A STUDY OF THE SELF-DIFFUSION OF CERTAIN OF THE LOWER ALKYL HALIDES

BY

L.H. STEIN

Thesis Presented to

The University of Capetown

For the Degree of Doctor of Philosophy

The University of Cape Town

Modderfontein September, 1955

The copyright of this thesis vests in the author. No quotation from it or information derived from it is to be published without full acknowledgement of the source. The thesis is to be used for private study or non-commercial research purposes only.

Published by the University of Cape Town (UCT) in terms of the non-exclusive license granted to UCT by the author.

The University of Cape Town

SUMMARY

The self-diffusion coefficients of MeI, and Et-, nPr- isoPr-, nBu-, isoBu- and secBu-iodides and bromides were determined by application of the capillary tube method and using iodine-131 and bromine-82 for labelling the compounds. Viscosities were measured for those compounds for which the data in the literature were insufficient for calculation of energies of activation.

The diffusion coefficients were of the order of 2×10^{-5} $cm.^2 sec.^{-1}$ with activation energies of 2 kcal./mole; determined from plots of log D/T versus 1/T. The temperatures at which coefficients were measured were 7.35, 19.35 and 30.00°C. The activation energies measured agreed with those for viscous flow as is required by the theories of Frenkel and Eyring. It was found that $D\eta/T$ was reasonably constant for each compound as is to be expected from the relationships derived by these workers and from the Stokes-Einstein equation. Parameter values calculated from these various relationships were, however, in very poor agreement with the expected values; those for the Stokes-Einstein equation were the most reasonable. Further application of the Frenkel and Eyring theories to the experimental results and to the results in the literature, indicate that these theories are only very approximate.

Self-diffusion coefficients of ethyl and n-butyl iodides were measured in mixtures of different compositions. These coefficients differed from one another and were concentration dependent. Viscosities were also measured at different compositions of the mixture and $D\eta$ values at a fixed temperature were found to be reasonably constant for both series of results. Activation energies for the self-diffusion of the two compounds at a fixed composition were in fair agreement with those for the pure compounds as well as with that for the viscosity of the mixture. The self-diffusion coefficients were discussed in relation to the intrinsic and interdiffusion coefficients. On the assumption that these mixtures are very nearly ideal the self-diffusion coefficients

were taken to be equal to the intrinsic coefficients and interdiffusion coefficients were calculated at different compositions. These interdiffusion coefficients were found to be concentration dependent but to a lesser degree than the self-diffusion coefficients.

ACKNOWLEDGEMENTS

I wish to acknowledge my indebtedness to the following organisation and persons:

1. Dr. P.C. Carman for suggesting the problem, for his interest in the investigation and for the invaluable advice and criticism he so generously offered.

2. Dr. A.H. Spong for his patience in reading through the manuscript and for the advice, suggestions and criticism which resulted therefrom.

3. Mr. A. White for the construction of glass apparatus.

4. Mr. E.A. Hecker, of the N.P.L., for the precision grinding of the diffusion tubes.

5. The Council for Scientific and Industrial Research, in whose laboratories the investigation was undertaken, for permission to present the findings in this thesis.

CONTENTS

PART I

THE THEORETICAL BACKGROUND

1.1. A Theoretical Discussion

1.1.1. Introduction

In the study of surface diffusion[1] of gases in a porous material it was found that the diffusion coefficient obtained in the multilayer region gave values which were of the same order, though higher, than those to be expected for self-diffusion coefficients of liquids. In a search of the literature for self-diffusion data, with which the results could be compared, the paucity of results was immediately apparent. The present work was accordingly undertaken in an attempt to furnish further data.

The lower alkyl halides chosen for this study are liquids at normal temperatures and can be readily labelled with radioactive isotopes. The self-diffusion coefficients have been measured as carefully as possible and considerable attention paid to reproducibility and accuracy of results. In this investigation the techniques for handling the isotopes concerned and of measuring self-diffusion coefficients were successfully mastered and it was felt that similar methods should be applied to the study of binary mixtures. A suitable system was selected and the self-diffusion coefficients of the individual constituents determined.

1.1.2. Definition of Diffusion and Viscosity

Diffusion is the process in which a material progresses by nature of its thermal motion from a position of higher to one of lower concentration. In a solution, therefore, whilst the solute moves in one direction, the solvent moves the opposite way. The rate of movement is dependent on a diffusion coefficient which is a constant at a fixed temperature. According to Fick's Law[2] the quantity ds of substances diffusing from an area A, in time dt, when the concentration gradient is $-\, da/dx$, is given by

$$ds = -DA \frac{da}{dx}\, dt \qquad \ldots\ldots\ldots\ldots\ 1.$$

The diffusion coefficient D thus has the dimensions length^2 x time^{-1} (measured in the c.g.s. system in $cm^2. sec.^{-1}$) and is numerically equal to the quantity of material which passes through unit area in unit time when the concentration gradient is unity. The gradient is always negative since diffusion occurs only in the direction of decreasing concentration.

Though diffusion must be measured for molecules* that differ from one another, it is obvious that even in an homogeneous medium thermal motion must cause each molecule to move through the whole volume occupied by the medium, at a definite rate. Diffusion of a material in itself is named self-diffusion and cannot be measured for molecules completely identical with one another, but, if a group of molecules can be labelled in such a way that the molecular weight is virtually unchanged, it is possible to measure a diffusion coefficient which can be regarded as a close approximation to the self-diffusion coefficient of the compound concerned. In the present case, halogen atoms in the lower alkyl bromides and iodides have been replaced by Br^{82} and I^{131} isotopes, the half-lives of which are respectively, 35.87[(3)] and 192.06 hours[(4)]. Molecular weights have thus been increased by two and four for the bromides and iodides, respectively. This increase should have only a slight effect on the coefficients.

In the investigation of thermal molecular motion, diffusion, viscosity and heat conductivity are grouped as transport properties and are thus related. Data on viscosities of pure liquids are fairly extensive and where deficient can be readily supplemented, so that it was decided to compare self-diffusion coefficients with the corresponding viscosities. Viscosities have had to be evaluated for the temperatures at which diffusion coefficients were determined and the energies of activation calculated. For four of the compounds the available data were insufficient and viscosities were determined at the required temperatures.

---

*The term "molecule" is used throughout and should be taken as a synonym for the terms "atom" and "particle".

In the equation

$$P_{xy} = -\eta dv/dx \qquad \ldots\ldots\ldots\ldots\ldots 2$$

η is the coefficient of viscosity which is numerically equal to the force per unit area P_{xy}, measured in dynes cm.$^{-2}$, acting on one square cm. parallel to the reference plane and such that the velocity gradient dv/dx, between the two parallel planes separated by unit distance, is unity. In the c.g.s. system the unit of viscosity, the poise, is expressed as gram cm.$^{-1}$ sec.$^{-1}$ The reciprocal of the viscosity coefficient is known as the fluidity.

1.1.3. Diffusion and Viscosity in the Gaseous and Liquid States

Although the interest of this work is centred primarily on diffusion in liquids it is of interest to consider the relationship between the above two properties in the gaseous state.

In a gas it is only because each molecule undergoes continuous collisions with its fellows that diffusion takes place at a slower rate than the average molecular velocity $\bar{c}$. It is clear from this that the mean free path, l, of the molecule is closely connected with the rate of diffusion. Application of simple kinetic theory leads to the relationship that

$$D = \tfrac{1}{3}\,\bar{c}\,l \qquad \ldots\ldots\ldots\ldots\ldots 3$$

By applying the Maxwellian distribution of velocities, a coefficient of $\frac{1}{2}$ is obtained. A coefficient equal to 0.601 is derived by Chapman[5] for rigid elastic spheres in an elaborate and rigorous treatment which takes into account that the distribution of velocities, in transport processes, is no longer purely Maxwellian.

Viscosity or internal friction arises as a shear force between parts of a fluid moving at different relative speeds. Imagine two parallel planes in a gas, such that molecules in one plane have a constant and unidirectional velocity impressed upon them relative to those in the other plane. The kinetic energy due to this motion is additional to the average kinetic energy which is common to molecules in both planes. Owing to random thermal motion molecules in either plane will, from time to time, collide and interchange with those in the other plane. This interchange produces a constant transfer of translational momentum, which would cause the relative translational velocity of the planes to approach zero, unless it were maintained by some external agency. The force required to overcome the transfer of momentum is measured as viscosity.

Simple kinetic theory leads to the relationship

$$\eta = \tfrac{1}{3}\rho \bar{c} l \qquad \ldots\ldots\ldots\ldots 4$$

where ρ is the density. If a Maxwellian velocity distribution is assumed, the numerical coefficient is $\frac{1}{2}$. The Chapman-Enskog[6] theory leads to a coefficient equal to 0.499 for rigid spheres.

In general, η is independent of pressure or density at a given temperature, and D is inversely proportional to pressure. From equation 3 and 4, $\rho D = \eta$ and, in the rigorous theory,

$$\rho D = K\eta \qquad \ldots\ldots\ldots\ldots 5$$

where K depends on the law of interaction between molecules and is equal to 1.204 for rigid spheres.

The foregoing treatment cannot be applied to liquids, since it takes no account of the facts that (i) the volume of the molecules is a large fraction of the total volume, (ii) each molecule moves continuously in a field of intermolecular forces. The former of these effects have been approached quantitatively by Enskog's theory[7] for dense gases consisting of rigid, spherical molecules. In such gases, intermolecular forces are ignored, and attention is directed wholly to the effects of molecular size. Two effects can be distinguished. First, if a gas is compressed until the volume of the molecules is an appreciable fraction of the total gas volume, collisions take place at Y times the rate expected if the gas consisted of point molecules, where $Y > 1$ and Y tends to 1 at low pressures. This slows down the rate of molecular interchange, so that the self-diffusion coefficient decreases to 1/Y times the value calculated for point molecules. Since the kinetic transport of momentum which gives rise to gaseous viscosities is influenced the same way, a corresponding decrease of viscosity is to be expected.

A second effect, however, also comes into play which affects viscosity but not diffusion. When rigid molecules collide, there is an instantaneous transfer of momentum from the centre of one to the centre of the other. This "collisional transport" of momentum is additional to the kinetic transport, and so tends to increase viscosity. It is negligible for point molecules i.e. for gases at low pressures, but it becomes the dominant mode of transport of momentum in dense gases.

Thus, as a gas is compressed, diffusion and viscosity vary in different ways. This is illustrated by calculated values of η and of relative values of ρD for nitrogen at 50°C.[8] in table 1. For an ideal gas, both of these should be constant at the values for low pressures; taken arbitrarily as unity for ρD. Actually, in the dense gas, ρD decreases steadily, while η, on the other hand increases.

Table 1 :

Calculated values of η and relative values of ρD for N_2 at 50°C.

Pressure atmos.	η obs. μ poise	η calc. μ poise	ρ g./ml.	$\rho D_{relative}$
15.37	191.3	181	0.01623	0.99
57.60	198.1	190	0.06049	0.96
104.5	208.8	205	0.1083	0.95
212.4	237.3	224	0.2067	0.795
320.4	273.7	266	0.2875	0.755
430.2	312.9	308	0.3528	0.725
541.7	350.9	348	0.4053	0.69
630.4	378.6	380	0.4409	0.67
742.1	416.3	418	0.4786	0.64
854.1	455.0	455	0.5117	0.61
965.8	491.3	492	0.5404	0.59
True $\rho D_{lim} = 239 \times 10^{-6}$ c.g.s. units				

The agreement between experimental and calculated values of η shows that Enskog's theory is remarkably successful. In applying his theory to the results of Warburg and Babo[9] on the viscosity of carbon dioxide, Enskog attained the same degree of success at a temperature (40.3°C.) slightly above the critical temperature (31.1°C.), even at a pressure (115 atmospheres) which is about one and a half times the critical pressure (73 atmospheres)[10].

It might thus appear that Enskog's theory bridges the main gap between the behaviour of gases and of liquids. If this were the case, the position could be summarised briefly by stating that there is no fundamental change in the mechanism of diffusion, but that viscosity undergoes a marked change of mechanism and, in so doing, loses its close relationship to diffusion.

The inadequacy of the theory appears when we turn to temperature coefficients. In gases consisting of rigid spheres, both diffusion and viscosity increase in proportion to the square root of the absolute temperature, and the same applies to Enskog's dense gas. In liquids, (i) temperature coefficients are very much larger and variation with temperature generally follows an exponential relationship, indicating that an energy of activation is involved; (ii) while diffusion continues to increase with temperature, viscosity decreases; (iii) diffusion and viscosity do not appear to be unrelated, since there is plentiful evidence that diffusion and reciprocal viscosity (fluidity) vary with temperature at much the same rate, a behaviour which may be contrasted with equation 5 (p.4). Thus for a gas $D/\eta = \frac{K}{\rho}$ whilst for a liquid $D\eta$ = a constant dependent on equations 16, 18 and 23 (pp.15 and 17). Effects (i) and (ii) also characterise dense gases. Thus, while viscosity of carbon dioxide at 40°C agrees well with Enskog's theory, Phillips[11] has shown that its temperature coefficient in the same range changes from a small positive value at low pressures to large negative values at pressures above 80 atmospheres. Similar results for ether vapour have been obtained by Schroer and Becker[12]. It is clear that Enskog's theory breaks down with respect to temperature coefficient due to its neglect of the intermolecular field of force.

1.1.4. Andrade's Theory of Liquid Viscosities[13]

Enskog's theory of viscosity in dense gases indicates that the dominant mechanism is collisional transfer of momentum. Andrade has developed a theory of viscosity in liquids which assumes that collisional transfer is dominant, but employs it in a different way.

He visualises a transfer of momentum between molecules in two parallel planes, one of which has a constant unidirectional velocity impressed upon it relative to the other. In a liquid, as in a solid, each molecule is confined to a relatively fixed position by its neighbours and the transfer of momentum cannot occur by molecular interchange between the planes. Because of its thermal energy, however, each molecule vibrates rapidly and collides with its neighbours, both in its own plane and in the adjacent planes. The period of contact is, he assumes, of sufficient duration for two colliding molecules to acquire a common translational velocity. In this way momentum is transferred between the adjacent planes, and the tangential force between them is equivalent to the viscosity.

Andrade assumes that planes of molecules are moving relatively to one another in viscous flow and exchanging momentum by collisions, but he finds no necessity to provide a molecular mechanism for their motion. Neither does he derive a relationship between diffusion and viscosity. These features are to be expected of a mechanism of collisional transfer of momentum and apply equally well to Enskog's more rigorous theory for dense gases. Andrade's theory of liquid viscosities must therefore be regarded as arising from analogy between liquid and gaseous states rather than between liquid and solid states.

Theories of viscosity based on analogy to the solid state ignore transfer of momentum by either a kinetic or a collisional mechanism. Instead, viscous flow is considered to take place as a relaxation of shear stress brought about by the same processes as are responsible for diffusion, so that fluidity and diffusion vary in proportion to one another. Before dealing with relaxation theories of viscosity, diffusion in solids and extension of similar ideas to the liquid state will first be considered.

1.1.5. Diffusion in the Solid State

In a perfect crystalline solid every molecule occupies a regular equilibrium position and thermal motion is confined to vibration about that position. It stands to reason that for a molecule to move it must have somewhere to move to. Thermal motion must produce a certain proportion of defects due to motion of the most energetically vibrating molecules. In addition to these defects there are imperfections which have been produced during the life of the solid, for example, in growth.

Let us consider these defects as holes in the lattice, that is, vacant sites or interstitial positions of sufficient size to accommodate a molecule. Molecules possessing sufficient thermal energy to escape from their equilibrium positions can then move into these holes. Frenkel[14] envisaged this as an activated process and in order to get an idea of the frequency of escape, $1/\tau$, he used a simplified approximate equation derived according to the concept of a potential barrier (see figure 1). The time between escapes from the trough is $\tau = \tau_0 e^{\varepsilon/kT}$ so that the frequency of escape is

$$1/\tau = 1/\tau_0 \, e^{-\varepsilon/kT} \qquad \ldots\ldots\ldots\ldots\ 6$$

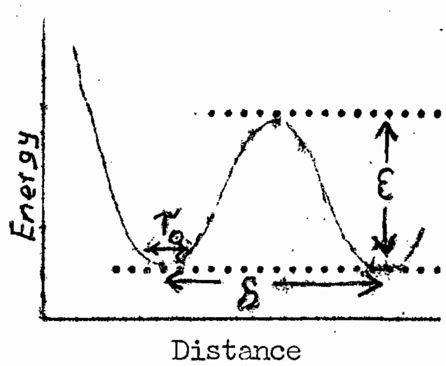

Fig.1 : Potential-energy barrier for molecular movement.

where ε, the energy of activation for a single molecule, is the depth of the trough and τ_0 is the period of free vibration of the molecule in the bottom of the trough.

Any molecule possessing the energy ε is able to move from its equilibrium position to the top of the barrier. From there it may, of course, return to its original position, but if it possesses an energy slightly in excess of ε, it can move the distance δ into an adjacent hole or, if there is no immediately available hole, the movement will take place interstitially into a more distant hole. Alternatively, and of some importance for diffusion in the liquid state, another mode of movement is that of interchange of position of two adjacent molecules. In these ways the molecules diffuse through the solid and since each molecule moving into a hole must have left a vacant site, one can also regard it as diffusion of holes in the opposite direction.

By virtue of thermal motion, the foregoing processes produce continual random interchange in position of the molecules. In the presence of a concentration gradient this interchange gives rise to diffusion. In relating this motion to the diffusion coefficient, Frenkel[14] made use of the Einstein relationship[15]. As motions are completely random the displacement of an individual molecule along any given axis, say the x-axis, will be nullified by an equal movement of another molecule in the opposite direction so that in time t the average displacement for all molecules will be zero. Each individual molecule, however, will have moved a certain distance, and the most probable value of this, irrespective of direction along the chosen axis, will be given by the root mean square displacement, Δ_x.

It has been shown by Einstein[15] and Smoluchowski[16] that the relationship between self-diffusion and the root mean square displacement parallel to the x-axis is

$$D = \frac{\Delta_x^2}{2t} \qquad \text{.............} \quad 7.$$

If Δ is the root mean square displacement in space, then $\Delta^2 = \Delta_x^2 = \Delta_y^2 = \Delta_z^2$, where Δ_y and Δ_z are the root mean square displacements parallel to the y- and z-axes. In purely random motion the statistical average $\overline{\Delta_x^2} = \overline{\Delta_y^2} = \overline{\Delta_z^2} = \frac{1}{3}\overline{\Delta^2}$ and by substitution in equation 7, we have

$$D = \frac{\overline{\Delta^2}}{6t} \qquad \text{.............} \quad 8.$$

The usefulness of this expression depends on measurements of Δ in an arbitrary time t. This has been possible in the case of colloid particles, the Brownian movement of which can be followed in a microscope, as has been used in the classical experiments of Perrin[17] to calculate the diffusion coefficient.

Frenkel[14] has utilised this relationship to obtain an expression for D in solids:

$$D = \frac{\delta^2}{6\tau} \qquad \text{.............} \quad 9.$$

This is obtained by taking the arbitrary time, t, as the average time,

τ, between successive jumps. In each jump, a molecule moves a distance δ, which is therefore substituted for Δ. Assumptions made are that (i) an arbitrary fixed time may be replaced by an average time of jumping, and (ii) a fixed distance of jump may replace an average displacement. Furthermore the relationship $D = \delta^2/6\tau$ assumes completely random motion which is not possible in crystals in which the hole is surrounded by a regular arrangement of molecules which may jump into it. The equation can therefore only be regarded as an approximate type and the last objection is best covered by using a numerical factor other than 6, particularly as Frenkel's use of this factor is not justified on the basis of the derivation of equation 8 but is dependent on the assumption that 1/6 of the molecules move in one direction along one axis. Thus for body-centred and face-centred cubic crystals, factors of 24 and 12, respectively, have been derived by Wert and Zener[18].

Frenkel assumes that since the interchange of molecules involves an activation energy, the time τ in equation 9 may be related to the time of vibration and the temperature as is given in equation 6. Thus

$$D = \frac{\delta^2}{6\tau_o} e^{-\mathcal{E}/kT} \qquad \ldots\ldots\ldots\ldots\ldots 10.$$

In solids, therefore, D is expected to increase exponentially with temperature. This is in contrast to the slow increase in gases which is proportional to the square root of the absolute temperature. The temperature relationship for solids has been repeatedly established and is generally accepted.

1.1.6. Analogy between the Liquid and Solid States

That the liquid state is similar to the solid rather than to the gaseous state is borne out by the fact that on fusion the volume of a solid is increased by only a small amount; about 10 per cent. The molecular arrangement in a liquid near the temperature of crystallisation must therefore be very like that of the solid.

As heats of fusion are very much smaller than heats of vaporisation, this indicates that cohesive forces between the molecules must decrease only slightly on fusion. Further evidence of the similarity of the liquid to the solid state is that the specific heat of a condensed body is only altered slightly on fusion. This means that the heat motion in a liquid remains fundamentally the same as in a solid, reducing mainly to small vibrations about equilibrium positions and in the case of diatomic or more complex molecules, to rotational oscillations about certain equilibrium orientations.

A practical consideration is that X-ray structure analysis has indicated that the molecular arrangement of a liquid is very different from the disorder of the gaseous state. Over short distances it is similar to that of the solid to which the liquid crystallises. Short range or local order is evident but there is a loss of long range order which gives a liquid its amorphous structure and in minor respects, its similarity to a gas. Solids themselves are seldom found in the form of a single crystal but are composed of polycrystalline aggregates and from a roughly macroscopic point of view are as isotropic as liquids.

With increasing temperature solids and liquids expand normally and in solids this expansion may be due to increase in the intermolecular distance as well as to increase in the number of holes. In a liquid, however, the expansion is due almost entirely to the latter process and further, whereas the holes in a solid can be distinguished and referred to lattice or interstitial positions, in a liquid any rupture of sufficient magnitude is in fact a hole.

From the foregoing it is evident that a liquid is similar to a solid in particular near the point of crystallisation. With rise in temperature, however, the liquid must approach more closely to a gas since the number of holes becomes larger and larger and short range order tends to disappear so that the molecules moving individually are in random motion akin to that in a gas. This condition will only be approached in the vicinity of the critical density.

Analogy between liquid and gaseous states is based mainly on the fact that both are fluid and do not possess rigidity. This is not a satisfactory basis because no substance is completely rigid. As is emphasised later rigidity is essentially a manifestation of high viscosity. It is true that the fluidity of liquids is higher than would be expected for their densities in comparison with crystalline solids. This is unquestionably connected with the random structure and the absence of fixed positions in space which characterise a crystal lattice. As in a solid each molecule is contained by its neighbours and must spend most of its time oscillating in an approximately constant position. The difference from a solid is that this position is not fixed in space but is itself slowly drifting about.

1.1.7. Application to Diffusion and Viscosity in Pure Liquids

As has been shown it is to be expected that in liquids as in solids, there are vacant sites although these are not as definite in size and character as in solids. It is not unreasonable to assume that the main factor in diffusion is an occasional jump from a position in which a molecule vibrates amongst neighbouring molecules, to an adjacent hole. This step by step wandering which is the basis of the kinetic theory of liquids must be faster than in solids. In addition this movement will be of a simpler nature in liquids due to the absence of definite lattice sites and interstices. Movement may also occur by interchange of position of two adjacent molecules, the one molecule rolling around the other. In this way movement can take place without there being a full size hole into which the molecule can move.

Frenkel(14) has used the foregoing analogy to apply equations 9 and 10, which were derived for solids, to liquids. Thus

$$D = \frac{\delta^2}{6\tau_0} e^{-\mathcal{E}/kT} \qquad \text{.............. } 11$$

where δ is an average distance between adjacent equilibrium positions. In the application of this equation to the case of a liquid the use of the factor 6 is perhaps more valid since there is no definite molecular arrangement and hence fewer limitations on the direction of jumping. In cases where steric hindrance might restrict movement the factor might well vary between the extreme values which are encountered for solids[18] and 6, as progress is made from the melting to the boiling point.

Let us now consider viscous flow and the relationship which exists between diffusion and viscosity. This can be approached by regarding viscosity as a relaxation process. The idea of viewing viscosity in this way was first put forward by Maxwell[19]. Suppose that a rigid body is placed under a shear stress. As a result, it undergoes a shear strain and if it is completely rigid a constant shear stress will be necessary to maintain a constant shear strain. Suppose, however, that processes take place in the body so that at constant shear strain the shear stress decreases, that is, it is said to undergo relaxation and after a time the deformed shape will be retained permanently without any stress. Conversely, if a constant shear stress is maintained the same process of relaxation will give rise to a constant rate of shear, that is viscous flow. It follows from this view that rigidity and viscosity are not mutually exclusive but that rigidity is a manifestation of high viscosity.

Maxwell's theory was essentially phenomenological as it did not deal with the mechanism of relaxation. We can see, however, that if a solid body is exposed to a shear stress the continual molecular interchange, which is responsible for diffusion in solids will also lead to relaxation and hence to viscous flow. Since the same process is responsible for both, a direct relationship between diffusion and fluidity should result. In crystalline solids such a relationship between diffusion and viscosity is in actual fact obscured since flow or plastic deformation in such solids is characterised by the process of "slip". It should apply, however, to amorphous solids such as glasses, and to liquids.

Frenkel first applied this concept to liquid viscosities[14] and derived his equation as follows: Let the flow of a liquid take place in a positive direction along the x-axis with the average velocity, superimposed on the normal thermal motion, increasing in the direction of the y-axis. Consider a layer of liquid with thickness δ, enclosed between the planes $y = y_o$ and $y = y_o + \delta$, where δ is the average distance between two equilibrium positions. If the lower plane is regarded as stationary then the plane under consideration moves with a velocity $v_x = \left(\frac{\partial v_x}{\partial y}\right) \delta$. This motion must be ascribed to the force by which the plane is pulled in the positive direction by the shearing force. If the shearing force referred to unit area is P_{xy}, then the force acting on each molecule is $F = P_{xy} \delta^2$ since δ^2 may be taken as an approximate measure of the area of a molecule in a plane. Each molecule vibrates about its equilibrium position, occasionally jumping to the next equilibrium position. The effect of F is to favour jumps in the direction of F, with the result that the molecule drifts in this direction with a jerky motion, but at a constant average speed. As all molecules in the plane are similarly affected, this is the velocity of movement of the plane as a whole, that is v_x. We can write

$$v_x = qF = qP_{xy} \delta^2 \qquad \text{............. 12}$$

if q is the mobility produced, that is, the rate with which a molecule must move when unit force is impressed upon it.

Putting $v_x = \left(\frac{\partial v_x}{\partial y}\right) \delta$ we obtain the usual relationship between the velocity gradient and the shearing force

$$\frac{\partial v_x}{\partial y} = q \delta P_{xy} \qquad \text{............. 13}$$

By definition $\frac{\partial v_x}{\partial y} = \frac{1}{\eta} P_{xy}$ and therefore

$$\eta = \frac{1}{q\delta} \qquad \text{............. 14}$$

which is always applicable when the relaxation process is involved.

For a colloidal suspension in which the colloid particles were moving randomly, Einstein[15] found the diffusion coefficient, D, to be given by

$$D = \frac{kT}{f} \qquad \text{............. 15}$$

where k is Boltzmann's constant and f is the frictional resistance of the medium on a moving particle when this moves with an average velocity $\bar{v}$ under the force exerted on it by the osmotic pressure. If this force moves the particle against the frictional resistance at unit velocity it will be equal to f and the mobility $q = 1/f$. The Einstein equation thus becomes $D = qkT$ for these conditions.

Frenkel uses this relationship between the diffusion coefficient and the mobility for the evaluation of η by substitution in equation 14. Thus :

$$\eta = \frac{kT}{D\delta} \qquad \text{.............} \ 16$$

and since $D = \dfrac{\delta^2}{6\tau_0} e^{-\mathcal{E}/kT}$ according to equation 10

$$\eta = \frac{6kT\tau_0}{\delta^3} e^{\mathcal{E}/kT} \qquad \text{.............} \ 17.$$

The Einstein relationship was not derived originally for molecules which require an energy of activation. Frenkel derived a general relationship between D and q for such moleoules, and showed that it reduced to the Einstein equation when F is very much smaller than kT as is true for all normal cases of viscous flow. He assumed that this equation is equally applicable for a molecule moving in a medium which consists of identical molecules.

