measurements with this liquid were made with the 0.20 mm. gap. The limiting value of the increase of apparent viscosity was 15.3% for the 0.22 mm. gap and 11.9% for the 0.28 mm. gap.

With chloroform the results with the different gaps are shown in figure 14. The value of the increase of apparent viscosity at 30 kV/cm. was 31.7% for the 0.20 mm. gap, 25.8% for the 0.22 mm. gap and only 21.0% for the 0.28 mm. gap. The dotted line represents the variation of the current with field, which is the same for all three gaps. It will be seen that the current is only 13 μA for a field of 30 kV/cm.
The effect of an electric field on the viscosity of liquids

Moist monochlorobenzene

\[ \frac{\Delta \eta}{\eta} \]

Field (kV/cm.)

Figure 12

N-propyl chloride

gap 0.22 mm.

gap 0.28 mm.

\[ \frac{\Delta \eta}{\eta} \]

Field (kV/cm.)

Figure 13
Effect with alternating fields

In a first attempt to find out if any of the effects obtained could be attributed to peculiarities of the apparatus, the effect of reversing the direction of the field was tried. It was found that the increase of apparent viscosity was exactly the same for either direction, as would be expected. We then proceeded to try the effect of an alternating voltage.

In the first case the supply from the mains was used, namely, 220 V at a frequency of 50 cyc./sec., and acetonitrile was adopted as the liquid. Assuming a simple harmonic wave form and that the voltage at any instant produced the static effect appropriate to that voltage, the increase calculated was 53.6%. The increase actually found was 52.7%, which agrees well within the limits to be expected.

The effect of varying the frequency of the field was then investigated. The source of supply of the alternating voltage was a large Sullivan oscillator, an input of about 10 V being applied to a valve amplifier by means of a potentiometer arrangement. The output from the amplifier was applied across the apparatus, chloroform being the liquid adopted. The magnitude and wave form of the potential difference between the plates were found by means of a cathode-ray oscillograph incorporating a linear time-base circuit. The wave form was made as nearly sinusoidal as possible, to simplify the calculation of the increase in viscosity to be expected on a static basis. The peak voltage was determined by photographing the trace and then placing on
The effect of an electric field on the viscosity of liquids

the same plate three lines corresponding to zero voltage and to a known steady field applied first in one and then in the other direction.

Beginning with a low frequency, the increase in the time of flow of the liquid in the apparatus was found for a given voltage amplitude. Experiments were then carried out over a range of increasing frequencies. The increase of time of flow caused

<table>
<thead>
<tr>
<th>frequency cyc./sec.</th>
<th>$\Delta \eta / \eta$ experimental</th>
<th>$\Delta \eta_s / \eta_s$ predicted on static basis</th>
<th>$\Delta \eta / \eta$</th>
<th>$\Delta \eta_s / \eta_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.317</td>
<td>0.317</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.210</td>
<td>0.208</td>
<td>1.009</td>
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<tr>
<td>100</td>
<td>0.185</td>
<td>0.185</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.241</td>
<td>0.243</td>
<td>0.990</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0.235</td>
<td>0.243</td>
<td>0.963</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>0.149</td>
<td>0.243</td>
<td>0.615</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.088</td>
<td>0.248</td>
<td>0.355</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>0.045</td>
<td>0.235</td>
<td>0.191</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>0.015</td>
<td>0.182</td>
<td>0.080</td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>0.015</td>
<td>0.195</td>
<td>0.077</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>0.016</td>
<td>0.222</td>
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</tr>
<tr>
<td>1000</td>
<td>0.013</td>
<td>0.190</td>
<td>0.068</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>0.007</td>
<td>0.192</td>
<td>0.037</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>0.005</td>
<td>0.195</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>4000</td>
<td>0.000</td>
<td>0.182</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

gap = 0.20 mm. $T = 15^\circ$ C

chloroform

gap 0.22 mm.
$15^\circ$ C

by the alternating field diminished as the frequency rose and ultimately became zero. The static curve was then obtained and the increases in apparent viscosity for the various applied alternating voltages calculated on a static basis. The actual increase was expressed as a fraction of the increase predicted on a static basis, and this ratio was found to decrease rapidly after a certain critical frequency had been reached. The results are expressed in table 3 and in figure 15.
INFLUENCE OF TEMPERATURE ON THE CRITICAL FREQUENCY

Since it had been found that the increase in apparent viscosity in an alternating field diminished rapidly once a definite critical frequency was exceeded, it was decided to determine how this critical frequency depended on the temperature of the liquid.

The previous experiment was therefore conducted at 25° C, and it was again found that the full increase was obtained up to a critical frequency, but for higher frequencies the increase rapidly diminished. The critical frequency was much higher in this case, being about 450 cyc./sec. as compared with 250 cyc./sec. at 15° C (see figure 16).

![Graph of chloroform viscosity change with frequency at 25° C, gap 0.20 mm.](image)

**Figure 16**

VARIATION OF CRITICAL FREQUENCY WITH SIZE OF GAP

The increase of viscosity for chloroform for various frequencies was determined in the apparatus having a deeper gap, namely, 0.28 mm.

Again it was found that the full effect was only obtained for frequencies below a certain critical frequency. The temperature of the liquid was made the same as that in the previous experiment (25° C); the value for the critical frequency was lower, being only about 350 cyc./sec., as compared with 450 cyc./sec. for the apparatus with a gap of 0.20 mm. (figure 17).

