X. BAKERIAN LECTURE.—*On the Relations between the Viscosity (Internal Friction) of Liquids and their Chemical Nature.*

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[PLATE 8.]

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PART I.

INTRODUCTION.

DURING the half century which has elapsed since HERMANN KOPP directed attention to the connection which exists between the molecular weights of substances and their densities, the attempts which have been made to establish similar relationships between the magnitudes of other physical constants and chemical composition have shown that probably all physical constants are to be regarded as functions of the chemical nature of molecules, and that the variations in their magnitude observed in passing from substance to substance are to be attributed to changes in chemical composition.

The physical properties first investigated from this point of view were naturally those either often measured or at least capable of being easily measured. To this class belong such determinations as density, boiling-point, refractive index, &c., &c. On the other hand, properties not so clearly understood, or less readily perceived, received little or no attention. An example of this kind occurs in connection with the viscosity of liquids.

When a liquid flows, or when its form is altered, forces are called into play within the liquid which offer resistance to the force causing flow or change of form. The viscosity of the liquid may be taken as a measure of these internal forces, but, although the common use of the terms "viscid," "oily," "mobile," "limpid," &c. shows that the endeavour has not been wanting to indicate the different character of liquids in respect to this property, it is only within quite recent times that the attempt to obtain quantitative measures of the viscosity, or viscosity-coefficients, for a large number of liquids has been made. This is due to a variety of reasons. To begin with, physio-chemical inquiries have been almost exclusively carried out by chemists, who have hitherto had little cause to study such a property as viscosity, the conception and mode of quantitative expression of which have been developed by physicists. Moreover, even from a purely physical point of view, the accurate determination of absolute coefficients of viscosity has been beset with difficulties, both in the theory and practice of the methods employed. Viscosity is, no doubt, the nett result of at least two distinct causes. When a liquid flows, during the actual collision or contact of its molecules, a true friction-like force will be called into play, opposing the movement. But, in addition to this force, even after the actual collisions, molecular attractions will exercise a resistance to forces which tend to move one molecule past another, and hence it may have been surmised that, even if accurate values of the coefficients of viscosity could be obtained, they might not exhibit simple relationships to chemical composition.*

Although few absolute measures of viscosity have been hitherto published, several researches have been made which may be regarded, in certain cases at least, as being concerned with the relations of viscosity to the chemical characters of substances. That they may be so regarded arises from the circumstance that the observers have incidentally made use of one of the methods for obtaining the viscosity-coefficient, which consists in noting the time which a definite volume of liquid takes to flow

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* Comp. GRAETZ, 'WIEDEMANN'S Annalen,' 24, 25, 1888; MÜTZEL, 'WIEDEMANN'S Annalen,' 43, 35, 1891.

through a capillary tube of known size under definite conditions of temperature, pressure, &c. By suitably arranging the experimental conditions, the relative times of flow, or, as they have been somewhat inaptly termed, the relative times of transpiration, through the same tube may be considered as proportional to the coefficients of viscosity.

Hence it happens that the historical treatment of the investigations which are related to that described in this paper opens with some account of the researches which have been undertaken to obtain the so-called transpiration-times of liquids. It has to be borne in mind, in dealing with this part of the subject, that in many cases the observers were apparently unaware that they might obtain relative measures of viscosity by the method they employed. They simply ascertained the time of flow of a liquid, and considered this value as a physical constant under the experimental conditions. In most cases, as will be made clear subsequently, these conditions were probably not such as would admit of the transpiration-time being regarded as a relative measure of the coefficient of viscosity—that is, of the real physical constant which was influencing the experiments.

That the flow of liquids, and especially of water, through channels, conduits, and pipes should have received so much attention in the early days of experimental science is, of course, due to the economic importance of the subject. The main result of these observations was to show that the resistance offered to the flow of the liquid was as the square of the velocity, the velocity being in these cases considerable.

About fifty years ago, however, POISEUILLE, starting from physiological considerations, attempted to discover the law of the flow in tubes of very narrow bore where the velocity of exit was but small, and here he found the resistance to vary not as the square of the velocity, but directly as the velocity. It was thus evident that the character of the motion of a liquid in a capillary tube where the velocity is small, differed essentially from that occurring in the cases of rapid flow in tubes of large diameter. As is well known, POISEUILLE found that the volume of liquid, in cub. millims., which flows in the unit of time through a tube of circular section, the walls of which it wets, may be expressed by the formula $V = K D^4 H/L$, in which D is the diameter in millims. of the tube, L its length in millims., H the pressure in millims. of mercury, and K (which POISEUILLE regarded as a measure of the fluidity of the liquid) a constant which varies with the nature of the liquid and its temperature.

The meaning and validity of this empirical expression have been established by the theory of hydrodynamics, and it has been shown that from observations made by POISEUILLE's method, under suitable conditions and with certain corrections, to be explained hereafter, the viscosity of a liquid may be ascertained.*

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* STOKES, 'Cambridge Phil. Trans.,' 8, 304, 1847; G. WIEDEMANN, 'Pogg. Ann.,' 99, 177, 1856; E. HAGENBACH, 'Pogg. Ann.,' 109, 385, 1860; STEFAN, 'Wien. Ber.,' 46, II., 495, 1862; COUETTE, 'Ann. de Chimie et de Phys.' (6), 21, 433, 1890; WILBERFORCE, 'Phil. Mag.' (5), 31, 407, 1891.

The attempts made by POISEUILLE to connect the magnitude of K with the nature of the liquid were practically restricted to an extension of the prior experiments of GIRARD on the influence of dissolved foreign substances in modifying the velocity of flow of water. POISEUILLE confirmed the fact that certain of these substances, like common salt, accelerate, whilst others, like nitre, retard the rate of flow of water, and that in general the action increases, within certain limits, with the amount of substance added. At first sight it may seem remarkable that POISEUILLE should have sought to elucidate the problem by attacking its most complicated side; that is, by studying the mutual action of heterogeneous molecules; but the circumstance is explained when we remember that his primary object was to establish the causes which determine the flow of blood in the capillaries, and to trace the influence of different alimentary substances and medicaments on its movement. Although no fundamental relations of the kind looked for were discovered, certain facts of a remarkably significant character were brought to light. Thus it was found that in the case of mixtures of alcohol and water, there is a certain mixture for which the time of flow measured at a definite temperature is a maximum, and that this maximum of transpiration-flow corresponds with the mixture which shows the maximum degree of contraction, or in other words is connected with the existence of an apparently definite hydrate, $C_2H_6O.3H_2O$. Hence it was inferred that such observations might throw considerable light on the molecular constitution of liquids.

The subject was next attacked from this point of view by THOMAS GRAHAM ('Phil. Trans.,' 1861, p. 373). By a method of observation identical in principle with that of POISEUILLE, he confirmed the fact that in the case of mixtures of alcohol and water, the composition of the mixture which had the maximum transpiration-time corresponded with the hydrate $C_2H_6O.3H_2O$; and he showed that similar relationships were to be found in the case of mixtures of nitric, sulphuric, hydrochloric, acetic, butyric, valeric, and formic acids with water, although the connection of the phenomenon with definite degrees of hydration was not always so well marked as it apparently is in the case of alcohol and water. Although we are not immediately concerned with this aspect of the subject, it may here be stated that subsequent investigation has shown that GRAHAM'S main conclusion is not capable of the simple expression which he gave to it. WIJKANDER ('Lund. physiogr. Sällsk. Jubelskrift.,' 1878, Abstr. in 'Wied. Beiblätter,' vol. 3, p. 8, 1879) confirmed GRAHAM'S observation that in the case of a mixture of acetic acid and water, the maximum transpiration-time occurs at 20° with the monohydrate $C_2H_4O_2.H_2O$, but it was also found that at another temperature, the composition of the mixture having a maximum transpiration-time was not that of a definite hydrate, showing that the phenomenon is probably dependent on or modified by dissociative changes in the liquid. (Compare also J. TRAUBE, 'Chem. Ber.,' vol. 19, p. 871, 1886; PAGLIANI and E. ODDONE, 'Atti R. Acc. delle Scienze di Torino,' vol. 22, 314, 1887, Abstr. in 'Beibl.,' 1887, p. 415; ARRHENIUS, 'Zeit. für physikal. Chem.,' vol. 1, p. 285, 1887.) Further investigation is required to show

how far determinations of viscosity may be taken as the measure of such dissociative changes; up to the present no simple expression for the relation of the viscosity coefficient of a mixture to those of its components has been deduced.

A point of more immediate importance is that in this Memoir, GRAHAM, for the first time, directed attention to the desirability of studying the transpirability of homogeneous liquids in connection with their other physical properties, and in respect to their chemical nature. He determined the transpiration-times of a number of such liquids at the uniform temperature of 20° C., and compared the observed times with that of water in the same apparatus, at the same temperature. From observations made on methyl, ethyl, and amyl alcohols; on acetic, butyric, and valeric acids, and on the ethyl esters of these acids he found that the transpiration-time of an alcohol, ester, or acid, increases as its boiling-point under ordinary pressure increases, from which he inferred that a connection exists between transpirability and molecular weight of a kind analogous to that which subsists between boiling-point and composition, and he suggested the advisability of determining the transpiration-times of homologous series of substances at a fixed and relatively high temperature.

In 1868, RELLSTAB ('Ueber Transpiration homologer Flüssigkeiten, Inaug.-Dissert.,' Bonn, 1868) attempted to develop the subject in the manner indicated by GRAHAM, and at the same time to determine the influence of temperature on the efflux-times of the liquids studied. POISEUILLE, as already stated, had traced this influence in the case of water; GRAHAM had repeated the observations on water, and had further studied the case of ethyl alcohol. RELLSTAB'S method was essentially that of POISEUILLE, the main difference being that the effective pressure was established by means of a column of mercury instead of by compressed air, and that the observations were made, as a rule, at various temperatures between 10° and 50°. The intermediate values for every 5° were obtained by graphical interpolation, and the times were compared with that occupied by water at 0° in flowing through the same apparatus under the same pressure (*circa* 500 millims.). The experiments gave directly what PRIBRAM and HANDL subsequently designated (*vide supra*) by the somewhat arbitrary term *specific viscosity* of the liquids at the temperature of observation. Calling the specific viscosity Z, it is expressed by the formula $Z = t\ 100/t_w$, in which t is the time of flow of the constant volume of liquid at the temperature of observation, and t_w is the time occupied by the same volume of water at 0°, the pressure which determines the flow being the same in both cases. RELLSTAB was of opinion that the connection between composition and transpiration would be best traced by comparing the efflux-times of "equivalent amounts" instead of the efflux-times of equal volumes of liquids. The efflux-times of equivalent amounts were assumed to be obtained by multiplying the observed efflux-times of equal volumes by the molecular weight, and dividing by the density; in other words, multiplying the observed time by the specific volume at that temperature. The values of Z, for so-called "equivalent amounts," were not given with the highest attainable accuracy, inasmuch as the thermal expansion of certain of the liquids was unknown. As the range of temperature over which RELLSTAB'S observations extended was only from 10° to 50°, and as the relative densities of all the liquids experimented upon were known at 20°, he employed in all cases the specific volume at 20°, instead of the true specific volume at the temperature of observation. The error thus introduced depends upon the difference between the coefficients of thermal expansion of the liquids under investigation, and may amount to three or four per cent. at the higher temperatures. The liquids investigated by RELLSTAB were alcohols of the $C_nH_{2n+2}O$ series, certain of the fatty acids, a number of compound ethers (esters), aldehydes, and a few aromatic derivatives.

Since the transpiration-time necessarily alters with the temperature, and at a rate varying with each liquid, it was of fundamental importance to determine the particular temperature at which the comparison between the individual results should be made. RELLSTAB assumed, with KOPP, that the temperatures at which the various liquids possessed the same vapour-pressure might be considered as comparable, and adopting LANDOLT'S values for the vapour-pressures, he compared the transpiration-times of "equivalent amounts" of the acids of the $C_nH_{2n}O_2$ series at a number of comparable temperatures between 0° and 50°.

The general result of the observations was to show that in the case of this series of acids the transpiration-time *decreases* with increasing molecular weight in passing from formic acid to acetic acid, and from acetic acid to propionic acid, but that the differences between the values for the several pairs of acids become less and less as the temperature rises until they become constant. On passing from propionic acid to normal butyric acid, from butyric acid to valeric acid, from valeric acid to caproic acid, the transpiration-times *increase* with increasing molecular weight, and the differences between the values for any pair of successive homologues at "comparable temperatures" become less and less with increasing temperature, as in the first case, and tend apparently to become constant. No simple relation either between the transpiration-times and the molecular weights or between these times and the vapour-pressures could be traced by RELLSTAB. Hence, in the rest of his memoir, RELLSTAB simply follows GRAHAM'S suggestion, and compares the transpiration-times of "equivalent amounts" of the various liquids, whenever possible, at 50°, the highest temperature to which his experiments extended.

The main conclusions which RELLSTAB deduces from his observations may be thus summarised :—

1. The transpiration-time of all liquid substances decreases with the temperature. The decrease for equal intervals is most marked, the longer the time of efflux and the lower the temperature.

2. An increment of CH_2, in an homologous series, is in general accompanied by an

increase in the time of efflux. This increase in efflux-time is greater when the increment of CH_2 takes place in an alcohol radicle than when it takes place in an acid radicle.

3. An increase in the transpiration-time also accompanies an increment of CHOH, of H_2, and of O.

4. A decrease of efflux-time accompanies an increment of C.

5. Metameric bodies have, in general, different efflux-times. These are nearer together, the nearer the boiling-points of the liquids.

6. Substances containing double-linked carbon have a greater efflux-time than those of equal molecular weight containing single-linked carbon.

7. An increase or diminution of velocity of transpiration corresponds with an increase or decrease of boiling-point without being a simple function of the latter.

8. In any particular homologous series it is possible to determine the direction of the alteration in transpiration-velocity on passing from a lower to a higher member, but not the magnitude of the change.

GUEROUT ('Compt. Rend.,' vol. 81, p. 1025, 1875; and vol. 83, p. 1291, 1876) also determined the value of K in POISEUILLE's formula $K = VL/HD^4$ (taking H as the height of a water column) at ordinary temperatures (13°–15°) for a number of the liquids investigated by RELLSTAB, and from the data PRIBRAM and HANDL have calculated the "specific viscosities" for equal volumes so as to make the results more directly comparable with those of RELLSTAB. The numerical values thus given by the two observers are, for the most part, widely different, although certain of their general conclusions are in agreement. Both find that, as a rule, in an homologous series, an increase of molecular weight is accompanied by an increase of transpiration-time, and GUEROUT confirms the exceptions in the cases of formic and acetic acids. GUEROUT's numbers are, with one exception, considerably higher than those of RELLSTAB. In the series of the alcohols the difference is as high as 40 per cent. in the case of butyl alcohol, and is about 20 per cent. in most of the others; in the series of the acids the discrepancy amounts to 5 or 6 per cent. It is impossible to determine exactly to what these divergencies are due, since GUEROUT gives no details either of the character of his preparations or of his method of observation.

GUEROUT found that isomeric esters give the same value for K, but RELLSTAB's observations lend no support to this conclusion.

The most extensive investigation hitherto published on this subject is that by PRIBRAM and HANDL ('Wien. Ber.,' Part II., vol. 78, p. 113, 1878; Part II., vol. 80, p. 17, 1879; Part II., vol. 84, p. 717, 1881), who have determined the "specific viscosity" of a large number of liquid substances at different temperatures. Their methods, in principle, were identical with that of POISEUILLE, although it must be admitted that their apparatus was hardly capable of furnishing results at all comparable in point of accuracy with that of their predecessor. Indeed, the test-observations which they adduce differ among themselves by from 2 to 3 per cent., and, under certain conditions of measurement, successive observations on the same liquid vary by as much as 12 per cent.

The comparisons of the specific viscosities were given at temperatures differing by a 5° interval between the maximum limits of 10° and 60°. The main conclusions which may be deduced from their work, which of course refers to specific viscosities measured at one and the same temperature, are stated by them as follows :—

1. The substitution in a molecule of Cl, Br, I, and NO_2 for H, in all cases increases the specific viscosity of the substance. This increase is smallest on the introduction of Cl, and increases on the introduction of Br, I, and NO_2, and in the order given. The absolute amount of the increase depends not only upon the nature of the substituting radicle but also upon its position in the molecule.

2. Isomeric esters have nearly the same specific viscosity. Of two isomeric esters that possesses the greater specific viscosity which contains the higher alcohol radicle.

3. The ester containing the normal radicle has always a greater specific viscosity than the isomeride containing the iso-radicle, and this obtains no matter whether the isomerism is in the alcohol or the acid radicle.

4. The normal aldehydes have invariably a greater specific viscosity than the iso-compounds. In the case of the alcohols the results are conflicting, although as a rule the normal compounds have a greater specific viscosity than the iso-alcohols.

5. The alcohols have a greater specific viscosity than the corresponding aldehydes and ketones.

6. In homologous series, in general, the increase in specific viscosity is proportional to the increase in molecular weight ; the actual amount of increase is, however, dependent upon the constitution of the molecule, and only becomes constant when the members of the homologous series, considered as binary compounds, contain one constant and one variable member.

PRIBRAM and HANDL's work undoubtedly constitutes a great advance upon that of their predecessors. But whilst it establishes the broad fact of a connection between the viscosity of a liquid and the chemical nature of its molecules, it cannot be said that the numerical results afford us any accurate means of determining the quantitative character of this connection. This is probably due partly to the imperfection of their observational methods and to their mode of treating their results, and partly also to the uncertainty of the basis of comparison ; possibly, also the nature of the liquids themselves may have occasioned, to some extent, the equivocal character of the results, for it is impossible to gather from such data as are given that the liquids approached the standard of purity which is desirable in an investigation of this kind.

R. GARTENMEISTER (' Zeits. für physik. Chemie,' vol. 6, p. 524, 1890) has also determined the viscosity of a large number of organic substances and has expressed his results in absolute measure. His method consisted in allowing the liquid to flow from bulb-shaped pipettes through capillary tubes in the manner already adopted by

OSTWALD and ARRHENIUS ('Zeits. für physik. Chemie,' vol. 7, p. 285, 1887). The greater number of the determinations were made at the temperature of 20°, but in the cases of formic and butyric acids, and in those of methyl, ethyl, propyl, iso-propyl, and iso-butyl alcohols, a series of estimations at every 10° between 10° and 50° was made.

GARTENMEISTER finds that although, in general, viscosity may be said to increase with molecular weight, there are apparently numerous exceptions to this rule. These are seen not only among the initial members of the fatty acid series, but also among the esters of aceto-acetic acid. Metameric esters frequently possess different viscosities, as already observed by RELLSTAB. On the other hand, RELLSTAB'S conclusion that the viscosities more nearly approximate the smaller the difference in boiling-point is only generally true. On comparing the boiling-points of the aceto-acetic esters with their viscosities, it is found that the boiling-point of the ethyl ester is always an equal number of degrees higher than that of the methyl ester of the same acid, whereas, in the case of the viscosities, the relations are of quite another order. BRÜHL ('Ber.,' 13, 1529) has pointed out that it is probable that in the case of isomeric bodies more time would be required for an equal number of molecules to flow through a capillary tube of that particular compound which has the higher boiling-point, the greater relative density, and the greater refractive index; or, in other words, that the viscosity of a liquid stands in the same relation to its chemical constitution as do its other physical constants. GARTENMEISTER finds that, although the statement may be taken as generally true, there are numerous exceptions.

RELLSTAB concluded that substances containing so-called double-linked carbon transpire more slowly than those of equal molecular weight containing single-linked carbon. PRIBRAM and HANDL, however, found that the "specific viscosity" of allyl alcohol (C_3H_6O) is less than that of propyl alcohol (C_3H_8O), and GARTENMEISTER observed that diallyl $CH_2 : CH(CH_2)_2CH : CH_2$ has a lower viscosity than dipropyl $CH_3(CH_2)_4CH_3$. On the other hand, the viscosity of benzene (C_6H_6) is more than double that of dipropyl. If it is assumed that there is double linking in both allyl compounds and in benzene, it would seem to follow that the relatively high viscosity of benzene cannot be ascribed wholly to double linking, but is dependent rather on those properties that we associate with the ring mode of atomic grouping. This view of the influence of the ring grouping is confirmed by the study of other aromatic compounds.

GARTENMEISTER further concludes from PRIBRAM and HANDL'S observations that, within the limits of temperature at which the determinations have been made, the viscosity of compounds containing an equal number of carbon atoms in which Cl, Br, and I replace each other is proportional to the molecular weight. In the case of homologous series the viscosity is proportional to the square of the molecular weight.

The introduction of the hydroxyl group into the molecule greatly increases the viscosity of the liquid. This is strikingly illustrated by the instances of propyl alcohol $C_3H_7(OH)$, propylene glycol $C_3H_6(OH)_2$, and glycerin $C_3H_5(OH)_3$. Indeed, the high viscosity of solutions of carbohydrates, *e.g.*, the sugars, gums, &c., is probably dependent on the relatively numerous hydroxyl groups present in the molecule. The manner in which the hydroxyl group is combined seems, however, to have considerable influence on the viscosity. Thus, in the cases of the isomeric substances, benzyl alcohol and metacresol, it is found that, in the first-named substance, in which the hydroxyl group occurs in the side chain, the viscosity is very much less than that of the second, in which the hydroxyl group is attached to a carbon atom in the benzene ring.

The foregoing observations practically include all that may be regarded as attempts to determine the connection between the viscosity and the chemical nature of homogeneous liquids. A very large amount of experimental work has been done, especially in the physical laboratories of OSCAR E. MEYER, WIEDEMANN, and OSTWALD, on saline solutions and mixtures, in order to trace analogies and relations between viscosity and electric conductivity, temperature, concentration, &c.; but while these researches have been of great service in regard to the applicability and value of observational methods, they have added little to our knowledge of the special question with which we are more immediately concerned.

Although it is manifest from the foregoing account that relationships do exist between the chemical character of liquid substances and that property which is related to their times of transpiration, it must be admitted that these relationships are not very precisely defined by such experimental evidence as we have at present. Instances have been given in which the results of different observers, and in some cases even those of the same observer, differ among themselves by amounts which cannot be reasonably attributed to imperfections in the principle of the methods employed. As a general rule, the plan adopted seems to have been to make relatively rough observations on as many liquids as could be obtained, rather than to institute a careful and systematic comparison between a few of well established purity. Moreover, the nature of the conditions by which truly comparable results could alone be obtained, has received but scant consideration. For example, it seems futile to expect that any definite stoichiometric relations should become evident by comparing observations taken at the same temperature. A few attempts have been made to ascertain the influence of temperature on the time of transpiration, but these are insufficient both in number and temperature range to admit of a trustworthy deduction of the law of the variation. It seemed obvious therefore that in order to investigate the subject with reasonable hope of discovering stoichiometric relations, one essential point was to ascertain more precisely the influence of temperature on viscosity, and then to compare the results under conditions which have been found to be suitable in similar investigations in chemical physics.

DEFINITION OF THE VISCOSITY COEFFICIENT.

It has already been stated that the time which a liquid takes to flow through a capillary tube, is, under certain conditions, a measure of its viscosity. The necessary conditions will be given at length subsequently. It will be sufficient here to indicate the meaning of viscosity, and the principles involved in measuring it.

In the case of an ideal solid, the value of the fraction

$$\frac{\text{Force producing deformation}}{\text{Deformation produced}}$$

is a constant; whereas in the case of a liquid this ratio depends on the time during which the force acts. Determined for unit-time, the fraction may be taken in the case of a liquid as a measure of its viscosity or its resistance to change of form. The coefficient of viscosity η* is thus given by the expression

$$\eta = \frac{\text{Deforming force}}{\text{Deformation per unit time.}}$$

Consider a quantity of liquid contained between two parallel planes of unit area at a distance δ apart, and let a tangential force act on the liquid so that the planes move parallel to one another, and let the displacement of one plane relative to the other, which may be considered at rest, be δ'.

If the velocity of any stratum be assumed to be proportional to its distance from the fixed plane, then the deformation of the substance between the planes per unit time, or the rate of shear, is measured by the velocity of displacement of any stratum divided by its distance from the fixed plane, and thus by δ'/δ, so that, if F be the tangential force per unit area acting on either of the planes, and exerted by the substance in resisting deformation,

$$\eta = \frac{\mathrm{F}}{\delta'/\delta}.$$

If $\delta'/\delta = 1$, that is, if the displacement is equal to the distance from the fixed plane, $\eta = \mathrm{F}$, and the coefficient of viscosity can then be defined. It is the force which is necessary to maintain the movement of a layer of unit area past another of the same area with a velocity numerically equal to the distance between the layers, when the space between them is continuously filled with the viscous substance. Or η may be defined as the tangential force which must be exerted on unit area of each stratum of liquid in order to maintain the flow when the velocity is changing in a

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* Different symbols have been used in different countries to indicate the coefficient of viscosity. In France ϵ, in Germany η, and in this country μ, have been commonly employed. The use of μ seems objectionable as it is now largely employed for the refractive index of a substance; it is also sometimes used to denote magnetic permeability and also the micro-millimeter. We therefore prefer, in conformity with German custom, to make use of η to denote the coefficient of viscosity.

direction normal to the movement in such a way that strata at unit distance apart have velocities which differ by unity. The dimensions of η are therefore $[ML^{-1}T^{-1}]$.

It seemed advisable to design an apparatus which would admit of the determination, in absolute measure, of this coefficient for different substances and for a temperature range from 0° up to the ordinary boiling-point of the particular liquid. In this way instead of finding, as has been the usual custom, relative times of flow through the same apparatus under the same external conditions of temperature and pressure, and which might or might not be taken, as will be shown later, as measures of a single physical magnitude of the substance, that is, of its viscosity, the physical magnitude itself could be measured and the various influences which have been found to affect its value could be allowed for. The physical constants thus obtained could then be treated from the point of view of the chemist and the comparison would thus be of the same kind as that employed in connection with other physical magnitudes, such as densities or refractive indices.

MODES OF MEASURING VISCOSITY.

Although the transpiration method has been almost exclusively used in researches of this kind, there are other methods of obtaining the value of η. One of the oldest methods is due to COULOMB ('Mém. de l'Inst. Nat.,' vol. 3, p. 261, 1800). It consisted in suspending a disc or cylinder within a mass of liquid and setting the disc or cylinder oscillating. From the diminution in the amplitude of the oscillations the value of the coefficient of viscosity may be calculated.

Another method depending on observations of the oscillation of a liquid in a U-shaped tube was first proposed by LAMBERT (Mém. de l'Acad. de Berlin, 1784). The COULOMB method was modified by MAXWELL. PIOTROWSKI, at HELMHOLTZ's suggestion, instead of oscillating a regular solid in the liquid, obtained values of η by oscillating a hollow sphere filled with the liquid; and quite recently O. E. MEYER has shown that by the use of a hollow cylinder instead of a sphere, the accuracy obtainable in the theoretical treatment of the observations is considerably increased.

None of these methods was suited for obtaining values of η over wide temperature ranges; moreover, the large volume of liquid required to carry them out precluded their use in our case, owing to the difficulty of obtaining such large quantities of liquid in a state of sufficient purity. The tube method was therefore alone available for our purpose. It is satisfactory to note that MÜTZEL has obtained with the hollow cylinder a value for η at 20° which is identical with that deduced from the tube observations of POISEUILLE.

GENERAL PRINCIPLE OF THE METHOD AND DESCRIPTION OF THE APPARATUS EMPLOYED IN THIS INVESTIGATION.

The principle of the method employed by us consists in observing the time required for a definite volume of liquid, under a definite pressure, to pass through a capillary tube of known size, the temperature being known and kept uniform during the interval.

The liquid under observation is contained in a vessel fitted with a capillary tube. This instrument, on the suggestion of Principal BODINGTON, we propose to term a *glischrometer*. It is immersed in a bath of water or glycerin, the temperature of which can be altered as desired. The definite volume of liquid which is forced through the capillary tube is measured by suitable marks etched upon the instrument. A head of water serves to set up the pressure, which is ascertained by a water manometer, and the time of flow is noted by means of a stop-watch.

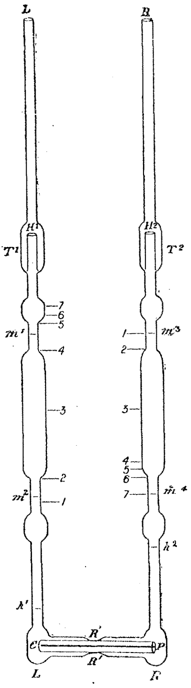
In deciding upon the form of the glischrometer several conditions had to be observed. In most of the instruments used by previous observers, the liquid after passing through the capillary was allowed to escape, and hence the apparatus had to be re-charged before another observation could be made. In the form adopted by us the time spent in re-charging was saved, by arranging that in all the observations on any one liquid the same sample could be used repeatedly; and further economy in time was obtained by arranging that observations could be taken while the liquid was flowing in either direction through the capillary tube, and that while an observation was in progress, and liquid was leaving one portion of the instrument, it was entering another portion and getting into position for a fresh observation. It was also desirable to avoid the use of corks or caoutchouc, at least in such parts as would be in contact with the liquid; it was therefore necessary that the instrument should be made entirely of glass. This condition presented the first serious difficulty in construction. To obtain absolute values of the coefficient of viscosity the exact dimensions of the capillary tube had to be known, and the problem to be solved was, how to seal the capillary tube to the other parts of the instrument in such a way that the direction and size of its bore should not be altered.

The form of apparatus designed to meet these requirements is shown in fig. 1. It consists of two upright limbs, L, and R, (left and right), connected near their lower ends by a cross-piece. Within the cross-piece is the capillary tube, C, P, the bore of which is about ·008 centim. radius, and the thickness of the wall about 2 millims., the internal radius of the cross-piece being a millimeter or so greater than the external radius of the capillary. At the zone, R, R′, the walls of the cross-piece are constricted and made continuous with those of the capillary, the latter is thus gripped at its middle portion and held axially within the cross-piece. The use of the cross-piece will now be obvious, for by its means the risk of altering the bore of the capillary tube was lessened, as only one sealing operation was necessary in order to make the capillary tube the sole means of communication from the one limb to the other.

To ascertain that this was really the case and that the capillary was quite continuous with the cross-piece all the way round, two simple tests were applied. A deeply-coloured liquid was introduced into the instrument, when it was observed that the colour was stopped entirely at the zone, R, R′. The second test consisted in half filling one limb with water and blowing air from the empty limb through the water in the other. Bubbles of air issued through the bore of the capillary tube only; of course, if any passage had existed across the zone, its presence would have been revealed by a stream of bubbles.

On one side of each limb of the instrument three fine horizontal lines were etched, m^1, m^2, k^1, on the left limb; m^3, m^4, k^2, on the right limb. The volumes of the limbs between m^1 and m^2 and between m^3 and m^4 were carefully determined; these represent the volumes of liquid which flow through the capillary. The time taken by the level of the liquid to pass from the upper to the lower of either of these pairs of marks is the time observed in the experiments. The limb is constricted in the vicinity of the marks, in order to give sharpness in noting the coincidence of the meniscus with the mark. The shape of the limb between the marks was made cylindrical rather than spherical, in order that the contained liquid might the more readily acquire the temperature of the bath in which the glischrometer was placed during an observation.

Fig. 1.



It will be seen from the figure that the upper ends of the limbs H^1, H^2 terminate within the glass traps T^1, T^2. These traps admit of slight adjustments of the volumes of liquid contained in the limbs, and their use, which is connected with that of the marks k^1 and k^2, will be evident at a later stage. During an experiment the levels of liquid in the two limbs are continually altering. It will be sufficient here to state that the object of these marks and traps is to ensure that at the beginning of any observation in a particular limb the effective head of the liquid contained in the glischrometer shall be constant and shall be known. Let us suppose that an observation is to be made in the right limb; the liquid level in the left limb is just brought into coincidence with the mark k^1, when any excess of liquid will flow over into the trap T^2; hence the effective head of liquid extends from H^2 to k^1, and is thus known. A similar proceeding is carried out for the left limb observations, using the mark k^2 and trap T^1. The marks k^1 and k^2 have been placed by trial in such positions that the volume from k^1 to H^2 is almost equal to, but slightly greater than, that from k^2 to H^1. The reason for this will be given subsequently. The volumes $k^1 H^2$ and $k^2 H^1$ are the working volumes of liquid used in the observations.

From what has been said it will be seen that at the beginning of an observation in the right limb the liquid level is at H^2. In order to allow the observer time to get ready to take the necessary readings before the liquid level falls to m^3, which time is but short in the case of mobile liquids, the limb is expanded into a bulb, as shown in fig. 1, just above m^3. After the liquid has fallen to m^4 and the time has been noted, readings of temperature, pressure, &c., have to be taken immediately; to give the necessary time for these readings, the limb is again enlarged below the mark, so that they can be taken before the level in the right limb falls to k^2, and the level in the left rises to H^1. Similar reasons explain the shape of the left limb. The lower extremities of the limbs are also expanded and bulb-shaped. This form was given to them, so that, if by any mischance any solid particles were present in the liquid under experiment, they would tend to collect in the hollow under the end of the capillary.

The instrument was made of thin glass to facilitate the passage of heat through its walls. It was therefore somewhat fragile, and would probably not have lasted throughout the observations had pains not been taken in its treatment. When immersed in the bath it was attached by light brass clips to a brass framework (see fig. 3). Whenever possible it was only manipulated when attached to this frame, and in this way it could be filled with liquid and cleaned with little risk of breakage.

The general arrangement of the whole apparatus is shown in fig. 2. The scale is $\frac{1}{10}$ A bath B, which for observations at temperatures below 100° contains water, and for higher temperatures glycerin, is supported on an iron stand, which is placed on a table in front of a window.* The bath is divided into two compartments. The inner compartment is provided back and front with plate glass walls; the rest of the bath is made of brass. The outer compartment bounds the inner at the sides, and underneath, and is fitted with a tap for adjusting the quantity of liquid which it contains. The brass framework carrying the glischrometer, and thermometer T, can be lowered into vertical slots in the lateral walls of the inner compartment; when thus situated the glischrometer occupies a central position in the bath. The walls of both compartments are provided with guides, along which move stirrers consisting of brass plates pierced with holes, which are attached to suitable rods and cross pieces, and are worked by a small water-motor W, M, which is connected with the upper cross piece

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* In practice two baths were used, one containing water, the other glycerin.

by a cord and pulley arrangement as shown in the figure. The length of the cord, which varies with the atmospheric conditions, is adjusted by a hook and chain. Two sets of stirrers fixed to the rods at different heights move in front of and behind the glischrometer in the inner compartment, and of course at the sides in the outer compartment.

Lids pierced with holes for the stirring rods, thermometer T, and india-rubber tubes E, E′, cover in the top of the bath. The lids covering the outer compartment can be removed or replaced, even while the stirrers are in motion, without disturbing anything.

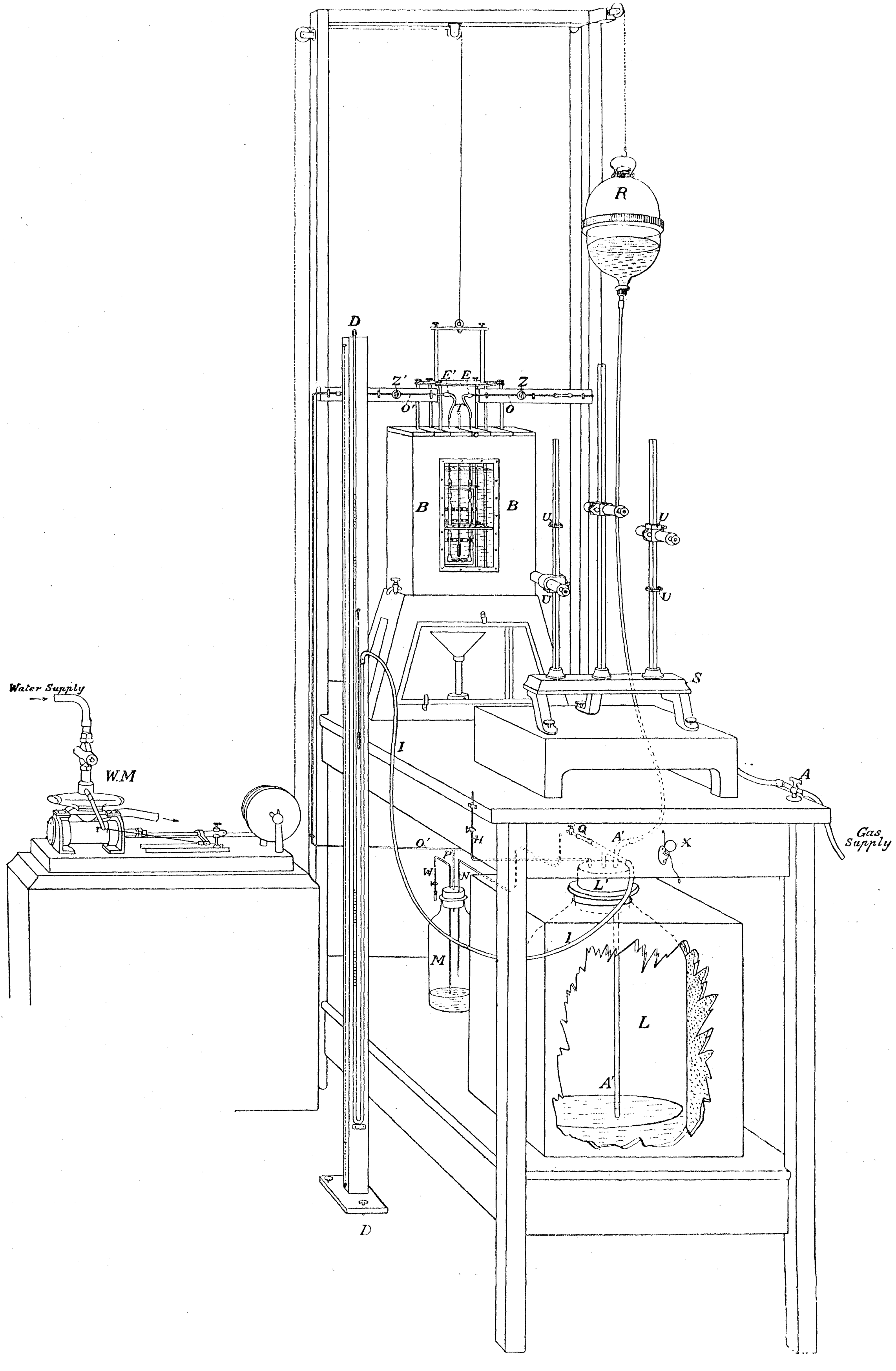
The rubber tube E connects the right limb of the glischrometer with the glass tube O, in which is inserted the three-way cock Z. In the same way E′ connects the left limb of the glischrometer with the tube O′ fitted with the three-way cock Z′. At P, O and O′ are united by a T-piece which leads to the bottle M containing a quantity of sulphuric acid, which can be abstracted or replaced by means of the siphon W. The acid serves to dry air in its passage from the reservoir L to the glischrometer. When hygroscopic liquids are being experimented upon, the exit tubes of the three-way cocks are provided with small tubes filled with calcium chloride to prevent access of atmospheric moisture to the glischrometer. In this way it is insured that dry air only is in contact with the liquid under examination.

By means of the tube N, which extends from within a few millimeters of the surface of the acid in M to a centimeter or so below the cork L′, and which is fitted with the cock Q, the air in M may be put into communication with the large air reservoir L. This consists of a glass bottle of about 30 litres capacity, encased in a wooden box, and surrounded with sawdust to prevent excessive fluctuation of temperature. A glass tube A′, which reaches to within 5 millims. of the bottom of L, is connected, as shown, by india-rubber tubing with the water reservoir R. The air in L is compressed by raising the water reservoir, the height of which can be regulated by a cord leading by a system of pulleys to the stud X, in close proximity to the position occupied by the observer, and to the water manometer D, D, which indicates the pressure set up in the confined air-space. The manometer is connected with the air reservoir by the tube I, I, which has a common termination with the tube N.

Leading from L to the air is the tube H furnished with a stop-cock. This tube is but seldom used; it serves to make fine adjustments of the pressure by allowing small quantities of air to escape from L, and it is also useful when it is necessary to quickly bring the air in L to atmospheric pressure. The three-way cocks Z and Z′ serve to put either limb of the glischrometer in connection with the atmosphere or with the air reservoir, or to cut off communication of either limb with the reservoir or the atmosphere. By their means the air reservoir may also be put into connection with the atmosphere.

When the apparatus is not in use, and the glischrometer has been removed from the bath, the cocks Z and Z′ are turned so as to cut off communication from L to the air, and the reservoir R is hung upon a peg which is attached to the table at a level

Fig. 2.


R
D
Z'
E'
E
Z
O'
O
B
B
U
U
U
U
S
Water Supply
W.M
I
A
Gas Supply
O'
H
Q
A'
X
P
W
N
L'
M
I
L
A'
D

below that of the bottom of the air reservoir. After water has siphoned over from L to R, and the air in the former has thus been reduced to atmospheric pressure, the cock Q is turned to prevent unnecessary absorption of water from L by the acid in M.

In front of the bath is placed the iron stand S, which is fitted with levelling screws and rests on the low wooden support shown. Fixed to the stand are three vertical brass rods each carrying a telescope. The telescope on the middle rod is used for reading the thermometer T. The telescope on the rod to the right of the middle rod is used for viewing the marks m^3, m^4 on the right limb of the glischrometer, that on the rod on the left for the marks on the left limb. On these outer rods are fitted the stops U, U, which have been so placed that, after levelling the stand S, when a telescope and a stop are in contact, one of the marks m of the glischrometer is in the field of view. The stop-watch is kept on the table just to the right of the telescope support.

To obtain observations at temperatures above that of the atmosphere, the bath is heated by Bunsen burners, which are protected from draughts by a zinc screen fitted with glass windows, in order that the flames may be seen. The gas supply is regulated by a quadrant tap, A, fixed to the side of the table close to the observer's hand. Temperatures below that of the atmosphere are obtained by introducing fragments of ice into the outer compartment of the bath, this compartment being kept uncovered by the lids at such times.

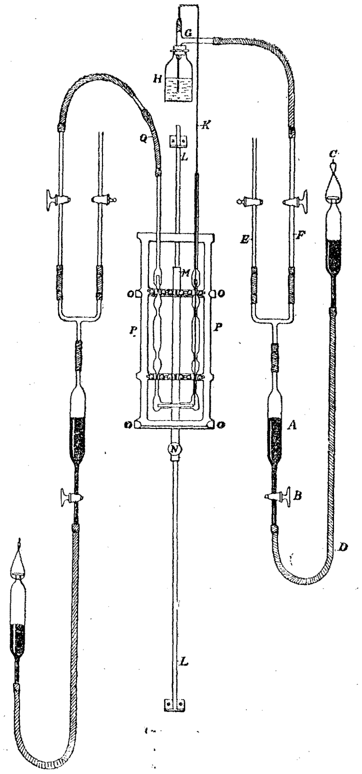
The double bath not only tends to keep the liquid round the glischrometer of a more uniform temperature, but it also has the advantage that the liquid in the inner compartment need not be renewed very frequently, as any dust or dirt introduced while regulating the temperature is confined to the outer compartment, and thus in no way interferes with the telescope readings.

Method of Experiment.

Before introducing the liquid to be examined, it was essential that the glischrometer should be perfectly clean and dry. The instrument was first rinsed out by successive quantities of dust-free water, alcohol, and ether, or, under ordinary circumstances, alcohol and ether only, and allowed to drain. It was then transferred to a specially constructed air-bath, heated to about 80° or 100°, and a current of air, filtered through cotton wool, and dried by oil of vitriol, was drawn through it for some time.

The liquids used for washing were obtained dust-free by distillation in an apparatus made entirely of glass, consisting of a large Wurtz flask, fitted with a well-ground glass stopper, the exit tube being sealed to a glass tube, which was passed through a Liebig's condenser. They were stored in ether bottles which, in addition to well-fitting glass stoppers, had glass caps ground on to their necks. The liquid is gently distilled in this apparatus and, after sufficient time has been allowed for the tube of the condenser to be rinsed out, the distillate is collected in the clean and dry store bottle. A small quantity of liquid is allowed to collect, and the bottle is then rinsed out. After this process has been repeated three or four times, the bottle is allowed to fill up with the distillate, and if on examination with a lens, when the bottle is held up to the light, the liquid shows no trace of suspended matter, it is regarded as dust-free. If suspended matter is present the distillation is repeated. As a rule, by the use of this glass apparatus, one distillation of liquid, which has been distilled in the ordinary way, gives a sample free from dust.

Fig. 3.



A special piece of apparatus was made in order to introduce and withdraw liquid from the glischrometer. The essential parts of the apparatus are seen in fig. 3. On one side of a mahogany stand, which is 75 centims. high and 17 centims. square, is fitted, by brass clips, a 20 cub. centim. pipette, A, which serves as an air reservoir. Connecting this pipette with a similar one containing mercury, is a short straight glass tube with a stop-cock, B, and a rubber tube. The mercury pipette can be hung upon either of the hooks C or D, and in this way the air in the reservoir can be put under increased or diminished pressure.

Connected by a T-piece with the air reservoir, are the two vertical glass tubes, E and F, each provided with stop-cocks. One of these tubes can be joined by rubber tubing to the horizontal limb of a small T-piece, G, the vertical limb of which passes through until it is just underneath the cork of the bottle, H, containing the liquid to be introduced into the glischrometer. A light glass bottle of about 25 cub. centims. capacity, to the base of which a disc of lead has been cemented to give it increased stability, was found of convenient size as a filling bottle. To the upper or free end of the vertical branch of the small T-piece, G, 2 centims. or so of narrow rubber tubing are fixed, which allow the short branch of a narrow siphon, K, to pass air-tight into the liquid in the filling bottle. The siphon was made by pulling out a piece of quill tubing in the blow-pipe flame, and bending it twice at right angles. The long branch extends downwards some 35 centims. or so, parallel to the front side of the mahogany stand. The second vertical tube, E, leading to the air reservoir, is useful for quickly putting the air in the reservoir to atmospheric pressure. It can also be used to introduce dry air, or other gas, to the reservoir and filling bottle when a hygroscopic or decomposable liquid is being employed.

The other side of the stand is fitted with an exactly similar arrangement of pipettes and stop-cocks. A vertical brass rod, L, L, extends along the middle of the entire length of the front side of the stand at a distance of 2 or 3 millims. from it. Along this rod slides a closely-fitting brass tube, M, which can be clamped to the rod by a screw and milled head, N. Two cross-arms, O, O, are attached to the brass tube, and the ends of these arms have been so constructed that they may be readily made to support and hold vertically the brass frame, P, P, carrying the glischrometer.

By means of this arrangement the glischrometer can be brought under the long branch of the siphon, and can be fixed with the end of the latter at any desired height within the right or the left limb. On regulating the heights of the mercury reservoir on the stand, and of the glischrometer, and manipulating the stop-cocks, a definite quantity of liquid can with ease be introduced or withdrawn from the instrument.

On several occasions, during the course of the investigation, the glischrometer was treated with hot, strong nitric acid, in order to remove grease, free alkali, &c.

While the glischrometer was drying, the filling bottle and siphon, which, of course, had been rinsed out with the same liquids as the glischrometer, were also being dried. The bottle was heated on a steam tray, in a glass crystallizing dish, the top of which was covered by a glass plate to exclude dust. When warm, a stream of air filtered through cotton wool was blown through it. It was then corked, the ends of the T-piece being closed with short lengths of rubber tubing plugged by pieces of glass rod.

The liquid under investigation was then distilled, in the apparatus described later, into the filling bottle. The latter having been repeatedly rinsed out with the dust-free liquid, a suitable quantity was then collected and the bottle corked.

The siphon, which meanwhile had been kept on glass supports in a cupboard out of the way of dust, was now suspended over the steam tray, and a current of filtered air was then driven through it. When dry it was wiped on the outside with a clean silk cloth, and fitted to the filling bottle in the manner already described. The siphon was rinsed out by allowing a few drops of the liquid to be examined to run through it. It was then slowly emptied by putting the filling bottle under diminished pressure. When it is empty, and bubbles are just about to be drawn through it into the liquid in the bottle, the latter is put to air and the air current thus stopped. This method has always to be used in order to empty the siphon, and the process must be slow in the case of volatile liquids, otherwise evaporation takes place so quickly at the free end of the siphon that ice crystals form and the siphon has to be dried anew.

The quantity of liquid necessary to carry out an observation is greater than can be contained in any one limb of the glischrometer. Instead, however, of filling the requisite amount into each limb by means of the siphon, time is saved, and risk of introducing dust is lessened, by filling liquid into one limb and by putting the other limb to reduced pressure, the requisite quantity of liquid being aspirated into it through the capillary tube. The method uniformly employed was to allow the siphon to extend to the bottom of the right limb, the filling bottle being attached to the pressure arrangement on the right side of the stand. The left limb of the apparatus was then connected by the rubber tube Q, fig. 3, to the pressure arrangement on the left side of the stand. The siphon was slowly set in action, and, after the liquid level had risen above the capillary, the left limb was put under diminished pressure. It was necessary to allow but a small quantity of liquid to enter the left limb; when sufficient was introduced the pressure was brought up to that of the atmosphere and the filling of the right limb proceeded with. During this process, by lowering the glischrometer, the end of the siphon was kept just below the surface of the liquid; in this way only a short length of the outside of the siphon was wetted, and risk of introducing adherent dust minimised. When almost enough liquid had been introduced the frame carrying the glischrometer was clamped, so that the end of the siphon was at the height to be occupied finally by the liquid level. When the level of liquid had reached the end of the siphon the latter was emptied in the manner indicated. The volume of liquid to be introduced was found by trial; it was slightly more than was necessary for the purpose of observation when the liquid has the lowest temperature at which experiments were made. The quantity had not to exceed a certain limit, for, as will be seen presently, the traps T^1, T^2, fig. 1, would thus be filled, and the observations would be interrupted before they had extended over the requisite range of temperature. It was also found convenient, in order to avoid the possible introduction of liquid into the trap during filling, to aspirate such a quantity of liquid into the left limb that the necessary volume of liquid was introduced into the glischrometer when the right limb was filled up to about the mark m^3. Mobile liquids run so quickly through the siphon that when the liquid has reached the desired level, before the action of the siphon can be reversed, so much liquid may enter the glischrometer that if the volume of the limb up to the trap is not considerable, the latter may be filled, and must be emptied before the observations can be commenced.

When the volume of liquid in the glischrometer had been adjusted, the rubber tube Q was detached from the glischrometer, which was then lowered, the siphon moved aside, the tubes E and E′ (fig. 2) fitted to the right and left limbs, and the ends of each stopped with a glass rod. The frame and glischrometer were now removed from the filling stand, and any small air bubbles which occasionally lodged in the interspace between the capillary tube and the cross piece of the glischrometer were removed. The thermometer was now fitted to the frame, which was next lowered into the slots in the sides of the bath. The water-bath was used for low temperature observations, and in the case of this bath, the stirrers were next introduced. The lid of the inner compartment, which was pierced with holes for the rubber tubes and the thermometer, was then fitted on, and the bath placed in position directly under the pulley over which passes the cord leading to the motor.

In the case of the glycerin bath, the stirrers remain permanently in the liquid, the glischrometer being introduced by unscrewing the cross pieces connecting the stirring rods and taking off the lid covering the inner compartment. This lid is made in one piece, and can only be removed in this way, or along with the stirrers as is done in the case of the water-bath. After adjusting the position of the bath, the rubber tubes E, E′ (fig. 2) were at once fitted to the glass tubes O, O′ respectively, and the cocks Z, Z′ turned so as to put the limbs of the glischrometer in connection with the air reservoir L, and thus under equal pressures. The water reservoir was then raised to the required height, care being taken to wet the walls of the manometer for some distance above the points where readings were to be made. In this way, before the first observation was started, and in the interval between subsequent observations the experimental liquid was kept under the increased pressure of the air in the reservoir. Two advantages arise from this arrangement. In the first place, the air in contact with the liquid is dry, which would not be the case if the pressure in each limb were kept equal by putting the three-way cocks to air, and secondly, evaporation of the liquid in the glischrometer under the increased pressure is retarded. At high temperatures the loss of liquid by evaporation during the interval between two observations, when the temperature is being raised, and afterwards when it is becoming steady, would in some cases be so great as to impair the volume necessary for the next observation if the liquid were kept at atmospheric pressure for such a length of time. Having established the pressure and having adjusted the length of the cord leading from the stirrers to the motor, the latter was put on to the water main and the stirrers set in motion.

If the experimental liquid did not solidify above 0° ice was now introduced into the outer compartment of the bath, and as it melted the supply was replenished, the water formed being removed at intervals by the tap. The motor was easily controlled. The rate of stirring was altered by regulating the water supply and the length of stroke adjusted by attending to the cut-off.

By rapid stirring the temperature soon falls, and becomes steady at 0°·3 or 0°·5, the exact temperature depending on the temperature of the laboratory. As a general rule, observations at as nearly as possible the same temperature were taken in both limbs of the glischrometer; for this purpose, as will be evident from what follows, the first observation at a given temperature had to be taken in the right limb.

When the liquid in the glischrometer had acquired the constant temperature of the bath, the first point to be attended to was the adjustment of the working volume of liquid. During the time that the glischrometer had been standing after being filled, the liquid was slowly flowing through the capillary, and the level, which after filling was much higher in the right limb, had been falling and approaching that in the left limb. The cock Z was now turned so as to put the right limb of the glischrometer to air. The pressure of the air reservoir, which was acting upon the liquid in the left limb, caused the level in this limb to fall, and as soon as the meniscus, as seen by a lens through the glass wall of the bath, touched the mark k^1, fig. 1, the pressure on both limbs was equalized. The slight excess of liquid over the volume k^1H^2 which was introduced in filling the glischrometer, escaped into the trap T^2. This process was carried out before observing the time of flow at any temperature, and in this way at the beginning of any experiment, the head of liquid in the limb, subject to a small correction for expansion of the glass of the glischrometer, was constant. As will be shown later, by this means a pressure correction for the effect of the varying head of liquid in the limbs of the glischrometer during the time of flow can be evaluated.

The head of liquid having been adjusted, the left limb was now put to air. Under the pressure of the air reservoir the level in the right limb, which meanwhile had been slowly filling, descended more rapidly.

The telescope on the right-hand outer rod was now clamped against the upper stop, when the mark m^3 was in the field. As soon as the meniscus was seen through the telescope to touch this mark the stud of the stop-watch was pressed and the hands started. Readings of the thermometer T through the telescope, of the water levels in the manometer, and of the manometer thermometer through a lens, were immediately taken. The telescope on the right hand rod was unclamped and allowed to slide down to the lower stop, the mark m^4 being then in view. During the experiment, attention was directed to keeping the temperature of the bath as uniform as possible. This temperature was noted at regular intervals during the flow, and if the latter were long, the manometer readings were also repeated. When the meniscus was seen through the telescope to touch the mark m^4 the hands of the watch were arrested and readings of the thermometer and manometer noted immediately as before. The time indicated by the watch was next taken, and the hands brought back to zero. If it was judged that these final readings could be taken and noted before the level in the limb fell to k^2 the disposition of the cocks Z, Z′ was left unaltered; if the level, however, was falling too rapidly to admit of these observations, both limbs were put under the same pressure before the level fell to the mark k^2.

To take an observation in the left limb, precisely similar operations were gone through. The volume of liquid was first adjusted by bringing the level in the right limb to k^2. Since, under ordinary circumstances, the left limb observation was taken at the same temperature as the previous one in the right limb, and from the fact that the limb is expanded below the mark m^4, sufficient time is given to the observer before the meniscus passes from m^4 to k^2 to enable him to begin the observation in the left limb, the cocks, Z, Z′, having remained undisturbed from the beginning of the right limb observation. The working volume, k^2 H^1, is, as already stated, slightly less than k^1 H^2. This was necessary because at high temperatures during the flow from the right limb a small but appreciable loss of liquid by evaporation took place, chiefly from the left limb, which was, of course, at atmospheric pressure. It was necessary, therefore, in order that observations might be taken at the same temperature in either limb, that the working volume in the left limb should be the smaller.

Care had to be taken not to make the difference of the volumes too great, for in order that the right limb observation may be taken after a left limb observation, the difference between the volumes must be made up by the expansion of the liquid in attaining the next higher temperature of observation, and in some cases this temperature interval is small—some 5° or so.

Having taken the necessary readings in the left limb, the pressure was equalised on the two limbs before the level of liquid fell to k^1 and the bath was now raised to the next temperature of observation.

To obtain temperatures between 0° and the atmospheric temperature, hot water, and, when necessary, ice were introduced into the outer compartment of the bath, and after several trials the quantity of boiling water needed to effect a given rise of temperature, and the quantity of ice which had to be added from time to time in order to maintain it constant, were ascertained with considerable precision. After the temperature of the bath had become steady and the liquid in the glischrometer had had time to acquire it, the head of liquid was adjusted and the observations taken as already described.

To maintain the temperature just above that of the atmosphere small quantities of boiling water were from time to time introduced into the outer compartment of the bath; for higher temperatures up to 100°, the water-bath was heated by small Bunsen burners.

Temperatures above 100° were obtained by the use of the glycerin bath, the water bath containing the glischrometer being allowed to cool to about 40°, and the glischrometer then transferred to the glycerin bath, which had been previously warmed over a steam tray. The glycerin bath was heated by a large Bunsen burner with a spreading flame.

During its flow the liquid in one limb of the glischrometer was at atmospheric pressure, an observation could therefore not be taken at a temperature above the ordinary boiling-point of the liquid. The highest temperature at which an observation was taken depended on the appearance of bubbles of vapour in the liquid. It invariably happened that bubbles began to form in the left limb, never near the capillary, but in the region of the mark m^2. The temperature was raised till bubbles appeared in the left limb. A right limb observation was then taken, a few bubbles forming in the left limb while the flow was in progress, these bubbles affecting but slightly, if at all, the validity of the observation. A left limb observation was then taken at the same temperature, and could always be carried on without the appearance of bubbles. The fact that the results of these two observations are concordant proves that the effect of bubbles during the right limb observation is inappreciable.

As a general rule, duplicate observations—one in each limb—were taken at the same temperature in the case of each liquid, and these observations were made at twelve temperatures, occurring at approximately regular intervals between 0° and the boiling-point of the liquid. It was found, however, that the variation of the coefficient of viscosity with the temperature was of such a kind that it was needless for the purpose of the research to take observations at temperatures separated by intervals smaller than 5°. When, therefore, the range of temperature between 0° and the boiling-point of the liquid was but short, fewer than twelve pairs of observations were made, the number being regulated by the 5° interval.

In all cases the time of flow decreases as the temperature rises. In the case of relatively viscous liquids, at low temperatures, single observations only were taken, alternately from the right and left limbs. When, however, by rise in the temperature the time of flow was reduced to a convenient amount, duplicate observations were again taken.

If during a series of observations on any liquid the latter had to stand overnight in the glischrometer, the cocks Z, Z′ were turned so as to prevent all passage from the limbs of the glischrometer, and the apparatus was then disposed as when not in use. When the cocks Z, Z′ were placed as described above, the bottle M was in communication with the atmosphere, and, therefore, to prevent access of moisture, the exits of the cocks were joined by a piece of rubber tubing. If the temperature of the bath was below that of the air, it was advisable to make the levels of the liquid in the two limbs about the same before turning the cocks, otherwise, on the temperature rising during the night to that of the atmosphere, the expansion of the air in the limb containing the smaller quantity of liquid might force the liquid from the other limb into the trap, and thus affect the working volume.

CONDITIONS DETERMINING THE DIMENSIONS OF THE APPARATUS.

The fundamental measurement which regulated the degree of accuracy aimed at, and therefore the dimensions of the apparatus, was that of time. Since a comparatively large number of liquids was to be examined, and since it was considered to be necessary to make, as a rule, twenty-four observations on the same liquid in order that the law of the change of viscosity with temperature might be ascertained, it was desirable that the times of flow should be as short as possible, consistent with an accuracy sufficient to satisfy the requirements of the research. Considering the conditions of the problem, we may assume an accuracy of one part in 1000 as sufficient; indeed, when we have regard to the imperfection and uncertainty of the theory, this degree of accuracy is probably the utmost that we can at present legitimately aspire to. Since the watch was graduated into fifths of a second, and could be read to one-tenth, it followed, on the assumption that one-fifth of a second was the probable error in time of an estimation, and that two observations were to be taken at each temperature, that the minimum time of an observation, even at the highest temperature, should never be less than three minutes. At the lower temperatures, where the efflux times would be greater, the same absolute error in time, other things being equal, would of course have a smaller percentage effect.

On the basis of POISEUILLE's observations, we first made a trial apparatus, and with such a working volume of liquid as seemed suitable (determined approximately in the manner given below), we ascertained the size of capillary needed to give an efflux time of three minutes in the case of water at 100°. Observations with benzene, which is less viscous at its boiling-point than water, showed that the same apparatus could still be made to give efflux times within the minimum limit with liquids much less viscous than water at its boiling-point, provided that means were devised for slightly altering the pressure under which the flow took place. With the knowledge acquired by the use of this model the apparatus described was designed.

As regards the *volume of liquid* to be taken, it is obvious that, other dimensions being constant, the larger the volume of liquid employed, the smaller is the percentage effect of an error in the time; on the other hand, the larger the volume the greater becomes the difficulty of keeping the temperature uniform during the flow and of ensuring that the whole of the liquid has taken up the temperature of the bath. A relatively small volume meets the requirements, and it may be made to give sufficiently long times by using long and narrow capillary tubes. But in the case of a small apparatus the relative amount of liquid which adheres to the walls is greater than in a large apparatus of similar shape. On the assumption of the degree of accuracy above given we are thus able to fix the minimum limit. Considering all things the best volume to take appeared to be about 2·5 c.c. So small a quantity had the further advantage that it enabled observations to be made on liquids which were difficult to obtain in large quantities in a state of sufficient purity. The *shape of the vessel* had also to be considered. As regards rapidity of acquiring a constant temperature, a long cylinder is better than a sphere; in the case of a sphere, however, less liquid adheres to the walls than in that of a cylinder of equal capacity. Experiments made with water determined the relations of length and breadth of cylinder such that the observations should not be influenced, within the limits of accuracy aimed at, by the liquid left adhering to the walls.

Having fixed the working volume, the other factors to be considered in maintaining the time of flow at any temperature within the three minutes limit were the *pressure* and the *dimensions of the capillary tube.*

As already stated the pressure employed was a head of water. The minimum head should be capable of measurement with an accuracy well within 1 in 1000. The scales of the manometer were divided into millimeters and could be easily read by a lens to 0·2 millim. The minimum pressure head usually employed was about 100 centims., which was found a convenient height to measure; hence the error in reading the manometer did not exceed 1 in 5,000.

The dimensions of the capillary could now be fixed from POISEUILLE'S observations and from the results of the experiments with the model. Since the time of flow depends on both the length and radius, it is obvious that the same time could be obtained by means of tubes of very different dimensions. It was advisable, however, to have the length as short as possible consistently with the considerations given below, for then the limbs of the apparatus could be placed near together, and could be kept more readily at the same temperature, and the temperature, indicated by a thermometer placed between them, could be taken as that of each. The length chosen was about 5 centims., and with this length the radius had to be about ·008 centim.

It will be obvious from the above dimensions that the velocity of flow of liquids which have efflux times near the minimum limit is considerable.

$$\text{Mean velocity} = \frac{V}{\pi r^2 t} = \frac{2\cdot 5}{\pi \times (\cdot 008)^2 \times 180} = 66 \text{ centims. per second.}$$

In connection with this relatively high velocity two questions present themselves:

(1) The formula used in obtaining the coefficient of viscosity is deduced on the assumption that the motion of the fluid within the tube is linear, and that the stream does not break up into eddies. OSBORNE REYNOLDS ('Phil. Trans.,' 1883 and 1886) has shown, experimentally, that if the velocity of efflux is greater than that given by the expression $V = 2000\eta/2rd$, the motion is probably turbulent, and therefore the formula will not hold. In this expression η is the viscosity coefficient, and d the density of the liquid; r is the radius of the tube. By taking observations under different pressures, it has been shown, as is described later, that the flow in the apparatus employed by us is linear. In the case of water the critical velocity at 100° in our apparatus is about 400 centims. a second, the velocity

actually observed is about 70 centims. In the case of ether, one of the most mobile of liquids, the critical velocity at 32°, as given by the above formula, is 360 centims., the actual value in the apparatus employed, even under the greatest head, is 93 centims. It is evident, therefore, that our apparatus falls well within the requirements necessary for a stream without eddies.

(2) On account of the high value for the velocity of efflux the kinetic energy correction (see p. 435) becomes in some cases comparatively large. Thus, in the extreme case of ether at 32°, under the highest pressure it is about 4 per cent.; this is also the value of the correction in the case of water at 100°, although at 5° it is only ·16 per cent. On the other hand, the recent investigations by FINKENER, COUETTE, and WILBERFORCE have shown that the theoretical basis upon which the evaluation of the correction depends is valid, and that the actual determination of the numerical value can be made with a high degree of accuracy. In any case, the stoichiometric relations deduced from coefficients of viscosity thus obtained will in all probability be unaffected by any modification of the theory relating to the correction. For this modification can at most lead to a correction on a correction, because it is obvious that the liquid does carry away kinetic energy, which must be allowed for.

Moreover the legitimate use of the correction will give a means of testing its validity, as the final results thus obtained can be compared with those observations in which this correction is less important. Dearth of experimental data has been the main obstacle in deciding the worth of the correction, and if, as has been the custom, its effect were in all cases to be evaded instead of ascertained, the problem would never be brought nearer to solution.

DETERMINATION OF THE CONSTANTS OF THE GLISCHROMETER.

Volumes of Liquid Passing through the Capillary Tube.—The volumes of liquid contained between the marks m^1 and m^2 on the left limb, and the marks m^3 and m^4 on the right limb, were obtained by gauging with water. Three weights were ascertained—(1) The weight of water filling the glischrometer up to the lower marks m^2 and m^4; (2) the weight of water filling the right limb up to the lower mark m^4, and the left limb up to the upper mark m^1; and (3) the weight of water filling the glischrometer up to the upper marks m^1 and m^3. In determining any of these weights a quantity of freshly distilled water was introduced by means of the filling apparatus into the clean and dry glischrometer, which had been carefully weighed. The quantity of water introduced was adjusted until the levels of liquid in either limb nearly coincided with the desired marks, pains being taken not to wet the glischrometer above these marks. To obtain perfect coincidence between the liquid levels and the marks, the glischrometer was transferred to the water-bath, and by slightly altering the temperature and adjusting the quantity of liquid in either limb, by causing a small quantity to pass through the capillary tube, the temperature was obtained at which the quantity of liquid introduced into the glischrometer exactly filled it up to the marks, all the observations being made through the reading telescopes. The glischrometer was next withdrawn from the bath, its open ends closed by india-rubber caps, and allowed to take up the temperature of the balance case; the caps were then removed and the weight ascertained. Knowing the weight of the glischrometer alone, the weight of water (reduced to a vacuum) which at the temperature of the water-bath filled the instrument up to the marks could be ascertained, and on introducing corrections for the expansion of the water and of the glass, the volume at 0° could be readily calculated.

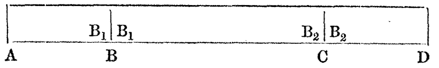
From two concordant sets of observations carried out in this way the mean volumes were found to be

Right limb, m^3, m^4, 2·6731 cub. centims.
Left limb, m^1, m^2, 2·5513 ,,

The amount of liquid which in any observation flows through the capillary tube is, of course, less than either of the above volumes by the quantity which adheres to the wall of the glischrometer-limb between the upper and lower marks. To obtain some idea of the amount thus adhering, a glass vessel was made of as nearly as possible the same shape and size as a limb of the glischrometer. This vessel was fixed vertically, filled with water, and the amounts which at ordinary temperatures adhered to the sides when the times taken by the water to flow from the vessel were about the same as that of the actual viscosity observations were determined by weighing. About ·002 grm. was found to adhere, and with rise in temperature the amount appeared to diminish. The error thus introduced in the case of water corresponds to 1 in 1300, and is within the limits of the accuracy to which we could attain.

Dimensions of the Capillary Tube.—It was expected, and it so happened, that several tubes would be broken before one was successfully sealed into the glischrometer in the manner already described. On this account measurements of the mean diameter and length of the capillary were deferred till the sealing in had been accomplished.

Having ascertained, by rough optical measurements, that the section of the bore of a piece of capillary tubing was nearly circular, and that its mean diameter was suitable, before cutting off the required length, the tubing was marked as shown. BC being



the length required, at these points two cuts were made with a sharp file, and on either side of each cut, the same letter, B_1 or B_2, was etched on the tube with glass-ink. The length, BC, was then broken off, carefully protected from dust, and sent to the glass-blower. Optical measurements made on the section of the pieces AB and CD at their marked ends served, of course, to give the dimensions of the bore at the ends of the length BC. In each case the length of the major and minor axis of the elliptical section of the bore was determined. The method employed was as follows :—

One of the pieces, AB or CD, was fixed vertically in a cork, the marked end uppermost, and projecting a millimeter or so above the cork. The cork was placed centrally in a circular brass disc, on the circumference of which were four marks 90° apart. This disc stood on a piece of paper, on which were ruled two lines at right angles to one another, the marks on the disc coinciding with the lines on the paper, and the whole arrangement placed so that the section of the bore of the tube was in the field of the telescope of a horizontal cathetometer, which was graduated to read to ·0001 centim. By rotating the cork, the major axis was, by trial, brought parallel to the cross-hair of the telescope, and the minor axis was then measured. On rotating the disc through 90° by means of the marks on its circumference and the lines on the paper, the major axis could next be ascertained.

Some thirty measurements made in this way gave the following mean values observed at 17°·2 :—

	Major axis.	Minor axis.
End B_1	·017207	·016175
End B_2	·017200	·016412

Correcting for the expansion of the glass and of the scale of the cathetometer, these numbers give at 0° as values for the mean section of the bore of the tube

Semi-major axis, ·008603 ; semi-minor axis, ·008148.

If these measurements could have been taken as absolute lengths in centimeters, no further observations need have been made on the dimensions of the section of the tube. It is very difficult, however, to obtain an instrument which will give such readings for lengths so small; we have, therefore, regarded the above as relative measurements, and have obtained the true lengths of the semi-axes by combining the preceding measurements with what we have taken as the true mean radius of the tube as determined by weighing with mercury, in the manner shortly to be described.

On receiving the glischrometer from the maker, the first point to decide was whether the bore of the tube had been modified in the process of sealing. A thread of mercury was introduced into the tube of such a length that it could be measured when on either side of the zone of sealing, or when its central portion was in the region of the zone. Eighteen measurements were taken by the horizontal cathetometer, six when the thread was in somewhat different positions in each of the three regions indicated above. The following mean values were obtained :—

Thread towards end B_1	1·5602 centims.
Thread at zone of sealing	1·5573 „
Thread towards the end B_2	1·5581 „

It is evident that no appreciable modification in the dimensions of the bore had been brought about in making the glischrometer. The measurements indicate also the increase in the section of the tube towards the end B_2, which was apparent from the previous optical measurements.

Length of the Bore of the Capillary Tube.—From the fact that the ends of the tube were somewhat oblique, it was a matter of some difficulty to find the exact length of the bore. When the glischrometer was laid flat on the table with that side undermost upon which the various marks m^1, m^2, &c., were etched, owing to the obliquity of the ends the termination of the bore could not be seen, and even with the etched side uppermost the termination was not quite definite. Accurate readings were obtained, however, by introducing a thread of mercury into the tube, the quantity of mercury being so arranged that at either end the thread expanded into a spherical globule. With the etched side uppermost the points where the bore ended and this expansion took place could be clearly made out. Measurements were then made with a Brown's calibrating instrument of the length of the bore indicated in this way, when the bore was parallel to the line of motion of the reading microscope and when different parts of the scale of the instrument were used.

From twelve measurements the mean observed length at 15°·95 was

4·9318 centims.

Corrected for the expansion of the brass scale and the expansion of glass, at 0° this value became

4·9326 centims.

Mean Radius of the Bore of the Tube.—The mean radius was determined by weighing a globule of mercury which occupied a known length of the bore of the tube. After several trials the method adopted was as follows:—The glischrometer, perfectly clean and dry, was fixed with the capillary tube vertical, the left limb being uppermost, and, of course, horizontal. Into this limb was next introduced a long piece of drawn-out glass tubing containing a small globule of pure re-distilled mercury. One end of this piece of tubing was placed on the flat end of the capillary, and to the other end was attached a piece of rubber tubing. By gently compressing the rubber tubing the globule was transferred to the flat end of the capillary. The drawn-out tube was then removed, and a small india-rubber ball, which could be used as a compressing syringe, was attached to the free end of the left limb. By gently tapping the glischrometer the globule was brought over the bore of the capillary, and, when in this position, by compressing the ball it was slowly driven into the tube. After a sufficient length of mercury had been introduced, by quickly laying the glischrometer flat on the table, the excess of mercury contained in the globule was detached into the left limb. The position of the thread which nearly filled the bore was then made as nearly as possible equidistant from the ends of the capillary.

The length l of the thread was then ascertained by the calibrating instrument, eight measurements, as a rule, being made when the thread was parallel to the line of motion of the reading microscope and when either side of the glischrometer was uppermost.

When the length had been accurately measured, by tilting the glischrometer the thread was completely transferred, in the form of a globule, into the right limb. By judiciously tapping and tilting the glischrometer, the globule was next very gradually moved to the free end of the limb, its course being followed with a lens in order to see that no separation into smaller globules took place. The globule was finally received in a small weighed glass tube which fitted into a slightly wider tube. The tubes together weighed less than 1 gram.

The weight W of the globule, which was but some ·013 grm., was then ascertained. The weighings were performed on an assay balance by the method of vibrations. The sensibility of the balance was about 7 (1 scale division corresponded to less than ·00014 grm.) The zero point and the sensibility were determined before and after each weighing. Reduction of the observed weight to a vacuum was unnecessary since mercury was weighed against platinum. By the use of the ordinary formula, $R = \sqrt{(W/\pi\rho l)}$, on introducing the necessary corrections for the expansion of the brass scale of the calibrating instrument, and for the expansion of glass and change in ρ, the density of mercury, the mean of two concordant determinations carried out as above gave for R the mean radius of the capillary at 0°,

$$\cdot 0082018 \text{ centim.}$$

If A and B are the semi-axes of the elliptical section of the tube, on taking the value of the ratio A/B, as already obtained by the optical method, and using the above value of R as the true mean radius of the tube, the values of A and B are found to be

$$A = \cdot 0084374 \text{ centim.} \qquad B = \cdot 0079728 \text{ centim.}$$

At 0° the constants of the glischrometer thus obtained were as under :—

Volume, right limb $= V_{R.} = 2{\cdot}6731$ cub. centims.
Volume, left limb $= V_{L.} = 2{\cdot}5512$,, ,,
Length of capillary $= l = 4{\cdot}9326$ centims.
Section of Capillary $\begin{cases} \text{Major axis} = A = \cdot 0084374 \text{ centim.} \\ \text{Minor axis} = B = \cdot 0079728 \text{ ,,} \end{cases}$

Determination of Temperature.—Two sets of thermometers, each consisting of two instruments, were employed. The working range of the first instrument extended from 10° to 110°; that of the second from 100° to 210°. They were of the Geissler pattern, made of Jena glass, and had been compared with standards at the Physikalisch-Technische Reichsanstalt at Charlottenburg. Each thermometer was provided with two fixed points and was divided into half-degrees and could be read by the telescope to hundredths. The position of the two fixed points was ascertained from time to time, and the necessary corrections introduced into the temperature readings. During the time over which the observations extended there was no appreciable alteration in the capacity of the bulbs.

In considering the influence of thermometric errors it must be remembered that $d\eta/d\mathrm{T}$ varies for different liquids, and moreover for any one liquid varies greatly with the temperature. Thus for water the value of this rate of change is about 18 times as large at 0° as it is at 100°. This example serves to illustrate the general rule that $d\eta/d\mathrm{T}$ is much larger at low than at high temperatures. On the other hand, in considering the effect of possible errors due to this circumstance, it must be remembered that it is much easier to keep the temperature constant at low temperatures, and that the accuracy of the final result is increased by the multiplication of thermometer readings at the low temperatures, and that the longer times of flow tend to ensure that the liquid has actually the temperature of the bath in which the whole is immersed. An error of $0^\circ{\cdot}1$ in observing the temperature may be taken for an average value of the viscosity as corresponding to about 1 part in 1000 in the value of η.

Determination of Pressure.—The pressure under which the liquid was driven through the capillary tube was measured by means of a water-manometer. This consisted of a glass U-tube fixed, as shown in fig. 2, to a stout wooden frame, provided with a plummet and levelling screws. The shorter limb of the manometer was connected with the air-reservoir, and between the limbs was a thermometer to determine the temperature of the water. Two millimeter scales, each 10 centims. long, were etched on each limb, the middle points of the inner pair and of the outer pair being equidistant from the middle point of the longer limb. The two upper scales were read from below upwards, the two under scales from above downwards. The pressure head was thus the sum of the scale-readings, *plus* the distance between the zeros of the scales. The quantity of water was adjusted so that the levels were always on corresponding scales, *i.e.*, either on both of the inner or on both of the outer scales. Pressure heads of *circa* 130 centims. were measured by the outer scales, and those of *circa* 100 centims. by the inner. The inner scales were principally used for such liquids as would, under the higher pressures corresponding to the outer scales, give times of flow under the three minutes limit. The lengths of the scales were tested and the distance between their zero-points measured by means of a De La Rive cathetometer. As the pressure head was to be expressed finally in terms of water at 4°, the scale of the manometer was corrected to 4°. This was done once and for all from the cathetometer readings at the mean atmospheric temperature by applying a correction, which also included a small scale error, to the distance between the scales. The variation in length of the manometer between the mean and extreme temperatures of the laboratory may be neglected. The true length of the water column on a scale correct at 4°, having the temperature of the atmosphere, could thus be got with ease. To express this as a head of water at the temperature of 4°, advantage was taken of the fact that when the same two scales were used the pressure head was almost the same, and thus the correction of the head for change in density of the water depended only on the temperature. A table was therefore constructed from which by inspection the correction to be applied to the head at any temperature in order to give the height of a column of unit density could be obtained. In order to find the mean effective pressure, two corrections have to be applied to this head of water.