It is of interest to note that equation 16 may be compared with the <u>Stokes-Einstein</u> relationship for D and η. In this the proportionality constant is derived by assuming that the particles moving in an essentially homogeneous viscous medium, are small spheres of radius r. Applying Stokes' law[20] for the evaluation of the resistance suffered by a particle moving with average relative velocity $\bar{v}$,

$$f = 6\pi r \eta \bar{v} \qquad \text{.............} \ 18$$

and since from equation 15, $D = kT/f$

$$D = \frac{kT}{6\pi r \eta} \qquad \text{.............} \ 19$$

for unit relative velocity. This equation has been shown to hold good for diffusion of colloids where relatively large particles are moving through a medium of smaller molecules. Since Stokes' law is a hydrodynamical equation, the molecular nature of the medium is not considered and one would not necessarily expect it to hold for a molecule moving amongst its fellows of equal size, as is the case in self diffusion.

In equation 9, the average frequency of jump by a single molecule is $1/\tau$. Since there are six main directions, we can assume that, on the average, the frequency b, with which a molecule jumps in one direction is given by

$$b = 1/6\tau \qquad \ldots\ldots\ldots\ldots\ldots \; 20$$

whence, from equation 9

$$D = \delta^2 b \qquad \ldots\ldots\ldots\ldots\ldots \; 21.$$

Now, Frenkel evaluates τ by equation 6, in which he relates it to τ_o, the mean period of vibration. This is a very approximate relationship, and is intended only to give the right order of magnitude. Eyring's[21] contribution is an attempt to make a more accurate evaluation of the frequency of jumping by applying the theory of rate processes, leading to the equation

$$b = \frac{kT}{h} \; \frac{Q_{\ddagger} e^{-\mathcal{E}/kT}}{Q} \qquad \ldots\ldots\ldots\ldots\ldots \; 22$$

which can be substituted in equation 21. In this, h is Planck's constant and $Q_{\ddagger}$ and Q are the partition functions, for unit volume, in the activated and initial states, respectively. $\mathcal{E}$ is the activation energy per molecule.

It may be noted that, in the publications of Eyring and his school[22], the expression on the right-hand side of equation 22 represents the frequency with which a molecule passes over the potential energy barrier i.e. jumps into a hole. In its deduction no limitation seems to be made on the direction of this jump, and the frequency in question would thus be the frequency in <u>any</u> direction and should correspond to $1/\tau$, that is to 6b. This means that the Eyring equation is incorrect to at least a factor of 6. Since, however, both the Frenkel and Eyring theories are probably only good as order of magnitude theories the introduction or omission of this factor should not be important.

Since Eyring uses the same mechanism for viscosity, essentially the same equation relating viscosity and diffusion is obtained as equation 16. A minor difference is that Eyring differentiates between the distance of jump δ, and the spacing of the molecules. If the distance between adjacent planes is taken as λ_1, λ_2 is the lateral distance between neighbouring molecules at right angles to the direction of motion and λ_3 is the distance between successive molecules in the direction of flow. The effective area of a molecule in a plane is thus $\lambda_2 \lambda_3$ and in place of equation 16, one obtains

$$\eta = \frac{\lambda_1 kT}{\lambda_2 \lambda_3 D} \quad \ldots\ldots\ldots\ldots\ 23.$$

Eyring applied the theory to calculations and found it necessary to assume that λ_1, λ_2 and λ_3 were all approximately equal to δ, as there were no data for these spacings. On the basis of this assumption one comes back, in practice, to equation 16.

The approaches detailed above are attempts which proceed by analogy and are not direct applications of the kinetic theory to the problem of the liquid state. In actual fact their agreement with experimental results has not been very satisfactory. More rigorous and mathematically detailed approaches have been made by Born and Green[23,24], and by Kirkwood[25], but, though these theories are undoubtedly more rigorous, they have not as yet led to expressions which can be tested with experimental data since they deal with monatomic particles or rigid spherical molecules. Furthermore, the required molecular distribution functions and intermolecular forces cannot be readily evaluated for more complex molecules because the data for these are not available and an attempt could not be made to obtain them from, for example, X-ray scattering of the liquids concerned.

1.1.8. Self-diffusion in a Binary Mixture

So far attention has been focussed on self-diffusion as such and it is now desirable to consider the self-diffusion of a component in a binary mixture.

The use of isotopes for labelling is the only method by which the self-diffusion coefficient can be obtained in a pure compound. For mixtures, however, where concentration gradients can be measured by chemical and physical means, interdiffusion coefficients can be evaluated from these measurements. At first sight there is no particular scope for isotopes in these measurements which would involve the use of expensive equipment and would mean the replacement of relatively simple techniques by the complex process of labelling.

If the interdiffusion coefficient is dependent on concentration, however, some difficulties occur since it is necessary, in order to obtain accurate results, to restrict the concentration differences, with the result that the desirable difference might be too small to be measured accurately. The procedure which should strictly be adopted is that, at each average concentration, progressively smaller concentration differences should be used and the resulting interdiffusion coefficients extrapolated to zero concentration difference. This is, however, difficult and cumbersome and by use of isotopes self-diffusion coefficients of the individual constituents can be determined under conditions of negligible concentration gradient.

These self-diffusion coefficients are necessarily individual to each constituent but as will be discussed more fully in 4.1.3 (p. 91), they are related to the interdiffusion coefficient. Interdiffusion is a complex process and it has been increasingly realised in recent years that the self-diffusion coefficients of the individual constituents have more significance than the interdiffusion or the "composite" coefficient. As the greater majority of diffusion coefficients are measured in solutions, i.e. in mixtures, a very wide field of study may be investigated by measuring the self-diffusion coefficients of the constituents by the methods applied to pure liquids.

In order to see in how far these methods could be applied to a mixture and to illustrate the inter-relationship of the various coefficients of a binary mixture, a suitable pair of liquids was chosen. The self-diffusion coefficients of these pure liquids had been determined and self-diffusion coefficients of each were determined at different compositions of the mixture. The full discussion of self-diffusion in a binary mixture is given in Part IV (p. 89 seq.).

1.2. Correlation of Published Diffusion Coefficients and their Relation to Eyring's Views

Ample data on liquid viscosity are available in the literature and have frequently been discussed with respect to the Eyring equations[e.g.26]. Few self-diffusion coefficients of liquids are available, and work on these will be summarised in some detail with particular reference to the Eyring type of equation.

1.2.1. Published Results

The self-diffusion coefficient of liquid lead was measured at a single temperature by Groh and Hevesy[27] who obtained a value of 2.55×10^{-5} cm.^{2}sec.$^{-1}$ at 343°C. Mercury has been investigated by Haissinsky and Cottin[28], and by Hoffman[29]. The work of the former pair was based on isotopic exchange between mercury and an aqueous solution of mercurous nitrate. They assumed that diffusion in the mercury was the rate determining step and put forward arguments to justify their assumptions. The results they obtained differ markedly from those of Hoffman, who used the capillary tube method[30] and so obtained direct values. These values are preferred and are given in the following table:

Table 2: Values for Hg at different temperatures

Temperature °C.	2.5	16.4	23.0	31.9	41.5	66.1	91.2
D x 10^5 cm.^{2}sec.$^{-1}$	1.52	1.68	1.79	1.88	1.98	2.24	2.57

Drickamer and his school have reported values for CS_2[31] and H_2O[32] under pressure and for liquid sulphur[33] at normal and high pressures. Their results will not be quoted but are discussed later (p. 26, the

the second and third paragraphs).

Of all the liquids investigated water has been examined most extensively and results obtained by the different observers are to be found in table 3 together with the tracer used. These tracers were either deuterium, D, tritium, T, or oxygen-18, O^{18}. The superscripts on the column numbers refer to the methods adopted.

Water is, however, not an ideal liquid for measurement of self-diffusion by tracer elements, since substitution of D, T or O^{18} alters its molecular weight and its physical properties measurably. As will be seen from the methods of Temkin(34) and of Lamm(35), differences in density, and in refractive index are sufficiently large to allow for direct measurement of the change in concentration. Lamm indicates that for a ten per cent. concentration of D_2O the viscosity is two per cent. higher than that of normal water. It follows that diffusion coefficients of HTO, HDO and H_2O^{18} in H_2O are not necessarily the same and that none may correspond to the true self-diffusion coefficient for H_2O. Differences were found by Wang(36) in his later work, using diffusion of trace quantities of HDO, HTO and H_2O^{18} in a medium of normal H_2O. In his earlier work(37), he diffused nearly pure D_2O and water containing a high concentration of D_2O into normal H_2O, and this might also be expected to lead to different results from diffusion of trace quantities of HDO. Graupner and Winter(38) report diffusion of D_2O into H_2O, but do not give concentrations. It is probable that the concentration of alleged D_2O was not high, in which case, by exchange between H and D, the deuterium would be mainly present as HDO. Similar remarks apply to the data of Partington et al.(39). In all other cases(40 - 42), concentrations of trace elements were low enough for deuterium to be present predominantly as HDO.

As may be seen from table 3, the results of Orr and Butler are on the whole higher than those reported by the other workers. Graupner and Winter point out that Orr and Butler based their calculations on a diffusion coefficient for KCl which has

Table 3 : Diffusion coefficients of water as $D \times 10^5$ $cm^2 sec^{-1}$

1 Author	2* Orr & Butler	3= Temkin	4° Lamm	5° Rogener	6* Wang	7@ Wang	8@ Wang	9@ Wang	10@ Wang	11* Graupner & Winter	12* Partington et al.	13* Partington et al.	14° Longsworth
Compound	HDO	HDO	HDO	HDO	HDO	D_2O	HDO	HDO	H_2O^{18}	D_2O	H_2O^{18}	HDO	HDO
Temp. °C.													
0.0		1.1				1.00							
0.1	1.46												
1.0													1.13
1.11									1.44				
4.9									1.55				
5.0								1.39					
5.2					1.29	1.23							
10.00							1.57		1.90				
14.3	1.94												
15.0								1.83		1.62		1.90	
16.1						1.65							
17.5				1.77	1.77								
18.0							2.06		2.35				
20.0			2.00										
25.0	2.64				2.12	2.14	2.34	2.44	2.66	2.04	2.09	2.43	2.26
28.0		2.5											
35.0	3.88				2.75	2.76		3.04	3.49	2.73		2.98	
45.0	4.75				3.52	3.45	3.87	3.83	4.38	3.34	3.20	3.60	
55.0					4.39	4.12	4.95		5.45				

*: diaphragm. =: hydrostatic. °: optical. @: capillary tube.

since been shown to be incorrect. Application of the necessary correction factor, 0.974, however, yields values which are still higher than the others. Cuddeback, Koeller and Drickamer[32] in a study on the effect of pressure on diffusion in water, obtained values in agreement with those of Orr and Butler, but this is hardly surprising since they used the results of these authors for purposes of calibration.

Compared graphically, the results of Temkin and Lamm agree with those in columns 8 and 9, and Rogener's result agrees with that in column 6. Longsworth obtained his values by extrapolation to zero concentration and these values are closest to those in columns 8 and 9. For the sake of obtaining better intercomparison the results in columns 6 to 13 have been converted to logarithmic values and are plotted versus the reciprocal of the absolute temperature in figure 2.

Wang's results for the higher concentrations of deuterium agree with one another but are lower than the values obtained for trace concentration studies with D and T, which are in turn lower than the values for H_2O^{18}. Graupner and Winter obtained results in agreement with those in the lowest curve although they also worked with H_2O^{18}. Their method was different but, if there is a definite difference between the diffusion coefficients of the compounds, this should have been apparent in their two sets of results. The values given by Partington et al. cut across the two lower curves. The activation energy is thus lower than is the case for the other curves which agree well in this respect.

In spite of the mass of results for water it appears that agreement for the different methods is poor. Even in diffusion of heavy molecules (like proteins) in water, different methods of measuring diffusion coefficients give different results. It may be queried whether the theory of all methods has as yet been examined with sufficient care. There is certainly a need for critical examination in the case of water as also for a rigorous investigation of the role played by the different tracers.

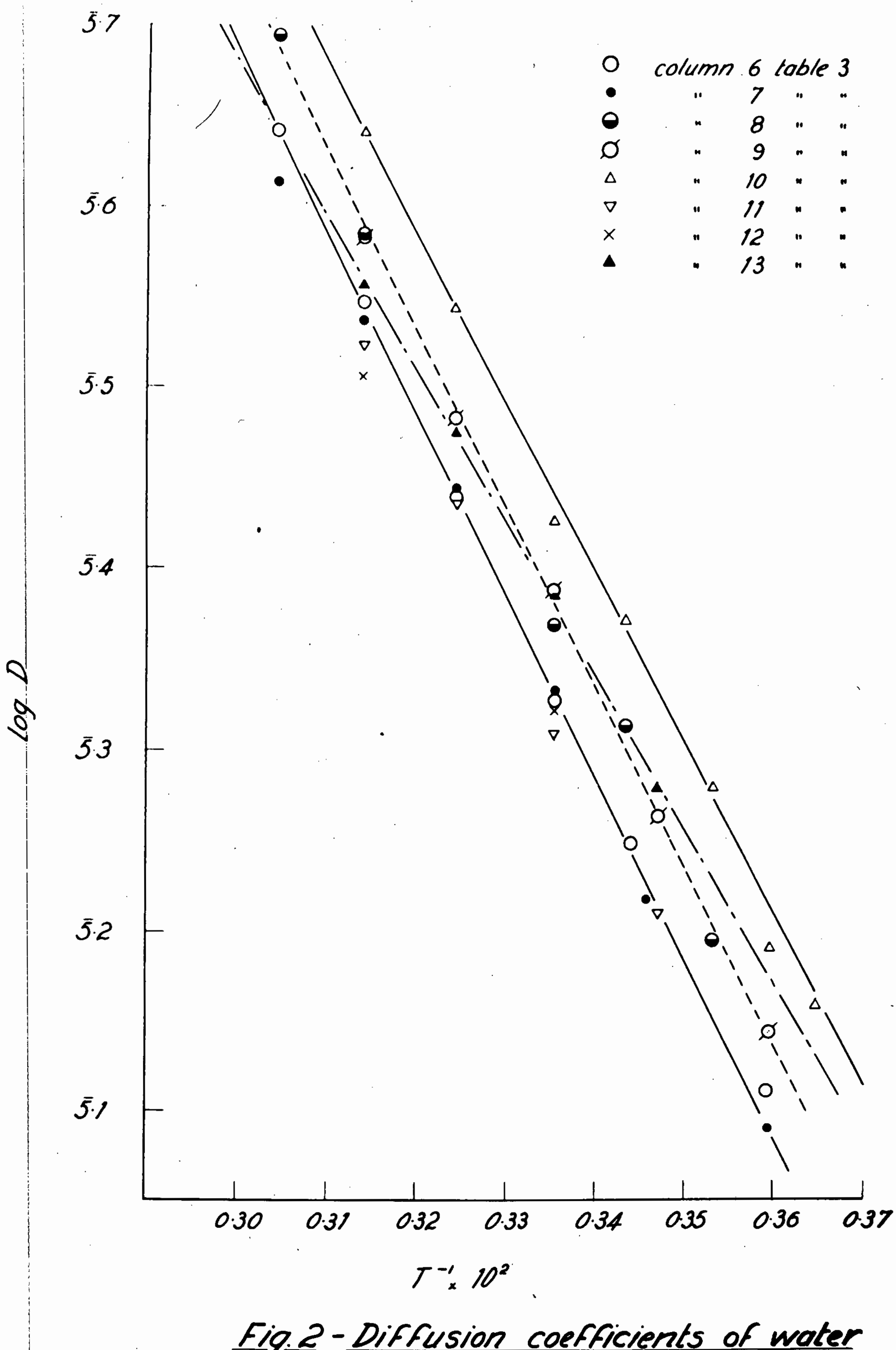

Fig. 2 - Diffusion coefficients of water

Certain organic liquids have also been investigated by Graupner and Winter[38], and by Partington et al.[39]. The former school examined benzene, ethyl bromide and ethyl alcohol using dueterium as tracer. The latter school also used this isotope in their study of methyl, ethyl, n-propyl, iso-propyl, n-butyl and tert-butyl alcohols. Methyl alcohol was also labelled with carbon-14 and results obtained for the two isotopes were in approximate agreement. The following table lists the results reported by these two groups.

Table 4: Diffusion coefficients of some organic liquids

Compound	$D \times 10^5$ cm.^{2}sec.$^{-1}$							Authors
	15°C.	22.5°C.	25°C.	30°C.	35°C.	45°C.	55°C.	
C_6H_6	1.88		2.15		2.40	2.67		Graupner and Winter
EtBr	3.60	3.80		3.96				
EtOH	0.80		1.05		1.31	1.70		
MeOH	1.93		2.27		2.65			Partington et al.
EtOH	0.768		1.01		1.30			
nPrOH	0.504		0.646		0.814	1.017		
isoPrOH	0.474		0.649		0.867	1.145		
nBuOH			0.504		0.649	0.822		
tertBuOH					0.497	0.744	1.07	

Graupner and Winter give errors which were generally better than 3 per cent. for benzene and the alcohol. The errors in the ethyl bromide results are 10, 7 and 5 per cent. Partington et al. obtained internal agreement of 0.3 per cent. with an overall accuracy of 0.5 per cent.

1.2.2. Temperature Dependence of Diffusion and Viscosity

It has been well established experimentally that both diffusion and viscosity coefficients obey an exponential variation with temperature[e.g. 43,44].

$$D = D_o \, e^{-E_D/RT} \qquad \ldots\ldots\ldots\ldots\ 24$$

$$\eta = \eta_o \, e^{E_\eta/RT} \qquad \ldots\ldots\ldots\ldots\ 25$$

Straight lines are normally obtained on plotting log D or log η versus 1/T, and the equations are written in the above form to show that they are activated processes with E_D and E_η as the energies of activation. In some cases E is not independent of temperature. This is especially so for strongly associated liquids.

In the theories of Frenkel and Eyring the same frequency of jump is postulated for both processes, so that E_D and E_η should be the same. It is important to note here, however, that these quantities are obtained experimentally from the gradient of log D or log η versus 1/T. If D_o is not temperature independent, but is proportional to T^n, then, over the limited temperature range of a normal series of experiments, the above plot gives a gradient corresponding to $(E_D + nRT)$. Since, in general, E_D is not many times greater than RT, the correction cannot be ignored. It follows from the theories of Frenkel and Eyring that $D\eta/T$ should be independent of temperature, and, as will be seen in the following section, there is much experimental evidence in favour of this. Thus, if $E_D = E_\eta$, D_o and η_o must vary with temperature in such a way that $D_o\eta_o$ is proportional to T. Conversely, apparent values, E_D' and E_η' obtained experimentally as described above should be related by

$$E_D' = E_\eta' + RT \qquad \ldots\ldots\ldots\ldots\ 26.$$

The difficulty is to decide whether E_D' or E_η' is the correct value of $E_D = E_\eta = E$, or whether the correct value differs from them by nRT. This can be well illustrated by a rather extreme case. Hoffman,(29) from the data in table 2, found $D\eta/T$ constant for mercury over a wide range of temperature. Assuming D_o constant, he found $E_D' = 1.16$ kcal. and he obtained an agreeing value of 1.25 kcal. by plotting log η/T versus 1/T. Alternatively, he could have obtained agreement by plotting log D/T versus 1/T and log η versus 1/T, respectively, but the values would then have both been lower by about 0.64 kcal., the value of RT at 47°C., the mid-point of the temperature range. In the case of mercury, the value of E_D' is so little above the value of RT that it can be questioned if diffusion and viscosity require an energy of activation at all.

In the case of water, Wang(36) obtained straight lines on plotting log D versus 1/T although the results indicate that below capillary method. It was found that $D\eta/T$ at constant pressure increased only a few per cent. over a temperature range of $30^{\circ}C.$, and that, if temperatures were chosen so that comparison was made at constant molecular volume, values of $D\eta/T$ were almost independent of pressure. Before the results of Drickamer's school can be accepted, they should be confirmed by other workers using other substances and, preferably, other methods.

From equation 27 molecular parameters which are of interest may be calculated. Assuming that $\lambda_1 = \lambda_2 = \lambda_3 \simeq 2r$, Hoffman calculated the value of r to be 7.54 A. The expected value for the mercury atom is 1.5 A, and the value derived from the molecular volume is 1.45 A. Agreement is not good particularly as Eyring[48] has suggested that in a liquid metal the unit of flow is the ion rather than the atom, in which case the radius should be about 0.7 A.

On the basis of the results of Orr and Butler for water, Eyring[21,49] calculated that $\lambda_2 \lambda_3 / \lambda_1 = 1.4 \times 10^{-7}$ cm. On assuming as did Hoffman that $\lambda_1 = \lambda_2 = \lambda_3 = 2r$, a value of 7 A. is obtained for the radius of the water molecule. This is very much larger than the expected value of 1.4 A. obtained from the van der Waals' radii or that calculated from the molecular volume, namely 1.55 A. From the value for $\lambda_2 \lambda_3/\lambda_1$ Eyring, assuming that $\lambda_1 \lambda_2 \lambda_3$ was equal to the effective volume of a single molecule, calculated a value of $\lambda_1 = 1.45$ A. and $(\lambda_2 \lambda_3)^{\frac{1}{2}} = 4.52$ A. λ_1 is thus smaller than $(\lambda_2 \lambda_3)^{\frac{1}{2}}$ and probably smaller than either λ_2 or λ_3. This he maintained was in agreement with the expectation that the plane of flow in diffusion tends to coincide with the plane of the water molecule. The value of λ_1 is, however, very much less than the expected value of 2r and though there is justification for assuming a planar configuration due to the strongly directional field of force around the water molecule, the smallest diameter possible is that of the co-valently bound oxygen viz. 2.64 A., which is greater than the value of λ_1. The value of $(\lambda_2 \lambda_3)^{\frac{1}{2}}$ is, on the other hand considerably greater than expected.

These calculations were based on diffusion coefficients which are higher than those found by modern workers. On the basis of Wang's results for HTO, however, it can be calculated that since $D\eta/T = 7.29 \times 10^{10}$, $\lambda_2\lambda_3/\lambda_1 = 1.89 \times 10^{-7}$ cm., $\lambda_1 = 1.26$ A. and $(\lambda_2\lambda_3)^{\frac{1}{2}} = 4.88$ A. These values are in no better agreement with the expected results than are the above. Wang calculated a value for $\delta = 1.5$ A., for the distance of jump, from an equation by Eyring[45] relating diffusion to the time of dielectric relaxation. This value is also smaller than the diameter of the water molecule. It is apparent therefore, that though the Eyring equation allows one to differentiate between λ_1 and $\lambda_2\lambda_3$ neither these values nor those from the simpler Frenkel equation are satisfactory.

The Stokes-Einstein equation, $D\eta/kT = 1/6\pi r$, gives a similar relationship and, if applied, the radius for mercury is 0.80 A. as compared with the expected ionic radius of 0.7 A. Hoffman also calculated a value for lead from the result of Groh and Hevesy and found $r = 0.84$ A., which lies between the expected values of 1.18 and 0.7 A. for bivalent and tetravalent lead ions. The value for water calculated according to this equation is 0.75 A. On the whole, radii calculated according to the Stokes-Einstein equation seem to be more reasonable despite its lack of a plausible theoretical background.

1.2.4. Comparison between Experimental Measurements and the Eyring Equation

The equation for diffusion is developed further by Eyring[50] on a quasi-thermodynamical basis in the following manner:

$$D = \delta^2 \frac{kT}{h} \frac{Q^{\ddagger}}{Q} e^{-\mathcal{E}/kT} \qquad \text{.............. 28}$$

and since

$$\frac{Q^{\ddagger}}{Q} e^{-\mathcal{E}/kT} = e^{-\Delta G^{\ddagger}/RT} \qquad \text{.............. 29}$$

$$D = \delta^2 \frac{kT}{h} e^{-\Delta G^{\ddagger}/RT} \qquad \text{.............. 30}$$

and $$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \text{.............} \; 31$$

so that $$D = \delta^2 \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \qquad \text{............} \; 32$$

where $\Delta G^{\ddagger}$ is the free energy of activation, $\Delta H^{\ddagger}$ the heat of activation and $\Delta S^{\ddagger}$ the entropy change of activation. Since diffusion is accompanied by a negligible volume change[50] it follows that $\Delta H^{\ddagger} = \Delta E^{\ddagger}$, where $\Delta E^{\ddagger}$ is the internal energy of activation. If E_D' is the experimental energy of activation obtained by plotting log D versus 1/T and $\Delta S^{\ddagger}$ is independent of temperature, then $\Delta E^{\ddagger} = E_D' - RT$. It may be noted in passing that, according to this, we should get correct values of E_D and E' by plotting log D/T versus 1/T and log η versus 1/T.

Eyring assumes that $\lambda_1 = \lambda_2 = \lambda_3 = \delta = (V/N)^{\frac{1}{3}}$, the cube root of the molecular volume, and $\Delta G^{\ddagger}$ may be evaluated by substitution in equation 30 at a given temperature. $(E_D'-RT)$ is known experimentally so that $\Delta S^{\ddagger}$ can be obtained by substitution in equation 31 since $\Delta H^{\ddagger} = E_D' - RT$.

Values for $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ have been calculated by Partington et al.[39] at 35°C. and are tabulated below:

Table 6: Free energy and change in entropy

Compound	H_2O	MeOH	EtOH	nPrOH	isoPrOH	nBuOH	tertBuOH
$\Delta G^{\ddagger}$ kcal./mole	3.26	3.66	4.25	4.63	4.60	4.85	5.03
$\Delta S^{\ddagger}$ E.U.	0.20	-4.87	-0.78	-3.21	0.29	-2.79	6.04

The most striking feature is the small, but regular, increase in $\Delta G^{\ddagger}$ with increasing molecular weight although the individual values of energy and entropy of activation vary in an irregular manner. Values for two pairs of isomers are recorded in table 6 and it will be noted that the values of $\Delta G^{\ddagger}$ are, in each case, approximately the same, although the activation energies for the butyl alcohols differ widely.

An alternative way[51] of dealing with Eyring's equation is to evaluate the partition function ratio $Q_{\ddagger}/Q$ in equation 28 and hence calculate a value for D. If we adopt the simple cage model for a liquid in which each molecule is envisaged as confined to, but moving within a free volume v_f, it can be shown that the contribution Q_{tr} to the partition function, corresponding to the three translational degrees of freedom, is the same as for a gas molecule moving within a volume v_f. That is

$$Q_{tr} = \frac{(2\pi mkT)^{3/2}}{h^3} v_f \qquad \text{.............} \quad 33.$$

Contributions due to inner rotations and vibrations of the molecules may be neglected, if we consider them the same for the normal and activated states. The activated state, according to Eyring's theory has one degree of freedom less, whence

$$Q_{tr}{}^{\ddagger} = \frac{(2\pi mkT)}{h^2} (v_f)^{\frac{2}{3}} \qquad \text{.............} \quad 34.$$

Substituting in equation 28,

$$D = \delta^2 \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} (v_f)^{-\frac{1}{3}} \; e^{-E_D/RT} \qquad \text{.............} \quad 35.$$

For the evaluation of this equation it is necessary to know E_D and v_f. For a rigid molecular lattice, E_D should equal E_{vap}, the energy of vaporisation. That is to say the energy necessary to form a hole of molecular dimensions equals that of a molecule leaving the surface. It has been found, however, that the energy for movement in a material is not as high as for movement out of it. One can only assume that holes of molecular size are not required for movement within the material. Assuming that the energy of activation for viscous flow is nearly that for diffusion, Eyring shows that for non-metallic liquids the ratio of the energy of evaporation to that for viscous flow is on the average about 3.5. Graupner and Winter[38] obtained results varying from 2.5 to 3.5 for E_{vap}/E'_{η} and for E_{vap}/E'_D the variation was even greater.

An estimate of the free volume v_f, may be obtained by various methods. One of these is the comparison of the velocity of sound in gases and in liquids as given by Kincaid and Eyring[52]. As this comparison is difficult to make without the relevant data, other equations have been derived by Eyring and co-workers[53].

