

# THERMAL CONDUCTIVITY OF ORGANIC LIQUIDS

A thesis presented for the Degree of

Doctor of Philosophy

of the University of London

in the Faculty of Science

by

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December 1962.

## ABSTRACT

The liquid state is discussed with reference to its importance in determining the transport properties. Existing quasi gaseous and quasi crystalline theories of energy transport in liquids are outlined and their predictions for simple molecular systems discussed.

The methods available for measuring thermal conductivity have been critically surveyed and the advantages of the selected transient conduction method are presented and analysed in detail.

In addition to measurements upon the well studied compounds toluene and water the group of compounds benzene, diphenyl, ortho-, meta- and para-terphenyl and triphenylene have been studied over a range of temperature including the supercooled state. The thermal conductivities and viscosities of the isotopically substituted pairs benzene and perdeutero benzene, cyclohexane and perdeutero-cyclohexane have been measured. Existing diffusion data on ethyl iodide n-butyl iodide mixtures have been supplemented by viscosity and thermal conductivity measurements.

In Part 3 existing theories of liquid thermal

conduction are extended for liquids containing simple molecules. An expression is derived in terms of a mean molecular vibration frequency calculated from known pair forces assuming a quasi crystalline liquid structure. A close relationship between the temperature coefficient of thermal conductivity and the thermal expansion coefficient is indicated.

The contrasting behaviour of energy and momentum transport in molten polyphenyls is discussed and the thermal conductivities compared with the existing theories.

The ratios of the transport coefficients of energy and momentum in isotopically substituted benzene and cyclohexane are discussed with reference to mechanisms of transport in condensed phases and the experimental results are compared with a specific model due to Valleau.

Some relationship between the transport coefficients of mass momentum and energy in binary regular solutions have been extracted from a theory of Bearman and compared with the values obtained experimentally for ethyl iodide, n butyl iodide mixtures.

ACKNOWLEDGMENTS:

The author wishes to express his thanks to Professor A.R. Ubbelohde, F.R.S., who supervised this work, for his help and encouragement throughout.

The author also wishes to record his indebtedness to Dr. E. McLaughlin for his active interest in the work and for much valuable advice and discussion.

Thanks are also due to the National Coal Board for the award of a bursary during the period in which this research was carried out.

Two papers based on the work presented in this thesis have been published jointly with Dr. E. McLaughlin:

Transactions of the Faraday Society, 1960, 56, 446

Transactions of the Faraday Society, 1962, 58, 1357

Reprints are appended at the end of the thesis.

A further paper in collaboration with Dr. E. McLaughlin on the transport coefficients of isotopically substituted molecules has been accepted for publication by the Faraday Society.

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## CHAPTER 1.1 THE THEORY OF LIQUIDS

### 1.1.1 Introduction

At the present time the kinetic theory of gases and theories of the solid state have reached a degree of completeness which is totally lacking in theories of liquids. In the liquid there are no laws which parallel, either in power or simplicity, the gas laws or the Debye theory of specific heats. Liquid behaviour, in its widest sense, ranges from the solid, in glasses at low temperatures, to the dense gas, at the critical point. The thermal conductivity and viscosity in particular are sensitive to the details of molecular interaction and to the typical distribution of molecules in space. It is the complexity of this distribution which distinguishes liquid theories from those of the solid or gas.

The task of liquid theory is to provide a framework which will explain the diversity of liquid behaviour, ultimately in terms of molecular properties. Two lines of approach may be distinguished. The one, a complete statistical description of the liquid not dependent upon imperfect analogies with solids or gases. This approach has been

developed particularly by Kirkwood<sup>(1)</sup> and his co-workers and by Born and Green<sup>(2)</sup>. The other, obligatory for all but the simplest molecules, relies upon judicious comparison with gases and crystals to illuminate problems which lie ahead of rigorous theory.

A detailed review of liquid theory is not undertaken here. Attention is concentrated upon those properties of molecules and liquids which have a direct bearing upon the development of transport theories.

### 1.1.2 Intermolecular Potentials

The potential energy of a pair of molecules which depends in general both upon their separation and upon their relative orientation, contains both repulsive and attractive terms. For simple molecules (monatomic diatomic and symmetrical polyatomic molecules) the angular dependence may be neglected to a first approximation.

Information about intermolecular potentials comes from a study of both gases and solids<sup>(3)</sup> where theory is sufficiently advanced to permit detailed comparison with experiment.

Major sources of information are the thermodynamic properties (virial coefficients and Joule Thomson coefficients), of gases, the transport properties of dilute gases, and the low temperature properties of crystalline solids.

The macroscopic properties do not lead directly to a knowledge of the potential but to integrals involving it. It is therefore customary to adopt as simple a model potential as possible and to compare the predicted properties with experiment. Typical potentials which have been postulated are the so called Lennard-Jones 6-12 potential,<sup>(4)</sup> the Sutherland<sup>(5)</sup> potential and the square well potential. These

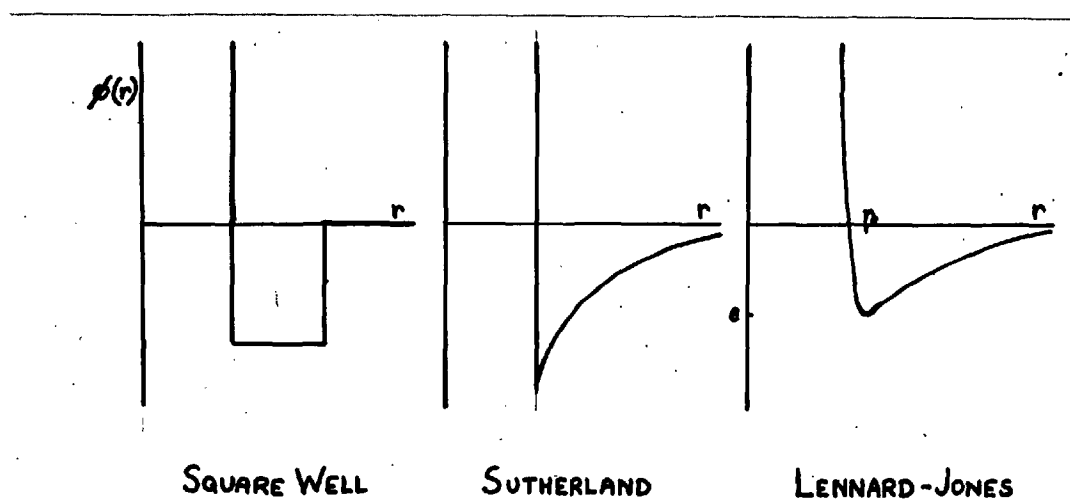
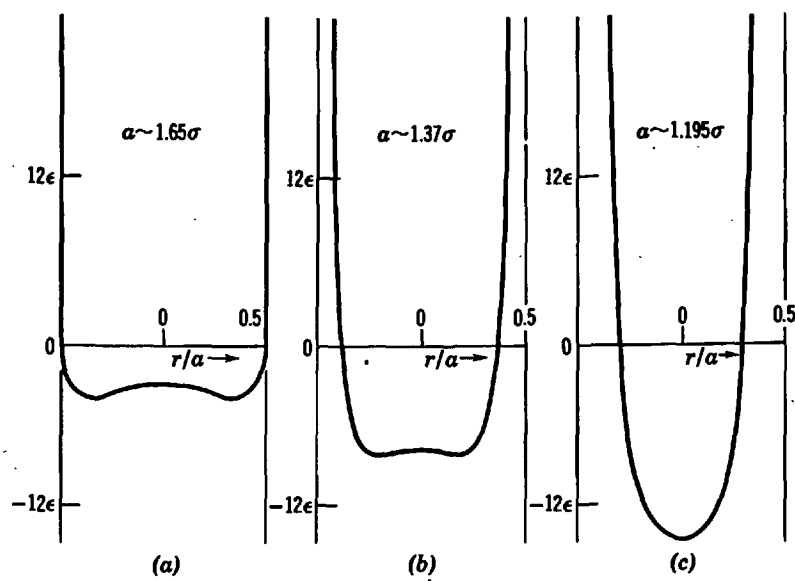


Figure 1.1 Model Potentials



The potential field within a cell for various cell sizes.

Figure 1.2

are illustrated in figure 1.1. Second virial coefficients may be adequately explained<sup>(6)</sup> using any of these potentials with suitably disposed parameters. However the viscosity of dilute gases is very sensitive to the shape<sup>(7)</sup> and experimental data support the choice of the Lennard Jones 6-12 potential (N.B. It is reported for the inert gases that the true potential has a rather steeper repulsion term and wider minimum). Additional information<sup>(3)</sup> in support of the 6-12 has been obtained from the properties of crystals at low temperatures. Although more adjustable potentials<sup>(8)</sup> have been used in particular instances the 6-12 is the most comprehensively successful. It is characterised by two parameters  $\epsilon$  and  $r_0$ , and has the form

$$\phi(r) = \epsilon \left[ 2 \left( \frac{r_0}{r} \right)^{12} - \left( \frac{r_0}{r} \right)^6 \right] \quad (1.1)$$

$\epsilon$  and  $r_0$  are simply the co-ordinates (figure 1.1) of the potential energy minimum.

Although the interactions of more complicated molecules are not spherically symmetric it is sometimes possible to treat each atom in a molecule as the centre of a Lennard-Jones interaction with each atom of a neighbouring molecule<sup>(9)</sup>.

In terms of the molecular size the overall repulsive interactions of large molecules are rather steeper<sup>(10)</sup> than those of simple ones.

### 1.1.3 The Structure of Liquids

By the mean structure of a liquid is meant the typical arrangement of molecules in relation to any one molecule. In the case of spherically symmetric molecules the description involves only the relative locations of molecules, but for molecules of complex shape mutual orientations enter into the complete description. The mean structure varies markedly throughout the liquid range being indistinguishable from the gas at the critical point while near the melting point it is more closely akin to the crystalline solid. Despite the similarity between the liquid and crystal at the melting point there is no evidence that the liquid may pass continuously into a completely ordered state, although the possibility of such a "critical" point for liquid-solid transitions has been discussed <sup>(11)</sup>. A degree of ordering in the disposition of molecules is now seen to be a consequence of the similarity in density between the liquid and the crystal. Gases compressed to liquid densities show <sup>(12)</sup> x-ray diffraction patterns similar to those found in liquids.

At high densities the hard core of each molecule excludes other molecules from its immediate vicinity. Its

nearest neighbours tend to congregate in a spherical shell surrounding the central molecule and they in turn exclude other molecules which form a second shell surrounding the first. In the crystal the molecules are situated on a well defined lattice and the co-ordination shells are determined by the nearest neighbour distance and the crystal symmetry. Apart from the effect of lattice imperfections the shells remain clear at large distances from the central molecule. In the liquid which has a similar nearest neighbour distance the molecules are not situated on a lattice, but co-ordination shells are still evident although much broader and less distinguished from one another. Long range order completely disappears and it is usually only possible to identify a few initial co-ordination shells beyond which the disposition of molecules becomes effectively random.

The local structure of liquids is of great importance in determining transport processes (e.g. viscous flow does not occur in a perfectly ordered state), and rigorous theories of these phenomena are concerned with its perturbation in the steady state.

A statistical description of liquid structure has been recently developed in terms of configurational distribution

functions <sup>(2,3,13,14,15)</sup>. These define the probability of a given arrangement of molecules. For instance, the distribution function of  $h$  order,  $n^{(h)}(\underline{r}_1 \underline{r}_2 \dots \underline{r}_h)$  expresses the probability  $n^{(h)}(\underline{r}_1 \underline{r}_2 \dots \underline{r}_h) d\underline{r}_1 d\underline{r}_2 \dots d\underline{r}_h$  of finding molecules  $1, 2, 3 \dots h$  at positions  $\underline{r}_1, \underline{r}_2 \dots \underline{r}_h$  simultaneously, the positions of all other molecules in the system being undefined. Where the intermolecular energy of the system may be expressed as a sum of pair potentials a knowledge of the first two distribution functions  $n^{(1)}(\underline{r})$  and  $n^{(2)}(\underline{r}_1, \underline{r}_2)$  is sufficient to determine the equilibrium properties of the system. In an isotropic system  $n^{(1)}(\underline{r})$  is independent of position and is simply the number density of molecules.

In isotropic systems containing spherically symmetric molecules the pair distribution function  $n^{(2)}(\underline{r}_1, \underline{r}_2)$  is frequently written in terms of the related radial distribution function  $g(r)$  in which  $r = |\underline{r}_2 - \underline{r}_1|$ .

$$g(r) = \frac{n^{(2)}(r)}{[n^{(1)}(r)]^2} \quad (1.2)$$

is a quantitative description of the co-ordination shells surrounding a given molecule. It is the ratio of the mean molecular density in a shell distance  $r$  from the central

molecule to the average molecular density over a finite region.

Information on radial distribution functions has been obtained from x-ray and neutron diffraction studies<sup>(19)</sup>.

The analysis required for the interpretation of liquid diffraction patterns was developed by Debye<sup>(16)</sup>, Manke<sup>(17)</sup>, Zernike and Prins<sup>(18)</sup>. A review of this work and experimental results stemming from it, has been compiled by Green<sup>(20)</sup>.

Theories of transport based on molecular distribution functions have been developed by Born and Green<sup>(2)</sup>, and by Kirkwood<sup>(1)</sup> and his collaborators. Their method and results for liquid argon are discussed in section 1.2.

#### 1.1.4 Cell Lattice Models of the Liquid Structure

The application of a distribution function approach to evaluating the properties of real fluids is subject to two major limitations.

1. The theory as at present developed, applies rigorously only to spherically symmetric structureless molecules.
2. Even for systems which satisfy this condition (e.g. inert gas molecules) the radial distribution function has not yet been determined with sufficient accuracy either experimentally or theoretically.

In view of this it is frequently more useful to adopt an approximate model which satisfies the density of the fluid and which permits an easy description of the structure. Such are the cell lattice models of liquids.

The main feature of these theories is that they consider the molecules to be confined within small volumes or cells in the vicinity of lattice sites. Eyring<sup>(21,22,23)</sup> and others developed the idea of a regular lattice structure and postulated the existence of vacant sites or holes which were important in determining the behaviour near the critical point. These ideas were used to deduce relationships

between various macroscopic properties. In 1937, Lennard-Jones and Devonshire<sup>(24)</sup> placed the theory on a more quantitative basis and it became possible to calculate bulk properties of the liquid in terms of the molecular forces.

The assumptions of the Lennard-Jones and Devonshire theory are:

- (1) Each molecule is confined to a cell by its neighbours
- (2) The volume of a cell,  $\nu$ , is defined by the molar volume  $\nu = V/N$ . Thus all cells are assumed to be occupied. If the cells are situated on a face centered cubic lattice each has twelve neighbouring cells separated from its centre by a distance,  $(\sqrt{2} V/N)^{1/3}$
- (3) The cell potential (i.e. the potential of a molecule in the field of its neighbours) is spherically symmetrical. It may be calculated by averaging over all angles the potential due to twelve neighbours each at a distance,  $(\frac{\sqrt{2} V}{N})^{1/3}$ , from the centre of the cell. The additional potential due to more distant molecules has also been calculated.

Various modifications<sup>(23,25-29)</sup> of the initial theory have been put forward which allow for the possibility of vacant

cells and the movement of molecules between cells. These modifications improve to varying extents the calculation of macroscopic properties but none are comprehensively satisfactory.

#### 1.1.4a The Lennard-Jones and Devonshire Cell Potential

The average potential energy,  $\omega(r)$ , of a molecule displaced a distance,  $r$ , from the centre of a cell is obtained by summing the potential due to  $z$  neighbours smeared over the surface of a sphere radius,  $a$ .

$$\omega(r) = \frac{z \int_0^{2\pi} \int_0^\pi \phi(r^2 + a^2 - 2ar \cos \theta) \sin \theta \, d\theta \, d\phi}{\int_0^{2\pi} \int_0^\pi \sin \theta \, d\theta \, d\phi} \quad (1.3)$$

$\phi$  is the pair potential which if replaced by the 6-12

law (equation 1.1) gives

$$\begin{aligned} \frac{z\epsilon}{2} \left\{ \frac{r_0^6}{r} \frac{1}{2a^5} \left[ \left(1 - \frac{r}{a}\right)^{-4} + \left(1 + \frac{r}{a}\right)^{-4} \right] \right. \\ \left. + \frac{r_0^{12}}{r^{10}a^{11}} \left[ \left(1 - \frac{r}{a}\right)^{-10} - \left(1 + \frac{r}{a}\right)^{-10} \right] \right\} \quad (1.4) \end{aligned}$$

Putting  $r^2/a^2 = y$  and using the f.c.c. values  $v = a^3/\sqrt{2}$  and  $v_0 = r_0^3/\sqrt{2}$ , equation 1.4 may be simplified to read

$$\omega(r) = z\epsilon \left[ \left( \frac{v_0}{v} \right)^4 (l(y)+1) - 2 \left( \frac{v_0}{v} \right)^2 (m(y)+1) \right] \quad (1.5)$$

in which

$$\ell(y) = (1 + 12y + 25 \cdot 2y^2 + 12y^3 + y^4)(1-y)^{-10} - 1 \quad (1.6)$$

$$m(y) = (1 + y)(1-y)^{-4} - 1 \quad (1.7)$$

The potential relative to that at the centre of the cell is given by

$$\omega(r) - \omega(0) = Ze \left[ \left( \frac{U_0}{U} \right)^4 \ell(y) - 2 \left( \frac{U_0}{U} \right)^2 m(y) \right] \quad (1.8)$$

The effect of more distant shells has also been discussed <sup>(30)</sup>. For three shells the corresponding equation for the potential is

$$\omega(r) - \omega(0) = Ze \left[ \left( \frac{U_0}{U} \right)^4 L(y) - 2 \left( \frac{U_0}{U} \right)^2 M(y) \right] \quad (1.9)$$

where

$$L(y) = \ell(y) + \frac{1}{128} \ell(y/2) + \frac{2}{729} \ell(y/3) \quad (1.10)$$

$$M(y) = m(y) + \frac{1}{16} m(y/2) + \frac{2}{27} m(y/3) \quad (1.11)$$

In figure 1.2 the potential  $\omega(r)$ , for the three shell approximation, is shown as a function of  $r/a$  for various values of  $U/U_0$ . The shape of the potential depends strongly on the volume per particle and at high

densities is well represented by a parabola. The parabolic term in the expansion of  $\omega(r)$  is shown dotted in the figure. At lower densities the cell potential is better approximated by a square well.

By fitting square & harmonic potential wells to the potential, the partition function and thermodynamic properties may be simply determined<sup>(31)</sup>. Hirschfelder<sup>(30)</sup> and his co-workers have calculated the thermodynamic properties using the exact form of the potential  $\omega(r)$ .

#### 1.1.4b The Harmonic Oscillator Model

The cell potential may be expanded as a Taylor series in  $r^2/a^2$ . The harmonic oscillator model<sup>(32)</sup> is obtained by retaining only the first term (parabolic in  $r$ ) of this expansion

$$^* \omega(r) - \omega(0) \doteq Z\epsilon \left[ 22 \left( \frac{v_0}{v} \right)^4 - 10 \left( \frac{v_0}{v} \right)^2 \right] \frac{r^2}{a^2} \quad (1.12)$$

As may be seen from figure 1.2 this is only a satisfactory approximation at high densities and hence low temperatures.

The frequency,  $\nu$ , of the molecule in this harmonic well is given by

$$\nu^2 = \frac{Z\epsilon}{2\pi^2 m a^2} \left[ 22 \left( \frac{v_0}{v} \right)^4 - 10 \left( \frac{v_0}{v} \right)^2 \right] \quad (1.13)$$

\* this corresponds to the single shell approximation of equation 1.8.

The effect of more distant shells of molecules has been calculated by Corner<sup>(33)</sup>. The coefficient of the attractive part (  $(U_0/U)^2$  ) is increased by 20% but that of the repulsive part by only 1%.

## CHAPTER 1.2 TRANSPORT PROCESSES IN FLUIDS

Two transport processes characteristic of pure fluids are thermal conduction and viscosity. The former process describes a flow of energy occasioned by a temperature gradient and the latter, a flow of momentum arising from a velocity gradient. These flows are directed so as to restore thermal and mechanical equilibrium and are accompanied by an irreversible increase in the entropy of the system.

A third transport process, diffusion, is strictly possible only in a system of more than one component since it describes the elimination of a concentration gradient by the relative motion of distinguishable molecular species. The process of diffusion may be imagined to occur even in a pure system if the molecules are conceived to be labelled in different ways. In this sense one may speak of a self diffusion coefficient, meaning the diffusion of a molecular species into an identical species. It can never be directly observed although types of experimental labelling exist which alter the physical properties of the molecule very little.

### 1.2.1 The Phenomenological Equations of Transport

The three major transport processes are described by the phenomenological equations of Fourier, Newton and Fick:

$$Q = -\lambda \frac{dT}{dx} \quad \text{Fourier's Law} \quad (1.14)$$

$$P_T = -\eta \frac{dV_T}{dx} \quad \text{Newton's Law} \quad (1.15)$$

$$J_i = -D \frac{dc_i}{dx} \quad \text{Fick's Law} \quad (1.16)$$

$Q$  is the flux of heat along  $x$  due to the temperature gradient  $dT/dx$ .  $P_T$  is the transverse stress (equivalent to a flux of transverse momentum along  $x$ ) occasioned by a gradient of transverse velocity  $dV_T/dx$ .  $J_i$  is the flux of matter (species  $i$ ) along  $x$  occasioned by the concentration gradient  $dc_i/dx$ .

Equations 1.14 to 1.16 are the one dimensional equations applicable to isotropic bodies for which  $\lambda$ ,  $\eta$  and  $D$  are scalar constants called respectively the coefficients of thermal conductivity, viscosity and diffusion.

If the equations 1.14 to 1.16 are written so that the fluxes and gradients refer to the same property they become

$$Q = - \frac{\lambda}{\rho C_v} \frac{d}{dx} (\rho C_v T) \quad (1.17)$$

$$P_t = - \frac{\eta}{\rho} \frac{d}{dx} (\rho V_t) \quad (1.18)$$

$$J_i = - D_i \frac{dc_i}{dx} \quad (1.19)$$

where  $\rho$  is the density and  $C_v$  the specific heat. All three equations satisfy the general diffusion equation

$$D_g \nabla^2 G = \frac{dG}{dt} \quad (1.20)$$

The transport coefficients have a positive sign which is a consequence of the necessary increase in entropy of systems which are not in equilibrium. Thermodynamics however gives no information about the magnitude of the coefficients which depends on the detailed molecular processes involved.

### 1.2.2 The Quasi Gaseous Approach: Transport Phenomena in Gases

1.17-1.19

The formal similarity of equations <sub>1.17-1.19</sub> does not, per se, infer a relationship between the three transport coefficients. However if the same molecular mechanism is responsible for each, a close relationship may be expected. Such is the case in a dilute monatomic gas. All three types of transport are caused by the random motion of individual molecules throughout the system. Such molecules carry not only their mass but also the momentum and energy corresponding to their original location. It is not surprising that the crude kinetic theory of gases leads to equality of the transport coefficients of equations 1.17 to 1.19

$$D = \frac{\eta}{\rho} = \frac{\lambda}{\rho C_v} = \frac{\Omega l}{3} = \frac{\left\{ \sqrt{\pi m k T} \right\}}{\pi \sigma^2} \frac{1}{\rho} \quad (1.21)$$

$\Omega$  is the mean molecular velocity and  $l$  is the mean distance traversed between collisions.

More rigorous kinetic theory of gases reveals certain differences between the three transport coefficients. The differences are comparatively minor because the dominant mechanism in the gas phase is the motion of molecules between encounters and not the encounters themselves.

### 1.2.3 Transport in Dense Gases and Liquids

At liquid densities the diffusion coefficient is some five orders of magnitude smaller than in the gas phase at normal pressures. The corresponding values of  $\eta/\rho$  and  $\lambda/\rho C_v$  are only reduced by three orders, so that the coefficients of viscosity and thermal conductivity are actually greater. This arises because, as the density increases an alternative molecular mechanism becomes important for the transport of energy and momentum but not for diffusion. This mechanism is the transport of energy and momentum at encounters over the distance separating the molecules. In the extreme example of colliding rigid spherical molecules transfer occurs instantaneously across the diameter of a molecule.

A satisfactory kinetic theory of transport in dense fluids of real molecules has not been developed, but Enskog<sup>(42)</sup> has developed a theory for rigid spherical molecules with particular regard to the collisional contribution.

#### (a) Enskog's Theory for a Dense Rigid Sphere Fluid

As a fluid is compressed at constant temperature the molecular collision frequency increases due to the reduction in space available to the molecules. However the

increase is less than might be supposed because as the available volume approaches molecular proportions shielding of one molecule by another occurs.

Enskog showed that the collision frequency in a dense gas of rigid spheres differed from the dilute gas expression by a factor,  $\chi$ , depending only on the density and the molecular diameter,  $\sigma$ , and mass,  $m$ ,

$$\chi = 1 + \frac{5}{8} \rho b + 0.2869 \rho^2 b^2 \quad (1.22)$$

where  $b = 2\pi\sigma^3/3m$

Enskog modified the Boltzmann equation for high densities and by the method of Chapman and Enskog<sup>(1)</sup> derived equations for the transport coefficients including contributions due to both the dilute gas mechanism involving molecular motion and the dense gas collisional mechanism. These expressions are

$$\frac{\eta}{\eta_0} = \frac{1}{\chi} + 0.8 b \rho + 0.7614 (b \rho)^2 \chi \quad (1.23)$$

$$\frac{\lambda}{\lambda_0} = \frac{1}{\chi} + 1.2 b \rho + 0.7674 (b \rho)^2 \chi \quad (1.24)$$

where  $\eta_0$  and  $\lambda_0$  are the viscosity and thermal conductivity

of a dilute gas of rigid spheres.

$$\eta_0 = 1.016 \frac{5}{16\sigma^2} \left( \frac{mkT}{\pi} \right)^{1/2} \quad (1.25)$$

$$\lambda_0 = 1.025 \frac{25}{32\sigma^2} \left( \frac{mkT}{\pi} \right)^{1/2} \frac{3k}{2m} \quad (1.26)$$

The contributions due to molecular motion and to collisions in equations 1.23 and 1.14 may be separated giving

$$\frac{\eta_{\text{mot}}}{\eta_0} = \frac{1}{\chi} + \frac{2}{5} \rho b \chi \quad (1.27)$$

$$\frac{\eta_{\text{coll}}}{\eta_0} = 0.4 \rho b \chi + 0.7616 \rho^2 b^2 \chi \quad (1.28)$$

and 
$$\frac{\lambda_{\text{mot}}}{\lambda_0} = \frac{1}{\chi} + 0.4 b \rho \chi \quad (1.29)$$

$$\frac{\lambda_{\text{coll}}}{\lambda_0} = 0.6 \rho b \chi + 0.7557 \rho^2 b^2 \chi \quad (1.30)$$

In both transport processes the term involving molecular motion decreases and that involving collisions increases as the density and hence  $\chi$  also is raised.

Enskog's diffusion coefficient is simply

$$\frac{D}{D_0} = \frac{1}{\chi} \quad (1.31)$$

where  $D_0$  is the diffusion coefficient of the dilute gas.

(b) Theory of Longuet-Higgins and Pople for a Dense Rigid Sphere Fluid

Longuet-Higgins and Pople<sup>(43)</sup> assumed that the molecular motion contribution to energy and momentum transport is negligible at high densities. They showed that it was possible to evaluate the collisional contribution under the assumptions:

1. that the spatial pair distribution function depends only on the local temperature and density and not on the gradients of temperature and velocity,
2. that the velocity distribution function is Maxwellian corresponding to the local temperature and velocity.

They pointed out that the latter assumption can only lead to a solution in the rigid sphere approximation.

Their expressions for the thermal conductivity and viscosity are

$$\eta = \frac{2\sigma}{5} \left( \frac{mkT}{\pi} \right)^{1/2} \left( \frac{P}{kT} - \frac{N}{V} \right) \quad (1.32)$$

$$\lambda = \sigma k \left( \frac{kT}{\pi m} \right)^{1/2} \left( \frac{P}{kT} - \frac{N}{V} \right) \quad (1.33)$$

Using Enskog's expression for  $P$ ,

$$P = \frac{NkT}{V} \left( 1 + \frac{2}{3} \frac{N}{V} \pi \sigma^3 \chi \right) \quad (1.34)$$

and the definitions of  $\lambda_0$ ,  $\eta_0$  and  $\chi$ , equations 1.32 and 1.33 may be written

$$\frac{\eta}{\eta_0} = 0.6016 (b\rho)^2 \chi \quad (1.35)$$

$$\frac{\lambda}{\lambda_0} = 0.3457 (b\rho)^2 \chi \quad (1.36)$$

It has been shown that these expressions correspond to a part of the Enskog expressions which does not depend upon the perturbed portion of the distribution function. They therefore neglect a substantial part of the total contribution to transport in a rigid sphere fluid.

### (c) Comparison of Dense Gas Theories with Experiment

The dense gas theories predict that the transport properties should be related to the dilute gas values by terms involving only the density. In figure 1.3 Enskog's expression for  $\lambda/\lambda_0 b\rho$ ,  $\eta/\eta_0 b\rho$  and  $D/D_0 b\rho$  are plotted as a function of  $b\rho\chi$ .  $\lambda/\lambda_0 b\rho$  has a minimum value 2.938 at  $b\rho\chi = 1.151$ .  $\eta/\eta_0 b\rho$  has a minimum 2.545 at  $b\rho\chi = 1.146$ . The diffusion coefficient decreases monotonically with  $b\rho\chi$ .

Minima in  $\lambda/\rho$  and  $\eta/\rho$  are observed

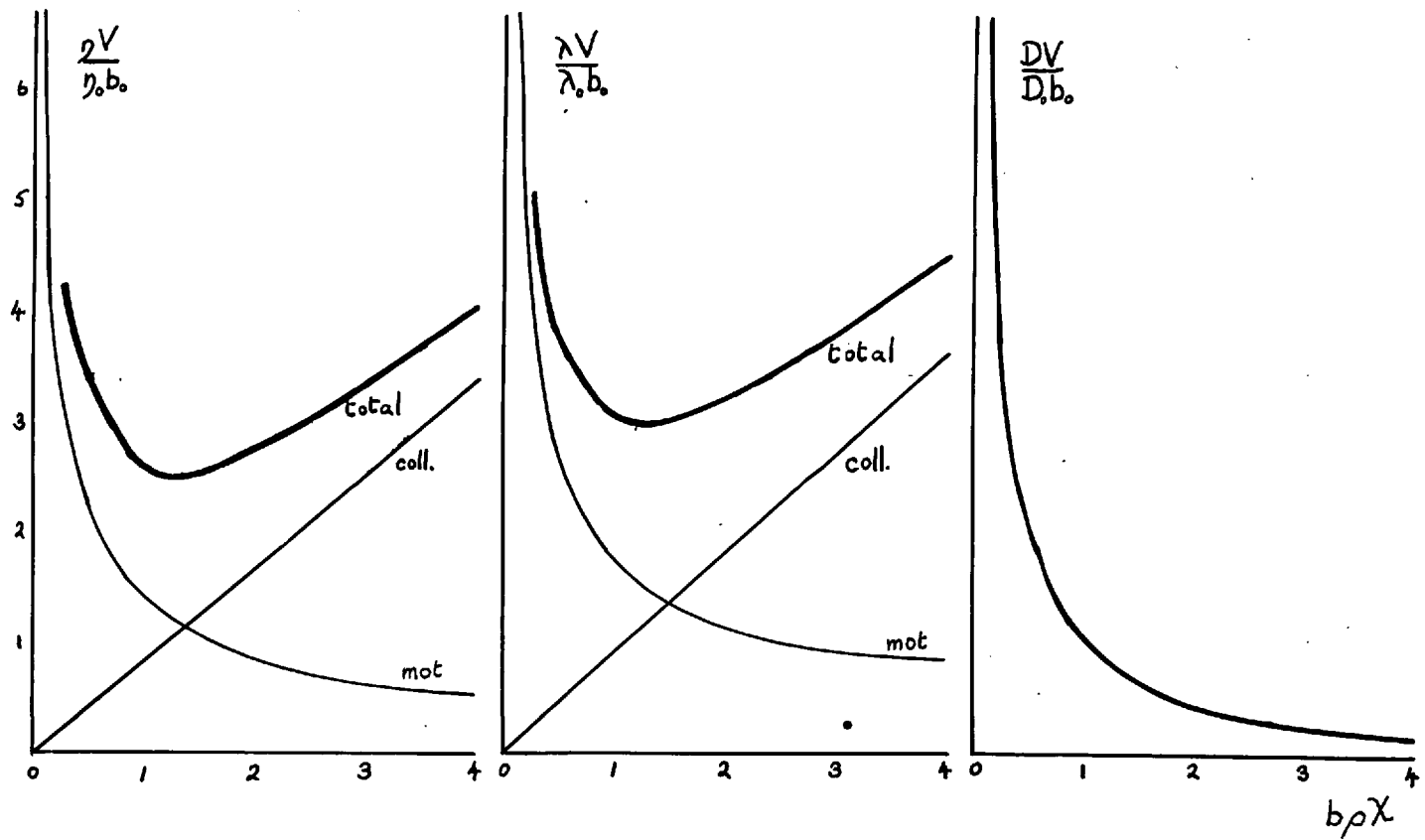


Figure 1.3

experimentally for real gases well above the critical temperature.

In making a numerical comparison between the results of Enskog's theory and experiment, difficulties arise in assigning effective values of  $b$  and  $\chi$  to systems of real molecules which are characterised by a potential containing both attractive and repulsive parts. For real molecules Enskog allowed for the effect of attractive interactions by replacing  $P$  in equation 1.34 by  $P + a\rho^2$  giving

$$P + a\rho^2 = \frac{RT}{M} \rho (1 + b\rho\chi) \quad (1.37)$$

where  $M$  is the molecular weight. Using the experimental pressures and densities corresponding to the minima in  $\eta/\rho$  or  $\lambda/\rho$  for a gas at the temperature required, and using the theoretical value of  $b\rho\chi$  for the minima, the constant,  $a$ , in equation 1.37 may be calculated. The value of  $b\rho\chi$  at other densities is then found by substituting this value of  $a$  back into the equation. An alternative but similar method for calculating suitable values of  $b\rho\chi$  has been used by Michels and Bötzen<sup>(44)</sup>.

Experimental viscosities and thermal conductivities

for compressed nitrogen are compared with calculated values in table 1.1. The viscosity comparison is due to Michels and Gibson<sup>(45)</sup> and the thermal conductivity comparison to Michels and Botzen.

TABLE 1.1

| p(ats) | $\eta \times 10^6$ (exp) | $\eta \times 10^6$ (calc) | p(ats) | $\lambda \times 10^6$ (exp)                                                | $\lambda \times 10^6$ (calc)                                               |
|--------|--------------------------|---------------------------|--------|----------------------------------------------------------------------------|----------------------------------------------------------------------------|
|        | poise                    | poise                     |        | $\frac{\text{cal. cm}^{-1}}{\text{sec}^{-1} \text{ } ^\circ\text{C}^{-1}}$ | $\frac{\text{cal. cm}^{-1}}{\text{sec}^{-1} \text{ } ^\circ\text{C}^{-1}}$ |
| 15.37  | 191.3                    | 181                       | 12.2   | 67.6                                                                       | 72.0                                                                       |
| 57.60  | 198.1                    | 190                       | 62.6   | 73.4                                                                       | 76.8                                                                       |
| 104.5  | 208.8                    | 205                       | 116.5  | 82.8                                                                       | 85.3                                                                       |
| 212.4  | 237.3                    | 224                       | 228.1  | 102                                                                        | 104                                                                        |
| 320.4  | 273.7                    | 266                       | 300    | 115                                                                        | 115                                                                        |
| 430.2  | 312.9                    | 308                       | 453    | 142                                                                        | 140                                                                        |
| 541.7  | 350.9                    | 348                       | 521    | 152                                                                        | 150                                                                        |
| 630.4  | 378.6                    | 380                       | 603    | 165                                                                        | 163                                                                        |
| 742.1  | 416.3                    | 418                       | 783    | 189                                                                        | 189                                                                        |
| 854.1  | 455.0                    | 455                       | 889    | 203                                                                        | 204                                                                        |
| 965.8  | 491.3                    | 492                       | 1080   | 222                                                                        | 228                                                                        |

Sangers has determined the viscosity and thermal conductivity of compressed argon between 25°C and 30°C. Experiment and theory agree within 2-3% up to moderate pressures. At a 600 Amagats the predicted viscosity and thermal conductivity are 15% and 20% low respectively.

For simple molecules at moderate densities it may be concluded that the most important features of the viscosity and thermal conductivity are included in Enskog's theory. It is not, however, adequate to deal with systems near to criticality.

(d) The Temperature Dependence of Viscosity and Thermal Conductivity on Enskog's Model

Enskog's equations 1.23 and 1.24 may be written

$$\lambda = \text{Constant } T^{1/2} f(\rho) \quad (1.38)$$

$$\eta = \text{Constant } T^{1/2} g(\rho) \quad (1.39)$$

The temperature dependences of  $\eta$  and  $\lambda$  may be obtained by differentiation in the form

$$\frac{1}{\lambda} \frac{d\lambda}{dT} = \frac{1}{2T} + \frac{f'}{f} \propto \quad (1.40)$$

$$\frac{1}{\eta} \frac{d\eta}{dT} = \frac{1}{2T} + \frac{g'}{g} \propto \quad (1.41)$$

where the differentiation is understood to be at constant

pressure and thus  $\alpha = \rho^{-1} (d\rho/dT)_p$ . Since  $\alpha$  is negative the temperature dependences will be positive or negative according to whether the first or second term in each of equations 1.40, 1.41 is the greater. Both  $f'/f$  and  $g'/g$  increase from low densities and lead to a change in sign of the temperature coefficients at high densities.

This change of sign is observed in experimental work on dense gases and accords with the observed negative temperature coefficients in the liquid state.

The detailed expressions for  $f$  and  $g$  indicate that both  $\eta$  and  $\lambda$  should have a similar dependence on temperature and that the ratio  $\lambda/\eta C_v$  should reach a limiting value, 2.5, at infinite compression. 2.5 is also the limiting value of this ratio in the dilute gas but at intermediate densities it passes through a maximum at 2.98.

Sengers<sup>(46)</sup> has compared the experimental values of  $\lambda/\eta C_v$  for argon at 50°C with those predicted by the Enskog expressions. He showed that the experimental values fall increasingly below the theoretical ones as the density increases. However, if instead of using experimental values of  $C_v$  for argon, one compares the ratio  $m\lambda/1.5k\eta$

with the theoretical curve  $\lambda/c_v\eta$  good agreement is obtained over the whole range of densities (1 to 600 Amagat). This agreement suggests that the effective molecular specific heat for thermal conduction remains  $3k/2$  (specific heat of translation) even at densities where the total specific heat of argon contains a considerable potential energy contribution. Whether this situation obtains at even higher densities and in the liquid state is of considerable interest.

TABLE 1.2 - Experimental Values of  $m\lambda/k\eta$  for Simple Liquids

| <u>Liquid</u>        | Temp.<br>°K | $m\lambda/k\eta$ |
|----------------------|-------------|------------------|
| Benzene              | 288.2       | 2.02             |
|                      | 298.2       | 2.28             |
|                      | 308.2       | 2.55             |
|                      | 318.2       | 2.83             |
| Carbon Tetrachloride | 298.2       | 2.19             |
|                      | 308.2       | 2.42             |
|                      | 318.2       | 2.78             |
| Argon                | 84.2        | 2.16             |
|                      | 87.3        | 2.31             |
| Nitrogen             | 69.1        | 2.20             |
|                      | 71.4        | 2.39             |
|                      | 77.3        | 2.98             |
| Carbon Monoxide      | 72.0        | 2.19             |
|                      | 77.7        | 2.64             |
|                      | 80.8        | 2.80             |
| Methane              | 93.2        | 2.21             |
|                      | 103.2       | 2.75             |
|                      | 108.2       | 2.98             |

The ratio seems to have roughly the value 2.5 predicted by Longuet-Higgins and Pople for rigid spheres although the temperature dependence even for the simplest molecule, argon, is marked, reflecting the different temperature coefficients of  $\lambda$  and  $\eta$  which are always found in real liquids.

It must be remembered that the above theory can only be reasonably applied to simple, quasi spherical molecules. For molecules of complex shape at liquid densities departures from simple behaviour are to be expected. A study of these departures may point the way to a more rigorous theory of complicated systems which is at present lacking. The behaviour of  $m\lambda/k\eta$  for the large polyphenyl molecules is discussed in section 3.2.

#### 1.2.4 Kirkwood's Theory of Transport for Liquids of more Realistic Molecules

The calculation of transport coefficients requires the specific consideration of molecular dynamics. The rigid sphere assumption which allowed Enskog to develop a theory of dense fluids is sufficient to ensure that only binary encounters occur. If this assumption is relaxed it is not possible to avoid considering the dynamics of multiple collisions for which no rigorous treatment has yet proved possible.

Kirkwood<sup>(1)</sup> has developed a theory of transport in non rigid monatomic fluids by analogy with the theory of Brownian motion. A molecule moving with a velocity exceeding that of its neighbours is retarded by its interaction with them. The retardation is characterised, according to Kirkwood, by a molecular friction coefficient similar to that which arises in the theory of Brownian motion. The self diffusion coefficient is related directly to this friction coefficient,  $\zeta$ , by the relation

$$D = \frac{kT}{\zeta} \quad (1.42)$$

Using  $\zeta$ , an expression for the non-equilibrium distribution function was derived in terms of the equilibrium

distribution function  $g(r)$ . An equation for the pressure tensor was derived in terms of the non-equilibrium distribution function and by comparing this equation with the phenomenological equation an expression for the shear viscosity was obtained. In a similar manner Irving and Kirkwood<sup>(47)</sup> derived an expression for the heat flux vector which by comparison with phenomenological equation 1.17 yields the thermal conductivity.

