

SELF-DIFFUSION STUDIES IN
BINARY NON-ELECTROLYTE MIXTURES.

A Thesis submitted to the University
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Philosophy

by

Ismat Kamal

Department of Chemical Engineering and
Chemical Technology,
Imperial College of Science & Technology,
London, S.W.7.

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ABSTRACT

Existing theories of the liquid state have been briefly summarised with reference to their importance in the understanding of transport behaviour. Theories of transport in liquids have been discussed with particular emphasis on the theories of diffusion. Attention has been focussed on the concentration dependence of self-diffusion coefficients with reference to its importance in testing relationships among the various transport coefficients in binary mixtures.

Experimental methods of measuring self-diffusion coefficients have been critically surveyed and advantages of the porous diaphragm cell method have been enumerated. A modification of Stokes' method for determining diffusion coefficients in magnetically-stirred diaphragm cells has been described. Measurements of the self-diffusion coefficients have been reported at various concentrations in the binary systems benzene-cyclohexane, toluene-cyclohexane and benzene-toluene at 25°C. A paper based on the present results for the benzene-cyclohexane system is in the course of publication in the Transactions of the Faraday Society.

The experimental results have been discussed in terms of existing theories with particular reference to Bearman's theory of transport phenomena in mixtures. It has been shown that the theories are applicable only to regular solutions such as benzene-toluene, and that modifications in Bearman's equations allowing

for the departure of simple binary solutions from 'regular' behaviour are required in order to make the theory applicable to non-regular solutions.

In addition to the experimental work on diffusion in three binary systems presented in this thesis, two additional problems in the theory of transport phenomena have been considered. The first is the effect of pressure and volume on the thermal conductivity of liquids. This is given in Appendix 3, as reprinted from the Transactions of the Faraday Society, 1964, 60, 809. The second on the behaviour of the ratio of thermal conductivity λ to the viscosity η as a function of density according to the theory of Enskog has been published in Chemical Reviews, 1964, 64, p.403. This is given in Appendix 2.

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CHAPTER 1.THE STRUCTURE OF LIQUIDS.1.00 Introduction.

Self-diffusion in liquids takes place as a result of the stochastic motion of molecules which is caused by the kinetic energy possessed by them in all states of aggregation. By virtue of their movements molecules participate in the transfer of mass (diffusion), heat (thermal conductivity) and momentum (viscosity). The extent to which an individual molecule contributes to mass, heat or momentum transport depends upon the spatial configuration of neighbours about that molecule. Thus the first step in a theoretical approach to transport phenomena in liquids is to obtain a description of the liquid structure at equilibrium. Both the thermal motions of the liquids and their interactions with each other must be considered in order to obtain a thermodynamic picture of the liquid state. The theoretical methods which have been used to characterize the structure of liquids may be divided into two main classes:

(a) The method of the pair distribution function, which is a direct attempt to develop the theory of liquids from the fundamentals of statistical mechanics and inter-molecular forces, and

(b) an indirect approach, starting from a simplified physical description of the structure, usually based on the kinship of the liquid to the crystalline solid near its melting point. Theories of this class are generally known as "lattice theories".

The theories and properties of liquids which are important in the understanding of transport phenomena will be discussed in this chapter.

1.10. The Forces between Molecules.

When two molecules approach very closely they repel each other. At larger distances the repulsion is replaced by an attraction owing to the "van der Waals" or "dispersion" forces. The forces between molecules are electrostatic in origin, and the nature of the attractive forces has been elucidated by F. London¹. In the simplest case of highly symmetrical molecules, it may be safely assumed that the forces between molecules are independent of the molecular orientations and depend only on the distance between the centres of the two molecules.

The forces between molecules may be expressed as the gradient of a potential function, $f = -\partial U/\partial r$, and it is generally convenient to describe the potential energies rather than the forces themselves. Although qualitative information on the variation of the potential energy with

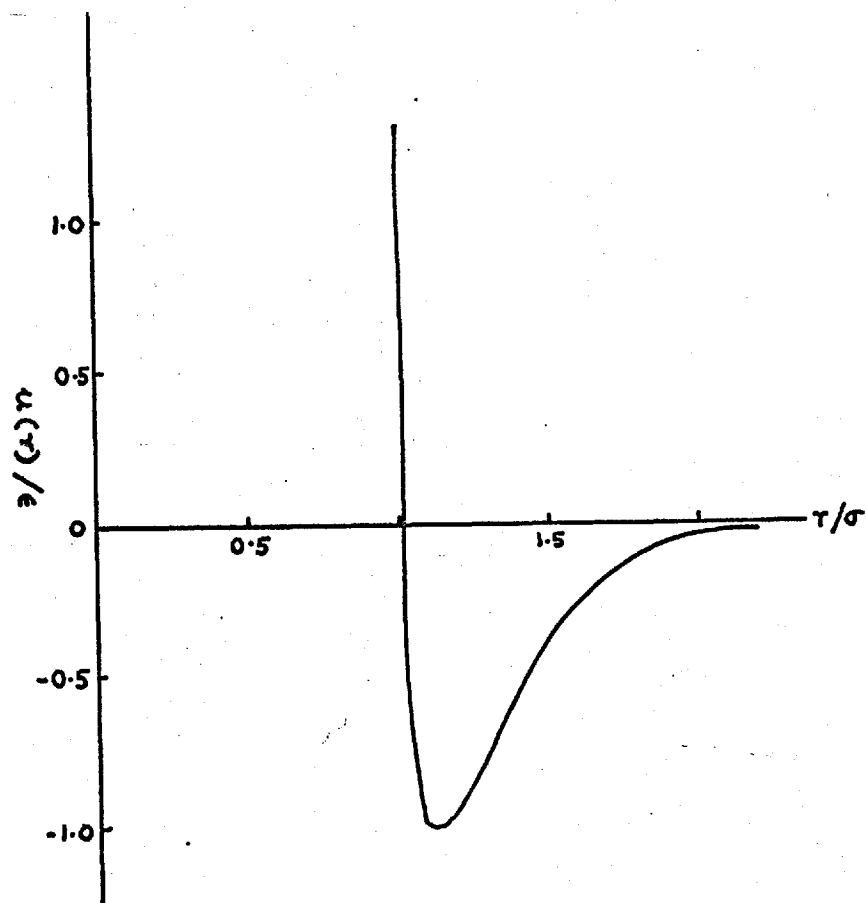


FIG. 1-1. THE LENNARD-JONES (12,6) POTENTIAL

the separation between molecules may be obtained from quantum mechanical calculations^{2, 3, 4}, it is at present not possible to obtain detailed quantitative information on the inter-action potential between many-electron molecules from quantum mechanics. Therefore it is usual to use a suitable simple empirical formula, expressing the potential energy as a function of distance, that will reproduce the experimental results. When a simple potential is found to be inadequate then comparison with experimental results yields information for its improvement.

A simple empirical formula is the Lennard-Jones (12; 6) potential (Fig.1.1) on which much of the work on the theory of liquids has been based. It is described by the equation

$$u(r) = 4 \epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right] \quad \dots (1.1)$$

where r is the distance between the centres of the two molecules, σ is the value of r for which $u(r) = 0$ and ϵ is the maximum energy of attraction (or depth of the potential well) which occurs at $r = 2^{1/6}\sigma$.

With suitably chosen constants this potential gives a reasonably accurate description for inert gases and for simple non-polar molecules such as nitrogen and methane. For instance, it reproduces the second virial coefficient of the inert gases over very wide ranges of temperature^{2, 5, 6} and, with the same parameters as are used to fit the second virial coefficients, it reproduces the viscosity, thermal conductivity and coefficient

10.

of self-diffusion of the dilute gases ^{3, 7, 8}. The latter is strong evidence in favour of the (12,6) potential as it has been shown ^{9, 10} that neither an (8,4) nor a "square well" potential will do this. However, the (12,6) potential is not adequate for giving an exact description of all real systems, particularly in the calculation of the more sensitive bulk properties. For instance, Guggenheim ⁵ and Kihara ⁶ have shown that the experimental results for the third virial coefficients of the inert gases cannot be fitted with this potential, even within the large experimental errors.

In calculating the properties of liquids it is generally assumed that the potential energies of interaction are additive, that is,

$$U = \sum_{i < j} u(r_{ij}) \quad \dots (1.2)$$

where U is the total potential energy and $u(r_{ij})$ is the potential energy of interaction of molecules i, j , which depends on their separation r_{ij} . This assumption is not strictly true, since at any instance the force between the molecules i and j would depend on whether or not molecule j is being also polarized by molecules k, l , etc. The extent of the error involved in the assumption is not known, but the fact that the (12-6) potential derived from gas properties of argon also fits the crystal data ¹¹ suggests that it is small for simple molecules.

1.11. The Forces between unlike Molecules

The potential energy between a pair of simple unlike molecules can be described in the same way as that between a pair of molecules of the same species. In the generalised Lennard-Jones potential

$$u(r) = \lambda r^{-n} - \nu r^{-m} \quad (n > m) \quad \dots (1.3)$$

λ and ν are parameters characteristic of the interaction and the indices n and m are usually assumed to be the same for all chemical species. For a pair of unlike molecules the parameters of equation (1.3) are determined by the chemical species of both molecules and may be written as $\lambda_{\alpha\beta}$ and $\nu_{\alpha\beta}$. In a binary mixture of two components 1 and 2 there are three kinds of intermolecular potentials, represented by (λ_{11}, ν_{11}) , (λ_{22}, ν_{22}) and (λ_{12}, ν_{12}) . The relationship of λ_{12} to λ_{11} and λ_{22} is not known, but London's theory of dispersion forces¹ suggests that ν_{12} is close to the geometric mean of ν_{11} and ν_{22} .

From a study of the properties of gaseous mixtures, two empirical rules have been obtained for the calculation of the mixed parameters ϵ and σ (of equation 1.1.).

These rules are

$$\epsilon_{12} = \sqrt{\epsilon_{11} \epsilon_{22}} \quad \dots (1.4)$$

$$\sigma_{12} = \frac{1}{2} \sigma_{11} + \frac{1}{2} \sigma_{22} \quad \dots (1.5)$$

The arithmetic mean rule (1.5) was first proposed by Lorentz¹² and the geometric mean rule (1.4) was first used by Berthelot¹³

for energies of interaction -- hence the name "Lorentz-Berthelot" mixture sometimes used for a mixture of Lennard-Jones molecules in which the unlike parameters are given by equations (1.4) and (1.5). Studies on the second virial coefficient of simple, binary gaseous mixtures and the rate of interdiffusion of two gases^{2,7,14} show that Lorentz-Berthelot equations give ϵ_{12} and σ_{12} with an accuracy of about 2 percent for simple molecules.

1.20. Distribution Function Theories of Liquids.

The spatial arrangement of molecules may be described in terms of molecular distribution functions. Thus the pair distribution function $n^{(2)}(r)$ is defined as the probability of finding two molecules simultaneously at two given points separated by a distance r . It is often convenient to use a normalised pair function $g(r)$, equal to $n^{(2)}(r)/n^2$, which approaches unity for large values of r . Taking the centre of one atom as the origin, $g(r)$ gives the probability of finding the centre of another atom at the end of a vector of length r drawn from the origin.

Statistical mechanics enables one¹⁵ to express thermodynamic functions such as the internal energy, pressure and chemical potential of liquids in terms of the radial distribution function $g(r)$ and the potential of intermolecular forces $u(r)$. An accurate evaluation of these two factors would provide a complete theory of the liquid state, but is beset with enormous difficulties.

1.21. The Radial Distribution Function.

The evaluation of the radial distribution function has been made possible by X-ray diffraction experiments^{16*}. The arrangement of electrons in a molecule resembles a diffraction grating from which X-rays are reflected. A second diffraction grating is provided by the coarser spacing between the individual molecules. The observed scattering of X-rays in X-ray diffraction experiments is due to the superposition of these two gratings. Measurements on the liquid itself and on the dilute vapour (in which the interference of X-rays by different molecules is absent and the scattering shows the contribution of the internal molecular structure to the total scattering observed in the liquid) enable one to decompose the diffraction pattern of the liquid into its two component parts.

Equations have been derived^{17, 18, 19} to obtain the distribution function from the intensity of the X-radiation scattered by the liquid, and have lead to results²⁰ valuable in the understanding of liquid structure.

1.22. The Superposition Principle.

From the definitions of the pair distribution function and the intermolecular potential equations can be derived¹⁵ for the internal energy, pressure and the chemical potential of the liquids in terms of these two quantities. These equations could then be used to calculate all the thermodynamic properties of a liquid.

Experimentally determined values of $g(r)$, however, are not sufficiently accurate to make these calculations possible. The theoretical evaluation of $g(r)$, a formidable task, has therefore been undertaken. Integro-differential equations can be derived for the pair distribution function, but these also involve $n^{(3)}(r_{12}, r_{13}, r_{23})$, the probability that three molecules will be so located that their separations are given by r_{12} , r_{13} and r_{23} . In turn the integral equation for $n^{(3)}$ would involve $n^{(4)}$, and so on. A complete solution of this family of integro-differential equations seems impossible and some means of terminating the series has to be sought. The series may be terminated by applying the superposition approximation of Kirkwood²¹, which equates the probability of the simultaneous presence of three molecules whose separations are given by r_{12} , r_{13} and r_{23} to the product of the probability of the independent occurrence of pairs of molecules separated by r_{12} , r_{13} and r_{23} , that is,

$$n^{(3)}(r_{12}, r_{13}, r_{23}) = n^{(2)}(r_{12}) \cdot n^{(2)}(r_{13}) \cdot n^{(2)}(r_{23}) / n^3 \quad \dots (1.6)$$

On substituting this relationship in the equation for the pair distribution function an ordinary integral equation is obtained. Starting from two different but entirely equivalent sets of integral equations, Kirkwood²¹ and Born and Green²² arrived at two different integral equations for the pair distribution functions. The two equations can be solved by numerical methods and their results used for the calculation of the thermodynamic properties of the liquid.

1.23. Tests of the Distribution Function Theories.

On substituting for the pair distribution function in the equation expressing the pressure in terms of $n^{(2)}(r)$ and $u(r)$ a virial equation is obtained for the pressure. It is found that use of the superposition approximation gives correctly the second and third virial coefficients but only approximately the fourth and fifth virial coefficients ²³.

A crude estimate of the error involved in the superposition principle may be made from the differences between the predictions of Kirkwood's and of Born's and Green's methods. The radial distribution function and the thermodynamic functions of a liquid composed of rigid spheres* has been calculated on the basis of the two methods ²⁴. It is found that the predictions of the two theories are scarcely distinguishable at low densities (where the superposition principle is a valid approximation), but the agreement is less satisfactory at higher densities. This shows the limitation of the superposition principle when it is applied to the liquid state.

Kirkwood, Lewinson and Alder ²⁵ have obtained numerical solutions for an assembly of molecules interacting with a modified Lennard-Jones potential where

$$\begin{aligned} u(r) &= 4 \epsilon (\sigma/r)^{12} - (\sigma/r)^6 & ; r \leq \sigma \\ &\dots & \dots (1.7) \\ u(r) &= + \infty & ; r < \sigma \end{aligned}$$

Fig.1.2 compares their theoretical predictions for the radial

*A rigid sphere model is one where the potential energy of molecular interaction is taken to be positively infinite if the separation is less than the molecular diameter, and zero otherwise.

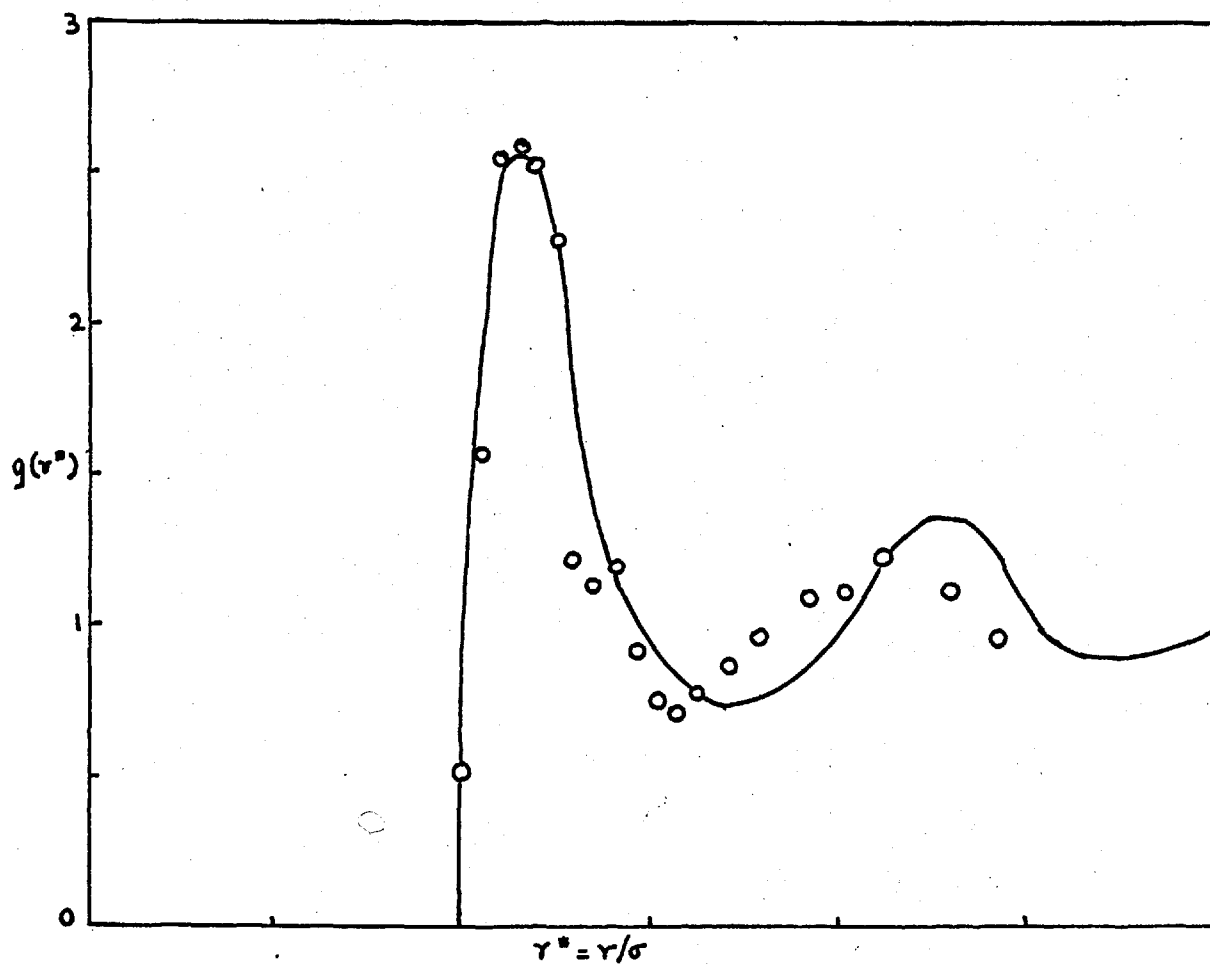


FIG. 1-2. A COMPARISON OF EXPERIMENTAL AND THEORETICAL RADIAL DISTRIBUTION FUNCTIONS FOR LIQUID ARGON AT 91.8°K AND 1.8 ATM. ²⁵

distribution function in liquid argon with the experimentally determined values of Eisenstein and Gingrich²⁰. The agreement is fairly good, but the derived thermodynamic functions do not show such good agreement with theory since they are very sensitive to minor variations in $g(r)$.

The qualitative success of the superposition approximation has provided an incentive for investigations leading to the formulation of a modified theory which would ensure a higher degree of quantitative success. Several attempts have been made in this direction, but only limited progress has as yet been made.

1.30 Lattice Theories of Liquids.

In its present state the distribution function theory is best suited for liquids at low densities but, owing to the nature of the approximation involved, it fails at higher densities. The lattice theories adopt the alternate approach of starting with a description of the liquid state which is suitable at high densities and applying corrections for decreasing density.

Unlike solids, which have a static crystal structure only slightly blurred by thermal motions, the "structure" of liquids changes continuously because of the random thermal motions of the molecules. In solids the molecules vibrate about fixed equilibrium positions, and jumps from these positions are rare — hence diffusion in solids is slow. In liquids there are no fixed lattice sites and diffusion is fairly rapid. Nevertheless experimental evidence from the scattering of slow neutrons by liquids suggests that the molecular motions in liquids may be described

approximately as vibrations interrupted by jumps. In dealing with time-averaged equilibrium properties the occasional jumps may be disregarded, but they become important in transport properties such as diffusion. This viewpoint is adopted by the lattice theories, which are therefore more suitable for dealing with equilibrium properties than with transport properties.

The lattice theories may be classified into the "cell" or "free volume" theories which are based on a regular crystalline lattice structure with all the lattice sites occupied, the "hole" theories, which allow for some vacant lattice sites, the "tunnel theory", which is based on a partially disordered lattice structure and "Monte Carlo" and "molecular dynamics" methods, in which the available volume is divided into large cells containing many molecules and averaging is performed by direct numerical methods.

1.31 Theory of Lennard-Jones and Devonshire.

Lennard-Jones and Devonshire^{26,27} made the first detailed calculations of thermodynamic properties based on the cell model for molecules interacting with the $(12-6)$ potential. Most of the subsequent developments in the lattice theory of liquids have arisen from attempts to justify or to improve the L-J-D theory.

The basic assumptions in this theory are:-

- (i) that the available volume may be divided into identical cells, and only configurations in which each cell contains just one molecule need be considered. (Hence the volume v of a cell is V/N where V is the molar volume and N is Avagadro's Number).

(ii) that the cells can be chosen so that their centres form a regular lattice, and

(iii) that the molecules can be regarded as moving independently in their cells.

The last assumption implies that the total potential energy U of the system may be approximated by a sum of terms each depending on the position of just one molecule. (If this were not so the force on one molecule would depend on its separation from others and the motions of molecules would not be independent). Hence it is assumed that

$$U = U_0 + \sum_{i=1}^N [\psi(\underline{r}_i) - \psi(o)] \quad \dots (1.8)$$

where $\underline{r}_i$ is the vector displacement of molecule i from its centre, U_0 is the lattice or configurational energy of the assembly when all the molecules are in their lattice sites and $[\psi(\underline{r}_i) - \psi(o)]$ is the change of potential energy when the molecule i moves from its cell centre to the point $\underline{r}_i$, with all other molecules at their cell centres.

If U_0 is the energy of interaction for two molecules on neighbouring sites then, neglecting interactions between all but nearest neighbours,

$$U_0 = Nz u_0 / 2 \quad \dots (1.9)$$

where z is the number of nearest neighbours or the co-ordination number. In a closed packed lattice with co-ordination number z equal to 12 the separation between neighbouring sites, a , is

related to the volume per molecule, v , by

$$a^3 = v \sqrt{2} \quad \dots (1.10)$$

Substituting for $r = a$ in equation (1.1) for the (12, 6) potential, we get

$$u_o = \epsilon \left[\left(\frac{\sigma^3}{v} \right)^4 - 2 \left(\frac{\sigma^3}{v} \right)^2 \right] \quad \dots (1.11)$$

It is evident from equation (1.8) that each molecule moves in a potential energy field defined by the function $[\psi(\underline{r}) - \psi(o)]$.

Lennard-Jones and Devonshire assumed that this is the field which the neighbours would exert on a molecule if they were at rest on their lattice sites. They also assumed that this field, which has dodecahedral symmetry (in a closed packed lattice with co-ordination number $z = 12$) could be replaced by its average over all angles to give a field of spherical symmetry. With these assumptions, and a 12, 6 potential

$$\psi(\underline{r}) - \psi(o) = z\epsilon \left[\left(\frac{\sigma^3}{v} \right)^4 \ell(y) - 2 \left(\frac{\sigma^3}{v} \right)^2 m(y) \right] \dots (1.12)$$

The functions ℓ and m arise from the averaging over all angles and are given by

$$\ell(y) = (1 + 12y^2 + 25.2y^4 + 12y^6 + y^8)(1-y^2)^{-10} - 1 \quad \dots (1.13)$$

$$m(y) = (1+y^2)(1-y^2)^{-4} - 1 \quad \dots (1.14)$$

These results enable one to calculate the "free volume" V_f which is the volume available to the centre of the molecule and is given by

$$V_f = \int \exp \left\{ - \left[\psi(\underline{r}_i) - \psi(o) \right] / kT \right\} d\underline{r}_i \quad \dots (1.15)$$

Hirschfelder and his colleagues⁽²⁸⁾ have carried out extensive calculations to compute the free volume on the basis of the above

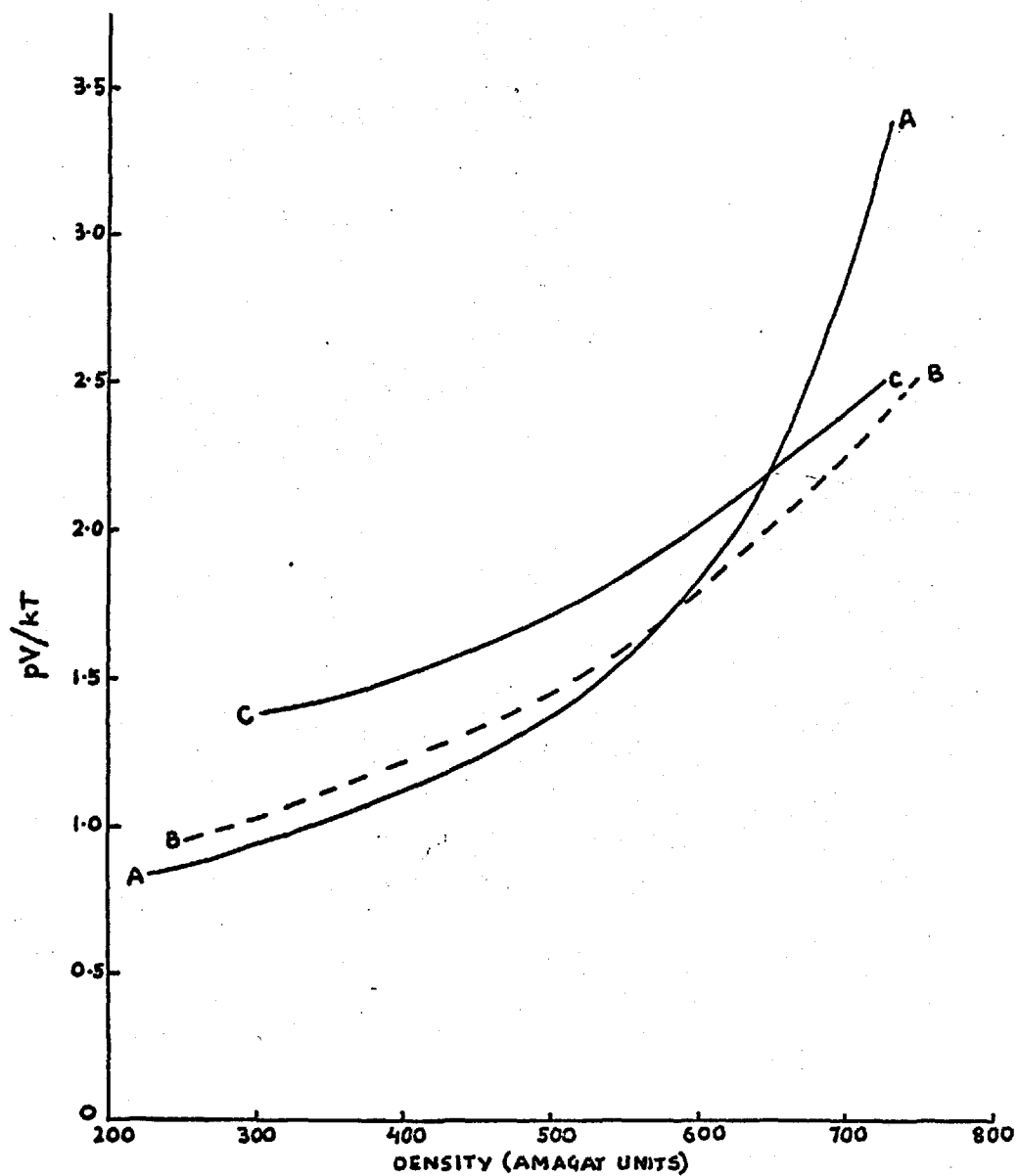


FIG.1-3. A COMPARISON OF EXPERIMENTAL AND THEORETICAL EQUATIONS OF STATE FOR ARGON AT 273 ° K.

A, EXPERIMENTAL VALUES³⁰; B, RADIAL DISTRIBUTION FUNCTION METHOD; C, CELL THEORY²⁵.

approximations. They have also applied corrections to allow for molecules which are not in the first co-ordination shell.

1.32. Tests of the L-J-D Theory.

All of the thermodynamic properties of a liquid may be expressed in terms of the free volume²⁹. The equation of state for argon at 273°K has been calculated by Wentorf, Buehler, Hirschfelder and Curtiss²⁸ and is compared in fig.1.3 with experimental values³⁰ and values calculated by the radial distribution function method. Generally it is found that at very high densities the theory of Lennard-Jones Devonshire is more successful than that of the superposition principle. At low densities where the cell model becomes physically unrealistic the predictions of the L-J-D theory become very unsatisfactory.

Numerous extensions of the cell theory have been proposed in an effort to achieve a theory which would be truly applicable over the entire range of the liquid and vapour densities. Attempts have been made to improve the L-J-D theory by allowing for the presence of empty cells ("hole" theories)^{31,32,33}, but improvements achieved are not very significant. The "hole" theories and other developments in the lattice theories of liquids have been critically reviewed by Barker³⁴. Compared with the distribution function theory (the best achievement of which has been the calculation of radial distribution functions which agree well with experiment) the lattice theory has produced more numerical results that can be compared with experiments.

CHAPTER 2

TRANSPORT PROCESSES IN LIQUIDS

2.00 Introduction

Transport processes are concerned with the flux of mass, momentum and energy in a system perturbed from equilibrium by the existence of gradients of concentration, mass velocity and temperature respectively. The gradients may be regarded as 'forces' which produce 'fluxes'. Linear relationships were shown to exist between the 'forces' and fluxes and may be stated as

$$J_m = -D \cdot \partial c / \partial x \quad (\text{Fick's Law}) \quad \dots (2.1)$$

$$J_{mv} = -\eta \partial v / \partial z \quad (\text{Newton's Law}) \quad \dots (2.2)$$

$$J_q = -\lambda \partial T / \partial x \quad (\text{Fourier's Law}) \quad \dots (2.3)$$

where D , η and λ are the coefficients of diffusion, viscosity and thermal conductivity respectively. $\partial c / \partial x$, $\partial v / \partial z$, $\partial T / \partial x$ are the gradients of concentration, velocity and temperature and J_m , J_{mv} and J_q are the corresponding fluxes of mass, momentum and energy. Various "cross-effects" (such as thermal diffusion) may also occur as a result of combined gradients such as those of concentration and temperature. It can be shown from irreversible thermodynamics³⁵ that the direct transport coefficients D , η and λ are positive whereas the cross-coefficients can be of either sign.

A primary aim of theoretical investigations on transport processes is to obtain the transport coefficients in terms of molecular scale processes and in terms of molecular parameters such as

intermolecular potentials. Theories that have been developed in the attempt to predict transport coefficients include lattice theories which are based on a quasi-crystalline model of liquid structure, dense gas theories which are an extension of the transport theory of gases to liquids and theories based on the use of a non-equilibrium distribution function.

2.10. Quasi-Crystalline Models for Transport Processes.

In transport theories based on quasi-crystalline models of liquid structure a molecular mechanism of transport is first assumed, and empirical methods are then used to estimate terms (in the derived equation) depending on the intermolecular potential and the quasi-lattice geometry of the liquid. Of these theories the one due to Eyring^{36,37} has been most widely used for viscosity and diffusion and will be discussed in Chapter 3. Andrade³⁸ presented a theory of viscosity which is generally applied to metals at their melting point. Theories of thermal conductivity have been put forward by Bridgman³⁹, by Kincaid and Eyring⁴⁰ and by Horrocks and McLaughlin⁴¹.

2.11. The Theory of Horrocks and McLaughlin.

In this theory the molecules of a liquid are assumed to be located on a face centred cubic pseudo-lattice. The molecules vibrate about their mean positions and transfer energy when they collide with adjacent molecules at the extremities of their motion. By this mechanism the excess energy due to a temperature gradient

is transferred down the gradient with a frequency ν , which is the frequency of vibration and is determined by the molecular mass and intermolecular forces. In addition to the above mechanism for heat flow there is a contribution from the convective motion of the molecules from site to site in the pseudo lattice. Thus the thermal conductivity of a liquid may be represented as the sum of two terms:

$$\lambda = \lambda_{\text{conv.}} + \lambda_{\text{vib.}} \quad \dots (2.4)$$

The equations derived by Horrocks and McLaughlin for the two contributions are

$$\lambda_{\text{conv.}} = \sqrt{2} K_o C_v / a \quad \dots (2.5)$$

$$\text{and } \lambda_{\text{vib.}} = \sqrt{2} \nu C_v / a \quad \dots (2.6)$$

where $a = (\sqrt{2} V/N)^{1/3}$ is the nearest neighbour distance and K_o is the frequency of diffusive displacement. V is the molar volume, N Avagadro's number and C_v the specific heat per molecule. K_o has been calculated from McLaughlin's theory of self-diffusion⁴² and used to evaluate $\lambda_{\text{conv.}}$ which is found to be negligible amounting, for example, for argon at its normal boiling point to less than 1% of the total conduction. ν has been evaluated on a harmonic oscillator model and used to calculate the thermal conductivity of a series of simple liquids for which experimental data is available. Calculated values of λ agree on average within 20% of experimental values compared with values from Bridgman's theory³⁹ which are within about 35%. The theory has been usefully applied by

Horrocks and McLaughlin⁴³ in studying the temperature dependence of thermal conductivity and by Kamal and McLaughlin⁴⁴ in studying the pressure and volume dependence. The theory, however, is not applicable beyond the high density end of the liquid range (i.e., beyond the normal boiling point of the liquid) when the concept of a lattice-type structure becomes physically unrealistic.