Thus

$$v_f = \frac{cRT}{E_{vap}} \left(\frac{V}{N}\right)^{\frac{1}{3}} \quad \ldots\ldots\ldots\ldots\ldots\ 36$$

or

$$v_f = \frac{RT}{NP_v} e^{-(E_{vap} + RT)/RT} \quad \ldots\ldots\ldots\ldots\ldots\ 37$$

where c is a constant depending on the packing of the molecules and P_v is the vapour pressure of the liquid. For cubical packing c is taken as 2. Agreement between values for the free volume obtained by different methods is not good. Since, however, the free volume enters into results only as the cube-root, an uncertainty is not of very great importance.

By putting $\delta = (V/N)^{\frac{1}{3}}$, D can be evaluated by substitution of one or other of the v_f equations in equation 35. In Glasstone, Laidler and Eyring[22] values of D have been calculated for various cases of interdiffusion by using v_f as given in equation 36, and $E_{vap}/3$ for E_D. On the whole the calculated values are about twice as large as the observed.

The only application of equation 35 to self-diffusion has been carried out by Graupner and Winter using equation 37 for the evaluation of v_f, that is

$$D = \left(\frac{V}{N}\right)^{\frac{2}{3}} \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \left(\frac{RT}{NP_v} e^{-(E_{vap} + RT)/RT}\right)^{-\frac{1}{3}} e^{-E_D/RT}$$

$$\ldots\ldots\ldots\ldots\ldots\ 38$$

Instead of using E_{vap}/n for the evaluation of E_D they employed their own experimental values. In table 7 their observed and calculated values for D_o are given together with the ratio $R = D_{obs.}/D_{calc.}$ The authors have pointed out that R is greater than one for associated liquids and R is less than one for the normal liquid.

Table 7: Comparison of calculated and observed values of diffusion constants and coefficients

Compound	Temp. °C.	D_o calculated $cm^2sec.^{-1}$	D_o observed $cm^2sec.^{-1}$	R
C_6H_6	15	2.75×10^{-3}	7.75×10^{-4}	0.261
	25	2.63 "		0.278
	35	2.49 "		0.291
	45	2.38 "		0.305
EtOH	15	6.10 "	2.37×10^{-2}	3.24
	25	6.52 "		3.06
	35	6.59 "		2.95
	45	6.35 "		3.16
H_2O	15	4.87 "	3.78×10^{-2}	9.76
	25	4.63 "		9.99
	35	4.42 "		10.8
	45	4.24 "		10.7

It has been seen in equation 28, that D_o is approximately proportional to T and, depending on the temperature dependence of v_f, it is proportional in equation 38 to some power of T between $\frac{1}{2}$ and unity. A criticism of Graupner and Winter's calculation is thus that their "experimental" value of E_D is really E_D', and should thus be decreased by approximately RT. This would mean dividing all values of R in table 7 by approximately e = 2.72.

A further consideration in calculating absolute values of D is the error introduced where the factor of 1/6 has been omitted from Eyring's equation as discussed earlier. (p.16, paragraph below equation 22). In table 7 its introduction would cause all values of R to be multiplied by 6.

PART II

EXPERIMENTAL

2.1. Preparation, Purification and Labelling of Materials

Only relevant details are given with regard to the work carried out since the methods and techniques involved were those used in general practice in organic chemistry[54].

2.1.1. Synthesis of Alkyl Halides

Though most of the halides used were eventually obtained from overseas, only methyl iodide, ethyl bromide and sec-butyl bromide were initially available. In order to have a wider variety of materials with which to work, ethyl iodide, n-propyl bromide and n-propyl iodide were synthesised from readily available starting materials. For the later interdiffusion work it was also found necessary to prepare n-butyl iodide.

Ethyl iodide was synthesised according to the following reaction:

$$(C_2H_5)_2SO_4 + 2KI \longrightarrow 2C_2H_5I + K_2SO_4$$

n-Propyl bromide was similarly prepared but with n-propyl alcohol as the starting material. This was purified before use in order to preclude the formation of isomeric products. The sulphate was formed in situ in the presence of potassium bromide solution.

In the case of n-propyl iodide and n-butyl iodide, esterification was carried out according to the following reaction:

$$3ROH + PI_3 \longrightarrow 3RI + P(OH)_3$$

where R refers to the alkyl group. The phosphorus tri-iodide was prepared in situ by addition of iodine to red phosphorus in the presence of the purified alcohols.

2.1.2. Purification of Materials

The halides were, where necessary, washed repeatedly with a ten per cent. solution of sodium carbonate, dried over anhydrous potassium carbonate or calcium chloride, filtered and fractionally distilled at normal or reduced pressures. The latter procedure was essential in the case of the higher boiling compounds as these decomposed so readily. All materials had to be purified from time to time as they became coloured with use and storage, even though contained in brown glass bottles and kept in the dark. Purity criteria were the boiling points[10,55] of the constant boiling fractions related to the pressure at which they were distilled, and the refractive indices[10,55] for the D-line measured with an Abbé refractometer.

The materials used either as solvents in the labelling of the halides (p. 36) or as standards for viscosity measurements (2.4.3.(a), p. 67 and 2.4.3.(c), p. 68) were purified by distillation. Commercial chloroform was used for sample preparation and was recovered by fractional distillation. The chemical purity of the solvent was unimportant but fractionation was necessary to remove active iodides so that on re-use there would be no contribution of activity by the solvent. Solvent contaminated with bromides was allowed to stand until the bromine activity had decayed.

2.1.3. Labelling of Halides

(a) General considerations

Labelling was carried out by an exchange reaction between the labelled lithium salt of the halogen concerned and the desired compound in a suitable solvent[56]. The choice of solvent was dependent on the boiling point of the alkyl halide as it had to be readily separable from this by fractional distillation.

In preparing samples of the alkyl halides for counting (2.3.3.(a), p. 53), dilutions of 10^4 were necessary at the start of an experiment so that the activity of the original material had to be fairly high, about 1.5 millicuries. The fraction of the total activity to be expected in the alkyl halide after complete exchange is equal to the molal concentration of alkyl halide relative to the total molal concentration of iodide in the mixture. The lower the lithium halide concentration, therefore, the higher will be the fraction of active iodine in the organic material. Use of lithium halides of high specific activity thus avoided unnecessary waste and reduced handling risks.

In the case of I^{131} high specific activities were obtainable since this material is received from the Atomic Energy Research Establishment in England, as an aqueous solution of iodide and is virtually free of stable iodine by virtue of the fact that it is prepared from tellurium by the following nuclear reaction:[57]

$$Te^{130}\,(n,\gamma)\;\; Te^{131} \xrightarrow[\beta^-]{25\ \text{min.}} I^{131}.$$

Then I^{131} is separated from the tellurium by chemical methods[58].

Radioactive bromine is, however, prepared from the stable isotopes Br^{79} and Br^{81}, the natural abundances of which are 50.51 and 49.49 per cent. respectively, and the specific activities are not high. The reactions involved are[57]

$$Br^{79}\,(n,\gamma)\;\; Br^{80}$$

and

$$Br^{81}\,(n,\gamma)\;\; Br^{82}.$$

Br^{80} has a half-life of 4.4 hours[57] and though the activity due to this isotope is initially high, by the time a sample is counted in Pretoria it has decayed 16 half-lives and less than 1/65536 of the original activity is left. In this time the Br^{82} has decayed through two half-lives and the contribution from the Br^{80} is negligible.

Since the specific activity of the bromide was poor, larger amounts of this had to be used in the exchange reaction and as the activity decreased fairly rapidly with time it was necessary to use still higher activities and longer times of exchange when a second compound was to be labelled from the one batch of active material.

(b) Preparation of the lithium halides

Lithium iodide was obtained by adding 0.1 ml. of a 0.1N solution of lithium hydroxide to a suitable aliquot of I^{131} solution. Evaporation of this mixture resulted in solid lithium iodide and hydroxide.

The first two shipments of active bromine were in the form of the potassium salt in solution and thereafter it arrived as solid ammonium bromide. In most cases the material was shared with Dr. le Roux of Pretoria University. The first three shipments were converted to lithium bromide by him on the basis of the following reactions:

$$KBr + AgNO_3 \longrightarrow AgBr + KNO_3$$

or

$$NH_4Br + AgNO_3 \longrightarrow AgBr + NH_4NO_3$$

$$AgBr + H_2 \xrightarrow{700^\circ C} HBr + Ag$$

$$HBr + LiOH \longrightarrow LiBr + H_2O$$

This method was cumbersome and exposed the operator to large doses of activity, vide 2.2.5. p. 47, particularly when ammonium bromide was used as this was of higher activity than the potassium solutions. The preparation was then undertaken by myself. Lithium hydroxide solution was added to an aqueous solution of the ammonium salt in sufficient quantity to liberate all the ammonia. Evaporation of water and ammonia from suitable aliquots yielded dry lithium bromide and a small amount of lithium hydroxide.

(c) The exchange reaction

Addition of 5 ml. of acetone, methyl ethyl ketone or ethylene glycol diacetate to the dry salts, ensured solution of the halogenated salt, but left the hydroxide undissolved. 5 to 10 ml. of the compound were added and the mixture was heated for about an hour at a temperature of from 40 to 60°C, at which stage sufficient exchange had occurred. The solvent and compound were carefully separated by fractional distillation at reduced pressure and the pure fraction so obtained was ready for use. Purity was checked as in 2.1.2. above and since the volume of fractions was generally in the region of 0.75 ml. good separation was achieved and redistillation

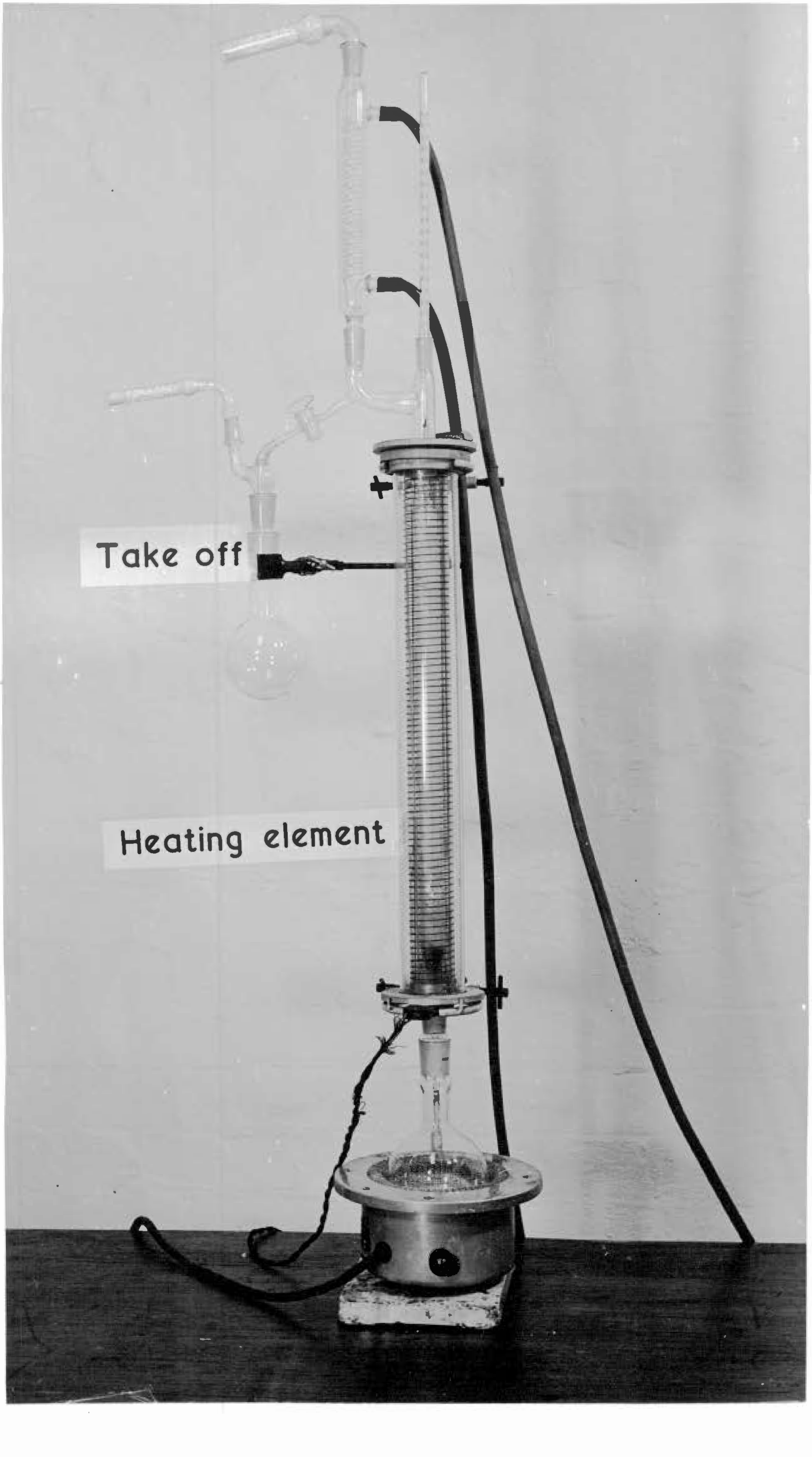

Fig.3-Fractionating column

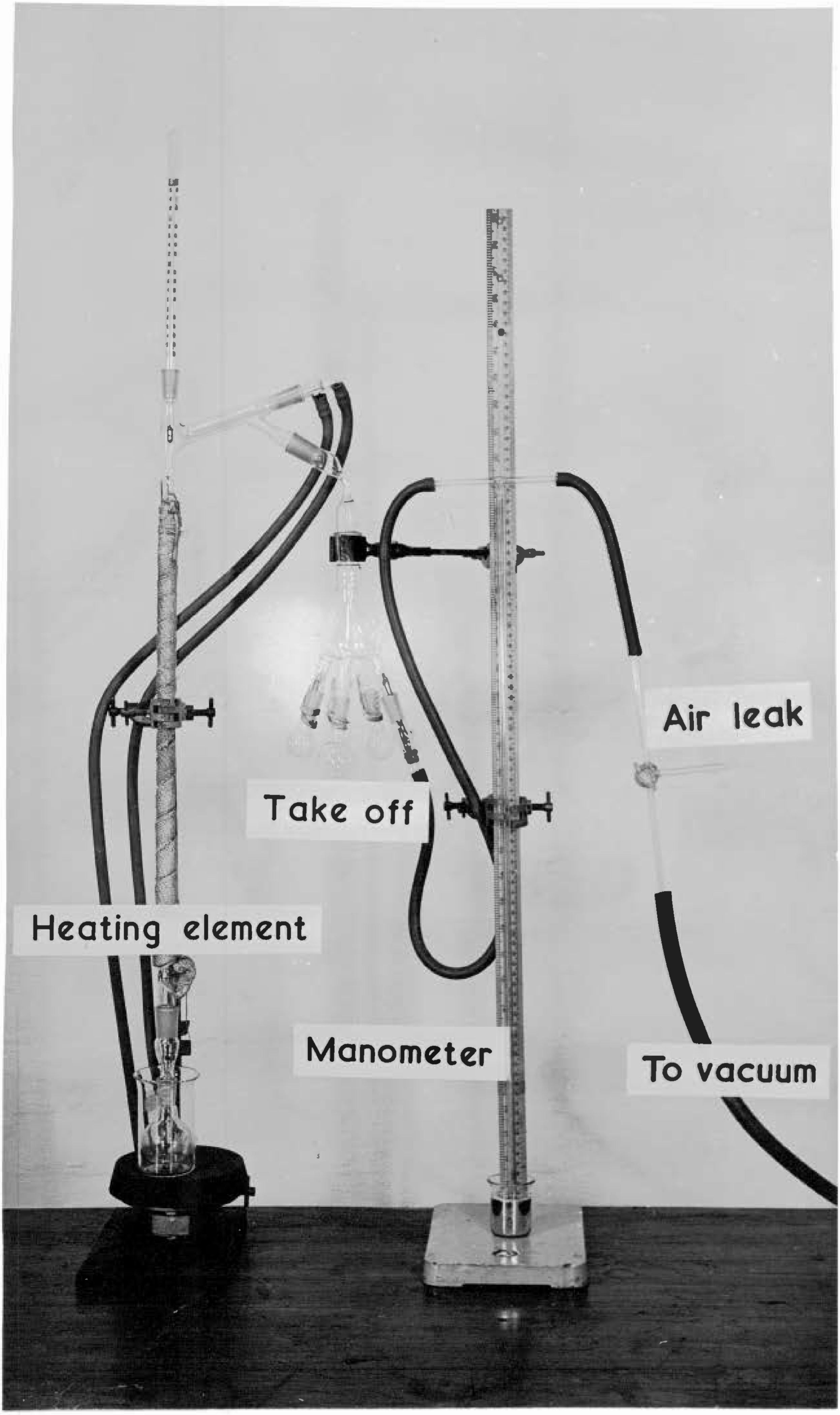

Fig.4 - Small fractionating column

2.2. Measurement of Radioactivity

2.2.1. Choice of Counter

The types of instrument and the methods available for assessing radiation from radioactive materials have been competently dealt with in the literature(59) and further discussion of these is beyond the scope of this work. By virtue of the amount of radioactive material which could be safely and conveniently handled, a Geiger-Muller type of counter was selected. These counters are reasonably sensitive and the electronic equipment associated with their use is of fairly rugged design and gives good continuous service if properly maintained.

Since both Br^{82} and I^{131} are γ and β emitters the consideration of design of counter resolved itself into a choice between solid counting with an end-window counter and liquid counting with a solution counter. The latter method was adopted since the samples were liquid and could be readily brought into solution whereas the conversion of 0.01 ml. of a volatile liquid into a solid sample would have been very difficult. In addition it is easier to attain reproducibility of geometry with a liquid counter.

The counters used were of the self-quenching type with an external quenching time superimposed on them to ensure uniformity as each counter has its own individual dead-time. The correction which must be applied to a count to allow for those incidents which occur during the dead-time, is discussed in 2.2.4.(d) (pp. 45, 46).

2.2.2. Apparatus

(a) Counters

Liquid counters of type M6 and M12, as manufactured by 20th Century Electronics following the design of Veall(60), consist of a glass skirt around a cylindrical Geiger-Muller tube. This skirt protrudes slightly beyond the counter as may be seen from

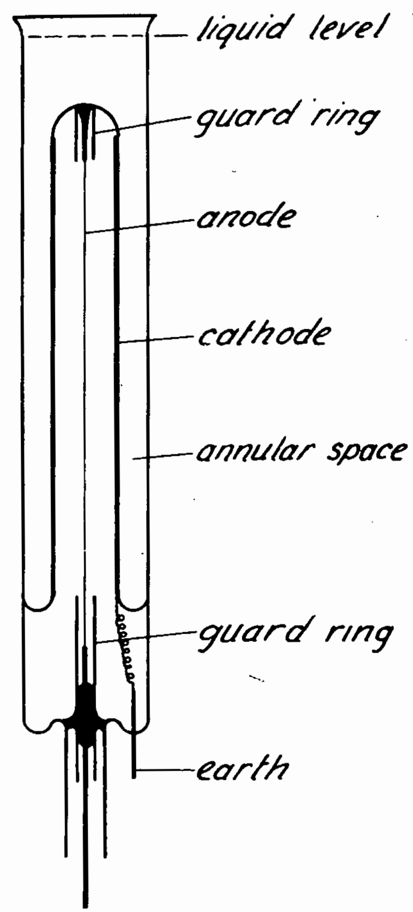

Fig. 5 - Liquid counter

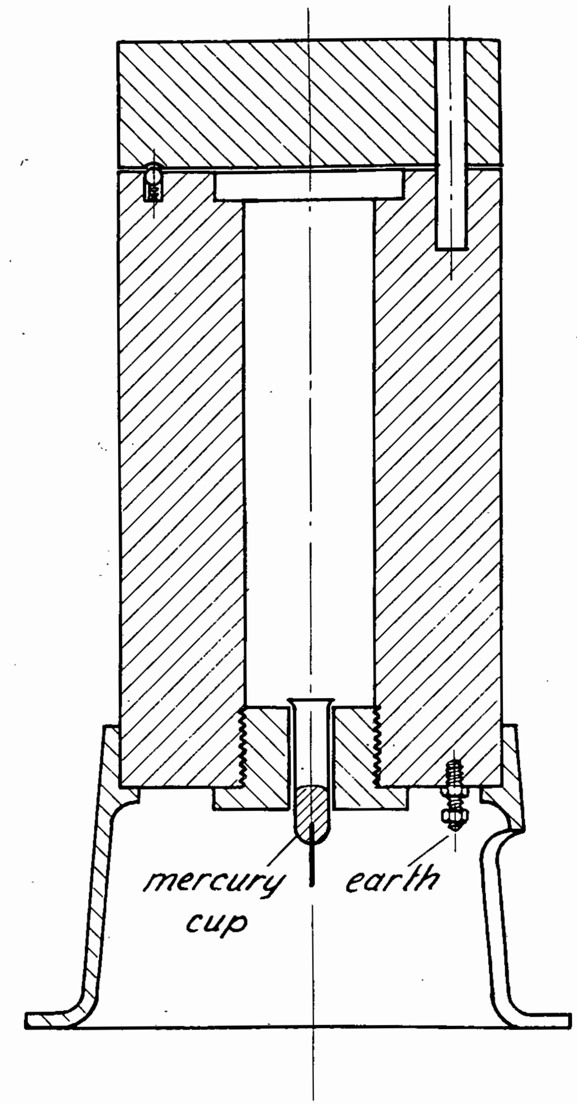

Fig. 6 - Lead castle

figure 5, and liquid is contained in the annular space between the counter and the skirt. Providing the liquid is always at the same level in the tube the geometry is fixed. The M6 and M12 counters have capacities of about 12 ml. and 17 ml., respectively.

(b) Lead Castle

In order to protect the counter from external radiation either of cosmic, laboratory source or of light origin, it is enclosed in lead in what is referred to as a castle. The design of one type is given in figure 6 and follows the pattern as manufactured by ERD Engineering Company, Slough. It consists of a hollow lead cylinder with a sliding cover and the wall thickness is about $1\frac{1}{2}$ inches. A glass cup with platinum electrode, and partly filled with mercury, is held at the bottom of the castle in a threaded brass container. The counter, with anode connection in the mercury is supported on the cathode connector which rests on the brass. Since the brass is screwed into the castle and this is in turn earthed, the cathode is at earth potential. The anode is connected via the platinum electrode and a screened cable to the probe unit and high tension supply.

(c) Electronic equipment

The Dynatron type 200A <u>scaling unit</u> was used to count and register the number of pulses arriving in a random manner over a period of time. The design consists of two electronic scales of ten with neon indicators which successively register units and tens and are followed by a mechanical register of four digits. For use with the counters described, the paralysis time was set at 300 μs.

A type 1014A <u>probe unit</u> was used to reduce the potential applied to the anode of the counter by some 240 volts (for a dead-time setting of 300 μs.) following each registered pulse. This unit provided an output pulse suitable for operating the scaling unit from which it drew the necessary power for operation.

The power unit was a Dynatron type P200A, and provided a stable voltage source for operating the counters. Regulation was such that 10 per cent. variations in mains voltages were reduced to fluctuations of not more than 0.66 per cent. in the output voltage.

The counting set up can be seen in figure 7.

(d) Standard

For checking day to day stability a reference source or standard was constructed from a thin brass tube of dimensions such that it fitted into the annular space in the counters. At a point on this tube a groove was cut so that when in position in a counter it was well within the counting volume. This ensured that a cobalt-60 source (5.3 years half-life[57]) sealed into this groove, was always in a position of reproducible geometry.

2.2.3. Procedure

The electronic equipment was allowed to warm up for a few minutes and the high tension adjusted to the required value for the counter chosen. The standard was counted for a period such that at least 10,000 counts were registered and the rate was calculated. If this did not agree with previous results within the statistical error to be expected, vide 2.2.4.(a), the count was repeated until the required reproducibility had been attained or the reason for bad behaviour ascertained, and rectified. When the instruments were found to be satisfactory, the standard was removed and the counter filled with the solvent to be used for the preparation of samples. This was counted for a period of approximately the same duration as estimated for subsequent samples. Reduced to a counting rate this was the blank or background and is due to radiation which has penetrated the lead screening.

The sample to be counted, having been made up to a desired volume (2.3.3.(a), p. 53) was used to rinse out the counter at least three times. The counter was filled to a predetermined level and the sample counted at the same voltage in the castle for

Fig. 7- Counting Equipment

a period of time sufficient to give the statistical accuracy desired. The counting rate was calculated and corrected for background.

2.2.4. Sources of Error and their Experimental Assessment

(a) Statistical

All physical measurements are subject to error, and it is desirable that the magnitude of this possible deviation of the observed result from the true one, be known. The errors associated with Geiger-Muller radioactivity measurements are due largely to the random nature of the disintegration and background processes. The most useful error formula is that for the standard deviation of a series of observations, the figure obtained being a measure of the relative precision of all the measurements and their internal consistency. If n determinations of a certain quantity x are made, the standard deviation of the mean value $\bar{x}$ is given by the relation:

$$\text{Standard deviation} = \sqrt{\frac{\sum_{i=o}^{n} (\bar{x} - x_i)^2}{n(n-1)}} \qquad \text{.......... 39.}$$

Since individual nuclei decay independently of one another, the laws of probability can be applied to the observed results from counting these random incidents. Errors due to the measuring instruments can be noted because they cause large or erratic departure from the deviations calculated on the assumption of a random disintegration process. A series of similar determinations on a sample result in a number of different values which, if we assume that decay is not appreciable, will be distributed about an average value in a random manner.

Suppose that $\bar{n}$ is the average number of particles detectable in a given time interval, the probability P_n that n particles will actually be detected in this interval is given by the Poisson relation[61]

$$P_n = \frac{(\bar{n})^n e^{-\bar{n}}}{n!} \qquad \text{.......... 40.}$$

to background of 20, the errors in background determination could be neglected.

(b) Radioactive decay

Radioactivity is a chance phenomenon, and the rate of disintegration cannot be affected by any known physical or chemical process or condition. It has been shown that the rate of decay at any instant is proportional to the number of unstable nuclei present[62]. The relation is expressed as follows:

$$-dN/dt = KN \qquad \text{.............. 42}$$

Integration of this equation gives

$$N = N_o e^{-Kt} \qquad \text{.............. 43}$$

where N_o is the original number of unstable nuclei at time $t = 0$, N is the number present after time t, and K is the disintegration constant. The half-life $t_{\frac{1}{2}}$ is the time in which the activity of an isotope has decreased to half and $t_{\frac{1}{2}} = \ln 2/K$. Equation 43 can thus be written as

$$0.4343 \log N/N_o = \frac{-0.6931}{t_{\frac{1}{2}}} t \qquad \text{.............. 44}$$

and by plotting $\log N/N_o$ versus t, the half-life can be evaluated from the slope of the resultant straight line. Alternatively, if the half-life is known, any results obtained can be corrected to $t = 0$.

While the half-life of I^{131} is well established[4] the value for Br^{82} as given in the literature when this work was commenced, varied from 34 to 36.1 hours. Two determinations were carried out and the results obtained were plotted according to the above equation. The results obtained were 36.05 and 36.1 hours as calculated from the plots in figure 8. Subsequently a report[63], of an accurate determination, was obtained and the value as given there of 35.9 hours, has been used throughout. Using the correct half-lives, the error due to decay should not exceed that due to randomisation.