1. *Correction for Inequalities in the Atmospheric Pressure on the Liquid Surfaces in the Manometer and Glischrometer.*—A head of air, assumed to have the mean atmospheric temperature and pressure, and having a height equal to the difference between the upper level of liquid in the manometer and the mean level of liquid in the glischrometer, opposes the flow of liquid through the capillary. Acting in the same direction is a head of air having the atmospheric temperature and a pressure equal to that of the atmosphere *plus* that indicated by the manometer, and having a height equal to the difference in level of the lower liquid surface of the manometer and the mean liquid level in the glischrometer. The mean value of this correction for the outer scales was 0·17 centim. of water at 4°; for the inner scales the correction was 0·13 centim.

These values are not appreciably affected by changes in atmospheric density, and were therefore applied once and for all as corrections to the distance between the scales.

2. *Correction for Change of Head of Liquid in the Glischrometer.*—This correction, which is needed to eliminate the effect of the alteration in the heads of liquid in the two limbs, is by far the more difficult to ascertain.

If the limbs of the glischrometer had been identical in all respects, it would have been possible to arrange the working volume of liquid before each flow, so that the pressure produced by the head of liquid acting in unison with the pressure of the air-reservoir during the first half of the time of flow, would have been cancelled by an equal back pressure during the second half. As it was impossible to obtain the limbs exactly similar, and as on this account the mean head of liquid accelerating the flow differed from that retarding it, it became necessary to estimate the exact value of the effective pressure due to this cause, and provide some means of ascertaining its effect at any temperature with any liquid. This was rendered possible by the use in each flow of a constant working volume of liquid, as already described. To obtain the effective pressure called into play during the flow from, say, the right limb, it was necessary to take account of the fact that the rate of change of pressure was largely influenced by the varying diameter of the limb. A paper millimeter scale, 1 millimeter broad, was gummed along the entire length of each limb of the glischrometer. A quantity of water was then introduced into the instrument, which was transferred to the bath, and after a constant state of temperature (that of the atmosphere) had been obtained, the working volume of liquid was adjusted. The position occupied by the mark M^3 was ascertained by a cathetometer, the level of liquid in the right limb brought just into contact with the mark M^3, and the position of the level in the left limb read off. As the level fell in the right limb to the mark M^4, readings were taken on the cathetometer and paper scales, of the levels in both limbs, when that in any one limb was leaving a narrow portion of the limb to enter a wide portion, or *vice versâ*. Finally the cathetometer reading of the mark M^4 was observed, the level brought into contact with it, and the position of the corresponding level in the left limb noted. The positions of corresponding levels are numbered alike, and are roughly indicated in fig. 1, p. 410. The temperature remaining unaltered, the time was next observed, by fixing the cross hair of the observing telescope on the corresponding reading of the paper scale, which the liquid took to pass from 1 to 2, 2 to 3, &c., under a constant pressure. It was then possible to plot out a curve having as abscissæ the times, and as ordinates the heads of liquid, $1_R - 1_L$, $2_R - 2_L$, &c., representing the variation in the head of liquid with the time throughout the entire flow, the curve between any two consecutive ordinates being assumed to be straight. The curve consisted, of course, of two portions, one above, the other below the axis of abscissæ. On dividing the difference in the area enclosed between the upper part of the curve and the axis of abscissæ, and that enclosed between the lower part of the curve and the axis of abscissæ, by the total time of flow, the mean head of water of density corresponding to the temperature of the experiment which influences the flow is obtained. In the case of the left limb this was found to be $-\cdot139$ centim. at $19^\circ\cdot15$; in the case of the right limb it was $-\cdot253$ centim. It is obvious that with the same liquid this height will be subject to a correction for expansion of the glass of the glischrometer, but as the height is small compared with the total pressure, 130 centims. or so, the correction may be neglected. Thus, for any liquid for any temperature $-\cdot139$ centim. represents the mean head of liquid opposing the flow from the left limb. In order to put this head into the form of a correction to be applied to the reduced reading of the water manometer, account has to be taken of the densities of the different liquids, and of the variation in density of each liquid with change of temperature. A table has been constructed for each limb of the glischrometer, from which, knowing ρ, the density of the liquid at 0°, and s, the volume which 1 cub. centim. at 0° occupies at the temperature of experiment, it is possible to obtain by inspection the value, in centims., of water at 4°, corresponding to the mean effective pressure head of any liquid at any temperature. The tables include densities from 0·7 to 3·0, and volumes from 1 at 0°, to 1·2 at the highest point of observation.

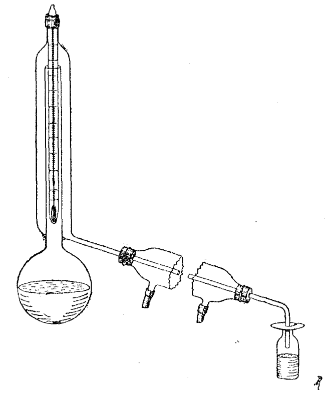
Determination of Time.—Two stop watches supplied by DENT were used. The rate of each was determined from time to time by running it for 12 hours against an astronomical clock controlled by hourly signals from the Royal Observatory, Greenwich, and suitable corrections, which were in all cases very slight, were introduced into the observed times of flow.

PURITY OF THE LIQUIDS EMPLOYED.

As regards the purity of the liquids investigated, we mainly relied upon their origin and mode of preparation, but we give, whenever possible, as criteria, the boiling-point and vapour density, and in some cases the density of the liquid employed for the viscosity determinations.

The boiling-point was in almost all cases determined by means of the apparatus seen in fig. 4, constructed on a principle similar to that already employed by BERTHELOT. It is made entirely of glass in order to exclude dust and extraneous organic matter, and is so arranged that the mercurial column of the thermometer is jacketed for by far the greater part of its length, and is completely surrounded by vapour during a distillation. Hence the correction for the emergent column, which is especially unsatisfactory in the case of thermometers of the Geissler pattern, is obviated. For this reason it is only in the case of a few liquids which were distilled from ordinary flasks that there is any correction for emergent column involved in the boiling-points as given by us.

Fig. 4.



The neck of the flask is constricted just below the cork supporting the thermometer, so that the cork may never be moistened by the liquid.

The observations on boiling-points are reduced to a standard atmosphere by the formulæ of CRAFTS ('Ber.,' 20, 709) and of RAMSAY and YOUNG ('Phil. Mag.,' 1885, 515). In certain cases where the vapour pressures have been studied the corrections have been deduced from the curves of vapour pressure.

In cases in which it was necessary to carry out a fractionation the same apparatus was employed; on account of the large radiating surface and the peculiar construction of its neck, the flask was found to be very well adapted to this purpose.

The vapour density was ascertained by means of the modified Hofmann apparatus already described by one of us (THORPE, 'Chem. Soc. Trans.,' 1880), which allows of the introduction of all the corrections necessary to obtain normal values. The formula used in the reduction of the observations is

$$D = 760W\,(1 + \alpha T)/{\cdot}0_4 8957V\,\{H - h\,(1 - \beta T)\},$$

where

D = required vapour density,
W = weight of substance taken,
α = ·003665,
T = temperature of vapour-jacket,
V = observed volume, corrected for meniscus and volume of bottle × (1 + ·000025T),
H = barometric height corrected for scale error and reduced to 0°,
h = height of mercury in experimental tube corrected for scale error at the temperature T of the vapour-jacket,
β = ·00001808.

It will be seen that the agreement between the observed and theoretical values is, as a rule, very satisfactory.

DEDUCTION OF THE WORKING FORMULA.

When a stream of liquid flows through a tube of uniform section, so far as experiments have been able to show, the liquid molecules appear either to move in straight lines parallel to the axis of the tube, *i.e.*, the motion is linear; or the stream breaks up into eddies, *i.e.*, the motion is turbulent.

With a given liquid flowing through a given tube, linear movement corresponds to the lowest velocities, turbulent movement to the highest, and for intermediate values of the velocity, the two kinds of movement may occur alternately.

In order to deduce the value of the viscosity coefficient from the time of flow, it is essential that the movement be linear.

If a horizontal tube of indefinite length and of radius R be traversed by a constant current of liquid, pressure falls in passing along the tube in the direction of the movement, and if measurements of pressure be made at any two sections of the tube distant l from one another, the difference of pressure observed, if the movement is linear, may be attributed to two causes :—

1. To friction of the liquid against the walls of the tube (external friction).
2. To the viscosity of the liquid (internal friction).

Experiment seems to show, however, that (1) is inoperative, because it is found that if the tube be wetted by the liquid, the loss of pressure is independent of the nature of the material of which the tube is made. It is, therefore, assumed that the layer of liquid in immediate contact with the wall of the tube is stationary, and the experiments of KOCH ('Wied. Ann.,' 14, 1) on the flow of mercury through glass tubes, and those of COUETTE on the flow of water through paraffin tubes, seem to show that even when the tube is not wetted the same state of things prevails.*

Under the conditions above given, the loss of pressure may thus be wholly attributed to overcoming the viscosity of the liquid.

Assume the velocity of the liquid molecules to be the same at points equidistant from the axis of the tube, and to be zero at the wall of the tube and greatest at the axis, and consider the forces acting upon an elementary cylinder of liquid situated between the two sections of the tube at which pressure is measured, and having for its axis the axis of the tube.

If r be the radius of such an elementary hollow cylinder, dx its length, measured in the direction of the axis of the tube, dr its thickness, and P the pressure exerted on one end of the cylinder, then the total pressure on this end will be $2\pi r\mathrm{P}dr$. On the other end of the cylinder the pressure will be $2\pi r\,[\mathrm{P} + (d\mathrm{P}/dx)\,dx]\,dr$. The difference of these two pressures $2\pi r\,(d\mathrm{P}/dx)\,dxdr$ is spent in overcoming viscosity or internal friction, inasmuch as the external pressures which are normal to the direction of movement must be in equilibrium with the weight of the liquid.

Within the cylinder, the adjacent liquid is moving more freely and tends to carry the cylinder along with it, whereas on the exterior surface of the cylinder the adjacent liquid, which is moving more slowly, exerts a retarding effect. The difference of these two friction-effects corresponds to the loss of pressure.

In order to estimate the magnitude of the friction-effects assumptions have now to be made. When a liquid is at rest its surface is plane, the force between two contiguous strata of liquid is therefore normal to their surface of separation. It is only when the liquid moves that this force has a tangential component. It is thus assumed that the magnitude of this component is a function of the relative velocity of the strata, becoming zero when the relative velocity is zero. For small velocities, such as those usually attained in capillary tubes, it is further assumed that the tangential component is simply proportional to the relative velocity. The tangential component is also assumed to be proportional to the area of the surface of contact, and to be independent of the curvature of the surface. After making these assumptions it may readily be shown that if p be the difference in the pressures at two sections of the tube distant l from one another, then V, the volume of liquid carried through the tube per unit time, is given by

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* The question of slipping at a liquid boundary has recently been raised by BASSETT ('Roy. Soc. Proc.,' 52, 273, 1893). Trustworthy experimental support to the idea that slipping really takes place seems, however, to be wanting. Besides the results quoted above, and those summarised by COUETTE (Ann. de Chimie et de Phys. [6], 21, 490, 1890), the work of WHETHAM ('Phil. Trans.,' vol. 181, A. (1890), p. 559) is conclusive in showing that during linear movement the liquid layer in contact with the solid wall is stationary, and from the experiments of COUETTE, the same condition appears to hold even when the movement is turbulent.

$$V = \pi R^4 p/8\eta l,$$

and thus, that

$$\eta = \pi R^4 p/8Vl.$$

It is also possible to obtain the same expression for η by integrating the simplest of the fundamental hydrodynamical equations of NAVIER ('Mém. Acad. des Sciences,' vol. 6, 1822), after making the assumptions that when a permanent current of liquid passes through a tube the velocities of the molecules are parallel to the axis of the tube and zero at the sides (COUETTE, 'Bull. des Sci. Phys.,' 1888).

If, instead of considering a tube of indefinite length, and the loss of pressure taking place between two sections of such a tube, we deal with a system consisting of two reservoirs, connected by a tube of finite length, the difference of pressure measured being that between the two reservoirs, then the above formula will in general not apply unless suitable corrections be introduced. This arises from the fact that the observed difference of pressure will, in general, not be entirely spent in overcoming viscosity within the tube, for, besides this cause of loss of pressure, the following have to be taken into account:—

(1.) If the liquid flows through the tube with a finite velocity, at the entrance to the tube pressure will be spent in imparting kinetic energy to the liquid.

(2.) Owing to modifications of the stream-lines, especially at the entrance, pressure will be spent to some small extent in overcoming friction outside the tube, in the neighbourhood of its ends.

It is possible to arrange the experimental conditions so that corrections for these disturbing causes may be neglected. The observations made by POISEUILLE, with long and narrow tubes, are in perfect accord with the preceding formula. In these experiments the velocity of efflux was so small that the kinetic energy correction was inappreciable, and, owing to the length and narrowness of the tubes, the pressure spent in friction outside the tubes was negligible in comparison with that spent within them. When, however, the velocity of efflux is considerable, and the tube is as short as that of our glischrometer, the magnitudes of these disturbing effects have to be ascertained and, if necessary, corrections have to be applied.

(1.) A correction for the kinetic energy imparted to the liquid was first deduced by HAGENBACH ('Pogg. Ann.,' 109, 385, 1860). His conclusion may be thus stated. If, in the formula for an indefinitely long tube, l be taken as the length of a finite tube, and p the difference of pressure between the reservoirs which the tube connects, then the value of this correction, which has to be applied to the formula, is

$$-\rho V/2^{10/3}\pi l,$$

in which ρ is the density of the liquid.

In a communication ('Ann. de Chim. Phys.' (6), 21, 433, 1890), which must be regarded as containing the most complete theoretical discussion, which has hitherto appeared, of the formula applicable to the case of a finite tube, COUETTE finds that

$$-\rho V/8\pi l$$

is the true value of the kinetic energy correction. This value is greater than that given by HAGENBACH in the ratio of $\sqrt[3]{2}$ to 1.

Simultaneously with the publication of COUETTE's paper, GARTENMEISTER ('Zeit. für physik. Chem.,' 6, 524, December, 1890), stated that, from considerations not then published, Professor FINKENER, of Berlin, had arrived at a correction which is identical with that given by COUETTE, and, more recently, WILBERFORCE ('Phil. Mag.,' 5, 31, 407, 1891) has shown that, from HAGENBACH's assumptions, the value of the correction, as given by COUETTE and FINKENER is correct, as there is a slip in the reasoning employed by HAGENBACH. What may be termed the COUETTE-FINKENER value of the correction is the one adopted in this paper. It is shown by COUETTE to give much better results than that of HAGENBACH when applied to observations made with two of the shortest tubes used by POISEUILLE, in which the velocity of efflux was large and varied considerably.

The formula corrected for kinetic energy is therefore

$$\eta = \pi R^4 p/8Vl - \rho V/8\pi l.$$

(2.) COUETTE alone seems to have attempted to obtain a measure of the friction near the ends of the tube. What actually takes place in this region is not sufficiently known to admit of the magnitude of the effect being theoretically deduced. COUETTE concludes, however, that in order to assess its value experimentally, it may be regarded as the same as that of a slight alteration in the length of the tube employed, and the formula for a finite tube containing the corrections for kinetic energy and the influence of the ends, he gives as

$$\eta = \left(\frac{\pi R^4 p}{8Vl} - \frac{\rho V}{8\pi l}\right)\frac{l}{l + L}.$$

Here, L is the length which must be taken in a tube indefinitely long and of the same radius as the finite tube in order that when V volumes of liquid flow per unit time through the tube the work spent in friction per unit time for the length L will be the same as that dissipated by the influence of the ends. The magnitude of L which takes note of this friction effect he attempted to deduce from such experimental data as were available. Two sets of observations were made by POISEUILLE with short tubes (say A and B) of the same radius but of different lengths. From observations made with these short tubes at a uniform temperature of 10°, the values of η calculated by the formula for an indefinitely long tube vary with the velocity of efflux. On introducing the COUETTE-FINKENER correction for kinetic energy, unless in the case of the highest velocities, the value of η is constant for either tube, but is different in the case of tube A from that in the tube B, and in both cases it differs from the true value of η, as deduced from POISEUILLE's observations with long tubes in which the corrections are negligible.

These differences COUETTE attributes to the effect of the magnitude L. Let η_A be the constant value obtained for η by the above process in the case of tube A, η_B its value in the case of tube B. On assuming that L has the same value for both tubes, seeing that the diameter of each tube is the same, from the preceding equation the true value of η should be given by

$$\eta = \eta_A \frac{l_A}{l_A + L} = \eta_B \frac{l_B}{l_B + L}.$$

This was found to be the case; the true value of η thus deduced was identical with that obtained by POISEUILLE in the case of long tubes. On solving for L, its value was found to be 2·868 times the diameter of the tubes.

From a set of experiments made by himself in which the diameter was seven times that of the tubes used by POISEUILLE, COUETTE found that L was 3·2 times the diameter. COUETTE concludes from this evidence that, unless the velocity of efflux be considerable, the value of L is constant and about three times the diameter of the tube. Probably its magnitude becomes somewhat larger as the diameter increases.

The conditions of velocity in our observations and the diameter of our tube are similar to those for which the above constant value of L seems to hold, and, on applying the correction $l/(l + L)$ to our results, after correcting for kinetic energy, they would be diminished by about 1 per cent. We find, however, that without applying this correction for L, our observations give results for water identical with those of POISEUILLE.

It need not follow, however, that our results are in opposition to the idea that the source of error denoted by the correction is inoperative. We are rather inclined to believe that its effect is made negligible in our case by another source of error which acts in the same sense, and which it seems impossible to allow for. The radius of our tube was obtained by weighing with mercury, a method which gives low results, due to the film of condensed air which invariably intervenes between the mercury and the glass. The radius thus obtained will be too small, and seeing that the fourth power of the radius is employed in determining η, the percentage error made in observing R will be magnified.

For this reason, we have neglected the correction for L in deducing the value of η; this was indeed the only course which appeared to be open. The correction L is an experimentally determined quantity, which was introduced in order to make observations taken with short tubes coincide with those taken by the long tubes of POISEUILLE; in our case this coincidence exists without the use of the correction.

The formula used by us to obtain η was thus

$$\eta = \pi R^4 tp/8lV - \rho V/8\pi lt,$$

where V is now the volume of the liquid passing through the tube in time t. This formula was deduced for a circular tube of radius R, but it is almost impossible to obtain narrow tubes of perfectly circular section. The tube employed, as already stated, was elliptical. In such a case the semi-axes of the ellipse being A and B, Professor RÜCKER was good enough to show that $R^4/8$ in the above formula should be replaced by $\frac{A^3B^3}{4(A^2+B^2)}$ which, when $A = B = R$, is, of course, $R^4/8$.

Since observations were made at different temperatures, a correction for expansion of glass, and for changes in ρ, the density of the liquid, must be introduced into the formula.

If A, B, V, l and ρ are determined for 0°, if θ be the temperature of observation, β the coefficient of linear expansion of glass between 0° and θ, and s the volume which 1 cub. centim. of liquid measured at 0° occupies at θ, then η_θ the coefficient of viscosity measured at θ will be given by

$$\eta_\theta = \frac{\pi A^3B^3tp(1+\beta\theta)^6}{4(A^2+B^2)lV(1+\beta\theta)^3(1+3\beta\theta)} - \frac{V\rho(1+3\beta\theta)}{8\pi lts(1+\beta\theta)}.$$

Neglecting quantities of the second order,

$$\eta_\theta = \frac{\pi A^3B^3tp}{4(A^2+B^2)lV} - \frac{V\rho}{8\pi lts}(1+2\beta\theta).$$

This formula may be written

$$\eta_\theta = Kpt - k\rho \, . \frac{1+2\beta\theta}{ts}.$$

K and k are constants having different values for each limb of the glischrometer, and ρ is, of course, constant for the same liquid.

$1 + 2\beta\theta$ could be taken with sufficient accuracy from a table constructed for every 5 degrees; s was obtained from observations on the thermal expansion of the liquid.

Details of the measurements made in order to determine the constants K and k have already been described. Their values are given by

$$\log K_L = \bar{7}\cdot140937 \qquad \log k_L = \bar{2}\cdot313429,$$
$$\log K_R = \bar{7}\cdot120666 \qquad \log k_R = \bar{2}\cdot333699.$$

ON THE MATHEMATICAL EXPRESSION OF THE RELATION OF THE VISCOSITY OF LIQUIDS TO TEMPERATURES.

Our observations on the several liquids were, as already stated, taken at intervals of temperatures varying between 5° and 15°. In order to obtain viscosity coefficients at any desired temperature from these observations, we have used both graphical and algebraical methods. It may be convenient to discuss here the reasons which led to our adoption of the particular type of algebraical expression which we employ.

Most of the formulæ which have hitherto been proposed have been devised from a study of the effect of temperature on the viscosity of water. POISEUILLE (*loc. cit.*) used an expression of the form

$$\eta_t = \eta_0/(1 + \alpha t + \beta t^2).$$

O. E. MEYER (' WIED. Ann.,' vol. 2, p. 387, 1877) showed that although this formula gave good results for the temperature range over which POISEUILLE's observations extended, namely 0° to 45°, yet for higher temperatures it was inapplicable.

For such temperatures MEYER proposed the hyperbolic expression

$$\eta_t = \eta_0/(1 + \alpha t).$$

To cover the entire temperature range from 0° to 100°, SLOTTE (' WIED. Ann.,' vol. 14, p. 13, 1881) suggested the expression

$$\eta_t = \mathrm{C}/(\alpha + t) - b,$$

which gives numbers in fair agreement with the observed values.

The preceding formulæ were all deduced empirically and were applied only to a particular case. GRAETZ (' WIED. Ann.,' vol. 34, p. 25, 1888), starting from MAXWELL's formula (' Phil. Mag.,' (4), vol. 35, p. 129), $\eta = \mathrm{ET}$ (in which E is the modulus of rigidity, and T is the time of relaxation, or the time which a stress excited in the fluid takes to fall to $1/e$ of its original value), shows that as a first approximation

$$\eta_t = \mathrm{A}\,(\theta - t)/(t - t_1),$$

in which θ is the critical temperature of the substance expressed on the centigrade scale, and t_1 is an unknown temperature below the melting-point. A is a constant. In deducing the formula GRAETZ assumes that the viscosity of liquids is mainly due to molecular attractions, and that molecular impacts, which in the case of gases are all important, play only a subordinate part in the case of liquids. It would follow from the formula that at the critical temperature η is zero, and at t_1 is infinitely great. A and t_1 have, of course, to be determined experimentally for each liquid.

On applying his formula to the results obtained by RELLSTAB and by PRIBRAM and HANDL, in which the temperature range did not exceed 60°, GRAETZ found that in some fifty cases it was satisfactory. In the case of the fatty alcohols and ethyl ether the formula was inapplicable. That GRAETZ's formula appeared to fail in the case of ether was no doubt due to the imperfect data by means of which he tested it. We find that the formula $\eta_t = \cdot 0_2 3338\,(194 \cdot 4 - t)/(t - 227 \cdot 8)$ deduced from our observations reproduces them with an average divergence of less than 0·3 per cent. For many of the other liquids, especially for water and the alcohols, the formula is unsatisfactory. GRAETZ's formula may be transformed into the preceding expression given by SLOTTE on putting $A = b$, $\theta = (C - ab)/b$, and $-t_1 = a$.

In a subsequent communication, SLOTTE ('Beibl.,' vol. 16, p. 182, 1892) reviews the position of the question of viscosity as a function of the temperature, and concludes that none of the preceding formulæ gives satisfactory results with liquids such as the oils where the viscosity alters rapidly with change in temperature.

We had ourselves ascertained that an expression of the type given by POISEUILLE, even when four constants were introduced, failed to reproduce the results for water within the limits of experimental error.

SLOTTE finds, however, that an expression of the form

$$\eta_t = \eta_0/(1 + \beta t)^n$$

gives better results than any of the others. It differs from POISEUILLE's formula in containing in the denominator the general exponential term $(1 + \beta t)^n$ instead of $1 + \alpha t + \beta t^2$.

We have employed this last expression given by SLOTTE as being the most satisfactory of those at our disposal.

The formula may be written in the shape

$$\eta = c/(a + t)^n.$$

In order to determine the values of the constants, two values of η, viz., η_1 and η_3, are chosen which correspond respectively with the temperatures t_1 and t_3; a third value of η, viz., η_2, is then found from the equation,

$$\eta_2 = \sqrt{\eta_1 \eta_3},$$

and the temperature t_2 corresponding with this value η_2 is found graphically. a and n are then deduced from the equations,

$$a = \frac{t_2^2 - t_1 t_3}{t_1 + t_3 - 2t_2} \qquad n = \frac{\log \eta_1 - \log \eta_3}{\log(a + t_3) - \log(a + t_1)}.$$

In connection with each substance we give the data used in deducing the formula, and the values of the constants for the expression $\eta_t = \frac{c}{(a + t)^n}$. A table is also given which contains the values of the constants when the formula is put into the shape $\eta_t = \frac{\eta_0}{(1 + \beta t)^n}$. The general applicability of SLOTTE's formula as a means of expressing η as a function of the temperature is discussed at a later stage.

SCHEME OF WORK.

With a view of testing the conclusions set out at length in the introduction to this paper, and in particular of tracing the influence of homology, substitution, isomerism, molecular complexity, and, generally speaking, of changes in the composition and constitution of chemical compounds upon viscosity, we drew up a scheme of work which has involved the determination in absolute measure of the viscosity of some seventy liquids at all temperatures between 0° (except in cases where the liquid solidified at that temperature) and their respective boiling-points.

This list is as follows :—

Water	H_2O.
Bromine	Br_2.
Nitrogen peroxide	N_2O_4.

Paraffins and Unsaturated Fatty Hydrocarbons.

Pentane	$CH_3.(CH_2)_3.CH_3$.
Isopentane	$(CH_3)_2CH.CH_2.CH_3$.
Hexane	$CH_3.(CH_2)_4.CH_3$.
Isohexane	$(CH_3)_2CH.(CH_2)_2.CH_3$.
Heptane	$CH_3.(CH_2)_5.CH_3$.
Isoheptane	$(CH_3)_2CH.(CH_2)_3.CH_3$.
Octane	$CH_3.(CH_2)_6.CH_3$.
Trimethyl Ethylene (β-isoamylene)	$(CH_3)_2C:CH.CH_3$.
Isoprene (Pentine)	C_5H_8.
Diallyl (Hexine)	$CH_2:CH.(CH_2)_2.CH:CH_2$.

Iodides.

Methyl iodide	CH_3I.
Ethyl iodide	$CH_3.CH_2I$.
Propyl iodide	$CH_3.CH_2.CH_2I$.
Isopropyl iodide	$(CH_3)_2CHI$.
Isobutyl iodide	$(CH_3)_2CH.CH_2I$.
Allyl iodide	$CH_2:CH.CH_2I$.

Bromides.

Ethyl bromide	$CH_3.CH_2Br$.
Propyl bromide	$CH_3.CH_2.CH_2Br$.
Isopropyl bromide	$(CH_3)_2CHBr$.
Isobutyl bromide	$(CH_3)_2CH.CH_2Br$.
Allyl bromide	$CH_2:CH.CH_2Br$.
Ethylene bromide	$CH_2Br.CH_2Br$.
Propylene bromide	$CH_3.CHBr.CH_2Br$
Isobutylene bromide	$(CH_3)_2CBr.CH_2Br$.
Acetylene bromide	$CHBr:CHBr$.

Chlorides.

Propyl chloride	$CH_3.CH_2.CH_2Cl$.
Isopropyl chloride	$(CH_3)_2CHCl$.
Isobutyl chloride	$(CH_3)_2CH.CH_2Cl$.
Allyl chloride	$CH_2{:}CH.CH_2Cl$.
Methylene chloride (Dichlormethane)	CH_2Cl_2.
Ethylene chloride	$CH_2Cl.CH_2Cl$.
Ethylidene chloride	$CH_3.CHCl_2$.
Chloroform (Trichlormethane)	$CHCl_3$.
Carbon tetrachloride (Tetrachlormethane)	CCl_4.
Carbon dichloride (Tetrachlorethylene)	$CCl_2{:}CCl_2$.

Sulphur Compounds.

Carbon bisulphide	CS_2.
Methyl sulphide	$(CH_3)_2S$.
Ethyl sulphide	$(CH_3.CH_2)_2S$.
Thiophen	$\underline{CH{:}CH.S.CH{:}CH}$.

Acetaldehyde and Ketones.

Acetaldehyde	$CH_3.COH$.
Dimethyl ketone	$CH_3.CO.CH_3$.
Methyl ethyl ketone	$CH_3.CH_2.CO.CH_3$.
Diethyl ketone	$CH_3.CH_2.CO.CH_2.CH_3$.
Methyl propyl ketone	$CH_3.(CH_2)_2.CO.CH_3$.

Acids.

Formic acid	$H.COOH$.
Acetic acid	$CH_3.COOH$.
Propionic acid	$CH_3.CH_2.COOH$.
Butyric acid	$CH_3.(CH_2)_2.COOH$.
Isobutyric acid	$(CH_3)_2CH.COOH$.

Oxides (Anhydrides).

Acetic anhydride (Acetyl oxide)	$(CH_3.CO)_2O$.
Propionic anhydride (Propionyl oxide)	$(CH_3.CH_2.CO)_2O$.
Ethyl ether	$CH_3.CH_2.O.CH_2.CH_3$.

Aromatic Hydrocarbons.

Benzene	C_6H_6.
Toluene (Methyl benzene)	$C_6H_5.CH_3$.
Ethyl benzene	$C_6H_5.C_2H_5$.
Ortho-xylene	$C_6H_4(CH_3)_2(1:2)$.
Meta-xylene	$C_6H_4(CH_3)_2(1:3)$.
Para-xylene	$C_6H_4(CH_3)_2(1:4)$.

Alcohols.

Methyl alcohol	CH_3OH.
Ethyl alchohol	$CH_3.CH_2OH$.
Propyl alcohol	$CH_3.CH_2.CH_2OH$.
Isopropyl alcohol	$(CH_3)_2CHOH$.
Butyl alcohol	$CH_3.(CH_2)_2.CH_2OH$.
Isobutyl alcohol	$(CH_3)_2CH.CH_2OH$.
Trimethyl carbinol	$(CH_3)_3COH$.
Amyl alcohol (active)	$CH_3.CH_2.CH(CH_3).CH_2OH$.
Amyl alcohol (inactive)	$(CH_3)_2CH.CH_2.CH_2OH$.
Dimethyl ethyl carbinol	$(CH_3)_2C(OH).CH_2.CH_3$.
Allyl alcohol	$CH_2:CH.CH_2OH$.

Of course such a list might be greatly extended, and might be made to comprise other well-defined groups of correlated substances. It must, however, be remembered that we are limited in our selection by the difficulty of obtaining many substances in a state of sufficient purity to warrant the expenditure of the labour necessary to determine their viscosity. Moreover, we were desirous that the upper limit of temperature in our observations should not exceed that which could be conveniently ascertained in a glycerin bath: hence the boiling-point should not be higher than 160° or 170°.

PART II.—RESULTS OBTAINED.

WATER.

The viscosity of water has been frequently measured; indeed, no other liquid has been made the subject of so many determinations of this property. As the measurements hitherto published extend, for the most part, over a comparatively limited range of temperature, we have considered it desirable to make an additional series of observations from about 0° up to the ordinary boiling-point, partly to gain more information as to the effect of temperature in altering the viscosity of water, and partly to test the validity of our experimental method as well as the accuracy with which the constants of the apparatus had been determined.

The sample of water used was distilled just before its introduction into the glischrometer from a quantity which had been repeatedly distilled in order to free it from dust. Special pains were taken in the final distillation to obtain a sufficient quantity of air-free as well as dust-free liquid.

The details of the observation are stated below. On the left-hand side of the table are given the results obtained from observations made in the left limb of the glischrometer, *i.e.*, when the liquid was flowing from the left limb to the right limb. On the right-hand side are the corresponding results of observations in the right limb. In the first column is given the mean corrected temperature at which the observation was made; in the second is the mean effective pressure in grms. per square centim.; under Corr. is given the value in dynes of the correction for the kinetic energy of the liquid flowing through the capillary. Under η, in the last column, is given in dynes per square centim. the value of the viscosity-coefficient after all corrections have been applied.

In calculating the results, the values used for the density and expansion of water have been taken from the mean results of different observers given in ROSETTI's tables ('Annales de Chimie et de Phys.' (4), 17, 370).

VISCOSITY of Water between 0° and 100°.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η	Temp.	Press.	Corr.	η
°				°			
5·47	128·64	·0000237	·014929	5·44	128·54	·0000237	·014949
13·52	128·65	·0000300	·011814	13·54	128·54	·0000300	·011801
22·04	128·64	·0000370	·009544	22·00	128·56	·0000370	·009556
30·72	128·48	·0000447	·007859	30·73	128·40	·0000447	·007861
39·29	128·39	·0000527	·006627	39 35	128·31	·0000527	·006618
47·03	128·70	·0000605	·005761	47·03	128·61	·0000605	·005760
55·53	128·67	·0000690	·005010	55·54	128·55	·0000690	·005010
63·98	128·73	·0000777	·004416	64·05	128·64	·0000777	·004412
72·57	128·73	·0000870	·003909	72·51	128·67	·0000870	·003921
80·74	128·81	·0000956	·003522	80·76	128·73	·0000956	·003526
89·87	128·85	·0001052	·003164	89·94	128·75	·0001052	·003167
98·12	128·90	·0001144	·002879	98·06	128·82	·0001144	·002899
99·97	128·90	·0001150	·002859	91·51	128·79	·0001150	·002845

The results of these observations are graphically represented in Plate 8; viscosity coefficients $\times 10^5$ being taken as ordinates and temperatures as abscissæ.

By taking

$$\eta_1 = 0{\cdot}14939 \qquad \eta_3 = {\cdot}002889 \qquad \eta_2\,(\text{calculated}) = {\cdot}006569$$

$$t_1 = 5^\circ{\cdot}45 \qquad t_3 = 98^\circ{\cdot}09 \qquad t_2\,(\text{from curve}) = 39^\circ{\cdot}72,$$

we obtain the formula

$$\eta = \frac{5{\cdot}9849}{(43{\cdot}252 + t)^{1{\cdot}5423}} .$$

The agreement between the Observed and Calculated values is seen in the following Table :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
5°·45	·01494	·01494	·00000
13·53	·01181	·01179	− ·00002
22·02	·00955	·00951	− ·00004
30·72	·00786	·00784	− ·00002
39·32	·00662	·00662	·00000
47·03	·00576	·00577	+ ·00001
55·53	·00501	·00502	+ ·00001
64·01	·004415	·00442	+ ·000005
72·54	·003915	·00393	+ ·000015
80·75	·003525	·003535	+ ·00001
89·90	·003165	·003165	·00000
98·09	·00289	·00289	·00000
100·00	·00283	·00283	·00000

Moritz (‘ Pogg. Ann.,’ 70, 1847) from observations made by the method of Coulomb (oscillating disc), inferred that water had a maximum viscosity in the neighbourhood of 4°. Other observers, and more especially Poiseuille and Sprung, using the tube method, were unable to detect any peculiarity in the rate of change of viscosity at temperatures at about the point of maximum density.

We have made a special series of observations to test this question, the results of which are seen in the following table :—

Viscosity of Water between 0° and 8°.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
1°·13	130·16	·000021	·017094	0°·37	130·01	·000020	·017570
2·41	130·26	·000022	·016395	1·86	130·04	·0000215	·016701
4·47	129·935	·000023	·015351	3·09	130·10	·000022	·016079
5·94	129·95	·000024	·014639	3·84	129·83	·000023	·015678
7·41	129·98	·000026	·014006	5·19	129·82	·000024	·015005
				6·67	129·845	·000025	·014331
				8·01	129·87	·000026	·013766

The results of the viscosity observations between 0° and 8°, by taking

$$t_1 = 0^\circ{\cdot}37 \qquad t_3 = 7^\circ{\cdot}41 \qquad t_2 = 3^\circ{\cdot}79$$
$$\eta_1 = {\cdot}017570 \qquad \eta_3 = {\cdot}014006 \qquad \eta_2 = {\cdot}015687,$$

may be represented by the formula

$$\eta = \frac{58{\cdot}7375}{(58{\cdot}112 + t)^{1{\cdot}9944}},$$

which gives results in fair accord with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·37	·01757	·01757	·00000
1·13	·01710	·01712	+ ·00002
1·86	·01670	·01671	+ ·00001
2·41	·01640	·01641	+ ·00001
3·09	·01608	·01605	− ·00003
3·84	·01568	·01566	− ·00002
4·47	·01535	·01535	·00000
5·19	·01500	·01500	·00000
5·94	·01464	·01465	+ ·00001
6·67	·01433	·01433	·00000
7·41	·01401	·01401	·00000
8·01	·01377	·01375	− ·00002

The curve representing the change in viscosity was originally plotted on as large a scale as was consistent with the accuracy of the observations, but no indication was given by this curve that any anomalous change occurred in the viscosity at temperatures between 0° and 8°. It must be borne in mind, however, that the anomalous change in the density of water amounts only to about 1 part in 10,000; hence, since the accuracy attained in these special observations of viscosity probably does not exceed 1 in 5,000, it may be doubted whether any anomalous change in viscosity of the same order of magnitude as that observed in the case of the density would be detected by any of our present experimental methods.

Measurements of the viscosity of water by the tube method have been made by the following observers:—

Poiseuille	'Mém. des Sav. Étrang.,' 9, 433 (1846)
Graham.	'Phil. Trans.,' 151, 373 (1861).
Rellstab	'Inaug. Diss. Bonn.' (1868).
Sprung	'Pogg. Ann.' 159, 1 (1876).
Rosencranz (comm. by O. E. Meyer) .	'Wied. Ann.,' 2, 387 (1877).
Grotrian	'Wied. Ann.,' 8, 536 (1879).

STEPHAN	'Wied. Ann.,' 17, 680 (1882).
WAGNER	'Wied. Ann.,' 18, 259 (1883).
SLOTTE	'Wied. Ann.,' 20, 262 (1883).
KÖNIG	'Wied. Ann.,' 25, 620 (1885).
TRAUBE	'Ber.,' 19, 871 (1886).
NOACK	'Wied. Ann.,' 28, 666 (1886).

In order to compare our results with those of our predecessors, we have made a careful critical examination of certain of these memoirs, and more particularly of those in which the observations extend over a moderate range of temperature, which are expressed in absolute measure, and which, so far as can be judged, were made with sufficient care. In all cases where the values are given in gravitation measure they have been reduced to dynes, and when a correction for kinetic energy is necessary, the more accurate values deduced from the expression of COUETTE and FINKENER have been substituted for those obtained by the formula of HAGENBACH.

POISEUILLE.—The observations made by POISEUILLE in 1846 are still regarded as the standard data from which the coefficients of viscosity of water for the temperature range over which the experiments extended, viz., from 0° to 45°, may be deduced. POISEUILLE found the number of milligrams of water which could be driven through tubes of different dimensions under definite conditions of temperature and pressure. From four sets of observations in tubes of different diameters, O. E. MEYER ('Wied. Ann.,' 2, 387) has calculated the values of the viscosity-coefficients at the different temperatures of observation, and, by graphical interpolation, has found from each set the values at the same temperature 5° apart. The numbers obtained for the different sets are in close agreement, and from these the mean values of the coefficients are calculated.

On plotting these mean values as ordinates against temperatures as abscissæ on the same sheet as that containing the curve for our observations, the agreement between the two series is seen to be remarkably close. POISEUILLE'S observation at 0°·6 lies exactly on our curve, that at 0°·5, which is not quite concordant with that at 0°·6, is somewhat larger than our observation at that temperature. From 5° to 30° the observations lie slightly to the right of our curve; from 30° to 40° they are coincident with it, and the observation at 45° lies slightly to the left. In no single case does the difference between our observations and those of POISEUILLE at the same temperature exceed 1 per cent. Comparing observations at intervals 5° apart at temperatures between 0° and 45°, the mean difference between our observations and those of POISEUILLE is less than 0·4 per cent., POISEUILLE'S values being, on the average, greater by this amount.

We have examined the values of the coefficients, as calculated by MEYER, from POISEUILLE'S observations, in order to ascertain if they lend any support to the correction for friction-effects outside the tube, as given by COUETTE. The coefficients determined with one pair of tubes should be on the average about 0·2 per cent. greater than those determined by the other pair if the correction were operative. No such difference is apparent; hence the value of the correction probably falls within the limits of the experimental error.

SPRUNG (*loc. cit.*) gives a series of values for water extending from 0° to 50° which are expressed in gravitation measure. On introducing the necessary corrections to reduce these values to dynes, we find that from 0° to 15° they are practically identical with ours; from 20° to 50° they are slightly larger, the deviation increasing as the temperature rises, until at 50° it is about 0·9 per cent. At 40° and 45° our curve passes between those of SPRUNG and POISEUILLE. The Couette correction would diminish SPRUNG'S results by about 0·46 per cent.

ROSENCRANZ (*loc. cit.*) made a series of observations on water, at temperatures between 40° and 90°, with a view of supplementing POISEUILLE'S observations between 0° and 45°. On plotting ROSENCRANZ'S values it is at once seen that individual results differ widely from the values deduced from a mean curve. At the higher temperatures, the mean values are also considerably higher than those obtained by SLOTTE (*v. infra*) and ourselves at these temperatures. ROSENCRANZ'S value at 42°9 is identical with ours at that temperature, but at 80° his result differs by some 10 per cent. from that of SLOTTE and ourselves. The discrepancy between ROSENCRANZ'S values and those of later observers is to be ascribed to the imperfections of his experimental method. There can be little doubt, from the construction of his apparatus, that he failed to ascertain the real temperature of the water flowing through the capillary tube.

SLOTTE (*loc. cit.*) is the only observer who has hitherto attempted to determine the viscosity of water at all temperatures between its ordinary freezing and boiling-points. His results are expressed in dynes, and we have modified them by substituting the COUETTE-FINKENER values of the kinetic energy correction for those of HAGENBACH. This makes a difference of about 1 per cent. in the value of η at the higher temperatures. At 0°·2, SLOTTE'S value for η differs by about 1·5 per cent. from ours; at higher temperatures, his numbers are about 0·7 per cent. greater. The application of the correction for friction effects outside the tube would diminish his values to the extent of about 0·4 per cent., *i.e.*, make them about 0·3 per cent. greater than our own.

TRAUBE (*loc. cit.*) gives two sets of values for η, determined with two different tubes, at temperatures between 0° and 60°. At the same temperature, the observations of the one series agree to within 1 per cent. with those of the other. TRAUBE compares his numbers with those of POISEUILLE (as given by HAGENBACH), SPRUNG, and SLOTTE. From this comparison TRAUBE'S values appear to be larger than SLOTTE'S by amounts varying between 2 and 3 per cent., but agree more closely with those of the other observers. This agreement, however, is not real, since POISEUILLE and SPRUNG'S values are expressed in gravitation measure. As a matter of fact, when the results of all the observers are expressed in dynes, TRAUBE'S numbers differ more widely from the values afforded by POISEUILLE and SPRUNG'S observations than they do from those of SLOTTE. The introduction of the Couette-Finkener correction reduces TRAUBE'S coefficients at the higher temperatures by about 1 per cent. On comparing these corrected values, which vary irregularly with the temperature, with our own, they are found to be uniformly greater to the extent of from 1·5 to 4·2 per cent. These differences cannot be attributed to friction outside the tube ; the effect of this would diminish the values by about 0·8 per cent.

The following table, showing the viscosity of water in dynes at every 5° between 0° and 100°, is based upon the observations of POISEUILLE, SPRUNG, SLOTTE, and ourselves. The values due to POISEUILLE are those calculated by OSCAR MEYER, with the exception of that at 0°, which has been obtained by graphical extrapolation. SPRUNG'S values are those given in his paper, with the substitution of the Couette-Finkener correction for that of HAGENBACH ; SLOTTE'S numbers have been corrected in like manner, and the values for every 5° obtained graphically. The values given by ourselves have been obtained in the same way.

TABLE showing the Viscosity of Water in Dynes per square centim. between 0° and 100°.

Temperature.	POISEUILLE.	SPRUNG.	SLOTTE.	THORPE and RODGER.
°				
0	·01776*	·01778	·01808	·01778†
5	·01515	·01510	·01524	·015095†
10	·01309	·01301	·01314	·013025
15	·01146	·01135	·01144	·011335
20	·01008	·01003	·01008	·010015
25	·00897	·00896	·00896	·00891
30	·00803	·00802	·00803	·007975
35	·00721	·00723	·00724	·00720
40	·00653	·00657	·00657	·006535
45	·00595	·00602	·00602	·00597
50		·00553	·00553	·005475
55			·00510	·005055
60			·00472	·00468
65			·00438	·004355
70			·00408	·00406
75			·00382	·003795
80			·00358	·00356
85			·00337	·00335
90			·00318	·003155
95			·00301	·002985
100			·00285	·00283

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* The observation at 0°·6 was used in extrapolating this value. POISEUILLE gives in addition a result at 0°·5, but as it is considerably greater than it ought to be, having regard to the curve drawn through the other observations, it has been neglected.

† These values are taken from the curve connecting the special series of observations made on water between the temperatures of 0° and 8°.

BROMINE.

About 600 grms. of "pure" bromine were repeatedly shaken with pure oil of vitriol during four days. It was then separated from the acid and distilled in a reflux condenser, made entirely of glass, with pure potassium bromide, for eleven days. The product was next distilled into a bottle and treated with phosphoric oxide for four days. On siphoning off the bromine from the phosphoric oxide it was found to boil absolutely constantly at 58°·81. Bar. 756·3 millims. Corrected and reduced b.p. = 58°·91.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·55	130·20	·000094	·012433	0·58	129·78	·000094	·012461
5·38	129·94	·000099	·011710	5·25	129·65	·000099	·011754
10·46	129·93	·000105	·011027	10·44	129·59	·000105	·011047
16·18	129·93	·000111	·010347	16·14	129·57	·000111	·010362
21·09	129·94	·000116	·009822	21·05	129·60	·000116	·009838
25·98	129·92	·000121	·009332	26·00	129·57	·000121	·009346
31·18	129·33	·000126	·008880	31·22	128·99	·000126	·008884
35·81	129·40	·000131	·008483	35·92	129·04	·000131	·008486
40·95	129·44	·000136	·008084	40·92	129·11	·000136	·008107
46·19	130·33	·000143	·007715	46·20	130·00	·000143	·007723
50·30	130·31	·000148	·007431	50·27	130·02	·000147	·007442
56·44	130·32	·000154	·007049	56·38	129·99	·000154	·007065

In reducing the observations we have employed the value $d\,(0^\circ/4^\circ) = 3{\cdot}18828$ for the density, and the expression

$$V = 1 + 0{\cdot}0_2 106218t + 0{\cdot}0_5 187714t^2 - 0{\cdot}0_8 3085t^3$$

for the thermal expansion. (THORPE, 'Chem. Soc. Trans.,' 1880, 172.)

By taking

$$\eta_1 = {\cdot}012447 \qquad \eta_3 = {\cdot}007057 \qquad \eta_2\,(\text{calculated}) = {\cdot}009372$$
$$t_1 = 0^\circ{\cdot}56 \qquad t_3 = 56^\circ{\cdot}41 \qquad t_2\,(\text{from curve}) = 25^\circ{\cdot}68,$$

we obtain the formula

$$\eta_t = \frac{9{\cdot}6002}{(111{\cdot}92 + t)^{1{\cdot}4077}},$$

by means of which the calculated values in the following table are obtained :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·56	·01245	·01245	·00000
5·31	·01173	·01177	+ ·00004
10·45	·01104	·01105	+ ·00001
16·16	·01035	·01037	+ ·00002
21·07	·00983	·00983	·00000
25·99	·00934	·00934	·00000
31·20	·00888	·00887	− ·00001
35·86	·00848	·00848	·00000
40·93	·00809	·00808	− ·00001
46·19	·00772	·00771	− ·00001
50·28	·00744	·00744	·00000
56·41	·00706	·00706	·00000

NITROGEN PEROXIDE. N_2O_4.

A quantity of this substance, prepared by heating carefully dried lead nitrate, was distilled, after having been frozen in a mixture of calcium chloride and ice. It boiled between 21°·53 and 23°·43. Bar. 763·7 millims. Corrected and reduced b.p. = 21°·97.

Observations on its viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·70	100·14	·000078	·005214	0·75	99·97	·000078	·005227
5·07	100·17	·000081	·004947	5·11	100·02	·000081	·004960
9·14	100·15	·000085	·004718	9·16	99·99	·000085	·004722
11·88	100·14	·000087	·004573	11·86	100·00	·000087	·004583
15·33	100·13	·000090	·004395	15·39	99·99	·000090	·004408

The attempt was made to extend the readings up to within a degree or so from the boiling-point of the substance. The vapour of the nitrogen peroxide, however, acted so rapidly upon the caoutchouc connections at the higher temperatures that further observation was rendered impossible.

In reducing the observations we have employed the value $d\,(0°/4°) = 1{\cdot}4903$ for the density, and the expression

$$V = 1 + 0{\cdot}0_{2}1591t - 0{\cdot}0_{5}397015t^2 + 0{\cdot}0_{6}2153t^3$$

for the thermal expansion (THORPE, *loc. cit.*, p. 225).

Taking

$$\eta_1 = \cdot005220 \qquad \eta_3 = \cdot004401 \qquad \eta_2\,(\text{calculated}) = \cdot004793$$
$$t_1 = 0^\circ\cdot72 \qquad t_3 = 15^\circ\cdot36 \qquad t_2\,(\text{from curve}) = 7^\circ\cdot86,$$

we obtain

$$\eta_t = \frac{28\cdot155}{(140\cdot89 + t)^{1\cdot7349}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·72	·005220	·005220	·000000
5·09	·004954	·004952	−·000002
9·15	·004720	·004722	+·000002
11·87	·004578	·004577	−·000001
15·36	·004401	·004401	·000000

HYDROCARBONS.

Pentane. $CH_3.(CH_2)_3.CH_3$.

The specimen of normal pentane used by us was supplied by the late Professor SCHORLEMMER. Re-distilled from sodium wire, it boiled between 36° and 38°. Bar. 765·5 millims. Corrected and reduced b.p. = 36°·3.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·77	99·80	·000064	·002802	° 0·71	99·73	·000064	·002808
7·46	99·79	·000068	·002617	7·48	99·72	·000068	·002623
13·13	99·78	·000071	·002480	13·20	99·73	·000071	·002482
18.89	99·76	·000074	·002352	18·93	99·69	·000074	·002351
26·40	99·71	·000078	·002188	26·21	99·68	·000078	·002195
30·38	99·73	·000080	·002111	30·44	99·69	·000080	·002110
32·65	99·69	·000081	·002072	32·67	99·62	·000081	·002069

PERKIN'S value for the relative density, $d\,(15^\circ/15^\circ) = 0\cdot63373$ ('Chem. Soc. Trans.,' 1884), and the expression

$$V = 1 + \cdot0_2 14646t + \cdot0_5 209319t^2 + \cdot0_7 16084t^3$$

for the thermal expansion (THORPE and L. M. JONES, 'Chem. Soc. Trans.,' 1893, p. 273), were used in the reduction of the observations.

Taking

$$\eta_1 = \cdot 002805 \qquad \eta_3 = \cdot 002070 \qquad \eta_2 \text{ (calculated)} = \cdot 002410$$
$$t_1 = 0^\circ\cdot 74 \qquad t_3 = 32^\circ\cdot 66 \qquad t_2 \text{ (from curve)} = 16^\circ\cdot 00,$$

we obtain

$$\eta_t = \frac{19\cdot 459}{(165\cdot 59 + t)^{1\cdot 7295}},$$

which gives results in very close agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·74	·002805	·002805	·000000
7·47	·002620	·002619	—·000001
13·16	·002481	·002476	—·000005
18·91	·002351	·002344	—·000007
26·30	·002192	·002191	—·000001
30·41	·002110	·002111	+·000001
32·66	·002070	·002070	·000000

Isopentane (Dimethyl-Ethyl-Methane). $(CH_3)_2CH.CH_2.CH_3$.

Obtained from Professor SCHORLEMMER. On distillation from sodium wire it boiled between 29° and 32°. Bar. 763·4 millims. Corrected and reduced b.p. = 30°·4. Dr. PERKIN, who examined the magnetic rotation of the same sample, found the same boiling-point.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·69	100·05	·000066	·002704	0·73	100·01	·000066	·002702
6·41	100·02	·000069	·002546	6·40	99·95	·000069	·002549
11·89	100·01	·000072	·002407	11·94	99·95	·000072	·002408
15·80	100·00	·000074	·002323	15·85	99·95	·000074	·002321
21·05	99·99	·000077	·002209	20·91	99·95	·000077	·002215
24·20	99·96	·000079	·002143	24·34	99·89	·000079	·002145
26·33	99·98	·000080	·002101	26·44	99·90	·000080	·002103

In reducing the observations, PERKIN'S value for the relative density,

$$d\,(15^\circ/15^\circ) = 0\cdot 62479,$$

and the expression

$$V = 1 + 0{\cdot}_2 14683t + {\cdot}0_5 509626t^2 + {\cdot}0_8 6979t^3$$

(THORPE and L. M. JONES, *loc. cit.*) for the thermal expansion have been used.

By taking

$$\begin{array}{lll} \eta_1 = {\cdot}002703 & \eta_3 = {\cdot}002102 & \eta_2 \text{ (calculated)} = {\cdot}002384 \\ t_1 = 0^{\circ}{\cdot}71 & t_3 = 26^{\circ}{\cdot}38 & t_2 \text{ (from curve)} = 12^{\circ}{\cdot}92, \end{array}$$

we obtain

$$\eta_t = \frac{1{\cdot}2903}{(118{\cdot}56 + t)^{1{\cdot}2901}},$$

which gives values in very close agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0·71	·002703	·002703	·000000
6·40	·002547	·002545	— ·000002
11·91	·002407	·002407	·000000
15·82	·002322	·002317	— ·000005
21·03	·002212	·002207	— ·000005
24·27	·002144	·002142	— ·000002
26·38	·002102	·002102	·000000

Hexane. $CH_3.(CH_2)_4.CH_3$.

Obtained by SCHORLEMMER by the action of zinc and dilute hydrochloric acid on secondary hexyl iodide from mannite; it boiled at 71°·5 ('Phil. Trans.,' 1872, p. 111). Observations with the glischrometer gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0·83	99·95	·000048	·003926	0·77	99·89	·000048	·003935
9·11	100·03	·000052	·003578	9·19	99·95	·000052	·003584
14·72	100·10	·000055	·003379	14·78	99·98	·000055	·003377
19·99	100·18	·000058	·003201	19·97	100·11	·000058	·003203
25·40	100·29	·000060	·003034	25·39	100·25	·000060	·003036
30·20	100·35	·000063	·002899	30·27	100·28	·000063	·002890
36·76	100·39	·000066	·002718	36·76	100·32	·000066	·002726
43·48	99·98	·000069	·002560	43·46	99·90	·000069	·002553
47·42	99·97	·000071	·002468	47·43	99·90	·000071	·002472
52·90	100·03	·000074	·002349	52·89	99·97	·000074	·002353
58·78	100·06	·000077	·002230	58·74	100·00	·000077	·002232
63·64	100·10	·000079	·002144	63·54	100·03	·000079	·002142

Zander's value (Annalen, 214, 165) $d\,(0°/0°) = 0{\cdot}6753$ and his expression

$$V = 1 + {\cdot}0_2 12665t + {\cdot}0_5 17113t + {\cdot}0_7 12315t^3$$

or the thermal expansion have been used in the reduction of the observations.

Taking

$$\eta_1 = {\cdot}003931 \qquad \eta_3 = {\cdot}002143 \qquad \eta_2\,(\text{calculated}) = {\cdot}002902$$
$$t_1 = 0°{\cdot}80 \qquad t_3 = 63°{\cdot}59 \qquad t_2\,(\text{from curve}) = 29°{\cdot}96,$$

ve obtain

$$\eta_t = \frac{276{\cdot}01}{(189{\cdot}42 + t)^{2{\cdot}1264}},$$

vhich gives the following values as compared with those obtained by observation :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·80	·003931	·003930	− ·000001
9·15	·003581	·003587	+ ·000006
14·75	·003378	·003381	+ ·000003
19·98	·003202	·003204	+ ·000002
25·39	·003035	·003034	− ·000001
30·23	·002894	·002893	− ·000001
36·76	·002722	·002719	− ·000003
43·47	·002557	·002556	− ·000001
47·42	·002470	·002466	− ·000004
52·90	·002351	·002349	− ·000002
58·76	·002231	·002232	+ ·000001
63·59	·002143	·002143	·000000

Isohexane (Dimethyl-propyl-methane). $(CH_3)_2CH.(CH_2)_2.CH_3$.

Obtained from Professor Schorlemmer, who found its boiling-point to be 62°·0. Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·48	100·08	·000051	·003692	0·75	100·02	·000052	·003684
5·56	100·09	·000054	·003488	5·58	100·00	·000054	·003487
10·22	100·02	·000056	·003314	10·28	99·99	·000056	·003318
15·21	99·98	·000059	·003147	15·31	99·94	·000059	·003146
20·51	99·92	·000061	·002985	20·52	99·91	·000061	·002988
25·48	99·95	·000064	·002841	25·43	99·87	·000064	·002841
31·96	99·99	·000067	·002673	31·98	99·91	·000067	·002667
36·64	99·96	·000070	·002549	36·62	99·92	·000070	·002550
41·07	99·96	·000072	·002449	41·08	99·93	·000072	·002451
45·38	99·90	·000074	·002354	45·39	99·87	·000074	·002356
51·14	99·46	·000077	·002233	51·20	99·40	·000077	·002237
55·43	99·41	·000079	·002153	55·43	99·37	·000079	·002150

In reducing the observations we have adopted $d\,(15^\circ/15^\circ) = 0{\cdot}6633$ (which gives $d\,(0^\circ/4^\circ) = 0{\cdot}6766$) (PERKIN, 'Chem. Soc. Trans.,' 1884, 447) for the relative density, and the expression

$$V = 1 + {\cdot}0_2137022t + {\cdot}0_697649t^2 + {\cdot}0_729819t^3$$

(THORPE and JONES, *loc. cit.*) for the thermal expansion.

Taking

$$\eta_1 = {\cdot}003688 \qquad \eta_3 = {\cdot}002151 \qquad \eta_2\,(\text{calculated}) = {\cdot}002817$$
$$t_1 = 0^\circ{\cdot}61 \qquad t_3 = 55^\circ{\cdot}43 \qquad t_2\,(\text{from curve}) = 26^\circ{\cdot}43,$$

we get

$$\eta_t = \frac{917{\cdot}96}{(209{\cdot}35 + t)^{2{\cdot}3237}};$$

which gives values in close agreement with those obtained by observation :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·61	·003688	·003688	·000000
5·59	·003487	·003493	+ ·000006
10·25	·003316	·003323	+ ·000007
15·26	·003147	·003153	+ ·000006
20·51	·002987	·002988	+ ·000001
25·45	·002841	·002844	+ ·000003
31·97	·002670	·002669	− ·000001
36·63	·002550	·002553	+ ·000003
41·07	·002450	·002449	− ·000001
45·38	·002355	·002354	− ·000001
51·17	·002235	·002234	− ·000001
55·43	·002151	·002151	·000000

Heptane. $CH_3.(CH_2)_5.CH_3$.

A specimen of pure normal heptane, from *Pinus Sabiniana*, was distilled from sodium wire. It boiled at 98°·4 (corrected and reduced).

Determination of vapour density :—

	I.		II.
Found	50·11		50·19.
Calculated		50·00	

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
6·49	128·40	·000051	·004797	6·36	128·36	·000051	·004797
6·56	128·35	·000051	·004790	6·56	128·33	·000051	·004801
13·49	128·34	·000055	·004418	13·41	128·29	·000055	·004419
21·74	128·34	·000059	·004023	21·74	128·28	·000059	·004031
30·29	128·32	·000064	·003690	30·24	128·26	·000064	·003679
38·34	128·50	·000069	·003396	38·34	128·45	·000069	·003399
47·24	128·51	·000074	·003112	47·26	128·43	·000074	·003112
55·06	128·54	·000078	·002885	54·99	128·50	·000078	·002895
62·04	129·59	·000082	·002719	62·04	128·55	·000082	·002709
70·04	129·59	·000087	·002527	70·14	128·52	·000087	·002526
77·69	129·31	·000091	·002372	77·71	128·17	·000091	·002372
85·46	128·05	·000096	·002222	85·51	127·91	·000096	·002214
92·24	127·57	·000100	·002093	92·19	127·49	·000100	·002100

In the reduction of the observations the value for the density $d\,(0^\circ/4^\circ) = 0{\cdot}70048$, and the expression for the thermal expansion

$$V = 1 + {\cdot}0_2121023t + {\cdot}0_511133t^2 + {\cdot}0_71174t^3,$$

already given by one of us (THORPE, *loc. cit.*), have been employed.

Taking

$$\eta_1 = {\cdot}004797 \qquad \eta_3 = {\cdot}002096 \qquad \eta_2 \text{ (calculated)} = {\cdot}003171$$
$$t_1 = 6^\circ{\cdot}43 \qquad t_3 = 92^\circ{\cdot}22 \qquad t_2 \text{ (from curve)} = 45^\circ{\cdot}28,$$

we obtain

$$\eta_t = \frac{445{\cdot}97}{(180{\cdot}14 + t)^{2{\cdot}1879}},$$

which gives numbers in good agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
6·43	·004797	·004797	·000000
6·56	·004795	·004790	− ·000005
13·45	·004418	·004425	+ ·000007
21·74	·004027	·004037	+ ·000010
30·27	·003685	·003687	+ ·000002
38·34	·003397	·003396	− ·000001
47·25	·003112	·003112	·000000
55·03	·002890	·002891	+ ·000001
62·04	·002714	·002711	− ·000003
70·09	·002526	·002524	− ·000002
77·70	·002372	·002363	− ·000009
85·49	·002218	·002214	− ·000004
92·21	·002096	·002096	·000000

Isoheptane (Dimethyl-Butyl-Methane). $(CH_3)_2CH.(CH_2)_3.CH_3$.

Made for us by Mr. W. A. C. ROGERS, Assoc. R.C.S., by WURTZ's reaction. In its preparation pure inactive amyl alcohol was used; this was obtained by PASTEUR's method of fractional crystallization of the barium salts of amyl-sulphuric acid. The alcohol was converted partly into bromide and partly into iodide, and these were purified by fractional distillation before treatment with ethyl iodide or bromide and sodium. The sodium, in thin slices, was gradually added to the mixed halogen compounds in a flask connected with a reflux condenser. The reaction was more vigorous in the case of the iodides than in that of the bromides. The contents of the flask were distilled over in an oil-bath and the distillate heated in sealed tubes with sodium to decompose any unaltered halogen compounds. The product was further purified by JUST's method ('Annalen,' 220, 154) and finally fractionally distilled in order to separate the diamyl simultaneously formed in the reaction. It boiled between 90°·35 and 90°·75. Bar. 766·8 millims. Corrected and reduced b.p. = 90°·2.

A determination of vapour density gave: Found 49·47. Calculated 50·00.

The observations for viscosity gave:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·41	103·45	·000043	·004743	0°·44	103·39	·000043	·004744
7·69	103·33	·000046	·004339	7·71	103·31	·000046	·004347
15·92	103·30	·000050	·003955	15·85	103·24	·000050	·003963
24·66	103·23	·000054	·003602	24·61	103·18	·000054	·003613
32·32	102·79	·000058	·003332	32·30	102·74	·000058	·003335
40·06	102·71	·000062	·003089	40·05	102·70	·000062	·003095
49·03	102·64	·000066	·002838	49·00	102·56	·000066	·002840
56·47	102·56	·000070	·002652	56·45	102·52	·000069	·002650
63·91	102·47	·000073	·002483	63·93	102·42	·000073	·002485
71·82	102·42	·000077	·002314	71·86	102·35	·000077	·002319
80·65	102·26	·000082	·002146	80·66	102·21	·000082	·002153
88·39	102·21	·000086	·002010	88·43	102·14	·000086	·002015

In reducing the observations we have used $d\,(0°/4°) = 0{\cdot}6969$ for the density, and the expression

$$V = 1 + {\cdot}0_2 12394t + {\cdot}0_5 119318t^2 + {\cdot}0_7 13058t^3$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking $\eta_1 = {\cdot}004743$ $\eta_3 = {\cdot}002012$ η_2 (calculated) $= {\cdot}003089$

$t_1 = 0°{\cdot}42$ $t_3 = 88°{\cdot}41$ t_2 (from curve) $= 40°{\cdot}07$,

we get

$$\eta_t = \frac{362{\cdot}79}{(180{\cdot}47 + t)^{2{\cdot}1633}},$$

which gives numbers in fair agreement with the results of observation :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·42	·004743	·004743	·000000
7·70	·004343	·004355	+ ·000012
15·88	·003959	·003972	+ ·000013
24·63	·003607	·003615	+ ·000008
32·31	·003333	·003338	+ ·000005
40·05	·003092	·003090	— ·000002
49·01	·002839	·002835	— ·000004
56·46	·002651	·002646	— ·000005
63·92	·002484	·002474	— ·000010
71·84	·002316	·002309	— ·000007
80·66	·002149	·002144	— ·000005
88·41	·002012	·002012	·000000

Octane. $CH_3.(CH_2)_6.CH_3$.

A sample of normal octane, prepared by Professor SCHORLEMMER from capryl alcohol, was digested over phosphoric anhydride and distilled from sodium wire, and the fraction boiling between 124°·57 and 124°·73, which was more than half the total amount, was collected separately and used for the observations. Bar. 747·8 millims. Corrected and reduced b.p. = 125°·24.

Determination of vapour density:

Found, 56·54. Calculated, 57·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·23	104·48	·000030	·007001	0·28	104·39	·000030	·006999
12·18	104·52	·000035	·005944	12·19	104·44	·000035	·005944
22·92	104·58	·000040	·005198	22·92	104·53	·000040	·005200
32·97	104·64	·000044	·004623	32·96	104·56	·000044	·004630
43·89	104·73	·000049	·004108	43·90	104·64	·000049	·004107
54·72	104·89	·000054	·003673	54·74	104·82	·000054	·003675
66·47	104·99	·000059	·003282	66·46	104·90	·000059	·003289
77·83	104·99	·000065	·002957	77·82	104·92	·000065	·002961
88·33	103·76	·000069	·002694	88·34	103·69	·000069	·002697
98·52	103·74	·000074	·002473	98·52	103·69	·000074	·002474
109·03	103·70	·000079	·002270	109·11	103·71	·000079	·002272
122·08	103·82	·000086	·002039	122·07	103·75	·000086	·002043

In reducing the observations the value $d\,(0°/4°) = 0·71883$ for the density at 0°, and the expression

$$V = 1 + ·0_2118304t + ·0_6186648t^2 + ·0_712947t^3$$

for the thermal expansion (THORPE, *loc. cit.*), have been employed.

Taking

$$\eta_1 = ·007000 \qquad \eta_3 = ·002041 \qquad \eta_2\,(\text{calculated}) = ·003780$$
$$t_1 = 0°·25 \qquad t_3 = 122°·07 \qquad t_2\,(\text{from curve}) = 51°·98,$$

we obtain

$$\eta_t = \frac{171·82}{(145·50 + t)^{2·029}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·25	·00700	·00700	·00000
12·18	·00594	·00596	+ ·00002
22·92	·00520	·00522	+ ·00002
32·96	·00463	·00464	+ ·00001
43·89	·00411	·00411	·00000
54·73	·00367	·00367	·00000
66·46	·00328	·00327	– ·00001
77·82	·00296	·00295	– ·00001
88·33	·00269	·00269	·00000
98·52	·00247	·00246	– ·00001
109·07	·00227	·00226	– ·00001
122·07	·00204	·00204	·00000

Trimethyl Ethylene (β-Isoamylene). $(CH_3)_2C\!:\!CH.CH_3$.

Prepared by Dr. PERKIN from the iodide obtained from dimethyl ethyl carbinol. On distillation, it boiled between 35°·7 and 37°·9. Bar. 758·7 millims. Corrected and reduced b.p. = 36° 4.

Determination of vapour density :

Found, 35·19. Calculated, 35·00.

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·20	103·44	·000077	·002527	0·20	103·39	·000077	·002531
5·51	103·50	·000081	·002404	5·42	103·42	·000080	·002409
10·21	103·54	·000083	·002303	10·21	103·46	·000083	·002308
15·82	103·55	·000087	·002193	15·82	103·48	·000087	·002191
20·00	103·55	·000089	·002114	20·05	103·48	·000089	·002115
25·71	103·69	·000092	·002015	25·79	103·62	·000092	·002017
30·68	103·69	·000095	·001930	30·71	103·60	·000095	·001932
32·57	103·72	·000096	·001904	32·62	103·63	·000096	·001901

In reducing the observations we have employed PERKIN's value $d(15°/15°) = 0·67037$ for the relative density, and the expression

$$V = 1 + ·0_2145871t + ·0_5338435t^2 + ·0_8339536t^3$$

for the thermal expansion (THORPE and JONES, *loc. cit.*).

Taking

$$\eta_1 = ·002529 \qquad \eta_3 = ·001903 \qquad \eta_2 \text{ (calculated)} = ·002194$$
$$t_1 = 0°·20 \qquad t_3 = 32°·59 \qquad t_2 \text{ (from curve)} = 15°·75,$$

we obtain

$$\eta_t = \frac{28·916}{(187·24 + t)^{1·7855}},$$

which almost exactly reproduces the observed values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·20	·002529	·002529	·000000
5·46	·002406	·002407	+·000001
10·21	·002306	·002305	−·000001
15·82	·002192	·002192	·000000
20·03	·002114	·002113	−·000001
25·75	·002015	·002013	−·000002
30·69	·001931	·001932	+·000001
32·59	·001903	·001903	·000000

Isoprene (Pentine). C_5H_8.

We are indebted to Dr. TILDEN for a liberal supply of this hydrocarbon. It was obtained from turpentine. On distillation the greater part boiled between 35°·5 and 37°·0.

A determination of vapour density gave:

Found, 35·73 ; Calculated, 34·00.

As the hydrocarbon readily absorbs oxygen, which transforms it into a liquid of syrupy consistence and higher boiling-point, it was carefully redistilled in a current of dry carbon dioxide. The greater portion boiled regularly between 35°·38 and 36°·03. Bar. 758·5 millims. Corrected and reduced b.p. = 35°·76.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·36	101·71	·000075	·002587	0°·34	101·73	·000075	·002591
5·68	101·37	·000078	·002456	5·56	101·40	·000078	·002462
10·27	101·24	·000080	·002359	10·27	101·18	·000080	·002356
15·31	101·21	·000084	·002248	15·35	101·16	·000083	·002250
20·40	101·22	·000087	·002145	20·42	101·19	·000087	·002149
25·27	101·21	·000089	·002060	25·24	101.16	·000089	·002060
28·95	101·21	·000092	·001993	28·94	101·14	·000091	·001998
32·02	101·22	·000093	·001944	32·03	101·15	·000093	·001945
29·93	129·98	·000117	·001984	29·94	129·90	·000117	·001986

As isoprene is one of the least viscous of the liquids examined by us, it presented an excellent means of determining whether different velocities of flow in our apparatus led to identical values for the viscosity. For if with this substance concordant values of η were thus obtained, it would be indicated (1) that, even for the highest velocities we have employed, the character of the motion is still linear; and (2) that the mode of correcting for kinetic energy is valid. The observations made in the neighbourhood of 30° under the different pressures of 101·22 and 129·94 centims. show that the values of η thus obtained are identical.*

In reducing the observations of viscosity we have employed for the density at 0° the value 0·6912, and for the thermal expansion the expression

$$V = 1 + \cdot 0_2 14603t + \cdot 0_6 99793t^2 + \cdot 0_7 56015t^3$$

(THORPE and JONES, *loc. cit.*).

Taking

$$\eta_1 = \cdot 002589, \qquad \eta_3 = \cdot 001944, \qquad \eta_2 \text{ (calculated)} = \cdot 002244$$
$$t_1 = 0^\circ\cdot 35 \qquad t_3 = 32^\circ\cdot 02 \qquad t_2 \text{ (from curve)} = 15^\circ\cdot 40,$$

we obtain the formula

$$\eta_t = \frac{3\cdot 3891}{(144\cdot 01 + t)^{1\cdot 4433}},$$

which gives results in very good agreement with the observed values.

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* This fact is even more clearly established in the case of ether—also a very mobile liquid—where two independent samples, measured under similar wide variations of pressure, afforded perfectly concordant values of η (see pp. 519–520).

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0·35	·002589	·002592	+ ·000003
5·62	·002459	·002461	+ ·000002
10·27	·002358	·002355	− ·000003
15·33	·002249	·002248	− ·000001
20·41	·002147	·002148	+ ·000001
25·25	·002060	·002060	·000000
28·94	·001996	·001997	+ ·000001
32·02	·001944	·001946	+ ·000002
29·93	·001985	·001980	− ·000005

Diallyl (Hexine). $CH_2:CH.(CH_2)_2.CH:CH_2$.

Prepared for us by Mr. H. Grime, Assoc. R.C.S., by the action of sodium on allyl iodide. Portions of about 100 grams of the pure iodide were placed with about half their weight of sodium in a flask attached to a reflux condenser. Two drops of absolute alcohol were added and the contents of the flask maintained at 80° for 1½ hours in a water bath, and after standing for from 12 to 24 hours the diallyl was distilled off and subsequently rectified.

The sample was allowed to stand over sodium until required for our observations. On distillation, it boiled between 59°·3 and 60°·2, by far the greater portion coming over between 59°·45 and 59°·56. This fraction was redistilled and the portion boiling between 59°·38 and 59°·43 was employed for the observations. Bar. 760·1 millims. Corrected and reduced b.p. = 59°·4.

Determination of vapour density:

Found, 40·7 Calculated, 41·0.

The observations for viscosity gave the following results:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0·38	103·25	·000061	·003372	0·37	103·19	·000061	·003377
5·95	103·15	·000064	·003165	5·95	103·11	·000064	·003172
10·75	103·10	·000066	·003010	10·82	103·04	·000067	·003011
15·44	102·99	·000069	·002866	15·49	102·97	·000069	·002867
20·76	102·94	·000072	·002713	20·76	102·89	·000072	·002726
25·49	102·91	·000075	·002597	25·43	102·84	·000075	·002600
30·70	102·89	·000078	·002473	30·71	102·82	·000078	·002474
36·07	103·07	·000081	·002351	36·06	105·04	·000081	·002358
42·02	102·60	·000085	·002226	41·96	102·54	·000084	·002232
46·77	102·56	·000087	·002135	46·75	102·50	·000087	·002140
51·55	102·50	·000090	·002044	51·53	102·44	·000090	·002049
56·21	102·43	·000093	·001965	56·19	102·37	·000093	·001968

In reducing the observations we have adopted the value $d\,(0^\circ/0^\circ) = 0{\cdot}7074$ for the relative density, and the expression

$$V = 1 + 0{\cdot}0_2 13423t + 0{\cdot}0_6 34339t^2 + 0{\cdot}0_7 38693t^3$$

for the thermal expansion (ZANDER. 'Annalen.,' 214, 148).

Taking

$$\eta_1 = {\cdot}003374 \qquad \eta_3 = {\cdot}001966 \qquad \eta_2\,(\text{calculated}) = {\cdot}002576$$
$$t_1 = 0^\circ{\cdot}37, \qquad t_3 = 56^\circ{\cdot}20, \qquad t_2\,(\text{from curve}) = 26^\circ{\cdot}34,$$

we obtain the formula

$$\eta_t = \frac{72{\cdot}193}{(173{\cdot}01 + t)^{1{\cdot}9340}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·37	·003374	·003374	·000000
5·95	·003169	·003174	+ ·000005
10·78	·003010	·003014	+ ·000004
15·46	·002866	·002871	+ ·000005
20·76	·002719	·002721	+ ·000002
25·46	·002599	·002595	− ·000004
30·71	·002474	·002470	− ·000004
36·06	·002355	·002349	− ·000006
41·99	·002229	·002226	− ·000003
46·76	·002137	·002133	− ·000004
51·54	·002047	·002046	− ·000001
56·20	·001966	·001966	·000000

IODIDES.

Methyl Iodide. CH_3I.

A quantity of "pure" methyl iodide, after standing for some days over phosphoric oxide, was shaken with "molecular" silver and distilled. It boiled between 42°·36 and 42°·40. Bar. 746·2 millims. Corrected and reduced b.p. = 42°·91.

Vapour density :

Found, 70·49. Calculated, 70·75.

The liquid was quite colourless and remained so throughout the observations.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·43	101·02	·000111	·005905	0·42	100·81	·000111	·005923
6·06	100·89	·000117	·005568	6·06	100·68	·000117	·005582
6·04	100·86	·000117	·005572	6·08	100·65	·000117	·005580
10·54	100·82	·000121	·005326	10·53	100·57	·000121	·005335
15·85	100·77	·000127	·005057	15·78	100·54	·000127	·005071
21·37	100·75	·000132	·004808	21·37	100·53	·000132	·004813
27·18	100·70	·000138	·004562	27·26	100·49	·000138	·004567
33·41	100·63	·000144	·004316	33·36	100·40	·000144	·004330
39·95	100·56	·000150	·004089	39·97	100·28	·000150	·004092

In reducing the observations we have employed the value $d\,(0°/0°) = 2·3346$ for the relative density, and the expression

$$V = 1 + ·0_2 1144t + ·0_5 40465t^2 - ·0_7 27393t^3$$

for the thermal expansion (DOBRINER, 'Annalen,' 243, 23).