![Graph of chloroform viscosity change with frequency at 25° C, gap 0.28 mm.](image)

**Figure 17**

It was observed that the critical frequency was roughly inversely proportional to the size of the gap.
The effect of an electric field on the viscosity of liquids

Polar liquids showing no effect

1. Toluene. There was no change in the apparent viscosity of toluene with static field even when a field of 35 kV/cm. was applied to the apparatus. The current was small, being less than 0.5 μA with the largest field.

2. Metaxylene. There was no change in the apparent viscosity of metaxylene even when fields up to 40 kV/cm. were applied to the apparatus. Again the current was small, being less than 0.3 μA with the largest field.

3. Anisole (methyl phenyl ether). Fields up to 40 kV/cm. failed to produce any change in the apparent viscosity of anisole. The current was small, being only 0.8 μA under the largest field.

Longitudinal effect

Experiments with the direction of field parallel to the lines of flow were carried out with the apparatus described earlier, the source of potential being a Wommersdorf influence machine capable of giving about 100,000 V on moderate load. Acetonitrile was the first liquid tried, but it was found to conduct too well to allow the necessary potential difference to be established. Chloroform was then used, as being a liquid which showed a fairly large increase of apparent viscosity with a transverse field of 14 kV/cm. while conducting comparatively slightly. With an applied potential of 80 kV, giving a field of about 14 kV/cm., no change in apparent viscosity was detected. The time of flow was 250 sec.: a decrease in time of flow varying from 2 to 3 sec., according to the applied potential, was quantitatively explained by a slight rise of temperature that was found to take place. It can be said, then, that in the longitudinal case no change of apparent viscosity amounting to 1 part in 500 takes place under the conditions specified.

Part II. Discussion and Theory

Previous work

The early work on the effect of an electric field on the viscosity of liquids is not very convincing. König (1885), who seems to have been the first to work on the subject, used a glass capillary tube between condenser plates, about 1 cm. apart, to which a potential difference of about 14,000 V was applied. He found no change of viscosity with carbon disulphide. Duff (1896) used the falling sphere method, his spheres being of metal, and obtained an increase of viscosity with castor oil of about 0.5% and a possible decrease with paraffin oil with a field of 27 kV/cm. The method, which entails a conducting sphere entering and leaving a strong field, is obviously open to criticism. Quincke (1897) observed the damping of the oscillations of a glass sphere in a liquid between the plates of a condenser and found, with fields not exceeding 3.3 kV/cm., a very large increase of viscosity, with, among other liquids, carbon disulphide, ether and benzene; the results are certainly spurious. Pochettino (1903) enclosed the liquid between two metal disks held separate at a
distance of about 14 mm. by an ebonite ring; this arrangement was hung up by a 
bifilar suspension, the disks being horizontal, and the damping of the oscillations due 
to the enclosed liquid was measured. With about 15,000 V applied to the plates he 
obtained an increase of viscosity of 1·5 % with benzene and 4 % with xylol. There 
is, however, a total force of some 20 g. wt. between the plates with the field in ques-
tion, which, in the absence of precautions, may well have produced sufficient 
def ormation to account for the result. Ercolini (1903) used an apparatus in which 
the liquid was contained between insulated concentric cylinders. The whole system 
was suspended and the damping of the oscillations taken with and without the field 
of about 10 kV/cm. between the cylinders: he found no change in the viscosity of 
benzene within 1 %, about the limit of his accuracy. Pacher & Finazzi (1906) 
measured the time of axial flow between coaxial glass tubes. The potential difference 
was applied between mercury contained in the inner tube and tin foil wrapped round 
the outer one, so that the field in the liquid was uncertain but large. No effect was 
obtained with ether, benzene, carbon disulphide and other liquids. The early methods 
are all open to criticism and, in view of later results, little reliance can be placed on 
the measurements, a possible exception being that of Pacher & Finazzi.

The subject was not taken up again until 1933. Herzog, Kudar & Paersch (1933, 
1934) used first of all an ordinary capillary tube between condenser plates, like 
König, but later a tube of square cross-section, two opposite walls being of glass and 
the other two of platinum, between which a field was established. This form is very 
unfavourable for qualitative work, since the viscous flow is as much influenced by the 
two opposite sides which are at the same potential as by the sides between which a 
large, but not uniform, difference of potential is maintained. We shall show that all 
the positive effects observed are due to a modification of the properties of the liquid in 
the neighbourhood of the electrodes: the square channel is unsuit to reveal such 
an effect. Herzog and his collaborators used a low field only, viz. 2200 V/cm., and 
found no effect with the non-polar liquids hexane, cyclohexane and carbon tetrachloride. 
With ether they obtained a large increase, about 18 %, which in view of 
our results and those of Dobinski (1935) can only mean that the ether was very wet. 
With a range of polar liquids they obtained an increase of viscosity varying from 
something less than 1 up to 17 %. Determinations were only taken at one field 
strength and the results do not take us very far. Sokolov & Sosinski (1935, 1936, 
1939), like Herzog et al., used a tube of square cross-section, the side length being 
0·6 mm., and applied fields up to 17 kV/cm. They obtained no effect with hexane, 
benzene, toluene and carbon tetrachloride. Having come to the conclusion that 
the increase in time of flow was a function of the conductivity of certain liquids, they 
arti ficially increased the conductivity by the use of HCl vapour. The vapour was 
passed through a given quantity of the liquid, and small quantities of this con-
taminated liquid were then added to the pure liquid; in this way a range of con-
ductivities was obtained. With chloroform and ether, which were particularly 
investigated, the increase of time of flow was plotted against √(λ/λ₀), where λ is 
the conductivity of the contaminated liquid and λ₀ that of the pure liquid. The
The effect of an electric field on the viscosity of liquids