2.20. Dense Gas Theories

2.21. Enskog's Theory

Enskog⁴⁵ extended the transport theory of dilute gases for hard spheres to dense gases, taking into account the effects of a change in density. In the kinetic theory of dilute gases the transfer of mass, momentum and energy is regarded as due to the free motion of molecules between collisions (convective contribution). There is, however, an instantaneous transfer of momentum and energy at collision (collisional contribution) between molecules over the distance separating them at contact. The collisional contribution may be neglected when considering a dilute gas, when the mean free path of the gas is large compared with molecular dimensions, but it becomes increasingly important as the gas is compressed to higher densities. The collisional mechanism of transport does not effect the diffusion coefficient, which is always controlled by a convective mechanism, but it has a marked effect on viscosity and thermal conductivity. The alteration in the collision frequency on compression is due to two causes :

- (i) it is increased due to the reduction in the mean free path and
 (ii) it is decreased due to the shielding of one molecule by another from collision with more distance neighbours.

Enskog showed that compression of the gas increases the collision frequency by a factor Y which is equal to unity for a rare gas and increases with increasing density to infinity when the molecules are packed so closely together as to exclude motion. Y depends only on the density ρ , the molecular diameter σ and the mass m and is given by

$$Y = 1 + 0.6250 \rho b + 0.2869 \rho^2 b^2 + 0.115 \rho^3 b^3 + \dots \quad (2.7)$$

where $b = 2\pi\sigma^3/3m$, being the rigid sphere diameter.

Using an extension of the theory of dilute gases, Enskog showed that the transport coefficients in a dense gas composed of rigid spheres are related to those in the dilute gas by the following equations:

$$\eta/\eta_0 = 1/Y + 0.8 \rho b + 0.7614 (\rho b)^2 Y \quad \dots \quad (2.8)$$

$$\lambda/\lambda_0 = 1/Y + 1.2 \rho b + 0.7574 (\rho b)^2 Y \quad \dots \quad (2.9)$$

$$D/D_0 = 1/Y \quad \dots \quad (2.10)$$

where η , λ and D are the transport coefficients in the dense gas and η_0 , λ_0 and D_0 are the coefficients in the dilute gas at the same temperature. For rigid spheres the values of η_0 and λ_0 in the fourth approximation and of D_0 in the first approximation are given by

$$\eta_0 = 1.016 \frac{5}{16\sigma^2} \left(\frac{mkT}{\pi} \right)^{1/2} \quad \dots \quad (2.11)$$

$$\lambda_0 = 1.02513 \frac{25}{32} \left(\frac{mkT}{\pi} \right)^{1/2} \frac{3k}{2m} \quad \dots \quad (2.12)$$

$$\text{and } D_o = \frac{3}{8n\sigma^2} \left(\frac{kT}{\pi m} \right)^{1/2} \quad \dots (2.13)$$

where n is the number density related to the mass density ρ by $n = \rho/m$.

Enskog's theory predicts that the transport coefficients in dense gases are related to those in dilute gases by terms involving only the density. In Fig.2.1 Enskog's expressions for λ/λ_o , η/η_o and D/D_o are plotted against bpY for a rigid sphere gas. The minima in the thermal conductivity and viscosity curve is due to the changing mechanism in heat and momentum transfer. The diffusion curve does not show a minimum as no change in mechanism takes place. Experimental results⁴⁶ obtained for the transport coefficients of carbon dioxide are plotted in fig.2.2 and the curves show the same characteristics as exhibited by the theoretical rigid spheres curves.

For rigid spheres Enskog related the quantity bpY to the compressibility by the equation

$$PV/RT - 1 = bpY = y \quad \dots (2.14)$$

In a real gas the pressure experienced by a molecule is the sum of the external pressure P exerted by the walls of the containing vessel and the internal pressure $(\partial U/\partial V)_T$ which represents the force of cohesion of the molecules. The thermal pressure as defined in thermodynamics is the sum of the external and internal pressures and is given by

$$T(\partial P/\partial T)_V = P + U(\partial U/\partial V)_T \quad \dots (2.15)$$

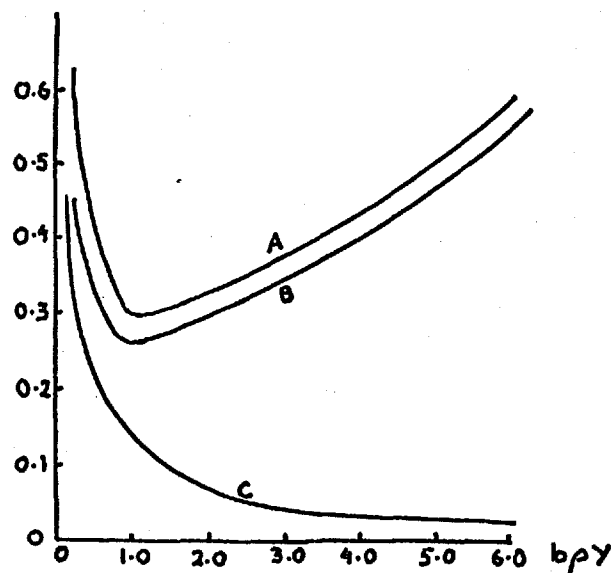


FIG. 2.1. THEORETICAL CURVE ON THE ENSKOG THEORY

Ordinate:

Curve A, reduced thermal conductivity $\lambda V / \lambda_{0b_0}$

Curve B, reduced viscosity $\eta V / \eta_{0b_0}$

Curve C, reduced self-diffusion coefficient $D_i^0 V / D_{0b_0}$

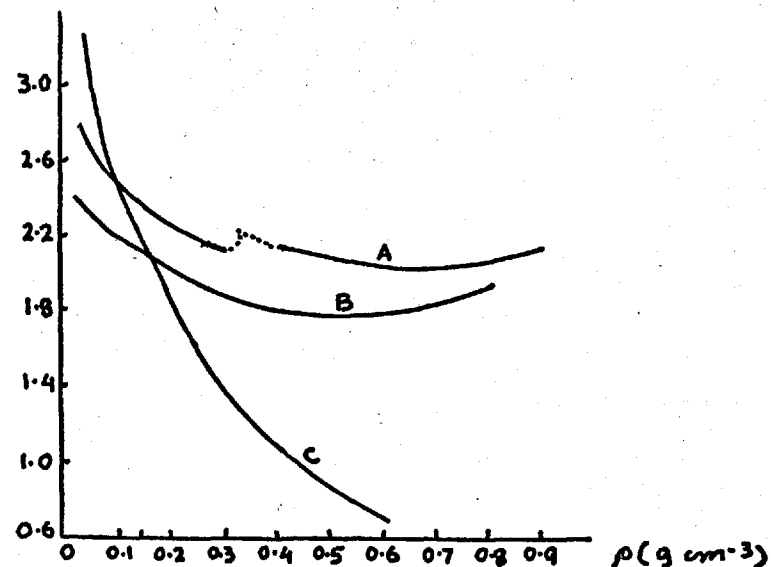


FIG. 2.2. EXPERIMENTAL CURVE ON THE ENSKOG THEORY

Ordinate:

Curve A: $\log (\lambda / \rho) \times 10^{-2} \text{ erg cm}^{-4} \text{ g}^{-1} \text{ sec}^{-1} \text{ } ^\circ\text{C}^{-1}$

Curve B: $\log (\eta / \rho) \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$

Curve C: $\log (D_i^0 / \rho) \times 10^4 \text{ cm}^5 \text{ g}^{-1} \text{ sec}^{-1}$

(Copied substantially from reference 168)

Enskog suggested that for real gases the pressure P in equation (2.14) should be replaced by the thermal pressure so that

$$\frac{V}{R} \left[\left(\frac{\partial P}{\partial T} \right)_V - 1 \right] = bpY = y \quad \dots (2.16)$$

In rigid spheres the internal pressure term is zero and Enskog's assumption implies that a real gas is equivalent to a rigid sphere gas in which the external pressure has been replaced by the thermal pressure. bpY may be evaluated from experimental pVT data using equation (2.16). Furthermore it follows from equations (2.8) and (2.9) that η/ρ and λ/ρ plotted as a function of the density ρ pass through minima at $bpY = 1.146$ and 1.151 respectively, with values

$$(\eta/\rho)_{\min.} = 2.545 b \eta_0 \quad \dots (2.17)$$

and

$$(\lambda/\rho)_{\min.} = 2.938 b \lambda_0 \quad \dots (2.18)$$

Using equations (2.17) and (2.18) equations (2.8) and (2.9) may be rewritten in the form

$$\eta/\rho = \frac{1}{2.545} \left(\frac{\eta}{\rho} \right)_{\min.} \left(\frac{1}{bpY} + 0.8 + 0.7614 bpY \right) \dots (2.19)$$

and

$$\lambda/\rho = \frac{1}{2.938} \left(\frac{\lambda}{\rho} \right)_{\min.} \left(\frac{1}{bpY} + 1.2 + 0.7574 bpY \right) \dots (2.20)$$

By fitting experimental minima to equations (2.19) and (2.20) and using values of bpY obtained as outlined above from PVT data, the viscosities and thermal conductivities of real molecules can be calculated. Comparison with available experimental data shows that this procedure reproduces the experimental results satisfactorily², and it can be concluded that Enskog's theory takes into account the main features in the transport phenomena of dense gases.

2.22. Theory of Longuet-Higgins and Pople

Longuet-Higgins and Pople⁴⁷ calculated the transport coefficients by introducing the radial distribution function for rigid spheres.

Assuming that the convective contribution to energy and momentum transport is negligible at high densities they derived the expressions

$$\eta = \left(\frac{2\sigma}{5}\right) \left(\frac{mkT}{\pi}\right)^{1/2} \left(\frac{P}{kT} - \frac{N}{V}\right) \quad \dots (2.21)$$

$$\lambda = \sigma k \left(\frac{kT}{\pi m}\right)^{1/2} \left(\frac{P}{kT} - \frac{N}{V}\right) \quad \dots (2.22)$$

Using Enskog's expression for P from equation (2.14) and the equations for λ_0 , η_0 and Y , equations (2.21) and (2.22) may be written in the form

$$\eta/\eta_0 = 0.6016 (bp)^2 Y \quad \dots (2.23)$$

$$\lambda/\lambda_0 = 0.3957 (bp)^2 Y \quad \dots (2.24)$$

One of the assumptions made in the theory of Longuet-Higgins and Pople is that the radial pair distribution function depends only on the temperature and density & not on the gradients of temperature and velocity. Thus this theory neglects the perturbed term of the distribution function and it has been shown by Dahler⁴⁸ that the results (2.23) and (2.24) are identical with that portion of the corresponding Enskog equations which do not depend on the perturbed term of the distribution function. The expressions of Longuet-Higgins and Pople, therefore, neglect a substantial part of the total contribution to transport in a rigid sphere fluid.

Elimination of the factor $\left(\frac{P}{kT} - \frac{N}{V}\right)$ in equations (2.21) and (2.22) leads to the result

$$\eta : \lambda = \frac{m}{5} : \frac{k}{2} \quad \text{or} \quad m\lambda/k\eta = 2.5 \quad \dots (2.25)$$

This is in substantial agreement with experimental results on a series of simple liquids at low temperature and high densities⁴⁹.

Longuet-Higgins and Pople⁴⁷ also derived an expression for self-diffusion starting from the random walk equation

$$D_1^0 = \langle r^2 \rangle / 6t \quad \dots (2.26)$$

where $\langle r^2 \rangle$ is the statistical average of the square of the distance travelled by a molecule in time t long compared with the time between collisions. Their expression for the self-diffusion coefficient is

$$D_1^0 = \frac{\sigma}{4} \left(\frac{\pi kT}{m} \right)^{\frac{1}{2}} \left(\frac{PV}{RT} - 1 \right)^{-1} \quad \dots (2.27)$$

This expression, unlike the ones derived for the viscosity and thermal conductivity, should be valid at low as well as at high densities. For a gas at low pressure $\frac{PV}{RT}$ may be equated to $1 + \frac{b_0}{V}$ where b_0 is the second virial coefficient, and hence the compressibility factor $(PV/RT - 1)$ in equation (2.27) may be replaced by b_0/V . For rigid spheres $b_0 = \frac{2}{3} \pi N \sigma^3$, and substitution in equation (2.27) yields

$$D_1^0 = \frac{3}{8n\sigma^2} \left(\frac{kT}{\pi m} \right)^{\frac{1}{2}} \quad \dots (2.28)$$

which is the same as Enskog's expression (2.13) for the self-diffusion coefficient of a dilute gas.

On comparing the expressions for η and D_1^0 in equations (2.21) and (2.27) a relationship is obtained between η and D_1^0 which may be written as

$$D_1^0 \eta = \frac{2a^2}{5} \cdot \frac{NkT}{V} \quad \dots (2.29)$$

where $a = \sigma/2$ is the molecular radius. The volume occupied by the molecules is given by $\frac{4}{3} \pi a^3 N$, and if c represents the ratio of the volume occupied by the molecules to the total volume

$$c = \frac{\frac{4}{3} \pi a^3 N}{V} \quad \dots (2.30)$$

$$\text{where } \frac{N}{V} = \frac{3c}{4\pi a^3} \quad \dots (2.31)$$

Substitution for N/V in equation (2.29) yields

$$D_1^0 \eta = 3kTc/10 \pi a \quad \dots (2.32)$$

which may be compared with the equation of Brownian motion,

$$D_1^0 \eta = kT/6 \pi a \quad \dots (2.34)$$

where D_1^0 and a refer to colloidal particles and η to the medium. Equation (2.34) holds rigorously for colloidal particles and applies reasonably well to self-diffusion (c.f. Chapter 3). The formal similarity of equations (2.32) and (2.34) lends weight to both of the theories concerned. The effective molecular radius calculated from (2.32) will be greater or less than the value calculated from equation (2.34) according as c is greater or less than $5/9$. Under ordinary pressures, when c may be expected to lie close to this ratio, the two calculations should give the same result.

2.30. Kirkwood's Theory of Transport Processes.

Until 1946 most of the work on transport properties was based on rather crude pictures of the liquid state and involved arbitrary assumptions regarding the molecular mechanism of transport. Since then considerable advances have been made in the

non-equilibrium statistical mechanical treatment of transport processes, a rigorous treatment which in principle is applicable to any class of liquid or liquid structure. In practice, owing to the mathematical difficulties, the discussion is usually confined to spherically symmetrical molecules where the force between two molecules can be derived from a potential which is a function of intermolecular distance alone.

The most successful development of these theories is based on analogies with theories of Brownian motion and is due to Kirkwood and his school. It has been reviewed by Cole⁵⁰, Collins and Raffel⁵¹ and Rice and Frisch⁵². A subset of molecules moving with a velocity exceeding that of the neighbouring molecules is retarded owing to the force exerted on it by the neighbours. Kirkwood assumed that the force exerted on the subset of molecules is analogous to the average frictional force on a particle of colloid dimensions undergoing Brownian motion. The frictional force is characterised by a friction coefficient ζ similar to that which arises in the theory of Brownian motion. The friction coefficient by Einstein's equation,

$$D_1^0 = kT/\zeta . \quad \dots (2.35)$$

When a system is perturbed by a transport process, the perturbation is characterised by a non-equilibrium radial distribution function g' . Using ζ and the equilibrium radial distribution function $g(r)$ an expression for g' has been derived. Expressions

for the momentum and energy fluxes in terms of non-equilibrium distribution functions have been derived^{52,53,54} and comparison with the phenomenological laws of viscous flow and heat conduction leads to expressions for viscosity and thermal conductivity.

One of the major obstacles in the development of this theory is the calculation of the friction constant ζ in terms of the intermolecular potential $u(r)$ and the equilibrium radial distribution function $g(r)$. It is generally agreed that the basic form of the friction constant is given by the equation

$$\zeta = \xi \zeta_0 \quad \dots (2.36)$$

where

$$\zeta_0^2 = \frac{Nm}{3V} \int_0^\infty \left[\frac{d^2 u(r)}{dr^2} + \frac{2du(r)}{rdr} \right] g(r) d^3 r \quad \dots (2.37)$$

V is the volume of the liquid and m the molecular mass. Different authors have given different values to ξ . While the value of unity has been most favoured^{55,56,57}, values of $(1/\pi)^{\frac{1}{2}}$ and $(2/\pi)^{\frac{1}{2}}$ have been obtained by Anderson et al.⁵⁸ and by Rice⁵⁹ respectively. Recently Rice⁶⁰ has derived an expression for

$$\xi = (4 \pi m^2 C^3 \rho)^{-1} \zeta_0^3 \quad \dots (2.38)$$

where C is the velocity of sound and ρ the density of the medium.

Using a development due to Rowlinson⁶¹, McLaughlin⁴⁹ has evaluated the integral in equation (2.37) in terms of experimentally available quantities. For a (12,6) potential

$$\zeta_0^2 = \frac{2mkT}{2} \left[-24 \frac{U'}{NkT} + 17 \left(\frac{pV}{NkT} - 1 \right) \right] \quad \dots (2.39)$$

where U' is the average configurational energy. Using

experimentally available values of U' and pV/NkT for a number of simple molecules. Table 2.1 (copied from reference 49) compares the experimental self-diffusion coefficients of liquid argon with calculated values from Einstein's equation (2.35) using values of ζ evaluated as outlined above (equation 2.34)

Table 2.1. Comparison of Calculated and Experimental Self-Diffusion

Coefficients of Liquid Argon.

Temp. °K	Pressure (atm.)	$D_1^0 \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$			Exptl. ⁵⁷
		$= 1$	$= (2/\pi)^{\frac{1}{2}}$	$= (4\pi m^2 c^3 \rho)^{-1}$	
84.3	0.722	2.35	2.95	0.97	1.77
87.3	1.000	2.45	3.07	0.91	2.10
90.0	1.319	2.55	3.20	0.85	2.43
100	3.20	2.95	3.70	0.72	3.54
110	6.58	3.40	4.26	0.69	4.80
120	11.98	3.88	4.86	0.61	6.06
130	20.00	4.53	5.68	0.42	7.45

Only moderate agreement is shown between the experimental and calculated values in Table 2.1 and between experimental and calculated values of the viscosity and thermal conductivity of liquid argon along the saturation curve⁴⁹. A more realistic appraisal of the friction coefficient is required for the further refinement of the theory.

In spite of the mathematical difficulties theories based on non-equilibrium statistical mechanics are the most attractive and promising of the transport theories and are expected to ultimately

provide for liquids the corresponding framework that the Chapman-Enskog theory provided for the transport theory of dilute gases.

2.40. Temperature Dependence of the Transport Properties.

There is a radical difference between the temperature coefficients of transport properties in gases and in liquids. In the gas phase the coefficients of diffusion, viscosity and thermal conductivity increase with increase of temperature. In liquids the coefficient of diffusion increases with increasing temperature while the coefficient of viscosity decreases. The experimentally determined temperature dependence of D and η

for many simple liquids can be represented by equations of the

$$\text{form} \quad \eta = \eta_K \exp E_\eta / RT \quad \dots (2.40)$$

$$\text{and} \quad D = D_K \exp (-E_D / RT) \quad \dots (2.41)$$

where η_K and D_K are constants characteristic of a particular species and E_η and E_D are temperature independent activation energies per mole for viscous flow and diffusion respectively.

The exponential dependence of the viscosity and diffusion coefficients of liquids upon the temperature lends weight to Eyring's theory of transport processes which is based upon analogies with chemical reaction kinetics. The temperature dependence of the thermal conductivity of liquids is more complicated. At atmospheric pressure the temperature coefficient of the thermal conductivity of liquids, other than water, is

negative and is given by

$$\lambda = \lambda_0 - BT \quad \dots (2.42)$$

where λ_0 and B are constants characteristic of the particular species considered. Bridgman³⁹ has shown, however, that the temperature coefficient of most common liquids becomes positive at a pressure of about 5000 atmospheres. The problem has been dealt with by Horrocks and McLaughlin⁴³. According to their theory λ for a f.c.c. lattice structure liquid is given by equation (2.6) of section 2.11. Since C_v is a constant the temperature dependence of thermal conductivity may be obtained, on differentiating equation (2.6), as

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial T} \right)_P = -\alpha \left[\frac{1}{3} - \left(\frac{\partial \ln v}{\partial \ln T} \right)_P \right] \quad \dots (2.43)$$

where $\left(\frac{\partial \ln v}{\partial \ln T} \right)_P$ is Gruneisen's constant.

Equation (2.43) shows the importance of α , the coefficient of thermal expansion, in controlling the temperature dependence of the thermal conductivity. As Gruneisen's constant can, in the first approximation, be regarded as constant, equation (2.43) predicts that a plot of $(1/\lambda) (\partial \lambda / \partial T)_P$ must be linear in α . This has been shown to be the case for a wide variety of liquids⁴³. The plot does not pass through the origin but intersects the α -axis at a value of α of about $5.5 \times 10^{-4} \text{ deg}^{-1}$. This means that when the coefficient of thermal expansion falls below this value (as at very high pressures for many liquids) the temperature coefficient of thermal conductivity reverses sign and begins to increase

with increasing temperature, explaining Bridgman's observations at high pressures.

2.50. Pressure Dependence of the Transport Properties.

On the basis of transport theories based on the "hole" structure of liquids (see section 3.22), which would require work done against the external pressure in forming a hole which must precede convective molecular motion, an exponential dependence of D_i^0 and η on pressure at constant temperature is to be expected. This behaviour has been confirmed for many simple liquids^{57,62}. Naghizadeh and Rice⁵⁷ have measured the self-diffusion coefficients of liquid Ar, Kr, Xe and CH_4 as functions of pressure and temperature. They showed that a plot of $\log D_i^0$ against p is linear and that for Ar, Kr and Xe

$$\log \tilde{D}_i^0 = 0.05 + 0.07 \tilde{p} - (1/\tilde{T})(1.04 + 0.1\tilde{p}) \quad \dots (2.44)$$

where $\tilde{D}_i^0$, $\tilde{T}$ and $\tilde{p}$ are the reduced diffusion coefficient, temperature and pressure given by

$$\tilde{D}_i^0 = (m/\epsilon \sigma^2)^{1/2} D_i^0 \quad \dots (2.45)$$

$$\tilde{T} = kT/\epsilon \quad \dots (2.46)$$

$$\tilde{V} = V/\sigma^3 \quad \dots (2.47)$$

$$\text{and } \tilde{p} = p\sigma^3/\epsilon \quad \dots (2.48)$$

The pressure and volume dependence of thermal conductivity has been investigated by Kamal and McLaughlin⁴⁴ who showed that appropriate differentiations of equation (2.6) give

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial p} \right)_T = \beta_T \left[\frac{1}{3} - \left(\frac{\partial \ln v}{\partial \ln v} \right)_T \right] \quad \dots (2.49)$$

and

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial v} \right)_T = \frac{1}{v} \left[\frac{1}{3} - \left(\frac{\partial \ln v}{\partial \ln v} \right)_T \right] \quad \dots (2.50)$$

where β_T is the isothermal compressibility. Again, $(\partial \ln v / \partial \ln v)_T$ may be treated as constant in the first approximation and linear relationships should exist between the pressure and volume dependence of thermal conductivity. Using thermal conductivity data obtained by Bridgman³⁹ at 30° and pressures upto 10,000 atm. it has been shown that for a number of simple organic liquids $(1/\lambda)$ $(\partial \lambda / \partial p)_T$ is linear in the isothermal compressibility and $-(1/\lambda) (\partial \lambda / \partial v)_T$ is linear in the reciprocal of molecular volume. The slopes of the two curves are equal as follows from the thermodynamic relationship.

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial p} \right)_T = -\beta_T v \frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial v} \right)_T \quad \dots (2.51)$$

Both the curves pass through the origin, showing that the pressure and volume coefficients of thermal conductivity would always be expected to be positive (as found experimentally), unlike the temperature dependence which can be negative. $(\partial \ln v / \partial \ln v)_T$ has been evaluated on the harmonic oscillator and rectangular cell potential models, and the resulting expressions for the pressure and volume dependence of thermal conductivity are closely similar to corresponding expressions derived from the theories of Enskog and of Longuet-Higgins and Pople.

CHAPTER 3

THEORIES OF DIFFUSION IN LIQUIDS.

In the absence of a rigorous theory of the liquid state the understanding of the factors influencing diffusion in a binary system can be only partial. Attempts to formulate theories of diffusion have been mainly based on either a hydrodynamic or a kinetic approach to the problem. Initial kinetic approaches applied to gaseous systems resulted in the well known Graham's Law of Diffusion. The law is valid for gaseous diffusion and reasonably applicable to the case of gases diffusing in a liquid, but it is wholly inadequate for liquid systems.

3.10. Hydrodynamic Theories.

G. Wiedemann⁶³ was the first to suggest a hydrodynamic basis to the problem of diffusion in liquids when he observed that in the dilute solutions then studied D varied inversely as the viscosity of the solvent. Walden⁶⁴ combined this observation with Graham's Law and postulated that $D\eta M^{\frac{1}{2}}$ is a constant for a given solvent where η is the viscosity of the solvent and M the molecular weight of the solute.

The classical hydrodynamic theory of diffusion is due independently to Sutherland⁶⁵ and to Einstein⁶⁶. They regarded diffusion flow as a balance between a driving force and a resistance to flow which produces a constant average diffusion velocity. In general if a force K is acting on a molecule 1 in solution it will impart to the molecule a proportional velocity v_1 given by

$$v_1 = K/\zeta \quad \dots (3.1)$$

where ζ is a constant representing the frictional resistance which the solvent offers to the movement of the molecule.

In the original papers of Einstein and Sutherland the driving force in diffusion was taken to be the gradient of osmotic pressure but the works of Gibbs⁶⁷, Hartley⁶⁸ and of Onsager and Fuoss⁶⁹ have shown that, in the light of modern thermodynamics, the force is the gradient of chemical potential of the diffusing species i . Since the chemical potential may be written as

$$\mu = \mu_i^0(p, T) + RT \ln f_i c_i \quad \dots (3.2)$$

where f is the activity coefficient on a molar scale and c is the molar concentration, it can be easily shown that for a one dimensional system the diffusion force per molecule of component i is

$$K = -(\text{grad } \mu_i)_{T,P} = -\left(\frac{d\mu}{dx}\right)_{T,P} = -\frac{RT}{Nc_i} \left[1 + \left(\frac{\ln f_i}{\ln c_i} \right)_{T,P} \right] \frac{dc_i}{dx} \quad \dots (3.3)$$

where N is Avagadro's Number. The activity term in the bracket is unity for ideal mixtures such as those considered by Sutherland and by Einstein. For such mixtures substitution for K in equation (3.1) given

$$v_i = \frac{1}{\zeta} \frac{RT}{Nc_i} \frac{dc_i}{dx} \quad \dots (3.4)$$

v_i is the velocity with which the solute i is carried forward by the process of diffusion. Since c_i gram molecules are present per unit volume, $c_i v_i$ is the mass of the dissolved substance (in gram molecules) which is carried per unit time by diffusion

through unit area of cross-section. This quantity is also given by Fick's fundamental law of diffusion,

$$J = c_i v_i = - D \frac{dc_i}{dx} \quad \dots (3.5)$$

On equating the two expressions for $c_i v_i$ one obtains

$$- \frac{Rc_i}{N\zeta} \cdot \frac{dc_i}{dx} = - D \frac{dc_i}{dx} \quad \dots (3.6)$$

$$\text{or} \quad D = kT/\zeta \quad \dots (3.7)$$

An analysis of ζ is required in order to make further progress with this theory. Stokes⁷⁰ calculated by classical hydrodynamic methods the frictional force acting on a spherical particle of radius a moving in a continuous medium of viscosity η and showed that

$$\zeta = 6\pi\eta a \cdot \frac{1 + 2\eta/\beta a}{1 + 3\eta/\beta a} \quad \dots (3.8)$$

where β is the coefficient of sliding friction between the molecule and its surroundings. Two limiting cases may be considered, namely,

$$\beta = 0, \quad \zeta = 4\pi\eta a \quad \dots (3.9)$$

$$\beta = \infty, \quad \zeta = 6\pi\eta a \quad \dots (3.10)$$

In the case of a large spherical molecule diffusing in a medium of low molecular weight there would be very little "slipping" of the solution at the surface of the molecule and the coefficient of friction β may be considered equal to infinity. If the corresponding value of β is substituted in Einstein's equation, one gets the Stokes-Einstein equation

$$D = kT/6\pi\eta a \quad \dots (3.11)$$

When the activity correction is included

$$D = \frac{kT}{6\pi\eta a_i} \left[1 + \left(\frac{\partial \ln f_i}{\partial \ln c_i} \right)_{T,P} \right] \quad \dots (3.12)$$

Equation (3.12) has been shown to apply accurately to particles of colloidal size by a number of investigators, but its accuracy decreases with decreasing particle size. This is not unexpected since Stoke's law is based on the assumption that the solvent is a continuum, an assumption which is not valid when the solute and solvent particles are of comparable size. Ordinarily the viscosity considered is that of the solvent alone, and this further restricts the applicability of equation (3.11) to dilute solutions.

Sutherland⁶⁵ pointed out that in the case of a small solute molecule diffusing through a solvent of comparable molecular size β is given fairly closely by its limiting value of zero, since the solute molecules can move freely in the small spaces between the solvent molecules. In this case

$$D = kT/4\pi\eta a \quad \dots (3.13)$$

Other theories of viscosity give values of the numerical coefficient which differ from both 4 and 6. Lamm⁷¹ has shown that it is 1.64 according to Andrade's theory of viscosity³⁸ and 4.5 according to Jäeger's theory⁷². Collins and Raffel⁷³ made a kinetic calculation of the self-diffusion coefficient of a liquid consisting of perfectly elastic cubically packed spheres with a Boltzmann distribution of energy and showed that

$$D = kT/2.77 \sigma \eta_c \quad \dots (3.14)$$

where σ is the collision diameter and η_c the collisional contribution to viscosity⁷⁴. η_c has been found to be between 0.25 and 0.5 of the viscosity η for a number of organic liquids. On putting

$\sigma = 2a$ equation (3.14) takes the form of equation (3.11) with the numerical factor lying between 1.385 and 2.77.

The evaluation of the friction coefficient ζ is a fundamental problem in the statistical mechanical theories of transport based on analogies with Brownian motion. The problem is still unsolved and has hampered attempts at numerical calculations of transport coefficients even for simple monatomic fluids for which such theories are valid.

3.20. Kinetic Theories of Diffusion.

3.21. Kinetic Theory of Arnold.

Arnold⁷³ made the first successful attempt at developing a kinetic theory of diffusion in liquids. He applied the method used in the kinetic theory of gaseous diffusion to liquids after making certain corrections for the shorter distance between molecules. He made the following assumptions:

- (a) all collisions are binary,
- (b) the collision rate is unaffected by the volume occupied by the molecules, and
- (c) intermolecular attractions are negligible, and deduced the equation

$$D = \frac{B \sqrt{(1/M_1 + 1/M_2)}}{S^2} V_1 \quad \dots (3.15)$$

where M_1 , M_2 are the molecular weights of the solvent and solute respectively, V_1 is the molar volume of the solvent, S is the sum

of the molecular diameters and B a proportionality constant. In liquids collisions of higher order than two must also take place, the volumes occupied by the molecules cannot be neglected and the molecules will exert forces on each other. In order to allow for the consequential defects in Arnold's theory an empirical correction was applied by inserting a correction factor F, chosen to give good agreement between experimental and calculated values in the denominator. Arnold used $A_1 A_2 V_1 \eta_1^{1/2}$ for F and wrote the final equation for D as

$$D = \frac{B \sqrt{1/M_1} + (1/M_2)}{A_1 A_2 \eta_1^{1/2} s^2} \quad \dots (3.16)$$

where η_1 is the solvent viscosity, and A_1, A_2 are empirical factors characteristic of the solvent and the solute. Arnold examined much of the data available at the time he presented his theory and found that experimental values showed reasonably good agreement with his theory. Caldwell and Babb⁷⁴ showed that the Arnold equation predicted diffusion coefficients correct to about 10 per cent in three ideal systems at dilute concentrations. Trevo and Drickamer⁷⁵ used the equation to correlate experimental data for some equimolar mixtures with considerable success. The agreement of Arnold's theory with experiment is not altogether surprising as his final equation for D contains 3 adjustable parameters.

On the basis of the limited amount of experimental data over a range of temperature available to him, Arnold proposed that the variation of D with temperature was linear. Later work

has clearly established that the temperature variation is exponential and has showed that in this respect Arnold was in error. In spite of the arbitrary assumptions made, Arnold's theory provides a good means of predicting diffusion coefficients in dilute solutions, when the necessary correction factors can be correctly assigned.