(c) Reliability of counting

When the voltage applied to a counter, exposed to a source of radiation, is increased from zero, a threshold value is

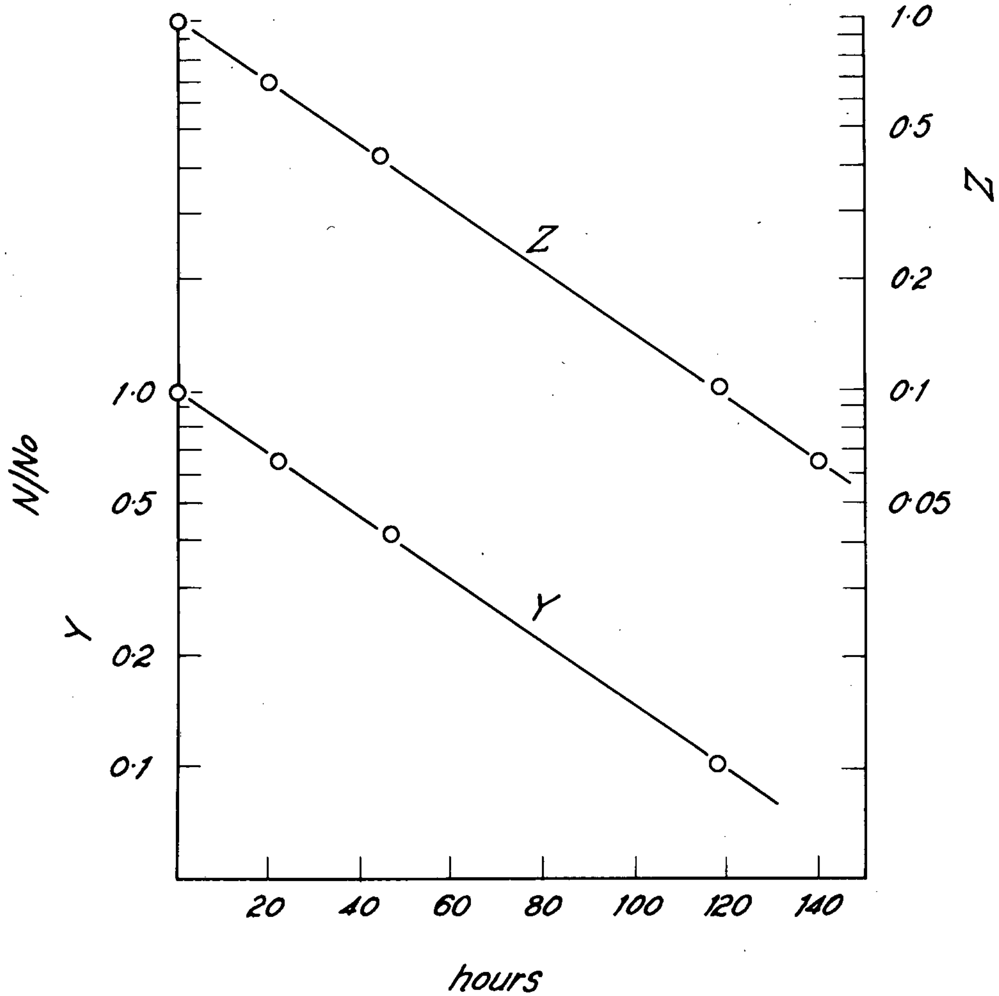

Fig. 8- Decay curves for Br^{82}

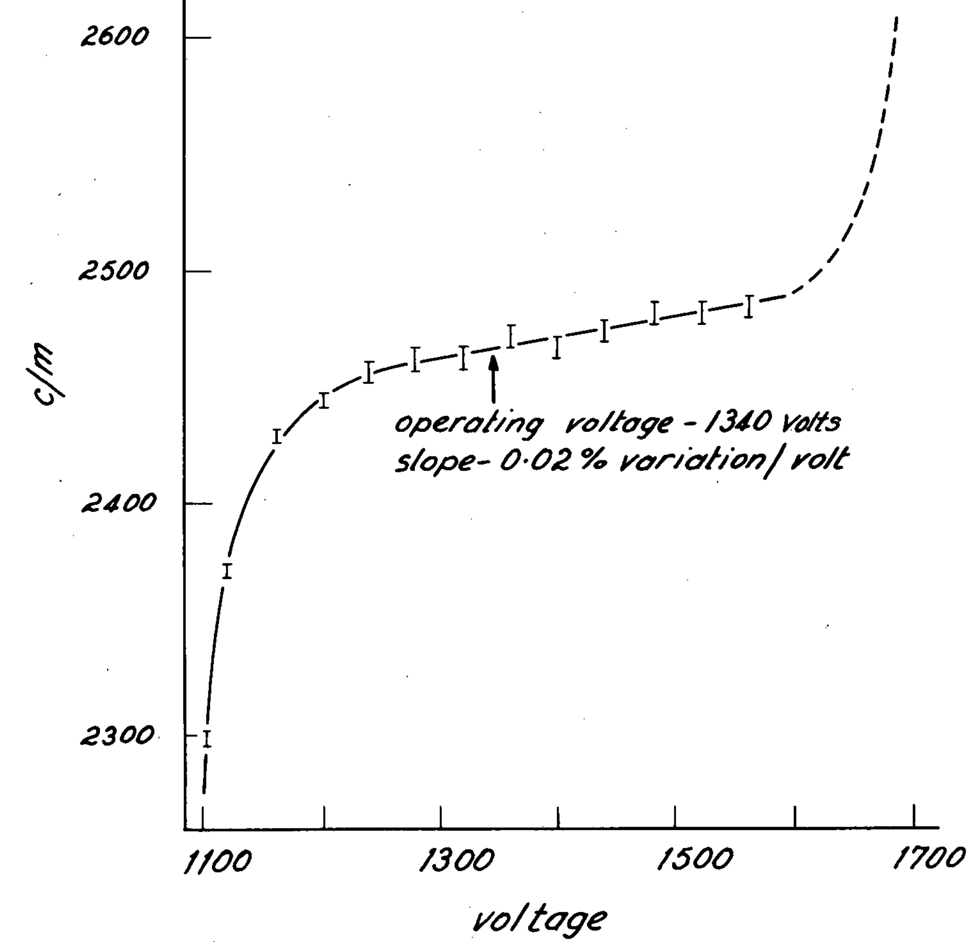

Fig. 9 - Counter plateau

reached at which the counter begins to operate. Further slight increases result in a rapid rise in counting rate to a value which should only increase gradually with further increases of the voltage. This latter region is referred to as the plateau and it is necessary to select a position on this plateau at which to operate the counter. This voltage is generally 60 volts above that at which the first reliable count is obtained. It is also necessary to select counters such that the plateau slope is less than 0.05 per cent. for the rise in counting rate per volt increase. For a 20 volt change in mains voltage of 220 volts, therefore, the error due to the resultant variation of 0.66 per cent. in the counter voltage, will not exceed 0.4 per cent. of the counting rate since the counters used were normally operated in the region of 1150 volts.

An example of a plateau is given in figure 9 in which the counting rate is plotted versus voltage applied. The plateau which extends over at least 300 volts was not completed but the full curve is indicated to illustrate the region of continuous discharge. Counters were checked from time to time to ensure that the characteristics were still suitable and conformed to the limits set.

To check overall reliability of the complete equipment, the standard was counted at various periods during a day and for a number of successive days. The results are given in table 8.

Table 8: Counting reproducibility

Experiment 1				Experiment 2			
Date	Time	c./m.	Mean	Date	Time	c./m.	Mean
13	9	1764		13	9	1764	
	10	1771			12	1777	
	11	1765			16	1758	
	12	1777		14	9	1801	
	14	1778	1768 ± 3		12	1775	1766 ± 6
	15	1759			16	1753	
	16	1758		15	9	1746	
	17	1759			12	1777	
	18	1781			16	1738	
Maximum deviation		13		Maximum deviation		35	

The standard deviation in both cases is well within the expected statistical error of 0.8 per cent. This type of test indicated two sources of error, namely that overheating of the scaling unit caused a bias in the results during the course of a day, and that after some 23 months of continuous operation the scaler valves were becoming unreliable as fluctuations in the counting rates were greater than was expected from the number of incidents observed. By directing a fan onto the scaling unit the first source of error was minimised and by replacing the suspect valves the instrument was again brought into reliable operation.

(d) Coincidence correction

All instruments of detection have a finite resolving time which limits their ability to respond separately to events occurring close together, and corrections for this effect must be made where it exceeds the desired accuracy. Several authors [(64)] have reviewed the techniques available for determining the dead-time. These in order of accuracy and difficulty are: (i) single paired-source measurements, (ii) measurement of sources of known relative intensity and (iii) multiple paired-source measurements with least-squares analysis of the data.

The probe and scaling units used were set for 300 μs. and as it was intended that counting rates should not exceed 2,000 c./m. and thus involve corrections of less than 1 per cent., the first method was adopted to check the resolving time for the counting equipment. This method is based on the following argument: During each dead-time interval ϕ, the number of lost counts will depend on the true counting rate N, and on the average will be ϕN. If n is the observed counting rate, there will be n intervals per unit of time when this loss occurs. The total loss will therefore be ϕNn counts per unit of time, and the true counting rate $N = n + \phi Nn$ or, since N is approximately equal to n,

$$N = n + \phi n^2 \qquad \text{.............. 45.}$$

For nett counting rates the background count must be subtracted.

If two samples A and B, of approximately equal strength are counted independently and together, counting rates n_A, n_B and n_{AB} counts per sec, are obtained. (Care must be taken to maintain the same goemetry.) With both samples removed the background count n_b c./s. can be measured. According to equation 45 nett counting rate

$$N_A = n_A + \phi n_A^2 - n_b ,$$

$$N_B = n_B + \phi n_B^2 - n_b ,$$

and $$N_{AB} = n_{AB} + \phi n_{AB}^2 - n_b$$

and, since $N_{AB} = N_A + N_B$, the dead-time can be determined. Thus

$$\phi = \frac{n_A + n_B - n_{AB} - n_b}{n_{AB}^2 - n_A^2 - n_B^2} \qquad \ldots\ldots\ldots\ldots\ 46.$$

Two experiments were carried out, the same equipment being used in both cases except that the counters were changed in order to make certain that the dead-time measured was that of the electronic apparatus and not the counter. The results are given in table 9.

Table 9: Dead-time determination

Experiment 1 Sample	c./s.	Experiment 2 Sample	c./s.
A	131.3 ± 0.5	A	128.9 ± 0.5
AB	239.7 ± 0.5	AB	192.3 ± 0.6
B	117.4 ± 0.4	B	68.3 ± 0.3
Backgnd.	1.25	Backgnd.	1.26
ϕ = 298 μs. (± 10%)		ϕ = 307 μs. (± 9%)	

The dead-time was thus taken as 300 μs. and where the counting rate exceeded 2,000 c./m. corrections were applied according to equation 45.

(e) Choice of solvent and technique of handling samples

As comparatively cheap and readily available solvents for sample preparation, alcohol and aqueous alcohol mixtures were thought to offer possibilities. It was found, however, that when counting methyl iodide in alcohol, there was loss of activity with time as may be seen from the following table:

Table 10: Activity loss from alcohol solution

Time after start minutes	Counting rate c./m.
10	1356
15	1331
23	1314
29	1326
44	1284
89	1215
101	1147
190	968

Chloroform, being similar to the materials being investigated, was then tried and the tops of the counters were ground flat so that a glass plate, moistened with glycerine, would seal the sample in the counter when placed on top of it. Tests carried out under these conditions gave reproducible results even when the solution was left in the counter overnight. As a further precaution the stoppers of the measuring flasks were also coated with glycerine to improve the seal of these. These precautions were taken throughout the experiments irrespective of the volatility of the compounds being dealt with.

2.2.5. Hazards

The counter efficiency for the isotopes handled, was low and as the active material had, in the initial stages of an experiment, to be diluted 10^4 times, alkyl halide was required with a specific activity of about 1.5 mc./5ml. An initial activity of 2 mc. of lithium iodide and 2.5 to 3 mc. of the bromide was, therefore, necessary.

The radiation from 1 mc. of I^{131} or Br^{82} at a distance of 1 foot is equivalent to 2.8 and 16.1 milliroentgen/hour, respectively(65). The tolerance dose rate which should not be exceeded for personnel exposed to radioactive materials has been laid down as 12.5 mr./hour by the International Committee on

Radiological Protection[66]. At all times it is desirable to keep well within this limit.

During the process of labelling alkyl halides, the times of exposure were short; the main reaction vessel was also masked with lead bricks as an added precaution, so that the hazard involved was negligible. The iodine was received as an aliquot from the Biophysics section of the N.P.L. and constituted virtually no hazard. The active bromide, however, was received as a direct shipment and as the activity on arrival was usually in the region of 40 mc., exposure at short range except for very short periods, was out of the question.

The intensity of radiation decreases with distance according to an inverse square law and distance is used as a means of protection where it is not possible to handle material behind lead screening. All handling tools and opening devices were of such a design as to allow the operator to be at least one metre from the source when dealing with it, and for most of the operations further protection was achieved with lead bricks.

2.3. Measurement of Diffusion Coefficients

2.3.1. Selection of Method

Three methods have been reported for work of this nature incorporating the use of radioactive materials:

(a) Jehle[67] allowed active material to diffuse vertically from one tube into another across an originally sharp boundary. He measured the change of concentration with time, at a known distance from the original boundary on the initially active half. A screened, collimated counter was used and a diffusion coefficient calculated from the data obtained. The method, though feasible, raises great difficulties of operation due to the necessity of eliminating convection in the tube and in limiting vibration in the apparatus. Jehle used tubes of 11 cm. diameter in his work but Wang and Kennedy[68] reported that, using tubes of only

1.5 cm. diameter, they had difficulty in obtaining 1 per cent. accuracy and considered the method inconvenient for ordinary laboratories.

(b) Porous diaphragms between the active and inactive liquids establish a well defined boundary and successfully eliminate the effects of convection and vibration by virtue of the small capillaries in the diaphragm. In this method[69], however, each cell has to be calibrated with a material of known diffusion coefficient and thus offers only a relative method.

(c) Anderson and Saddington[30] developed the capillary tube method and this was later modified by Wang[37]. This method gives direct results and is the method which has been adopted. Tubes of small enough diameter to ensure that effects of convection and vibration are eliminated, are sealed off at one end and ground to a suitable length. These tubes are filled with labelled material and immersed in unlabelled material of sufficient bulk to ensure that the diffusing labelled material does not affect the originally established concentration gradient of active to inactive material. Convection or stirring in the bulk liquid prevents any local concentration. The activity in a tube is determined before and after diffusion has occurred, and the diffusion coefficient calculated according to an equation derived for these particular conditions[70], viz.:

$$\frac{C_{AV}}{C_o} = \gamma = \frac{8}{\pi^2} \sum_{n=0}^{n=\infty} \frac{1}{(2n+1)^2} e^{-(2n+1)^2 \pi^2 Dt/4l^2} \qquad \ldots\ldots\ 47$$

where C_o and C_{AV} are the concentrations before and after diffusion has occurred, D is the diffusion coefficient in cm.^{2}sec.$^{-1}$, t is time in seconds and l the length of the diffusion path in cm.

2.3.2. Apparatus

(a) Diffusion tubes

Twenty-seven of these tubes were constructed from capillary tubing which had been checked for uniformity of bore by measuring the length of a mercury thread at different points in the tube. Flat-topped pieces of glass rod were sealed into one end of short lengths of the capillary and the tubes were ground to required lengths. To prevent damage of the capillary by the grinding paste, the tubes were partly filled with beeswax. Removal of the wax was difficult and particularly in the case of the smallest diameter tubes only two of the original five could be used as the others were damaged.

Table 11: Tube lengths and volume ratios

Tube	Length	Volume ratio to tube 1 according to: Mercury	Active solution
1	2.792 ± .002	1.0000	1.0000
2	2.806 ± .003	1.0000	0.9914
3	2.806 ± .003	0.9993	0.9945
4	2.813 ± .001	1.0241	1.0281
5	2.671 + .003	1.0663	1.0788
6	2.794 ± .002	1.0153	1.0171
7	2.805 ± .001	1.0262	1.0333
8	2.808 ± .002	1.0153	1.0085
11	3.986 ± .002	0.7908	
12	3.979 ± .002	0.7915	
13	3.996 ± .001	0.7901	
14	3.973 ± .001	0.7901	
16	2.832 ± .002	0.5627	0.5652
17	2.795 ± .001	0.5619	0.5711
18	2.785 ± .002	0.5554	0.5583
19	2.793 ± .002	0.5561	0.5582
20	1.997 ± .001	0.3972	
21	1.997 ± .001	0.4023	
22	1.988 ± .001	0.4001	
23	1.991 ± .001	0.4009	
24	1.992 ± .001	0.3994	
25	2.783 ± .005	0.4249	
27	2.812 ± .001	0.4242	

Three sets of tubes, 3 cm. long, were made from capillaries of 0.6794 ± .0006, 0.5084 ± .0002 and 0.4382 ± .0061 mm. diameter, respectively. Two further sets of 0.5084 mm. diameter, were 2 and 4 cm. long, respectively. All tubes were calibrated with mercury and a radioactive solution and their length accurately measured with a travelling microscope. After these tubes had been in use for some time it was observed that the openings had been damaged by repeated use and they were reground and recalibrated. This meant a great deal of repetitive measurement to ensure accuracy and retarded the work by more than a month. From time to time the 11 tubes in major use were checked one against the other with active solutions. In table 11 the lengths and the intervolume relationship for the reground tubes are given.

(b) Diffusion cells

The design of these cells was altered a good deal in the initial stages of the experiments. The designs used by previous workers were unsatisfactory for the purpose of this work; they used volumes of bulk liquid far in excess of the amounts of alkyl halides which could be used economically. Certain of the materials used in construction of the cells could not be utilised because of their solubility in, or reaction with the organic liquids. All-glass apparatus was necessary and the first type of cell used is shown in figure 10. This cell consisted of a flat-bottomed containing vessel made from a B-50 socket. The upper portion of the cell consisted of a B-50 cone, rounded over, and carrying a mercury seal and hollow central tube, to which two cups were fitted in such a manner as to allow the stirrer to operate between them when driven through the seal. The cups were only large enough to hold one diffusion tube each and ensured that this was kept in a vertical position. Each cup was approximately 1.5 cm. deep.

These cells were about 5.5 cm. in diameter and 15 cm. in height and 100 ml. of material were required to ensure that the tubes were immersed to a sufficient depth. For each run with eight tubes, therefore, 400 ml. were necessary. Difficulty was also experienced with the mercury seals when the more volatile

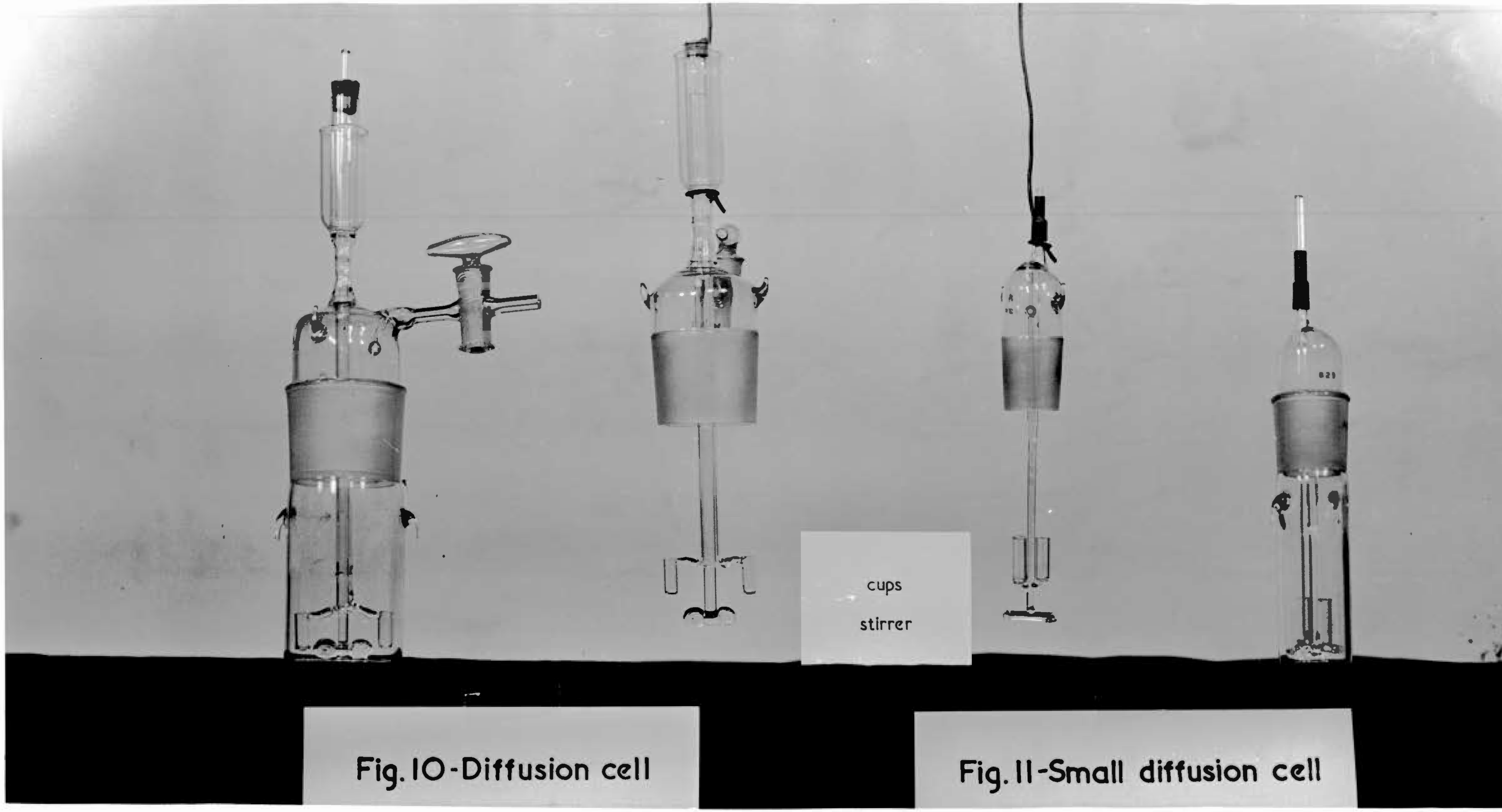

Fig. 10-Diffusion cell

Fig. 11-Small diffusion cell

compounds were used, as the build-up of pressure in the cell forced liquid through the seal. Taps were fitted so that the excess pressure could be released but these made the cells even more cumbersome.

After the necessary experimental tests, (2.3.5.(b), pp. 61 and 62), these cells were replaced by the smaller type shown in figure 11. The containing vessel was in this case made from a B-29 socket and the cell, which required 33 ml. of liquid, was about 3 cm. in diameter and 13 cm. high. The domed portion was made from a B-29 cone and carried a centrally placed rod to which two cups were attached. Relative to the rod, a sleeve was offset on the dome and a stirrer passed through this and was held in position by a rubber collar. The stirrer was a rectangle of glass which passed around the cups. Stirring was achieved by vertical movement. Lugs were attached to both portions of the cells so that these could be held together by springs to prevent loss of vapour.

(c) Pipettes and micro-syringe

Pipettes were drawn out of 4 mm. glass tubing so that the first 4 cm. were sufficiently fine to pass through a capillary of 0.44 mm. diameter. The internal diameter was tested by observing the size of resultant bubbles when air was blown through them whilst the tip was immersed in chloroform.

The micro-syringe consisted of an aluminium barrel, to which a micrometer head carrying a fibre piston of small diameter, was fitted. Control was good and small volumes could be readily handled. The pipettes were attached to the syringe by means of a shaped piece of pressure tubing and thus formed a rigid unit with the syringe.

(d) Constant temperature baths

Three water-filled baths were fitted with heating elements, stirrers and toluene- or mercury-filled regulators. The heaters and regulators were coupled up through "Sunvic" relays and temperatures were maintained with fluctuations of less than 0.03°C. The baths were in temperature controlled rooms and were run at 7.35, 19.35 and 30.00°C. These temperatures were measured and checked from time to time with N.P.L. standard thermometers.

2.3.3. Procedure

This was carried out in three stages:

(a) Measurement of initial concentration, C_o

Active material and standard tubes were placed in a bath at the desired temperature and allowed to reach equilibrium. The tubes were overfilled with active material by means of the pipette and micro-syringe described above. The excess of liquid was allowed to evaporate and each full tube immediately immersed in approximately 15 ml. of chloroform. Active material was expelled with air and uncontaminated solvent into the surrounding chloroform, which was then poured off and made up to a volume of 100, 50 or 25 ml. These solutions were counted as detailed earlier (p. 40 , paragraph 4). This procedure was repeated until reproducible values were obtained and after suitable correction the values for C_o were calculated by means of the calibration figures for the tubes used in the next stage.

(b) Measurement of the final concentration, C_{AV}

Four diffusion cells, each containing 33 ml. of inactive compound were placed, together with the active compound and the tubes to be used, in the required bath. After temperature equilibrium had been reached, the tubes were overfilled, placed in the cups and lowered carefully into the cell. The two portions of the cell were rotated slowly in opposite directions to remove excessive active material from the tops of the tubes and so establish the diffusion boundary at the mouth of the tube. After attaching the springs, the cell was replaced in the bath. An hour later, the cell liquid was gently stirred with the vertical stirrer in order to remove any local concentrations due to diffusion from the tubes.

After a prescribed time the tubes were removed from the cells, immersed in chloroform, emptied as in (a) above, and counted. For each run eight results were obtained; four for the largest diameter tubes and four for the 0.51 mm. diameter tubes. The tubes of 3 cm. length were used in the majority of the experiments. Using tubes of different diameters ensured that there was always a check on the general conditions of the experiment as any irregularity resulted in high diffusion coefficients for the larger diameter tubes, relative to the others. Unless results for both sets of tubes agreed within experimental error, they were discarded.

(c) Special considerations

The general procedure described above could not always be carried out. With methyl iodide, for example, the tubes had to be tied in position with pipe cleaners as the density of this compound is greater than that of the tubes. This, in addition to the high volatility of the compound, caused great difficulty and only a limited number of results could be obtained.

In order to use the radioactive materials to the best advantage, each labelled compound was generally used to carry out a series of experiments at the different temperatures. This necessitated working to a tight schedule and it was not possible to calculate results for each experiment as this was completed, with the result that where faults arose they were not readily detected until a series of experiments were evaluated. Results were thus depleted throughout a series by a persistent fault in one of the tubes, for example, the experiments on n-butyl iodide at 7 and 30°C., vide table 18 (p. 72).

(d) Calculation of the diffusion coefficient and energy of activation

Equation 47 can be transformed as follows:

$$\gamma = \frac{8}{\pi^2} \sum_{n=0}^{n=\infty} \frac{1}{(2n+1)^2} e^{-(2n+1)^2 \pi^2 Dt/4l^2} \quad \ldots\ldots\ 48$$

$$= \frac{8}{\pi^2} \left(\frac{e^{-\theta}}{1} + \frac{e^{-9\theta}}{9} + \frac{e^{-25\theta}}{25} + \frac{e^{-49\theta}}{49} + \ldots\ldots \right) \quad \ldots\ldots\ 49$$

where $\theta = \pi^2 Dt/4l^2$. Thus

$$\gamma = \frac{8}{\pi^2} e^{-\theta} \left(1 + \frac{e^{-8\theta}}{9} + \frac{e^{-24\theta}}{25} + \frac{e^{-48\theta}}{49} + \ldots\ldots \right) \quad \ldots\ldots\ 50$$

$$= \frac{8}{\pi^2} e^{-\theta} F \quad \ldots\ldots\ 51$$

$$= \frac{8}{\pi^2} e^{-\pi^2 Dt/4l^2} F \quad \ldots\ldots\ 52$$

and $\log \gamma = \log \frac{8}{\pi^2} - (\pi^2 Dt/4l^2) \log e + \log F \quad \ldots\ldots\ 53$

and thus $D = \frac{4l^2}{\pi^2 t \log e} \left(\log \frac{8}{\pi^2} - \log \gamma + \log F\right) \quad \ldots\ldots\ 54.$

For a given temperature D is a constant and for a given tube so is l, and the only variable in θ, therefore, is t. By choosing suitable values of θ over a wide range, corresponding values of F were calculated and curves drawn of θ versus F. From the value of γ determined experimentally, and assuming a value of F = 1, an approximate value can be calculated for θ from equation 51. With this a value of F can be obtained from the curves and by resubstitution in 51 an improved value of θ calculated. Thus by successive approximation an accurate value of F can be obtained.