authors also carried out experiments on the increase of time of flow (apparent viscosity) with applied potential at frequencies of 0, 50 and 1000 sec.$^{-1}$. The curves for the three frequencies cross one another in an unsystematic way for different liquids, so that nothing can be deduced from their results as to variation of the effect with frequency. They also increased the conductivity of hexane with HCl vapour, and found an effect on viscosity, which is in contradiction to our experiments on wet non-polar liquids. Their final conclusion is that the dependence of the effect on the purity of the liquid is an exceedingly complicated problem. Considering the results, they decide correctly that the effect cannot be explained by an orientation of the molecules, a direct transport of momentum by ions, or various other mechanisms which they consider. They finally come to the conclusion that the electric current causes a general convection of the fluid parallel to the electrodes, that the effect is "a pure hydrodynamic phenomenon due to the convection of a non-homogeneous liquid placed in an electric field", although they admit that there is so far no satisfactory explanation of such movement. We consider that our results, which establish that with many liquids the current increases linearly with the field while the apparent viscosity reaches a limiting value, show that this explanation cannot be correct. Later we will bring other arguments against it. The chief significance of the work of Sokolov & Sosinski is that they draw attention to the fact that a current accompanies the effect.

Alcock (1936) used a rotating cylinder apparatus unsuited to accurate work: he took no steps to purify his liquids or to control the temperature. He applied a steady field only, not exceeding 2500 V/cm., and found no effect with carbon tetrachloride and benzene. As regards other liquids, in some cases he found first of all a small decrease and then an increase of viscosity with increasing field.* With polar liquids such as diethyl ether (presumably wet), chloroform and acetone he obtained results which he interpreted as increases of viscosity exceeding 100 % at fields of 1600 V/cm. or so.

Dobinski (1935) used the method of flow, parallel to the axis, in the space between a cylindrical metal rod 1 mm. in diameter and a coaxial metal cylinder of 2 mm. internal diameter, the potential difference being applied across the gap, which involves a non-uniform field. His field did not exceed 4400 V/cm. He found no effect with benzene, carbon tetrachloride and carbon disulphide. With dry ether there was no change of viscosity, but with wet ether (1·2 % water) there was an increase of 12 % at 2200 V/cm. Acetone likewise showed no change when dry, but an increase when wet. He found an increase of viscosity at 2200 V/cm. with chloroform, methylene chloride and nitromethane, which are polar, while, as regards aromatic polar fluids, he found no change with xylene, toluene and nitrobenzene and a decrease of viscosity with aniline and o-nitrotoluene. Sokolov & Sosinski have shown that these decreases are to be attributed to heating effects. Within their limited range Dobinski's results, which are mostly carried out at one field only, are in agreement

* We suggest that the decrease was probably a temperature effect, due to heating of the liquid by the current.
with ours except for this decrease. Kimura (1937) has published a note on the effect of an electric field on a solution of stearic acid in benzene, with which he went up to 30 kV/cm.* With increasing field he obtained an increase of viscosity which reached a limiting value. We have not dealt with solutions, and merely cite this note since it is the first record of a limiting value.

Björnståhl & Snellman (1935, 1937) used a form of apparatus different from those of all other workers, viz. a suspended disk parallel to a uniformly rotating disk, and made extensive use of alternating fields. The method seems open to criticism on the ground that small asymmetries may produce spurious forces when the strong electric field is applied. In any case the results are hard to reconcile among themselves: for instance, with monochlorbenzene the authors find with a steady field of 10 kV/cm. an increase of viscosity of 189 %, while with the same field at 25 eyc./sec. they find an increase of 440 %. There seems every reason to suppose that with such slow fluctuations of field the effect must be the same as in the static case, that is, less than the static effect if the recorded voltage is the peak voltage, instead of being considerably more than twice as great. Again, with a solution of monochlorbenzene in benzene they found no effect at all, while with nitrobenzene, which gave a smaller effect in the pure state, they obtained a large increase with the solution in benzene. Further, the way in which, with nitrobenzene, the viscosity first decreased and then increased to the normal value as the voltage was raised, and the whole variation of the effect with frequency in the case of chlorbenzene and of bromobenzene, which shows, in both cases, the most capricious changes, point to some fundamental irregularity in the method of measurement. The curves do not form a self-consistent system.

The result of all this previous work is that there is general agreement among the more careful workers that there is no effect with certain non-polar liquids. Great discrepancies are shown by the results on polar liquids. There is, however, general agreement that with some polar liquids there is a very large apparent increase of viscosity with field, although complete disagreement as to the magnitude of the effect, and as to its variation with field strength. Such measurements as have been made on the effect of alternating field are unsystematic and discordant. The marked differences and inconsistencies show clearly that there are factors involved which have not been taken into account by previous experimenters.