3.22. Kinetic Theory of Eyring.

Eyring and his collaborators have developed a kinetic theory of diffusion which is far more general than Arnold's approach and is based on Eyring's theory of absolute reaction rates. The theory has been reviewed by Kincaid, Eyring and Stearn³⁶ and summarised in the textbook by Glasstone Laidler and Eyring³⁷. Eyring's theory of absolute reaction rates postulates that most processes which occur at a measurable rate can be regarded as proceeding through an intermediate transition state, the energy of which exceeds that of the initial state by an amount ϵ^0 per molecule. the velocity constant for the rate at which the transition state is attained (and hence the overall rate of change) is given by

$$k^v = \kappa \frac{kT}{h} \frac{F^\ddagger}{F} \exp \left(\frac{-\epsilon^0}{kT} \right) \quad \dots (3.17)$$

where κ is a transmission coefficient normally assumed to be unity in the application of the theory to diffusion and viscosity, h is Planck's constant and $F^\ddagger$, F are partition functions per unit volume of the molecule in the activated and normal states respectively.

Eyring's development is based on the 'hole' theory of the liquid state which regards a liquid as made up of 'holes' moving about in matter. The holes in a liquid are considered similar to gas molecules in their behaviour but, since the translational motion in a liquid is more restricted than in a gas, the partition function for holes in liquids is less than that for gases.

Eyring described diffusion as a process in which molecules move from a given equilibrium position into an adjacent hole in the liquid structure. The energy of activation for diffusion is the energy required to make a hole in a liquid of a size to accommodate a single molecule and has been shown³⁷ to be some fraction of the energy of vaporization, i.e.,

$$\Delta E_{\text{diff}} = \Delta E_{\text{vap}}/n \quad \dots (3.18)$$

If λ is the distance between two successive equilibrium positions of a molecule diffusing in the x-direction from an initial concentration of c , the concentration at the next equilibrium stage will be $c + dc/dx$. The net flow through unit area of cross-section in this process can be shown to be

$$J_N = -Nc\lambda^2 k^v \text{ molecules cm}^{-2} \text{ sec}^{-1} \quad \dots (3.19)$$

where N is Avagadro's number and k^v is the specific rate for diffusion, i.e., the number of times a molecule moves from one position to the next per second.

From the Fick's Law definition of the diffusion coefficient D ,

$$J_N = -DN \frac{dc}{dx} \text{ molecules cm}^{-2} \text{ sec}^{-1} \quad \dots (3.20)$$

Avagadro's number being introduced to change moles to molecules.

Thus

$$DN \frac{dc}{dx} = N \lambda^2 k^v \frac{dc}{dx} \quad \dots (3.21)$$

or

$$D = \lambda^2 k^v \quad \dots (3.22)$$

Equations (3.22) and (3.17) can be combined to give

$$D = \lambda^2 \frac{kT}{h} \frac{F^\ddagger}{F} \exp(-\xi_0/kT) \quad \dots (3.23)$$

It is assumed that the transition state differs from the normal state only in that it has one less degree of translational freedom.

With this assumption it can be shown³⁷ that

$$\frac{F}{F^\ddagger} = \frac{(2\pi mkT)^{1/2}}{h} v_f^{1/3} \quad \dots (3.24)$$

where v_f is the free volume⁷⁶. Upon writing $\Delta E_{\text{diff}}/RT$ in place of ξ_0/kT , replacing ΔE_{diff} by $\Delta E_{\text{vap}}/n$ and substituting for the ratio of partition functions from equation (3.24), equation (3.23) becomes

$$D = \frac{\lambda^2}{v_f^{1/3}} \left(\frac{kT}{2\pi m} \right)^{1/2} \exp(-\Delta E_{\text{vap}}/nRT) \quad \dots (3.25)$$

The distance λ may be taken approximately as $(V/N)^{1/3}$ where V is the molecular volume, and the free volume v_f may be estimated by several methods³⁷. Eyring and Hirschfelder⁷⁶ showed that it may be approximated by the equation

$$v_f^{1/3} = (cRTV^{1/3}) / (N^{1/3} \Delta E_{\text{vap}}) \quad \dots (3.26)$$

where c is a constant depending on the molecular arrangement, having a value of 2 for a simple cubical lattice with 6 nearest

neighbours. Kincaid and Eyring⁷⁷ also suggested the relation

$$V_f = V^{1/3} (U_{\text{gas}}/U_{\text{liq}}) \quad \dots (3.27)$$

where U is the velocity of sound.

For diffusion involving two types of molecules Eyring has suggested the employment of weighed mean values of λ , V_f and ϵ_0 given by the expressions

$$\lambda = N_1 \lambda_1 + N_2 \lambda_2 \quad \dots (3.28)$$

$$V_f^{1/3} = N_1 V_{f1}^{1/3} + N_2 V_{f2}^{1/3} \quad \dots (3.29)$$

$$\Delta E_{\text{vap}}^{1/2} = N_1 \Delta E_{\text{vap.1}}^{1/2} + N_2 \Delta E_{\text{vap.2}}^{1/2} \quad \dots (3.30)$$

Correlation of experimental data with Eyring's equation by a number of investigators^{74,75,78,79} has shown that the method yields values only of the proper order of magnitude. The Eyring equation predicts an exponential temperature dependence of diffusion rates which has been confirmed by the results of Cohen and Bruins⁸⁰, Caldwell and Babb⁷⁴, Graupner and Winter⁷⁹ and several other investigators.

Equation (3.22) may be combined with the equation developed by Eyring for viscosity⁸¹ to give

$$D = \lambda_1 kT / \lambda_2 \lambda_3 \eta \quad \dots (3.31)$$

when it has been assumed that λ and k^v are the same for the processes of diffusion and viscous flow. λ_1 , λ_2 and λ_3 are the distances between molecules in the 3 planes. The product $\lambda_1 \lambda_2 \lambda_3$ is usually identified with the volume per molecule and, in the

case of the self-diffusion of spherical molecules λ_1 , λ_2 and λ_3 may be each equated to the effective molecular diameter. In this case equation (3.31) reduces to

$$D = kT/2a \quad \dots (3.32)$$

where a is the radius of the diffusing molecule. Equation (3.32) is of a form similar to the one obtained on the basis of hydrodynamic theories. The numerical factor on the right hand side is different and Hammond and Stokes⁸² have shown that the hydrodynamic theory gives much better agreement with their experimental results than Eyring's theory. Li and Pin Chang⁸³ have shown that the discrepancy may be attributed to an error in Eyring's theory of viscosity, and their revised equation⁸³ gives better agreement with experimental data.

3.23. McLaughlin's Modification.

A modified rate-theory approach to the calculation of transport coefficients of molecules interacting with spherically symmetric fields of force was made by McLaughlin⁴². A face-centred cubical lattice type of structure was assumed, so that intermolecular distances in the liquid could be calculated. The transmission coefficient κ was assumed to be given not by unity (as in Eyring's approach) but by the proportion of vacant sites or holes in the liquid quasi-lattice, and the intermolecular interaction was represented by a Lennard-Jones (12,6) potential. The derived equation for the coefficient of self-diffusion may be written

$$D_1^0 = \left(\frac{kT}{2\pi m} \right)^{1/2} \frac{\lambda^2}{V_f^{1/3}} \frac{n_h}{N} \exp(-U_0/3NkT) \quad \dots (3.33) \quad 55.$$

λ was taken to be the nearest neighbour distance, $(\sqrt{2} V/N)^{1/3}$, and the fraction of holes n_h/N , free volume V_f and U_0 (the energy of the system when all the molecules are in their equilibrium positions at the centres of their cells) were calculated from the Lennard-Jones and Devonshire theory of liquids²⁶. Calculated self-diffusion coefficients at various temperatures for argon, carbon tetrachloride and benzene agreed with experimental values to within 10 per cent.

3.30. Self-diffusion in Binary Mixtures.

The measurement of self-diffusion, which does not require an overall concentration gradient, gives the nearest available approach to the observation of the magnitude of actual molecular motion in a gross sense. The relationships between the mutual and the two self-diffusion coefficients in a binary mixture have been a subject of wide investigations and equations relating these quantities have been proposed by Prager⁸⁴, Lamm^{85,86}, Darken⁸⁷, Hartley and Crank⁸⁸, Eyring³⁷, Gordon⁸⁹ and several others. The equations are similar in form and Bearman⁹⁰ has shown that, for regular solutions where the different molecules have similar size, shape and interaction potentials, the equations derived by Eyring et al., Hartley and Crank and by Gordon (loc.s cit.) for the concentration dependence of diffusion coefficients in binary liquid solutions are basically equally to each other and to corresponding equations derived on the basis of the statistical mechanical theory of transport⁹¹.

Bearman's expressions for mutual and self-diffusion coefficients can be simplified subject to the following assumptions:

- (a) the solutions are regular with spherically symmetric interaction potentials,
- (b) the radial distribution function is independent of composition and
- (c) no volume change occurs on mixing.

Under these conditions the following equations were derived:

$$D_1/D_2 = V_2/V_1 \quad \dots (3.34)$$

$$\lim_{c_1 \rightarrow 0} D = D_1^\infty \quad \dots (3.35)$$

$$\lim_{c_1 \rightarrow 0} D = D_2^\infty \quad \dots (3.36)$$

$$D = D_1 (\partial \ln a_1 / \partial \ln c_1)_{T,P} \quad \dots (3.37)$$

D_1 and D_2 are the self-diffusion coefficients of species 1 and 2 respectively, D the mutual diffusion coefficient and V_1 and V_2 the molecular volumes of species 1 and 2 respectively. D_1^∞ and D_2^∞ are the coefficients of self-diffusion of species 1 and 2 at infinite dilution and a_1 and c_1 the activity and concentration (moles per unit volume) of species 1.

Horrocks and McLaughlin⁹³ have shown that since

$$\left(\frac{\partial \ln a_1}{\partial \ln c_1} \right)_{T,P} = \left(\frac{\partial \ln a_1}{\partial \ln x_1} \right) \frac{x_1 V_1 + x_2 V_2}{V_2}, \quad \dots (3.38)$$

where x_1 is the mole fraction of species 1, it follows from equation (3.37) that

$$D = \left(\frac{\partial \ln a_1}{\partial \ln x_1} \right)_{T,P} \left[x_1 D_2 + x_2 D_1 \right] \quad \dots (3.39)$$

The ratio D_1/D_2 from Carman and Stein's data⁹² on the ethyl iodide + n-butyliodide system at 19.35°C. is found to be 1.1, on average, whereas V_2/V_1 is 1.41. The agreement is encouraging considering that in this system the radial distribution function is not expected to be independent of composition, since the molar volume of n-BuI is one and a half times greater than that of EtI. Mutual diffusion coefficients for this system have not been measured and hence the validity of equation (3.39) cannot be tested.

3.40. Relationships between the transport coefficients in mixtures.

Bearman's general theory also provides expressions for the viscosity and thermal conductivity in binary mixtures, and Horrocks and McLaughlin⁹³ have shown that the expressions for the three transport coefficients may be combined to give the following relationships:

$$\eta D_1 = \eta_1 D_1^0 = \eta_2 D_1^\infty \quad \dots (3.40)$$

$$\lambda D_1 = \lambda_1 D_1^0 = \lambda_2 D_1^\infty \quad \dots (3.41)$$

$$\text{and } D_1/D_2 = D_1^\infty/D_2^0 = D_1^0/D_2^\infty \quad \dots (3.42)$$

where η and λ are the viscosities and thermal conductivities of mixtures of species 1 and 2, with coefficients in the pure state of $\eta_1, \eta_2, \lambda_1$ and λ_2 . D_1^0 and D_2^0 are the self-diffusion coefficients of species 1 and 2 in the pure state. It can be shown from equations (3.40) - (3.42) that the ratios D_1^∞/D_1^0 , D_2^0/D_2^∞ , η_1/η_2 and λ_2/λ_1 should all be equal. Experimental data on the carbon tetrachloride-cyclohexane and carbon-tetrachloride-benzene system shows an

agreement of the ratio within 5 percent; whereas in the n-BuI + EtI system the thermal conductivity ratio differs by about 50% from the other three ratios which are almost identical⁹³. For the purpose of calculating the mutual diffusion coefficient from more readily available experimental data the following equations can be derived:

$$D = \frac{\eta_2}{\eta} D_1^\infty \left(\frac{\partial \ln a_1}{\partial \ln x_1} \right) \left[x_1 \frac{V_1}{V_2} + x_2 \right] \quad \dots (3.43)$$

$$D = \frac{\lambda}{\lambda_2} D_1^\infty \left(\frac{\partial \ln a_1}{\partial \ln x_1} \right) \left[x_1 \frac{V_1}{V_2} + x_2 \right] \quad \dots (3.44)$$

The validity of equation (3.43) has been tested by means of experimental data which are available for the carbon tetrachloride-cyclohexane system⁹⁴. If the molecular volumes in equation (3.43) are replaced by the partial molecular volumes $\bar{V}_1$ and $\bar{V}_2$ (since the system does exhibit a volume change on mixing, contrary to the assumption made in the derivation of the equation) agreement between the experimental and calculated values of the mutual diffusion coefficient is on average within 0.5 percent.

The paucity of experimental results on the concentration dependence of self-diffusion coefficients in mixtures has hindered comprehensive tests of the theory and the present work has been undertaken in order to provide such data for some simple binary systems.

CHAPTER 4.METHODS OF MEASURING SELF-DIFFUSION.4.00 The Diffusion Equations.

The fundamental law of diffusion, based on an analogy with Fourier's law of heat conduction, was given by A. Fick⁹⁵ in 1855 and is expressed by the equation

$$J_m = - D \frac{\partial c}{\partial x} \quad \dots (4.1)$$

for unidirectional diffusion in an isotropic fluid. J_m is the flux or rate of transfer per unit area of cross-section, $\partial c / \partial x$ the concentration gradient in a direction normal to the section and D the diffusion coefficient. D was originally assumed to be constant for a given system, but experimental evidence has shown that D is generally a function of concentration and may be regarded as a constant only in the limiting case, i.e., at infinite dilution.

Equation (4.1) may be written dimensionally in c.g.s. units as

$$\frac{\frac{(g)}{(cm)^2}}{(sec)} = \frac{D(g)}{(cm^3)(cm)}, \quad \dots (4.2)$$

showing that D has the dimensions $cm^2 \cdot sec^{-1}$. When determined as an average value over a range of concentration, D is known as an integral diffusion coefficient; if calculated for a specific concentration it is known as a differential diffusion coefficient.

Now the hydrodynamic equation of continuity for an isotropic fluid is⁹⁶

$$\frac{D\rho}{Dt} = - \frac{\partial v}{\partial x} \quad \dots (4.3)$$

where ρ is the fluid density, v its hydrodynamic (i.e. centre of mass) velocity, and t the time. The derivative $\frac{D}{Dt}$ is given by

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + v \frac{\partial}{\partial x} \quad \dots (4.4)$$

Equation (4.3) may be written in the expanded form as

$$\frac{\partial \rho}{\partial t} = -\rho \frac{\partial v}{\partial x} - v \frac{\partial \rho}{\partial x} = \frac{\partial}{\partial x} (\rho v) \quad \dots (4.5)$$

The product (ρv) expresses the flux J_m per unit area of cross-section (see section 3.10) and, since the density ρ of the fluid at constant temperature and pressure is a measure of its concentration c , equation (4.5) becomes

$$\frac{\partial c}{\partial t} = - \frac{\partial J_m}{\partial x} \quad \dots (4.6)$$

Equations (4.1) and (4.6) can be combined to give

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad \dots (4.7)$$

which is known as Fick's second law of diffusion. If, as in the case of small concentration ranges, very dilute solutions and self-diffusion, D is a constant equation (4.7) may be written as

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \dots (4.8)$$

D can be determined from measurements of $\frac{\partial c}{\partial x}$ (of or) c as a function of x or t provided equation (4.8) can be solved. Solutions of the equation can be obtained for a number of geometric possibilities and take different forms according to the boundary conditions⁹⁷.

4.10. Classification of Experimental Methods.

Experimental methods of measuring diffusion coefficients differ according to the selected boundary conditions and may be classified as follows:

(i) Free diffusion or the case of the infinite cylinder,

in which a sharp boundary is allowed to form within a diffusion cell. The concentration on either side of the boundary changes with time and diffusion is allowed to proceed for such a time that the concentrations at the ends of the cell remain unchanged.

The solution of equation (4.8) has the form⁹⁸

$$c = c''_0 + \frac{c'_0 - c''_0}{2} \left[1 - \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{Dt}} e^{-\beta^2} d\beta \right] \quad \dots (4.9)$$

where c''_0 and c'_0 are the initial concentrations of the upper and lower (more concentrated solutions, respectively, and c is the concentration at the level x at time t after diffusion commences. The second term in the bracket is the error function* in which β is an arbitrary integration variable, so that equation (4.9) may be written as

$$c = c''_0 + \frac{c'_0 - c''_0}{2} \left[1 - \operatorname{erf} (x/2\sqrt{Dt}) \right] \quad \dots (4.10)$$

The diffusion coefficient D can therefore be readily obtained from experimental values of c'_0 , c''_0 , x and t by reference to error function tables^{99, 100}.

If D is to be determined from measurements of concentration of gradients along the diffusion column, rather than that of

*The error function, a standard mathematical function of which standard tables are available^{99,100}, is defined by

$$\operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z e^{-\beta^2} d\beta$$

concentration, it is convenient to use a solution of equation (4.8) in the form⁹⁸

$$\frac{\partial c}{\partial x} = \frac{c'_0 - c''_0}{2\sqrt{Dt}} \exp(-x^2/4Dt) \quad \dots (4.11)$$

Most of the experiments on diffusion in which an optical technique of analysis is used are based on free diffusion methods.

(ii) Restricted diffusion or the case of the finite cylinder.

If, in the experiment described in section 4.10 (i), diffusion is allowed to proceed for a sufficiently long time, concentration changes begin to occur at the ends of the cell, and free diffusion becomes restricted. The general solution of equation (4.8) in this case is a Fourier series of the form

$$c = A + \sum_{n=0}^{\infty} B_n \exp \left[-\left(\frac{n}{l}\right)^2 Dt \right] \cos \frac{n\pi x}{l} \quad \dots (4.12)$$

where l is the length of the diffusion column and A and B_n are constants depending on the special case under consideration. For a cylinder of length l closed at one end with concentration maintained zero at the open end, the average concentration of material left in the cylinder at the end of time t (after the commencement of diffusion) is given by

$$c_{\text{avg}} = \frac{8 c'_0}{2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-\left\{ \frac{(2n+1)}{2l} \right\}^2 Dt \right] \quad \dots (4.13)$$

where c'_0 is the concentration at $t = 0$. The widely used capillary cell technique of measuring self-diffusion coefficients is based on this method.

(iii) Steady-state methods are based on solutions of Fick's law of diffusion given by equation (4.1), which may be integrated provided D is assumed constant and the concentration is a linear function of the distance. The latter condition is achieved in the steady state in which the flux of solute J_m in moles per unit area is constant at all planes in the diffusion column perpendicular to the direction of flow. The most useful application of steady-state diffusion is with diaphragm cells, which have been largely used for the measurement of diffusion coefficients.

4.20. Measurement of Self-Diffusion Coefficients.

Self-diffusion is the phenomenon of diffusion in a system of identical molecules, and its measurement by conventional methods is impossible. In practice the measurement is usually made by adding a small number

~~small number~~ of labelled molecules as tracers to a system of otherwise uniform chemical composition, and observing the net displacement of the tracers. The smaller the differences between the labelled and the unlabelled molecules the closer the experimental diffusion coefficient approximates to the true self-diffusion coefficient. Ordinarily the labelling is achieved by means of an isotope with a different mass than the parent, which allows analysis by density measurements, or by a radioactive isotope, when analysis can be carried out by appropriate radioactivity measurements. The behaviour of the tracer will be always slightly different from that of the unlabelled species since radioactive atoms emit energy and have slightly different masses. It is generally agreed, however, that the differences are slight and that measurements with labelled molecules may be regarded as measurements of true self-diffusion coefficients.

In recent years the discovery of the spin-echo phenomenon in the field of nuclear magnetic resonance¹⁰¹ and its ensuing theoretical analysis^{102,103} in terms of a diffusion process has led to a new technique^{102,104} for measuring self-diffusion coefficients which does not require the presence of unusual isotopes. In this case diffusion of molecules in a sample is followed by its effect in altering the nuclear magnetic properties of the sample and hence the true self-diffusion coefficient is directly measured. The spin-echo technique may be used to

measure self-diffusion coefficients rapidly and under a variety of experimental conditions. Self-diffusion coefficients in water¹⁰² and in some paraffin hydrocarbons¹⁰⁴ and primary alcohols¹⁰⁵ have been measured by this method. Although the experimental error is considerably large^{*}, the values obtained, where comparison is possible, are very close to those obtained by other methods.

Any of the conventional methods of measuring diffusion in which the analytical technique allows a distinction to be made between labelled and unlabelled isotopes can be used for the measurement of self-diffusion coefficients. This generally rules out the various optical methods. The principal techniques that have been used for measuring self-diffusion coefficients will be discussed in the next section.

4.21. Physical Micromethod.

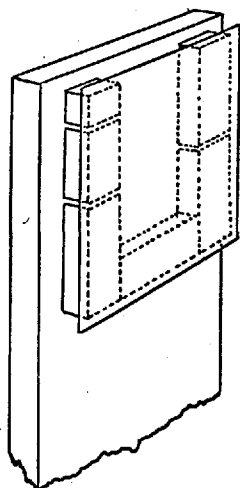
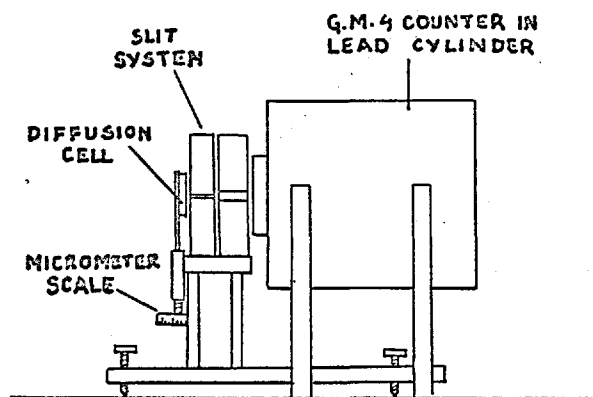
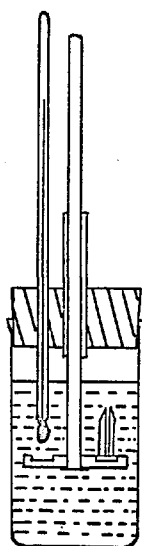
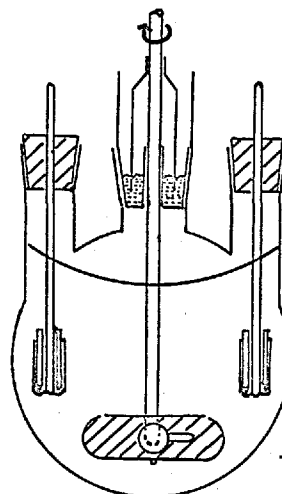
In the measurements of diffusion coefficients by free diffusion methods, the formation of a sharp boundary between adjacent phases in the system is of primary importance. In most of the earlier work, boundary formation was carried out by carefully flowing in the heavier solution under the lighter one by means of a pipette or a small connecting tube. However, in following this procedure, the avoidance of boundary disturbances is difficult. Considerable effort has been devoted to refinement of cell design. The F^urth cell was developed by F^urth^{106,107}

for use in the microcolorimetric method. It is suitable for aqueous systems but difficulties due to leakage are encountered if organic liquids are used.

Furth's method has been modified by Rolfe¹⁰⁸ for self-diffusion measurements on sodium iodide labelled with I-131 and on orthophosphoric acid labelled with P-32 with an accuracy of about 2 per cent. The cell used by Rolfe consists of two compartments separated by means of a thin stainless steel sliding partition (fig.4.1), and is mounted in a scanning apparatus (fig.4.2) so that it can be raised or lowered past the scanning slit by means of micrometer screw. The slit system, the walls of which have to be strong enough to absorb any gamma rays which may be given off, is formed by four lead blocks separated by spacers.

Radiation through the slits is measured with a Geiger counter in conjunction with a counting-rate meter. The counting rate was found to be directly proportional to the concentration of radioactive tracer.

Small pipettes are used to fill the lower half of the cell with a radioactive solution of known concentration, the slide closed and the excess solution removed from the upper half with pipettes and strips of filter paper. The upper half of the cell is filled with non-radioactive solution of the same concentration. It was found that, owing to the low sensitivity of the apparatus,

FIG. 4.1. ROLFE'S DIFFUSION CELL¹⁰⁸FIG. 4.2. THE SCANNING APPARATUS¹⁰⁸FIG. 4.3. OPEN-ENDED CAPILLARY
CELL¹⁰⁹FIG. 4.4. WANG'S CAPILLARY APPARATUS¹¹⁰

radioactive solutions of very high activity (20 mc. per ml.) were required.

The initial count rate from the undiffused solution in the lower half of the cell is determined in 0.5 mm. steps for distances of 1.0 to 4.0 mm. below the slide. After the start of diffusion by removal of the slide, the counting rates are taken for different times, t , and distances, x , below the slide. The diffusion coefficient is calculated by using the solution of equation (4.8) given by equation (4.10). Since the concentration (of the radioactive tracer) in the upper compartment of the cell is zero, equation (4.10) reduces to

$$c = 0.5 c_0' \left[1 - \operatorname{erf} (x/2 \sqrt{Dt}) \right], \quad \dots (4.14)$$

which, when solved for D , becomes

$$D = \frac{x^2}{4t} \left[\operatorname{erf}^{-1} (1 - 2c/c_0') \right]^2 \quad \dots (4.15)$$

where erf^{-1} is the inverse error function.

If r is the ratio of the counting rate relative to the initial rate at concentration c_0' , then $r = c/c_0'$ and equation (4.15) becomes

$$D = \frac{x^2}{4t} \left[\operatorname{erf}^{-1} (1 - 2r) \right]^2 \quad \dots (4.16)$$

Rolfe had to apply some corrections for gamma-rays transversing the lead blocks forming the slit walls and affecting the count rate. Corrections were also necessary to allow for back-scattering of beta-rays in the solution. Rolfe's technique also suffers from the usual disadvantage of Furth's micromethod, in that measurements

are made in a region in which errors due to boundary disturbances are pronounced.

4.22. Capillary Cells.

A widely used method of measuring self-diffusion coefficients is due to Anderson and Saddington¹⁰⁹ and employs narrow thick-walled capillaries (fig.4.3), sealed at the bottom and of uniform diameter, which are filled with the radioactive solution. The capillaries are then lowered vertically into a large volume of inactive solution having the same chemical composition as the active one. Diffusion of the radioactive solution takes place from the capillary into the bulk of the solution and, at the end of the experiment, the amount remaining in the capillary is measured. A diffusion period of about three days is usually required.

Since the volume in the capillary is so small compared to that in the vessel, the concentration of the active solution in the latter may safely be assumed to remain constant at zero throughout the experiment. The effective boundary conditions in a capillary cell are, therefore, those of a cylinder of length l closed at one end with concentration maintained zero at the open end, and the appropriate solution of Fick's equation (4.8) is given by equation (4.13), viz.

$$c_{\text{avg}} = \frac{8c'_0}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[- \left\{ \frac{(2n+1)^2 \pi^2}{2l^2} \right\} Dt \right] \dots (4.13)$$

where c_{avg} is the average final concentration, c'_0 the initial

(uniform) concentration and t the time. Putting $\theta = \pi^2 Dt / 4l^2$, the first three terms in the series are

$$\gamma = \frac{8}{\pi^2} \left[e^{-\theta} + \frac{1}{9} e^{-9\theta} + \frac{1}{25} e^{-25\theta} + \dots \right] \quad \dots (4.17)$$

where γ is the fraction of the original amount of radioactive isotope which is left in the capillary cell at the end of the diffusion run.

The series is rapidly Convergent and, when Dt/l^2 is sufficiently great (> 0.2 , c.f. Wang¹¹⁰), only the first term, $\gamma = 8e^{-\theta}/\pi^2$, need be considered.

In obtaining solution (4.13) for Fick's second law it has been assumed that throughout the diffusion period the concentration of the tracer at the upper end of the capillary was kept at zero by convection currents in the large bath. Wang¹¹⁰ has observed that this boundary condition can be fulfilled by using a slowly rotating mercury seal stirrer with a large paddle (fig.4.4) which can produce sufficient convection in the bath without causing appreciable vibrations. He found that when there is insufficient or no stirring the actual length of the diffusion path is $(l + \delta l)$, longer than the length l of the capillary and, if this occurrence is not taken into account, erroneous results will be obtained. If however the solution is stirred at a gradually increasing speed at a certain stage it might be possible that a little solution in and near the top of the capillary be swept

out by the convection current so that the actual diffusion path could be $(l - \delta l)$, shorter than the length of the capillary. In order to find c_{avg} the total amount of labelled material L in the capillary is determined and divided by the length and the area of cross-section a . The effective length can be written $(l \pm \delta l)$ and hence, using the first term approximation of equation (4.17),

$$Dt/l^2 = \frac{4}{\pi^2} \ln \left\{ \frac{8}{\pi^2} \frac{c_0' (l \pm \delta l)a}{L} \right\}, \quad \dots (4.18)$$

ignoring the uncertainty in δl on the left hand side of the equation¹¹¹. D and δl may be found by using capillaries of different lengths and the stirring speed is chosen so as to make δl negligible.

For self-diffusion measurements the capillary cell technique has the economic advantage of requiring only small amounts of diffusing solution. Recent improvements in the technique^{112,113} have resulted in marked improvements in the precision of successive measurements made by this method. A limiting factor in further improvement is the accuracy with which the contents in the capillary (approximately 10^{-2} ml volume) can be analysed. It is not practical to increase the volume of the capillary because an increase in length increases the diffusion time, while an increase in the internal diameter produces problems of convection.

4.23. Diaphragm Cells.

Because of the relatively poor accuracy which has usually been characteristic of the capillary tube method, a straightforward

adaptation of the diaphragm cell method used for the measurements of mutual diffusion coefficients has been widely used for the measurement of self-diffusion coefficients. The diaphragm cell technique, introduced by Northrup and Anson¹¹⁴ in 1929, overcomes the chief experimental difficulty in the measurement of diffusion coefficients, viz., the elimination of convection which will be produced to some extent by temperature fluctuations or vibrations however small, and particularly by the process of dividing up the diffusing solution when this is necessary for analysis. The diaphragm, through which the diffusion proceeds, serves as a permeable membrane between two compartments in which the respective liquid concentrations are maintained uniform. The diaphragm presents an effective cross-section and path length to the diffusing liquids which cannot be directly measured but must be determined by calibration with a system whose diffusion coefficient is known.

Northrup and Anson assumed that the diffusional process in the diaphragm can be treated as a steady-state problem, and obtained a solution of the diffusion equation on the basis of this assumption. The theory of the method will be discussed in the next chapter.

4.24. Advantages of the Diaphragm Cell Method.

The diaphragm cell method was adopted in the present work because it has certain advantages, which are listed

below, over the other methods which are available for the measurement of self-diffusion coefficients.

1. Convection, which can be caused by mechanical and thermal disturbances, is completely absent within the diaphragm, which forms the diffusion column.

2. In the capillary technique, unless great care is taken, the process of immersing the capillaries in the large bulk of solvent might produce mechanical convection. In the diaphragm cell method mixing in any way other than by diffusion at the beginning and throughout the course of diffusion is prevented. Minor vibrations do not effect the transport of material in the diffusion column.

3. The ability to withdraw samples for isotopic analysis is convenient, as 'in situ' measurements of isotopic concentrations (as required in Rolfe's micromethod) by radioactive or other means pose difficult problems.

4. The time required for sufficient diffusion is less than that for most other methods because of the relatively high concentration gradients that can be established in the diaphragm. Accurate thermostating of the diffusion cells over very long periods of time would be difficult.

5. Relatively large volumes of solutions are available for analysis, which can therefore be made with greater accuracy than in the case of capillary cells.

CHAPTER 5

SELF-DIFFUSION MEASUREMENTS.5.10 Theoretical Considerations5.11 Steady-State Diffusion

In theory the steady state may be realised by allowing diffusion to take place through a plane sheet or membrane of thickness l , whose surfaces $x = 0$, $x = l$ are maintained at concentrations c_1 , c_2 respectively.

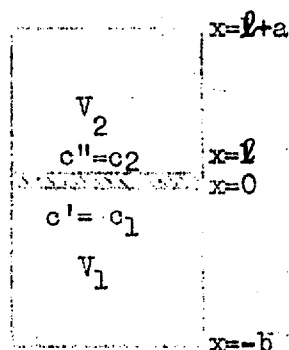


Fig. 5.1.a

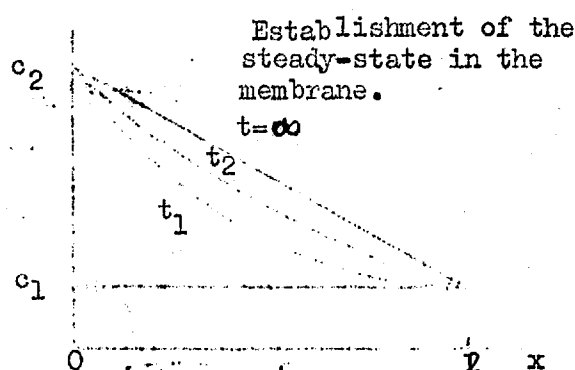


Fig. 5.1.b.

This may be achieved by having two large reservoirs filled with solutions of concentration c_1 and c_2 touching the lower and upper surface of the membrane (fig. 5.1a) until a steady state is reached in which the concentration remains constant at all points of the sheet, i.e., $\partial c / \partial t = 0$. The value of the flux J_m will be constant at all levels and, if D is constant, the concentration gradient will be linear along the column. The concentration distribution in the column until the establishment of the steady state is shown in fig. 5.1b.