Taking

$$\eta_1 = ·005914 \qquad \eta_3 = ·004090 \qquad \eta_2 \text{ (calculated)} = ·004918$$
$$t_1 = 0°·42 \qquad t_3 = 39°·96 \qquad t_2 \text{ (from curve)} = 18°·92,$$

we obtain the formula

$$\eta_t = \frac{6·6577}{(134·32 + t)^{1·4329}},$$

which almost exactly expresses the observed values.

Mean. temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·42	·005914	·005914	·000000
6·06	·005576	·005576	·000000
10·53	·005330	·005332	+ ·000002
15·81	·005064	·005065	+ ·000001
21·37	·004810	·004808	— ·000002
27·22	·004564	·004560	— ·000004
33·38	·004323	·004322	— ·000001
39·96	·004090	·004090	·000000

Ethyl Iodide. $CH_3.CH_2I$.

A quantity of ethyl iodide, made for us by Mr. A. GREEVES, was dried over calcium chloride, and finally over phosphoric oxide. On distilling, it boiled between 72°·38 and 72°·44, Bar. 756·2 millims. Corrected and reduced b.p. = 72°·57.

The sample was quite colourless and remained so throughout the observations.

Vapour density :

Found, 77·39. Calculated, 77·77.

Observations of viscosity :

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·27	101·53	·000079	·007164	0·30	101·31	·000079	·007171
7·70	101·63	·000085	·006601	7.70	101·40	·000085	·006610
13·19	101·69	·000089	·006231	13·18	101·46	·000089	·006240
20·83	101·84	·000096	·005778	20·77	101·60	·000096	·005787
26·08	101·85	·000100	·005494	26·10	101·64	·000100	·005499
32·96	101·89	·000105	·005150	32·99	101·64	·000105	·005153
38·74	101·92	·000110	·004888	38·74	101·74	·000110	·004896
45·27	101·24	·000114	·004619	45·22	101·08	·000114	·004623
51·39	101·08	·000119	·004383	51·40	100·94	·000119	·004390
57·51	101·07	·000124	·004168	57·51	100·88	·000124	·004166
63·76	100·98	·000129	·003963	63·69	100·82	·000129	·003969
69·35	100·93	·000134	·003790	69·42	100·75	·000134	·003794

In reducing the observations we have used the value $d\,(0°/0°) = 1·9795$ for the relative density, and the expression

$$V = 1 + \cdot 0_2 11520t + \cdot 0_6 26032t^2 + \cdot 0_7 14181t^3$$

for the thermal expansion (DOBRINER, *loc. cit.*).

Taking

$$\eta_1 = \cdot 007167 \qquad \eta_3 = \cdot 003792 \qquad \eta_2 \text{ (calculated)} = \cdot 005213$$
$$t_1 = 0°\cdot 28 \qquad t_3 = 69°\cdot 38 \qquad t_2 \text{ (from curve)} = 31°\cdot 70,$$

we obtain

$$\eta_t = \frac{50\cdot 810}{(157\cdot 42 + t)^{1\cdot 7520}},$$

which gives results in good agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·28	·007167	·007167	·000000
7·70	·006605	·006613	+ ·000008
13·18	·006235	·006245	+ ·000010
20·80	·005782	·005785	+ ·000003
26·09	·005496	·005497	+ ·000001
32·98	·005151	·005152	+ ·000001
38·74	·004891	·004890	— ·000001
45·24	·004621	·004619	— ·000002
51·39	·004387	·004383	— ·000004
57·51	·004168	·004167	— ·000001
63·72	·003966	·003964	— ·000002
69·38	·003792	·003792	·000000

Propyl Iodide. $CH_3.CH_2.CH_2I$.

A quantity of this liquid, obtained from KAHLBAUM, after drying over phosphoric oxide, was carefully fractionated, and the greater portion was eventually found to boil between 102°·34 and 102°·44. Bar. 756·5 millims. Corrected and reduced b.p. = 102°·23.

Vapour density:

Found, 84·17. Calculated, 84·77.

The liquid remained quite colourless during the observations for viscosity. These gave:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·31	101·17	·000055	·009327	° 0·30	100·99	·000055	·009345
10·95	101·17	·000062	·008165	11·01	100·99	·000062	·008173
20·82	101·17	·000068	·007294	20·80	101·01	·000068	·007306
28·33	101·19	·000073	·006728	28·30	101·01	·000073	·006738
38·83	101·15	·000081	·006044	38·83	101·01	·000081	·006054
46·16	100·75	·000085	·005631	46·18	100·62	·000085	·005639
55·59	100·82	·000092	·005159	55·60	100·64	·000092	·005166
65·45	100·93	·000099	·004739	65·48	100·73	·000099	·004742
74·39	101·00	·000105	·004390	74·37	100·81	·000105	·004396
83·86	101·11	·000112	·004065	84·01	100·90	·000112	·004066
90·78	101·32	·000118	·003842	90·79	101·13	·000118	·003847
98·87	101·38	·000123	·003626	98·92	101·18	·000123	·003616

In reducing the observations we have adopted $d\,(0^\circ/0^\circ) = 1{\cdot}7829$ for the relative density, and the expression

$$V = 1 + \cdot0_{2}10276t + \cdot0_{5}18658t^{2} - \cdot0_{10}508t^{3}$$

for the thermal expansion (DOBRINER, *loc. cit.*).

Taking

$$\eta_1 = \cdot009336 \qquad \eta_3 = \cdot003621 \qquad \eta_2\ (\text{calculated}) = \cdot005814$$

$$t_1 = 0^\circ{\cdot}30 \qquad t_3 = 98^\circ{\cdot}89 \qquad t_2\ (\text{from curve}) = 42^\circ{\cdot}96,$$

we obtain

$$\eta_t = \frac{50{\cdot}893}{(136{\cdot}84 + t)^{1{\cdot}7483}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·30	·00934	·00934	·00000
10·98	·00817	·00819	+ ·00002
20·81	·00730	·00732	+ ·00002
28·31	·00673	·00674	+ ·00001
38·83	·00605	·00605	·00000
46·17	·00564	·00564	·00000
55·59	·00516	·00516	·00000
65·46	·00474	·00473	− ·00001
74·38	·00439	·00439	·00000
83·88	·00406	·00406	·00000
90·78	·00384	·00385	+ ·00001
98·89	·00362	·00362	·00000

Isopropyl Iodide. $(CH_3)_2CHI$.

A quantity of isopropyl iodide, obtained from KAHLBAUM, was placed for some days over phosphoric oxide, and after decantation shaken with "molecular" silver to remove free iodine. It was then fractionated, when the main portion was found to boil between 89°·40 and 89°·58. Bar. 753·5 millims. Corrected and reduced b.p. = 89°·7.

No valid determination of vapour density could be obtained, or indeed expected, owing to the rapidity with which the iodide changes on exposure to heat and light.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·28	101·55	·000057	·008747	0·32	101·38	·000057	·008752
9·22	101·54	·000063	·007814	9·15	101·35	·000063	·007824
15·91	101·52	·000068	·007216	15·94	101·35	·000068	·007229
23·36	101·32	·000073	·006642	23·50	101·15	·000073	·006637
32·71	99·88	·000079	·006004	32·67	99·71	·000079	·006019
40·63	101·70	·000086	·005548	40·71	101·52	·000086	·005549
49·49	101·64	·000092	·005090	49·38	101·46	·000092	·005099
57·07	101·73	·000098	·004746	56·95	101·56	·000097	·004753
66·67	101·75	·000105	·004356	64·22	101·58	·000103	·004455
71·39	101·76	·000108	·004194	71·59	101·58	·000108	·004175
80·57	101·79	·000115	·003864	80·33	101·62	·000115	·003887
88·67	101·78	·000122	·003607	88·77	101·62	·000122	·003605

The liquid was quite colourless to begin with, but in the course of the observations it became tinted, and at the close was of the colour of pale sherry.

In reducing the observations we have employed the value $d\,(0^\circ/0^\circ) = 1{\cdot}7440$ for the relative density, and the relative volumes given by F. D. Brown ('Roy. Soc. Proc.,' 36, 245) for the thermal expansion.

Taking

$$\eta_1 = {\cdot}008749 \qquad \eta_3 = {\cdot}003606 \qquad \eta_2 \text{ (calculated)} = {\cdot}005617$$

$$t_1 = 0^\circ{\cdot}30 \qquad t_3 = 88^\circ{\cdot}72 \qquad t_2 \text{ (from curve)} = 39^\circ{\cdot}42,$$

we obtain

$$\eta_t = \frac{129{\cdot}85}{(150{\cdot}03 + t)^{1{\cdot}9161}},$$

which gives values in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·30	·00875	·00875	·00000
9·18	·00782	·00784	+ ·00002
15·92	·00722	·00724	+ ·00002
23·43	·00664	·00665	+ ·00001
32·69	·00601	·00602	+ ·00001
40·67	·00555	·00555	·00000
49·43	·00509	·00509	·00000
57·01	·00475	·00474	− ·00001
65·44	·00440	·00439	− ·00001
71·49	·00418	·00416	− ·00002
80·45	·00388	·00386	− ·00002
88·72	·00361	·00361	·00000

Isobutyl Iodide. $(CH_3)_2CH.CH_2I$.

About 500 cub. centims. of isobutyl iodide, boiling between 119° and 121° were fractionated. The greater portion boiled between 120° and 120°·5. This was shaken with mercury, to remove any free iodine, decanted, and treated with phosphoric oxide, and the portion boiling at 119°·75 and 119°·95 collected separately. Bar. 762·0 millims. Corrected and reduced b.p. = 119°·94.

The iodide was re-distilled under diminished pressure before being introduced into the glischrometer. The portion collected came over, without actual boiling, between 57° and 71° under a pressure of from 85 to 141 millims.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·45	100·22	·000040	·011534	0·45	100·08	·000040	·011544
				11·23	100·66	·000047	·009784
22·46	100·59	·000054	·008430	22·43	100·48	·000054	·008441
33·84	100·56	·000061	·007385				
44·54	100·58	·000067	·006578	44·59	100·42	·000067	·006577
54·68	100·52	·000074	·005933	54·63	100·36	·000073	·005938
65·17	100·53	·000080	·005364	65·06	100·36	·000080	·005371
77·31	100·56	·000088	·004801	77·35	100·40	·000088	·004805
86·92	100·55	·000095	·004416	86·74	100·37	·000094	·004427
97·84	100·61	·000102	·004032				
109·20	100·57	·000109	·003683	109·20	100·46	·000109	·003687
116·04	100·54	·000114	·003493	116·09	100·39	·000114	·003486

The liquid at the outset was perfectly colourless, but in the course of the work it gradually became yellow and ultimately dark red at the higher temperatures. It remained, however, transparent to the end.

In reducing the observations, we employed the value $d\,(0^\circ/0^\circ) = 1{\cdot}6345$ for the relative density, and the numbers given by PIERRE and PUCHOT ('Ann. de Chim. et de Phys.,' 4, 22, 318) as expressing the thermal expansion.

Taking

$$\eta_1 = {\cdot}011539 \qquad \eta_3 = {\cdot}003489 \qquad \eta_2 \text{ (calculated)} = {\cdot}006345$$

$$t_1 = 0^\circ{\cdot}46 \qquad t_3 = 116^\circ{\cdot}05 \qquad t_2 \text{ (from curve)} = 47^\circ{\cdot}95,$$

we obtain

$$\eta_t = \frac{27{\cdot}652}{(108{\cdot}86 + t)^{1{\cdot}6577}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·45	·01154	·01154	·00000
11·23	·00978	·00987	+ ·00009
22·44	·00844	·00852	+ ·00008
33·84	·00739	·00742	+ ·00003
44·56	·00658	·00658	·00000
54·65	·00593	·00592	– ·00001
65·11	·00536	·00534	– ·00002
77·33	·00480	·00477	– ·00003
86·83	·00442	·00440	– ·00002
97·84	·00403	·00402	– ·00001
109·20	·00368	·00367	– ·00001
116·07	·00349	·00349	·00000

Allyl Iodide. $CH_2:CH.CH_2I$.

A quantity of allyl iodide, made by the method of Tollens and Henninger ('Annalen,' 156, 134), which boiled between 102°·5 and 103°·0, was shaken with a small quantity of mercury and distilled; the greater portion was found to boil between 102°·05 and 102°·55. Bar. 747·7 millims. Corrected and reduced b.p. = 102°·79. The distillate was next treated with "molecular" silver and redistilled under diminished pressure (*circa* 190 millims.) immediately before its introduction into the glischrometer.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·34	102·61	·000059	·009253	0·32	102·37	·000059	·009262
9·36	102·64	·000065	·008239	9·31	102·45	·000065	·008266
16·82	102·61	·000071	·007530	16·73	102·41	·000070	·007548
26·16	102·65	·000078	·006782	26·08	102·45	·000077	·006798
35·76	102·66	·000085	·006132	35·78	102·48	·000085	·006139
44·16	102·17	·000090	·005647	44·20	101·98	·000091	·005648
55·17	102·11	·000099	·005093	55·15	101·93	·000099	·005101
63·43	102·09	·000104	·004773	63·45	101·91	·000104	·004742
71·16	102·14	·000111	·004436	71·13	101·93	·000111	·004435
81·31	102·22	·000118	·004113	81·28	102·03	·000118	·004083
91·83	102·24	·000127	·003750	91·90	102·04	·000127	·003748
98·45	102·26	·000131	·003584				

In reducing the observations, we employed the value $d\,(0°/0°) = 1·8696$ for the relative density, and the expression

$$V = 1 + 0{\cdot}0_{2}10539t + 0{\cdot}0_{6}63572t^{2} + 0{\cdot}0_{7}10036t^{3}$$

given by ZANDER ('Annalen,' 214, 146) for the thermal expansion.

Taking

$$\eta_t = {\cdot}009257 \qquad \eta_3 = {\cdot}003749 \qquad \eta_2 \text{ (calculated)} = {\cdot}005891$$

$$t_1 = 0^{\circ}{\cdot}33 \qquad t_3 = 91^{\circ}{\cdot}86 \qquad t_2 \text{ (from curve)} = 39^{\circ}{\cdot}90,$$

we obtain the formula

$$\eta_t = \frac{28{\cdot}411}{(126{\cdot}05 + t)^{1{\cdot}6592}},$$

which affords the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
$0^{\circ}{\cdot}33$	·00926	·00926	·00000
9·33	·00825	·00826	+ ·00001
16·77	·00754	·00756	+ ·00002
26·12	·00679	·00680	+ ·00001
35·77	·00614	·00614	·00000
44·18	·00565	·00565	·00000
55·16	·00510	·00509	− ·00001
63·44	·00476	·00473	− ·00003
71·14	·00443	·00443	·00000
81·29	·00410	·00407	− ·00003
91·86	·00375	·00375	·00000
98·45	·00358	·00357	− ·00001

BROMIDES.

Ethyl Bromide. $CH_3.CH_2Br$.

A sample made by the action of bromine and phosphorus on alcohol, after drying over phosphoric oxide and rectifying, boiled between $38^{\circ}{\cdot}23$ and $38^{\circ}{\cdot}58$. Bar. 764·9 millims. Corrected and reduced b.p. = $38^{\circ}{\cdot}22$.

Vapour density :

Found, 54·56. Calculated, 54·5.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·34	102·38	·000086	·004755	° 0·34	102·22	·000086	·004764
5·21	101·46	·000089	·004517	5·16	101·31	·000089	·004533
9·68	101·39	·000092	·004320	9·66	101·30	·000092	·004334
15·47	101·37	·000097	·004085	15·45	101·21	·000097	·004090
20·54	101·35	·000100	·003900	20·54	101·21	·000100	·003906
25·30	101·31	·000104	·003728	25·26	101·17	·000104	·003740
30·07	101·33	·000108	·003577	30·00	101·17	·000107	·003585
36·20	101·35	·000112	·003391	36·09	101·20	·000112	·003397

In reducing the observations the value $d\,(0°/0°) = 1{\cdot}4733$ for the relative density, and the expression

$$V = 1 + {\cdot}0_2 13376t + {\cdot}0_5 15013t^2 + {\cdot}0_7 169t^3$$

for the thermal expansion (Pierre, 'Annales de Chim. et de Phys.,' 3, vol. 15, 369), have been adopted.

Taking

$$\eta_1 = {\cdot}004759 \qquad \eta_3 = {\cdot}003394 \qquad \eta_2 \text{ (calculated)} = {\cdot}004019$$
$$t_1 = 0^\circ{\cdot}34 \qquad t_3 = 36^\circ{\cdot}15 \qquad t_2 \text{ (from curve)} = 17^\circ{\cdot}22,$$

we obtain the formula

$$\eta_t = \frac{6{\cdot}8898}{(138{\cdot}65 + t)^{1{\cdot}4749}},$$

which almost exactly reproduces the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·34	·004759	·004759	·000000
5·18	·004525	·004525	·000000
9·67	·004327	·004324	− ·000003
15·46	·004087	·004087	·000000
20·54	·003903	·003896	− ·000007
25·28	·003734	·003731	− ·000003
30·03	·003581	·003577	− ·000004
36·15	·003394	·003394	·000000

Propyl Bromide. $CH_3.CH_2.CH_2Br$.

A quantity of this substance, obtained from Kahlbaum, after standing over phosphoric oxide, boiled between 70°·76 and 70°·93. Bar. 754·6 millims. Corrected and reduced b.p. = 71°·07.

Vapour density :

Found, 60·79. Calculated, 61·38.

Observations for viscosity :—

Left limb.				Right limb.			
Temp. °	Press.	Corr.	η.	Temp. °	Press.	Corr.	η.
0·46	100·50	·000059	·006408	0·43	100·41	·000059	·006419
7·85	100·43	·000064	·005878	7·87	100·31	·000064	·005890
13·67	100·39	·000068	·005513	13·65	100·27	·000067	·005534
19·19	100·30	·000071	·005199	19·15	100·19	·000071	·005219
25·46	100·21	·000075	·004896	25·43	100·07	·000075	·004910
31·90	100·19	·000079	·004580	31·87	100·07	·000079	·004595
38·62	100·14	·000083	·004294	38·59	100·01	·000083	·004307
45·66	100·12	·000088	·004027	45·65	99·99	·000088	·004036
51·11	100·30	·000092	·003835	50·91	100·16	·000091	·003852
57·34	100·31	·000096	·003629	57·41	100·17	·000096	·003638
61·99	100·41	·000099	·003491	61·98	100·25	·000099	·003499
67·84	100·43	·000103	·003324	67·88	100·28	·000103	·003333

In reducing the observations the value 1·3835 for the relative density at 0°, and the expression

$$V = 1 + \cdot 0_2 12239t + \cdot 0_6 56696t^2 + \cdot 0_7 1369t^3$$

for the thermal expansion (Zander, 'Annalen,' 214, 159), have been adopted.

Taking

$$\eta_1 = \cdot 006414 \qquad \eta_3 = \cdot 003328 \qquad \eta_2 \text{ (calculated)} = \cdot 004620$$
$$t_1 = 0^\circ\cdot 45 \qquad t_3 = 67^\circ\cdot 86 \qquad t_2 \text{ (from curve)} = 31^\circ\cdot 14,$$

we obtain the formula

$$\eta_t = \frac{65\cdot 713}{(155\cdot 75 + t)^{1\cdot 8282}},$$

which gives results in good agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·45	·006414	·006414	·000000
7·86	·005884	·005893	+ ·000009
13·66	·005523	·005529	+ ·000006
19·17	·005209	·005215	+ ·000006
25·44	·004903	·004890	− ·000013
31·88	·004588	·004587	− ·000001
38·60	·004300	·004301	+ ·000001
45·64	·004032	·004030	− ·000002
51·01	·003844	·003841	− ·000003
57·37	·003633	·003634	+ ·000001
61·98	·003495	·003495	·000000
67·86	·003328	·003328	·000000

Isopropyl Bromide. $(CH_3)_2CHBr$.

Obtained from KAHLBAUM. After drying over phosphoric oxide, the liquid boiled between 59°·26 and 59°·30. Bar. 748·4 millims. Corrected and reduced b.p. = 59°·73.

Vapour density:

Found, 61·28. Calculated, 61·38.

The observations for viscosity were :—

Left limb.				Right Limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·31	101·10	·000061	·006013	° 0·35	100·91	·000061	·006029
5·13	100·95	·000065	·005683	5·11	100·84	·000064	·005694
10·16	100·75	·000068	·005363	10·13	100·64	·000068	·005379
15·30	100·61	·000071	·005061	15·30	100·50	·000071	·005075
20·32	100·60	·000074	·004796	20·24	100·45	·000074	·004811
25·50	100·56	·000078	·004543	25·43	100·43	·000078	·004558
30·00	100·56	·000081	·004337	29·91	100·45	·000081	·004350
35·96	100·39	·000085	·004087	35·84	100·33	·000085	·004104
41·19	100·21	·000089	·003886	41·16	100·15	·000088	·003902
46·34	99·91	·000092	·003698	46·39	99·79	·000092	·003709
50·89	99·71	·000095	·003550	50·93	99·59	·000095	·003558
56·80	99·50	·000099	·003366	56·73	99·45	·000099	·003376

In reducing the observations, the value 1·3397 for the relative density at 0°, and the expression

$$V = 1 + \cdot0_2 12494t + \cdot0_5 1887t^2 + \cdot0_8 6365t^3,$$

for the thermal expansion (ZANDER, 'Annalen,' 214, 161), have been adopted.

Taking

$$\eta_1 = {\cdot}006021 \qquad \eta_3 = {\cdot}003371 \qquad \eta_2\,(\text{calculated}) = {\cdot}004505$$
$$t_1 = 0^\circ{\cdot}33 \qquad t_3 = 56^\circ{\cdot}76 \qquad t_2\,(\text{from curve}) = 26^\circ{\cdot}52,$$

we obtain the formula

$$\eta_t = \frac{188{\cdot}08}{(169{\cdot}03 + t)^{2{\cdot}0166}},$$

which gives values in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·33	·006021	·006021	·000000
5·12	·005688	·005691	+ ·000003
10·14	·005371	·005374	+ ·000003
15·30	·005068	·005076	+ ·000008
20·28	·004803	·004810	+ ·000007
25·46	·004551	·004555	+ ·000004
29·94	·004343	·004350	+ ·000007
35·90	·004095	·004099	+ ·000004
41·17	·003894	·003894	·000000
46·36	·003704	·003707	+ ·000003
50·91	·003555	·003554	− ·000001
56·76	·003371	·003371	·000000

Isobutyl Bromide. $(CH_3)_2CH.CH_2Br$.

After drying with phosphoric oxide, the liquid boiled between 91°·80 and 90°·96. Bar. 763·8 millims. Corrected and reduced b.p. = 91°·7.

Vapour density :

Found, 67·24. Calculated, 68·50.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·33	100·32	·000042	·008190	° 0·36	100·19	·000042	·008203
7·39	100·29	·000046	·007447	7·42	100·18	·000046	·007459
16·11	100·26	·000050	·006679	16·05	100·13	·000050	·006692
23·70	100·22	·000055	·006103	23·72	100·12	·000055	·006121
32·18	100·81	·000060	·005551	32·16	100·69	·000060	·005564
40·33	100·67	·000064	·005094	40·35	100·49	·000064	·005105
48·42	100·72	·000069	·004692	48·36	100·57	·000069	·004703
56·11	99·94	·000073	·004348	56·18	99·83	·000073	·004355
64·16	99·96	·000078	·004035	64·18	99·82	·000078	·004039
72·59	100·14	·000083	·003724	72·55	100·02	·000083	·003735
80·16	100·19	·000088	·003480	80·21	100·06	·000088	·003489
87·92	100·18	·000093	·003225	87·94	100·05	·000093	·003233

In reducing the observations, the value of 1·249 for the density at 0°, and the volumes given by PIERRE and PUCHOT ('Annales de Chim. et de Phys.' (4), 22, 314) for the thermal expansion, have been made use of.

Taking

$$\eta_1 = \cdot008196 \qquad \eta_3 = \cdot003229 \qquad \eta_2 \text{ (calculated)} = \cdot005145$$
$$t_1 = 0^\circ\cdot34 \qquad t_3 = 87^\circ\cdot93 \qquad t_2 \text{ (from curve)} = 39^\circ\cdot42,$$

we obtain the expression

$$\eta_t = \frac{472\cdot23}{(161\cdot62 + t)^{2\cdot1547}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·34	·00820	·00820	·00000
7·40	·00745	·00747	+ ·00002
16·08	·00669	·00671	+ ·00002
23·71	·00611	·00613	+ ·00002
32·17	·00556	·00557	+ ·00001
40·34	·00510	·00509	− ·00001
48·39	·00470	·00468	− ·00002
56·14	·00435	·00433	− ·00002
64·17	·00404	·00401	− ·00003
72·57	·00373	·00370	− ·00003
80·18	·00348	·00346	− ·00002
87·93	·00323	·00323	·00000

Allyl Bromide. $CH_2:CH.CH_2Br$.

Prepared by Mr. J. G. SALTMARSH, Assoc. R.C.S., by GROSHEINTZ's method ('Bulletin de la Soc. Chim. de Paris,' 30, 98). After drying and distillation the liquid boiled between 69°·58 and 70°·28. Bar. 745·7 millims. Corrected and reduced b.p. = 70°·5.

Vapour density :

Found, I. 59·40 ; II. 59·11 ; Calculated, 60·40.

The mercury in both cases was found to be slightly attacked by the vapour of the allyl bromide.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·30	101·12	·000068	·006162	0·30	100·93	·000068	·006174
6·60	101·18	·000073	·005734	6·69	101·01	·000073	·005727
12·42	101·24	·000077	·005367	12·42	101·05	·000077	·005376
18·36	101·26	·000081	·005040	18·33	101·11	·000081	·005054
24·72	101·50	·000086	·004721	24·75	101·34	·000086	·004733
30·87	101·66	·000091	·004444	30·81	101·50	·000091	·004453
37·22	101·77	·000095	·004207	37·22	101·61	·000095	·004190
42·87	101·80	·000099	·003996	42·81	101·64	·000099	·003980
47·88	100·61	·000102	·003803	47·85	100·49	·000102	·003807
54·46	100·36	·000107	·003589	54·65	100·27	·000107	·003586
61·12	100·16	·000111	·003403	61·18	100·03	·000111	·003401
68·67	99·97	·000117	·003192	68·67	99·83	·000117	·003195

In reducing the observations the value $d\,(0°/0°) = 1{\cdot}4593$ for the relative density, and the expression

$$V = 1 + {\cdot}0_2 12275t - {\cdot}0_6 44365t^2 + {\cdot}0_7 25843t^3$$

for the thermal expansion, were used (Zander, 'Annalen,' 214, 145).

Taking

$$\eta_1 = {\cdot}006168 \qquad \eta_3 = {\cdot}003193 \qquad \eta_2 \text{ (calculated)} = {\cdot}004438$$

$$t_1 = 0°{\cdot}30 \qquad t_3 = 68°{\cdot}67 \qquad t_2 \text{ (from curve)} = 31°{\cdot}20,$$

we obtain the formula

$$\eta_t = \frac{30{\cdot}360}{(145{\cdot}03 + t)^{1{\cdot}7075}},$$

which gives values in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·30	·006168	·006168	·000000
6·64	·005730	·005735	+ ·000005
12·42	·005372	·005380	+ ·000008
18·34	·005046	·005051	+ ·000005
24·73	·004727	·004731	+ ·000004
30·84	·004449	·004454	+ ·000005
37·22	·004198	·004191	− ·000007
42·84	·003988	·003979	− ·000009
47·86	·003805	·003804	− ·000001
54·55	·003587	·003589	+ ·000002
61·15	·003402	·003395	− ·000007
68·67	·003193	·003193	·000000

Ethylene Bromide. $CH_2Br.CH_2Br$.

A considerable quantity of ethylene dibromide was dried over phosphoric oxide and frozen. By repeated freezing and partial liquefaction a fraction was eventually obtained which melted constantly at 9°·25. This was again dried over phosphoric oxide and distilled; it boiled between 130°·28 and 130°·60. Bar. 761·2 millims. Corrected and reduced b.p. = 130°·39.

Vapour density :

Found, 93·07 Calculated, 93·74.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
9·48	130·07	·000038	·020511	9·51	129·45	·000038	·020543
20·66	129·73	·000046	·016964	20·61	129·62	·000046	·017005
31·27	130·51	·000053	·014440	31·16	130·36	·000053	·014463
41·64	130·03	·000061	·012508	41·64	129·95	·000061	·012529
51·93	129·65	·000068	·010980	51·69	129·46	·000068	·011006
62·97	129·01	·000076	·009655	62·78	128·84	·000076	·009685
73·44	129·71	·000085	·008623	73·53	129·49	·000085	·008624
85·95	129·56	·000094	·007607	85·80	129·42	·000094	·007632
95·86	129·46	·000102	·006939	95·77	129·26	·000102	·006940
105·74	129·38	·000110	·006336	105·68	129·17	·000110	·006342
117·08	129·45	·000119	·005769	116·75	129·25	·000119	·005782
126·71	129·51	·000127	·005323	126·72	129·29	·000127	·005321

In reducing the observations the value 2·2132 for the density at 0°, and the expression

$$V = 1 + \cdot 0_3952845t + \cdot 0_6683455t^2 + \cdot 0_83947t^3$$

for the thermal expansion, were adopted (THORPE, *loc. cit.*).

Taking

$$\eta_1 = \cdot 020527 \qquad \eta_3 = \cdot 005322 \qquad \eta_2 \text{ (calculated)} = \cdot 010452$$

$$t_1 = 9^\circ\cdot 49 \qquad t_3 = 126^\circ\cdot 71 \qquad t_2 \text{ (from curve)} = 56^\circ\cdot 08,$$

we obtain the formula

$$\eta_t = \frac{30\cdot 535}{(80\cdot 802 + t)^{1\cdot 6222}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
9·49	·02053	·02053	·00000
20·63	·01698	·01699	+ ·00001
31·21	·01445	·01447	+ ·00002
41·64	·01252	·01252	·00000
51·81	·01099	·01100	+ ·00001
62·87	·00967	·00966	— ·00001
73·48	·00862	·00861	— ·00001
85·97	·00762	·00759	— ·00003
95·81	·00694	·00691	— ·00003
105·71	·00634	·00633	— ·00001
117·01	·00577	·00575	— ·00002
126·71	·00532	·00532	·00000

Propylene Bromide. $CH_3.CH\,Br.CH_2Br$.

Prepared by KAHLBAUM. After drying over phosphoric oxide the liquid boiled between 140°·90 and 141°·17. Bar. 753·9 millims. Corrected and reduced b.p. = 141°·35.

Vapour density:

Found 100·7. Calculated 100·76.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·37	129·56	·000031	·022838	0·35	129·39	·000031	·022856
12·91	130·46	·000040	·018147	12·91	130·24	·000040	·018166
25·27	130·44	·000046	·014937	25·27	130·23	·000046	·014937
38·00	130·47	·000054	·012472	38·04	130·27	·000054	·012469
50·18	130·00	·000062	·010703	49·99	129·79	·000062	·010732
63·20	130·12	·000072	·009185	63·19	129·89	·000072	·009183
76·47	130·06	·000081	·007974	76·45	129·90	·000081	·007966
89·46	130·10	·000090	·007046	88·80	129·89	·000090	·007044
101·16	130·13	·000100	·006287	101·20	129·96	·000100	·006281
113·61	130·15	·000109	·005636	113·81	129·99	·000109	·005624
127·97	130·12	·000121	·005010	127·98	129·92	·000121	·005010
136·62	130·08	·000127	·004687	136·72	129·92	·000127	·004681

In reducing the observations, the value 1·9617 for the relative density at 0°, and the expression

$$V = 1 + \cdot 0_3 91672 t + \cdot 0_5 12277 t^2 + \cdot 0_8 12010 t^3$$

for the thermal expansion (ZANDER, 'Annalen,' 214, 175), were adopted.

Taking

$$\eta_1 = ·022847 \qquad \eta_3 = ·004684 \qquad \eta_2 \text{ (calculated)} = ·010345$$
$$t_1 = 0°·36 \qquad t_3 = 136°·67 \qquad t_2 \text{ (from curve)} = 52°·98,$$

we obtain the formula

$$\eta_t = \frac{48·803}{(88·757 + t)^{1·7075}},$$

which gives the following values :—

Mean temp.	η		Difference.
	Observed (mean).	Calculated.	
°			
0·36	·02285	·02285	·00000
12·91	·01816	·01824	+ ·00008
25·27	·01494	·01499	+ ·00005
38·02	·01247	·01249	+ ·00002
50·08	·01072	·01072	·00000
63·19	·00918	·00919	+ ·00001
76·46	·00797	·00796	– ·00001
89·13	·00704	·00702	– ·00002
101·18	·00628	·00628	·00000
113·71	·00565	·00563	– ·00002
127·97	·00501	·00501	·00000
136·67	·00468	·00468	·00000

Isobutylene Bromide. $(CH_3)_2CBr.CH_2Br$.

A quantity of this substance, procured from KAHLBAUM, was placed over phosphoric oxide for some days and then distilled. It boiled completely between 148°·85 and 149°·60. Bar. 752·5 millims. Corrected and reduced b.p. = 149°·6.

Before introducing it into the glischrometer, it was again distilled under reduced pressure, and the portion coming over between the pressures 77 and 91 millims. was employed for the experiments.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η	Temp.	Press.	Corr.	η
°				°			
13·67	130·52	·000026	·024558	0·39	130·25	·000020	·032903
40·80	129·97	·000041	·015278	26·94	129·83	·000033	·019163
66·90	129·84	·000057	·010648	53·18	129·73	·000049	·012741
80·64	129·63	·000066	·009027	80·56	129·53	·000066	·009032
93·67	129·57	·000076	·007809	93·60	129·40	·000075	·007821
107·15	130·52	·000086	·006808	107·16	130·37	·000086	·006803
121·72	130·57	·000097	·005933	121·76	130·38	·000097	·005923
133·75	130·59	·000106	·005321	133·76	130·42	·000106	·005322
142·46	130·59	·000113	·004946	142·42	130·41	·000112	·004936

In reducing the observations we employed the value $d\ (15^\circ/15^\circ) = 1{\cdot}74343$ given by Perkin ('Chem. Soc. Trans.,' 45, 525) for the relative density, and the expression

$$V = 1 + {\cdot}0_3 95566t + {\cdot}0_6 31753t^2 + {\cdot}0_8 500821t^3$$

for the thermal expansion (Thorpe and L. M. Jones, *loc. cit.*).

Taking

$$\eta_1 = {\cdot}032903 \qquad \eta_3 = {\cdot}004941 \qquad \eta_2\ \text{(calculated)} = {\cdot}012750$$
$$t_1 = 0^\circ{\cdot}39 \qquad t_3 = 142^\circ{\cdot}44 \qquad t_2\ \text{(from curve)} = 53^\circ{\cdot}12,$$

we obtain

$$\eta_t = \frac{79{\cdot}485}{(75{\cdot}60 + t)^{1{\cdot}7988}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·39	·03290	·03290	·00000
13·67	·02456	·02463	+ ·00007
26·94	·01916	·01919	+ ·00003
40·80	·01528	·01528	·00000
53·18	·01274	·01274	·00000
66·90	·01065	·01062	− ·00003
80·60	·00903	·00900	− ·00003
93·63	·00781	·00779	− ·00002
107·15	·00680	·00679	− ·00001
121·74	·00593	·00591	− ·00002
133·75	·00532	·00532	·00000
142·44	·00494	·00494	·00000

Acetylene Bromide. (Symmetrical Dibromethylene.) (CHBr:CHBr.)

Prepared by Dr. Plimpton, to whom our thanks are due for the specimen. The liquid boiled between 108°·9 and 109°·7. Bar. 757·8 millims. Corrected and reduced b.p. = 109°·4.

Vapour density :

Found, 92·04. Calculated, 92·77.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·84	128·99	·000070	·012163	0·88	128·73	·000070	·012171
11·02	129·07	·000078	·010693	10·88	128·76	·000078	·010701
19·94	129·07	·000086	·009592	19·93	128·84	·000086	·009603
30·15	129·17	·000096	·008579	30·13	128·93	·000096	·008594
39·45	129·22	·000104	·007812	39·53	128·96	·000104	·007820
47·80	129·19	·000111	·007222	47·81	128·99	·000111	·007224
58·00	129·25	·000120	·006588	57·92	129·00	·000120	·006595
67·21	129·26	·000128	·006099	67·17	129·02	·000128	·006102
76·65	129·37	·000137	·005651	76·79	129·10	·000136	·005650
85·95	129·37	·000145	·005249	85·95	129·13	·000145	·005256
97·10	129·20	·000155	·004831	97·10	128·99	·000154	·004839
105·74	129·22	·000163	·004538	105·71	129·01	·000162	·004542

The published determinations of the density of acetylene bromide are somewhat discordant. Two independent estimations of the sample employed by us gave d (0°/4°) = 2·29866 and 2·29847 ; mean = 2·2986, which we have adopted in the calculations. This agrees closely with WEGER's value, d (0°/0°) = 2·2983.

For the thermal expansion we have used WEGER's expression ('Annalen,' 221, 72)

$$V = 1 + {\cdot}0_3 99103t + {\cdot}0_5 17519t^2 + {\cdot}0_8 11776t^3.$$

Taking

$$\eta_1 = {\cdot}012167 \qquad \eta_3 = {\cdot}004540 \qquad \eta_2 \text{ (calculated)} = {\cdot}007432$$
$$t_1 = 0^\circ{\cdot}86 \qquad t_3 = 105^\circ{\cdot}72 \qquad t_2 \text{ (from curve)} = 44^\circ{\cdot}77,$$

we obtain the formula

$$\eta_t = \frac{14{\cdot}868}{(112{\cdot}29 + t)^{1{\cdot}5032}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·86	·01217	·01217	·00000
10·95	·01070	·01070	·00000
19·93	·00960	·00963	+ ·00003
30·14	·00859	·00861	+ ·00002
39·49	·00782	·00782	·00000
47·80	·00722	·00722	·00000
57·96	·00659	·00658	— ·00001
67·19	·00610	·00608	— ·00002
76·72	·00565	·00563	— ·00002
85·95	·00525	·00523	— ·00002
97·10	·00483	·00482	— ·00001
105·72	·00454	·00454	·00000

CHLORIDES.

Propyl Chloride. $CH_3.CH_2.CH_2Cl$.

A quantity of the chloride obtained from KAHLBAUM was dried by phosphoric oxide and distilled. It boiled between 46°·1 and 46°·3. Bar. 754·4 millims. Corrected and reduced b.p. 46°·47.

Vapour density :

Found, 39·56. Calculated, 39·18.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·43	100·00	·000057	·004325	0·47	99·95	·000057	·004330
5·25	99·95	·000060	·004103	5·23	99·85	·000060	·004106
10·08	99·80	·000063	·003893	10·05	99·73	·000063	·003896
14·68	99·74	·000065	·003706	14·63	99·66	·000065	·003711
20·74	100·01	·000069	·003491	20·68	99·94	·000069	·003499
25·80	99·99	·000071	·003340	25·73	99·92	·000071	·003347
30·33	99·95	·000074	·003178	30·44	99·86	·000074	·003177
35·36	99·90	·000077	·003040	35·40	99·84	·000077	·003037
40·81	99·89	·000080	·002882	40·83	99·81	·000080	·002892
44·67	99·89	·000082	·002786	44·69	99·79	·000082	·002783

In reducing the observations the value d (0°/0°) = 0·9123 for the relative density, and the expression :

$$V = 1 + \cdot 0_2 13306 t + \cdot 0_5 38313 t^2 - \cdot 0_7 13859 t^3$$

for the thermal expansion (ZANDER, 'Annalen,' 214, 157), were used.

Taking

$$\eta_1 = \cdot 004327 \qquad \eta_3 = \cdot 002784 \qquad \eta_2 \text{ (calculated)} = \cdot 003471$$
$$t_1 = 0^\circ\cdot 45 \qquad t_3 = 44^\circ\cdot 68 \qquad t_2 \text{ (from curve)} = 21^\circ\cdot 48,$$

we obtain

$$\eta_t = \frac{662\cdot 52}{(203\cdot 36 + t)^{2\cdot 2453}},$$

from which the following calculated values are obtained :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·45	·004327	·004327	·000000
5·24	·004104	·004108	+ ·000004
10·06	·003894	·003902	+ ·000008
14·65	·003709	·003720	+ ·000011
20·71	·003495	·003498	+ ·000003
25·76	·003344	·003327	− ·000017
30·38	·003178	·003181	+ ·000003
35·38	·003038	·003034	− ·000004
40·82	·002887	·002884	− ·000003
44·68	·002784	·002784	·000000

Isopropyl Chloride. $(CH_3)_2CHCl$.

A sample from KAHLBAUM, after drying over phosphoric oxide, was distilled. It boiled between 35°·80 and 35°·86. Bar. 762·1 millims. Corrected and reduced b.p. = 35°·74.

Vapour density :

Found, 38·92. Calculated, 39·18.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·27	100·38	·000060	·003996	0°·27	100·32	·000060	·004003
6·68	100·35	·000064	·003712	6·69	100·25	·000064	·003716
11·02	100·34	·000067	·003540	11·02	100·25	·000067	·003540
16·46	100·33	·000070	·003341	16·48	100·25	·000070	·003341
22·53	100·31	·000074	·003133	22·47	100·22	·000074	·003143
28·22	100·32	·000077	·002960	28·22	100·21	·000077	·002964
33·05	100·31	·000080	·002827	33·00	100·23	·000080	·002832

In reducing the observations, the value $d\,(0°/0°) = 0·8825$ for the relative density, and the expression

$$V = 1 + ·0_2 13696t + ·0_5 55287t^2$$

for the thermal expansion (ZANDER, ' Annalen,' 214, 158), were employed.

Taking

$\eta_1 = ·004000$ $\eta_3 = ·002829$ η_2 (calculated) $= ·003364$

$t_1 = 0°·27$ $t_3 = 33°·02$ t_2 (from curve) $= 15°·75$, we obtain

$$\eta_t = \frac{9{\cdot}2541}{(133{\cdot}60 + t)^{1{\cdot}5819}},$$

which gives an extremely good agreement with the observed values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·27	·004000	·004000	·000000
6·68	·003714	·003714	·000000
11·02	·003540	·003540	·000000
16·47	·003341	·003338	− ·000003
22·50	·003137	·003137	·000000
28·22	·002962	·002963	+ ·000001
33·02	·002829	·002829	·000000

Isobutyl Chloride. $(CH_3)_2CH.CH_2Cl$.

A sample from KAHLBAUM, after standing over phosphoric oxide for several days, was distilled, and the fraction boiling between 68°·33 and 69°·03 was used for the experiments. Bar. 750·7 millims. Corrected and reduced b.p. = 69°·02.

Vapour density :

Found, I. 47·07 ; II. 46·90. Calculated, 46·20.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·35	100·70	·000043	·005814	0·36	100·91	·000043	·005817
5·96	100·59	·000045	·005397	5·98	100·69	·000045	·005404
11·93	101·40	·000049	·005016	11·98	101·45	·000049	·005014
18·70	99·54	·000051	·004638	18·69	99·60	·000051	·004636
23·41	98·68	·000053	·004386	23·55	98·75	·000053	·004386
29·47	100·88	·000058	·004104	29·46	100·95	·000058	·004101
37·33	100·17	·000062	·003766	37·32	100·32	·000062	·003770
42·43	100·94	·000065	·003576	42·44	101·08	·000065	·003575
48·70	100·06	·000068	·003357	48·73	100·14	·000068	·003361
53·77	99·30	·000070	·003194	53·72	99·39	·000070	·003200
60·40	101·00	·000075	·003002	60·13	98·76	·000075	·003012
65·34	101·28	·000078	·002882	65·27	101·22	·000078	·002873

In reducing the observations, the value 0·8953 for the density at 0°, and the relative volumes at different temperatures given by PIERRE and PUCHOT ('Ann. de Chim. et de Phys.' (4) 22, 310), were employed.

Taking

$$\eta_1 = \cdot 005816 \qquad \eta_3 = \cdot 002877 \qquad \eta_2\,(\text{calculated}) = \cdot 004091$$
$$t_1 = 0^\circ\cdot 35 \qquad t_3 = 65^\circ\cdot 30 \qquad t_2\,(\text{from curve}) = 29^\circ\cdot 78,$$

we obtain the expression

$$\eta_t = \frac{61\cdot 940}{(141\cdot 87 + t)^{1\cdot 8706}},$$

which gives values agreeing closely with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·35	·005816	·005816	·000000
5·97	·005401	·005409	+·000008
11·95	·005015	·005022	+·000007
18·69	·004637	·004635	−·000002
23·47	·004386	·004388	+·000002
29·46	·004102	·004105	+·000003
37·32	·003768	·003775	+·000007
42·43	·003575	·003581	+·000006
48·71	·003359	·003364	+·000005
53·74	·003197	·003204	+·000007
60·26	·003007	·003013	+·000006
65·30	·002877	·002877	·000000

Allyl Chloride. $CH_2{:}CH.CH_2Cl$.

Made by the action of phosphorus trichloride on allyl alcohol by Mr. J. G. SALTMARSH, A.R.C.S., to whom we are indebted for the preparation of the other haloid derivatives of allyl employed by us. The purified product boiled between 44°·95 and 45°·13. Bar. 752·4 millims. Corrected and reduced b.p. = 45°·29.

Vapour density:

Found, 38·54. Calculated, 38·18.

Observations for viscosity:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 0·50	100·53	·000067	·004036	° 0·56	100·44	·000067	·004035
5·95	100·38	·000070	·003797	6·02	100·32	·000070	·003804
11·19	100·21	·000074	·003596	11·20	100·15	·000074	·003600
16·68	100·06	·000077	·003406	16·64	100·05	·000077	·003409
21·94	99·92	·000080	·003228	21·93	99·87	·000080	·003232
28·34	98·69	·000083	·003038	28·31	98·68	·000083	·003039
33·98	98·48	·000086	·002884	33·96	98·40	·000086	·002887
38·34	98·31	·000089	·002775	38·41	98·24	·000089	·002773
42·10	98·08	·000091	·002680	42·11	98·02	·000091	·002683

The value 0·9610 for the relative density at 0°, and the expression

$$V = 1 + {\cdot}0_{2}13218t + {\cdot}0_{5}5078t^{2} - {\cdot}0_{7}41915t^{3}$$

for the thermal expansion (ZANDER, 'Annalen,' vol. 214, p. 143), have been employed in the reduction of the observations.

Taking

$$\eta_1 = {\cdot}004035 \qquad \eta_3 = {\cdot}002681 \qquad \eta_2\ (\text{calculated}) = {\cdot}003289$$
$$t_1 = 0^\circ{\cdot}53 \qquad t_3 = 42^\circ{\cdot}10 \qquad t_2\ (\text{from curve}) = 20^\circ\ 10,$$

we obtain the formula

$$\eta_t = \frac{27{\cdot}705}{(157{\cdot}08 + t)^{1{\cdot}7459}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·53	·004035	·004035	·000000
5·98	·003800	·003803	+ ·000003
11·19	·003598	·003599	+ ·000001
16·66	·003408	·003404	− ·000004
21·93	·003230	·003231	+ ·000001
28·32	·003039	·003039	·000000
33·97	·002885	·002884	− ·000001
38·37	·002774	·002771	− ·000003
42·10	·002681	·002681	·000000

Methylene Chloride. CH_2Cl_2.

A quantity of this liquid, obtained from KAHLBAUM, was placed over phosphoric anhydride and distilled. It boiled between 40°·68 and 40°·88. Bar. 769·2 millims. Corrected and reduced b.p. = 40°·41.

Vapour density:

Found, 42·42. Calculated, 42·37.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·49	100·42	·000071	·005335	0·44	100·35	·000071	·005324
5·76	100·33	·000074	·005017	5·71	100·23	·000074	·005028
10·15	100·31	·000077	·004793	10·22	100·17	·000077	004796
15·45	100·28	·000081	·004548	15·45	100·14	·000081	·004552
20·53	100·25	·000084	·004327	20·54	100·09	·000084	·004333
25·60	100·16	·000087	·004131	25·58	100·02	·000087	·004144
30·96	100·01	·000091	·003930	31·00	99·93	·000091	·003936
37·53	99·98	·000095	·003703	37·50	99·84	·000095	·003712

In reducing the observations we have adopted PERKIN's value for the relative density $d\,(15^\circ/15^\circ) = 1·3377$, and the expression

$$V = 1 + {\cdot}0_2 130805t + {\cdot}0_5 2735t^2 - {\cdot}0_8 133t^3,$$

already given by one of us (THORPE, *loc. cit.*), for the thermal expansion.

Taking

$$\eta_1 = {\cdot}005329 \qquad \eta_3 = {\cdot}003707 \qquad \eta_2\,(\text{calculated}) = {\cdot}004445$$
$$t_1 = 0^\circ{\cdot}46 \qquad t_3 = 37^\circ{\cdot}51 \qquad t_2\,(\text{from curve}) = 17^\circ{\cdot}82,$$

we obtain the formula

$$\eta_t = \frac{5{\cdot}8778}{(128{\cdot}88 + t)^{1{\cdot}4408}},$$

which gives values in close agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·46	·005329	·005329	·000000
5·73	·005023	·005031	+ ·000008
10·18	·004794	·004801	+ ·000007
15·45	·004545	·004551	+ ·000006
20·53	·004330	·004329	— ·000001
25·59	·004137	·004126	— ·000011
30·98	·003933	·003928	— ·000005
37·51	·003707	·003707	·000000

Ethylene Chloride. $CH_2Cl.CH_2Cl$.

A specimen of this liquid was dried over phosphoric anhydride and distilled. It boiled between 83°·91 and 84°·08. Bar. 761·0 millims. Corrected and reduced b.p. 83°·93.

Vapour density :

Found, I. 48·99 ; II. 49·29. Calculated, 49·37.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·33	128·09	·000042	·011194	0·30	127·96	·000042	·011229
7·22	128·13	·000046	·010020	7·24	127·97	·000046	·010022
14·71	128·13	·000051	·008959	14·75	127·99	·000051	·008964
21·84	128·26	·000056	·008126	21·85	128·13	·000056	·008132
28·78	128·21	·000061	·007408	28·78	128·11	·000061	·007426
36·90	128·21	·000066	·006684	36·87	128·09	·000066	·006707
43·88	128·22	·000071	·006163	43·90	128·07	·000071	·006168
51·78	128·14	·000077	·005670	51·69	128·07	·000076	·005666
58·52	128·19	·000082	·005265	58·55	128·05	·000082	·005273
65·56	128·23	·000087	·004907	65·51	128·08	·000087	·004917
72·98	128·28	·000092	·004552	72·93	128·14	·000092	·004564
81·06	128·35	·000098	·004213	81·09	128·20	·000099	·004221

In reducing the observations the value 1·28082 for the density at 0°, and the expression

$$V = 1 + \cdot0_2115303t + \cdot0_6825693t^2 + \cdot0_89625t^3$$

(THORPE, *loc. cit.*) for the thermal expansion, have been adopted.

Taking

$$\eta_1 = \cdot011211 \qquad \eta_3 = \cdot004217 \qquad \eta_2\ (\text{calculated}) = \cdot006876$$
$$t_1 = 0^\circ\cdot31 \qquad t_3 = 81^\circ\cdot07 \qquad t_2\ (\text{from curve}) = 34^\circ\cdot80,$$

we obtain the formula

$$\eta_t = \frac{24\cdot256}{(100\cdot67 + t)^{1\cdot6641}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·31	·011211	·011211	·000000
7·23	·010021	·010041	+ ·000020
14·73	·008961	·008978	+ ·000017
21·84	·008129	·008128	− ·000001
28·78	·007417	·007416	− ·000001
36·88	·006695	·006704	+ ·000009
43·89	·006166	·006171	+ ·000005
51·74	·005668	·005652	− ·000016
58·53	·005239	·005256	+ ·000017
65·53	·004912	·004893	− ·000019
72·95	·004558	·004550	− ·000008
81·07	·004217	·004217	·000000

Ethylidene Chloride. $CH_3.CHCl_2$.

A sample, prepared from paraldehyde and free from phosphorus, was fractionated, and the portion boiling between 56°·84 and 57°·24 was employed for the experiments. Bar. 753·0 millims. Corrected and reduced b.p. = 57°·32.

Vapour density :

Found, 49·38. Calculated, 49·37.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·06	128·11	·000073	·005682	7·06	128·11	·000073	·005690
11·34	127·97	·000077	·005400	11·14	127·94	·000077	·005426
15·34	128·25	·000080	·005153	15·34	128·22	·000080	·005160
19·31	128·25	·000083	·004933	19·31	128·14	·000083	·004934
23·24	128·15	·000086	·004730	23·21	128·87	·000086	·004742
27·84	128·11	·000089	·004503	27·86	128·02	·000090	·004510
31·51	128·02	·000092	·004338	31·59	127·97	·000092	·004337
35·57	128·00	·000095	·004156	35·66	127·88	·000096	·004165
40·21	127·82	·000099	·003973	40·16	127·75	·000099	·003980
43·74	128·41	·000102	·003834	43·74	128·35	·000102	·003838
47·96	128·15	·000105	·003694	47·94	128·06	·000105	·003696
54·54	127·94	·000110	·003476	54·54	127·86	·000110	·003476

In reducing the observations the value 1·2049 for the density at 0°, and the expression

$$V = 1 + \cdot 0_2 128402 t + \cdot 0_5 189062 t^2 + \cdot 0_8 7848 t^3$$

(THORPE, *loc. cit.*) for the thermal expansion, were used.

Taking

$$\eta_1 = \cdot 005686 \qquad \eta_3 = \cdot 003476 \qquad \eta_2 \,(\text{calculated}) = \cdot 004446$$

$$t_1 = 7^\circ \cdot 06 \qquad t_3 = 54^\circ \cdot 54 \qquad t_2 \,(\text{from curve}) = 29^\circ \cdot 06,$$

we obtain the formula

$$\eta_t = \frac{22 \cdot 247}{(132 \cdot 02 + t)^{1 \cdot 6762}},$$

which gives values in close agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 7·06	·005686	·005686	·000000
11·24	·005413	·005411	− ·000002
15·34	·005156	·005161	+ ·000005
19·31	·004934	·004936	+ ·000002
23·22	·004736	·004729	− ·000007
27·85	·004506	·004502	− ·000004
31·55	·004337	·004333	− ·000004
35·61	·004160	·004158	− ·000002
40·18	·003976	·003975	− ·000001
43·74	·003836	·003841	+ ·000005
47·95	·003695	·003693	− ·000002
54·54	·003476	·003476	·000000

Chloroform. $CHCl_3$.

We are indebted to Mr. DAVID HOWARD for the sample of pure chloroform which has served for our experiments. It was placed over phosphoric oxide for some hours and distilled. It boiled completely between 61°·43 and 61°·58. Bar. 764·0 millims. Corrected and reduced b.p. = 61°·34.

Vapour density:

Found, 59·40. Calculated, 59·55.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·33	100·46	·000060	·006975	0°·33	100·44	·000060	·006984
5·27	100·53	·000063	·006590	5·26	100·47	·000063	·006598
10·24	100·23	·000066	·006240	10·29	100·09	·000066	·006245
15·89	100·16	·000070	·005873	15·95	100·01	·000070	·005879
21·42	100·11	·000073	·005558	21·42	99·98	·000073	·005566
25·93	100·01	·000076	·005307	25·94	99·89	·000076	·005321
31·45	99·99	·000079	·005037	31·49	99·83	·000079	·005042
36·81	99·90	·000083	·004784	36·83	99·79	·000083	·004791
42·07	99·81	·000086	·004563	42·05	99·66	·000086	·004565
46·88	100·66	·000089	·004376	46·88	100·53	·000089	·004380
52·75	100·67	·000093	·004152	52·70	100·53	·000093	·004160
56·95	100·66	·000096	·004000	56·94	100·52	·000096	·004012

In reducing the observations we have employed the value 1·52637 for the density at 0°, and the expression

$$V = 1 + \cdot 0_2 123024t + \cdot 0_5 171383t^2 + \cdot 0_8 8338t^3$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking

$$\eta_1 = \cdot 006979 \qquad \eta_3 = \cdot 004006 \qquad \eta_2 \text{ (calculated)} = \cdot 005288$$
$$t_1 = 0^\circ\cdot 33 \qquad t_3 = 56^\circ\cdot 94 \qquad t_2 \text{ (from curve)} = 26^\circ\cdot 48,$$

we obtain the formula

$$\eta_t = \frac{70\cdot 4244}{(158\cdot 33 + t)^{1\cdot 8196}},$$

which gives results in very good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·33	·006979	·006979	·000000
5·26	·006594	·006601	+ ·000007
10·26	·006242	·006250	+ ·000008
15·92	·005876	·005885	+ ·000009
21·42	·005562	·005562	·000000
25·93	·005314	·005316	+ ·000002
31·47	·005039	·005037	− ·000002
36·82	·004787	·004789	+ ·000002
42·06	·004565	·004564	− ·000001
46·88	·004378	·004370	− ·000008
52·72	·004156	·004153	− ·000003
56·94	·004006	·004006	·000000

Carbon Tetrachloride. CCl_4.

The sample employed for our observations was obtained by repeatedly agitating a quantity of the rectified liquid with potash solution, decanting, drying over phosphoric oxide, and fractionating. The liquid was eventually found to boil constantly at 76°·76. Bar. 755·4 millims. Corrected and reduced b.p. = 76°·96.

Vapour density:

Found, 76·62. Calculated, 76·74.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·61	129·68	·000045	·013320	0°·60	129·48	·000045	·013323
7·20	129·47	·000050	·011864	7·10	129·33	·000045	·011905
14·90	129·32	·000056	·010467	14·88	129·23	·000056	·010487
21·20	129·34	·000061	·009513	21·23	129·17	·000061	·009522
27·55	129·13	·000066	·008705	27·57	129·02	·000066	·008706
35·21	128·97	·000072	·007847	35·22	128·88	·000073	·007864
42·08	128·71	·000078	·007194	42·08	128·69	·000078	·007202
49·52	128·52	·000084	·006565	49·50	128·39	·000084	·006569
56·26	128·36	·000090	·006075	56·31	128·26	·000090	·006080
62·88	128·17	·000096	·005653	62·87	128·06	·000096	·005666
69·87	127·76	·000102	·005243	69·91	127·59	·000101	·005250
74·21	127·64	·000106	·005013	74·12	127·53	·000105	·005020

In reducing the observations we have adopted the value $d(0°/4°) = 1·63195$ for the density, and the expression

$$V = 1 + \cdot 0_2 120719t + \cdot 0_6 67109t^2 + \cdot 0_7 13478t^3$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking

$$\eta_1 = \cdot 013322 \qquad \eta_3 = \cdot 005017 \qquad \eta_2 \text{ (calculated)} = \cdot 008175$$
$$t_1 = 0^\circ\cdot 60 \qquad t_3 = 74^\circ\cdot 16 \qquad t_2 \text{ (from curve)} = 32^\circ\,17,$$

we obtain the expression

$$\eta_t = \frac{32\cdot 780}{(95\cdot 05 + t)^{1\cdot 7121}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·60	·013322	·013322	·000000
7·15	·011884	·011893	+ ·000009
14·89	·010476	·010496	+ ·000020
21·21	·009517	·009538	+ ·000021
27·56	·008705	·008708	+ ·000003
35·21	·007855	·007851	− ·000004
42·08	·007198	·007190	− ·000008
49·51	·006567	·006569	+ ·000002
56·29	·006078	·006073	− ·000005
62·87	·005659	·005646	− ·000013
69·89	·005246	·005241	− ·000005
74·16	·005017	·005017	·000000

Carbon Dichloride. $CCl_2:CCl_2$.

A large quantity of this liquid was distilled, washed with water and a dilute solution of potassium carbonate, dried over phosphoric anhydride and carefully fractionated. Eventually, after repeated fractionation, a portion was obtained which boiled between 120°·73 and 120°·85. Bar. 761·15 millims. Corrected and reduced b.p. = 120°·74.

Vapour density :

Found, 82·21. Calculated, 82·74.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·41	130·62	·000054	·011331	0·46	130·46	·000054	·011329
11·44	130·60	·000061	·009854	11·41	130·43	·000061	·009870
22·30	130·56	·000069	·008683	22·30	130·42	·000069	·008700
32·39	130·46	·000075	·007821	32·28	130·34	·000075	·007858
42·76	130·41	·000082	·007068	42·80	130·25	·000082	·007074
52·68	130·37	·000089	·006448	52·69	130·21	·000089	·006456
64·16	130·68	·000097	·005839	64·13	130·55	·000097	·005852
74·69	130·61	·000104	·005349	74·66	130·47	·000104	·005363
85·71	130·64	·000112	·004914	85·80	130·47	·000112	·004908
95·59	130·62	·000119	·004549	95·62	130·46	·000119	·004554
106·04	130·50	·000126	·004218	106·03	130·32	·000126	·004224
117·06	130·46	·000134	·003902	117·13	130·33	·000134	·003900

The published determinations of the density of carbon dichloride are very discrepant, owing, doubtless, to the difficulty of obtaining this substance pure. Two determinations of the sample used by us gave at 0° the values 1·65514 and 1·65505, the mean of which (1·6551) has been employed in the reductions.

For the thermal expansion we have adopted PIERRE's observations ('Annales de Chim. et de Phys.' (3), 33, 233).

Taking

$$\eta_1 = \cdot 011330 \qquad \eta_3 = \cdot 003901 \qquad \eta_2 \text{ (calculated)} = \cdot 006648$$

$$t_1 = 0^\circ \cdot 43 \qquad t_3 = 117^\circ \cdot 09 \qquad t_2 \text{ (from curve)} = 49^\circ \cdot 32,$$

we obtain the formula

$$\eta_t = \frac{30\cdot 656}{(126\cdot 17 + t)^{1\cdot 6325}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean.)	Calculated.	
° 0·43	·01133	·01133	·00000
11·24	·00986	·00991	+ ·00005
22·30	·00869	·00874	+ ·00005
32·34	·00784	·00785	+ ·00001
42·78	·00707	·00707	·00000
52·68	·00645	·00645	·00000
64·14	·00585	·00582	− ·00003
74·67	·00536	·00533	− ·00003
85·75	·00491	·00489	− ·00002
95·60	·00455	·00454	− ·00001
106·03	·00422	·00421	− ·00001
117·09	·00390	·00390	·00000

SULPHUR COMPOUNDS.

Carbon Bisulphide. CS_2.

A sample from Dr. PERKIN, after digestion with phosphoric oxide, was distilled. It boiled between 46°·63 and 46°·68. Bar. 766·0 millims. Corrected and reduced b.p. = 46°·42.

Vapour density :

Found, 37·59. Calculated, 38·00.

The observations for viscosity gave :—

Right limb.				Left limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·40	100·15	·000082	·004274	0·39	100·01	·000082	·004287
4·87	100·22	·000085	·004122	4·90	100·09	·000085	·004128
9·44	100·57	·000087	·003968	9·46	100·42	·000088	·003977
14·93	100·65	·000091	·003807	14·89	100·51	·000091	·003815
19·93	100·63	·000093	·003666	19·96	100·50	·000093	·003675
25·33	100·39	·000096	·003559	25·36	101·28	·000096	·003552
30·31	100·94	·000099	·003415	30·30	100·82	·000099	·003426
35·52	100·91	·000102	·003281	35·50	100·78	·000102	·003287
40·65	100·82	·000105	·003168	40·59	100·71	·000105	·003180
45·98	100·57	·000107	·003057	45·94	100·51	·000107	·003062

In reducing the observations we employed $d\,(0°/4°) = 1{\cdot}29215$ for the density, and the expression

$$V = 1 + {\cdot}0_2115056t + {\cdot}0_5111621t^2 + {\cdot}0_717455t^3$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking

$$\eta_1 = {\cdot}004280 \qquad \eta_3 = {\cdot}003060 \qquad \eta_2\ (\text{calculated}) = {\cdot}003619$$
$$t_1 = 0^\circ{\cdot}40 \qquad t_3 = 45^\circ{\cdot}96 \qquad t_2\ (\text{from curve}) = 22^\circ{\cdot}01,$$

we obtain the formula

$$\eta_t = \frac{24{\cdot}379}{(199{\cdot}17 + t)^{1{\cdot}6328}},$$

which gives numbers in very close accord with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·40	·00428	·00428	·00000
4·88	·00413	·00413	·00000
9·45	·00397	·00398	+ ·00001
14·91	·00381	·00382	+ ·00001
19·94	·00367	·00368	+ ·00001
25·34	·00356	·00353	− ·00003
30·30	·00342	·00341	− ·00001
35·51	·00328	·00328	·00000
40·62	·00317	·00317	·00000
45·96	·00306	·00306	·00000

Methyl Sulphide. $(CH_3)_2S$.

A quantity of methyl sulphide was dried over phosphoric oxide and fractionated. The greater portion was eventually found to boil between 37°·13 and 37°·45. Bar. 765·4 millims. Corrected and reduced b.p. = 37°·52.

A determination of vapour density gave :—

Weight of liquid	0·0614 gram.
Volume of vapour	81·61 cub. centim
Temperature	14°·8.
Pressure	215·93 millims.

Found, 31·17. Calculated, 31·00.

The vapour density observation was made at 14°·8—the atmospheric temperature, as the substance was completely volatilised under the diminished pressure (215·9 millims.) employed in the experiment.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·25	101·64	·000070	·003528	0·29	101·55	·000070	·003530
5·56	101·62	·000073	·003349	5·56	101·53	·000073	·003353
10·04	101·59	·000076	·003210	10·07	101·51	·000076	·003208
14·75	101·59	·000078	·003071	14·75	101·50	·000078	·003079
20·18	101·61	·000081	·002927	20·20	101·50	·000081	·002927
26·13	101·61	·000085	·002774	26·15	101·50	·000085	·002779
31·35	101·60	·000088	·002651	31·35	101·51	·000088	·002659
35·78	101·61	·000090	·002559	35·84	101·51	·000090	·002559

In reducing the observations the density was taken as $d\,(0°/4°) = 0{\cdot}8702$ and the thermal expansion as

$$V = 1 + \cdot 0_2 132607t + \cdot 0_5 2130214t^2 + \cdot 0_7 232968t^3.$$

(THORPE and L. M. JONES, *loc. cit.*).

Taking

$$\eta_1 = \cdot 003529 \qquad \eta_3 = \cdot 002559 \qquad \eta_2 \text{ (calculated)} = \cdot 003005$$
$$t_1 = 0°{\cdot}27 \qquad t_3 = 35°{\cdot}81 \qquad t_2 \text{ (from curve)} = 17°{\cdot}20,$$

we obtain the formula

$$\eta_t = \frac{21\cdot768}{(170\cdot34 + t)^{1\cdot6981}},$$

which gives results in excellent agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·27	·003529	·003529	·000000
5·56	·003351	·003351	·000000
10·05	·003209	·003210	+ ·000001
14·75	·003075	·003073	− ·000002
20·19	·002927	·002926	− ·000001
26·14	·002776	·002777	+ ·000001
31·35	·002655	·002656	+ ·000001
35·81	·002559	·002559	·000000

Ethyl Sulphide. $(CH_3.CH_2)_2S$.

About 200 grams of ethyl sulphide were dried over phosphoric oxide and distilled, By far the greater portion boiled between 91°·23 and 91°·53. Bar. 743·7 millims Corrected and reduced b.p. = 92°·1.

Vapour density :

Found, 44·73. Calculated, 45·0.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·19	101·99	·000044	·005570	0°·23	101·92	·000044	·005580
8·34	101·98	·000047	·005056	8·30	101·90	·000047	·005062
15·84	101·97	·000051	·004644	15·87	101·89	·000051	·004646
24·65	101·91	·000055	·004234	24·63	101·85	·000055	·004240
32·64	101·84	·000059	·003897	32·63	101·78	·000059	·003900
40·25	101·81	·000063	·003625	40·13	101·73	·000062	·003631
47·74	101·49	·000066	·003381	47·76	101·43	·000066	·003381
56·51	101·47	·000070	·003122	56·47	101·39	·000070	·003129
63·54	101·46	·000074	·002943	63·40	101·38	·000074	·002951
71·21	101·47	·000078	·002762	71·30	101·39	·000078	·002761
80·28	101·48	·000082	·002563	80·35	101·39	·000082	·002562
87·95	101·49	·000086	·002405	88·04	101·44	·000086	·002407

In reducing the observations we have adopted PIERRE's value $d\,(0^\circ/0^\circ) = 0\cdot83672$ for the relative density, and his expression

$$V = 1 + \cdot0_{2}11964t + \cdot0_{5}18065t^{2} + \cdot0_{8}78821t^{3}$$

for the thermal expansion ('Annales de Chim. et de Phys.,' (3), 33, 215).

Taking

$$\eta_1 = \cdot005575 \qquad \eta_3 = \cdot002406 \qquad \eta_2 \text{ (calculated)} = \cdot003663$$
$$t_1 = 0^\circ\cdot21 \qquad t_3 = 87^\circ\cdot99 \qquad t_2 \text{ (from curve)} = 39^\circ\cdot05,$$

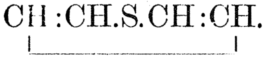
we obtain the formula

$$\eta_t = \frac{49\cdot886}{(149\cdot15 + t)^{1\cdot8175}},$$

which gives results in good agreement with the values obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·21	·005575	·005575	·000000
8·32	·005059	·005064	− ·000005
15·85	·004645	·004652	+ ·000007
24·64	·004237	·004233	− ·000004
32·63	·003899	·003901	+ ·000002
40·19	·003628	·003623	− ·000005
47·75	·003381	·003374	− ·000007
56·49	·003126	·003118	− ·000008
63·50	·002947	·002933	− ·000014
71·25	·002761	·002749	− ·000012
80·31	·002563	·002555	− ·000008
87·99	·002406	·002406	·000000

Thiophen. CH:CH.S.CH:CH.



A quantity of thiophen, after drying, was carefully fractionated, and the portion boiling between 84°·18 and 84°·38 was collected and employed for the viscosity observations. Bar. 759·0 millims. Corrected and reduced b.p. 84°·3.

Vapour density :—

Found, 41·57. Calculated, 42·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·24	102·43	·000036	·008672	0·25	102·30	·000036	·008680
8·39	102·41	·000041	·007688	8·40	102·33	·000041	·007697
16·66	102·03	·000045	·006869	16·56	101·92	·000045	·006883
22·55	102·10	·000048	·006381	22·45	101·96	·000048	·006388
31·15	102·16	·000053	·005749	31·09	102·00	·000053	·005758
37·85	101·77	·000056	·005324	37·82	101·67	·000056	·005332
44·93	101·72	·000060	·004934	44·95	101·61	·000060	·004935
53·14	101·75	·000065	·004539	53·02	101·62	·000064	·004541
61·85	101·83	·000070	·004162	61·48	101·69	·000069	·004179
68·61	101·89	·000073	·003907	68·60	101·78	·000073	·003907
75·10	101·88	·000077	·003679	75·03	101·77	·000077	·003685
82·50	101·93	·000081	·003448	82·56	101·81	·000081	·003446

In reducing the observations we have employed SCHIFF'S values for the thermal expansion ('Ber.', 18, *a*, 1605), and the number $d\,(0°/0°) = 1·0884$ for the relative density.

Taking

$$\eta_1 = ·008676 \qquad \eta_3 = ·003447 \qquad \eta_2\ (\text{calculated}) = ·005469$$

$$t_1 = 0°·24 \qquad t_3 = 82°·53 \qquad t_2\ (\text{from curve}) = 35°·52,$$

we obtain the formula

$$\eta_t = \frac{15·677}{(105·87 + t)^{1·6078}},$$

which gives results in good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·24	·008676	·008676	·000000
8·39	·007692	·007703	+ ·000011
16·61	·006876	·006889	+ ·000013
22·50	·006384	·006388	+ ·000004
31·12	·005754	·005754	·000000
37·83	·005328	·005328	·000000
44·94	·004934	·004930	− ·000004
53·08	·004540	·004531	− ·000009
61·66	·004170	·004163	− ·000007
68·60	·003907	·003900	− ·000007
75·06	·003682	·003679	− ·000003
82·53	·003447	·003447	·000000

KETONES.

Dimethyl Ketone (Acetone). $CH_3.CO.CH_3$.

A sample lent to us by Dr. PERKIN was distilled: all came over between 55°·3 and 55°·5. It was redistilled: the portion collected for the observations boiled between 55°·49 and 55°·54. $n = 8°$, $t = 25°{\cdot}5$ (emergent column). Bar. 742·6 millims. Corrected and reduced b.p. = 56°·22.

Vapour density:

Found, 28·51. Calculated, 29·00.

Observations for viscosity gave:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·94	128·68	·000078	·003634	7·79	128·61	·000078	·003641
11·71	128·70	·000080	·003497	11·74	128·62	·000080	·003495
15·24	128·72	·000082	·003383	15·24	128·61	·000082	·003370
19·04	128·85	·000085	·003254	19·01	128·76	·000085	·003262
23·04	128·84	·000088	·003129	22·99	128·76	·000088	·003132
27·21	129·09	·000091	·003004	27·24	129·05	·000091	·003010
32·31	128·62	·000094	·002861	32·56	128·61	·000094	·002865
35·94	128·51	·000096	·002774	36·06	128·46	·000096	·002770
40·04	128·40	·000099	·002683	40·04	128·34	·000099	·002678
44·09	128·34	·000101	·002586	44·16	128·29	·000102	·002583
47·61	128·30	·000104	·002501	47·64	128·21	·000104	·002506
52·16	128·18	·000107	·002405	52·24	128·10	·000107	·002406
				53·86	128·06	·000108	·002377

In reducing the observations we have adopted the value $d\ (0°/4°) = 0{\cdot}81858$ for the density, and the expression

$$V = 1 + {\cdot}0_{2}135293t + {\cdot}0_{5}302426t^{2} - {\cdot}0_{9}29t^{3}$$

for the thermal expansion (THORPE, *loc. cit.*).

Taking

$$\eta_1 = {\cdot}003637 \qquad \eta_3 = {\cdot}002405 \qquad \eta_2 \text{ (calculated)} = {\cdot}002958$$
$$t_1 = 7°{\cdot}86 \qquad t_3 = 52°{\cdot}20 \qquad t_3 \text{ (from curve)} = 29°{\cdot}00,$$

we obtain the formula

$$\eta_t = \frac{572{\cdot}63}{(209{\cdot}08 + t)^{2{\cdot}2244}},$$

which gives results in very good agreement with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
7°·86	·003638	·003638	·000000
11·72	·003495	·003498	+·000003
15·24	·003376	·003377	+·000001
19·02	·003258	·003254	−·000004
23·01	·003131	·003130	−·000001
27·22	·003007	·003008	+·000001
32·43	·002863	·002865	+·000002
36·00	·002772	·002773	+·000001
40·04	·002675	·002674	−·000001
44·12	·002584	·002579	−·000005
47·62	·002503	·002502	−·000001
52·20	·002405	·002405	·000000
53·86	·002377	·002372	−·000005

Methyl Ethyl Ketone. $CH_3.CH_2.CO.CH_3$.

A quantity of this ketone, obtained from Professor JAPP, and prepared by KAHLBAUM from ethylic methaceto-acetate by BÖKING's method ('Annalen,' 204, 17) was dried by means of anhydrous copper sulphate and submitted to fractional distillation. Eventually a portion was obtained which boiled between 79° and 83°. Bar. 772·88 millims.

The quantity of the material was insufficient to allow of further treatment.

A vapour density determination gave 35·14. Calculated, 36·00.

The observations for viscosity gave :—

Right limb.				Left limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				0°·32	101·04	·000044	·005361
7·04	101·08	·000048	·004923	7·04	100·99	·000048	·004923
14·09	101·02	·000051	·004524	14·11	100·95	·000051	·004520
21·26	100·87	·000055	·004172	21·36	100·82	·000055	·004167
28·39	100·73	·000059	·003860	28·34	100·69	·000059	·003862
35·44	100·45	·000062	·003588	35·41	100·40	·000062	·003583
42·44	100·33	·000066	·003342	42·54	100·30	·000066	·003343
48·70	100·28	·000069	·003152	48·75	100·20	·000069	·003146
55·93	100·21	·000073	·002945	55·91	100·13	·000073	·002944
63·74	101·32	·000078	·002751	63·75	101·25	·000078	·002750
70·36	101·28	·000081	·002596	70·16	101·16	·000081	·002595
76·28	101·11	·000085	·002464	76·23	101·09	·000085	·002466

In reducing the observations we have adopted the value $d\ (0°/4°) = 0·8296$ for the density, and the expression

$$V = 1 + \cdot 0_{2}11865t + \cdot 0_{5}33704t^{2} - \cdot 0_{8}53364t^{3}$$

for the thermal expansion (THORPE and L. M. JONES, *loc. cit.*).

Taking

$$\eta_1 = \cdot 005361 \qquad \eta_3 = \cdot 002465 \qquad \eta_2 \text{ (calculated)} = \cdot 003653$$
$$t_1 = 0^{\circ}\cdot 32 \qquad t_3 = 76^{\circ}\cdot 25 \qquad t_2 \text{ (from curve)} = 34^{\circ}\cdot 18,$$

we obtain the formula

$$\eta_t = \frac{36\cdot 972}{(139\cdot 33 + t)^{1\cdot 7895}},$$

which gives values in good agreement with those obtained by observation.

Mean temp.	η		Difference.
	Observed (mean).	Calculated.	
°			
0·32	·005361	·005361	·000000
7·04	·004923	·004929	+ ·000006
14·10	·004522	·004530	+ ·000008
21·31	·004170	·004173	+ ·000003
28·36	·003861	·003864	+ ·000003
35·42	·003586	·003589	+ ·000003
42·49	·003342	·003343	+ ·000001
48·72	·003149	·003148	− ·000001
55·92	·002944	·002943	− ·000001
63·74	·002750	·002743	− ·000007
70·26	·002595	·002592	− ·000003
76·25	·002465	·002465	·000000

Diethyl Ketone. $CH_3.CH_2.CO.CH_2.CH_3$.