As in Enskog's theory two distinct contributions arise: the one from individual molecular motion, the other from the interaction of molecular pairs.

One of the major obstacles in the development of this theory is the calculation of  $\eta$  in terms of the intermolecular forces and the radial distribution function.

Kirkwood, Buff and Green<sup>(48)</sup> have suggested the relation

$$\eta = \frac{4\pi\sigma\rho}{3} \int_c^\infty \left[ \frac{d^3\phi}{dx^3} + \frac{2}{x} \frac{d\phi}{dx} \right] x^3 g(x) dx \quad (1.43)$$

where  $\phi$  is the intermolecular potential,  $x = r/\sigma$

where  $\sigma$  is the low velocity collision diameter.

Using the experimental data of Eisenstein and Gingrich<sup>(49)</sup> supplemented by experimental information,

Kirkwood, Buff and Green calculated the radial distribution function for liquid argon at 89°K which together with intermolecular force constants they used to calculate  $\eta$  by numerical integration of equation 1.43. They obtained a value  $4.84 \times 10^{-10} \text{ g. sec}^{-1}$ . An alternative calculation has yielded a value  $2.85 \times 10^{-10} \text{ g. sec}^{-1}$ . These values may be compared with the value  $5.93 \times 10^{-10} \text{ g. sec}^{-1}$  obtained from self diffusion data using equation 1.42, Calculated values of  $\eta$  and  $\lambda$  based on these estimates of  $\eta$  are given in table 1.3.

TABLE 1.3 - Calculated and Experimental Transport Coefficients of Liquid Argon at 89°K

|                                                                                          | $\eta$<br>g. sec. $^{-1}$ | Calc. | Exp. |
|------------------------------------------------------------------------------------------|---------------------------|-------|------|
| $\eta \quad 10^{-3} \text{ poise}$                                                       | 4.84                      | 1.27  | 2.39 |
|                                                                                          | 2.85                      | 0.73  |      |
| $\lambda \quad 10^{-4} \text{ J. cm}^{-1} \text{ sec}^{-1} \text{ } ^\circ\text{C}^{-1}$ | 2.85                      | 4.1   | 2.94 |

### 1.2.5 Transport Coefficients in Liquid Mixtures

To avoid the introduction of a detailed rigorous theory of the non equilibrium distribution function an alternative approach was introduced by Bearman and Kirkwood<sup>(50)</sup> and subsequently developed by Bearman<sup>(51)</sup> for the transport properties of mixtures. The expressions for viscosity and thermal conductivity reduce in the limit to equations of Kirkwood, Buff and Green and Irving and Kirkwood for a pure liquid. The equations are complex but undergo considerable simplification for binary regular solutions in which the radial distribution function is independent of composition and no volume change on mixing occurs. Under these conditions the following relationships were derived:

#### Diffusion

$$\frac{D_{12c}}{D_{2c}} = \frac{v_2}{v_1} \quad (1.44)$$

#### Viscosity

$$\frac{x_1}{x_2} v_1^2 \left[ D_{12} \eta - D_1^0 \eta_1 \right] + 2 v_1 v_2 D_{12} \eta + \frac{x_2}{x_1} v_2^2 \left[ D_{12} \eta - D_1^0 \eta_2 \right] = A_{12} \quad (1.45)$$

#### Thermal Conductivity

$$\frac{x_1}{x_2} v_1^2 \left[ \frac{\lambda}{D_{12c}} - \frac{\lambda_1}{D_1^0} \right] + 2 v_1 v_2 \frac{\lambda}{D_{12c}} + \frac{x_2}{x_1} v_2^2 \left[ \frac{\lambda}{D_{12c}} - \frac{\lambda_2}{D_1^0} \right] = B_{12} \quad (1.46)$$

$D_{1x}$  and  $D_{2x}$  are self diffusion coefficients of species 1 and 2 in the mixture;  $D_1^\infty$  and  $D_2^\infty$  are the self diffusion coefficients of species 1 and 2 at infinite dilution;  $D_1^0$  and  $D_2^0$  are self diffusion coefficients in the pure state.  $v_1$  and  $v_2$  are the molecular volumes of species 1 and 2 and  $x_1$  and  $x_2$  are the mole fractions.  $\lambda$ ,  $\lambda_1$  and  $\lambda_2$  are the thermal conductivities in the mixture and in species 1 and 2 respectively. Similar meanings apply to the viscosities.  $A_{12}$  and  $B_{12}$  are constants independent of the mole fraction.

Equations 1.45, 1.46 may be rewritten to give the viscosity,  $\eta$ , and thermal conductivity,  $\lambda$ , of the mixture

$$\eta = x_1^2 \eta_1 \frac{v_1^2}{v^2} \frac{D_1^0}{D_{1x}} + x_1 x_2 A_{12} \frac{1}{D_{1x} v^2} + x_2^2 \eta_2 \frac{v_2^2}{v^2} \frac{D_2^\infty}{D_{1x}} \quad (1.47)$$

$$\lambda = x_1^2 \lambda_1 \frac{v_1^2}{v^2} \frac{D_{1x}}{D_1^0} + x_1 x_2 B_{12} \frac{D_{1x}}{v^2} + x_2^2 \lambda_2 \frac{v_2^2}{v^2} \frac{D_{1x}}{D_2^\infty} \quad (1.48)$$

where  $v = x_1 v_1 + x_2 v_2$

Using equations 1.47 and 1.48, it has been shown<sup>(52)</sup> that a complete set of relationships between the transport coefficients can be derived.

### CHAPTER 1.3 QUASI CRYSTALLINE MODELS FOR THE THERMAL CONDUCTIVITY OF LIQUIDS

Debye<sup>(53)</sup> conceived the solid to be an elastic continuum with various modes of vibration which were equivalent to the passage of acoustic waves. Such waves were scattered by mutual interaction and gave rise over a sufficiently large region to a diffusional process of energy transfer. If the amplitude of a wave is reduced by scattering to  $e^{-1}$  of its value in length,  $\ell$ , the thermal conductivity is given by

$$\lambda = C \ell U \nu C_v \quad (1.49)$$

in which  $U$  is the wave velocity,  $\nu C_v$  the heat capacity per unit volume, and  $C$  a numerical factor.

The three theories of liquids to be described arrive at expressions of the same fundamental form.

#### 1.3.1 Bridgman's Theory (1931)

Bridgman<sup>(40)</sup> was the first to put forward a theory of liquid thermal conduction with a plausible basis. He supposed that the liquid would be represented by a simple cubic array of molecules separated by a minimum distance,  $\delta$ . In a temperature gradient,  $dT/dx$ , the energy difference

between molecules in adjacent layers perpendicular to the gradient is  $C_v \delta dT/dx$ . (He further assumed the effective specific heat for thermal conduction to be  $3k$  corresponding to 3 kinetic and 3 potential degrees of freedom.) The energy unit,  $\delta C_v dT/dx$ , is conceived to be handed down a row of molecules with the velocity of sound in the liquid,  $U$ . Thus the total energy transferred per unit time across a unit plane (containing  $\delta^{-2}$  molecules) is given by

$$\left(3k \frac{dT}{dx} \delta\right) \cdot \frac{U}{\delta} \frac{1}{\delta^2} \quad (1.50)$$

and hence by the definition of thermal conductivity this is also equal to  $\lambda dT/dx$

whence 
$$\lambda = \frac{3kU}{\delta^2}$$

or, writing  $\delta = (V/N)^{1/3}$  where  $V$  is the molar volume, and  $N$ , Avogadro's Number,

$$\lambda = 3kU \left(\frac{N}{V}\right)^{2/3} \quad (1.51)$$

Jeffreys<sup>(54)</sup> has pointed out that this picture is oversimplified, and has shown that a similar formula may be reached using a slightly more sophisticated approach. The liquid is

likened to the solid where the thermal motion is successfully treated as the motion of "elastic" waves. Jeffreys suggests that in the liquid disorder is so great that these waves are scattered in lengths comparable with the distance separating molecules.

In this picture liquids are indistinguishable from amorphous solids, for which the thermal conductivity has been calculated with some success using Debye's expression

$$\lambda = \frac{v C_v \ell U}{2} \quad (1.52)$$

( $C_v$  is put equal to  $\frac{1}{2}$  by analogy with kinetic theory)

With a specific heat of  $3k$  ergs. per molecule, per  $^{\circ}\text{C}$ ,

$v C_v = 3k N/V$  and the expression becomes

$$= \frac{3k N \ell U}{2V} \quad (1.53)$$

which is equivalent to Bridgman's expression if  $\ell$  is put equal to  $2(V/N)^{1/3}$  i.e., twice the intermolecular spacing.

Bridgman's calculated values and measured values are compared in table 1.4, column 5. In table 3.5 experimental values for a number of simple liquids are compared with values calculated using Bridgman's equation. It is seen that for these molecules agreement is less good

than for the more complicated molecules on which Bridgman originally tested his equation.

### 1.3.2 Theory of Kincaid and Eyring

Kincaid and Eyring<sup>(55)</sup> derived an equation for liquid thermal conductivity by analogy with gas kinetic theory. Their equation\* is similar to that of Bridgman but contains a correction for the internal specific heat of the molecules akin to Eucken's correction for the thermal conductivity of gas.  $\gamma'$  is the ratio  $C_P/C_V$  in the vapour phase and  $\gamma$  the same ratio obtained from velocity of sound data. The term  $\alpha C_V$  is the effective specific heat for the thermal conduction. In assigning a value to this term Kincaid and Eyring differ from Bridgman on a fundamental point. They assume that only kinetic terms are important, but, that in addition to vibrational modes, those of rotation and liberation also contribute. Like Bridgman they attribute a value of  $3k$  to polyatomic

---

\*

$$\lambda = \frac{1}{12} (9\gamma' - 5) \left( \frac{S}{\pi \gamma} \right)^{\frac{1}{2}} \left( \frac{N}{V} \right)^{\frac{2}{3}} U(\alpha C_V) \quad (1.54)$$

molecules and in these cases the two theories differ by only a small numerical factor.

TABLE 1.4 - Calculated and Experimental Values of  $\lambda$

| Exp.<br>refs. | Liquid            | T<br>°C | $\lambda$ exp.                                                     | $\lambda$ Bridgman                                                 | $\lambda$ Kincaid<br>Eyring |
|---------------|-------------------|---------|--------------------------------------------------------------------|--------------------------------------------------------------------|-----------------------------|
|               |                   |         | $10^{-4} \text{J cm}^{-1} \text{sec}^{-1} \text{ } ^\circ\text{C}$ | $10^{-4} \text{J cm}^{-1} \text{sec}^{-1} \text{ } ^\circ\text{C}$ |                             |
| 56            | Methyl Alcohol    | 30      | 20.15*                                                             | 27.4                                                               | 22.3                        |
| 40            | Ethyl Alcohol     | 30      | 16.1                                                               | 21.8                                                               | 19.2                        |
| 56            | Acetone           | 30      | 16.1*                                                              | 18.5                                                               | 16.3                        |
| 40            | Carbon disulphide | 30      | 15.9                                                               | 21.9                                                               | 16.1                        |
| 56            | Ethyl Bromide     | 30      | 10.2*                                                              | 14.5                                                               | 12.8                        |
| 56            | Ethyl Iodide      | 30      | 8.9*                                                               | 12.1                                                               | 10.6                        |

\* Values at 20°C, nevertheless more accurate than Bridgman's measured values at 30°C

However, to monatomic and diatomic molecules they attribute values of  $3k/2$  and  $5k/2$  respectively.

Results for these molecules based on equation 1.61 are given in table 3.5, column 6. With the exception of methane the values are considerably better than those of Bridgman.

An extension of the quasi crystalline approach advanced by Horrocks and McLaughlin<sup>(57)</sup> is discussed in section 3.1.

## CHAPTER 1.4 THERMAL CONDUCTIVITY OF DIELECTRIC LIQUIDS

A discussion of liquid thermal conductivity is restricted by the availability and reliability of data. Although during the last decade various workers have claimed accuracies of 1 or 2% much previous work must be regarded with reserve. The results for water compiled by Powell<sup>(34)</sup> illustrate the discrepancies which can occur. Since much of the work, even recently, has been carried out over a small range near room temperatures the variation of  $\lambda$  with temperature is even less reliable,

All liquids have thermal conductivities lower than the corresponding solids (N.B. An exception is liquid bismuth, but this does not rank as a dielectric liquid). The majority have thermal conductivities in the range  $8 \times 10^{-4} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$  to  $3 \times 10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ . Exceptions are water and liquid ammonia which have anomalously high thermal conductivities ( $\sim 6 \times 10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ ) and the lower alkyl halides which have extremely low thermal conductivities ( $\sim 6 \times 10^{-4} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ )

The thermal conductivities of nearly all liquids decrease with temperature in marked contrast to the behaviour of gases. A similar contrast occurs between the temperature

dependence of liquid and gas viscosities.

The temperature dependence of thermal conductivity may usually be expressed with sufficient accuracy in the form

$$\lambda = A + B\theta \quad (1.52)$$

where  $\theta$  is the temperature in  $^{\circ}\text{C}$  and  $A$  is the conductivity at  $0^{\circ}\text{C}$ .  $B$  is a negative constant lying between  $-5 \times 10^{-4}$  and  $-2 \times 10^{-3}$ .

#### 1.4.1 Liquids having Anomalous Thermal Conductivities

Water and sulphur have positive temperature coefficients: both are associated in the liquid phase and dissociate as the temperature is raised.

The thermal conductivity of sulphur shows a small anomaly at  $160^{\circ}\text{C}$ . This is at a temperature where the viscosity indicates that the molecular structure of the liquid changes radically. Prins<sup>(36)</sup> has studied liquid sulphur using x-ray diffraction techniques and reports that change is not so abrupt as the viscosity behaviour suggests.

Anomalies have been reported<sup>(37)</sup> in the thermal conductivity of liquid paraffins (chain lengths 12 to 18). They take the form of a downward step of some 3% covering a temperature range of roughly  $15^{\circ}\text{C}$ . However, since the

method of determination employed a temperature interval of  $10^{\circ}\text{C}$  it is possible that the step is much sharper, even discontinuous. It has been suggested that the solid state transition which occurs in paraffins<sup>(38,39)</sup> with chain lengths exceeding 25 carbon atoms occurs in the liquid phase for shorter chain paraffins with lower melting points.

#### 1.4.2 The Pressure Dependence of Thermal Conductivity

The effect of pressure on the thermal conductivity of liquids has been less studied than that of temperature. An important series of investigations was made by Bridgman<sup>(40,41)</sup> up to pressures of  $12,000 \text{ kg. cm}^{-2}$ . He found that the thermal conductivity of all liquids increased with pressure and that the effect was greater at higher temperatures. The isobaric temperature coefficient decreased rapidly and changed sign for all the liquids investigated at pressures near to  $3,000 \text{ kg. cm}^{-2}$ .

## CHAPTER 1.5 : A REVIEW OF EXISTING METHODS FOR THE MEASUREMENT OF LIQUID THERMAL CONDUCTIVITIES

The measurement is frequently undertaken by comparative methods. However, since it is not uncommon to find reported values which differ by several percent, greater importance attaches to absolute methods of determination. Discrepancies in values obtained by different workers probably arise from inadequate suppression of heat losses and convection in different types of apparatus. A brief survey of the methods available is not out of place and serves to focus attention upon the nature of the difficulties inherent in the measurement.

The thermal conductivity of a liquid may in principle be determined in any apparatus which furnishes suitable boundary conditions to the heat conduction equation

$$\frac{\partial T}{\partial t} = \kappa \nabla^2 T \quad (1.53)$$

The solution of this equation together with a knowledge of the temperature and heat flux at the boundaries leads to a value of  $\kappa = \lambda / \rho C$ , the thermal diffusivity. To evaluate  $\lambda$  additional knowledge of the heat capacity per unit volume is required. This approach to  $\lambda$  has been

(42)  
rarely used in studying liquids and a method is usually sought  
which provides  $\lambda$  directly.

#### 1.5.1 Steady State Methods

The heat capacity may be avoided by using the so called steady state methods in which the temperature distribution is stationary and solutions of equation 1.53 contain only  $\lambda$ .

To facilitate interpretation of the measurements the apparatus is invariably of simple geometry. Commonly used are parallel plates, concentric cylinders and even concentric spheres; the heat flux possessing plane, cylindrical and spherical symmetry respectively. Boundary temperatures are usually measured with the aid of thermocouples whose space requirements are small and which may be situated very close to the boundaries themselves. The gradient of refractive index in the liquid medium has also been used<sup>(43, 44)</sup> but this entails an additional knowledge of the liquid and is, in any case, unsuitable for mixtures in which Soret demixing may cause confusion (page 63, ref. 13). Where electrical heating is used it is customary to measure the heat input directly but heat lost to cooling fluids at the cold

boundary has also been measured.<sup>(43)</sup>

Since a considerable period is required to establish steady state conditions the geometry must be such as to eliminate convection.

Parallel Plate Apparatus: Parallel plate boundaries are mounted horizontally and heated vertically from above. Extremely accurate levelling is required and the surfaces must be accurately flat and parallel. In the absence of horizontal temperature gradients such an arrangement is not susceptible to convection. However horizontal gradients are difficult to avoid at the edges of the liquid layer<sup>(45)</sup> particularly where this is of considerable thickness. Moreover, in transparent media direct radioactive heat transfer between the boundaries becomes increasingly important as the layer<sup>(47)</sup> thickness increases; although both conduction and radiation decrease with the separation of the plates the latter falls off less rapidly than the former. Corrections for the contribution of radiation are difficult to make since they depend upon the nature of the boundary surfaces as well as that of the medium. Extremely thin layers ( $< 1 \text{ mm}$ ) have been used to minimise this effect although they have<sup>(46)</sup>

the disadvantage of demanding greater precision in the construction of the apparatus and measurement of the liquid layer thickness. The most recent and probably the best determinations have been made using layers of intermediate depth (  $\sim$  3 mms).

The Concentric Cylinder Apparatus: Much that has been said about parallel plates applies also to concentric cylinders . They must be precisely centred and of accurately known dimensions. Mounted vertically a sufficient condition for the absence of convection in this apparatus is that the product of the Grashof and Prandtl numbers should be less than 1000. This condition limits the temperature differential and the thickness of the annular liquid layer to values even smaller than are necessary in the parallel plate apparatus.

In both parallel plate and concentric cylinder methods the ideally simple geometry of the temperature field is modified by the proximity of the ends. Edge effects have already been mentioned as determining the onset of convection in horizontal liquid layers but, even in the absence of convection, they limit the accuracy of the simple steady state equations. Many of the ingenious methods used in the past to compensate these end effects (notably that of Bridgman

and subsequently Smith<sup>(51)</sup> are now known to be inadequate.

More recently, much improved methods have been devised.

The parallel plate apparatus of Challoner and Powell<sup>(52)</sup> and that then  
(53, 54)  
of Riedel are among the best of these.

(55)  
The Concentric Sphere Apparatus: Riedel measured the heat flux through a spherical shell of liquid enclosed between two spherical copper walls. The results obtained compared well with those previously obtained by him using concentric cylinders and parallel plates. Although this geometry overcomes the edge effects difficulties of construction preclude its more frequent use.

The Hot Wire Method: In an increasingly popular modification of the concentric cylinder method, the inner cylindrical boundary is reduced to a fine wire whose temperature is determined either by means of an attached thermocouple or by measuring its resistance. To avoid convection the outer cylindrical boundary must also be reduced in diameter. The method is thus useful where only small quantities of material are available. As a result of the overall reduction in size the steady state is established more quickly so that measurements may be made with greater speed.

End effects are localised by the greater ratio of length to diameter and by measuring temperatures away from the ends, they may be eliminated. Measurement of the outer boundary temperature presents some difficulty and not infrequently the temperature of the containing thermostat is measured and a correction applied for conduction through the cylinder walls. In order to apply the radial flow equation a very high degree of precision in boring the outer cylinder and in centering the axial wire is needed. This precision is so difficult to achieve that studies have recently  
(56)  
been made on eccentrically mounted wires and are said to give satisfactory results.

### 1.5.2 Non-Steady State Methods

Of non-steady state methods which have found application in studying liquids the majority employ a hot wire cell. An exception is the transient conduction method (57) of Schmidt and Sellschöpp with which they measured the thermal conductivity of water. Their method called for a detailed knowledge of the dimensions of the apparatus in the case of steady state measurements.

The Transient Conduction Hot Wire Method The rise in temperature of a fine electrically heated wire immersed in the liquid is measured as a function of time following the initiation of heating. The primary objection to transient methods, namely that they yield the thermal diffusivity, is removed in this case, since it is possible to choose the cell dimensions and operating conditions in such a way that the measurement yields  $\lambda$  directly. (60)

The History of the Method: (58) In 1931 Stalhane and Pyk showed empirically that the rise in temperature of a discontinuously heated wire varied logarithmically with time at a rate depending upon the thermal conductivity of the medium. (59) Attention was drawn (1932) to the solution of the heat equation

for a mathematical line source in an extended medium and its modification for a source of finite but small diameters. Subsequently Pfriem<sup>(61)</sup> and Fischer<sup>(62)</sup> developed solutions describing the rise in temperature in a laterally restricted medium covering the approach to the steady state. Van der Held and van Drunen<sup>(63)</sup> (1949) further developed the analysis of the method and made measurements on several liquids using an electrically heated source which incorporated a thermocouple. They showed in a subsequent paper that<sup>(64)</sup> their original approach was over-simplified and put forward an improved analysis which unfortunately lacked the computational simplicity of its predecessor. These difficulties arose because the compound heat source was necessarily of considerable diameter. In 1955, a much smaller diameter source was successfully used by Gillam and Lamm<sup>(65)</sup>. Resistance was used as measure of the wire temperature. "Instantaneous" resistance measurements were made by photographing the deflection of a galvanometer detector in a bridge circuit containing the hot wire. Corrections were applied for the response of the galvanometer. Although satisfactory results were obtained for water and glycerine no further work has been published.

### 1.5.3 Reasons for Adopting the Transient Hot-Wire Method

The transient conduction method has certain advantages which will be stated here and subsequently justified in a detailed consideration of the method.

1. Although delicacy is needed in the construction of a cell, precise centering of the heater and detailed knowledge of the dimensions are not required.
2. Construction may be of glass and noble metals only and so resistant to chemical attack and easily cleaned.
3. The cell is of moderate size (15 cms. long, 1 cm. diameter) and so does not present insuperable problems of temperature control even at high temperatures.
4. End effects and extraneous heat losses are negligible.
5. The contribution of infra red radiation to the heat transfer may be neglected up to fairly high temperatures (page 103 ).
6. Convection may be avoided by limiting the duration of measurement to a short interval following the initiation of heating.
7. The short period of measurement is particularly suited to studying mixtures temperature gradients established over

long periods may, in certain cases, result in considerable demixing.

It will be shown that with the aid of modern recording equipment the technique is comparable in accuracy with the best available steady state methods.

## CHAPTER 2.1: THERMAL CONDUCTIVITY MEASUREMENT

### 2.1.1 Theory of the Selected Method

#### a. The Transient Conduction hot wire cell

The equation for heat conduction problems of cylindrical symmetry may be written

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} - \frac{1}{k} \frac{\partial T}{\partial t} = 0 \quad (2.1)$$

The solution of this equation for an infinite line source of heat, under the initial condition of uniform temperature, is<sup>(1)</sup>

$$T(r,t) = \frac{q_L}{4\pi\lambda} \left( Ei \left( \frac{-r^2}{4\kappa t} \right) \right) \quad (2.2)$$

$T$  being referred to the initial temperature.  $-Ei(-x)$  is the exponential integral<sup>(6)</sup> which for a fixed radius  $r=a$  may be expanded<sup>(2)</sup> as a series in  $1/t$ .

$$T(a,t) = \frac{q_L}{4\pi\lambda} \left( \ln t + \ln \frac{4\kappa}{a^2} + \frac{a^2}{4\kappa t} \dots \right) \quad (2.3)$$

Thus provided that  $\kappa t/a^2$  is sufficiently large, in the range  $t_1 < t_2$ ,

$$T(a,t_2) - T(a,t_1) = \frac{q_L}{4\pi\lambda} \ln \frac{t_2}{t_1} \quad (2.4)$$

It is noteworthy that this approximate expression does not contain the thermal diffusivity.

The behaviour of a hot wire cell limited both in

length and diameter will, under certain conditions, be shown to satisfy equation (2.4).

### Effect of Finite Source Diameter

A finite diameter source introduces an inner boundary condition for the solution of (2.1). For a wire of radius,  $a$ , the following solution is given by Carslaw and Jaeger<sup>(3)</sup>

$$T(a,t) = \frac{q_0}{4\pi\lambda} \left( \ln t + \ln \frac{4\kappa}{a^2} + \frac{a^2}{4\kappa t} + \frac{\alpha-2}{2\alpha} \frac{a^2}{\kappa t} \ln \frac{4\kappa t}{a^2} \right) \quad (2.5)$$

The wire is assumed to be perfectly conducting and thus

$T(a,t)$  is the temperature over the whole cross section

It can be shown<sup>(2)</sup> that the finite thermal conductivity of

platinum does not invalidate equation (2.5).  $\alpha = 2c\rho/c_0\rho_0$

where  $c\rho$  and  $c_0\rho_0$  are the volume heat capacities of the medium and wire respectively.

For sufficiently large values of  $t$  the term involving the heat capacities tends to zero and (2.5) approaches (2.4).

### Effect of Limited Extension of the Medium

In practice, because of the limited extension of the medium surrounding the heat source, a steady state is eventually established. The approach to this condition has been discussed both by Pfriem<sup>(4)</sup> and Fischer<sup>(5)</sup> for an

annulus of material whose outer surface ( at  $r = b$  )

is held at constant temperature. Fischer's expression

for the wire temperature  $T(a,t)$  may be written in the

form

$$T(a,t) = \frac{q_0}{4\pi\lambda} \left[ 2 \ln \frac{b}{a} - 4 \sum_{n=1}^{\infty} \frac{e^{-\kappa k_n^2 t}}{k_n^2 a^2 \left( \left( \frac{J_1(k_n a)}{J_0(k_n b)} \right)^2 - 1 \right)} \right] \quad (2.6)$$

where the running terms  $k_n$  in the series are roots of the equation

$$J_0(k_n b) N_1(k_n a) - N_0(k_n b) J_1(k_n a) = 0 \quad (2.7)$$

$J_i(x)$  and  $N_i(x)$  are the  $i$ th order Bessel

Functions of the first and second kinds<sup>(1a)</sup> respectively.

Equation (2.6) tends toward the solution (2.5) for sufficiently

short times. For large values of  $t$  the summation

disappears leaving the familiar equation for steady state

heat flow between coaxial cylinders.

Equation (2.6) may be simplified for the purposes

of calculation provided that

$$\frac{a}{b} g_n \ll 1 \quad (2.8)$$

where  $g_n = k_n b$  and hence  $a g_n / b = k_n a$

Using (2.8) and (2.7)

$$\frac{J_0(g_n)}{N_0(g_n)} \doteq - \frac{\pi a^2 g_n^2}{4 b^2} \quad (2.9)$$

Substituting (2.9) in the original expression (2.6) and remembering that  $\lim_{\lambda \rightarrow 0} \int_0^\lambda J_0(x) N_0(x) dx = 2/\pi$

yields

$$T(a,t) = \frac{q_0}{4\pi\lambda} \left[ 2 \ln \frac{b}{a} - 4 \sum_{n=1}^{\infty} \frac{e^{-\kappa g_n^2 t/b^2}}{\left( \frac{2}{\pi N_0(g_n)} \right)^2 - \frac{g_n^2 a^2}{b^2}} \right] \quad (2.10)$$

which, with the  $g_n$  given by equation (2.9), is valid up to terms in the series for which condition (2.3) fails,

For times which are not too short, the series converges sufficiently rapidly to be sensibly unaffected by the truncation. It follows from the inequality (2.8) that

$$a^2 g_n^2 / b^2 \ll 1 \quad \text{and thus it is possible to}$$

approximate (2.9) by

$$J_0(g_n) = 0 \quad (2.11)$$

the roots of which are well known<sup>(6)</sup>.

In figure 2.1 equations (2.10) and (2.5) are used to plot  $4\pi\lambda T(a,t)/q_0$  against  $\kappa t/a^2$  over a wide range.

For a considerable interval, depending upon the parameters

$\alpha$  and  $b/a$ , the temperature is closely

represented by (2.4). The limitations of the present

apparatus are discussed further on page 80.

### End Effects

So far the heat source has been assumed infinitely

$$\frac{4\pi\lambda T}{q_L}$$

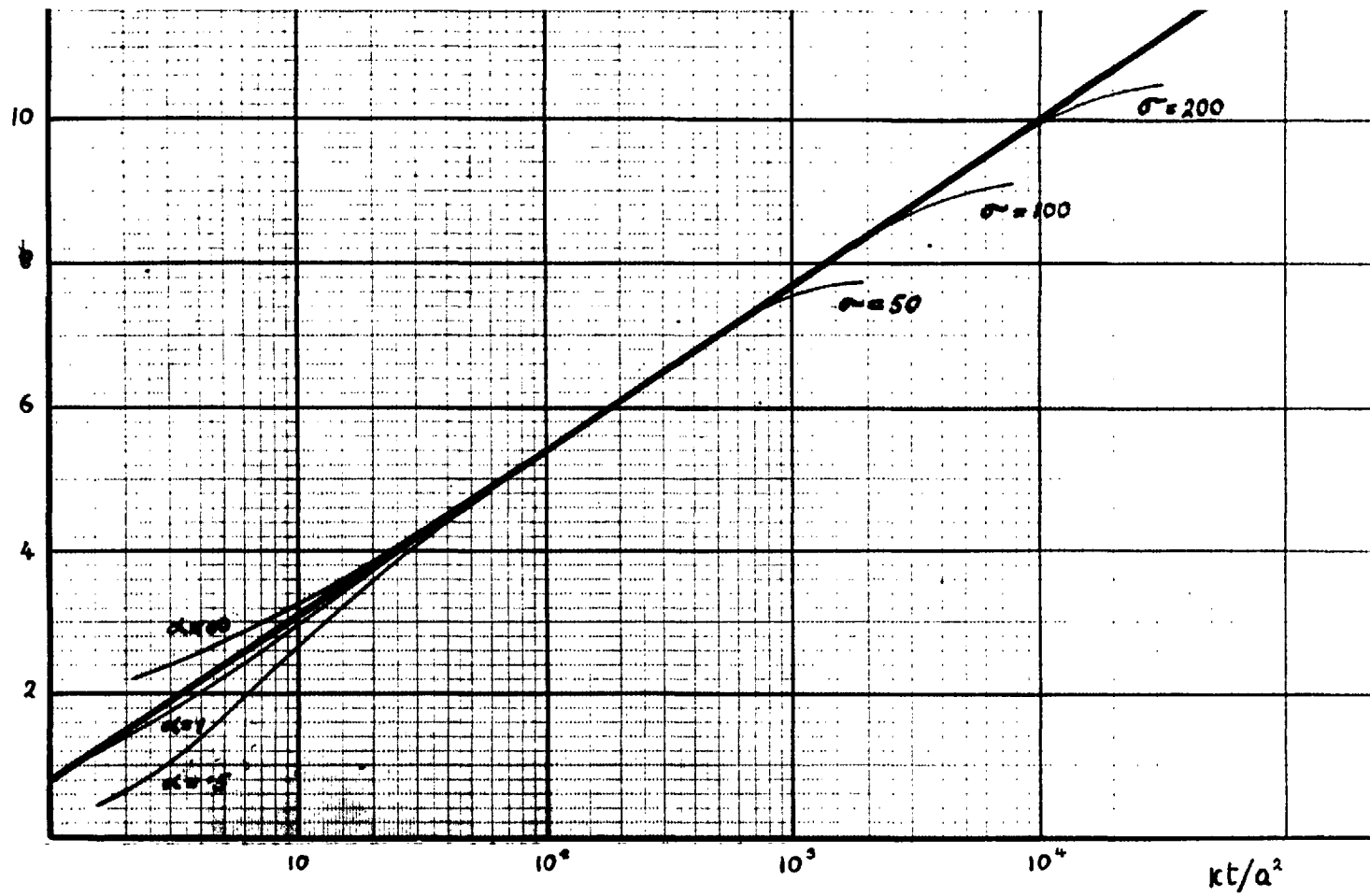


Figure 2.1

long. In practice the ends influence the temperature distribution in two ways. Firstly, the discontinuity in heating distorts the radial temperature field in the vicinity of each end; secondly, heat is conducted away along the heater itself.

The first effect will not be substantially different for a finite heater than for a line source of the same length. Such a line source may be imagined (figure 22) to coincide with the  $y$  axis between  $y_1$  and  $y_2$ , and to be made up of point sources each of power  $q_L dy$ , distributed along the line.

The temperature at a point  $(y', r)$  may after  $t$  secs. heating be written (1)

$$T_f(y', r, t) = \frac{q_L}{\rho c 8 \pi^{3/2} K^{3/2}} \int_{y_1}^{y_2} \int_0^t \exp\left[\frac{-R^2}{4K(t-t')}\right] \frac{1}{(t-t')^{3/2}} dt' dy \quad (2.12)$$

in which  $R^2 = r^2 + (y - y')^2$ . The subscript,  $f$ , is to indicate that the heat source is finite.

Assuming for simplicity that  $y'$  is the origin of co-ordinates and writing  $\Upsilon = (t - t')^{-1/2}$  equation (2.12) becomes

$$T_f(r, t) = \frac{q_L}{8(\pi K)^{3/2} \rho c} \int_{y_1}^{y_2} \int_{t^{-1}}^{\infty} 2 \exp\left[-\frac{R^2 \Upsilon^2}{4K}\right] d\Upsilon \quad (2.13)$$

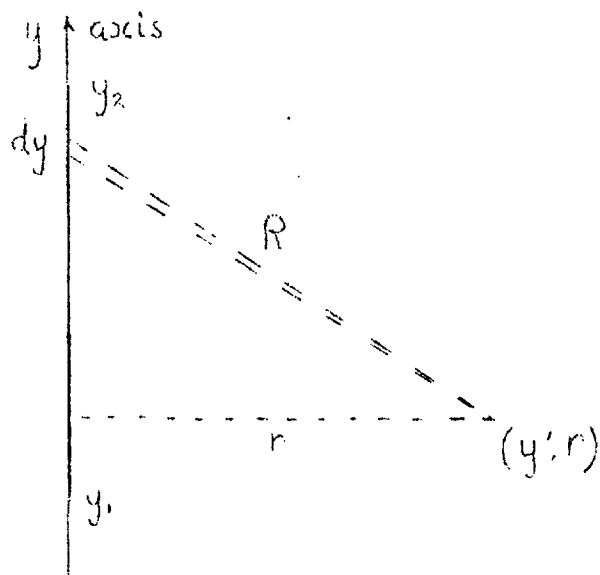


Figure 2.2

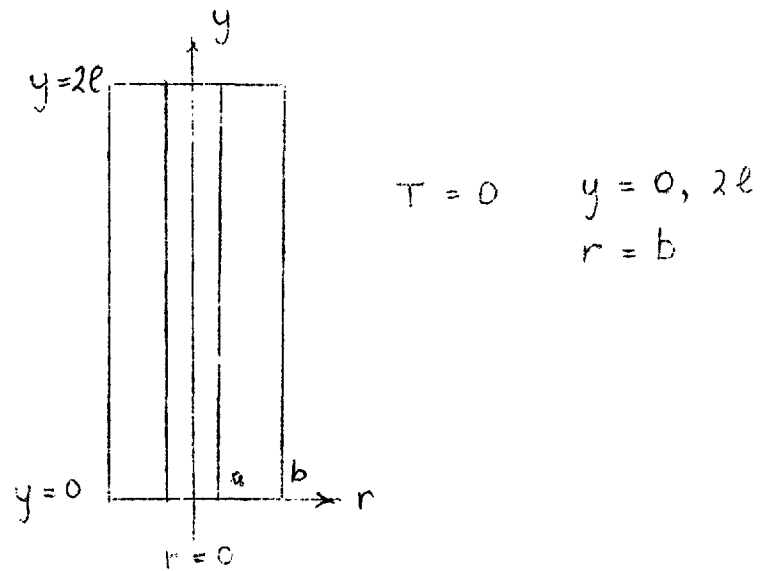


Figure 2.3

which on integration over  $\Upsilon$  and the substitution

$Z = \sqrt{R^2/4\kappa t}$  gives

$$T_f(y_1, y_2, r, t) = \frac{q_L}{4\pi\lambda} \int_{Z_1}^{Z_2} \frac{\operatorname{erfc} Z}{\sqrt{Z^2 - \frac{r^2}{4\kappa t}}} dz \quad (2.14)$$

(The principal part)

$\operatorname{Erfc}(Z)$  is the error function<sup>(7)</sup>.

Writing  $T_\infty(r, t)$  for the temperature due to an infinite source, the defect introduced by terminating the source at  $y_1$  and  $y_2$  may be written

$$T_\infty - T_f = \frac{q_L}{4\pi\lambda} \left( \int_{Z_1}^{\infty} \frac{\operatorname{erfc} z}{\sqrt{z^2 - r^2/4\kappa t}} dz + \int_{-\infty}^{Z_2} \frac{\operatorname{erfc} z}{\sqrt{z^2 - r^2/4\kappa t}} dz \right) \quad (2.15)$$

The fractional defect  $(T_\infty - T_f)/T_\infty$  is given by

$$\frac{T_\infty - T_f}{T_\infty} = \left[ \int_{Z_2}^{\infty} \frac{\operatorname{erfc} z}{\sqrt{z^2 - \frac{r^2}{4\kappa t}}} dz + \int_{-\infty}^{Z_1} \frac{\operatorname{erfc} z}{\sqrt{z^2 - \frac{r^2}{4\kappa t}}} dz \right] \frac{\ln 4\kappa t}{\gamma r^2} \quad (2.16)$$

The integrals decrease rapidly with increasing  $Z_1$  and  $Z_2$ . Thus for  $Z_1 \ll Z_2$  only one integral need be considered. This situation obtains near each end of a long heat source.

The second end effect may be estimated using a steady state approximation. The ends of the heat source and the boundaries of the medium are held at a constant temperature (figure 2.3)

Assuming that the flow of heat over the surface of the heater is everywhere in proportion  $H$  to its excess temperature at the point, the temperature along the heater<sup>(8)</sup> is

$$T(y) = \frac{q_L}{2\pi a H} \left[ 1 - \frac{\cosh a'(\ell-y)}{\cosh a'\ell} \right], \quad a' \sqrt{\frac{2H}{aK}} \quad (2.17)$$

$K$  is the thermal conductivity of the heater. Since the region of interest is near the ends of the heater where  $y \approx 0$  or  $y \approx 2\ell$

$$\frac{\cosh a'(\ell-y)}{\cosh a'\ell} \approx \exp(-a'd)$$

where  $d$  is the distance from the nearer end (assumed small).

Under the additional assumption that the surface heat transfer coefficient,  $H$ , is equal to that for steady state radial heat flow, i.e.  $H = \lambda/a \ln b/a$ , equation (2.17) may be written in terms of the distance,  $d$ , from the ends

$$T_d = \frac{q_L}{2\pi\lambda} \ln \frac{b}{a} \left[ 1 - \exp - \frac{d}{a} \left[ \frac{2\lambda}{K} \left( \ln \frac{b}{a} \right)^{-1} \right]^{\frac{1}{2}} \right] \quad (2.18)$$

As in the previous case a fractional defect at a distance,  $d$ , from the end of the heater may be calculated.

$$\frac{T_\infty - T_d}{T_\infty} = \exp - \frac{d}{a} \left[ \frac{2\lambda}{K} \left( \ln \frac{b}{a} \right)^{-1} \right]^{\frac{1}{2}} \quad (2.19)$$

Application of this equation to the present apparatus is discussed in section 2.1.2a (page 83 ).

### 2.1.1b. Theory of Measurement

The measurement of the heater temperature as a function of time poses the major experimental problem. Assuming for the present that equation (2.4) is valid,

$$\lambda = \frac{q_L}{4\pi} \frac{\Delta(\ell n t)}{\Delta T} \quad (2.20)$$

where  $t = 0$  at the initiation of heating. The heater resistance,  $R$ , is a property conveniently related to  $T$  and its measurement has the advantage of giving a temperature averaged over a finite length of wire.

Provided that the increments are not too large

$$\Delta T = \frac{dT}{dR} \Delta R$$

and

$$\lambda = \frac{q_L}{4\pi} \cdot \frac{\Delta \ell n t}{\Delta R} \cdot \frac{dR}{dT} \quad (2.21)$$

From Ohm's Law (again assuming small increments)

$$\Delta R = \frac{\Delta V}{I} - \frac{V}{I^2} \Delta I \quad (2.22)$$

in which  $V$  and  $I$  are respectively the potential across and the current in the heater.

(2.21) and (2.22) yield

$$\lambda = \frac{q_L}{4\pi} \frac{dR}{dT} \left[ \frac{1}{I} \frac{\Delta V}{\Delta \ell n t} - \frac{V}{I^2} \frac{\Delta I}{\Delta \ell n t} \right]^{-1} \quad (2.23)$$

Details of the practical application of the equation are given in section 2.1.3(d).