Since $\partial c / \partial t = 0$, the diffusion equation $\partial c / \partial t = D \partial^2 c / \partial x^2$ reduces to

$$\partial^2 c / \partial x^2 = 0$$

(5.1)

Integration of equation (5.1) w.r.t. x gives

$$\partial c / \partial x = \text{constant}, k_1 \text{ (say)} \quad \dots (5.2)$$

By a further integration the equation

$$c = k_1 x + k_2 \quad \dots (5.3)$$

is obtained, where k_2 is another constant of integration.

Substitution of the boundary conditions, $c = c_1$ at $x = 0$ and $c = c_2$ at $x = l$, in equation (5.3) yields the equations

$$c_1 = k_2 \quad \dots (5.4)$$

$$c_2 = k_1 l + k_2 = k_1 l + c_1 \quad \dots (5.5)$$

Hence

$$k_1 = (c_2 - c_1) / l = \partial c / \partial x \quad \dots (5.6)$$

If the flux, F , and the concentration gradient, $\partial c / \partial x$, are measured experimentally, D can be calculated from Fick's first law of diffusion, $F = -D \cdot \partial c / \partial x$.

5.12. Derivation of the Diaphragm Cell Equation.

The diaphragm is considered to be equivalent to a collection of parallel pores of average effective length l and of total effective cross-sectional area A . Both solutions are assumed to be of uniform composition right up to the entrance of the pores, and transport from one compartment to the other is assumed to take place solely by diffusion, i.e., it is assumed that streaming in the pores and surface transport along their walls are absent. Strictly speaking, the porous diaphragm does not reproduce conditions of a steady

state except as a limiting case in which the change in concentration becomes zero. For large enough volumes of the lower and upper solutions, however, their concentration will change so slowly that the distribution of concentration across the diaphragm will not differ appreciably from that for a steady-state.

The porous diaphragm method is based on the assumption that by allowing a preliminary diffusion a linear concentration gradient is established in the diaphragm, and that linearity is maintained during diffusion. Thus the concentration gradient at any given time is $(c' - c'')/l$ where c' and c'' are the concentrations of the denser and lighter solutions respectively and l is the length of the diaphragm.

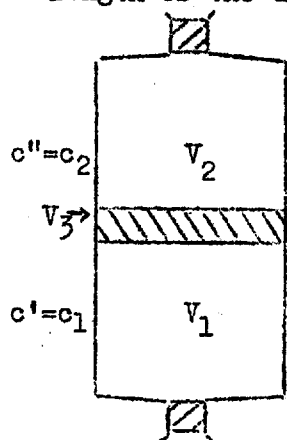
Initial conditions ($t=0$)

Fig.5.2.a

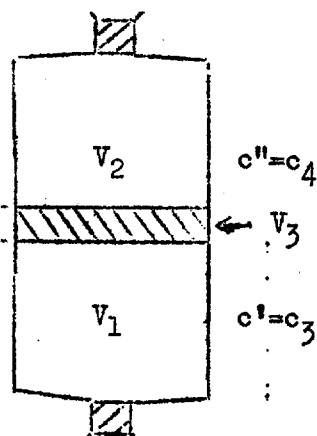
Final conditions ($t=t$)

Fig.5.2.b.

The rates of change in concentration in the upper and lower compartments, dc'/dt and dc''/dt , are given by

$$dc'/dt = -F.A/V_1 \quad \dots (5.7)$$

$$dc''/dt = +F.A/V_2 \quad \dots (5.8)$$

respectively, where F is the flux per unit area and V_1, V_2 are the volumes of the lower and upper compartments respectively.

Equations (5.7) and (5.8) can be combined to give ...

$$d(c' - c'')/dt = -FA(1/V_1 + 1/V_2) \quad \dots (5.9)$$

Now

$$F = -D \cdot dc/dx = -D(c'' - c')/\ell = D(c' - c'')/\ell \quad \dots (5.10)$$

which, when substituted in equation (5.9), gives

$$\frac{d(c' - c'')}{dt} = -D \left(\frac{c' - c''}{\ell} \right) \cdot A \cdot \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \quad \dots (5.11)$$

or

$$\frac{1}{(c' - c'')} d(c' - c'') = -D \beta dt \quad \dots (5.12)$$

where $\beta = A/\ell (1/V_1 + 1/V_2)$ is the cell constant which must be determined by calibration with a solution of known diffusion coefficient.

Since it has been assumed that D is independent of concentrations, equation (5.12) can be integrated to give

$$\ln(c' - c'') = -\beta Dt + K \quad \dots (5.13)$$

where K is the constant of integration which is determined by applying the boundary conditions

$$(c' - c'') = (c_1 - c_2) \text{ at } t = 0, \quad \dots (5.14)$$

$$\text{and } (c' - c'') = (c_3 - c_4) \text{ at } t = t, \quad \dots (5.15)$$

(c.f. fig.5.2), so that

$$K = \ln(c_1 - c_2) \quad \dots (5.16)$$

and

$$D = \frac{1}{\beta t} \ln \left(\frac{c_1 - c_2}{c_3 - c_4} \right) \quad \dots (5.17)$$

Equation (5.17) is rigorous if D is constant and conditions in the diaphragm are those of a steady-state. Since concentration changes

occur continuously, a steady-state may exist at any instant if the concentration changes take place sufficiently slowly so as not to alter the linearity of the concentration at that instant. Barnes¹¹⁵ has shown in a rigorous solution of the problem that this assumption does not lead to an appreciable error if the volumes of the solution are relatively large compared to that of the space in the diaphragm. This condition is easily realised in practice. Furthermore, deviations from the steady state are likely to be compensated for in the manner of calibration.

In practice the exact initial concentration c_1 can be found from c_2 (usually kept at zero), c_3 , c_4 and the volumes of the upper and lower compartments, and of the pores in the diaphragm. The concentration in the diaphragm is assumed to be the average of the concentrations in each compartment and it follows that, since no solute is lost,

$$c_1 V_1 + c_2 V_2 + (c_1 + c_2) V_3/2 = c_3 V_1 + c_4 V_2 + (c_3 + c_4) V_3/2 \quad \dots (5.18)$$

or

$$c_1 = c_3 + (c_4 - c_2)(V_2 + 0.5V_3)/(V_1 + 0.5V_3) \quad \dots (5.19)$$

where V_3 is the effective volume of the pores in the diaphragm.

If $c_2 = 0$,

$$c_1 = c_3 + c_4 (V_2 + 0.5V_3)/(V_1 + 0.5V_3) \quad \dots (5.20)$$

5.13. Case of Variable D

If $\bar{D}(t)$ denotes the average value of the diffusion coefficient D with respect to concentration over the concentration range

c'' to c' prevailing at the time considered, then

$$\bar{D}(t) = \frac{1}{c' - c''} \int_{c''}^{c'} d \, dc \quad (5.21)$$

The average value is written as $\bar{D}(t)$ because it is also a function of time, decreasing as the process of diffusion reduces the concentration difference.

Using the conditions $x = 0$ at $c = c'$, $x = l$ at $c = c''$, equation (5.21) may be written in terms of the variable x instead of c , so that

$$\bar{D}(t) = - \frac{1}{c' - c''} \int_{x=0}^{x=l} D \left(\frac{\partial c}{\partial x} \right) dx \quad (5.22)$$

$$= - \frac{1}{c' - c''} \int_{x=0}^{x=l} F \, dx \quad (5.23)$$

Since F is constant for all points in the diaphragm at time t , equation (5.23) may be integrated to give

$$\bar{D}(t) = lF/(c' - c'') \quad (5.24)$$

Substitution for F in equation (5.9) yields

$$d \ln(c' - c'')/dt = -\frac{A}{l} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \bar{D}(t) = -\beta \bar{D}(t) \quad (5.25)$$

Integration of equation (5.25) between the initial and final conditions shown in fig. 5.2 gives

$$\ln \frac{c_1 - c_2}{c_3 - c_4} = \beta \int_{t=0}^{t=t} \bar{D}(t) dt. \quad (5.26)$$

$\frac{1}{t} \int_{t=0}^{t=t} \bar{D}(t) dt$ is the time average of $\bar{D}(t)$

(which is itself a concentration average). If this time average is denoted by $\bar{D}$, equation (5.26) reduces to

$$\bar{D} = \frac{1}{\beta t} \ln \left(\frac{c_1 - c_2}{c_3 - c_4} \right) \quad (5.27)$$

The value $\bar{D}$ calculated from the initial and final concentrations and the time of diffusion in diaphragm cells is therefore a rather complicated ~~double~~ average known as the diaphragm cell integral coefficient, which it is not easy to convert immediately into the more fundamental differential diffusion coefficient D . Gordon¹¹⁶ has shown, however, that a negligible error is introduced in all ordinary cases if instead of using the exact relation

$$\bar{D} = \frac{1}{t} \int_0^t \bar{D}(t) dt \quad (5.28)$$

we treat the integrand as having a constant value equal to its value when the concentrations c' and c'' are half way between their initial and final values. This constant value is then equal to $\bar{D}$ as given by equation (5.27) and is related to the differential diffusion coefficient by

$$\bar{D} = \frac{1}{c_m' - c_m''} \int_{c_m''}^{c_m'} D \cdot dc \quad (5.29)$$

where $c_m' = \frac{c_1 + c_2}{2}$ and $c_m'' = \frac{c_3 + c_4}{2}$

Methods involving approximations can be employed for computing D at various values of c from a set of $\bar{D}$ values obtained experimentally. For instance, some suitable analytical expression with arbitrary coefficients may be assumed for D as a function of c and the coefficients determined so that equation (5.29) will fit the $\bar{D}$ values¹¹⁷.

This discussion of conditions prevailing when D is a variable is included here because it is applicable to the diffusion of potassium chloride solutions which were used to calibrate diaphragm cells in the present work. In the case of self-diffusion D may safely be regarded as constant for a given concentration, and calculated directly from equation (5.17), viz.,

$$D = \frac{1}{\theta t} \ln \left(\frac{c_1 - c_2}{c_3 - c_4} \right)$$

5.14 Exact theory of the Diaphragm Cell

C. Barnes¹¹⁵ has treated the problem of diffusion in the diaphragm cell without the assumption of the steady state. Diffusion occurs in a membrane extending from $x=0$ to $x=l$ in contact on both sides with well-stirred solutions which extend from $x=0$ to $x=-b$ and $x=l$ to $x=l+a$ (fig.5.1a). The concentrations of the two solutions are c_1 and c_2 , respectively, at $t=0$. The two compartments of the cell and the membrane are assumed to have unit cross-section. The initial distribution of concentration across the membrane is $c(x)$. After a time t the concentrations in the lower and upper solutions are denoted by $c'(t)$ and $c''(t)$, respectively, and the distribution in the membrane by $c(x,t)$.

It is required to solve

$$\partial c / \partial t = D \partial^2 c / \partial x^2 \quad (4.8)$$

with the following conditions

$$c(x,t) \rightarrow c(x) \text{ as } t \rightarrow 0, \quad 0 \leq x \leq l \quad (5.30)$$

$$c(0,t) = c'(t), \quad c(l,t) = c''(t), \quad t < 0 \quad (5.31)$$

$$c'(0) = c_1, \quad c''(0) = c_2 \quad (t=0) \quad (5.32)$$

The rate of change of concentration in both solutions is proportional to the rate of supply of material from the membrane (at $x = 0, l$) so that

$$\frac{\partial c'}{\partial t} = \frac{D}{b} \left(\frac{\partial c}{\partial x} \right)_{x=0}; \quad \frac{\partial c''}{\partial t} = -\frac{D}{c} \left(\frac{\partial c}{\partial x} \right)_{x=l}, \quad t > 0 \quad (5.33)$$

The solution of (4.8) ignoring the boundary conditions is obtained⁹⁸

$$\text{by the Laplace method. Let } c = u + v \quad (5.34)$$

$$\text{where } \frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2} \quad 0 < x < l \quad (5.35)$$

$$u = 0 \text{ when } x = 0 \text{ and } x = l$$

$$u = f(x) \text{ when } t = 0$$

$$\text{and } \frac{\partial v}{\partial t} = D \frac{\partial^2 v}{\partial x^2} \quad 0 < x < l \quad (5.36)$$

$$v = c'(t) \text{ when } x = 0$$

$$v = c''(t) \text{ when } x = l$$

$$v = 0 \text{ when } t = 0$$

It can then be shown⁹⁸ that

$$u = \frac{2}{l} \sum_{n=1}^{\infty} \exp(-Dn^2 \pi^2 t/l^2) \sin \frac{n\pi x}{l} \int_0^l f(x') \sin \frac{n\pi x'}{l} dx' \quad (5.37)$$

$$\text{and } v = \int_0^t c'(\tau) \frac{\partial}{\partial t} F_1(x, t-\tau) + c''(\tau) \frac{\partial}{\partial x} F_2(x, t-\tau) \quad (5.38)$$

$$\text{where } F_1(x, t-\tau) = 1 - \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \exp[-n^2 \pi^2 D(t-\tau)/l^2] \sin \frac{n\pi x}{l} \quad (5.39)$$

$$\text{and } F_2(x, t-\tau) = \frac{x}{l} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \cos n\pi \exp[-n^2 \pi^2 D(t-\tau)/l^2] \sin \frac{n\pi x}{l} \quad (5.40)$$

Introducing the conditions represented in equation (5.33) Barnes (loc.cit.) obtained, assuming $c_2=0$, the following expressions for c' and c''

$$c' = 0.5c_1 \left[1 + \left(1 - \frac{\alpha^2}{180} \right) \exp \left\{ -2\alpha Dt (1 - \alpha/6 + \alpha^2/45) / l^2 + \frac{\alpha^2}{2} \sum_{i=1}^{\infty} \frac{1}{i^4} \exp \left(-\frac{4i^2 \pi^2 Dt}{l^2} \right) \right\} \right] \quad (5.41)$$

$$c'' = 0.5c_1 \left[1 - \left(1 - \frac{\alpha^2}{180} \right) \exp \left\{ -2\alpha Dt (1 - \alpha/6 + \alpha^2/45) / l^2 + \frac{\alpha^2}{2} \sum_{i=1}^{\infty} \frac{1}{i^4} \exp \left(-\frac{4i^2 \pi^2 Dt}{l^2} \right) \right\} \right] \quad (5.42)$$

where $\alpha = c_1 = \alpha_2$; $\alpha_1 = \frac{1}{b}$; $\alpha_2 = \frac{1}{a}$

To compare this analysis with the steady state theory expressions for c' and c'' may be obtained from the latter as follows:-

$$\text{Let } V_1 = V_2 = Ab \text{ (c.f. fig. 5.1a)} \quad (5.43)$$

$$\text{and } \alpha = \frac{1}{b} = \frac{1}{a} \quad (5.42)$$

Equations (5.7) and (5.8) may then be written as

$$dc'/dt = -F\alpha/l = -D(c' - c'')\alpha/l^2 \quad (5.44)$$

$$dc''/dt = +F\alpha/l = +D(c' - c'')\alpha/l^2 \quad (5.45)$$

Now the initial concentration in the lower compartment is c_1 and, since c' , c'' are the concentrations in the two compartments at any instant t we have, from equation (5.20),

$$c'' = c_1 - c' \quad (5.46)$$

$$\text{and } c' = c_1 - c'' \quad (5.47)$$

Substitution for c'' in equation (5.44) gives

$$dc'/dt = -D(2c' - c_1)\alpha/l^2 \quad (5.48)$$

or

$$\frac{dc'}{2c' - c_1} = -\frac{D\alpha}{l^2} dt \quad (5.49)$$

Integration of equation (5.49) gives

$$\ln(2c' - c_1) = -2\alpha Dt/l^2 + k' \quad (5.50)$$

k' , the constant of integration, is evaluated by applying the condition

$c' = c_2$ when $t=0$, so that equation (5.50) becomes

$$\ln \left(\frac{2c' - c_1}{c_1} \right) = -2\alpha Dt/l^2 \quad (5.51)$$

or

$$\exp(-2\alpha Dt/l^2) = (2c' - c_1)/c_1 \quad (5.52)$$

$$\text{so that } c' = 0.5c_1[1 + \exp(-2\alpha Dt/l^2)] \quad (5.53)$$

Similarly, from equation (5.45) it can be shown that

$$c'' = 0.5c_1 [1 - \exp(-2\alpha Dt/l^2)] \quad (5.54)$$

Equations (5.53) and (5.54) should be compared with Barnes' equations (5.41) and (5.42). The change from the exponential factor $\alpha(1-\alpha/6+\alpha^2/45)/l^2$ to α/l^2 is of no experimental significance, since both quantities represent cell constants determined by calibration. The series in Barnes' equations converges rapidly and is multiplied by a factor $\alpha^2/2\pi^4$ which, for the cells used in the present work, is of the order of 10^{-4} , so that it can be neglected. Thus the error in equations (5.53) and (5.54) arises through the neglect of $\alpha^2/180$ in comparison with unity. In our diffusion cells $\alpha = l/a$ was of the order of 10^{-2} . The deviations from Barnes' equations do not become appreciable until α exceeds 0.1. Thus, provided there is a linear concentration ^{gradient} in the membrane at $t=0$ (as assumed by Barnes), the assumption of a steady state is justified. Gordon¹¹⁶ has suggested that a calculation similar to Barnes' but assuming D

to be variable would lead to equations similar to (5.41) and (5.42). Gordon has reported some experimental work which suggests that even in the case of a greatly varying D the membrane could safely be treated as a steady state problem.

5.20 The Mechanism of Transport in the Diaphragm

The accuracy of the diaphragm cell technique depends chiefly upon the transfer of material through the diaphragm being due entirely to diffusion. Bulk streaming of one solution into the other may occur if improper or imperfect membranes are used. Thus some results obtained by Hartley and Runnicles¹¹⁸ indicated that streaming may not be entirely absent with leak-free G-3 diaphragms (15-20 microns porosity), but it is negligible with G-4. To investigate the occurrence of streaming Dawson¹¹⁹ has recommended calibration of the cell first in its normal position (with the diaphragm horizontal) and then inclined at an angle of 30°. Gordon¹¹⁶ has suggested that the best precaution is always to work with a group of cells so that, if any cell has an imperfect diaphragm, this will be apparent at once in its high and erratic cell constant.

Errors may also arise from part of the transfer of solute taking place by surface transport along the walls of the pores, which have an enormous surface area (of the order of one square metre in a typical diaphragm cell). The possibility of surface transport, specially at low concentrations, has been considered by various workers. McBain and Liu¹²⁰ did not find any apparent drift in the diffusion

coefficient ratio for two solutes on passing from a more porous to a less porous diaphragm, or from a glass to a sintered alumina diaphragm. Since in the presence of surface transport the ratio would depend on the nature and magnitude of the pores, they concluded that surface transport was negligible. Stokes¹²¹ has concluded that surface transport does occur and has recommended that, at least in the case of electrolytes, the diaphragm cell technique must be restricted to solutions of concentration greater than 0.05N if a high accuracy is desired.

The theory of the diaphragm cell discussed in the last section assumes that both solutions are of uniform composition throughout. Most users of diaphragm cells in the past assumed that mounting of the cell in a horizontal plane, with the denser solution upper most, resulted in the circulation of the liquid in each compartment owing to the density changes caused by diffusion. While this may be true for the greater bulk of liquid in each compartment, there is the possibility that stagnant layers may exist for short distances on either side of the diaphragm surface, through which diffusion will proceed as well as in the pores themselves. Gordon¹¹⁶ has pointed out that, although such layers have been proved to behave reproducibly, it is by no means certain that they are of equal importance at all concentrations or for different solutions. Mouquin and Cathcart¹²² accomplished stirring in their diaphragm cell by means of glass spheres which move through the liquid when the cell is rotated end-

over-end by a belt and pulley mechanism. Hartley and Runnicles¹¹⁸ performed the stirring in a similar manner by rotating the cell in an inclined position about the longitudinal axis. Stokes¹²³ contends that while this method ensures adequate mixing within each compartment, it does not entirely eliminate the possibility of stagnant layers being present on the diaphragm surface. Stokes¹²³ introduced a system of stirring which makes it possible to keep the diaphragm horizontal and to have the denser solution on the lower side, thus using gravity as a stabilising rather than a disturbing force. Stokes' method of stirring has been adapted for use in the present work and will be described in Section 5.30.

5.30 Apparatus

5.31 The Thermostat

As accurate temperature control is of fundamental importance in measurements of diffusion coefficients, considerable attention was given to accurate thermostating of the apparatus. The results of Graupner and Winter⁷⁹ on the self-diffusion coefficients of benzene and some other liquids and of Caldwell and Babb¹²⁴ on mutual diffusion coefficients in the benzene-carbon tetrachloride system at various temperatures show that the change in the value of D per degree rise in temperature is in the region of $0.025 \times 10^{-5} \text{ cm}^2/\text{sec}$. These observations indicate that for sufficient accuracy the temperature of the thermostat must be kept constant to within 0.01°C or better for the duration of the experiment (20 to 36 hours).

A cylindrical glass tank, 12" in diameter and 18" long, was used as the thermostat bath (fig. 5.3). It was lagged on the outside by a cylinder of soft asbestos board, a small 3" x 6" section of which was cut out at the front to permit inspection of the apparatus in the thermostat. The glass tank was placed on 3" thick insulating bricks so as to be in the centre of an 18" x 18" x 21" box made of plywood and supported by 'Handy' angle bars. The wooden box rested on a wooden platform supported on a 'Handy' angle frame work. A 6" x 3" window was cut through the plywood box in front of the opening in the asbestos cylinder. A lamp was placed inside the box, in front of another opening cut out in the asbestos cylinder, for illuminating the bath when necessary. A 3" x 3" x 6" piece of expanded polystyrene (Spandoplast) was used to block the window when not in use. The space between the plywood and the soft asbestos sheet was insulated with vermiculite.

The water inside the glass tank was stirred by means of an immersion pump, the shaft of which was connected through a 2 ft. long flexible drive to a $1/30$ h.p. motor. The flexible drive was incorporated in the stirring pump in order to reduce vibration in the apparatus. The motor was fixed to the frame through rubber pads for the same reason. The rate of stirring was controlled by means of a rheostat; a rate of about 800 r.p.m. was found to be sufficient for adequate circulation of the water and did not produce any eddies or whirls on the surface. A thermometer graduated in tenths of a degree was

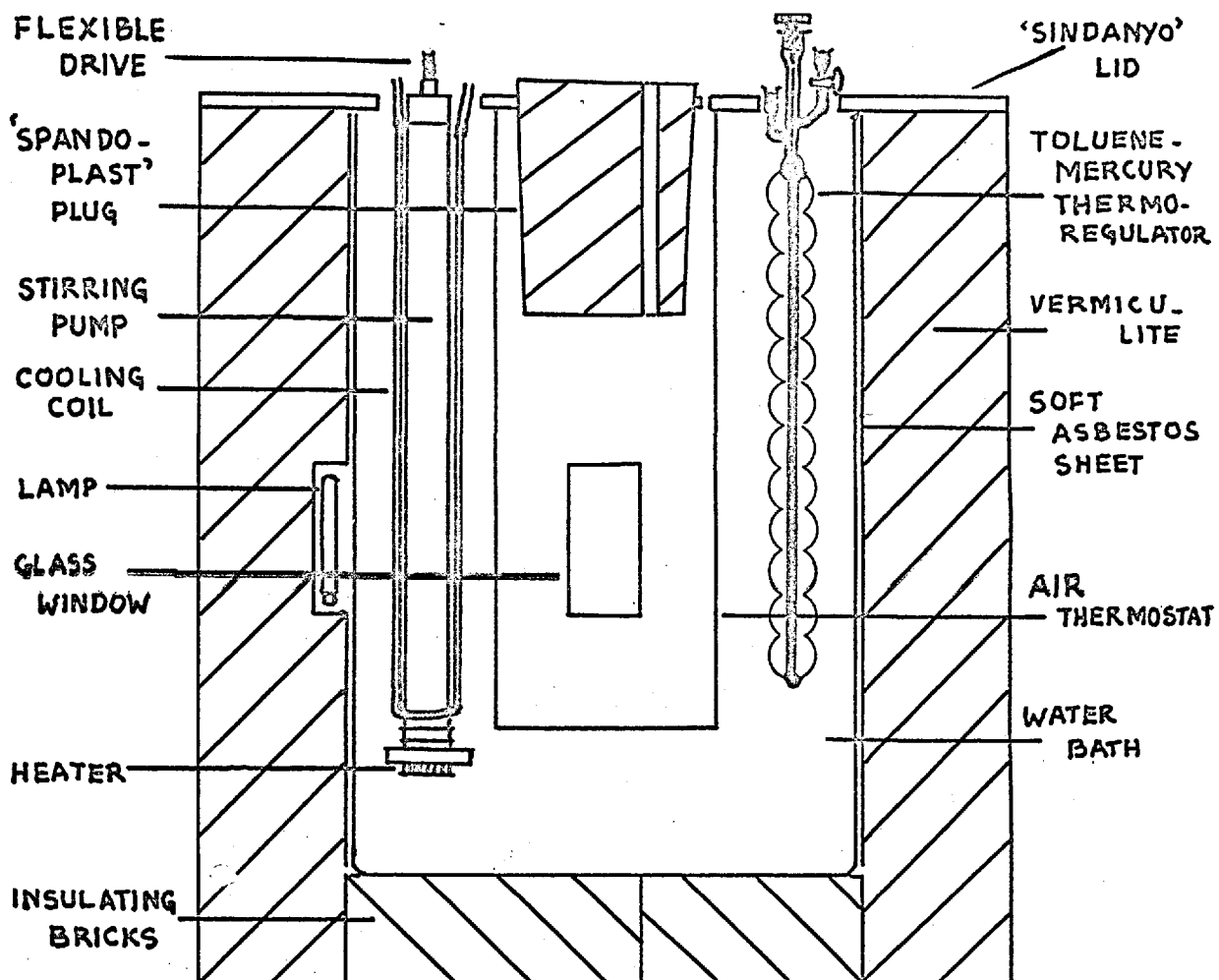


FIG. 5-3

THE THERMOSTAT

inserted in the bath to give a rough indication of the temperature inside the thermostat.

The water in the thermostat was heated by means of a small 20 watt insulated heating coil attached to the base of the stirring pump. The heating coil was attached to the mains through a Variac so that its power could be increased if necessary. Cooling of the water, which was necessary to counteract the gradual build-up of heat due to thermal inertia, especially during the summer months, was effected by means of a thin U-shaped copper tube running along the length of the stirring pump. Tap water was passed through the copper tube at a regulated rate, and a constant head device was used to maintain a uniform pressure head of water.

The temperature was controlled by means of a toluene mercury thermoregulator. The length of the regulator was made as long as possible (approximately 15"); the portion containing toluene consisted of bulbs, so that a large surface area of contact between the controller and the temperature controlled bath was provided. Contact with the mercury column in the thermoregulator was made and broken by means of a needle fitted to a proportionating head operating through a 'Sunvic' electronic relay type EA3T.

5.32 The Air-Thermostat

The diffusion measurements were to be made in two-compartment glass cells closed by stopcocks. An air-thermostat was immersed in the water bath to hold the diffusion cell. This prevented any possible leakage of water into the cells.

The air-thermostat consisted of a cylindrical copper vessel (fig. 5.4), 5" in diameter and 15" in length, with two glass windows, 3" x 6" and 2" x 2" in size to facilitate inspection of the cells from outside. The smaller window was used for illumination. The air-thermostat was suspended inside the water bath from an 18" x 18" x $\frac{1}{2}$ " Sindanyo lid resting on the steel framework of the plywood box, and stoppered with a 6" long x 5" diameter 'Spandoplast' plug, through which a hole was made for the insertion of the cell holder.

The base of the air-thermostat was fitted with a permanent U-shaped steel magnet, 3" in length and $2\frac{1}{4}$ " in diameter. A $\frac{5}{16}$ " diameter shaft running down the copper vessel was used to rotate the magnet by means of pulleys and ball-bearings attached to the shaft and to the axis of the magnet. A geared motor (h.p. approximately $\frac{1}{20}$, torque 10 lbs) was used to rotate the shaft. The speed of rotation could be varied by using pulleys of different diameter and by means of a rheostat.

In preliminary experiments with cells having a diaphragm porosity of 5-15 microns the precision on successive cell constant determinations was of the order of 4%. This large variation was attributed in part to vibrations conveyed to the cells from the immersion pump- and geared-motors, which were mounted on the same framework as the thermostats. The motors were mounted on a separate framework rigidly fixed to the wall in the laboratory to overcome this difficulty.

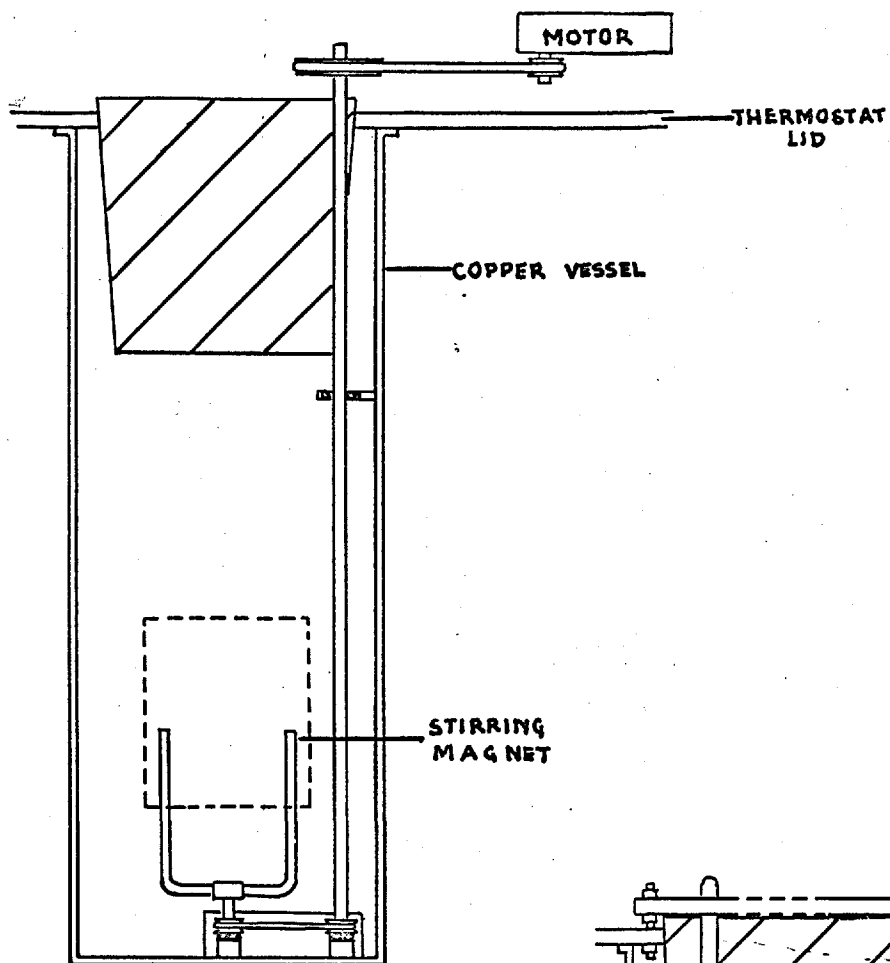


FIG. 5-4. THE AIR THERMOSTAT

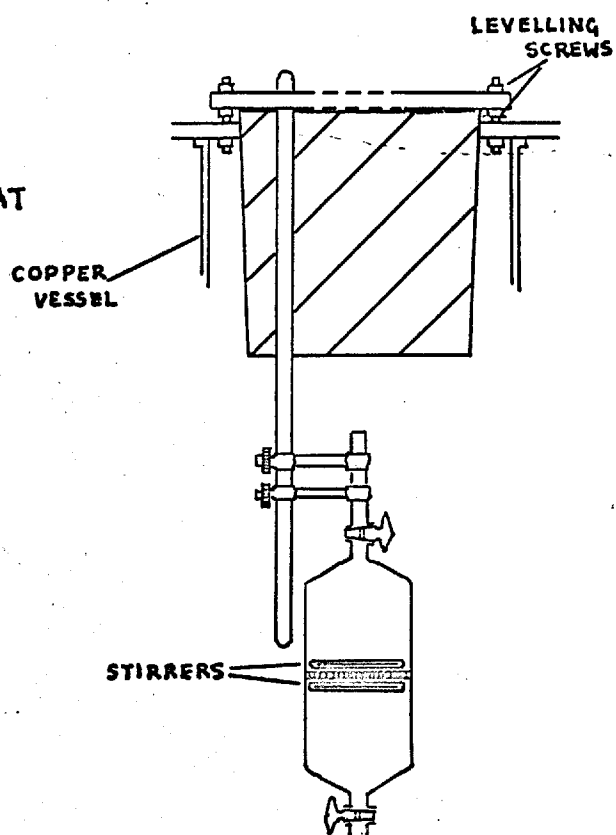


FIG. 5-6. THE CELL AND CELL HOLDER

5.33 The Cells

Two double-compartment cells were used in the self-diffusion measurements. This type of cell constitutes a closed system and therefore has certain advantages over the single-compartment cell in that the possibility of mass flow is minimized, the volumes of both compartments are fixed, and evaporation and contact of the liquids with air is avoided.

The effective diameter of the pores in the diaphragm must be such that gross streaming through the diaphragm is avoided but, at the same time, the pores must be large in comparison with molecular dimensions so that the diffusion will take place under conditions comparable with those obtained in free diffusion. The size most frequently used has been G-4 (pore diameter 2-5 microns). Diaphragms of a coarser porosity (5-15 microns) supplied by Messrs. Baird and Tatlock were used in preliminary experiments for the determination of the cell constant. The values obtained in successive measurements were erratic.