A sample of this compound, lent to us by Dr. JAPP, and prepared by KAHLBAUM from barium propionate by KRAFFT'S method, was carefully fractionated, and eventually a portion was obtained which boiled between 100°·9 and 101°·95. Bar. 745·3 millims. Corrected and reduced b.p. = 102°·1.

A determination of its vapour density gave 41·98. Calculated, 43·0.

The viscosity observations gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·45	100·33	·000040	·005913	0·47	100·26	·000040	·005915
9·10	100·29	·000044	·005299	9·11	100·22	·000044	·005305
18·70	100·28	·000049	·004746	18·71	100·20	·000049	·004750
27·07	100·33	·000053	·004328	27·07	100·21	·000053	·004329
36·20	100·39	·000057	·003937	36·22	100·31	·000057	·003941
44·70	100·42	·000061	·003619	44·70	100·34	·000061	·003627
53·46	100·35	·000066	·003336	53·42	100·27	·000066	·003342
62·41	100·36	·000070	·003077	62·46	100·26	·000070	·003082
72·21	100·17	·000075	·002832	72·19	100·10	·000075	·002835
81·51	99·90	·000079	·002623	81·43	99·86	·000079	·002624
90·97	99·69	·000084	·002426				
98·79	99·53	·000088	·002279	98·85	99·46	·000088	·002280

In reducing the observations we have adopted the value d (0°/4°) = 0·8335 for the density, and the expression

$$V = 1 + \cdot 0_2 115342 t + \cdot 0_5 188396 t^2 + \cdot 0_8 32021 t^3$$

for the thermal expansion (THORPE and L. M. JONES, *loc cit.*).

Taking

$$\eta_1 = \cdot 005914 \qquad \eta_3 = \cdot 002279 \qquad \eta_2 \text{ (calculated)} = \cdot 003671$$
$$t_1 = 0^{\circ}\cdot 46 \qquad t_3 = 98^{\circ}\cdot 82 \qquad t_2 \text{ (from curve)} = 43^{\circ}\cdot 38,$$

we obtain the formula

$$\eta_t = \frac{64\cdot 487}{(146\cdot 67 + t)^{1\cdot 8626}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·46	·005914	·005914	·000000
9·10	·005302	·005318	+ ·000016
18·70	·004748	·004757	+ ·000009
27·07	·004328	·004339	+ ·000011
36·21	·003939	·003944	+ ·000005
44·70	·003623	·003624	+ ·000001
53·44	·003339	·003335	— ·000004
62·43	·003079	·003073	— ·000006
72·20	·002834	·002822	— ·000012
81·47	·002623	·002613	— ·000010
90·97	·002426	·002411	— ·000015
98·82	·002279	·002279	·000000

Methyl Propyl Ketone. $CH_3.(CH_2)_2.CO.CH_3$.

A sample lent to us by Dr. JAPP was placed over anhydrous copper sulphate and submitted to fractional distillation, and eventually a portion was obtained boiling between 102°·25 and 102°·55. Bar. 775·4 millims. Corrected and reduced b.p. = 101°·7.

Determinations of its vapour density gave (1) 42·97 ; (2) 42·78. Calculated 43·00.

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·41	100·49	·000037	·006400	0·35	100·41	·000037	·006409
9·34	100·45	·000041	·005697	9·46	100·35	·000041	·005688
18·30	100·42	·000045	·005108	18·30	100·34	·000045	·005111
27·79	100·39	·000049	·004589	27·76	100·32	·000049	·004594
35·44	100·38	·000053	·004231	35·42	100·32	·000053	·004237
45·27	100·33	·000057	·003829	45·31	100·25	·000058	·003832
53·90	100·29	·000062	·003525	53·98	100·24	·000062	·003525
62·26	100·19	·000066	·003261	62·23	100·11	·000066	·003262
72·79	100·62	·000071	·002979	72·69	100·58	·000071	·002982
80·65	100·51	·000075	·002785	80 63	100·44	·000075	·002788
90·08	100·49	·000080	·002574	90·04	100·41	·000080	·002573
98·78	100·50	·000084	·002399	98·77	100·40	·000084	·002401

In reducing the observations we have adopted PERKIN's value d (15°/15°) = 0·8124 (which gives d (0°/4°) = 0·8258) for the relative density, and the expression

$$V = 1 + \cdot0_2 113087t + \cdot0_5 21255t^2 + \cdot0_9 98644t^3,$$

for the thermal expansion (THORPE and L. M. JONES, *loc. cit.*).

Taking

$$\eta_1 = \cdot006404 \qquad \eta_3 = \cdot002400 \qquad \eta_2 \text{ (calculated)} = \cdot003920$$
$$t_1 = 0^\circ\cdot38 \qquad t_3 = 98^\circ\cdot77 \qquad t_2 \text{ (from curve)} = 43^\circ\cdot00,$$

we obtain the formula

$$\eta_t = \frac{51\cdot543}{(137\cdot75 + t)^{1\cdot8248}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·38	·006404	·006404	·000000
9·40	·005692	·005706	+·000014
18·30	·005109	·005126	+·000017
27·77	·004592	·004604	+·000012
35·43	·004234	·004239	+·000005
45·29	·003831	·003831	·000000
53·94	·003525	·003522	−·000003
62·24	·003262	·003260	−·000002
72·74	·002980	·002969	−·000011
80·64	·002787	·002776	−·000011
90·06	·002574	·002570	−·000004
98·77	·002400	·002400	·000000

Acetaldehyde. $CH_3.COH$.

A considerable quantity of aldehyde, obtained from KAHLBAUM, was distilled from a water-bath, the temperature of which was not allowed to rise above 30°, and the fraction distilling between 20° and 23° was collected separately. This portion was then shaken for a few minutes with calcium chloride (comp. PERKIN, 'Chem. Soc. Trans.,' 1884, p. 475), filtered into a stoppered bottle, and placed in ice for about four hours to promote the separation of any metaldehyde. The liquid was again distilled, and the portion boiling between 20°·45 and 21°·93 was collected. Bar. 755·6 millims. Corrected and reduced b.p. = 21°·4.

A determination of the vapour density of this fraction gave 22·49 ; calculated 22·00. The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0°·32	100·78	·000081	·002666	0°·35	100·76	·000081	·002659
5·34	100·65	·000084	·002540	5·36	100·60	·000084	·002536
9·55	100·54	·000086	·002440	9·57	100·49	·000087	·002443
13·91	100·47	·000089	·002346	13·93	100·41	·000089	·002343
19·20	100·31	·000092	·002232	19·14	100·23	·000092	·002237

In reducing the observations, we have employed the value $d\,(0°/0°) = 0·80092$ for the relative density, and the expression

$$V = 1 + \cdot 0_2 15464t + \cdot 0_5 69745t^2$$

for the thermal expansion (KOPP, 'Jahresbericht,' 1847–48, p. 66).

Taking

$$\eta_1 = \cdot 002663 \qquad \eta_3 = \cdot 002234 \qquad \eta_2 \text{ (calculated)} = \cdot 002439$$
$$t_1 = 0^\circ\cdot 33 \qquad t_3 = 19^\circ\cdot 17 \qquad t_2 \text{ (from curve)} = 9^\circ\cdot 60,$$

we obtain the formula

$$\eta_t = \frac{15652\cdot 2}{(286\cdot 11 + t)^{2\cdot 7550}},$$

which gives numbers in almost exact agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·33	·002663	·002663	·000000
5·35	·002538	·002538	·000000
9·56	·002442	·002440	— ·000002
13·92	·002345	·002344	— ·000001
19·17	·002234	·002234	·000000

ACIDS.

Formic Acid. H.COOH.

We are indebted to Dr. PERKIN for the sample of formic acid which has served for our observations. It was a portion of that employed by him in determining the magnetic rotary polarization of this substance. It boiled at 101° (corrected).

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 7·59	128·61	·000018	·023864	° 7·59	128·50	·000018	·023837
15·94	128 66	·000021	·019513	15·99	128·52	·000021	·019503
24·16	128·70	·000026	·016336	24·16	128·60	·000026	·016353
32·89	128·35	·000031	·013777	32·84	128·29	·000031	·013811
40·44	128·32	·000035	·012058	40·29	128·19	·000035	·012092
48·06	128·37	·000039	·010628	48·01	128·21	·000039	·010654
56·31	128·26	·000044	·009359	56·29	128·13	·000044	·009380
64·16	128·22	·000049	·008373	64·24	128·07	·000049	·008379
72·06	128·21	·000054	·007537	72·04	128·08	·000054	·007546
80·24	128·00	·000059	·006801	80·19	127·86	·000059	·006817
88·24	128·17	·000064	·006176	88·14	127·90	·000064	·006195
97·19	128·18	·000071	·005582	97·26	128·05	·000071	·005586

In reducing the observations, ZANDER'S expression ('Annalen,' 224, 59, 1884) for the thermal expansion,

$$V = 1 + ·0_3 95794t + ·0_6 9647t^2 + ·0_8 45729t^3,$$

was employed: this affords values closely concordant with those given by that of KOPP: for the relative density we have adopted the mean of the concordant observations of LANDOLT and ZANDER, viz., d (0°/0°) = 1·2424.

Taking

$$\eta_1 = ·023851 \qquad \eta_3 = ·005584 \qquad \eta_2 \text{ (calculated)} = ·011540$$
$$t_1 = 7°·59 \qquad t_3 = 97°·23 \qquad t_2 \text{ (from curve)} = 43°·07$$

we obtain the formula

$$\eta_t = \frac{32·8143}{(59·799 + t)^{1·7164}},$$

which gives calculated values which agree closely with those obtained by observation.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 7·59	·02385	·02385	·00000
15·96	·01951	·01951	·00000
24·16	·01635	·01635	·00000
32·86	·01379	·01381	+ ·00002
40·36	·01208	·01208	·00000
48·03	·01064	·01064	·00000
56·30	·00937	·00938	+ ·00001
64·20	·00838	·00837	− ·00001
72·05	·00754	·00754	·00000
80·22	·00681	·00680	− ·00001
88·19	·00619	·00618	− ·00001
97·23	·00558	·00558	·00000

Acetic Acid. $CH_3.COOH$.

A quantity of "pure" glacial acetic acid was cooled below its freezing point, and the liquid portion drained from the crystals. These were melted, again frozen, and drained as before, the process being repeated four times. The residual portion was then melted and placed over anhydrous copper sulphate for several days. The clear liquid was decanted and distilled. It boiled at 117°·8. Bar. 754·2 millims. Corrected and reduced b.p. = 118°·1.

As is well known the vapour density of acetic acid is anomalous. The observations of RAMSAY and YOUNG, however, render it possible to calculate the vapour density of the pure acid at different temperatures and pressures. We accordingly made a determination of the vapour density of the acid employed by us with the following results :—

Weight of liquid, 0·0755 grm.	Volume of vapour, 79·8 cub. centims.
Temperature, 100°·66.	Pressure, 240·3 millims.

Found, 45·73.	Calculated (R. and Y.), 45·8.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
13·23	128·79	·000028	·013577	13·70	128·73	·000028	·013605
21·90	128·68	·000031	·011761	21·93	128·60	·000032	·011761
30·87	128·63	·000036	·010247	30·86	128·54	·000036	·010257
39·91	128·59	·000040	·009026	39·85	128·47	·000040	·009037
48·50	128·51	·000045	·008055	48·45	128·42	·000045	·008059
57·46	128·33	·000049	·007201	57·45	128·39	·000049	·007221
68·15	128·59	·000055	·006373	68·06	128·50	·000055	·006383
76·60	128·60	·000060	·005807	76·72	128·47	·000060	·005800
84·52	128·64	·000064	·005338	84·55	128·52	·000064	·005344
93·96	128·72	·000070	·004844	93·99	128·60	·000070	·004845
103·90	128·90	·000076	·004409	101·89	128·70	·000075	·004490
112·47	128·92	·000081	·004067	112·67	128·83	·000081	·004056

For the relative density we have adopted the mean of the closely concordant values of ROSCOE, LANDOLT, OUDEMANS, and ZANDER, viz., $d\,(0°/0°) = 1·0711$, and for the thermal expansion the mean of the formulæ given by KOPP and ZANDER :

$$V = 1 + {·0_2}106001t + {·0_6}15479t^2 + {·0_7}102597t^3.$$

Taking

$$\eta_1 = ·010252 \qquad \eta_3 = ·004062 \qquad \eta_2\ (\text{calculated}) = ·006453$$
$$t_1 = 30°·86 \qquad t_3 = 112°·57 \qquad t_2\ (\text{from curve}) = 67°·12,$$

we obtain the formula

$$\eta_t = \frac{267·814}{(112·207 + t)^{2·0492}},$$

which gives values which agree closely with those obtained by observation at temperatures above 30°.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
30·86	·01025	·01025	·00000
39·88	·00903	·00905	+ ·00002
48·47	·00806	·00808	+ ·00002
57·46	·00721	·00723	+ ·00002
68·10	·00638	·00638	·00000
76·66	·00580	·00580	·00000
84·53	·00534	·00534	·00000
93·97	·00484	·00486	+ ·00002
102·89	·00445	·00445	·00000
112·57	·00406	·00406	·00000

Propionic Acid. $CH_3.CH_2.COOH$.

A sample of the pure acid received from Dr. PERKIN was distilled, and the portion boiling between 140°·52 and 140°·65 was collected separately. n = 10°·5, t = 32°·5 (emergent column). Bar. 758·1 millims. Corrected and reduced b.p. = 140°·76.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
4·54	128·66	·000026	·014076	4·86	128·62	·000026	·014008
16·83	128·61	·000031	·011504	16·91	128·52	·000031	·011508
28·19	128·87	·000036	·009790	28·23	128·80	·000036	·009785
40·04	128·96	·000041	·008387	40·05	128·85	·000041	·008399
52·04	128·71	·000047	·007280	52·02	128·57	·000047	·007297
63·60	128·81	·000052	·006423	63·67	128·69	·000052	·006423
76·35	128·87	·000058	·005644	77·05	128·77	·000058	·005604
88·94	128·88	·000066	·004989	90·19	128·79	·000066	·004939
101·04	128·49	·000071	·004478	100·99	128·39	·000071	·004481
112·98	128·43	·000077	·004034	112·98	128·32	·000077	·004033
				112·37	128·32	·000077	·004049
123·63	128·37	·000083	·003676	123·71	128·30	·000083	·003679
137·02	128·42	·000091	·003297	137·09	128·45	·000091	·003294
100·47	128·52	·000071	·004508	100·08	128·58	·000071	·004521
113·04	128·46	·000078	·004026	113·07	128·41	·000078	·004027
125·33	128·37	·000084	·003633	125·41	128·33	·000084	·003623
135·90	128·26	·000090	·003322	136·28	128·21	·000090	·003321

After the observations were finished it was discovered that a minute quantity of the mercury of the thermometer had distilled up into the vacuous space. It was considered desirable, therefore, to repeat such of the observations as might possibly have been affected by this circumstance. The repetition of all above 100° showed, however, that the distillation which had occurred was too insignificant in amount to influence the results. In all subsequent observations over 100° the thermometer was inverted and replaced in the bath just before the observation of temperature.

Observations of the thermal expansion of propionic acid have been made by KOPP ('Annalen,' 95, 309), by PIERRE and PUCHOT ('Annales de Chimie et de Phys.,' 4, 28, 71), and by ZANDER ('Annalen,' 224, 91). As the results are very concordant, the mean value of the different expressions has been employed. For the relative density we have adopted $d\,(0°/0°) = 1·0170$, the mean of the values given by KOPP, LANDOLT, LINNEMANN, and ZANDER.

Taking

$$\eta_1 = ·014042 \qquad \eta_3 = ·003295 \qquad \eta_2 \text{ (calculated)} = ·006802$$
$$t_1 = 4°·70 \qquad t_3 = 137°·05 \qquad t_2 \text{ (from curve)} = 58°·30,$$

we obtain the formula

$$\eta_t = \frac{105·746}{(109·53 + t)^{1·8840}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 4·70	·01404	·01404	·00000
16·87	·01151	.01156	+ ·00005
28·21	·00979	·00987	+ ·00008
40·04	·00839	·00845	+ ·00006
52·03	·00729	·00731	+ ·00002
63·63	·00642	·00641	— ·00001
76·70	·00562	·00559	— ·00003
89·56	·00496	·00493	— ·00003
101·01	·00448	·00444	— ·00004
112·98	·00403	·00400	— ·00003
112·37	·00405	·00402	— ·00003
123·67	·00368	·00366	— ·00002
137·05	·00329	·00329	·00000

Butyric Acid. $CH_3.(CH_2)_2.COOH$.

From Dr. PERKIN. It was found to boil at 161°·5. $n = 29°·5$, $t = 28°$ (emergent column). Bar. 759·5 millims. Corrected and reduced b.p. = 162°·02.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
3·26	128·62	·000016	·021257	3·16	128·54	·000016	·021306
18·01	128·44	·000021	·015907	18·03	128·42	·000021	·015921
31·84	128·81	·000027	·012624	31·82	128·66	·000027	·012643
44·53	128·83	·000032	·010474	44·45	128·73	·000032	·010498
59·40	128·89	·000038	·008587	59·39	128·78	·000038	·008604
73·25	128·25	·000044	·007277	73·47	128·20	·000044	·007268
86·56	128·20	·000050	·006274	86·54	128·12	·000050	·006276
101·49	128·45	·000057	·005367	101·60	128·40	·000058	·005368
115·42	128·49	·000065	·004689	115·06	128·48	·000064	·004705
130·29	128·29	·000073	·004075	130·23	128·27	·000072	·004087
144·97	128·23	·000081	·003583	144·97	128·15	·000081	·003579
155·78	128·22	·000087	·003267	155·74	128·12	·000087	·003266

The relative density of butyric acid has been frequently determined, and there seems little reason to prefer any one value to the exclusion of the others from among the concordant observations of DELFTS, PIERRE, MENDELÉEFF, LANDOLT, LINNEMANN, and BRÜHL. We have, therefore, adopted the mean of the different results, namely, $d\,(0°/0°) = 0·9786$, which is almost identical with the observations of LANDOLT and BRÜHL.

For the thermal expansion we have taken the means of the very concordant observations of PIERRE ('Annales de Chimie et de Phys.,' (3). 31, 127), and ZANDER ('Annalen,' 234, p. 91).

Taking

$$\eta_1 = ·021282 \qquad \eta_3 = ·003267 \qquad \eta_2 \text{ (calculated)} = ·003338$$
$$t_1 = 3°·21 \qquad t_3 = 155°·76 \qquad t_2 \text{ (from curve)} = 61°·87,$$

we obtain the formula

$$\eta_t = \frac{195·765}{(94·462 + t)^{1·99205}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 3·21	·02128	·02128	·00000
18·02	·01591	·01607	+ ·00016
31·83	·01263	·01276	+ ·00013
44·49	·01049	·01055	+ ·00006
59·39	·00860	·00861	+ ·00001
73·36	·00727	·00724	− ·00003
86·55	·00628	·00623	− ·00005
101·55	·00537	·00531	− ·00006
115·24	·00470	·00465	− ·00005
130·26	.00408	·00405	− ·00003
144·97	·00358	·00357	− ·00001
155·76	·00327	·00327	·00000

Isobutyric Acid. $(CH_3)_2CH.COOH$.

From Dr. PERKIN. On distillation the sample boiled between 152°·5 and 154°. $n = 23°·2$, $t = 31°$ (emergent column). Bar. 751·5 millims. Corrected and reduced b.p. = 154°·03. A second observation of the boiling-point in another apparatus gave as the boiling-point limits 152°·4 and 154°·3. $n = 23°0$, $t = 27°·5$. Bar. 746·1 millims. Corrected and reduced b.p. = 154°·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
° 3·71	128·63	·000019	·017584	° 3·68	128·58	·000019	·017626
16·97	128·60	·000024	·013827	17·04	128·50	·000024	·013830
29·31	128·55	·000029	·011379	29·36	128·47	·000029	·011365
42·54	128·37	·000035	·009450	42·52	128·30	·000035	·009456
54·31	128·61	·000040	·008123	54·77	128·56	·000040	·008096
70·48	128·57	·000047	·006729	70·51	128·53	·000047	·006756
88·08	128·72	·000055	·005592	88·04	128·64	·000055	·005605
99·07	128·57	·000061	·004977	98·82	128·54	·000061	·005004
109·56	128·36	·000066	·004512	110·00	128·35	·000066	·004496
121·04	128·33	·000072	·004057	120·90	128·27	·000072	·004074
134·52	128·55	·000080	·003608	134·48	128·48	·000080	·003610
147·56	128·39	·000087	·003223	147·77	128·28	·000087	·003231
96·49	128·61	·000060	·005119	96·43	128·56	·000060	·005118
107·71	128·57	·000065	·004602	107·54	128·49	·000065	·004606
122·16	128·58	·000073	·004027	122·50	128·49	·000073	·004012
135·37	128·55	·000080	·003588	135·47	128·48	·000080	·003582
147·21	128·57	·000087	·003244	147·45	128·47	·000087	·003239

The repetition of the observations from about 100° upwards was made in consequence of a minute quantity of the mercury of the thermometer having distilled into the vacuous space (comp. p. 511). In the second series the thermometer was inverted and replaced in position just before the observation of temperature and flow. The second set of observations lie exactly on the curve which expresses the first series; no sensible error in the determination of the temperature had therefore been made.

In reducing the observations we have employed for the thermal expansion the mean values obtained from the concordant results of PIERRE and PUCHOT ('Annales de Chim. et de Phys.,' (4) 28, 366), and of ZANDER ('Annalen,' 224, 91).

For the relative density we have adopted $d\,(0^\circ/0^\circ) = 0{\cdot}9670$, the mean of the closely agreeing values given by PIERRE and PUCHOT, LINNEMANN, BRÜHL, and MARKOWNIKOFF.

Taking

$$\eta_1 = {\cdot}017605 \qquad \eta_3 = {\cdot}003234 \qquad \eta_2 \text{ (calculated)} = {\cdot}007545$$
$$t_1 = 3^\circ{\cdot}69 \qquad t_3 = 147^\circ{\cdot}47 \qquad t_2 \text{ (from curve)} = 60^\circ{\cdot}62,$$

we obtain the formula

$$\eta_t = \frac{212{\cdot}41}{(104{\cdot}63 + t)^{2{\cdot}00595}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
3.69	·01761	·01761	·00000
17·00	·01383	·01386	+ ·00003
29·33	·01137	·01150	+ ·00013
42·53	·00945	·00952	+ ·00007
54·54	·00811	·00814	+ ·00003
70·49	·00674	·00672	— 00002
88·06	·00560	·00544	— ·00016
98·94	·00499	·00497	— ·00002
109·78	·00450	·00448	— ·00002
120·97	·00407	·00404	— ·00003
134·50	·00361	·00360	— ·00001
147·47	·00323	·00323	·00000
96·46	·00512	·00509	— ·00003
107·62	·00460	·00457	— ·00003
122·33	·00402	·00399	— 00003
135·42	·00359	·00357	— ·00002

OXIDES.

Acetic Anhydride. $(CH_3.CO)_2O$.

A large quantity of this liquid was shaken for a few minutes with phosphoric oxide and distilled. It boiled between 138°·50 and 138°·77. Bar. 749·5 millims. Corrected and reduced b.p. = 139°·13.

Observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr	η.	Temp.	Press.	Corr.	η.
°				°			
0·19	132·09	·000033	·012379	0·18	131·99	·000033	·012376
12·52	132·14	·000040	·010067	12·53	132·04	000040	·010078
24·13	132·16	·000047	·008509	24·08	132·03	·000047	·008524
35·43	132·03	·000054	·007333	35·38	131·91	·000053	·007347
48·13	132·22	·000061	·006296	48·17	132·08	·000062	·006299
60·40	132·36	·000069	·005506	60·38	132·23	·000069	·005505
71·05	132·45	·000076	·004941	71·04	132·31	·000076	·004941
84·40	132·90	·000085	·004339	84·44	132·78	·000085	·004345
95·08	133·37	·000092	·003936	95·10	133·26	·000093	·003939
108·92	131·52	·000100	·003513				
120·23	131·45	·000108	·003198	120·23	131·34	·000108	·003199
133·43	131·46	·000116	·002893	133·36	131·35	·000116	·002892

In reducing the observations we have employed KOPP's value $d\,(0°/0°) = 1{\cdot}0969$ for the relative density, and his expression

$$V = 1 + 0{\cdot}0_2 105307t + 0{\cdot}0_5 18389t^2 + 0{\cdot}0_9 79165t^3$$

for the thermal expansion ('Annalen,' 94, 295).

Taking

$$\eta_1 = {\cdot}0123774 \qquad \eta_3 = {\cdot}002893 \qquad \eta_2\,(\text{calculated}) = {\cdot}005984$$
$$t_1 = 0°{\cdot}18 \qquad t_3 = 133°{\cdot}39 \qquad t_2\,(\text{from curve}) = 52°{\cdot}64,$$

we obtain the formula

$$\eta_t = \frac{27{\cdot}713}{(97{\cdot}10 + t)^{1{\cdot}6851}},$$

which gives results in good agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·18	·01238	·01238	·00000
12·52	·01007	·01012	+ ·00005
24·10	·00852	·00856	+ ·00004
35·40	·00734	·00735	+ ·00001
48·15	·00630	·00630	·00000
60·39	·00551	·00550	− ·00001
71·04	·00494	·00492	− ·00002
84·42	·00434	·00433	− ·00001
95·09	·00394	·00393	− ·00001
108·92	·00351	·00350	− ·00001
120·23	·00320	·00319	− ·00001
133·39	·00289	·00289	·00000

Propionic Anhydride. $(CH_3.CH_2.CO)_2O$.

A quantity of this liquid, obtained from Kahlbaum, was shaken with a small quantity of phosphoric oxide for a few minutes, decanted and submitted to fractional distillation. The portion employed for the observations boiled between 168°·30 and 169°·25. Bar. 765·1 millims. Corrected and reduced b.p. = 168°·56.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·45	132·85	·000024	·015918	0·49	132·75	·000025	·015923
14·71	132·92	·000032	·012187	14·69	132·82	·000031	·012207
29·98	132·87	·000039	·009559	29·96	132·80	·000039	·009581
44·83	132·83	·000047	·007790	44·89	132·72	·000047	·007797
59·48	132·78	·000056	·006509	59·56	132·70	·000056	·006509
74·92	132·38	·000065	·005492	74·82	132·29	·000064	·005497
94·88	132·38	·000077	·004498	94·86	132·29	·000076	·004507
104·50	133·11	·000083	·004119	104·55	133·05	·000083	·004124
119·54	133·02	·000092	·003603	119·60	132·94	·000092	·003613
134·59	132·91	·000102	·003187	134·71	132·84	·000102	·003194
148·66	132·91	·000111	·002864	148·66	132·82	·000111	·002869
				164·56	132·71	·000121	·002545

In reducing the observations we have employed the value $d\,(0°/4°) = 1{\cdot}0336$ for the density, and the expression

$$V = 1 + 0{\cdot}0_{2}109109t + 0{\cdot}0_{6}38295t^{2} + 0{\cdot}0_{8}651461t^{3}$$

for the thermal expansion (Thorpe and L. M. Jones, *loc. cit.*).

Taking

$$\eta_1 = \cdot015921 \qquad \eta_3 = \cdot002867 \qquad \eta_2 \text{ (calculated)} = \cdot006755$$
$$t_1 = 0^\circ\cdot47 \qquad t_3 = 148^\circ\cdot66 \qquad t_2 \text{ (from curve)} = 56^\circ\cdot32,$$

we obtain the formula

$$\eta_t = \frac{31\cdot312}{(85\cdot011 + t)^{1\cdot7049}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·47	·01592	·01592	·00000
14·70	·01220	·01225	+ ·00005
29·97	·00960	·00960	·00000
44·86	·00780	·00780	·00000
59·52	·00651	·00650	− ·00001
74·87	·00549	·00547	− ·00002
94·87	·00450	·00449	− ·00001
104·52	·00412	·00410	− ·00002
119·57	·00361	·00360	− ·00001
134·65	·00319	·00319	·00000
148·66	·00287	·00287	·00000
164·56	·00254	·00256	+ ·00002

Ethyl Ether. $CH_3.CH_2.O.CH_2.CH_3$.

Two independent preparations of ethyl ether have been made use of in our observations on the viscosity of this substance.

The first, made specially for us by Professor DUNSTAN, after standing in contact with sodium wire for a day was distilled. It boiled completely between 34°·3 and 35°·0 ; on redistillation the greater portion boiled between 34°·5 and 34°·7. Bar. 764·3 millims. Corrected and reduced b.p. = 34°·48.

Vapour density :

Found, 36·66. Calculated, 37·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
6·74	128·48	·000094	·002664	6·64	128·43	·000094	·002671
				6·89	128·37	·000094	·002660
9·49	128·43	·000096	·002590	9·46	128·38	·000096	·002599
11·81	128·29	·000097	·002534	11·81	128·24	·000097	·002530
14·24	128·28	·000099	·002472	14·19	128·20	·000099	·002478
17·16	128·70	·000101	·002409	17·09	128·66	·000101	·002411
19·61	128·52	·000103	·002350	19·59	128·54	·000103	·002352
21·81	128·47	·000104	·002314	21·84	128·41	·000104	·002310
24·34	128·43	·000106	·002255	24·36	128·37	·000106	·002254
25·46	128·33	·000107	·002233	25·44	128·36	·000107	·002233
27·24	128·29	·000108	·002201	27·21	128·27	·000108	·002202
29·04	128·24	·000109	·002165	28·91	128·20	·000109	·002165
30·24	128·18	·000110	·002140	30·21	128·16	·000110	·002138
				32·04	128·28	·000112	·002096

In reducing the observations we have employed KOPP's value $d\,(0°/0°) = 0{\cdot}73658$ for the relative density, and his expression

$$V = 1 + 0{\cdot}0_2 148026t + 0{\cdot}0_5 350316t^2 + 0{\cdot}0_7 27007t^3$$

for the thermal expansion ('Pogg. Ann.,' 72, 1 and 223).

We are indebted for the second sample of ether to Dr. PERKIN. After standing for a night over sodium wire it was distilled; it boiled completely between 34°·8 and 35°·8. Bar. 768·0 millims. Corrected and reduced b.p. = 35°·0.

The slight difference in the boiling point of the two samples may be due to superheating. It is noteworthy that TAMMAN (Wied. 'Ann.,' 32, 683) and BECKMANN ('Zeits. f. physik. Chemie,' 4, 536), independently, found very great difficulty in obtaining ether of a constant vapour pressure.

A determination of the vapour density of Dr. PERKIN's sample gave 36·88. Calculated, 37·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·24	99·95	·000074	·002658	7·11	99·89	·000074	·002662
9·60	99·91	·000075	·002593	9·49	99·90	·000075	·002598
11·74	99·91	·000076	·002537	11·69	99·85	·000076	·002544
13·84	99·95	·000078	·002485	13·81	99·89	·000078	·002492
15·91	99·99	·000079	·002437	15·86	99·93	·000079	·002440
18·06	99·97	·000080	·002387	18·04	99·90	·000080	·002392
20·56	99·90	·000082	·002332	20·54	99·83	·000081	·002336
23·13	99·85	·000083	·002274	23·06	99·79	·000083	·002277
24·81	99·82	·000084	·002244	24·94	99·73	·000084	·002242
27·04	99·82	·000085	·002196	27·04	99·75	·000085	·002197
29·26	100·01	·000087	·002150	29·36	99·97	·000087	·002154
31·14	100·02	·000088	·002116	31·14	99·94	·000088	·002119
				20·72	128·48	·000103	·002341
21·96	128·60	·000104	·002317	21·82	128·51	·000104	·002310
26·04	128·60	·000108	·002225	26·02	128·51	·000108	·002224

In reducing the observations we have employed the same values for the density and thermal expansion as in the reduction of the first series.

Taking mean values from the two series of observations we get

$$\eta_1 = {\cdot}002664 \qquad \eta_3 = {\cdot}002128 \qquad \eta_2\ (\text{calculated}) = {\cdot}002381$$
$$t_1 = 6^\circ{\cdot}93 \qquad t_3 = 30^\circ{\cdot}68 \qquad t_2\ (\text{from curve}) = 18^\circ{\cdot}35,$$

from which we obtain the formula

$$\eta_t = \frac{3{\cdot}8307}{(136{\cdot}38 + t)^{1{\cdot}4644}},$$

which reproduces the observed values in both cases with great accuracy:—

Sample I.				Sample II.			
Mean temp.	η.		Difference.	Mean temp.	η.		Difference.
	Observed (mean).	Calc.			Observed (mean).	Calc.	
°				°			
6·69	·002668	·002670	+ ·000002	7·17	·002660	·002657	− ·000003
6·89	·002660	·002665	+ ·000005	9·54	·002595	·002594	− ·000001
9·47	·002594	·002596	+ ·000002	11·71	·002540	·002539	− ·000001
11·81	·002532	·002536	+ ·000004	13·82	·002489	·002487	− ·000002
14·21	·002475	·002477	+ ·000002	15·88	·002438	·002438	·000000
17·12	·002410	·002409	− ·000001	18·05	·002389	·002388	− ·000001
19·60	·002351	·002353	+ ·000002	20·55	·002334	·002332	− ·000002
21·82	·002312	·002305	− ·000007	23·09	·002276	·002278	+ ·000002
24·35	·002254	·002252	− ·000002	24·87	·002243	·002241	− ·000002
25·45	·002233	·002230	− ·000003	27·04	·002196	·002198	+ ·000002
27·22	·002201	·002194	− ·000007	29·31	·002152	·002154	+ ·000002
28·97	·002165	·002160	− ·000005	31·14	·002118	·002120	+ ·000002
30·22	·002139	·002137	− ·000002				
32·04	·002096	·002103	+ ·000007				

AROMATIC HYDROCARBONS.

Benzene. C_6H_6.

A sample of carefully purified and thiophen-free benzene which had stood over sodium wire for many months, was distilled. It boiled completely between 80°·04 and 80°·14. Bar. 757·4 millims. Corrected and reduced b.p. = 80°·2.

Determination of vapour density :—

Found, 38·63. Calculated, 39·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				7·64	128·12	·000040	·007889
7·71	128·21	·000040	·007881	7·65	128·10	·000040	·007889
13·44	128·07	·000043	·007169	13·49	127·98	·000043	·007175
19·39	127·84	·000047	·006539	19·39	127·99	·000047	·006550
26·01	128·06	·000051	·005943	25·91	127·97	·000051	·005950
32·06	128·10	·000055	·005469	32·09	128·02	·000055	·005471
38·54	128·37	·000060	·005013	38·41	128·30	·000060	·005029
45·36	128·35	·000065	·004615	45·34	128·24	·000064	·004616
51·69	128·34	·000069	·004284	51·64	128·27	·000069	·004286
57·36	128·34	·000073	·004016	57·39	128·26	·000073	·004017
63·29	128·37	·000077	·003766	63·29	128·30	·000077	·003767
69·41	128·28	·000081	·003534	69·41	128·22	·000081	·003537
				75·36	128·19	·000085	·003329

Observations on the thermal expansion of benzene have been made by KOPP ('Jahr.,' 1847–48, 66); LOUGUININE ('Ann. de Chimie et de Phys.,' 4, 11, 465, 1867); ADRIENZ ('Ber.,' 1873, 441); PISATI and PATERNO ('Chem. Soc. Trans.' (2), 12, 686); and LACHOWICZ ('Ber.' 21, b. 2206). As KOPP's values approximate very closely to the mean of all the other observations, they have been made use of in the reduction. His expression for the thermal expansion is

$$V = 1 + \cdot 0_2 117626t + \cdot 0_5 127755t^2 + \cdot 0_8 80648t^3.$$

We have also employed his value d (0°/0°) = 0·89911 for the density.

By taking

$\eta_1 = \cdot 0078903$ $\eta_3 = \cdot 003329$ η_2 (calculated) $= \cdot 005125$

$t_1 = 7°\cdot 67$ $t_3 = 75°\cdot 36$ t_2 (from curve) $= 36°\cdot 85$,

we obtain the formula

$$\eta_t = \frac{8\cdot8415}{(83\cdot92 + t)^{1\cdot5554}},$$

which gives results in close agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
7·67°	·007890	·007899	+ ·000009
13·46	·007172	·007178	+ ·000006
19·39	·006544	·006546	+ ·000002
25·96	·005946	·005945	− ·000001
32·07	·005470	·005464	− ·000006
38·47	·005021	·005025	+ ·000004
45·35	·004615	·004614	− ·000001
51·66	·004285	·004284	− ·000001
57·37	·004017	·004017	·000000
63·29	·003767	·003768	+ ·000001
69·41	·003535	·003536	+ ·000001
75·36	·003329	·003332	+ ·000003

Toluene (Methyl benzene). $C_6H_5.CH_3$.

We are indebted to Dr. PERKIN for the sample of this hydrocarbon which has served for our experiments. It was prepared from pure sodium parasulphonate. Placed over sodium wire and distilled, it boiled between 110°·37 and 110°·40. Bar. 756·6 millims. Corrected and reduced b.p. = 110°·56.

Determinations of its vapour density gave :—

Found, I. 46·67 ; II. 46·44. Calculated, 46·00.

The observations with the glischrometer gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
0·27°	104·23	·000034	·007648	0·25°	104·14	·000034	·007663
9·89	104·21	·000039	·006675	9·88	104·10	·000039	·006691
19·52	104·18	·000043	·005893	19·42	104·11	·000043	·005906
30·28	104·21	·000049	·005183	30·22	104·10	·000049	·005186
39·88	104·24	·000053	·004666	39·84	104·13	·000053	·004669
49·43	104·29	·000061	·004218	49·44	104·18	·000061	·004219
60·17	104·32	·000064	·003797	60·20	104·23	·000064	·003801
69·13	104·35	·000068	·003501	69·14	104·28	·000068	·003505
80·62	103·19	·000074	·003162	80·57	103·14	·000074	·003165
91·72	103·17	·000079	·002880	91·76	103·07	·000079	·002875
99·92	103·07	·000083	·002695	99·99	102·99	·000084	·002694
107·06	102·93	·000087	·002554	107·10	102·87	·000087	·002554

In reducing the observations, PERKIN'S value $d\,(4°/4°) = 0·8817$ for the relative density ('Chem. Soc. Trans.,' *loc. cit.*), and LOUGUININE'S values ('Ann. de Chim. et de Phys.,' 4, 11, 468) for the thermal expansion were adopted.

Taking

$$\eta_1 = ·007655 \qquad \eta_3 = ·002554 \qquad \eta_2 \text{ (calculated)} = ·004422,$$
$$t_1 = 0°·26 \qquad t_3 = 107°·08 \qquad t_2 \text{ (from curve)} = 44°·88,$$

we obtain the formula

$$\eta_t = \frac{18·954}{(112·99 + t)^{1·6522}},$$

which gives results in good agreement with the observed values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 0·26	·007655	·007655	·000000
9·88	·006683	·006691	+ ·000008
19·47	·005900	·005909	+ ·000009
30·25	·005184	·005193	+ ·000009
39·86	·004667	·004664	− ·000003
49·43	·004219	·004219	·000000
60·18	·003799	·003795	− ·000004
69·13	·003503	·003492	− ·000011
80·59	·003164	·003157	− ·000007
91·74	·002877	·002878	+ ·000001
99·95	·002695	·002697	+ ·000002
107·08	·002554	·002554	·000000

Ethyl Benzene. $C_6H_5.C_2H_5$.

A quantity of this hydrocarbon, obtained from KALHBAUM, was placed over sodium for a couple of days and then submitted to careful fractionation. The portion boiling between 135°·25 and 136°·25 was re-distilled, and the fraction boiling between 135°·85 and 136°·09 was collected separately and digested with sodium wire for four days and again distilled. The greater portion boiled between 136°·15 and 136°·27. Bar. 766·3 millims. Corrected and reduced b.p. = 135°·9.

Determination of its vapour density :

Found, 52·93. Calculated, 53·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·40	102·43	·000029	·008690	0·43	102·33	·000030	·008697
11·46	102·46	·000034	·007436	11·37	102·34	·000034	·007452
21·70	102·55	·000039	·006528	21·63	102·46	·000038	·006543
32·86	102·65	·000043	·005722	32·95	102·54	·000043	·005725
47·17	102·55	·000050	·004904	47·05	102·51	·000050	·004919
60·52	102·42	·000056	·004297	60·51	102·35	·000056	·004305
73·89	102·97	·000062	·003801	73·73	102·88	·000062	·003813
83·60	102·99	·000067	·003496	83·65	102·91	·000067	·003490
95·60	102·81	·000073	·003162	95·60	102·74	·000072	·003161
107·68	102·70	·000078	·002873	108·26	102·57	·000078	·002864
119·14	102·73	·000084	·002627	119·24	102·69	·000084	·002628
131·40	102·78	·000090	·002405	131·41	102·71	·000090	·002409

In reducing the observations, we have employed WEGER's expression for the thermal expansion—

$$V = 1 + \cdot 0_3 86172 t + \cdot 0_5 25344 t^2 - \cdot 0_8 18319 t^3,$$

and the relative density $d\,(0°/0°) = 0{\cdot}8832$ ('Annalen,' 221, 67).

Taking

$$\eta_1 = \cdot 008693 \qquad \eta_3 = \cdot 002407 \qquad \eta_2 \text{ (calculated)} = \cdot 004574$$

$$t_1 = 0°{\cdot}41 \qquad t_3 = 131°{\cdot}4 \qquad t_2 \text{ (from curve)} = 54°{\cdot}10,$$

we obtain the formula,

$$\eta_t = \frac{41{\cdot}215}{(121{\cdot}68 + t)^{1{\cdot}7616}},$$

by means of which the calculated values given below are obtained.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·41	·00869	·00869	·00000
11·41	·00744	·00750	+ ·00006
21·66	·00654	·00655	+ ·00001
32·90	·00572	·00576	+ ·00004
47·11	·00491	·00491	·00000
60·51	·00430	·00427	− ·00003
73·81	·00381	·00379	− ·00002
83·62	·00349	·00348	− ·00001
95·60	·00316	·00315	− ·00001
107·97	·00287	·00286	− ·00001
119·19	·00263	·00263	·00000
131·40	·00241	·00241	·00000

Ortho-xylene (Ortho-dimethyl benzene). $C_6H_4(CH_3)_2(1:2)$.

Two specimens of this hydrocarbon were employed in the determination of its viscosity. The first was prepared for us by Dr. G. T. Moody from Witte's "pure" ortho-xylene. The hydrocarbon was sulphonated with ordinary sulphuric acid, and the product converted into the barium salt, and ultimately into the sodium salt, which was then repeatedly crystallised from water. The pure sodium salt, which forms large, characteristic plates, was hydrolysed by mixing it with sulphuric acid and injecting steam into the solution. The hydrocarbon thus obtained was dried over sodium and distilled, the first and last portions of the distillate being collected apart.

The middle fraction was placed over sodium wire for about a fortnight and again distilled. It boiled between 144°·00 and 144°·08. Bar. 759·1 millims. Corrected and reduced b.p. = 144°·09.

The determination of the boiling-point was subsequently repeated. The hydrocarbon was found to boil at 144°·35 under a barometric pressure of 766·2 millims. Corrected and reduced b.p. = 144°·05.

Observation of vapour density :—

Found, 52·59. Calculated, 53·00.

The observations for viscosity gave the following results :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·45	102·78	·000024	·010927	0·54	102·65	·000024	·010928
13·87	102·70	·000029	·008805	13·89	102·62	·000029	·008814
26·53	102·96	·000034	·007379	26·55	105·25	·000035	·007386
39·35	102·95	·000040	·006279	39·32	102·85	·000040	·006284
51·92	103·00	·000046	·005437	51·97	102·89	·000045	·005441
65·40	103·02	·000051	·004728	65·42	102·94	·000052	·004735
78·78	103·14	·000058	·004156	78·79	103·03	·000058	·004159
90·82	103·22	·000063	·003726	90·82	103·13	·000063	·003733
101·80	103·38	·000068	·003403	101·76	103·35	·000068	·003403
116·49	103·40	·000076	·003023	116·74	103·31	·000075	·003015
128·33	103·44	·000081	·002762	127·98	103·31	·000081	·002769
140·99	103·44	·000087	·002519	141·29	103·35	·000087	·002515

In reducing the observations, Pinette's expression for the thermal expansion,

$$V = 1 + {\cdot}0_3 91734t + {\cdot}0_5 13245t^2 + {\cdot}0_8 19586t^3,$$

and his value for the relative density, $d\,(0°/0°) = 0{\cdot}8932$, have been employed ('Annalen,' 243, 50, 1884).

As the boiling-point of the ortho-xylene employed (144°·07) is nearly 2° higher than that usually assigned to this hydrocarbon, Dr. MOODY was good enough to prepare a second sample from the sulpho-chloride. This was reconverted into the acid by boiling with alcohol, and the acid was afterwards hydrolised. The hydrocarbon was dried over sodium wire and distilled. It boiled between 143°·75 and 144°·02. Bar. 757·6 millims. Corrected and reduced b.p. = 144°·01.

It will be observed that the boiling-point of the second sample is almost identical with that of the first.

An observation of its vapour density gave :—

Found, 52·88. Calculated, 53·00.

Observations on the viscosity of the second sample were made with the following results :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·35	103·41	·000024	·010969	0.35	103·34	·000024	·010978
13·04	103·47	·000029	·008936	12·97	103·37	·000029	·008950
26·97	103·54	·000035	·007337	26·80	103·44	·000035	·007358
38·73	103·57	·000040	·006313	38·73	103·49	·000040	·006323
51·18	103·40	·000045	·005483	51·13	103·35	·000045	·005488
65·95	103·22	·000052	·004695	65·89	103·16	·000052	·004703
77·46	103·13	·000057	·004203	77·50	103·07	·000057	·004205
90·32	103·02	·000063	·003741	90·42	102·96	·000063	·003740
100·68	102·73	·000067	·003430	100·75	102·65	·000068	·003428
115·67	102·54	·000075	·003032	115·64	102·47	·000075	·003036
128·75	102·37	·000081	·002748	128·63	102·31	·000080	·002749
139·89	102·23	·000086	·002533	139·90	102·17	·000086	·002536

In reducing the observations the same values for the relative density and thermal expansion were used as in the first series.

On plotting the results, the observations on the second sample are seen to be practically identical with those of the first. For temperatures up to 20° those of the second are about 0·1 per cent. greater than those of the first; from this point up to about 100° the curves are absolutely coincident; from 100° up to the boiling-point the observations of the second series are about 0·3 per cent. less than those of the first.

The case is interesting as showing the practical identity of the two samples, and as proving that a substance prepared in totally different ways may be obtained in a condition so closely approximating to absolute purity that the degree to which it may fall short of this ideal state is without appreciable effect on the property we are measuring.

Taking

$$\eta_1 = {}^{\cdot}010950 \qquad \eta_3 = {}^{\cdot}002526 \qquad \eta_2 \text{ (calculated) } = {}^{\cdot}005259$$
$$t_1 = 0^{\circ}{\cdot}42 \qquad t_3 = 140^{\circ}{\cdot}52 \qquad t_2 \text{ (from curve) } = 55^{\circ}{\cdot}05,$$

we obtain the expression

$$\eta_t = \frac{19{\cdot}644}{(96{\cdot}352 + t)^{1{\cdot}6386}},$$

which gives values in good agreement with those obtained by observation.

Specimen I.				Specimen II.			
Mean temp.	η.		Difference.	Mean temp.	η.		Difference.
	Observed (mean).	Calculated.			Observed (mean).	Calculated.	
°				°			
0·49	·01093	·01094	+ ·00001	0·35	·01097	·01096	– ·00001
13·88	·00881	·00885	+ ·00004	13·00	·00894	·00896	+ ·00002
26·54	·00738	·00740	+ ·00002	26·88	·00735	·00737	+ ·00002
39·33	·00628	·00629	+ ·00001	38·73	·00632	·00634	+ ·00002
51·94	·00544	·00544	·00000	51·15	·00549	·00549	·00000
65·41	·00473	·00472	– ·00001	65·92	·00470	·00469	– ·00001
78·78	·00416	·00414	– ·00002	77·48	·00420	·00419	– ·00001
90·82	·00373	·00372	– ·00001	90·37	·00374	·00373	– ·00001
101·78	·00340	·00339	– ·00001	100·71	·00343	·00342	– ·00001
116·61	·00302	·00301	– ·00001	115·65	·00303	·00303	·00000
128·15	·00276	·00276	·00000	128·69	·00275	·00275	·00000
141·14	·00252	·00252	·00000	139·89	·00254	·00254	·00000

Meta-xylene (Meta-dimethyl benzene). $C_6H_4(CH_3)_2(1:3)$.

We are indebted to Dr. Moody for a liberal supply of this hydrocarbon. It was prepared from Witte's "pure" meta-xylene. The hydrocarbon was sulphonated with ordinary sulphuric acid and the resulting sulphonic acid was recrystallised nine or ten times from a mixture of two parts of ordinary sulphuric acid and one part of water. The pure meta-acid was converted into the sodium salt which was thrice recrystallised. The pure sodium salt was reconverted into the hydrocarbon by hydrolysis with sulphuric acid and steam, dried over sodium and distilled.

On redistillation, after standing for some time over sodium wire, the meta-xylene boiled between 137°·95 and 138°·10. Bar. 744·3 millims. Corrected and reduced b.p. = 138°·8.

Determinations of its vapour density gave :

Found I. 53·36 ; II. 52·69. Calculated, 53·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·21	128·89	·000039	·007992	0·27	128·86	·000039	·007993
11·54	128·69	·000045	·006836	11·50	128·61	·000045	·006848
23·36	128·58	·000051	·005912	23·37	128·53	·000051	·005996
37·19	128·44	·000059	·005062	34·76	128·39	·000058	·005194
48·72	128·32	·000065	·004501	48·71	128·28	·000065	·004501
59·94	128·11	·000071	·004043	59·94	128·06	·000071	·004046
60·35	99·98	·000056	·004013	60·10	99·92	·000056	·004046
71·16	99·93	·000061	·003659	71·24	99·87	·000061	·003659
85·50	101·25	·000068	·003241	87·20	100·26	·000068	·003202
98·68	100·41	·000074	·002925	98·68	100·35	·000074	·002927
109·92	100·47	·000079	·002687	109·58	100·39	·000079	·002697
123·50	100·55	·000085	·002438	123·56	100·47	·000085	·002434
135·25	100·55	·000090	·002251	135·31	100·47	·000090	·002252

In reducing the observations we have employed PINETTE's value for the relative density, $d\,(0°/0°) = 0·8812$, and his expression

$$V = 1 + ·0_3 94866t + ·0_6 97463t^2 + ·0_8 51933t^3$$

for the thermal expansion ('Annalen,' 243, 51, 1884).

Taking

$\eta_1 = ·007992$ $\quad \eta_3 = ·002251$ $\quad \eta_2$ (calculated) $= ·004242$

$t_1 = 0°·24$ $\quad t_3 = 135°·28$ $\quad t_2$ (from curve) $= 54°·88$,

we obtain the formula

$$\eta_t = \frac{19·395}{(115·66 + t)^{1·6400}},$$

by means of which the calculated values given below are obtained.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·24	·00799	·00799	·00000
11·52	·00684	·00686	+ ·00002
23·36	·00595	·00593	— ·00002
35·97	·00513	·00514	+ ·00001
48·71	·00450	·00451	+ ·00001
59·94	·00404	·00404	·00000
60·27	·00403	·00403	·00000
71·20	·00366	·00365	— ·00001
86·35	·00322	·00321	— ·00001
98·68	·00293	·00292	— ·00001
109·75	·00269	·00269	·00000
123·53	·00244	·00244	·00000
135·28	·00225	·00225	·00000

Para-xylene (Para-dimethyl benzene). $C_6H_4(CH_3)_2(1:4)$.

We are indebted to Dr. Moody for a sample of this hydrocarbon. It was prepared from Kahlbaum's "pure" para-xylene; this gave on sulphonation a clean sodium salt, which was nearly, if not quite, pure. The sodium salt was re-crystallised twice, and then hydrolysed. The regenerated hydrocarbon was dried and placed in a freezing mixture. By constant stirring the solid hydrocarbon was obtained in small crystals. When about half the liquid had solidified, the crystals were separated by a filter-pump and allowed to drain for over an hour at the ordinary temperature; the crystals were then melted and distilled over sodium.

On redistillation, after standing over sodium wire for several hours, the hydrocarbon boiled between 138°·37 and 138°·67. Bar. 766·4 millims. Corrected and reduced b.p. = 138°·23.

Determination of vapour density:—

Found, 52·84. Calculated, 53·00.

An attempt was made to take the first viscosity observation at 0°·35, but although the para-xylene was liquid to begin with, it solidified shortly after starting the experiment. The crystals began to soften at about 10°, and were completely melted at 15°. After complete liquefaction the temperature was allowed to fall to about 8°, and the first observation was then made.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
8·31	104·15	·000034	·007513	8·25	104·05	·000034	·007522
20·52	104·19	·000040	·006387	20·54	104·12	·000040	·006395
31·20	104·20	·000045	·005611	31·26	104·11	·000045	·005615
41·92	104·21	·000050	·004975	41·78	104·11	·000050	·004989
53·61	104·19	·000055	·004410	53·57	104·10	·000055	·004415
64·82	104·19	·000061	·003958	64·93	104·12	·000061	·003956
77·38	104·46	·000067	·003532	77·16	104·35	·000067	·003536
88·88	104·58	·000073	·003197	88·87	104·52	·000073	·003201
100·81	104·71	·000079	·002903	100·87	104·62	·000079	·002902
111·76	104·03	·000084	·002665	111·90	103·94	·000084	·002661
123·23	104·15	·000090	·002447	123·29	104·04	·000090	·002448
135·19	104·19	·000096	·002249	135·24	104·11	·000096	·002247

In reducing the observations, Pinette's expression for the thermal expansion,

$$V = 1 + \cdot 0_3 97013t + \cdot 0_6 8714t^2 + \cdot 0_8 5287t^3,$$

and his value for the relative density, $d(0°/0°) = 0·8801$, have been employed ('Annalen,' 243, 51, 1884).

Taking

$\eta_1 = {\cdot}007517$ $\eta_3 = {\cdot}002248$ η_2 (calculated) $= {\cdot}004111$

$t_1 = 8^\circ{\cdot}28$ $t_3 = 135^\circ{\cdot}21$ t_2 (from curve) $= 60^\circ{\cdot}80$,

we obtain the formula

$$\eta_t = \frac{32{\cdot}7453}{(117{\cdot}730 + t)^{1{\cdot}7326}},$$

from which the calculated values given below are obtained :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated	
° 8·28	·00752	·00752	·00000
20·53	·00639	·00640	+ ·00001
31·23	·00561	·00562	+ ·00001
41·85	·00498	·00499	+ ·00001
53·59	·00441	·00441	·00000
64·87	·00396	00395	– ·00001
77·27	·00353	·00353	·00000
88·87	·00320	·00319	– ·00001
100·84	·00290	·00290	·00000
111·83	00267	·00266	– ·00001
123·26	·00245	·00244	– ·00001
135·21	·00225	·00225	00000

ALCOHOLS.

Methyl Alcohol. CH_3OH.

A quantity of acetone-free methyl alcohol (from KAHLBAUM) was converted into the oxalate by DITTMAR and FAWSITT's process ('Trans. Roy. Soc. Edin.,' 33, 2, 510). After standing for two months over dry potassium carbonate, the product was cohobated with quicklime, and allowed to remain in contact with fresh lime for a week. This process was repeated, and the resulting liquid was put over anhydrous copper sulphate for ten days; the alcohol, which was coloured bluish-green from the presence of a small quantity of dissolved $CuSO_4.2\,CH_3OH$ (FORCRAND, 'Compt. Rend.,' 102, 551), was siphoned off and distilled. It boiled between 65°·24 and 65°·49; $n = 25^\circ{\cdot}3$; $t = 28^\circ$ (emergent column). Bar., 771·7 millims. Corrected and reduced b.p. = 64°·96.

Vapour density :—

Found, 15·72. Calculated, 16·00.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
3·51	128·70	·000038	·007647	4·04	128·67	·000038	·007563
9·75	129·22	·000041	·006991	9·73	129·14	·000041	·006991
14·54	129·06	·000045	·006402	14·52	129·01	·000044	·006407
19·46	128·98	·000047	·005951	19·49	128·89	·000048	·005952
25·42	128·65	·000051	·005492	25·42	128·57	·000051	·005494
30·32	128·61	·000054	·005131	30·32	128·50	·000054	·005133
35·71	128·55	·000058	·004767	35·74	128·48	·000058	·004764
40·81	128·53	·000061	·004463	41·01	128·45	·000061	·004451
46·14	128·46	·000065	·004156	46·07	128·40	·000065	·004163
52·29	128·36	·000070	·003844	52·29	128·29	·000070	·003847
57·66	128·74	·000074	·003596	57·72	128·68	·000074	·003594
61·56	128·72	·000077	·003442	61·57	128·62	·000077	·003438
63·26	128·71	·000079	·003358				

In reducing the observations KOPP'S value for the relative density, $d\,(0^\circ/4^\circ) = 0{\cdot}81796$, and his expression for the thermal expansion ('Jahresbericht,' 1847, 66) were employed. There is, however, reason to believe that the methyl alcohol employed by KOPP was not wholly free from water, in spite of the care employed in its preparation. We, therefore, recalculated the value of the kinetic energy correction by means of the more recent determinations of the relative density and expansion of methyl alcohol given by DITTMAR and FAWSITT, but found that the coefficients were not affected within the limits of experimental error.

Taking

$$\eta_1 = {\cdot}007605 \qquad \eta_3 = {\cdot}003440 \qquad \eta_2 \text{ (calculated)} = {\cdot}005115$$
$$t_1 = 3^\circ{\cdot}77 \qquad t_3 = 61^\circ{\cdot}36 \qquad t_2 \text{ (from curve)} = 30^\circ{\cdot}53,$$

we obtain the formula

$$\eta_t = \frac{6940{\cdot}8}{(163{\cdot}93 + t)^{2{\cdot}6793}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
3·77	·00761	·00761	·00000
8·74	·00699	·00703	+ ·00004
14·53	·00641	·00644	+ ·00003
19·47	·00595	·00598	+ ·00003
25·42	·00549	·00549	·00000
30·32	·00513	·00513	·00000
35·72	·00477	·00477	·00000
40·91	·00446	·00445	− ·00001
46·10	·00416	·00416	·00000
52·29	·00385	·00383	− ·00002
57·69	·00360	·00360	·00000
61·56	·00344	·00344	·00000
63·26	·00336	·00337	+ ·00001

Ethyl Alcohol. $CH_3.CH_2OH$.

A quantity of "pure" absolute alcohol was boiled with quicklime for eight hours in a reflux condenser, and decanted on to fresh lime, over which it was allowed to stand for about a month, again decanted and distilled from freshly burnt lime. It boiled constantly at 78°·24. Bar. 748·9 millims. Corrected and reduced b.p. = 78°·63.

Vapour density:

Found, 22·70. Calculated, 23·00.

The observations for viscosity gave:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
7·19	128·55	·000019	·015318	7·14	128·46	·000019	·015338
13·21	128·66	·000021	·013570	13·26	128·58	·000021	·013577
19·24	128·64	·000023	·012096	19·21	128·57	·000023	·012093
25·24	128·66	·000026	·010787	25·24	128·56	·000026	·010798
31·89	128·58	·000029	·009556	31·89	128·53	·000029	·009564
37·49	128·53	·000032	·008646	37·54	128·46	·000032	·008643
42·84	128·47	·000035	·007878	42·84	128·39	·000035	·007872
49·39	128·41	·000038	·007049	49·34	128·36	·000038	·007046
55·56	128·30	·000042	·006351	55·59	128·21	·000042	·006358
61·14	127·97	·000046	·005806	61·01	127·93	·000046	·005825
67·51	128·35	·000050	·005252	67·59	128·31	·000050	·005253
73·59	128·51	·000055	·004758	73·56	128·30	·000055	·004771

The observations were reduced by means of KOPP'S values for the density $d\,(0^\circ/4^\circ) = 0{\cdot}8095$, and his expression for the thermal expansion

$$V = 1 + {\cdot}0_2104139t + {\cdot}0_67836t^2 + {\cdot}0_717618t^3$$

('Jahresbericht,' 1847, 66).

Taking

$$\eta_1 = {\cdot}015328 \qquad \eta_3 = {\cdot}004764 \qquad \eta_2\,(\text{calculated}) = {\cdot}009545$$
$$t_1 = 7^\circ{\cdot}16 \qquad t_3 = 73^\circ{\cdot}57 \qquad t_2\,(\text{from curve}) = 38^\circ{\cdot}15,$$

we obtain the formula

$$\eta_t = \frac{251908000{\cdot}0}{(209{\cdot}63 + t)^{4{\cdot}3731}},$$

which gives the following calculated values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 7·16	·015328	·015328	·000000
13·23	·013573	·013584	+ ·000011
19·22	·012094	·012097	+ ·000003
25·24	·010792	·010798	+ ·000006
31·89	·009560	·009557	— ·000003
37·51	·008644	·008642	— ·000002
42·84	·007875	·007872	— ·000003
49·37	·007047	·007041	— ·000006
55·57	·006354	·006349	— ·000005
61·07	·005815	·005804	— ·000011
67·55	·005253	·005233	— ·000020
73·57	·004764	·004764	·000000

Propyl Alcohol. $CH_3.CH_2.CH_2OH$.

Received from Dr. PERKIN. After standing over anhydrous copper sulphate for some time it was distilled. It boiled between 95°·5 and 96°·5, $n = 51^\circ$, $t = 29^\circ{\cdot}5$ (emergent column). Bar. 755·9 millims. Corrected and reduced b.p. = 96°·6.

Determinations of vapour density :—

Found, I., 29·51 ; II., 29·44. Calculated, 30·00.

Observations for viscosity :—

Left limb.				Right Limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·40	128·58	·000009	·031362	7·22	128·49	·000009	·031542
15·06	128·63	·000011	·025547	15·07	128·52	·000011	·025561
22·90	128·62	·000014	·020986	22·81	128·52	·000014	·021043
30·77	128·90	·000016	·017344	30·89	128·80	·000016	·017304
31·04	128·89	·000016	·017230	31·01	128·84	·000016	·017258
38·79	128·47	·000019	·014372				
38·81	128·86	·000020	·014373	38·76	128·78	·000019	·014433
46·45	128·82	·000023	·012180	46·49	128·74	·000023	·012184
54·31	128·94	·000027	·010292	54·36	128·86	·000027	·010300
61·74	128·93	·000031	·008875	61·74	128·87	·000031	·008884
69·04	128·46	·000035	·007706	69·04	128·44	·000035	·007712
76·78	128·20	·000040	·006658	76·73	128·17	·000040	·006666
84·90	128·11	·000046	·005752	84·74	128·04	·000046	·005772
93·09	128·17	·000052	·004984	93·11	128·10	·000052	·004995
95·59	128·24	·000054	·004771				

Observations on the relative density and thermal expansion of propyl alcohol have been made by PIERRE and PUCHOT ('Annales de Chim. et de Phys.,' (4), 22, 276), and by ZANDER ('Annalen,' 214, 154). The observations are not in very good agreement. As there seemed to be doubt as to the individuality of the specimen of alcohol employed by PIERRE and PUCHOT, the numbers given by ZANDER have been adopted, viz. :—

$$V = 1 + \cdot0_3 74601t + \cdot0_5 49478t^2 + \cdot0_7 13929t^3.$$

We have also employed his value d (0°/0°) = 0·8177 for the relative density. It happens to be the mean of the observations of BRÜHL and LINNEMANN.

Taking

$$\eta_1 = \cdot031452 \qquad \eta_3 = \cdot004990 \qquad \eta_2 \text{ (calculated)} = \cdot012527$$
$$t_1 = 7^\circ\cdot31 \qquad t_3 = 93^\circ\cdot10 \qquad t_2 \text{ (from curve)} = 45^\circ\cdot19,$$

we obtain the formula

$$\eta_t = \frac{8801350\cdot0}{(135\cdot75 + t)^{3\cdot9188}},$$

which gives the following observed values :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
7·31	·03145	·03144	− ·00001
15·06	·02555	·02556	+ ·00001
22·86	·02101	·02098	− ·00003
30·83	·01732	·01731	− ·00001
31·02	·01724	·01724	·00000
38·79	·01440	·01442	+ ·00002
46·47	·01218	·01218	·00000
54·33	·01030	·01032	+ ·00002
61·74	·00888	·00889	+ ·00001
69·04	·00771	·00771	·00000
76·75	·00666	·00667	+ ·00001
84·82	·00576	·00576	·00000
93·10	·00499	·00499	·00000
95·59	·00477	·00478	+ ·00001

Isopropyl Alcohol. $(CH_3)_2$ CHOH.

A quantity of isopropyl alcohol from KAHLBAUM was heated in a sealed tube with caustic baryta at 100°. A crystalline alcoholate separated out on cooling. This, together with the residual alcohol, was heated over a steam-bath and the product re-distilled and dried. It boiled between 82°·4 and 83°·4. Bar. 754·4 millims. Corrected and reduced b.p. = 82°·9.

Vapour density :

Found, 29·38. Calculated, 30·00.

As the liquid was very viscid at low temperatures, and as the times of flow were therefore comparatively great (about 42 mins. at 0°·4), duplicate observations were not made below 66°. The observations for viscosity are as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
0·44	130·28	·000006	·044861	0·28	130·44	·000006	·045174
7·21	130·55	·000008	·035568				
				14·41	130·53	·000010	·028157
22·22	130·73	·000013	·022204				
				30·55	130·65	·000016	·017275
37·92	130·42	·000020	·014053				
				45·15	130·29	·000024	·011604
51·97	130·43	·000028	·009771				
				59·39	130·38	·000033	·008157
66·61	130·59	·000038	·006921	66·60	130·53	·000038	·006925
72·04	130·58	·000043	·006138	72·01	130·50	·000043	·006144
78·10	130·59	·000048	·005409	78·08	130·51	·000048	·005405

The observations have been reduced by means of ZANDER's values for the relative density at 0°, 0·7996, and his expression for the thermal expansion,

$$V = 1 + \cdot0_2 10534t + \cdot0_6 4430t^2 + \cdot0_7 27274t^3$$

('Annalen,' 214, 154).

Two formulæ are required to reproduce the values with sufficient accuracy. The first extends from 0° to 40°, the second from 40° to 78°.

They are respectively as follows:

$$\text{I.}\ \eta_t = \frac{2175320000\cdot0}{(141\cdot72 + t)^{4\cdot9635}}, \qquad \text{II.}\ \eta_t = \frac{192398\cdot0}{(86\cdot259 + t)^{3\cdot4079}}.$$

The agreement between the observed and calculated values is seen in the following table:—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·36	·045018	·045018	·000000
7·21	·035568	·035635	+ ·000067
14·41	·028157	·028191	+ ·000034
22·22	·022204	·022126	− ·000078
30·55	·017275	·017301	+ ·000026
37·92	·014053	·014053	·000000
45·15	·011604	·011589	− ·000015
51·97	·009770	·009753	− ·000017
59·39	·008157	·008161	+ ·000004
66·60	·006923	·006938	+ ·000015
72·02	·006141	·006147	+ ·000006
78·09	·005407	·005407	·000000

Butyl Alcohol. $CH_3.(CH_2)_2.CH_2OH$.

A quantity of the alcohol obtained from KAHLBAUM was dehydrated by caustic baryta. It boiled between 117°·25 and 117°·90. Bar. 764·6 millims. Corrected and reduced b.p. = 117°·42.

Vapour density:

Found, I., 36·02; II., 36·13. Calculated, 37·00.

As the alcohol is rather viscous at low temperatures, the time of flow at 0°·27 being nearly 50 minutes, single observations only were made up to 83°. The results are as follows:—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				0·27	130·28	·000006	·051539
10·69	130·68	·000008	·037958				
				21·83	130·65	·000010	·028017
31·73	130·33	·000013	·021718				
				42·91	130·30	·000017	·016611
52·17	130·47	·000021	·013438				
				61·99	130·46	·000026	·010903
72·24	130·69	·000031	·008860				
83·11	130·77	·000038	·007184	83·15	130·66	·000038	·007182
94·86	130·50	·000046	·005817	94·90	130·43	·000046	·005817
102·98	130·69	·000052	·005094	102·94	130·57	·000052	·005099
114·08	130·91	·000061	·004259	114·14	130·80	·000061	·004259

In the reduction of the observations we have employed ZANDER's value, 0·8233, for the density at 0°, and his expression

$$V = 1 + \cdot 0_3 83751t + \cdot 0_5 28634t^2 - \cdot 0_8 12415t^3$$

for the thermal expansion ('Annalen,' 224, 80).

Two formulæ are required to reproduce the values with sufficient accuracy. The first extends from 0° to 52°, the second from 52° to 114°.

They are respectively as follows :—

$$\text{I.}\ \eta_t = \frac{65187500 \cdot 0}{(139 \cdot 05 + t)^{4 \cdot 2452}}, \qquad \text{II.}\ \eta_t = \frac{117255 \cdot 0}{(91 \cdot 997 + t)^{3 \cdot 2150}}.$$

The agreement between the observed and calculated values is seen in the following table :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·27	·051539	·051562	+ ·000023
10·69	·037957	·037961	+ ·000004
21·83	·028016	·027992	− ·000024
31·73	·021718	·021724	+ ·000006
42·91	·016611	·016597	− ·000014
52·17	·013438	·013438	·000000
61·99	·010903	·010872	− ·000031
72·24	·008860	·008838	− ·000022
83·13	·007183	·007190	+ ·000007
94·88	·005817	·005835	+ ·000018
102·96	·005096	·005092	− ·000004
114·11	·004259	·004259	·000000

Isobutyl Alcohol. $(CH_3)_2CH.CH_2OH$.

A sample received from Dr. PERKIN was placed over anhydrous copper sulphate for a month, decanted, and distilled. It boiled between 107°·02 and 107°·42 (therm. 567). Bar. 749·8 millims. Corrected and reduced b.p. = 107°·6.

Vapour density :

Found, 36·30. Calculated, 37·00.

As the liquid is very viscous at low temperatures, the time of flow at 0°·45 being more than 77 minutes, only single observations were made in this series.

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
9·90	129·65	·000005	·055735	0·45	129·30	·000004	·079111
27·82	130·19	·000009	·030641	38·38	129·86	·000013	·022263
47·44	130·01	·000016	·017217	56·59	129·96	·000021	·013502
65·95	129·96	·000025	·010697	74·61	128·64	·000031	·008748

The sample was redistilled nearly two years after the first series of observations, and a second series taken. The alcohol was now found to boil between 107°·5 and 108°·0 (therm. 1518). Bar. 769·1 millims. Corrected and reduced b.p. = 107°·5. This result agrees almost exactly with that first obtained.

The following observations were made in the glischrometer :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				27·72	129·94	·000010	·030675
37·94	130·27	·000013	·022522				
				56·48	129·40	·000021	·013571
83·95	129·61	·000038	·007173				
93·90	129·04	·000046	·005854	93·81	128·96	·000046	·005874
105·07	128·84	·000070	·004751	105·08	128·72	·000070	·004755

In reducing the observations the density and values for the relative volumes at different temperatures given by PIERRE and PUCHOT ('Ann. de Chim. et de Phys.,' (4), 22, 306) were employed.

On plotting the two series of observations they are found to lie on exactly the same curve. This agreement shows (1) that the sample was uniform in character, and that it had suffered no change during the two years; and (2) that the dimensions of the glischrometer had experienced no appreciable alteration during the same period, although it must have been washed and dried, heated and cooled, many hundreds of times during the interval.

Three formulæ of the SLOTTE type are required to reproduce the values with even approximate accuracy. The first extends from 0° to 38°, the second from 38° to 75°, the third from 75° to 105°.

They are respectively as follows:—

$$\text{I. } \eta_t = \frac{1486370{\cdot}0}{(92{\cdot}248 + t)^{3{\cdot}6978}}, \qquad \text{II. } \eta_t = \frac{1112440{\cdot}0}{(86{\cdot}751 + t)^{3{\cdot}6708}}, \qquad \text{III. } \eta_t = \frac{29790{\cdot}3}{(63{\cdot}14 + t)^{3{\cdot}0537}}.$$

The agreement between the observed and calculated values is seen in the following table:—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·45	·079111	·079111	·000000
9·90	·055735	·055250	—·000485
19·01	·039779	·040285	+·000506
27·77	·030658	·030439	—·000219
38·16	·022392	·022392	·000000
47·44	·017217	·017212	—·000005
56·48	·013571	·013549	—·000022
56·59	·013502	·013511	+·000009
65·95	·010697	·010711	+·000014
74·61	·008748	·008748	·000000
83·95	·007173	·007160	—·000013
93·85	·005864	·005868	+·000004
105·07	·004753	·004753	·000000

Trimethyl Carbinol. $(CH_3)_3COH$.

A sample of this substance received from Dr. PERKIN, which had been distilled with baryta and kept in a fused state over anhydrous copper sulphate for six to seven weeks, was distilled. It boiled between 81°·83 and 82°·33. Bar. 756·1 millims. Corrected and reduced b.p. = 82°·25.

Determinations of its vapour density showed that the sample was probably still imperfectly dehydrated.

	I.	II.
Weight of liquid . . .	0·0329 grms.	0·0572 grms.
Volume of vapour . . .	65·77 cub. centims.	81·42 cub. centims.
Temperature	100°·12	100°·12
Pressure	166·6 millims.	233·0 millims.

Found, I. = 34·62; II. = 34·97. Calculated 37·00.

Unfortunately the quantity of the substance at our disposal was insufficient to enable us to submit it to further dehydration.

The observations for viscosity were as follows :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				22·41	130·67	·000005	·058877
27·47	130·93	·000006	·045505				
				32·08	129·21	·000010	·030047
37·22	129·32	·000012	·023676				
				42·41	129·26	·000015	·019094
47·82	129·27	·000018	·015501				
				52·99	129·25	·000021	·012961
57·94	129·24	·000025	·010976				
				62·09	129·25	·000028	·009678
				68·35	129·67	·000033	·008102
73·47	129·50	·000038	·007058	73·47	129·45	·000038	·007057
77·07	129·37	·000041	·006448	77·03	129·32	·000041	·006447

As the time of flow, especially at the low temperatures, was so considerable (at 22°·41 it was nearly 57 minutes), only single observations were made up to 73°·47.

In reducing the observations, the relative density $d(25°/25°) = 0·7836$, given by PERKIN ('Chem. Soc. Trans.,' 45, 469), which gives $d(0°/4°) = 0·8072$, and the expression

$$V = 1 + \cdot 0_{2}13126t - \cdot 0_{6}88155t^{2} + \cdot 0_{7}36121t^{3}$$

(THORPE and JONES, *loc. cit.*) for the thermal expansion, have been employed.

Two formulæ are required to reproduce the values with sufficient accuracy. The first extends from 20° to 50°, and the second from 50° to 77°.

They are, respectively, as follows :—

$$\text{I. } \eta_t = \frac{2\cdot 05152}{(-7\cdot 803 + t)^{1\cdot 3242}}, \qquad \text{II. } \eta_t = \frac{46\cdot 3090}{(5\cdot 077 + t)^{2\cdot 0143}}.$$

The agreement between the observed and calculated values is seen in the following table :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
22·41	·058876	·058876	·000000
32·08	·030047	·030045	—·000002
37·22	·023676	·023298	—·000378
42·41	·019094	·018788	—·000306
47·82	·015501	·015501	·000000
52·99	·012961	·012961	·000000
57·94	·010976	·010992	+·000016
62·09	·009678	·009667	—·000011
68·35	·008102	·008079	—·000023
73·47	·007057	·007053	—·000004
77·05	·006447	·006447	·000000

Amyl Alcohol (optically active). $CH_3.CH_2.CH(CH_3).CH_2OH$.

We are indebted to Mr. J. E. MARSH, Oxford, for the specimen of optically active amyl alcohol which has served for our observations. Its rotatory power for sodium light was — 7° 34′ for 20 centims. at 10°. It was placed over fused potassium carbonate for 18 days, and after decantation from the carbonate was distilled. It boiled between 127°·25 and 129°·25. Bar. 751·8 millims. Corrected and reduced b.p. = 128°·7.

Vapour density :—

Found, 43·46. Calculated, 44·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				0·40	130·35	·000003	·109672
11·63	130·45	·000004	·069581				
				23·30	130·30	·000007	·045372
34·75	129·85	·000010	·030788				
				47·40	129·73	·000014	·020880
56·94	129·82	·000018	·015956				
				67·52	129·76	·000024	·012183
79·25	129·95	·000031	·009254				
				91·88	129·87	·000031	·007075
100·03	130·09	·000046	·006033				
112·79	130·13	·000056	·004814	112·78	130·02	·000056	·004824
124·40	130·16	·000066	·004003	124·32	130·07	·000066	·004013

The time of flow of this alcohol at low temperatures is so great—at 0°·40 it was over 106 minutes—that only single observations were taken up to 112°·78.

In reducing the observations we employed PERKIN'S value, $d\,(15°/15°) = 0·81495$, for the relative density, which gives $d\,(0°/4°) = ·8330$, and for the thermal expansion the expression

$$V = 1 + ·0_{3}89023t + ·0_{5}114376t^{2} + ·0_{7}10170t^{3}$$

(THORPE and JONES, *loc. cit.*).

Three formulæ are required to reproduce the values with sufficient accuracy. The first extends from 0° to 35°, the second from 35° to 73°, the third from 73° to 124°.