### 2.1.1c Non Uniformity of the Heater

The previous treatment has assumed that the heat source is of uniform cross-section. It is worthwhile considering to what extent non uniformity will affect the measurement.

Let the cross sectional area be  $\chi(x)$ , the resistance per unit length  $r(x)$ , and the heat generation per unit length  $q(x)$ ,

$$r(x) = \frac{\sigma}{\chi(x)} \quad , \quad q(x) = \frac{I^2 \sigma}{\chi(x)} \quad (2.24)$$

$\sigma$  is the electrical resistivity of the heater. The total resistance,  $R$ , of the length,  $\ell$ , is

$$R = \int_0^{\ell} r(x) dx \quad (2.25)$$

During the experiment the increment  $\Delta r$  in  $r$  is given by

$$\Delta r = \frac{\partial r}{\partial T} \Delta T \quad (2.26)$$

$\Delta T$  is the experimental increment in temperature and dependent on  $x$ . Thus by (2.25) and (2.26)

$$\Delta R = \int_0^{\ell} \frac{\partial r}{\partial T} \Delta T dx \quad (2.27)$$

Assuming that, even in the non uniform case, the

heat flux is radial and given by equation (2.20),

$$\Delta T = \frac{q(x)}{4\pi\lambda} \Delta \ell_{nt} \quad (2.28)$$

Substituting (2.28) and (2.24) in (2.27) yields

$$\begin{aligned} \Delta R &= \int_0^{\ell} \frac{I^2}{4\pi\lambda} \frac{\sigma}{(\chi(x))^2} \frac{\partial \sigma}{\partial T} dx \\ &= \frac{I^2}{4\pi\lambda} \sigma \frac{d\sigma}{dT} \int_0^{\ell} \frac{1}{(\chi(x))^2} dx \end{aligned} \quad (2.29)$$

In actual practice the equation used is

$$\Delta R = \frac{q_L}{4\pi\lambda} \frac{dR}{dT} \Delta \ell_{nt} \quad (2.30)$$

in which  $q_L$  and  $dR/dT$  have the following significance:

$$\begin{aligned} q_L &= \frac{I^2 R}{\ell} = \frac{I^2 \sigma}{\ell} \int_0^{\ell} \frac{1}{\chi(x)} dx \\ \frac{dR}{dT} &= \frac{d}{dT} \left[ \sigma \int_0^{\ell} \frac{dx}{\chi(x)} \right] \end{aligned}$$

On substitution (2.30) becomes

$$\Delta R = \frac{I^2 \sigma}{4\pi\lambda} \frac{d\sigma}{dT} \frac{1}{\ell} \left[ \int_0^{\ell} \frac{1}{\chi(x)} dx \right]^2 \quad (2.31)$$

For a uniform wire ( $\chi(x) = \text{constant}$ ) equations (2.31)

and (2.29) are identical.

The assumption of radial flow even in the non uniform case somewhat exaggerates the effect of non uniformity, so that the difference between (2.31) and (2.29) sets an upper limit on its importance. The effect has not been previously discussed in the literature but could be significant if the fragile heater were stretched or damaged in the construction of the cell. To assess the extent of such damage in the construction of the present apparatus a typical cell was dismantled and examined (page 84 ).

### 2.1.2 Apparatus

#### a. The Cell Design (Figures 2.4, 2.5, 2.10)

Cells were constructed of which the following details are typical. The body of the cell was of 1 cm bore glass tubing approximately 15 cms long and provided with a side arm close to the upper end. B.T.H. C9 glass was found to be more easily worked than soda or lead glass and made reliable pinch-seals to the platinum leads. The electrical circuit of the cell resembled a 4 lead platinum resistance thermometer. The axial heater, (figure 2.4) of 46 S.W.G. platinum wire was maintained under a light tension ( $\sim 5$  grms) by a spring of 36 S.W.G. platinum 10% iridium wire. To prevent heating of the spring and consequent thermal E.M.F.'s at its junctions with the platinum leads, electrical shunts, S, of platinum foil (.1 cm x .051 cm) were provided. These were placed symmetrically to avoid a lateral movement of the tensioned spring. (Figure 2.4 shows a single shunt but the design was rejected for the above reason, and the one shown enlarged in figure 2.5 was adopted.)

The potential leads, (figure 2.10) of 46 S.W. G. platinum were spot welded to the heater approximately



Figure 2.5

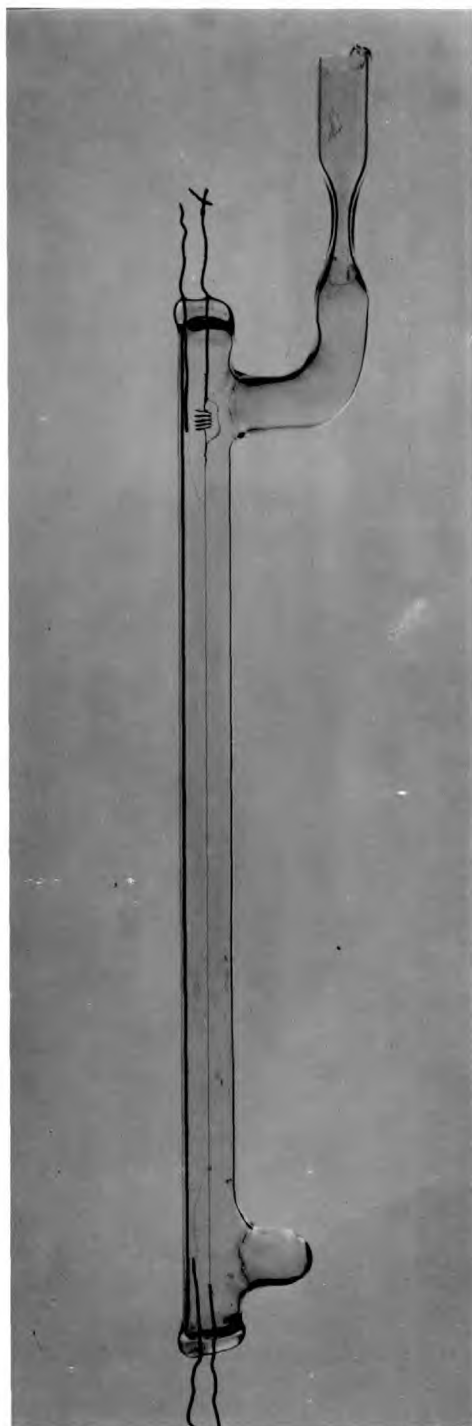


Figure 2.4

1 cm from each end, care being taken to avoid distorting the wire during the welding process. All connections to the cell were made via stout (26 S.W.G.) platinum leads sealed through the glass at each end.

The glass to metal seals were made individually. For the second seal the cell was mounted in a vertical position and a small weight suspended from the heater to ensure tautness over a wide range of temperature. Small holes were left in the cell wall at each end to facilitate manual adjustment of the heater after making the seals. The heater was annealed in situ by passing a current for about an hour during which time the temperature was reduced gradually from white heat to normal.

(i) The Wall Effect

This was investigated on the basis of equations (2.10) and (2.11). In the present apparatus  $a/b \doteq .005$ , thus equation (2.11) was deemed to hold up to  $\gamma = 8$  (for which  $a\gamma/b = 0.1$ ). These eight terms were sufficient to evaluate the series with .01% accuracy for all times exceeding 2 secs. The Bessel Functions were taken from the tables of Jahnke and Emde<sup>(6)</sup>.

Table 2.1 below contains values of  $4\pi\lambda T/q_L$

calculated from equations (2.10) and (2.3).

TABLE 2.1

| $\frac{\kappa t}{a^2}$ | $\frac{4\pi\lambda T}{q_L}$<br>(2.10) | $\frac{4\pi\lambda T}{q_L}$<br>(2.3) | t<br>(secs.) |
|------------------------|---------------------------------------|--------------------------------------|--------------|
| 320                    | 6.577                                 | 6.577                                | 2            |
| 640                    | 7.269                                 | 7.271                                | 4            |
| 1,280                  | 7.962                                 | 7.964                                | 6            |
| 2,560                  | 8.655                                 | 8.657                                | 8            |
| 5,120                  | 9.348                                 | 9.350                                | 16           |
| 10,240                 | 10.010                                | 10.053                               | 32           |
| 20,480                 | 10.463                                | 10.736                               | 64           |

Agreement is close up to  $\kappa t/a^2 = 5120$   
 which for the majority of organic liquids (where  $\kappa = 10^{-3}$ )  
 corresponds to a time of about 30 seconds (N.B. for water  
 where  $\kappa \approx .0014$  this time is reduced to about 20  
 secs). In general it may be said that, in a cell of the  
 present dimensions, the walls will have negligible ( $\approx .1\%$ )  
 effect for a period of about 30 seconds following the  
 initiation of heating. Under these circumstances precise  
 centering of the heater is unnecessary.

(ii) End Effects

It has been shown that the heater temperature falls off at a distance,  $d$ , from the ends such that

$$\frac{T_{\infty} - T_f(d)}{T_{\infty}} = \frac{\int_{Z_1}^{\infty} \frac{\operatorname{erfc} z}{(z^2 - \frac{a^2}{4\kappa t})^{1/2}} dz}{\ln 4\kappa t/a^2}, \quad Z_1^2 = \frac{d^2 + a^2}{4\kappa t}$$

The defect in temperature at the point of attachment of the potential leads is found by putting  $d = 1$  cm.

Relevant values of the integral are tabulated as a function of  $Z_1$ , in table 2.2.

TABLE 2.2

| $Z_1$ | $\frac{\operatorname{erfc} Z_1}{\sqrt{Z_1^2 - \frac{a^2}{4\kappa t}}}$ | $\int_{Z_1}^{\infty} \frac{\operatorname{erfc} z}{\sqrt{z^2 - \frac{a^2}{4\kappa t}}} dz$ |
|-------|------------------------------------------------------------------------|-------------------------------------------------------------------------------------------|
| 1.0   | .157                                                                   |                                                                                           |
| 1.2   | .0750                                                                  | .020                                                                                      |
| 1.4   | .0344                                                                  | .009                                                                                      |
| 1.6   | .0144                                                                  | .0032                                                                                     |
| 1.8   | .0062                                                                  | .0013                                                                                     |
| 2.0   | .0025                                                                  | .0005                                                                                     |
| 3.0   | .0000                                                                  | .0000                                                                                     |

For the purposes of calculation one may put

$K = 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$  and  $t = 30 \text{ secs.}$  With these values  $Z = 2$  and  $\ln 4\kappa t/a^2 \doteq 10$ , therefore using table 2.2

$$\frac{T_{\infty} - T_f(1)}{T_{\infty}} = .00005$$

This is obviously of negligible importance.

A second defect results from conduction along the heater itself.

Equation (2.19) shows

$$\frac{T_{\infty} - T_f}{T_{\infty}} = \exp - \frac{d}{a} \left[ \frac{2\lambda}{K} \left( \ln \frac{b}{a} \right)^{-1} \right]^{\frac{1}{2}}$$

where  $K$  is the thermal conductivity of platinum equal to  $.17 \text{ calcs. cm}^{-1} \text{ sec}^{-1} \text{ } ^\circ\text{C}^{-1}$ .

In the worst example measured, (n BuI )

$\lambda = 2 \times 10^{-4} \text{ calcs cm}^{-1} \text{ sec}^{-1} \text{ } ^\circ\text{C}^{-1}$ . Putting the geometrical constants of the apparatus (  $a = 2.5 \times 10^{-3} \text{ cms}$ ;  $b = .5 \text{ cms}$ ;  $d = 1 \text{ cm.}$ ) into the equation gives

$$\frac{T_{\infty} - T_f(1)}{T_{\infty}} = .0014$$

the defect at the junction of the potential leads.

The temperature as a function of the distance,  $x$ , from one end of the wire is given by

$$T(x) = T_{\infty} (1 - \exp(-qx)) \quad (2.32)$$

$T_{\infty}$  is the temperature far removed from an end.

Integration of (2.32) over the length shows that the average temperature over the whole wire errs by less than 2% and over the centre section by less than .01%.

Thus, even in the most unfavourable examples considered here, the end effects are negligible.

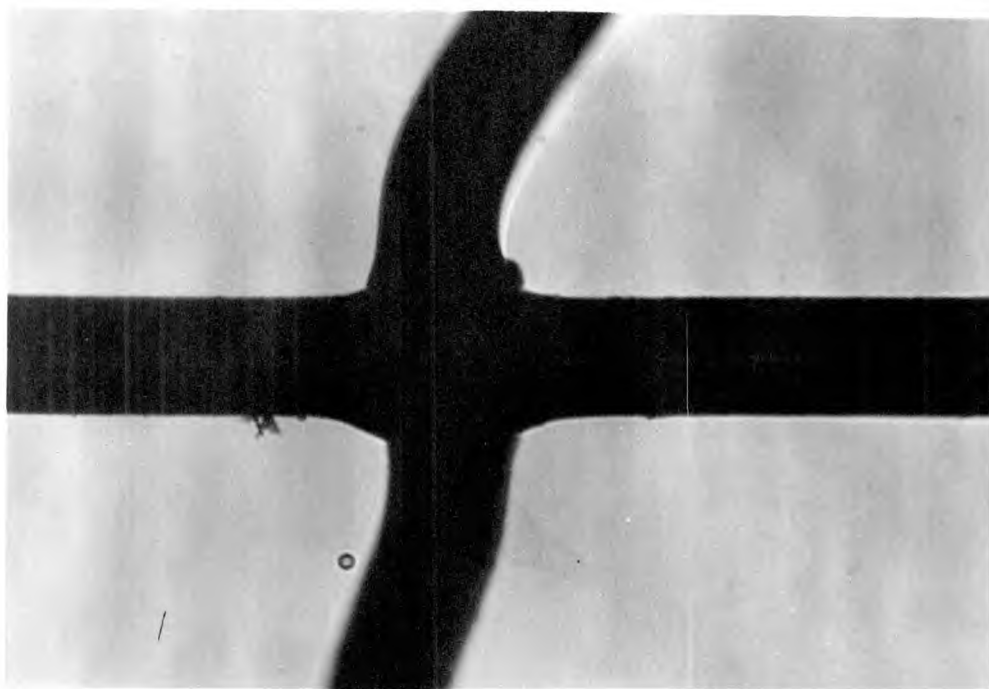
### Uniformity of the Heater

Because of the importance which attaches to the uniformity of the heater a cell was dismantled and the heater examined under a microscope. Photographs (figures 2.6a, 2.6b) show a typical section of the wire and a potential lead junction magnified 500 times.

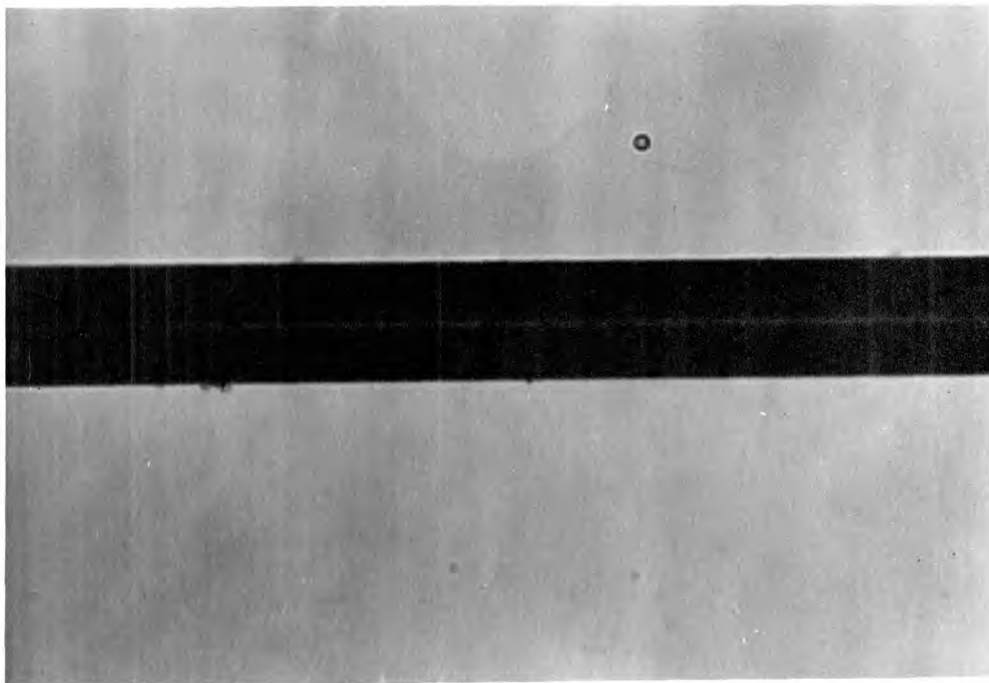
The weld was found to be localised in the region of contact and there was no detectable crushing of the wire. Non-uniformity did not exceed 2% anywhere and was for the most part not measurable. This causes no significant difference between equations (2.29) and (2.31).

### b. The Thermostat

This consisted (figure 2.7) of two vessels one enclosing the other and thermally insulated from it. A Sunvic bimetallic element, T.C., was used to control the outer bath within  $\pm \frac{1}{2}^{\circ}\text{C}$  of a desired temperature. Oil from



a



b

Figure 2.6 Cell heater and welded junction (x 500)

the outer bath was circulated through the hollow lid, X , so that the inner bath was completely surrounded by a constant temperature jacket. No control heat was supplied to the inner bath which was allowed to adopt the mean temperature of the surrounding jacket. Boost heaters, H and h , were provided in both baths.

The temperature of the inner bath was measured with a 25 platinum resistance thermometer, R , and a Smith's Bridge. The calibration accuracy of the thermometer was  $\pm .015^{\circ}\text{C}$  (maximum errors).

Fluctuations in temperature could be measured to within  $.002^{\circ}\text{C}$ . Short period fluctuations due to imperfect stirring did not exceed this value. The thermal time constant of the inner bath was about two hours, so that after changing the temperature a considerable period had to elapse before a steady temperature was reached. It was found convenient to change the temperature overnight.

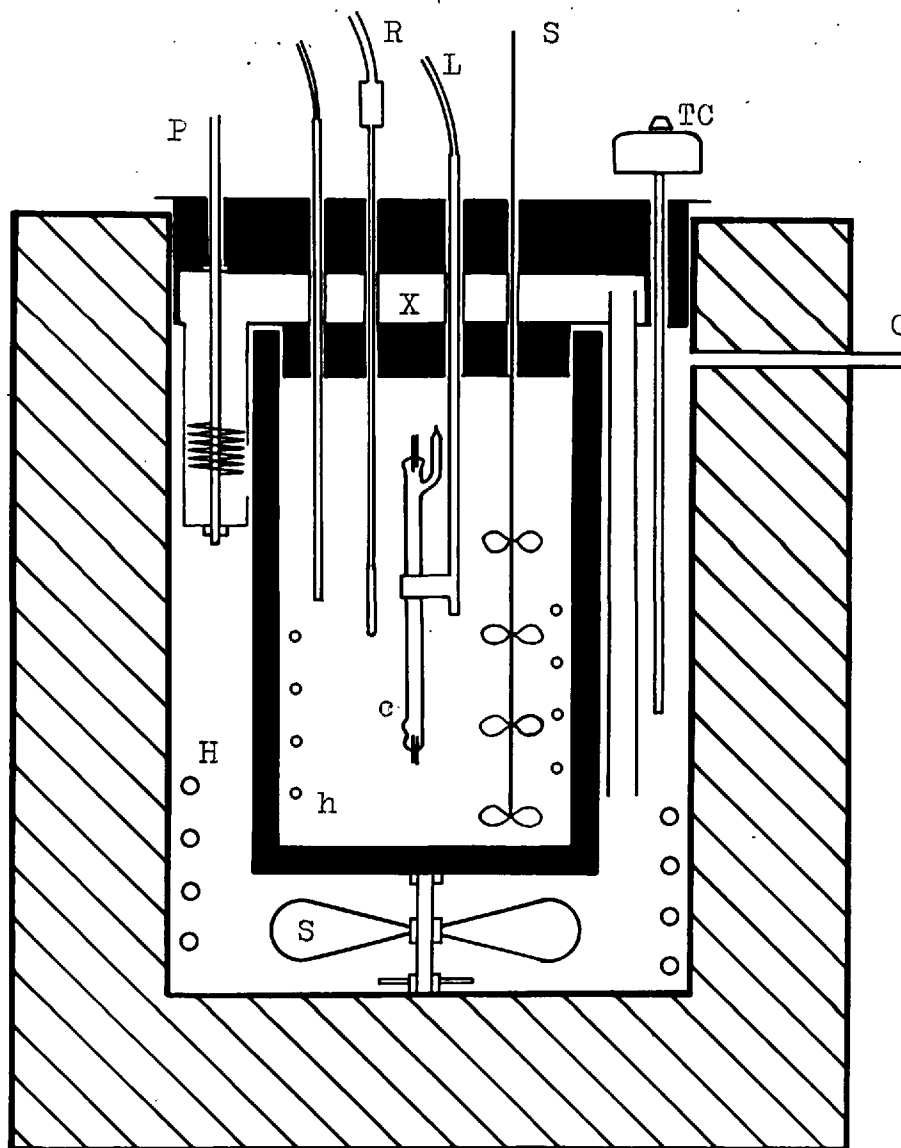


Figure 2.7

### 2.1.3 Details of Operation

#### a. Temperature Control

During the period of measurement the heater temperature increases by  $0.25^{\circ}\text{C}$  approximately. For 0.1% accuracy the variation of the ambient temperature must not exceed  $0.00025^{\circ}\text{C}$ . To remain within this limit, measurements were not made unless the temperature drift of the thermostat was less than  $0.001^{\circ}\text{C}/\text{minute}$  during the five preceeding minutes.

#### b. Minimum Period between Measurements

The time of equilibration of the cell depends upon  $\kappa/b^2$ . It can be shown<sup>(9)</sup> that, after a time  $\kappa t/b^2 = 1$ , the temperature in a cell, initially uniformly hotter than its surroundings, will nowhere exceed 1% of its initial value. With  $b = 0.5 \text{ cms}$ ,  $\kappa = .001 \text{ cm}^2 \text{ sec}^{-1}$  this gives a time of 250 seconds.

In practice a minimum period of 10 minutes was allowed between measurements.

#### c. Convection Criteria

It has been shown<sup>(10, 11, 12)</sup> that, in the steady state heat transfer by convection between horizontal cylinders is negligible below a critical value (1000) of the product of the

Grashof and Prandtl numbers. These are defined:

$$Gr = \frac{g \rho^2 \beta \delta^3 \Delta \theta}{\eta^2}, \quad Pr = \frac{\eta}{k}$$

$g$  is the acceleration due to gravity

$\rho$  is the density

$\beta$  is the coefficient of thermal expansion

$\Delta \theta$  is the temperature differential across  $\delta$

$$\delta = b - a$$

$\eta$  is the coefficient of viscosity

Since the tendency to convect is less marked<sup>(13)</sup> in vertical than in horizontal cylinders, the criterion may be used to determine experimental limits in vertical cells.

To the instantaneous non steady temperature field of the experiment there may be found<sup>(2)</sup> an equivalent steady state situation and to this situation the above criterion may be applied.

In the steady state

$$\Delta \theta = \frac{q_L}{2\pi\lambda} \ln \frac{b}{a} \quad (2.33)$$

In the non steady state the effective outer radius  $b_{eff}$  is that of the expanding cylinder of high temperature which surrounds

the heating wire. The effective value of  $\Delta\theta$  in the non steady state may be equated to the instantaneous temperature  $T(a, t)$  of equation (2.3).  $b_{eff}$  is found by putting this temperature into equation (2.33) giving

$$T(a, t) = \frac{q_L}{2\pi\lambda} \ln \frac{b_{eff}}{a}$$

and hence

$$\delta_{eff} = b_{eff} - a = a \left[ \exp \frac{2\pi\lambda T(a, t)}{q_L} - 1 \right]$$

This is more conveniently written

$$\delta_{eff} = a \left[ \exp \frac{T^*}{2} - 1 \right]$$

where  $T^* = 4\pi\lambda T / q_L$

Substituting  $\delta_{eff}$  and  $T(a, t)$  into the convection criterion yields a critical  $T^*$

$$1000 = GrPr = \frac{g\beta q_L a^3}{\eta k 4\pi\lambda} \left[ T^* \left( \exp \frac{T^*}{2} - 1 \right) \right]^3 \quad (2.34)$$

A plot (figure 2.8) of the function  $T^* (\exp T^*/2 - 1)^3$  versus  $4\pi k t / a^2$  was prepared.

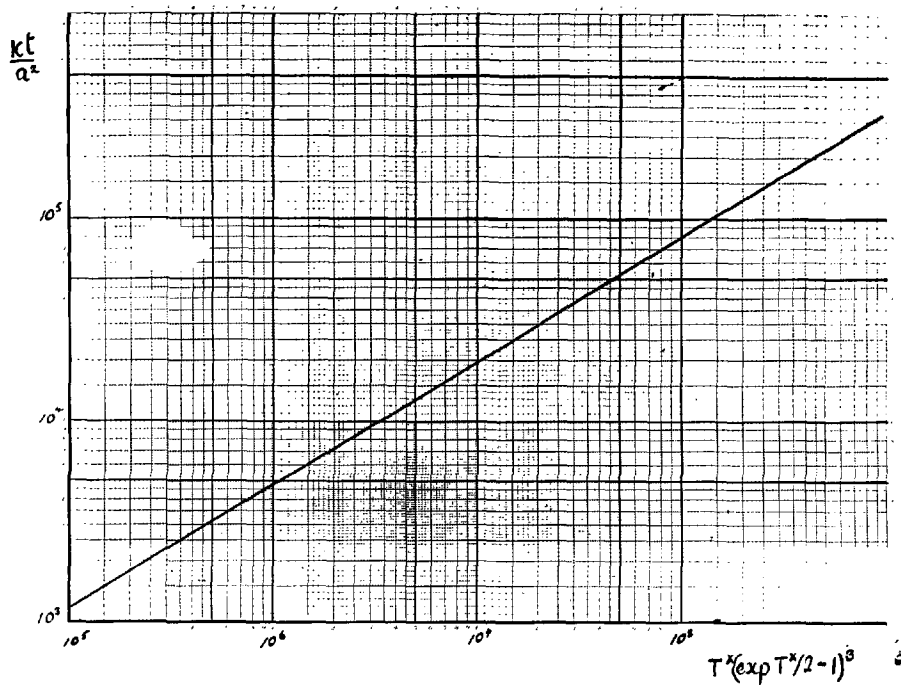


Figure 2.8

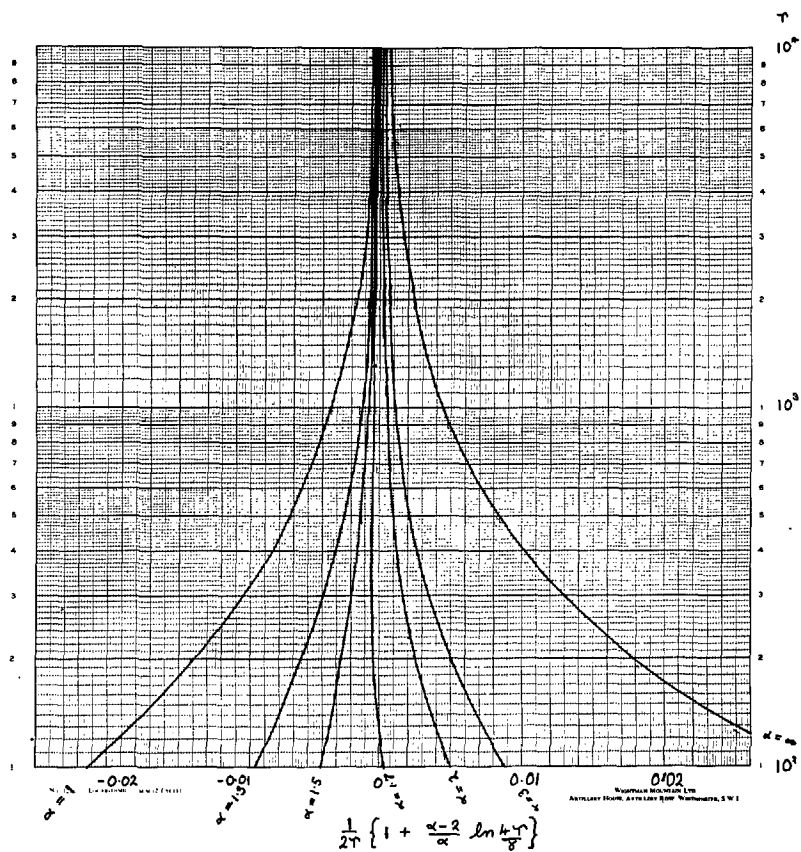


Figure 2.9

TABLE 2.3

| $\frac{4\kappa t}{a^2}$ | $T^* = \ln \frac{4\kappa t}{8a^2}$ | $T^* \left( \exp \frac{T^*}{2} - 1 \right)^3$ |
|-------------------------|------------------------------------|-----------------------------------------------|
| 4.9                     | 1                                  | .273                                          |
| 13.2                    | 2                                  | 10.1                                          |
| 35.9                    | 3                                  | 126.3                                         |
| 97.5                    | 4                                  | 1,044                                         |
| 265.1                   | 5                                  | 7,000                                         |
| 725                     | 6                                  | 41,820                                        |
| 1,950                   | 7                                  | 231,000                                       |
| 5,250                   | 8                                  | 1,230,000                                     |
| 14,500                  | 9                                  | $6.3 \times 10^6$                             |
| 38,900                  | 10                                 | $32 \times 10^6$                              |
| 100,600                 | 11                                 | $159 \times 10^6$                             |

By substituting the parameters  $g$ ,  $\beta$ ,  $q_L$  etc. in equation 2.34 a critical value of  $T^* \left( \exp T^*/2 - 1 \right)^3$  was calculated for each experiment. Interpolating this quantity in figure 28 yielded the critical period preceeding convection. The relevant parameters and the results of the calculation for the phenyl derivatives at the highest temperatures are given below.

TABLE 2.4 : Onset of Convection Parameters

|             | $T$<br>$^{\circ}\text{C}$ | $\rho$<br>$\text{g cm}^{-3}$ | $\eta$<br>$10^{-2} \text{P}$ | $\lambda$<br>$10^{-3} \text{J cm}^{-1} \text{s}^{-1} \text{C}^{-1}$ | $\alpha$<br>$10^{-4} \text{C}^{-1}$ | $\kappa$<br>$10^{-4} \text{cm}^2 \text{s}^{-1}$ |
|-------------|---------------------------|------------------------------|------------------------------|---------------------------------------------------------------------|-------------------------------------|-------------------------------------------------|
| Benzene     | 70                        | 0.82                         | 0.35                         | 1.3                                                                 | 12                                  | 9                                               |
| Diphenyl    | 130                       | 0.94                         | 0.6                          | 1.3                                                                 | 8                                   | 7.5                                             |
| o-terphenyl | 140                       | 0.99                         | 1.9                          | 1.25                                                                | 7                                   | 7                                               |
| n-terphenyl | 140                       | 1.01                         | 1.8                          | 1.35                                                                | 6                                   | 7                                               |
| p-terphenyl | 250                       | 0.94                         | 0.6                          | 1.25                                                                | 9                                   | 6                                               |

|             | $T$<br>$^{\circ}\text{C}$ | $q_L$<br>$10^{-3} \text{J cm}^{-1}$ | $4\pi\eta\kappa\lambda/g\beta q_L$ | $t_{\text{crit.}}$<br>secs. |
|-------------|---------------------------|-------------------------------------|------------------------------------|-----------------------------|
| Benzene     | 70                        | 2.5                                 | $1.6 \times 10^6$                  | 10                          |
| Diphenyl    | 130                       | 3.0                                 | $2.3 \times 10^6$                  | 16                          |
| o-terphenyl | 140                       | 2.5                                 | $8.1 \times 10^6$                  | 38                          |
| n-terphenyl | 140                       | 3.5                                 | $6.5 \times 10^6$                  | 32                          |
| p-terphenyl | 250                       | 2.2                                 | $2.1 \times 10^6$                  | 18                          |

Only in the case of benzene at  $70^{\circ}\text{C}$  is the critical period as short as ten seconds. (Similar values were obtained for cyclohexane and toluene near their boiling points.)

Where experiments were of sufficient duration it was noticed that the critical period calculated corresponded closely with a sudden departure from linearity of the experimental curves

$V$  versus  $\ell n t$ , (e.g. in benzene this occurred at 8.5 secs.)

Using more accurate values of the parameters (Table 2.4) extremely close agreement between calculated and observed critical periods has been obtained <sup>(1)</sup>.

### The Measurement

In the present experimental arrangement (figure 2.10) the parameters in equation (2.23) written thus

$$\lambda = \frac{IV}{4\pi L} \frac{dR}{dT} \left[ \frac{1}{I} \frac{\Delta V}{\Delta \ell n t} - \frac{V}{I^2} \frac{\Delta I}{\Delta \ell n t} \right]^{-1} \quad (2.35)$$

have the following significance.  $I$  and  $V$  are respectively the current in and the potential across the central portion (length  $l$  and resistance  $R$ ) of the heater. The validity of equation (2.35) depends upon small increments.

$\Delta V/V$  and  $\Delta I/I$  have not exceeded .002 and .0002 respectively, so that  $I$ ,  $V$  and  $Q = IV$  have been replaced by their average values during measurement.

The current,  $I$ , was measured in terms of the voltage,  $V_I$ , developed across a standard resistance,  $S$ , in series with the cell. Both  $V_I$  and  $I$  were measured using a precision vernier potentiometer, V.P., of quoted accuracy 1 part in  $10^5$ .

In order to measure  $\Delta V/\Delta \ell n t$  and  $\Delta V_I/\Delta \ell n t$  during

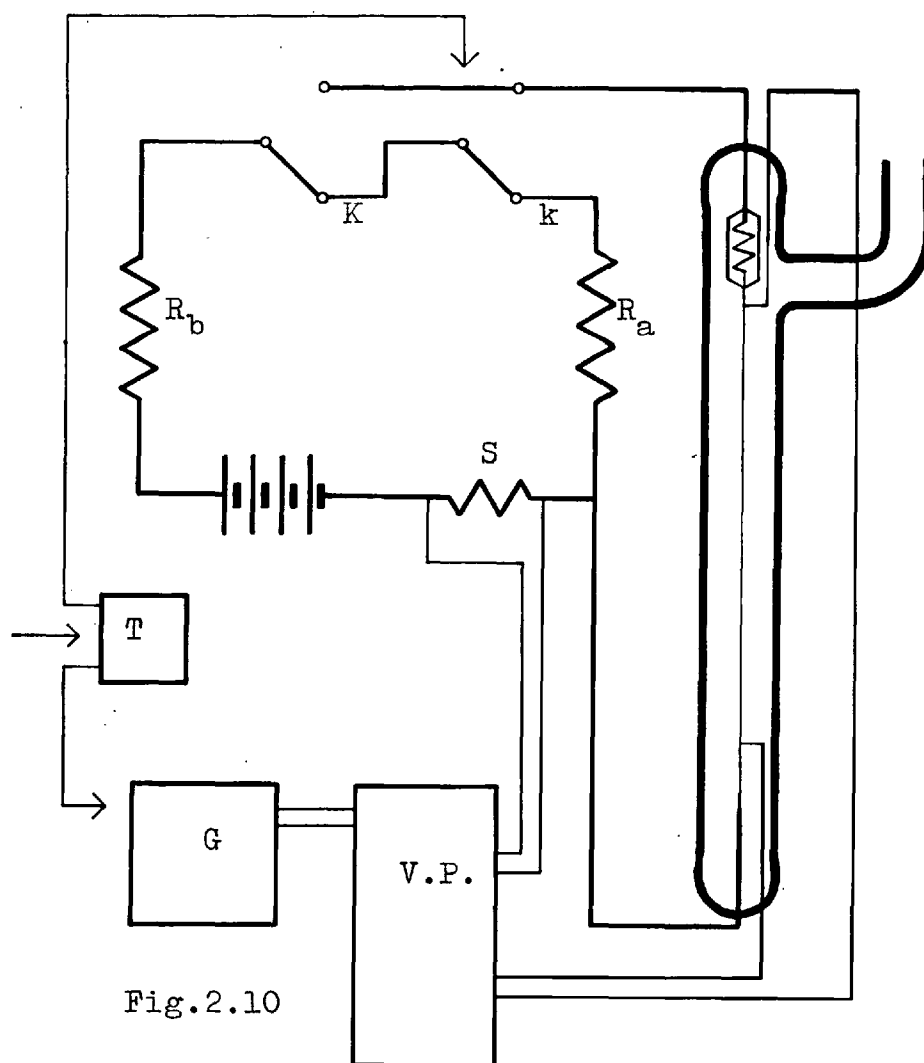


Fig.2.10

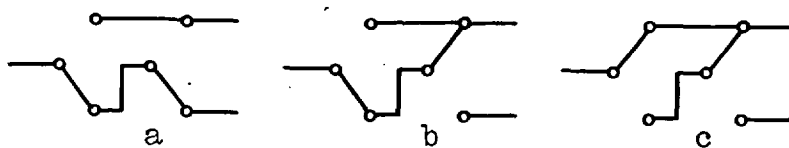


Fig.2.11

a run, the unbalanced output from the vernier potentiometer was measured on a Sunvic recording potentiometer, G (F.S.D. = 1 MV), which had been modified to read at high speed. Time intervals were marked on the trace by lifting the pen at  $\frac{1}{2}$ -second intervals.

Extreme care was taken to ensure the stability of the accumulators supplying both the potentiometer and the cell. Since the cell current must be interrupted the heating circuit was provided with an alternative electrical path,  $R_a$ , matched to the cell resistance, maintaining a continuous and constant current drain. The accumulators were protected from thermal fluctuations.

### Switching

It was found that interrupting the current for even short periods (.1 secs) was sufficient to change the E.M.F. of the accumulators significantly. On re-establishing the current, the changed E.M.F. did not immediately assume its original value, but returned to it over a period of several seconds. To avoid this, an electrical relay, k, with rapid change over time ( $2 \times 10^{-3}$  seconds) was used. The unreliable contact resistance of this high speed switch

was by-passed during measurement by a manually operated rotary stud switch, K, with "make before break" contacts.

The sequence of operations is shown in figures 2.11a, 2.11b, 2.11c.

The relay was arranged to coincide with one of timing pulses so that accurate intervals from the initiation of heating were directly available.

e. Measurement of  $dR/dT$

Since the heater is under tension it is not sufficient to take the maker's values of the temperature coefficients of the unstrained platinum wire.

The cell resistance was measured at intervals of  $10^{\circ}\text{C}$  or  $20^{\circ}\text{C}$  using a small calibrating current. Assuming only the quadratic dependence of  $R$  on  $T$ ,  $dR/dT$  was calculated from the equation

$$\left(\frac{dR}{dT}\right)_{\frac{T_1+T_2}{2}} = \frac{R_1 - R_2}{T_1 - T_2}$$

A typical curve of  $dR/dT$  against temperature is shown (page 108 ). The value of  $R_{100}/R_0$  for this cell was 1.385 which compares not unfavourably with the value for an unstrained platinum resistance thermometer which should exceed 1.39.

#### 2.1.4 Corrections to the Simple Measurement

##### 1. Lag in the recorder

The recording potentiometer is a servo-mechanism which moves in response to a difference between the voltage applied and the voltage indicated. This difference suitably amplified drives the pen until the two voltages are equal. It follows that while the pen is moving the recorded voltage cannot be exactly equal to that applied. In the present experiments this discrepancy takes the form of a "lag" which is greatest initially and which gives rise to a curvature of the  $V$  versus  $\ln t$  graphs. In principle it is possible to make a theoretical prediction of this lag but in practice not enough is known about the behaviour of the instrument. Attempts to measure the "out of balance" of the instrument during the actual measurements disturbed the operation. An initial-calibration of the instrument proved to be the most successful.

With the instrument slightly underdamped a varying voltage derived from a motor driven potential divider was applied to the recorder. A pair of contacts, operated by

means of a cam on the spindle of the potential divider, actuated the pen lift mechanism and marked the record at a fixed value of the applied voltage. By driving the motor at different speeds the difference between the applied and recorded voltages was determined as a function of the traverse speed of the recorder. (See Table 2.5 and figure 2.12a).

Using figure 2.12a, corrections were applied to each point on the record appropriate to the value of  $dV/dt$  at the point.  $dV/dt$  is given by

$$\frac{dV}{dt} = \frac{1}{t} \frac{\Delta V}{\Delta \ln t}$$

Rough values of  $\Delta V/\Delta \ln t$  obtained from the uncorrected record were used to evaluate the correction.