G-4 diaphragms, 3cm in diameter and fused to the middle of 20cm long glass tubes, were obtained from Messrs. Jena Glass Works (London Agents: C.Z. Scientific Instruments, Ltd.) and used to make diffusion cells, one of which is shown in fig. 5.5. The two compartments had a capacity of about 20ml each and were closed by small high vacuum stopcocks greased with the minimum necessary amount of Apiezon L grease for calibration with KCl solutions diffusing into water. The volumes

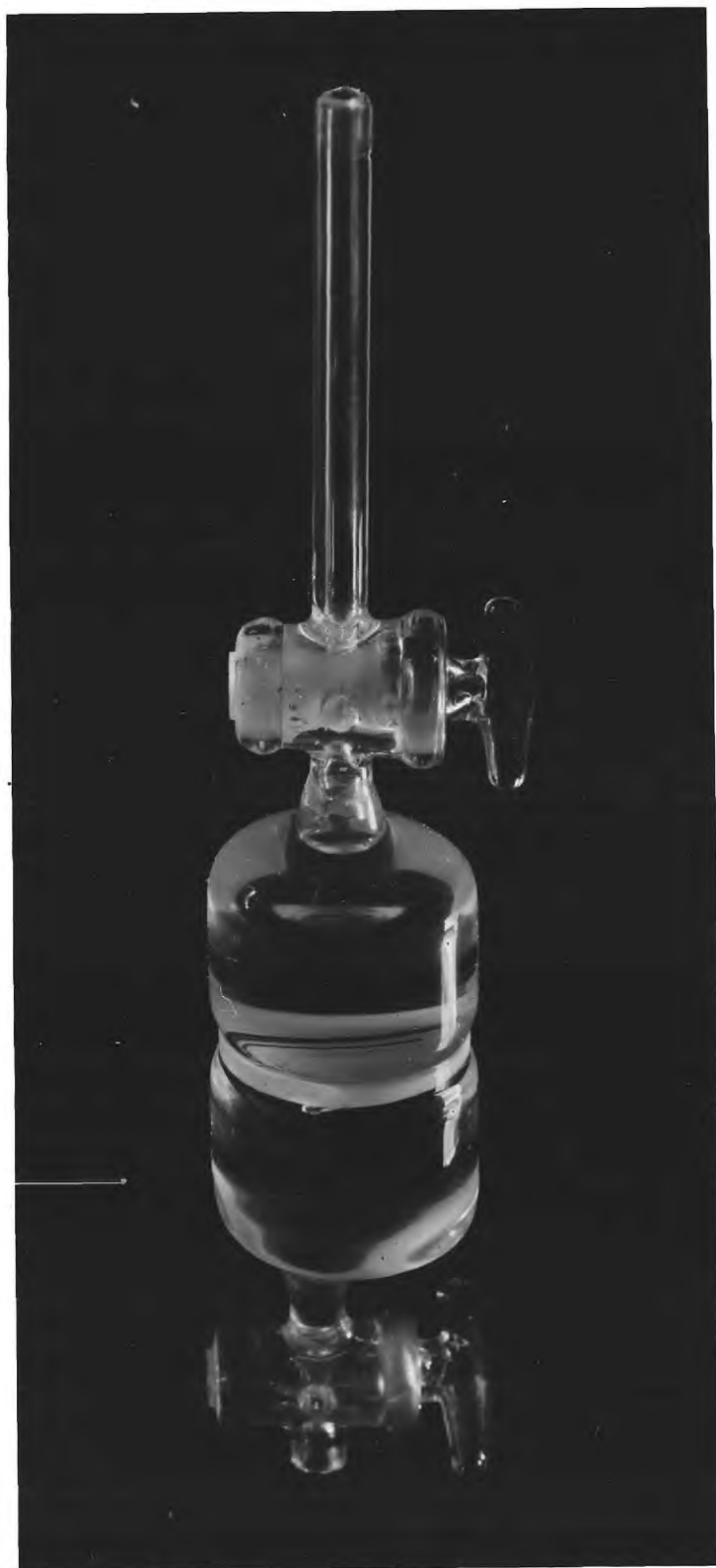


FIG. 5.5. GAS CYLINDER.

of the two compartments could be thus fixed by stopcocks because no volume changes on mixing were envisaged in the case of self-diffusion. The stopcocks, obtained from Springham and Co., Ltd., were of size MSTV₄ and had an extra wide bore, 2mm in diameter.

5.3₄ The Stirrers

Stirring of the diffusing solutions is necessary in order to maintain uniform concentration in the two compartments of the cells and to eliminate any stagnant layers that might form on the diaphragm surface. A stirrer of glass tubing, about 2mm in diameter and of length slightly less than the diameter of the diaphragm, was used in each compartment of the cell. Inside each stirrer was sealed a length of soft iron wire. The thicknesses of the wire and the walls of the glass tube were adjusted so that the stirrer in the upper compartment sank while the one in the lower floated. As mixtures of varying density were to be used in the experiments the density of the lower stirrer was made such that it would float on the lightest liquid (cyclohexane) while the density of the upper stirrer was made such that it would sink in the heaviest (water).

Stirrers with the soft iron wire enclosed in thin 'teflon' (polytetrafluorethylene) tubing were also tried, since glass stirrers have been known to cause slow wear in the diaphragm. These stirrers were sealed by etching the ends of the teflon tube in a two percent solution of sodium in liquid ammonia, and then closing the ends with Araldite. It was found, however, that these stirrers were not suitable,

as a leak invariably developed after a few months of use.

5.35 The Cell Holder

The cell was held at the centre of the stirring magnet inside the copper air-thermostat by means of rigid clamps attached to the stem of a viscometer holder (fig. 5.6). The upper end of the viscometer holder contained a ring joined at right angles to the stem. A sindanyo ring was made to fit the viscometer ring and fixed to the lid of the thermostat by means of three adjustable screws. The levelling screws were adjusted using a spirit level so that the cell was held with the sintered glass diaphragm in a horizontal position. The level of the cell itself was adjusted by altering the positions of the clamps so that the ends of the stirrers were near the poles of the stirring magnet. In this position the stirrers were rotated by the magnet, both sides of the diaphragm being wiped twice per revolution of the magnet.

5.40 Details of Operation

5.41 Determination of Cell Volume

The diaphragm was at first tested for leaks by filling the upper compartment of the cell with potassium permanganate solution and applying a small suction through the lower. The cell was cleaned by filling it with nitrating acid cleaning mixture and allowing to stand for some time. It was then thoroughly washed with copious amounts of distilled water, sucking the water through the sinter in both directions. The cell was dried in an electric oven and then cooled

in a vacuum dessicator. This procedure of cleaning and drying the cell was repeated before each diffusion measurement.

The taps were greased with a minimum amount of stopcock grease and the cell weighed. The upper compartment of the cell was carefully filled with clean dry mercury and the cell reweighed. The volume of the upper compartment was obtained from the weight of the mercury contained in it. The volume of the lower compartment was determined similarly. The volumes of the upper and lower stirrers were determined separately by means of an R.D. Bottle. Subtraction of the volumes of the stirrers from the volumes of the respective compartments gave V_1 and V_2 , the volumes of the lower and upper compartments respectively.

The volume (V_3) of the pores in the diaphragm was determined by degassing the diaphragm (according to the method described in the next section) and weighing the cell with distilled water filled in the diaphragm pores and in the two compartments of the cell upto the level of the stopcocks. The results were:-

	Cell I (No. 554)	Cell II (No. 52)
Volume of upper compartment A	19.1934ml	19.0553ml
Volume of upper stirrer	<u>0.0933ml</u>	<u>0.1153ml</u>
V_2 , the volume of liquid in the upper compartment	<u>19.1001ml</u>	<u>18.9400ml</u>
Volume of lower compartment B	20.4810ml	18.3610ml
Volume of lower stirrer	<u>0.1052ml</u>	<u>0.1238ml</u>
V_1 , the volume of liquid in the lower compartment	20.3758ml	18.2372ml
V_3 , the volume of the pores in the diaphragm	0.5098ml	0.4965ml

5.42 Temperature Control

The height of the mercury column in the large toluene-mercury thermoregulator used for controlling the thermostat temperature fluctuated considerably with minor variations in temperature, providing a good temperature control. The temperature inside the air-thermostat was measured by means of a platinum resistance thermometer used in conjunction with a Smith's bridge which could be used to one hundredth of a degree. Over a period of 24 hours the maximum variation was found to be 0.008° at a temperature of about 25°C .

To set the thermostat at the true 25°C temperature, the resistance thermometer was calibrated using another thermometer of known ice, steam and sulphur points. A graph of resistance vs. temperature gave a straight line (fig. 5.7), and the value of the resistance at 25°C read off from this graph was found to be 28.2688 ohms. At the beginning of each diffusion run the thermostat was set at 25°C using the calibrated resistance thermometer.

5.43 Calibration of the Cells

The cells were calibrated with approximately 0.2N potassium chloride solutions diffusing into water, using values of D given by Stokes¹²¹.

Analar potassium chloride was heated in an oven at $400-450^{\circ}\text{C}$ for about two hours and cooled in a dessicator. An approximately 0.2N solution was made up in a graduated flask. Silver nitrate solution, approximately 0.05N, was made up in another graduated flask

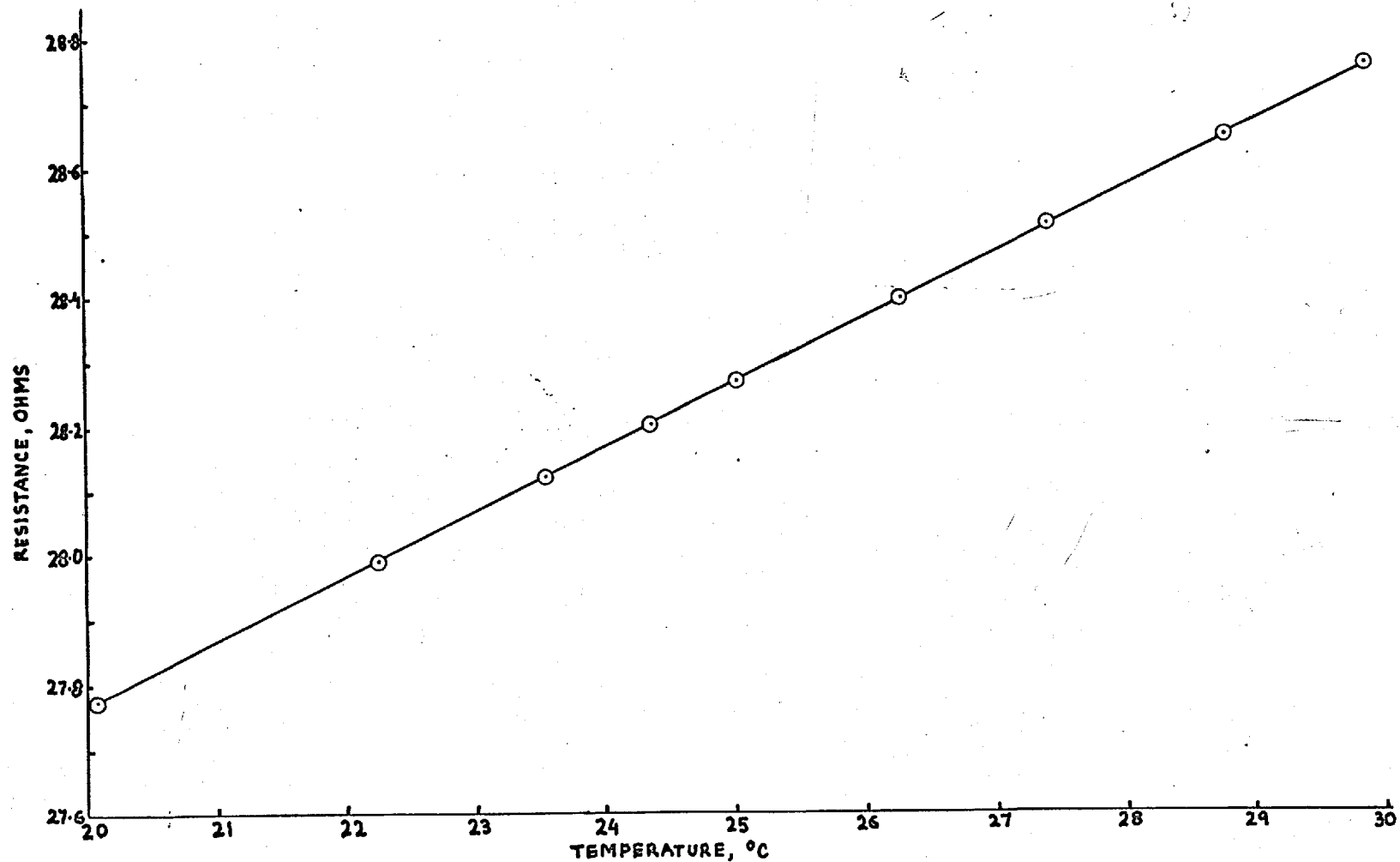


FIG. 5-7. PLATINUM THERMOMETER RESISTANCE VS. TEMPERATURE

and standardised according to the method described by Kolthoff and Stenger¹²⁵ using potassium chromate as indicator.

The cell was cleaned and dried as described in the preceding section and the stopcocks were greased with the minimal requirement of Apeizon 'L' grease. The diaphragm was degassed by sucking a large quantity of distilled water, freed from dissolved gas by boiling, through it. Bubbles of air were dislodged by sudden increase in suction, which also served as a test for complete removal of air. After the diaphragm had been thus degassed, the cell was completely filled with distilled water and the stopcocks closed. For degassing and filling, the cell was held upside down and the suction applied through compartment B. Some gas was usually left in compartment A after the operation. It was allowed to escape by bringing the cell back to the upright position. Excess water in the stem above the stopcock in each compartment was removed by means of a syringe fitted with a long needle which could go through the narrow bore of the stopcock. The presence of a very small quantity of liquid in the bores of the stopcocks could not be avoided and must have contributed towards the error in the precision of the diffusion measurements.

The cell was thermostatted with the upper stopcock open for about ten minutes. This allowed the cell to come to the thermostat temperature (25°C). Expansion of the liquid took place and the excess liquid was removed from the bore of the upper stopcock by means of a syringe, as before. The water in the lower compartment was replaced

by degassed potassium chloride solution, which had been previously cooled to the thermostat temperature. The strength of the potassium chloride solution was approximately 0.1-0.2N.

In order to use the solution of the diffusion equation for the steady state, a linear distribution of concentration in the disc must be first ensured. This was achieved by setting the cell in the air thermostat for a preliminary diffusion of about three to four hours duration. (The time required for preliminary diffusion was calculated from Gordon's rough empirical rule¹¹⁶, which is to set $Dt/l^2 = 1.2$ where D is the diffusion coefficient, t the time, and l the effective pore length of the diaphragm.) The magnet was rotated at a rate of 50 r.p.m. in order to stir the solutions in both compartments. After the preliminary diffusion the cell was removed from the thermostat and the solution in the upper compartment was replaced, after several rinses, with gas-free water at the thermostat temperature. It was found by experiment that six rinses were sufficient to reduce the concentration of potassium chloride in the upper compartment effectively to zero. In withdrawing liquid from the compartment care was taken not to allow the syringe needle to rest on the diaphragm as this might have disturbed the liquid in it. The run was taken as beginning when the final replacement occurred. The cell was then quickly set up again in the thermostat and the stirring restarted. After a run of about twenty four hours (found by experiment to be the time in which the concentration in the lower compartment was reduced by approximately 0.4

of its initial value) the cell was removed and the upper compartment drained by means of a syringe into a sample bottle.

The run was taken to end at this point. The time at the beginning and the end of the diffusion run was noted correct to the nearest minute. After withdrawing the sample from the upper compartment the cell was held with compartment B uppermost and the stopcock in compartment A was opened. This stopped any further diffusion from the diaphragm into B during the removal of a sample from this compartment. The whole operation to this point could be completed within two minutes of the removal of the cell from the thermostat, so that no significant error was introduced by the slightly indefinite nature of the exact moment of beginning or ending of a run of twenty four hours' duration. Two 5ml-samples from each compartment were titrated with approximately 0.05N silver nitrate solution using the same technique as used in the standardisation of this solution. Concurrent titrations agreed to within 0.4 percent so that the samples were analysed with an accuracy of about 0.2 percent.

The formulae used for calculating the cell constant- β were:

For Cell I (No.554)

$$\begin{aligned}\beta &= \frac{1}{\bar{D}t} \ln \frac{c_1 - c_2}{c_3 - c_4} = \frac{1}{\bar{D}t} \ln \frac{c_3 + c_4 \times \left(\frac{19.1001 + 0.2549}{20.3758 + 0.2549} \right)}{c_3 - c_4} \\ &= \frac{1}{\bar{D}t} \ln \frac{c_3 + 0.93816 c_4}{c_3 - c_4} \quad (5.55)\end{aligned}$$

For Cell II (No.52)

$$\begin{aligned}\beta &= \frac{1}{\bar{D}t} \ln \frac{c_1 - c_2}{c_3 - c_4} = \frac{1}{\bar{D}t} \ln \frac{c_3 + c_4 \times \left(\frac{18.9400 + 0.2485}{18.2372 + 0.2485} \right)}{c_3 - c_4} \\ &= \frac{1}{\bar{D}t} \ln \frac{c_3 + 1.03802 c_4}{c_3 - c_4} \quad (5.56)\end{aligned}$$

c_3 and c_4 were the normalities of the lower and upper solutions respectively at the end of the diffusion period of time t seconds. The standard value of $\bar{D}$, the diaphragm cell integral diffusion coefficient, was obtained according to the procedure described in the next section.

5.431 Choice of Standard for Calibration

In the past there has been some disagreement over the choice of a standard for the calibration of diaphragm cells, and the problem has been discussed by several authors^{116, 126}. The question has been finally settled by Stokes' analysis^{121, 127} of Gordon's equation (5.29) for $\bar{D}$ and of the experimental results obtained by Gosting¹²⁸ and by Harned and Nuttal¹²⁹.

Gordon¹¹⁶ has shown that $\bar{D}$ is related to the true or differential diffusion coefficient D by the equation

$$\bar{D} = \frac{1}{\frac{cm'}{cm''} - \frac{cm''}{cm'}} \int_{cm''}^{cm'} D dc \quad (5.29)$$

where cm' is the mean of the initial and final concentrations on the solution side of the diaphragm, and cm'' is the mean concentration on the other side. Since the latter side contains pure water initially, cm'' is half of the final concentration on this side.

Stokes has defined a new integral coefficient $\bar{D}_{(c)}^o$ as that which would be found in a run of 'vanishingly short duration' between concentration c and pure water. According to equation (5.29) $\bar{D}_{(c)}^o$ is related to D by

$$\bar{D}_{(c)}^o = \frac{1}{c} \int_0^c D \, dc \quad (5.57)$$

Stokes¹²⁷ has shown that, for diaphragm cell measurements which start with KCl solution on one side and pure water on the other side of the diaphragm

$$\bar{D}_{(cm')}^o = \bar{D} - \frac{cm''}{cm'} [\bar{D} - \bar{D}_{(cm'')}^o] \quad (5.58)$$

or

$$\bar{D} = \frac{[\bar{D}_{(cm')}^o - \frac{cm''}{cm'} \bar{D}_{(cm'')}^o]}{1 - cm''/cm'} \quad (5.59)$$

Gosting¹²⁸ has made absolute measurements of the differential diffusion coefficient of KCl solutions in water at 25°C from 0.1 N to 3.9N by the Guoy interference technique and Harned and Nuttal¹²⁹ have obtained values of D at 25°C for KCl solutions over the range 0.00125N to 0.5N by a conductimetric method. There is extraordinarily good agreement between the results obtained by the two different methods in the over-

lapping part of the range, and the combined results can be used for the calibration of diaphragm cells. The results have been used by Stokes¹²³ to calculate $\bar{D}_{(c)}^0$ for KCl solutions by graphical and tabular integration according to the formula

$$\bar{D}_{(c)}^0 = \frac{1}{c} \int_0^c D dc \quad (5.57)$$

In the present work Stokes' results for $\bar{D}_{(c)}^0$ were plotted against c (fig. 5.8) and values of $\bar{D}_{(c_{II})}^0$ and $\bar{D}_{(c_{II})}^0$ were read off for each run from the graph. The value of $\bar{D}$ for the run was then calculated from equation (6.5), and substituted in equation (6.1) or (6.2) to obtain the cell constant. The results obtained were

	Cell Constant	
	Cell I (554)	Cell II (52)
Run I	0.5084	0.5838
Run II	0.5000	0.5799
Run III	0.5034	0.5923
Run IV	-	0.5869
Average	<u>0.5032</u>	<u>0.5857</u>

The average deviation from the mean cell constant was thus 0.6 per cent for Cell I and 0.7 per cent for Cell II.

The cell constant increases slowly owing to the reduction in the length of the diaphragm pores caused by wear. After every eight or nine runs the cells were recalibrated with carbon-14 labelled benzene. The value obtained in the present work for the self-diffusion coefficient of benzene was substituted

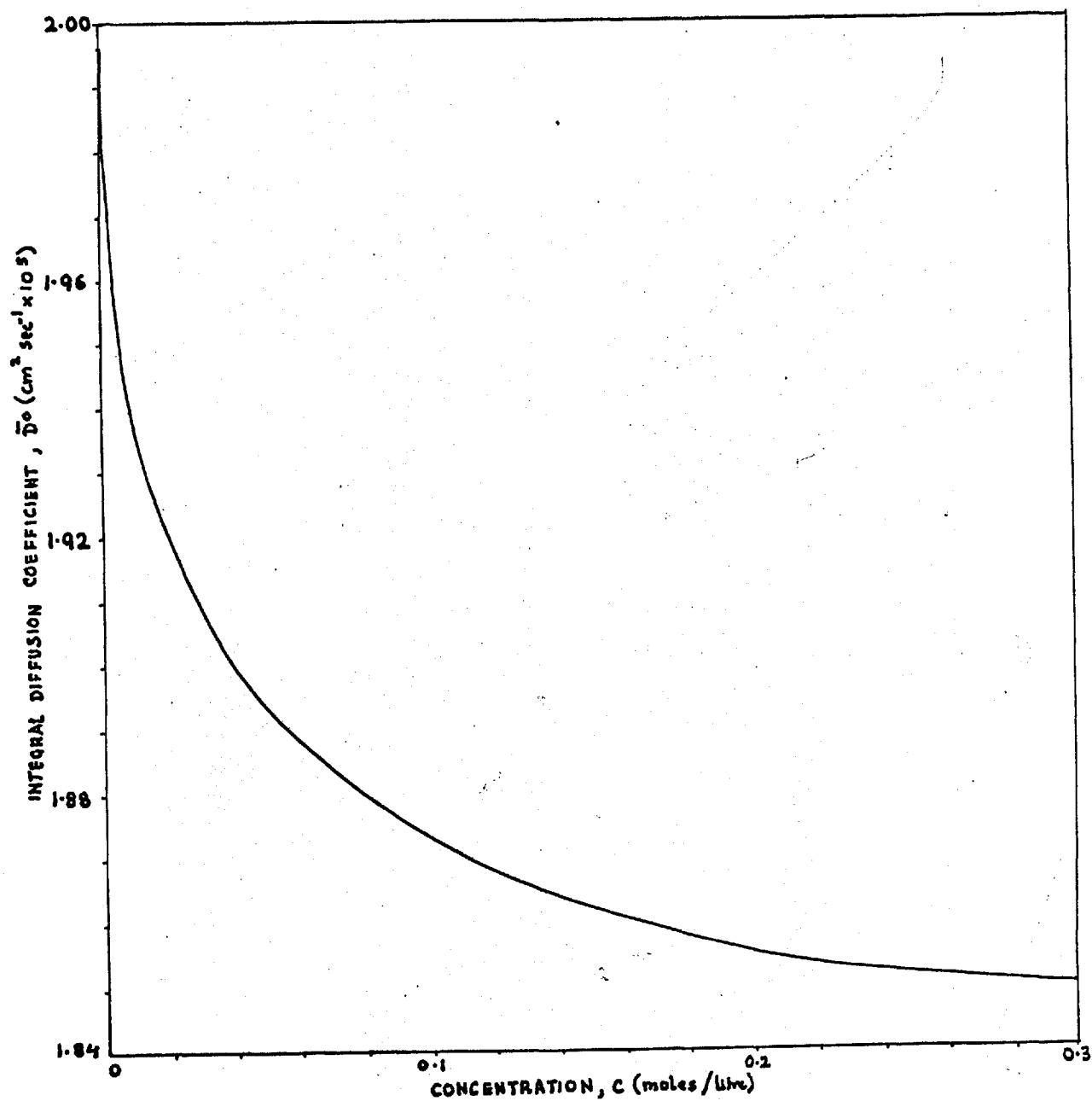


FIG. 5-8. INTEGRAL DIFFUSION COEFFICIENTS OF KCL SOLUTIONS AT 25°C. 121

in the diaphragm cell equation (5.17) to obtain the new cell constant. The increase in the value of β was found to be small, about 0.2 per cent per hundred hours of use. A graph of cell life vs. cell constant was used to interpolate the value of β for a particular run. Since few of the runs exceeded twenty four hours' duration, no correction for the change of cell constant during any individual run was necessary.

5.44 Effect of Stirring Rate

The cell constant is known to increase with stirring rates upto a threshold value above which it remains constant over a wide range. Stokes¹²³ observed a plateau in the range 30-80 r.p.m., but Lewis¹³⁰ found that the cell constant goes on increasing even upto 100 r.p.m. The effect of stirring rate on the cell constant was therefore studied in the present work.

The cell constant was determined at various stirring rates from 0 to 125 r.p.m., and a graph of stirring rate vs. cell constant relative to the cell constant at 50 r.p.m. was plotted (fig. 5.9). A sharp plateau was observed beyond a stirring rate of about 15 r.p.m. Stirring rates even as high as 125 r.p.m. did not seem to have any adverse effects such as 'forcing' the liquid through the diaphragm. A rate of 50 r.p.m., which lies within the plateau and, at the same time, is not so fast as to cause excessive wear in the diaphragm, was chosen for the present diffusion measurements.

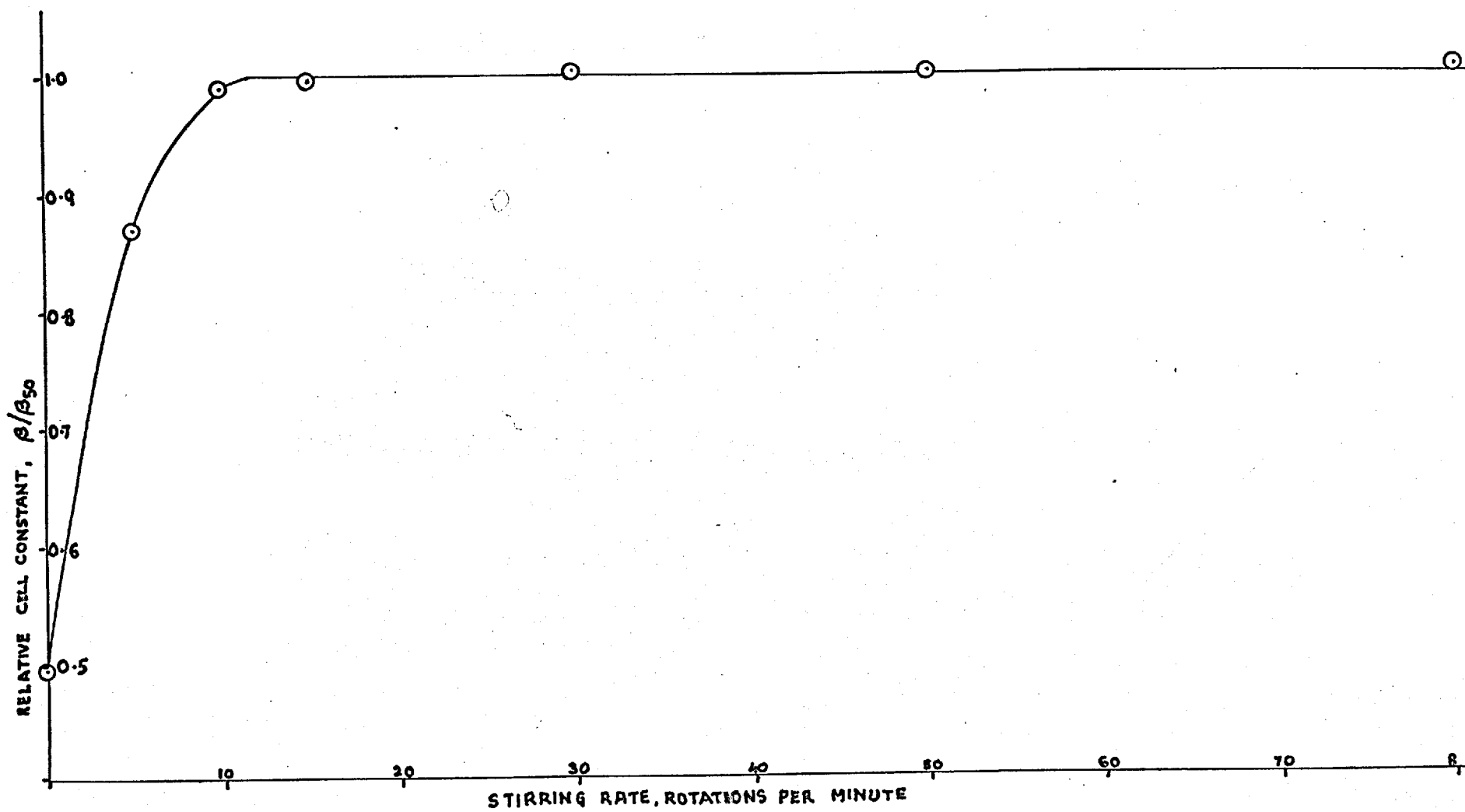


FIG. 5-9. VARIATION OF CELL CONSTANT WITH RATE OF STIRRING

5.45 Technique of filling the Cells

A large quantity of liquid (approximately $1\frac{1}{2}$ litres) is required in order to degas the diaphragm by the method used for the potassium chloride solutions. If this method were to be applied to organic liquids it would lead to the wastage of large quantities of solvents. Another method of degassing the diaphragm was therefore sought.

The cell was cleaned and dried and the stopcocks greased with a special starch-glycerol grease which, unlike Apiezon or silicone greases, is impervious to the organic solvents used in the present measurements. The grease is suitable for using with a vacuum of the order of 10^{-3} to 10^{-4} mm Hg pressure and was prepared¹³¹ by heating dried and evacuated starch with anhydrous glycerol (8.25g starch, 25g glycerol) to 140° until the mixture became stiff. The heating was carried out in an evacuated test tube in which the final product was stored. The grease was applied quickly and the tube re-evacuated as it readily absorbs moisture. A protective coating of Apiezon grease was applied on the outside of the stopcock key in order to prevent ingress of moisture.

The upper compartment of the cell was connected to a vacuum line through a B7 quickfit joint, while the lower compartment was connected to a piece of glass tubing through teflon tubing which was sealed to the glass with Araldite.

Thin rubber tubing was used to secure the teflon tube to the end of the lower compartment with copper wire tightened round the rubber tubing to make the system as air-tight as possible.

Liquid was filled upto just above the level of the lower stopcock which was then closed and the cell evacuated with the glass tube still dipping in the liquid. Evacuation by means of a mercury diffusion pump was carried out until a vacuum of about 10^{-3} mm Hg pressure had been obtained. Pumping was continued for a further 20 to 30 minutes. The upper stopcock was then closed and the cell filled with the liquid by slowly opening the lower stopcock. Attempts at degassing and filling the cell by this method were not very successful, however, as a few bubbles of air were always found to remain in the cell.

An extension was made to the high vacuum line as shown in fig. 5.10. A wide glass container was connected to the vacuum line by means of a B55 'Quickfit' cone and socket joint. The size of the socket was large enough for the cell with the stopcocks closed to be raised or lowered through it. The cell could be suspended into the wide glass container by means of nylon thread tied to and wound round a glass rod sealed to a B14 socket. The B14 socket could be rotated round a B14 cone, thus raising or lowering the cell. The system was connected by a side arm carrying a small tap, through which dried air could be admitted, to a calcium chloride tube. The upper part of the drying tube

had a plug of glass wool to entrap any dust particles. The cell was cleaned and dried and the stirrers were placed in their respective compartments. The taps were greased with a minimum amount of the starch-glycerol grease and the cell was then suspended inside the B55 cone with compartment B upper most, and the tap in compartment B closed and that in compartment A open, by means of the nylon thread. 50ml of the liquid were taken in the wide glass container which was connected to the vacuum line through the B55 socket. The liquid was frozen, using solid CO_2 /acetone for cyclohexane and benzene and liquid nitrogen for toluene. The apparatus was evacuated by means of the mercury diffusion pump until a vacuum better than 10^{-3} mm Hg had been obtained. Tap S was then closed and the solid allowed to melt. The process of melting and freezing followed by evacuation was repeated a few times to remove all the dissolved gas from the system. The frozen liquid was finally allowed to melt, and warm to near the room temperature, while still under vacuum. The cell was slowly lowered into the liquid till its stem nearly touched the base of the wide glass container. Dried air was slowly admitted and it forced the liquid into the cell. The cell was thus completely filled with the degassed liquid, it being quite certain at the same time that the diaphragm was air-free.