For sufficiently large values of t, such that γ is less than 0.4, F tends to unity and the correction, being log F, is zero. For reasons of necessity, however, values of t had to be chosen such that the value of γ fell between 0.4 and 0.55. In most cases, therefore, F had to be evaluated and since the method of successive approximation is laborious, a curve relating γ and F was drawn and is given in figure 12.

Equation 54 can now be solved as the only unknown is D. Following the above procedure diffusion coefficients for the various tubes were evaluated at the three temperatures selected. The

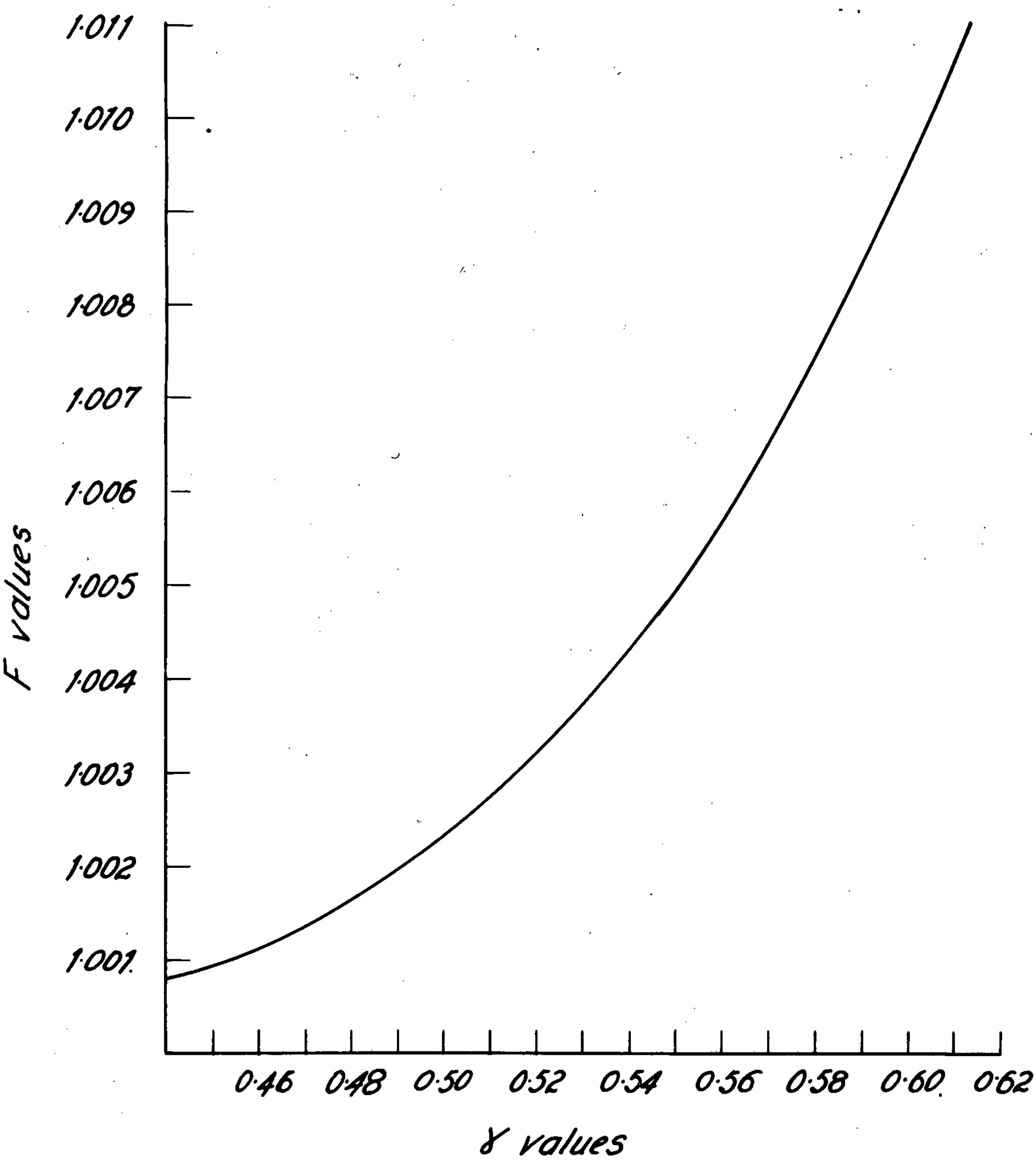

Fig. 12 - F values for solution of diffusion equation

Tube	Filling	Vol. ml.	N c./m.	Date	Time h.	Zero + h.	θ	e^{θ}	N c./m. in 50 ml.
1	C_o	100	1443	25	1521	0.35	.00125	1.0013	2890
2	"	"	1437	"	1533	0.55	.00197	1.0020	2880
3	"	"	1446	"	1544	0.73	.00261	1.0026	2900
8	"	"	1447	"	1555	0.93	.00329	1.0033	2904
4	C_{AV}	50	1644	"	1608	1.01	.00362	1.0036	1650
5	"	"	1670	"	1618	1.3	.00466	1.0047	1678
6	"	"	1662	"	1628	1.47	.00527	1.0053	1671
7	"	"	1641	"	1639	1.65	.00591	1.0059	1651
16	"	"	912.0	"	1653	1.88	.00674	1.0067	918.0
17	"	"	871.4	26	0900	18.00	.06449	1.0666	929.5
18	"	"	841.7	"	0920	18.33	.06567	1.0679	898.9
19	"	"	841.5	"	0945	18.75	.06717	1.0695	900.0
1	C_o	100	1341	"	1438	23.63	.08465	1.0884	2920
2	"	"	1326	"	1449	23.83	.08534	1.0890	2890
3	"	"	1312	"	1506	24.01	.08602	1.0900	2856
8	"	"	1308	"	1519	24.32	.08713	1.0910	2854
4	C_{AV}	50	1518	"	1531	24.52	.08784	1.0918	1657
5	"	"	1538	"	1544	24.73	.08860	1.0926	1680
6	"	"	1486	"	1557	24.95	.08938	1.0935	1625
7	"	"	1505	"	1609	25.02	.08963	1.0937	1646
16	"	25	1637	"	1621	25.35	.09082	1.0951	896.5
17	"	"	1674	"	1632	25.53	.09146	1.0958	917.0
18	"	"	1632	"	1644	25.73	.09218	1.0966	895.5
19	"	"	1655	"	1654	25.9	.09279	1.0972	908.0

Values for tubes 2, 3 and 8 are converted to values for tube 1 according to the ratios in table 11 (p. 54); thus we find

2890	and	2920
2906		2916
2916		2872
2880		2830

The value of 2830 has been discarded since it differs from the mean of 2900 by far more than the expected deviation of 0.8 per cent. The standard deviation of this mean calculated according to equation 39 (p. 41) is 7.3 or less than 0.3 per cent. From this figure for tube 1, the C_o values for the tubes used in the experiment have been calculated and the C_{AV}/C_o or γ values derived. From a knowledge of γ, the value for F in equation 51 (p. 55), has been obtained from figure 12 (follows p. 56). In equation 54 (p. 55) the only unknown is thus D and this can then be calculated according to the following equation:

$$D = \frac{4l^2}{\pi^2 t \log e} \left(\log \frac{8}{\pi^2} - \log \gamma + \log F\right) \quad \ldots\ldots\ldots\ldots \quad 58$$

where l is the length in cm. of the capillary, given in table 11 (p. 50), and t is the duration of the experiment in seconds.

Table 12: Calculated values of C_o, γ, F and D

Tube	C_o c./m.	γ	$\log \gamma$	F	log F	$D \times 10^5$ $cm^2 sec^{-1}$
4	2983	.5533	$\bar{1}$.7429	1.0052	.0022	1.567
5	3128	.5364	$\bar{1}$.7295	1.0041	.0017	1.522
6	2968	.5630	$\bar{1}$.7505	1.0059	.0025	1.480
7	2968	.5529	$\bar{1}$.7426	1.0052	.0022	1.562
16	1639	.5601	$\bar{1}$.7483	1.0057	.0024	1.540
17	1656	.5612	$\bar{1}$.7492	1.0058	.0024	1.492
18	1618	.5552	$\bar{1}$.7445	1.0053	.0022	1.523
19	1618	.5560	$\bar{1}$.7451	1.0054	.0023	1.527
4	2982	.5557	$\bar{1}$.7448	1.0053	.0022	1.551
5	3128	5371	$\bar{1}$.7301	1.0042	.0018	1.518
6	2968	.5475	$\bar{1}$.7384	1.0048	.0020	1.587
7	2968	.5546	$\bar{1}$.7440	1.0053	.0022	1.549
16	1639	.5470	$\bar{1}$.7380	1.0048	.0020	1.634
17	1656	.5537	$\bar{1}$.7432	1.0052	.0022	1.545
18	1618	.5528	$\bar{1}$.7425	1.0052	.0022	1.541
19	1618	.5609	$\bar{1}$.7489	1.0057	.0024	1.493

(b) Results for iso-butyl iodide at 30°C.

In the following table the $D \times 10^5$ values in $cm.^2 sec.^{-1}$ are given for all the experiments carried out for iso-butyl iodide at 30°C., together with their deviation Δ, from the mean.

In calculating the mean, the values for tubes 3, 5 and 6 in experiment 6, were disregarded as being obviously suspect. The standard deviation was calculated according to equation 39 (p. 41). Thus

$$\text{standard deviation} = \sqrt{\frac{\sum_{0}^{n} \Delta^2}{n(n-1)}} \quad \ldots\ldots\ldots\ldots \quad 59$$

where n is the number of observations considered.

Table 13: Diffusion coefficients for iso-butyl iodide at 30°C. and values of Δ

Expt.	Tube	$D \times 10^5$ $cm.^2 sec.^{-1}$	Δ	Expt.	Tube	$D \times 10^5$ $cm.^2 sec.^{-1}$	Δ
5	3	1.551	.008	12	4	1.567	.024
	5	1.505	.038		5	1.522	.021
	6	1.583	.040		6	1.480	.037
	7	1.511	.032		7	1.562	.019
	15	1.487	.056		16	1.540	.003
	16	1.507	.036		17	1.492	.051
	17	1.569	.026		18	1.523	.020
	19	1.583	.040		19	1.527	.016
6	3	1.741	-	13	4	1.551	.008
	5	1.383	-		5	1.518	.025
	6	1.404	-		6	1.587	.044
	7	lost	-		7	1.549	.006
	15	1.615	.072		16	1.634	.091
	16	1.528	.015		17	1.545	.002
	17	1.523	.020		18	1.541	.002
	19	1.608	.065		19	1.493	.050

The mean for the above values is 1.543. The sum of the squares of the individual deviations from the mean is 0.040337 so that

$$\text{standard deviation} = \sqrt{\frac{0.040337}{28(28 - 1)}} = \sqrt{0.00053}$$

The result for iso-butyl iodide at 30°C. is thus

$$D \times 10^5 = 1.543 \pm 0.007 \ cm.^2 sec.^{-1}$$

The internal error is thus better than 0.5 per cent. whilst the worst result has a deviation from the mean of less than 6 per cent.

2.3.5. Sources of Error and their Experimental Assessment

From equation 54 (p. 55) it can be readily seen that the accuracy with which D can be measured is dependent on the accuracy with which t, l and γ can be evaluated. In addition to their direct effect in the equation there are numerous errors which may arise from the design of the experiments as a whole and in technique.

(a) Effect of time

The measurement of t was accurate to at least one part in a thousand and, in most cases, was better than this. The time factor in itself, thus constitutes only a very small error.

The actual value of t chosen for a particular value of D was, however, important as the value of C_{AV} varies exponentially with t. Since the negative log is involved in the final evaluation, and log $8/\pi^2$ and log F are small, the smaller the value of log γ the smaller will be the relative error in -log γ and hence in D. By virtue of the diffusion rates, however, low values of γ would have necessitated large values of t. This would have incurred large losses due to decay with corresponding counting difficulties and in the case of the bromides, loss of opportunity for replication.

It was, therefore, necessary to choose a value of γ which could be evaluated in a reasonable time with accuracy. By determining γ values at different times, values for D were calculated and an indication obtained of the upper limit at which γ could be measured with reasonable accuracy. Furthermore, by measuring D over different periods it was possible to assess whether convection or vibration was affecting results since D would increase with time if either effect was marked.

Results tabulated below reflect values of γ and D measured for ethyl bromide in the large diameter tubes, 1 and 2, for different times of diffusion. Other similar experiments were also carried out but as these gave similar results to those tabulated, they are not quoted.

Table 14: Values of γ and D determined at different values of t

Time h.	6	9	12	15	20	22	24	36
γ_1	.6030	.5809	.5463	.4998	.3929	.3975	.3541	.2264
γ_2	.6521	.5663	.5528	.4681	.3983	.3916	.3813	.2319
$D \times 10^5$	5.17	3.80	3.37	3.26	3.64	3.28	3.47	3.43
$cm^2 sec^{-1}$	3.98	3.62	3.16	3.73	3.60	3.35	3.19	3.53

It is apparent that for a γ value of 0.55 or less, reasonable results could be expected. No marked effect due to vibration or convection was noticeable though it was apparent that greater replication was necessary to achieve accuracy in the evaluation of D.

(b) The influence of stirring and cell design

Assuming that there is little convection in the bulk liquid, diffusion of material from the tubes will result in a concentration of active material at the tube openings with a resultant suppression of diffusion rate. This would probably be marked only in the early stages and the effect would tend to disappear with long periods of diffusion, due partly to convection in the bulk liquid and to the decreasing rate of diffusion with time. In order to reduce the times of diffusion, tests were carried out to ascertain the amount of stirring required to obtain accurate values of γ in the region of 0.5. At the same time the smaller cells, with their different method of stirring, were also tested.

The initial experiments carried out will not be quoted as these were useful only in the development of the methods adopted. The main experiments using sec-butyl bromide are given as examples and these were followed by experiments with ethyl iodide which confirmed the results for the butyl bromide, and have consequently been omitted. Large cells containing sec-butyl bromide were left untouched for 18 and 36 hours, whilst another was stirred mechanically for 18 hours. Small cells were carefully hand-stirred at the start of the experiment and again an hour later and were left for a further 23 hours. Results for these runs are tabulated in table 15.

Table 15: Effect of stirring

Time h.	Conditions	$D \times 10^5$ $cm^2 sec^{-1}$
18	Static	1.805 ± .026
36	"	1.939 ± .018
18	Mechanically stirred	1.933 ± .036
24	Small cell; hand-stirred	1.951 ± .011

Providing, therefore, that stirring was carried out in the initial stages or the times taken increased considerably, either cell type could be used. The hand-stirred smaller cell was the most convenient and was used in all subsequent experiments. During the course of these experiments further observations were made with regard to stirring but in all cases, except where this was excessive, the results were constant.

(c) The effect of length of diffusion path

The actual length of the capillaries was determined with good accuracy as may be seen from table 11 (p. 50). Since D is proportional to l^2 the error introduced is very small, namely $(.02\%)^2$. Wang[36] considers, however, that the diffusion path may be affected by an accumulation of active material above the mouth of the tube when there is no stirring, or by a sweeping out of material from the tube mouth when stirring is excessive. He eliminates any errors by using tubes of different lengths to obtain the necessary corrections. As may be seen from table 16 the results for tubes of different lengths do not differ significantly and the effects found by Wang are not apparent under the conditions adopted here.

Table 16: Tube length and variation in D

Compound	Temperature °C.	Length cm.	D x 10^5 $cm^2 sec^{-1}$
EtI	19.35	2	2.226 ± .010
		3	2.212 ± .014
		4	2.200 ± .009
nPrBr	7.35	2	1.995 ± .014
		3	2.026 ± .009
		4	2.015 ± .011
secBuBr	7.35	2	1.602 ± .009
		3	1.600 ± .013
		4	1.615 ± .017

(d) The effect of vibration and convection as checked with tubes of different diameters

As an additional check to that in (a), on the effect of vibration and convection, tubes of different diameters were used since the smaller the diameter of the tubes the smaller should be the effect produced by either convection or vibration. The smaller the diameter, however, the greater are the difficulties of filling and emptying of the tubes and any errors in analysis are proportionally higher because of the smaller volume. Tubes of three diameters were used and results are given in table 17.

Table 17: Tube diameter and variation in D

Compound	Temperature $^{\circ}C.$	Diameter mm.	$D \times 10^5$ $cm^2 sec.^{-1}$
EtI	30.00	0.44	2.561 ± .021
		0.51	2.579 ± .012
		0.68	2.594 ± .015
secBuBr	19.35	0.44	1.819 ± .009
		0.51	1.940 ± .011
		0.68	1.929 ± .010
secBuBr	30.00	0.44	2.163 ± .017
		0.51	2.231 ± .012
		0.68	2.220 ± .015

It will be seen that though the two larger diameter tubes are in good agreement the smallest diameter tubes are decidedly lower for sec-butyl bromide. Other experiments were attempted but in most cases there was always doubt as to the reliability of the results and it was not possible to obtain the necessary replication. In view of the agreement of the two other sets throughout the investigation the discrepancy due to the smallest tubes was disregarded. Four of each of the larger diameter tubes were used in most of the experiments and it was observed that if anything untoward occurred during an experiment, this was reflected as a large discrepancy between the results obtained with each set of tubes. In these cases the results were discarded and the experiment repeated after the fault had been recognised and rectified.

(e) Hydrostatic effect and purity of the bulk liquid

Bearing in mind that limited volumes were available, suitable volumes had to be selected to ensure sufficient coverage of the tubes. Results for volumes of 30, 33 and 35 ml. were 2.236, 2.233 and 2.232 x 10^5 $cm.^2 sec.^{-1}$, respectively. The volume of 33 ml. used was thus well within any limit there might be. Due to inequalities in the lengths of the solid portions of the tubes and in the levels of the tube holders, tubes were not always immersed to the same depth in the bulk liquid. A note was made of the relative positions of tubes in a cell but over a period of months no correlation was found between the results obtained for those tubes immersed to a lesser depth, relative to the others. It is thus evident that no effect due to differences in hydrostatic pressure was noticeable under the conditions adopted.

In certain cases repeat runs had to be carried out in the same bulk liquid. Considering the largest tubes used, with volumes of 0.01 ml., two of which were immersed in 33 ml. of bulk liquid, the highest concentration of labelled compound in the bulk liquid could be only one-thousandth of that in the tubes at the end of a second run. This should have no measurable effect on the diffusion rate and this was in fact found to be the case.

It was virtually impossible to prevent actinic decomposition of some of the higher homologues. This manifested itself as a colour in the liquid but had no apparent effect on the refractive indices at the concentrations encountered. Slight impurity of this nature in the bulk liquid should have no effect on the diffusion of the labelled material. This was checked by using coloured and pure materials as bulk liquids in two successive experiments but no significant differences could be detected.

Purity of the labelled material was, however, always maintained since any free halogen would lead to the measurement of a coefficient due partly to free halogen and partly to alkyl halide.

Any foreign impurity such as the alcohol, the solvent or water would result in the measurement of the interdiffusion of the alkyl halide in the resultant mixture.

(f) Turbulence effects

It was thought that the movement of the tubes into and through the bulk liquid during the establishment of the boundary and subsequent removal from the cell, might cause turbulence in the liquid. This might then result in the removal of liquid from the tubes and affect results. In order to check this, tubes were filled and counted, and after drying them they were overfilled and introduced into the cells, rotated in the usual way and immediately removed and counted. There was a slight difference in the counting rates before and after immersion but this was so small that the change in D was negligible and well within the normal error.

(g) Effect of errors in γ

As is apparent from the above, the expected errors can all be reduced to low values. The error in γ, which is due to technique and to errors in counting (2.2.4.(a), pp.41, 42), can, however, not be reduced to below that of the combined errors involved in the evaluation of C_o and C_{AV} and this error is the limiting factor in the accurate determination of D. The error in counting rate was about 0.8 per cent. In the evaluation of C_o this error could be reduced by repetition but, except by replication the expected error in C_{AV} could not be less than 0.8 per cent. In combining the errors of a quotient the error is given by the square root of the sum of the squared percentage errors and it is estimated that the error in γ was thus seldom less than 1 per cent. For a value of γ = 0.55 the resultant error in D was slightly greater than 3 per cent. By keeping γ as low as possible and repeating measurements, it was possible to reduce the internal error and evaluate D with fair accuracy. It is realised, however, that the results might be biased, but it is estimated that this would not be by more than 1.5 per cent.

2.4. Measurement of Viscosity Coefficients

Methods and apparatus for the evaluation of viscosities are many and varied and with the theory have been comprehensively dealt with in the literature[71]. It is considered unnecessary to give further details here and only pertinent information is given.

2.4.1. Apparatus

Two Ostwald type viscometers were used of 12.282 and 11.981 ml. capacity and with capillaries of 12.5 and 12.3 cm. length, respectively. The times of flow for water at 19.35°C. were 357.6 and 2,010 seconds, respectively.

2.4.2. Procedure

Viscometers were cleaned with filtered chromic acid solution, washed with filtered distilled water and dried, where necessary, with pure acetone and a stream of dust-free air. The viscometer was filled, allowed to reach temperature equilibrium and, after ensuring that the volume was correct, it was vertically aligned. Liquid was transferred to the upper bulb by suction with a syringe and the free flow of liquid timed between two marks on either side of this bulb. This was repeated until the accuracy of the value was satisfactory. Values were obtained both for the liquid of known and for that of unknown viscosity at the three temperatures concerned and the unknown viscosity was evaluated by application of the following equation:

$$\eta_2 = \frac{\rho_2 \quad t_2 \, \eta_1}{\rho_1 \quad t_1} \qquad \ldots\ldots\ldots\ldots\ 60.$$

The viscosity of the unknown η_2, can be determined if the densities ρ, and the times of flow t, are known for the known and unknown liquids here designated by the subscripts 1 and 2, respectively.

Where the times of flow differ greatly a correction for the kinetic end effects, as indicated in 2.4.3.(b), has to be applied. The energy of activation is evaluated from equation 25, viz. $\eta = \eta_0 \ e^{E_\eta/RT}$, by plotting log η versus 1/T and calculating E_η from the slope of the straight line obtained.

2.4.3. Sources of Error and Experimental Details

(a) The effect of errors in the physical constants used

From equation 60 it is apparent that the accuracy with which η_2 can be determined, depends on the accuracy with which the viscosity of the standard and the densities of the compounds are known. The viscosity of water, which was used as the standard, is known to four figures with a presumed accuracy of 0.1 per cent. The densities are known to five figures with a presumed accuracy of 0.05 per cent. The effect of these errors should be negligibly small.

(b) The effect of times of flow

Assuming that there are no other effects due to times of flow the effect of errors in t should be very small since these were measured to an accuracy of 0.05 per cent. Combining this error and those given in (a) the combined error should not be greater than 0.11 per cent. Where the times of flow for the two liquids concerned differ and are relatively short, however, kinetic end effects due to the different flow velocities become apparent and must be allowed for.

Poiseuille's equation[72] for the relationship between viscosity and other factors for flow of a Newtonian liquid through a capillary, is

$$\eta = \frac{hgr^4t\rho\pi}{8lv} \qquad \text{.............} \ 61$$

where h is the liquid head, g the gravitational constant, r the radius of the capillary, v the volume of flow and l the length of the capillary. In applying this, however, one does not encounter a situation in which the flow of the liquid is confined within a length of capillary. Corrections due to the net energy losses sustained in establishing flow in the capillary, and in returning to flow in the wider tube beyond the capillary, must be applied. Discussion of the effects involved are to be found in the literature[71] and the correction which should be applied is derived below:

$$\eta = \frac{hgr^4 t\rho\pi}{8lv} - \frac{v\rho}{8lt\pi} \qquad \ldots\ldots\ldots\ldots\ 62$$

or $$\eta = C\rho t - (B\rho/t) \qquad \ldots\ldots\ldots\ldots\ 63.$$

Thus $$\eta_1 = C\rho_1 t_1 - (B\rho_1/t_1) \qquad \ldots\ldots\ldots\ldots\ 64$$

and $$\eta_2 = C\rho_2 t_2 - (B\rho_2/t_2) \qquad \ldots\ldots\ldots\ldots\ 65.$$

Now if $$C = \frac{\eta_1}{\rho_1 t_1} - \frac{B}{t_1^2} \qquad \ldots\ldots\ldots\ldots\ 66$$

$$\eta_2 = \left(\frac{\eta_1}{\rho_1 t_1} + \frac{B}{t_1^2}\right)\rho_2 t_2 + \frac{B\rho_2}{t_2} \ldots\ldots\ldots\ldots\ 67$$

and $$\eta_2 = \frac{\eta_1\,\rho_2\,t_2}{\rho_1\,t_1} + B\,\rho_2\left(\frac{t_2^2 - t_1^2}{t_1^2\,t_2}\right) \ldots\ldots\ 68$$

which is equation 60 plus a correction term. Where t_1 and t_2 are similar this correction is practically zero and can be omitted but in the compounds investigated they were widely different and it was necessary to apply the correction. The viscosity of benzene is accurately known over a wide range of temperatures and this compound was measured as a check on the accuracy of the method and the applied correction. Agreement with the data in the literature was good.

(c) Surface tension effect

In an endeavour to reduce the effect of the widely differing times of flow, a smaller bore capillary viscometer was tried as the relative difference in times would be reduced. With water as the standard, however, the results obtained were high and this was attributed to the difference in surface tension between this liquid and the organic materials being investigated. Values for benzene were also high but by using benzene as the standard, values for the liquid investigated, namely n-butyl iodide, were brought into line with the previous determination as can be seen from figure 13 (follows p. 70). The surface tension of benzene and n-butyl iodide are very similar. With the wider bore capillary the effect due to the difference in surface tension was assumed to be negligible since results were the same whether water or benzene were used as standards.

PART III

VISCOSITY AND SELF-DIFFUSION COEFFICIENTS OF PURE ALKYL HALIDES

3.1. Viscosity Coefficients

The results have been presented in graphical form in figure 13 in which log η is plotted versus the reciprocal of the absolute temperature. The data in Timmermans[55] have been included for the sake of comparison. The four liquids investigated were n- and sec-butyl bromides and n- and sec-butyl iodide. Results for n-butyl iodide are given for the two viscometers both for water and benzene as the standards. The discrepancy in the case of the smaller capillary with water is clearly noticeable. It is apparent, however, that the slopes of the curves are similar so that activation energies would in any case be comparable.

A marked discrepancy between the values determined and those from Timmermans is apparent only in the case for sec-butyl iodide. This set of measurements was repeated and the values obtained verified those previously determined at the lower temperatures. The value at 30°C. lined up with these, where previously it had been higher. The line through these points is virtually parallel to that of n-butyl iodide. It will be seen that for the bromides measured, the slopes are also the same and on this basis it is felt that the results obtained for sec-butyl iodide are more likely to be correct than those quoted in the literature.

The activation energies calculated from the above results are tabulated together with those calculated from published data for the other alkyl halides in table 21 (p. 76). They are there discussed and compared with the values obtained for the diffusion process.