They are respectively as follows :—

$$\text{I. } \eta_t = \frac{66652700·0}{(101·51 + t)^{4·3736}}, \quad \text{II. } \eta_t = \frac{97413·3}{(64·67 + t)^{3·2542}}, \quad \text{III. } \eta_t = \frac{71·8436}{(7·838 + t)^{2·0050}}.$$

The agreement between the observed and calculated values is seen in the following tables :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·40	·109672	·109811	+ ·000139
11·63	·069581	·069517	− ·000064
23·30	·045372	·045253	− ·000119
34·75	·030788	·030788	·000000
47·40	·020880	·020850	− ·000030
56·94	·015956	·015983	+ ·000027
67·52	·012183	·012183	·000000
79·25	·009254	·009264	+ ·000010
91·88	·007075	·007061	− ·000014
100·03	·006033	·006032	− ·000001
112·78	·004819	·004821	+ ·000002
124·36	·004008	·004012	+ ·000004

Amyl Alcohol (optically inactive). $(CH_3)_2CH.CH_2.CH_2OH$.

Two samples of optically inactive amyl alcohol have served for our observations. For the first we are indebted to Dr. PERKIN. It was a portion of that prepared by Professor PEDLER by PASTEUR'S method of fractional crystallisation from the various sulphamylates ('Chem. Soc. Trans.,' vol. 6, p. 74, 1868). When tested in a LAURENT'S polarimeter with monochromatic sodium light it was found to be quite inactive.

It was placed over anhydrous copper sulphate for three weeks, and distilled. It boiled between 131°·15 and 131°·35. Bar. 759·4 millims. Corrected and reduced b.p. 131°·29.

Vapour density :—

Found, I. 42·17 ; II. 42·31. Calculated, 44·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				0·39	129·76	·000004	·086402
11·40	129·96	·000005	·058225				
				23·70	129·34	·000008	·039222
34·67	129·44	·000010	·028239				
				45·90	129·44	·000014	·020719
57·72	129·63	·000019	·015303				
69·70	129·48	·000025	·011582				
				81·69	129·75	·000031	·008925
92·17	129·87	·000038	·007240				
				102·97	130·22	·000046	·005942
115·53	130·30	·000056	·004804				
125·64	130·30	·000064	·004107	125·68	130·24	·000064	·004101

On account of the length of time of flow (about 84 minutes at 0°·39) only single observations were made except at about 125°, when duplicate readings were taken in both limbs. In reducing the observations we have used the value $d\,(0^\circ/4^\circ) = {\cdot}8254$ for the density, and the expression

$$V = 1 + {\cdot}0_3 92410 t + {\cdot}0_6 264281 t^2 + {\cdot}0_7 13486 t^3$$

for the thermal expansion (THORPE and JONES, *loc. cit.*).

The second sample of inactive amyl alcohol was prepared for us by Mr. GREEVES in the laboratory of the Royal College of Science, by PASTEUR'S method. When examined in the Soleil-Duboscq Polarimeter with a sodium flame, not the least indication of rotation was apparent.

It was carefully dehydrated by copper sulphate and distilled, when it was found to boil almost constantly between 131°·50 and 131°·55. Bar. 762·0 millims. Corr. and red. b.p. = 131°·44.

Vapour density :

Found, 44·18. Calculated, 44·00.

The observations for viscosity gave :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				0·24	130·82	·000004	·084610
11·91	131·35	·000005	·056249				
				23·83	130·71	·000008	·038633
34·25	130·99	·000011	·028303				
				47·66	130·67	·000015	·019654
58·74	130·88	·000020	·014847				
				71·05	130·94	·000026	·011210
81·87	131·35	·000032	·008888				
94·95	131·54	·000041	·006870	94·93	131·42	·000041	·006874
104·57	130·30	·000047	·005791	104·58	130·22	·000047	·005798
117·66	130·20	·000058	·004645	117·54	130·11	·000057	·004663
128·15	130·24	·000066	·003970	128·06	130·15	·000066	·003979

In reducing the observations the same values for the density and thermal expansion were used as in the case of the first sample.

The results of the two series of observations show that the samples were not absolutely identical in character, although the general form of the curves is almost the same. From 0° up to about 80° the first sample is more viscous than the other. At 0° the difference amounts to about 2·5 per cent., this gradually diminishes up to about 80° when the curves cross; above 80° the first sample is slightly less viscous than the other, the extreme difference being about 1 per cent. at the boiling point.

These differences may possibly be owing to the presence of a minute quantity of water in the first sample, which seemed moreover to be indicated by its lower vapour density and boiling-point. We prefer, therefore, to adopt the values afforded by the second sample as expressing the true viscosity of the inactive alcohol prepared by PASTEUR'S method.

Three formulæ, given by the observations on the second sample, are required to reproduce the values with sufficient accuracy. The first extends from 0° to 40°, the second from 40° to 80°, the third from 80° to 128°. They are, respectively, as follows:—

$$\text{I. } \eta_t = \frac{77360200{\cdot}0}{(117{\cdot}79 + \ )^{4{\cdot}3249}}, \qquad \text{II. } \eta_t = \frac{211442{\cdot}0}{(79{\cdot}872 + t)^{3{\cdot}3395}}, \qquad \text{III. } \eta_t = \frac{1156{\cdot}78}{(37{\cdot}682 + t)^{2{\cdot}4618}}.$$

The agreement between the observed and calculated values is seen in the following tables:—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
0°·24	·084610	·084610	·000000
11·91	·056249	·056276	+ ·000027
23·83	·038633	·038475	− ·000158
34·25	·028303	·028303	·000000
47·66	·019654	·019654	·000000
58·74	·014847	·014881	+ ·000034
71·05	·011210	·011200	− ·000010
81·87	·008888	·008888	·000000
94·94	·006872	·006885	+ ·000013
104·57	·005795	·005793	− ·000002
117·60	·004654	·004669	+ ·000015
128·10	·003974	·003974	·000000

Dimethyl Ethyl Carbinol. $(CH_3)_2C(OH).CH_2.CH_3$.

Received from Dr. PERKIN. After standing over dehydrated copper sulphate for five months it was found to boil between 101°·62 and 102°·52. Bar. 766·9 millims. Corrected and reduced b.p. = 101°·81.

Two determinations of its vapour density gave the following results :—

	I.	II.
Weight of liquid	0·0478 grm.	0·0476 grm.
Volume of vapour	75·02 c.c.	74·36 c.c.
Temperature	99°·18	99°·22
Pressure	179·8 millims.	179·0 millims.

Found, I. 41·00 ; II. 41·37. Calculated, 44·00.

In spite of the prolonged treatment with copper sulphate the liquid was evidently not completely dehydrated.

The observations for viscosity gave the following results :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
				0·49	128·79	·000002	·137969
9·31	129·15	·000004	·082034				
				18·48	128·73	·000006	·049978
27·24	128·86	·000009	·033643				
				36·42	128·79	·000013	·023322
45·05	128·87	·000017	·017135				
				53·18	128·79	·000022	·013199
62·95	128·87	·000028	·009943				
71·91	129·08	·000035	·007931				
				81·06	128·95	·000043	·006400
89·94	129·09	·000051	·005301				
95·69	129·18	·000056	·004722	95·72	129·08	·000056	·004714
				96·70	128·98	·000057	·004643

In reducing the observations we have taken PERKIN'S value $d\ (15°/15°) = \cdot 8144$ for the relative density ('Chem. Soc. Trans.,' 45, 471), which gives $d\ (0°/4°) = \cdot 8269$, and the expression

$$V = 1 + \cdot 0_2 10661 t + \cdot 0_5 17643 t^2 + \cdot 0_7 14119 t^3$$

(THORPE and JONES, *loc. cit.*) for the thermal expansion.

Three formulæ are required to reproduce the values with approximate accuracy. The first extends from 0° to 27°, the second from 27° to 63°, the third from 63° to 95°. They are respectively as follows :—

$$\text{I. } \eta_t = \frac{35091\cdot 0}{(47\cdot 922 + t)^{3\cdot 2081}}, \quad \text{II. } \eta_t = \frac{3255\cdot 20}{(37\cdot 007 + t)^{2\cdot 7578}}, \quad \text{III. } \eta_t = \frac{2159\cdot 86}{(38\cdot 340 + t)^{2\cdot 6611}}.$$

The agreement between the observed and calculated values is seen in the following table :—

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
°			
0·49	·137969	·137969	·000000
9·31	·082034	·080650	− ·001384
18·48	·049978	·050067	+ ·000089
27·24	·033643	·033643	·000000
36·42	·023322	·023278	− ·000044
45·05	·017135	·017133	− ·000002
53·18	·013199	·013204	+ ·000005
62·95	·009943	·009943	·000000
71·91	·007931	·007935	+ ·000004
81·06	·006400	·006418	+ ·000018
89·94	·005301	·005303	+ ·000002
95·70	·004718	·004718	·000000
96·70	·004643	·004625	− ·000018

Allyl Alcohol. $CH_2:CH.CH_2OH$.

A portion of a sample received from Dr. PERKIN. It was carefully dehydrated by lime. On distillation it boiled between 95°·74 and 96°·64, $n = 51°$, $t = 30°$ (emergent column). Bar. 764·6 millims. Corrected and reduced b.p. = 96°·4. This number agrees closely with that previously found for this substance by one of us, viz., 96°·6 (THORPE, 'Chem. Soc. Trans.,' 1880, 210).

Vapour density :

Found, 28·41. Calculated, 29·00.

Observations for viscosity :—

Left limb.				Right limb.			
Temp.	Press.	Corr.	η.	Temp.	Press.	Corr.	η.
°				°			
7·49	128·22	·000017	·018065	7·34	128·14	·000017	·018139
15·31	128·22	·000020	·015079	15·31	128·12	·000020	·015084
22·76	128·25	·000023	·012842	22·86	128·16	·000023	·012819
30·49	128·14	·000027	·010959	30·51	128·08	·000027	·010953
38·04	128·22	·000031	·009463	38·06	128·12	·000031	·009456
46·41	128·00	·000036	·008096	46·31	127·93	·000036	·008126
54·14	128·37	·000041	·007067	54·06	128·37	·000041	·007096
60·71	128·06	·000045	·006337	60·84	128·06	·000045	·006329
68·84	128·66	·000051	·005565	68·89	128·67	·000051	·005582
76·79	128·30	·000057	·004922	76·84	128·25	·000057	·004927
84·54	128·22	·000063	·004388	84·46	128·14	·000063	·004402
92·14	128·12	·000069	·003945	92·39	128·05	·000069	·003936
				95·24	127·99	·000072	·003792

The observations have been reduced by means of the value $d\,(0°/4°) = 0{\cdot}8699$ and the expression

$$V = 1 + \cdot0_3 99371t + \cdot0_6 599861t^2 + \cdot0_7 12285t^3$$

(THORPE, *loc. cit.*).

Taking

$$\eta_1 = \cdot018102 \qquad \eta_3 = \cdot003941 \qquad \eta_2 \,(\text{calculated}) = \cdot008446,$$
$$t_1 = 7°{\cdot}41 \qquad t_3 = 92°{\cdot}26 \qquad t_2 \,(\text{from curve}) = 44°{\cdot}08,$$

we obtain the formula

$$\eta_t = \frac{10748{\cdot}4}{(109{\cdot}42 + t)^{2{\cdot}7925}},$$

which gives numbers in good agreement with the observed values.

Mean temp.	η.		Difference.
	Observed (mean).	Calculated.	
° 7·41	·01810	·01810	·00000
15·31	·01508	·01508	·00000
22·81	·01283	·01281	– ·00002
30·50	·01096	·01094	– ·00002
38·05	·00946	·00945	– ·00001
46·36	·00811	·00811	·00000
54·10	·00708	·00708	·00000
60·77	·00633	·00633	·00000
68·86	·00557	·00556	– ·00001
76·81	·00492	·00492	·00000
84·50	·00440	·00440	·00000
92·26	·00394	·00394	·00000
95·24	·00379	·00378	– ·00001

PART III.—DISCUSSION OF RESULTS.

INTRODUCTION.

Before proceeding to the discussion of the results obtained, it may be advisable to indicate briefly the factors upon which the magnitude of the viscosity may probably depend.

Unlike several of the properties which have been investigated from a physico-chemical point of view, viscosity depends essentially on the forces in play between molecules—it is the result of extra-molecular actions. It has long been conjectured that the fundamental molecules of some liquids, at least, are really congeries of gaseous molecules. NAUMANN, from the boiling-points of isomers; RAMSAY and YOUNG from the variations of saturated vapour densities; GUYE and YOUNG from critical densities, and others, have given evidence in favour of this conclusion. The most significant contribution to the subject, however, was made as long ago as 1886, by EÖTVÖS ('Wied. Ann.,' 27, 452). He was able to show that for many liquids the rate of change of molecular surface energy with temperature was independent of the temperature and of the chemical nature of the liquids ; whereas for other liquids, like water, the fatty alcohols and the fatty acids, this was no longer the case. EÖTVÖS attempted to show theoretically that to the former class belonged substances for which the complexity of the liquid molecule was the same as that of the gaseous molecule, while to the latter class belonged substances for which the complexity of the liquid molecule was the greater. He also indicated how the degree of complexity at any temperature might be ascertained.

Quite recently, RAMSAY and SHIELDS ('Phil. Trans.,' 1893), by means of the principle used by EÖTVÖS, have largely supplemented the observations of the Hungarian physicist. Their results serve to confirm the idea that the fatty acids, the fatty alcohols, and water, are liquids which contain congeries of gaseous molecules, and that acetone, glycol, propionitrile, and nitroethane belong to the same category. Thirty-six other liquids examined by them give, on the other hand, little evidence of association of molecules. Although this method of estimating molecular complexity has not been established by rigorous theoretical considerations either by Eötvös, or by Ramsay and Shields, it must be granted that there is now strong experimental support to the contention that liquids may differ from one another in regard to the complexity of their molecules.

Since surface energy resembles viscosity, inasmuch as both are the result of extra-molecular effects, it is almost certain that the one as well as the other will be affected by molecular complexity.

Hence, in dealing with viscosity, we must be prepared to find its magnitude influenced not only by the nature, number, and arrangement of the atoms composing gaseous molecules—intra-molecular factors which alone seem to operate in the case of properties like specific molecular volume and molecular refraction—but also by the extent to which the gaseous molecules become associated into complex groups in passing from gas to liquid.

Graphical Representation of Results.

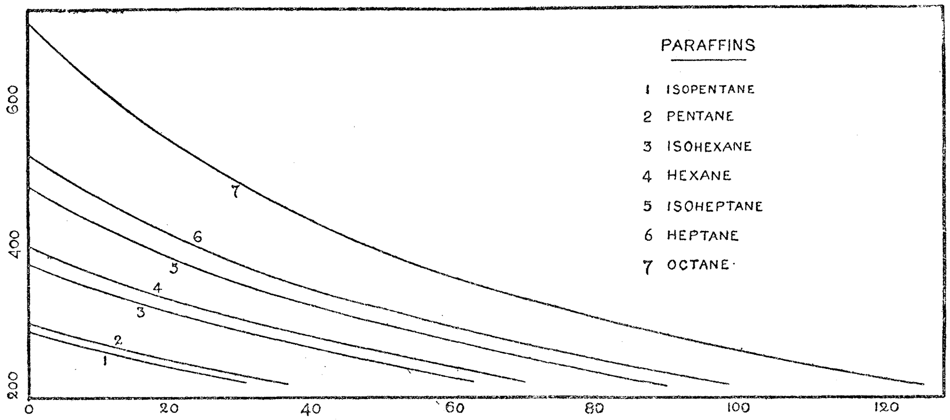
After the observations of viscosity had been reduced, curves extending from 0° to the boiling-points of the particular liquids were plotted against viscosity coefficients as ordinates and temperatures as abscissæ. On the scale adopted, 1 millim. corresponded to 0°·2 in temperature, and to ·00002 in the viscosity coefficient. On this scale a continuous curve could be drawn through the experimental points with little difficulty, as the observations taken in different limbs at the same temperature were often coincident, and were never so far apart as to admit of the introduction of any appreciable error by an arbitrary method of smoothing.

On plotting the curves for a group of related substances on the same sheet of paper, marked regularities were often apparent between the relative disposition of the curves for the different members and their chemical nature. These regularities will be apparent from the reduced representations of the curves given in the following pages. To avoid complication, the experimental points through which the curves are drawn have not been indicated; it has to be remembered, however, that each curve represents on the average some 24 observations of the viscosity coefficient. The ordinates are multiplied by 10^5. We now proceed to indicate the general features of these curves.

Paraffins.

The paraffins investigated were isopentane, pentane, isohexane, hexane, isoheptane, heptane, and octane. Fig. 5 represents the results obtained. In the case of the paraffins the curves are all of the same general shape; their order and disposition are such as to exhibit a direct connection between the chemical nature of the substances and the magnitudes of their viscosity coefficients. The curve for any paraffin always lies below and to the left of that of its next higher homologue; and, further, the curve for the isoparaffin always lies below and to the left of that for the normal paraffin. All the curves tend to approach as the temperature rises, but it is noticeable that at the same temperature the distance between the curves of isomeric paraffins is larger the higher the molecular weight. At the same temperature the viscosity is greater the higher the molecular weight and is lower for an iso- than for a normal compound. Another striking feature in the series is that all the curves stop almost exactly on a line drawn parallel to the horizontal axis. This means, of course, that at their respective boiling points the paraffins have almost exactly the same viscosity coefficient.

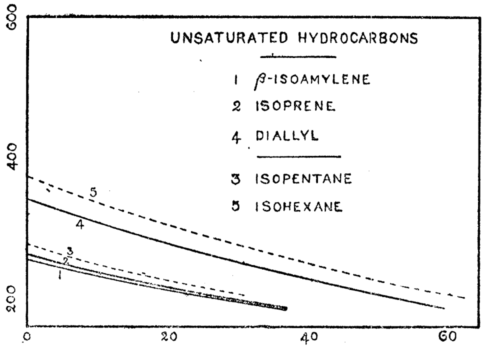
Fig. 5.



Unsaturated Hydrocarbons.

Only three unsaturated hydrocarbons were investigated, viz., isoprene, β-isoamylene, and diallyl. Fig. 6 represents the results. As in the case of the paraffins, the curve for isoprene C_5H_8 lies to the left of that for diallyl C_6H_{10}; each of these curves is also disposed in the same way with reference to the corresponding isoparaffin; that of isoprene being to the left of that of isopentane; and that of diallyl to the left of that of isohexane. The curve for β-isoamylene lies also to the left of that of isopentane, and is very close to that of isoprene. Isoprene C_5H_8 gives a curve, however, which lies uniformly to the right of that for isoamylene C_5H_{10}, although the molecular weight of the latter compound is very slightly the higher. Hence it would appear that differences in constitution may, in some cases, modify the influence of molecular weight. When, however, we compare strictly homologous hydrocarbons, it would appear that the relative position of the viscosity curves is mainly dependent on molecular weight.

Fig. 6.

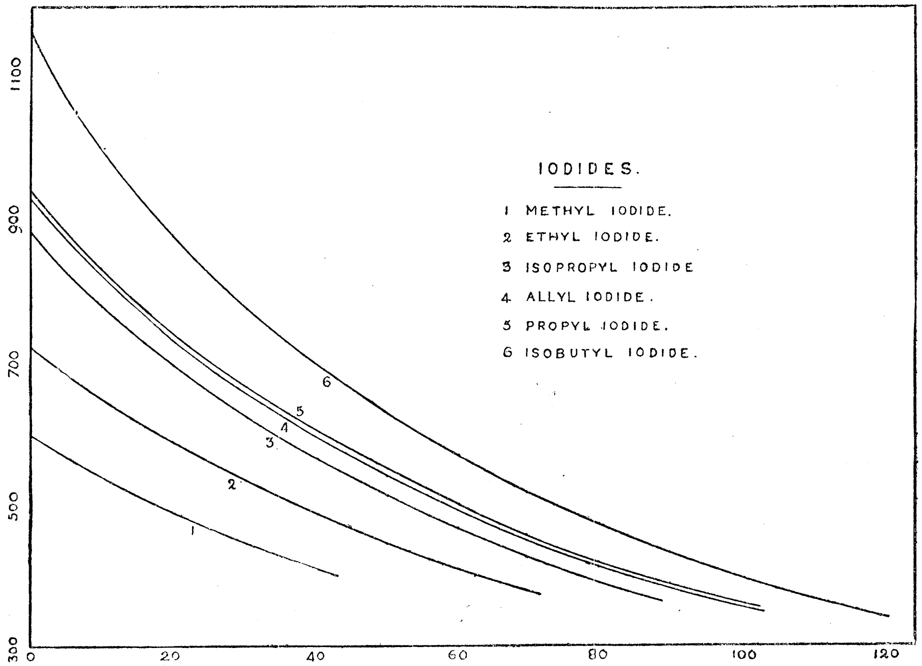


The position of the curve for diallyl is interesting, for when one allyl group only occurs in the molecule, as in the case of the allyl halides (*v. infra*), the curve for the allyl compound lies between the curves for the corresponding normal and isopropyl compounds, and is thus to the left of that for the normal compound only. When, however, two allyl groups occur in the molecule, as in the case of diallyl, the curve obtained lies to the left of that of the isopropyl (isohexane) as well as that of the normal propyl compound (hexane).

Iodides.

The iodides investigated were methyl iodide, ethyl iodide, isopropyl iodide, propyl iodide, isobutyl iodide, and allyl iodide. Fig. 7 represents the results obtained. Here striking regularity is again obvious. The curves are all of the same general

Fig. 7.



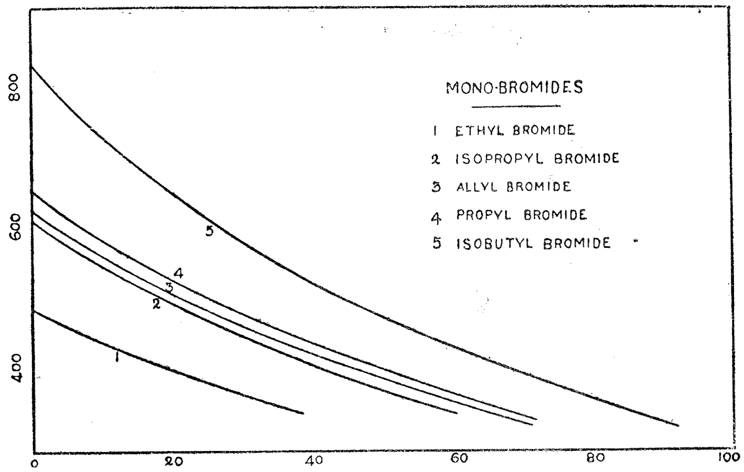
shape, and those for the saturated iodides are disposed in accordance with the molecular weights.

Isopropyl iodide, as in the case of the paraffins, has at the same temperature always a lower coefficient than normal propyl iodide. The position of allyl iodide between normal and isopropyl iodides, and nearer to the normal than the iso-iodide, is noteworthy, and again indicates the influence of constitution on the viscosity coefficient.

Bromides.

Monobromides.—Five monobromides were examined, viz., ethyl bromide, isopropyl bromide, propyl bromide, isobutyl bromide, and allyl bromide. Fig. 8 represents the results obtained.

Fig. 8.



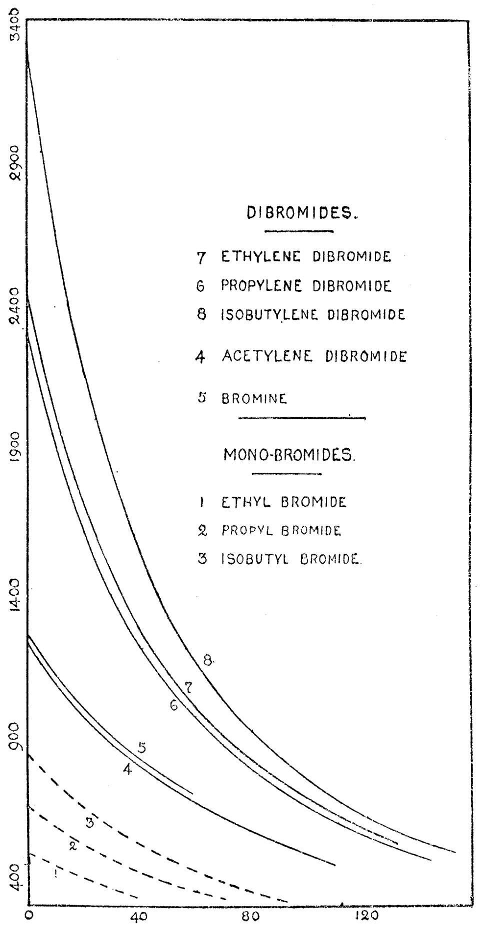
On comparing the curves for the monohalogen compounds, the same kind of regularity as in the case of the iodides is apparent, both as regards their shape and order. The allyl curve occupies a position between those of the normal and isopropyl compounds as before, but is now about midway between the two. It is also to be noted that at the boiling-point the bromides have almost the same viscosity coefficient. This regularity, so marked in the case of the paraffins, was not apparent in the case of the iodides, but as the molecular weight falls it again asserts itself, not only in the case of the bromides, but also, as will be seen later, in the case of the chlorides.

Dibromides.—The dibromides investigated were acetylene dibromide, ethylene dibromide, propylene dibromide, and isobutylene dibromide. The results obtained are given in fig. 9, which also contains several of the monobromides, and in which, for the sake of comparison, the curve for bromine is also inserted.

In order to keep the curves of somewhat the same size as in previous diagrams, the scale of ordinates and abscissæ in this figure is two-and-a-half times as close as it has hitherto been. Although the scale has thus been reduced, the general shape of the curves, since both ordinates and abscissæ have been altered in the same ratio, is the same as it would have been on the previous scale.

The marked effect of replacing an atom of hydrogen in a monobromide by an atom of bromine, is evident on comparing the curves of ethyl, propyl, and isobutyl bromides with the corresponding dihalogen compounds; at 0°, for example, ethylene bromide has a coefficient five times as great as that of ethyl bromide. Indeed, the entire shape of the dihalogen curves differs from that of the mono-derivatives. For the latter, the slope of the curve varies little from member to member, and is comparatively speaking small. The slope, of course, is $d\eta/dt$ and is the measure of the rate of change of the viscosity coefficient with temperature. In the case of the mono-derivatives, $d\eta/dt$ is not only small but varies little as the temperature rises. For dihalogen derivatives the slope is considerably increased, and with it, its variation with temperature.

Fig. 9.

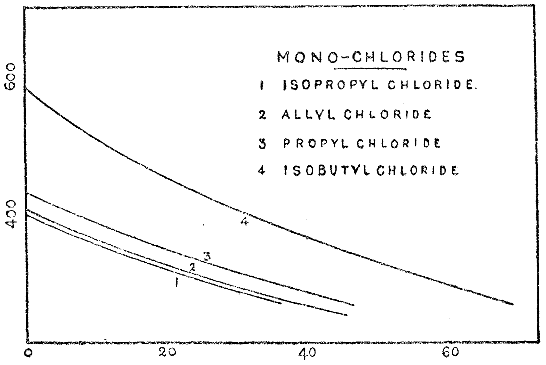


It is also apparent that constitution exercises a marked effect in the case of the dibromides, for although the curves for acetylene, ethylene, and isobutylene bromides follow in the order of the molecular weights of the substances, that for propylene bromide lies to the left instead of the right of the curve for ethylene bromide. From such data as can be obtained on this point, the divergence is more probably due to the difference in symmetry between the structure of the molecules of ethylene and propylene bromides than to any possible difference in the complexity of the liquid molecules of these substances. It is significant that the curves for substances of which the molecules contain two atoms of bromine have such a different shape from those of mono-derivatives. Bromine itself, as shown by the similarity of its curve to that of acetylene bromide, behaves like a dibromide. This fact may be held to indicate the diatomic nature of its molecule.

Chlorides.

Four monochlorides were examined, viz., isopropyl chloride, propyl chloride, isobutyl chloride, and allyl chloride. Fig. 10 represents the results obtained. The order of the curves for the monohalogen compounds shows the same regularity as is exhibited by the paraffins. The curve for the allyl compound is nearer the isopropyl than the normal propyl curve. It is therefore evident that although in the case of monohalogen compounds the allyl curve always lies between the propyl curves, there is a regular alteration in its relative position. It is nearer the normal curve in the case of the iodides, but nearer the iso curve in the case of the chlorides. At the boiling point the saturated mono-chlorides have, as in the case of the parent paraffins, almost the same viscosity coefficient.

Fig. 10.

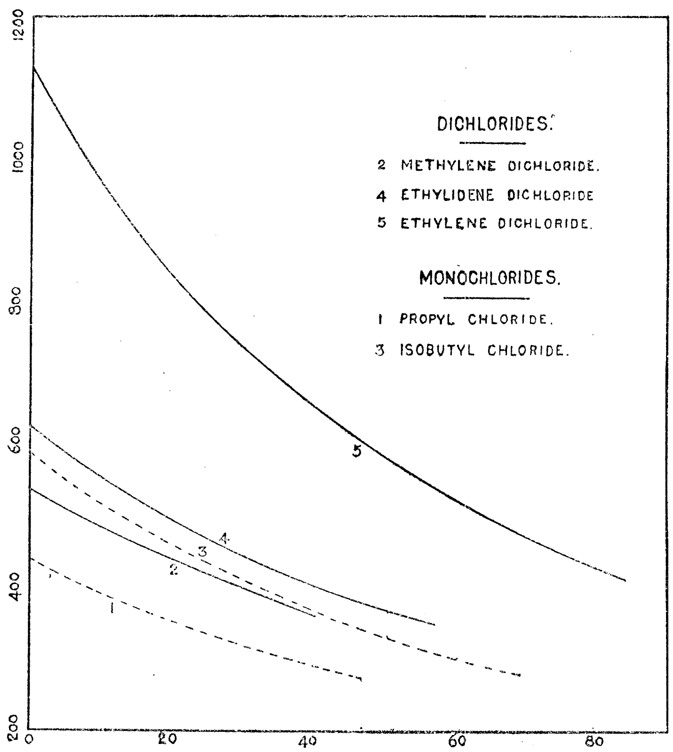


Dichlorides.

Three dichlorides were investigated, viz., methylene dichloride, ethylene dichloride, and ethylidene dichloride. The results obtained are represented in fig. 11, in which the curves for propyl and isobutyl chlorides are inserted for the sake of comparison.

The same effects as in the case of the dibromides are here traceable, the introduction of a second atom of chlorine exercising a marked increase in the viscosity constants. The curve for dichlormethane occurs to the right of the normal propyl curve, and both the dichlorethanes are to the right of the isobutyl curve.

Fig. 11.

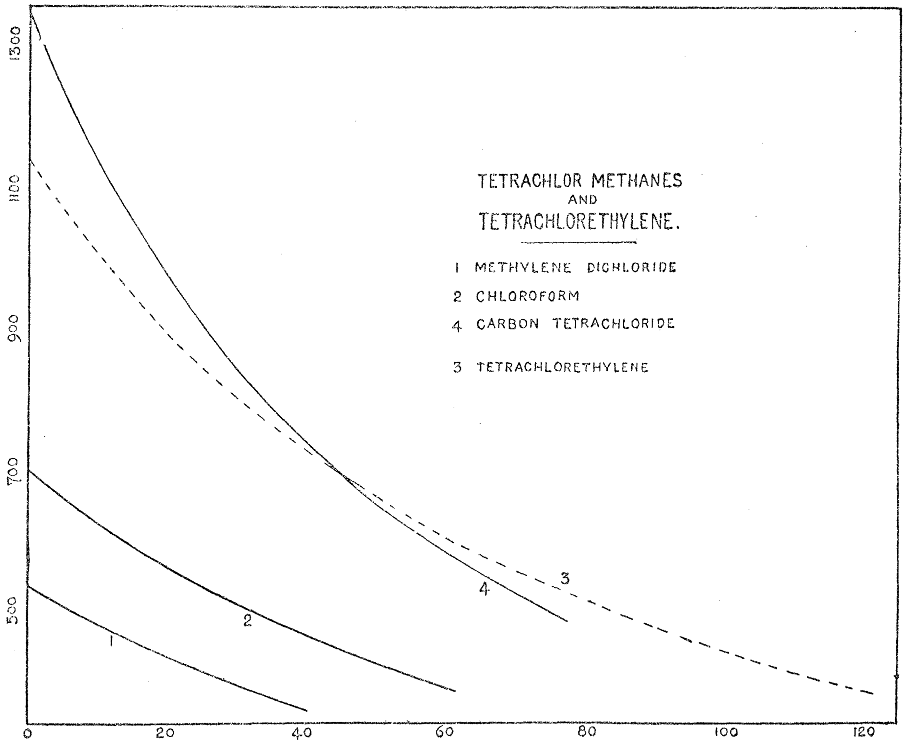


The distance between the curves for the dichlorethanes indicates a difference in the characters of the two substances which seems almost too great to be accounted for by the mere difference in their chemical constitutions. Probably the molecular complexities of the two substances may not be the same. SCHIFF's values for the surface tension of ethylene chloride give, however, no indication of molecular aggregation, and as yet there are no other data on this point. It is noteworthy that the curve of the symmetrical isomer lies to the right of that of the unsymmetrical isomer, a position analogous to that of the curve for symmetrical ethylene dibromide as compared with that of propylene dibromide.

Poly-chlorinated Compounds.

Measurements were made on the di-, tri-, and tetra-chlormethanes, and also on tetrachlorethylene. The curves obtained are represented in fig. 12. The curves for the chlormethanes follow one another in the order of their molecular weights. The distance apart of the curves for the tri- and tetra-chlor compounds is much greater than that of the curves for the di- and tri- compounds, and points to the fact that the effect produced by the introduction of a chlorine atom into the molecule of a compound depends on the number of chlorine atoms already present.

Fig. 12.



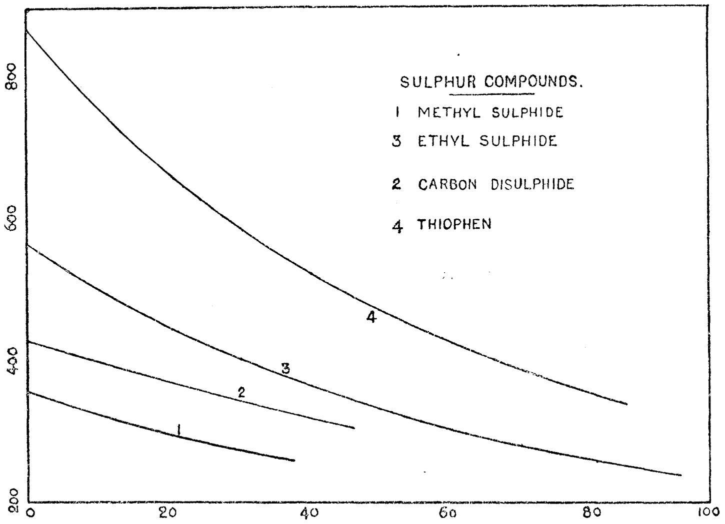
The comparison of the curves for tetrachlorethylene, C_2Cl_4, and tetrachlormethane, CCl_4, is significant, as illustrating the effect of constitution in counteracting that of molecular weight, and also the effect of temperature on the relative viscosities of two substances. At low temperatures the compound of higher molecular weight has the lower viscosity, but, as the temperature rises, the curves cross, and the viscosity at the same temperature is in the order of the molecular weights. No crossing of the curves takes place in the case of any of the strictly comparable compounds which have hitherto been considered.

Sulphur Compounds.

Four compounds containing sulphur were investigated, viz., methyl sulphide, ethyl sulphide, carbon disulphide, and thiophen. The results obtained are represented in fig. 13. The curves for methyl and ethyl sulphides exhibit the same regularities in shape and position as other homologous compounds.

Carbon bisulphide gives a somewhat steeper curve than the alkyl sulphides, but the position of the curves for the three substances is in accordance with their molecular weights.

Fig. 13.

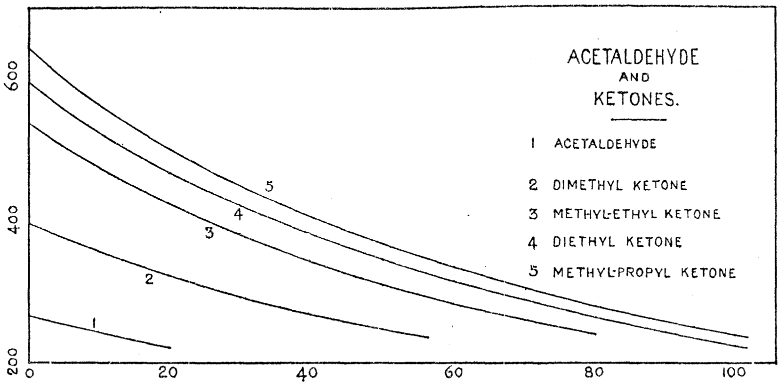


The curve for thiophen, C_4H_4S, is considerably to the right of that for ethyl sulphide, $C_4H_{10}S$, and exemplifies the probable effect of the ring grouping of atoms in increasing the viscosity constants (*vide infra*).

Aldehydes and Ketones.

Observations were made on acetaldehyde and four ketones, viz., dimethyl ketone, methyl-ethyl ketone, diethyl ketone, and methyl-propyl ketone. Fig. 14 represents the results obtained.

Fig. 14.

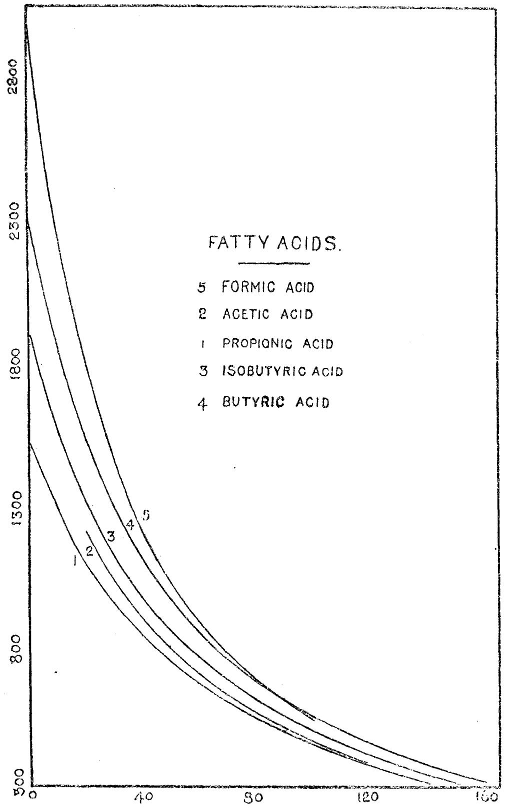


Aldehyde and the ketones give curves which closely resemble one another, and in which $d\eta/dt$ is very small. The curves follow regularly in the order of increasing molecular weight. Methyl-propyl and diethyl ketones give curves of almost the same shape, the latter lying uniformly to the left of the former; unlike the dichlorethanes, the symmetrical compound has in this case the smaller viscosity at the same temperature. It should be stated, however, that the validity of this conclusion may be affected by the great difficulty of obtaining diethyl ketone in a condition of sufficient purity.

Fatty Acids.

Five members of this series were investigated, viz., formic acid, acetic acid, propionic acid, isobutyric acid, butyric acid. Fig. 15 represents the results obtained, on a scale two and a half times as close as that usually employed.

Fig. 15.



The character of the curves for the acids presents a marked difference from that of the paraffins and such of their derivatives as have hitherto been considered. One of the most important features is seen in the largely increased effect of temperature on the value of the viscosity coefficients of all the acids. In the case of formic acid, which most clearly indicates this point, the change in the coefficient between 0° and 100° is ·0244; whilst in the case of heptane, which has about the same boiling-point as formic acid, the change is only about ·0032, or about one-eighth of the change in the case of formic acid.

The most striking feature, however, in connection with the curves for the acids, is their relative disposition, which is exceptional, the anomaly being due to the peculiar behaviour of the lowest members of the series. Except at temperatures close to the boiling point, the curve for formic acid is to the right of all the others ; at the same temperatures it has the *greatest* viscosity. On passing to acetic acid the viscosity falls, the curve for this acid lying uniformly to the left of the formic acid curve. The curve for propionic acid, in a similar way, comes to the left of that for acetic acid. The order of the curves for the three acids is exactly the opposite to what invariably obtains in the case of strictly homologous substances. The curve for butyric acid, however, takes up a normal position to the right of that for propionic acid ; isobutyric acid also conforms to the general rule, the curve being uniformly to the left of that of butyric acid, and to the right of that of propionic acid.

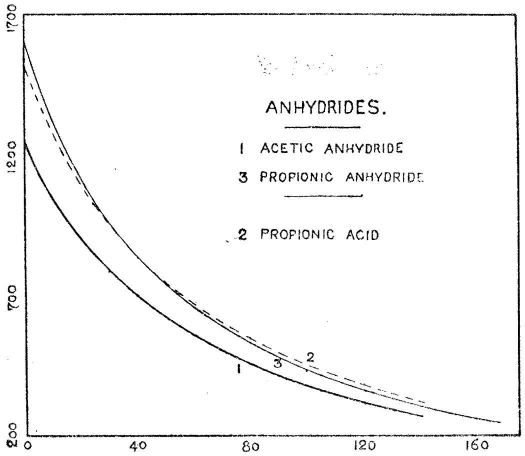
This exceptional behaviour of the fatty acids is in all probability to be traced to differences in molecular complexity. Eötvös first suggested that the fatty acids contain complex molecules, and according to Ramsay and Shields all the acids we have examined contain molecular aggregates, and at all temperatures the complexity of formic and acetic acids is somewhat the same, and more than twice as great as that of any of the other acids, so that at all temperatures the weights of the liquid molecules of these two acids are greater than those of the others. It is thus possible to give a definite reason for the apparently anomalous position of the curves of the lowest acids. In the case of the normal paraffins and their monohalogen derivatives we are dealing with liquids which in all likelihood contain simple molecules, the molecular weights of the gas and the liquid are here the same, and here the curves are disposed in accordance with the ordinary gaseous molecular weights.

In the case of the acids, however, the effect of the complexity of the liquid molecule is superadded, the molecular weights of gas and liquid are no longer the same, and the curves no longer follow one another in the order of the theoretical molecular weights, but their disposition evidently depends upon the weights of the liquid molecules. Although this reasoning indicates why the viscosity curve of formic acid should lie to the right of the others, it does not explain why the curve for formic should lie to the right of that for acetic acid, because from the measurements of Ramsay and Shields, the molecular weight of liquid acetic acid is at all temperatures greater than that of formic acid, and its viscosity at any temperature would thus be expected to be greater instead of being less than that of formic acid. It is noticeable from the numbers given by Ramsay and Shields that with the exception of acetic acid the complexity of the first four acids diminishes with rise in molecular weight. If the anomalous position of the viscosity curves is due solely to the effect of complexity, it is indicated that acetic acid is really no exception to this rule. If, however, the results obtained by the surface-energy method of estimating complexity are valid, it must be admitted that the anomalous position of the curve for formic acid, with relation to that of acetic acid, is due to some peculiarity in the constitution of formic acid, which may be associated with the fact that it is the initial member of the homologous series, and does not contain a CH_2 or a CH_3 group.

Anhydrides.

Acetic anhydride and propionic anhydride were the only members of this series which were examined. The curves obtained, together with that of propionic acid, which is inserted for the sake of comparison, are given in fig. 16.

Fig. 16.



The curves for propionic anhydride and acetic anhydride are disposed in the order of the molecular weights. On comparing the dotted curve for propionic acid with those for the two anhydrides, it is evident that the absolute values of the coefficients for propionic anhydride are not very different from those for propionic acid at the same temperature, although the theoretical molecular weights of the substances differ widely. This is probably another instance of the marked effect of molecular complexity.

From surface energy measurements it appears that liquid acetic anhydride contains simple molecules, and from the position and course of the viscosity curve for propionic anhydride with reference to that of acetic anhydride, it is probable that liquid propionic anhydride is also simply constituted. Propionic acid on the other hand contains molecular aggregates, and from surface-energy measurements the average molecular weight of the liquid is almost 130, a number which is exactly the same as the molecular weight of gaseous and probably of liquid propionic anhydride.

This is probably the reason for the proximity of the curves of propionic acid and propionic anhydride.

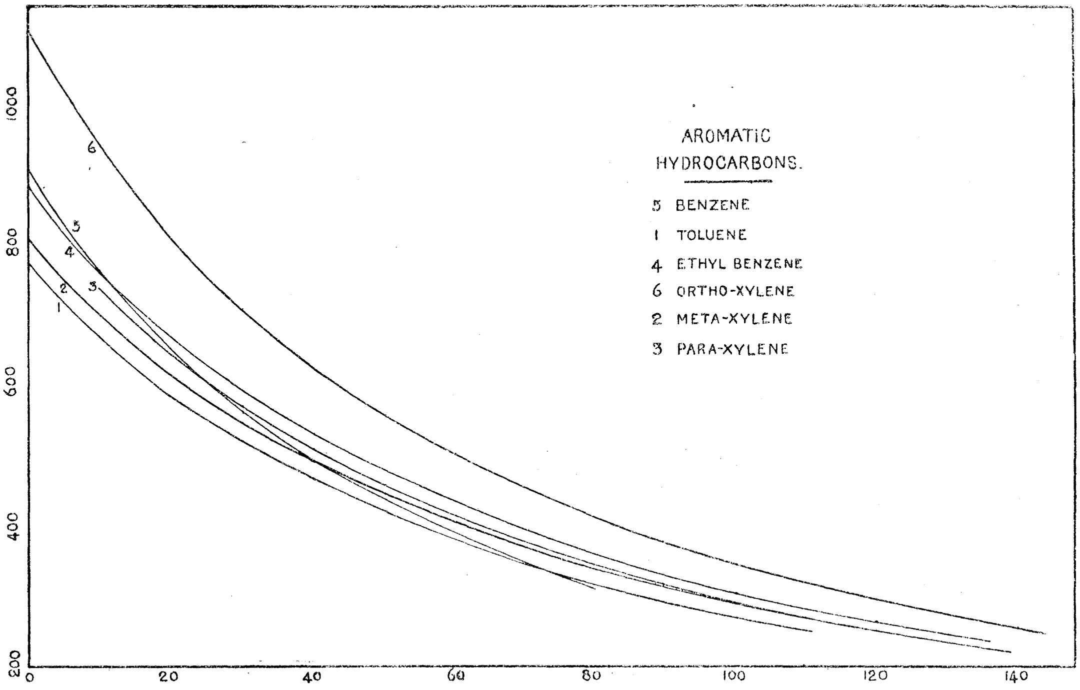
Aromatic Hydrocarbons.

Six members of this series were investigated, viz.: benzene, toluene, ethyl benzene, ortho-xylene, meta-xylene, and para-xylene.

The results obtained are represented in fig. 17.

The general character of the curves for the aromatic hydrocarbons is similar to that of the paraffins: $d\eta/dt$ is comparatively small. One of the most striking points in connection with them is the anomalous course of the benzene curve. At 0° benzene has a greater viscosity than ethyl benzene ; at about 10° the curves cross and for the greater part of its course the benzene curve lies between those of ethyl benzene and toluene. At about 80°, however, it cuts across the toluene curve, so that at the boiling point of benzene the viscosity constants of benzene, toluene, and ethyl benzene are in the order of the molecular weights. The curve for toluene is uniformly to the left of that for ethyl benzene. Another striking point is the disposition of the curves for the three isomeric xylenes. The curves for the meta- and para-isomers lie between those of toluene and ethyl benzene, and thus uniformly to the left of the curve for the latter. The curve for the ortho-isomer however, is widely separated from the other two and lies considerably to the right of the curve for ethyl benzene. It is also interesting, as emphasising the similarity between the meta- and para-compounds and the separation from them of the ortho-compound, that although at low temperatures para-xylene gives slightly larger coefficients than meta-xylene, yet between 110° and the boiling-point the two curves for the meta- and para-isomers are practically identical.

Fig. 17.



The peculiar course of the benzene curve might at first sight appear to indicate molecular complexity; an extensive series of surface-energy measurements made by Ramsay and Shields would appear to show however that this disturbing factor does not here exist. If we accept this conclusion, then difference in chemical constitution must be taken to be the cause of the peculiarity, for it is easy to conceive that a property like viscosity will be affected by the general *contour* of the moving molecule. The benzene molecule differs from those of all its homologues in containing no side chains, and since the curves for the isomeric xylenes show that even a difference in the position of the side chains exerts a decided effect on the viscosity, the entire want of side chains may be expected to bring about a marked influence.

The curve for benzene, the initial member of the homologous series of aromatic hydrocarbons, thus resembles formic acid, the initial member of the series of fatty acids, in having an anomalous position with respect to that of higher homologues.

Alcohols.

Eleven alcohols were examined, viz., methyl alcohol, ethyl alcohol, isopropyl alcohol, propyl alcohol, trimethyl carbinol, isobutyl alcohol, butyl alcohol, di-methyl ethyl carbinol, active amyl alcohol, inactive amyl alcohol, and allyl alcohol. Fig. 18 represents the results obtained for methyl, ethyl, isopropyl, propyl, isobutyl, butyl and allyl alcohols. The scale in this diagram, as in all those relating to the alcohols, is two and a half times as close as that usually employed.

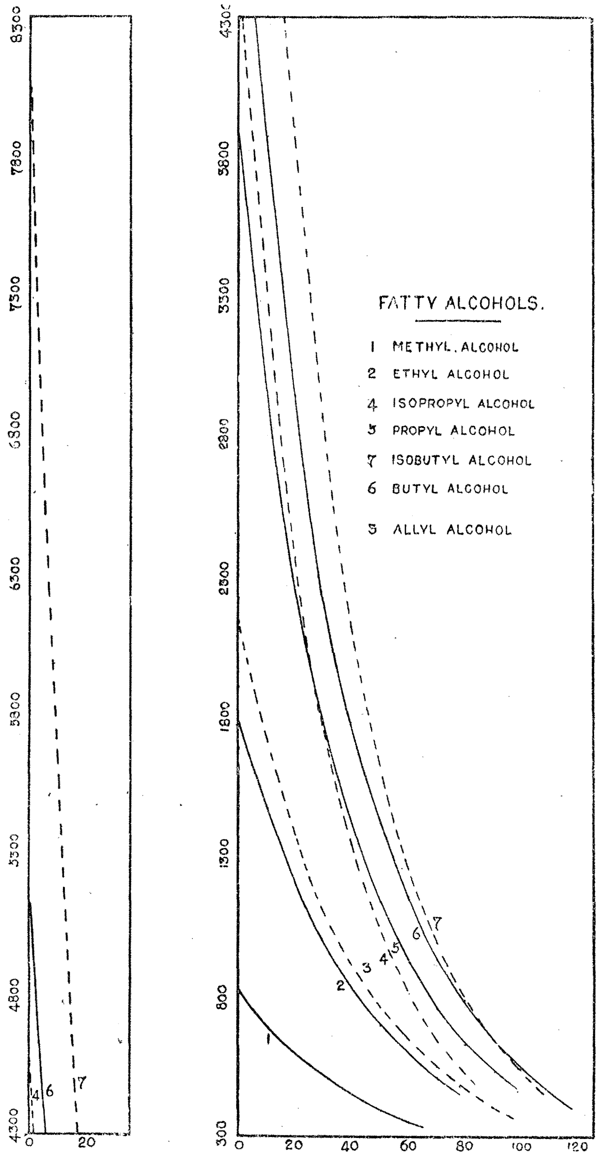
The peculiar character of the alcohol curves is at once evident. Here the tendency of the slope to deviate from the small values which it has in the case of the paraffins and their monohalogen derivatives reaches a maximum. Even methyl alcohol, over the comparatively short temperature range between 0° and its boiling point, gives large values of $d\eta/dt$, the curve being of the same general shape as the high temperature regions of the curves of the higher alcohols. In the case of isobutyl alcohol, for example, the change in viscosity between 0° and 100° is ·0751 ; over the same temperature range heptane has a viscosity change of ·0032, so that the same temperature change exerts almost twenty-five times as great an effect on the viscosity coefficient in the case of the alcohol as it does in the case of the hydrocarbon.

The continuous curves in the diagram refer to the four lowest members of the series of normal alcohols. It will be seen that the curves are disposed in accordance with the theoretical molecular weights of the alcohols. There is no anomaly such as that which occurs in the case of formic and acetic acids, although there is every reason to believe that molecular grouping takes place in the case of the alcohols just as in the case of the acids.

From RAMSAY and SHIELDS' observations on the four normal alcohols at low temperatures, methyl alcohol is the most complex, and the complexity steadily diminishes with rise in molecular weight, so that in the case of butyl alcohol it is only about half what it is in the case of methyl alcohol. Although this is assumed to be the case, the molecular weights of the liquid alcohols still follow one another in the order of the theoretical molecular weights, so that the disposition of the viscosity curves is in conformity with the weights of the liquid molecules indicated by surface-energy observations.

The curves for the lower iso alcohols lie no longer uniformly on one side of those of the corresponding normal alcohols. The two available comparisons show that the iso-curve cuts that of the normal isomer, so that at high temperatures the iso-curve, as is generally the case, lies to the left of the normal curve, whilst at low temperatures

Fig. 18.



it lies to the right. $d\eta/dt$ at any temperature is uniformly greater for the iso- than for the normal alcohol.

The crossing of the curves is probably also to be traced to different rates of decomposition of liquid molecular aggregates. RAMSAY and SHIELDS' observations indeed indicate that the molecular weight of liquid isobutyl alcohol is greater at low temperatures, and less at high temperatures than that of butyl alcohol. In the absence of any satisfactory theory little stress can, however, be laid upon the numbers given by surface-energy observations in so far as they relate to the *extent* of molecular aggregation or to its variation with temperature. RAMSAY and SHIELDS' observations indicate that in some cases complexity increases with rise in temperature; viscosity gives no indication of such an increase. Their measurements also show that liquid isopropyl alcohol has a higher molecular weight than either normal or isobutyl alcohol: the viscosity curve of isopropyl alcohol is, however, to the left of those for alcohols higher in the series.

The curve for allyl alcohol is still between those of ethyl and propyl alcohols, just as in the case of the paraffins and their derivatives; its position relative to the isomeric propyl alcohols is, however, no longer the same, a fact no doubt due to molecular complexity. According to RAMSAY and SHIELDS' observations, the molecular weight of liquid allyl alcohol is almost the same as that of liquid methyl alcohol; the position of the curves for these two alcohols is, however, very different, the difference being due, in part at least, to the influence of chemical constitution.

The profound effect of constitution and molecular complexity on the relative disposition of the alcohol curves, and also the effect of temperature in altering this disposition, is evident on comparing the isomeric butyl and amyl alcohols.

Butyl Alcohols.

Three isomeric butyl alcohols, viz.: trimethyl carbinol, isobutyl alcohol, and normal butyl alcohol were examined. The results are represented in fig. 19. Tertiary butyl alcohol at low temperatures, just above its freezing-point, has the largest viscosity; as the temperature rises, however, its viscosity curve cuts across those of the iso- and normal isomers, so that at temperatures near its boiling-point it has the lowest viscosity. Isobutyl alcohol at low temperatures has, in a similar way, a much greater viscosity coefficient than the normal isomer, but, as already shown, the curve for the former crosses that of the latter as temperature rises.

Ether.

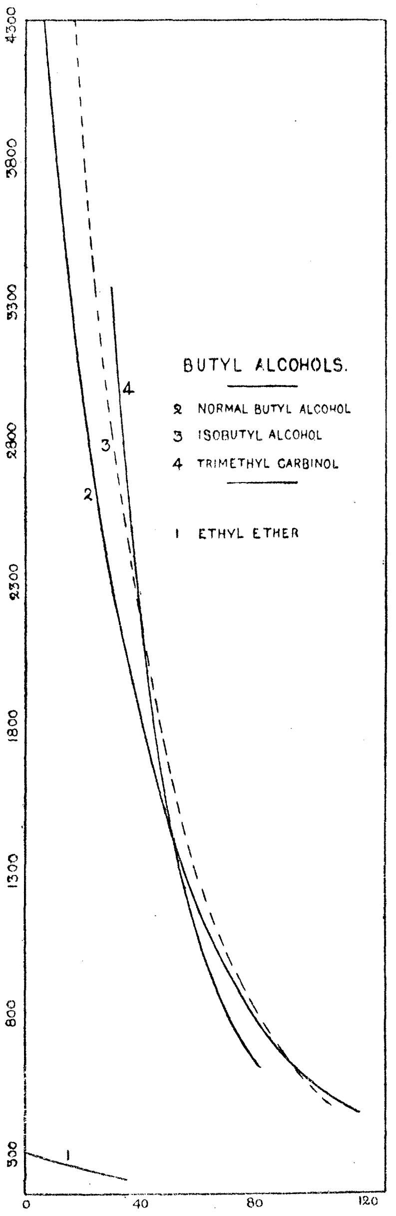
The curve for ether which is, of course, isomeric with the butyl alcohols, is introduced to show how markedly the chemical constitution and the molecular complexity of a liquid affect its viscosity.

Amyl Alcohols.

Fig. 20 represents the results of the determinations on di-methyl ethyl carbinol, active amyl alcohol, and inactive amyl alcohol.

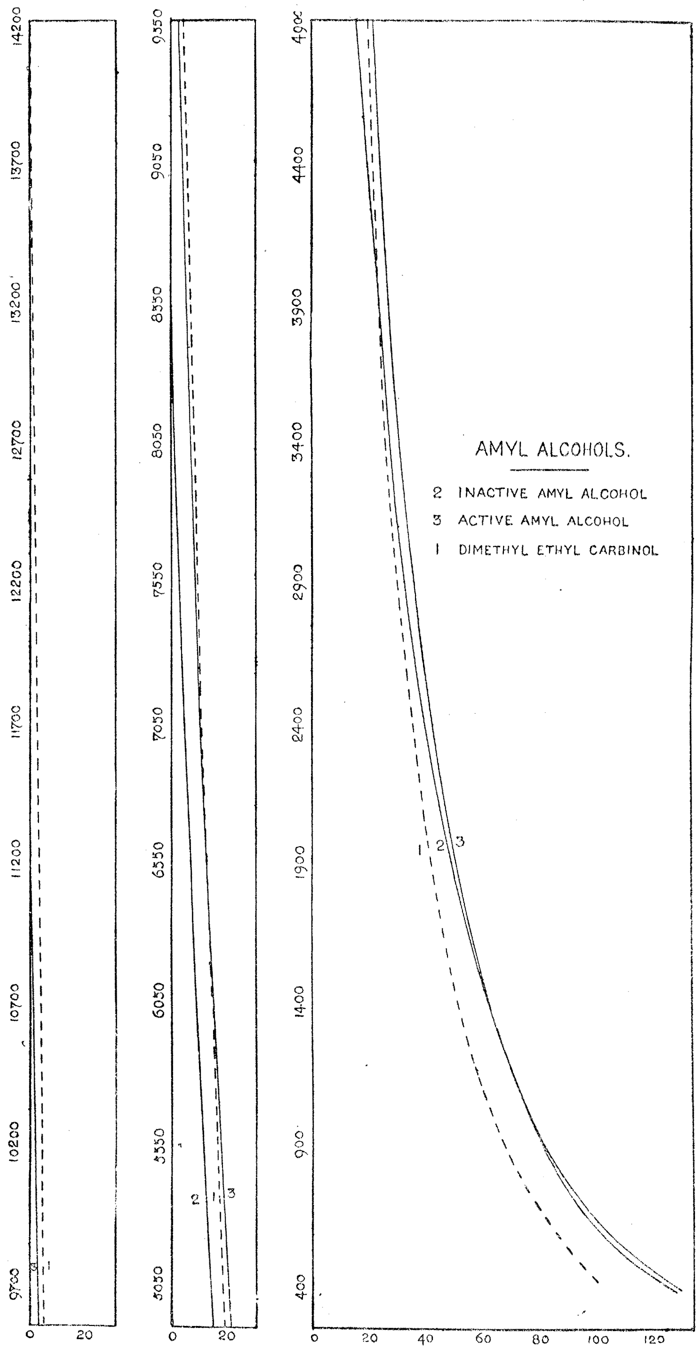
As in the case of the butyl alcohols, the tertiary isomer has at low temperatures the largest viscosity. Eventually, however, its viscosity curve crosses those for the inactive and active alcohols, and at higher temperatures it has the smallest viscosity. The curve of the active alcohol stands in the same relation to that of the inactive alcohol as that of isobutyl alcohol does to that of normal butyl alcohol. Of all the liquids examined, dimethyl ethyl carbinol exhibits in the most marked degree the effect of temperature on the viscosity coefficient. At 0°, the value of the coefficient is ·14179 dyne, while at 101°·9, the boiling-point of the alcohol, the coefficient is only ·00418 dyne, or only about $\frac{1}{34}$th of the value which it has at 0°.

Fig. 19.



The general character of the curves for the alcohols clearly shows that even in monohydric alcohols there is the indication of the high values of the viscosity coefficient which are known to characterise the glycols, glycerin, and other polyhydric alcohols.

Fig. 20.



The feature which is common to all those curves, as has been already stated, is the large value of the slope. Temperature exerts a profound effect on the value of the viscosity, and thus we have peculiar steep curves indicating at low temperatures values for the viscosity coefficient which are enormous when compared with those of, say, the paraffins. This rapid increase in the value of the viscosity is, in all probability, to be associated with increasing complexity in the molecule of the liquid alcohol, a complexity which is probably much greater in the case of the polyhydric alcohols.

It is further to be noted that the viscosity curves which most closely resemble those of the alcohols are those of water and the fatty acids, and these are just the liquids which, along with the alcohols, have, on independent grounds, been held to consist of complex molecules. There is thus strong support to the idea that large values in $d\eta/dt$ are to be ascribed to changes of molecular complexity, and, further, that marked change of complexity is exhibited so far as our viscosity observations go by only one type of substances, namely, those which, like water, an acid, or an alcohol, contain a hydroxyl group. The peculiarities above referred to are thus related to the chemical nature of the substances, and comparisons of the curves for hydroxy compounds such as water, formic acid, and propyl alcohol with that of heptane, all of which substances have boiling points which differ at most by only 4°, makes evident at a glance the peculiarity here considered.

The following tables contain values of the coefficients of viscosity read off at intervals of 10° from the curves originally plotted. Besides giving an idea of how the viscosity coefficient varies from substance to substance the numbers may serve as data for ascertaining, either graphically or by the ordinary interpolation formulæ, the values of the coefficients at particular temperatures :—

Coefficients of Viscosity (dynes per sq. centim.).

Hydrocarbons.

Paraffins.

Temp.	Pentane.	Hexane.	Heptane.	Octane.	Isopentane.	Isohexane.	Isoheptane.
° 0	·00283	·003965	·00519	·00703	·00273	·00371	·00477
10	·002555	·00355	·00460	·006125	·00246	·003325	·00423
20	·00232	·00320	·004105	·00538	·00223	·00300	·00379
30	·00212	·00290	·00369	·004785	·00204	·002725	·003415
40	..	·00264	·00334	·00428	..	·00247	·00309
50	..	·00241	·00303	·003855	..	·002255	·002815
60	..	·00221	·00276	·003495	..	·00208	·00257
70	..	..	·00253	·00318	..	..	·00235
80	..	..	·00232	·002905	..	..	·00216
90	..	..	·00214	·00266	..	..	·00200
100	..	..	..	·002445			
110	..	..	..	·002255			
120	..	..	..	·002075			

UNSATURATED HYDROCARBONS.

Temp.	Isoprene.	Diallyl.	β-Isoamylene.
°			
0	·00260	·00339	·00254
10	·00236	·003035	·00231
20	·002155	·00274	·002115
30	·00198	·00249	·00194
40	..	·00227	
50	..	·002075	

IODIDES.

Temp.	Methyl iodide.	Ethyl iodide.	Propyl iodide.	Isopropyl iodide.	Isobutyl iodide.	Allyl iodide.
°						
0	·005945	·00719	·00938	·008785	·011625	·00930
10	·00536	·00645	·00827	·00775	·00996	·00819
20	·00487	·00583	·00737	·00690	·00870	·007265
30	·00446	·00530	·006615	·00619	·007715	·006515
40	·00409	·00484	·005985	·00559	·006905	·005885
50	..	·00444	·005435	·00507	·00622	·005345
60	..	·00409	·00497	·00463	·005635	·004885
70	..	·00378	·00456	·00424	·005135	·004475
80	..	..	·004195	·00389	·004695	·00412
90	..	..	·00387	..	·00430	·00381
100	..	..	·00359	..	·00396	·00352
110	..	..	..	..	·00366	
120	..	..	..	..	·00338	

MONOBROMIDES.

Temp.	Ethyl bromide.	Propyl bromide.	Isopropyl bromide.	Isobutyl bromide.	Allyl bromide.
°					
0	·00478	·00645	·006045	·008235	·00619
10	·004315	·00575	·00538	·00721	·00552
20	·00392	·00517	·00482	·00638	·004955
30	·00357	·00467	·00435	·00569	·00449
40	..	·00425	·00394	·005115	·004095
50	..	·003875	·003585	·004625	·00374
60	..	·003555	..	·00419	·003435
70	..	·003275	..	·00382	·00316
80	..	..	..	·003485	
90	..	..	..	·003165	

DIBROMIDES AND BROMINE.

Temp.	Ethylene bromide.	Propylene bromide.	Isobutylene bromide.	Acetylene bromide.	Bromine.
°					
0	·02435	·022995	·03316	·01230	·012575
10	·02035	·01910	·02653	·01083	·01109
20	·01716	·01619	·02169	·009595	·009935
30	·01470	·01394	·01818	·00860	·008985
40	·01280	·012155	·015455	·00778	·00817
50	·01124	·01073	·01331	·007075	·00746
60	·009985	·009525	·01163	·00648	
70	·00895	·00853	·01025	·00596	
80	·00808	·00769	·00909	·00550	
90	·00733	·00697	·00813	·005095	
100	·00668	·00635	·007315	·004735	
110	·00611	·005815	·00662		
120	·00562	·005345	·00602		
130	·00518	·004935	·00550		
140	..	·00456	·00505		

MONOCHLORIDES AND CHLORETHANES.

Temp.	Propyl chloride.	Isopropyl chloride.	Isobutyl chloride.	Allyl chloride.	Ethylene chloride.	Ethylidene chloride.
°						
0	·00436	·00402	·005835	·00406	·01128	·006215
10	·00390	·00358	·00514	·003645	·00961	·00549
20	·00352	·00322	·004565	·003295	·00833	·00490
30	·00319	·002915	·00408	·00299	·00730	·004405
40	·00291	..	·003665	·002735	·006455	·003985
50	..	..	·00332	..	·005765	·003625
60	..	..	·003015	..	·00519	
70	..	..	..	..	·00470	
80	..	..	..	..	·00426	

CHLORMETHANES AND TETRACHLORETHYLENE.

Temp.	Methylene dichloride.	Chloroform.	Carbon tetrachloride.	Carbon dichloride.
°				
0	·00536	·00700	·013465	·01139
10	·004805	·00626	·01133	·010035
20	·004355	·00564	·00969	·008925
30	·003965	·00511	·008415	·00803
40	·00363	·004655	·00738	·007265
50	..	·00426	·006535	·00661
60	..	·00390	·005835	·00605
70	..	..	·00524	·005565
80	..	..	..	·00514
90	..	..	..	·00475
100	..	..	..	·00441
110	..	..	..	·004105
120	..	..	..	·003825

COMPOUNDS CONTAINING SULPHUR.

Temp.	Methyl Sulphide.	Ethyl Sulphide.	Thiophen.	Carbon Bisulphide.
°				
0	·00354	·00559	·00871	·004295
10	·00321	·00496	·00752	·00396
20	·00293	·004445	·00659	·00367
30	·002685	·00401	·00583	·00342
40	..	·00363	·00520	·00319
50	..	·00331	·00468	
60	..	·003035	·00424	
70	..	·00279	·003855	
80	..	·00257	·00350	
90	..	·00237		

ACETALDEHYDE AND KETONES.

Temp.	Aldehyde.	Dimethyl ketone.	Methyl-ethyl ketone.	Diethyl ketone.	Methyl-propyl ketone.
°					
0	·00267	·00394	·005385	·00595	·00644
10	·002435	·00356	·00475	·00525	·00565
20	·002215	·003225	·00423	·004655	·00501
30	..	·00293	·003795	·004195	·004485
40	..	·00268	·003425	·003795	·00404
50	..	·002455	·00311	·003445	·00366
60	..	..	·002845	·00315	·003335
70	..	..	·00260	·00289	·00305
80	..	..	·002395	·002655	·00280
90	..	..	..	·00245	·00258
100	..	..	..	·00226	·00238

FATTY ACIDS.

Temp.	Formic.	Acetic.	Propionic.	Butyric.	Isobutyric.
°					
0	(solid)	(solid)	·01519	·02284	·01885
10	·02245	(solid)	·01286	·01849	·01566
20	·01782	·01219	·01099	·01538	·01315
30	·01457	·01036	·00956	·01301	·01126
40	·012155	·00901	·00841	·011175	·00977
50	·010315	·00791	·00747	·009715	·00858
60	·00887	·00700	·006685	·008535	·00760
70	·00775	·00625	·006015	·00756	·00678
80	·00682	·00560	·005445	·00674	·00609
90	·00606	·00505	·00495	·006045	·00548
100	·00542	·004575	·00452	·00545	·00495
110	..	·004165	·004135	·00494	·00449
120	..	..	·003795	·004495	·00410
130	..	..	·003495	·00409	·003755
140	..	..	·003215	·00374	·00345
150	..	..	..	·00343	·00317
160	..	..	..	·00314	

ANHYDRIDES (Oxides).

Temp.	Acetic.	Propionic.
° 0	·012415	·01608
10	·01049	·01327
20	·00902	·01116
30	·00787	·00957
40	·006935	·008315
50	·006165	·00730
60	·00553	·00647
70	·00499	·00578
80	·00453	·00521
90	·004125	·004715
100	·00377	·004295
110	·00347	·00399
120	·00320	·003595
130	·002965	·00331
140	..	·00306
150	..	·00284
160	..	·002635

AROMATIC HYDROCARBONS.

Temp.	Benzene.	Toluene.	Ethyl benzene.	Ortho-xylene.	Meta-xylene.	Para-xylene.
° 0	·009025	·007685	·00874	·011025	·00802	(Solid at 0°)
10	·00759	·006675	·00758	·00934	·006975	·00735
20	·00649	·00586	·006665	·00807	·00615	·006435
30	·00562	·00520	·00592	·007055	·00547	·005695
40	·00492	·00466	·00529	·00623	·00491	·005085
50	·00437	004195	·00477	·005555	·004445	·004575
60	·003905	·00381	·00432	·004995	·00404	·00412
70	·00351	·003475	·00394	·004525	·00369	·00377
80	·00327	·00318	·00360	·00411	·00339	·00345
90	..	·002915	·003305	·00376	·00313	·00317
100	..	·002695	·003045	·003455	·00289	·00292
110	..	·00250	·002815	·00318	·00269	·00270
120	..	..	·00262	·00294	·00250	·002505
130	..	..	·002435	·00273	·00233	·00233
140	..	..	..	·00254		

FATTY ALCOHOLS.

Temp.	Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.	Butyl alcohol.	Allyl alcohol.	Isopropyl alcohol.
°						
0	·00813	·01770	·03882	·05185	·02144	·04564
10	·00686	·01449	·02917	·03872	·01703	·03245
20	·00591	·01192	·02255	·02947	·01361	·02369
30	·00515	·009895	·017775	·02266	·01165	·01755
40	·004505	·008275	·01403	·01780	·00911	·01329
50	·00396	·006975	·01128	·01409	·007595	·01026
60	·003495	·005915	·00919	·011365	·00642	·00804
70	..	·005045	·00757	·009265	·005475	·00642
80	..	..	·00628	·00762	·00470	·00520
90	..	..	·00526	·006335	·00407	
100	..	..	..	·005345		
110	..	..	..	·004545		

FATTY ALCOHOLS—(continued).

Temp.	Isobutyl alcohol.	Trimethyl carbinol.	No. I. Inactive amyl alcohol.	No. II. Inactive amyl alcohol.	Active amyl alcohol.	Dimethyl ethyl carbinol.
°						
0	·08038	(solid)	·08762	·08532	·11129	·14179
10	·05547	(solid)	·06107	·06000	·07425	·07860
20	·03906	(solid)	·04390	·04341	·05091	·04642
30	·02863	·03349	·03234	·03206	·03593	·03000
40	·02121	·02103	·02433	·02414	·02606	·02044
50	·01609	·014355	·01862	·01849	·019355	·01457
60	·01239	·010295	·01449	·01443	·01472	·010775
70	·00973	·00772	·011495	·01147	·01147	·00830
80	·00779	·005995	·00924	·009235	·00909	·006575
90	·00633	..	·00757	·007575	·00735	·00530
100	·00521	..	·00626	·006275	·00605	·00434
110	..	..	·005265	·00529	·00505	
120	..	..	·004475	·004505	·00429	
130	..	..	·003835	·00386		

ETHER AND NITROGEN PEROXIDE.

Temp.	Ether.	Nitrogen peroxide.
0	·00286	·005275
10	·002585	·00468
20	·002345	·00418
30	·00212	

Conclusions drawn from the Graphical Representation of the Results.

From the graphical representation of the results, we appear to be justified in assuming that the value of the viscosity coefficient depends not only on molecular weight and chemical constitution but also on molecular complexity.

For liquids which probably contain simple molecules, or for which there is, in any case, little evidence of the association of gaseous molecules, the following conclusions may be drawn :—

(1) In homologous series, or in series of related substances, the viscosity is greater the greater the molecular weight.

(2) An iso-compound has always a smaller viscosity coefficient than the corresponding normal compound.

(3) An allyl compound has in general a coefficient which is greater than that of the corresponding iso-propyl compound, but less than that of the normal propyl compound.

(4) Substitution of halogen for hydrogen raises the viscosity by an amount which is greater the greater the atomic weight of the halogen.

Successive substitution of hydrogen by chlorine in the same molecule brings about different increments in the viscosity coefficient.

(5) In some cases, as in those of the dichlorethanes, constitution exerts a marked influence on the viscosity; and in the case of the dibromides and benzene it may be so large that the compound of higher molecular weight has the smaller viscosity.

(6) Certain liquids, which probably contain molecular complexes, do not obey these rules. Formic and acetic acids are exceptions to rule (1). The alcohols conform at some, but not at all, temperatures to rule (2); at no temperature, however, do they conform to rule (3).

(7) Liquids containing molecular complexes have in general large values of $d\eta/dt$.

(8) In both classes of liquids the behaviour of the initial members of homologous series, such as formic acid and benzene, is in some cases exceptional when compared with that of higher homologues.

ALGEBRAIC REPRESENTATION OF RESULTS.

We have already discussed the various types of mathematical expression which have been suggested in order to represent the relation of viscosity to temperature. As already stated, we found that, on the whole, the most satisfactory formula hitherto devised is that due to SLOTTE. We, therefore, next sought to determine whether any connection could be traced between the magnitudes of the constants in this formula and the chemical nature of the substances. Writing the formula in the shape $\eta = C / (1 + bt)^n$, where C is η_0, the viscosity coefficient at 0°, it is seen—as, indeed, follows from the previous discussion of the disposition of the curves—that, in general, in any series of related substances :

(1) C increases as the molecular weight increases;

(2) C for an iso-compound is less than for the corresponding normal compound;

(3) C for an allyl compound is less than for the corresponding normal propyl compound but greater than for the isopropyl compound.

Exceptions to (1) occur in the case of lowest members of the series of fatty acids, aromatic hydrocarbons, and dibromides. Exceptions to (2) and (3) occur in the case of the alcohols.

As to the magnitude of C in passing from one series to another nothing very definite can be said. The corresponding iodides, bromides, and chlorides give values which are in the order of their molecular weights; the acids and alcohols, however, although possessing smaller theoretical molecular weights than the corresponding iodides, give larger values of C, due, doubtless, to the influence of molecular complexity.

As regards the other constants of the formula, n and b are terms connected with the temperature variation of η. It is evident, however, from the appended table that the magnitudes of these terms are not simply related to the chemical nature of the substances. Pentane and isopentane, for example, give different values for these constants, although the two experimental curves are almost superposable.

This is doubtless due partly to the facts—

(1) That SLOTTE's formula does not express the true law of the temperature change of the viscosity, and

(2) That only three observations are used in deducing the formula; but mainly to the circumstance

(3) That the values of n and b are interdependent, so that different pairs of values of n and b may be found which give, with the same value of C, practically the same viscosity curve, and, from the mode of deducing these constants, the individual values of n and b are often affected by influences which fall within the limits of experimental error.

(1) and (2). For short straight curves the formula gives numbers which closely agree with the observed values, the differences exhibiting no regularity. In the case of isopropyl chloride, for instance, the calculated values agree with those of observation to the fourth significant figure—that is, on an average, to 1 part in 2000; or with a degree of accuracy which is certainly as high as we may suppose the observations themselves to possess. As soon, however, as the length of the curve increases, and the slope begins to vary considerably as the temperature rises—that is, as soon as the observed curve commences to deviate to a marked extent from the linear type—the formula begins to break down, and the differences vary in a regular way, and indicate that at low temperatures the calculated curve is to the right and at high temperatures to the left of the observed curve. Attempts were made to obtain a better agreement in cases such as this. Professor HENRICI, to whom we are indebted for much assistance in the mathematical treatment of our results, spent some considerable time

in attempting to deduce a suitable formula; and on the publication of SLOTTE's paper he sought, by an application of the method of least squares, to employ the whole of the experimental results in arriving at the values of the constants. The improvement, however, was hardly commensurate with the arithmetical labour involved.

It follows by differentiating SLOTTE's formula in the shape

$$\eta = c/(a + t)^n$$

that

$$d\eta = \frac{\eta}{c}\, dc - \eta \log_e (a + t)\, dn - \frac{n\eta}{a + t}\, da,$$

and on using the differences between the observed values of η and those deduced by SLOTTE's formula as values for $d\eta$, as many equations as there were observations were obtained. These were then added together into three groups, the sums being solved for dc, dn, and da, the corrections to be applied to the constants in the original formula. The results obtained by this method were again but a slight improvement on those given by the unmodified constants. Of course, better agreement would be obtained by introducing more constants into the formula. Immediately this is done, however, the simple character of the formula disappears, and it is rendered unwieldy, and indeed, unsuited for carrying out a general physico-chemical inquiry as to the dependence of viscosity on temperature.