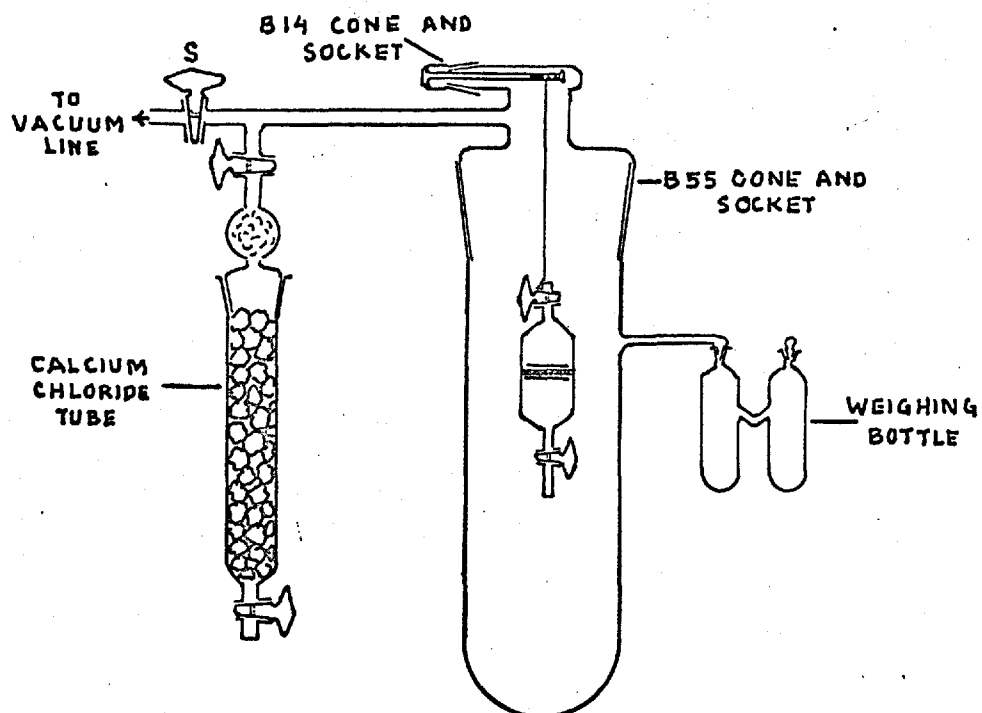


FIG. 5-10. APPARATUS FOR FILLING CELLS IN VACUO

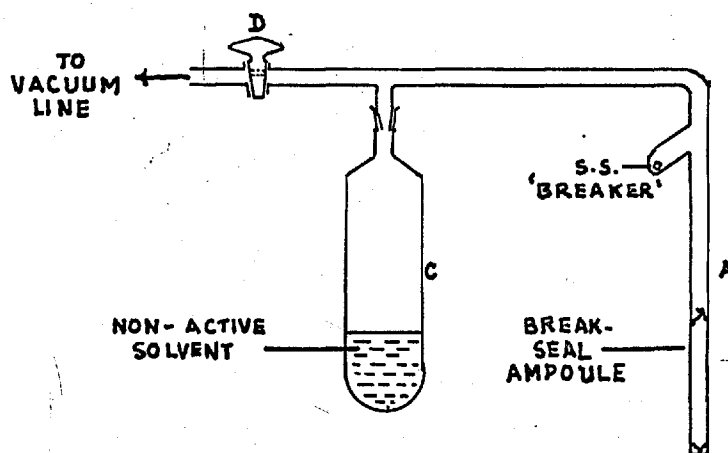


FIG. 5-11. APPARATUS FOR DILUTING C-14 LABELLED MATERIALS

5.46 Materials5.461 Purification of Solvents¹³²

(a) Benzene: 'Analar' benzene (Hopkin and Williams) was shaken with concentrated sulphuric acid until free from thiophene (as indicated by the isatin test). The benzene was further washed with water, dilute sodium hydroxide and several times with water until free from alkali. It was dried over phosphorous pentoxide for a few days and distilled over phosphorous pentoxide through a 5 ft. long x 1 in. diameter fractionating column packed with glass helices. The middle fraction of the distillate was taken and stored in a round-bottom flask closed by a calcium chloride drying tube.

B.p. of purified sample: $80.1 \pm (0.2^\circ)$ at 765mm Hg pressure

Refractive index : $n_{20}^D = 1.5011$

(Literature data for benzene) : $n_{20}^D = 1.5009 - 1.5011$ (Timmarmans¹³³)
 : $n_{20}^D = 1.50112$ (American Petroleum Inst.¹³⁴)

(b) Cyclohexane: 'Spectrosol' cyclohexane (Hopkin and Williams) was washed several times in the cold with a mixture of concentrated nitric acid and sulphuric acid to nitrate any benzene that may have been present. After repeated washings with distilled water it was dried and fractionally distilled over sodium using a 5 ft. long x 1 in. diameter fractionating column packed with glass helices. Again the middle fraction of the distillate was taken and stored over fused calcium chloride.

113.

B.p. of purified sample: $80.7 \pm 0.2^{\circ}\text{C}$ at 765mm Hg pressure

Refractive index : $n_{20}^D = 1.4262$

(Literature data for cyclohexane) : $n_{20}^D = 1.4263$ (Timmermans)

: $n_{20}^D = 1.42623$ (American Petroleum Inst.)

(c) Toluene: 'Analar' toluene (Hopkin and Williams) was washed twice with ten per cent of its volume of concentrated sulphuric acid, then with dilute sodium hydroxide solution and finally with water until free from alkali. It was dried and distilled over sodium using a 5 ft. long fractionating column as before. The middle fraction of the distillate was used for the diffusion measurements.

B.p. of purified sample: $110.6 \pm 0.2^{\circ}\text{C}$ at 765mm pressure

Refractive index : $n_{20}^D = 1.4967$

(Literature data for toluene) : $n_{20}^D = 1.4966-1.49693$ (Timmermans)

: $n_{20}^D = 1.49693$ (American Petroleum Inst.)

After every two or three diffusion measurements, the remaining stock of the solvent was distilled afresh in each case.

5.462 Dilution of Labelled Compounds

(a) Benzene: 0.1 Millicurie of Carbon-14(U) labelled benzene, prepared by the catalytic trimerisation of acetylene- $\text{C}^{14}(\text{U})$ by a method similar to that described by Pichat and Baret¹³⁵, was obtained from the Radiochemical Centre, Amersham. The benzene

had a specific activity of 9.6 millicuries per millimole and was supplied in a break-seal ampoule, sealed under vacuum.

It was diluted to 500ml in the following manner (c.f. fig.5.11):-

An extension was made to the vacuum line through a stopcock D. The extension consisted of two side arms. One side arm was fitted with a B19 cone while the other, which had an appendix containing a stainless steel ball bearing, was sealed to the open end of the break-seal ampoule tube A. 50ml of purified benzene were taken in a flask C which was connected to the vacuum line through the B19 cone.

The benzene in C was frozen using liquid nitrogen. The system was evacuated and the benzene degassed by alternate melting and freezing followed by evacuation. Finally the benzene in the flask C and the break-seal ampoule were frozen and the system evacuated till a vacuum better than that equivalent to 10^{-4} mm Hg pressure was obtained. Tap D was closed to cut off the vacuum pump and the steel ball bearing dropped by means of a magnet to break the ampoule seal. The dewar of nitrogen round the flask C was then removed and a few millilitres of benzene from C distilled into the ampoule to act as carrier. The labelled benzene and carrier were then allowed to melt and distil into the flask C. Liquid nitrogen was used to condense the distillate. The bottle was removed from the vacuum line and the volume of the benzene made up to 500ml. The bottle

was stoppered and stored in a fume cupboard.

(b) Cyclohexane: 0.1 mc of C-14(U) labelled cyclohexane, prepared by the reduction of benzene-C14(U) over a cobalt catalyst according to the method described by Rupprecht and Bergqvist¹³⁵ and treated with fuming sulphuric acid to remove the unreacted benzene, was obtained from the Radiochemical Centre, Amersham. It had a specific activity of 7.2mc per millimole, and was diluted to 100ml by the same procedure as for benzene.

(c) Toluene: 0.1mc of toluene (methyl-C14), prepared by catalytic hydrogenation of benzyl alcohol (carbinol-C14) with palladium on charcoal in ethyl alcohol and purified by successive distillations from calcium chloride and sodium metal, was obtained from the Radiochemical Centre. It had a specific activity of 11.1 mc per millimole and was diluted to 100 ml by the same procedure as for benzene.

5.47 Counting Technique

The counting of radioactive materials in the liquid form has the advantage of geometrical reproducibility but suffers from the problems of self absorption and the consequent reduction in sensitivity. In the liquid phosphor scintillation counting technique adopted in the present work the sample and scintillator are intimately mixed so that no correction is required for self-absorption. With the materials used in the present measurements - benzene, cyclohexane and toluene - the usual

problem of finding a solvent compatible with both phosphor and sample was easily solved, as toluene itself was used as the solvent for the phosphor. It was shown in the present work (Section 6.475) that mixtures having the same chemical composition are quenched in the same ratio so that, in the method of calculating self-diffusion coefficients from diaphragm cell measurements, where only the relative final concentrations in the upper and lower compartments are used, no corrections were required for quenching.

5.471 The Counter

The liquid scintillation beta counter is of special value for the measurement of soft beta emitters such as carbon-14. It depends on the property of certain organic substances ('phosphors') which absorb the energy of bombarding beta particles and transform it into light photons, several per particle. These scintillations are detected and converted into electrical pulses by a photo-multiplier tube.

In the present work a Universal Scintillation Counter Type N664A, supplied by Messrs. Ekco Electronics, was used. It consists of a 13-stage photo-multiplier connected to a compartment for the sample bottle, the assembly being enclosed in a lead shield fitted with a counter-balanced hinged lid, and mounted on a steel case which also contains a wide band linear amplifier. It was used in conjunction with an Ekco automatic

Scaler Type N530F.

The sample bottle compartment is separated from the photomultiplier tube by a light proof shutter fitted with a lock which is released by closing the lid of the compartment. This prevents the accidental exposure of the photomultiplier tube to light. A spring loaded carrier in the compartment supports the sample bottle by its external projections and allows it to be lowered through the open shutter into contact with the photomultiplier window when the lid of the lead shield is closed. To improve the light collection efficiency, silicone oil M.S.200/2cs was used as an optical coupling medium between the sample bottle and the photomultiplier. The oil served also to lubricate the shutter.

The N664A is a dual purpose instrument and, by a simple modification, may be adapted for gamma counting,

5.472 Determination of Optimum Working Conditions

The instrument was assembled for beta counting according to the makers' instructions¹³⁷ and then left for over forty hours for the photomultiplier tube to become dark adapted for maximum efficiency. Coated pyrex containers with a capacity of 20ml were used to count the samples. Uncoated containers were also obtained but not used, since in the absence of a constant level device for the coupling silicone fluid, the level of the fluid falls as fluid is removed with the container and leads

118.
to a variable loss of light through the cell walls, reducing the standard of reproducibility.

The phosphor solution consisted of 3g of PPO (diphenyl oxazole) plus 0.3g of POPOP (1, 4-di[2-(5 phenyl oxazoly1)] benzene) dissolved in 1 litre of triple distilled toluene. The PPO and POPOP were obtained from Messrs. Thorn Electronics.

The sample containers retained a slight residual phosphorescence after exposure to light, and were dark adapted for five to ten minutes before use. Care was taken to avoid exposure of the sample containers to daylight. They were stored in a black cardboard box and counted in a darkened room.

The counter was switched on and left for about half an hour to allow it to stabilise. Two sample containers were cleaned by rinsing with dilute nitrating acid and then several times with distilled water. Care was taken to avoid splashing the acid on to the coated outer wall of the containers which can be easily damaged. The containers were dried in an oven at 70° to 80°C and allowed to cool in the dark. 15ml of phosphor solution were pipetted into each container. 5ml of inactive benzene were added to one container to serve as a blank, and 5ml of carbon-14 labelled benzene (approximately 0.02 microcuries) to the other. The contents of the containers were mixed by shaking gently with a rotary motion, avoiding splashing the liquid on to the stopper where it may be lost by capillarity.

Care was taken to avoid introducing solid matter, which would contaminate the silicone fluid and reduce light transmission, on the sample containers. The containers were wiped immediately before introduction into the counter with a piece of chamois leather. Paper tissues were not used as they generally leave fibres sticking on the containers. From time to time the silicone fluid was replenished to make up for that lost each time the bottle was removed.

The active sample was placed in the counter and counting was commenced five to ten minutes afterwards, when the count rate became steady. Counts were recorded at various intervals of E.H.T. over the range 800 to 1800 volts with the discriminator bias set at 5, 10, 15, 20, 25 and 30 volts and with different settings of the amplifier gain over the range $\times 25$ to $\times 1000$. The procedure was repeated with the nonactive sample to obtain the background count rate at each setting.

For each value of discriminator bias curves were plotted, both for the active sample and the background, of count rate vs. E.H.T. At each setting the value of the 'figure of merit', R_s^2/R_B (where R_s is the count rate from the source and R_B is the background count rate) was calculated. It was necessary to avoid the steep part of the count rate vs. E.H.T. curves and, at the same time, to choose a setting where R_s^2/R_B was equal to, or near, its maximum. With this aim in view the setting chosen

for the present work was 1250 volts E.H.T. with a discriminator bias of 15 volts at an amplifier gain of x25. With the 0.02 microcurie source, a count rate of 540 c.p.s. with a background of 1.4 c.p.s. was obtained at this setting, showing an efficiency of about seventy per cent. The counting was carried out at room temperature. Minor variations of 1 to 2°C in temperature did not have any adverse effects such as increasing the background.

5.473 Reproducibility

To check the reproducibility of counting from different source containers, two different cells were filled with the same quantity of phosphor and active solution. The samples were taken volumetrically and the actual amount determined gravimetrically. A total of one million counts were recorded for each container, and the activity per g was calculated in each case. The following results were obtained:-

Container I : 110.24 c.p.s. per g of active solution

Container II : 111.42 c.p.s. per g of active solution

The results from the two containers were therefore consistent to about one percent.

5.474 Quenching Effect of Carbon tetrachloride

As it was intended to make some diffusion measurements in mixtures containing carbon tetrachloride, the quenching effect of this compound was studied. It was found that 1ml of carbon tetrachloride added to 5ml of C-14 labelled benzene with 15ml

of phosphor solution reduced the count rate from 454.25 c.p.s. to 1.4 c.p.s. The present technique of liquid scintillation counting was therefore considered unsuitable for mixtures containing carbon tetrachloride.

5.475 Quenching Effect of Cyclohexane

To observe the quenching effect of cyclohexane preliminary experiments were made on mixtures with benzene containing various mole fractions of cyclohexane from 0 to 0.9. 15ml of phosphor solution were taken, and the total volume of the samples in each container was kept constant as far as possible. The count rate from the same quantity of the active solution was calculated in each case.

The experiment was repeated with solutions containing two-fifths of the activity in the first experiment. Linear graphs (fig.5.12) were obtained for count rate vs. mole fraction of cyclohexane, showing that the amount of quenching increases linearly with rising mole fraction of cyclohexane. At each mole fraction the ratio of the count rates from samples containing the two different amounts of radioactivity remained constant. This showed that the counts from mixtures having different amounts of radioactivity but the same molar composition were quenched in the same proportion. Hence the observed count rates could be directly substituted in equation (5.17) for obtaining diffusion coefficients from measurements in diaphragm cells.

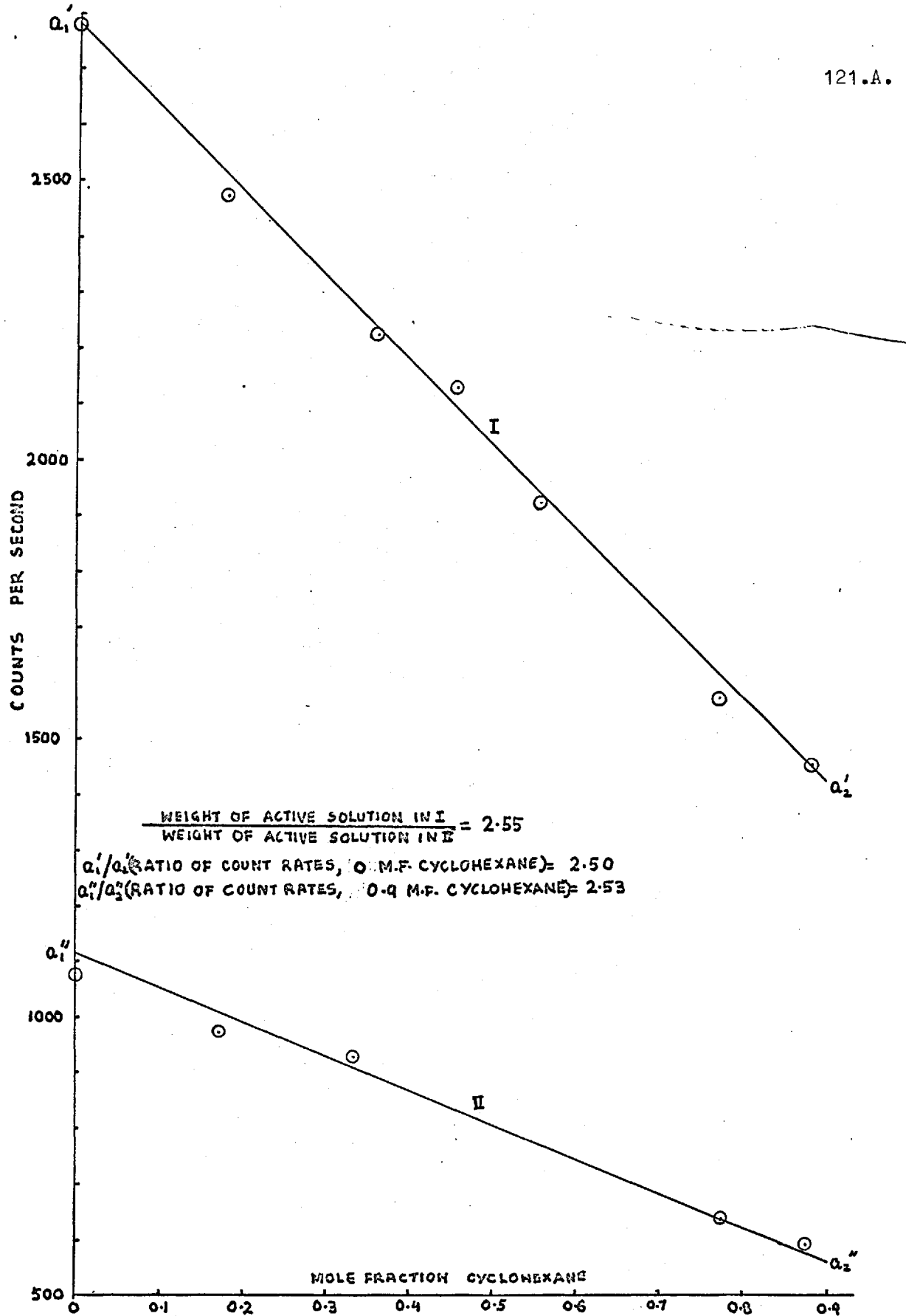


FIG. 5-17. 'QUENCHING' EFFECT OF CYCLOHEXANE IN ITS MIXTURES WITH BENZENE

5.48 Safety precautions

Although no particular health hazard was involved in working with the small quantity of carbon-14 employed (the maximum permissible total body burn for carbon-14 is 300 micro-curie¹³⁸), a few precautions were necessary.

All operations with the radioactive compounds were carried out in a fume cupboard in which the compounds were stored. As required by the Imperial College Code of Practice against Radiation Hazards¹³⁹, the fume cupboard had an air velocity exceeding 150 linear ft/min. across the front face with the window in the normal working position. The fume cupboard exhaust air was carried in independent ducting and discharged outside the building. The base of the cupboard had a 'Formica' covering and the floor near it was covered with a good quality linoleum. To avoid the spread of contamination in the event of breakage or spill all work was carried out in a tray which had an enamel surface and was lined with absorbent 'Kimwipe' paper.

Rubber gloves were worn while handling apparatus inside the fume cupboard. The surgical technique was used when putting on or removing the gloves, to avoid contaminating the hands and the inside surfaces of the gloves. The rubber gloves and the working surfaces inside the cupboard were occasionally monitored with a mica window G-M counter type MX123. The maximum permissible levels of contamination for carbon-14 are as follows:-¹³⁸

(a) Parts of body, personal clothing, inactive areas:

10^{-4} microcuries/cm²

(b) Protective clothing, active areas, glassware and other

apparatus: 10^{-3} microcuries/cm²

5.49I Self-diffusion Measurements in Pure Compounds

For the measurements of the self-diffusion coefficients of pure benzene, cyclohexane and toluene, the cell was degassed and filled with the pure compound according to the procedure described in Section 6.50. It was then clamped to the cell holder and, with the stopcock in the upper compartment A open, thermostatted at 25°C for ten minutes. Excess liquid from the bore of the upper stopcock was removed by means of a syringe and the cell transferred to the fume cupboard, where a few millilitres of liquid in the lower compartment B were replaced by the same quantity of the labelled compound. The cell was set up in the thermostat for a preliminary diffusion of three to four hours. At the end of this period it was removed from the thermostat and the solution in compartment A replaced, after six rinses, with the pure unlabelled compound at the thermostat temperature (25°C). The cell was quickly set up again in the thermostat and the stirring restarted. Two pairs of sample containers were cleaned, dried and weighed with 15ml of phosphor solution in each. After a diffusion run of about twenty four hours (the exact time of diffusion being recorded accurately to the nearest minute,

as in the 'calibration runs' with KCl solution) the cell was again transferred to the fume cupboard and two 5ml samples from each compartment were taken in separate source containers. The exact amount of sample taken in each case was determined gravimetrically. The samples were counted in the liquid scintillation counter, a total of at least 10^6 counts being recorded in each case in order to reduce the statistical error in the counting. The count rate per g of sample was calculated and the diffusion coefficient was calculated separately from the two different pairs of 'matched' source containers. The two results generally agreed to within one percent, and the average was taken as the diffusion coefficient of the pure compound.

5.492 Self-diffusion Measurements in Mixtures

Evaporation of the volatile solvents presents a problem in manipulation, and therefore special weighing bottles were made to minimise losses from prepared mixtures of known composition¹⁴⁹. The bottles consisted of two compartments connected by a U-tube (fig. 5.10). The U-tube was sealed with mercury in order to prevent losses of the component in one compartment while adding the second component to the other. Both compartments were stoppered with B7 stoppers which were greased with the starch-glycerol grease prepared as described in Section 6.50. After weighing, mixing was brought about by tilting the bottles to remove the mercury plug and transferring the liquid from one compartment to the other until complete mixing had been achieved. The bore of the U-tube was made as wide as

possible in order to facilitate transfer of the liquid between compartment

50ml of the mixture of required composition was made up in a weighing bottle the two compartments of which had a rounded base for strength. A wide glass container similar to that used in the filling of pure compound, but having an L-shaped side arm ending in a B7 cone, was employed for the filling of the cells with mixtures. The cell was suspended in the glass container as before and the weighing bottle containing the mixture connected to the B7 cone. The mixture was frozen and the system evacuated. Tap S was then closed and the refrigerant round the weighing bottle was removed and placed round the base of the container. The mixture slowly sublimed and condensed in the lower part of the glass container. The mixture and the diaphragm were then degassed as before and the cell filled by lowering it into the liquid mixture at room temperature by letting in dry air.

A mixture of the same chemical composition, but having a small amount of the appropriate tracer, was made up in another two-compartment weighing bottle. The contents of the bottles were mixed thoroughly and brought up to the thermostat temperature, 25°C. The cell filled with the non-active mixture was thermostatted for ten minutes as in previous measurements and the contents of compartment B were replaced by the radioactive mixture. After a preliminary diffusion of about three to four hours, the contents of compartment A were replaced, after six or seven rinses, with non-active mixture, again of the same chemical composition, prepared in separate weighing bottles. After

the diffusion run of about twenty four hours samples from the two compartments were analysed as in the case of the measurements on the pure components. Except in mixtures very dilute in the amount of tracer a total of 10^6 counts were recorded from each sample. Self-diffusion coefficients were determined from equation (5.17) as before. Measurements of the self-diffusion coefficients of each component were made at 25°C at various mole fractions in the systems benzene-cyclohexane, benzene-toluene and toluene-cyclohexane.

5.50 Results

5.51 Note on Symbology

Three non-electrolytes were considered in the present work. They are denoted as species 1 (benzene), species 2 (cyclohexane) and species 3 (toluene).

The self-diffusion coefficients of benzene, cyclohexane and toluene in the pure state are D_1^0 , D_2^0 and D_3^0 respectively. In binary mixtures the self-diffusion coefficients given as D_i in Chapter 3 are denoted in Chapters 5 and 6 as D_i^j , which are the self-diffusion coefficients of species i in a mixture of i and j . The self-diffusion coefficient of i in a mixture infinitely diluted by j is represented by D_i^{00j} .

The mutual diffusion coefficients of i and j given as D in Chapter 3 are denoted in Chapters 5 and 6 as D_{ij} . x_1 , x_2 and x_3 are the mole fractions of benzene, cyclohexane and toluene in binary mixtures.

5.52 Self-diffusion Coefficients of Pure Compounds

The self-diffusion coefficients of benzene, toluene and cyclohexane were determined at 25°C. The self-diffusion coefficient of benzene was measured in two different cells, and agreement between the two values (2.147×10^{-5} cm²/sec. and 2.093×10^{-5} cm²/sec.) is within the limit of accuracy (1 to 2 percent) estimated for the present work.

The results are given in Table 5.1.

TABLE 5.1

<u>Self-diffusion Coefficients at 25°C</u>		
		$D_i \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$
Benzene	D_1^0	2.12
Cyclohexane	D_2^0	1.41
Toluene	D_3^0	2.23

5.53 Self-diffusion Coefficients in Mixtures

Self-diffusion coefficients in benzene-cyclohexane, toluene-cyclohexane and the benzene-toluene systems were determined at 25°C. The two cells were alternately used for measuring the self-diffusion coefficients at varying mole fractions. The results are listed in Tables 5.2 - 5.4 and plotted against the composition of the mixture in figs. 5.13 - 5.15. In fig. 5.13 values of the self-diffusion coefficients in the benzene-cyclohexane system obtained by Mills¹⁴¹ are plotted for comparison with values obtained in the present work.

TABLE 5.2

Self-diffusion Coefficients of Benzene in Benzene-Cyclohexane Mixtures at 25°C

x_1	$D_1^2 \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$
0.120	1.97
0.264	2.07
0.419	2.22
0.542	2.365
0.665	2.40
0.799	2.30
0.917	2.165
1.000	2.12

TABLE 5.3

Self-diffusion Coefficients of Cyclohexane in
Benzene-Cyclohexane Mixtures at 25°C

x_1	$D_2^1 \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$
0	1.41
0.266	1.75
0.592	2.00
0.777	2.10
0.908	2.09
0.953	2.08

TABLE 5.4

Self-diffusion Coefficients of Toluene in Toluene-
Cyclohexane Mixtures at 25°C

x_3	$D_3^2 \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$
0.068	1.79
0.504	2.17
0.808	2.27
1.000	2.23

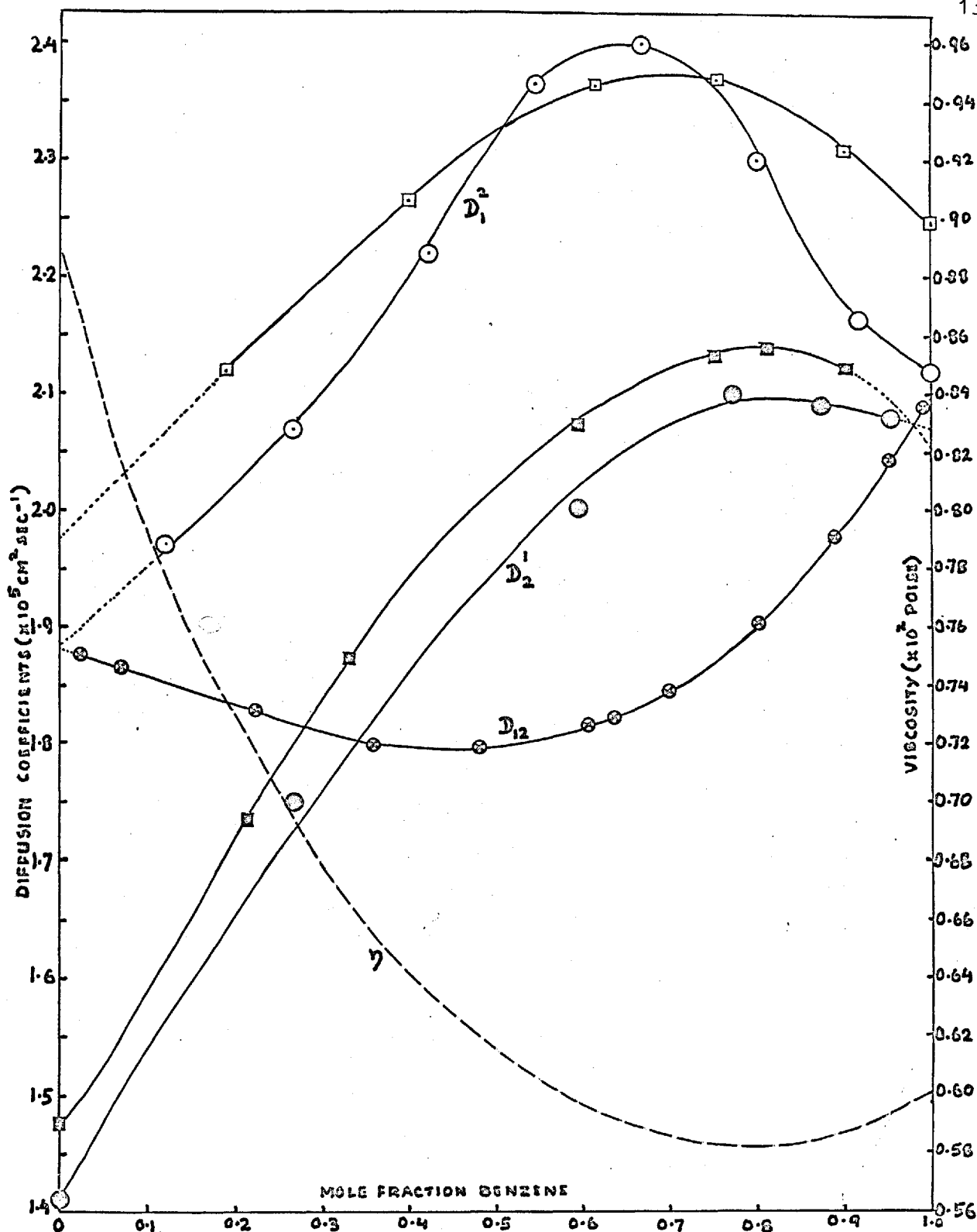


FIG. 5-13. DIFFUSION COEFFICIENTS IN THE SYSTEM BENZENE - CYCLOHEXANE AT 25°C

SELF-DIFFUSION COEFFICIENTS OF BENZENE : $\square$ MILLS¹⁴, $\circ$ PRESENT WORK
 SELF-DIFFUSION COEFFICIENTS OF CYCLOHEXANE : $\square$ MILLS, $\bullet$ PRESENT WORK
 $\otimes$ MUTUAL DIFFUSION COEFFICIENTS, LYONS AND RODWIN, --- VISCOSITY ¹⁶³
 --- INDICATES EXTRAPOLATIONS

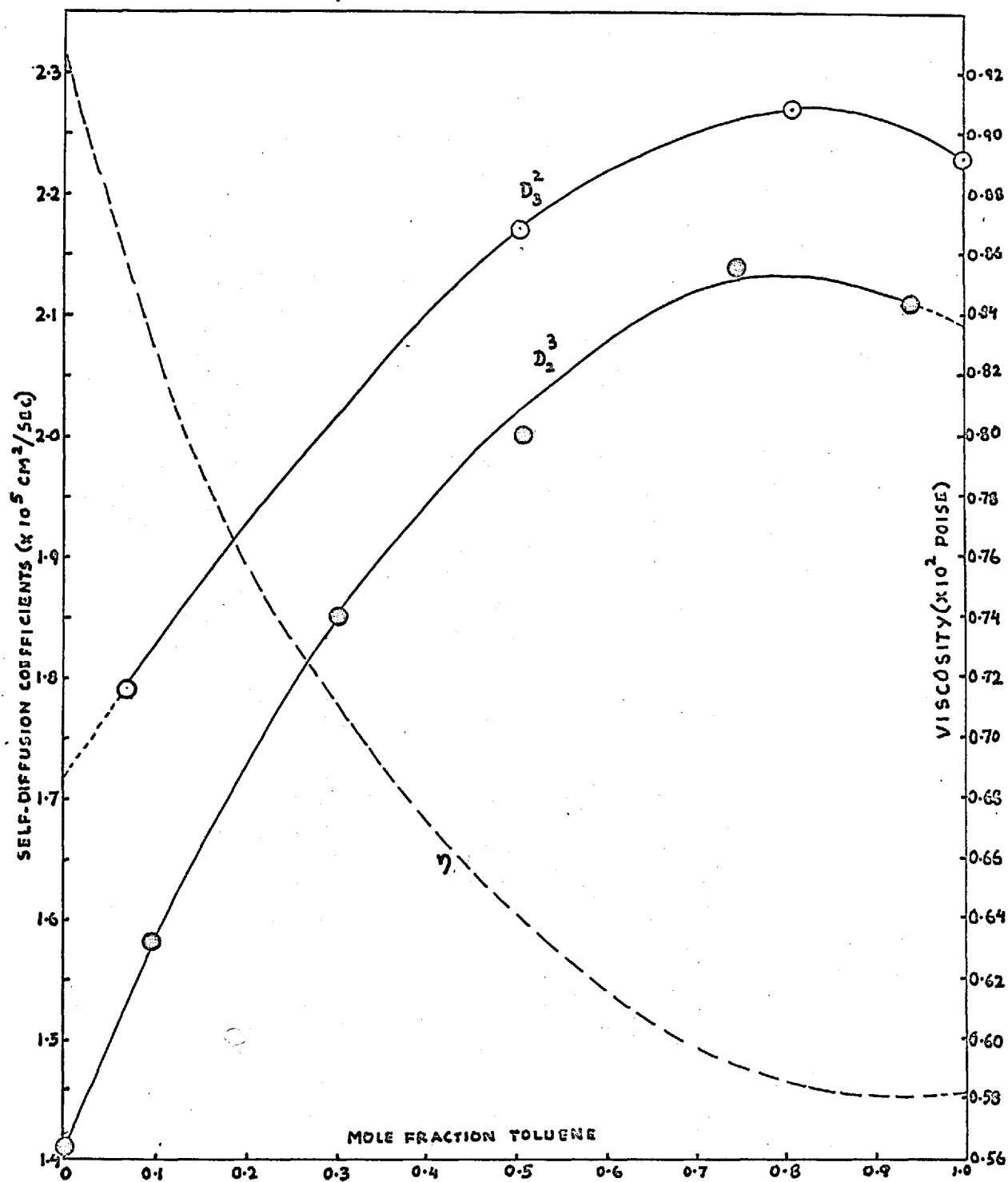


FIG. 5-14. SELF-DIFFUSION COEFFICIENTS IN THE SYSTEM TOLUENE- CYCLO HEXANE
AT 25°C

○ SELF-DIFFUSION COEFFICIENTS OF TOLUENE, ○ SELF-DIFFUSION
COEFFICIENTS OF CYCLOHEXANE, ——— VISCOSITY¹⁵⁵
----- INDICATES EXTRAPOLATIONS