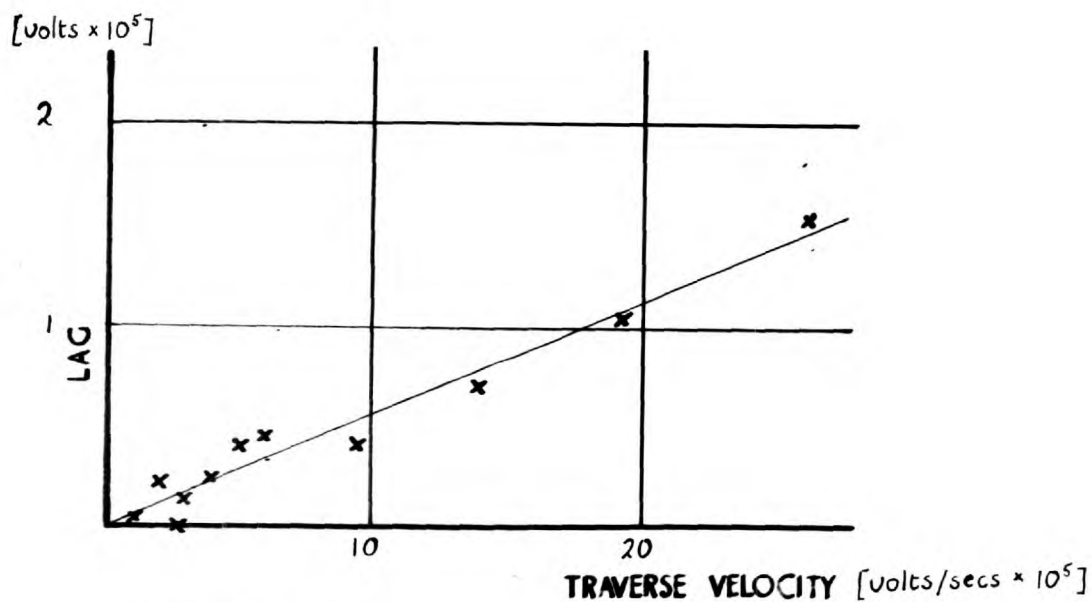


Figure 2.12 a

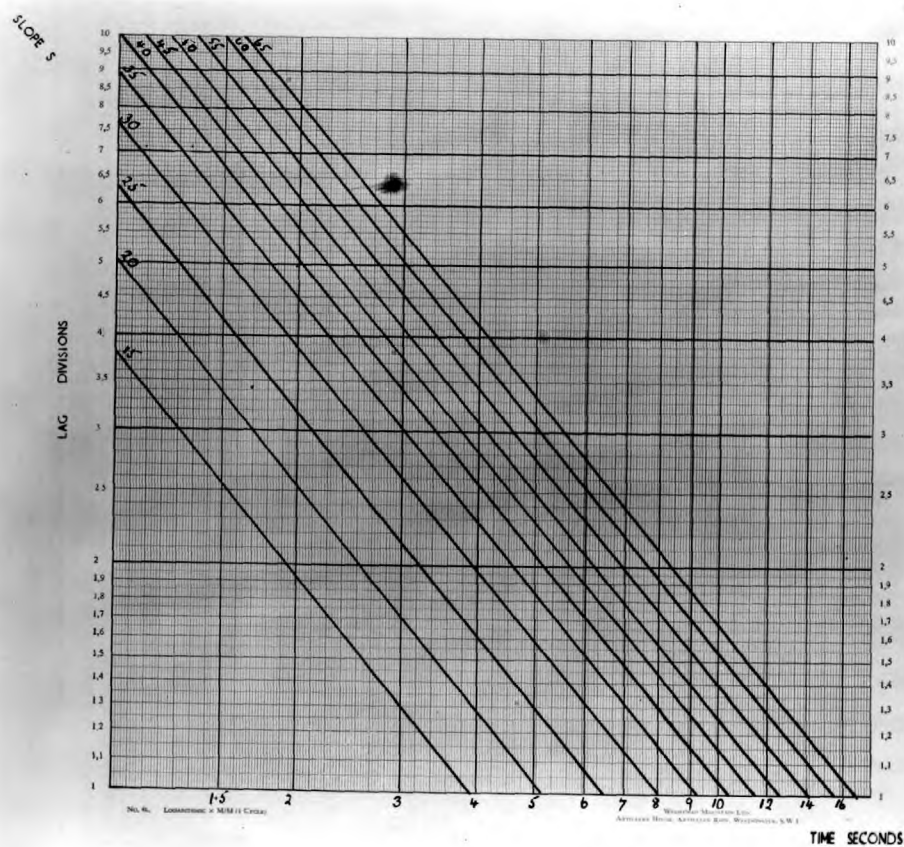


Figure 2.12 b

**TABLE 2.5 - Measured Values of the Lag as a Function of the Traverse velocity**

| Traverse<br>Velocity | Lag             |
|----------------------|-----------------|
| $10^{-5}$ volts/sec  | $10^{-5}$ volts |
| 1                    | .05             |
| 1.4                  | .00             |
| 2.0                  | .25             |
| 2.8                  | .15             |
| 5.2                  | .4              |
| 6.2                  | .45             |
| 9.5                  | .4              |
| 14.0                 | .75             |
| 19.0                 | 1.05            |
| 26.0                 | 1.6             |

2. The thermal capacity of the heater

Since convection restricts measurement to short times it has been found necessary to apply a correction for the thermal capacity of the heater.

Putting  $\epsilon(t) = \frac{a^2}{2\kappa t} + \frac{\alpha - 2}{2\alpha} \frac{a^2}{\kappa t} \ln \frac{4\kappa t}{a^2}$

equation (2.5) becomes

$$T(a, t) = \frac{q_L}{4\pi\lambda} \left[ \ln t + \ln \frac{\kappa}{\delta a^2} + \epsilon(t) \right]$$

and hence

$$T(a, t_2) - T(a, t_1) = \frac{q_L}{4\pi\lambda} \left[ \ln \frac{t_2}{t_1} + \epsilon(t_2) - \epsilon(t_1) \right] \quad (2.36)$$

The correction is too small (  $< .3\%$  ) to cause a detectable curvature in the plot  $V$  versus  $\ln t$  and therefore an overall correction to the slope of  $[\epsilon(t_2) - \epsilon(t_1)] / \ln t_2/t_1$  was used:  $t_2$  and  $t_1$  corresponding to the limits of the plot. To facilitate its estimation a plot (figure 2.9) of  $\epsilon(t)$  over a range of  $\kappa t / a^2$  and  $\alpha$  was used. Percentage corrections applied in the case of several liquids are shown in Table 2.6 .

TABLE 2.6 - Corrections applied to  $\lambda$  for the thermal capacity effect

| Material    | % correction to $\lambda$ |                         |
|-------------|---------------------------|-------------------------|
| Benzene     | 0.2                       |                         |
| p Terphenyl | 0.04                      |                         |
| m Terphenyl | 0.3                       |                         |
| o Terphenyl | 0.3                       | $t_2 = 10 \text{ secs}$ |
| Toluene     | 0.3                       | $t_1 = 1 \text{ secs}$  |
| Water       | -0.1                      |                         |
| Diphenyl    | 0.2                       |                         |
| Cyclohexane | 0.06                      |                         |

### 3. Contribution of Radiation to Heat Transfer

Suppose that the heater radiates into a "black" enclosure. The radiative heat loss per unit length is given by

$$q_r = 2\pi a \sigma (e T_1^4 - \alpha_{12} T_2^4) \quad (2.37)$$

For platinum wire  $e \doteq \alpha_{12} \doteq 0.1$  (14)

$T_1$  is the wire temperature and  $T_2$  the enclosure temperature.  $\sigma$  is Stefan's constant  $= 5.68 \times 10^{-5} \text{ erg sec}^{-1} \text{ } ^\circ\text{K}^{-4}$

For small differences

$$q_r = 0.8 \pi a \sigma T^3 \Delta T$$

Putting  $\Delta T$  equal to the experimental increment  
(equation 2.3)

$$\frac{q_r}{q_L} = \frac{2\sigma a T_i^3}{\lambda} \ln \frac{4\kappa t}{\gamma a^2} \quad (2.38)$$

In the least favourable case studied (para-terphenyl),

$$\lambda = 1.2 \times 10^{-3} \text{ /cm}^{-1} \text{ s}^{-1} \text{ } ^\circ\text{C}^{-1}, \quad T_i = 530^\circ\text{K}, \quad \ln 4\kappa t / \gamma a^2 = 0.8$$

Equation 2.38 gives

$$q_r/q_L = 2.5 \times 10^{-3}$$

Since hydrocarbons have a considerable absorption the actual contribution of radiation will be smaller. No corrections have therefore been applied.

### 2.1.5 A Specimen Determination

Records of a typical determination are reproduced in figures 2.13 and 2.14. The full scale deflection of the record corresponds to  $10^{-3}$  volts. The approximate slope  $\Delta V / \Delta \ln t$  was obtained by inspection and is written

$S_V = 40$  in figure 2.13 From this slope the lag corrections were calculated and marked on the record.  $V$  versus  $\ln t$  curves associated with the records are shown in figure 2.15. and the associated measurements and a specimen calculation are included on page 109 .

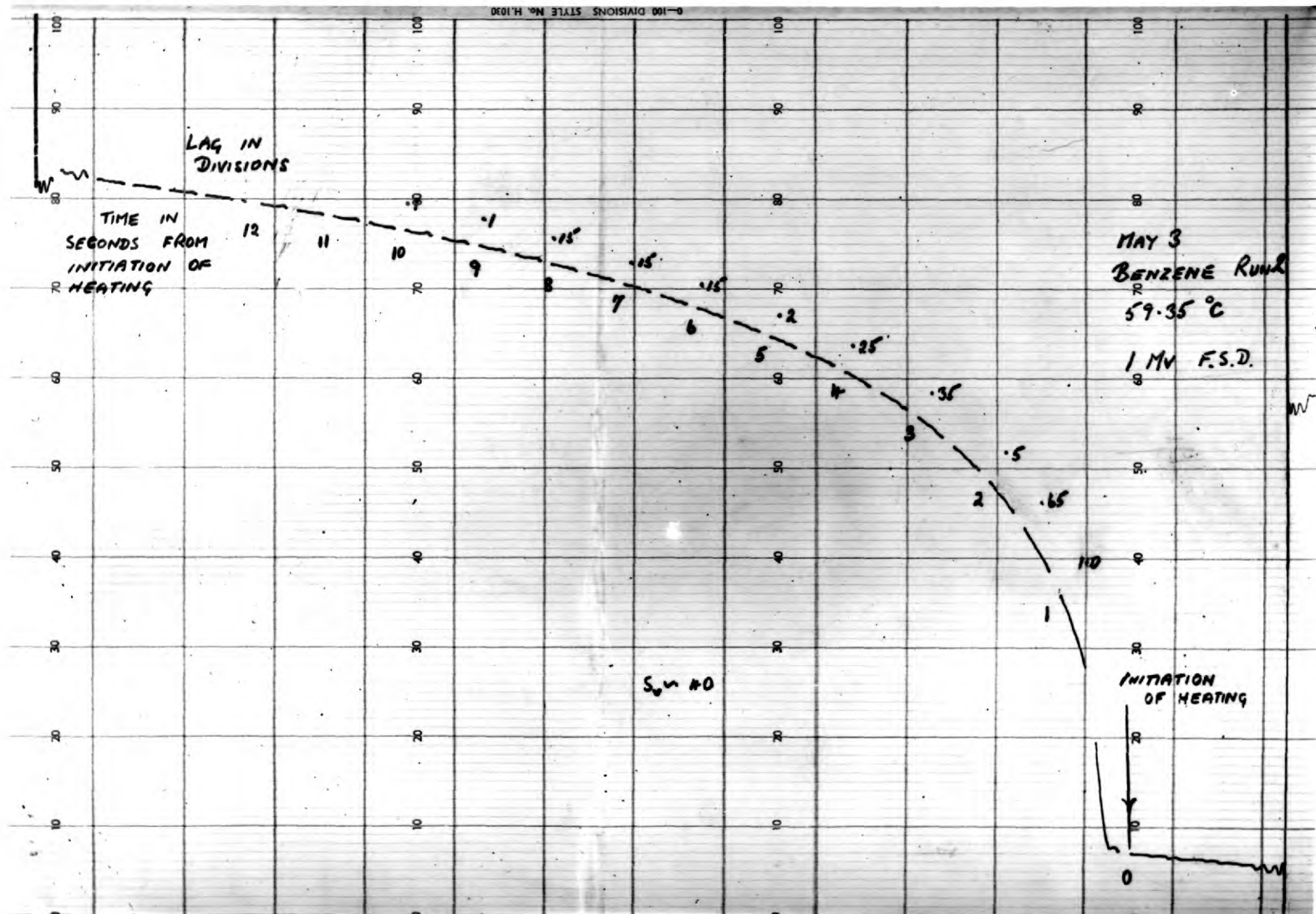
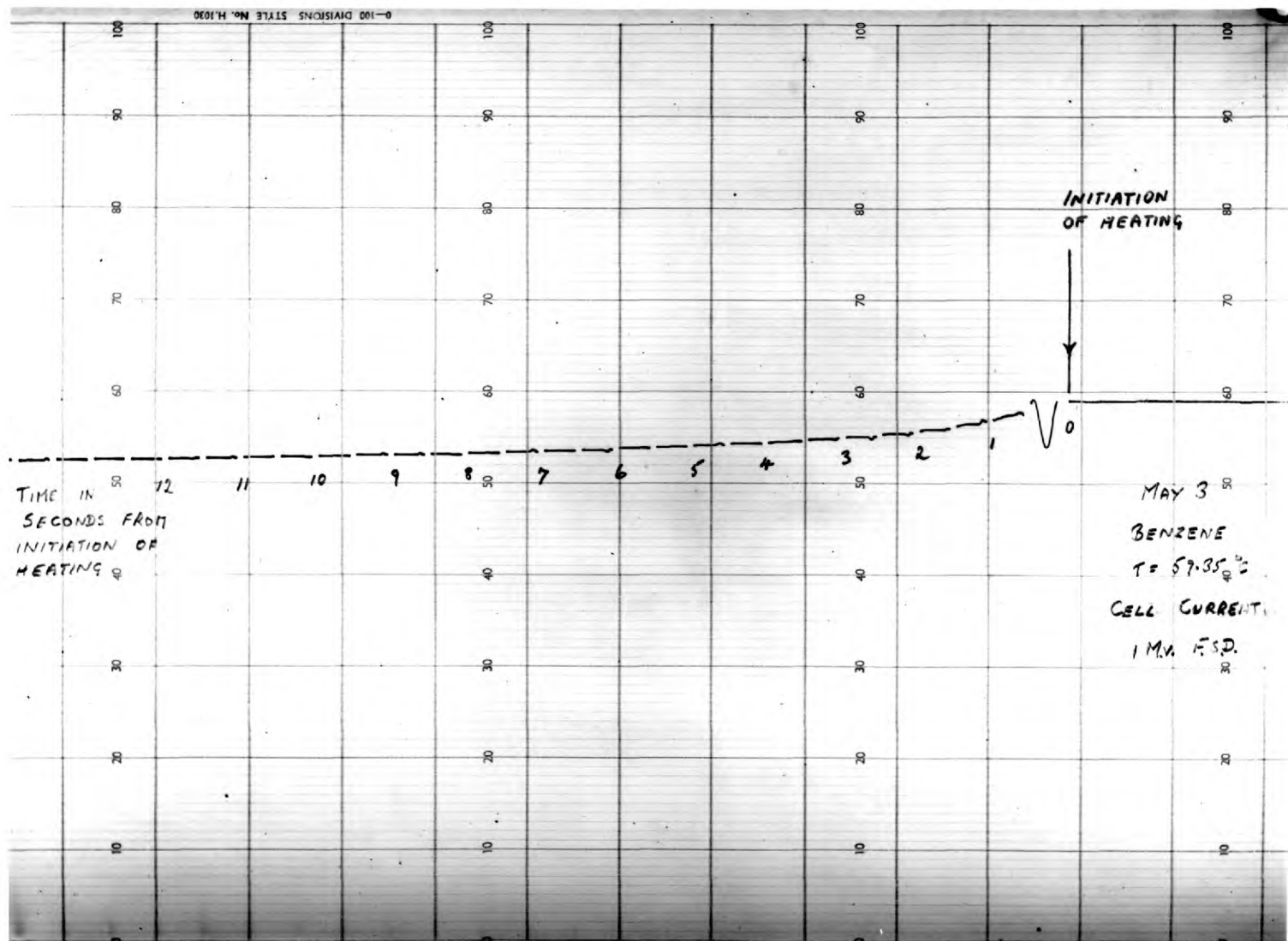


Figure 2.13

Figure 2.14



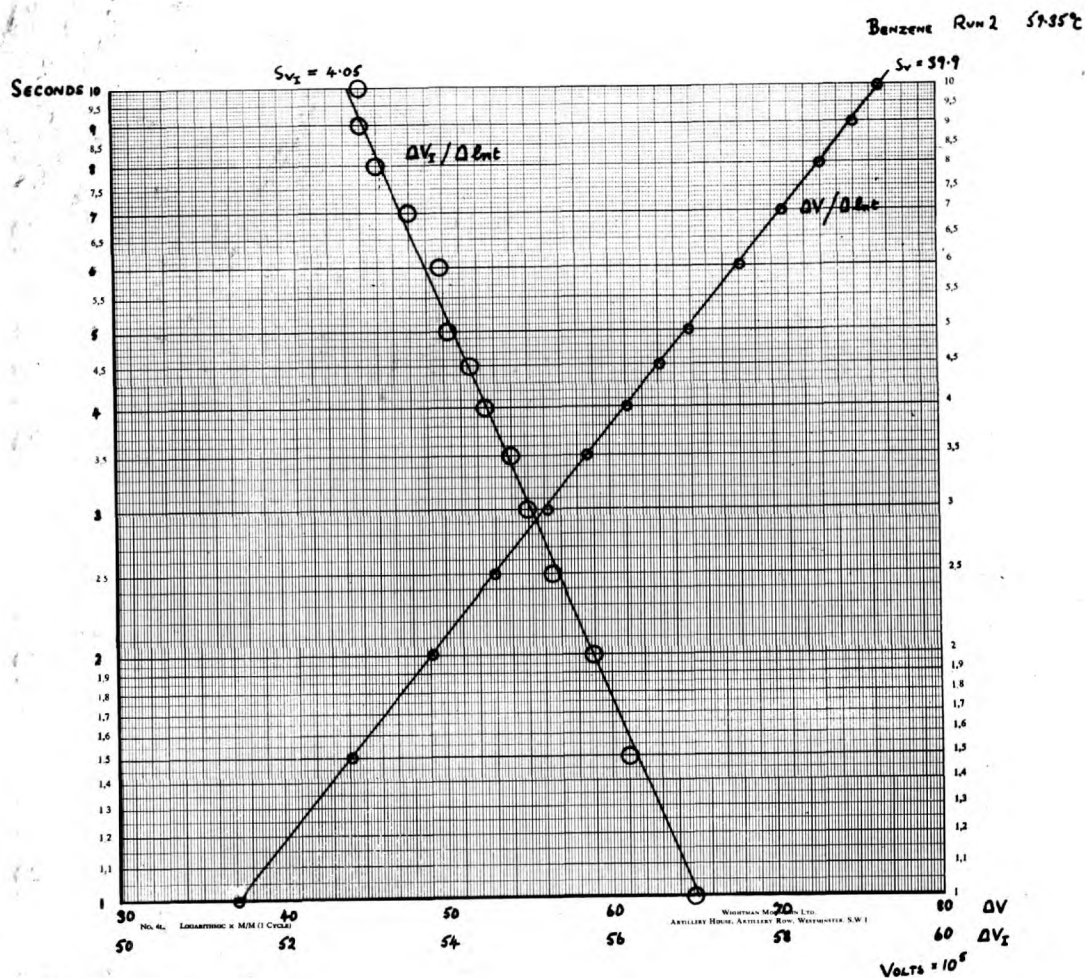


Figure-2.15-

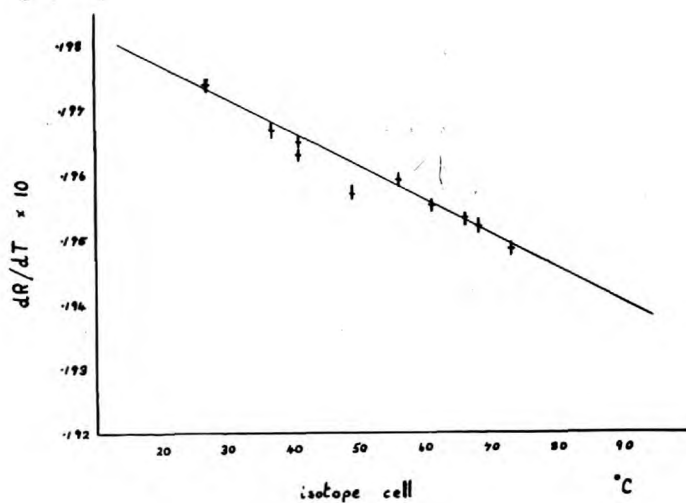


Figure 2.16

Specimen Calculation

Benzene 59.35°C

Potentiometer setting during  $\Delta V$  runs .40240 volts

Mean recorder deflection during measurement .00060 volts

Mean value of  $V$  during measurement .40300 voltsPotentiometer setting during  $\Delta V_I$  runs .63860 volts

Mean recorder deflection during measurement .00050 volts

Mean value of  $V_I$  during measurement .63910 voltsMean value of  $I = .1 V_I$  .06391 amps

| $\Delta V / \Delta \log t$ runs |                                                    | $\Delta V_I / \Delta \log t$ runs |                                                      |
|---------------------------------|----------------------------------------------------|-----------------------------------|------------------------------------------------------|
| Run                             | $\Delta V / \Delta \log t \times 10^5$ (volts/sec) | Run                               | $\Delta V_I / \Delta \log t \times 10^5$ (volts/sec) |
| I                               | 39.6                                               | I                                 | 4.05                                                 |
| II                              | 39.9                                               | II                                | 4.15                                                 |
| III                             | 40.3                                               |                                   |                                                      |
| Mean                            | 39.95                                              | Mean                              | 4.1                                                  |

$$\Delta I / \Delta \log t = 0.41$$

$$P_{\text{mean}} = V_{\text{mean}} \times I_{\text{mean}} = 0.02576 \text{ watts}$$

110.

$$dR/dT \text{ at } 59.35^{\circ}\text{C}$$

$$= 0.01956$$

$$\frac{1}{I} \frac{\Delta V}{\Delta \log t}$$

$$= 625.0 \times 10^{-5}$$

$$- \frac{V}{I} \frac{\Delta I}{\Delta \log t}$$

$$= 40.5 \times 10^{-5}$$

$$\frac{1}{I} \frac{\Delta V}{\Delta \log t} - \frac{V}{I} \frac{\Delta I}{\Delta \log t}$$

$$= 665.5 \times 10^{-5}$$

$$\lambda = \frac{.02576}{4\pi \times 10.52} \times \frac{.01956}{665.5 \times 10^{-5}}$$

$$= 1.316 \times 10^{-3} \text{ Jcm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$$

### 2.1.6 Thermal Conductivity Results

Except where otherwise stated the values of in the following tables are obtained by averaging two or three determinations of  $\Delta V / \Delta l \Delta t$  and  $\Delta I / \Delta l \Delta t$ . The spread of these quantities was used to calculate a probable error for the measurement. The average value of this error for all measurements on one compound is quoted at the head of each table. The temperatures quoted are those of the thermostat and are accurate to  $\pm .05^\circ\text{C}$ . The temperature of the wire during measurement is, on average,  $0.3^\circ\text{C}$  to  $0.4^\circ\text{C}$  higher than the bath temperature. Each graphical point is in the form of a cross, the vertical dimension of which is equivalent to the probable error in  $\lambda$ . The horizontal dimension is merely to mark the mid-point and has no significance for errors in temperature.

Wherever possible the thermal conductivities have been fitted to an expression of the form

$$10^{-3}\lambda = A + B\theta$$

$\lambda$  in  $\text{J. cm}^{-1}\text{sec}^{-1}^\circ\text{C}^{-1}$ ;  $\theta$  in  $^\circ\text{C}$ .

Values of  $A$  and  $B$  were obtained by a least squares calculation.

a. Toluene

Toluene obtained from Eastman Organic Chemicals Ltd. was dried over sodium wire. Analysis by gas chromatography at 50°C indicated a maximum impurity content of 0.05 mole %, probably benzene.

$$\text{Refractive index } n_{21}^D = 1.4967$$

TABLE 2.7 - Results

| T<br>°C | $\lambda \pm .21\%$<br>$10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ } ^\circ\text{C}^{-1}$ |                           |
|---------|--------------------------------------------------------------------------------------------------|---------------------------|
| 25.0    | 1.330                                                                                            |                           |
| 37.4    | 1.294                                                                                            | A = 1.403                 |
| 51.2    | 1.253                                                                                            | B = $2.92 \times 10^{-3}$ |
| 61.0    | 1.225                                                                                            |                           |

b. Water

Distilled water was passed through a mixed bed ion exchange column and subsequently boiled to remove traces of dissolved gas before sealing into the cell.

Several low temperature measurements have been

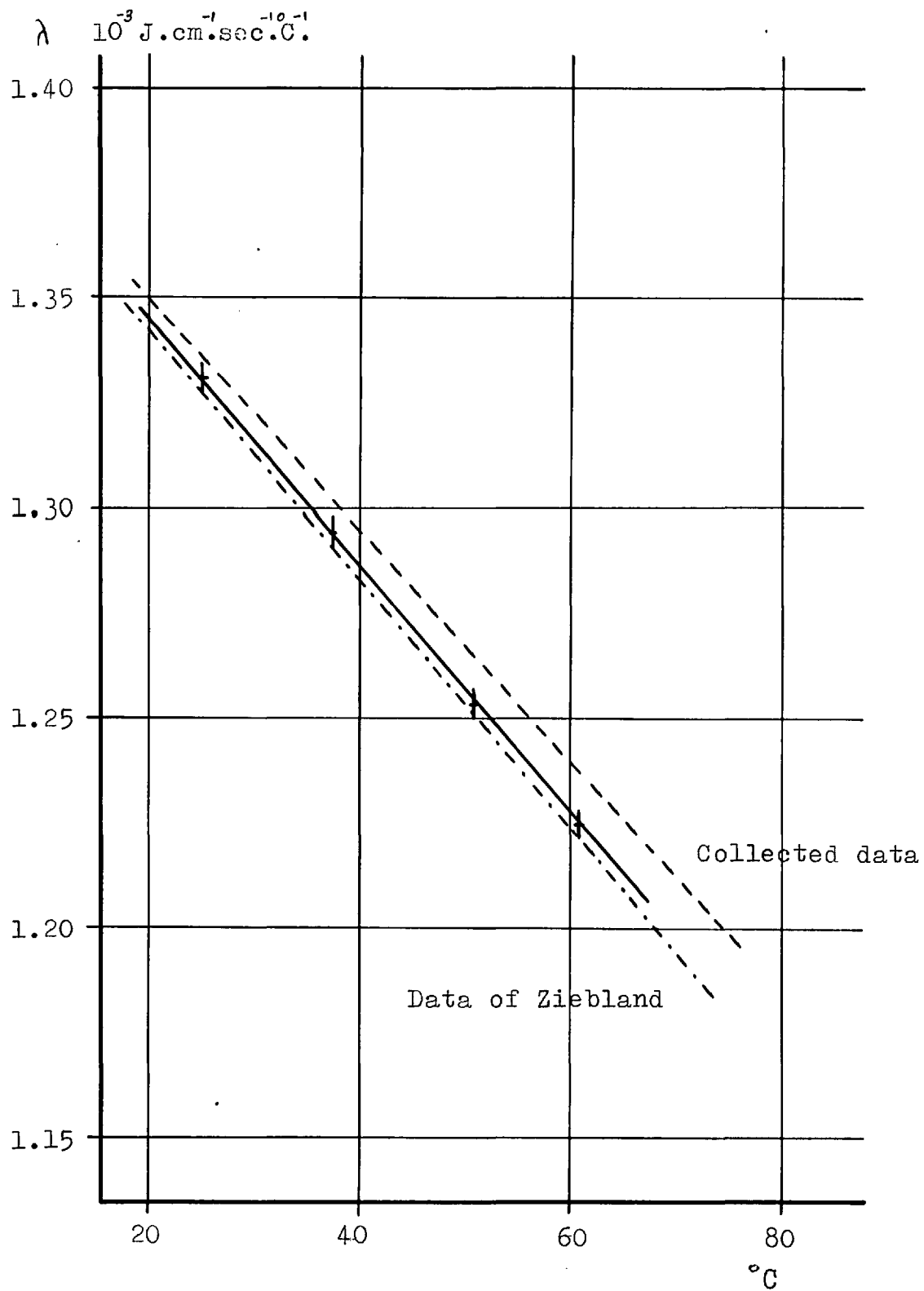


Figure 2.17

toluene

made using various cells. The high temperature region was studied using the isotope cell. Errors have been estimated only for these better measurements but those in the other points will not be significantly different.

TABLE 2.8 - Results  
The Thermal Conductivity of Water  
Single determinations at low temperatures

| Cell | L<br>cms | Other compounds<br>studied using the<br>same cell | T<br>°C | $\lambda$<br>$10^{-3}$<br>$\text{cm}^{-1}\text{sec}^{-1}\text{°C}^{-1}$ |
|------|----------|---------------------------------------------------|---------|-------------------------------------------------------------------------|
| I    | 9.12     | p-terphenyl                                       | 23.1    | 6.01                                                                    |
| II   | 10.145   | "                                                 | 22.3    | 5.09                                                                    |
|      |          |                                                   | 21.35   | 6.01                                                                    |
|      |          |                                                   | 21.35   | 5.97                                                                    |
| III  | 14.286   | diphenyl                                          | 30      | 6.07                                                                    |
|      |          | m-terphenyl                                       | 33.35   | 6.18                                                                    |
|      |          |                                                   | 33.35   | 6.18                                                                    |
| IV   | 15.3     | o-terphenyl                                       | 31.2    | 6.10                                                                    |
|      |          |                                                   | 20.8    | 5.90                                                                    |

Table 2.9 contains the results for water over a range of temperature made using the isotope cell (page 130 ).

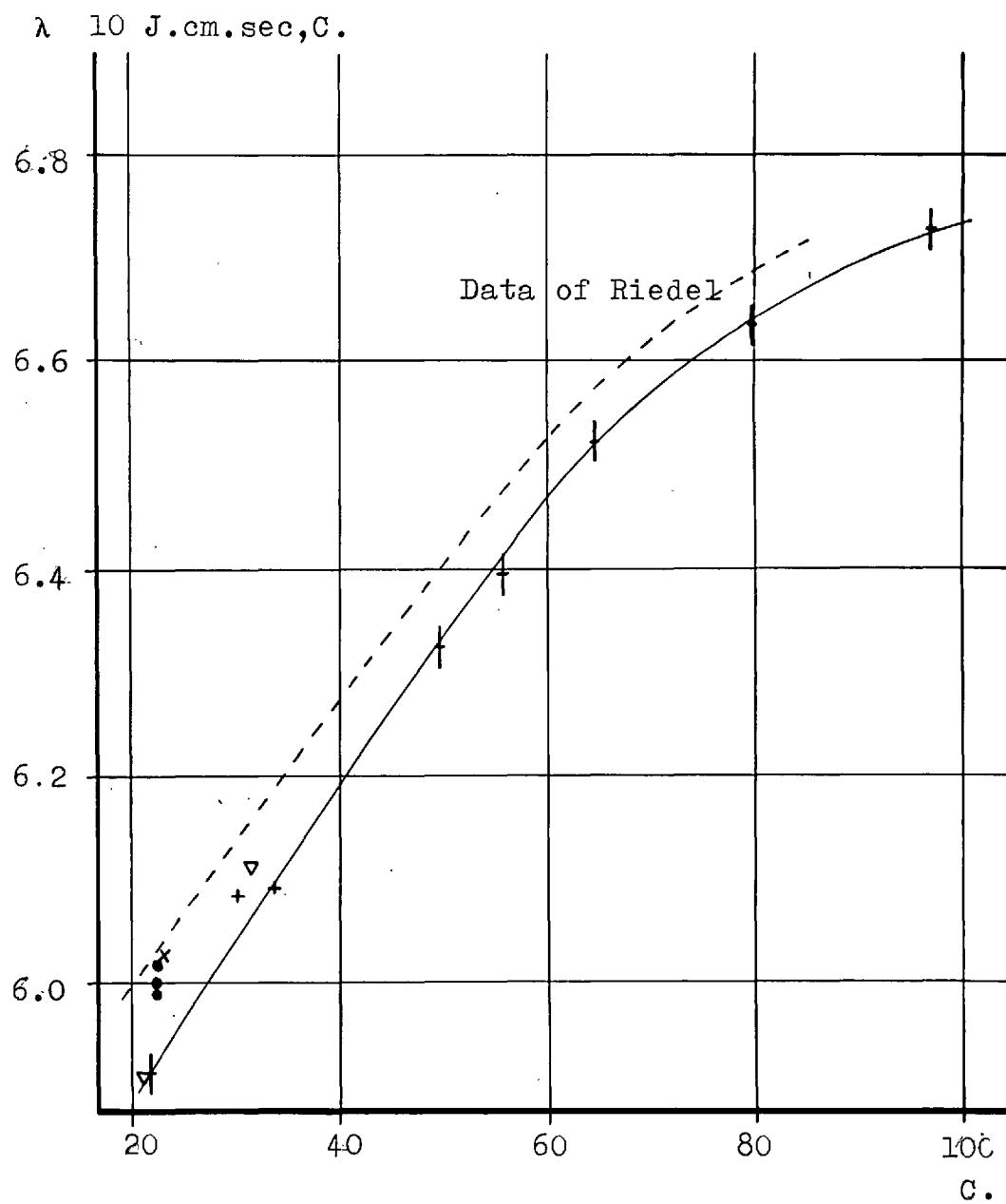


Figure 2.18      water

TABLE 2.9 - The thermal conductivity of water

| $T$<br>$^{\circ}\text{C}$ | $\lambda \pm 0.3\%$<br>$10^{-3} \text{ cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ |
|---------------------------|-------------------------------------------------------------------------------------------------|
| 21.8                      | 5.91                                                                                            |
| 49.3                      | 6.32                                                                                            |
| 55.3                      | 6.39                                                                                            |
| 64.5                      | 6.53                                                                                            |
| 79.8                      | 6.62                                                                                            |
| 96.9                      | 6.73                                                                                            |

c. The phenyl derivatives

The compounds studied were, benzene, diphenyl, o-terphenyl, m-terphenyl, p-terphenyl, cyclohexyl benzene, and triphenylene. Pure 20 grm. samples of each hydrocarbon were prepared. The stages of purification of the solid hydrocarbons were as follows:

1. Polar impurities were removed by elution through activated alumina in a non-polar solvent. In the case of materials of lower solubility the column and solvent were heated to  $50^{\circ}\text{C}$  or thereabouts.
2. After elution the solution was further purified by fractional recrystallisation.

3. The filtered crystals were dried under vacuum and collected by molecular distillation.

Where possible, melting points of the solids and refractive indices of the liquids were measured and compared with reported values.

Ultra violet spectra in the range  $50,000 - 30,000 \text{ cm}^{-1}$  were obtained for the polyphenyls.

No unusual peaks were detected except in the case of ortho-terphenyl which showed a small peak at  $40,000 \text{ cm}^{-1}$ . A sample was chromatographed and divided into fractions none of which however showed any enhancement or diminution of the peak, which was therefore assumed to be a genuine peak of ortho-terphenyl.

Diphenyl and the terphenyls were analysed by gas chromatography, in a 3' column containing a stationary phase of silicone oil on celite. The carrier gas was hydrogen, and the column was maintained at  $224^{\circ}\text{C}$ .

#### Results on the phenyl derivatives

Benzene : Two samples of benzene were measured, one in a conventional cell and the other in the isotope cell (page 130 )

The first sample was Hopkin and Williams Analar grade benzene used without further purification. The second sample was obtained from the same source but was purified by fractional freezing until the melting point remained constant. No significant difference was apparent in the measurements on the two samples.

Refractive Index  $n_{21}^D = 1.5005$  (Sample II)

TABLE 2.10 - Benzene (Sample I)

| $T$<br>$^{\circ}\text{C}$ | $\lambda \pm 0.25\%$<br>$10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ } ^{\circ}\text{C}^{-1}$ |
|---------------------------|-----------------------------------------------------------------------------------------------------|
| 31.1                      | 1.396                                                                                               |
| 33.5                      | 1.395                                                                                               |
| 41.3                      | 1.372                                                                                               |
| 48.4                      | 1.341                                                                                               |
| 60.7                      | 1.310                                                                                               |
| 67.8                      | 1.278                                                                                               |

The results for Sample II are included in the isotope section (page 133 ).

Diphenyl: This was obtained from Gesellschaft für Teerverwertung. It was purified by elution in benzene through activated alumina and subsequently recrystallised, filtered, and sublimed under vacuum.

A sample analysed by gas chromatography indicated a maximum molar impurity of .04%.

Melting point  $69.7^{\circ}\text{C}$ .

TABLE 2.11

| $T$<br>$^{\circ}\text{C}$ | $\lambda \pm 0.15\%$<br>$10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ |                            |
|---------------------------|----------------------------------------------------------------------------------------------------|----------------------------|
| 81                        | 1.367                                                                                              |                            |
| 89.7                      | 1.346                                                                                              |                            |
| 103.2                     | 1.332                                                                                              | $A = 1.477$                |
| 115.6                     | 1.318                                                                                              | $B = -1.41 \times 10^{-3}$ |
| 132.2                     | 1.291                                                                                              |                            |

o-terphenyl: This was obtained from British Drug Houses Ltd. (technical grade material). It was purified by elution in benzene through activated alumina and subsequently recrystallised, filtered and distilled under vacuum.

Molar impurities indicated by gas chromatography

were 0.5% unknown and 0.4% *m*-terphenyl.

Melting point 55.8°C.

TABLE 2.12

|              | $T$<br>°C | $\lambda \pm 0.11\%$<br>$10^{-3} \text{J cm}^{-1} \text{sec}^{-1} \text{ } ^\circ\text{C}^{-1}$ |                             |
|--------------|-----------|-------------------------------------------------------------------------------------------------|-----------------------------|
|              | 22.3      | 1.310                                                                                           |                             |
| super-cooled | 46.8      | 1.304                                                                                           |                             |
| liquid       | 51.7      | 1.300                                                                                           |                             |
| -----        |           |                                                                                                 |                             |
|              | 56.4      | 1.296                                                                                           |                             |
|              | 56.9      | 1.307                                                                                           |                             |
|              | 57.3      | 1.295                                                                                           |                             |
|              | 58.1      | 1.297                                                                                           |                             |
| 58           | 58.6      | 1.303                                                                                           | $A = 1.354$                 |
|              | 60.5      | 1.317                                                                                           | $B = -6.920 \times 10^{-4}$ |
|              | 60.6      | 1.309                                                                                           |                             |
|              | 60.8      | 1.310                                                                                           |                             |
|              | 68.8      | 1.307                                                                                           |                             |
|              | 78.2      | 1.299                                                                                           |                             |
|              | 85.0      | 1.293                                                                                           |                             |
|              | 97.7      | 1.280                                                                                           |                             |
|              | 123.3     | 1.270                                                                                           |                             |
|              | 140.6     | 1.255                                                                                           |                             |

m-terphenyl: This was obtained from British Drug Houses Ltd. (technical grade material). Purification was as for o-terphenyl.

Molar impurities indicated by gas chromatography were 1% para-terphenyl and 0.5% unknown.

Melting point  $87.0^{\circ}\text{C}$ .

TABLE 2.13

|                    | $T$                | $\lambda \pm 0.1\%$                                              |
|--------------------|--------------------|------------------------------------------------------------------|
|                    | $^{\circ}\text{C}$ | $10^{-3} \text{J cm}^{-1} \text{sec}^{-1} ^{\circ}\text{C}^{-1}$ |
| supercooled liquid | 82                 | 1.367                                                            |
|                    | 91.3               | 1.365                                                            |
|                    | 99.0               | 1.360                                                            |
|                    | 107.3              | 1.360                                                            |
|                    | 121.8              | 1.354                                                            |
|                    | 133.7              | 1.348                                                            |

$A = 1.397$   
 $B = -3.6 \times 10^{-4}$

p-terphenyl: The para-terphenyl was obtained from Eastman Organic Chemicals. It was eluted through alumina in benzene at  $50^{\circ}\text{C}$  and subsequently recrystallised, filtered and sublimed under vacuum.

A sample was analysed by gas chromatography at 220°C. No impurities were indicated.

Melting point 212°C

TABLE 2.14

| $T$<br>°C | $\lambda \pm 0.23\%$<br>$10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ } ^\circ\text{C}^{-1}$ |                            |
|-----------|---------------------------------------------------------------------------------------------------|----------------------------|
| 214.8     | 1.278                                                                                             |                            |
| 217.3     | 1.280                                                                                             |                            |
| 222.0     | 1.279                                                                                             | $A = 1.527$                |
| 231.0     | 1.259                                                                                             | $B = 1.144 \times 10^{-3}$ |
| 246.4     | 1.246                                                                                             |                            |

Triphenylene: The sample was obtained from Rutgerswerke Aktiengesellschaft (rein 99%). It was purified by elution in benzene and subsequently recrystallised and sublimed under vacuum.

One measurement was made.

$$\lambda = 1.337 \pm .3\% \quad 10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ } ^\circ\text{C} \quad \text{at } 208.9^\circ\text{C}$$

Cyclohexyl Benzene: The sample was not purified. The refractive index was  $n_{22}^D = 1.5266$ .

Two measurements were made.