The worth of the simple formula can only be tested when some means has been devised for employing all the observations in deducing it. In some cases it was obvious that all or most of the differences between observed and calculated values were of the same sign, so that by slightly altering the value of C, and thus shifting the calculated curve, a better agreement could be obtained. When possible this was done.

As stated before, the closeness of the agreement between the formula and observation depends on the slope. As the difference between the slopes at 0° and the boiling point increases, the deviations increase. For many liquids calculated and observed numbers only give a fair agreement in the fifth decimal place, and this has been thought sufficiently good. In these cases, the initial slope, in general, diminishes to about one-tenth of its value as the curves are descended. Although, for curves in which the slope varies to such a large extent as this, the results giving the comparison of calculated and observed numbers have only been given to the fifth decimal place, there is every reason to believe that the observed values are just as accurate as those for liquids giving short straight curves and where the agreement is satisfactory as far as the sixth place. In the case of the alcohols the slope changes so considerably as temperature rises, in some cases being at the boiling-point only $\frac{1}{50}$th of what it is at 0°, that the observed curve has had to be split up into two or three parts, and a separate formula calculated for each, in order to give the required degree of agreement. It is significant that when this is done the values of b and n vary according to the part of the curve chosen, a circumstance indicating that no great stress should be put upon the relative magnitudes of the constants in the ordinary formula. For, obviously their values depend so much upon the particular part of the curve used, that if it were possible to take observations below 0°, values different from those already given would be obtained.

In the following table are given the values of C, b, and n in SLOTTE's formula:—

CONSTANTS in SLOTTE's Formula, $\eta = C/(1 + bt)^n$.

	C.	b.	n.
Pentane	·002827	·006039	1·7295
Hexane	·003965	·005279	2·1264
Heptane	·005180	·005551	2·1879
Octane	·007025	·006873	2·0290
Isopentane	·002724	·008435	1·2901
Isohexane	·003713	·004777	2·3237
Isoheptane	·004767	·005541	2·1633
Isoprene	·002600	·006944	1·4433
Amylene	·002534	·005341	1·7855
Diallyl	·003388	·005780	1·9340
Methyl iodide	·005940	·007444	1·4329
Ethyl iodide	·007190	·006352	1·7520
Propyl iodide	·009372	·007308	1·7483
Isopropyl iodide	·008783	·006665	1·9161
Isobutyl iodide	·011620	·009186	1·6577
Allyl iodide	·009296	·007933	1·6592
Ethyl bromide	·004776	·007212	1·4749
Propyl bromide	·006448	·006421	1·8282
Isopropyl bromide	·006044	·005916	2·0166
Isobutyl bromide	·008234	·006187	2·1547
Allyl bromide	·006190	·006895	1·7075
Ethylene bromide	·024579	·012375	1·6222
Propylene bromide	·023005	·011267	1·7075
Isobutylene bromide	·033209	·013227	1·7988
Acetylene bromide	·012307	·008905	1·5032
Bromine	·012535	·008935	1·4077
Propyl chloride	·004349	·004917	2·2453
Isopropyl chloride	·004012	·007485	1·5819
Isobutyl chloride	·005842	·007048	1·8706
Allyl chloride	·004059	·006366	1·7459

Constants in Slotte's Formula, $\eta = C/(1 + bt)^n$ (continued).

	C.	b.	n.
Ethylene chloride	·011269	·009933	1·6640
Ethylidene chloride	·006205	·007575	1·6761
Methylene chloride	·005357	·007759	1·4408
Chloroform	·007006	·006316	1·8196
Carbon tetrachloride	·013466	·010521	1·7121
Carbon dichloride	·01139	·007925	1·6325
Carbon bisulphide	·004294	·005021	1·6328
Methyl sulphide	·003538	·005871	1·6981
Ethyl sulphide	·005589	·006705	1·8175
Thiophen	·008708	·009445	1·6078
Dimethyl ketone	·003949	·004783	2·2244
Methyl ethyl ketone	·005383	·007177	1·7895
Methyl propyl ketone	·006464	·007259	1·8248
Diethyl ketone	·005949	·006818	1·8626
Acetaldehyde	·002671	·003495	2·7550
Formic acid	·029280	·016723	1·7164
Acetic acid	·016867	·008912	2·0491
Propionic acid	·015199	·009130	1·8840
Butyric acid	·022747	·010586	1·9920
Isobutyric acid	·018872	·009557	2·0059
Acetic anhydride	·012416	·010298	1·6851
Propionic anhydride	·016071	·011763	1·7049
Ethyl ether	·002864	·007332	1·4644
Benzene	·009055	·011963	1·5554
Toluene	·007684	·008850	1·6522
Ethyl benzene	·008745	·008218	1·7616
Ortho-xylene	·011029	·010379	1·6386
Meta-xylene	·008019	·008646	1·6400
Para-xylene	·008457	·008494	1·7326
Water—			
0° to 8°	·017793	·017208	1·9944
0° to 100°	·017944	·023121	1·5423

CONSTANTS in SLOTTE'S Formula, $\eta = C/(1 + bt)^n$ (continued).

	C.	b.	n.
Methyl alcohol	·008083	·006100	2·6793
Ethyl alcohol	·017753	·004770	4·3731
Propyl alcohol	·038610	·007366	3·9188
Butyl alcohol—			
0° to 52°	·051986	·007194	4·2452
52° to 114°	·056959	·010869	3·2150
Isopropyl alcohol—			
0° to 40°	·045588	·007057	4·9635
40° to 78°	·048651	·011593	3·4079
Isobutyl alcohol—			
0° to 38°	·080547	·010840	3·6978
38° to 75°	·085365	·011527	3·6708
75° to 105°	·094725	·015838	3·0537
Inactive amyl alcohol—			
0° to 40°	·085358	·008488	4·3249
40° to 80°	·093782	·012520	3·3395
80° to 128°	·152470	·026540	2·4618
Active amyl alcohol—			
0° to 35°	·111716	·009851	4·3736
35° to 73°	·124788	·015463	3·2542
73° to 124°	·147676	·127583	2·0050
Trimethyl carbinol—			
20° to 50°	·135060	·128156	1·3242
50° to 77°	1·755458	·196967	2·0143
Dimethyl ethyl carbinol—			
0° to 27°	·142538	·020868	3·2080
27° to 63°	·154021	·027019	2·7578
63° to 95°	·131901	·026082	2·6610
Allyl alcohol	·021736	·009139	2·7925
Nitrogen peroxide	·005267	·007098	1·7349

(3.) The main cause of the want of regularity in the values of b and n is, no doubt, due to the fact that they are interdependent, and, as has been stated, that different pairs of values of these constants give practically the same curve. Moreover, from the mode of deducing their values, they are, in many cases, largely affected by influences which are within the limits of experimental error. On referring to p. 440 it will be seen that the denominator of the expression which serves to determine n is $(t_1 + t_3) - 2t_2$. In the case of curves which approach the linear type this denominator is but small, it may be but several tenths of a degree ; and, hence, since an error of one-twenty-fifth of a degree in reading off t_2 from the curve corresponds to one-tenth of a degree in the value of the denominator, in extreme cases the value of n may be altered by one-half by errors incidental to plotting and reading the curves employed. Thus, in the case of aldehyde, the denominator is 0°·3, and here an error of 0°·1 in obtaining t_2 would alter the value of n by more than 60 per cent. It is worth noting, however, that in spite of this uncertainty, which is, of course, greatest in the case of mobile liquids having low boiling-points, the value of n varies within comparatively narrow limits for all the liquids; if the alcohols investigated be excepted, the sixty-two remaining liquids give a mean value for n of 1·766. The maximum value 2·234 occurs in the case of isohexane, which has an extremely small value for b, and the minimum 1·408 in the case of bromine. Aldehyde gives the large value of 2·755 for n, but here the value of b is smaller than for any other substance; methyl alcohol gives a value similar to that given by aldehyde; but in the case of ethyl alcohol n is as high as 4·373. For the higher alcohols two or three formulæ are used in each case, but still the value of n remains in general high, its average value for the alcohols being 3·25. In the case of trimethyl carbinol the values of n are small; but here the values of b are enormous as compared with those given by the majority of the liquids. The alcohols thus differ from all the other liquids in giving larger values of n or of b, or of both these constants; they are thus characterised by the marked effect exerted by temperature on their viscosities.

From the fact that the values of n and b are small for the great majority of the substances, it became a matter of interest to ascertain if in the formula $\eta = \mathrm{C}/(1 + bt)^n$ a few terms in the expansion of $(1 + bt)^n$ would not suffice to denote the effect of temperature upon viscosity. For inasmuch as the coefficients of t, t^2, &c., in the expansion involve both n and b, it might be expected that the magnitudes of these coefficients would be related to the chemical nature of the substances.

The data given in the following table serve to test the above points when three terms in the expansion are employed.

In the columns headed β and γ are given, for all the liquids but the alcohols and water, the values of these coefficients in the expression

$$\eta = \mathrm{C}/(1 + nbt + \frac{n(n-1)}{1.2} b^2t^2) = \mathrm{C}/(1 + \beta t + \gamma t^2).$$

The remaining columns serve to give an idea of the accuracy with which this modified formula reproduces the observed values of η. Since the terms omitted in the formula are most important at high temperatures, the differences between observed and calculated values will be greatest at the highest temperatures. Under t are given temperatures as near as possible to the boiling points of the liquids and satisfying also the condition, which simplifies the calculations, that each is an integral product of 10. Under η (calculated) are given the values of η at the temperature t, as deduced from the above modified formula, and under η (observed) the values of η at t as read off from the curves. The differences obtained may be taken as the maximum differences between the observed and calculated values given at any temperature.

FORMULA, $\eta = C/(1 + \beta t + \gamma t^2)$.

	β.	γ.	t.	$\eta \times 10^5$ (Calc.).	$\eta \times 10^5$ (Obs.).	Difference $\times 10^5$.
Pentane	·01044	$\cdot 0_4 2301$	30	212	212	0
Hexane	·01122	$\cdot 0_4 3337$	60	221	221	0
Heptane	·01214	$\cdot 0_4 4004$	90	214	214	0
Octane	·01394	$\cdot 0_4 4926$	120	208	208	0
Isopentane	·01088	$\cdot 0_4 1331$	30	204	204	0
Isohexane	·01110	$\cdot 0_4 3509$	60	207	208	1
Isoheptane	·01199	$\cdot 0_4 3863$	80	216	216	0
Isoprene	·01002	$\cdot 0_4 1542$	30	198	198	0
Amylene	·00954	$\cdot 0_4 2000$	30	194	194	0
Diallyl	·01118	$\cdot 0_4 3017$	50	207	207	0
Methyl iodide	·01067	$\cdot 0_4 1719$	40	409	409	0
Ethyl iodide	·01113	$\cdot 0_4 2658$	70	377	378	1
Propyl iodide	·01278	$\cdot 0_4 3493$	100	358	359	1
Isopropyl iodide . . .	·01277	$\cdot 0_4 3899$	80	387	389	2
Isobutyl iodide . . .	·01523	$\cdot 0_4 4600$	120	333	338	5
Allyl iodide	·01316	$\cdot 0_4 3441$	100	349	352	3
Ethyl bromide	·01064	$\cdot 0_4 1822$	30	357	357	0
Propyl bromide . . .	·01174	$\cdot 0_4 3121$	70	326	327	1
Isopropyl bromide . .	·01193	$\cdot 0_4 3588$	50	358	358	0
Isobutyl bromide . . .	·01333	$\cdot 0_4 4762$	90	318	316	−2
Allyl bromide	·01177	$\cdot 0_4 2871$	70	315	316	1
Ethylene bromide . . .	·02007	$\cdot 0_4 7018$	130	513	518	5
Propylene bromide . .	·01924	$\cdot 0_4 7668$	140	444	456	12
Isobutylene bromide . .	·02379	$\cdot 0_3 12568$	140	489	505	16
Acetylene bromide . .	·01339	$\cdot 0_4 2999$	100	466	474	8
Propyl chloride . . .	·01104	$\cdot 0_4 3381$	40	291	291	0
Isopropyl chloride . .	·01185	$\cdot 0_4 2580$	30	291	291	0
Isobutyl chloride . . .	·01318	$\cdot 0_4 4045$	60	302	302	0
Allyl chloride	·01111	$\cdot 0_4 2639$	40	273	273	0
Ethylene chloride . . .	·01653	$\cdot 0_4 5451$	80	422	426	4
Ethylidene chloride . .	·01270	$\cdot 0_4 3252$	50	362	362	0
Methylene chloride . .	·01118	$\cdot 0_4 1866$	30	396	396	0
Chloroform	·01149	$\cdot 0_4 2588$	50	427	426	−1
Carbon tetrachloride .	·01801	$\cdot 0_4 6747$	60	520	524	4
Carbon dichloride . .	·01294	$\cdot 0_4 3243$	120	377	382	5

Formula, $\eta = C/(1 + \beta t + \gamma t^2)$—continued.

	β.	γ.	t.	$\eta \times 10^5$ (Calc.).	$\eta \times 10^5$ (Obs.).	Difference $\times 10^5$.
Methyl sulphide . . .	·00997	$\cdot 0_4 1584$	30	269	269	0
Ethyl sulphide	·01219	$\cdot 0_4 3340$	90	236	237	1
Carbon bisulphide . .	·00820	$\cdot 0_4 1302$	40	318	319	1
Dimethyl ketone . . .	·01064	$\cdot 0_4 3115$	50	245	245	0
Methyl ethyl ketone . .	·01284	$\cdot 0_4 3639$	80	238	239	1
Methyl propyl ketone .	·01325	$\cdot 0_4 3965$	100	238	238	0
Diethyl ketone	·01270	$\cdot 0_4 3734$	100	225	226	1
Acetaldehyde	·00963	$\cdot 0_4 2953$	20	222	222	0
Formic acid	·02870	$\cdot 0_3 16953$	100	526	542	16
Acetic acid	·01826	$\cdot 0_4 8537$	110	417	417	0
Propionic acid	·01720	$\cdot 0_4 6941$	140	319	322	3
Butyric acid	·02109	$\cdot 0_3 11073$	160	315	314	−1
Isobutyric acid . . .	·01917	$\cdot 0_4 9215$	150	317	317	0
Acetic anhydride . . .	·01735	$\cdot 0_4 6122$	140	268	275	7
Propionic anhydride . .	·02005	$\cdot 0_4 8315$	160	254	264	10
Ethyl ether	·01074	$\cdot 0_4 1828$	30	214	212	−2
Thiophen	·01518	$\cdot 0_4 4358$	80	349	350	1
Benzene	·01861	$\cdot 0_4 6181$	80	314	317	3
Toluene	·01462	$\cdot 0_4 4220$	110	246	250	4
Ethyl benzene	·01448	$\cdot 0_4 4530$	130	240	244	4
Ortho-xylene	·01701	$\cdot 0_4 5636$	140	249	254	5
Meta-xylene	·01418	$\cdot 0_4 3923$	130	229	233	4
Para-xylene	·01472	$\cdot 0_4 4578$	130	229	233	4
Bromine	·01258	$\cdot 0_4 2290$	50	743	746	3
Nitrogen peroxide . . .	·01231	$\cdot 0_4 3212$	20	418	418	0

Agreement of Observed and Calculated Values.

The differences given in the table show that in the great majority of cases the agreement is very close. Indeed it clearly points to the conclusion that an expression of the type

$$\eta = A/(1 + Bt + Ct^2)$$

will hold for most of the liquids.

Fifty-five of the liquids give differences which are not greater than 5 ; in most cases the differences are *nil.* Five of the liquids give differences greater than 5, the largest, viz., 3·6 per cent., being given by propionic anhydride. In most of the cases where the differences are greater than 2, slightly better agreement is obtained by introducing another term into the expansion. Since n is less than 2 for all of these liquids the additional term is negative, and the denominator in the formula is made smaller; the result is, that with the additional term the calculated values are all too large, whereas with three terms, as the table shows, they are all too small. In the case of ethylene bromide and ortho-xylene the negative differences obtained on using the additional term are greater than the positive differences given by the formula already used. Little advantage is therefore obtained by introducing another term into the formula, and in any case the small differences, given by all the substances in the preceding table indicate that the values of the coefficient β and γ closely represent the true effect of temperature upon viscosity, and that any connections which may be traced between the magnitudes of these coefficients and the chemical nature of the substances may therefore be regarded as valid relationships. The nature of these relationships is dealt with in what follows.

Relationships between the Magnitudes of the Temperature Coefficients β and γ.

On taking a general survey of the table it is evident that the fatty hydrocarbons and their monohalogen derivatives, the sulphides, the ketones, aldehyde and ether, are characterized by small values of the coefficients ; in these series temperature exerts the smallest effect on the viscosity. The aromatic hydrocarbons and thiophen have larger values of the coefficients, whilst the largest of all are given by the alkylene dibromides, the acids, and the anhydrides, to which may also be added ethylene dichloride and carbon tetrachloride.

On closer examination the following conclusions may be arrived at :

Homologues.—In general the coefficients increase as a homologous series is ascended. Exceptions to the rule occur in the case of the dibromides, formic and acetic acids, benzene and toluene, probably for the reasons already given when discussing the graphical representation of the results.

Corresponding Compounds.—In general the compound of higher molecular weight has the larger coefficients. This rule is obeyed by the chlorides, bromides, and iodides of the alkyls, by the allyl halogen compounds, and by ethylene chloride and bromide. The acids on the other hand, although they have smaller molecular weights, have much larger coefficients than the corresponding iodides.

Substitution of Halogen for Hydrogen.—On comparing the coefficients of the mono-bromides with those of the corresponding dibromides, the large increase in the values of the coefficients produced by the replacement of hydrogen by bromine is made evident. The chlormethanes also indicate that replacement of one atom of hydrogen by one atom of chlorine also raises the values of the coefficients; that the increase varies with the amount of chlorine already present in the molecule is shown by the large values of the coefficients given by carbon tetrachloride.

In connection with these substances the large coefficients of the alkylene dibromides as compared with those of acetylene dibromide and bromine, of ethylene dichloride as compared with ethylidene chloride, and of tetrachlormethane as compared with tetrachlorethylene, are noteworthy.

Isomers.—Normal and iso compounds have coefficients which are almost the same. The acids constitute the most marked exception, probably on account of the disturbing effect of molecular complexity.

Of the two isomeric ketones, diethyl ketone, the symmetrical isomer, has the smaller coefficients; the opposite conclusion holds in the case of the chlorethanes.

The values for the isomeric aromatic hydrocarbons clearly indicate the peculiar behaviour of ortho-xylene which has considerably larger values than the closely agreeing numbers given by the other isomers.

Water.

The values of the coefficients obtained for water are as follows:—

	β.	γ.	t.	$\eta \times 10^5$ (calc.).	$\eta \times 10^5$ (obs.).	Diff. × 10^5.
Water	·03580	$\cdot 0_3 2253$	100	263	283	20

The difference between the observed and calculated numbers is greater than that given by any of the substances in the preceding tables, and on introducing another term into the formula the difference is changed from + 20 to − 14, so that little advantage is thus derived. The above agreement is sufficiently close to allow β and γ to be regarded as expressing the temperature effect with sufficient accuracy for the end at present in view, and the magnitudes of these coefficients are particularly interesting. For, although γ is smaller than in the case of several of the liquids given in the first set of tables, the value of β given by water is the largest of any yet considered. At low temperatures, temperature has a large effect on the viscosity of water; at higher temperatures, however, the effect is relatively smaller than in the case of liquids with correspondingly large values of β. In its behaviour at low temperatures, water strongly resembles the acids, and more especially the alcohols, and there is little doubt that the peculiarities of all these liquids are to be ascribed to the presence of molecular aggregations.

The Alcohols.

The only two alcohols, which had values of n which were not very far removed from 2, coupled with moderately small values of b, and which, therefore, had any likelihood of giving a serviceable formula of the type already used, were methyl and allyl alcohols. The results for these two alcohols are given below :—

	β.	γ.	t.	$\eta \times 10^5$ (calc.).	$\eta \times 10^5$ (obs.).	Diff. × 10^5.
Methyl alcohol .	·01634	$\cdot 0_4 8371$	60	354	349	− 5
Allyl alcohol . .	·02552	$\cdot 0_3 20902$	90	436	407	− 29

Methyl alcohol gives a moderately small difference, the values of its coefficients being somewhat the same as those of the acids. Allyl alcohol gives a much larger difference, and has larger coefficients than methyl alcohol. It is to be noted that in both cases the values of γ are large, pointing to large temperature changes at the higher temperatures.

Of the remaining alcohols the values of n or of b, or of both, are so large as to preclude any chance of agreement between the results of observation and those given by a formula with three terms, and nothing would be gained by the use of formulæ involving such a number of terms as would make the agreement satisfactory. For the large values of n and b, given by the alcohols, clearly indicate that with them the effect of temperature upon viscosity is in general much more pronounced than in any other series. In the following table are given for each alcohol the values for β and γ, obtained, as before, from SLOTTE'S formula. Where several of these formulæ have been used only that corresponding to the lowest temperature range is given in each case. The range over which the original SLOTTE'S formula applied is indicated in the table. The values are given merely for the purpose of showing how the behaviour of the alcohols differs from that of the other substances.

FORMULA, $\eta = C/(1 + \beta t + \gamma t^2)$.

	Range.	β.	γ.
Ethyl alcohol	0° to 78°	·02086	·0016782
Propyl alcohol	0° to 98°	·02495	·0026818
Butyl alcohol	0° to 52°	·03054	·0035650
Isopropyl alcohol	0° to 40°	·03503	·0004898
Isobutyl alcohol	0° to 38°	·04008	·0005861
Inactive amyl alcohol	0° to 40°	·03671	·0005180
Active amyl alcohol	0° to 35°	·04308	·0007159
Trimethyl carbinol	20° to 50°	·16971	·0035257
Dimethyl ethyl carbinol	0° to 27°	·06694	·0015423

From the above table it follows that, although the values of β in the case of ethyl and propyl alcohols are somewhat less than those given by one or two of the liquids which had the largest values in the first table, yet in all cases the values of γ are much larger than for any of the liquids previously discussed. Here we have the indication of the persistence of large temperature alterations at high temperatures, which brings about the long steep curves so characteristic of the alcohols.

It is further evident from the table that the values of the coefficients of the normal alcohols increase with the rise in molecular weight and increase on passing to the corresponding iso-alcohol, and still further increase on passing to the corresponding tertiary alcohol. The largest values of all the temperature coefficients is possessed by tertiary butyl alcohol (trimethyl carbinol).

It is also noteworthy that inactive amyl alcohol has smaller coefficients than isobutyl alcohol, and, further, that the large differences between the coefficients of active and inactive amyl alcohols point to the markedly different courses taken by the curves of these closely-related isomers over the low temperature ranges.

The alcohols, like the acids, have much larger temperature coefficients, although smaller theoretical molecular weights than the corresponding iodides. This result is no doubt to be attributed to the presence of molecular aggregates in the liquid alcohols. It must be noted, however, that the behaviour of the alcohols differs from that of the acids, for, in the latter, the coefficients at first diminish in ascending the series of normal acids, and isobutyric acid has smaller coefficients than normal butyric acid; whereas, in the case of the alcohols, there is a persistent rise in the values of the coefficients as the series of normal alcohols is ascended, and isobutyl alcohol has larger coefficients than normal butyl alcohol. These results are no doubt to be ascribed to differences in the mode in which the complexity alters in the two series.

The preceding discussion serves to show that the effect which temperature exercises on the viscosity of a liquid substance is related to its chemical nature and physical constitution.

Conclusions concerning the Effect of Temperature on Viscosity.

1. SLOTTE's formula gives the best results in the case of observed viscosity curves in which the slope varies but little with the temperature.

Where the variation of the slope is considerable, as in the case of the alcohols, several formulæ of this type have to be employed in order to represent the effect of temperature upon viscosity with sufficient accuracy.

2. As regards the relations between the chemical nature of the substances, and the magnitudes of their temperature coefficients, it is evident that :—

(*a*) From the mode in which the constants n and b, in SLOTTE's formula, are derived, their individual values cannot be expected to be simply related to chemical nature ;

(*b*) For the majority of the liquids, the formula,

$$\eta = C/(1 + \beta t + \gamma t^2),$$

obtained from SLOTTE's formula by neglecting terms in the denominator involving higher powers of t than t^2, closely expresses the effect of temperature on viscosity, and, in this formula, the magnitudes of the coefficients β and γ are definitely related to the molecular weight and the constitution of the substances ;

(*c*) The substances, to which this modified formula does not apply, are characterized by large temperature coefficients, and these substances are in general those which, like water, the acids, and the alcohols, contain molecular aggregates.

COMPARISONS OF VISCOSITY MAGNITUDES AT COMPARABLE TEMPERATURES.

Comparable Temperatures.

The examination of the curves for families of related substances gives, of course, a general idea of how the viscosity varies from member to member. In order, however, to obtain quantitative relationships between viscosity and chemical nature, and to compare one group of substances with another, it was necessary to fix upon particular temperatures, and to obtain and compare the values corresponding with those temperatures.

The first point to decide was at what temperature viscosities should be compared.

In the past, owing to the fact that the temperature variation has been little studied, it has been customary to employ one and the same temperature for all substances.

The kind of relationships which are obtained by such a system of comparison have already been indicated in connection with the graphical representation of our observations. We have thought it needless to say anything further regarding this method, for, as has been shown, the viscosity curves, even in the same family of substances cross one another, so that quantitative relationships obtained at any single temperature of comparison can have no pretensions to generality, but must vary with the value of the particular temperature selected.

The first comparable temperature which suggested itself was the boiling-point, and the detailed examination of viscosity at the boiling-point is first set out. With such data as could be obtained relating to critical temperatures, we then calculated values of corresponding temperatures by the method indicated by VAN DER WAALS. The particular temperature adopted (·6) was such that it included the greatest number of cases. A very brief summary of the results obtained at the corresponding temperature of ·6 is next given. Following this are the results obtained by the use of a new system of deducing comparable temperatures, the details of which are given on pp. 622 and 623.

Viscosity Magnitudes dealt with at the Different Temperatures of Comparison.

At each of the different conditions of comparison the experimental results have been expressed according to the same system, in order to show at a glance relationships between the magnitudes of the viscosity constants and the chemical nature of the substances. The liquids are arranged so that chemically-related substances are grouped together—groups of homologues, chlorides, bromides, and iodides, propyl and allyl compounds, groups of isomers, &c. The alcohols, on account of their peculiar behaviour at all the conditions of comparison, are kept more or less separate from the other liquids. Tables are constructed in this way which give the values of three different magnitudes derivable from measurements of the viscosity of the substances.

(1) *Values of the Viscosity Coefficient.* (η.)

The first set of tables contains values of the viscosity coefficient in dynes per sq. centim. and exhibit how this physical constant varies from liquid to liquid at the temperature of comparison.

(2) *Values of* η × *Specific Molecular Area. The Molecular Viscosity.* (ηd^2.)

The second set of tables contains values of the coefficients η treated so as to quantitatively connect them with the chemical nature of the substances. The absolute coefficient η is the force in dynes which has to be exerted per unit area of a liquid surface in order to maintain its velocity relative to that of another parallel surface at unit distance equal to unity. It seemed, however, that relations between viscosity and chemical nature would best be brought to light if instead of adopting merely unit areas we selected areas which were related to the specific molecular volumes of the liquids. If M be in grams a weight of substance numerically equal to its molecular weight, and if ρ be the density of the liquid, M/ρ is the specific molecular volume d^3, or a volume of liquid in cub. centim. which contains for different substances the same number of gaseous molecules.

d^2 evidently gives in sq. centim. the area of the face of a cube which may be taken to represent the specific molecular volume. This area we term the specific molecular area and the product of η and the specific molecular area ($\eta \times d^2$) we term the molecular viscosity. With the units employed, it is the force in dynes which has to be exerted on a liquid surface equal to the specific molecular area in sq. centim. in order to maintain its velocity equal to unity under the unit conditions laid down in the definition of the viscosity coefficient.

In the absence of a dynamical theory of the nature of liquid viscosity if we assume, as has already been done by Eötvös, that on the specific molecular area there are distributed, on the average, the same number of molecules, the molecular viscosity may be taken as proportional to the force which has to be exerted on a liquid molecule in order to maintain its velocity equal to unity under unit conditions.

(3) *Values of* $\eta \times$ *Specific Molecular Volume. The Molecular Viscosity Work.* ($\eta \times d^3$.)

The product of η and the specific molecular volume exhibits relations to chemical nature of the same kind as those given by molecular viscosity. This product ηd^3 is evidently the molecular viscosity multiplied by d which is the length in centimeters of the edge of the cube which represents the specific molecular volume, and this length we term the specific molecular length. ηd^3 has evidently the dimensions of work, and for this reason we term it the molecular viscosity work. In ordinary units it is the work in ergs required to move a liquid surface equal to the specific molecular area in sq. centim. through the specific molecular length in centim. under unit conditions. If the specific molecular length be assumed to be proportional to the average distance between the centres of two adjacent molecules the molecular viscosity work is proportional to the work spent in moving a molecule through the average distance between two molecules under unit conditions.

In deducing the specific molecular volumes, specific molecular areas, etc., gaseous molecular weights were employed. It was therefore to be expected that the relationships between the magnitudes of the molecular viscosity and molecular viscosity work, existing in the case of liquids for which the liquid and gaseous molecular weights were identical, would no longer be the same when the liquids contained aggregates of gaseous molecules. By this mode of treatment it was hoped that if these magnitudes were simply related amongst themselves in the case of non-associated liquids, deviations from such regularities would be exhibited by complex liquids, and these deviations would give some indication of the existence and extent of the molecular grouping.

A. Comparisons of Viscosity Magnitudes at the Boiling-Point.

Following the suggestion of SCHRÖDER and KOPP, the temperature of the ordinary boiling-point has been largely used in the comparison of the physical constants of liquids; at this temperature the vapour pressures of the substances are, of course, the same, and this equality seemed to justify the use of the boiling-point as a comparable temperature.

GULDBERG has pointed out that the reason why KOPP obtained relationships between the densities of liquids and their chemical nature at the boiling-point, probably lies in the fact that the boiling-point is approximately a so-called corresponding temperature.

If the absolute boiling-point be divided by the absolute critical temperature, a quotient having the average value of 2/3 is obtained, so that the ordinary boiling-point is approximately the corresponding temperature of ·66. According to the theoretical views of VAN DER WAALS, the thermal properties of liquids should be compared at such corresponding temperatures, and the accidental agreement between the boiling-point and the corresponding temperature of ·66 is taken by GULDBERG as being the reason for the success of the boiling-point as a temperature of comparison.

It may be contended, however, that this argument is not altogether valid. Seeing that, in general, the higher the boiling-point the higher is the critical temperature and the larger is the difference between the two, the ratio of the absolute boiling-point to the absolute critical temperature cannot vary very much for different substances.

It may be written—

$$\frac{\text{B.P.} + 273}{\text{B.P.} + 273 + \text{C.T.} - \text{B.P.}}, \quad \text{or} \quad 1 - \frac{\text{C.T.} - \text{B.P.}}{\text{C.T.} + 273},$$

where B.P. is the ordinary boiling-point and C.T. the ordinary critical temperature expressed on the centigrade scale.

Here the ratio is seen to be unity diminished by a fraction in which the numerator increases along with the denominator, which latter contains a large constant term, viz., 273.

According to another deduction from VAN DER WAALS' theory substances may be compared when under corresponding pressures, or pressures which are the same fraction of their critical pressures. Comparisons at corresponding temperatures should lead to like results. If the boiling-point were a truly corresponding temperature, then the vapour pressure at the boiling-point should for all liquids be the same fraction of the critical pressure.

But at the boiling-point the vapour pressures of different substances are the same, and hence if the boiling-point be approximately a corresponding temperature, the critical pressures of substances ought to be approximately the same. This conclusion, however, is not supported by facts, and hence, having regard to the doctrine of corresponding pressures, GULDBERG'S view, that the boiling-point may be regarded as a corresponding temperature, receives no support from VAN DER WAALS' theory.

Hitherto the boiling-point has been mainly of value as a comparable temperature in dealing with properties which, like density or surface energy, vary but slowly with the temperature.

It was a matter of interest, therefore, to determine if it led to good results in the case of a property like viscosity, which alters rapidly with the temperature. No doubt physico-chemical relationships, even in the case of these slowly changing properties, are not so definite as might be desired, and the want of precision may in part be due to the fact that at the boiling-point the substances are not in really comparable conditions. Evidence on this point seemed most likely to be gained by the study of a property which, like viscosity, varies so largely with temperature.

In deciding upon the particular boiling-points to be adopted, we have made a careful critical examination of all existing data, and have selected the mean value of what seemed to be the best authenticated determinations, including our own.

In the following tables the values of η have been read from the curves, and are multiplied by 10^5 in order to avoid the use of decimals.

COEFFICIENTS OF VISCOSITY AT THE BOILING-POINT.

(η in dynes per sq. centim. × 10^5.)

HOMOLOGUES.

	η.	Difference.
Pentane	200	
Hexane	204	4
Heptane	199	− 5
Octane	198	− 1
Isopentane	203	
Isohexane	205	2
Isoheptane	198	− 7
Isoprene	188	
Diallyl	192	4

Homologues (continued).

	η.	Difference.
Methyl iodide	399	− 28
Ethyl iodide	371	− 18
Propyl iodide	353	
Isopropyl iodide	359	− 21
Isobutyl iodide	338	
Ethyl bromide	329	− 4
Propyl bromide	325	
Isopropyl bromide	329	− 18
Isobutyl bromide	311	
Ethylene bromide	514	− 64
Propylene bromide	450	
Isopropyl chloride	275	5
Isobutyl chloride	280	
Methylene dichloride	363	47
Ethylene dichloride	410	
Methyl sulphide	253	− (10)
Ethyl sulphide	234	
Dimethyl ketone	232	− (5)
Diethyl ketone	222	
Methyl ethyl ketone	239	− 5
Methyl propyl ketone	234	
Formic acid	536	− 151
Acetic acid	385	− 66
Propionic acid	319	− 10
Butyric acid	309	

Homologues (continued).

	η.	Difference.
Acetic anhydride	277	
		– (15)
Propionic anhydride	247	
Benzene	316	
		– 68
Toluene	248	
		– 15
Ethyl benzene	233	
Methyl alcohol.	329	
		112
Ethyl alcohol	441	
		22
Propyl alcohol	463	
		– 58
Butyl alcohol	405	
Isopropyl alcohol	491	
		– 39
Isobutyl alcohol	452	
		– 74
Isoamyl alcohol	378	
Trimethyl carbinol	566	
		– 148
Dimethyl ethyl carbinol	418	

It is apparent from the table that the effect on the viscosity-coefficient of an increment of CH_2 in molecular weight varies from series to series.

Paraffins.—In this series the viscosity-coefficient is practically the same, both in the case of normal and iso-hydrocarbons. Here we have the somewhat striking result that the magnitude of the coefficient is practically independent of molecular weight. A similar result holds for the two C_nH_{2n-2} hydrocarbons, isoprene and diallyl, and also for the alkyl chlorides, as the viscosity coefficient of propyl chloride, which does not occur in the table, is 274.

In all the other series, with the exception of methylene and ethylene chlorides and the alcohols—that is, in the case of the iodides, bromides, sulphides, ketones, acids, anhydrides and aromatic hydrocarbons, an increment of CH_2 brings about a diminution in the viscosity coefficient. Moreover, it is the general rule that the diminution becomes less and less as the series is ascended.

In the case of the dichlorides the compound of higher molecular weight has a decidedly higher coefficient. This difference is no doubt affected by the same cause which brings about the wide separation of the curves of the isomeric dichlorethanes.

If ethylidene chloride be used instead of ethylene chloride, a negative difference, — 25, as in most other series, is obtained for the effect of CH_2.

The fact, too, that methylene chloride is the lowest member of the series, and contains only one carbon atom, may be important.

The large differences brought about by the values for formic acid and benzene are further indications of the abnormal coefficients possessed by the initial members of homologous series.

Alcohols.—This series, as is the case under every condition of comparison, differs from all the others. An increment of CH_2 not only exercises great influence on the viscosity coefficient, but its effect is exceptional, inasmuch as the sign changes as the molecular weight increases.

The differences between the first three members are positive; all the others are negative. In the tertiary alcohols the effect of CH_2 is at a maximum, and reaches the large value of — 148.

CORRESPONDING Compounds.

	Iodide.	Diff.	Bromide.	Diff.	Chloride.	Diff.	Acid.	Diff.	Alcohol.
	η.		η.		η.		η.		η.
Methyl	399	..	..	..	..	−137	536	70	329
Ethyl	371	42	329	..	..	− 14	385	− 70	441
Propyl	353	28	325	51	274	34	319	−110	463
Butyl	..	..	..	..	..	..	309	..	405
Isopropyl . . .	359	30	329	54	275	..	..	−132	491
Isobutyl . . .	338	27	311	31	280	31	307	−114	452
Allyl	344	29	315	53	262	..	..	− 29	373
Ethylene . . .	..	..	514	(52)	410				

On comparing the coefficients of corresponding halogen compounds a marked regularity is apparent. The iodide has a coefficient which is invariably larger, in general, by some 30 units, than that of the corresponding bromide, while the bromide has in turn a coefficient which is invariably larger than that of the corresponding chloride, in general by some 50 units. There is here a close connection between the molecular weights of the halides and the magnitude of their coefficients, whether the compounds be normal or iso alkyl derivatives, or allyl or ethylene derivatives.

On comparing the acids with the iodides, the two lowest members exhibit a marked irregularity. Formic acid has a coefficient which is more than half as large again as that of methyl iodide, although the latter has the higher molecular weight. The coefficient of acetic acid is still larger than that of ethyl iodide, although the difference is only one-tenth of what it was in the case of the formic acid comparison. Propionic and isobutyric acid give values which are uniformly less by some 30 units than those of the corresponding iodides, so that sufficiently high up in the acid series the members conform to the rule that the compound of lower molecular weight has the lower viscosity.

This behaviour of the acids with reference to the iodides is very probably to be attributed to the high molecular complexity of the lowest acids. If the viscosity coefficient is greater the higher the molecular weight of the liquid molecule, on using RAMSAY and SHIELDS' observations to estimate the molecular complexity, it follows that acetic acid should have a slightly larger viscosity than ethyl iodide, and higher acids should have smaller viscosities than the corresponding iodides just as is the case in the above table. Formic acid, on the other hand, although its complexity appears from surface-energy observations to be about the same as that of acetic acid, has, at its boiling-point, a smaller liquid molecular weight than methyl iodide, and would be expected to have a correspondingly smaller viscosity. This is, however, not the case, and points either to the fact, as already stated, that the surface-energy observations employed do not give a correct measure of the complexity, or that formic acid, as initial member of the homologous series, gives a peculiar value of the viscosity coefficient.

On comparing the alcohols with the iodides, methyl alcohol is seen to have a much smaller coefficient than methyl iodide, but for the remaining alcohols given in the table the coefficients are decidedly greater than those of the iodides; for the saturated alcohols the difference is about 100 units.

These results cannot be easily explained. According to surface-energy measurements the weights of the molecules of the liquid alcohols are invariably lower than the ordinary molecular weights of corresponding iodides. Methyl alcohol, however, is the only alcohol which has a lower viscosity than the corresponding iodide.

In explanation of these anomalies the following points must be borne in mind :—

1. The degree of molecular complexity may not be accurately indicated by surface-energy measurements.

2. The molecular complexity of the alcohols may increase with rise in molecular weight.

3. The boiling-point may not be a suitable condition of comparison.

That the boiling-point is a suitable condition of comparison in the case of the chlorides, bromides, and iodides is shown by the fairly definite relations exhibited. Hence, it is probable that the molecular complexity of the alcohols does increase with rise in molecular weight, contrary to the conclusion arrived at from surface-energy measurements.

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	η.		η.
Hydrocarbons	204	(6)	192
Iodides	353	9	344
Bromides	325	10	315
Chlorides	274	12	262
Alcohols.	463	90	373

ETHYLENE and Acetylene Bromides.

	Ethylene.	Acetylene.	
Bromides	514	72	442

With the exception of the alcohols, a normal propyl compound has invariably a slightly larger coefficient than the corresponding allyl compound, the average difference being some 9 units. It is noteworthy that diallyl and normal hexane are related in the same way as the halogen derivatives. In the case of the alcohols, the difference is still in the same sense but has reached the value of 90 units, or 10 times its magnitude in the preceding comparisons, a result no doubt due to molecular complexity.

Ethylene and acetylene bromides may be compared here, as they differ in constitution in the same way as normal propyl and allyl compounds. The saturated compound has a coefficient which is the larger by some 72 units, a value comparable with that given by the alcohols.

ISOLOGOUS Hydrocarbons.

n.	(Normal) C_nH_{2n+2}.	Difference.	C_nH_{2n}.	Difference.	C_nH_{2n-2}.	Difference.	C_nH_{2n-6}.
	η.		η.		η.		η.
5	200	15	185	12	188		
6	204	. .	. .	12	192	−112	316
7	199	. .	. .	. .	. .	− 49	248
8	198	. .	. .	. .	. .	− 35	233

On comparing normal pentane with isoamylene, loss of hydrogen is attended by a slight fall in viscosity of some 15 units. Isoprene and diallyl give numbers which differ from those of the corresponding paraffins by about the same amount, some 12 units. It is thus evident, that in passing from amylene to isoprene, the effect of loss of hydrogen on the viscosity-coefficient is counterbalanced by constitutive influences.

The effects of constitution are well illustrated by the numbers given by the aromatic hydrocarbons which are decidedly larger than those of the corresponding paraffins, so that fall in molecular weight appears to be accompanied by rise in viscosity. The large difference given by benzene may be attributed to the anomalous behaviour exhibited in general by the lowest members of homologous series, to which reference has already been made.

SUBSTITUTION of Halogen for Hydrogen.

Bromine for hydrogen.				Chlorine for hydrogen.		
n.	$C_nH_{2n}Br_2$.	$C_nH_{2n+1}Br$.		Chlormethanes.		
	η.	Difference.	η.		η.	Difference.
2	514	185	329	Methylene chloride . .	363	23
3	450	125	325	Chloroform	386	102
4 (Iso)	467	156	311	Carbon tetrachloride .	488	

On comparing alkylene dibromides with alkyl bromides containing the same number of carbon atoms, it is evident that on replacing hydrogen by bromine the viscosity coefficient is largely increased. The variation of the effect with increase in molecular weight is, however, not regular; this is probably due, as already indicated, to the peculiar behaviour of propylene bromide.

The values for the chlormethanes indicate that, although the effect of substituting hydrogen by chlorine is to increase the coefficient, yet the magnitude of the effect depends to a great extent on the amount of halogen already present in the molecule.

COMPOUNDS Differing by 1 Carbon Atom.

	η.	Diff.		η.	Diff.
Tetrachlormethane . . .	488	−107	Methyl alcohol	329	−110
Tetrachlorethylene . . .	381		Aldehyde	219	

The introduction of a carbon atom and the occurrence of a double linkage, which takes place in passing from tetrachlormethane to tetrachlorethylene, is followed by a considerable lowering of the viscosity coefficient, viz., 107 units.

This effect is almost the same as that produced on passing from methyl alcohol to acetaldehyde, where O is replaced by CO. It must not be forgotten, however, that in the case of methyl alcohol the result is affected by molecular complexity.

ISOMERS.

NORMAL and Iso Compounds.

	Normal.	Difference.	Iso.
	η.		η.
Pentanes	200	− 3	203
Hexanes	204	− 1	205
Heptanes	199	1	198
Propyl iodides	353	− 6	359
Propyl bromides	325	− 4	329
Propyl chlorides	274	− 1	275
Butyric acids	309	2	307
Propyl alcohols	463	−28	491
Butyl alcohols	405	−47	452

Excluding the alcohols, the viscosity-coefficient of an iso compound is either slightly greater than, or almost equal to, that of the corresponding normal compound. In the seven cases cited, the coefficient of the iso compound is, on the average, greater by some two units. In the case of the alcohols the differences are in the same sense, but have considerably larger values, viz., 28 and 47 units.

BUTYL Alcohols and Ethyl Ether.

	η.	Difference.
Normal butyl alcohol	405	47
Isobutyl alcohol	452	114
Trimethyl carbinol	566	
Ethyl ether	205	

AMYL Alcohols.

	η.	Difference.
Inactive amyl alcohol	378	
		−4
Active amyl alcohol	374	
		44
Dimethyl ethyl carbinol	418	

On comparing the coefficients of the isomeric alcohols they seem to vary in a regular way with the constitution. The more branched the chain of atoms in the molecule the higher is the viscosity. A tertiary alcohol has a larger coefficient than an iso-alcohol, and an iso alcohol than a normal alcohol. Active and inactive amyl alcohols have almost the same coefficients at their boiling-points.

If the above relations are affected by complexity, it is evident that the extent of the complexity is dependent on the chemical nature of the substances.

ALLYL Alcohol and Acetone.

	η.	Difference.
Allyl alcohol	373	
		−141
Acetone	232	

Allyl alcohol has a value which is more than half as large again as that of acetone, and, as is shown in the preceding table, butyl alcohol a value which is more than twice as large as that of ethyl ether. These results are, no doubt, affected both by differences in chemical constitution and of molecular complexity.

DICHLORETHANES.

	η.	Difference.
Ethylene chloride	410	
		−72
Ethylidene chloride	338	

ISOMERIC Ketones.

	η.	Difference.
Diethyl ketone	222	12
Methyl propyl ketone	234	

Ethylene chloride gives a coefficient which is markedly larger than that of ethylidene chloride. Here the symmetrical isomer has the larger value. In the case of the isomeric ketones, however, the symmetrical compound has slightly the smaller coefficient. The probable cause of this result has already been indicated.

AROMATIC Hydrocarbons.

	η.	Difference.
Ortho-xylene	247	−28
Meta-xylene	219	1
Para-xylene	220	13
Ethyl benzene	233	

Meta- and para-xylene have identical coefficients, which are, however, removed from that of ortho-xylene, which is some 30 units larger. The value for ethyl benzene is between that of ortho-xylene and of the other two isomers.

General Conclusions relating to Viscosity Coefficients at the Boiling-point.

The results arrived at from the previous discussion may be summarized as follows:—

(1.) As an homologous series is ascended, in a few cases the viscosity coefficients remain practically the same, but in the greater number of series the coefficients diminish.

In one series the coefficients increase.

In the case of the alcohols the coefficients vary irregularly with ascent of the series.

(2.) Of corresponding compounds, the one having the highest theoretical molecular weight has in general the highest coefficient.

The acids and, to a much greater extent, the alcohols do not accord with this rule.

(3.) Normal propyl compounds have, as a rule, slightly higher values than allyl compounds; in the case of the alcohols propyl compounds have much the higher value.

(4.) The effect of molecular weight is in some cases more than counterbalanced by the effect of constitution or of complexity.

(5.) The lowest members of homologous series frequently exhibit deviations from the regularities shown by higher members.

(6.) An iso compound has, in general, a larger coefficient than a normal compound, and the differences reach their maximum in the case of the alcohols.

(7.) In the case of other metameric substances, branching of the atomic chain and the symmetry of the molecule influence the magnitudes of the coefficients; the ortho-position, in the case of aromatic compounds, appears to have a more marked effect on the coefficient than either the meta- or para-positions. The isomeric normal alcohols give values which are almost twice as large as those of acetone and ethyl ether.

(8.) One of the most striking points thus brought to light is the peculiar behaviour of the alcohols, and to some extent of the acids, as contrasted with that of other liquids.

MOLECULAR VISCOSITY (η × SPECIFIC MOLECULAR AREA = ηd^2) AT THE BOILING-POINT.

(η in dynes per sq. centim. × specific molecular area in sq. centims. × 10^4).

HOMOLOGUES.

	ηd^2.	Difference.
Pentane	480	70
Hexane	550	43
Heptane	593	53
Octane	646	
Isopentane	489	62
Isohexane	551	37
Isoheptane	588	
Isoprene	415	68
Diallyl	483	
Methyl iodide	639	82
Ethyl iodide	721	74
Propyl iodide	795	
Isopropyl iodide	816	46
Isobutyl iodide	862	

Homologues (continued).

	ηd^2.	Difference.
Ethyl bromide	597	89
Propyl bromide	686	
Isopropyl bromide	705	56
Isobutyl bromide	761	
Ethylene bromide	1089	– 4
Propylene bromide	1085	
Isopropyl chloride	567	90
Isobutyl chloride	657	
Methylene chloride	587	208
Ethylene chloride	795	
Methyl sulphide	450	(61)
Ethyl sulphide	572	
Dimethyl ketone	420	(57)
Diethyl ketone	533	
Methyl ethyl ketone	504	61
Methyl propyl ketone	565	
Formic acid	639	– 24
Acetic acid	615	15
Propionic acid	630	72
Butyric acid	702	
Acetic anhydride	635	(38)
Propionic anhydride	710	
Benzene	661	– 65
Toluene	596	28
Ethyl benzene	624	

Homologues (continued).

	ηd^2.	Difference.
Methyl alcohol	401	
		292
Ethyl alcohol	693	
		176
Propyl alcohol	869	
		14
Butyl alcohol	883	
Isopropyl alcohol	928	
		59
Isobutyl alcohol	987	
		– 51
Isoamyl alcohol	936	
Trimethyl carbinol	1243	
		– 219
Dimethyl ethyl carbinol	1024	

CORRESPONDING Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	$\eta\ d^2$.	Diff.	$\eta\ d^2$.	Diff.	$\eta\ d^2$	Diff.	$\eta\ d^2$.	Diff.	$\eta\ d^2$.
Methyl	639	..	..	..	..	0	639	238	401
Ethyl	721	124	597	..	..	106	615	28	693
Propyl	795	109	686	129	557	165	630	– 74	869
Butyl	..	..	..	..	..	..	702	..	883
Isopropyl	816	111	705	138	567	..	..	–112	928
Isobutyl	862	101	761	104	657	162	700	–125	987
Allyl	745	110	635	131	504	..	..	86	659
Ethylene	..	..	1089	(147)	795	..	..	..	..

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	$\eta\, d^2$.		$\eta\, d^2$.
Hydrocarbons	550	(34)	483
Iodides	795	50	745
Bromides	686	51	635
Chlorides	557	53	504
Alcohols	869	210	659

ETHYLENE and Acetylene Bromides.

	Ethylene.	Difference.	Acetylene.
	$\eta\, d^2$.		$\eta\, d^2$.
Bromides	1089	194	895

ISOLOGOUS Hydrocarbons.

n.	C_nH_{2n+2}.	Diff.	C_nH_{2n}.	Diff.	C_nH_{2n-2}.	Diff.	C_nH_{2n-6}.
	$\eta\, d^2$.		$\eta\, d^2$.		$\eta\, d^2$.		$\eta\, d^2$.
5	480	60	420	65	415		
6	550	..	..	67	483	−111	661
7	593	..	..	..	..	− 3	596
8	646	..	..	..	..	22	624

SUBSTITUTION of Halogen for Hydrogen.

Bromine for hydrogen.				Chlorine for hydrogen.		
n.	$C_nH_{2n}Br_2$.	Diff.	$C_nH_{2n}Br$.	Chlormethanes.		Diff.
	$\eta\, d^2$.		$\eta\, d^2$.		$\eta\, d^2$.	
2	1089	492	597	Methylene chloride . . .	587	156
3	1085	399	686	Chloroform.	743	334
4 (Iso)	1274	513	761	Carbon tetrachloride . .	1077	

COMPOUNDS differing by one Carbon Atom.

	$\eta\ d^2$.	Diff.		$\eta\ d^2$.	Diff.
Tetrachlormethane . . .	1077	−179	Methyl alcohol	401	−79
Tetrachlorethylene . . .	898		Aldehyde	322	

ISOMERS.

NORMAL and Iso Compounds.

	Normal.	Difference.	Iso.
	$\eta\ d^2$.		$\eta\ d^2$.
Pentanes	480	− 9	489
Hexanes	550	− 1	551
Heptanes	593	5	588
Propyl iodides	795	− 21	816
Propyl bromides . . .	686	− 19	705
Propyl chlorides . . .	557	− 10	567
Butyric acids	702	2	700
Propyl alcohols . . .	869	− 59	928
Butyl alcohols	883	−104	987

BUTYL Alcohols and Ethyl Ether.

	$\eta\ d^2$.	Difference.
Normal butyl alcohol	883	104
Isobutyl alcohol	987	256
Trimethyl carbinol	1243	
Ethyl ether.	459	

AMYL Alcohols.

	$\eta\ d^2$.	Difference.
Inactive amyl alcohol	936	− 16
Active amyl alcohol	920	104
Dimethyl ethyl carbinol	1024	

ALLYL Alcohol and Acetone.

	$\eta\ d^2$.	Difference.
Allyl alcohol	659	−239
Acetone	420	

DICHLORETHANES.

	$\eta\ d^2$.	Difference.
Ethylene chloride.	795	−121
Ethylidene chloride	674	

ISOMERIC Ketones.

	$\eta\ d^2$.	Difference.
Diethyl ketone	533	32
Methyl propyl ketone	565	

AROMATIC Hydrocarbons.

	$\eta\ d^2$.	Difference.
Ortho-xylene	660	−70
Meta-xylene	590	4
Para-xylene.	594	30
Ethyl benzene	624	

Conclusions relating to Molecular Viscosity at the Boiling-point.

(1.) The foregoing tables make it evident that, with the exception of the alcohols, the dibromides and the lowest members of homologous series, an increment of CH_2

in chemical composition corresponds with an increase in molecular viscosity. This increase is, however, far from being constant, even in the same series.

(2.) With the above exceptions, it is also apparent that the corresponding compound having the highest molecular weight has the highest molecular viscosity, and the differences between the members of two corresponding series are fairly constant.

(3.) The relationships shown in the other tables are substantially of the same nature as those given by the viscosity coefficients.

The comparisons which give the largest deviations from regularity contain those substances which have already been shown to exhibit a peculiar behaviour, namely, the alcohols, acids, propylene dibromide, ethylene dichloride, &c.

In order to give some idea of how far molecular viscosity at the boiling-point is quantitatively connected with chemical nature, attempts were made by the method given in detail at a later stage to calculate the probable partial effects of the atoms on the molecular viscosity. Values were also assigned to the effect of the iso grouping of atoms, the double linkage of carbon atoms, and the ring grouping. The values thus obtained are given in the following table :—

FUNDAMENTAL Viscosity Constants (Molecular Viscosity at the Boiling-point.)

Hydrogen	H	80
Carbon	C	− 98
Hydroxyl-oxygen . . . . . . C—O—H	$\diagdown O \diagup$	196
Ether-oxygen . . . . C—O—C	O<	35
Carbonyl-oxygen . . . . . . C=O	$\overset{\|}{O}$	248
Sulphur . . . . C—S—C	$\diagdown S \diagup$	155
Chlorine	Cl	284
Bromine (in monobromides)	Br	420
Bromine (in dibromides)	Br′	479
Iodine	I	520
Iso grouping	<	15
Double linkage	(=)	113
Ring grouping	ⓞ	610

The main points to be considered in connection with the meaning to be attached to fundamental viscosity constants in general, may be introduced here.

As has already been stated, viscosity may be taken as a measure of the attractive forces in play between molecules. Now the preceding tables, and more especially those given later, go to show that an increment of CH_2 in chemical composition, or the substitution of an atom of chlorine, bromine, or iodine for an atom of hydrogen, brings about a definite change in the viscosity magnitudes. It is therefore made evident that viscosity or intermolecular attraction is in reality a property of the atoms of which the molecules are composed.

But besides change in molecular weight, change in the mode of grouping of the same atoms also affects the values of the viscosity magnitudes. The observations show that iso compounds have values differing from those of isomeric normal compounds ; ring compounds have not the values which by the study of straight chain compounds they might be expected to have ; compounds containing hydroxyl oxygen give values differing from those containing carbonyl oxygen. The same atoms must therefore exert different effects when differently linked together. That the effects of the atoms in one portion of the molecule need not be affected by change in the mode of linkage of the atoms in another portion is proved by the fact that the effects of CH_2, of iodine, of bromine, etc., are the same in normal and in iso compounds. In the present state of the question it is impossible, however, to ascertain to what extent the individual effects of each atom are influenced by an alteration in the mode of grouping in a given portion of a molecule. Hence the method adopted in deducing fundamental constants is to assume that certain atoms retain the same values under all conditions whilst the collective change in the values of those atoms which are affected by the mode of linkage is, when possible, expressed either as a new constant —the value of an iso linkage, a double linkage, etc.—or by saying that a particular atom has assumed a new value, *e.g.*, carbonyl oxygen, hydroxyl oxygen, etc. In some cases the method of calculation may lead to the result that a negative constant is ascribed to a particular atom. In deducing the values of carbon and hydrogen, for example, it is implied that in a CH_2 group and in the molecule of a normal paraffin the individual effect of each atom of carbon or of hydrogen is the same. The above reasoning and the actual results show, however, that this is not the case. The effects exerted by carbon and hydrogen in a CH_3 group are different from those in a CH_2 group. Since this constitutive effect cannot be correctly apportioned amongst the atoms concerned in it, the fundamental constant of an element may for this reason come out negative although the absolute effect exerted by any atom is doubtless positive.

For these reasons fundamental constants are to be regarded as empirically ascertained magnitudes which are merely intended to indicate how far the observed results may be represented as the sum of partial values which are the same for all substances. They have no reference to the possible behaviour of the elements when in the free state ; they simply serve to show how far definite changes in chemical composition correspond with definite changes in the viscosity magnitudes.

The comparisons of the observed molecular viscosities and those calculated by means of the above fundamental constants are given in the following tables.

In the first, Table A, are set out those compounds for which the agreement is fairly satisfactory. With respect to the agreement it must be borne in mind that errors incidental to the determination of the boiling-point, density, and thermal expansion, as well as of viscosity, may affect the observed values.

In the second, Table B, are placed compounds which give differences which are far beyond the limits of the experimental errors involved.

MOLECULAR Viscosity at the Boiling-point.

TABLE A.

	Observed.	Calculated.	Difference per cent.
Pentane	480	470	2·1
Hexane	550	532	3·3
Heptane	593	594	− 0·1
Octane	646	656	− 1·5
Isopentane	489	485	0·8
Isohexane	551	547	0·7
Isoheptane	588	609	− 3·6
Amylene	420	438	− 4·3
Methyl iodide	639	662	− 3·6
Ethyl iodide	721	724	− 0·4
Propyl iodide	795	786	1·1
Isopropyl iodide	816	801	1·8
Isobutyl iodide	862	863	− 0·1
Allyl iodide	745	739	0·8
Ethyl bromide	597	624	− 4·5
Propyl bromide	686	686	0
Isopropyl bromide	705	701	0·6
Isobutyl bromide	761	763	− 0·3
Allyl bromide	635	639	− 0·6
Ethylene dibromide	1089	1082	0·6
Isobutylene dibromide	1274	1221	4·2
Propyl chloride	557	550	1·2
Isopropyl chloride	567	565	0·3
Isobutyl chloride	657	628	4·4
Allyl chloride	504	503	0·2
Ethylidene dichloride	674	692	− 2·7
Carbon tetrachloride	1077	1038	3·6

TABLE A (continued).

	Observed.	Calculated.	Difference per cent.
Methyl sulphide	450	439	2·4
Ethyl sulphide	572	583	− 1·9
Dimethyl ketone	420	434	− 3·3
Methyl ethyl ketone	504	496	1·5
Methyl propyl ketone	565	558	1·2
Diethyl ketone	533	558	− 4·6
Propionic acid	630	630	0
Butyric acid	702	692	1·4
Isobutyric acid	700	707	− 1·0
Acetic anhydride	635	619	2·5
Propionic anhydride	710	743	− 4·6
Ethyl ether	459	443	3·5
Toluene	596	564	5·3
Ethyl benzene	624	626	− 0·3
Ortho-xylene	660	626	5·1
Meta-xylene	590	626	− 6·1
Para-xylene	594	626	− 5·4
Bromine	981	958*	2·3
Methyl alcohol	401	421	− 5·0

* Calculated from the value of bromine in dibromides.

MOLECULAR Viscosity at the Boiling-point.

TABLE B.

	Observed.	Calculated.	Difference per cent.
Isoprene	415	376	9·4
Diallyl	483	438	9·3
Propylene dibromide	1085	1144	− 5·4
Acetylene dibromide	895	1035	− 15·6
Ethylene dichloride	795	692	12·9
Methylene dichloride	587	630	− 7·3
Chloroform	743	834	− 12·2
Carbon dichloride	898	1053	− 17·2
Carbon disulphide	478	218	54·4
Acetaldehyde	322	372	− 15·5
Formic acid	639	506	20·8
Acetic acid	615	568	7·6
Benzene	661	502	24·0
Water	199	359	− 80·4
Ethyl alcohol	693	483	30·3
Propyl alcohol	869	545	37·3
Butyl alcohol	883	607	31·2
Isopropyl alcohol	928	560	39·6
Isobutyl alcohol	987	622	36·9
Inactive amyl alcohol	936	684	26·9
Active amyl alcohol	920	684	25·6
Trimethyl carbinol	1243	637	48·8
Dimethyl ethyl carbinol	1024	699	31·7
Allyl alcohol	659	498	24·4

1. It will be seen from the first table that, in the case of forty-five liquids, the difference between the observed and calculated values rarely exceeds 5 per cent. Here molecular weight and chemical constitution exert effects upon the magnitude of the molecular viscosity which can be quantitatively expressed with moderate exactness.

In the case of the isomeric ketones and aromatic hydrocarbons the differences are in part due to constitutive influences which, as yet, on account of lack of data it is not possible to allow for in obtaining the calculated values.

2. In the second table are found those substances which give differences exceeding this 5 per cent. limit. These may be roughly classed as unsaturated hydrocarbons, polyhalogen compounds, formic and acetic acids, benzene, water, and the alcohols.

In many cases the differences are the result of constitutive influences. The same calculated value is used for ethylidene and ethylene dichloride. The large difference given by the latter is the result of the difference in the structure of the two compounds. The calculated values for the chlormethanes are obtained by means of the value possessed by chlorine in monochlorides. The differences are seen to increase as chlorine accumulates in the molecule, pointing to the conclusion, supported by other physico-chemical comparisons, that the effect produced on substituting hydrogen by halogen depends on the number of hydrogen atoms previously substituted. In calculating the value of carbon bisulphide, the value of sulphur in alkyl sulphides was employed. The large difference may be attributed, in part at least, to the difference in the mode of linkage of sulphur in the bisulphide. Benzene gives a large difference, probably for the reasons given when discussing the graphical representation of the results.

The calculated value of aldehyde is obtained in the same way as that of a ketone. The difference obtained is, therefore, an indication of the generic difference in the chemical constitution of the two classes of substances.

The calculated values of all the hydroxyl compounds given in the table are obtained by means of the constant for hydroxyl oxygen deduced from the higher fatty acids. It will be seen that in the case of the lower acids, of water, and of all the alcohols but methyl alcohol, there is no indication of agreement. For the lowest acid chemical constitution, as already mentioned, may in part be the cause of the difference, but for the other substances difference in molecular complexity at the boiling-point is doubtless the main factor in producing the large divergences above obtained.

As the stoichiometric relationships exhibited by molecular viscosity at the boiling-point are on the whole not very definite, we do not intend to further discuss the results given in the above tables.

MOLECULAR VISCOSITY WORK ($\eta \times$ SPECIFIC MOLECULAR VOLUME $= \eta d^3$) IN ERGS $\times 10^3$ AT THE BOILING-POINT.

(η in dynes per sq. centim. $\times$ specific molecular volume in cub. centims. $\times 10^3$.)

HOMOLOGUES.

	ηd^3.	Difference.
Pentane	235	50
Hexane	285	38
Heptane	323	46
Octane	369	
Isopentane	240	46
Isohexane	286	35
Isoheptane	321	
Isoprene	195	47
Diallyl	242	
Methyl iodide	256	62
Ethyl iodide	318	59
Propyl iodide	377	
Isopropyl iodide	389	46
Isobutyl iodide	435	
Ethyl bromide	255	60
Propyl bromide	315	
Isopropyl bromide	326	50
Isobutyl bromide	376	
Ethylene bromide	501	32
Propylene bromide	533	
Isopropyl chloride	258	60
Isobutyl chloride	318	
Methylene chloride	236	114
Ethylene chloride	350	

Homologues (continued).

	ηd^3.	Difference.
Methyl sulphide	190	(46)
Ethyl sulphide	283	
Dimethyl ketone	179	(41)
Diethyl ketone	261	
Methyl ethyl ketone	231	46
Methyl propyl ketone	277	
Formic acid	221	25
Acetic acid	246	28
Propionic acid	274	60
Butyric acid	334	
Acetic anhydride	304	(38)
Propionic anhydride	381	
Benzene	302	– 9
Toluene	293	30
Ethyl benzene	323	
Methyl alcohol	140	135
Ethyl alcohol	275	101
Propyl alcohol	376	34
Butyl alcohol	410	
Isopropyl alcohol	404	57
Isobutyl alcohol	461	5
Isoamyl alcohol	466	
Trimethyl carbinol	582	– 75
Dimethyl ethyl carbinol	507	

CORRESPONDING Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.
Methyl . . .	256	..	..	..	..	35	221	116	140
Ethyl	318	63	255	..	..	72	246	43	275
Propyl . . .	377	62	315	64	251	103	274	1	376
Butyl	..	..	..	..	..	..	334	..	410
Isopropyl . . .	389	63	326	68	258	..	..	− 15	404
Isobutyl . . .	435	59	376	58	318	101	334	− 26	461
Allyl	347	62	285	63	222	..	..	70	277
Ethylene . . .	..	..	501	(75)	350				

NORMAL Propyl and Allyl Compounds.

	Normal Propyl.	Difference.	Allyl.
	ηd^3.		ηd^3.
Hydrocarbons	285	(22)	242
Iodides	377	30	347
Bromides	315	30	285
Chlorides	251	29	222
Alcohols	376	99	277

ETHYLENE and Acetylene bromides.

	Ethylene.	Difference.	Acetylene.
	ηd^3.		ηd^3.
Bromides	501	98	403

ISOLOGOUS Hydrocarbons.

n.	(Normal) C_nH_{2n+2}.	C_nH_{2n}.		C_nH_{2n-2}.		C_nH_{2n-6}.	
	ηd^3.	Difference.	ηd^3.	Difference.	ηd^3.	Difference.	ηd^3.
5	235	35	200	40	195		
6	285	..	..	43	242	− 17	302
7	323	..	..	..	..	30	293
8	369	..	..	..	..	46	323

SUBSTITUTION of Halogen for Hydrogen.

Bromine for hydrogen.				Chlorine for hydrogen.		
n.	$C_nH_{2n}Br_2$. ηd^3.	Difference.	$C_nH_{2n+1}Br$. ηd^3.	Chlormethanes.	ηd^3.	Difference.
2	501	246	255	Methylene chloride . .	236	90
3	533	218	315	Chloroform	326	180
4 (Iso)	666	290	376	Carbon tetrachloride . .	506	

COMPOUNDS Differing by One Carbon Atom.

	ηd^3.	Difference.		ηd^3.	Difference.
Tetrachlormethane. . .	506	−70	Methyl alcohol	140	−16
Tetrachlorethylene. . .	436		Aldehyde	124	

ISOMERS.

NORMAL and Iso compounds.

	Normal. ηd^3.	Difference.	Iso. ηd^3.
Pentanes	235	− 5	240
Hexanes	285	− 1	286
Heptanes	323	2	321
Propyl iodides	377	−12	389
Propyl bromides	315	−11	326
Propyl chlorides	251	− 7	258
Butyric acids	334	0	334
Propyl alcohols	376	−28	404
Butyl alcohols	410	−51	461

BUTYL Alcohols and Ethyl Ether.

	ηd^3.	Difference.
Normal butyl alcohol	410	51
Isobutyl alcohol	461	121
Trimethyl carbinol	582	
Ethyl ether	218	

AMYL Alcohols.

	ηd^3.	Difference.
Inactive amyl alcohol	466	−10
Active amyl alcohol	456	51
Dimethyl ethyl carbinol	507	

ALLYL Alcohol and Acetone.

	ηd^3.	Difference.
Allyl alcohol	277	−98
Acetone	179	

DICHLORETHANES.

	ηd^3.	Difference.
Ethylene chloride	350	−49
Ethylidene chloride	301	

ISOMERIC Ketones.

	ηd^3.	Difference.
Diethyl ketone	261	16
Methyl propyl ketone	277	

AROMATIC Hydrocarbons.

	ηd^3.	Difference.
Ortho-xylene	341	
Meta-xylene	306	−35
Para-xylene	308	2
Ethyl benzene	323	15

Conclusions in reference to Molecular Viscosity Work at the Boiling-point.

By means of the numbers given in the preceding tables the following probable values for fundamental constants are deduced :—

FUNDAMENTAL Viscosity Constants (Molecular Viscosity Work at the Boiling-point.)

Hydrogen	H	−1·5
Carbon	C	50
Hydroxyl-oxygen C—O—H	$\overset{\diagdown\diagup}{O}$	102
Ether-oxygen C—O—C	O<	27
Carbonyl-oxygen C=O	$\overset{\|}{O}$	41
Sulphur C—S—C	$\diagdown S \diagup$	99
Chlorine	Cl	109
Bromine (in monobromide)	Br	176
Bromine (in dibromides)	Br′	212
Iodine	I	233
Iso grouping	<	5
Double linkage	(=)	−31
Ring grouping	ⓞ	−60

In the following tables is given the comparison of the observed and calculated numbers.

The substances are classified into two groups—Table A and Table B—as in the case of molecular viscosity, according as the differences are less or greater than about 5 per cent.

MOLECULAR Viscosity Work at the Boiling-point.

TABLE A.

	Observed.	Calculated.	Difference per cent.
Pentane	235	232	1·2
Hexane	285	279	2·1
Heptane	323	326	− 0·9
Octane	369	373	− 1·1
Isopentane	240	237	1·2
Isohexane	286	284	0·7
Isoheptane	321	331	− 3·1
Amylene	200	209	− 4·5
Methyl iodide	256	278	− 8·6
Ethyl iodide	318	325	− 2·2
Propyl iodide	377	377	1·3
Isopropyl iodide	389	372	4·4
Isobutyl iodide	435	424	2·5
Allyl iodide	347	344	0·8
Ethyl bromide	255	268	− 5·1
Propyl bromide	315	315	0
Isopropyl bromide	326	320	1·8
Isobutyl bromide	376	367	2·4
Allyl bromide	285	287	− 0·7
Ethylene dibromide	501	518	− 3·4
Propyl chloride	251	248	1·2
Isopropyl chloride	258	253	1·9
Isobutyl chloride	318	300	5·7
Allyl chloride	221	220	0·5
Ethylidene dichloride	308	312	− 1·3
Carbon tetrachloride	506	486	3·9
Methyl sulphide	190	190	0
Ethyl sulphide	283	284	− 0·4
Dimethyl ketone	179	181	− 1·1
Methyl ethyl ketone	231	228	1·3
Methyl propyl ketone	277	275	0·7
Diethyl ketone	261	275	− 5·4

MOLECULAR Viscosity Work at the Boiling-point.

TABLE A (continued).

	Observed.	Calculated.	Difference per cent.
Acetic acid	246	237	3·6
Propionic acid	274	284	– 3·6
Butyric acid	334	331	0·9
Isobutyric acid	334	336	– 0·6
Acetic anhydride	304	301	1·0
Propionic anhydride	381	395	– 3·7
Ethyl ether	217	211	2·7
Toluene	293	278	5·1
Ethyl benzene	323	325	– 0·6
Ortho-xylene	341	325	4·7
Meta-xylene	306	325	– 6·2
Para-xylene	308	325	– 5·5
Bromine	370	352	4·9
Methyl alcohol	140	146	– 4·3

MOLECULAR Viscosity Work at the Boiling-point.

TABLE B.

	Observed.	Calculated.	Difference per cent.
Isoprene	195	176	9·7
Diallyl	242	223	7·9
Propylene dibromide	533	565	− 6·0
Isobutylene dibromide . . .	666	617	7·3
Acetylene dibromide	403	484	− 20·1
Ethylene dichloride	350	312	10·8
Methylene dichloride	236	265	− 12·3
Chloroform	326	375	− 15·0
Carbon dichloride	436	505	− 15·7
Carbon bisulphide	189	250	− 32·3
Acetaldehyde	124	135	− 8·8
Formic acid	221	190	14·0
Benzene	302	237	21·5
Water	53	99	− 86·8
Ethyl alcohol	275	193	29·8
Propyl alcohol	376	240	36·2
Butyl alcohol	410	287	30·0
Isopropyl alcohol	404	245	39·3
Isobutyl alcohol	461	292	36·6
Inactive amyl alcohol	466	339	27·2
Active amyl alcohol	456	339	25·7
Trimethyl carbinol	582	302	48·1
Dimethyl ethyl carbinol . . .	507	349	31·1
Allyl alcohol	277	211	23·9

The degree of agreement between the observed and calculated values of the molecular viscosity work is practically the same as in the case of molecular viscosity, and the same striking exceptions occur in the case of hydroxy compounds, &c.

General Conclusions relating to Molecular Viscosity and Molecular Viscosity Work at the Boiling-point.

On taking a general survey of the comparisons at the boiling-point, it is evident that for the majority of the substances examined—the paraffins and their monohalogen derivatives, the sulphides, the ketones, the oxides, and most of the acids and aromatic hydrocarbons—molecular viscosity and molecular viscosity work may, with moderate exactness, be quantitatively connected with chemical nature.

The remaining substances—unsaturated hydrocarbons, di- and polyhalogen compounds, formic acid, benzene, water, and the alcohols—present marked exceptions to the foregoing regularities. Most of these substances have already been shown, both in the graphical and algebraical portions of this memoir, to be peculiar; hydroxy compounds, and, in particular, the alcohols, exhibiting in all cases the most pronounced deviations from regularity.

B. Comparison of Viscosity Magnitudes at the corresponding Temperature of ·6.

Tables similar to those already given were constructed showing the various viscosity magnitudes at the corresponding temperature ·6. When satisfactory observed or calculated data could not be obtained, the critical temperature was deduced by means of the formula of THORPE and RÜCKER (Jour. Chem. Soc., vol. 45, p. 135, 1884)

$$\Theta = \frac{(t + 273)\,V_t - 273}{1{\cdot}995\,(V_t - 1)}.$$

Θ is the absolute critical temperature, V_t is the volume that unit-volume of liquid measured at 0° occupies at t°.

From the values of the critical temperatures thus obtained, T, the corresponding temperature of ·6 on the ordinary scale, was given by $T = {\cdot}6\,(\Theta) - 273$.

THORPE and RÜCKER's formula is inapplicable to the case of water. To make the calculated critical temperature for water harmonise with the observed value, a instead of being 1·995 would require to be 4·2. The alcohols in general give values of a which are also larger than 2 by about 10 per cent.

The critical data are too unsatisfactory to warrant us in laying any particular stress on the relationships obtained under this condition of comparison. We think, therefore, that no useful purpose can be served by reproducing the tables. Partial and imperfect as the available data are, the relationships however are similar to, even if less definite than, those obtained at the boiling-point. For a property like viscosity, which alters so rapidly with temperature, a corresponding temperature is certainly no better as a condition of comparison than the boiling-point.

C. Comparisons of Viscosity Magnitudes at Temperatures of Equal Slope.

On comparing the viscosity curves of those substances which gave the best physico-chemical relationships at the boiling-point, it was at once seen that the general shape of these curves towards the boiling-point was practically the same. If tangents were drawn to the curves at points corresponding with the boiling-points of the liquids, the inclinations of the tangents to the axes, that is the *slopes* of the curves, varied but little. On the other hand, the curves for liquids such as the alcohols or the lowest members of homologous series, which gave little indication of physico-chemical relationships, had invariably a different shape. The entire course of these curves was indeed exceptional, and the inclinations of tangents drawn at the boiling-point were markedly different from those of the majority of substances. It seemed probable, therefore, that the discrepancies were related to this difference in the value of the slopes, and that if the temperatures of comparison were chosen so as to eliminate this difference better relationships might be obtained. This idea led to the adoption of temperatures of equal slope as comparable temperatures, and indeed apart altogether from considerations such as the above, which refer to the particular case of viscosity, much may be said from a theoretical point of view in favour of employing such temperatures for physico-chemical comparisons in general. To begin with, at the temperature of equal slope, the effect of temperature upon the property examined is the same for different substances. In the case of viscosity, for instance, $d\eta/dt$, or the rate at which viscosity is being altered by the temperature, has the same value for all the liquids, and this equality might be taken as sufficient justification for supposing that at temperatures of equal slope the substances, so far as viscosity is concerned, are in comparable states. Another argument which may be advanced in favour of such a method of treatment is that the comparable temperatures are chosen by means of a study of the effect of temperature on the property actually examined. The main objection which can be urged against the boiling-point as a comparable temperature even when, as in the case of such a property as density, it gives comparatively definite stoichiometric relationships is that these relationships may not be general. If a pressure other than the atmospheric is employed at which to determine the boiling-point and density the relationships initially obtained may no longer hold. Whether they hold or not can only be decided by a study, not only of the effect of temperature on density, the property under consideration, but also of the effect of temperature on vapour pressure, a property which, at first sight at least, need not be connected with density. If, however, comparable temperatures be chosen, as in the case of slope, by a study of the property considered, the generality of the relationships obtained can be ascertained without the study of other properties of the substances. Moreover it is possible to devise a system of choosing slopes such that the relationships obtained at any series of slopes chosen in this way shall be the same as those obtained at any other series of slopes, provided that the method of choosing is the same throughout. This last point is treated in detail at a later stage.