Table 5.5

Self-diffusion Coefficients of Cyclohexane in Toluene-
Cyclohexane Mixtures at 25°C.

x_3	$D_2^3 \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$
0	1.41
0.098	1.58
0.301	1.85
0.508	2.00
0.746	2.14
0.940	2.11

Table 5.6

Self-diffusion Coefficients of Benzene in Benzene-
Toluene Mixtures at 25°C.

x_1	$D_1^3 \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$
0.076	2.33
0.439	2.28
0.707	2.19
0.830	2.13
0.913	2.19
1.000	2.12

Table 5.7

Self-diffusion Coefficients of Toluene in Benzene-
Toluene Mixtures at 25°C.

x_1	$D_3^1 \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$
0	2.23
0.192	2.20
0.559	2.14
0.948	2.05

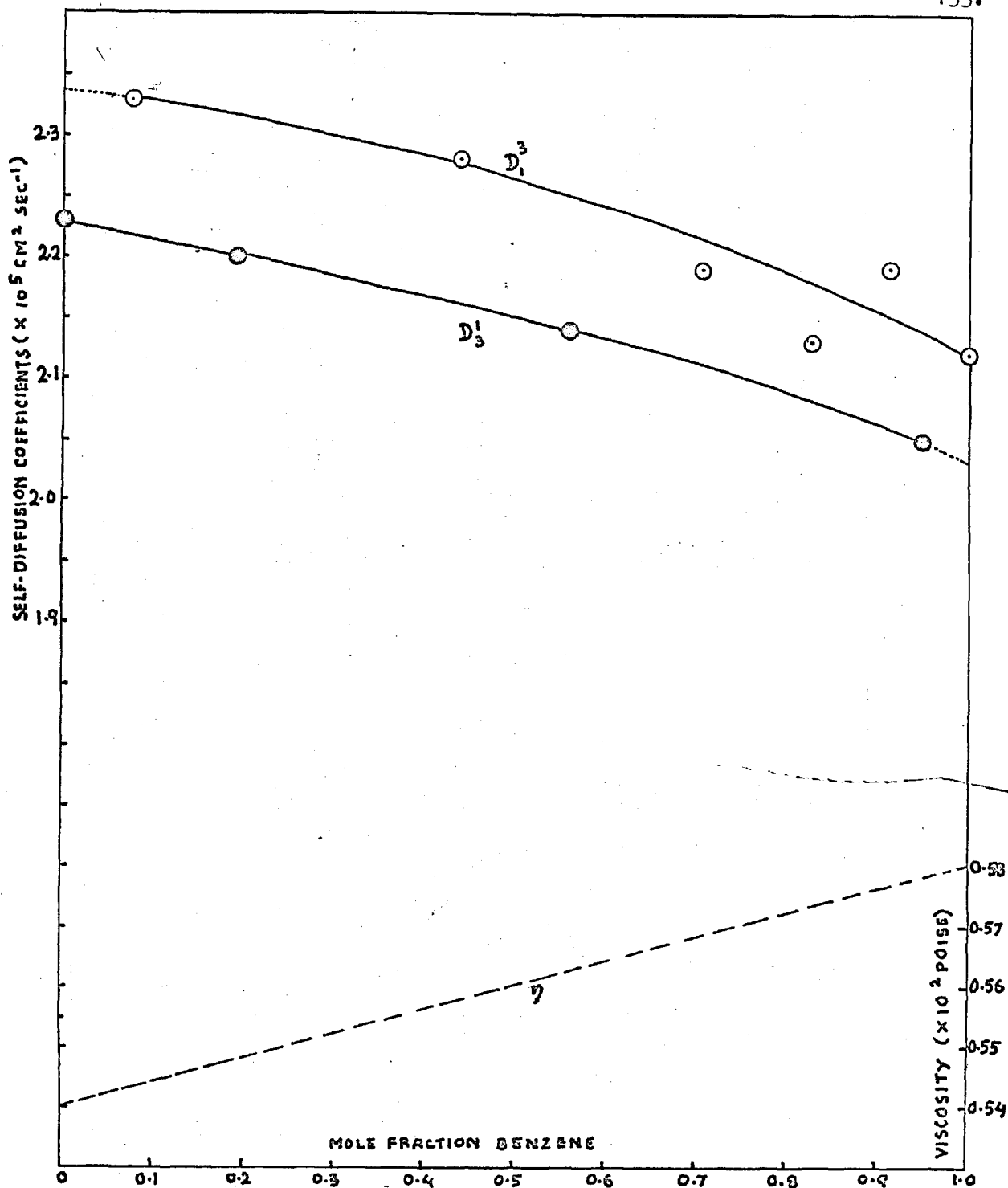


FIG. 5-15 SELF-DIFFUSION COEFFICIENTS IN THE SYSTEM BENZENE-TOLUENE AT 25°C

⊙ SELF-DIFFUSION COEFFICIENTS OF BENZENE, ⊙ SELF-DIFFUSION COEFFICIENTS OF TOLUENE, --- VISCOSITY, ... INDICATES EXTRAPOLATIONS.

CHAPTER 6.DISCUSSION OF THE RESULTS.

Since the present experimental work on the benzene-cyclohexane system was completed, measurements on the same system at the same temperature have been published by Mills¹⁴¹. As seen from Table 6.1, which compares the present self-diffusion results for pure benzene and cyclohexane with existing values, Mills' results for the self-diffusion coefficient of ~~cyclohexane~~ benzene D_1^0 and the self-diffusion coefficient of cyclohexane D_2^0 are significantly different from the other values, being approximately 4 percent higher in each case than the average values of $D_1^0 \times 10^5$ and $D_2^0 \times 10^5$ from other investigations which are respectively 2.16 ± 0.03 and 1.41 ± 0.02 .

Table 6.1.Self-diffusion Coefficient of Benzeneat 25°C.

	$D_1^0 \times 10^5 \text{ cm}^2/\text{sec.}$	Precision %	Method
Graupner and Winter ⁷⁹	2.15	$\pm 2-3$	Diaphragm Cell
Johnson and Babb ¹⁴²	2.18	± 6	Capillary
Hiraoka, Osugi and Jono ¹⁴³	2.13	± 3	Capillary
Rathbun and Bab ¹⁴⁴	2.21	± 5	Capillary
Mills ¹⁴¹	2.247	± 0.3	Diaphragm Cell
Present work	2.12	$\pm 1-2$	Diaphragm Cell

Self-diffusion Coefficient of Cyclohexane at 25°C.

	$D_2^0 \times 10^5 \text{ cm}^2/\text{sec}^{-1}$	Precision %	Method
McCall, Douglass & Anderson ¹⁴⁵	1.38	-	Spin echo
Mills ¹⁴¹	1.475	± 0.3	Diaphragm Cell
Kulkarni, Allen & Lyons ¹⁴⁶	1.433	-	Diaphragm Cell
J.D. Birkett	1.42	-	See ref.146
Present work	1.41	$\pm 1-2$	Diaphragm Cell

The present values of D_1^2 and D_2^1 in benzene-cyclohexane mixtures differ from Mills' over the composition range as seen from fig.5.13. For cyclohexane the difference is by an approximately constant factor corresponding to the differences in the D_2^0 values. For D_1^2 wider discrepancies occur, particularly in the benzene rich mole fractions. Since the conceivable sources of error (such as an imperfect membrane, vibrations and temperature fluctuations) in the diaphragm cell method are more likely to raise the measured value of the diffusion coefficient than to lower it, there is some justification for preferring the present results. More recently self-diffusion data in the benzene-cyclohexane systems at 25°C. has been reported by McCall and Anderson¹⁴⁷. Their data shows good agreement with our results. No previous measurements of diffusion coefficients in the benzene-toluene and cyclohexane-toluene systems exist.

All the equations which have been proposed relating the processes of mutual and self-diffusion (see section 3.30) predict that $D_i^{\infty j}$ and $D_j^{\infty i}$, the limiting values of D_i^j and D_j^i , should correspond with the end values of the mutual diffusion coefficient for the system. Thus

$$\lim_{c_i \rightarrow 0} D_{ij} = D_i^{\infty j} \quad \dots (6.1)$$

$$\text{and } \lim_{c_i \rightarrow 1} D_{ij} = D_j^{\infty i} \quad \dots (6.2)$$

It should be remembered¹⁴⁸, however, that for parent and isotopic molecules of masses m_p and m_i respectively where the molecular diameters and intermolecular forces are the same and the molecule is strictly spherically symmetric, then the ratio of the self-diffusion coefficients is given by the square root of the ^{inverse} mass ratio $D_p^0 / D_i^0 = (m_i / m_p)^{\frac{1}{2}}$, so that the self-diffusion coefficient of the heavier isotopic molecule would be smaller than that of the parent by the factor $(m_p / m_i)^{\frac{1}{2}}$. This applies, however, only to systems of the pure parent or pure isotopic species and so an exact correction factor cannot be applied to the present type of measurements where the isotopic species is diffusing in a medium of light parent molecules. While it cannot quantitatively be taken into account, we would expect $D_i^{\infty j}$ and $D_j^{\infty i}$ as determined from extrapolated tracer diffusion results to be slightly lower than the extrapolated end values of D_{ij} as determined by optical methods.

Equations (6.1) and (6.2) can be tested with the present results only for the benzene-cyclohexane system, for which the

relevant mutual diffusion data is available. Table 6.2 compares our extrapolation of values of $D_1^{\infty 2}$ and $D_2^{\infty 1}$ from the present work and from the results of Mills¹⁴¹ with those from the mutual diffusion values of Lyons and Rodwin¹⁴⁹.

Table 6.2

Comparison of $D_1^{\infty 2}$ and $D_2^{\infty 1}$ from mutual and self-diffusion data.

	$D_1^{\infty 2} \times 10^5$ $\text{cm}^2 \text{sec}^{-1}$	$D_2^{\infty 1} \times 10^5$ $\text{cm}^2 \text{sec}^{-1}$
Lyons and Rodwin	1.880	2.101
Mills	1.975	2.052
Present work	1.885	2.07

These results show that $D_1^{\infty 2}$ from the present work agrees with Lyons' and Rodwin's value than do Mills' results. The extrapolated values for $D_2^{\infty 1}$ are not significantly different and are both slightly lower than Lyons' and Rodwin's value.

In figs. 5.13 - 5.14 the viscosities of the mixtures are plotted against mole fraction along with the diffusion results. It is noteworthy that, for the benzene-cyclohexane and toluene-cyclohexane systems, the maxima in the self-diffusion curves occurs in the same concentration range as the minima in the respective viscosity curves. Moreover, for the benzene-cyclohexane system the curve for the "activity-corrected" mutual diffusion coefficient D_{12}' ($D_{12}' = D_{12} / \partial \ln a_1 / \partial \ln x_1$), where D_{12} is the observed mutual diffusion coefficient¹⁴⁹ and a_1 and x_1 are the thermodynamic activity and mole fraction,

respectively, of component 1) also has a maximum in the same concentration range as the maxima in the self-diffusion curves for benzene and cyclohexane. Since, according to the various theories of diffusion discussed in Chapter 3, the self-diffusion coefficient varies inversely as the viscosity of the solvent, it is reasonable to expect the self-diffusion coefficient in a mixture to show a trend with composition in the opposite sense to viscosity. Benzene-cyclohexane and toluene-cyclohexane mixtures show a volume expansion in mixing, with maxima of 0.66 cc/mole and 0.59 cc per mole respectively^{150,151} at a composition very close to equimolar. The excess heat of mixing for the two systems is also a maximum at approximately equimolar composition^{152,153}. These observations imply that the energy of interaction between a benzene and a cyclohexane molecule is less than that between two benzene or two cyclohexane molecules. A similar argument applies to the toluene-cyclohexane system. Thus there should be a maximum in the diffusion coefficient and a minimum in the viscosity at the same composition as the maxima in volume change of mixing and enthalpy of mixing. At first sight, the minima in the viscosity and the maxima in the self-diffusion curves would seem to occur at a composition different from the maxima in the thermodynamic functions. It must be remembered, however, that the volume change in mixing is the excess volume of mixing over that for an ideal solution, in

which the total volume is given by

$$v_{ij} = x_i v_i + x_j v_j \quad \dots (6.3)$$

where x_i and x_j are the mole fractions and v_i and v_j the molar volumes of the two pure components. Therefore two arbitrary quantities, the excess viscosity η_{ij}^{xs} and the excess self-diffusion coefficient D_i^{jxs} may be defined by

$$\eta_{ij}^{xs} = \eta_{ij} - x_i \eta_i - x_j \eta_j \quad \dots (6.4)$$

and

$$D_i^{jxs} = D_i^j - x_i D_i^0 - x_j D_i^{\infty j} \quad \dots (6.5)$$

where η_i and η_j are the viscosities of the pure components 1 and 2 and η_{ij} is the viscosity of the mixture.

Tables 6.3 and 6.4 show that, for the benzene-cyclohexane and toluene-cyclohexane systems, the maxima in η_{ij}^{xs} and the minimum in η_{ij}^{xs} occur in the same concentration range (approximately equimolar, to within 10 percent) as the maxima in the excess thermodynamic functions. The viscosity data used are those of Rodwin Harpst and Lyons¹⁵⁴ for the benzene-cyclohexane system and of Linke¹⁵⁵ for the toluene-cyclohexane system.

Table 6.3Excess transport properties in the benzene-cyclohexane systemat 25°C.

Mole fraction benzene, x_1	D_1^{2xs} ($x_1 10^5 \text{ cm}^2 \text{ sec}^{-1}$)	D_2^{1xs} ($x_1 10^5 \text{ cm}^2 \text{ sec}^{-1}$)	η_{12}^{xs} ($\times 10^2 \text{ poise}$)
0	0	0	0
0.1	0.05	0.08	-0.062
0.2	0.11	0.14	-0.101
0.3	0.15	0.13	-0.124
0.4	0.23	0.18	-0.133
0.5	0.32	0.19	-0.211
0.6	0.37	0.20	-0.236
0.7	0.35	0.19	-0.102
0.8	0.23	0.16	-0.071
0.9	0.08	0.09	-0.042
1.0	0	0	0

Table 6.4Excess transport properties in the toluene-cyclohexane systemat 25°C.

Mole fraction	D_3^{2xs} ($\times 10^5 \text{ cm}^2 \text{ sec}^{-1}$)	D_2^{3xs} ($\times 10^5 \text{ cm}^2 \text{ sec}^{-1}$)	η_{23}^{xs} ($\times 10^2 \text{ poise}$)
0	0	0	0
0.1	0.06	0.10	-0.065
0.2	0.10	0.17	-0.101
0.3	0.14	0.23	-0.109
0.4	0.25	0.26	-0.112
0.5	0.20	0.29	-0.112
0.6	0.19	0.26	-0.103
0.7	0.18	0.24	-0.088

(Table 6.4 - contd.)

Mole fraction toluene, x_3	D_{33}^{2xs} D_{33}^{2xs} 3 5 2 (x 10 cm sec)			D_{22}^{3xs} D_{22}^{3xs} -1 (x 10 poise)		η_{23}^{xs} η_{23}^{xs} 2 (x 10 poise)	
0.8				0.15	0.18	-	0.065
0.9				0.08	0.10	-	0.034
1.0				0	0	-	0

Beaman⁹⁰ has pointed out that the product $D_i^j \eta_{ij}$ should be independent of composition for a regular solution. The systems benzene-cyclohexane and toluene-cyclohexane are far from regular, and hence $D_i^j \eta_{ij}$ is not constant. The assumption of Glasstone Laidler and Eyring³⁷ that $D_j^i \eta_{ij}$ is a linear function of mole fraction for self-diffusion in a mixture is only approximately true for these systems (see tables 6.5 and 6.6, where the viscosity data of Radwin, Harpst and Lyons¹⁵⁴ have been used for benzene cyclohexane mixtures. The viscosities in toluene-cyclohexane mixtures have been obtained by interpolation from Linke's data¹⁵⁵).

The lack of constancy of $D_i^j \eta_{ij}$ is due to the fact that the relative increase in viscosity is more rapid than the decrease in the diffusion rate. This is in agreement with Onsager's prediction¹⁵⁶ that a positive deviation from Raoult's law (as shown by the benzene cyclohexane systems) corresponds to "local segregation of the components, which might well facilitate diffusion and yet impede viscous flow"

Table 6.5

Self-diffusion ratios and the product $D_i^j \eta_{ij}$ in the
benzene-cyclohexane system at 25°C.

Mole fraction Benzene, x_1	$D_1^2 \eta_{12}$ ($\times 10^7$ cm ² poise sec ⁻¹)	$D_2^1 \eta_{12}$	D_1^2/D_2^1
0	1.67	1.25	1.34
0.1	1.55	1.24	1.25
0.2	1.48	1.23	1.20
0.3	1.43	1.21	1.18
0.4	1.41	1.19	1.18
0.5	1.42	1.18	1.20
0.6	1.42	1.19	1.19
0.7	1.40	1.22	1.15
0.8	1.33	1.22	1.09
0.9	1.28	1.23	1.04
1.0	1.27	1.24	1.03

Table 6.6

Self-diffusion ratios and the product $D_i^j \eta_{ij}$ in the
toluene-cyclohexane system at 25°C.

Mole fraction toluene, x_3	$D_3^2 \eta_{23}$ ($\times 10^7$ cm ² poise sec ⁻¹)	$D_2^3 \eta_{23}$	D_3^2/D_2^3
0	1.59	1.30	1.22
0.1	1.50	1.30	1.15
0.2	1.45	1.30	1.12
0.3	1.44	1.32	1.09
0.4	1.42	1.32	1.08
0.5	1.39	1.31	1.06

Mole fraction toluene, x_3	$D_3^2 \eta_{23}$ ($\times 10^7$ cm ² poise sec ⁻¹)	$D_2^3 \eta_{23}$	D_3^2/D_2^3
0.6	1.37	1.28	1.07
0.7	1.34	1.26	1.06
0.8	1.33	1.25	1.06
0.9	1.32	1.23	1.07
1.0	1.30	1.22	1.07

In the toluene-benzene system, which has been shown to obey Raoult's law quite closely^{157,158} and may be regarded as a regular solution, the product $D_i^j \eta_{ij}$ is constant to within one percent, on average (table 6.7). As can be seen in fig. 5.15, the self-diffusion curves in this system are nearly linear, with a slope which is nearly equal and opposite in sign to the viscosity curve. The viscosity data at 25°C. have been obtained by interpolation from measurements made by Mamedov and Panchenkov¹⁵⁹ at various temperatures. The slightly positive deviations of the self-diffusion curves from linearity in the benzene-toluene system are in accord with the observation that its excess volume, though very small, is slightly positive¹⁵⁰. The ideal behaviour shown by the self-diffusion curves in this system, in comparison to the other two systems investigated in the present work, supports the thesis of Rowlinson¹⁶¹ that the molecular interaction between an aromatic and an aliphatic molecule is relatively weak compared to the average of the energies of interaction of like pairs of molecules.

Table 6.7

Self-diffusion ratios and the product $D_i^j \eta_{ij}$ in the
benzene-toluene system at 25°C.

Mole fraction benzene, x_1 .	$D_1^3 \eta_{13}$ ($\times 10^7 \text{ cm}^2 \text{ poise sec}^{-1}$)	$D_3^1 \eta_{13}$	D_1^3/D_3^1
0	1.26	1.20	1.04
0.1	1.27	1.20	1.05
0.2	1.27	1.21	1.05
0.3	1.27	1.21	1.05
0.4	1.27	1.20	1.05
0.5	1.27	1.20	1.05
0.6	1.27	1.20	1.05
0.7	1.26	1.20	1.05
0.8	1.25	1.20	1.05
0.9	1.24	1.19	1.05
1.0	1.23	1.18	1.04

Bearman's theory of diffusion in mixtures⁹⁰ predicts that, for regular solutions, the ratio D_i^j/D_j^i should be constant over the entire concentration range. Tables 6.5 - 6.7 show that this ratio is virtually constant for benzene-toluene mixtures, but not for the toluene-cyclohexane and benzene-cyclohexane systems.

According to Bearman's theory

$$D_i^j/D_j^i = v_j/v_i \quad \dots (6.6)$$

for regular solutions. This equation is tested with the present

results in table 6.8, where the average values of self-diffusion ratios are listed against the ratio of molecular volumes. Also included are values of the ratios for the ethyl iodide-n-butyl iodide system at 19.35°C., obtained by Carman and Stein⁹².

Table 6.8

Self-diffusion and molar volume ratios in binary systems
at 25°C.

<u>System</u>	
Benzene-cyclohexane	$D_1^2/D_2^1 = 1.18, \quad v_2/v_1 = 1.22$
Toluene-cyclohexane	$D_3^2/D_2^3 = 1.09, \quad v_2/v_3 = 1.02$
Toluene-benzene	$D_1^3/D_3^1 = 1.05, \quad v_3/v_1 = 1.20$
EtI-n-BuI	$D_{\text{BuI}}^{\text{BuI}}/D_{\text{EtI}}^{\text{EtI}} = 1.14, \quad v_{\text{BuI}}/v_{\text{EtI}} = 1.41$

The agreement shown by the two ratios in the first two systems must be regarded as fortuitous, since the self-diffusion ratios vary widely in these systems (see tables 6.5 and 6.6). It has been pointed out by Bearman¹⁶² that in binary mixtures where the molar volumes of the two components are appreciably different, the radial distribution function is not expected to be independent of composition. This may be the reason for the equation (6.6) not applying to benzene-toluene and ethyliodide-n-butyl iodide systems.

According to Bearman's theory of transport in binary mixtures the ratios $D_i^{\infty j}/D_i^0$, $D_j^0/D_j^{\infty i}$, η_i/η_j and λ_j/λ_i should all be equal as can be seen from equations (3.40) to (3.42). These values are given

in table 6.9 where the thermal conductivity data of Horrocks, McLaughlin and Ubbelohde¹⁶³ have been used. The references for the viscosity data are cited in the table. Values of the ratios for the benzene-carbon tetrachloride and carbon tetrachloride-cyclohexane system given by Horrocks and McLaughlin⁹³ are also included for comparison. Carbon tetrachloride is denoted as species 4.

Table 6.9

Values of the transport coefficient ratios for
various systems at 25°C.

Benzene - cyclohexane				
$D_1^{\infty 2}/D_1^0$	$D_2^0/D_2^{\infty 1}$	η_1/η_2	λ_2/λ_1	Reference for viscosity data
0.89	0.68	0.68	0.84	163
Toluene-cyclohexane				
$D_3^{\infty 2}/D_3^0$	$D_2^0/D_2^{\infty 3}$	η_3/η_2	λ_2/λ_3	
0.77	0.67	0.63	0.90	155
Benzene-toluene				
$D_1^{\infty 3}/D_1^0$	$D_3^0/D_3^{\infty 1}$	η_1/η_3	λ_3/λ_1	
1.10	1.10	1.07	0.94	159
Benzene-carbon tetrachloride				
$D_1^{\infty 4}/D_1^0$	$D_4^0/D_4^{\infty 1}$	η_1/η_4	λ_4/λ_1	
0.65	0.73	0.66	0.73	163
Carbon tetrachloride-cyclohexane				
$D_4^{\infty 2}/D_4^0$	$D_2^0/D_2^{\infty 4}$	η_4/η_2	λ_2/λ_4	
1.05	1.09	1.02	1.16	163

The results for the nearly ideal benzene-toluene system show good agreement with theory. Among the remaining systems listed

in table 6.9, the theory is most closely obeyed for the cyclohexane-carbon tetrachloride system. This is to be expected because, although none of the systems conform exactly to the assumptions of the theory, excess volumes are smallest for the carbon tetrachloride-cyclohexane.¹⁶⁴ One of the requirements for the applicability of Bearman's transport theory is that the ratio of the coefficient of thermal expansion to the isothermal compressibility, α/B_T , be independent of composition¹⁶⁵.

Values of this ratio for benzene, carbon tetrachloride and cyclohexane are 1.27, 1.14 and 1.07 respectively with available experimental data¹⁶⁶ on the mixtures of cyclohexane-benzene and benzene carbon tetrachloride exhibiting shallow curvature so that it is reasonable to assume that the composition independence of

α/B_T is most closely followed by the carbon tetrachloride cyclohexane system. This is an additional reason for the latter system showing better agreement with theory than the benzene-cyclohexane and toluene-cyclohexane systems.

The benzene-cyclohexane system is the first simple system for which complete mutual and self-diffusion data are available, hence it is useful to compare calculated and experimental mutual diffusion coefficients. The equations

$$D = \left(\frac{\partial \ln a_i}{\partial \ln x_j} \right)_{T,p} (x_i D_j^i + x_j D_i^j) \quad (6.7)$$

and

$$D = \frac{\eta_i}{\eta_{ij}} D_i^{caj} \left(\frac{\partial \ln a_i}{\partial \ln x_i} \right)_{T,P} \left[\frac{x_i v_i}{v_j} + x_j \right] \quad (6.8)$$

which expresses the mutual diffusion coefficients in terms of different transport coefficients (see chapter 3) will be checked for this system. Table 6.10 contains a comparison of the calculated and experimental values which show better agreement for equation (6.8) than for equation (6.7). It is noteworthy that the experimental values of D lie between the values calculated from equation (6.7) and equation (6.8). The $(\partial \ln a_1 / \partial \ln x_1)$ data were calculated from equations given by Scatchard, Wood and Mochel¹⁶⁶.

TABLE 6.10

Comparison of calculated and experimental mutual diffusion
coefficients for the system benzene-cyclohexane at 25°C

x_1	$D_{12} \times 10^5$ $\text{cm}^2 \text{ sec}^{-1}$ (exp.)	$D_{12} \times 10^5$ $\text{cm}^2 \text{ sec}^{-1}$ (eqn. 6.7)	$D_{12} \times 10^5$ $\text{cm}^2 \text{ sec}^{-1}$ (eqn. 6.8)	$D_{12} \times 10^5$ $\text{cm}^2 \text{ sec}^{-1}$ (eqn. 6.9)
0	1.88	1.88	1.88	1.88
0.1	1.86	1.75	1.86	1.77
0.2	1.85	1.66	1.86	1.72
0.3	1.81	1.60	1.84	1.70
0.4	1.80	1.58	1.85	1.71
0.5	1.80	1.60	1.86	1.76
0.6	1.815	1.63	1.90	1.80
0.7	1.85	1.68	1.96	1.85
0.8	1.90	1.75	2.03	1.89
0.9	1.99	1.87	2.15	1.96
1.0	2.10	2.07	2.29	2.07

McCall and Anderson¹⁴⁷ have given an empirical equation
 for the mutual diffusion coefficient in binary mixtures showing

a viscosity defect defined by $1 - \eta_{ij} / (x_i \eta_i + x_j \eta_j)$.

Their equation is

$$D_{ij} = (x_i D_j + x_j D_i) \eta_{ij} / (x_i \eta_i + x_j \eta_j) \quad (6.9)$$

Values of D_{ij} calculated from equation (6.9), which are listed in table 6.8, show good agreement with experimental data in benzene-rich mole fractions. The viscosity data of Rodwin, Harpst and Lyons¹⁵⁴ have been used in the calculation of D from equation 6.9

Activity data at 25°C is not available for the toluene-cyclohexane system. Mutual diffusion coefficients have been calculated from equation (6.9) using Linke's viscosity data¹⁵⁵ and are listed in Table 6.11. It is noteworthy that the calculated mutual diffusion curve passes through a minimum like the experimental mutual diffusion curve for the benzene-cyclohexane system. A true test of the theory, however, must await the measurement of mutual diffusion coefficients in the toluene-cyclohexane system.

TABLE 6.11

Calculated Mutual diffusion coefficients in the toluene-
cyclohexane system at 25°C

Mole fraction toluene	$D_{23} \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$
0	1.71 ₅
0.1	1.66
0.15	1.65
0.2	1.66
0.3	1.70
0.4	1.75
0.5	1.79
0.6	1.83
0.7	1.88
0.8	1.95
0.9	2.01
1.0	2.09

The benzene-toluene system is nearly ideal, and the activity factor ($\partial \ln a_1 / \partial \ln x_1$) may be taken as unity. Values of D calculated from equation (6.7) with this assumption are listed in table 6.12.

TABLE 6.12

Calculated Mutual diffusion coefficients in the benzene-toluene system at 25°C

Mole fraction benzene	$D_{12} \times 10^5 \text{ cm}^2 \text{ sec}^{-1}$
0	2.33 ₅
0.1	2.32
0.2	2.29
0.3	2.27
0.4	2.23
0.5	2.20 ₅
0.6	2.17
0.7	2.14
0.8	2.11
0.9	2.07
1.0	2.03

According to the theory of Hartley and Crank⁸⁸ the mutual diffusion coefficient in a binary mixture is given by

$$D_{ij} = \frac{RT}{N\eta_{ij}} \left(\frac{\partial \ln a_i}{\partial \ln x_i} \right) \left(\frac{x_i}{\sigma_j} + \frac{x_j}{\sigma_i} \right) \quad (6.10)$$

where σ_i is termed the intrinsic frictional coefficient of species i . (Carman and Stein⁹² have equated $RT/N\sigma_i \gamma_{ij}$ to the self-diffusion coefficient D_i^j to obtain equation (6.7) which is also Bearman's equation for D). One of the difficulties in the prediction of mutual diffusion coefficients from equation (6.11) is the nonconstancy of the frictional coefficients, as it has been shown⁹³ that, even for the nearly ideal cyclohexane-carbon tetrachloride system, $D_{ij} \gamma_{ij} / (\partial \ln a_i / \partial \ln x_i)$ is not linear in x_i . Harpst¹⁶⁷ has proposed that, in ideal systems, a sensible first order approximation would be to assume the frictional coefficients to vary linearly between their limiting values at $x_i = 0$ and 1. At $x_i = 0$, σ_i may be obtained from the limiting value of the binary diffusion coefficient ($D_i^{\infty j}$) as $x_i \rightarrow 0$. At $x_i = 1$, σ_i may be obtained from the self-diffusion coefficient of species i . This procedure fits the carbon tetrachloride-cyclohexane system very well¹⁴⁶, and it will be useful to apply it to other **ideal** systems. This has been done for the toluene-benzene system. The results are tabulated in table 6.13 where species 1 is benzene and species 3 toluene. The viscosity data employed are those of Mamedov and Panchenkov¹⁵⁹ and the activity factor $(\partial \ln a_i / \partial \ln x_i)$ is assumed to be unity.

TABLE 6.13

x_1	$\eta_{13} \times 10^{-2}$ poise	$\sigma_1 \times 10^8$	$\sigma_3 \times 10^8$	$D_{13} \times 10^5$ cm ² sec ⁻¹
0	0.541	32.58	34.12	2.335
0.1	0.545	32.67	34.20	2.30
0.2	0.549	32.75	34.28	2.27
0.3	0.552	32.84	34.36	2.24
0.4	0.556	32.92	34.43	2.21
0.5	0.560	33.00	34.51	2.18
0.6	0.565	33.09	34.59	2.14
0.7	0.569	33.17	34.66	2.12
0.8	0.572	33.25	34.74	2.09
0.9	0.576	33.34	34.82	2.06
1.0	0.580	33.42	34.90	2.03

Values of D_{13} shown in table 6.11 agree quite closely with the values calculated from equation (6.7) and shown in table 6.12. However no definite conclusions can be made in the absence of mutual diffusion data for the benzene-toluene system.

From the present observations it may be concluded that Bearman's equations can be applied only to a narrow class, that of regular solutions for which the theory is only applicable. Even for systems where the departures from the assumptions of a regular solution are not large, agreement between theory and experiment while encouraging is not completely exact. The discrepancies may have their origin in the transport equations derived on the basis of the molecular friction coefficient $\zeta = kT/D_i^0$ as it has been shown⁴⁹ that when ζ is evaluated from the various expressions which have been proposed poor agreement is obtained between calculated and observed self-diffusion coefficients of liquid argon (see Chapter 2).