**GENERAL RESULTS OF OUR EXPERIMENTS**

We have established that an electric field transverse to the flow has no effect on the viscosity of non-polar liquids. This has been found by the previous workers just cited, but we have widened the limits within which this can be stated. With transformer oil any change of viscosity must be less than 1 in 5000 for a field of

* Probably. The intensity of the field as given is in volts, not V/cm., and there is a contradiction between the table and the diagram as to the strength.
50 kV/cm., with carbon disulphide less than 1 in 6000 at 32 kV/cm. With carbon tetrachloride and benzene the change of viscosity is also within this limit at about 40 kV/cm.

These non-polar liquids are, when dry, very bad conductors of electricity compared to polar liquids such as acetonitrile, chloroform and others that show a large change of apparent viscosity with field. When saturated with water, however, they pass currents of the same order as these polar substances, that is, thousands of times as great as they do when dry, but still show no change of viscosity with field. This proves definitely that the viscosity effect is not a consequence of the current passing, as Sokolov & Sosinski have suggested.

A large class of polar liquids, when dry and pure, by ordinary standards, show a big increase of apparent viscosity with electric field, the increase reaching a limiting value as the field increases, and also conduct relatively well: acetonitrile (3·16), acetone (2·74), dimethylamine (0·96), ethylene dichloride (1·51), methyl acetate (1·67), ethyl acetate (1·76), propyl acetate (1·89), butyl acetate (1·84), amyl acetate (1·91), n-propyl chloride (1·94), chloroform (1·18). The figures in brackets give the dipole moments when multiplied by $10^{-18}$. In the case of the two liquids first named it has been shown that, with specimens at different stages of purification, the limiting increase of viscosity at high fields is proportional to the conductivity, the result indicating that a specimen so pure as not to conduct at all, if it could be obtained, would show very small or no change of apparent viscosity with field.

Certain polar liquids, e.g. ether (1·15), monochlorobenzene (1·56), show no effect of an electric field on viscosity when dry, and also conduct very badly. When saturated with water they conduct much better and show the same type of increase of apparent viscosity with field as the large class of conducting polar liquids cited in the preceding paragraph. Toluene (0·4), metaxylene (0·4) and anisole (1·2) are likewise polar and neither conduct nor show a viscosity effect: the effect of wetting them was not tried.

The liquids fall, then, into three classes:

(1) Non-polar liquids, which show no viscosity effect, whether they are dry and non-conducting, or wet and conducting.

(2) Polar liquids which do not conduct and which show no viscosity effect.

(3) Polar liquids which conduct, either as ordinarily termed 'pure' or on the addition of moisture. These show the characteristic viscosity effect, approaching a limiting value at high fields. Successive purifications indicate that if the specimen could be prepared so as not to conduct at all, there would be little or no effect.

The general conclusion is, then, that for an effect to exist, neither conduction nor polar molecules alone suffices, but that both must be present.

Conduction is, of course, an index of ionization, and the conducting behaviour of our liquids is in accordance with general chemical considerations from this point of view. Toluene, metaxylene and anisole should, from the point of view of chemical structure, show no, or very little, tendency to ionization. Ether and monochlor-
benzene should not ionize when dry, but may reasonably be expected to do so in
the presence of water. Thus ether should ionize according to the scheme
\[
\begin{align*}
\text{CH}_3\text{OH}^+ & | \text{OH}^- \\
\text{CH}_3 & \\
\end{align*}
\]
while as regards monochlorbenzene, which shows a comparatively small viscosity
increase, the conduction and viscosity changes may be due to the ionization of the
water alone. It is to be noted that conduction and viscosity effects are both much
larger with wet ether than with wet monochlorbenzene.

The liquids of class (3) ionize readily in the presence of a trace of water. Thus
acetonitrile \( \text{CH}_3\text{C}≡\text{N} \) probably goes to \( (\text{CH}_3\text{CNH})^+ \) and \( \text{OH}^- \). In the case of the
homologous series of alkyl acetates the effect systematically decreases as we go from
methyl to butyl, which is to be expected if the effect is connected with hydrolysis.
Thus the connexion of the viscosity effect with ionization, shown by the current, is
also in accord with general considerations of chemical structure. To know how the
ionization comes about is not, however, essential for our theoretical considerations;
it suffices to know that ions are there, without knowing exactly what ions they are.

Experiments with different depths of channel show that the limiting effect
diminishes with increasing depth.

Fundamental for our consideration is the result that with an alternating field
the viscosity effect begins to diminish when a certain critical frequency is reached,
and ultimately tends to become very small or vanish as the frequency is still further
increased. The critical frequency diminishes as the depth of the channel is increased,
and increases as the temperature is increased.

**General explanation of the effects**

It has been shown by many workers that poorly conducting liquids behave under
an electric field in a manner analogous to gases. Schweidler (1901a, b, 1904), working
with plates immersed in toluol, showed that the potential gradient was greatest at
the electrodes, and with petroleum that the current increased more slowly than the
applied potential. Jaffé (1908) and van der Bijl (1912) worked with liquids in which
the ions were produced by \( γ \)-rays from radium, and found values for ionic mobilities
and coefficient of recombination; van der Bijl, in particular, found that the recom-
bination obeyed the laws valid for ions in gases. That poorly conducting liquids
should behave like gases rather than like normal electrolytes is not astonishing, in
view of the fact that the difference between gases and normal electrolytes is due to
the relative scarcity of ions in the former.