The comparisons about to be given are made at temperatures at which $d\eta/dt$ is the same for the different liquids. Or graphically, the temperatures may be defined as those corresponding with points on the viscosity curves at which tangents are equally inclined to the axes of coordinates. The temperatures are therefore those at which temperature is exercising the same effect on viscosity, and for shortness may be termed *temperatures of equal slope.*

The temperatures were obtained by means of SLOTTE's formula.

On differentiating the formula in the shape

$$\eta = \frac{c}{(a+t)^n} \quad \text{we obtain} \quad -\frac{d\eta}{dt} = \frac{nc}{(a+t)^{n+1}}.$$

On choosing a particular value of $-d\eta/dt$, say S, values of t corresponding with this value of the slope were deduced from the equation

$$t = (nc/\mathrm{S})^{1/(n+1)} - a,$$

$$\text{or} \quad \log(a+t) = \frac{\log nc - \log \mathrm{S}}{n+1}.$$

Slopes at which Comparisons were made.

The first point to decide was what particular value of the slope should be employed. It was apparent from the shape of the curves that all the liquids could not be compared at any one value of the slope, because the effect of temperature on viscosity varied so much from substance to substance. In some cases, the whole of the alcohols for example, the slope at the boiling-point was considerably greater than that at 0° in the case of some of the less viscous liquids.

The question then resolved itself into choosing, in the first instance, a slope at which the viscosity of as many liquids as possible might be compared. From a study of the curves the particular value fixed upon was S = ·0000323, which happens to be the value possessed by methyl iodide at its boiling-point.

Comparisons were then made at the slope ·0000987, which was chosen in order that the liquids which could not be included at the smaller slope might be compared with as large a number as possible of the other liquids.

The values of the temperature at these slopes, and of the specific molecular areas and specific molecular volumes for the various liquids are given in the appendix. The following tables contain the various viscosity magnitudes at this system of comparable temperatures for as many liquids as could be compared at each value of the slope. In some cases the curves have had to be extrapolated for a short distance beyond the ordinary range from 0° to the boiling-point.

Viscosity Coefficients at Slope $\cdot 0_4 323$.

(η in dynes per sq. centim. × 10^5).

Homologues.

	η.	Difference.
Pentane	299	
Hexane	318	19
Heptane	330	12
Octane	336	6
Isopentane	286	
Isohexane	312	26
Isoheptane	322	10
Isoprene	295	
Diallyl	304	9
Methyl iodide	399	
Ethyl iodide	404	5
Propyl iodide	407	3
Isopropyl iodide	390	
Isobutyl iodide	404	14
Ethyl bromide	368	
Propyl bromide	372	4
Isopropyl bromide	353	
Isobutyl bromide	360	7
Ethylene bromide	455	
Propylene bromide	441	− 14
Isopropyl chloride	317	
Isobutyl chloride	331	14
Methylene chloride	372	
Ethylene chloride	377	5

Homologues (continued).

	η.	Difference.
Methyl sulphide	335	(6)
Ethyl sulphide	346	
Dimethyl ketone	329	(7)
Diethyl ketone.	343	
Methyl ethyl ketone	330	14
Methyl propyl ketone	344	
Formic acid	373	− 3
Acetic acid	370	20
Propionic acid	390	− 11
Butyric acid.	379	
Acetic anhydride	378	(1)
Propionic anhydride	379	
Benzene	330	24
Toluene	354	13
Ethyl benzene	367	

At this condition of comparison the effect which an increment of CH_2 in chemical composition exerts on the magnitude of η varies within much narrower limits than when the boiling-point is used as the temperature of comparison. With the exception of the acids, which are still peculiar, and the dibromides, the effect in all cases is positive, and, in general, diminishes as the series is ascended. The large differences which exist at the boiling-point between the lowest members of series have now disappeared.

The paraffins have no longer almost the same constants, but have values which vary regularly with the molecular weight. With the exception of propionic acid, the acids and anhydrides, which at the boiling-point had values which differed considerably from each other, have now practically the same viscosity coefficients.

The alcohols, as already stated, cannot be compared at this particular value of the slope. This is significant as indicating that even at this new condition of comparison the behaviour of the alcohols, as at the comparable temperatures already employed, is anomalous.

CORRESPONDING Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	η.	Diff.	η.	Diff.	η.	Diff.	η.	Diff.	η.
Methyl	399	..	..	..	..	26	373	109	290
Ethyl	404	36	368	..	..	34	370		
Propyl	407	35	372	42	330	17	390		
Butyl	..	..	..	..	..	..	379		
Isopropyl	390	37	353	36	317	..	..		
Isobutyl	404	44	360	29	331	26	378		
Allyl	406	35	371	43	328				
Ethylene	..	..	455	(39)	377				

Corresponding iodides, bromides, chlorides, and acids now give constants which are closely related to one another. The large discrepancies given at the boiling-point by the lowest acids have now disappeared, and in all cases the differences between corresponding members of two different series of compounds are much more nearly constant, the largest variations being given by the acids.

An iodide has, on the average, a coefficient which is 37 units greater than that of the corresponding bromide. Practically, the same average difference, 38, exists between corresponding bromides and chlorides. Here, the difference in η is strictly proportional to the difference in molecular weight. The difference between an iodide and an acid, 26, on the average, though uniform, is not so large as that between an iodide and a bromide, viz., 37, although the differences in the theoretical molecular weights are respectively 106 and 47. This indicates that in general η is not a simple function of theoretical molecular weight. Methyl alcohol, the only member of the alcohol series which could be included at slope $\cdot 0_4 323$, gives a value considerably below that of methyl iodide or formic acid, the difference being in the direction of the change in molecular weight but showing no proportionality. Here, as with homologues, the relationships are much more regular than at the boiling-point.

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	η.		η.
Hydrocarbons	318	(7)	304
Iodides	407	1	406
Bromides	372	1	371
Chlorides	330	2	328

ETHYLENE and Acetylene Bromides.

	Ethylene.	Difference.	Acetylene.
	η.		η.
Bromides	455	−8	463

Here again, is a decided regularity; the coefficient of the propyl compound is uniformly larger, and the difference tends to increase as the molecular weight decreases, the iodides exhibiting the smallest, and the hydrocarbons the largest differences.

In the case of ethylene and acetylene bromides, where the molecular weights are higher than in the case of the iodides, the difference for the loss of a double linkage and the addition of H_2 has become negative. At the boiling-point this difference was in no way comparable with that of normal propyl and allyl compounds.

ISOLOGOUS Hydrocarbons.

n.	C_nH_{2n+2}.	C_nH_{2n}.		C_nH_{2n-2}.		C_nH_{2n-6}	
		Diff.	η.	Diff.	η.	Diff.	η.
5	299	−12	311	4	295		
6	318	..	..	14	304	−12	330
7	330	..	..	..	..	−24	354
8	336	..	..	..	..	−31	367

On passing from pentane to amylene the viscosity rises by some 12 units. When, however, by the loss of four hydrogen atoms the corresponding paraffin passes into isoprene or diallyl the viscosity falls, the fall increasing with the molecular weight. Constitution here evidently comes into play. An aromatic hydrocarbon has a coefficient which is greater than that of the corresponding paraffin by an amount which increases with increase of molecular weight; the differences now vary within much narrower limits than at the boiling-point.

SUBSTITUTION of Halogen for Hydrogen.

n.	$C_nH_{2n}Br_2$.	Diff.	$C_nH_{2n+1}Br$.	Chlormethanes.	η.	Diff.
	η.		η.			
2	455	87	368	Methylene chloride . .	372	16
3	441	69	372	Chloroform	388	−11
4 Iso	426	66	360	Carbon tetrachloride .	377	

The conversion of a monobromide into a dibromide is accompanied by a marked rise in viscosity, which is less the higher the molecular weight.

On the conversion of dichlormethane into the tri- and tetra-chlor compounds the change is very slight. As, however, the results for chloroform and carbon tetrachloride are extrapolated, the small difference may be due to errors thus introduced.

COMPOUNDS differing by one Carbon Atom.

	η.	Difference.		η.	Difference.
Tetrachlormethane . .	377	69	Methyl alcohol . . .	290	26
Tetrachlorethylene . .	446		Aldehyde	316	

The differences here obtained are now far removed from one another, no doubt for the reason given in the case of these comparisons at the boiling-point.

ISOMERS.

NORMAL and Iso Compounds.

	Normal.	Difference.	Iso.
	η.		η.
Pentanes	299	13	286
Hexanes	318	6	312
Heptanes	330	8	322
Propyl iodides	407	17	390
Propyl bromides	372	19	353
Propyl chlorides . . .	330	13	317
Butyric acids	379	1	378

Normal compounds have higher values than the corresponding iso-compounds. The small difference for the butyric acids may be the result of molecular complexity.

AROMATIC Hydrocarbons.

	η.	Difference.
Ortho-xylene	372	−5
Ethyl benzene	367	1
Meta-xylene	368	−8
Para-xylene	360	

Of the four isomeric C_8H_{10} substituted benzenes, ortho-xylene has decidedly the largest coefficient, and para-xylene the lowest coefficient, whilst meta-xylene and ethyl benzene have intermediate and almost identical values.

ISOMERIC Ketones.

	η.	Difference.
Diethyl ketone	343	1
Methyl propyl ketone	344	

The isomeric ketones give identical coefficients, the effect of constitution being apparently inoperative, probably for the reason already given.

DICHLORETHANES.

	η.	Difference.
Ethylene chloride	377	− 22
Ethylidene chloride	355	

The isomeric dichlorethanes give values which differ widely, the symmetrical compound being the more viscous.

VISCOSITY COEFFICIENTS AT SLOPE $\cdot 0_4 987$.

(η in dynes per sq. centim. $\times 10^5$.)

As already stated, it was impossible to compare all the liquids at the same slope. The previous comparisons made at the slope $\cdot 0_4 323$ include all the liquids except bromine and the alcohols. The next step was to choose another value of the slope so that these outstanding liquids might be included in the comparison. In the case of the alcohols, the slope, even at the boiling-point, has a value which is larger than that given by many of the liquids at the lowest temperatures of observation. Obviously, therefore, in order that as many compounds as possible might be compared with the alcohols, the smallest possible value of the slope at which the alcohols could be compared had to be chosen. The value which satisfied this condition was $\cdot 0_4 987$, which happens to be the value possessed by isopropyl alcohol at its boiling-point. Besides the alcohols, it was found that 33 of the liquids, which were compared at slope $\cdot 0_4 323$, could be compared at this new value of the slope, and the first point to decide was whether the same relations existed between the magnitudes of the various viscosity constants at this new value of the slope as we had established at the previous value. This point was easily ascertained in the following way:—

On finding the value of the ratio,

$$\frac{\text{Viscosity coefficient at slope } \cdot 0_4 987}{\text{Viscosity coefficient at slope } \cdot 0_4 323},$$

a number was obtained which was practically the same for all the 33 liquids. The mean value of the ratio was 2·03 ; the average divergence from the mean being ·036, or about 1·7 per cent.

Making due allowance for experimental errors, and especially for imperfections in SLOTTE's formula, the constancy of the ratio is satisfactory, as it shows that the relationships established between the viscosity coefficients at slope $\cdot 0_4 323$ remain practically the same at slope $\cdot 0_4 987$, and indicates that the method of comparison is a general one, and is independent of the particular value of the slope at which the comparisons are made.

It is also noteworthy that the acids and water, the complexity of which is supposed to increase as temperature falls, give values of the ratio which do not differ more widely from the mean ratio than the values given by other types of substances such as the dibromides.

The values given by the alcohols and bromine which, of course, could not be compared at slope $\cdot 0_4 323$, are given below :—

	η.	Difference.
Bromine	953	
Methyl alcohol	650	
Ethyl alcohol	606	−46
Propyl alcohol	560	−46
Butyl alcohol	575	15
Isopropyl alcohol	490	
Isobutyl alcohol	525	35
Inactive amyl alcohol	574	49
Trimethyl carbinol	461	
Dimethyl ethyl carbinol	490	29

In the case of the primary alcohols, the table shows that up to propyl alcohol a rise in molecular weight is accompanied by a fall in the viscosity coefficient, but for all other higher alcohols a rise in molecular weight is accompanied by an increase in the coefficient. The alcohols, therefore, differ from most other homologous series where the value of CH_2 is positive, and tends to diminish as the series is ascended.

Conclusions relating to Viscosity Coefficients at Equal Slope.

1. It is evident, from the foregoing comparisons, that temperatures of equal slope tend to reveal much more definite relationships between the values of the viscosity coefficients and the chemical nature of the substances than were obtained at the boiling-points.

2. In all homologous series, with the exception of those of the alcohols, acids, and dichlorides, the effect of CH_2 on the value of the coefficient is positive and tends to diminish as the series is ascended.

3. Of corresponding compounds, the one of highest molecular weight has the highest coefficient.

4. Normal propyl compounds have slightly larger coefficients than the corresponding allyl compounds.

5. An iso compound has invariably a larger coefficient than a normal compound.

6. In the case of other isomers, the orientation of the molecule and branching of

the atomic chain influence the magnitudes of the coefficients. Similar effects of constitution are also exhibited on comparing saturated and unsaturated hydrocarbons, and the variable effects produced by successive substitution of halogen for hydrogen.

7. The alcohols, and to some extent the acids, still give results which are peculiar when compared with those of the other substances.

Molecular Viscosity ($\eta \times$ specific molecular area $= \eta d^2$) in dynes per sq. centim. $\times 10^4$ at slope $\cdot 0_4 323$.

(η in dynes per sq. centim. $\times$ specific molecular area in sq. centims. $\times 10^4$.)

Homologues.

	ηd^2.	Difference.
Pentane	687	
Hexane	818	131
Heptane	931	113
Octane	1035	104
Isopentane	663	
Isohexane	799	136
Isoheptane	908	109
Isoprene	620	
Diallyl	728	108
Methyl iodide	638	
Ethyl iodide	778	140
Propyl iodide	903	125
Isopropyl iodide	878	
Isobutyl iodide	1010	132
Ethyl bromide	663	
Propyl bromide	774	111
Isopropyl bromide	750	
Isobutyl bromide	877	127
Ethylene bromide	973	
Propylene bromide	1068	95

Homologues (continued).

	ηd^2.	Difference.
Isopropyl chloride	644	116
Isobutyl chloride	760	
Methylene chloride	600	137
Ethylene chloride	737	
Methyl sulphide	578	(117)
Ethyl sulphide	812	
Dimethyl ketone	572	(107)
Diethyl ketone	785	
Methyl ethyl ketone	671	125
Methyl propyl ketone	796	
Formic acid	456	137
Acetic acid	593	149
Propionic acid	742	100
Butyric acid	842	
Acetic anhydride	838	(99)
Propionic anhydride	1036	
Benzene	688	133
Toluene	821	118
Ethyl benzene	939	

It is evident from the table that the effect of an increment of CH_2 in chemical composition on the molecular viscosity is here much more definite than at the boiling-point. Although the numbers show that the effect apparently slowly diminishes as each homologous series is ascended, yet it may be taken as a first approximation that the effect of CH_2 is about the same in all the homologous series investigated. The mean difference for CH_2 is about 120 units, the largest differences from the mean being in the cases of the acids, the dibromides, and the anhydrides. In the case of the dibromides an unsymmetrical compound is compared with a symmetrical compound, so that the value for CH_2 is probably affected by constitutive influences, and, as regards the anhydrides, the unsatisfactory character of the propionic anhydride may be the cause of the smallness of the difference. It is significant that the differences given by homologous acids, although irregular, are not very far removed from those given by other series of homologues.

CORRESPONDING Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	ηd^2.	Diff.	ηd^2.	Diff.	ηd^2.	Diff.	ηd^2.	Diff.	ηd^2.
Methyl	638	..	..	..	..	182	456	280	358
Ethyl	778	115	663	..	..	185	593		
Propyl	903	129	774	116	658	161	742		
Butyl	..	..	..	..	..	..	842		
Isopropyl	878	128	750	106	644				
Isobutyl	1010	133	877	117	760	167	843		
Allyl	864	130	734	117	617				
Ethylene	..	..	973	(118)	737				

Here it is seen that an iodide has on the average a molecular viscosity which is about 127 units larger than that of the corresponding bromide.

A bromide gives a molecular viscosity which, on the average, is 115 units greater than that of the corresponding chloride, the average difference from this mean value being only some 3 units. An iodide has, on the average, a molecular viscosity which is 174 units greater than that of the corresponding acid. Methyl alcohol has a molecular viscosity which is also considerably lower than that of methyl iodide. It is, therefore, evident that the corresponding compound of higher molecular weight has the higher molecular viscosity, and where two series of corresponding compounds, the fatty acids included, can be compared, the differences obtained are approximately equal.

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	ηd^2.		ηd^2.
Hydrocarbons	818	(45)	728
Iodides	903	39	864
Bromides	774	40	734
Chlorides	658	41	617

ETHYLENE and Acetylene Bromides.

	Ethylene		Acetylene.
Bromides	973	41	932

It is evident that a normal propyl compound has a molecular viscosity which is, on the average, 41 units greater than that of the corresponding allyl compound. It is further indicative of the comparatively definite quantitative relations here exhibited that the difference between the molecular viscosities of ethylene and acetylene bromides, which are related in the same way as a normal propyl compound is to an allyl compound, is also 41 units.

ISOLOGOUS Hydrocarbons.

n.	C_nH_{2n+2}.	C_nH_{2n}.		C_nH_{2n-2}.		C_nH_{2n-6}.	
	ηd^2.	Difference.	ηd^2.	Difference.	ηd^2.	Difference.	ηd^2.
5	687	22	665	67	620		
6	818	..	..	90	728	130	688
7	931	..	..	..	..	110	821
8	1035	..	..	..	..	96	939

Loss of hydrogen is always attended by a fall in molecular viscosity. On comparing two series of corresponding hydrocarbons, the differences, although not quite constant, vary within comparatively narrow limits ; in the case of the aromatic hydrocarbons and the paraffins, the differences vary in a regular way, and diminish with rise in molecular weight. It is also evident that the removal in succession of two hydrogen atoms from a saturated hydrocarbon brings about a variable decrement in viscosity.

SUBSTITUTION of Halogen for Hydrogen.

Bromine for hydrogen.				Chlorine for hydrogen.		
n.	$C_nH_{2n}Br_2$. ηd^2.	Diff.	$C_nH_{2n+1}Br$. ηd^2.	Chloromethanes.	ηd^2.	Difference.
2	973	310	663	Methylene chloride . .	600	
3	1068	294	774	Chloroform.	747	147
4 (Iso)	1171	294	877	Carbon tetrachloride .	854	107

On converting a monobromide into the corresponding dibromide, the viscosity rises by an amount which is approximately constant and equal to 300 units. If, however, the hydrogen atoms present in the same molecule be substituted in succession by chlorine, it is evident from the comparisons given that the effect diminishes as the number of chlorine atoms in the molecule increases.

COMPOUNDS differing by a Carbon Atom.

	ηd^2.	Difference.		ηd^2.	Difference.
Tetrachlormethane . .	854	178	Methyl alcohol	358	90
Tetrachlorethylene. . .	1032		Aldehyde	448	

The different values given by the two comparisons may partly be due to the fact that the effect of the linkage of carbon atoms among themselves is different from that of a carbon atom to an oxygen atom, and partly to the effect of the molecular complexity of methyl alcohol.

Isomers.

Normal and Iso Compounds.

	Normal.	Difference.	Iso.
	ηd^2.		ηd^2.
Pentanes	687	24	663
Hexanes	818	19	799
Heptanes	931	23	908
Propyl iodides	903	25	878
Propyl bromides	774	24	750
Propyl chlorides	658	14	644
Butyric acids	842	− 1	843

With the exception of the butyric acids, which of those given above are probably the only liquids containing molecular aggregates, the normal compound has distinctly the higher molecular viscosity. In the case of the halogen compounds, the differences diminish with the fall in molecular weight; in the paraffins, however, there is no regularity in the variation of the differences.

It may thus be assumed, as a first approximation, that the average effect of the iso mode of grouping is constant and operates so as to diminish the molecular viscosity by about 21 units.

Aromatic Hydrocarbons.

	ηd^2.	Difference.
Ortho-xylene	954	
		−15
Ethyl benzene	939	
		0
Meta-xylene	939	
		−16
Para-xylene	923	

Of the four isomeric hydrocarbons, ortho-xylene has the largest, and para-xylene the lowest molecular viscosity. Ethyl benzene and meta-xylene give identical numbers, which are almost the mean of those of ortho- and para-xylene.

DICHLORETHANES.

	ηd^2.	Difference.
Ethylene chloride	737	-35
Ethylidene chloride	702	

The symmetrical compound has here decidedly the larger value.

ISOMERIC Ketones.

	ηd^2.	Difference.
Diethyl ketone	785	11
Methyl-propyl ketone	796	

Here the unsymmetrical compound, probably for the reason already given, has the larger molecular viscosity.

Quantitative relations fairly definite in character are thus exhibited in the preceding tables between the magnitudes of the molecular viscosities.

The tables of homologous and corresponding compounds show that molecular weight exerts an approximately regular effect, and the comparisons of normal and iso compounds, and of propyl and allyl compounds, indicate that the effect of constitution can also in some cases be quantitatively estimated.

We have, therefore, attempted to ascertain if molecular viscosity can be expressed as the sum of partial effects which may be ascribed to the atoms and to the modes of atom linkage which occur in the molecule. The details of the method of calculation, which is the same as that employed in the case of the comparisons at the boiling-point, are given in what follows.

METHOD OF DEDUCING THE FUNDAMENTAL VISCOSITY CONSTANTS (MOLECULAR VISCOSITY AT SLOPE $\cdot 0_4 323$).

Value of CH_2.

From the table of homologues the mean of the twenty-three values for the effect of CH_2 is 120. Neglecting signs, the average difference from the mean is 12. It is therefore assumed that

$$CH_2 = 120.$$

Influence of the Iso grouping.

Neglecting, for reasons already given, the butyric acids, the six available comparisons give 21 as the amount by which the molecular viscosity of a normal compound is greater than that of the isomeric iso compound. The mean difference from this value, neglecting signs, is about 3. It is therefore assumed that the value of the iso grouping is

$$-21.$$

Value of Hydrogen.

On deducting the value of $n\mathrm{CH}_2$ from the observed molecular viscosity of a normal paraffin $\mathrm{C}_n\mathrm{H}_{2n+2}$, a value is obtained for the effect of H_2.

On using the above measure of the effect of the iso mode of linkage, iso paraffins may also be included in the comparison. The available data are as under :—

	n.	$\mathrm{C}_n\mathrm{H}_{2n+2}$. ηd^2. (obs.).	$n\mathrm{CH}_2$ (calc.).	H_2.
Normal paraffins	5	687	600	87
	6	818	720	98
	7	931	840	91
	8	1035	960	75
Iso paraffins	5	663	579	84
	6	799	699	100
	7	908	819	89
Mean value of $\mathrm{H}_2 = 89$.				

Neglecting signs, the average divergence from this value is 7. It is therefore assumed that

$$\mathrm{H} = 44{\cdot}5$$

Value of Carbon.

From the two equations

$$\mathrm{CH}_2 = 120, \qquad \mathrm{H}_2 = 89,$$

it follows, on the assumption that the effect of CH_2 is additively composed of those of carbon and hydrogen, that the effect on the molecular viscosity of an atom of carbon may be taken as

$$\mathrm{C} = 31.$$

Influence of Double Linkage.

The four available comparisons show that the molecular viscosity of a normal propyl compound is 41 units larger than that of the corresponding allyl compound. The average difference from this mean value is less than 2. The value is exactly the same as that brought about by the change of ethylene into acetylene bromide. This value corresponds with the addition of H_2 and the loss of a double linkage of carbon atoms. Consequently if we take the value of H_2 as 89, we may assume that a double linkage of carbon atoms increases the molecular viscosity by 48 units.

The iso linkage of carbon atoms, as already seen, exercises an opposite effect to the extent of 21 units.

Values of the Halogens.

Adopting the values $H = 44{\cdot}5$, $C = 31$, iso linkage $= -21$, double linkage $= 48$, the values of the carbon-hydrogen "rests" in the molecules of the various haloid compounds may be calculated, and the atomic effects of the halogens may in this way be obtained; the data are given in the following tables:—

VALUE of Iodine.

	Iodide.	"Rest" (calculated).	I.
	ηd^2 (observed).		
Methyl	638	164	474
Ethyl	778	284	494
Propyl	903	404	499
Isopropyl	878	383	495
Isobutyl	1010	503	507
Allyl	864	363	501
Adopted value for I = 499.			

The value for methyl iodide, the lowest member of the series, varies so much from the closely concordant numbers given by the other iodides that it is omitted in taking the mean. With this omission, which will be referred to subsequently, the average divergence from the mean is about 4 units.

VALUES of Bromine.

	Bromide.	"Rest" (calculated).	Br.
	ηd^2 (observed).		
Ethyl	663	284	379
Propyl	774	404	370
Isopropyl	750	383	367
Isobutyl	877	503	374
Allyl	734	363	371
Ethylene	973	240	(367)
Propylene	1068	360	(354)
Isobutylene	1171	459	(356)
Acetylene	932	199	(367)

In monohalogen compounds bromine has thus the value of 372, the mean divergence from this value being about 3.

In dihalogen compounds, however, bromine would appear to have a slightly lower value, viz., 361, with a mean divergence of 6.

VALUES of Chlorine.

	Chloride.	"Rest" (calculated).	Cl.
	ηd^2 (observed).		
Propyl	658	404	254
Isopropyl	644	383	261
Isobutyl	760	503	257
Allyl	617	363	254
Ethylene	737	240	(248)
Methylene	600	120	(240)
Chloroform	747	76	(224)
Carbon tetrachloride	854	31	(206)
Carbon dichloride	1032	110	(230)

In saturated as well as unsaturated monohalogen compounds chlorine seems to have the value 256, the mean divergence being about 2 units.

For the two dihalogen compounds the number obtained is 244 ; from the trihalogen compound it is 224, and from the tetrahalogen compound 206 ; the value which may thus be ascribed to chlorine becomes less and less as chlorine accumulates in the molecule. In the unsaturated tetrahalogen compound, using the ordinary values of C and of a double linkage, the number obtained is 230, which is nearer that deduced from chloroform than from carbon tetrachloride, and is the same as the value (231) given by ethylidene chloride.

The values for the halogens obtained from monoderivatives are so related that the value for bromine, 372, is almost the mean of the values of chlorine and iodine viz., 377.

Values of Oxygen.

Carbonyl Oxygen.—On deducting the values of nCH_2 from the observed molecular viscosities of aldehyde and the ketones of the general formula $C_nH_{2n}\overset{\|}{O}$, the differences correspond with values of carbonyl oxygen $\overset{\|}{O}$.

	$C_nH_{2n}\overset{\|}{O}$.	nCH_2 (calculated).	$\overset{\|}{O}$.
	ηd^2 (observed).		
Dimethyl ketone	572	360	212
Aldehyde	448	240	208
Methyl ethyl ketone	671	480	191
Methyl propyl ketone	796	600	196
Diethyl ketone	785	600	185
Mean value for $\overset{\|}{O} = 198$			

The average divergence from the mean is about 9 units. The mean value is no doubt affected by constitutive causes, as aldehyde is not strictly comparable with the ketones, and the isomeric ketones do not give identical molecular viscosities. Moreover, acetone appears from surface-energy measurements to contain molecular aggregates. These effects are apparently small, however, and in a first approximation may be ignored.

Hydroxyl Oxygen.—On deducting nCH_2 from the observed molecular viscosities of the acids $C_nH_{2n}\overset{\|}{O}\overset{\diagdown\diagup}{O}$, values are obtained for the joint effect of an atom of carbonyl and an atom of hydroxyl oxygen in these compounds.

	Acids.	nCH_2 (calculated).	$\overset{\|}{O}\overset{\diagdown\diagup}{O}$.
	ηd^2 (observed).		
Formic acid	456	120	336
Acetic acid	593	240	353
Propionic acid	742	360	382
Butyric acid	842	480	362
Isobutyric acid	843	459	384
Mean value of $\overset{\|}{O}\overset{\diagdown\diagup}{O} = 364$			

Formic acid, the initial member of the series, presents the greatest divergence from the mean value, and the numbers on the whole are not so uniform as those given in previous comparisons, the average difference from the mean being 16 units. It is probable that the cause of these deviations is to be sought in differences in the molecular complexity of the acids.

From the relations

$\overset{\diagdown\diagup}{O} + \overset{\|}{O} = 364$ and $\overset{\|}{O} = 198$ it follows that the value of hydroxyl oxygen may be taken as

$$\overset{\diagdown\diagup}{O} = 166.$$

Ether Oxygen.—The study of several of the physical characters of substances, more especially their optical properties, has indicated that an oxygen atom, when linked to two carbon atoms, exercises an effect on the magnitude of a physical property which is different from that exerted when it is in the condition of carbonyl oxygen or hydroxyl oxygen. The number of compounds available to ascertain if such a difference exists in the case of the viscosity constants is hardly sufficient to warrant any definite conclusion as to the absolute magnitude of the effect so exerted. Using the values of C, H, and $\overset{\|}{O}$, and the observed numbers for acetic anhydride and ether, the mean value 58 is obtained for ether oxygen. So far as the data go, it would appear that ether oxygen, or oxygen linked to two carbon atoms, which may be represented as $O<$, has an extremely small value as compared with that of oxygen in a carbonyl group, or with that of hydroxyl oxygen as deduced from the acids.

If such differences are confirmed by more numerous observations, viscosity will rank as one of the most useful properties in determining the constitution of oxygen compounds. The values obtained for oxygen in different conditions are :—

Carbonyl oxygen . . . . $\overset{\|}{O} = 198$

Hydroxyl oxygen . . . . $\overset{\diagdown\diagup}{O} = 166$

Ether oxygen . . . . $O< = 58$

It is, of course, to be remembered here that the value of $\overset{\diagdown\diagup}{O}$ as it is derived from the acids is no doubt affected by molecular complexity.

Value of Sulphur.

Only two compounds are available for the estimation of the atomic value of sulphur $\overset{\diagdown\diagup}{S}$ which is singly linked to two carbon atoms.

	Sulphide.	" Rest " (calculated).	$\overset{\diagdown\,\diagup}{\mathrm{S}}$.
	ηd^2 (observed).		
Methyl	578	329	249
Ethyl	812	569	243

Mean value of $\overset{\diagdown\,\diagup}{\mathrm{S}} = 246$.

Influence of Ring-grouping.

HORSTMANN's discussion of the specific molecular volumes of liquids seems to show that in aromatic compounds the ring-grouping of atoms exerts a marked influence. On the other hand, BRÜHL concludes that, so far as refraction and dispersion constants go, there is no indication of this effect. BRÜHL assumes, however, that three double linkages occur in the benzene nucleus.

The data to test this point in connection with the viscosity constants are but scanty, and, further, four of the aromatic compounds—the methyl toluenes—are isomers, each having a different viscosity magnitude.

Since the value of CH_2 deduced from homologous aromatic hydrocarbons agrees with the values given by other homologous series, in the present state of the question it may be assumed that carbon and hydrogen have the same values in these compounds as they have in the others. In the following table the "rests" are calculated from the previously found values for carbon and hydrogen on the assumption that the constitution is the same as in an open straight chain compound. The differences in the last column represent the excess of the observed molecular viscosities over the values thus calculated, and may be taken as measures of the effect of the ring-grouping of atoms.

	ηd^2 (observed)	" Rest " (calculated).	Ring-grouping.
Benzene	688	453	235
Toluene	821	573	248
Ethyl benzene	939	693	246
Ortho-xylene	954	693	261
Meta-xylene	939	693	246
Para-xylene	923	693	230

Mean value for ring-grouping = 244.

Probably the first three hydrocarbons alone are comparable with one another as the xylenes contain two side chains. The general mean value is, however, almost the same as that deduced from the first three, as the meta-isomer gives almost the mean value, and the values of the ortho- and para-isomers lie to about the same extent on either side of the mean. Making due allowance for constitutive effects, it is evident, therefore, that the peculiar structure of aromatic compounds exercises an approximately constant and a most marked effect on their molecular viscosities, which are larger by some 244 units than the amounts calculated in the way already indicated.

The calculated increase, which would be brought about by three double linkages, is 144 units, so that the observed differences have to be sought for in some additional structural effect which acts in the same sense as double linkage inasmuch as it increases the molecular viscosity. The whole effect may at present be termed that of the ring-grouping of atoms, no assumption being made as to whether or not double linkage participates in bringing it about.

Thiophen gives the value 151 for the same kind of effect;

	ηd^3.	"Rest."	Ring-grouping.
Thiophen	699	548	151.

The effect produced by two double linkages is 96.

The fundamental constants thus obtained are given below.

FUNDAMENTAL Viscosity Constants. (Molecular Viscosity at Slope $\cdot 0_4 323$.)

Hydrogen	H	44·5
Carbon	C	31
Hydroxyl-oxygen . . . . . C—O—H	$\overset{\diagdown\diagup}{\text{O}}$	166
Ether-oxygen. . . . . . . C—O—C	O<	58
Carbonyl-oxygen . . . . . C=O	$\overset{\|}{\text{O}}$	198
Sulphur. . . . . C—S—C	$\overset{\diagdown\diagup}{\text{S}}$	246
Chlorine (in monochlorides)	Cl	256
Chlorine (in dichlorides)	Cl′	244
Bromine (in monobromides)	Br	372
Bromine (in dibromides).	Br′	361
Iodine	I	499
Iso grouping	<	− 21
Double linkage	(=)	48
Ring-grouping	ⓞ	244

The following tables show the numbers calculated by means of these constants, together with those actually observed :—

MOLECULAR Viscosity at Slope $\cdot 0_4 323$.

	Observed.	Calculated.	Difference per cent.
Pentane	687	689	– 0·3
Hexane	818	809	1·1
Heptane	931	929	0·2
Octane	1035	1049	– 1·3
Isopentane	663	668	– 0·7
Isohexane	799	788	1·4
Isoheptane	908	908	0·0
Isoprene	620	607	2·1
Diallyl	728	729	– 0·1
Methyl iodide	638	664	– 4·0
Ethyl iodide	778	784	– 0·8
Propyl iodide	903	904	– 0·1
Isopropyl iodide	878	883	– 0·6
Isobutyl iodide	1010	1003	0·7
Allyl iodide	864	866	– 0·2
Ethyl bromide	663	657	0·9
Propyl bromide	774	777	– 0·4
Isopropyl bromide	750	756	– 0·8
Isobutyl bromide	877	876	0·1
Allyl bromide	734	739	– 0·7
Ethylene bromide	973	962	1·1
Propylene bromide	1068	1082	– 1·3
Isobutylene bromide	1171	1181	– 0·9
Acetylene bromide	932	921	1·2
Propyl chloride	658	661	– 0·4
Isopropyl chloride	644	640	0·6
Isobutyl chloride	760	760	0·0
Allyl chloride	617	623	– 1·0
Ethylene chloride	737	728	1·2
Methylene chloride	600	600	0·0
Methyl sulphide	578	575	0·5
Ethyl sulphide	812	815	– 0·3

MOLECULAR Viscosity at Slope $\cdot 0_4 323$—(continued).

	Observed.	Calculated.	Difference per cent.
Dimethyl ketone	572	558	2·4
Methyl ethyl ketone	671	678	– 1·0
Methyl propyl ketone	796	798	– 0·2
Diethyl ketone	785	798	– 1·6
Acetaldehyde.	448	438	2·2
Formic acid	456	484	– 6·1
Acetic acid	593	604	– 1·8
Propionic acid	742	724	2·4
Butyric acid	842	844	– 0·2
Isobutyric acid	843	823	2·4
Acetic anhydride	838	845	– 0·8
Propionic anhydride	1036	1085	– 4·7
Ethyl ether	635	627	1·3
Benzene	688	697	– 1·3
Toluene	821	814	0·8
Ethyl benzene	939	934	0·5
Ortho-xylene.	954	934	2·1
Meta-xylene	939	934	0·5
Para-xylene	923	934	– 1·2

The fifty-one compounds named in the above table give an average divergence from the calculated values of about one per cent. (1·13 per cent.). It is also significant that the largest differences are given by methyl iodide, acetone, aldehyde, and formic acid, which are all the initial members of homologous series. The large difference given by propionic anhydride, as already indicated, is probably due to impurity.

In the following table are given the observed values of those substances which could not be included in deducing the fundamental constants and the values calculated for these substances after making certain assumptions as to their structure.

	Observed.	Calculated.	Difference per cent.
Amylene	665	627	5·7
Methylene dichloride	600	632	– 5·3
Chloroform	747	843	– 12·8
Carbon tetrachloride	854	1055	– 23·5
Carbon dichloride	1032	1134	– 9·9
Ethylidene chloride	702	728	– 3·7
Carbon bisulphide	618	521	15·7
Methyl alcohol	358	375	– 4·7
Water	206	255	– 23·8

The calculated value for amylene is obtained by assuming that an iso grouping and a double linkage occur in the molecule. If no iso group be assumed to exist, the calculated value is 648, which is considerably nearer that found. According to Dr. PERKIN, however, the sample is β isoamylene.

The values for the chlormethanes are calculated from the values of carbon and hydrogen, and the value of chlorine in monochlorides. The comparison is given in order to show that as chlorine accumulates in the molecule the observed values differ more and more from those calculated in this manner. In a similar way the value for carbon dichloride, calculated on the assumption that a double linkage occurs in the molecule, is also far in excess of the observed value. The observed value for ethylidene chloride is compared with that calculated for ethylene chloride; the difference is due to the difference in the constitution of the two isomers.

In calculating the value for carbon bisulphide, the value possessed by singly-linked sulphur in the alkyl sulphides has been used. The difference is, no doubt, due to the altered condition of sulphur in the bisulphide.

The values of methyl alcohol and water are calculated by means of the value of hydroxyl oxygen as deduced from the acids. It is evident, especially in the case of water, that the observed numbers differ widely from those calculated in this way.

As similar relationships are given by these substances when the values of the molecular viscosity work are compared, their behaviour will be discussed more fully at a later stage.

MOLECULAR VISCOSITY AT SLOPE $\cdot0_4987$.

(η in dynes per sq. centim. × specific molecular area in sq. centims. × 10^4.)

On finding the ratios of the molecular viscosities at the two slopes $\cdot0_4987$ and $\cdot0_4323$, a practically constant number was obtained as in the case of the viscosity coefficients. Its mean value was 1·928, the average difference being ·032 or 1·66 per cent. For this reason it was assumed that the fundamental constants which were employed at slope $\cdot 0_4 323$, if increased in the ratio of 1 : 1·928, would serve for the calculation of molecular viscosities at slope $\cdot 0_4 987$. This was the only course which could be taken in order to deduce fundamental constants, as the number of liquids was too small to enable them to be obtained in the manner already indicated. Fundamental constants had to be deduced in order that alcohols might be compared with the other liquids. The following are the values of the atomic constants at slope $\cdot 0_4 987$ calculated from the values at slope $\cdot 0_4 323$, on the assumption that molecular viscosity at the larger slope is 1·928 times that at the smaller.

FUNDAMENTAL Viscosity Constants (Molecular Viscosity at Slope $\cdot 0_4 987$).

Hydrogen	H	86
Carbon	C	60
Hydroxyl-oxygen C—O—H	$\overset{\diagdown\diagup}{\mathrm{O}}$	320
Ether-oxygen C—O—C	O<	112
Carbonyl-oxygen C=O	$\overset{\parallel}{\mathrm{O}}$	382
Sulphur C—S—C	$\overset{\diagdown\diagup}{\mathrm{S}}$	474
Chlorine (in monochlorides)	Cl	494
Chlorine (in dichlorides)	Cl′	470
Bromine (in monobromides)	Br	717
Bromine (in dibromides)	Br′	696
Iodine	I	962
Iso grouping	<	−40
Double linkage	(=)	92
Ring-grouping	ⓞ	465

The following table gives the comparison of the observed values with those calculated from the above fundamental constants :—

MOLECULAR Viscosity at Slope $\cdot 0_4 987$.

	Observed.	Calculated.	Difference per cent.
Octane	2055	2028	1·3
Ethyl iodide	1494	1510	−1·0
Propyl iodide	1734	1741	−0·4
Isopropyl iodide	1714	1701	0·8
Isobutyl iodide	1897	1932	−1·8
Allyl iodide	1642	1661	−1·1
Isobutyl bromide	1755	1687	3·9
Ethylene bromide	1828	1854	−1·5
Propylene bromide	2043	2085	−2·0
Isobutylene bromide	2270	2276	−0·3
Acetylene bromide	1713	1774	−3·6
Ethylene chloride	1401	1402	−0·1
Methyl propyl ketone	1535	1537	−0·1
Diethyl ketone	1539	1537	0·1
Formic acid	883	933	−5·6
Acetic acid	1188	1164	2·0
Propionic acid	1439	1395	3·1
Butyric acid	1671	1626	2·7
Isobutyric acid	1665	1586	4·7
Acetic anhydride	1595	1628	−2·0
Propionic anhydride	1976	2080	−5·3
Benzene	1299	1335	−2·8
Toluene	1572	1566	0·4
Ethyl benzene	1820	1797	1·3
Ortho-xylene	1806	1797	0·5
Meta-xylene	1794	1797	−0·2
Para-xylene	1796	1797	0·0

In the above table the agreement of calculated and observed values is practically the same as it was at the smaller slope, the mean percentage difference being 1·7. The largest differences, as at the smaller slope, are given by the acids and propionic anhydride. In the following table those liquids are compared which were not employed in deducing the fundamental constants. The calculated values are obtained in the same way as already indicated at slope $\cdot 0_4 323$.

	Observed.	Calculated.	Difference per cent.
Carbon tetrachloride	1627	2036	− 25·1
Carbon dichloride	1933	2188	− 13·2
Ethylidene chloride	1336	1402	− 4·9
Water	398	492	− 23·6

The behaviour of these substances is substantially what it was at the smaller slope, where the differences between the observed and calculated numbers were respectively − 23·5, − 9·9, − 3·7, and − 23·8.

The identical values given for the differences in the case of water are especially noteworthy, as the molecular complexity of water is supposed to alter as the temperature falls.

It has already been shown that the molecular viscosities of the acids—which, like water, are also supposed to contain molecular aggregates—are related to those of the other liquids in practically the same way at the two slopes. These points are of the highest importance in justifying the use of temperatures of equal slope as temperatures of comparison. For although the temperatures of slope, and thus the molecular viscosity corresponding with these temperatures, will be affected by the existence of molecular aggregates, yet the above facts indicate that the relationships obtained at any one value of the slope are general, and will be the same, no matter at what slope the comparisons are made.

Bromine and the Alcohols.

The comparison of the observed values for bromine and the alcohols with those calculated from the preceding fundamental constants, which were entirely deduced from the molecular viscosities of the other liquids, is given in the table.

	Observed.	Calculated.	Difference per cent.
Bromine	1317	1392	− 5·7
Methyl alcohol	760	720	5·3
Ethyl alcohol.	933	951	− 1·9
Propyl alcohol	1041	1182	− 13·5
Butyl alcohol	1232	1413	− 14·7
Isopropyl alcohol	930	1142	− 22·8
Isobutyl alcohol.	1137	1373	− 20·8
Inactive amyl alcohol . . .	1386	1604	− 15·8
Active amyl alcohol	1334	1604	− 20·2
Trimethyl carbinol.	1020	1333	− 30·7
Dimethyl ethyl carbinol . . .	1190	1564	− 31·4
Allyl alcohol	1047	1105	− 5·5

The calculated value for bromine is deduced from the dibromides, and its agreement with the observed value is satisfactory. In the case of the alcohols, however, it is at once evident that all trace of agreement between calculated and observed values has disappeared. The values of the alcohols, like that for water, are calculated by means of the constant for hydroxyl oxygen as derived from the acids. The calculated value for a tertiary alcohol is obtained on the assumption that two iso linkages occur in the molecule. In the case of the normal primary alcohols the first difference is positive, but all the others are negative, and increase as the series is ascended. It is also noticeable that an iso- or secondary isomer, gives a larger difference than the normal isomer, and a tertiary isomer gives the largest difference of any of the isomers. It is thus evident that there is a regularity in the magnitude of the deviations. Allyl alcohol also exhibits a comparatively large negative difference. As the behaviour of the alcohols is of the same nature with regard to the molecular viscosity work, we defer its detailed discussion till a later stage.

Conclusions relating to Molecular Viscosity at Equal Slope.

1. The tables indicate that at equal slope molecular viscosity for the great majority of the substances can be calculated from fundamental constants which express not only the partial effects of the atoms existing in the molecule, but also those due to different modes of atomic arrangement.

The large effects which can be attributed to the ring-grouping of atoms, to the iso linkage, to double linkage, and to changes in the condition of oxygen in its compounds, as well as the smaller effects due to the accumulation of an atom of halogen in a molecule, make evident the quantitative influence of constitution.

2. Of the remaining substances, the chlormethanes, tetrachlorethylene, ethylidene chloride, and carbon bisulphide, give deviations from the calculated values on account of constitutive influences, which for lack of sufficient data can not, as yet, be quantitatively expressed, and which are not allowed for in deducing the fundamental constants.

3. The alcohols and water give no agreement with the calculated values. The mode in which the deviations vary indicates, in the case of the alcohols, that the disturbing factor is related to their chemical nature.

MOLECULAR VISCOSITY WORK ($\eta \times$ SPECIFIC MOLECULAR VOLUME $= \eta d^3$) AT SLOPE $\cdot 0_4 323$.

(η in dynes per square centim. × specific molecular volume in cub. centims. × 10^3.)

HOMOLOGUES.

	ηd^3.	Difference.
Pentane	329	
		86
Hexane	415	
		80
Heptane	495	
		79
Octane	574	
Isopentane	320	
		85
Isohexane	405	
		77
Isoheptane	482	
Isoprene	284	
		72
Diallyl	356	
Methyl iodide	255	
		86
Ethyl iodide	341	
		84
Propyl iodide	425	
Isopropyl iodide	417	
		88
Isobutyl iodide	505	
Ethyl bromide	282	
		71
Propyl bromide	353	
Isopropyl bromide	346	
		87
Isobutyl bromide	433	
Ethylene bromide	450	
		76
Propylene bromide	526	
Isopropyl chloride	290	
		74
Isobutyl chloride	364	
Methylene chloride	241	
		85
Ethylene chloride	326	

Homologues (continued).

	ηd^3.	Difference.
Methyl sulphide	240	(77)
Ethyl sulphide	393	
Dimethyl ketone	238	(69)
Diethyl ketone	376	
Methyl ethyl ketone	302	81
Methyl propyl ketone	383	
Formic acid	160	77
Acetic acid	237	87
Propionic acid	324	73
Butyric acid	397	
Acetic anhydride	394	(74)
Propionic anhydride	542	
Benzene	314	82
Toluene	396	79
Ethyl benzene	475	

It is evident from the above table that in all homologous series CH_2 exerts an effect on the molecular viscosity-work which is approximately constant and is about 80 units, although, as in the case of molecular viscosity, there is a tendency for the value to diminish as the series is ascended.

CORRESPONDING Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.	Diff.	ηd^3.
Methyl	255	..	..	..	..	95	160	129	126
Ethyl	341	59	282	..	..	104	237		
Propyl	425	72	353	59	294	101	324		
Butyl	..	..	..	..	..	..	397		
Isopropyl	417	71	346	56	290	..			
Isobutyl	505	72	433	69	364	107	398		
Allyl.	397	70	327	59	268				
Ethylene	..	..	450	(62)	326				

The compound of higher molecular weight has invariably the higher molecular viscosity work. It is evident also that the same change in chemical nature corresponds approximately with the same change in molecular viscosity work.

The value for an iodide is about 70 units greater than that for a bromide, and the value for a bromide is about 60 units greater than that for a chloride.

The value for an iodide is greater by about 102 units than that for an acid, and methyl iodide has a value greater by some 130 units than that for methyl alcohol.

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	ηd^3.		ηd^3.
Hydrocarbons	415	(29)	356
Iodides	425	28	397
Bromides	353	26	327
Chlorides	294	26	268

ETHYLENE and Acetylene Bromides.

	Ethylene.	Difference.	Acetylene.
	ηd^3.		ηd^3.
Bromides	450	32	418

The five comparisons show that the loss of 2 atoms of hydrogen and the gain of a double linkage correspond to a definite change in molecular viscosity work of some 29 units.

ISOLOGOUS Hydrocarbons.

n.	C_nH_{2n+2}.	Difference.	C_nH_{2n}.	C_nH_{2n-2}.		C_nH_{2n-6}.	
	ηd^3.		ηd^3.	Difference.	ηd^3.	Difference.	ηd^3.
5	329	21	308	45	284	..	
6	415	..	..	59	356	101	314
7	495	..	..	..	..	99	396
8	574	..	..	..	..	99	475

Loss of hydrogen is accompanied by a fall in the value of the molecular viscosity work. A benzene hydrocarbon has a value which is invariably lower by almost 100 units than that of the normal paraffin containing the same number of carbon atoms. The values for isoprene and diallyl are some 52 units lower than those of the corresponding paraffins, and that of iso-amylene is some 21 units lower than that of normal pentane.

It is noteworthy that these numbers, 100, 52, and 21 are, in the same sense as, although not strictly proportional to, the corresponding differences in chemical composition, viz., H_8, H_4, and H_2.

SUBSTITUTION of Halogen for Hydrogen.

n.	$C_nH_{2n}Br_2$.	Difference.	$C_nH_{2n+1}Br$.	Chlormethanes.	ηd^3.	Difference.
	ηd^3.		ηd^3.			
2	450	168	282	Methylene chloride . .	241	87
3	526	173	353	Chloroform	328	78
4 (Iso.)	614	181	433	Carbon tetrachloride. .	406	

The mean increase in molecular viscosity work for the change of a monobromide into a dibromide is 174 : the increase, however, tends to become greater the higher the molecular weight.

As in the case of molecular viscosity the effect of substituting H by Cl in a chlormethane is smaller the larger the amount of chlorine in the molecule.

COMPOUNDS Differing by a Carbon Atom.

	ηd^3.	Diff.		ηd^3.	Diff.
Tetrachlormethane . .	406	90	Methyl alcohol . . .	126	43
Tetrachlorethylene . .	496		Aldehyde	169	

As in the case of molecular viscosity, the different values given by the comparisons may be partly due to the fact that the addition of a carbon atom to form the group C : C exerts a different effect from that produced when the carbon atom added forms the group C : O, and partly to the presence of molecular aggregates in the methyl alcohol.

ISOMERS.

NORMAL and Iso compounds.

	Normal.	Difference.	Iso.
	ηd^3.		ηd^3.
Pentanes	329	9	320
Hexanes	415	10	405
Heptanes	495	13	482
Propyl iodides	425	8	417
Propyl bromides	353	7	346
Propyl chlorides	294	4	290
Butyric acids	397	− 1	398

With the exception of the butyric acids, which are anomalous, probably for the reason already given, the normal compound has always the higher viscosity, the average difference being about 8 units. It is evident, however, that in the same family of compounds the difference tends to rise with the molecular weight.

AROMATIC Hydrocarbons.

	ηd^3.	Diff.
Ortho-xylene	483	− 8
Ethyl benzene	475	− 1
Meta-xylene	474	− 7
Para-xylene	467	

As in the case of molecular viscosity, ortho-xylene has the largest value and para-xylene the smallest; meta-xylene and ethyl benzene have practically the same value, and this is almost the mean of those of ortho- and para-xylene.

DICHLORETHANES.

	ηd^3.	Difference.
Ethylene chloride.	326	−14
Ethylidene chloride	312	

The symmetrical compound has, as before, the larger value.

ISOMERIC Ketones.

	ηd^3.	Difference.
Diethyl ketone	376	7
Methyl propyl ketone	383	

Probably for the reason already given, the unsymmetrical compound has the larger value.

It will be apparent from these tables that the relationships thus established are as definite as those given by the molecular viscosities of the substances, and justify the attempt to calculate atomic constants which is given in detail in what follows. The method is the same as that used in the case of molecular viscosity.

METHOD OF DEDUCING THE FUNDAMENTAL VISCOSITY CONSTANTS (MOLECULAR VISCOSITY WORK AT SLOPE $\cdot 0_4 323$).

Value of CH_2.

The mean of the twenty-three available values for CH_2 given in the table of homologues is practically 80 (79·52) and, neglecting signs, the average divergence from the mean is 5. Hence it is assumed that

$$CH_2 = 80.$$

Influence of the Iso grouping.

Excluding the butyric acids, for the reason already given, all the comparisons agree in showing that a normal compound has a higher value than an iso compound, the average difference being 8, from which the mean divergence, neglecting signs, is 3. The effect of introducing the iso arrangement of two carbon atoms into a straight chain compound is thus taken to be − 8.

Value of Hydrogen.

The data used in deducing the value of H are summarised below :—

	n.	C_nH_{2n+2}.	nCH$_2$.	H$_2$.
Normal paraffins . .	5	329	400	− 71
	6	415	480	− 65
	7	495	560	− 65
	8	574	640	− 66
Iso-paraffins	5	320	392	− 72
	6	405	472	− 67
	7	482	552	− 70
Mean value of H$_2$ = − 68.				

Neglecting signs, the average divergence from the mean is less than 3.

Value of Carbon.

Since $CH_2 = 80$ and $H_2 = -68$, it may be taken that $C = 148$.

Influence of a Double Linkage.

The four comparisons of normal propyl and allyl compounds show that the occurrence of a double linkage and the loss of two hydrogen atoms lower the molecular viscosity work by 27 units, the average divergence being about 1 unit. The same change in a substance like ethylene bromide affects its molecular viscosity work to about the same extent.

It follows, therefore, since the value of H$_2$ is − 68, that the value of a double linkage is − 95.

Values of the Halogens.

Adopting the values,

$H = -34$, $C = 148$, iso grouping = − 8, double linkage = − 95,

the data available for calculating the atomic constants of the halogens are collected in the tables given below :—

VALUE of Iodine.

	Iodide.	"Rest" (calculated).	I.
	ηd^3 (observed).		
Methyl	255	46	209
Ethyl	341	126	215
Propyl	425	206	219
Isopropyl	417	198	219
Isobutyl	505	278	227
Allyl	397	179	218
Mean value of I = 218.			

The average divergence from the mean is less than 4.

VALUES of Bromine.

	Bromide.	"Rest" (calculated).	Br.
	ηd^3 (observed).		
Ethyl	282	126	156
Propyl	353	206	147
Isopropyl	346	198	148
Isobutyl	433	278	155
Allyl	327	179	148
Ethylene	450	160	(145)
Propylene	526	240	(143)
Isobutylene	614	312	(151)
Acetylene	418	113	(152)

In monohalogen compounds bromine has the value 151, the average divergence being less than 4.

In dibromides the value for bromine is 148, with an average difference of less than 4.

This value is almost the same as that in monobromides, but the small difference is probably real, as comparisons of molecular viscosity, and also of chlorine compounds, &c., serve to show that in dihalogen compounds the halogen has a lower value than in monohalogen compounds.

VALUES of Chlorine.

	Chloride.	" Rest " (calculated).	Cl.
	ηd^3 (observed).		
Propyl	294	206	88
Isopropyl	290	198	92
Isobutyl	364	278	86
Allyl	268	179	89
Ethylene	326	160	(83)
Methylene.	243	80	(81)
Chloroform	328	114	(71)
Carbon tetrachloride	406	148	(64)
Carbon dichloride	497	201	(74)

In monohalogen compounds the value of chlorine by the method of calculation adopted is 89, and in carbon tetrachloride is 64.

It is thus apparent, as far as the data go, that as chlorine accumulates in a molecule its value becomes less and less, the values obtained being

In monochlorides, 89.	In trichlorides, 71.
In dichlorides, 82.	In tetrachlorides, 64.

In the unsaturated compound, C_2Cl_4, chlorine appears to have about the same value as in chloroform and in ethylidene chloride (76).

The mean of the values for iodine and chlorine in monohalogen compounds is 153, which is almost identical with that obtained for bromine, viz., 151.

Values of Oxygen.

Carbonyl Oxygen.—On deducting, as before, $n\mathrm{CH}_2$ from the observed numbers for aldehyde and the ketones, values are obtained for $\overset{\|}{\mathrm{O}}$.

	$C_nH_{2n}\overset{\|}{O}$.	nCH_2 (calculated).	$\overset{\|}{O}$.
	ηd^3 (observed).		
Aldehyde	169	160	+ 9
Dimethyl ketone	238	240	− 2
Methyl ethyl ketone	302	320	−18
Methyl propyl ketone	383	400	−17
Diethyl ketone	376	400	−24

Mean adopted value of $\overset{\|}{O} = -19$.

Methyl ethyl ketone and methyl propyl ketone give almost the same value for carbonyl oxygen; the value of diethyl ketone, on making allowance for the effect of constitution, also indicates that the value of $\overset{\|}{O}$ is about − 19.

The values for $\overset{\|}{O}$ obtained from dimethyl ketone, the initial member of the series, which from surface-energy measurements appears to contain molecular aggregates, and aldehyde, which, of course, has a different constitution from that of the ketones, are not included in the adopted mean.

These two substances will be referred to later.

It is assumed that the probable value for carbonyl oxygen is

$$\overset{\|}{O} = -19.$$

Hydroxyl Oxygen.—On deducting the values of nCH_2 from the observed numbers for the fatty acids, the differences obtained correspond with the joint effect of an atom of carbonyl and an atom of hydroxyl oxygen $\overset{\|}{O}\overset{\diagdown\diagup}{O}$.

	Acids.	nCH_2 (calculated).	$\overset{\|}{O}\overset{\diagdown\diagup}{O}$.
	ηd^3 (observed).		
Formic	163	80	83
Acetic	237	160	77
Propionic	324	240	84
Butyric	397	320	77
Isobutyric	398	312	86

Mean value of $\overset{\|}{O}\overset{\diagdown\diagup}{O} = 81$.

The average divergence from the mean is less than 4. The percentage variation is greater, however, than for most of the other atomic constants. The value is probably affected by the complexity of the acids.

Taking $\overset{\|}{\mathrm{O}} = -19$, and $\overset{\|}{\mathrm{O}} + \overset{\diagdown\diagup}{\mathrm{O}} = 81$, it follows that in the acids $\overset{\diagdown\diagup}{\mathrm{O}} = 100$.

Ether Oxygen.—Using the preceding values of C, H, and $\overset{\|}{\mathrm{O}}$, the observed numbers for acetic anhydride and ether give respectively 44 and 42 as values for ether oxygen ; with such scanty data as are to hand it is therefore probable that

$$\mathrm{O}< \; = 43.$$

The mean values thus obtained for oxygen in different conditions are

$$\overset{\|}{\mathrm{O}} = -19, \quad \overset{\diagdown\diagup}{\mathrm{O}} = 100, \quad \mathrm{O}< \; = 43.$$

Value of Sulphur.

The two comparisons available for obtaining values for singly-linked sulphur are given below :—

	Sulphide.	" Rest " (calculated).	$\overset{\diagdown\diagup}{\mathrm{S}}$.
	ηd^3 (observed).		
Methyl	240	92	148
Ethyl	393	252	141

Mean value of $\overset{\diagdown\diagup}{\mathrm{S}} = 144$.

Influence of Ring-Grouping.

On calculating values for the molecular viscosity work of the aromatic hydrocarbons in the same way as has been described when dealing with molecular viscosity, the differences given in the subjoined table, representing the effect of the ring-grouping, are obtained.

	ηd^3 (observed).	" Rest " (calculated).	Ring-grouping.
Benzene	314	684	−370
Toluene	396	764	−368
Ethyl benzene	475	844	−369
Ortho-xylene	483	844	−361
Meta-xylene	474	844	−370
Para-xylene	467	844	−377

Mean value of ring-grouping = − 369.

Probably the first three hydrocarbons are alone strictly comparable, as the others contain two side chains. The mean of all the differences is, however, exactly the same as that deduced from the first three. The average difference from the mean, which in the case of the xylenes is mainly due to constitutive influences, is only some 3 units.

It is thus evident that the ring-grouping of atoms exerts a definite and profound influence on the magnitude of the molecular viscosity work.

If it is assumed that three double linkages occur in benzene, the differences would be reduced to

$$369 - 3 \times 95 = 84 \text{ units},$$

so that the original difference is in the same sense as that which would be produced by double linkage, but evidently it can not be explained on the assumption that double linkages alone produce it.

As in the case of aromatic hydrocarbons the calculated value for thiophen is largely in excess of that observed :

$$\text{Thiophen}\left\{\begin{array}{lr}\text{Calculated} & .\ \ 600\\ \text{Observed} & .\ \ 305\end{array}\right\}\text{Difference, 294.}$$

The value of the effect of two double linkages is 190, so that here also it is impossible to attribute the observed difference to the double linkage of carbon atoms alone.

The values thus obtained for the fundamental constants are summarized in the following table :—

FUNDAMENTAL Viscosity Constants (Molecular Viscosity Work at Slope $\cdot 0_4 323$).

Hydrogen		H	$-$ 34
Carbon		C	148
Hydroxyl-oxygen	C—O—H	$\overset{\diagdown\,\diagup}{\mathrm{O}}$	100
Ether-oxygen	C—O—C	O<	43
Carbonyl-oxygen	C=O	$\overset{\Vert}{\mathrm{O}}$	$-$ 19
Sulphur	C—S—C	$\overset{\diagdown\,\diagup}{\mathrm{S}}$	144
Chlorine (in monochlorides)		Cl	89
,, (in dichlorides)		Cl′	82
Bromine (in monobromides)		Br	151
,, (in dibromides)		Br′	148
Iodine		I	218
Iso grouping		<	$-$ 8
Double linkage		(=)	$-$ 95
Ring-grouping		⊙	$-$ 369

The comparison of the observed values of the molecular viscosity work with those calculated by means of the above fundamental constants is given in the following table :—

MOLECULAR Viscosity Work at Slope $\cdot 0_4 323$.

	Observed.	Calculated.	Difference per cent.
Pentane	329	332	– 0·9
Hexane	415	412	0·7
Heptane	495	492	0·6
Octane	574	572	0·3
Isopentane	320	324	– 1·2
Isohexane	404	404	0·0
Isoheptane	482	484	– 0·4
Isoprene	284	278	2·1
Diallyl	356	358	– 0·5
Methyl iodide	255	264	– 3·5
Ethyl iodide	341	344	– 0·9
Propyl iodide	425	424	0·2
Isopropyl iodide	417	416	0·2
Isobutyl iodide	505	496	1·8
Allyl iodide	399	397	0·5
Ethyl bromide	282	277	1·8
Propyl bromide	353	357	– 1·1
Isopropyl bromide	346	349	– 0·9
Isobutyl bromide	433	427	1·4
Allyl bromide	327	330	– 0·9
Ethylene bromide	450	456	– 1·3
Propylene bromide	526	536	– 1·9
Isobutylene bromide	614	608	1·0
Acetylene bromide	418	409	2·0
Propyl chloride	294	295	– 0·3
Isopropyl chloride	290	287	1·0
Isobutyl chloride	364	367	– 0·8
Allyl chloride	268	268	0·0
Methylene chloride	241	244	– 1·2
Ethylene chloride	326	324	0·6

MOLECULAR Viscosity Work at Slope $\cdot 0_4323$—(continued).

	Observed.	Calculated.	Difference per cent.
Methyl sulphide	240	236	1·7
Ethyl sulphide	393	396	– 0·8
Methyl ethyl ketone	302	301	0·3
Methyl propyl ketone	383	381	0·5
Diethyl ketone	376	381	– 1·3
Formic acid	160	159	0·6
Acetic acid	237	239	– 0·8
Propionic acid	323	319	1·2
Butyric acid	397	399	– 0·5
Isobutyric acid	398	391	1·8
Acetic anhydride	394	393	0·3
Propionic anhydride	542	553	– 2·0
Ethyl ether	295	295	0·0
Benzene	314	315	– 0·3
Toluene	395	395	0·0
Ethyl benzene	475	475	0·0
Ortho-xylene	483	475	1·7
Meta-xylene	474	475	– 0·2
Para-xylene	467	475	– 1·7

The average difference between the observed and calculated numbers given by the above compounds is less than 1 per cent.; in one or two cases, as the isomeric ketones and isomeric xylenes, the differences are partly due to effects of constitution which are ignored in obtaining the calculated values.

Several compounds are worthy of special discussion, and are considered in what follows.

Isoprene.—The calculated value for isoprene is deduced on the assumption that it is a straight chain compound containing two double linkages. Of the five possible formulæ for isoprene (see TILDEN, 'Proc. Birmingham Phil. Soc.,' vol. 8, 1892), one contains, in addition to the double linkages, an iso linkage of carbon atoms. If an iso linkage occurred in the chain the calculated value for the molecular viscosity work would be reduced to 270, and the difference between the observed and calculated values raised to 14 units, or 5 per cent. Viscosity observations therefore favour the view which is indicated by chemical methods, that no iso linkage occurs in the molecule. It is noteworthy that the difference between the values of the molecular viscosity work of diallyl and isoprene is 72, a number which is lower than the mean value for a difference in composition corresponding to CH_2, viz., 80. If diallyl be represented as

$$CH_2 : CH.CH_2.CH_2.CH : CH_2,$$

the above small difference may be taken to indicate that isoprene is not a true homologue of diallyl, and probably, therefore, that the formula for isoprene which most closely resembles the formula for diallyl, viz.,

$$CH_2 : CH.CH_2.CH : CH_2,$$

is not the correct formula. The conclusions which follow from the viscosity of isoprene, taken in conjunction with the fact that isoprene yields acetic acid as an oxidation product, point to

$$CH_3.CH : C : CH.CH_3$$

or

$$CH_3.CH : CH.CH : CH_2$$

as the most probable formula for this hydrocarbon.

Methyl Iodide.—The difference between the theoretical and calculated values for methyl iodide is considerably above the average.

This is no doubt due to the fact that methyl iodide is a substituted methane; it is, indeed, the only monocarbon compound given in the table; in all the other iodides iodine has been introduced into a methyl group. (Compare what follows with regard to carbon tetrachloride, which is also a monocarbon compound.)

Fatty Acids.—As has already been stated, the acids most probably contain molecular aggregates at the temperatures of comparison. The fairly regular values given by the normal acids for the effect of CH_2 and $\overset{\diagdown\diagup}{O}$ indicate, however, that at temperatures of equal slope the extent of the molecular aggregation if not quite the same is not very different for the various liquids.

Isobutyric acid has probably a slightly different molecular complexity at equal slope from that of the corresponding normal acid. The same result, indeed, follows from surface-energy observations. This is no doubt the reason why in all comparisons nto which this iso acid enters it gives values which appear more or less anomalous when compared with those given by non-associated liquids or by liquids like the normal acids, which are probably of about the same degree of association at equal slope.

Isomeric Aromatic Hydrocarbons.—The calculated value is the same for all the compounds, and is deduced from the values of carbon, hydrogen, and the effect of the ring-grouping.

Ethyl benzene and meta-xylene give observed values which are identical with those calculated, whereas ortho-xylene gives a number which is as far above the calculated value as that of para-xylene is below it. The differences give a measure of the variation in constitution of these substances. In the following table is given the comparison of the molecular viscosity work and several other physical properties of these isomers :—

	Molecular viscosity work.		Critical temperatures.*		Critical pressures.*		Boiling-point.	
			°				°	
Ortho-xylene	483		358		36·9		144·0	
		9		13		1·1		5·0
Meta-xylene	474		345		35·8		139·0	
		7		1		·8		·8
Para-xylene	467		344		35·0		138·2	
Ethyl benzene	475	8	346	12	38·1	−1·2	136·1	7·9

	Molecular magnetic rotation.†		Specific molecular volume at boiling-point.		Molecular refraction.‡	
Ortho-xylene	13·306		138·2		36·050	
		·575		−1·5		·444
Meta-xylene	12·731		139·7		35·606	
		−·058		− ·5		·031
Para-xylene	12·789		140·2		35·575	
Ethyl benzene	13·327	−·021	138·7	− ·5	35·332	·718

As regards the metameric xylenes, except in the case of magnetic rotation, the differences are of the same sign; this, of course, is the result of the fact that the ortho-isomer has either the largest value, and the meta compound the smallest value, or *vice versâ*. The magnetic rotation of the meta isomer is exceptional, and is slightly smaller than that of the para isomer. It is also invariably the case that the difference between the values of the ortho- and meta isomers is larger than the difference between the meta- and para isomers.

The relation in which the magnitude of the value for ethyl benzene stands to those of the other compounds varies with the particular property dealt with.

The difference given in the table is that between ethyl benzene and ortho-xylene; from the magnitude and sign of this difference as compared with those of the other differences it is evident that, in the case of molecular viscosity work, critical temperature, and specific molecular volume, the value for ethyl benzene is intermediate between those of ortho- and meta-xylenes.

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* ALTSCHUL, 'Zeit. für physik. Chemie,' 11, 577.

† LANDOLT and JAHN, 'Zeit. für physik. Chemie,' 10, 311 (n^2_α formula).

‡ SCHÖNROCK, 'Zeit. für physik. Chemie,' 11, 753.

In the case of critical pressure and magnetic rotation ethyl benzene has the largest, and in the case of boiling-point and molecular refraction the smallest, value of all the isomers. The relations between the magnitudes of the viscosity constants of these substances is thus in harmony with their other physical properties.

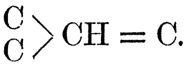
In what follows the observed values of substances which are not included in the preceding table, and which were not employed in deducing the fundamental constants, are compared with the values given by the other substances.

Amylene.—Assuming that the substance employed is a straight chain compound containing one double linkage,

$$\left.\begin{array}{ll}\text{the calculated value is} & 305\\ \text{the value found is} & 307\end{array}\right\}\text{Difference . 2.}$$

On Dr. PERKIN'S authority, however, the sample is tri-methyl ethylene, and if, in addition to a double linkage, an iso linkage be taken to exist in the molecule, the calculated value is modified to 297, and the difference raised to 10, or about 3 per cent. This difference is somewhat greater than those usually found in the preceding table, and it is noteworthy that Dr. PERKIN found that the magnetic rotation of this sample was anomalous (compare 'Journ. Chem. Soc.,' 45, p. 561, 1884).

It may also be pointed out that this substance is the only one examined in which an iso linkage is associated with a double linked carbon atom; of all the substances investigated by us it alone contains the group



$$\begin{matrix}C\\C\end{matrix}\!\!>CH = C.$$

The same remarks apply in the case of molecular viscosity.

Chlormethanes.—In deducing the values of the fundamental constants it has been established that if the values of carbon and hydrogen be taken as constant, the value of the halogen in a dihalogen compound is invariably lower than the value in a monohalogen compound.

From the values afforded by the chlormethanes it would appear that a similar decrease still takes place in the case of tri- and tetra-halogen compounds. In order to indicate this change in the value of the halogen, we give in the following table the observed values of the chlormethanes and the values calculated by using the value possessed by chlorine in monochlorides.

	ηd^3 (observed).	ηd^3 (calculated).	Difference.
Methylene chloride	241	258	−17
Chloroform	328	381	−53
Carbon tetrachloride	406	504	−98

As the number of hydrogen atoms displaced by the halogen increases, the differences augment at an increasing rate.

If the values of carbon and hydrogen be taken as normal in these compounds, on introducing the value of chlorine obtained from monohalogen compounds the following numbers represent the respective effects on the molecular viscosity work of 1, 2, 3, and 4 atoms of chlorine when linked to one carbon atom.

	Effect upon molecular viscosity work.	Difference.
Cl	89	
		75
Cl_2	164	
		50
Cl_3	214	
		44
Cl_4	258	

It is instructive to note that the magnitudes of several of the other physical properties of these and similar substances exhibit the same kind of relationships.

From determinations of the heats of formation of halogen compounds at constant volume, THOMSEN concludes that the respective thermal effects which may be attributed to the fixation of different numbers of chlorine atoms in the same molecule are as follows:—

	Thermal effect.	Difference.
Cl	138 K	
		192
Cl_2	330 K	
		144
Cl_3	474 K	
		126
Cl_4	600 K	

Here, precisely as in the case of molecular viscosity work, the differences diminish at a decreasing rate.

The numbers given in the following table indicate also a parallelism between the magnitudes of the boiling-points, specific molecular volumes, and magnetic rotatory powers of the chlormethanes and the values of the molecular viscosity work.

Critical temperatures might also be included in the comparisons, but the values for the higher chlorinated compounds, especially that of methylene chloride, are untrustworthy, as the observations were made over heated mercury, whereby the substances are partially decomposed. The value for the molecular viscosity work of methyl chloride is calculated from that of monohalogen compounds.

	Molecular viscosity-work.	Difference.	Boiling-point.	Difference.
Methyl chloride	(135)		° – 23·7	
Methylene dichloride . .	243	108	40·2	63·9
Chloroform	328	85	61·3	21·1
Carbon tetrachloride. . .	406	78	76·8	15·5

	Molecular magnetic rotation.	Difference.	Specific molecular volume at boiling-point.	Difference.
Methyl chloride	..	..	50·8	
Methylene chloride . . .	4·313		65·6	14·8
Chloroform	5·559	1·246	84·5	18·9
Carbon tetrachloride. . .	6·582	1·023	103·7	19·2

In all cases the differences are not constant, but alter progressively as substitution goes on; and for all the properties but specific molecular volume the differences diminish.

Other properties, which are less influenced by differences in constitution than those mentioned above, also give indication of effects of a similar kind. Observations on molecular refraction show, although not so definitely as the above properties, that as an element, or radicle, accumulates in a molecule the effect of each increment is not the same (Comp. BRÜHL, 'Zeit. f. physik. Chem.,' 7, 178; ARMSTRONG, 'Proc. Chem. Soc.,' 1892–3, 57).

In the case of specific molecular volume and molecular refraction, unlike what takes place in the case of molecular viscosity work, the value of chlorine, say, increases as successive atoms are linked to the same carbon atom. This difference is significant, as viscosity and boiling-point are doubtless to be referred to inter-molecular effects, whereas specific molecular volume, and, as there is reason to believe, refraction as well, are to be associated with intra-molecular effects (compare p. 549).

The surface tensions of two only of the chlormethanes, viz., chloroform and carbon tetrachloride, have been determined by SCHIFF. He has shown that, according to his method of treating surface tension measured at the boiling-point, the value of chlorine in chloroform is the same as in carbon tetrachloride. It would thus appear that, as regards the surface tensions of these two substances, the effect of the accumulation of chlorine in the molecule is inoperative.

The values for the molecular viscosity work of the chlormethanes are thus in harmony with those of all other properties which are largely affected by constitutive influences, and conform to the general rule that the extent to which the magnitude of a property is affected by the displacement of one atom of hydrogen by one atom of halogen is not constant, but varies in a regular way according as the first, second, third, or fourth hydrogen atom is replaced.

Chlorethanes.—The molecular viscosity work of ethylene chloride is distinctly greater than that of ethylidene chloride.

Ethylene chloride	326	14
Ethylidene chloride	312	

With the exception of heats of combustion, where it has to be noted that chlorine takes no part in the chemical change, the magnitudes of several of the other physical properties of these metamers exhibit similar striking differences, as the following table shows :—

	Boiling-point.	$\frac{\text{Surface tension}}{\text{Molecular weight}}$ at b.p.	Molecular magnetic rotation.	Heat of combustion.	Specific molecular volume at b.p.	Molecular refraction.
Ethylene chloride .	84·0°	24·6	5·485	272	85·0	20·92
Ethylidene chloride.	57·5	20·8	5·335	272	89·3	21·08
Difference	26·5	3·8	·150	0	−4·3	−·16

Here again the change in specific molecular volume and molecular refraction is in the opposite sense to the change in the other properties.

The cause of these remarkable differences is no doubt to be traced to the fact that the effect of introducing chlorine in place of hydrogen into ethane varies according as it is the first, second, or third atom of chlorine which is united to the same carbon atom. Thus the effect of substituting hydrogen by chlorine in the compounds, RCH_3, RCH_2Cl, $RCHCl_2$, is doubtless different in each case.

Moreover, it is also conceivable that the effect may depend on the nature of R, *i.e.*, whether it be CH_3, CH_2Cl, $CHCl_2$, or CCl_3. To test these two points it would be necessary to investigate as many of the various chlormethanes as possible.

This has only been done in the case of specific molecular volumes, and here the results clearly point to the conclusion that if we start with ethyl chloride the nature of R is inoperative, and that the effect of introducing Cl into ethyl chloride, or its chlorine derivatives, simply depends on whether it is the first, second, or third chlorine atom which has been introduced into a particular methyl group.

Using the value for ethyl chloride calculated by KOPP from PIERRE'S values for its thermal expansion, and the values obtained by STAEDEL, the following are the data which serve to establish the foregoing conclusion :—

Chlorethane.	Differences in specific molecular volume.	Where R may be
RCH_3		CH_2Cl, $CHCl_2$, or CCl_3.
	14·1 ± ·3	
RCH_2Cl		CH_3, CH_2Cl, $CHCl_2$, or CCl_3.
	16·9 ± ·4	
$RCHCl_2$		CH_3, CH_2Cl, $CHCl_2$, or CCl_3.
	19·2 ± ·4	
$RCCl_3$		CH_3, CH_2Cl, or $CHCl_2$.

Here the effect of substituting chlorine, as in the case of the chlormethanes, is greater, according as the first, second, or third hydrogen atom in the original methyl group is replaced by the chlorine.

The cause of the difference between the specific molecular volumes of ethylene chloride and ethylidene chloride is to be sought for in the fact that in the former substitution has taken place in two methyl groups, whereas in the latter it has only taken place in one methyl group. There is no doubt that the difference in the magnitudes of the viscosity and other physical properties is to be ascribed to the same fact. Whether the magnitude of the effect of substituting chlorine in the case of these properties depends also on the nature of R, *i.e.*, on the halogen contents of the other methyl group, can best be decided by investigations similar to those of STAEDEL. There is indication, however, that this effect is operative in the case of viscosity, as it appears that dihalogen derivatives of ethane give a smaller value for the atomic constant of the halogen than monohalogen compounds. If the effect of the nature of R were inoperative, the compound $CH_3.CH_2Cl$ should yield the same value for chlorine as $CH_2Cl.CH_2Cl$, for in each case the first hydrogen atom in a methyl group has alone been replaced. Indeed, it may be the case that specific molecular volume is also affected in the same way. The volume-change in passing from ethane itself, $CH_3.CH_3$, to ethyl chloride, $CH_3.CH_2Cl$, may perhaps differ from the change produced in passing from $CH_3.CH_2Cl$. to $CH_2Cl.CH_2Cl$. This point can only be settled when the specific molecular volume of ethane is determined.