The Hartley-Crank equations (6.10) as modified by Carman and Stein⁹² is also expected to apply only to regular solutions. This is because in order to equate D_i^j with $RT/N\sigma_i \eta_{ij}$ deriving equation (6.8) Carman and Stein assume that at a given concentration the mobility of species i in mutual diffusion u_i , is the same as the mobility of the tagged species u_i^* in the measurement of self-diffusion coefficients. This equality, however, is not justified for non-ideal solutions. In mutual diffusion, transport through the solution occurs only by the exchange of molecules of species i and j . In self-diffusion experiments, such transport depends on the exchange of the

tagged species i^* with molecules of both species i and j .

In regular solutions where the radial distribution function are independent of composition, molecules of species i and j are expected to have similar size, shape and interaction potentials. In this particular case the mobilities for the two different types of exchange may be assumed approximately equal, and Carman's and Stein's approximation is then justified.

Adopting approaches similar to that of McCall and Anderson¹⁴⁷ the mutual diffusion coefficient in non-regular solutions may be expressed in terms of the self-diffusion coefficients and the viscosity or the density "defect". However more experimental results on mutual and self-diffusion coefficients in simple binary mixtures are required in order to formulate and test such equations.

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APPENDIX 1

SPECIMEN CALCULATION OF THE SELF-DIFFUSION COEFFICIENT

RUN 8, CELL 554

For cell 554, D is given by

$$D = \frac{1}{\beta t} \ln \frac{c_3 + 0.93812 c_4}{c_3 - c_4}$$

At the end of the run c_3 and c_4 were determined as count rates per g of sample.

c_3 and c_4 as obtained by counting do not give the true activity, but a 'quenched' value of the activity. It is assumed that c_3 and c_4 are quenched in the same ratio since the amount of the quenching agent (cyclohexane) is in the same proportion in each sample.

This assumption is justified by Fig. 5.12, where at a mole fraction (say) of 0.3, the count rate is reduced from 1110 to 925 c.p.s. at a certain activity and from 2780 to 2325 c.p.s. at an activity approximately three times higher

$$1110/925 = 1.200$$

$$2780/2325 = 1.196$$

Experimental Data

$$c_4 = 467.50 \text{ c.p.s. per g of sample}$$

$$c_3 = 732.79 \text{ c.p.s. per g of sample}$$

$$t = 34 \text{ hours } 47 \text{ min.} = 2087 \text{ min}$$

β (determined from fig. APl, showing the dependence of cell constant on cell life) = 0.5039

$$D = \frac{10^{-5}}{0.5039 \times 2.087 \times 0.6} \ln \frac{1171.362}{265.293}$$

$$= 2.35 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$$

On the basis of c_3 and c_4 obtained from a different pair of matched source containers

$$D = 2.38 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$$

Taking the average, $D = 2.36_5 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$

APPENDIX 2

From the phenomenological laws of Fourier and Newton for the thermal conductivity and viscosity respectively, (see Chapter 2) the dimensions of the two transport coefficients may be expressed in terms of fundamental quantities by the equation

$$\lambda = m l t^{-3} T^{-1} \quad (\text{AP.1})$$

$$\eta = m l^{-1} t^{-1} \quad (\text{AP.2})$$

where the fundamental quantities chosen are mass m , length l , time t , and temperature T .

The time dimension in equation (AP.1) and (AP.2) can be eliminated¹¹⁹ using the definition of absolute temperature ($\frac{1}{2} m v^2 = 3/2 kT$) to give

$$t = m^{\frac{1}{2}} l k^{-\frac{1}{2}} T^{-\frac{1}{2}} \quad (\text{AP.3})$$

and the transport coefficients rewritten as

$$\lambda = m^{-\frac{1}{2}} l^{-2} k^{3/2} T^{\frac{1}{2}} \quad (\text{AP.4})$$

and

$$\eta = m^{\frac{1}{2}} l^{-2} k^{\frac{1}{2}} T^{\frac{1}{2}} \quad (\text{AP.5})$$

From equations (AP.4) and (AP.5) the ratio of λ to η is given by the dimensionless quantity $m \lambda / k \eta$ which is of fundamental importance in considering the transport properties of dense gases and liquids. The ratio has been shown to be constant within about 10 percent of 2.48 for a series of simple liquids at low temperatures and normal liquid densities, and

to increase with increase in temperature in all cases ¹⁶⁸.

According to Enskog's theory of dense gases and liquids ⁴⁵ the thermal conductivity and viscosity are given respectively by the equations

$$\lambda = 1.025 \times \frac{25}{32\sigma^2} \left(\frac{mkT}{\pi} \right)^{\frac{1}{2}} \times \frac{3k}{2m} \times b\rho(1/y + 1.2 + 0.7557 y) \quad (\text{AP.6})$$

and

$$\eta = 1.016 \times \frac{5}{16\sigma^2} \left(\frac{mkT}{\pi} \right)^{\frac{1}{2}} \times b\rho(1/y + 0.8 + 0.7615 y) \quad (\text{AP.7})$$

where ρ is the density, $b = b_0 M$ where $b_0 = 2/3 \pi N \sigma^3$ is the rigid sphere second virial coefficient and $y = b\rho Y$ where Y is Enskog's compressibility factor. σ is the molecular diameter

From equations AP.6 and AP.7 the ratio $m\lambda/K\eta$ on the Enskog theory is given by the equation

$$\frac{m\lambda}{k\eta} = \frac{15}{4} \left[\frac{1+1.2y + 0.7574 y^2}{1+0.8 y + 0.7614 y^2} \right] \quad (\text{AP.8})$$

which shows that the ratio is solely a function of y . This equation has a maximum of 4.333 at $y = 1.126$

As

$$p = nkT (1 + b\rho Y) \quad (\text{AP.9})$$

on the hard sphere model

$$\left(\frac{\partial p}{\partial T} \right)_p = nk (1 + b\rho Y)$$

so that

$$y = b_p Y = \frac{M}{R\rho} \left(\frac{\partial p}{\partial T} \right)_p - 1 \quad (\text{AP.11})$$

Using equation (AP.11) y can be obtained for real molecules from experimented (pVT) data. This has been done for argon and the values of y used to calculate $m\lambda/k\eta$ at various values of ρ and T . The calculated values are compared with the experimental values of Michels, Sengers and Van de Klundert¹⁷⁰ in Table AP.1.

TABLE AP.1

Comparison of Experimental and Calculated Values of the
Ratio $m\lambda/K\eta$ for Argon.

	0°		25°	
ρ	Exp.	Calc.	Exp.	Calc.
1	3.733	3.753	3.753	3.753
10	3.801	3.781	3.807	3.780
25	3.854	3.825	3.878	3.822
40	3.930	3.866	3.946	3.866
60	4.002	3.920	4.029	3.917
80	4.081	3.972	4.095	3.965
100	4.171	4.016	4.159	4.009
120	4.230	4.060	4.226	4.053
160	4.340	4.135	4.336	4.128
200	4.425	4.197	4.425	4.191
240	4.503	4.247	4.493	4.242
280	4.551	4.285	4.535	4.282
320	4.563	4.312	4.557	4.310
360	4.555	4.328	4.561	4.327

0°

25°

	Exp.	Calc.	Exp.	Calc.
400	4.551	4.333	4.545	4.343
440	4.539	4.328	4.533	4.329
480	4.519	4.314	4.513	4.317
520	4.477	4.295	4.485	4.299
560	4.435	4.271	4.449	4.276
600	4.374	4.244	4.402	4.250
640	4.288	4.218	4.328	4.224

50°

75°

	Exp.	Calc.	Exp.	Calc.
1	3.773	3.753	3.795	3.753
10	3.815	3.779	3.840	3.778
25	3.884	3.820	3.898	3.819
40	3.952	3.861	3.962	3.858
60	4.031	3.911	4.035	3.910
80	4.099	3.959	4.109	3.955
100	4.161	4.004	4.167	3.999
120	4.221	4.046	4.234	4.070
160	4.330	4.121	4.340	4.116
200	4.431	4.186	4.447	4.181
240	4.501	4.238	4.519	4.235
280	4.549	4.279	4.569	4.276
320	4.569	4.308	4.593	4.306
360	4.573	4.326	4.601	4.325
400	4.571	4.346	4.597	4.340
440	4.561	4.330	4.593	4.331
480	4.543	4.319	4.571	4.321
520	4.521	4.302	4.549	4.305
560	4.489	4.281	4.512	4.285
600	4.447	4.256	4.459	4.262
601	4.347	4.229	4.419	4.235

The table shows that the calculated maxima occur at a slightly higher density than that found experimentally, and, in addition, below the maximum the ratio decreases with increase of temperature contrary to experiment. Overall, however, the largest discrepancy between calculated and experimental values of the ratio is only about 5 per cent, showing that equation AP.11 is a surprisingly good approximation for y .

It should be remembered that these values of M/ρ are for the transition from the dilute to the dense fluid. As the density is further increased and the temperature lowered, the value becomes about 2.5 as stated earlier.

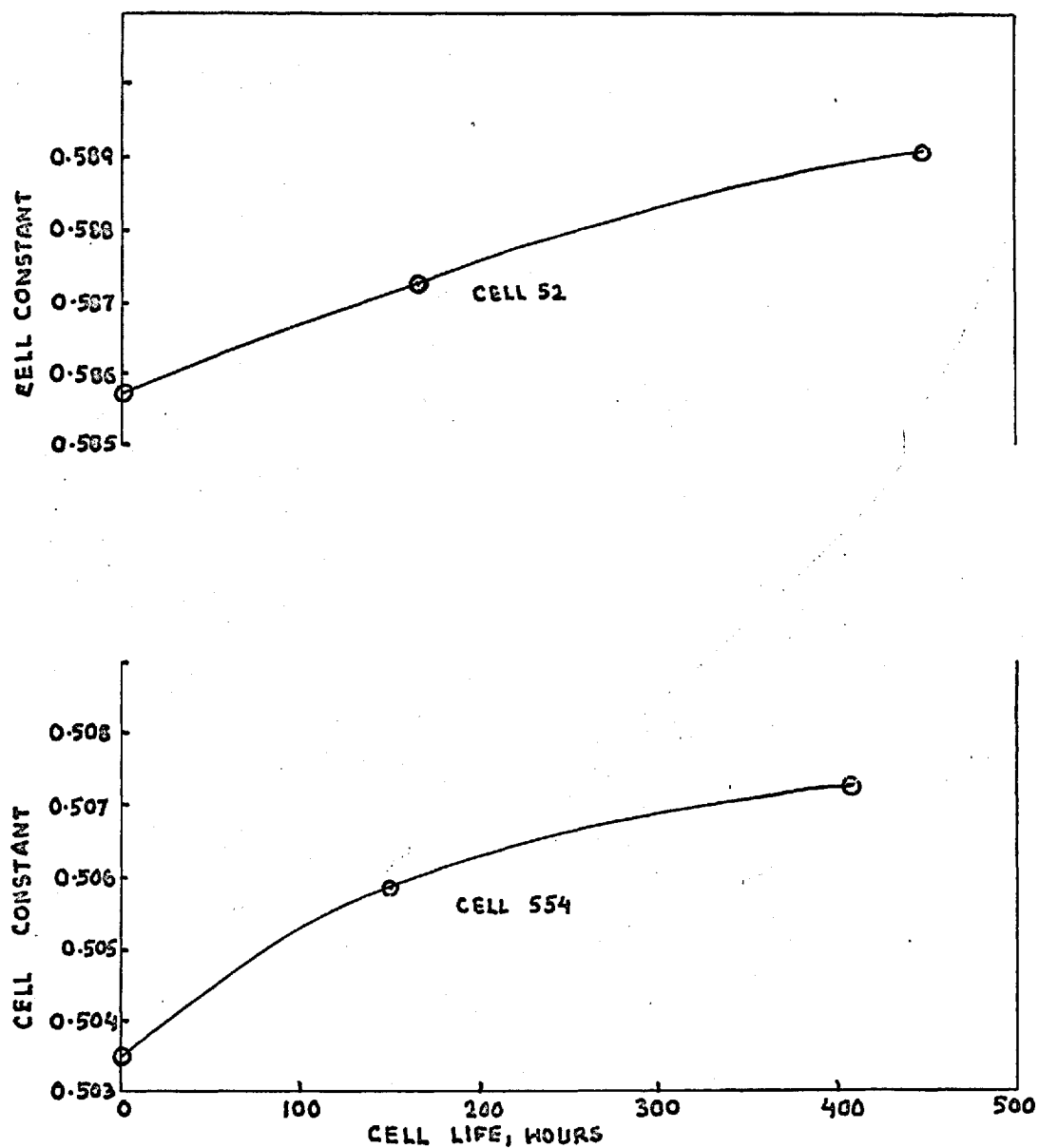


FIG. AP-1. CELL LIFE VS. CELL CONSTANT

APPENDIX 3.

Pressure and Volume Dependence of the Thermal Conductivity of Liquids

BY I. KAMAL AND E. McLAUGHLIN

Dept. of Chemical Engineering and Chemical Technology, Imperial College,
London, S.W.7

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The pressure dependence of the thermal conductivity of a liquid at constant temperature is shown to be controlled by the coefficient of isothermal compressibility, and the volume dependence at constant temperature by the reciprocal of the molecular volume. Expressions for these coefficients have been derived by assuming the harmonic oscillator and rectangular cell potential models of the liquid. The results on the rectangular cell potential model are closely similar to the corresponding expressions derived from the statistical theories of Enskog and of Longuet-Higgins and Pople. Experimental results show a large measure of agreement with the theory for both simple and complex liquids.

The temperature dependence of the thermal conductivity λ of a liquid is substantially controlled¹ by the coefficient of thermal expansion according to the equation

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial T} \right)_p = -\alpha \left[\frac{1}{3} - \left(\frac{\partial \ln \nu}{\partial \ln v} \right)_p \right], \quad (1)$$

where ν is the vibrational frequency of the liquid quasi-lattice. This equation results from the vibrational theory² of thermal conductivity, according to which λ is given by

$$\lambda = \sqrt{2} \nu C_v / a. \quad (2)$$

On this model the excess energy, due to the temperature gradient, is assumed to be transferred down the gradient when molecules oscillating about their equilibrium positions collide with their neighbours at the extremities of their vibrations. a is the nearest neighbour distance in the lattice, which is assumed to be f.c.c., and C_v is the specific heat operative in the transport process.

In the first approximation this specific heat is assumed to be constant and given by the lattice contribution alone, as studies³ of the ratio $m\lambda/k\eta$ and the thermal conductivities of isotopic molecules⁴ suggest that rotational and internal bond vibrational contributions do not participate in energy transport, at least for simple molecules.

In the present paper the pressure and volume dependence of thermal conductivity are examined on the same model and comparisons made with experiment and with existing statistical theories.

PRESSURE AND VOLUME COEFFICIENTS OF THERMAL CONDUCTIVITY

The pressure and volume coefficients of thermal conductivity can be obtained by taking the appropriate derivatives of eqn. (2) and using standard thermodynamic

formulae. As C_v is independent of V and T , the results are given by the equations

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial p} \right)_T = \beta_T \left[\frac{1}{3} - \left(\frac{\partial \ln v}{\partial \ln v} \right)_T \right], \quad (3)$$

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial v} \right)_T = -\frac{1}{v} \left[\frac{1}{3} - \left(\frac{\partial \ln v}{\partial \ln v} \right)_T \right], \quad (4)$$

where β_T is the isothermal compressibility and $v = V/N = a^3/\sqrt{2}$ is the volume per molecule. To complete the set of equations that are directly useful the temperature dependence at constant volume is

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial T} \right)_v = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_v. \quad (5)$$

The equations are connected by the thermodynamic properties of the system, e.g.,

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial p} \right)_T = -\beta_T v \left(\frac{\partial \lambda}{\partial v} \right)_T, \quad (6)$$

but before discussing these relationships in terms of experimental results for specific systems it is of interest to evaluate the coefficients themselves according to various models of the liquid cell potential which determines the frequency. This also enables comparisons to be made with existing statistical theories. Two models which are limiting cases of the cell potential are considered below, the harmonic oscillator and the rectangular cell potential model.

EVALUATION OF THE COEFFICIENTS ON MODELS OF THE LIQUID CELL POTENTIAL

HARMONIC OSCILLATOR MODEL

On the Lennard-Jones and Devonshire model⁵ of a liquid, assuming a 12:6 potential for the intermolecular interaction, the expression for the change in potential energy $\psi(r) - \psi(0)$, for a molecule of the liquid quasi-lattice displaced a distance r from the centre of its cell, to terms in r^2 gives the harmonic frequency

$$\nu = \frac{1}{2\pi\sqrt{m}} \left[\frac{2Ze}{a^2} \{L_1 v^{*4} - M_1 v^{*2}\} \right]^{\frac{1}{2}}. \quad (7)$$

The coefficients L_1 and M_1 have values 22.11 and 10.56 respectively, e is the intermolecular force constant and σ the molecular diameter. $Z = 12$ is the co-ordination number and $v^* = v_0/v$, where $v_0 = \sigma^3$.

Eqn. (7) shows that in this approximation ν is a function of volume alone, hence $(\partial \nu / \partial T) = 0$ and the $(\partial \ln \nu / \partial \ln v)$ terms in eqn. (1), (3) and (4) are equal and given by

$$\gamma^{\text{H.O.}} = - \left(\frac{\partial \ln \nu}{\partial \ln v} \right)^{\text{H.O.}} = \frac{1}{2} \left[\frac{103.18 v^{*2} - 28.16}{L_1 v^{*2} - M_1} \right], \quad (8)$$

where the superscript H.O. stands for harmonic oscillator and γ is Gruneisen's constant.

RECTANGULAR CELL POTENTIAL MODEL

In this case the cell model is that of a hard sphere in a box so that

$$\begin{aligned} \psi(r) - \psi(0) &= 0, & 0 < r < (a - \sigma), \\ \psi(r) - \psi(0) &= \infty, & (a - \sigma) < r. \end{aligned}$$

By taking the mean molecular velocity as determining the frequency this gives

$$v = \sqrt{\frac{8kT}{\pi m}} \frac{1}{4(a-\sigma)} \quad (9)$$

and hence

$$\frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_v = \frac{1}{2T} \quad (10)$$

$$\gamma_p^{\text{H.S.}} = - \left(\frac{\partial \ln v}{\partial \ln v} \right)_p^{\text{H.S.}} = \left[-\frac{1}{2T\alpha} + \frac{1}{3}(y+1) \right] \quad (11)$$

$$\gamma_T^{\text{H.S.}} = - \left(\frac{\partial \ln v}{\partial \ln v} \right)_T^{\text{H.S.}} = \frac{1}{3}(y+1) \quad (12)$$

y is given by $(pV/RT)-1$ and has been taken from the free volume theory⁶ for a fluid of rigid spheres where $pV/RT = [1-(\sigma/a)]^{-1}$. The superscript H.S. stands for the hard-sphere model.

By using eqn. (8), (10), (11) and (12) the corresponding equations for the various pressure, volume and temperature coefficients of thermal conductivity can be obtained on the two models.

COMPARISON WITH EXISTING STATISTICAL THEORIES

At present only comparisons on the hard-sphere model can be made. In this case two theories can be considered, the first due to Enskog⁷ and the second due to Longuet-Higgins and Pople.⁸ On the Enskog theory, the coefficient of thermal conductivity of a dense fluid λ can be written in terms of the corresponding coefficient λ_0 of the infinitely dilute gas, at the same temperature, as

$$\lambda = \frac{\lambda_0 b_0}{V} \left[\left\{ \frac{1}{y} + \frac{3}{5} \right\} + \left\{ \frac{3}{5} \left(1 + \frac{3}{5}y \right) + 0.3957y \right\} \right] \quad (13)$$

where

$$\lambda_0 = 1.025 \frac{25}{32\sigma^2} \left(\frac{kT}{\pi m} \right)^{\frac{1}{2}} \frac{3k}{2m} \quad (14)$$

$y = (pV/RT)-1$ and b_0 is the rigid sphere second virial coefficient. The first bracket term is the convective contribution to thermal conductivity which arises from the motion of molecules between collisions, and the second is the collisional contribution due to energy transfer across the centres of colliding molecules at impact. On the vibrational model of thermal conductivity the convective contribution has been shown to be small² and is not included in eqn. (2), hence on discarding the appropriate term in eqn. (13) the various derivatives can be calculated.

Close similarities between the results on the present hard-sphere model and the Enskog model result, e.g., for the pressure dependence at constant temperature the Enskog theory gives the expression

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial p} \right)_T = \beta_T \left[1 + \frac{1}{3}(y+1) \left\{ \frac{5y(0.7557)}{5y(0.7557)+3} \right\} \right] \quad (15)$$

which compared with the present hard-sphere eqn.,

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial p} \right)_T = \beta_T \left[\frac{1}{3} + \frac{1}{3}(y+1) \right] \quad (16)$$

show a difference of a constant factor in the initial term similar to that obtained previously in the temperature-dependence result. The curly bracket term in eqn. (15) arises from the use of a non-equilibrium distribution function and so would not be expected on the present theory.

The Longuet-Higgins and Pople expression for thermal conductivity which considers the collisional contribution to thermal conductivity alone is given by

$$\lambda = \sigma k \left(\frac{kT}{\pi m} \right)^{\frac{1}{2}} \left(\frac{pV}{RT} - 1 \right) \frac{N}{V}, \quad (17)$$

and hence

$$\frac{1}{\lambda} \left(\frac{\partial \lambda}{\partial p} \right)_T = \beta_T \left[1 + \frac{1}{3}(\gamma + 1) \right], \quad (18)$$

which is also closely similar to the present expression except for a constant factor. Complete identity would not be expected between eqn. (16) and (18) as eqn. (16) includes an intracellular convective term¹ as well as the usual collisional contribution. All three expressions tend to the same value in the limit of high densities ($\gamma \gg 1$). These similarities correspond to those which were previously noted in comparing the corresponding expressions for the temperature dependence of thermal conductivity at constant pressure. A similar correspondence is found when the other coefficients are examined.

COMPARISON WITH BRIDGMAN'S THEORY

It has commonly been assumed in earlier theories of thermal conductivity that, in a liquid, energy was transmitted with the velocity of sound down the temperature gradient. One of the earliest of these theories is due to Bridgman^{9a} who derived the equation

$$\lambda = 3kU_s/\delta^2, \quad (19)$$

where δ is the distance between adjacent molecules and U_s is the velocity of sound. This equation is basically the same as eqn. (2) when the velocity is replaced by the frequency U_s/δ and C_v is given the lattice equipartition value, hence the temperature, volume and pressure coefficients will be similar to those of the present theory.

COMPARISON OF THEORY WITH EXPERIMENT

The present theory can be tested at two levels. In the first case, without detailed assumptions of the cell potential for the evaluation of the frequency, the quantities γ_p and γ_T can be assumed constant. In this approximation, linear relationships should exist between the pressure and volume coefficients of thermal conductivity and the thermodynamic properties of the liquid as given by eqn. (3) and (4).

Bridgman^{9b} has made thermal conductivity measurements on a number of organic liquids at pressures up to 10,000 kg cm⁻² which are suitable for testing eqn. (3) and (4). According to eqn. (3) with the assumption of constant γ_T then $(1/\lambda)(\partial\lambda/\partial p)_T$ should be linear in β_T , the isothermal compressibility. The results for methanol, ethanol, ether, acetone and carbon disulphide at 75°C are given in fig. 1, which are seen to conform with the theoretical prediction.

Alternatively, the volume dependence $(1/\lambda)(\partial\lambda/\partial v)_T$ should be linear in $1/v$. This is confirmed in fig. 2 for the same liquids at 75°C. These two results are not independent. Eqn. (6) provides the appropriate connection and implies that if linear relationships hold as illustrated in fig. 1 and 2 then the slopes are identical.

FIG. 1.—Plot of $(1/\lambda)(\partial\lambda/\partial p)_T$ against β_T for:

ether, ○; acetone, ●;
carbon disulphide, □;
methanol, ▲; ethanol, ■.

Units are in $\text{kg}^{-1} \text{cm}^2$.

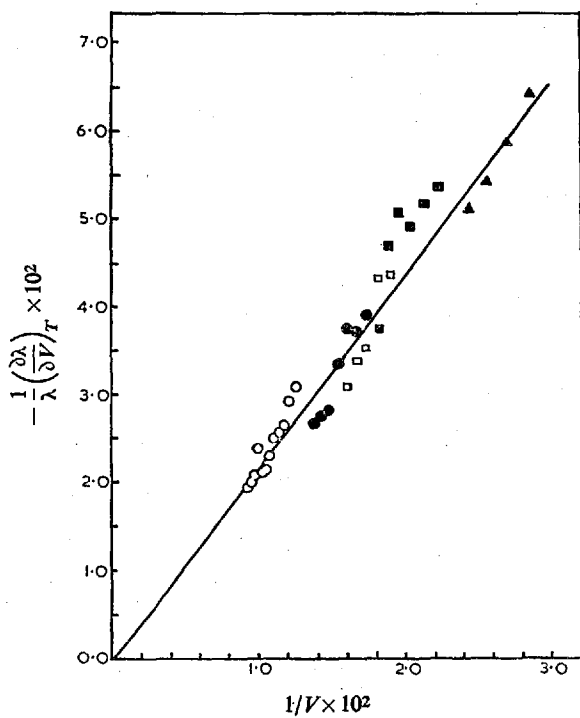
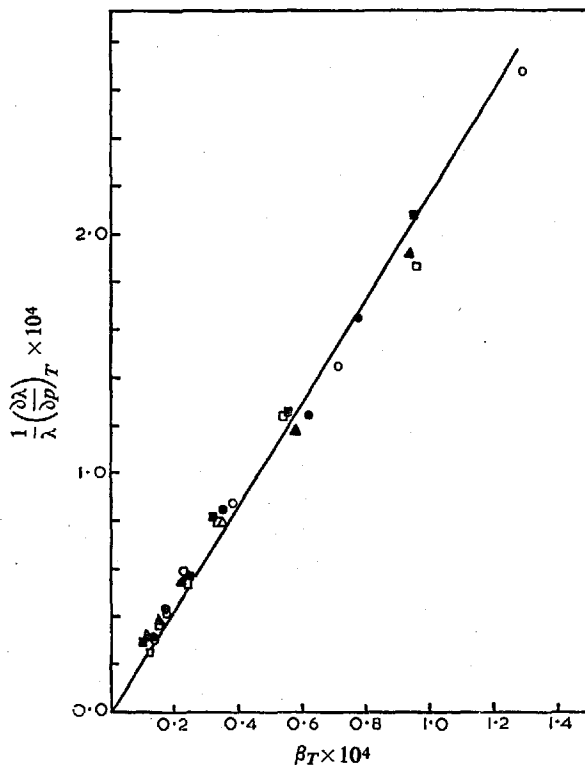


FIG. 2.—Plot of $(1/\lambda)(\partial\lambda/\partial V)_T$ against $1/V$ for:

ether, ○; acetone, ●;
carbon disulphide, □;
methanol, ▲; ethanol, ■.

Units are in $\text{cm}^{-3} \text{mole}$.

In fact, in fig. 2 the solid line through the experimental data has been drawn with the same slope as in fig. 1 and is seen to pass satisfactorily through the points.

While the results quoted conform satisfactorily with the theoretical predictions, Bridgman's measurements at atmospheric pressure are in error in the absolute values of thermal conductivity by about 10 %. This error is not very important provided the coefficients are correct, but full confirmation must await new measurements on the pressure dependence of thermal conductivity.

The results in fig. 1 and 2 differ significantly from the corresponding plot of $(1/\lambda)(\partial\lambda/\partial T)_p$ as a function of α previously reported¹ for the series of liquids, argon, nitrogen, carbon monoxide, methane, toluene, benzene, carbon tetrachloride, diphenyl, o-terphenyl, m-terphenyl and p-terphenyl. In this case, while a linear relationship is also obtained the curve does not pass through the origin but intersects the coefficient of expansion abscissa at a value of $\alpha = 5.5 \times 10^{-4} \text{ deg.}^{-1}$. Fig. 3

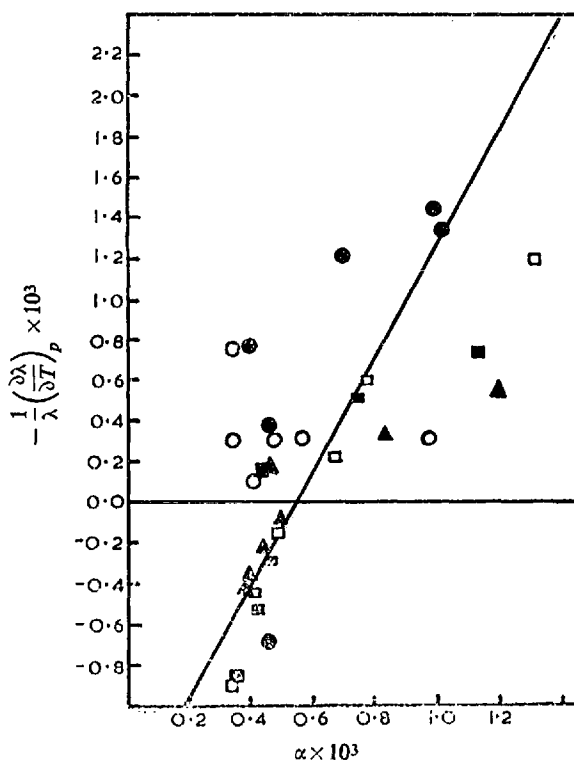


FIG. 3.—Plot of $(1/\lambda)(\partial\lambda/\partial T)_p$ against α for: ether, $\circ$; acetone, $\bullet$; carbon disulphide, $\square$; methanol, $\blacktriangle$; ethanol, $\blacksquare$. Units are in deg.^{-1} .

gives a plot of $(1/\lambda)(\partial\lambda/\partial T)_p$ for ether, acetone, carbon disulphide, methanol and ethanol for a series of pressures. The solid curve in this case is the one previously obtained for the simple liquefied gases and aromatic hydrocarbons. The scale in this case is substantially magnified. It can be seen in this case also that the data, while more scattered, do cut the abscissa at the value $5.5 \times 10^{-4} \text{ deg.}^{-1}$ previously reported for the other substances. This means¹⁰ that as the pressure is increased, the temperature dependence of thermal conductivity reverses sign and begins to increase with increase of temperature when the coefficient of thermal expansion

falls below the value $5.5 \times 10^{-4} \text{ deg.}^{-1}$. The greater scatter in this curve can be largely attributed to the fact that measurements were made at two widely spaced temperatures only, 30 and 75°, and hence unlike the pressure and volume results, where up to seven values are available, they are more liable to be in error. It may be significant that beyond about 5000 atm the scatter of the results is substantially reduced.

It is unfortunate that the existing data are not sufficiently precise to enable these inter-relationships to be explored more fully, in particular those involving the connection

$$\left(\frac{\partial \ln v}{\partial \ln v}\right)_p = \left(\frac{\partial \ln v}{\partial \ln v}\right)_T + \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p \frac{1}{\alpha}, \quad (20)$$

which could be helpful in testing particular models of the frequency.

At the second level of testing, comparisons can be made on the basis of the specific form assumed for the cell potential. In the present work only two limiting cases have been examined, the harmonic oscillator and rectangular cell model, whereas in reality the intermediate case of an anharmonic cell potential is likely to be a better approximation. While this problem is at present being studied it is still of interest to examine experimental results in the light of the present models.

Ideally the theory should be tested on thermal conductivity results for simple systems at high densities. Such information is, however, extremely scarce and the results which do exist are concentrated principally in the region from the dilute to the moderately dense gas where the harmonic oscillator approximation, in particular, is the worst.

For the present, attention will be restricted to the temperature dependence at constant volume, where results of interest have been obtained. On the harmonic oscillator model $(\partial \lambda / \partial T)_V = 0$ and on the hard sphere model it is $\lambda / 2T$. A number of studies have been made on oxygen, nitrogen, argon and ammonia by Ziebland and co-workers who have suggested¹¹ that when the thermal conductivity is plotted against the density for the liquid and dense-gas regions for various temperatures then, within experimental error, the isotherms are coincident. This result agrees with the harmonic oscillator model. Michels, Sengers and Van de Klundert¹² have also studied the density dependence of the thermal conductivity of argon from the dilute gas to a density of 600 amagat (*ca.* 1.07 g cm^{-3}) at 0, 25, 50 and 75°C. Even at the highest densities the isotherms are not coincident. For example, at 600 amagat, $(\partial \lambda / \partial T)_V$ is $1.7 \times 10^{-7} \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg.}^{-1}$ which compares with a $\lambda / 2T$ value of $3.2 \times 10^{-7} \text{ cal cm}^{-1} \text{ sec}^{-1} \text{ deg.}^{-1}$ at the mean temperature of 37.5°C. These values suggest that rather than the rectangular cell potential, which can be looked on as a limiting case of anharmonicity, better results will be obtained from the work at present in progress which includes the quatic term in $\psi(r) - \psi(0)$.

The agreement between experiment and theory given above tends to support the conclusion previously advanced¹³ that the imposition of a temperature gradient on a liquid is a small perturbation of the structure compared with the imposition of a velocity gradient. This makes thermal conductivity comparatively structure insensitive and the pressure, volume and temperature coefficients dependent mainly on volume parameters. Viscosity, on the other hand, is dependent on energy parameters because of the disruption of the intermolecular forces by the velocity gradient.

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