Our results have led us independently to the conclusion that the liquids we have
used conduct ionically, in the gaseous manner. Under the influence of the field, local
concentrations of ions appear at the electrodes, giving rise to abnormal cathode and
anode fall of potential, as widely observed in gases and as measured by Schweidler,
in a particular case, with liquids. The field gradient is greatest at an electrode, and
The effect of an electric field on the viscosity of liquids

diminishes as the distance from the electrode increases until a region is reached where it is zero.

The general nature of our results can be explained by the concentration of ions in the neighbourhood of the electrodes that takes place in a conducting liquid, if one makes the supposition that such ions, in consequence of the intense local field, act as centres around which polar molecules, if present, cluster. The viscosity of a liquid containing an appreciable quantity of such clusters will exceed that of the normal liquid. On this basis it is seen, in the first place, why, for a marked viscosity effect, it is necessary to have both conduction and polar molecules, since without conduction there is no local concentration of ions and without polar molecules no clusters are formed. In the second place this general picture explains why, in the case of alternating fields of increasing frequency, after a certain frequency $\nu_c$ is reached the viscosity effect diminishes and ultimately becomes negligible. For the establishment of the full effect it is necessary for the ions to move through a distance approximately equal to the depth of the channel. When the half-period is of the order of the quantity depth-of-channel/velocity-of-ion, the effect will begin to diminish and will vanish when the period is so small that the ions do not move appreciably.

The order of the ionic mobility—nothing more can be attempted in view of the complications due to non-uniformity of field and to the fact that equilibrium is not reached—derived from this point of view turns out to be reasonable. Table 4 shows the approximate figures. These values of $k$ are of the right order. For instance, the mobility of the NO$_3^-$ ion in water at infinite dilution is about $6 \times 10^{-4}$, and the viscosity of water is about twice that of chloroform. For the CS$_3$ ion produced in CS$_2$ by radium radiation, van der Bijl found $k = 6.6 \times 10^{-4}$, the viscosity of CS$_2$ being about 0.6 times that of chloroform. The increase of mobility with increasing temperature, indicated by the experimental results, is explained by the decrease of viscosity. Discussion of the difference of mobility found with the two different depths of channel would demand a more detailed analysis of the distribution of field under changing voltage than is possible at present.

<table>
<thead>
<tr>
<th>depth of channel (cm.)</th>
<th>peak voltage</th>
<th>temp. °C</th>
<th>critical frequency</th>
<th>mobility $k$ (cm./sec.)/(V/cm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>327</td>
<td>15</td>
<td>235</td>
<td>$9 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.020</td>
<td>333</td>
<td>25</td>
<td>450</td>
<td>$17 \times 10^{-4}$</td>
</tr>
<tr>
<td>0.028</td>
<td>344</td>
<td>25</td>
<td>350</td>
<td>$25 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

The lack of a longitudinal effect is also consistent with the general theory here put forward.

Before passing on to a more detailed discussion of our theory it may be pointed out that the effects cannot be explained by the transport of momentum consequent on the transport of ions. In the first place wet CCl$_4$ and wet C$_6$H$_4$ carry currents of the same order as the liquids that show the viscosity effects, and have ions of the same
order of mass, but show no effect. In the second place we have calculated the viscosity effect to be anticipated as due to the transfer of momentum by ions of the kind of mass in question, and with chloroform, for instance, the change of viscosity due to the drift of ions with the highest field would be about 1 part in 4000, and so quite negligible compared to the effects found experimentally.

**Theory of the Viscosity Increase**

The greatly increased time of flow which occurs when an electric field is applied at right angles to the direction of flow we have attributed to the concentrations of free ions in the neighbourhood of the electrodes, which leads to clusters of polar molecules involving local increases of viscosity. This theory explains qualitatively the class of liquid that shows the effect and also the fact that in an alternating field the field begins to diminish at a certain frequency and vanishes at a still greater frequency. It remains to show why the increase of apparent viscosity tends to a limiting value and why the effect diminishes as the channel in the viscometer is made deeper. These problems will now be handled quantitatively, but it may be said at once that the limiting value is due to the decreased velocity of the ions in the neighbourhood of the electrodes which is a direct consequence of a local increase of viscosity. This decrease of velocity tends to diminish the local concentration of ions, which in its turn tends to decrease the local viscosity, and so in the end, with very large fields, the apparent viscosity tends to a saturation value.

The treatment follows the lines first laid down by J. J. Thomson (cf J. J. Thomson and G. P. Thomson, vol. I, chapter IV) for conduction in an ionized gas, but certain essential modifications have to be made, owing to the fact that the ionic mobility is variable.

Let $n_1$, $n_2$ be the number per unit volume of positive and negative ions, each carrying charge $e$, and let $\alpha$ be the coefficient of recombination. Let $X$ be the local strength of the electric field in the direction $x$, normal to the direction of flow, $x$ being measured from the anode. Then $dX/dx = 4\pi(n_1 - n_2)e$. If the rate of formation of ions be $q$ per unit volume, then

$$\frac{d}{dx}(k_1 n_1 X) = q - \alpha n_1 n_2, \quad \frac{d}{dx}(k_2 n_2 X) = -q + \alpha n_1 n_2,$$

where $k_1$, $k_2$ are the respective mobilities of the two kinds of ions.