From a study of the chlorethanes and chlormethanes it is thus evident that, as in the case of specific molecular volume, the magnitude of the effect which is exerted on the molecular viscosity work when chlorine is united to carbon, hydrogen being expelled, depends on whether the first, second, or third hydrogen atom is replaced.

Tetrachlorethylene.—The mean value of chlorine in tetrachlorethylene $CCl_2:CCl_2$ is 74.

This value is almost the same as the value of chlorine in ethylidene chloride, viz., 76.

It is probable, therefore, that in substituting hydrogen by chlorine in ethylene, the same or similar variations take place, as in the case of ethane ; for on producing

$$CH_3.CHCl_2 \text{ and } CCl_2{:}CCl_2,$$

the first and second hydrogen atoms attached to a given carbon atom have alone been substituted, and the above numbers show that the mean value of the chlorine is about the same in both cases.

The following table contains the values of chlorine calculated from the molecular viscosity work of the chlorine compounds examined :—

N = atoms of hydrogen substituted in each methyl group.	Chlormethanes.		Chlorethanes.		Chlorethylene.	
1	*($H.CH_2Cl$)	89	$CH_2Cl.CH_2Cl$	83		
2	$H.CHCl_2$	83	$CH_3.CHCl_2$	76	$CCl_2{:}CCl_2$	74
3	$H.CCl_3$	71				
4	$Cl.CCl_3$	64				

It will be seen in conformity with the conclusions already stated that as N increases the value of chlorine always diminishes. It is also noticeable that when N is the same, the value of chlorine varies slightly with the series to which the substance belongs. This is again evidence of the fact already mentioned that on substituting hydrogen in a methyl group, the effect also depends upon the nature of the radicle to which the methyl group is attached.

On comparing the differences between the specific molecular volumes of compounds belonging to the above series a similar variation is noticeable, as is seen in the following table :—

N.	Chlormethanes.			Chlorethanes.		Chlorethylene.		
		Specific molecular volume.	Difference.		Difference.		Specific molecular volume.	Difference.
1	$H.CH_2Cl$	50·8	14·9	$R.CH_2Cl$	16·9	$CHCl : CHCl.$	79·6	(17·5)
2	$H.CHCl_2$	65·7	18·8	$R.CHCl_2$	19·2	$CCl_2 : CCl_2$	114·6	
3	$H.CCl_3$	84·5		$R.CCl_3$				

---

* The value of chlorine here used is that given by the monohalogen compounds examined.

The effect of introducing chlorine increases as N increases, and, N remaining the same, it is greatest in an ethylene compound and least in a methane compound. Here, as is always the case, the direction of the change in specific molecular volume is the reverse of that exhibited in the case of molecular viscosity work.

It is evident that the condition of chlorine in carbon tetrachloride is different from that in tetrachlorethylene. Indeed, CCl_4 is hardly comparable with the other substances where substitution in methyl groups is considered.

On comparing the physical properties of these two substances with those of compounds which are related in the same way so far as chemical composition goes, in all cases, as the following table shows, the behaviour of these chlorine compounds is peculiar.

The peculiarity is doubtless to be attributed to the different conditions of chlorine in the two compounds, a difference which is ignored when the compounds are simply regarded as differing in chemical nature by an atom of carbon and a double linkage.

	Molecular viscosity work.	Difference.	Boiling-point.	Difference.	$\frac{\text{Surface tension}}{\text{Molecular weight}}$ at b.p.	Difference.
Ethyl bromide . .	282	45	38·4°	32·1	20·5	− 1·7
Allyl bromide . .	327		70·5		18·8	
Ethyl iodide . .	341	56	72·4	30·4	14·7	− 1·7
Allyl iodide . . .	397		102·8		13·0	
Tetrachlormethane	406	91	76·8	43·9	13·3	·1
Tetrachlorethylene	497		120·7		13·4	

	Heat of combustion.	Difference.	Specific molecular volume at b.p.	Difference.
Ethyl bromide . .	341·8	120·3	77·5	13·0
Allyl bromide . .	462·1		90·5	
Ethyl iodide . .	..	..	85·8	15·1
Allyl iodide . . .	..	..	100·9	
Tetrachlormethane	75·9	119·2	103·7	10·9
Tetrachlorethylene	195·1		114·6	

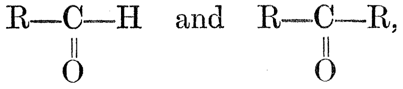
The differences between the magnitudes of the properties of the two chlorine compounds are never in harmony with the fairly concordant differences obtained from the other pairs of compounds, the members of which differ in composition by a carbon atom and a double linkage.

Aldehyde and Acetone.—As already stated, the observed values of these substances were not employed in deducing the fundamental constants.

Using the values for C, H, and $\overset{\|}{O}$, the observed and calculated numbers are :—

	Observed.	Calculated.	Difference per cent.
Aldehyde	169	141	16
Acetone	238	221	7

This large difference in the case of aldehyde points to the difference in constitution between the aldehydes and the ketones, as the value of oxygen used in obtaining the calculated number is that of ketonic oxygen. The difference is to be ascribed to the fact that different values have to be given to carbonyl in the groups



$$R—\underset{\underset{O}{\|}}{C}—H \quad \text{and} \quad R—\underset{\underset{O}{\|}}{C}—R,$$

just as different values have to be given to oxygen in the groups R.O.H (hydroxyl oxygen) and R.O.R (ether oxygen). A study of other aldehydes would have to be undertaken to decide this point. The large observed value for acetone is somewhat difficult to explain on purely chemical grounds. It is possibly due to the symmetry of the molecule, although the evidence is somewhat unsatisfactory. The symmetrical compound Et.CO.Et. gives an observed value which is smaller than that obtained by calculation; possibly, as already mentioned, the character of the diethyl ketone may have affected the result. On comparing ethylene and ethylidene chlorides it has been seen that the symmetrical compound differs from the unsymmetrical compound just as acetone appears to differ from ketones like Me.CO.Et. and Me.CO.Pr; the symmetrical compounds having the larger values. The most probable cause of the peculiar behaviour of acetone is indicated, however, by surface-energy measurements, which point to the conclusion that acetone contains molecular aggregates, whereas methyl propyl ketone, and thus presumably higher homologues of acetone, do not. (RAMSAY and SHIELDS, *loc. cit.*)

Carbon Bisulphide.—The calculated value for carbon bisulphide, using the constant for singly-linked sulphur, is 436. The observed value is 241.

It is evident, however, that in carbon bisulphide we are dealing with doubly-linked sulphur, which, employing the ordinary values for carbon and hydrogen, apparently has the value

$$\overset{\|}{\mathrm{S}} = \tfrac{1}{2}(241 - 148) = 47.$$

The values thus obtained for sulphur are related to one another in a similar way to those already given for ether oxygen and carbonyl oxygen.

	Molecular viscosity work.		Molecular refraction.
	Oxygen.	Sulphur.	Oxygen.
Singly-linked	39	144	1·655
Doubly-linked	−19	47	2·328
Difference.	58	97	− ·673

Brühl arrives at corresponding values in the case of oxygen from a study of molecular refraction; his numbers are given in the last column of the above table. In conformity with what has already been said, the difference in the case of molecular refraction is negative, while in the case of viscosity it is positive.

Water.

The observed value for water is 55.

The calculated value, using the value for hydroxyl oxygen, and the ordinary value of hydrogen, is 30, so that the observed number is twice as large as that calculated in this way. Having regard to the general physical behaviour of liquid water as indicating the existence of molecular aggregates, and also to the mode in which the fundamental constants were deduced, this difference is what might have been anticipated. The value for hydroxyl oxygen was deduced from the observed numbers given by the acids on the assumption that in these liquids C, H, and $\overset{\|}{\mathrm{O}}$ had the same values as in simply constituted liquids. Seeing, however, that the acids contain molecular aggregates, the value of $\diagdown\mathrm{O}\diagup$ will be affected by this influence and cannot, therefore, be expected to apply to liquids containing molecular aggregates which differ in complexity from those of the acids.

The large difference obtained above may, in the main, be attributed to the fact that at equal slope the complexity of water is different from that of the acids, a conclusion which is supported by surface-energy observations. The fact also that in the simple water molecule OH is linked to hydrogen and not to an unsaturated "rest" as in the simple molecule of an acid may also exert some effect.

Molecular Viscosity work at Slope $\cdot 0_4 987$.

(η in dynes per sq. centim. $\times$ specific molecular volume in cub. centims. $\times 10^3$.)

In order to compare the alcohols with the other liquids, and to test if the comparisons at slope $\cdot 0_4 323$ still held at different values of the slope, the magnitudes of the molecular viscosity work were ascertained at slope $\cdot 0_4 987$. The reason for choosing this particular value has already been given.

On finding values of the ratio

$$\frac{\text{Molecular viscosity work at slope } \cdot 0_4 987}{\text{Molecular viscosity work at slope } \cdot 0_4 323},$$

for as many substances as could be compared at the two slopes, numbers which were practically the same were obtained; the mean value of the ratio being 1·880, with an average divergence of ·034, or 1·8 per cent.

As the number of liquids was insufficient to admit of an independent determination of the fundamental constants, from the constancy of the above ratio it was assumed that the fundamental constants obtained at slope $\cdot 0_4 323$, if multiplied by 1·88, would apply at slope $\cdot 0_4 987$; the values thus obtained are given below.

Fundamental Viscosity Constants (Molecular Viscosity work at Slope $\cdot 0_4 987$).

Hydrogen	H	− 64
Carbon	C	278
Hydroxyl-oxygen . . . . . C—O—H	$\overset{\diagdown\ \diagup}{\mathrm{O}}$	188
Ether-oxygen . . . . C—O—C	O<	73
Carbonyl-oxygen . . . . . C=O	$\overset{\Vert}{\mathrm{O}}$	− 36
Sulphur	$\overset{\diagdown\ \diagup}{\mathrm{S}}$	271
Chlorine (in monochlorides)	Cl	167
Chlorine (in dichlorides)	Cl′	154
Bromine (in monobromides)	Br	284
Bromine (in dibromides)	Br′	278
Iodine	I	410
Iso grouping	<	− 15
Double-linkage	(=)	− 179
Ring-grouping	ⓞ	− 694

The comparison of the observed numbers with those calculated by means of the above constants is given in the following table :—

MOLECULAR Viscosity-work at Slope $\cdot 0_4 987$.

	Observed.	Calculated.	Difference per cent.
Octane	1113	1072	3·7
Ethyl iodide	637	646	− 1·4
Propyl iodide	794	796	− 0·2
Isopropyl iodide	790	781	1·1
Isobutyl iodide	924	931	− 0·8
Allyl iodide	737	745	− 1·1
Isobutyl bromide	841	805	4·3
Ethylene bromide	821	856	− 4·3
Propylene bromide	977	1006	− 2·9
Isobutylene bromide	1157	1141	1·4
Acetylene bromide	747	705	5·6
Ethylene chloride	603	608	− 0·8
Methyl propyl ketone	721	714	1·0
Diethyl ketone	718	714	0·5
Formic acid	301	298	1·0
Acetic acid	462	448	3·0
Propionic acid	610	598	2·0
Butyric acid	766	748	2·3
Isobutyric acid	764	733	4·1
Acetic anhydride	731	729	0·2
Propionic anhydride	1006	1029	− 2·3
Benzene	579	587	− 1·4
Toluene	740	737	0·4
Ethyl benzene	900	887	1·4
Ortho-xylene	895	887	0·9
Meta-xylene	886	887	− 0·1
Para-xylene	890	887	0·3

In the above tables the agreement between observed and calculated values is practically the same as at the smaller slope; the mean percentage difference is about 1·8 per cent. It is noticeable that in the case of the dibromides the differences are uniformly larger than in the case of the other liquids.

It is also evident that although the relations between the isomeric chlorethanes are the same as at the smaller slope, the values of the isomeric aromatic hydrocarbons do not arrange themselves in the same order. Of the isomeric xylenes the ortho-isomer has still the largest molecular viscosity work, but para-xylene has now a value which is slightly larger than that of meta-xylene. The value for ethyl benzene is no longer intermediate to that of ortho- and meta-xylenes, but is the greatest of all the values given by the four isomers. The numbers are now in the same order as the magnetic rotations of the substances. Whether these small variations in the relative magnitudes of the values of the molecular viscosity work are real, or merely the result of imperfections in SLOTTE'S formula, cannot at present be definitely decided.

The halogen compounds, and water, which are not included in the preceding table, give values which are related to those of the other compounds in the same way as at slope $\cdot 0_4 323$. This is seen in the following table, where the observed values of the halogen compounds at the two different slopes are compared with the values calculated by using the value of chlorine in monochlorides. The calculated value for water is obtained from the value of hydroxyl oxygen deduced from the acids.

	Slope $\cdot 0_4 323$.			Slope $\cdot 0_4 987$.		
	Obs.	Cal.	Diff. per cent.	Obs.	Cal.	Diff. per cent.
Ethylidene chloride . .	312	338	8·3	578	634	9·7
Chloroform	328	381	16·1	615	715	16·2
Carbon tetrachloride .	406	504	24·1	751	946	26·0
Tetrachlorethylene . .	497	557	12·1	903	1045	15·7
Water	55	30	— 45.5	105	56	— 46·6

From the agreement between the magnitudes of the percentage differences given at the two slopes, it is evident that the peculiarities exhibited by these substances at the smaller slope still persist at the large slope, and are thus independent of the value of the slope at which the comparisons are made. The discussion of the values of these substances already given at slope $\cdot 0_4 323$ is thus applicable to the values at slope $\cdot 0_4 987$.

As already pointed out, the agreement of the differences in the case of water and the behaviour of the fatty acids at the widely separated temperatures of the two slopes indicate that even in the case of liquids such as these which contain molecular aggregates, the relationships obtained are also independent of the particular value of the slope at which the comparisons are made.

Bromine and the Alcohols.

In the following table the observed values of bromine and the alcohols are compared with the values calculated from the fundamental constants, which it must be remembered have been exclusively deduced from observations on the other liquids.

	Observed.	Calculated.	Difference per cent.
Bromine	490	556	− 13·5
Methyl alcohol	260	206	20·8
Ethyl alcohol	367	356	3·0
Propyl alcohol	449	506	− 12·7
Butyl alcohol	570	656	− 15·1
Allyl alcohol	434	455	− 4·8
Isopropyl alcohol	405	491	− 21·2
Isobutyl alcohol	529	641	− 21·2
Inactive amyl alcohol	681	791	− 16·1
Active amyl alcohol	654	791	− 20·9
Trimethyl carbinol	480	611	− 27·3
Dimethyl ethyl carbinol	527	761	− 44·4

Bromine.—The calculated number for bromine is deduced from the dibromides.

It is evident that the value calculated in this way differs considerably from that of free bromine. The divergence is much greater than in the case of molecular viscosity.

The Alcohols.

The results given by the alcohols show that the behaviour of this series of substances is peculiar at this as at other conditions of comparison. The large differences between the calculated and observed values prove that the fundamental constants which served for calculating the values of the other substances do not apply in the case of the alcohols. The divergences are no doubt to be attributed to the presence in the liquid alcohols of molecular aggregates which have a complexity different from those of the acids, and in what follows the attempt is first made to ascertain if the magnitudes of the numbers given by the alcohols, affected as they are by complexity, are related to one another or to the chemical nature of the alcohols.

Normal Alcohols.—On comparing the values given by the normal primary alcohols, the effect of CH_2 still appears to be constant, but instead of being 150, as in the case of other homologous series, is now reduced to 104. The comparison of the observed and calculated values using $CH_2 = 104$ is given in the following table, the value of methyl alcohol being taken as the starting point of the calculated numbers :—

	ηd^3. Observed.	ηd^3. Calculated.	Difference.
Methyl alcohol	260	260	
Ethyl alcohol	367	364	3
Propyl alcohol	449	468	− 19
Butyl alcohol	570	572	− 2

In deducing the value of CH_2 the molecular viscosity work of propyl alcohol was ignored, as there is little doubt, from the low boiling-point of the sample, that its viscosity is affected by impurity. It is conceivable, of course, that the discrepancy in the case of this alcohol may be due to mathematical treatment of the results, for in the case of the alcohols SLOTTE's formula is least satisfactory, as $d\eta/dt$ is so large that a small error in determining the slope corresponds to a large error in the ascertained viscosity. In this particular case, however, a graphical method of obtaining the slope led to practically the same result as the analytical method. The difference in the case of propyl alcohol is about 4 per cent., and in the case of ethyl and butyl alcohols the differences are only about ·6 per cent. It is therefore probable, that in normal primary fatty alcohols, CH_2, as in other homologous series, corresponds to a constant change in molecular viscosity work, and that the magnitude of this change differs from that in other series, and is about 104 units.

A primary straight chain alcohol may be represented as

$$H(CH_2)_nOH,$$

on deducting values of nCH_2, that is, $n(104)$, from the observed values of the alcohols, the differences obtained correspond with the value of H . . . OH.

The data are given in the table :—

n.	$H(CH_2)_nOH$. ηd^3 (observed).	nCH_2 (calculated).	H . . . OH.
1	260	104	156
2	367	208	159
3	449	312	137
4	570	416	154

Propyl alcohol, as before, gives a number differing considerably from the others; excluding this, we conclude that the probable value of H . . . OH is 156.

Isomeric Alcohols.—The following table contains the observed values for the different groups of isomeric alcohols :—

Propyl alcohol	449	44
Isopropyl alcohol	405	
Butyl alcohol	570	41
Isobutyl alcohol	529	49
Trimethyl carbinol	480	
Inactive amyl alcohol	681	27
Active amyl alcohol	654	127
Dimethyl ethyl carbinol	527	

It is evident that although simple quantitative relations do not exist between corresponding members of the different classes of isomeric alcohols, yet the magnitudes of the molecular viscosity work vary in a regular way with the chemical nature of the substances.

A normal alcohol has a larger value of the molecular viscosity-work than an isomeric iso-primary, or iso-secondary alcohol, and an iso alcohol has in turn a larger value than an isomeric tertiary alcohol. Of the two primary amyl alcohols, isobutyl carbinol has a larger value than secondary butyl carbinol. All the values conform to the rule that the higher the boiling-point, the higher is the molecular viscosity work. It is also seen from the table that the difference between a normal and an iso alcohol is now about 40 units as compared with 15 in the case of other compounds.

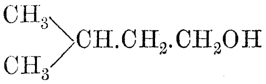
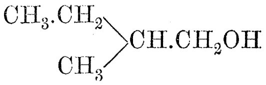
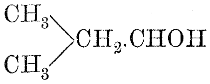
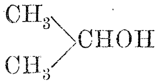
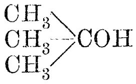
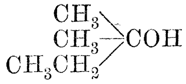
On comparing the values of allyl alcohol and normal propyl alcohol with those of the corresponding iodides, the behaviour of the alcohols is again seen to be peculiar.

	Alcohol.	Iodide.
Propyl	449	794
Allyl	434	737
	15	57

From the whole of these comparisons it is clear that in the case of the alcohols the values of the molecular viscosity work vary largely with the chemical nature of the substance. In order to obtain some estimate of these variations and to see if they are subject to any general rule, the observed values for the branched-chain alcohols are, in the following table, compared with those calculated by means of the numbers obtained from the normal primary alcohols for CH_2 and H . . . OH, no allowance being made for the branching of the atomic chain, &c.

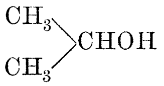
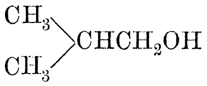
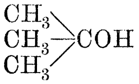
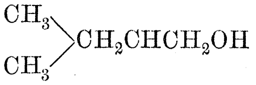
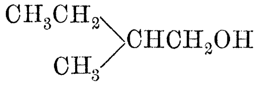
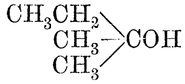
	ηd^3 (observed).	ηd^3 (calculated).	Difference.
Isopropyl alcohol	405	468	− 63
Isobutyl alcohol	529	572	− 43
Tertiary butyl alcohol . . .	480	572	− 92
Inactive amyl alcohol . . .	681	676	5
Active amyl alcohol	654	676	− 22
Dimethyl ethyl carbinol . . .	527	676	−149

If the alcohols be now arranged in the order of the divergences from the calculated values, on writing out their formulæ at length and so arranging that the HO group is placed at the end of each formula, there is at once an obvious relation between the constitution and the magnitude of the divergences.

	Divergence.	Formula.
Inactive amyl alcohol . .	+ 5	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH.CH_2.CH_2OH$
Active amyl alcohol . . .	− 22	 $\left.\begin{matrix}CH_3.CH_2\\CH_3\end{matrix}\right\rangle CH.CH_2OH$
Isobutyl alcohol	− 43	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH_2.CHOH$
Isopropyl alcohol . . .	− 63	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH$
Trimethyl carbinol . . .	− 92	 $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\rangle COH$
Dimethyl ethyl carbinol .	−149	 $\left.\begin{matrix}CH_3\\CH_3\\CH_3CH_2\end{matrix}\right\rangle COH$

In alcohols with two branches in the chain the more nearly the branching takes place to the HO group, or the nearer the rest of the molecule is to the HO group the larger is the divergence. If there are three branches in the chain the divergence is greater than if only two branchings occur, and is also greater the higher the molecular weight of the alcohol. The divergence of the value for an alcohol with a branched chain from that of the corresponding straight chain compound is thus a function of the proximity of the rest of the molecule to the HO group. In the case of inactive amyl alcohol, the branching takes place so far from the HO group that it gives practically the value of a straight chain alcohol.

The same result is apparent on comparing the deviations from the calculated values of the isomeric alcohols.

	Divergence.	Formula.
Propyl alcohol.	− 19	$CH_3CH_2CH_2OH$
Isopropyl alcohol. . . .	− 63	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHOH$
Butyl alcohol	− 2	$CH_3CH_2CH_2CH_2OH$
Isobutyl alcohol	− 43	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CHCH_2OH$
Trimethyl carbinol . . .	− 92	 $\left.\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right\rangle COH$
Inactive amyl alcohol . .	5	 $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH_2CHCH_2OH$
Active amyl alcohol . . .	− 22	 $\left.\begin{matrix}CH_3CH_2\\CH_3\end{matrix}\right\rangle CHCH_2OH$
Dimethyl ethyl carbinol .	−149	 $\left.\begin{matrix}CH_3CH_2\\CH_3\\CH_3\end{matrix}\right\rangle COH$

The divergence is least in the case of the primary alcohols and is less for a secondary than for a tertiary alcohol. Of isomeric primary alcohols the one in which the branching of the chain occurs nearest to the hydroxyl group exhibits the largest deviation. Only one secondary alcohol occurs in the table, but of the two tertiary alcohols the one of higher molecular weight has the larger deviation.

The values given by the alcohols although at first sight apparently anomalous are thus seen to be subject to regularity; moreover they indicate most clearly that to the presence and relationships of the (HO) group in the fundamental molecule are to be ascribed the apparent discrepancies.

Now it has already been indicated that the slope of the alcohol curves and indeed the whole general behaviour of the alcohols point to the presence of molecular aggregates in these liquids. It has also been stated that those liquids, which from various independent considerations give the most marked indication of containing such aggregates, are hydroxyl compounds. Hence it is most probable that the anomalous values for the viscosity magnitudes exhibited by the alcohols, more especially since they can be connected with the presence of HO, are the result of the presence of molecular aggregates in the alcohols at the temperature of comparison. The values used for the molecular viscosity work in the case of the alcohols are therefore not the actual values of this quantity, since they involve the theoretical molecular weights instead of the actual liquid molecular weights of the substances. They can, therefore, not be taken to represent the same magnitude as is dealt with in the case of simply constituted liquids, but serve only to indicate how the simple relationships which hold for such substances are complicated by the presence of molecular complexes.

It would be interesting, no doubt, to ascertain with such data as are to hand, the actual value of the viscosity magnitudes, calculated from liquid molecular weights. But until the theoretical basis of EÖTVÖS's method of estimating molecular complexity has been definitely established we do not see that much will be gained by instituting such a comparison.

We are indeed inclined to believe that the question of the actual extent of the complexity will not be settled by the study of one single property but by a comparison of as many properties as are more or less immediately related to the acting molecule of a liquid substance.

Results Obtained from Associated Liquids.

The most satisfactory method of showing the presence of complexes in the hydroxy liquids which we have examined would be to compare the observed values with those calculated by means of the effect produced by hydroxyl oxygen in simply constituted liquids. The general conclusion which seems to flow from the physico-chemical evidence at present accumulated is, however, that a simply constituted hydroxy compound does not exist; all hydroxy compounds seem to contain molecular aggregates. Hence, the most that can be done is to show that the value of hydroxyl oxygen which applies to one series of substances, does not apply to another, and that, in the case of the same series, owing to variations in the complexity of individual members, the differences between the observed and calculated values are larger than in similar comparisons involving simply constituted liquids. Evidence may also be obtained on comparing the effects produced by a definite change in chemical composition on the viscosity magnitudes of the hydroxy liquids with those produced by the same change in the case of simply constituted liquids.

The varying values which, by the preceding mode of treatment, may be ascribed to hydroxyl oxygen in the acids, water, and the alcohols, and which may be affected to some extent by chemical constitution as well as molecular complexity are as follows. The value of hydroxyl oxygen originally used was derived from the numbers given by the acids wherein the "rest" contained the unsaturated carboxyl group, so that the value of $\overset{\diagdown\diagup}{\mathrm{O}} = 184$ refers only to the acids. In the case of water, it has been shown that here the value of $\overset{\diagdown\diagup}{\mathrm{O}}$ derived from the acids no longer applies. If the value of hydrogen be taken to be normal, and to be $H = -64$, the value of oxygen in water is $105 + 128 = 233$.

In the normal alcohols, since $H \ldots OH = 156$, using the normal value for hydrogen,

$$\overset{\diagdown\diagup}{\mathrm{O}} = 156 + 128 = 284.$$

The values which may thus be ascribed to oxygen, when linking hydrogen to the various groups in these compounds, are given below.

(CO)—O—(H). Linking hydrogen to carboxyl in an acid = 180.
(H)—O—(H) „ „ hydrogen in water = 233.
(R)—O—(H) „ „ a saturated rest in a normal alcohol = 284.

The value which, by the above method of calculation, may be ascribed to $\overset{\diagdown\diagup}{\mathrm{O}}$, is seen from the table to be larger for water than for an acid, and largest of all for an alcohol. The preceding discussion has also shown how the behaviour of the alcohols is probably related to the effect which the (HO) group exerts upon the rest of the molecule, and it is now indicated that this effect is greater in the case of an alcohol than in that of any other of the liquids examined.

The values for CH_2 given by the viscosity coefficients of the acids, it will be remembered, varied irregularly as the series was ascended. The same is true for the values given by molecular viscosity and molecular viscosity work.

Although in these latter cases the mean effect of CH_2 is not far removed from that of simply-constituted liquids, coupled with the peculiar behaviour of isobutyric acid as compared with other iso compounds, the irregularities observed point to the peculiar behaviour of the acids which is so obvious in glancing at their viscosity-curves and which is no doubt to be ascribed to molecular complexity.

The normal alcohols appear to give a constant value for CH_2, which is decidedly different from that given by simply-constituted liquids. Moreover, the variation in the numbers for isomeric alcohols is enormous when compared with that given by the other liquids, the acids included.

All the above facts point to the molecular complexity of the hydroxy liquids which we have examined, and also to the conclusion that if complexity, as distinguished from the purely chemical constitution of simple molecules, is the sole cause of the irregularities, it exerts a much more profound effect in the case of the alcohols than in any of the other liquids. This last conclusion is further supported by the comparisons made at different slopes.

It will be remembered that, on passing from one slope to another, the viscosity magnitudes of water and the acids alter to the same extent as those of the other liquids. The alcohols, however, do not follow the same rule, for, as will be seen later (p. 692), on passing to a new slope, the extent to which the viscosity alters is different for each alcohol and is related to its chemical nature. These results are but additional expressions of the marked differences which obviously exist between the viscosity-curves of the alcohols and those of all the other liquids.

Conclusions relating to Molecular Viscosity Work at Equal Slope.

The results here obtained are of precisely the same nature as those discussed under molecular viscosity. More detail has been given to show that the substances which give deviations from the calculated values fall into two classes. In the first the deviations are to be attributed to chemical constitution, as similar disturbing effects may be detected in the magnitudes of other physical properties which do not seem to be affected by molecular complexity. In the second are those substances like the acids, water, and the alcohols, for which the disturbing factor is, no doubt, molecular complexity, the effect produced in this way, in the case of the alcohols, being dependent upon their chemical nature.

GENERALITY OF THE RESULTS OBTAINED AT EQUAL SLOPE.

One of the most important points which has to be discussed in connection with any physico-chemical investigation is the question of the generality of the results. Will the relationships obtained at one series of comparable temperatures be the same at any other series chosen according to the same system, but having different magnitudes from those first employed? For example, will relations between specific molecular-volume measured at the ordinary boiling-point be the same at other temperatures of equal vapour pressure?

In the case of viscosity the question is: Are the results obtained independent of the magnitude of the slope? It has already been shown that on comparing as many liquids as could be compared at slopes $\cdot 0_4 323$ and $\cdot 0_4 987$, practically the same results are obtained in each case. Instead, however, of testing the question by means of a method like the above, which relates to particular cases, it is possible to treat the question in a general way by employing SLOTTE's formula.

From $\eta = c/(a + t)^n$, it follows that $- d\eta/dt$, or the slope S, is given by

$$S = \frac{nc}{(a + t)^{n+1}}, \quad \text{and}$$

$$S^{n/(n+1)} = \left(\frac{n^n}{c}\right)^{1/(n+1)} \times \frac{c}{(a + t)^n} = \frac{1}{\rho} \frac{c}{(a + t)^n}, \quad \text{where}$$

$$\rho = \left(\frac{c}{n^n}\right)^{1/(n+1)}.$$

Consequently,

$$\eta = \rho\, S^{n/(n+1)}$$

where η is expressed in terms of the slope.

Let η_{A_1}, η_{B_1}, η_{C_1}, &c., be the viscosity coefficients of the liquids A, B, C, &c., measured at the slope S_1, and let η_{A_2}, η_{B_2}, η_{C_2}, &c., be the corresponding coefficients at the slope S_2.

Then, if the relations between η_{A_1}, η_{B_1}, η_{C_1}, &c., are the same as those between η_{A_2}, η_{B_2}, η_{C_2}, &c., that is, if the relations are to be independent of the value of the slope, it is evident that the ratios

$$\eta_{A_1}/\eta_{A_2},\ \eta_{B_1}/\eta_{B_2},\ \eta_{C_1}/\eta_{C_2}, \text{ \&c., must be equal.}$$

But η_{A_1}, η_{B_1}, &c., can be expressed in terms of the slope S_1, and may be written

$$\rho_A S_1{}^{n_A/(n_A+1)},\ \rho_B S_1{}^{n_B/(n_B+1)}, \text{ \&c.,}$$

and η_{A_2}, η_{B_2}, &c., can be in the same way expressed in terms of the slope S_2 and written

$$\rho_A S_2{}^{n_A/(n_A+1)},\ \rho_B S_2{}^{n_B/(n_B+1)}, \text{ \&c.,}$$

and hence, if the relationships between η_{A_1}, η_{B_1}, η_{C_1}, &c., are to be the same as those between η_{A_2}, η_{B_2}, η_{C_2}, &c., it follows that the values of ratios

$$(S_1/S_2)^{n_A/(n_A+1)},\ (S_1/S_2)^{n_B/(n_B+1)}, \text{ \&c., must be equal,}$$

and since in comparisons at equal slopes S_1 and S_2 have the same value for all the liquids, it follows that the comparisons will be independent of the slope if

$$n_A/(n_A + 1) = n_B/(n_B + 1) = \text{\&c.}$$

That is, if $n_A = n_B = n_C$, &c.

So far as SLOTTE's formula goes, it is thus indicated that for the comparisons to be general the value of n should be the same for all the liquids.

It has already been stated that, from the mode in which n is deduced, its value is affected by circumstances more or less accidental. It is satisfactory, however, to find, on comparing the values of n for all the liquids, with the exception of aldehyde and the alcohols, that the variation is comparatively small.

The following table contains the mean value of n as given by the different series of liquids, the alcohols and aldehyde excluded :—

	Values of n.
10 Fatty hydrocarbons	1·9
6 Iodides	1·7
9 Bromides	1·8
10 Chlorides	1·7
5 Acids	1 9
4 Ketones	1·9
2 Anhydrides	1·7
4 Sulphur compounds	1·7
6 Aromatic hydrocarbons	1·7
Nitrogen peroxide	1·7
Water	1·5
Ethyl ether	1·5
Bromine	1·4
Mean of means	1·76

From the 60 liquids above given, it is evident that the value of n is, in general, between 1·6 and 1·9, and does not differ much from 1·76.

From this mean value it is possible to calculate the value of the ratio of the viscosities at the slopes employed, that is, the value of

$$\frac{\text{Viscosity coefficient at slope } {\cdot}0_4987}{\text{Viscosity coefficient at slope } {\cdot}0_4323},$$

for, by the previous discussion, the ratio is equal to

$$(S_1/S_2)^{n/(n+1)} \quad \text{or} \quad ({\cdot}0_4987/{\cdot}0_4323)^{1{\cdot}76/2{\cdot}76},$$

which is equal to 2·04.

The mean value of this ratio obtained directly for the 33 liquids which could be compared at the two slopes, was, as already stated, 2·03, which closely agrees with the value obtained above by using the value of n deduced from the whole of the 60 liquids included in the table.

From the reasons already given regarding the unsatisfactory character of the method of obtaining the constants in SLOTTE's formula, this agreement is of considerable importance, and seems to indicate that formulæ may yet be obtained of the type used by SLOTTE in which n is the same for all substances such as those under consideration.

If this should be possible, since

$$\eta = \rho\, S^{n/(n+1)},$$

it is evident that ρ is the quantity peculiar to each liquid which should be used in chemico-physical comparisons. If, at present, values of ρ be found for each liquid by means of the varying numbers obtained for n, these values can in general not be directly connected with the chemical nature of the substances, for such fortuitous variations in the value of n as those given by pentane and isopentane mask general relationships.

It is also indicated that the general relation which connects the viscosities of all the foregoing liquids with the slope is

$$(\eta_1/\eta_2) = (S_1/S_2)^{\cdot 6377},$$

so that knowing η_1 at the slope S_1, it is possible to calculate η_2 its value at the new slope S_2.

The Alcohols.—As already stated, one formula of the type used by SLOTTE was not capable of representing with sufficient accuracy the observed values for the higher alcohols over the entire range between 0° and the boiling-point. It has already been stated, and it is evident from the table on p. 578, that even when several short range formulæ are employed the values obtained for n are markedly in excess of the average value 1·76 obtained from the other substances. It is also evident from the different formulæ obtained from the same alcohol that the value of n is not constant but falls as the temperature rises. This variation would probably take place in the case of any experimental curve if several formulæ were deduced according to the method employed, inasmuch as a similar change is noticeable in the values of n as given by the formulæ for water.

This variation indicates that the magnitude of n is dependent upon the particular region of the curve to which the formula refers, and when it is remembered that for no two liquids is the portion of the curve compared between 0° and the boiling-point of the same extent, the variation lends further support to the idea that with such a method as that employed in deducing SLOTTE'S formula, little stress need be put upon such slight changes in the value of n as have been found for the majority of the liquids.

The general mean of the 22 values obtained for n in all the formulæ relating to the alcohols is 3·53, and this value differs so much from the mean value 1·76 obtained for the other liquids, that it is without doubt connected with the generic difference in the behaviour of the alcohols which is expressed in the peculiar shape of their viscosity curves.

This large value for n, especially when it is borne in mind that for the alcohols b has also large values, also indicates that at a larger value of the slope their viscosity coefficients will not be related to those of the other liquids in the same way as at slope $\cdot 0_4 987$, but will be relatively larger.

From the unsatisfactory nature of the formula for the alcohols, it was not possible to estimate this difference by a general method. A new value of the slope was therefore chosen, and the corresponding values of η determined for the alcohols, and as many as possible of the other liquids.

The value of the slope which appeared to be the most suitable was $\cdot 0_3 7498$, viz., that possessed by butyric acid at 0°. At this value of the slope, only 5 liquids other than the alcohols could be compared, and in the following tables are given the values of η and t the temperature, for these liquids at the previous slope $\cdot 0_4 987$, and the new slope $\cdot 0_3 4798$. As before, η is expressed in dynes per sq. centim. $\times 10^5$.

	Slope $\cdot 0_4 987$.		Slope $\cdot 0_3 4798$.		η''/η'.
	t'.	η'.	t''.	η''.	
	°		°		
Formic acid	71·7	758	13·7	2057	2·77
Butyric acid	65·7	796	0·	2283	2·87
Ethylene bromide	68·8	906	0·9	2397	2·65
Propylene bromide	65·7	893	− 2·7	2425	2·71
Isobutylene bromide . . .	83·3	875	14·7	2400	2·74
				Mean	2·74

Here it is again evident that the coefficients are related at slope $\cdot 0_3 4798$, in practically the same way as at slope $\cdot 0_4 987$, as the value of the ratio of the viscosities at the two slopes is practically constant and equal to 2·74. It is also significant that the value of the ratio calculated on the assumption that n has the mean value 1·76, by means of the formula

$$(\cdot 0_3 4798/\cdot 0_4 987)^{1\cdot 76/2\cdot 76}$$

is exactly the value found above, viz., 2·74.

This goes to show that at temperatures which differ so widely as those of the original slope $\cdot 0_4 323$ and of the final slope $\cdot 0_3 4798$, the difference being about 140°, the viscosity coefficients are related in practically the same way, even in the case of liquids like the acids and the dibromides.

With the alcohols, however, this is not the case. The following table contains the values of the alcohols at slopes $\cdot 0_4 987$ and $\cdot 0_3 4798$. Methyl alcohol is not included in the tables, as the temperature corresponding with the larger slope appears to be as low as − 48°.

	Slope $\cdot 0_4 987$.		Slope $\cdot 0_3 4798$.		η'/η''.
	t'.	η'.	t''.	η''.	
	°		°		
Ethyl alcohol	58·5	606	− 9·85	2191	3·61
Propyl alcohol	86·5	560	25·4	1976	3·53
Butyl alcohol	95·6	575	35·6	1980	3·44
Isopropyl alcohol	82·9	490	31·7	1673	3·41
Isobutyl alcohol	99·6	525	46·9	1747	3·33
Inactive amyl alcohol . . .	105·2	574	49·7	1865	3·25
Active amyl alcohol . . .	104·7	555	53·7	1745	3·14
Trimethyl carbinol	90·9	461	49·0	1495	3·24
Dimethyl ethyl carbinol . .	93·9	490	49·1	1500	3·06
Allyl alcohol	63·1	610	4·3	1946	3·19

The value of the ratio η''/η', instead of being 2·74, is now considerably greater, being on the average 3·33. It is thus evident that the mode in which the magnitude of the viscosity coefficients of the alcohols varies with the value of the slope is different from that of the whole of the other liquids. It is further indicated that, although the value of the ratio is somewhat the same for all the alcohols, yet it depends to some extent on their chemical nature, as it is smaller the higher the molecular weight for alcohols of like constitution, and, in the case of alcohols of the same molecular weight, it is smaller the more branched the atomic chain, or the lower the boiling-point, as is seen from the following table :—

Propyl	3·53	Butyl.	3·44	Inactive amyl	3·25
Isopropyl	3·41	Isobutyl	3·33	Active amyl	3·14
		Trimethyl carbinol .	3·24	Dimethyl ethyl carbinol .	3·06

It is thus apparent that not only are the magnitudes of the viscosity coefficients of all the alcohols determined at any one slope, peculiar, but also the manner in which the values of the coefficients change with the slope. With such data as are to hand, it would seem that relations between the viscosity coefficients of the other liquids are of the same kind, no matter what slope be used. The mode in which the values for the alcohols are related to those for the other liquids depends, however, on the slope, and, further, the relations between the values for the alcohols themselves seem to depend on the value of the slope, and to suffer slight variations which are related to their chemical nature.

There is little doubt that methyl alcohol behaves in the same way as the higher alcohols, for the value given by it for the quotient

$$\frac{\eta \text{ at slope } \cdot 0_4 987}{\eta \text{ at slope } \cdot 0_4 323}$$

was 2·24, which is higher than the mean value given by the other liquids, viz., 2·03.

Here we again have definite evidence that the alcohols exhibit peculiarities which have no existence in the case of the other liquids. Even the acids which, like the alcohols, contain molecular aggregates, give no marked indication of exceptional behaviour at different slopes. Between the groups of acids and alcohols there must, therefore, be a generic difference which may ultimately be related to the fact that for an alcohol the HO group, which is the most active part of the molecule so far as viscosity is concerned, is in connection with a saturated "rest," whereas, for an acid the "rest" is unsaturated.

In the preceding discussion regarding the generality of the results, viscosity coefficients only have been dealt with; similar conclusions hold, however, for molecular viscosity and molecular viscosity work, as the molecular area and molecular volume vary so slowly with temperature as compared with viscosity, and the relations between them at the temperatures of equal slope are so nearly independent of the magnitude of the slope, that the change in the viscosity coefficient itself need alone be considered.

COMPARISONS IN WHICH A DIFFERENT SLOPE IS EMPLOYED FOR EACH LIQUID.

If it is eventually established that a formula of the type used by SLOTTE represents the true temperature-function of viscosity, and also that in such a formula n varies from liquid to liquid, from what has been said it is evident that comparisons at the same slope will not be general, but will vary with the magnitude of the slope. Under such conditions it is obvious, therefore, that to obtain general results the slope must vary from liquid to liquid, and the following method indicates how the question may be approached, the conditions to be fulfilled being :—

(1.) That the comparisons shall be general.

(2.) That the results obtained shall be related to the chemical nature of the substances.

(1.) For generality, it has already been shown that the following relation must hold

$$(S_{A_1}/S_{A_2})^{n/n+1} = (S_{B_1}/S_{B_2})^{p/p+1} =, \&c.$$

Now if S_{A_1}, &c., differ from S_{B_1}, &c., that is, if the slope varies from liquid to liquid, slopes can be chosen so as to satisfy the above relation in an indefinite number of ways.

(2.) It appears, however, from all the preceding comparisons that chemical relations will only be made evident when the slopes are nearly the same; hence for chemical relations S_{A_1}, S_{B_1}, &c., must be approximately equal, and, of course, S_{A_2}, S_{B_2}, &c., must be approximately equal.

If slopes be chosen, therefore, according to some definite system, and fulfilling the above conditions, the results will be general, and related to the chemical nature of the substance.

By trial we have found that if slopes be chosen which satisfy the relationship

$$\left(S_{A_1} \, . \, n_A \, . \, c_A{}^{1/(n_A+1)}\right)^{n_A/(n_A+1)} = \left(S_{B_1} \, . \, n_B \, . \, c_B{}^{1/(n_B+1)}\right)^{n_B/(n_B+1)} = \&c.,$$

or,

$$\left(S_{A_2} \, . \, n_A \, . \, c_A{}^{1/(n_A+1)}\right)^{n_A/(n_A+1)} = \left(S_{B_2} \, . \, n_B \, . \, c_B{}^{1/(n_B+1)}\right)^{n_B/(n_B+1)} = \&c.,$$

the condition for generality is fulfilled, the slopes obtained are almost the same, and they are chosen according to a system, as the constants employed are c and n, which occur in the formulæ of the particular liquids.

The same conditions are also satisfied if instead of $nc^{1/(n+1)}$ either $(n+1)\,c^{1/(n+1)}$ or $(c/n)^{1/(n+1)}$ be substituted in the above equations.

At all these conditions of comparisons, however, the stoichiometric relationships are no more definite than at temperatures of equal slope. We do not propose, therefore, in the present state of the question, to give details of the results obtained. The above discussion, however, may serve to show how it is possible by means of slope comparisons, and with a simple formula like that of SLOTTE'S, to insure that the results obtained shall be general, even when n varies.

The fact that the above somewhat complex methods lead to no better physico-chemical relations than the simple method of equal slopes, may also be taken as a further indication that, at least for liquids in which the molecular complexity does not change with the temperature, in a formula of the type employed, if it could be made to agree more closely with actual observations, the constant n would be the same. This again indicates that at temperatures of equal slope the results may be taken to be general as well as comparable.

Conclusions relating to the Generality of the Results Obtained at the Temperatures of Equal Slope, and to the Comparisons in which a Different Slope is Employed for each Liquid.

1. From the preceding discussion it is evident that over such temperature-ranges as our observations extend the results obtained at a particular value of the slope may be regarded as general for all liquids, with the exception of the alcohols where the relationships vary slightly as the slope alters.
2. It is further indicated that in the present state of the question equal slope is the most suitable condition at which to compare the viscosities of different liquids.

COMPARISONS OF THE MAGNITUDES OF THE TEMPERATURES OF EQUAL SLOPE.

In the preceding comparisons we have been concerned with the values of the various viscosity magnitudes corresponding with points on the viscosity curves at which $d\eta/dt$ is the same for the different substances. Instead of comparing the values of the viscosity at these points we may equally well deal with the magnitudes of the temperatures at which the slope is the same for the various substances. In what follows an attempt is made to show how the magnitudes of the temperatures of equal slope are related to the chemical nature of the substances, and, also, how the relationships obtained at any one slope are affected on passing to a new value of the slope.

TEMPERATURES = t' IN DEGREES CENTIGRADE AT WHICH THE SLOPE IS ·0000323.

HOMOLOGUES.

	t'.	Difference.
	°	°
Pentane	− 5·4	
		25·9
Hexane	20·5	
		20·6
Heptane	41·1	
		23·0
Octane	64·1	
Isopentane	− 4·4	
		20·4
Isohexane	16·0	
		19·7
Isoheptane	35·7	
Isoprene	− 12·1	
		21·8
Diallyl	9·7	
Methyl iodide	42·9	
		18·6
Ethyl iodide	61·5	
		22·1
Propyl iodide	83·6	
Isopropyl iodide	79·9	
		17·7
Isobutyl iodide	97·6	
Ethyl bromide	26·9	
		27·8
Propyl bromide	54·7	
Isopropyl bromide	51·6	
		24·8
Isobutyl bromide	76·4	
Ethylene bromide	147·8	
		− 3·2
Propylene bromide	144·6	

Homologues (continued).

	t'.	Difference.
Isopropyl chloride	21·4°	28·8
Isobutyl chloride	50·2	
Methylene chloride	37·1	56·6
Ethylene chloride	93·7	
Methyl sulphide	5·7	(19·8)
Ethyl sulphide	45·2	
Dimethyl ketone	17·8	(16·3)
Diethyl ketone	50·5	
Methyl ethyl ketone	43·7	12·8
Methyl propyl ketone	56·5	
Formic acid	138·7	−15·8
Acetic acid	122·9	− 6·2
Propionic acid	116·7	21·6
Butyric acid	138·3	
Acetic anhydride	99·8	(7·1)
Propionic anhydride	114·0	
Benzene	75·9	− 8·1
Toluene	67·8	10·1
Ethyl benzene	77·9	

From the above table it is seen that for most series an increment of CH_2 brings about an increase in the temperature of slope, which varies within moderate limits on passing from one series to another. The dibromides, the acids, and benzene give, however, negative differences, and the dichlorides a large positive difference. These irregularities are but further indications of the peculiarities which have already been noted in connection with these substances.

CORRESPONDING Compounds.

	Iodide.	Bromide.		Chloride.		Acid.		Alcohol.	
	t'.	Diff.	t'.	Diff.	t'.	Diff.	t'.	Diff.	t'.
	°	°	°	°	°	°	°	°	°
Methyl . .	42·9	..	..	..	..	−95·8	138·7	−33·6	76·5
Ethyl . .	61·5	34·6	26·9	..	..	−61·4	122·9		
Propyl . .	83·6	28·9	54·7	28·3	26·4	−33·1	116·7		
Butyl . .	..	..	..	..	..	..	138·3		
Isopropyl .	79·9	28·3	51·6	30·2	21·4				
Isobutyl .	97·6	21·0	76·6	26·4	50·2	−31·5	129·1		
Allyl. . .	82·0	31·2	50·8	30·5	20·3				
Ethylene .	..	..	147·8	(27·0)	93.7				

In the case of simply constituted liquids, the same alteration in molecular weight brings about approximately the same alteration in temperature. The compound of highest molecular weight has also the highest temperature. The complex liquids—methyl alcohol and the acids—do not obey these rules, but give large negative differences which, in the case of the acids, diminish with rise in molecular weight.

NORMAL Propyl and Allyl Compounds.

	Normal propyl.	Difference.	Allyl.
	t'.		t'.
	°	°	°
Hydrocarbons	20·5	(5·4)	9·7
Iodides	83·6	1·6	82·0
Bromides.	54·7	3·9	50·8
Chlorides	26·4	6·1	20·3

ETHYLENE and Acetylene Bromides.

	Ethylene.	Difference.	Acetylene.
	t'.		t'.
Bromide	° 147·8	° 44·8	° 103·0

A normal propyl compound has invariably a slightly higher temperature than the corresponding allyl compound. The differences thus obtained, unlike what holds for the differences in the viscosity magnitudes at equal slope, show no agreement with that given by the dibromides.

ISOLOGOUS Hydrocarbons.

n.	C_nH_{2n+2}.	C_nH_{2n}.		C_nH_{2n-2}.		C_nH_{2n-6}.	
	t′.	Diff.	t′.	Diff.	t′.	Diff.	t′.
	°	°	°	°	°	°	°
5	− 5·4	14·8	−20·2	6·7	−12·1		
6	20·5	..	..	10·8	9·7	−55·4	75·9
7	41·1	..	..	..	..	−26·7	67·8
8	64·1	..	..	..	..	−13·8	77·9

On converting a saturated into a straight-chain unsaturated hydrocarbon the temperature of slope is lowered, amylene giving a larger difference than isoprene or diallyl. The large negative values of the differences given by the aromatic hydrocarbons point to the influence of the ring-grouping, and their variation to the anomalous behaviour of benzene already noted.

SUBSTITUTION of Halogen for Hydrogen.

n.	$C_nH_{2n}Br_2$.	Diff.	$C_nH_{2n+1}Br$.	Chlormethanes.		
	t′.		t′.		t′.	Diff.
	°	°	°		°	°
2	147·8	120·9	26·9	Methylene chloride .	37·1	29·5
3	144·6	89·9	54·7	Chloroform	66·6	38·3
4 Iso.	161·3	84·9	76·4	Carbon tetrachloride .	104·9	

On substituting bromine for hydrogen the temperature is largely increased, and the amount varies somewhat with the chemical nature of the substance. The successive replacement of hydrogen by chlorine increases the temperature by different amounts.

COMPOUNDS differing by a Carbon Atom.

	t′.	Difference.		t′.	Difference.
	°	°		°	°
Tetrachlormethane . .	104·9	−6·5	Methyl alcohol	76·5	−93·3
Tetrachlorethylene . .	98·4		Aldehyde	−16·8	

The entire want of agreement between the values of the differences given in the above comparisons is, no doubt, the result both of chemical constitution and of the molecular complexity of methyl alcohol.

ISOMERS.

NORMAL and Iso Compounds.

	Normal.		Iso.
	t'.	Difference.	t'.
	°	°	°
Pentanes	− 5·4	− 1·0	− 4·4
Hexanes	20·5	4·5	16·0
Heptanes	41·1	5·4	35·7
Propyl iodides	83·6	3·7	79·9
Propyl bromides	54·7	3·1	51·6
Propyl chlorides	26·4	5·0	21·4
Butyric acids	138·3	9·2	129·1

A normal compound has a temperature which is in general slightly larger than that of the corresponding iso compound. The large difference given by the acids is, in all probability, the result of complexity.

AROMATIC Hydrocarbons.

	t'.	Difference.
	°	°
Ortho-xylene	91·3	−13·4
Ethyl benzene	77·9	− 7·3
Meta-xylene	70·6	4·5
Para-xylene	75·1	

The large difference given by ortho-xylene is connected with the striking peculiarity in the course of the curve for this substance, as compared with those of the other isomers. The temperatures of the other isomers differ at most by some 8°.

DICHLORETHANES.

	t'.	Difference.
	°	°
Ethylene chloride	93·7	−41·5
Ethylidene chloride	52·2	

The symmetrical compound has here by far the higher temperature.

ISOMERIC Ketones.

	t'.	Difference.
	°	°
Diethyl ketone	50·5	6·0
Methyl propyl ketone	56·5	

Of the two ketones, the symmetrical compound has slightly the lower temperature. Here, as in the case of all other comparisons, the chlorethanes differ from the ketones.

TEMPERATURES $= t''$ IN DEGREES CENTIGRADE AT WHICH THE SLOPE IS ·0000987.

At slope $\cdot 0_4 987$ the temperature differences obtained on making comparisons of the kind given in the preceding tables are practically of the same order as are there represented. This result follows from the fact that the ratios of the absolute temperatures of the two slopes are practically constant.

The mean value of the ratio,

$$\frac{\text{Absolute temperature at slope } \cdot 0_4 323}{\text{Absolute temperature at slope } \cdot 0_4 987}$$

for the thirty-four possible comparisons is 1·23, the average divergence from the mean being ·017, or about 1·4 per cent. It is also worthy of note that the liquids giving the largest divergences were water, benzene, and formic acid; the differences were all negative, and about 5·7 per cent. in the case of water, and 3·3 per cent. in the case of the other two liquids.

That the temperature differences are of the same order at any slope was also verified by comparisons made at various slopes which are not discussed in this paper.

It now remains to examine how the temperatures given by the alcohols at slope $0_4 987$ are related to one another. The results are expressed in the following tables :—

HOMOLOGUES.

	t''.	Difference.
	°	°
Ethyl alcohol	58·5	28·0
Propyl alcohol	86·5	9·1
Butyl alcohol	95·6	
Isopropyl alcohol	82·9	16·7
Isobutyl alcohol	99·6	5·6
Inactive amyl alcohol	105·2	
Trimethyl carbinol	90·9	2·9
Dimethyl ethyl carbinol . . .	93·8	

It is seen from the above table that the differences, although always positive, vary to a most marked extent in the case of the alcohols as compared with simply constituted liquids.

NORMAL and Iso alcohols.

	Normal.	Difference.	Iso.
	t''.		t''.
	°	°	°
Propyl	86·5	3·6	82·9
Butyl	95·6	− 4·0	99·6

Here again the alcohols are peculiar, as the differences are positive and negative, whereas for the other liquids the corresponding differences are, in general, positive.

NORMAL Propyl and Allyl Alcohols.

	t''.	Difference.
	°	°
Propyl alcohol	86·5	23·4
Allyl alcohol	63·1	

The large value of the difference given by the comparison of normal propyl and allyl alcohols is a further instance of the peculiarities of the alcohols.

TEMPERATURES = t''' IN DEGREES CENTIGRADE AT WHICH THE SLOPE IS ·000479.

In order to ascertain if the values of the temperature differences given by the alcohols would be of the same nature at another slope, values were obtained for the ratio

$$\frac{\text{Absolute temperature at slope } \cdot 0_4 987}{\text{Absolute temperature at slope } \cdot 0_3 479}.$$

Five liquids other than the alcohols, namely, formic and butyric acids, and ethylene, propylene, and isobutylene bromides, were also available for this comparison. These five liquids gave practically the same values for the ratio, the mean value being 1·24, and the average divergence ·012, or about ·90 per cent. These liquids behave, therefore, at the large slope $\cdot 0_3 479$ just as they did at the smaller slopes. The alcohols, however, do not obey this rule, for they give ratios which are not the same, but vary from liquid to liquid, and are in general less than 1·24.

The values of t'' the ordinary temperatures at slope $\cdot 0_4 987$, and the values of t''' the ordinary temperatures at slope $\cdot 0_3 479$, together with the ratios of these temperatures on the absolute scale, are given in the following table:—

	t''	t'''.	Ratio.
	°	°	
Ethyl alcohol	58·5	− 9·8	1·26
Propyl alcohol	86·5	25·4	1·20
Butyl alcohol	95·6	35·6	1·19
Isopropyl alcohol	82·9	31·7	1·17
Isobutyl alcohol	99·6	46·9	1·17
Isoamyl (inactive) alcohol .	105·2	49·7	1·17
Active amyl alcohol . . .	104·7	53·7	1·16
Trimethyl carbinol . . .	90·9	49·0	1·13
Dimethyl ethyl carbinol .	93·8	49·1	1·14
Allyl alcohol	63·1	4·3	1·21

For a normal alcohol the ratio is about 1·21; for an isoalcohol, about 1·17; and for a tertiary alcohol, about 1·13. The alcohols again differ in their behaviour from the great majority of the other liquids, and their peculiarities, as is shown in the above table, are related to their chemical nature.

Conclusions relating to Temperatures of Equal Slope.

The preceding tables show that:

1. The magnitudes of the temperatures of equal slope vary in a regular way with the chemical nature of the substances, except in the case of liquids like formic acid,

benzene, and propylene dibromide, giving viscosity curves which are abnormal when compared with those of their homologues.

2. The temperature relationships may also be regarded as general, and thus independent of the value of the slope, except in the case of the alcohols, which, in this respect, as in that of viscosity at equal slope, are anomalous.

GENERAL CONCLUSIONS REGARDING PHYSICO-CHEMICAL COMPARISONS.

It is evident from the foregoing tables that the liquids showing irregularity in the magnitudes of their temperatures of equal slope are the dihalogen compounds, the acids, benzene, ortho-xylene, the alcohols, &c., and these are the liquids which were shown both by the graphical and algebraical treatment of our results to possess viscosity-curves having courses which were peculiar as compared with those of the majority of other related substances. Although at equal slope the viscosity-magnitudes of many of these compounds, the acids included, exhibit more or less different relationships, yet when we consider the magnitudes of the temperatures at equal slope, the peculiarities of the substances stand out as clearly as before. This points to the conclusion that, if the disposition of the curve of a substance is peculiar as compared with those of related substances, then no matter how we choose the conditions of comparison the original peculiarity expressed by the curve must still exist and may be discovered by regarding the results from different points of view.

Since the magnitude of the boiling-point of a substance is more or less definitely related to its chemical nature, if we choose the boiling-point as the condition of comparison, we insure that the temperatures of the substances will exhibit more or less definite physico-chemical relationships; and hence the viscosity-magnitudes of those liquids which give peculiar viscosity-curves will not be definitely related at the boiling-point. This we have seen to be the case. Similar considerations apply in the case of other physical properties.

At equal slope, on the other hand, we have found that the viscosity-magnitudes of many of the peculiar substances accord with the regular behaviour of those of most of the other liquids, but, as has just been shown, the peculiarities, although they no longer exist in magnitudes of the viscosities, are clearly indicated by the magnitudes of the temperatures.

This argument does not necessarily prove that for the purposes of physico-chemical comparisons the boiling-point has as much to recommend it as a temperature of equal slope; indeed, the latter, both by the results obtained and from general considerations, seems to be by far the more preferable. The real conclusion indicated is that to use a system of temperatures of comparison merely for the sake of obtaining and discussing the magnitudes of physical properties at those temperatures, is but a partial method of arriving at a true estimate of the behaviour of the substances, for that behaviour is expressed, not only in the magnitude of the physical property, but also in the magnitude of the temperature. At equal slope the viscosity of benzene, say, although its viscosity curve is peculiar, accords with those of higher homologues, and, indeed, of most homologous substances. Benzene may therefore be said to be comparable with other substances at equal slope, but it has still to be explained why the temperature of benzene is higher than that of its higher homologue at equal slope, for this temperature relation is the reverse of what holds for almost all simply-constituted liquids.

It follows, therefore, from the above general discussion, (1) that a comprehensive view of the physico-chemical relationships of a series of substances can only be obtained by studying the variation of the physical property over as wide a range of temperature as possible; (2) that the graphical or algebraical representation of the results so obtained will indicate whether particular members of a series are exceptional in behaviour as compared with their congeners; and (3) if such exceptional behaviour occurs, it may be detected either in the viscosity-magnitude or the temperature, no matter whether we use the boiling-point, a corresponding temperature, or a temperature of equal slope as the condition of comparison.

OTHER METHODS OF OBTAINING AND COMPARING VISCOSITY-MAGNITUDES.

It might at first sight be supposed that the most suitable method of obtaining physico-chemical relationships would have been to deal with the curves expressing the relations between temperature and the molecular viscosity (ηd^2) or the molecular viscosity work (ηd^3), instead of concerning ourselves, as we have done, with the curves for η, the viscosity coefficient.

From the fact, however, that molecular aggregation affects the values of d^2 and d^3 to an extent which cannot at present be satisfactorily estimated, we concluded that the question should, in the first instance, be approached by deducing slopes from the curves for the viscosity coefficients, and not from curves involving the quantities d^2 and d^3.

We have, however, made a series of comparisons using curves for molecular viscosity, theoretical values of d^2 being used in obtaining them. The result of this method is, that the constants in SLOTTE's formula, and the coefficients β and γ in the modified formula, the values of the temperatures of equal slope, and the values of the molecular viscosity read off at these temperatures, although differing in magnitude from those already given, exhibit amongst themselves practically the same general relationships as have already been described.

The same conclusions apply to the method in which curves for molecular viscosity work are employed.

APPENDIX.

In the following tables are given the values of the temperatures, viscosity coefficients, specific molecular areas, and specific molecular volumes employed in the comparisons at the boiling-point and equal slope. The last column in the tables contains the contractions for the names of the observers whose data were used in calculating the specific molecular areas and specific molecular volumes. The contractions and the names to which they refer are as follows :—

Br., Brown; B., Buff; D., Dobriner; K., Kopp; L., Lossen; Lo., Louguinine; M., Mendeléef; N., Neubeck; P., Pinette; Pr., Pierre; P. & P., Pierre and Puchot; R., Rosetti; S., Schiff; T., Thorpe; T. & J., Thorpe and L. M. Jones; W., Weger; Z., Zander.

The prefix a. before the contraction, as a.K., denoting after Kopp, indicates that in the mean values given by the observer the results of previous investigators have been included. Except in cases marked (*), the viscosity coefficients have been read from the curves; in these cases the temperature of comparison lies slightly beyond the range over which observations were actually made, and the coefficients have been calculated by means of Slotte's formula.

	Boiling-point.				Slope $\cdot 0_4323$.				Slope $\cdot 0_4987$.				
	Tempe-rature.	Viscosity coefficient × 10⁵.	Specific molecular area.	Specific molecular volume.	Tempe-rature.	Viscosity coefficient × 10⁵.	Specific molecular area.	Specific molecular volume.	Tempe-rature.	Viscosity coefficient × 10⁵.	Specific molecular area.	Specific molecular volume.	
	°				°				°				
Pentane	36·3	200	24·00	117·6	— 5·4	299*	22·97	110·06	..	..	..	..	T. & J.
Hexane	69·4	204	26·94	139·8	20·5	318	25·74	130·56	..	..	..	..	S., Z.
Heptane	98·4	199	29·78	162·5	41·1	330	28·22	149·92	..	..	..	..	T.
Octane	125·3	198	32·62	186·3	64·1	336	30·80	170·94	— ·4	703*	29·24	158·18	T.
Isopentane	30·4	203	24·10	118·3	— 4·4	286*	23·20	111·74	..	..	..	..	T. & J.
Isohexane	62·0	205	26·87	139·3	16·0	312	25·62	129·66	..	..	..	..	T. & J.
Isoheptane	90·3	198	29·72	162·0	35·7	322	28·21	149·83	..	..	..	..	T.
Isoprene	36·2	185	22·10	103·9	—12·1	295*	21·02	96·38	..	..	..	..	T. & J.
Amylene	36·1	188	22·69	108·1	—20·2	311*	21·38	98·89	..	..	..	..	T. & J.
Diallyl	59·2	192	25·15	126·1	9·7	304	23·95	117·22	..	..	..	..	B., S., Z.

APPENDIX (continued)

	Boiling-point.				Slope $\cdot 0_4323$.				Slope $\cdot 0_4987$.				
	Tempe-rature. °	Vis-cosity coeffi-cient × 10^5.	Specific mole-cular area.	Specific mole-cular volume.	Tempe-rature. °	Vis-cosity coeffi-cient × 10^5.	Specific mole-cular area.	Specific mole-cular volume.	Tempe-rature. °	Vis-cosity coeffi-cient × 10^5.	Specific mole-cular area.	Specific mole-cular volume.	
Methyl iodide	42·9	399	16·02	64·1	42·9	399	15·98	63·91	..	..	..	..	a. D.
Ethyl iodide	72·4	371	19·45	85·8	61·5	404	19·25	84·44	−11·6	822*	18·18	77·49	a. S., a. D.
Propyl iodide	102·4	353	22·51	106·8	83·6	407	22·18	104·43	10·0	827	20·97	96·04	a. D.
Isopropyl iodide . . .	89·2	359	22·73	108·4	79·9	390	22·52	106·90	6·7	807	21·24	97·89	Z., Br.
Isobutyl iodide	120·2	338	25·50	128·8	97·6	404	24·99	124·94	26·7	801	23·69	115·29	a. K., P. & P.
Allyl iodide	102·8	344	21·67	100·9	82·0	406	21·28	98·19	10·5	814	20·17	90·56	Z.
Ethyl bromide	38·4	328	18·18	77·5	26·9	368	18·02	76·53	..	..	..	..	a. K., Pr.
Propyl bromide . . .	71·0	325	21·11	97·0	54·7	372	20·81	94·96	..	..	..	..	Z.
Isopropyl bromide . .	59·7	329	21·43	99·1	51·6	353	21·25	98·01	..	..	..	..	Z.
Isobutyl bromide . . .	91·9	311	24·46	121·0	76·6	360	24·36	120·25	5·5	764	22·97	110·10	S., P. & P.
Allyl bromide	70·5	315	20·16	90·5	50·8	371	19·79	88·03	..	..	..	..	Z.
Ethylene bromide . . .	131·0	514	21·18	97·5	147·8	455*	21·39	98·93	68·8	906	20·18	90·64	a. K., T.
Propylene bromide . .	141·8	450	24·11	118·4	144·6	441*	24·23	119·28	65·7	893	22·88	109·44	a. K., Z.
Isobutylene bromide . .	149·6	467	27·29	142·6	161·3	426*	27·48	144·03	83·3	875	25·95	132·19	T. & J.
Acetylene bromide . .	109·5	442	20·25	91·1	103·0	463	20·13	90·32	25·5	902	18·99	82·79	W.
Propyl chloride . . .	46·4	274	20·32	91·6	26·4	330	19·93	88·95	..	..	..	..	a. K., Z.
Isopropyl chloride . .	36·3	274	20·66	93·9	21·4	317	20·31	91·51	..	..	..	..	a. K., Z.
Isobutyl chloride . . .	68·6	280	23·47	113·7	50·2	331	22·95	109·95	..	..	..	..	S., P. & P.

APPENDIX (continued).

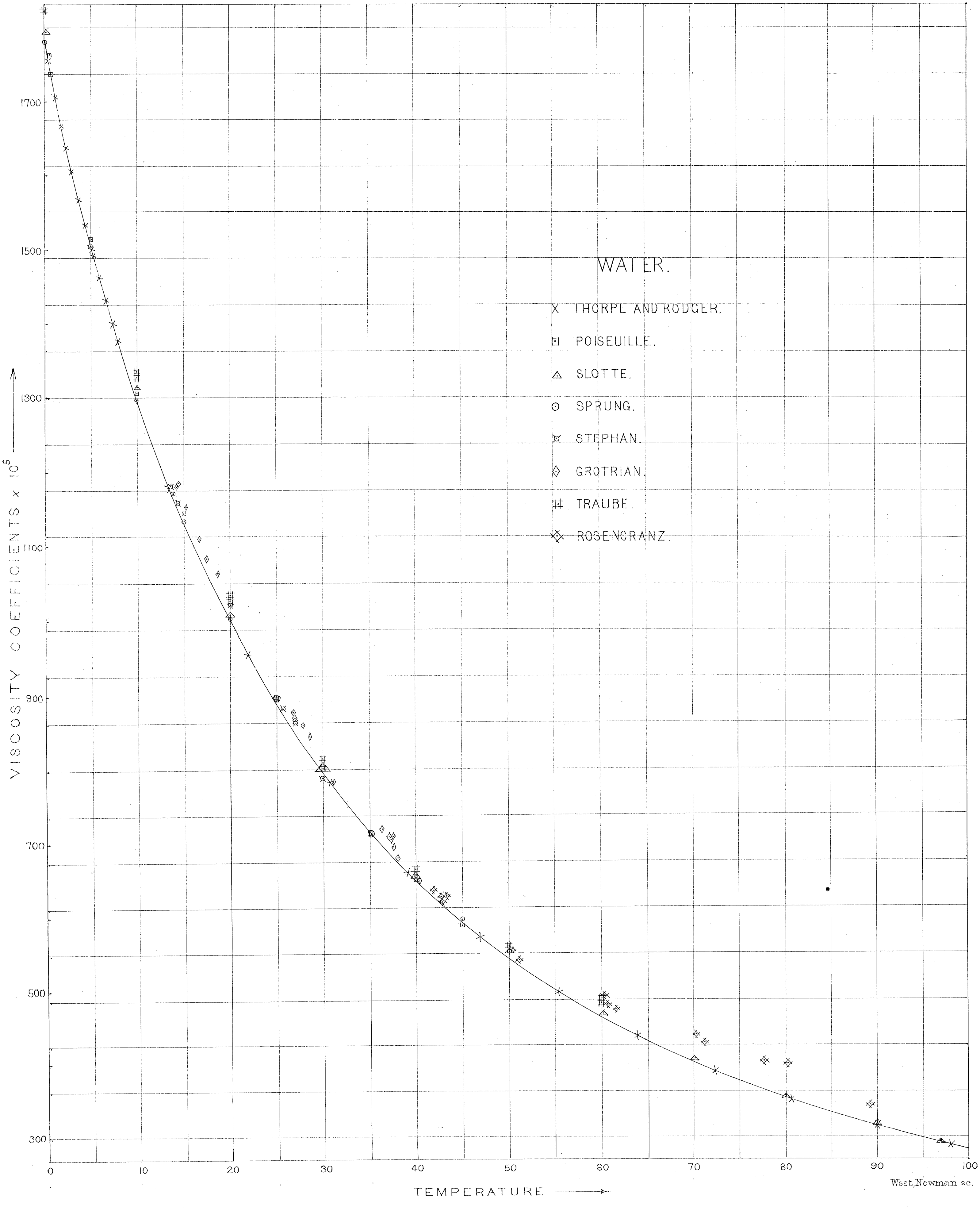
	Boiling-point.				Slope $\cdot 0_4 323$.				Slope $\cdot 0_4 987$.				
	Tempe-rature.	Vis-cosity coeffi-cient × 10^5.	Specific mole-cular area.	Specific mole-cular volume.	Tempe-rature.	Vis-cosity coeffi-cient × 10^5.	Specific mole-cular area.	Specific mole-cular volume.	Tempe-rature.	Vis-cosity coeffi-cient × 10^5.	Specific mole-cular area.	Specific mole-cular volume.	
	°				°				°				
Allyl Chloride	45·5	261	19·29	84·7	20·3	328	18·82	81·64	..	..	..	..	Z.
Ethylene chloride . . .	84·0	410	19·38	85·3	93·7	377*	19·55	86·46	27·1	758	18·49	79·52	T.
Ethylidene chloride . .	57·5	338	19·93	89·0	52·2	355	19·78	87·94	−10·7	715*	18·69	80·83	T.
Methylene chloride . .	40·2	363	16·18	65·1	37·1	372	16·12	64·70	..	..	..	..	T.
Chloroform	61·3	386	19·25	84·5	60·6	388	19·25	84·47	−11·0	799*	18·09	76·95	T., S.
Carbon tetrachloride . .	76·8	488	22·07	103·7	104·9	377*	22·65	107·77	37·4	763	21·32	98·43	T., S.
Carbon dichloride . . .	120·7	380	23·59	114·6	98·4	446	23·14	111·33	20·7	885	21·84	102·04	a. K., S., PR.
Methyl sulphide	37·5	253	17·80	75·1	5·7	335	17·26	71·71	..	..	..	..	T. & J.
Ethyl sulphide	92·0	234	24·44	120·8	45·2	346	23·47	113·68	..	..	..	..	a. K., PR.
Carbon disulphide . .	46·2	305	15·68	62·1	6·6	407	15·19	59·21	..	..	..	..	T., S.
Dimethyl ketone . . .	56·3	232	18·10	77·0	17·8	329	17·39	72·50	..	..	..	..	T.
Methyl ethyl ketone . .	80·0	239	21·07	96·7	43·7	330	20·32	91·61	..	..	..	..	T. & J.
Methyl propyl ketone .	102·0	234	24·13	118·5	56·5	344	23·13	111·27	− 6·9	699	21·99	103·18	T. & J.
Diethyl ketone	102·1	222	24·02	117·7	50·5	343	22·89	109·49	−13·1	708	21·74	101·38	T. & J.
Aldehyde	21·1	219	14·71	56·4	−16·8	316*	14·17	53·36	..	..	..	..	a. L., K.
Formic acid	101·0	536	11·93	41·2	138·7	373*	12·24	42·83	71·7	758	11·65	39·75	a. Z., S.
Acetic acid	118·1	385	15·97	63·8	122·9	370*	16·03	64·16	50·7	784	15·15	58·96	a. Z., K.

APPENDIX (continued).

	Boiling-point.				Slope $\cdot 0_4 323$.				Slope $\cdot 0_4 987$.				
	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	Temperature.	Viscosity coefficient × 10^5.	Specific molecular area.	Specific molecular volume.	
Propionic acid	° 141·0	319	19·45	85·8	° 116·7	390	19·02	82·94	° 44·0	801	17·97	76·16	K., a. Z., P. & P.
Butyric acid	162·1	309	22·71	108·2	138·3	379	22·22	104·74	65·7	796	20·99	96·19	a. Z., PR.
Isobutyric acid. . . .	154·0	307	22·80	108·9	129·1	378	22·31	105·36	56·5	792	21·03	96·47	P. & P., a. Z., S.
Acetic anhydride . . .	139·1	277	22·93	109·8	99·8	378	22·16	104·29	32·7	760	20·99	96·15	K.
Propionic anhydride . .	168·6	247	28·75	154·2	114·0	379	27·34	142·94	46·6	762	25·93	132·04	T. & J.
Ethyl ether	34·8	205	22·41	106·1	— 2·7	295*	21·52	99·84	..	..	..	..	a. D.
Thiophen	84·1	336	19·32	84·9	75·9	364	19·20	84·10	12·5	727	18·27	78·08	S.
Benzene	80·2	316	20·92	95·7	75·9	330	20·85	95·23	19·4	654	19·87	88·58	N., K.
Toluene	110·7	248	24·05	118·0	69·8	354	23·19	111·71	5·6	710	22·15	104·27	a. N., Lo.
Ethyl benzene	136·1	233	26·80	138·7	77·9	367	25·60	129·53	11·4	744	24·46	120·97	a. W.
Ortho-xylene	144·0	247	26·73	138·2	91·3	372	25·64	129·80	26·6	737	24·51	121·38	S., P., N.
Meta-xylene	139·0	219	26·92	139·7	70·6	368	25·51	128·86	6·3	734	24·43	120·73	S., P., N.
Para-xylene	138·2	220	26·99	140·2	75·1	360	25·64	129·79	10·2	733	24·51	121·37	S., P., N.
Bromine	58·9	691	14·20	53·5	..	..	..	..	24·0	953	13·82	51·36	T.
Water.	100·0	283	7·05	18·73	96·8	292	7·04	18·69	46·9	577	6·90	18·14	a. R.

APPENDIX (continued).

	Boiling-point.				Slope $\cdot 0_4 323$.				Slope $\cdot 0_4 987$.				
	Temperature. °	Viscosity coefficient $\times 10^5$.	Specific molecular area.	Specific molecular volume.	Temperature. °	Viscosity coefficient $\times 10^5$.	Specific molecular area.	Specific molecular volume.	Temperature. °	Viscosity coefficient $\times 10^5$.	Specific molecular area.	Specific molecular volume.	
Methyl alcohol	65·0	328	12·20	42·6	76·5	290*	12·34	43·36	13·5	650	11·70	40·03	a. Z., K.
Ethyl alcohol	78·4	441	15·72	62·3	..	..	..	..	58·5	606	15·41	60·51	M., K.
Propyl alcohol	97·4	463	18·77	81·3	..	..	..	..	86·5	560	18·59	80·18	a. Z., P. & P.
Butyl alcohol	117·3	405	21·80	101·8	..	..	..	..	95·6	575	21·42	99·12	a. Z.
Isopropyl alcohol . . .	82·9	490	18·92	82·3	..	..	..	..	82·9	490	18·98	82·68	a. L., a. Z.
Isobutyl alcohol . . .	107·8	452	21·84	102·1	..	..	..	..	99·6	525	21·66	100·81	a. L., P. & P.
Inactive amyl alcohol .	131·4	378	24·77	123·3	..	..	..	..	105·2	574	24·15	118·67	T. & J.
Active amyl alcohol . .	128·7	374	24·60	122·0	..	..	..	..	104·7	555	24·03	117·80	T. & J.
Trimethyl carbinol . .	82·4	566	21·96	102·9	..	..	..	..	90·9	461	22·12	104·04	T. & J.
Dimethyl ethyl carbinol	101·9	418	24·50	121·4	..	..	..	..	93·8	490	24·29	119·71	T. & J.
Allyl alcohol	96·6	373	17·66	74·2	..	..	..	..	63·1	610	17·17	71·17	T.



West, Newman sc.