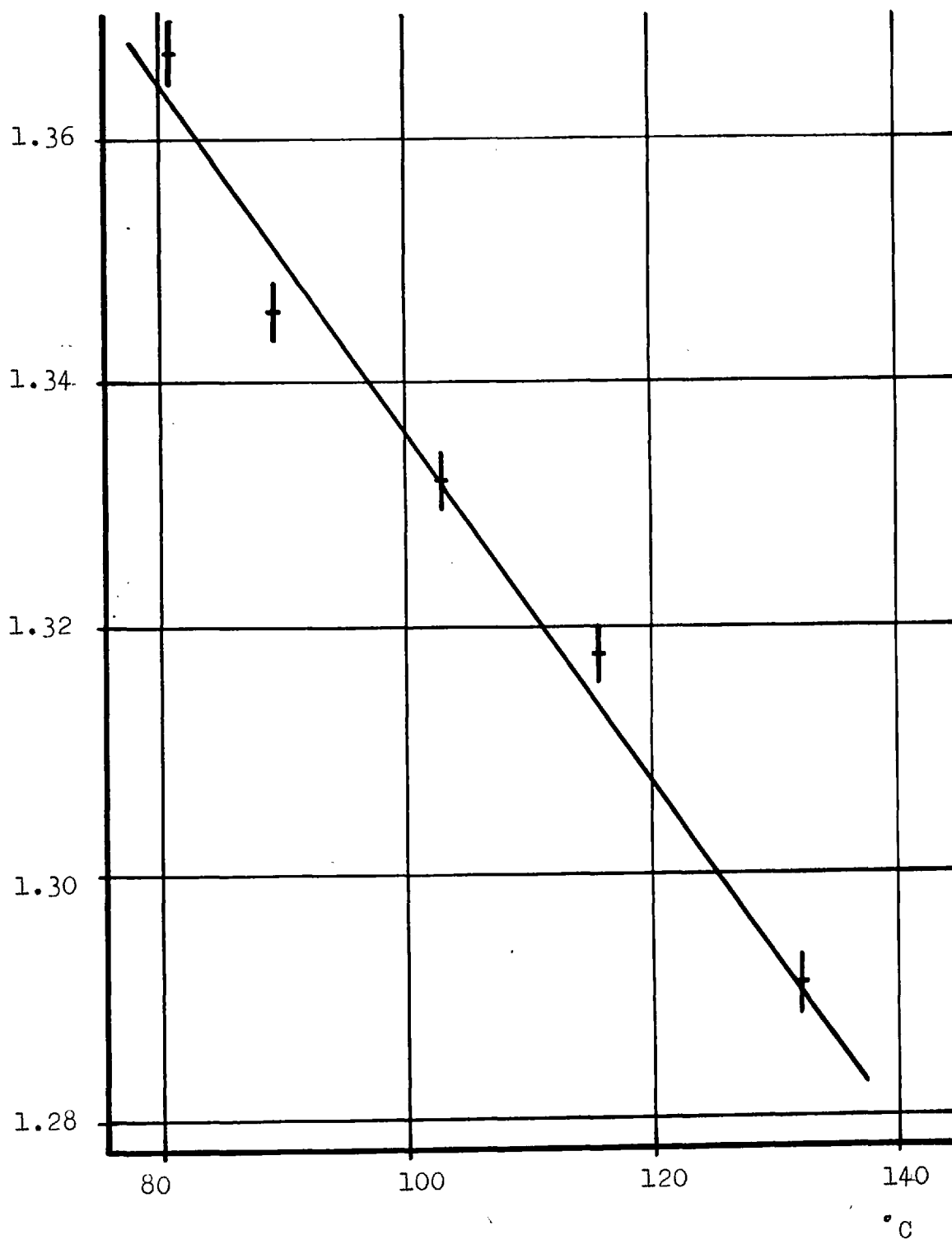


Figure 2.19

diphenyl

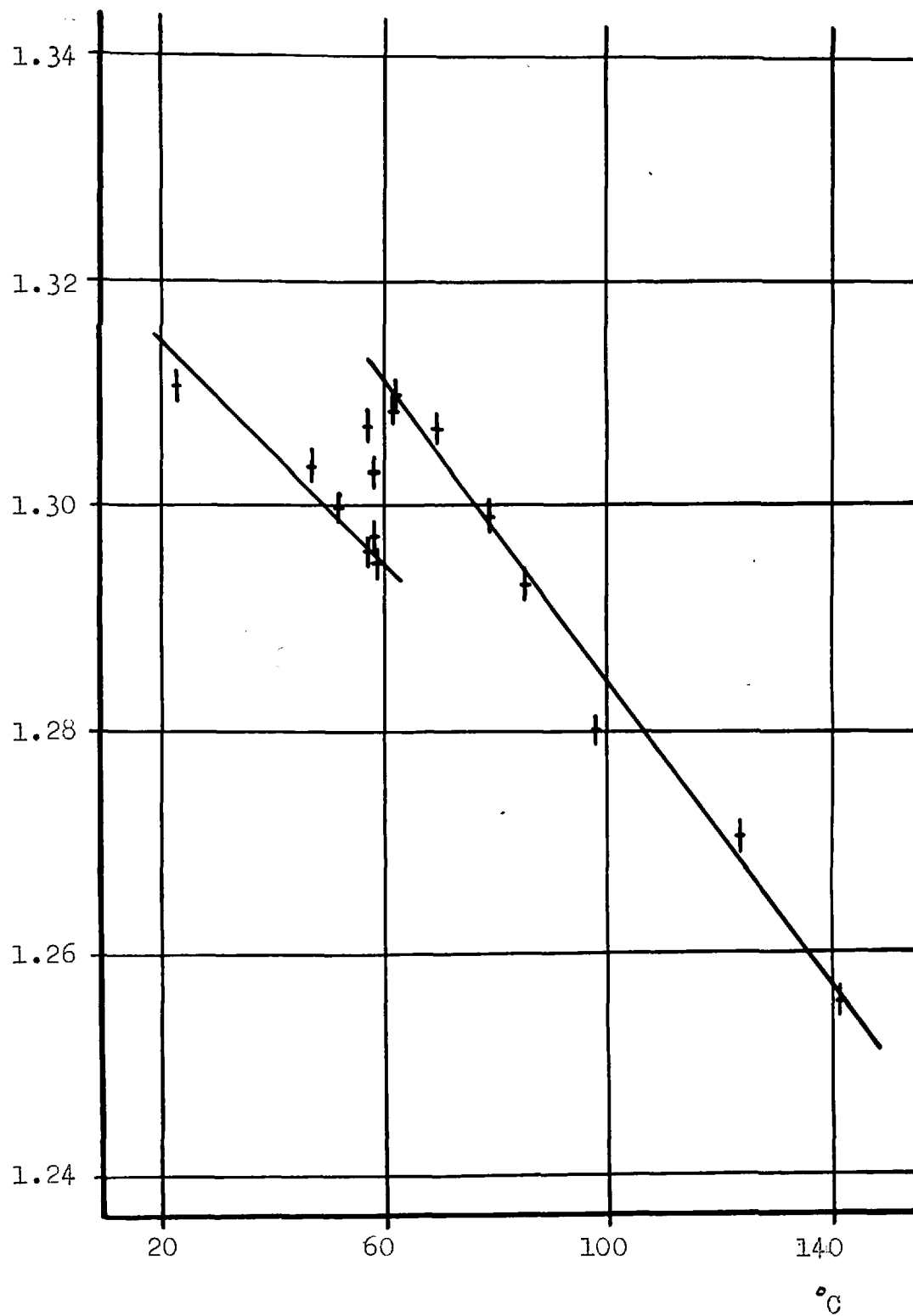
$\lambda \quad 10^{-9} \text{ J.cm}^{-1}.\text{sec}^{-1}.\text{ }^{\circ}\text{C}^{-1}$ 

Figure 2.20

ortho-terphenyl

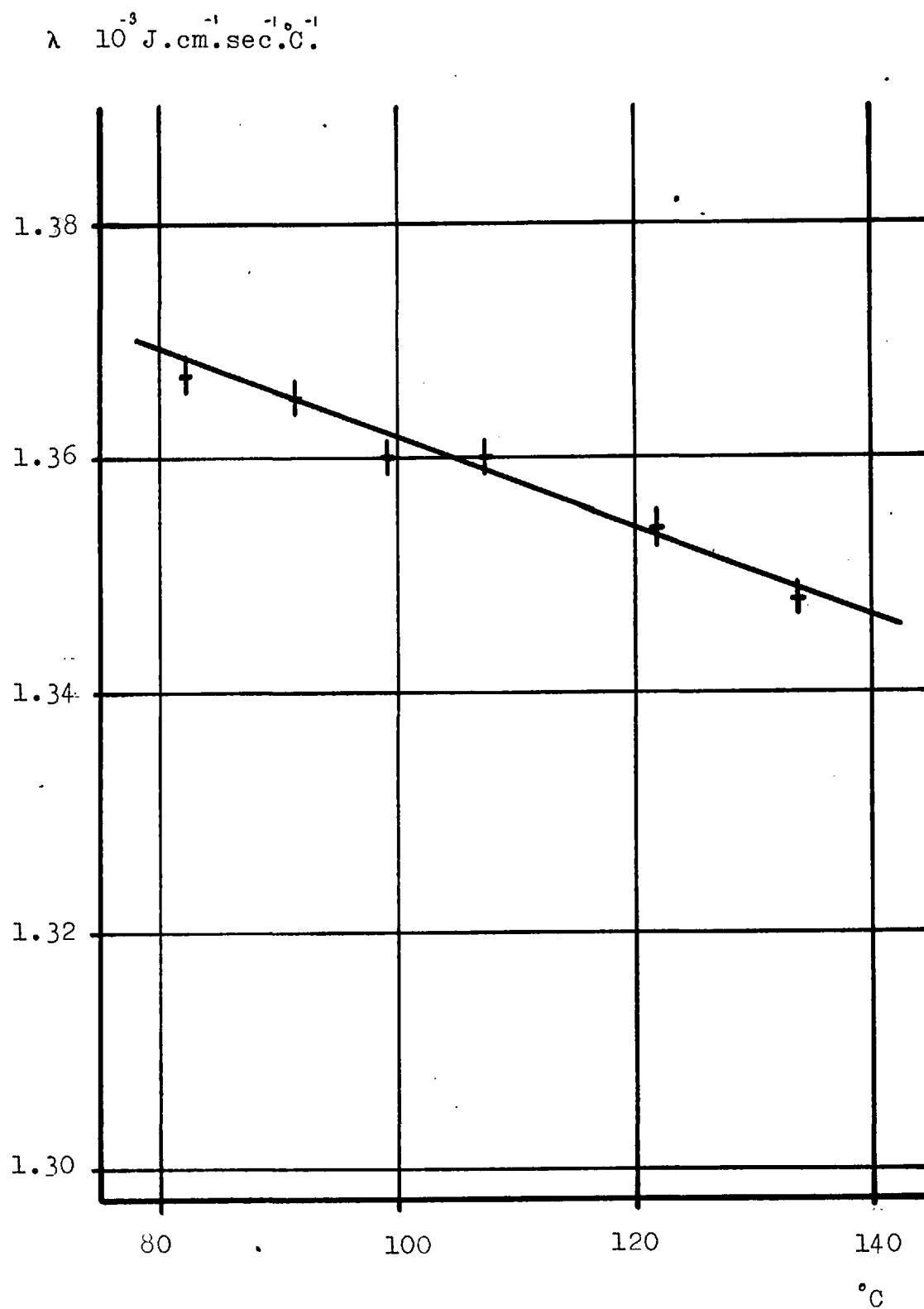


Figure 2.21

meta - terphenyl

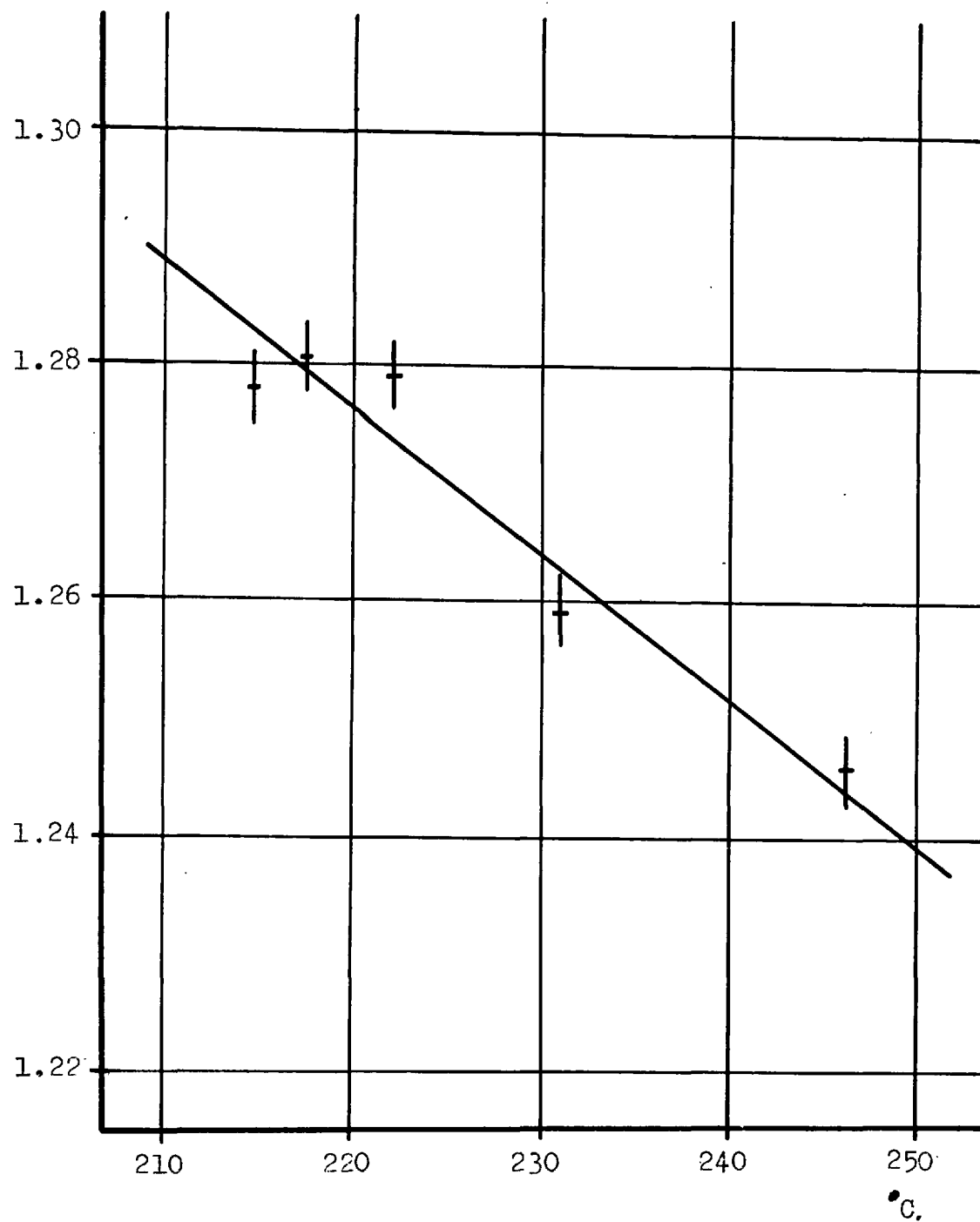
$\lambda \cdot 10^3 \text{ J.cm}^{-1}\text{sec}^{-1}\text{.}^\circ\text{C}^{-1}$ 

Figure 2.22

para - terphenyl

TABLE 2.15

| $T$<br>$^{\circ}\text{C}$ | $\lambda \pm 0.3\%$<br>$10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$ |                                                                                                          |
|---------------------------|---------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------|
| 22                        | 1.203                                                                                             | $d\lambda/dT = 1.1 \pm .3$<br>$10^{-6} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-2}$ |
| 36                        | 1.188                                                                                             |                                                                                                          |

Ethyl Iodide, n Butyl Iodide measurements

Both compounds were obtained from Hopkins and Williams Ltd. and each was treated<sup>(15)</sup> with sodium to remove free hydrogen iodide and water. They were cooled in ice during the treatment to avoid Wurtz formation of butane and octane.

The decanted liquors were fractionated in a column containing copper turnings. They were stored in the dark under an atmosphere of nitrogen and in the presence of calcium. Before making up mixtures for measurement the appropriate quantity of material was refractionated. Properties of the purified materials were,

|                |                                                              |
|----------------|--------------------------------------------------------------|
| ethyl iodide   | 1.5104, b.p. $72.6 \pm 0.2^{\circ}\text{C}$ at 770 mms. Hg.  |
| n-butyl iodide | 1.4967, b.p. $130.8 \pm 0.2^{\circ}\text{C}$ at 770 mms. Hg. |

The measurements were carried out at  $19.35^{\circ}\text{C}$  (to compare with previous work<sup>(16)</sup> on diffusion coefficients) in a conventional water thermostat which was cooled below the ambient temperature. The cell itself was immediately surrounded by an oil filled jacket which insulated the leads and served to attenuate thermal fluctuations in the water bath.

TABLE 2.16 - Results  
Thermal conductivity of EtI + n BuI mixture

| mole fraction<br>EtI ( $x_1$ ) | $\lambda \pm 0.25\%$<br>$10^{-4}\text{J cm}^{-1}\text{sec}^{-1}\text{ }^{\circ}\text{C}^{-1}$ |
|--------------------------------|-----------------------------------------------------------------------------------------------|
| 0.000                          | 8.90                                                                                          |
| 0.183                          | 8.80                                                                                          |
| 0.336                          | 8.75                                                                                          |
| 0.589                          | 8.60                                                                                          |
| 0.835                          | 8.58                                                                                          |
| 1.000                          | 8.57                                                                                          |

A quadratic curve was fitted by least squares to the above results.

$$\lambda (10^{-4} \text{ cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}) = 8.91 - .661 x_1 + .33 x_1^2$$

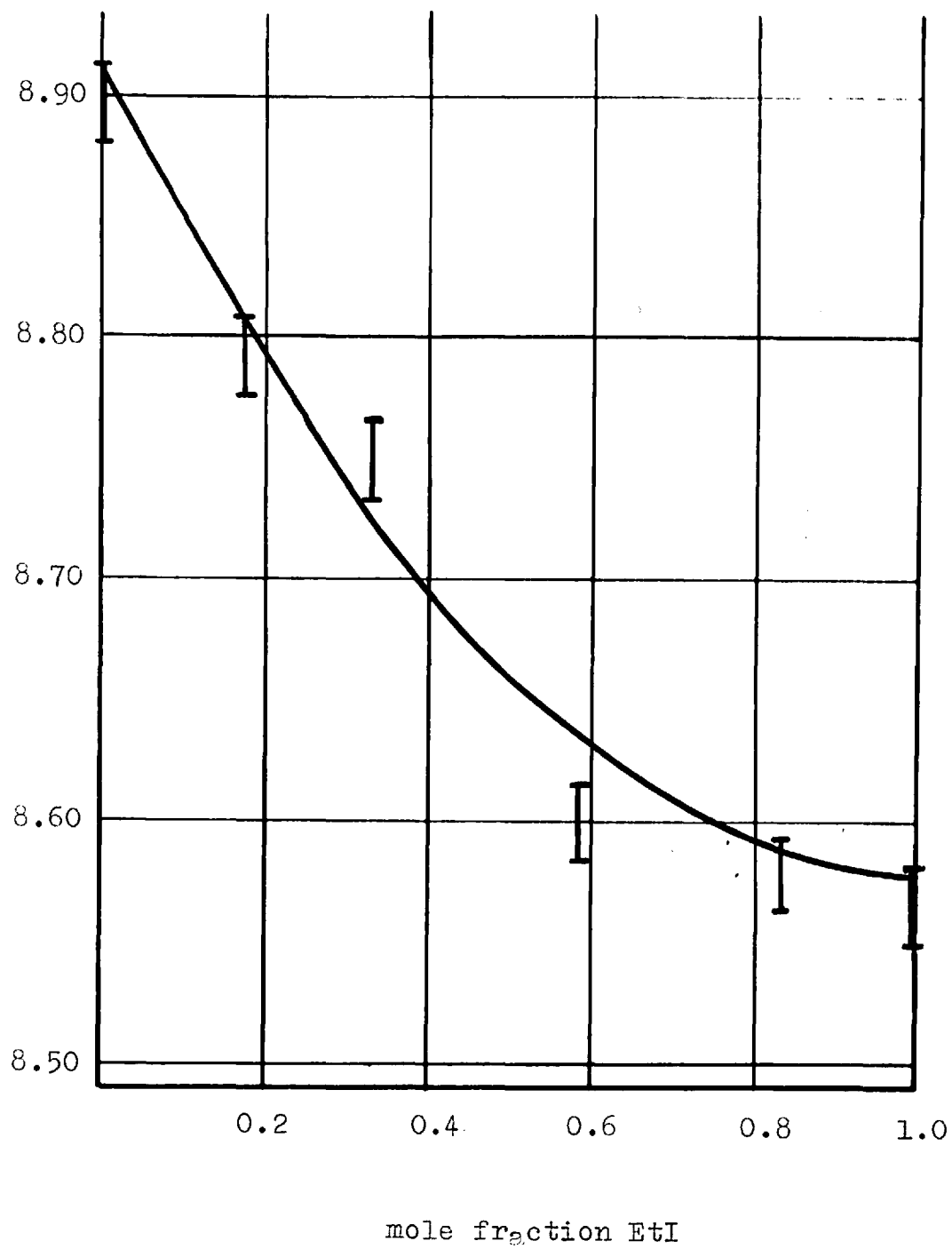
$\lambda$  10 J.cm.sec.C.

Figure 2.23

Measurements on Cis Dekalin, Trans Dekalin and Di-cyclohexyl

The Dekalins were obtained from Esso Research Ltd., and the Di-cyclohexyl from Monsanto Ltd. They were not purified.

TABLE 2.18 - Results

| Material       | Ref. Index            | $\lambda$ at 25.1°C                                                   |
|----------------|-----------------------|-----------------------------------------------------------------------|
|                |                       | $10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}$ |
| Cis Dekalin    | $n_{25}^D = 1.4800$   | 1.147                                                                 |
| Trans Dekalin  | $n_{24.2}^D = 1.4677$ | 1.080                                                                 |
| Di cyclohexyl  | $n_{24.1}^D = 1.4771$ | 1.156                                                                 |
| m.p. 3.4°C     |                       |                                                                       |
| b.p. 237-239°C |                       |                                                                       |

Measurements on the isotopically substituted benzene and cyclohexane

Measurements were made on benzene, cyclohexane, per-deuterobenzene and per-deuterocyclohexane over the range 20°C to 80°C.

Details of the Isotope Cell: The cell (figure 2.24) was modified to accommodate the small volumes available and to facilitate filling and emptying without loss. The diameter was reduced to 0.5 cms which was the minimum compatible with accurate

measurement over a period of 10 secs. The glass to metal seals were covered with a layer of Araldite to render them vacuum tight. A break seal was provided to aid recovery of the materials and an additional arm containing sodium for drying was sealed on immediately prior to filling the cell.

Filling Procedure: The arrangement is shown in figure 2.25 .

The deuterated compounds which were contained in sealed tubes were frozen in liquid nitrogen and opened under vacuum. They were sublimed over gradually into the arm of the cell. The arm only was cooled in liquid nitrogen so that the cell itself was not subjected to extremes of temperature. The whole cell assembly was sealed off under half an atmosphere of dry nitrogen.

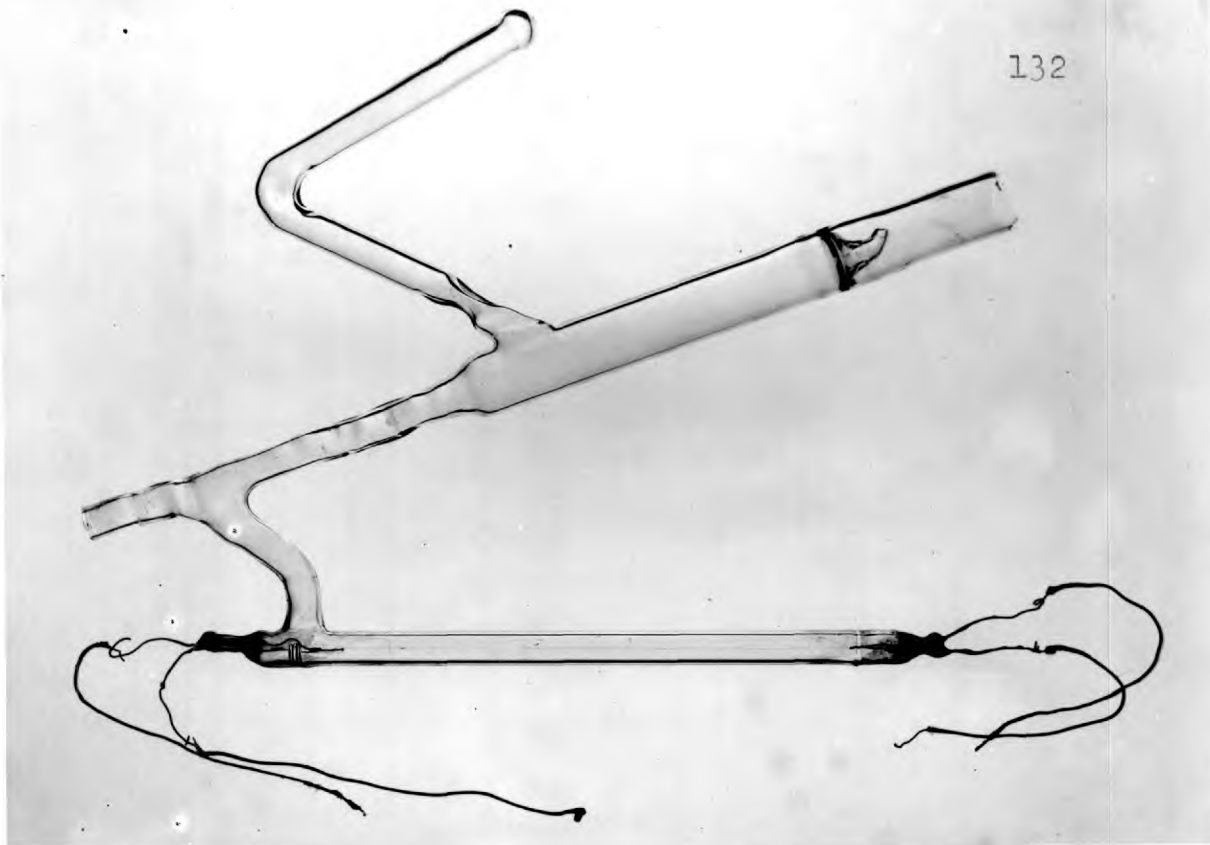


Figure 2.24

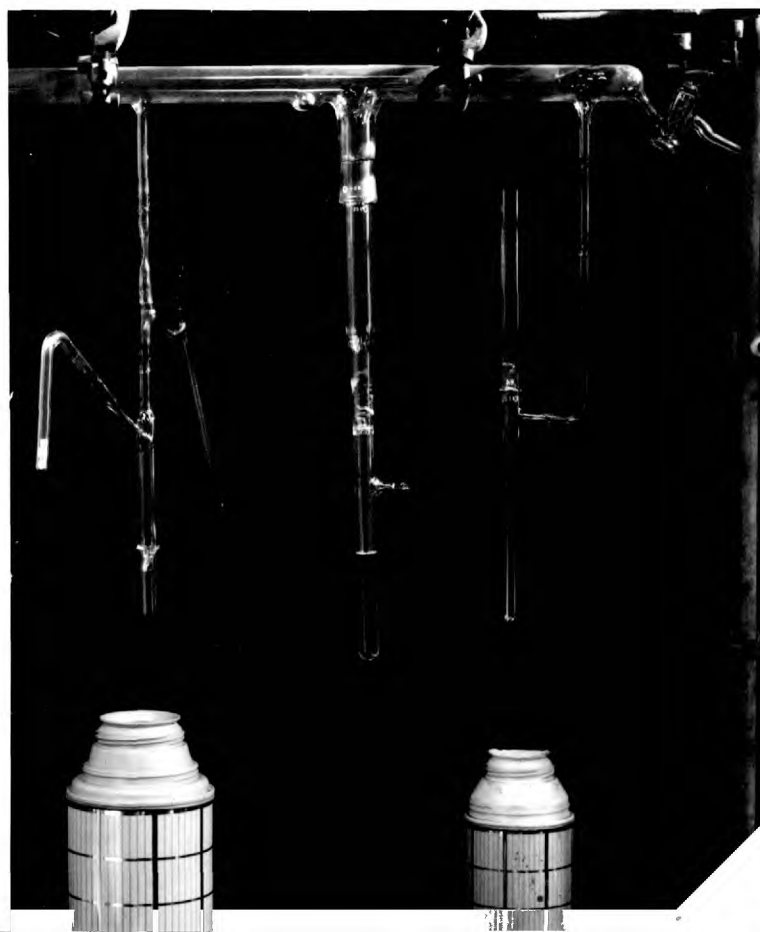


Figure 2.25

Results:    Benzene     $C_6H_6$

TABLE 2.19

| $T$         | $\lambda$                                   |                           |
|-------------|---------------------------------------------|---------------------------|
| $^{\circ}C$ | $10^{-3} J cm^{-1} sec^{-1} ^{\circ}C^{-1}$ |                           |
| 22.7        | 1.426                                       |                           |
| 34.9        | 1.387                                       |                           |
| 50.1        | 1.344                                       | $A = 1.501$               |
| 59.35       | 1.316                                       | $B = -3.2 \times 10^{-3}$ |
| 75.3        | 1.255                                       |                           |

$C_6D_6$

TABLE 2.20

| $T$         | $\lambda$                                   |                            |
|-------------|---------------------------------------------|----------------------------|
| $^{\circ}C$ | $10^{-3} J cm^{-1} sec^{-1} ^{\circ}C^{-1}$ |                            |
| 22.8        | 1.373                                       |                            |
| 33.8        | 1.338                                       |                            |
| 42.2        | 1.311                                       | $A = 1.437$                |
| 56.4        | 1.267                                       | $B = -2.89 \times 10^{-3}$ |
| 66.7        | 1.249                                       |                            |
| 74.3        | 1.223                                       |                            |

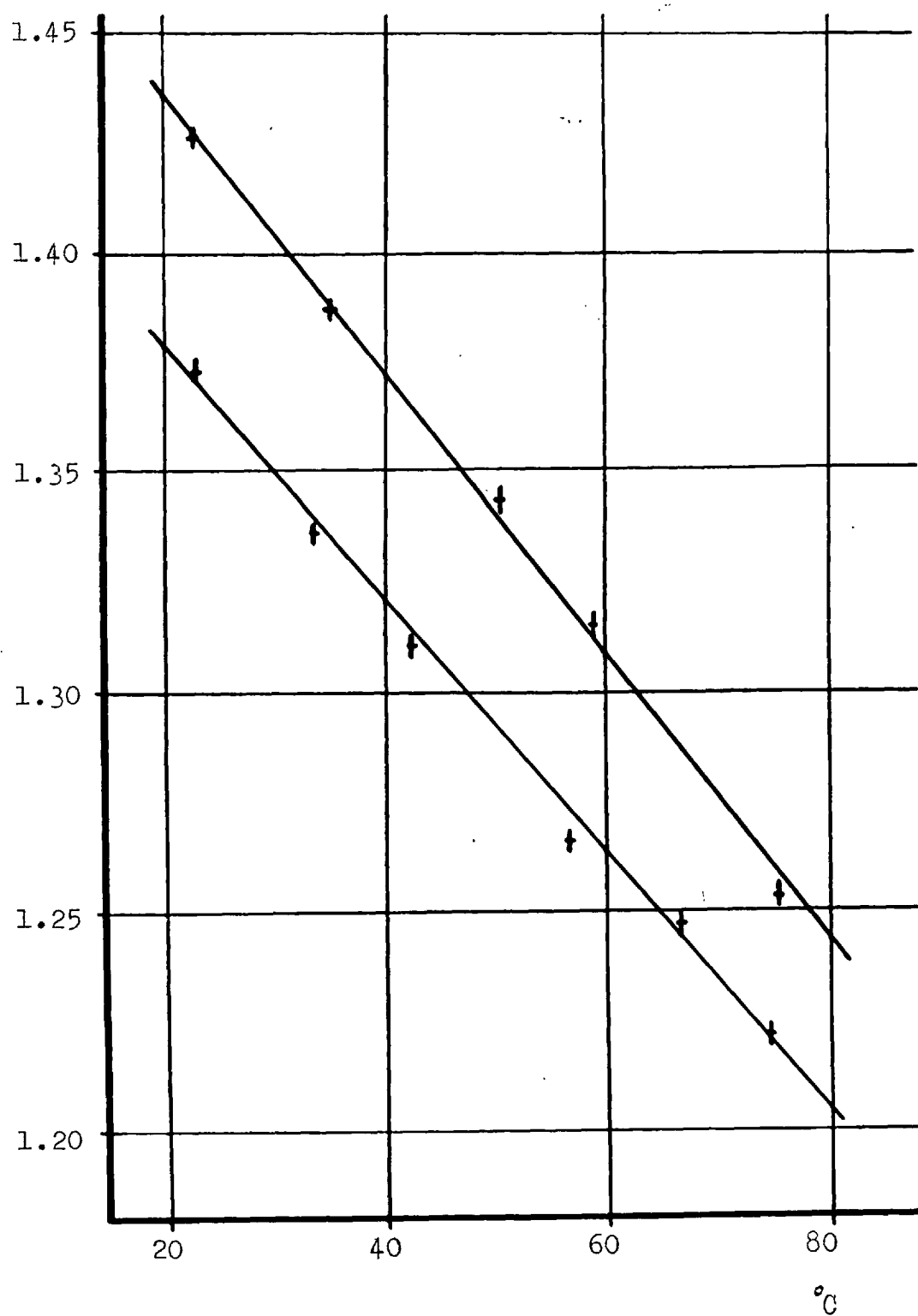
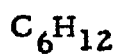
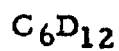


Figure 2.26 benzene &amp; per deuterio-benzene

CyclohexaneTABLE 2.21

| $T$<br>$^{\circ}C$ | $\lambda$<br>$10^{-3} J\ cm^{-1}\ sec^{-1}\ ^{\circ}C^{-1}$ |                            |
|--------------------|-------------------------------------------------------------|----------------------------|
| 21.4               | 1.201                                                       |                            |
| 31.0               | 1.187                                                       | $A = 1.259$                |
| 44.5               | 1.142                                                       | $B = -2.55 \times 10^{-3}$ |
| 59.2               | 1.107                                                       |                            |
| 71.5               | 1.078                                                       |                            |

TABLE 2.22

| $T$<br>$^{\circ}C$ | $\lambda$<br>$10^{-3} J\ cm^{-1}\ sec^{-1}\ ^{\circ}C^{-1}$ |                            |
|--------------------|-------------------------------------------------------------|----------------------------|
| 22.2               | 1.133                                                       |                            |
| 31.0               | 1.113                                                       |                            |
| 41.5               | 1.086                                                       | $A = 1.183$                |
| 50.5               | 1.061                                                       | $B = -2.31 \times 10^{-3}$ |
| 60.9               | 1.040                                                       |                            |
| 74.3               | 1.015                                                       |                            |

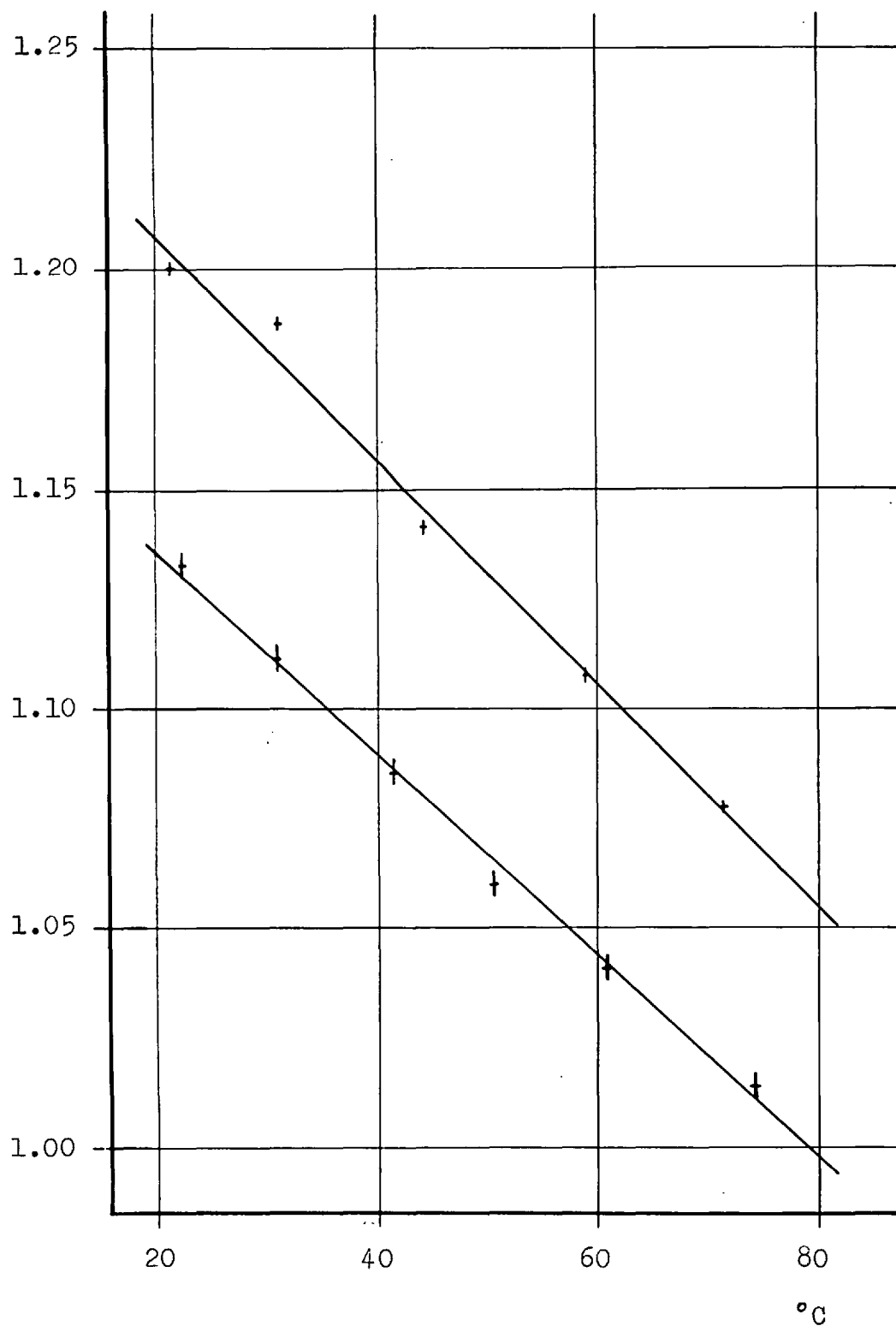


Figure 2.27      cyclohexane & per deuterio-cyclohexane

## CHAPTER 2.2: VISCOMETRIC MEASUREMENTS

### Capillary Viscometers

The streamline laminar flow of a liquid through a capillary of radius  $r$  and length  $\ell$  under an applied pressure  $P$  is described by

$$V = \frac{\pi P r^4 t}{8 \ell \eta} \quad (2.39)$$

in which  $V$  is the volume and  $t$  the duration of flow, and  $\eta$  is the viscosity of the medium.

Equation (2.39) is valid<sup>(17)</sup> under the following conditions:

- (a) The pressure,  $P$ , refers only to the pressure required in overcoming the viscous resistance of the liquid within the capillary.
- (b) The flow is everywhere parallel to the axis of the capillary.
- (c) No slipping occurs between the liquid and the walls.

In a practical viscometer only condition (c) is satisfied under all circumstances, conditions (a) and (b) are not completely satisfied and some correction to equation (2.39) is required.

### The Kinetic Energy Correction

Since the liquid bores the capillary with a finite velocity, some of the work done by the applied pressure is not dissipated within the capillary but in the viscometer reservoir. Thus the effective pressure for inclusion in equation (2.39) is somewhat less than the total applied pressure and is given by:

$$P_{eff} = P = \frac{m \rho V^2}{\pi r^4 t} \quad (2.40)$$

$m$  is a factor depending on the shape of the capillary entrances, introduced because the flow at the entrances and exits is modified by their shape.

### Couette Correction

Liquid entering the capillary does not immediately assume parallel streamlines<sup>(18)</sup>. This results in an additional resistance to flow which may be corrected by the addition of a small length to that of the capillary; the length being proportional to the radius<sup>(19)</sup>.

The finally corrected form of equation (2.31) is

$$\eta = \frac{\pi r^4 P t}{8 V (l + \alpha r)} - \frac{m \rho V}{8 \pi t (l + \alpha r)} \quad (2.40)$$

For comparative measurement it is unnecessary to determine all the constants in equation (2.40). Provided that flow times are measured for several values of  $P$  and the product  $Pt$  extrapolated to zero pressure, the equation (2.40) may be written

$$\eta = K (Pt)_0 \quad (2.41)$$

where  $K$  is an apparatus constant and  $(Pt)_0$  the extrapolated product. By calibrating against a liquid of known viscosity

$$\frac{\eta}{\eta_s} = \frac{(Pt)_0}{(P_s t_s)_0} \quad (2.42)$$

subscript  $s$  referring to the calibrating liquid.

#### Condition for Stream line Flow

The criterion which determines that the flow is stream-line has been given by Reynolds <sup>(2)</sup> to be that the dimensionless group  $R < 2000$ .  $R$  is defined, in the case of a capillary, as

$$R = \frac{u \rho d}{\eta} \quad (2.43)$$

where  $u$  is the linear velocity on the axis and  $d$  is the

capillary diameter.

In the present measurements the value of  $R$  has  
never exceeded 250

### 2.2.1. Apparatus

#### The Ubbelohde Viscometer <sup>(21)</sup>

This consisted (figure 2.28) of two parallel 8 cm. lengths of Veridia capillary (.3 mm. bore) joined at the base. The upper ends of the capillaries were ground flat and sealed at the rims into two bulbs, A and B, of approximately 1 ml. capacity. Three levels,  $L_1$ ,  $L_2$ ,  $L_3$ , were marked on the viscometers at the constrictions. The time of flow of an accurately known volume was measured between levels  $L_1$  and  $L_2$ .