For simplicity take $k_1 = k_2$ and suppose that the ions are removed so rapidly that the recombination can be neglected, i.e. confine attention to the case of large field strength, for which alone the conclusions here reached will be valid. Then

$$k_1 n_1 X = qx, \quad \text{since } n_1 = 0 \text{ at } x = 0,$$

and

$$k_2 n_2 X = \frac{i}{e} - qx, \quad \text{where } i \text{ is the current density},$$

$$\begin{align*}
(n_2 - n_1) &= \left(\frac{i}{2qe - x}\right) \frac{2q}{kX}.
\end{align*}$$

(i)
The effect of an electric field on the viscosity of liquids

The local mobility of the ions may be assumed to be inversely as the local viscosity or \( k = a/\eta \), where \( a \) is constant. Assume, and this is an essential assumption, that the local viscosity is increased by an amount proportional to the number of excess ions, in accordance with the previous argument, or

\[
\eta = \eta_0 + b(n_2 - n_1),
\]

where \( \eta_0 \) is the viscosity, in the absence of field, and \( b \) is a constant. Then from (i),

\[
n_2 - n_1 = \frac{2\eta_0 qx'}{aX - 2qbx'}, \quad \text{where} \quad x' = \frac{i}{2qe} - x,
\]

whence

\[
\frac{dX}{dx'} = \frac{Ax'}{X - Bx'}, \quad \text{(ii)}
\]

where \( A = \frac{8\pi\varepsilon\eta_0 q}{a} \), \( B = \frac{2qb}{a} \) and \( A \) and \( B \) are both positive.

The integration of (ii) gives

\[
\frac{X^2 - Bx'X - A x'^2}{2X + (c - B)x'} = \frac{X_0^2}{c}, \quad \text{where} \quad c = \sqrt{(B^2 + 4A)} \quad \text{(iii)}
\]

within the region \( x = 0 \) to \( x = i/2qe \), i.e. \( x' = i/2qe = x_0 \) to \( x' = 0 \). For negative values of \( x' \), i.e. \( x > x_0 \), \( X \) has an approximately constant value \( X_0 \); in other words, \( X_0 \) is the approximately constant value which the field has in the central region.

The field markedly exceeds the value \( X_0 \) throughout a layer of thickness \( x_0 \) adjacent to the electrode. If \( I \) is the saturation current density, then \( 2dqe = I \), where \( 2d \) is the separation of the electrodes. Hence \( x_0 = (i/I)d \). Thus \( x_0 \) is proportional to \( i \), or the distance that the layer extends from the electrode increases linearly with the current.

In principle, equation (iii) enables one to find the distribution of \( X \) against \( x \) for a given voltage \( V \) applied to the electrodes. The distribution of \( X \) gives the number of excess ions at any point and hence, for an assumed value of \( b \), gives the viscosity as a function of \( x \). From this the time of flow can be found as follows.

Consider any layer distant \( \xi = d - x \) from the centre of the channel and let the viscosity be \( \eta \) in this layer. The velocity of this layer along the channel is

\[
v = \int_{\xi}^{d} \frac{p}{\eta} \xi d\xi,
\]

where \( p \) is the pressure gradient along the channel. If \( Q_0 \) is the volume per second delivered at this pressure gradient without electric field, then

\[
p = 3Q_0 \eta_0/2d^3.
\]
Volume per second with electric field \( Q = 2 \int_0^d v d \xi \)

\[
= 2 \int_0^d \int_0^d \int_0^d \frac{p}{\eta} \xi d \xi d \xi.
\]

But

\[
\eta = \eta_0 + b(n_2 - n_1) = \eta_0 \left(1 - \frac{B d X}{A dx}\right),
\]

therefore

\[
t = t_0 = \frac{3d^3}{\int_0^d \int_0^d \int_0^d \frac{1}{\xi d \xi d \xi}} 
\]

Hence a knowledge of the value of \( B/A \), together with the distribution of \( dX/dx \) against \( x \), i.e. against \( \xi \), gives the required \( t/t_0 \) and hence \((t - t_0)/t_0\) for comparison with observations.

In order to trace the effect of applied voltage on rate of flow, proceed with a numerical example, since the matter is too complicated to permit of a general expression. Take the following estimated values, suggested by acetonitrile:

\[
I = 8.4 \times 10^4 \text{ e.s.u./cm.}^2, \quad k = 0.67 \text{ cm./sec./e.s.u.,}
\]

\[
\eta_0 = 3.6 \times 10^{-3} \text{ c.g.s. units,} \quad d = 10^{-2} \text{ cm.,}
\]

whence \( A = 1.57 \times 10^8 \). To evaluate \( B \) an assumption must be made which gives \( b \). Assume that at the electrodes \( \eta = 1.35\eta_0 \); as this is merely to derive a general form for the variations of apparent viscosity with field any reasonable value will do. Since the denominator of the left-hand side of equation (iii) is always less than 1 and near the electrodes \( X \) is large compared to \( X_0 \), an approximate solution of (iii) is the positive solution of the quadratic

\[
X^2 - Bx'X - A x'^2 = 0,
\]

or

\[
\frac{X}{x'} = \frac{B + \sqrt{(B^2 + 4A)}}{2}.
\]