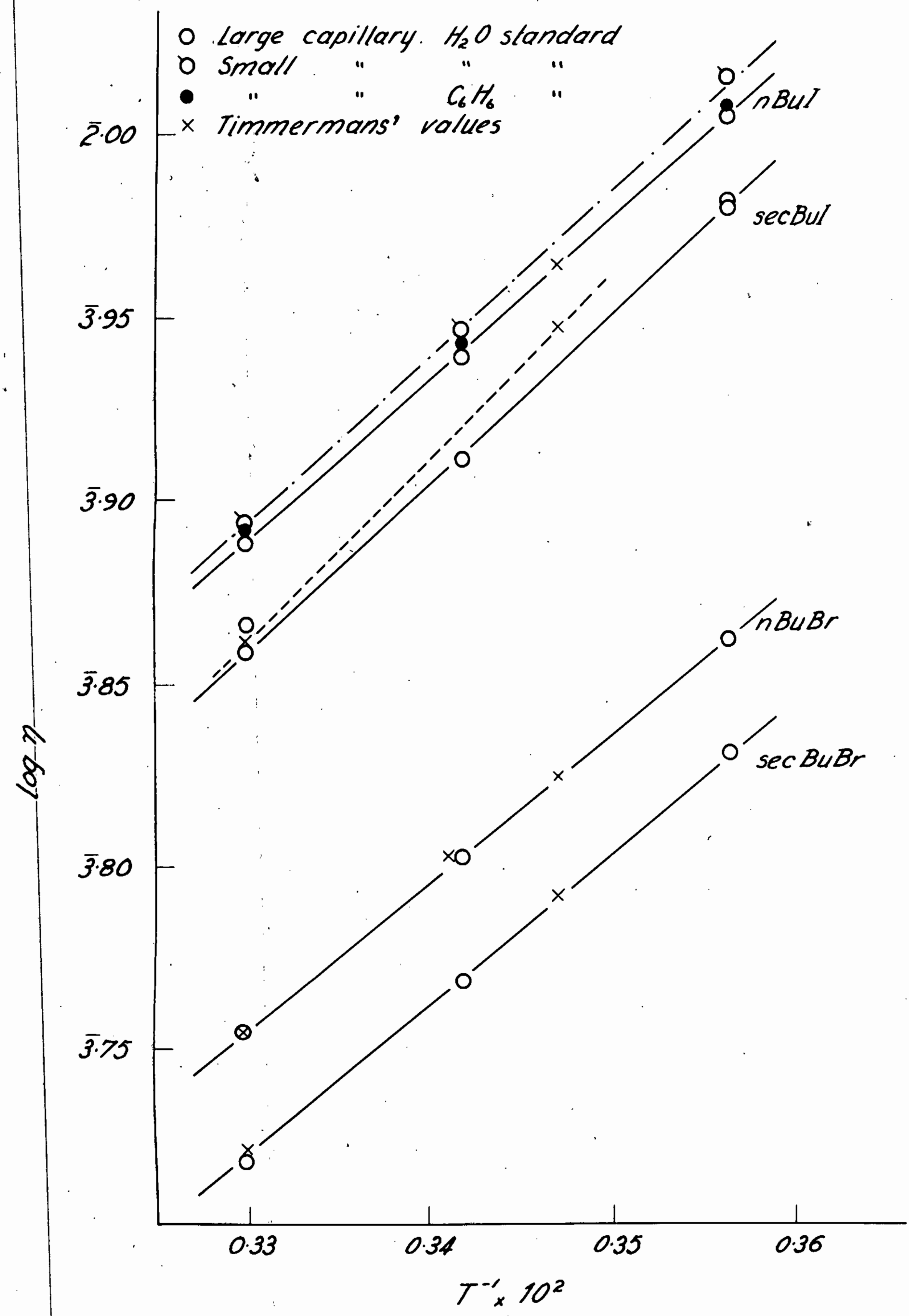

Fig. 13 - Viscosity coefficients of alkyl halides

3.2. Self-diffusion Coefficients

3.2.1. Experimental Details

As indicated in 2.3.5.(g) (p. 65) there are certain limitations to the accuracy which can be attained in the evaluation of the diffusion coefficients. In order to obtain results with a reasonable degree of accuracy it was necessary to make a large number of observations and to treat them statistically. The amount of work involved was considerable and the number of observations made and used in each determination has been listed together with reasons for the non-inclusion of certain of the observations. This list includes actual results only, and does not take into consideration experiments which had to be discontinued due to breakages, failure of air conditioning plant, thermostats or stirring devices.

In certain cases additional problems arose and a number of experiments were lost. The experiments with methyl iodide were complicated by the high density of the liquid and although the tubes were fastened in position these did on occasions float loose. The low boiling points of this material, ethyl and n-propyl bromide, increased the difficulties and on occasion caused the loss by evaporation of labelled material before sufficient measurements of the concentrated material had been made. In the case of the bromides this led to considerable loss of time as Br^{82} was not readily available.

No explanation has been offered in the table in cases where two or three results have not been taken into consideration. These were generally inadmissable due to bad technique or loss of the individual sample by spillage or accident.

Table 18: Reasons for disregarding certain of the observations

Compound	Temp. °C.	No. of observations Made	Used	Remarks
MeI	7	16	16	
	19	26	14	First ten discarded as technique and apparatus were being developed.
	30	16	13	Near boiling point. Bubbles formed in three tubes.
EtI	7	26	18	An experiment of 8 results was disregarded as the counter was suspect.
	19	34	32	
	30	32	29	
nPrI	7	28	28	
	19	36	32	Incorrect time chosen for first 4 with resultant poor accuracy.
	30	40	40	Increased replication was found to be necessary at this temperature.
isoPrI	7	24	24	
	19	24	20	Results for one cell obviously false due to excessive stirring.
	30	24	20	Repetitive fault due to decreased volume in two capillaries because of glass splinters from pipette.
nBuI	7	32	28	Two tubes faulty.
	19	32	31	
	30	32	25	Same two tubes faulty as in experiments at 7°C. and bubbles found in two others.
isoBuI	7	32	24	Eight discarded as material found to be coloured i.e. impure.
	19	24	23	
	30	32	28	Group of 4 obviously false.
secBuI	7	32	32	
	19	32	31	
	30	32	31	
EtBr	7	24	16	Eight results not considered as serious discrepancy between smaller and wider diameter tubes.
	19	50	48	Major portion of earlier tests carried out with this material but reproducibility poor.
	30	16	15	Further replication not attempted because of low boiling point.
nPrBr	7	32	31	Difficulty found in obtaining this compound pure due to azeotropic mixture.
	19	48	39	Reproducibility poor; 8 disregarded as solution found to be impure.
	30	40	31	Eight disregarded as same solution used as above.
isoPrBr	7	16	15	
	19	16	16	
	30	16	16	

Compound	Temp. °C.	No. of observations Made	Used	Remarks
nBuBr	7	16	16	
	19	16	16	
	30	16	16	
isoBuBr	7	32	24	Solution found to be coloured for one set of 8.
	19	32	27	Set of 4 obviously false.
	30	32	23	Same solution as used at 7°C., and 8 disregarded.
secBuBr	7	16	16	
	19	44	19	Sixteen results disregarded as part of initial experiments on stirring. Another 8 lost due to counting difficulties.
	30	28	20	Serious discrepancy between larger and smaller diameter tubes for set of 8 results.

From the above table it is evident that it would be impracticable to detail all the observations made and unnecessary to give all the calculations leading up to the individual results. The values obtained in two successive experiments were detailed in 2.3.4.(a), (pp. 56 to 58) and this was followed by all the results obtained for the substance at one temperature together with the method of calculating the mean and the standard deviation associated with it (2.3.4.(b), pp. 58, 59).

3.2.2. Results

Mean values of the diffusion coefficients measured for the thirteen compounds examined are listed in table 19, together with the standard deviations calculated for the number of replications indicated.

None of the results for the iodides have an internal deviation of greater than 1 per cent. irrespective of whether the replication was large or not. For the bromides the number of replicates was in general not as large due to the greater difficulty of obtaining bromine-82 and the limited usage that could be made of a batch of this material.

Table 19: Self-diffusion coefficients of the lower alkyl halides

Temp. °C.	Compound	D x 10^5 $cm^2 sec^{-1}$	Reps	Compound	D x 10^5 $cm^2 sec^{-1}$	Reps
7.35	MeI	2.166 ± .013	16			
19.35		2.671 ± .018	14			
30.00		3.241 ± .025	13			
7.35	EtI	1.838 ± .015	18	EtBr	2.847 ± .035	16
19.35		2.212 ± .014	32		3.483 ± .033	48
30.00		2.589 ± .013	29		4.176 ± .084	15
7.35	nPrI	1.362 ± .011	28	nPrBr	2.026 ± .009	31
19.35		1.623 ± .011	32		2.380 ± .014	39
30.00		1.922 ± .016	40		2.751 ± .014	31
7.35	isoPrI	1.435 ± .012	24	isoPrBr	2.077 ± .012	15
19.35		1.725 ± .008	20		2.467 ± .012	16
30.00		2.049 ± .011	20		2.893 ± .012	16
7.35	nBuI	1.135 ± .008	28	nBuBr	1.588 ± .008	16
19.35		1.347 ± .007	31		1.872 ± .011	16
30.00		1.685 ± .007	25		2.222 ± .011	16
7.35	isoBuI	1.044 ± .007	24	isoBuBr	1.495 ± .014	24
19.35		1.263 ± .007	23		1.800 ± .013	27
30.00		1.543 ± .007	28		2.170 ± .018	23
7.35	secBuI	1.124 ± .006	32	secBuBr	1.600 ± .013	16
19.35		1.353 ± .009	31		1.936 ± .011	19
30.00		1.607 ± .012	31		2.255 ± .022	20

Reps = Replications.

The internal deviations were well below 1 per cent. in all cases except that of ethyl bromide where they were 1.5 and 2. per cent. for the 7.35 and 30.00°C. experiments, respectively. These results are an improvement on those of Graupner and Winter[38] which were:

Table 20: Graupner and Winter's values of D for EtBr

Temperature °C.	15	22.5	30
D x 10^5 $cm^2 sec^{-1}$	3.60 ± 0.37	3.80 ± 0.26	3.96 ± 0.19

The relation of these results to those in table 19 may be more readily judged from figure 15 (follows p.76) where the log D/T values have been plotted versus 1/T.

3.2.3. General Discussion

(a) Variation of D with chain length

There is a definite decrease in D with increase in molecular weight in both the iodides and the bromides. The number of homologous compounds is, however, too limited to give more than an indication of the manner of this variation. In the case of the iodides D appears to decrease linearly with increase in the number of carbon atoms in the chain length but for the bromides the decrease is very much greater between ethyl and n-propyl than between n-propyl and n-butyl bromide. The values obtained by Partington et al.[39] for the first four alkyl alcohols in the homologous series decreased progressively less as the chain length increased. It is of interest to note that the viscosity of both the halide series, and the alcohols increases linearly with chain length over the range considered here.

(b) Variation of D between isomers

Both the iso-propyl compounds have significantly higher diffusion coefficients than the corresponding normal compounds but in the butyl group, the iso-compounds are both lower than either the normal or secondary ones which are themselves not significantly different. From table 4 (p. 23) it may be seen that the values for iso-propyl alcohol are higher than for the normal alcohol. Those for the tert-butyl alcohol are lower than those for the normal compound. This fact coupled with the results for the iso-butyl compounds given above might be taken as an indication that the branching in the chain restricts movement of these compounds, which is what would be expected.

3.2.4. Discussion of Results in Relation to Existing Theories

The Eyring and Frenkel theories give the only basis of calculation upon which diffusion results can be related and it is proposed to carry out calculations similar to those made by previous workers in this field.

(c) Evaluation of Activation Energies

In view of the discussion in 1.2.2., (p. 23) on the temperature dependence of D_0, it has been decided to plot log D/T versus 1/T and log η versus 1/T. In figures 14 and 15 the results given in table 19 (p. 74) have been plotted on this basis and the errors indicated. It will be seen that straight lines have been obtained in all cases. The 19°C. results seem in general to be slightly low but this can probably be attributed to experimental error rather than to deviation from linearity. The results obtained by Graupner and Winter(38) for ethyl bromide have also been plotted and agree with the present results within their experimental error, which is very much larger than found in the present work.

The energy of activation for diffusion has been calculated from the slope of the plots in the two figures and an error has been attributed to them on the basis of the maxima and minima of the diffusion coefficients at the extreme temperatures. The energy of activation for viscosity has been calculated from plots, the values for which were taken either from the literature or the work reported in 3.1. (p. 70). These results are given in the following table:

Table 21: Values for E_D and E'_η for the lower alkyl halides

Compound	E_D kcal.	E'_η kcal.	Compound	E_D kcal.	E'_η kcal.
MeI	2.43 ± .10	1.58			
EtI	1.98 ± .10	1.52	EtBr	2.28 ± .14	1.90
nPrI	1.99 ± .12	2.20	nPrBr	1.71 ± .07	1.99
isoPrI	2.08 ± .10	1.96	isoPrBr	1.88 ± .09	1.84
nBuI	2.01 ± .09	1.95	nBuBr	1.93 ± .07	1.83
isoBuI	2.34 ± .08	1.95	isoBuBr	2.20 ± .14	1.98
secBuI	2.09 ± .10	2.13	secBuBr	1.99 ± .14	1.85

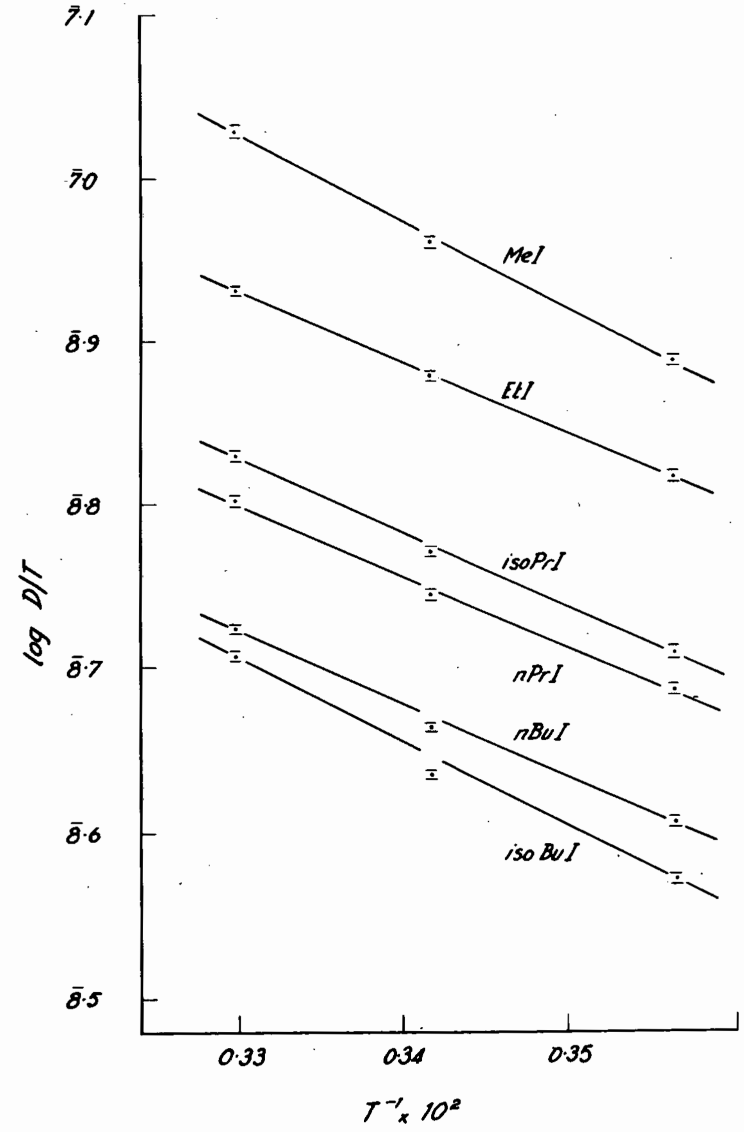

Fig. 14 - Self-diffusion coefficients of alkyl iodides

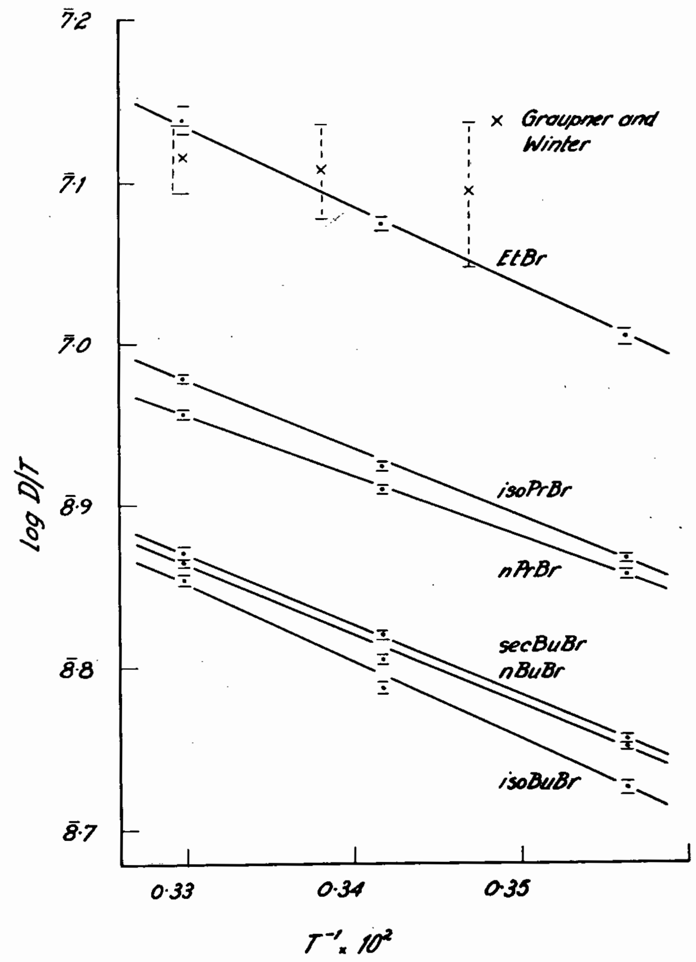

Fig. 15 - Self-diffusion coefficients of alkyl bromides

The E_D values, both in the iodide and bromide series are all similar although the values for the iso- compounds are slightly higher than those for their isomers. The lower boiling compounds have higher values than the others but this seems unlikely since one would expect any variation to lie in the opposite direction. This discrepancy is probably due to experimental error particularly as one would expect the agreement which is found in the E_η values to be reflected in the values for the diffusion process. That the activation energies are similar throughout the series might be ascribed to the predominant size of the halide atoms in the compounds.

The similarity of E_D in the series does not agree with the observation made by Oholm[73] that solutes possessing large diffusion coefficients usually have smaller temperature coefficients, but the range of diffusion coefficients is not very wide and the present results are not really suitable as a test of this broad generalization. Longsworth[42], however, examined a series of materials with molecular weights ranging from 19 to 68,000 and his findings also disagree with those of Oholm in that the temperature coefficients he measured increased only slightly with increasing particle size.

The similarity between the activation energies for the two processes is reasonably good. This is what is to be expected from the theories of Frenkel and Eyring which require them to be the same for the two processes.

On page 494 of the book by Glasstone, Laidler and Eyring[22] values for the ratio of the energy of activation for viscous flow are given as lying between 3 and 4 for unassociated liquids other than metals. From the published data for the enthalpy of vaporisation given in table 26 (p. 85), ΔE_{vap} values have been calculated and the ratio of these to the E'_η values given above, are, except for ethyl iodide, within the limits quoted. The ratios for methyl, ethyl and sec-butyl iodide are 3.76, 4.33 and 4.03 and for ethyl, n-propyl, iso-propyl and n-butyl bromide, 3.16, 3.29, 3.37 and 3.39, respectively.

(b) Constancy of $D\eta/T$ and Parameters Derived from these Values

The calculated values of $D\eta/T$ are presented in the table below. In agreement with the fact that E_D and E'_η are consistent with one another the $D\eta/T$ values, except for methyl iodide, are fairly constant for each of the compounds. The variation probably does not exceed the experimental error, indicating reasonable agreement in contrast to the values for the organic liquids discussed on page 25 (paragraph below table 5).

Table 22: Values of $D\eta/T$ for the lower alkyl halides

Compound	Temp. °C.	$D\eta/T \times 10^{10}$	Compound	$D\eta/T \times 10^{10}$
MeI	7.35	4.250		
	19.35	4.477		
	30.00	4.766		
EtI	7.35	4.388	EtBr	4.598
	19.35	4.460		4.717
	30.00	4.523		4.800
nPrI	7.35	4.195	nPrBr	4.292
	19.35	4.149		4.229
	30.00	4.188		4.225
isoPrI	7.35	4.114	isoPrBr	4.116
	19.35	4.103		4.092
	30.00	4.173		4.144
nBuI	7.35	4.061	nBuBr	4.104
	19.35	3.997		4.006
	30.00	4.113		4.155
isoBuI	7.35	3.896	isoBuBr	4.198
	19.35	3.838		3.955
	30.00	3.954		4.067
secBuI	7.35	3.810	secBuBr	3.981
	19.35	3.765		4.026
	30.00	3.827		3.995

In calculating the parameters for the molecules we apply the equation developed by Eyring for the case of self-diffusion. This is

$$\frac{D\eta}{kT} = \frac{\lambda_1}{\lambda_2\,\lambda_3} \quad \ldots\ldots\ldots\ldots\ldots \quad 69$$

and yields a value of $\lambda_2\lambda_3/\lambda_1$ from which λ_1 and $\lambda_2\lambda_3$ can be evaluated if we assume that $\lambda_1\lambda_2\lambda_3 = V/N$. Values of λ_1 and $(\lambda_2\lambda_3)^{\frac{1}{2}}$ calculated for 19.35°C. are listed in table 23 and it will be seen that $\lambda_1 \ll (\lambda_2\lambda_3)^{\frac{1}{2}}$, and is probably smaller than either λ_2 or λ_3. On the basis that λ_2 is the lateral distance between neighbouring molecules and resistance to motion would be least if this were not the largest value, it was assumed that $\lambda_2 < \lambda_3$. Scale models(74) of the stretched molecules have been measured in order to obtain relative values for comparison with λ_1, λ_2 and λ_3.

Table 23: Eyring values of λ_1, $(\lambda_2\lambda_3)^{\frac{1}{2}}$ and $\lambda_2\lambda_3/\lambda_1$

Compound	From exptl. $D\eta/T$ values λ_1 (A)	$(\lambda_2\lambda_3)^{\frac{1}{2}}$ (A)	$\lambda_2\lambda_3/\lambda_1$ (A)	Estimated from models λ_1 (A)	$(\lambda_2\lambda_3)^{\frac{1}{2}}$ (A)	$\lambda_2\lambda_3/\lambda_1$ (A)
MeI	1.83	7.58	31.3	3.50	4.27	5.28
EtI	2.08	8.02	31.3	3.50	5.41	8.40
nPrI	2.20	8.56	33.3	3.50	5.61	9.01
isoPrI	2.22	8.64	34.5	4.60	6.36	8.77
nBuI	2.34	8.99	34.5	3.50	6.03	10.42
isoBuI	2.30	9.10	35.7	4.83	6.65	9.17
secBuI	2.28	9.15	37.0	5.21	6.46	8.00
EtBr	2.06	7.76	29.4	3.50	5.23	7.81
nPrBr	2.15	8.38	32.3	3.50	5.48	8.55
isoPrBr	2.14	8.51	33.3	4.60	6.19	8.33
nBuBr	2.27	8.85	34.5	3.50	5.96	10.10
isoBuBr	2.27	8.90	34.5	4.86	6.50	8.70
secBuBr	2.29	8.87	34.5	5.00	6.26	7.87

The agreement between the results calculated from the experimental $D\eta/T$ values and the values estimated from the models is not good even though the fact that the estimated values should be slightly less, is considered. The ratios $\lambda_2\lambda_3/\lambda_1$ should, however, be comparable with those for the estimated values but as may be seen they differ widely. This ratio is also a mean value of δ if we assume $\lambda_1 = \lambda_2 = \lambda_3 = \delta$, and is the value obtained by applying Frenkel's equation, i.e. equation 16 (p. 15).

The experimentally derived values are based on the use of the molecular volume V/N and this implies that the molecules are symmetrical and that the packing is near-cubical. This is by no means true for the present case and all that may be expected is some relationship between the values obtained and the molecular dimensions. The product $\lambda_2 \lambda_3$ appears to increase fairly regularly with chain length and if the lateral distance between chains, λ_2, is nearly constant in each series this product would be approximately proportional to the length of the molecule. Exact proportionality should, however, not be expected as some freedom of rotation about C-C bonds may be retained.

The fact that λ_1 is the smallest value bears out the Eyring definition of this parameter for molecules of a non-spherical nature. The values are, however, very much smaller than the diameters of the halogens concerned although they are larger than their radii.

Applying the Stokes-Einstein relationship

$$\frac{D\eta}{kT} = \frac{1}{6\pi r} \qquad \text{.............. 70}$$

the radius r has been calculated at 19.35°C. and a comparison made with the values of $\frac{1}{2}(V/N)^{\frac{1}{3}}$ and values of the maximum radii for both the stretched and coiled configurations of the molecules as derived from scale models[74]. As may be seen the values obtained from equation 70 are smaller than the estimated values. This might be taken as an indication that the factor 6 is too large and that the equation should be modified for self-diffusion conditions. The values are, however, more realistic than those derived from the Eyring equation. This was also found to be the case for the materials considered in 1.2.3. (p. 28, paragraph 2).

Table 24: Stokes-Einstein values of r

Compound	From exptl. D η/T values r Å	$\frac{1}{2}(V/N)^{\frac{1}{3}}$ Å	Estimated from models $r_{stretched}$ Å	r_{coiled} Å
MeI	1.64	2.35	2.64	2.64
EtI	1.64	2.55	3.33	3.14
nPrI	1.77	2.72	3.93	3.33
isoPrI	1.79	2.75	3.32	3.15
nBuI	1.83	2.87	4.54	3.25
isoBuI	1.91	2.88	3.93	3.35
secBuI	1.95	2.88	3.70	3.30
EtBr	1.55	2.50	3.60	3.01
nPrBr	1.73	2.66	3.25	3.18
isoPrBr	1.78	2.69	3.19	3.02
nBuBr	1.83	2.82	4.44	3.25
isoBuBr	1.85	2.82	3.75	3.18
secBuBr	1.82	2.83	3.70	3.30

(c) Values of Derived Thermodynamic Quantities

A similar type of calculation to that carried out by Partington et al.[39] for the evaluation of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ the free energy and entropy of activation, has been made on the basis of equations 30 and 31 (pp.28,29). As suggested by Eyring, δ has been evaluated by assuming that $\delta = (V/N)^{\frac{1}{3}}$. The values obtained were calculated at 19.35°C. and are listed in table 25.

Table 25: Values of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ for the lower alkyl halides

Compound	$\Delta G^{\ddagger}$ kcal./mole	$\Delta S^{\ddagger}$ E.U.	Compound	$\Delta G^{\ddagger}$ kcal./mole	$\Delta S^{\ddagger}$ E.U.
MeI	3.61	-4.02			
EtI	3.82	-6.32	EtBr	3.53	-4.28
nPrI	4.08	-7.10	nPrBr	3.83	-7.27
isoPrI	4.05	-6.71	isoPrBr	3.82	-6.56
nBuI	4.11	-7.22	nBuBr	4.03	-7.22
isoBuI	4.29	-6.69	isoBuBr	4.06	-6.35
secBuI	4.25	-7.41	secBuBr	4.02	-7.27

As found by Partington et al. for the homologous series of alcohols there is a small but steady increase in $\Delta G^{\ddagger}$ in spite of there being no trend of variation in E_D. Contrary to their findings though, the variation is $\Delta S^{\ddagger}$ is not haphazard but decreases with increasing molecular weight of the compounds. The values for the iso-butyl compounds in each series resemble those of the iso-propyl, and this is of interest when one considers that these compounds have C_3 chains with a substituent on the C_2 carbon atom.

The values of $\Delta S^{\ddagger}$ are negative and this might imply some degree of ordering or loss of rotation of the molecules. It is of interest to note that for the similar process of viscous flow, Bondi[26] also found that the values for $\Delta S^{\ddagger}$ were negative for the lower molecular weight hydrocarbons.

In calculations carried out by Eyring of the entropy factor for diffusion on page 525 of the book "Theory of Rate Processes"[22], he evaluated $(e^{\Delta S^{\ddagger}/R})^{\frac{1}{2}}$ for phenol in methyl alcohol, phenol in benzene, tetrabrom- in tetrachlor-ethane and bromine in carbon disulphide and obtained values of 1.4, 1.4, 1.0 and 0.4 A, respectively. He states that these results "indicate that $\Delta S^{\ddagger}$ cannot differ appreciably from zero; i.e. $e^{\Delta S^{\ddagger}/R}$ is approximately unity, and the figures given are roughly equal to δ, the distance from one equilibrium position to the next in diffusion." As may be seen these values are very much smaller than would be expected for the systems under consideration. If, as was found above, the value for $\Delta S^{\ddagger}$ is taken not as unity but as a negative value, the resultant value of δ would be greater and hence more realistic.