A fixed total volume was always used in the viscometer since the validity of the comparative method depends on this. The fixed volume was determined by allowing excess liquid to overflow through T until the level  $L_3$  was exactly reached. This was repeated at every increased temperature.

#### Arrangement for supplying a constant pressure of Nitrogen <sup>(22)</sup>

Each of the glass tubes  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ , in figure 2.29 contained a 3 foot head of water. With  $T_1$  initially open to air, nitrogen introduced through valve V raised the pressure in the system up to that of the water head in  $C_1$ . The pressure was controlled at this value by allowing gas to

escape into the atmosphere. Increased pressures were obtained by closing  $T_1$ ,  $T_2$ ,  $T_3$ , in succession bringing in each case an additional 3 foot head of water into the system. Fluctuations due to bubbles of escaping gas were smoothed out in the filters  $F_1$  and  $F_2$ , and in the 20 litre reservoir R. The exit from the reservoir was connected to a mercury manometer and via a dual two-way tap system to the viscometer. Connections to the viscometer were made via P.V.C. flexible tubing. The ends of these were flamed and thoroughly blown out to minimise the possibility of introducing dust particles into the capillaries. Pressures were measured using a cathetometer to an accuracy of  $\pm .003$  cms. Hg. Meniscus corrections were applied.

#### The Thermostat

So that the maximum variation of viscosity during measurement should not exceed  $\pm 0.1\%$  the viscometer temperature was controlled to within  $\pm 0.5^\circ\text{C}$  in an oil filled thermostat fitted with a toluene mercury regulator. The temperatures were measured with mercury thermometers calibrated by N.P.L. to an accuracy  $\pm .1^\circ\text{C}$ .

In the case of the Ethyl Iodide, n-Butyl Iodide mixtures

Figure 2.29

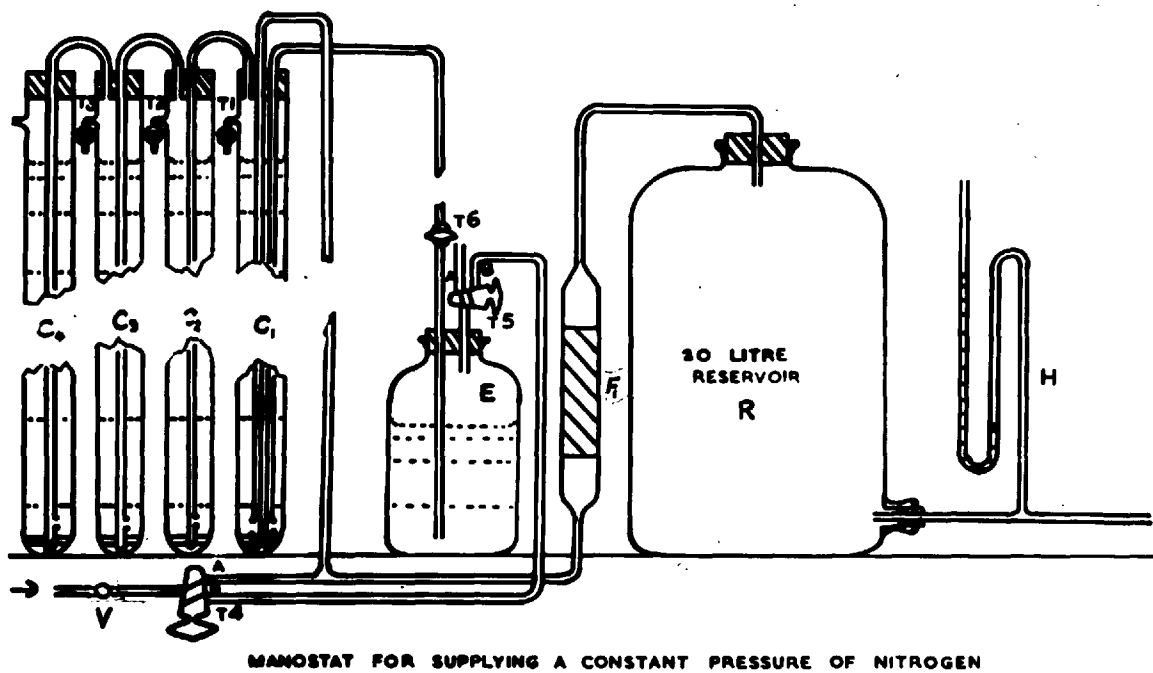
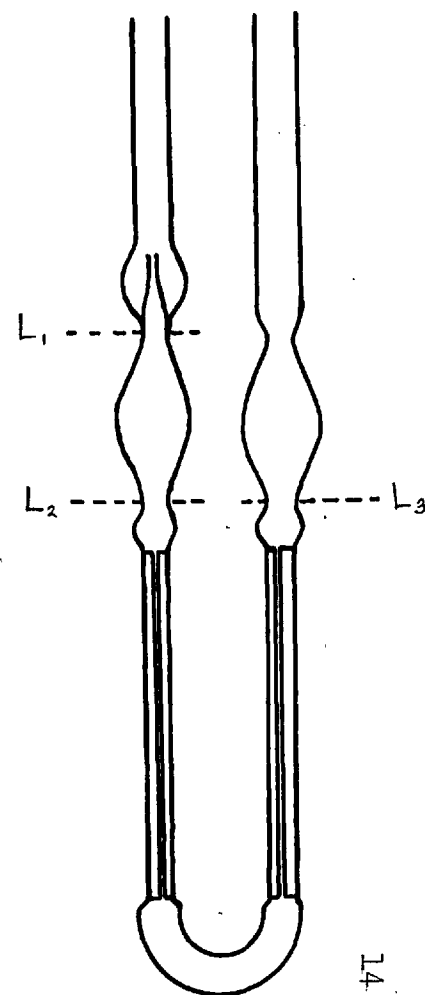


Figure 2.28



where the ambient temperature exceeded that required, the thermostat was cooled by circulating iced water through an external jacket.

### 2.2.3. The Measurements

Liquids were introduced into the viscometer through a sintered disc to remove any particles of solid matter. The viscometer was calibrated at two temperatures using distilled water. Measurements were made using three driving pressures each of which was applied more than once in each direction. At each pressure the mean product ( $Pt$ ) was plotted against  $P$  and extrapolated to zero  $P$  to get  $(Pt)_0$ . From the known absolute viscosity of water the viscometer constant

$$K = \frac{\eta}{(Pt)_0}$$

was calculated at each temperature and the mean value taken. Values of  $P$  and  $1/t$  for water are plotted in figure 2.30

### Viscosity Measurements

Viscosity measurements were made on the Ethyl Iodide n-Butyl Iodide system and on the deuterated hydrocarbons benzene and cyclohexane.

Ethyl Iodide n-Butyl Iodide System: The source and purification of the compounds has already been discussed (page 127 ). The measurements were made under the same conditions as were those of the thermal conductivity.

P cms. Hg

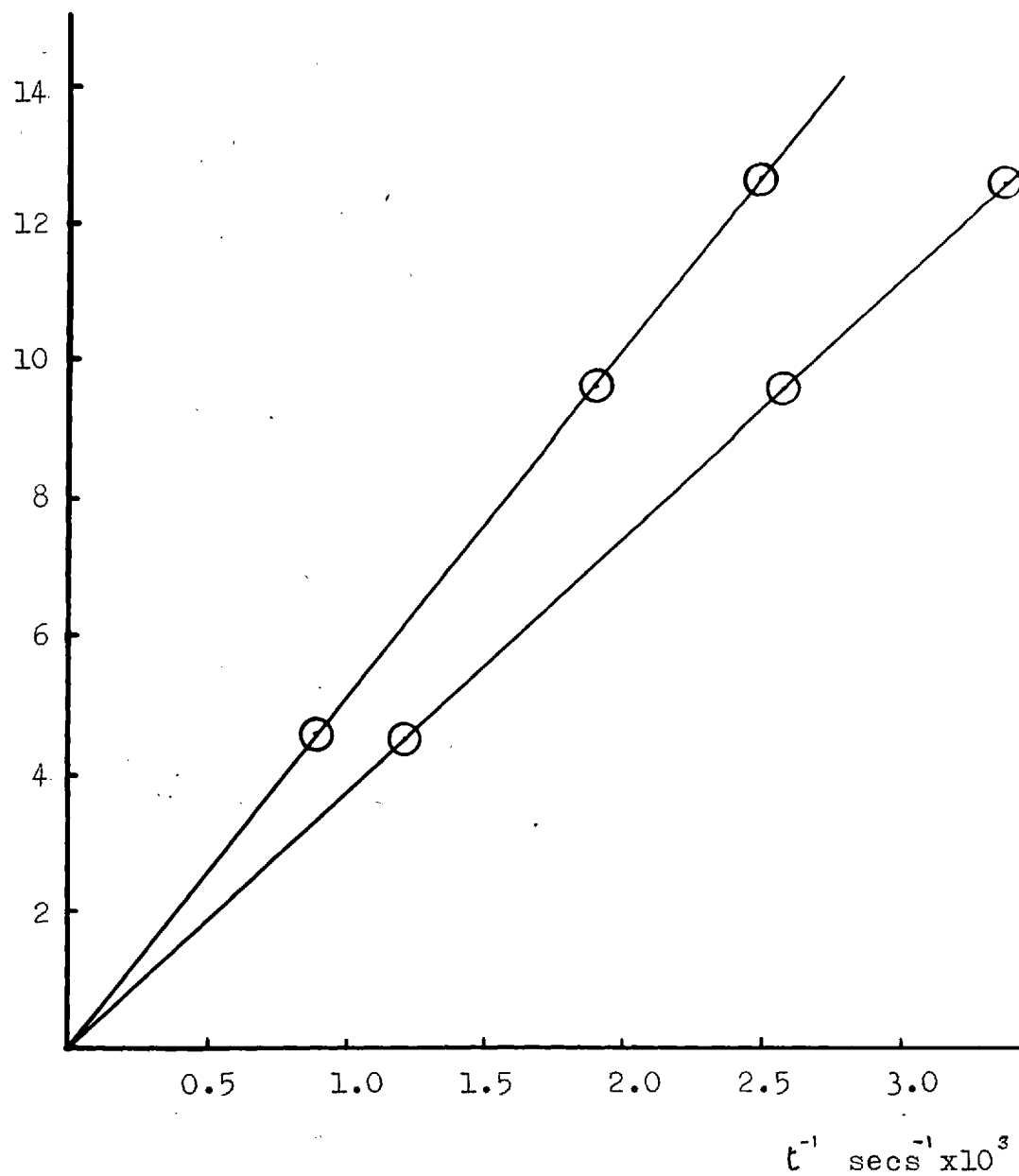


Figure 2.30

Viscometer Calibration

ResultsTABLE 2.23 - Viscosity of E<sub>1</sub>I (x<sub>1</sub>), n BuI mixtures

| mole fraction<br>Et I | $\eta$<br>millipoise |
|-----------------------|----------------------|
| 0.000                 | 8.87                 |
| 0.212                 | 8.21                 |
| 0.397                 | 7.74                 |
| 0.589                 | 7.12                 |
| 0.628                 | 7.04                 |
| 0.796                 | 6.55                 |
| 1.000                 | 5.89                 |

The following quadratic curve was fitted by least squares  
to the above results

$$\eta [10^{-3} \text{P}] = 8.78 - 2.583 x_1 - 0.283 x_1^2$$

per-deuterobenzeneTABLE 2.24 - Viscosity of  $C_6D_6$  as a function of temperature

| T<br>°C | $\eta$<br>$10^{-2}$ poise |
|---------|---------------------------|
| 21.8    | 0.682                     |
| 36.7    | 0.551                     |
| 51.15   | 0.463                     |
| 61.0    | 0.416                     |
| 71.6    | 0.371                     |

A least squares fit to  $\ln \eta = A + B/T$  gave

$$A = -.9903; \quad B = 5.375 \times 10^{-2}$$

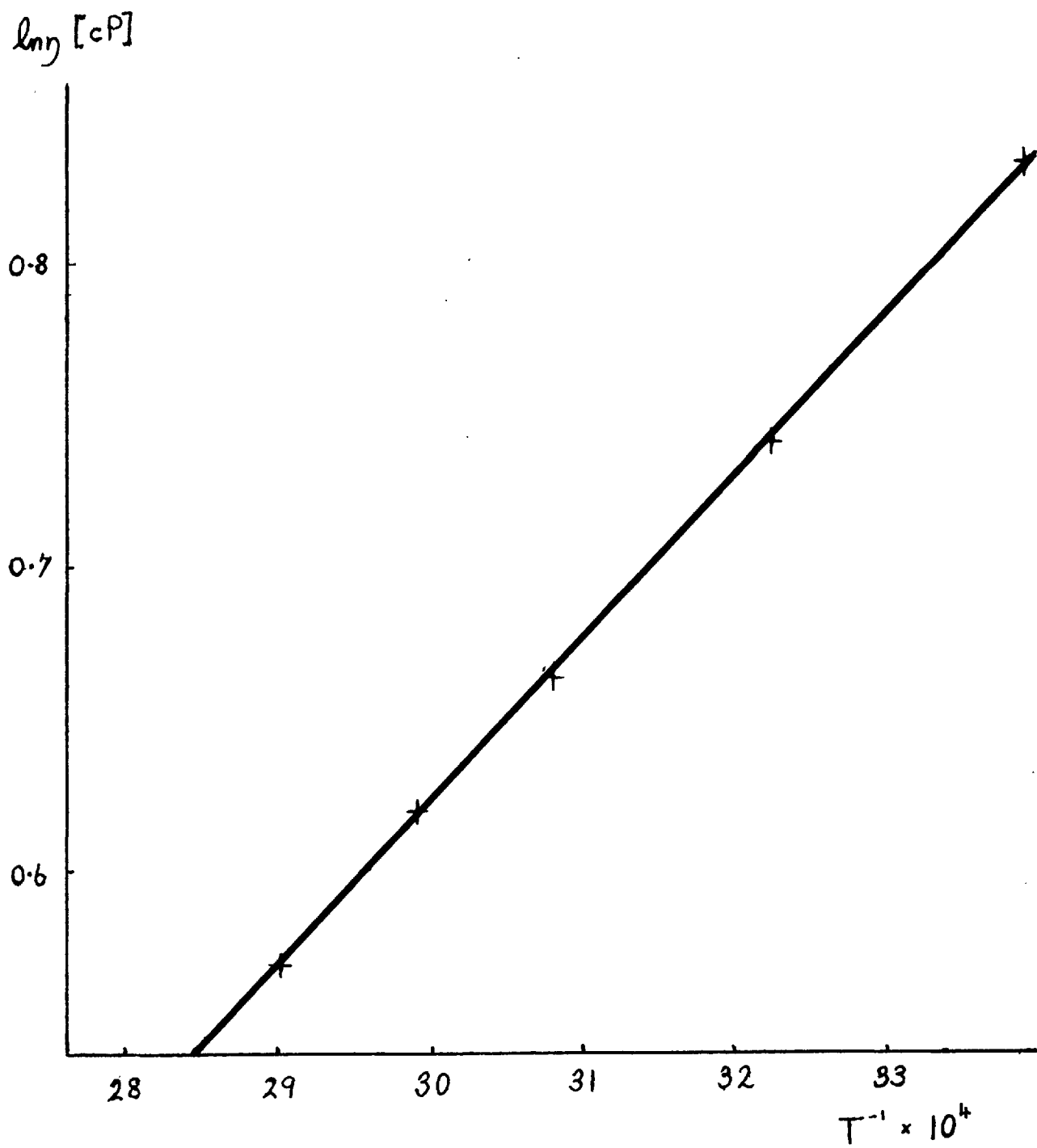


Figure 2.31

 $C_b D_b$

per-deuterocyclohexane

TABLE 2.25 - Viscosity of  $C_6D_{12}$  as a function of temperature

| $T$<br>$^{\circ}C$ | $10^{-2}$ poise |
|--------------------|-----------------|
| 27.1               | 0.925           |
| 41.95              | 0.733           |
| 51.15              | 0.641           |
| 59.8               | 0.568           |
| 68.9               | 0.507           |

$$A = -1.181; \quad B = 6.448 \times 10^2$$

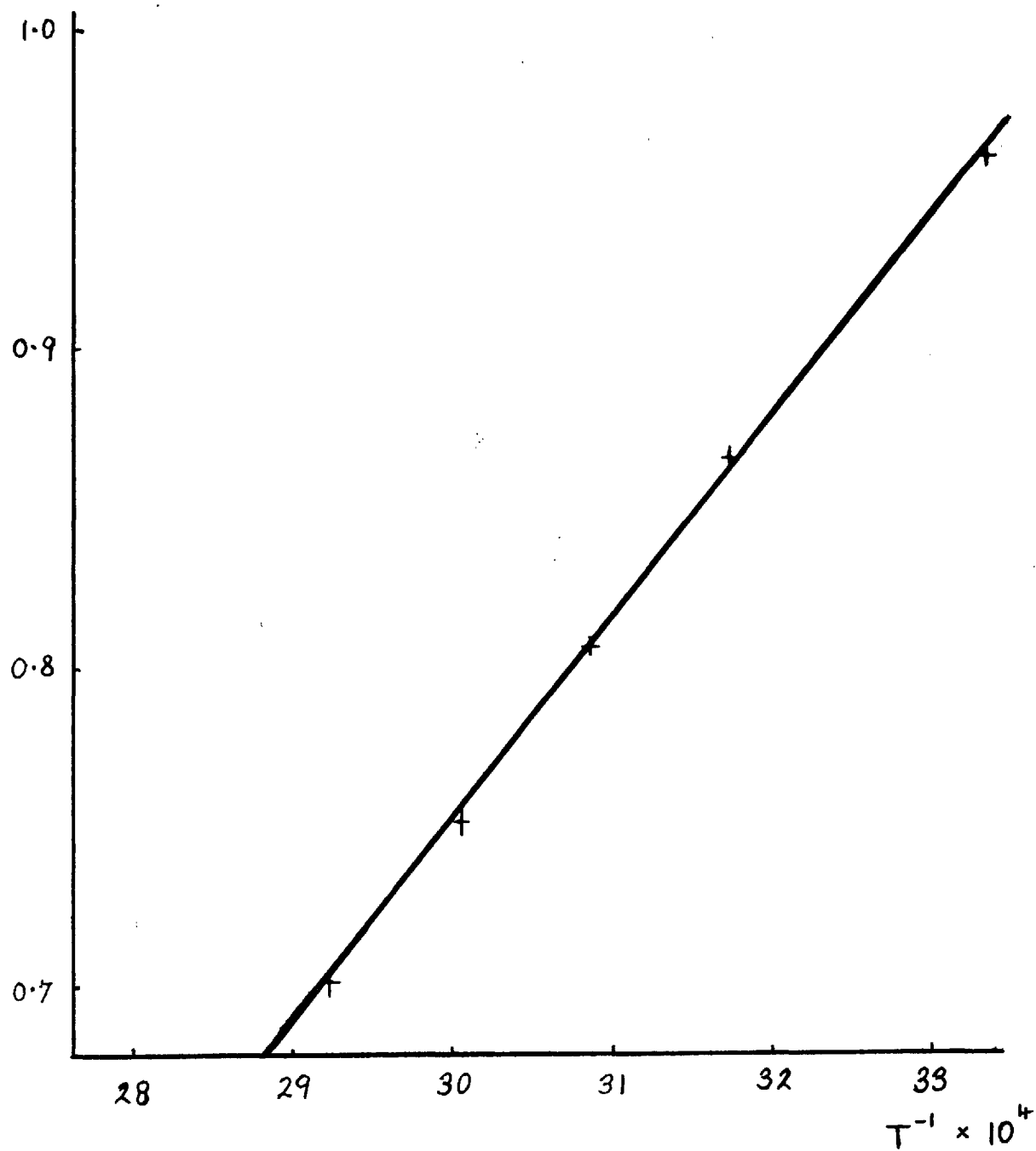
$\ln \eta [\text{cP}]$ 

Figure 2.32

 $C_b D_{12}$

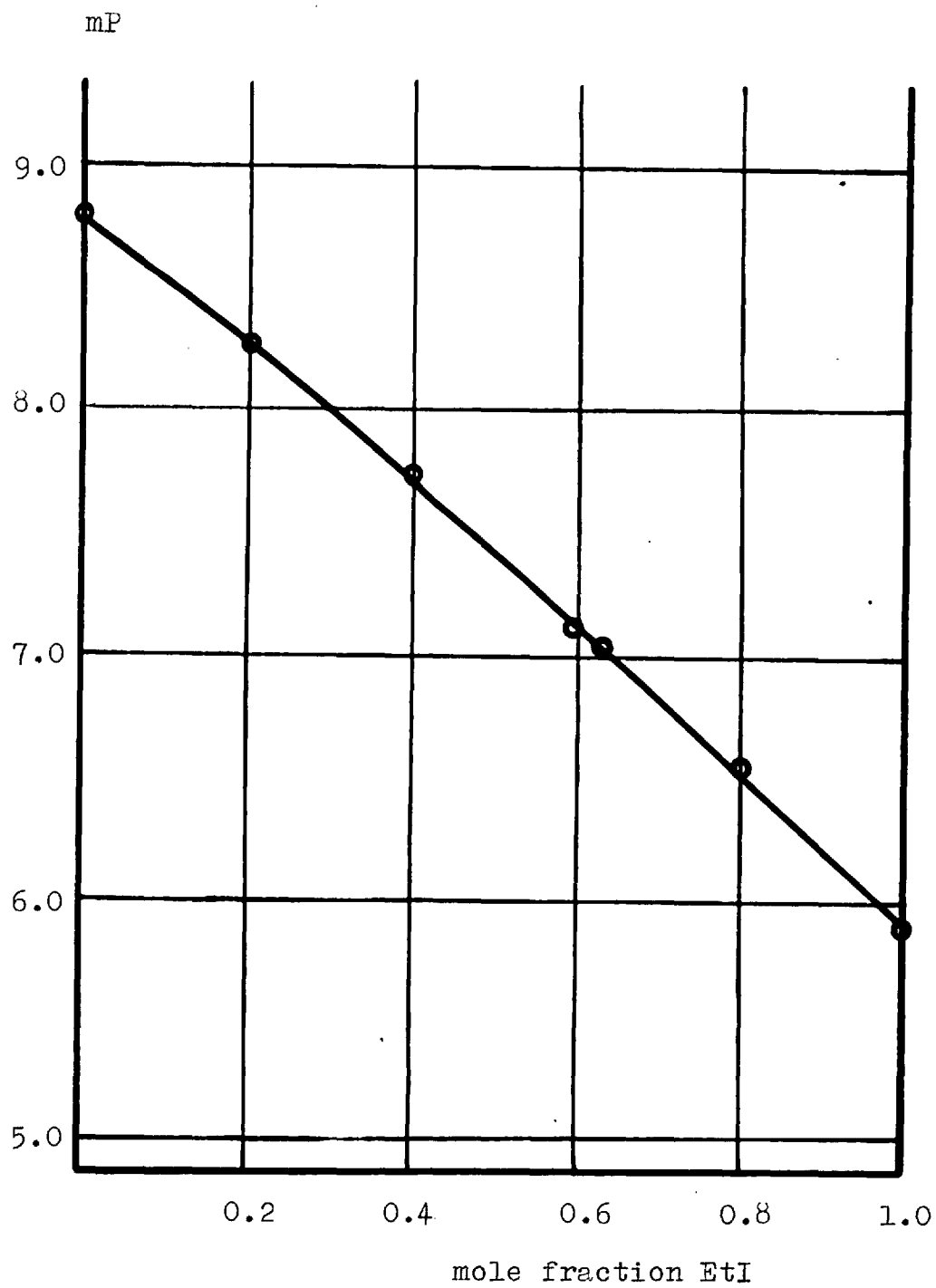


Figure 2.33

## CHAPTER 3.1 EXTENSION OF EXISTING THEORIES OF ENERGY TRANSPORT IN LIQUIDS

### 3.1.1 The Theory of Horrocks and McLaughlin

The disadvantage of the theories of Bridgman and of Kincaid and Eyring is that they correlate the thermal conductivity with the velocity of sound which is itself an experimental parameter. The highest experimental frequencies are several orders of magnitude lower than the frequencies associated with the thermal motion of the molecules. If as may well be the case dispersion occurs at very high frequencies the low frequency sound velocity is not directly relevant.

Horrocks and McLaughlin<sup>(1)</sup> put forward a description of thermal conduction in simple liquids which avoids the sound velocity and uses instead a vibration frequency calculated from molecular force constants. The frequency is that of a single particle in an average environment and will correspond to the highest frequencies in the vibration spectrum.

#### (a) Derivation of the Thermal Conductivity Expression

The molecules of the liquid are imagined to be located on a face centred cubic pseudo-lattice with nearest

neighbour distance,  $a$ . The molecules vibrate about their mean positions and at the extremities of their motion are imagined to collide with adjacent molecules and to transfer energy.

The difference in molecular energy between adjacent planes in the pseudo-lattice (spacing  $l$ ) is given by

$$C_v \frac{dT}{dx} l \quad (3.1)$$

where  $C_v$  is the molecular specific heat. The above unit of energy is imagined to be handed on between molecules at collision. If the vibration frequency is  $\nu$ , the energy flux,  $Q$ , is given by

$$Q = -2 n \nu l C_v \frac{dT}{dx} \quad (3.2)$$

in which the factor 2 accounts for their being two collisions per vibration.  $n$  is the number of molecules per unit area of the pseudo-lattice. Using the definition of thermal conductivity (1.14) equation 3.2 may be written

$$\lambda = 2 n \nu l C_v \quad (3.3)$$

Assuming that there are no holes in the lattice  $n$  may be written  $1/a^2$  and  $l$  may be written  $a/\sqrt{2}$ .

Thus

$$\lambda = \frac{\sqrt{2} \nu C_v}{a} \quad (3.4)$$

In addition to the above mechanism for heat flow there is a contribution from the diffusive hopping of the molecules themselves from site to site in the pseudo-lattice. The diffusion coefficient in simple liquids has already been calculated by McLaughlin<sup>(2)</sup>, and the thermal diffusivity of the hopping mechanism is numerically equivalent. In comparison with collisional contribution it is negligible.

#### (b) The Vibration Frequency in Terms of Molecular Parameters

The potential of a molecule in the field of its neighbours may be calculated as a function of its displacement from equilibrium if it is assumed that the neighbours remain on their lattice sites. Assuming Lennard-Jones 12-6 pair interaction, Corner<sup>(3)</sup> expressed this potential in ascending even powers of the displacement and gave an expression for the vibration frequency corresponding to the harmonic term

$$\nu^2 = \frac{\epsilon}{\pi^2 r_0^2 m} \left[ 11 C_{14} \left( \frac{r_0}{a} \right)^{14} - 5 C_8 \left( \frac{r_0}{a} \right)^8 \right] \quad (3.5)$$

$C_{14}$  and  $C_8$  are lattice summation constants given by 12.06 and 12.80 respectively.  $\epsilon$  and  $r_0$  are defined by equation 1.1. Substitution of (3.5) in

(3.4) yields

$$\lambda = \left[ \frac{\epsilon}{\pi^2 r_0^3 m} \left\{ 14 C_{14} \left( \frac{r_0}{a} \right)^{14} - 5 C_8 \left( \frac{r_0}{a} \right)^8 \right\} \right]^{\frac{1}{2}} \frac{\sqrt{2}}{a} C_v \quad (3.6)$$

### (c) Application of the Theory to Simple Liquids

To remain consistent with the harmonic approximation  $C_v$  has been equated with the specific heat per molecule of a system of harmonic oscillators.

$\lambda$  has been calculated for several simple liquids in table 3.1. Values obtained using the expressions of Bridgman and Kincaid and Eyring (see section 1.3.1) are given for comparison.

TABLE 3.1 - Thermal Conductivities of Simple Liquids

|                         | T<br>°K | $\lambda$ exp.                                                            | $\lambda$ (H & McL) | $\lambda$ (B) | $\lambda$ (K&E) |
|-------------------------|---------|---------------------------------------------------------------------------|---------------------|---------------|-----------------|
|                         |         | (10 <sup>-4</sup> J cm <sup>-1</sup> sec <sup>-1</sup> °C <sup>-1</sup> ) |                     |               |                 |
| argon                   | 84.2    | 12.6                                                                      | 9.92                | 27.77         | 14.3            |
|                         | 87.3    | 12.16                                                                     | 9.25                |               |                 |
| nitrogen                | 69.1    | 15.11                                                                     | 10.28               | 27.33         | 19.3            |
|                         | 71.4    | 14.8                                                                      | 9.77                |               |                 |
|                         | 77.3    | 13.96                                                                     | 8.49                |               |                 |
| carbon<br>monoxide      | 72.0    | 15.89                                                                     | 7.70                |               |                 |
|                         | 77.7    | 15.05                                                                     | 6.59                |               |                 |
|                         | 80.8    | 14.21                                                                     | 5.96                |               |                 |
| methane                 | 93.2    | 21.53                                                                     | 17.24               | 42.5          | 34.0            |
|                         | 103.2   | 20.27                                                                     | 15.27               |               |                 |
|                         | 108.2   | 19.64                                                                     | 14.36               |               |                 |
| benzene                 | 288.2   | 14.94                                                                     | 12.26               | 20.11         | 16.0            |
|                         | 298.2   | 14.63                                                                     | 11.71               |               |                 |
|                         | 308.2   | 14.24                                                                     | 11.24               |               |                 |
| carbon<br>tetrachloride | 298.2   | 10.64                                                                     | 10.18               | 12.9          | 10.3            |
|                         | 308.2   | 10.51                                                                     | 9.77                |               |                 |
|                         | 318.2   | 10.39                                                                     | 9.42                |               |                 |

References for experimental thermal conductivities:

A (4); N<sub>2</sub>(5); CO (6); CH<sub>4</sub> (6); C<sub>6</sub>H<sub>6</sub> (7); CCl<sub>4</sub> (8);

References for sound velocities:

A,  $N_2$ ,  $CH_4$  (9);  $CCl_4$ ,  $C_6H_6$  (10)

In comparison with the experimental values the present calculations are 30% low on average. Bridgman's calculation for these simple molecules gives results which are about 100% high but the comparable calculation of Kincaid and Eyring is on average only 25% high.

The present theory differs from that of Kincaid and Eyring in the effective specific heat assumption and in using a molecular vibration frequency in place of the experimental velocity of sound. The comparison in table 3.1 fails to confirm either approach as the more correct. Other factors not included in the above theories require consideration. In order to illuminate these deficiencies extensions of the present theory are suggested along the following lines

- (a) The effect of molecular shape and the detailed structure of the liquid upon the "mean free path" for energy exchange (here assumed to be one pseudo-lattice spacing).
- (b) The effect of anharmonic terms in the cell potential upon the mean molecular vibration frequency and

effective specific heat.

The latter effect is discussed in some detail in section 3.1.2. The former is difficult to treat in terms of the present crude model of the liquid but it is noteworthy that the effects of molecular shape causing substantial differences between different liquids may not vary rapidly with temperature within a given liquid. This being so a study of  $\lambda^{-1} d\lambda/dT$  in terms of the present theory is of interest.

(d) The Temperature Coefficient of Thermal Conductivity in Relation to the Coefficient of Thermal Expansion

The equation 3.4 for thermal conductivity contains only molecular parameters and the volume so that differentiation at constant pressure gives

$$\frac{1}{\lambda} \left( \frac{d\lambda}{dT} \right)_P = \alpha \left[ \frac{1}{3} + \left( \frac{\partial \ln v}{\partial \ln V} \right)_P \right] \quad (3.7)$$

Since the differentiation with respect to  $T$  is always carried out at constant pressure the subscript  $P$  will subsequently be omitted. The quantity  $\partial \ln v / \partial \ln V$  is known as Gruneiser's ratio,  $\gamma$ . Its value lies between -2 and -3 for most simple solids and metals.

Using Corner's expression (3.5) for  $\gamma$  gives

$$\frac{d \ln \gamma}{d \ln V} = \frac{1858 \left( \frac{v_0}{v} \right)^{6/3} - 512}{132.7 \left( \frac{v_0}{v} \right)^{4/3} - 64} \quad (3.8)$$

in which  $C_8$  and  $C_{14}$  have been replaced by their numerical values, and  $a^3 = \sqrt{2} v$ ,  $v_0^3 = \sqrt{2} v_0$ .

Values of the function are tabulated below.

TABLE 3.2

| $\frac{r_0}{a}$ | $\frac{v_0}{v}$ | $\frac{d \ln \gamma}{d \ln V}$ | $-\frac{1}{3} + \frac{d \ln \gamma}{d \ln V}$ |
|-----------------|-----------------|--------------------------------|-----------------------------------------------|
| 1.15            | 1.52            | -2.6                           | -2.93                                         |
| 1.10            | 1.33            | -2.7                           | -3.04                                         |
| 1.05            | 1.16            | -2.9                           | -3.24                                         |
| 1.02            | 1.06            | -3.05                          | -3.42                                         |
| 1.01            | 1.03            | -3.16                          | -3.50                                         |
| 1.00            | 1.00            | -3.26                          | -3.60                                         |
| 0.99            | 0.97            | -3.39                          | -3.71                                         |
| 0.98            | 0.94            | -3.53                          | -3.86                                         |
| 0.97            | 0.91            | -3.72                          | -4.04                                         |
| 0.96            | 0.88            | -3.94                          | -4.26                                         |
| 0.95            | 0.85            | -4.21                          | -4.55                                         |
| 0.93            | 0.80            | -5.22                          | -5.56                                         |
| 0.90            | 0.73            | -12.1                          | -12.4                                         |
| 0.85            | 0.61            | +2.29                          | +1.95                                         |

Values of the ratio  $\lambda' d\lambda/dT$  have been

calculated for the simple liquids argon, nitrogen, carbon monoxide, methane, benzene, cyclohexane (table 3.3)

**TABLE 3.3**

|                      | $T^{\circ}K$ | $\frac{v_0}{v}$ | $-\frac{1}{\lambda} \frac{d\lambda}{dT} \times 10^3$ | $\alpha \times 10^3$ | $-\frac{1}{\lambda} \frac{d\lambda}{dT} / \alpha$ |
|----------------------|--------------|-----------------|------------------------------------------------------|----------------------|---------------------------------------------------|
| argon                | 85           | 0.884           | 11.2                                                 | 4.40                 | 2.55                                              |
|                      | 87           | 0.872           | 11.5                                                 | 4.48                 | 2.57                                              |
| nitrogen             | 70           | 0.900           | 9.3                                                  | 5.18                 | 1.80                                              |
|                      | 72           | 0.895           | 9.5                                                  | 5.33                 | 1.78                                              |
|                      | 74           | 0.882           | 9.7                                                  | 5.46                 | 1.77                                              |
|                      | 76           | 0.872           | 9.9                                                  | 5.60                 | 1.77                                              |
| carbon monoxide      | 72           | 0.827           | 12.1                                                 | 4.8                  | 2.5                                               |
|                      | 74.          | 0.819           | 12.4                                                 | 5.0                  | 2.5                                               |
|                      | 76           | 0.810           | 12.7                                                 | 5.1                  | 2.5                                               |
|                      | 78           | 0.802           | 13.6                                                 | 5.3                  | 2.5                                               |
|                      | 80           | 0.795           | 13.4                                                 | 5.4                  | 2.5                                               |
| methane              | 94           | 0.921           | 5.9                                                  | 3.01                 | 1.95                                              |
|                      | 98           | 0.910           | 6.0                                                  | 3.05                 | 1.96                                              |
|                      | 102          | 0.898           | 6.2                                                  | 3.12                 | 1.98                                              |
|                      | 106          | 0.877           | 6.3                                                  | 3.20                 | 1.99                                              |
| benzene              | 293.3        | 1.122           | 2.23                                                 | 1.225                | 1.87                                              |
|                      | 313.2        | 1.097           | 2.34                                                 | 1.256                | 1.86                                              |
|                      | 333.2        | 1.067           | 2.45                                                 | 1.288                | 1.89                                              |
|                      | 353.2        | 1.032           | 2.51                                                 | 1.323                | 1.90                                              |
| cyclohexane          | 293.2        | 1.240           | 2.12                                                 | 1.227                | 1.73                                              |
|                      | 313.2        | 1.210           | 2.21                                                 | 1.257                | 1.76                                              |
|                      | 333.2        | 1.180           | 2.32                                                 | 1.289                | 1.80                                              |
| carbon tetrachloride | 298.2        | 1.260           | 1.18                                                 | 1.231                | 0.96                                              |
|                      | 308.2        | 1.246           | 1.20                                                 | 1.255                | 0.95                                              |
|                      | 318.2        | 1.232           | 1.21                                                 | 1.280                | 0.95                                              |

Table references:  $\lambda$  : argon, nitrogen, carbon monoxide, methane, carbon tetrachloride, see table 3.5: benzene, cyclohexane, present work.

$\alpha$  : argon, nitrogen, methane, ref. 11: carbon monoxide ref. 12: benzene, cyclohexane ref. 13.

In figure 3.1  $\lambda^{-1} d\lambda/dT$  is plotted as a function of  $\alpha$  for each of the simple molecules and the polyphenyls. The region in which, according to theory, the simple molecules ( $0.795 < \rho_0/\rho < 1.24$ ) should lie is enclosed between dotted lines.

The experimental ratio  $\lambda^{-1} d\lambda/dT$  and the equivalent theoretical ratio  $\gamma - \frac{1}{3}$  are plotted as a function of  $\rho_0/\rho$  in figure 3.2.

Although theory correctly predicts the rough proportionality of  $\lambda^{-1} d\lambda/dT$  and  $\alpha$ , the theoretical ratio  $\gamma - \frac{1}{3}$  is too large and does not fall below 2.9 anywhere in the region of normal liquid densities.

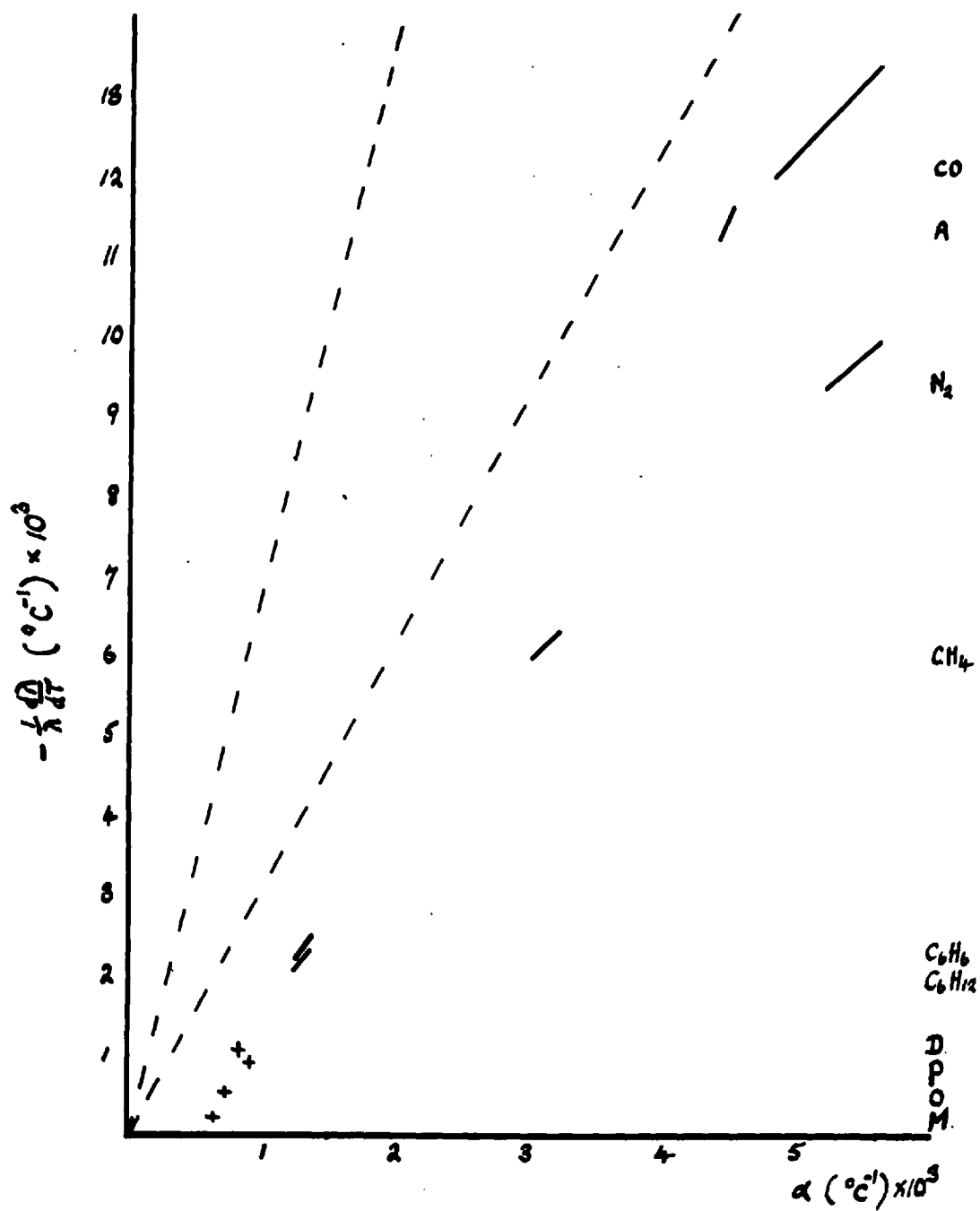


Figure 3.1

### 3.1.2 An Improved Calculation for the Vibration Frequency

The previously predicted ratio  $\lambda^{-1} d\lambda/dT$  increases to infinity in the region  $v_0/v = 0.7$  (figure 3.2). This behaviour has no experimental significance and is purely an artefact of the harmonic approximation to the cell potential. According to the cell lattice model of Lennard-Jones and Devonshire the potential of a molecule in the field of its neighbours may be developed as a series of even powers of its displacement from the centre of the cell. The harmonic oscillator model ignores all terms except the first squared term in this expansion. The coefficient of this term decreases rapidly with increasing volume and passes through zero near  $v_0/v = 0.7$ , so that at this density the calculated value of  $\lambda$  is zero and  $\lambda^{-1} d\lambda/dT$  infinite. Clearly approaching this condition, it is the higher order terms in the expansion which control the vibration frequency. In the quartic potential model these higher order terms are specifically introduced.