But, from (i)

\[
B = \frac{2qb}{k\eta} = \frac{X}{x'} \left(1 - \frac{\eta_0}{\eta}\right)
\]

\[
= \frac{X}{x'} \cdot 0.2593 = 0.13(B + \sqrt{B^2 + 4A}) \quad \text{approximately},
\]

whence

\[
B = 3.8 \times 10^3.
\]

This gives

\[
X_0^2 \left[ \frac{X - 14.6 \times 10^3 x'}{X + 10.8 \times 10^3 x'} \right]^{0.15} = X^2 - 3.8 \times 10^3 x'X - 157 \times 10^6 x'^2.
\]

In order to determine the distribution of field \( X \) for a given applied voltage \( V \) the constant value of the field \( X_0 \) in the central region must be chosen so that the area under the curve of \( X \) against \( x \) is equal to \( V \).
The effect of an electric field on the viscosity of liquids

A value of $X_0$ being chosen, values of $X$ against $x'$ are obtained from (iii$a$), remembering that $x' = (i/I)d = x_0$ at the electrode and $x' = 0, X = X_0$ towards the middle of the channel. Consistent values of $V$, $X_0$ and $X$ against $x'$ are obtained by successive approximations. Table 5 shows the values of $i$ for given values of $V$ taken as typical of a sample of acetonitrile.
E. N. da C. Andrade and C. Dodd

Table 5

<table>
<thead>
<tr>
<th>$V$ (V)</th>
<th>$i$ (e.s.u./cm.$^2$)</th>
<th>$x_0 = (i/I) d$ (cm.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>$3 \times 10^4$</td>
<td>$3.57 \times 10^{-3}$</td>
</tr>
<tr>
<td>176</td>
<td>4.5</td>
<td>5.35</td>
</tr>
<tr>
<td>230</td>
<td>5.4</td>
<td>6.43</td>
</tr>
<tr>
<td>304</td>
<td>6.45</td>
<td>7.68</td>
</tr>
<tr>
<td>370</td>
<td>7.05</td>
<td>8.40</td>
</tr>
<tr>
<td>saturation</td>
<td>8.4</td>
<td>10.00</td>
</tr>
</tbody>
</table>

The method indicated gave the curves of figure 18 for the field distribution at the various applied voltages. Putting appropriate values of $X$ and $x'$ in equation (ii) gives us the value of $dX/dx$ for various values of $x$ (see figure 19). Substituting in equation (iv) and integrating graphically, $t/t_0$ is obtained as a function of the applied voltage.
The effect of an electric field on the viscosity of liquids

The variation of \((t - t_0) / t_0\) with voltages from 100 to 370 is shown in figure 20. This curve clearly shows the tendency for the increase in time of flow to reach a limiting value for high voltages which is so marked a feature of the experimental curves. It will be remembered that the assumptions are valid for high fields only.

![Graph showing the variation of \((t - t_0) / t_0\) with applied voltage.](image)

**Figure 20**

The initial portion of the curve in figure 20 for low voltages lies above the values obtained experimentally. The reason for this is that in the above treatment no account has been taken of recombination of the ions. If the fields in the regions near to the electrodes are large, recombination of the swiftly moving ions will be negligible, as has been assumed in deducing the preceding formulae, but if the fields are small the ions will be moving much more slowly and hence some will be lost by recombination. The effect will then be everywhere to reduce the number of excess ions, and hence the viscosity, below the value previously obtained when this effect was neglected. The curve will thus tend to become concave upwards as indicated by the experimental curves. We hope on some future occasion to be able to give the theory
of the initial part of the curve, but it is not necessary for the general elucidation of the experimental effects under discussion.

LIQUIDS OBEYING OHM'S LAW

The attainment of a limiting value for the increase in the time of flow is independent of the exact relation between voltage and current. Even if Ohm's law holds at all the voltages used, a limiting value will still be obtained for the time of flow provided that the saturation current which the liquid can carry is not very much larger than the current produced by the largest applied voltage. This follows from the fact that the extent of the layer of high viscosity is governed by the ratio \( i/I \). Had the currents quoted for acetonitrile been proportional to the applied voltage, a curve such as that shown in figure 21 would be obtained as typical of a liquid obeying Ohm's law. The assumption that the increase of viscosity is proportional to the excess of ions of one sign existing locally, combined with the fact that the mobility of the ions is inversely proportional to the local viscosity leads to a relation of the general form found experimentally.

![Figure 21](http://rspa.royalsocietypublishing.org/)
The effect of an electric field on the viscosity of liquids

Effect of varying the conductivity

The limiting value for the increase in the time of flow is governed almost entirely by the value of the constant \( B = 2 q b / a \). For any organic liquid both \( a \) and \( b \) are fixed, but the rate at which the ions are produced, \( q \), is proportional to the electrical conductivity of the sample. The limiting value for the time of flow should therefore be proportional to the conductivity of the liquid, a fact which was observed experimentally for acetonitrile of different degrees of dryness (see figure 4).

Effect of size of gap

The extent of the region of increased viscosity measured from the electrode is given by

\[ x_0 = (\frac{i}{I}) d. \]

Now \( q \), the rate of formation of ions, is given by \( q = I / 2de \), and since this is constant for identical samples of liquid in two channels of different gaps, the saturation current \( I \) must be proportional to the size of the gap (2d). Now if the same mean field is applied to the two channels, the same current \( i \) will flow and thus \( x_0 \), the extent of the region of high viscosity, will be the same. Under these conditions the increase in the time of flow on applying the field will be less in the apparatus having the larger gap, as was observed. The limiting value of the time of flow should, however, be about the same for all gaps, since it is mainly determined by the value of \( B \), which is constant for identical samples of the liquid; with a larger gap, however, a larger mean field must be applied to produce this limiting value.