It must be noted, however, that the values for $\Delta S^{\ddagger}$, as calculated for the halides, cannot be taken as quantitative since the evaluation of $\Delta G^{\ddagger}$, upon which these are dependent, is by no means accurate. The dimension δ is not known and the value used assumes a compact molecule occupying a cubical space. The greater the value of δ, the larger the value of $\Delta G^{\ddagger}$ and the smaller the value of $\Delta S^{\ddagger}$. If one considers an elongated molecule moving in a direction such that the rest of the molecule offers least resistance to this movement, δ would be at least as great as the largest dimensions of the molecule. Using this value for δ, $\Delta S^{\ddagger}$ tends to a more negative value since $\Delta G^{\ddagger}$ increases considerably. Furthermore, as discussed on page 16 in the paragraph following equation 22, it is felt that a factor of 1/6 has been omitted from the Eyring equation. Inclusion of this factor reduces $\Delta G^{\ddagger}$, however, and $\Delta S^{\ddagger}$ is increased by approximately 3.5 E.U. thus becoming more positive.

(d) Evaluation of the Diffusion Constant, D_o

The experimental values of the diffusion constant D_o, have been calculated from the equation

$$D = D_o \, e^{-E_D/RT} \qquad \ldots\ldots\ldots\ldots\ldots \quad 71$$

where E_D has been obtained by the plot of log D/T versus 1/T. Values for D_o, calculated according to the Eyring theory (pp. 30,31) have been based on equation 38. As we are only concerning ourselves with the diffusion constant the equation has been reduced to:

$$D_o = \left(\frac{V}{N}\right)^{\frac{2}{3}} \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \left(\frac{RT}{NP_v} \quad e^{-(E_{vap} + RT)/RT} \right)^{-\frac{1}{3}} \qquad \ldots\ldots \quad 72.$$

For the evaluation of this equation it is necessary to know the latent heat of vaporisation. The data for these compounds are limited and it was considered best to estimate them by application of Trouton's equation[75] or preferably that of Hildebrand[76], which is a more accurate modification.

Trouton's rule states that the quotient of the heat of vaporisation and the absolute temperature of the boiling point is the same for all liquids. This means that the entropy of vaporisation for a fixed pressure, is constant. Results indicate that the rule is only approximately true. By assuming, as does Hildebrand, that the entropy of vaporisation for a fixed volume is constant, a more accurate relationship is obtained.

If the range of temperature is sufficiently small the heat of vaporisation of a liquid may be regarded as constant and the Clapeyron-Clausius equation may be integrated to the form

$$\ln \frac{p}{p_o} = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_o} - \frac{1}{T} \right) \quad \ldots\ldots\ldots\ldots\ 73$$

If T_o is taken to be the boiling point T_b so that p_o is an atmosphere, this becomes

$$\ln p = \frac{\Delta H_{vap}}{R\ T_b} \left\{ 1 - \frac{T_b}{T} \right\} \quad \ldots\ldots\ldots\ldots\ 74$$

$$= \frac{\Delta S}{R} \left\{ 1 - \frac{T_b}{T} \right\} \quad \ldots\ldots\ldots\ldots\ 75$$

where ΔS is the Trouton entropy normally taken as 23.

If we take T_o as the temperature at which the molar volume of the saturated vapour is 22.4 litres, then (if we assume the vapour to be ideal),

$$p_o = \frac{RT_o}{22.4} = \frac{T_o}{273.2} \text{ atmospheres} \quad \ldots\ldots\ldots\ 76$$

and the Clapeyron-Clausius equation becomes

$$\ln p = \ln \frac{T_o}{273.2} + \frac{\Delta S}{R} \left\{ 1 - \frac{T_o}{T} \right\} \quad \ldots\ldots\ 77$$

where ΔS is now the Hildebrand entropy, which for normal liquids may be taken as 22.1 so that equation 77 becomes

$$\log p = \log T_o + 2.40 - 4.83 \frac{T_o}{T} \quad \ldots\ldots\ldots\ 78$$

if p is in atmospheres.

With p as one atmosphere and T as the boiling point, T_b, values of T_o may be obtained by numerical solution of the above equation. Thus, if the vapour pressure of a liquid is known at different temperatures the heat of vaporisation can be evaluated from the Clapeyron-Clausius equation. If, however, only the boiling point is known, T_o can be evaluated and since $\Delta H_{vap} = T_o \Delta S$ where ΔS is the Hildebrand entropy, the heat of vaporisation can also be obtained and from this the energy of vaporisation, since $\Delta E_{vap} = \Delta H_{vap} - RT$.

In the following table the values for ΔH_{vap} and ΔE_{vap} calculated from equations 73 and 78, are given together with the maximum, minimum and mean values of the results in the literature[55].

Table 26: Latent heats and energies of vaporisation

Compound	Calculated ΔH_{vap} kcal./mole	Calculated ΔE_{vap} kcal./mole	Literature ΔH_{vap} kcal./mole Max.	Min.	Mean
MeI	7.06	6.43	6.54	6.51	6.52
EtI	7.79	7.10	7.85	7.11	7.17
nPrI	8.56	7.79	-	-	-
isoPrI	8.24	7.52	-	-	-
nBuI	9.26	8.46	8.45	8.43	8.44
isoBuI	9.03	8.25	-	-	-
secBuI	9.02	8.24	-	-	-
EtBr	6.96	6.34	6.72	6.38	6.58
nPrBr	7.78	7.10	-	-	7.13
isoPrBr	7.51	6.85	-	-	6.79
nBuBr	8.55	7.81	-	-	7.78
isoBuBr	8.31	7.59	-	-	-
secBuBr	8.31	7.59	-	-	-

The calculated values for ΔH_{vap} appear to be greater than the values in the literature by the amount RT since there is good agreement between ΔE_{vap} and the figures in the last column. Since this column is incomplete, however, the values calculated for the heat of vaporisation have been preferred for substitution in equation 72 since any error that is introduced by this would be uniform throughout the series.

The values of D_o calculated at 19.35°C. from the experimental values of D and E_D, together with the values calculated according to the Eyring equation are listed in table 27. The D_o value derived from the experimental values is temperature dependent and is lower than the value which would have been obtained had E_D been used in calculating it. Since the D_o in Eyring's equation is also temperature dependent it is felt that the value given here is the one with which the Eyring value should be compared although there might be a slight difference in the degree of the temperature dependence in the two cases.

An alternative method for the calculation of D_o is by application of Frenkel's equation

$$D = \delta^2 \frac{1}{6\tau_o} \quad e^{-E_D/RT} \quad \ldots\ldots\ldots\ldots\ldots \quad 79$$

whence $\quad D_o = \frac{\delta^2}{6\tau_o}$. In order to evaluate τ_o it has been assumed that this is the time taken for the molecule to travel a distance δ with an average thermal velocity of $(8RT/\pi M)^{\frac{1}{2}}$, where M is the molecular weight. The value of δ has been taken as equal to $(V/N)^{\frac{1}{3}}$ and the calculated values of D_o are also listed in table 27. By rights a D_o value should have been calculated from the experimental results on the basis of a temperature dependence of $T^{\frac{1}{2}}$ but it has been considered that, in view of the expected relationship with the calculated values which are at best only correct to the order or magnitude, this is unwarranted.

Table 27: Comparison of experimentally derived and calculated values of $D_o \times 10^4$ in $cm^2 sec^{-1}$

Compound	D_o Exptl.	D_o Eyring	D_o Frenkel	Compound	D_o Exptl.	D_o Eyring	D_o Frenkel
MeI	17.49	14.2	1.63				
EtI	6.68	16.5	1.70	EtBr	17.62	18.4	1.99
nPrI	4.98	18.8	1.73	nPrBr	4.51	20.5	1.99
isoPrI	7.78	18.9	1.75	isoPrBr	6.27	20.8	2.01
nBuI	4.28	20.7	1.76	nBuBr	5.18	22.6	2.00
isoBuI	7.08	20.5	1.76	isoBuBr	7.93	22.5	2.00
secBuI	4.93	20.7	1.76	secBuBr	5.94	22.6	2.00

The Frenkel equation is only intended to give a rough estimate, of the correct order of magnitude, and this is achieved. The Eyring equation is supposed to give a better estimate, but there is no evidence of this in table 27, thus confirming the deductions of Graupner and Winter[38]. It will be noted that, except for methyl iodide and ethyl bromide, which, owing to their volatility, give the least reliable results for D_o, the Eyring values are much larger than the experimental values and an order of magnitude larger than the Frenkel values. The use of the slightly high values of ΔH_{vap} in the calculation of the Eyring values will tend to make these smaller but as this is involved as the cube root it should have only a limited effect. As was discussed on page 16 in the paragraph after equation 22, it would seem that a factor 1/6 is missing from the Eyring equation, especially if it is to be brought in line with that of Frenkel. It is evident that division of all Eyring values for D_0 in table 27, by 6 would effect a much better agreement.

3.3. Conclusions regarding the Eyring Theory

By application of the Eyring equations it is possible to make an assessment of λ_1 and $(\lambda_2\lambda_3)^{\frac{1}{2}}$ from values of D, η and T. In the evaluation, however, experimental results bear out the type of model used in only very broad outline. From values of D, η and V/N, actual calculated values of λ_1 and $(\lambda_2\lambda_3)^{\frac{1}{2}}$ differ markedly from those expected. This is in part probably caused by considering that the molecules occupy a nearly cubic packing. Apart from methyl iodide, where the disagreement with Eyring is least, the molecules generally considered would in fact not occupy a cubic cell in a packing based on a nearly rectangular prism.

Eyring has made mention of an alternative mechanism by which diffusion can occur. This is the bimolecular process whereby two molecules roll around one another and thus change their relative positions. This is in contrast to the process of sporadic jumping on which his theory is based. It is possible that if the bimolecular mechanism were investigated more fully it would lead to a more precise model. It does allow for the comparatively small energy of activation for diffusion or viscosity when this is compared with that for vaporisation, i.e. with the energy necessary for the formation of a complete hole. Furthermore the bimolecular model would result in small values of λ_1.

It would, however, be necessary in applying this model, to review the process as the present theory has been derived ostensibly on the basis of the Einstein concept of D = qkT.

This concept would not necessarily apply to the bimolecular model, and if it did would have to be specially derived. This argument applies equally to other models which might be put forward and for which it is as difficult to cater.

The theory of Born and Green, while more rigorous than those which give only an order of magnitude, cannot be applied to experimental results as the distribution functions and internal forces have not been evaluated for complex molecules. Their theory does not lead to equations for the evaluation of diffusion and viscosity coefficients which are more accurate than those of Eyring.

For the evaluation of the frequency of jump, Eyring has used a more precise model than has Frenkel but this has not resulted in better results in the calculation of absolute values of the diffusion constant. The Eyring frequency is given in terms of the activated complex and enables one to calculate free energies and entropies of activation. The latter is of particular interest but when one comes to apply the Eyring equation, which appears to be a theoretical advance on that of Frenkel, there are too few measurable quantities to allow a reliable evaluation of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$ to be made.

The Eyring theory leads to values which are correct only to an order of magnitude and it is difficult to see how this can be avoided from the approximations which have to be employed in the evaluation.

PART IV

SELF-DIFFUSION IN A BINARY MIXTURE

4.1. Theoretical and Historical Background

4.1.1. General Considerations

In order to understand self-diffusion in a mixture it is necessary to consider the process of interdiffusion. This is actually rather complex. In a binary mixture of A and B, A and B diffuse individually along their own concentration gradients but in opposite directions. Each process will have an individual diffusion coefficient; Hartley and Crank(77) have called these "intrinsic" diffusion coefficients.

These intrinsic coefficients are not necessarily related. Associated with the movement of each molecule is a volume, and it is almost inevitable that the volume of A transported in one direction will not equal that of B transported in the other direction. As Hartley and Crank have pointed out, a mass-flow must take place in order to maintain balance. This mass-flow is to be distinguished from the random mixing process which characterises pure diffusion. Thus, an interdiffusion coefficient is a composite of the intrinsic diffusion coefficients and the mass-flow. Prior to Hartley and Crank's paper, the truth of this had already been realised in the case of metals and the existence of mass-flow had been demonstrated by the experiments of Smigelskas and Kirkendall(78). They showed that inert markers placed at the boundary between zinc and copper underwent progressive displacement as a result of mass-flow arising from lack of balance between the volume diffusion of zinc in one direction and of copper in the opposite direction. The solid state often cannot accommodate the amount of mass-flow required, with the result that metalic interdiffusion is then accompanied by formation of cavities.

It is clear that it would be preferable, on theoretical grounds at least, to measure intrinsic diffusion coefficients, as these refer to true diffusion of each constituent along its own concentration gradient. If some of the molecules A are labelled in one part of a uniform mixture of A and B, the self-diffusion coefficient of labelled A in the mixture will be a measure of the intrinsic coefficient of A. The same applies to B and the use of isotopes, therefore, presents itself as the only means of measuring intrinsic diffusion coefficients in liquid mixtures. Furthermore, the conditions required for carrying out experiments of this nature necessitate the absence of concentration gradients, so that, where the diffusion is strongly concentration dependent, only one measurement is required at each concentration instead of the cumbersome procedure mentioned in 1.1.8, (p. 18, paragraph 2). In the present instance, labelled material contained in a capillary tube was immersed in an unlabelled mixture of virtually the same composition and the self-diffusion coefficient was measured in the normal way. By choosing different compositions, diffusion coefficients of each component in the system could be determined over the complete range from 0 to 100 mole per cent. of each.

4.1.2. Literature Survey

In recent years, the significance of intrinsic diffusion coefficients and the use of isotopes to measure self-diffusion coefficients of individual constituents in mixtures have been increasingly appreciated. The greater proportion of the reported work has been carried out in ionic solutions[30,40,68, 79-88] where it is possible to evaluate these coefficients at very low concentrations. The theories of Nernst[89], Onsager and Fuoss[90], and Onsager[91] which are derived for these concentrations, have been examined and agreement with the experimentally derived values is good. Measurements have been made of the self-diffusion coefficients of both ionic species of a dissolved salt[32,67,88,92-94], and in a recent experiment Wang[95] has, in addition, evaluated the self-diffusion coefficient of the solvent, water, using H_2O^{18}, and he discusses the effect of the ionic hydration on this. He found that in certain cases the coefficient for water was higher than in the pure state. He has also measured the self-diffusion coefficient of ovalbumin and of water in aqueous solutions of the protein(96) and finds that the coefficient for water is, in this case, lower than in the pure state. His work is a step forward in the elucidation of the structure of water in different solutions.

In dealing with organic mixtures(97-101) the method of evaluation of diffusion coefficients have mostly been based on normal analytical procedures and the results are therefore mutual diffusion coefficients. Koeller and Drickamer(102) studied the self-diffusion of labelled carbon disulphide in organic mixtures under pressure.

4.1.3. Inter-relationship of the Various Diffusion Coefficients

The first appreciation of the distinction between intrinsic diffusion coefficients and the interdiffusion coefficient appeared in studies of diffusion in metals. In 1942 Johnson(103) measured self-diffusion coefficients of gold and of silver in an alloy containing 50.8 atomic per cent. silver using radio-isotopes, and showed that they were very different. They also differed from the "chemical diffusion coefficient", i.e. the inter-diffusion coefficient, measured in the usual way over a small concentration range to avoid effects due to concentration dependence. Some years after this excellent experimental study, Darken(104) showed a clear appreciation of the relationship between the intrinsic coefficient and the inter-diffusion coefficient in metals and the part played by mass-flow in the latter. He thus anticipated the paper of Hartley and Crank(77), and arrived at essentially the same equation relating the coefficients as they did. This equation has also been derived more recently by other workers(105,106,107). The relationship derived by Hartley and Crank may be written in the form

$$D_v = C_A V_A D_B + C_B V_B D_A \quad \ldots\ldots\ldots\ldots\ 80$$

where D_v is the mutual or interdiffusion coefficient, D_A and D_B are the two intrinsic coefficients, C_A and C_B the concentrations of each component in moles per unit volume and V_A and V_B the respective molar volumes of components A and B in the mixture of A and B. A defect of Darken's treatment is that he assumed equal molecular volumes for his two interdiffusing metals and thus arrived at the equation

$$D_v = N_A D_B + N_B D_A \quad \ldots\ldots\ldots\ldots\ 81$$

where N_A and N_B are the mole-fractions of A and of B, respectively. The assumption is quite unnecessary and equation 80 is therefore preferable to that proposed by Darken.

According to equation 80, interdiffusion coefficients should always lie between the intrinsic diffusion coefficients, D_A and D_B. The data of Johnson do not in fact appear to conform to this, since the interdiffusion coefficients for his alloy at various temperatures were roughly equal to the sum of the self-diffusion coefficient of silver and of gold. Darken[104] pointed out that, in a non-ideal mixture, the intrinsic diffusion coefficient is not identical with the self-diffusion coefficient and the latter must therefore be distinguished by the symbols D_A^* and D_B^*. It will be shown in 4.5. (p. 102), that

$$D_A = D_A^* \frac{d \ln a_A}{d \ln C_A} = D_A^* \frac{d \ln N_A f_A}{d \ln C_A} \quad \ldots\ldots\ldots 82$$

where a_A is the activity, N_A the mole fraction and f_A the activity coefficient of A in the mixture. A similar expression holds for D_B.

$$\text{Since } C_A = \frac{N_A}{N_A V_A + N_B V_B}, \quad N_A + N_B = 1 \text{ and } C_A/C_B = N_A/N_B$$

it can be shown that $d \ln C_A = \dfrac{V_B}{N_A V_A + N_B V_B} \, d \ln N_A$.

By substitution in equation 80,

$$D_V = \frac{d \ln N_A f_A}{d \ln N_A} \left(N_A D_B^* + N_B D_A^*\right) \quad \ldots\ldots\ldots\ldots\ 83$$

since according to the Duhem relationship[108] $\frac{d \ln N_A f_A}{d \ln N_A} = \frac{d \ln N_B f_B}{d \ln N_B}$.

Darken showed that, using the values of Wagner and Engelhardt[109] for activity coefficients of silver and of gold in an alloy, values of D_v calculated by equation 83, from Johnson's values of D_A^* and D_B^*, agreed well with the experimental values of D_v.

In liquids intrinsic diffusion coefficients cannot be measured directly, but in metals the extent of mass-flow can be followed by inert markers and used to evaluate D_A and D_B. In this way Seith and Kottmann[110] obtained D_A and D_B for a silver-gold alloy of the same composition as used by Johnson. They were able to prove that these values were related to D_A^* and D_B^* by equation 82.

In the present experiments, it can be assumed that mixtures were nearly ideal, that is f_A is unity, whence

$$D_v = N_A D_B^* + N_B D_A^* \qquad \text{............. 84.}$$

4.2. Experimental

4.2.1. General Procedure

Use has been made of two of the compounds for which self-diffusion coefficients have been determined and found to be reasonably different. Ethyl iodide and n-butyl iodide were chosen as being the most suitable as they have coefficients of 2.212 and 1.347 x 10^{-5} $cm.^2 sec.^{-1}$, respectively, at 19.35°C. The difference between the coefficients for methyl iodide and n-butyl iodide is greater but the low boiling point of methyl iodide would have complicated the technique unnecessarily. As it was, the preferential evaporation of ethyl iodide from the mixtures caused difficulty. The iodides were preferred to the bromides since iodine-131 has the longer half-life and was generally always available.

Self-diffusion coefficients were measured for the individual compounds at five different concentrations and values for the diffusion coefficients of each of the pure compounds into the other were obtained. On the whole the experiments were carried out at 19.35°C. but for the 1:1 mole ratio mixture, and pure ethyl iodide into pure n-butyl iodide, coefficients were measured at three temperatures so that the energies of activation could be evaluated.

The following viscosities were also determined: (a) viscosity of the equimolar mixtures at 7.35, 19.35 and 30.0°C., and, (b) viscosities of two other mixtures at 19.35°C. The former enabled comparison of activation energies to be made, and from a plot of viscosities at 19.35°C., see figure 17, the viscosity of any mixture at this temperature could be estimated and used to compute values of D. The procedure adopted for these determinations was the same as that detailed in 2.4.2. (pp. 66,67). For the purposes of calculation it was assumed that the heat of solution was negligible and that there was no resultant volume change on mixing. Densities were accordingly calculated on the basis of the weights and volumes of the compounds which constituted the mixtures.

4.2.2. Special Precautions

Although the method used was the same as was applied for the measurement of self-diffusion coefficients of the pure compounds, certain added precautions had to be taken to overcome problems peculiar to measurements in mixtures. These are discussed in detail in the following sub-sections:

(a) Evaporation losses

Because of the difference in boiling points, 72.3 and 130.4°C. for ethyl and n-butyl iodide, respectively, the loss of ethyl iodide from a mixture was greater than that of n-butyl iodide. For each experiment, therefore, fresh mixtures of labelled material were made up, so as to ensure that there were no great changes in concentration from one experiment in a series, to another. In the making up of a mixture precautions were taken to restrict evaporation losses and the n-butyl iodide was always weighed out first and the ethyl iodide added to it irrespective of which compound was labelled.

The evaluation of the initial concentration C_o was complicated by this loss of ethyl iodide as reproducibility could not be obtained due to the small change in concentration each time the bottle containing the active sample was opened. In the case of labelled ethyl iodide the concentration decreased and for labelled n-butyl iodide it increased. Solutions for the determination of the initial concentration were accordingly made up prior to and immediately after the experimental tubes were filled and the mean taken of these values. The difference was not great and over the eight tubes the error should have averaged out since those tubes filled first would have differed from the mean to the same extent, but in the opposite direction, as those tubes filled last. Internal errors for each experiment were on the whole fairly small but in certain cases the reproducibility between experiments was poor with the result that a large number of experiments had to be carried out.

(b) The effect of density

This effect was only evident in the experiments discussed in 4.4. (p. 101), in which pure n-butyl iodide was diffused into ethyl iodide. The densities for these two compounds are 1.6165 and 1.9383 g. per ml., respectively, at 19.35°C. with the result that when a tube containing n-butyl iodide was immersed in ethyl iodide the n-butyl iodide floated into the bulk liquid. It was therefore necessary to invert the tubes for this experiment and they were attached to the central stem of the cells with pipe cleaners and this meant that they were not always vertical. The introduction and removal of the full tubes from the cell liquid was difficult as liquid tended to drain out of them particularly on removal. The results were, however, reasonable and as they are intended only to give an indication of the type of result to be expected no attempt was made to improve the technique.

(c) Possibility of exchange

The addition of a labelled to another unlabelled compound gives rise to the possibility of exchange between the labelled iodine in the one and the unlabelled iodine in the other. If this occurs the diffusion coefficient measured is not that of the originally labelled compound alone but is that of a mixture. The composition of this mixture will depend on the degree to which exchange has occurred and might even vary during the course of an experiment.

Two 1:1 mole ratio mixtures were made up with labelled ethyl iodide. The one was used for measurement of the self-diffusion coefficient of ethyl iodide and the other was kept at 20°C. for five days. Had exchange occurred during this time, the diffusion coefficient subsequently measured for this material should have been lower than that obtained for the first mixture, since the diffusion coefficient of n-butyl iodide is lower than that of ethyl iodide. Any effect that might have been apparent was, however, masked by the loss of ethyl iodide from the mixture. In a later experiment in which a trace of n-butyl iodide was allowed to diffuse in ethyl iodide, two successive runs were carried out with the same active solution. Because of the low concentration, losses due to evaporation were negligible. The diffusion coefficient measured in the second run was, if anything, lower than in the first one whereas if exchange had occurred it should have been higher. Similar results were obtained when a trace of ethyl iodide was added to n-butyl iodide. Furthermore, in experiments carried out on the labelling of halides, in a case where no solvent was added the efficiency of labelling was found to be very poor. This would indicate that in the pure state little exchange occurs and this would be even less at the lower temperatures encountered in the diffusion measurements. It is felt, therefore, that over the period of the experiments and at the temperatures used the effect due to exchange can be neglected as being so limited as to be masked by the inaccuracies inherent in the method.

(d) Concentration differences

Diffusion was carried out from a mixture containing one labelled compound into a mixture of the unlabelled compounds. The composition of the two mixtures was as nearly the same as was possible but, since the two mixtures could not be made up simultaneously and the proportionate loss from the smaller volumes of the active mixtures was higher, there must always have been some slight discrepancy between them. From the results obtained it was obvious, though, that the effect of these small variations could be disregarded in establishing the different points since the dependence on concentration, though marked over the complete concentration range, was limited over small differences of concentration. In their experiments Mills and Kennedy[94] investigated the effect of concentration gradients on the measurement of individual diffusion coefficients and found that this was only appreciable at the high concentrations where the total change in concentration was relatively large.

The desirability of having the concentration of the bulk mixture equal to that of the labelled one, and the limited amount of material available, made it necessary to fractionate the mixtures after every three experiments. Pure compounds were thus repeatedly used to make up fresh mixtures when their activity had decreased sufficiently.

4.3. Results and Discussion

Although the number of independent results obtained in this investigation is limited to eighteen the amount of work involved in their determination was considerable, particularly as most of the results obtained in the first twenty experiments were carried out under conditions which made the results suspect. A great deal of trouble was also encountered with temperature control of the constant temperature room, and stirring motors either ran too hot and vibrated excessively or stopped altogether.

In all these cases results were suspect and had to be disregarded. In all some seventy-five experiments were carried out.

The mean values of the results measured at 19.35°C. are listed below together with the self-diffusion coefficients of the pure compounds as given in table 19 (p. 74), as these are the zero points for the two series of self-diffusion coefficients.