#### (a) The Quartic Potential Model

As before, a face centred cubic lattice is assumed with nearest neighbours distance,  $a$ . It was

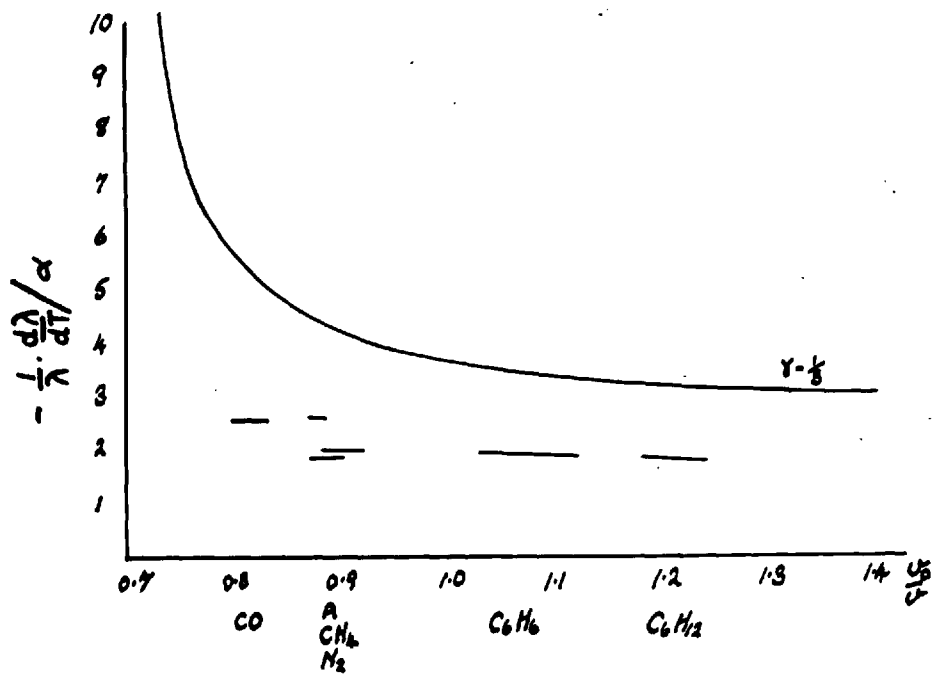


Figure 3.2

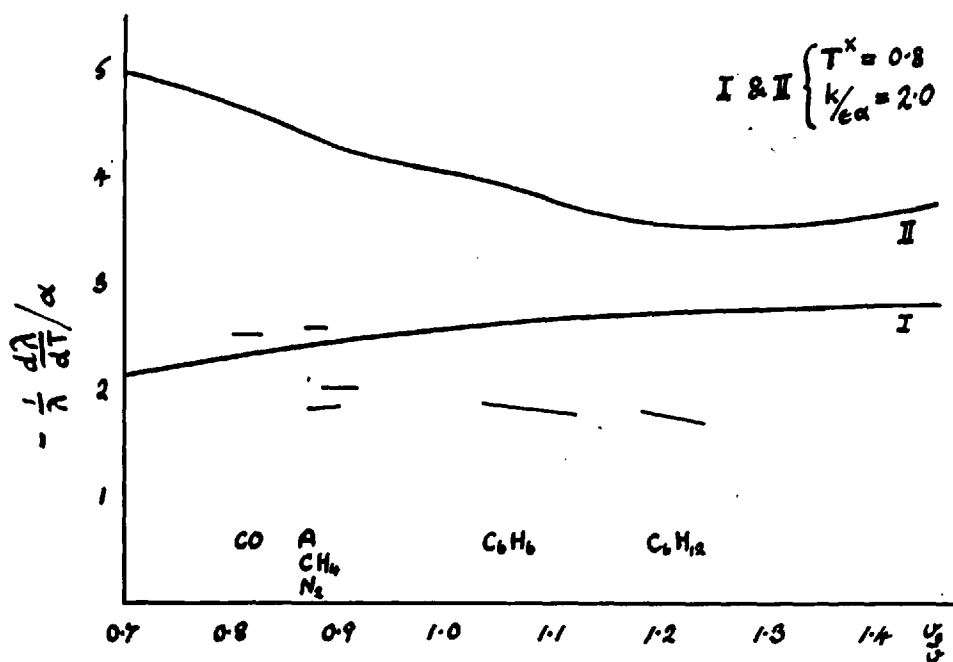


Figure 3.4

shown (section 1. 1.4 ) that the cell potential could be written

$$\omega(r) - \omega(0) = 12e \left[ \left( \frac{U_0}{U} \right)^4 L(y) - 2 \left( \frac{U_0}{U} \right)^2 M(y) \right] \quad (3.9)$$

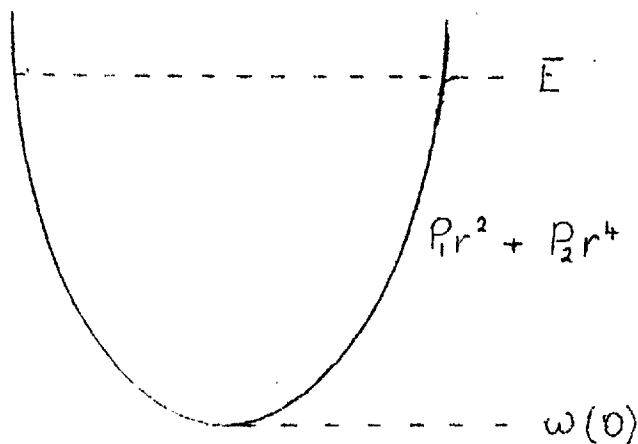
Three shells of neighbours are taken into account and  $L(y)$  and  $M(y)$  are defined by equations 1. 10 and 1. 11 . Using also equations 1. 6 and 1. 7  $L(y)$  and  $M(y)$  may be expanded as a series in  $y$

$$L(y) = 22.11 y + 200.6 y^2 + \dots \quad (3.10)$$

$$M(y) = 5.28 y + 14.33 y^2 + \dots \quad (3.11)$$

Replacing  $y$  by  $r^2/a^2$  and substituting 3.10 and 3.11 in equation 3.9 gives

$$\begin{aligned} \omega(r) - \omega(0) = & \frac{12e}{a^2} \left[ 22.11 \left( \frac{U_0}{U} \right)^4 - 10.56 \left( \frac{U_0}{U} \right)^2 \right] r^2 \\ & + \frac{12e}{a} \left[ 200.6 \left( \frac{U_0}{U} \right)^4 - 28.67 \left( \frac{U_0}{U} \right)^2 \right] r^4 \quad (3.12) \\ & + \dots \end{aligned}$$

(b) The Frequency of Vibration in a Quartic WellFigure 3.3

Suppose the potential well (figure 3.3) is described by

$$\omega(r) - \omega(0) = P_1 r^2 + P_2 r^4 \quad (3.13)$$

The kinetic energy of the oscillating particle may be written in terms of the total energy,  $E$

$$\frac{m \dot{r}^2}{2} = E - P_1 r^2 - P_2 r^4 \quad (3.14)$$

Separating the variables of time and displacement, and integrating gives the period of Vibration,  $T_p$ ,

$$T_p = \int_{\text{cycle}} dt = 4 \sqrt{\frac{m}{2}} \int_0^{r_1} \frac{dr}{\sqrt{E - P_1 r^2 - P_2 r^4}} \quad (3.15)$$

in which the integration over  $r$  has been divided into 4 quarter cycles  $0 \leq r \leq r_1$ .  $r_1$  is defined by the positive real roots of  $P_1 r_1^2 + P_2 r_1^4 = E$ . Equation 3.15 may be rewritten

$$T_p = 4 \sqrt{\frac{m}{2P_2}} \int_0^{r_1} \frac{dr}{\sqrt{\frac{E}{P_2} - \frac{P_1}{P_2} r^2 - r^4}} \quad (3.16)$$

and since  $P_1 > 0$   $P_2 > 0$ , the root in the integrand factorises so that

$$T_p = 4 \sqrt{\frac{m}{2P_2}} \int_0^b \frac{dr}{\sqrt{(a^2 + r^2)(b^2 - r^2)}} \quad (3.17)$$

$$a^2 = \frac{1}{2} \left\{ \frac{P_1}{P_2} \pm \sqrt{\frac{P_1^2}{P_2^2} + \frac{4E}{P_2}} \right\} \quad (3.18)$$

$$b^2 = \frac{1}{2} \left\{ -\frac{P_1}{P_2} \pm \sqrt{\frac{P_1^2}{P_2^2} + \frac{4E}{P_2}} \right\} \quad (3.19)$$

The integral in equation 3.17 is expressible as a complete elliptic integral<sup>(14)</sup>.

Thus

$$T_p = 4 \sqrt{\frac{m}{2E_2}} \frac{1}{\sqrt{a^2+b^2}} \operatorname{cn}^{-1}\left(0, \frac{b}{\sqrt{a^2+b^2}}\right) \quad (3.20)$$

in which

$$\operatorname{cn}^{-1}(0, k) = \int_0^{\pi/2} \frac{d\theta}{\sqrt{1 - k^2 \sin^2 \theta}} \quad (3.21)$$

$\operatorname{cn}^{-1}(0, k)$  is available in tabulated form for a range of  $k$ .

The frequency of vibration of a quartic oscillator is found by inverting equation 3.20, and substituting for  $a$  and  $b$

$$\nu_A = \frac{(P_1^2 + 4EP_2)^{1/4}}{2\sqrt{2m}} \times \frac{1}{\operatorname{cn}^{-1}\left(0, \frac{1}{\sqrt{2}} \left[1 - \frac{P_1}{\sqrt{P_1^2 + 4EP_2}}\right]^{1/2}\right)} \quad (3.22)$$

### (c) Calculation of $\nu_A$ in Terms of Molecular Parameters

In the quartic approximation to the cell potential

$P_1$  and  $P_2$  in equation 3.22 may be equated with the coefficients of  $r^2$  and  $r^4$  in equation 3.12.

$$P_1 = \frac{12\epsilon}{a^2} \left[ L_1 \left( \frac{v_0}{v} \right)^4 + M_1 \left( \frac{v_0}{v} \right)^2 \right] \quad (3.23)$$

$$P_2 = \frac{12\epsilon}{a^4} \left[ L_2 \left( \frac{v_0}{v} \right)^4 + M_2 \left( \frac{v_0}{v} \right)^2 \right] \quad (3.24)$$

where  $L_1 = 22.11$ ,  $L_2 = 200.6$ ,  $M_1 = -10.56$ ,  $M_2 = -28.67$ .

Unlike the frequency of the harmonic oscillator that of the quartic oscillator depends on the total energy, In the present case this is equated to the average total energy per particle in the system. The mean kinetic energy per particle is always  $1.5kT$  so that the mean total energy relative to particles at rest at the centres of their cells is

$$E = \frac{3}{2} kT + \chi(v, T) \quad (3.25)$$

$\chi(v, T)$  represents the mean potential energy per particle relative to the potential energy when the particles are at rest at the bottom of the potential well. It varies with anharmonicity of the cell potential.

$\chi(v, T)$  has been calculated by

Wentorf, Buehler, Hirschfelder and Curtiss<sup>(15)</sup> using the exact form of the cell potential (equation 3.9). Rather than attempt to calculate the energy appropriate to a system of pure quartic oscillators this value has been used. It is given by the expression

$$\chi(v, t) = 12\epsilon \left[ \left( \frac{v_0}{v} \right)^4 \frac{g_L}{G} - 2 \left( \frac{v_0}{v} \right)^2 \frac{g_M}{G} \right] \quad (3.26)$$

in which

$$G = \int_0^{0.30544} y^{\frac{1}{2}} \exp \{ - [\omega(r) - \omega(0)] / kT \} dy \quad (3.27)$$

$$g_L = \int_0^{0.30544} y^{\frac{1}{2}} L(y) \exp \{ - [\omega(r) - \omega(0)] / kT \} dy \quad (3.28)$$

$$g_M = \int_0^{0.30544} y^{\frac{1}{2}} M(y) \exp \{ - [\omega(r) - \omega(0)] / kT \} dy \quad (3.29)$$

All the quantities appearing in equation 3.22 for  $\nu_A$  have been defined in terms of the volume, temperature and the molecular parameters.

$$\nu_A = \frac{2^{1/3}}{4} \left( \frac{12\epsilon}{m} \right)^{1/2} \frac{v_0}{v^{2/3}} \frac{[f(v, T)]^{1/4}}{h(v, T)} \quad (3.30)$$

where

$$f(v, T) = \left[ L_1 \left( \frac{v_0}{v} \right)^2 + M_1 \right]^2 + \left[ L_2 + M_2 \left( \frac{v}{v_0} \right)^2 \right] \left[ \frac{kT}{2\epsilon} + \frac{\chi}{3\epsilon} \right] \quad (3.31)$$

$$h(v, T) = \omega' \left[ 0, \frac{1}{\sqrt{2}} \left\{ 1 - \left[ L_1 \left( \frac{v_0}{v} \right)^2 + M_1 \right] / (f(v, T))^{1/2} \right\}^{1/2} \right] \quad (3.32)$$

In the limit where the coefficient of  $r^4$  in the cell potential becomes zero, equation 3.30 reduces to the harmonic frequency

$$\omega_H = \frac{1}{2^{2/3}\pi} \left( \frac{12\epsilon}{m} \right)^{1/2} \frac{v_0}{v^{4/3}} \left[ L_1 \left( \frac{v_0}{v} \right)^2 + M_1 \right]^{1/2} \quad (3.33)$$

Values of  $f(v, T)$ ,  $h(v, T)$  and  $L_1 (v_0/v)^2 + M_1$  are tabulated below for a range of  $v_0/v$  and  $T^\times$ .

**TABLE 3.4 - Parameters for the Calculation of Vibration Frequencies**

| $\frac{v_0}{v}$ | $f(v, T)$   |             |             | $h(v, T)$<br>$0.7 < T^* < 0.9$ | $L_1 \left( \frac{v_0}{v} \right)^2 + M_1$ |
|-----------------|-------------|-------------|-------------|--------------------------------|--------------------------------------------|
|                 | $T^* = 0.7$ | $T^* = 0.8$ | $T^* = 0.9$ |                                |                                            |
| 1.57            | 2071        | 2089        | 2109        | 1.58                           | 44.0                                       |
| 1.41            | 1259        | 1278        | 1296        | 1.58                           | 33.6                                       |
| 1.18            | 527         | 544         | 562         | 1.60                           | 20.1                                       |
| 1.01            | 257         | 272         | 288         | 1.63                           | 12.0                                       |
| 0.942           | 191         | 205         | 219         | 1.65                           | 9.1                                        |
| 0.885           | 144         | 158         | 171         | 1.68                           | 6.1                                        |
| 0.788           | 96          | 108         | 120         | 1.75                           | 3.06                                       |
| 0.707           | 74          | 84          | 94          | 1.84                           | 0.5                                        |

references  $\gamma/\epsilon$  (16);  $m^{-1}(0, k)$  (14)

The ratio  $\gamma_A/\gamma_H$  may be found directly since it is only a function of volume and temperature.

$$\frac{\gamma_A}{\gamma_H} = \frac{\pi}{2} \frac{f^{\frac{1}{2}}}{h} \left/ \left( L_1 \frac{v_0^2}{v^2} + M_1 \right) \right. \quad (3.34)$$

TABLE 3.5 - The Ratio  $\nu_A/\nu_H$ 

|       | $\nu_A/\nu_H$ |             |             |
|-------|---------------|-------------|-------------|
|       | $T^x = 0.7$   | $T^x = 0.8$ | $T^x = 0.9$ |
| 1.57  | 1.011         | 1.013       | 1.015       |
| 1.41  | 1.021         | 1.026       | 1.029       |
| 1.15  | 1.049         | 1.058       | 1.066       |
| 1.01  | 1.115         | 1.139       | 1.147       |
| 0.942 | 1.182         | 1.199       | 1.211       |
| 0.885 | 1.252         | 1.285       | 1.310       |
| 0.788 | 1.639         | 1.698       | 1.727       |
| 0.707 | 3             | 3           | 3           |

Unlike  $\nu_H$  the quartic frequency  $\nu_A$  does not decrease through zero at low densities.

(d) The Thermal Conductivity Expression

By analogy with the derivation of equation 3.4

$$= 2^{1/3} \frac{\nu_A}{\nu_H} C_{VA} \quad (3.35)$$

where the subscript A refers to parameters derived from the anharmonic cell potential.

In the harmonic oscillator case the effective specific heat for thermal conduction was assumed to be

that appropriate to the model namely  $3k$ . In the present case, to be fully consistent, the specific heat per molecule appropriate to a system of quartic oscillators should be used. However there are available in tabulated form specific heats corresponding to the exact form of the cell potential (equation 3.9). These are defined by

$$C_{VA} = \frac{3k}{2} + \frac{\partial}{\partial T} (\chi(u, T)) \quad (3.36)$$

and are tabulated below.

TABLE 3.6

|       | $C_{VA}$    |             |
|-------|-------------|-------------|
|       | $T^x = 0.8$ | $T^x = 0.9$ |
| 1.57  | 2.966k      | 2.943k      |
| 1.41  | 2.947k      | 2.938k      |
| 1.18  | 2.772k      | 2.765k      |
| 1.01  | 2.668k      | 2.650k      |
| 0.942 | 2.554k      | 2.541k      |
| 0.885 | 2.480k      | 2.461k      |
| 0.788 | 2.295k      | 2.280k      |
| 0.707 | 2.128k      | 2.121k      |

The specific heat appropriate to a quartic oscillator will lie somewhere between the values in table 3.6 and 3k.

(e) Application of the Theory to Simple Liquids

In the following table the thermal conductivity of several simple liquids has been calculated.  $\lambda_A(I)$  uses a specific heat of 3k:  $\lambda_A(II)$  uses  $C_{VA}$  from table 3.6.

**TABLE 3.7 - Thermal Conductivities on the Quartic Oscillator Model**

|                         | $T$         | $\lambda_A(I)$ | $\lambda_A(II)$ | $\lambda_{exp}$ |
|-------------------------|-------------|----------------|-----------------|-----------------|
|                         | $^{\circ}K$ |                |                 |                 |
| argon                   | 84.2        | 12.5           | 10.7            | 12.60           |
|                         | 87.3        | 11.9           | 9.7             | 12.16           |
| nitrogen                | 69.1        | 12.8           | 10.7            | 15.11           |
|                         | 71.4        | 12.4           | 10.3            | 14.3            |
|                         | 77.3        | 11.2           | 9.1             | 13.96           |
| carbon<br>monoxide      | 72.0        | 10.6           | 8.5             | 15.89           |
|                         | 77.7        | 10.2           | 7.9             | 15.05           |
|                         | 80.8        | 10.4           | 7.8             | 14.21           |
| methane                 | 93.2        | 20.5           | 17.5            | 21.53           |
|                         | 103.2       | 19.0           | 15.8            | 20.27           |
|                         | 108.2       | 18.2           | 15.0            | 19.64           |
| benzene                 | 288.2       | 13.2           | 12.1            | 14.94           |
|                         | 298.2       | 12.6           | 11.5            | 14.63           |
|                         | 308.2       | 12.2           | 11.0            | 14.24           |
|                         | 318.2       | 11.8           | 10.7            | 13.89           |
| carbon<br>tetrachloride | 298.2       | 10.8           | 9.9             | 10.64           |
|                         | 308.2       | 10.4           | 9.6             | 10.51           |
|                         | 318.2       | 10.1           | 9.3             | 10.39           |

$\lambda_A(I)$  is on average within 14% of the experimental value but invariably low. This compares with the previous harmonic calculations of  $\lambda$  which were on average 30% low. It is noteworthy that in the use of the spherical molecule argon and the pseudo-spherical molecules methane and carbon tetrachloride,  $\lambda_A(I)$  is within 3% of the experimental value on average.

$\lambda_A(II)$  agrees well with the previous harmonic calculations. The effects of anharmonicity on the frequency, and on the specific heat per molecule, compensate each other.

In neither case is the overall agreement with experiment sufficiently good to draw definite conclusions about the effective specific heat for thermal conduction

(f) The Temperature Coefficient of Thermal Conductivity on the Quartic Potential Model

An expression for  $\lambda_A^{-1} d\lambda_A/dT$  is found by differentiating equation 3.35 in which  $\lambda_A$  has been substituted from (3.33)

$$\frac{1}{\lambda_A} \frac{d\lambda_A}{dT} = -\frac{5}{3}\alpha + \frac{1}{4f} \frac{df}{dT} - \frac{1}{h} \frac{dh}{dT} + \frac{1}{c_{VA}} \frac{dc_{VA}}{dT} \quad (3.37)$$

The derivatives of  $f$ ,  $h$  and  $c_{VA}$  were obtained by

graphical analysis of tables 3.4 and 3.6. Since these functions depend explicitly upon both the reduced temperature  $T^x$  and the reduced volume  $v_0/v$  their derivatives contain terms involving both  $\alpha$  and  $k/\epsilon$ .

In the case of the function  $h$  the dependence on  $T^x$  is slight, so that in the range  $0.8 < T^x < 0.9$  only the  $\alpha$  terms of  $dh/dT$  are important. Numerical values of  $(4f)^{-1} df/dT$ ,  $h^{-1} dh/dT$ , and

$c_{VA}^{-1} dc_{VA}/dT$  are given below in tables 3.8 and 3.9.

TABLE 3.8 - Derivatives of the Functions  $f$  and  $h$ .

| $(4f)^{-1} df/dT$       |             |             |       | $h^{-1} dh/dT$               |             |             |                         |
|-------------------------|-------------|-------------|-------|------------------------------|-------------|-------------|-------------------------|
| Coefficient of $\alpha$ |             |             |       | Coefficients of $k/\epsilon$ |             |             | Coefficient of $\alpha$ |
| $T^x = 0.7$             | $T^x = 0.8$ | $T^x = 0.9$ |       | $T^x = 0.7$                  | $T^x = 0.8$ | $T^x = 0.9$ | $0.7 < T^x < 0.9$       |
| 1.57                    | -1.16       | -1.16       | -1.16 | 0.023                        | 0.023       | 0.023       | 0                       |
| 1.41                    | -1.18       | -1.17       | -1.16 | 0.036                        | 0.036       | 0.035       | 0.035                   |
| 1.19                    | -1.20       | -1.16       | -1.13 | 0.083                        | 0.080       | 0.077       | 0.085                   |
| 1.01                    | -1.13       | -1.08       | -1.03 | 0.151                        | 0.142       | 0.135       | 0.17                    |
| 0.942                   | -1.06       | -1.00       | -0.95 | 0.191                        | 0.178       | 0.167       | 0.22                    |
| 0.885                   | -0.96       | -0.90       | -0.85 | 0.227                        | 0.207       | 0.192       | 0.30                    |
| 0.788                   | -0.76       | -0.71       | -0.68 | 0.308                        | 0.272       | 0.246       | 0.42                    |
| 0.707                   | -0.58       | -0.56       | -0.54 | 0.340                        | 0.300       | 0.268       | 0.57                    |

TABLE 3.9 - Derivatives of  $C_{VA}$ 

| $\frac{U_0}{U}$ | $C_{VA}^{-1} dC_{VA}/dT$ | $C_{VA}^{-1} dC_{VA}/dT$ |
|-----------------|--------------------------|--------------------------|
|                 | $0.7 < T^* < 0.8$        | $0.7 < T^* < 0.8$        |
| 1.57            | -0.2                     | -0.2                     |
| 1.41            | -0.4                     | -0.1                     |
| 1.19            | -0.3                     | -0.07                    |
| 1.01            | -1.1                     | -0.18                    |
| 0.942           | -1.2                     | -0.17                    |
| 0.885           | -1.5                     | -0.18                    |
| 0.788           | -2.0                     | -0.15                    |
| 0.707           | -2.3                     | -0.07                    |

Column 2  $\alpha$  termsColumn 3  $k/\epsilon$  terms

The values in table 3.9 are second derivatives of the original tabulated values of  $E$  and as such they contain considerable errors. The estimated errors are  $\pm 0.2$  and  $\pm 0.02$  in the coefficients of  $\alpha$  and  $k/\epsilon$  respectively.

In the calculation of  $\lambda_A^{-1} d\lambda_A/dT$  two separate specific heat assumptions have been used:

1. The specific heat is constant. This corresponds to the harmonic assumption of  $3k$  in the calculation of
2. The specific heat is given by the full expression

(equation 3.36) and hence its derivative is given by table 3.9.

Under either assumption the derivative of may be written,

$$\frac{1}{\lambda_A} \frac{d\lambda_A}{dT} = -X\alpha + Y\frac{k}{\epsilon} \quad (3.38)$$

Assumption 1

$X$  and  $Y$  are obtained from table 3.8

TABLE 3.10 -  $X$  and  $Y$  coefficients with zero specific heat terms

| $\frac{U_o}{U}$ | $X$       |           |           | $Y$       |           |           |
|-----------------|-----------|-----------|-----------|-----------|-----------|-----------|
|                 | $T^x=0.7$ | $T^x=0.8$ | $T^x=0.9$ | $T^x=0.7$ | $T^x=0.8$ | $T^x=0.9$ |
| 1.5             | 2.84      | 2.84      | 2.83      | 0.025     | 0.025     | 0.025     |
| 1.4             | 2.87      | 2.86      | 2.85      | 0.035     | 0.035     | 0.035     |
| 1.3             | 2.90      | 2.88      | 2.86      | 0.051     | 0.050     | 0.049     |
| 1.2             | 2.94      | 2.90      | 2.87      | 0.077     | 0.075     | 0.073     |
| 1.1             | 2.97      | 2.93      | 2.88      | 0.106     | 0.100     | 0.095     |
| 1.0             | 2.96      | 2.91      | 2.86      | 0.15      | 0.14      | 0.13      |
| 0.9             | 2.92      | 2.85      | 2.81      | 0.22      | 0.20      | 0.18      |
| 0.8             | 2.85      | 2.80      | 2.76      | 0.30      | 0.26      | 0.23      |
| 0.7             | 2.80      | 2.78      | 2.76      | 0.34      | 0.30      | 0.27      |

Assumption 2

To the values of  $X$  and  $Y$  in table 3.11, the coefficients of  $\alpha$  and  $k/\epsilon$  in  $C_{VA}^{-1} dC_{VA}/dT$  must be added. In view of the inaccuracy in these coefficients the dependence on  $T^X$  is no longer significant

TABLE 3.11 -  $X$  and  $Y$  coefficients including the specific heat term

|     | $X \pm 0.2$ | $Y \pm 0.04$ |
|-----|-------------|--------------|
| 1.5 | 3.1         | -0.13        |
| 1.4 | 3.3         | -0.06        |
| 1.3 | 3.3         | -0.03        |
| 1.2 | 3.3         | -0.00        |
| 1.1 | 3.6         | -0.02        |
| 1.0 | 4.0         | -0.04        |
| 0.9 | 4.4         | +0.02        |
| 0.8 | 4.8         | +0.14        |
| 0.7 | 5.1         | +0.23        |

Using  $X$  and  $Y$  from table 3.11 the ratio  $(\alpha\lambda_A)^{-1} d\lambda_A/dT$  is determined solely by the frequency effect and is equal to  $Y - \frac{1}{3}$  for the anharmonic oscillator. The

ratio depends upon both  $T^*$  and  $k/\epsilon\alpha$ . Values of  $k/\epsilon\alpha$  for simple molecules are listed below. They all lie in the region of 2.

TABLE 3.12

|                      | $T$<br>$^{\circ}\text{K}$ | $\epsilon/k$ | $k/\epsilon\alpha$ |
|----------------------|---------------------------|--------------|--------------------|
| argon                | 85                        | 116          | 1.96               |
| nitrogen             | 75                        | 91.5         | 1.96               |
| carbon monoxide      | 75                        | 110          | 1.92               |
| methane              | 100                       | 144          | 2.22               |
| benzene              | 313.2                     | 367          | 2.18               |
| cyclohexane          | 313.2                     | 324          | 2.45               |
| carbon tetrachloride | 308.2                     | 327          | 2.42               |

The ratio  $(\lambda_A \alpha)^{-1} d\lambda_A/dT$  is plotted against  $U_0/v$  in figure 3.4. Curve I corresponds to assumption 1 (table 3.10) for  $T^* = 0.8$  and  $k/\epsilon\alpha = 2$ . The ratio is not, in fact, very sensitive to these parameters. Curve II corresponds to assumption 2 (table 3.11).

The introduction of the quartic term removes the increase toward infinity at  $U_0/v \doteq 0.7$ . Under the constant specific heat assumption (curve I) the ratio

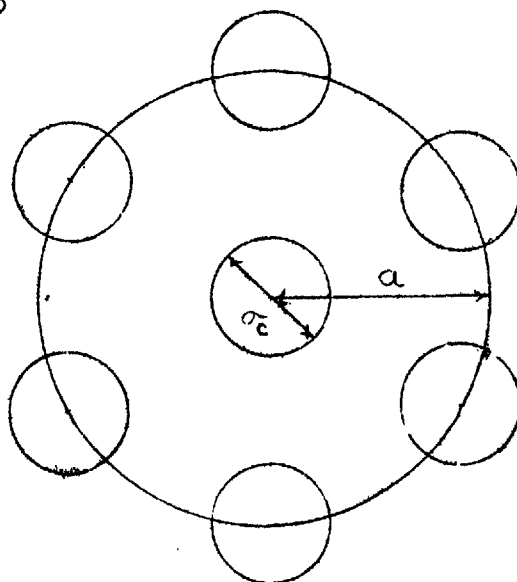
decreases slightly at low densities. Curve I is generally in better agreement with experiment than curve II.

The specific heat assumption is seen to be of major importance especially at low densities.

### 3.1.3 The Limiting Case of Anharmonicity: A Square Well Model

It is noticeable that even for the simple molecules, those of larger size lie well below the predicted line for  $\lambda_A^{-1} d\lambda_A/dT$ . For these molecules it is likely that the simple 12-6 pair interaction is not adequate and for even larger molecules (e.g. the polyphenyls) this is certainly the case. In terms of the molecular size the repulsive interactions of large molecules are considerably steeper than those of small molecules. For this reason although the molecules are too complicated to be satisfactorily described a rigid sphere interaction may better represent their behaviour. In the following model the cell is assumed to be a square well whose size is determined by the volume available per molecule and the molecular size.

Figure 3.5



A face centred cubic pseudo-lattice has been assumed in which packets of energy are exchanged between lattice planes  $l = a/\sqrt{2}$  apart at a ratio depending upon the frequency with which the molecule crosses a particular plane.

Fixing twelve nearest neighbours in their equilibrium positions leaves the central molecule free to move within a polyhedron determined by the nearest neighbour distance,  $a$ , and the molecular diameter,  $\sigma_c$ . At high densities this polyhedron may be approximated by a sphere, radius  $(a - \sigma_c)$  <sup>(18)</sup> in which the centre of the molecule moves freely.

The arithmetic mean velocity of rigid molecules is

$$\bar{U} = \sqrt{\frac{8kT}{\pi m}} \quad (3.39)$$

Thus the vibration frequency in a square well is given by

$$\nu = \frac{\bar{U}}{4(a - \sigma_c)} = \frac{1}{4} \sqrt{\frac{8kT}{\pi m}} \frac{1}{(a - \sigma_c)} \quad (3.40)$$

Substituting this value of  $\nu$  into equation 1, thermal conductivity gives

$$\lambda = C_v \sqrt{\frac{kT}{\pi m}} \frac{1}{(a - \sigma_c)} \quad (3.41)$$

where  $C_v$  may be written  $3k/2$  for a hard sphere system.

The derivative of equation 3.41 is given by

$$\frac{1}{\lambda} \frac{d\lambda}{dT} = \frac{1}{2T} - \frac{2a - \sigma_c}{a - \sigma_c} \alpha \quad (3.42)$$

This expression can give both positive or negative values of the temperature coefficient depending upon whether the term in  $1/T$  or  $\alpha$  is dominant. The results of this model will be further discussed in the next section.

## CHAPTER 3.2 THE THERMAL CONDUCTIVITY OF POLYPHENYL MELTS

### 3.2.1 The Contrasting Behaviour of Thermal Conductivity and Viscosity

Thermal conductivity and viscosity data for the polyphenyls are collected in table 3.13 and 3.14.  $A$  and  $B$  in table 3.13 refer to the coefficients in the linear equation

$$\lambda = A + B\theta \quad (3.43)$$

where  $\theta$  is the temperature in  $^{\circ}\text{C}$ .  $E_{\eta}$  and  $A_{\eta}$  in table 3.14 belong to the de Guzman equation

$$\eta = A_{\eta} \frac{E_{\eta}}{RT} \quad (3.44)$$

where  $T$  is the temperature in  $^{\circ}\text{K}$ .

TABLE 3.13 - Thermal Conductivity Parameters of the Polyphenyls

|             | $\lambda$ at melting point<br>$10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} ^{\circ}\text{C}$ | A<br>$10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} ^{\circ}\text{C}$ | B<br>$\text{ J cm}^{-1} \text{ sec}^{-1} ^{\circ}\text{C}^{-2}$ |
|-------------|---------------------------------------------------------------------------------------------|--------------------------------------------------------------------|-----------------------------------------------------------------|
| benzene     | 1.482                                                                                       | 1.500                                                              | 0.321                                                           |
| diphenyl    | 1.378                                                                                       | 1.477                                                              | 0.141                                                           |
| p terphenyl | 1.284                                                                                       | 1.527                                                              | 0.1144                                                          |
| m terphenyl | 1.366                                                                                       | 1.397                                                              | 0.03596                                                         |
| o terphenyl | 1.315                                                                                       | 1.354*                                                             | 0.0692*                                                         |

\* These refer to the region above the discontinuity.

TABLE 3.14 - Viscosity Parameters of the Polyphenyls<sup>(19)</sup>

|             | $\eta$ at melting point<br>$10^{-3}P$ | <u>High temperature</u>  |                          | <u>Near melting point</u> |                          |
|-------------|---------------------------------------|--------------------------|--------------------------|---------------------------|--------------------------|
|             |                                       | $E_{\eta}$<br>Kcals/mole | $A_{\eta}$<br>$10^{-3}P$ | $E_{\eta}$<br>Kcals/mole  | $A_{\eta}$<br>$10^{-3}P$ |
| benzene     |                                       | 2.42                     | $1.01 \times 10^{-3}$    | 2.53                      | $7.19 \times 10^{-4}$    |
| diphenyl    | 14                                    | 3.41                     | $9.57 \times 10^{-4}$    | 3.80                      | $5.43 \times 10^{-4}$    |
| p terphenyl | 8.0                                   | 3.76                     | $1.64 \times 10^{-3}$    | 3.80                      | $5.43 \times 10^{-4}$    |
| m terphenyl | 52                                    | 5.34                     | $2.7 \times 10^{-3}$     | 7.40                      | $1.73 \times 10^{-5}$    |
| o terphenyl | 280                                   | 7.93                     | $9.85 \times 10^{-6}$    | 16.04                     | $7.41 \times 10^{-11}$   |

Despite the variety of mass and molecular structure the thermal conductivities of all five compounds lie within  $\pm 10\%$  of  $1.4 \times 10^{-3} \text{ J cm}^{-1} \text{ sec}^{-1} \text{ }^{\circ}\text{C}^{-1}$  at their melting points. This similarity contrasts with the viscosity behaviour which varies markedly within the group.

At high temperatures  $\eta$  varies logarithmically with the inverse absolute temperature and  $A_{\eta}$  and  $E_{\eta}$  are constants. Near the melting point the molecules ortho-terphenyl and meta-terphenyl in particular show an exaggerated temperature dependence which may be formally described by making  $A_{\eta}$  and  $E_{\eta}$  vary with temperature.

This abnormality has been discussed by McLaughlin and Ubbelohde<sup>(20)</sup> on the basis of a partial clustering of the molecules, the clusters moving as whole units under shear and increasing the viscosity. These authors fitted the experimental data to an expression of Einstein<sup>(21)</sup>, for the viscosity of a suspension and were able to calculate the fraction of molecules associated at any given temperature.

Apart from the 1.5% discontinuity in orthoterphenyl, the thermal conductivity data give no indication that anything unusual is occurring in the liquid structure.

Most theories of transport in dense fluids predict a simple relationship between  $\lambda$  and  $\eta$ . The rigid sphere theories of Enskog and Longuet-Higgins and Pople give  $m\lambda/k\eta$  equal to 3.75 and 2.5 respectively. A combination of Andrade's viscosity expression and the expression of Horrocks and McLaughlin (equation 3.6) for thermal conductivity, both of which assume a molecular vibration mechanism, gives  $m\lambda/k\eta = 3$ . Liquids of simple molecules have already been shown to agree roughly with these predictions (table 1.2).

The experimental ratio  $m\lambda/k\eta$  for the polyphenyls

is given below.

TABLE 3.15

| T °C  | C <sub>6</sub> H <sub>6</sub> | $m\lambda/k\eta$ |      |      |      |
|-------|-------------------------------|------------------|------|------|------|
|       |                               | D                | P    | M    | O    |
| 40    | 2.74                          |                  |      |      |      |
| 50    | 3.00                          |                  |      |      |      |
| 60    | 3.28                          |                  |      |      | 0.16 |
| 70    |                               | 1.82             |      |      | 0.26 |
| 80    |                               | 2.11             |      | 0.59 | 0.41 |
| 90    |                               | 2.41             |      | 0.78 | 0.59 |
| 100   |                               | 2.75             |      | 1.01 | 0.83 |
| 110   |                               |                  |      | 1.25 | 1.11 |
| 120   |                               |                  |      | 1.54 | 1.44 |
| 130   |                               |                  |      | 1.85 |      |
| ----- |                               |                  |      |      |      |
| 220   |                               |                  | 4.7  |      |      |
| 230   |                               |                  | 5.1  |      |      |
| 240   |                               |                  | 5.85 |      |      |

D diphenyl; P para-terphenyl; M meta-terphenyl; O ortho-terphenyl

At high temperatures the ratio approaches values of the same order as those already encountered in simple liquids. There is a steep dependence on temperature and

in the case of *m*-terphenyl and *o*-terphenyl at low temperatures the ratio becomes extremely small. The abnormal behaviour of  $m\lambda/k\eta$  cannot be reconciled with theories of transport which attribute both thermal conduction and viscous flow to the same molecular mechanism. Moreover it is difficult to see how the formation of clusters invoked to explain the viscosity behaviour could fail also to affect the thermal conductivity. In this connection it is notable that Green's<sup>(22)</sup> rigorous approach to transport in simple liquids based upon the non-equilibrium distribution function makes an important distinction between the state of a fluid under shear and that of a fluid in a thermal in a thermal gradient. A velocity gradient causes a first order perturbation of the equilibrium pair distribution function, the magnitude of which is a measure of the fluid reaction to shear: a thermal gradient produces only a second order perturbation so that the thermal conductivity is determined largely by the equilibrium structure. It is possible that the structural perturbation under shear is greater in systems of complex molecules, where physical interlocking is possible, than in systems

of simple molecules. Thus, under shearing conditions groups of molecules may move (possibly rotate) in a correlated manner: the degree of correlation depending upon the molecular shape and upon the compression and therefore temperature of the system. Such a correlation is equivalent to the behaviour of a loosely knit cluster but it is not necessary to postulate the existence of distinguishable clusters under equilibrium conditions. The thermal conductivity which depends more upon the equilibrium structure may still be determined by the uncorrelated motion of single molecules.

### 3.2.2 The Theories of Bridgman and Kincaid and Eyring for Ortho-terphenyl

Velocity of sound data are available only for one member of the polyphenyl series, o-terphenyl. The thermal conductivity of melts of this molecule has been calculated at three temperatures using the methods of Bridgman and Kincaid and Eyring.

TABLE 3.16 - Thermal conductivity of o-terphenyl

| T<br>°C | Molar volume<br>ccs. | Velocity<br>of sound<br>m sec <sup>-1</sup> | <u><math>\lambda_{\text{calc. (B)}} \lambda_{\text{calc (K\&amp;E)}} \lambda_{\text{exp.}}</math></u><br><u>10<sup>-3</sup> J cm<sup>-1</sup>sec<sup>-1</sup> °C<sup>-1</sup></u> |      |      |
|---------|----------------------|---------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------|------|
|         |                      |                                             |                                                                                                                                                                                   |      |      |
| 60      | 219.5                | 1443                                        | 1.175                                                                                                                                                                             | 0.94 | 1.30 |
| 70      | 221.3                | 1408                                        | 1.135                                                                                                                                                                             | 0.91 | 1.30 |
| 85      | 223.7                | 1355                                        | 1.065                                                                                                                                                                             | 0.85 | 1.29 |

The calculated values are of the right order but show an exaggerated temperature dependence.

### 3.2.3 Application of the Theory of Horrocks and McLaughlin to the Polyphenyls

For molecules larger than benzene it is not possible to calculate vibration frequencies from molecular parameters. However, an empirical relation due to Lindemann<sup>(24)</sup> relates the frequency in the melting crystal to the absolute temperature  $T_f$  and the molecular weight  $M$ .

$$\gamma \text{ Lindemann} = \text{const.} \left( \frac{T_f}{M} \right)^{1/2} \frac{1}{V_f^{1/3}} \quad (3.45)$$

in which  $V_f$  is the molar volume.