The effect of the size of the gap on the maximum frequency of the alternating field which gives the full increase in time of flow is as follows. This frequency \( \nu_c \) must be proportional to \( X / x_0 \), where \( X \) is the mean field at a distance \( x_0 \) from the electrode. If, as a first approximation, the variation of current with applied field be expressed by means of an equation of the form

\[ X = \alpha i + \beta i^2, \]

where \( \alpha \) and \( \beta \) are positive constants, then

\[ \nu_c = A_0 \frac{\alpha i + \beta i^2}{i}, \]

since, as has just been seen, \( x_0 \) is proportional to \( i \). So

\[ \nu_c = A_0 (\alpha + \beta i), \]

and obviously decreases as the current decreases.

In the experiments with alternating fields, the applied voltage was approximately constant, and so in the smaller gap apparatus the current, and hence the maximum frequency \( \nu_c \), must be bigger than in the apparatus with the larger gap. This is borne out by the experiments on chloroform at 25°C, where the maximum frequency \( \nu_c \) was 450 sec.\(^{-1}\) for a gap of 0.20 mm. and 350 sec.\(^{-1}\) for a gap of 0.28 mm.
IS THERE A GENUINE EFFECT OF ELECTRIC FIELD ON VISCOSITY?

We have established the conditions under which large apparent increases of the viscosity of conducting liquids may take place in an electric field, and have shown that these effects occur in polar liquids only when there are large concentrations of ions in the neighbourhood of the electrodes.

The increase of viscosity observed is thus, in a sense, spurious, since the part of the liquid in which the increase of viscosity occurs is not normal but contains artificially produced clusters.

This spurious effect can be avoided by using a rapidly alternating field. This avoids concentrations of ions near the electrodes which not only gets rid of clusters but also ensures that the field shall be uniform.

In our experiments with chloroform the mean applied potential difference was about 10 kV/cm., and the total time of flow was about 300 sec. With care a difference of time of 0.2 sec. could have been detected, which means a change of viscosity of 1 part in 1500. However, at the time when the experiments on the effect of variation of frequency were being carried out a general survey only of the effect was in view, and the accuracy was not pressed to the limit. For chloroform at 15°C, $E/kT = 2.15$, and the mean field in the experiments was 10 kV/cm. $E$ thus has the value $8.5 \times 10^{-14}$ and $\mu$ is about $1 \times 10^{-19}$. This leads, on the considerations given at the beginning of this paper, to the value $d\eta/\eta = 8 \times 10^{-4}$, which is just on the limits of detection unless special precautions are taken. It should certainly not be beyond ultimate detection, since both the field and the time of flow can be increased.

In general, the way in which a true effect is to be sought has been established by these experiments. An alternating field must be used, whose frequency is well in excess of $uV/2D^2$, where $u$ is the mobility, $V$ is the applied potential and $D$ is the gap between the electrodes. If $D$ were reduced to 0.01 cm. and the gradient $V/D$ taken as 40 kV/cm., say, this means that a frequency well in excess of 1000 should be used. At the same time the frequency should not be high enough to produce effects involving the relaxation time. Luckily such effects do not set in below a frequency of about $10^7$ cyc./sec. Frequencies in the range $10^4$–$10^6$ cyc./sec. should, therefore, be suitable. Our experiments have suggested to us various ways in which the apparatus could be modified to increase somewhat the sensitiveness of the method. There is, therefore, every prospect that an effect of the order to be anticipated can be measured under precise and significant conditions, more especially as with an alternating field the potential gradient can probably be considerably increased without danger of electric breakdown.

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The thermochemistry of carbon: valence states, heats of sublimation and energies of linkage

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The controversy which exists at the present time between the figures 125 and 170 kcal./g.-atom for the latent heat of sublimation of carbon into monatomic vapour in the ground state originates largely from the neglect to take into consideration the energy required to raise the carbon atoms from the ground (\(^3\)P) state to the lowest tetravalent (\(^6\)S) electronic configuration corresponding to that in which it is normally found in chemical combination. Consideration of the energies of removal of a hydrogen atom from the methane and ethane molecules and of the energies of reorganization of the resulting radicals leads to the figure 190± about 10 kcal. for \(E_{P}\), the heat of sublimation into free atoms in the \(^6\)S state. This in turn leads to a satisfactory and unambiguous assignment of values to bond energies (as distinct from dissociation energies) which can now be expressed with an uncertainty of not more than a few kcal. In the light of the valency distinction there remains no sound evidence to maintain the higher value put forward for \(E_{P}\), and 125 kcal., is unquestionably of the right order. There are strong indications that an earlier estimate of 100 kcal. for the energy level of the \(^6\)S state above the \(^3\)P (ground) state is about 50% in excess of the true value.

The necessity for establishing this branch of thermochemistry on a sound theoretical and experimental footing has long been a very obvious need. The scheme here suggested reconciles points hitherto in apparent conflict, and brings virtually all established experimental knowledge into alignment.