Table 28: Values of D^* for ethyl and n-butyl iodide in a binary mixture

Cmpd.	Mole-fraction of EtI	$D^*_{EtI} \times 10^5$ $cm^2 sec^{-1}$	Cmpd.	Mole-fraction of EtI	$D^*_{nBuI} \times 10^5$ $cm^2 sec^{-1}$
EtI	1.00	2.212 ± .014	nBuI	.975 ± ?	2.046 ± .019
	.7995 ± .0001	2.060 ± .015		.8012 ± .0011	1.897 ± .016
	.6044 ± .0003	1.910 ± .012		.6029 ± .0021	1.677 ± .011
	.4948 ± .0047	1.840 ± .019		.4970 ± .0027	1.596 ± .010
	.2500 ± .0006	1.618 ± .011		.2460 ± .0018	1.500 ± .011
	.025 ± ?	1.510 ± .013		0.00	1.347 ± .007
EtI	into pure nBuI	1.764 ± .013	nBuI	into pure EtI	1.823 ± .011

It is apparent that the results for the two series are independent of one another and that they are significantly different over the whole concentration range. The coefficients for ethyl iodide decrease towards a value which is higher than the self-diffusion coefficient of n-butyl iodide in itself as the mole-fraction of ethyl iodide decreases from one to zero; that for n-butyl iodide increases to a value less than that of ethyl iodide in itself as the mole-fraction of n-butyl iodide decreases from one to zero. In their experiments on mixtures of water and alcohol, Hammond and Stokes[111] determined the limiting values of the interdiffusion coefficient by extrapolation and found that these differed from the self-diffusion coefficients of the two pure compounds in a similar fashion to that found here. The two values for the self-diffusion coefficients of trace amounts of the one compound in the other are in fact the limiting values for the

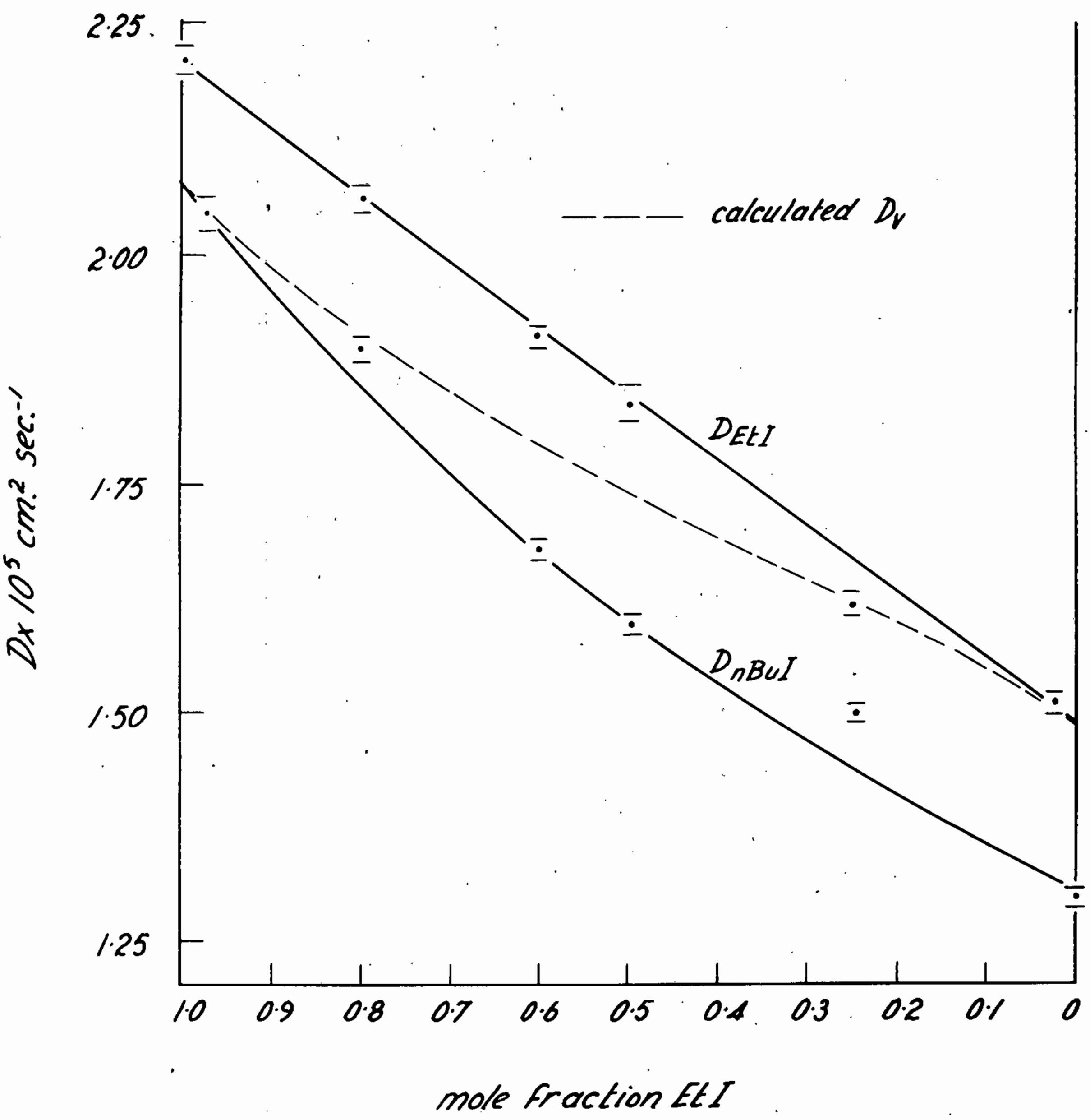

Fig. 16 - Diffusion coefficients for the binary system

interdiffusion coefficients as may be more readily seen from figure 16 where the values given above are plotted together with the curve for the interdiffusion coefficients calculated from equation 84. This interdiffusion curve is also dependent on concentration but to a lesser degree than the self-diffusion coefficients. Wang[112] measured the self-diffusion of glycine at low concentrations of the amino acid in water and his limiting value is in agreement with that found by Lyons and Thomas[113] for the interdiffusion coefficient. At finite concentration the interdiffusion coefficients are in this case less than the self-diffusion coefficients for glycine. According to equation 84 this is not possible since the self-diffusion coefficient of water is higher than that of glycine and the interdiffusion coefficient should lie between them. The solutions are, however, not ideal, and Wang has shown that, if this is taken into account by plotting $D_v \; d \ln N_A / d \ln N_A f_A$ in place of D_v, as required by equation 83, the resulting values lie above those for $D^*_{glycine}$, as would be expected; that is the case is similar to that of the silver-gold alloy, Darken's discussion of which is mentioned in paragraph 3 on page 91.

In the present work it has not been possible to determine the interdiffusion coefficients. Those would be obtained most conveniently by an optical method, but, as the refractive indices of the two compounds are not very different and the method could only be applied when the concentration differences were large, it would be of little value.

The results for ethyl and n-butyl iodide in the 1:1 mole ratio mixture were $(1.588 \pm .009) \times 10^{-5}$ and $(1.336 \pm .006) \times 10^{-5}$ cm.^{2}sec.$^{-1}$ at 7.35°C. and $(2.128 \pm .018) \times 10^{-5}$ and $(1.856 \pm .014) \times 10^{-5}$ cm.^{2}sec.$^{-1}$ at 30.00°C., respectively. The viscosity of this mixture at 7.35, 19.35 and 30.00°C. was found to be 0.8356, 0.7252 and 0.6521 centipoises. From plots of log D/T versus 1/T and log η versus 1/T, the energies of activation have been calculated and are given in table 29 together with the values previously given for the pure compounds in table 21. (p. 76).

Table 29: Values of E_D and E'_η

Compound	System	E_D kcal./mole	E'_η kcal./mole
EtI	Pure compound	1.98 ± .10	1.52
nBuI	" "	2.01 ± .09	1.95
EtI	Mixture	1.61 ± .11	1.84
nBuI	"	1.87 ± .09	1.84
EtI	Into pure nBuI	1.71 ± .08	-

As would be expected from the similarity of the E_D values for the pure compounds there is not an appreciable difference between these values and those for the mixture though the value for ethyl iodide is somewhat lower. The value of E'_η is also in good agreement with the E_D values and agrees with that for viscous flow in the pure n-butyl iodide. As a matter of interest the E_D value was also determined for the diffusion of pure ethyl iodide into pure n-butyl iodide and this was also in good agreement with the other values, which indicates that the energy of activation should be the same over a large concentration range, since the diffusion coefficient measured was a mean value over a wide variation in concentration (see 4.4.).

In the discussion of the values of $D\eta/T$ (pp. 25 - 28) the constancy of these values and their possible variation with temperature were pointed out. A natural extension to this is that at a given temperature in a series of mixtures $D^*\eta/T$ and hence $D^*\eta$ might well be independent of composition, providing that molecular packing and spacing do not vary with concentration. Viscosities were determined at different compositions of an ethyl iodide/n-butyl iodide mixture and are presented graphically in figure 17. From this curve and those in figure 16, $D^*\eta$ values have been calculated and are given in the following table:

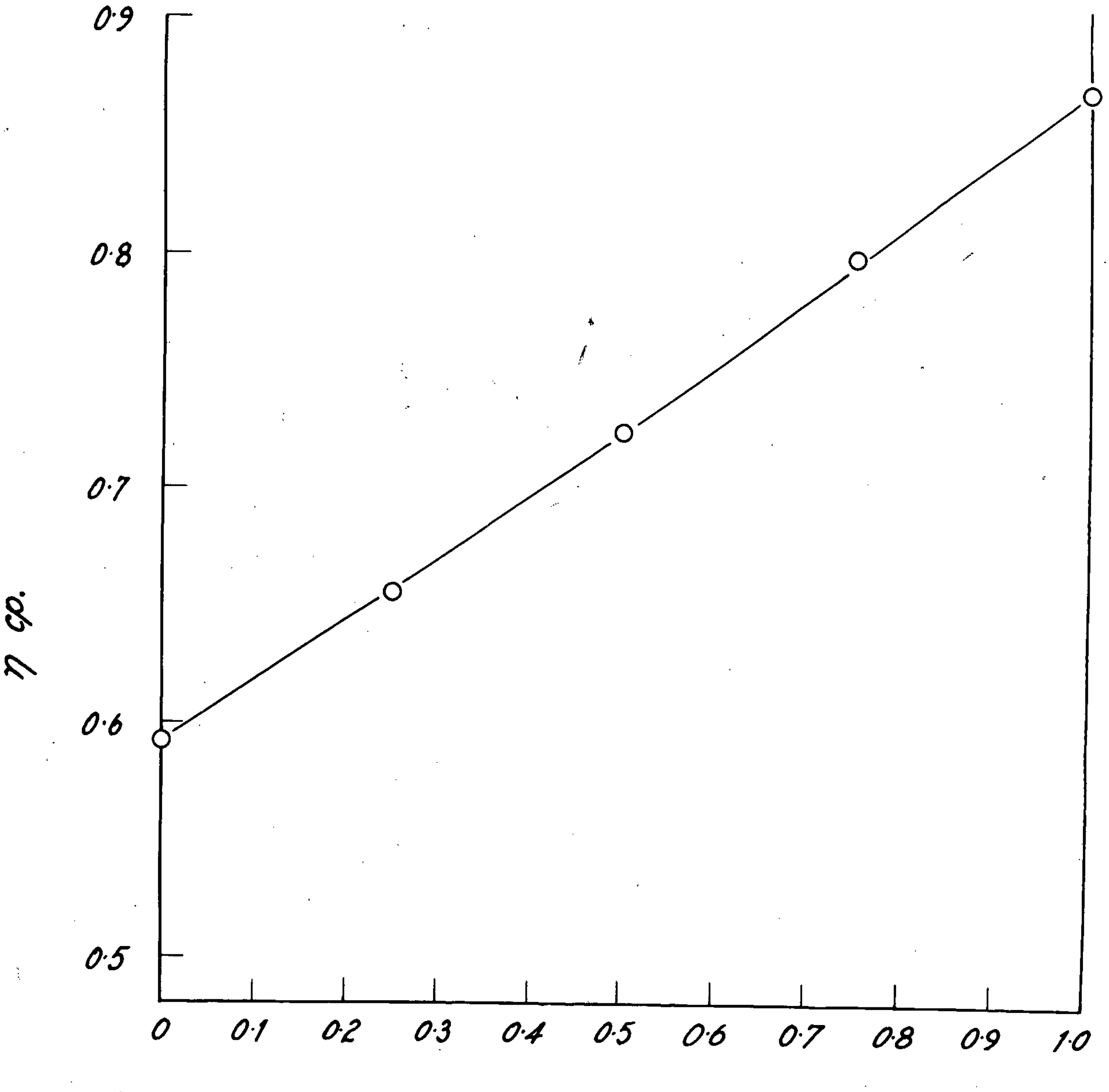

Fig.17 - Viscosity coefficients for EtI/nBuI mixtures

Table 30: Values of $D^{*}\eta$ for the binary system.

Mole fraction of EtI	$D^{*}_{EtI}\eta \times 10^{7}$	$D^{*}_{nBuI}\eta \times 10^{7}$
1.0	1.31	1.23
0.8	1.32	1.21
0.6	1.33	1.17
0.4	1.33	1.17
0.2	1.32	1.18
0.0	1.29	1.17

The values for ethyl iodide are reasonably constant but those for n-butyl iodide are high at the low concentrations of this material. This deviation is not unexpected since the change in D^{*}_{nBuI} with concentration is not linear whilst that for η is practically linear.

4.4. Interdiffusion between Pure Liquids

As mentioned in 1.1.8. (paragraph 2, p. 18), concentration dependence is an important factor in the measurement of diffusion coefficients in liquid mixtures. It is hardly likely that a dilute solution of ethyl iodide in n-butyl iodide will have the same interdiffusion coefficient as dilute n-butyl iodide in ethyl iodide, since in one the main process is diffusion of a small molecule in a medium of larger molecules and, in the other, the reverse is the case. The data recorded in table 28 (p. 98) and plotted on the following page in figure 16, gives a true picture for this system. It is perhaps noteworthy that the interdiffusion coefficient as depicted by the broken line curve, varies less than the self-diffusion coefficients, but is certainly not concentration independent.

Earlier workers have often been unable to avoid wide concentration differences because of experimental difficulties, and it therefore seemed desirable to include some measurements of this kind. The extreme cases, diffusion of pure labelled ethyl the number of molecules per unit area per second, is

$$\text{Flux} = -N\, D_A \frac{d\, C_A}{dx} \quad \ldots\ldots\ldots\ldots\ 86$$

where N is Avogadro's number. The flux is also equal to $v_A N C_A$ and hence

$$D_A = -\, v_A \frac{dx}{d \ln C_A} \quad \ldots\ldots\ldots\ldots\ 87$$

and if $v_A = q_A F_A$

$$= -\, q_A \frac{kT\, d \ln a_A}{dx} \quad \ldots\ldots\ldots\ldots\ 88$$

$$D_A = q_A \frac{kT \quad d \ln a_A}{d \ln C_A} \quad \ldots\ldots\ldots\ldots\ 89.$$

This will apply to any component A in a mixture and D_A is therefore the intrinsic diffusion coefficient of A.

Let us now consider a mixture in which component A is labelled with a small amount of radioactive A. For the labelled material we can similarly write

$$D_A^{*} = q_A^{*}\, kT \frac{d \ln a_A^{*}}{d \ln C_A^{*}} \quad \ldots\ldots\ldots\ldots\ 90,$$

but since q_A^{*} by its nature is equal to q_A and since the labelled material is only present in trace quantities we can take a_A^{*} as equal to C_A^{*} and hence

$$D_A^{*} = q_A\, kT \quad \ldots\ldots\ldots\ldots\ 91$$

and from equation 89, $D_A = D_A^{*} \dfrac{d \ln a_A}{d \ln C_A}$ 92

which is the relationship given in equation 82.

In equation 91 it is difficult to evaluate q_A. According to Stokes' law for a sphere $q_A = 1/6\,\pi r \eta$ and it is probable that in any relationship q_A will be inversely proportional to the viscosity of the medium and to a quantity σ_A which depends, according to Stokes[20], primarily upon a linear dimension of the diffusing molecule A, and to the inter-molecular distance according to Eyring[22]. It is thus legitimate to write $q_A = 1/\eta\sigma_A$ but in a mixture, σ_A is probably not independent of the composition though this may be assumed to be so as a first approximation. By substituting for q_A

$$D_A^* \eta = kT / \sigma_A \qquad \text{.............} \; 93$$

and, as was shown for the present case in table 30 (p. 101), $D_A^* \eta$ is in fact constant.

SUMMARY

The self-diffusion coefficients of MeI, and Et-, nPr- isoPr-, nBu-, isoBu- and secBu-iodides and bromides were determined by application of the capillary tube method and using iodine-131 and bromine-82 for labelling the compounds. Viscosities were measured for those compounds for which the data in the literature were insufficient for calculation of energies of activation.

The diffusion coefficients were of the order of 2×10^{-5} $cm^2 sec^{-1}$ with activation energies of 2 kcal./mole; determined from plots of log D/T versus 1/T. The temperatures at which coefficients were measured were 7.35, 19.35 and 30.00°C. The activation energies measured agreed with those for viscous flow as is required by the theories of Frenkel and Eyring. It was found that $D\eta/T$ was reasonably constant for each compound as is to be expected from the relationships derived by these workers and from the Stokes-Einstein equation. Parameter values calculated from these various relationships were, however, in very poor agreement with the expected values; those for the Stokes-Einstein equation were the most reasonable. Further application of the Frenkel and Eyring theories to the experimental results and to the results in the literature, indicate that these theories are only very approximate.

Self-diffusion coefficients of ethyl and n-butyl iodides were measured in mixtures of different compositions. These coefficients differed from one another and were concentration dependent. Viscosities were also measured at different compositions of the mixture and $D\eta$ values at a fixed temperature were found to be reasonably constant for both series of results. Activation energies for the self-diffusion of the two compounds at a fixed composition were in fair agreement with those for the pure compounds as well as with that for the viscosity of the mixture. The self-diffusion coefficients were discussed in relation to the intrinsic and interdiffusion coefficients. On the assumption that these mixtures are very nearly ideal the self-diffusion coefficients

were taken to be equal to the intrinsic coefficients and interdiffusion coefficients were calculated at different compositions. These interdiffusion coefficients were found to be concentration dependent but to a lesser degree than the self-diffusion coefficients.

REFERENCES

1. Carman, P.C. and Raal, F.A., Proc.Roy.Soc.,A, 209, 38 (1951)

2. Fick, A., Pogg. Ann., 94, 59 (1855)

3. Berne, E., Phys. Rev., 77, 568 (1950)

Cobble, J.W. and Atteberry, R.W., ibid., 80, 917 (1950)

Sinclair, W.K. and Holloway, A.F., Nature, 167, 365 (1951)

4. Lockett, E.E. and Thomas, R.H., Nucleonics, 11, No.3, 14 (1953)

5. Chapman, S. and Cowling, T.G., "The mathematical theory of non-uniform gases", Cambridge Univ. Press, (1939) P.198

6. Op. cit., ref. 5, P.218

7. Enskog, D., Uppsala Dissertation (1917)

8. Michels, A. and Gibson, R.O., Proc.Roy.Soc., A, 134, 288 (1931)

9. Warburg, and Babo, Wied. Ann., 17, 390 (1882)

10. N.R.C., "International Critical Tables", McGraw-Hill N.Y. (1923)

Landolt-Börnstein, "Physikalische-Chemische Tabellen" 5th Ed., Springer, Berlin (1923) et seq.

11. Phillips, P., Proc.Roy.Soc., A, 87, 48 (1912)

12. Schroer, E. and Becker, G., Z.phys.Chem., 173, 178 (1935)

13. Andrade, E.N.da C., Phil. Mag., 17, 497, 698 (1934)

14. Frenkel, J., Z. Physik, 35, 652 (1926)

Frenkel, J., "Kinetic theory of liquids", Oxford Univ. Press, (1946)

15. Einstein, A., Ann. Physik, 17, 549 (1905)

ibid. 19, 371 (1906)

16. Smoluchowsky, ibid. 21, 756 (1906)

17. Perrin, J., "Atoms" translated by Hammick, D.L., Ldn. (1920)

18. Wert, C. and Zener, C., Phys. Rev., 76, 1169 (1949)

19. Maxwell, J.C., Phil. Mag., 35, 133 (1868)

20. Stokes, G., Proc.Cambridge.Phil.Soc., 9, 5 (1856)

21. Eyring, H., J. Chem. Phys., 4, 283 (1936)

Hirschfelder, J., Stevenson, D. and Eyring, H., ibid., 5, 896 (1937)

22. Glasstone, S., Laidler, K.J. and Eyring, H., "The theory of rate processes", N.Y. (1941)

23. Born, M. and Green, H.S., Proc.Roy.Soc., A, 188, 10 (1946)

ibid., A, 190, 455 (1947)

Born, M. and Green, H. S., ibid., A, 191, 168 (1947)

24. Green, H.S., ibid., A, 189, 103 (1947)

25. Kirkwood, J.G., J.Chem.Phys., 14, 180 (1946)

26. Bondi, A., ibid., 14, 591 (1946)

27. Groh, J. and von Hevesy, G., Ann. Physik, 63, 85 (1920)

28. Haissinsky, M. and Cottin, M., J.phys.radium, 11, 611 (1950)

29. Hoffman, R.E., J.Chem.Phys., 20, 1567 (1952)

30. Anderson, J.S. and Saddington, K., J.Chem.Soc., (1949) S381

31. Koeller, R.C. and Drickamer, H.G., J.Chem.Phys., 21, 267 (1953)

32. Cuddeback, R.B. et al., ibid., 21, 589 (1953)

33. Saxton, R.L. and Drickamer, H.G., ibid., 21, 1362, 1364 (1953)

34. Temkin, M., Nature, 136, 552 (1938)

35. Lamm, O., Nova Acta Regiae Soc., Uppsala, 10, No.6 (1937)

36. Wang, J.H. et al., J.Am.Chem.Soc., 75, 466 (1952)

37. Wang, J.H., ibid., 73, 510 (1951)

38. Graupner, K. and Winter, E.R.S., J.Chem.Soc., (1952) 1145

39. Partington, J.R. et al., Nature, 169, 583 (1952)

40. Orr, W.J.C. and Butler, J.A.V., J.Chem.Soc., (1935) 1273

41. Rögener-Leipzig, H., Z.f.Elektrochem., 47, 164 (1941)

42. Longsworth, L.G., J.Phys.Chem., 58, 770 (1954)

43. Taylor, H.S., J.Chem.Phys., 6, 381 (1938)

44. Braune, H., Z.physik.Chem., 110, 147 (1924)

Bradley, R.S., J.Chem.Soc., (1934) 1910

Rabinowitz, E., Trans.Farad.Soc., 33, 1225 (1937)

45. Op. cit., ref. 22, P.524

Powell, R.E. and Eyring, H., "Advances in colloid science", N.Y. (1942) 213

46. Grunberg, L. and Nissan, A.H. Trans.Farad.Soc., 45, 125 (1949)

47. Haycock, E.W. et al., J.Chem.Phys., 21, 1601 (1953)

48. Ewell, R.H. and Eyring, H., ibid., 5, 726 (1937)

49. Op. cit., ref. 22, P.521

50. Op. cit., ref. 22, P.524, 188 and 195f

51. Stearn, A.E., Irish,E.M. and Eyring,H., J.Phys.Chem.,44,981 (1940)

52. Kincaid, I.F. and Eyring, H., J.Chem.Phys., 6,620 (1938)

53. Op. cit., ref. 22, P.479

Eyring, H. et al., J.Phys.Chem.,41,249 (1937)

54. Hartmann, W.W., Organic Synthesis,18,88 (1938)

Blatt, A.H., "Organic syntheses", Col.Vol.I and II, N.Y. (1946) Pages 29 and 404 resp.

Mann, F.G. and Saunders, B., "Practical organic chemistry", Oxford (1938)

55. Timmermans, J., "Physico-Chemical constants of pure organic compounds", Elsivier Pub. Co., N.Y., (1950)

56. Le Roux, L., Lu, C., Sugden, S. and Thompson, R., J.Chem.Soc.(1945) 586

Le Roux, L. and Sugden, S., J.chim.phys., 45, 147 (1948)

Evans, C. and Sugden, S., J.Chem.Soc., (1949) 270

57. Hollander, J.M. Perlman, I., and Seaborg, G.T., Rev.Mod.Phys., 25, 469 (1953)

58. Levy, M. and Keston, A.S. et al., J.Am.Chem.Soc., 70, 2289 (1948)

59. Korff, J.A., "Electron and nuclear counters" van Nostrand, N.Y. (1946)

Lewis, W.P., "Electrical counting", Cambridge Univ. Press, (1948)

Rossi,B.B. and Staub,H.H., "Ionization chambers and counters" McGraw-Hill, N.Y. (1949)

60. Veall, N., Brit.J.Radiol.,21, 347 (1948)

61. Bateman, H., Phil.Mag., 20, 704 (1910)

Rainwater, L.J. and Wu, C.S., Nucleonics,1, No.2, 60 (1947)

ibid., 2, No.1, 42 (1948)

62. Rutherford, E. et al., "Radiations from radioactive substances", Cambridge Univ.Press (1930)

63. Simons, D., Private communication; agrees with Cobble loc cit., ref.3

64. Moon, P.B., J.Sci.Inst., 14, 189 (1937)

Beer, V., Rev.Sci.Instr.,13, 72 (1942)

Kohman, T.P., Anal.Chem., 21, 352 (1949)

65. Evans, R.D. Nucleonics,1, No.9, 32 (1947)

66. Int.Committee on Rad.Protection, ibid., 8, No.1, 31 (1951)

67. Jehle, L., Ph.D. Thesis, Univ. of Calif. (1938)

68. Wang, J.H. and Kennedy, J.W., J.Am.Chem.Soc., 72, 2080 (1950)

69. Northrop, and Anson J.Gen.Physiol., 12, 543 (1929)

McBain, J., et al., J.Am.Chem.Soc., 53, 59 (1931)

ibid., 55, 432,545 (1933)

ibid., 56, 1041 (1934)

70. Carslaw, H. and Jaeger, J., "Conduction of heat in solids", Oxford Univ.Press (1947) P.79

71. Weissberger, A., "Technique of organic chemistry", Vol.1, Part 1, Interscience, N.Y. (1949) P.327f

Hatschek, E., "The viscosity of Liquids", Bell and Sons, Ldn (1928)

Barr, G., "A monograph of viscosity", Oxford Univ. Press (1931)

72. Poiseuille, J.C.M., Mem.Savants Etrangers, 9, 433 (1846)

73. Öholm, W., Z.physik.Chem., 50, 309 (1904)

ibid., 70, 378 (1910)

Meddel.Vetenskapsakad.Nobelinst., 2, 23 (1912)

74. Model sets made by Messrs. Waltham Enterprises, Ltd., Waltham Abbey, Essex.

Dimensions checked according to:

Hartley, G.S. and Robinson, C., Trans.Farad.Soc., 48, 847 (1952)

Syrkin, Y.K. and Dyatkina, M.E., "Structure of Molecules", Butterworth's Sci.Pub., Ldn (1950)

Coulson, C.A., "Valence", Oxford Univ. Press (1952)

Wells, A.F., "Structural Inorganic chemistry", Oxford Univ. Press (1945)

75. Trouton, F., Phil.Mag., 18, 54 (1884)

76. Hildebrand, J.H., J.Am.Chem.Soc., 37, 970 (1915)

ibid., 40, 45 (1918)

J.Chem.Phys., 7, 233 (1939)

77. Hartley, G.S. and Crank, J., Trans.Farad.Soc., 45, 801 (1945)

78. Smigelskas, A.D. and Kirkendall, E.O., Metals Tech. No.1, 13 Tech. publ. 2071 (1946)

79. Robinson, C.B. and Drew, J.B., J.Chem.Phys., 15, 417 (1947)

80. Adamson, A.W., ibid., 15, 762 (1947)

81. Gemant, A., J.Appl.Phys., 19, 1160 (1948)

82. Brady, A. and Salley, D., J.Am.Chem.Soc., 70, 914 (1948)

83. Adamson, A. et al. J.Chem.Phys., 70, 740 (1949)

84. Walker, L.A., Science, 112, 757 (1950)

85. Whiteway, S.G. et al., J.Chem.Phys., 18, 229 (1950)

86. Burkell, J.E. and Spinks, J.W.T., Can.J.Chem., 30, 311 (1952)

87. Krauss, C.J. and Spinks, J.W.T., ibid., 32, 71 (1954)

88. Wang, J.H., J.Am.Chem.Soc., 74, 1182, 1611, 1612 (1952)

89. Nernst, N., Z.physik.Chem., 2, 613 (1888)

90. Onsager, L. and Fuoss, R.M., J.Phys.Chem., 36, 2689 (1932)

91. Onsager, L., Ann.N.Y.Acad.Sci., 46, 241 (1945)

92. Nielson, J.M. and Adamson, A.W., J.Am.Chem.Soc., 74, 446 (1952)

93. Wang, J.H., ibid., 75, 1769 (1953)

94. Mills, R. and Kennedy, J.W., ibid., 75, 5696 (1953)

95. Wang, J.H., J.Chem.Phys., 58, 686 (1954)

96. Wang, J.H., J.Am.Chem.Soc., 76, 4775, 4763 (1954)

97. Cohen, E. and Bruins, H.R., Z.physik.Chem., 103, 404 (1923)

98. Lemonde, H., Ann.de Physique, 9, 539 (1938)

99. Trevoy, D.J. and Drickamer, H.G., J.Chem.Phys., 17, 1117 (1949)

100. Roseveare, W.E., Powell, R.E. and Eyring, H., J.App.Phys., 12, 669 (1941)

101. Kincaid, I.F., Eyring, H. and Stearns, I.E., Chem.Rev., 28, 301 (1941)

102. Koeller, R.C. and Drickamer, H.G., J.Chem.Phys., 21, 575 (1953)

103. Johnson, W.A., Trans.Am.Inst.Min.Met.Engrs., 147, 331 (1942)

104. Darken, L.S., ibid., 175, 184 (1948)

105. Prager, S., J.Chem.Phys., 21, 1344 (1953)

106. Lamm, O., Acta Chem.Scand., 8, 1120 (1954)

107. Seitz, F., J.Phys.Rev., 74, 1513 (1948)

108. Duhem, Compt.rend., 102, 1449 (1886)

109. Wagner, C. and Engelhardt, G., Z.f.phys.Chem., 159, 241 (1932)

110. Seith, W. and Kottman, A., Proc.Intl.Symposium on the reactivity of Solids, (1952) 63, Gottenburg (1954)

111. Hammond,B.R. and Stokes,R.H., Trans.Farad.Soc., 49, 890 (1953)

112. Wang, J.H., J.Am.Chem.Soc., 75, 2777 (1953)

113. Lyons,M.S. and Thomas,J.V., ibid., 72, 4506 (1950)