If the volume change on melting is small this frequency will be close to that in the liquid at the melting point. Equation 3.45 has been used<sup>(25)</sup> to calculate the vibration frequency in liquid metals and hence their viscosities.

In table 3.17 the vibration frequencies and hence the thermal conductivities of the polyphenyls were calculated. A value of the Lindemann constant appropriate to these molecules was obtained by taking benzene as a norm and fitting the thermal conductivity exactly to the experimental value. The value thus obtained was  $3.61 \times 10^{12}$ .

TABLE 3.17 - Lindemann frequencies and thermal conductivities of the polyphenyls

|             | $T_f$<br>°K | M   | $V_f$<br>(ccs) | $\gamma$<br>( $10^{11} \text{ sec}^{-1}$ ) | $\lambda$ calc.<br>( $10^{-4} \text{ Jcm}^{-1} \text{ sec}^{-1} \text{ } ^\circ\text{C}^{-1}$ ) | $\lambda$ exp. |
|-------------|-------------|-----|----------------|--------------------------------------------|-------------------------------------------------------------------------------------------------|----------------|
| benzene     | 278         | 78  | 87.3           | 15.6                                       | 15.0                                                                                            | 15.0           |
| diphenyl    | 343         | 154 | 155            | 10.0                                       | 8.06                                                                                            | 13.8           |
| p-terphenyl | 485         | 237 | 237            | 8.43                                       | 5.83                                                                                            | 12.9           |
| m-terphenyl | 360         | 232 | 221            | 7.44                                       | 5.27                                                                                            | 13.6           |
| o-terphenyl | 329         | 232 | 218            | 7.15                                       | 5.09                                                                                            | 13.1           |

The agreement is poor, becoming worse as the molecular weight increases. There are two possible reasons for this failure:

- (1) There may be in the larger polyphenyls a contribution to the effective specific heat from internal degrees of freedom.
- (2) The Lindemann frequency which varies as  $M^{-\frac{1}{2}}$  may be quite inaccurate for complex molecular systems.

All thermal conductivity theories neglect the internal specific heat of the molecules which are treated as rigid structureless particles. The justification for this omission lies partly in the success of the value  $3k$  in

predicting the thermal conductivity of fairly complex molecules like benzene where the internal specific heat is large, (benzene<sup>(26)</sup> at 20°C  $C_v$  internal = 7k/molecule). It has moreover been shown<sup>(27)</sup> by velocity of sound measurements in the vapour phase that the exchange of internal vibrational energy between molecules requires for its accomplishment of the order 1000 encounters.

These considerations can only apply to relatively simple polyatomic molecules otherwise the thermal conductivity of macromolecular systems would be infinitely small. Very large molecules have very low energy internal modes which are easily exchanged. There are however several indications that this is not the case in the polyphenyls.

- (1) In the case of ortho-terphenyl Bridgman's theory using  $C_v = 3k$  gives fairly good (15%) agreement with the experimental value.
- (2) The internal modes of the terphenyls which are most easily excited are connected with the relative motion of the phenyl rings. In the three isomers these modes suffer varying degrees of inhibition due to

mutual interference of the rings.<sup>(46,47)</sup> If the energy of these modes were handed on in thermal conduction a marked variation in the thermal conductivity of the three isomers would be expected. However, at their freezing points the values of  $\lambda$  lie within a range of  $\pm 2.5\%$ .

- (3) In this connection the thermal conductivity of triphenylene is of interest. In this molecule, whose mass differs by only two units from the mass of the terphenyls, the relative motion of the phenyl rings is suppressed by joining the outer rings. Nevertheless, triphenylene at its melting point has a thermal conductivity within the previously stated range ( $\pm 2.5\%$ ) of the terphenyl isomers.

It appears that the first possible cause of inaccuracy in the calculated value of  $\lambda$  has been eliminated.

### 3.2.4 The Temperature Coefficients of Thermal Conductivity in the Polyphenyls

The temperature coefficient of  $\lambda$  is more sensitive to molecular size and structure than is  $\lambda$  itself. It varies by a factor of 10 between benzene and meta-terphenyl (table 3.13). On the basis of the vibration frequency models of the previous section it was shown that a close correspondence should exist between the temperature coefficients of the thermal conductivity and of the volume. This was demonstrated for simple molecules in figure 3.1 which also included the polyphenyls. Figure 3.6 is a plot of  $\lambda' d\lambda/dT$  versus  $V^{-1} dV/dT$  on a larger scale including only the polyphenyls and toluene. Since the variation in those quantities is slight for the larger molecules they are represented by values appropriate to their melting points.

The values lie close to a straight line of slope 3.5. If extended this line cuts the  $\alpha$  axis at  $5.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ . This suggests that slightly larger molecules (e.g. 22 diphenyl-diphenyl) with a slightly smaller  $\alpha$  may have a positive temperature coefficient of thermal conductivity. Except in associated liquids such behaviour is not known at normal pressures. However, Bridgman<sup>(28)</sup> has shown

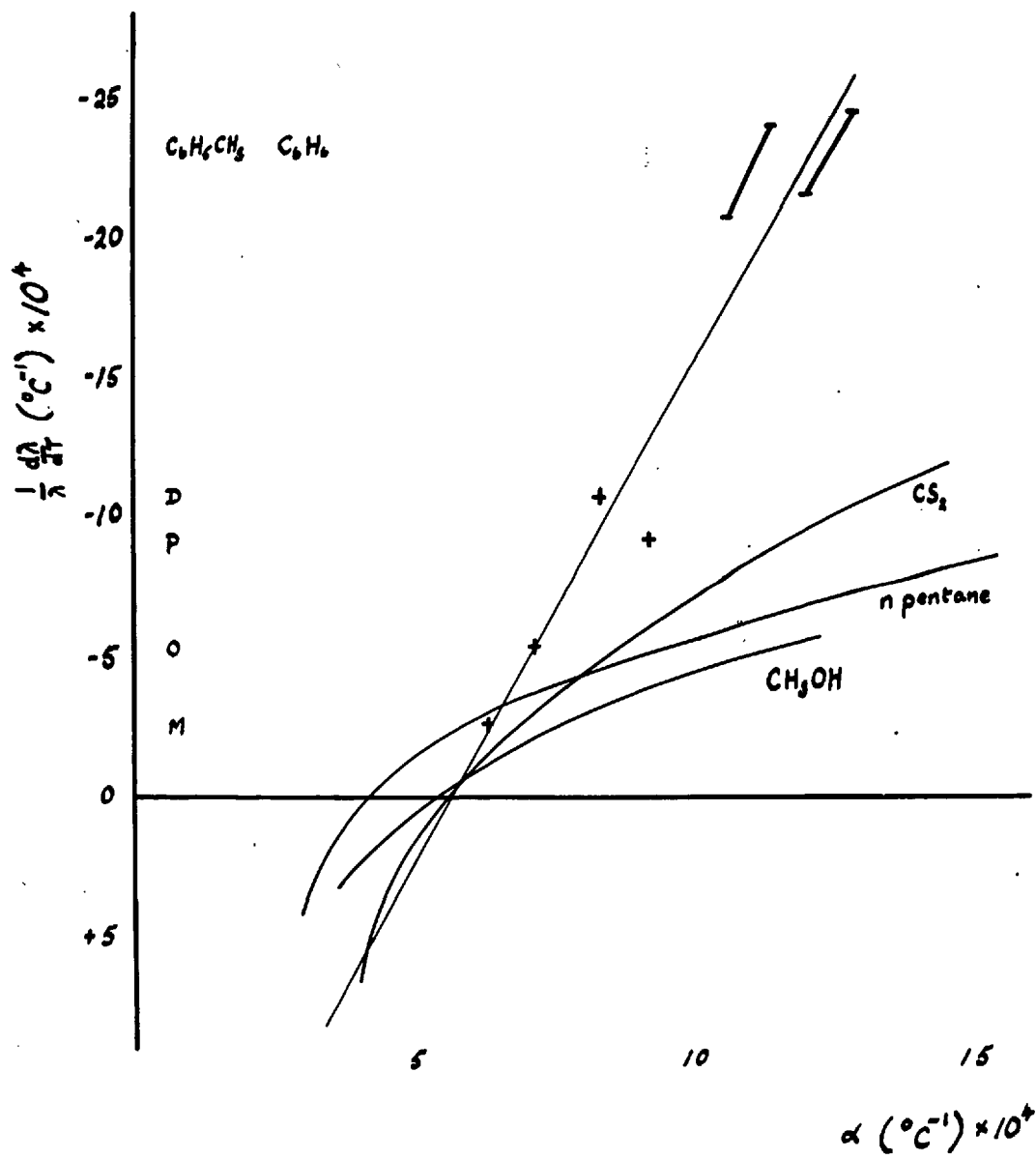


Figure 3.6

that for a number of liquids the temperature coefficient decreases in magnitude as the pressure is raised and becomes positive in the region  $3\,000\text{ kg/cm}^2$ .<sup>28</sup> Bridgman's data on carbon disulphide, n pentane and methyl alcohol have been analysed (table 3.18) to give  $\lambda^{-1} d\lambda/dT$  as a function of  $\alpha$  at various pressures.  $\alpha$  values were obtained from the measured volumes at  $20^\circ\text{C}$  and  $80^\circ\text{C}$  in the case of carbon disulphide and methyl alcohol and from the volumes at  $0^\circ\text{C}$  and  $95^\circ\text{C}$  in the case of n-pentane. Values of  $\lambda^{-1} d\lambda/dT$  were obtained from  $\lambda$  values at  $30^\circ\text{C}$  and  $75^\circ\text{C}$ .

TABLE 3.18

| Pressure<br>kg.cm <sup>-1</sup> | $\alpha \times 10^4$<br>°C <sup>-1</sup> | $\lambda^{-1} d\lambda/dT_x \times 10^4$<br>°C <sup>-1</sup> |
|---------------------------------|------------------------------------------|--------------------------------------------------------------|
| <u>Carbon disulphide</u>        |                                          |                                                              |
| 0                               | 14.8                                     | -12.0                                                        |
| 1                               | 3.4                                      | - 5.1                                                        |
| 2                               | 6.7                                      | - 2.2                                                        |
| 4                               | 4.9                                      | + 1.5                                                        |
| 6                               | 4.1                                      | + 4.5                                                        |
| 9                               | 4.1                                      | + 7.0                                                        |
| <u>n ethyl alcohol</u>          |                                          |                                                              |
| 0                               | 12.0                                     | - 5.3                                                        |
| 1                               | 8.5                                      | - 4.1                                                        |
| 2                               | 6.5                                      | + 0.3                                                        |
| 4                               | 4.9                                      | + 0.8                                                        |
| 6                               | 4.4                                      | - 0.5                                                        |
| 9                               | 3.9                                      | + 3.2                                                        |
| <u>n pentane</u>                |                                          |                                                              |
| 0                               | 19.8                                     | -10.5                                                        |
| 1                               | 9.0                                      | - 3.8                                                        |
| 2                               | 5.6                                      | - 3.2                                                        |
| 4                               | 4.0                                      | -                                                            |
| 6                               | 3.0                                      | + 4.2                                                        |

Smooth curves representing these tabulated values are included in figure 3.6. They cut the  $\alpha$  axis at approximately the same point as does the line for the polyphenyl molecules.

In the absence of further experimental data it is not possible to draw more general conclusions regarding the relationship between  $\alpha$  and  $\lambda^{-1}d\lambda/dT$ .

It is interesting to note that neither the harmonic oscillator model nor its modification to include quartic terms predict a change in sign of  $\lambda^{-1}d\lambda/dT$  within the normal range of liquid densities. However these theories were developed for simple molecules for which there are no data available at high pressures to show that the coefficient does change sign. It has been previously stated (page 185) that the square well model might be more suitable for large molecules. A calculation based upon equation 3.42 is included below for the polyphenyls.

In order to apply equation 3.42 it is necessary to estimate a rigid sphere collision diameter for these molecules. The volumes of the liquid polyphenyls are linearly dependent on temperature. By extrapolating the volume to 0°K, the volume which the close packed liquid would

occupy has been calculated. The ratio of this volume to that occupied by the liquid at its melting point has been equated to the equivalent ratio for a hard sphere fluid, namely  $(\sigma/a)^3$ . Using experimental values of  $\alpha$  at the melting point,  $\lambda' d\lambda/dT$  is estimated from equation 3.42 and compared with experiment in table 3.19.

TABLE 3.19

|                 | $\frac{1}{\lambda} \frac{d\lambda}{dT} \text{ exp. } \times 10^4$ | $\frac{1}{\lambda} \frac{d\lambda}{dT} \text{ calc. } \times 10^4$ |
|-----------------|-------------------------------------------------------------------|--------------------------------------------------------------------|
|                 | $^{\circ}\text{C}^{-1}$                                           |                                                                    |
| diphenyl        | 10.2                                                              | 13.8                                                               |
| para terphenyl  | 8.1                                                               | 9.2                                                                |
| meta terphenyl  | 2.6                                                               | 16.2                                                               |
| ortho terphenyl | 5.3                                                               | 14.7                                                               |

The calculated values are of the right order but individual agreement is poor which is not surprising in view of the crudity of the rigid sphere assumption.

### 3.2.5 The Discontinuity in the Thermal Conductivity of Ortho-terphenyl

Although striking, the discontinuity which occurs between 57 and 58°C is only 1.5% of the total thermal conductivity. However this considerably exceeds the experimental error of the present determinations and there seems no doubt that it is genuine. Measurements were made on three different samples of ortho-terphenyl using two different cells. The purity of the samples was never less than 99 mole %. In each case a discontinuity was observed.

It has already been mentioned that the long chain paraffins  $C_{12}$  and  $C_{18}$  possess anomalies in the thermal conductivities which may be discontinuous in character. Sakiadis and Coates<sup>(29)</sup> have suggested that this behaviour is connected with the anomalous specific heats observed in the solid paraffins.

Unfortunately there are no available measurements of specific heats or sound velocities in the temperature range 57 to 58°C for ortho-terphenyl. An attempt to observe a structural change in the melt by studying its ultra-violet spectrum in this range of temperature revealed

no significant change. However, since crystallisation of the material also failed to produce a shift of the spectrum, it may be surmised that the effect upon the electronic levels of a small change in the liquid structure is too small to be detected in this way.

### CHAPTER 3.3 THE TRANSPORT PROPERTIES OF ISOTOPICALLY SUBSTITUTED MOLECULES

In formulating theories of thermal conduction information is required on possible mechanisms of energy transport. Two translational mechanisms are generally recognised, one associated with the diffusional motion of molecules in the system, the other associated with the transport across centres of molecules at collision: the latter not involving a net displacement of the molecules themselves. In liquids it is well established that the contribution from the former mechanism is negligible compared with that from the latter.

However in liquids of assymmetric molecules the collisional mechanism is complicated by an additional possibility. The specific heats of such liquids suggest that the molecules possess rotational or librational motion, which may be expected to reinforce the heat transport in two ways.

1. It may contribute an additional "collision" mechanism to the actual mechanism of transport.

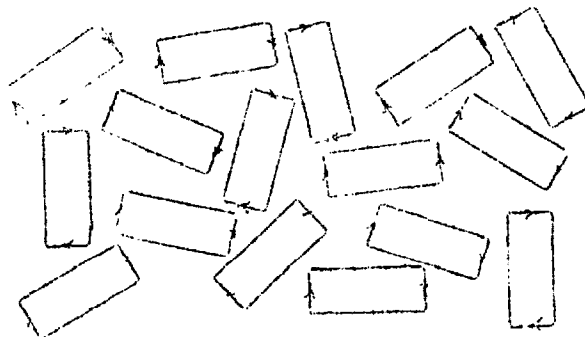


Figure 3.7

A system of partially interlocked bodies (figure 3.7 ) which are capable of libration may be expected to transmit this motion from one body to another in a similar manner to that in which translational motion is transmitted by collisions. The rate of energy transfer between molecules by this mechanism will be determined by the average frequency of librational motion.

2. The librations or rotations may be imagined also to contribute to the effective specific heat for thermal conduction: the magnitude of this contribution depending upon the number of rotational degrees of freedom of the molecule

In theories of liquid thermal conductivity, the direct transfer of librational motion has not so far been treated

as a distinct mechanism although the contribution of rotational motion to the effective specific heat has been postulated by Kincaid and Eyring<sup>50)</sup>. They assumed that the specific heat was made up of kinetic terms from both vibrations and rotations of the molecule. Although at the time thermal conductivities were not available on monatomic or diatomic molecules Kincaid and Eyring suggested that these molecules would provide a test of their specific heat assumption against that of Bridgman. Calculations on the basis of their model have been given in table 3.1 and are in better agreement with experiment than Bridgman's values for simple molecules. However in the same table it was shown that equally good results could be obtained using throughout a specific heat of  $3k$  in the harmonic oscillator model.

The evidence is conflicting, and the importance of rotational motion therefore requires investigation.

### 3.3.2 Corresponding States Behaviour in Thermal Conductivity

Rotational motion does not enter into the description of molecules which interact with central forces. The motions of the molecules in such a system are determined completely by the pair forces and the molecular mass. If a pair interact with a potential described by

$$\phi(r) = \epsilon F\left(\frac{\sigma}{r}\right) \quad (3.46)$$

where  $\epsilon$  and  $\sigma$  are respectively characteristic scale factors for the energy and separation of the pair, the thermal conductivity may be expressed<sup>(1)</sup> in dimensionless form

$$\lambda^* = \frac{\lambda \sigma^2 \sqrt{m}}{k \sqrt{\epsilon}} \quad (3.47)$$

in which  $\lambda^*$  is a universal function of the reduced state, i.e. of  $kT/\epsilon$  and  $V/N\sigma^3$ .

The ratio  $\lambda_1 : \lambda_2$  for two systems whose molecules are described respectively by  $\sigma_1, \epsilon_1$  and  $\sigma_2, \epsilon_2$  can be written

$$\frac{\lambda_1}{\lambda_2} = \left[ \frac{m_2}{m_1} \right]^{\frac{1}{2}} \left[ \frac{\epsilon_1}{\epsilon_2} \right]^{\frac{1}{2}} \left[ \frac{\sigma_2}{\sigma_1} \right]^2 \quad (3.48)$$

In the special case of isotopically substituted molecules

the force fields are essentially the same, and equation 3.48 reduces to

$$\frac{\lambda}{\lambda_i} = \left[ \frac{m_i}{m} \right]^{\frac{1}{2}} \quad (3.49)$$

Equation 3.49 would not be expected to hold for molecules whose force fields are assymmetric since in this case rotation enters into the description of the molecular motion. If thermal conduction is imagined to be occasioned by a librational mechanism only, the ratio will depend on the square root of the moment of inertia ratio. Only where the masses of all atoms in the molecule are altered in the same proportion will the mass ratio and moment of inertia ratio be identical<sup>(32)</sup>.

If librational or rotational motion as well as translational motion is effective in the actual mechanism of energy transport the thermal conductivity ratio will be expected to lie within the range  $\sqrt{m_i/m}$  and  $\sqrt{I_i/I}$

### 3.3.3. Thermal Conductivity Ratios of Isotopically Substituted Benzene, Cyclohexane and Water

Table 3.20 gives the thermal conductivity ratios for the isotopically substituted pairs; benzene, perdeuter<sup>10</sup>benzene; cyclohexane, perdeuterocyclohexane; water, deuterium oxide. The viscosity ratios and the square roots of the mass ratios and moment of inertia ratios are included, The subscript,  $i$ , refers to the deuterated compounds

TABLE 3.20

| <u>Pair</u>                                       | $T^{\circ}\text{K}$ | $\lambda/\lambda_i$ | $\eta_i/\eta$ | $(m_i/m)^{1/2}$ | $(\bar{I}_i/\bar{I})^{1/2}$ |
|---------------------------------------------------|---------------------|---------------------|---------------|-----------------|-----------------------------|
| $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6$       | 293.2               | 1.042               | 1.077         | 1.038           | 1.100                       |
|                                                   | 311.2               | 1.039               | 1.082         |                 |                             |
|                                                   | 332.2               | 1.036               | 1.080         |                 |                             |
| $\text{C}_6\text{H}_{12}/\text{C}_6\text{D}_{12}$ | 293.2               | 1.063               | 1.067         | 1.070           | 1.215                       |
|                                                   | 311.0               | 1.061               | 1.075         |                 |                             |
|                                                   | 333.2               | 1.059               | 1.080         |                 |                             |
| $\text{H}_2\text{O}/\text{D}_2\text{O}$           | 293.2               | 1.043               | 1.245         | 1.054           | 1.381                       |
|                                                   | 313.2               | 1.053               | 1.202         |                 |                             |
|                                                   | 333.2               | 1.060               | 1.178         |                 |                             |
|                                                   | 353.2               | 1.050               | 1.164         |                 |                             |

Table references 1:  $C_6D_6$   $C_6H_6$  (33);  $H_2O$   $D_2O$  (34);  
 $C_6H_{12}$  (35);  $C_6D_{12}$ , calculated from  $C_6H_{12}$ .

$\lambda$  and  $\eta$   $C_6D_6$   $C_6H_6$   $C_6D_{12}$   $C_6H_{12}$ , present work;  
 $H_2O$   $D_2O$  (36).

$\bar{I}$  in the table is the arithmetic mean moment of inertia.

Table 3.20 shows that on average over the liquid range the thermal conductivity ratio agrees with the corresponding square root of the mass ratio within 0.5%. This is a striking result in view of the diversity of structure in the three pairs and contrasts with the viscosity behaviour where only for the case of the pseudo-spherical cyclohexane pair is a similar correspondence achieved.

These results indicate that rotation or librations of the molecules do not contribute directly to the mechanism of energy transport although, as will be shown, a contribution to the actual amount of energy transported in a collision (via the specific heat) is not excluded.

### 3.3.3 A Rigid Sphere Model Including Rotation

At present the only statistical theory which has attempted to discuss transport in liquids where rotational motion is included, is due to Valleau<sup>(37)</sup> who studied the viscosity and thermal conductivity of a dense fluid of and rough spheres. The theory is an extension of the theory of Longuet-Higgins and Pople for smooth spheres and leads to the following modifications of their expressions for  $\lambda$  and  $\eta$ .

$$\lambda = \frac{4\sigma\chi Nk}{V} \left[ \frac{kT}{m} \right]^{\frac{1}{2}} \quad (3.50)$$

$$\eta = \frac{\sigma\chi N}{5V} \left\{ \frac{7I + m\sigma^2}{I + \frac{m\sigma^2}{4}} \right\} \left[ \frac{mkT}{\pi} \right]^{\frac{1}{2}} \quad (3.51)$$

where  $\chi = (PV/RT - 1)$  and  $I$  is the moment of inertia of the spheres.

The expression for the thermal conductivity is twice that for smooth spheres indicating that a full rotational specific heat is operative. The moment of inertia does not enter into the thermal conductivity since the basic

mechanism of energy transfer still depends upon the translational collision frequency which is unaffected by the rotation. Thus this model involving free rotation accords with equation 3.49.

Valleau's expression for the viscosity differs from that for smooth spheres by the factor

$$\frac{7I + m\sigma^2}{4I + m\sigma^2} \quad (3.52)$$

For the molecules studied this factor does not exceed

1. The predicted viscosity ratio for isotopic pairs is

$$\frac{\eta}{\eta} = \frac{7I_i + m\sigma^2}{4I_i + m\sigma^2} \left[ \frac{m_i}{m} \right]^{1/2} / \frac{7I + m\sigma^2}{4I + m\sigma^2} \quad (3.53)$$

Numerical values of equation 3.53 are 1.053, 1.105 and 1.063 for benzene, cyclohexane and water respectively.

Rigid sphere radii were obtained by equating experimental viscosities in the gas phase<sup>(38,39,40)</sup> at 25°C to the Chapman-Enskog equation for the viscosity of a dilute rigid sphere gas.

The poor agreement of this theory for the viscosity ratio suggests that rotation plays a more fundamental

role in the transport of momentum than a rough sphere model is able to describe.

Despite this reservation it is interesting to note the predictions of the hard sphere theories for  $m\lambda/k\eta$ .  
From equations 1.32, 1.33, 3.50 and 3.51.

$$\left[ \frac{m\lambda}{k\eta} \right]_{\text{rotating spheres}} = 2 \left[ \frac{4I + m\sigma^2}{7I + m\sigma^2} \right] \left[ \frac{m\lambda}{k\eta} \right]_{\text{smooth spheres}} \quad (3.54)$$

The multiplication factor varies between 2 and 1.25 as  $I$  increases from 0 to  $m\sigma^2$ .

The only molecule available for which rotation is definitely excluded is argon. Comparison of the specific heat of argon with that of nitrogen and methane<sup>(21)</sup> suggests that these two molecules are rotating freely in the liquid. However, experimental values of  $m\lambda/k\eta$  (table 1.2) for argon, nitrogen and methane are closely the same at corresponding temperatures within their liquid ranges. It may be tentatively surmised that the rotational specific heat, which gives rise to the factor 2 in equation 3.54, is not operative in the thermal conductivity of these molecules.

## CHAPTER 3.4 THE TRANSPORT PROPERTIES OF THE ETHYL IODIDE + N-BUTYL IODIDE SYSTEM

### 3.4.1 The Transport Properties of Mixtures

The transport properties of mixtures usually show a considerable departure from a linear concentration dependence. Frequently the simplest law which adequately describes the behaviour is quadratic, i.e. in the use of viscosity

$$\eta_{\text{mixture}} = x_1^2 \eta_1 + 2x_1(1-x_1)\eta_{12} + (1-x_1)^2 \eta_2 \quad (3.55)$$

where  $x_1$  is the mole fraction of species 1 and  $\eta_{12}$  is a constant having the dimensions of viscosity.

In section 2 the viscosity and thermal conductivity of the ethyl iodide + n butyl iodide system were fitted to a quadratic law of the above type.

Bearman<sup>(41,42,43)</sup> has derived on a statistical mechanical basis a mixing law for transport properties which is quadratic in form. The transport expressions and the assumptions on which they were derived have been stated in section 1, equations 1.47 and 1.48. Horrocks and McLaughlin<sup>(44)</sup> have shown that these expressions imply

a complete set of relations between the transport coefficients.

Equation 1. may be re-written in the form

$$\sigma^2 = x_1^2 v_1^2 \frac{\eta_1 D_1^0}{\eta D_{1x}} + x_1 x_2 \frac{A_{12}}{\eta D_{1x}} + x_2^2 v_2^2 \frac{\eta_2 D_1^\infty}{\eta D_{1x}} \quad (3.56)$$

which may be expanded in the variable  $x_1$  to give

$$\begin{aligned} & x_1^2 [v_1^2 - 2v_1 v_2 + v_2^2] + x_1 [2v_1 v_2 - 2v_2^2] + v_2^2 \\ &= \frac{1}{\eta D_{1x}} \left[ x_1^2 \{ \eta_1 v_1^2 D_1^0 + A_{12} + \eta_2 v_2^2 D_1^\infty \} + x_1 \{ A_{12} - 2\eta_2 v_2^2 D_1^\infty \} \right. \\ & \quad \left. + \{ \eta_2 v_2^2 D_1^\infty \} \right] \end{aligned} \quad (3.57)$$

Since this expression must hold for all values of  $x_1$ ,

$\eta D_{1x}$  must be constant and therefore equating coefficients of the powers of  $x_1$ ,

$$\eta D_{1x} = \eta_1 D_1^0 = \eta_2 D_1^\infty \quad (3.58)$$

and since the equation 1.47 must also hold with the species numbers interchanged,

$$\eta D_{2x} = \eta_2 D_2^0 = \eta_1 D_2^\infty \quad (3.59)$$

Equation 1.48 for the thermal conductivity may be

treated in the above manner and yields the relationships

$$\frac{\lambda}{D_{1x}} = \frac{\lambda_1}{D_1^0} = \frac{\lambda_2}{D_1^\infty} \quad (3.60)$$

and with the species numbers interchanged

$$\frac{\lambda}{D_{2x}} = \frac{\lambda_2}{D_2^0} = \frac{\lambda_1}{D_2^\infty} \quad (3.61)$$

A combination of these relationships leads also to

$$\lambda \eta = \lambda_1 \eta_1 = \lambda_2 \eta_2 \quad (3.62)$$

$$\frac{D_{1x}}{D_{2x}} = \frac{D_1^\infty}{D_2^0} = \frac{D_1^0}{D_2^\infty} \quad (3.63)$$

### 3.4.2 The System Ethyl Iodide + n-Butyl Iodide

This is the only system for which the necessary transport and thermodynamic data are available to test the equations (3.58) to (3.63). The viscosity and thermal conductivity data have been given in section 2. The self diffusion coefficients have been measured by Carman and Stein<sup>(45)</sup>

TABLE 3.21 - Transport coefficients of pure ethyl iodide and n-butyl iodide at 19.35°C

|                | $\eta$ (poise)<br>$\times 10^3$ | $\lambda$ (J.cm <sup>-1</sup> sec <sup>-1</sup> °C <sup>-1</sup> )<br>$\times 10^4$ | $D_1^0$ (cm <sup>2</sup> sec <sup>-1</sup> )<br>$\times 10^4$ |
|----------------|---------------------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------|
| ethyl iodide   | 5.91                            | 8.58                                                                                | 2.22                                                          |
| n-butyl iodide | 8.78                            | 8.91                                                                                | 1.37                                                          |

The  $\eta$  and  $\lambda$  values are end points of the quadratic curves fitted to the experimental results in tables 2.23 and 2.11

To obtain some indication of the general validity of equations 3.58 to 3.63 it is only necessary to compare the experimental ratios  $D_1^\infty/D_1^0$ ,  $D_2^0/D_2^\infty$ ,  $\eta_1/\eta_2$ , and

$\lambda_2/\lambda_1$ , which according to theory should be equal.

Table 3.22 gives these ratios for ethyl iodide (1) and n-butyl iodide (2).

TABLE 3.22

| $D_1 \text{ (cm}^2\text{sec}^{-1})$<br>$\times 10^5$ | $D_2 \text{ (cm}^2\text{sec}^{-1})$<br>$\times 10^5$ |      |      |      |      |
|------------------------------------------------------|------------------------------------------------------|------|------|------|------|
| 1.482                                                | 2.662                                                | 0.67 | 0.66 | 0.67 | 1.04 |

Agreement is good except for the ratio  $\lambda_2/\lambda_1$  which differs from the others by 50%.

Following the initial comparison it is necessary to test the validity of the transport expression over the whole mole fraction range. From equations 3.58 and 3.63 the viscosity of the mixture may be expressed

$$\eta = \frac{\eta_1 D_1^\circ}{D_{1x}} = \frac{\eta_2 D_2^\circ}{D_{2x}} = \frac{\eta_1 D_1^\circ}{D_{1x}} = \frac{\eta_2 D_2^\circ}{D_{2x}} \quad (3.64)$$

Tables 3.21 and 3.22 show that

$$\eta_1 D_1^\circ = \eta_2 D_2^\circ = 13.07$$

and

$$\eta_2 D_2^\circ = \eta_1 D_1^\circ = 12.11$$

so that using experimental values of  $D_{1x}$  and  $D_{2x}$ , the viscosities of the mixtures may be calculated. These are compared with experiment in table 3.23. Agreement is within 2% on average.

$\eta(\text{calc})$ 

TABLE 3.23

| $x_1$ | $D_{1x}(\text{expt})$ | $D_{2x}(\text{expt})$ | $\eta(\text{expt})$ | $\frac{13.07}{D_{1x}}$ | $\frac{12.11}{D_{2x}}$ |
|-------|-----------------------|-----------------------|---------------------|------------------------|------------------------|
|       |                       |                       |                     | $D_{1x}$               | $D_{2x}$               |
| 0.0   | 1.48                  | 1.37                  | 8.78                | 8.84                   | 8.84                   |
| 0.1   | 1.55                  | 1.40                  | 8.52                | 8.43                   | 8.65                   |
| 0.2   | 1.62                  | 1.45                  | 8.25                | 8.07                   | 8.35                   |
| 0.3   | 1.69                  | 1.50                  | 7.93                | 7.73                   | 8.07                   |
| 0.4   | 1.76                  | 1.56                  | 7.70                | 7.43                   | 7.76                   |
| 0.5   | 1.83                  | 1.62                  | 7.42                | 7.14                   | 7.47                   |
| 0.6   | 1.91                  | 1.70                  | 7.13                | 6.84                   | 7.12                   |
| 0.7   | 1.98                  | 1.78                  | 6.83                | 6.60                   | 6.80                   |
| 0.8   | 2.06                  | 1.86                  | 6.53                | 6.34                   | 6.51                   |
| 0.9   | 2.14                  | 1.96                  | 6.23                | 6.11                   | 6.13                   |
| 1.0   | 2.22                  | 2.06                  | 5.91                | 5.89                   | 5.88                   |

The thermal conductivity of the mixture may be calculated in a formally similar manner from either the viscosities or the diffusion coefficients using equations 3.62 or 3.60 and 3.61. As may be expected from the comparison of transport coefficient ratios in table 3.22, discrepancies of up to 50% occur between experimental thermal conductivities

of the mixtures and the calculated values.

It has been pointed out by Bearman (private communication) that for the theory to hold an additional restriction not previously stated is implied. This is that the ratio of thermal expansion and isothermal compressibility coefficients be independent of composition. There are no data available to check this for the present system.

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Offprinted from the *Transactions of the Faraday Society*,  
No. 446, Vol. 56, Part 2, February, 1960

**THERMAL CONDUCTIVITY OF SIMPLE MOLECULES IN  
THE CONDENSED STATE**

# THERMAL CONDUCTIVITY OF SIMPLE MOLECULES IN THE CONDENSED STATE

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*Received 14th September, 1959*

A model for the thermal conductivity of a liquid composed of spherically symmetric molecules is proposed. The theory permits calculation of the coefficient of thermal conductivity from the density, provided the force constants of the molecular interaction are known. The relative magnitude of "convective" and vibrational contributions is examined and the former is shown to be negligible. Calculated coefficients of thermal conductivity, for simple liquids, agree on average within approximately 20 % of experimental values. The theory has also been applied to solids composed of similar molecules.

In a previous paper<sup>1</sup> it was shown that the coefficients of self-diffusion and viscosity in a simple liquid could be calculated using a modified rate-theory approach. The model assumed that the liquid was quasi-crystalline and consisted of spherical molecules, interacting with a Lennard-Jones potential, located on a f.c.c. lattice in which there is a number of vacancies. The mechanism for the transport of both mass and momentum was assumed to be purely "convective", i.e. involved molecular hopping from occupied sites to holes in the liquid. This hopping was conditioned by a molecule having both sufficient energy to move and the presence of a nearest neighbour hole to accommodate it.

The assumptions of a specific lattice geometry and molecular force field, as in the theory of liquids of Lennard-Jones and Devonshire,<sup>2</sup> necessitated the estimation of only one parameter empirically in the evaluation of the coefficients of viscosity and self-diffusion from the final equations. In the present approach to calculate the thermal conductivity the same model of the liquid is retained.

## THE MECHANISM OF TRANSPORT AND THE COEFFICIENT OF THERMAL CONDUCTIVITY

If a temperature gradient  $dT/dx$  is applied to a liquid the average difference in thermal energy between successive molecules in adjacent planes a distance  $l$  apart is  $ldU/dx$ . This excess energy can be transported down the temperature gradient in two distinct ways, (a) by a vibrational mechanism and (b) by a convective mechanism.

### (a) VIBRATIONAL CONTRIBUTION

If the difference in energy  $ldU/dx$  between successive layers in the liquid quasi-lattice due to the temperature gradient is transferred down the gradient with a frequency  $Pv$  this gives rise to thermal conductance. The factor  $P$  is the probability that energy is transferred when two vibrating molecules collide and  $v$  is the mean vibrational frequency in the quasi-lattice. The rate of flow of heat  $dQ/dt$  across unit area of the liquid at right-angles to the temperature gradient is therefore given by

$$dQ/dt = -2nPvldu/dx. \quad (1)$$

The negative sign indicates that flow is down the temperature gradient. The factor 2 accounts for the fact that a molecule crosses a plane at right-angles to its direction

of motion twice in every complete vibration and  $n$  is the number of molecules per unit area of the liquid quasi-lattice. As

$$du/dx = du/dT \cdot dT/dx, \quad (2)$$

use of the one-dimensional Fourier equation for the heat flow per unit area, viz.,

$$dQ/dt = -\lambda dT/dx \quad (3)$$

enables  $\lambda$  the coefficient of thermal conductivity to be obtained from eqn. (1) as

$$\lambda_{\text{vib.}} = 2nPv l du/dT. \quad (4)$$

#### (b) CONVECTIVE CONTRIBUTION

In addition to the transfer due to molecular collision processes in the lattice heat can also be transferred down the temperature gradient by the hopping of molecules from occupied sites to vacancies in the liquid.

In the absence of a temperature gradient the frequency of movement  $k$  of atoms from one adjacent layer in the liquid to the next is given by

$$k = k_0 n_h / N \quad (5)$$

where  $n_h$  is the number of vacancies and  $N$  is Avogadro's number. From rate theory  $k_0$  can be written

$$k_0 = \left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}} \frac{1}{v_f} \exp(-e_0/kT), \quad (6)$$

where  $v_f$  is the free volume of the liquid and  $e_0$  the height of the boundary potential barrier restricting a molecule to its cell. As  $l$  is of the order of  $10^{-8}$  cm  $l dT/dx$  is small for normal gradients so that the frequencies  $k_f$  and  $k_r$  for forward and reverse motion across a reference plane at right-angles to the temperature gradient will not differ significantly and can each be replaced by a mean frequency given by (5). The rate of transport of energy across unit area of the reference plane is therefore given as before by

$$dQ/dt = -2nk l du/dx. \quad (7)$$

The factor 2 is included in eqn. (7) to account for the equivalence to the net transport of "hot" molecules moving across the reference plane down the temperature gradient to "cold" molecules moving up it. The convective contribution to the coefficient of thermal conductivity is then obtained from eqn. (7) using (2) and (3) as before and is

$$\lambda_{\text{conv.}} = 2nk l du/dT. \quad (8)$$

As the two mechanisms are independent, the coefficient of thermal conductivity may be written

$$\lambda = \lambda_{\text{vib.}} + \lambda_{\text{conv.}} \quad (9)$$

#### EVALUATION OF THE SEPARATE CONTRIBUTIONS

##### (a) VIBRATIONAL CONTRIBUTION

To obtain an expression for the vibrational contribution the liquid is considered quasi-crystalline, consisting of spherically symmetric molecules located on a f.c.c. lattice and interacting with a Lennard-Jones 12:6-potential. This point of view is justified in view of the similarities in properties of solids and liquids at the melting point.

If the lattice consisted of an infinite series of harmonic oscillators and had no structural defects, there would be no thermal resistance to the passage of heat and

no temperature-gradient could therefore be set up. In practice this situation does not arise due to anharmonicity of the oscillators, which introduces a thermal resistance and allows a temperature gradient to be set up leading to a finite thermal conductivity. While anharmonicity is essential therefore from the mechanistic point of view, the frequencies of the anharmonic and harmonic oscillators will not, however, be appreciably different for small vibrations. Under these conditions therefore the potential energy of the system may be written in terms of the displacement  $r$  from equilibrium as

$$V'(r) = V'_0 + \frac{1}{2}\bar{k}r^2, \quad (10)$$

where  $V'_0$  is the potential when all atoms are located on their lattice sites. For small vibrations the restoring force constant

$$\bar{k} = 4\pi^2\nu^2m,$$

where  $m$  is the mass of a molecule.

If the intermolecular potential  $\phi(r)$  is given by

$$\phi(r) = \varepsilon \left[ \left( \frac{r_0}{r} \right)^{12} - 2 \left( \frac{r_0}{r} \right)^6 \right], \quad (11)$$

where  $\varepsilon$  is the depth of the potential well at the equilibrium separation  $r_0$ , then it can be shown<sup>4</sup> that the vibrational frequency  $\nu$  is given by

$$\nu^2 = \frac{\varepsilon}{\pi^2 r_0^2 m} \left[ 11C_{14} \left( \frac{r_0}{a} \right)^{14} - 5C_8 \left( \frac{r_0}{a} \right)^8 \right], \quad (12)$$

where  $C_{14}$  and  $C_8$  are lattice summation constants of values<sup>3</sup> 12.05899 and 12.80194. The equilibrium diameter  $r_0$  of the molecule is related to its low velocity collision diameter by  $r_0^3 = \sqrt{2}\sigma^3$  and  $a$  the distance between nearest neighbour molecules is related to the molar volume  $V$  by  $a^3 = \sqrt{2}V/N$ . Provided  $\varepsilon$  and  $\sigma$  are known, the mean vibrational frequency can then be calculated from the density for use in eqn. (4).

The number of molecules per unit area of the reference plane  $n$  is determined by the geometry of the lattice and the number of holes and is

$$n = \frac{1}{a^2} \left( 1 - \frac{n_h}{N} \right). \quad (13)$$

In addition  $l$  the distance between planes is  $a\sqrt{2}/2$ . As  $du/dT$  is  $C_v$  this can be calculated, excluding internal contributions, by using the theory of Lennard-Jones and Devonshire<sup>6</sup> or alternatively taken in the first approximation as  $3k$  (assuming six vibrational degrees of freedom).

The vibrational contribution to the thermal conductivity can therefore be written finally as

$$\lambda_{\text{vib.}} = P \left[ \frac{\varepsilon}{\pi^2 r_0^2 m} \left\{ 11C_{14} \left( \frac{r_0}{a} \right)^{14} - 5C_8 \left( \frac{r_0}{a} \right)^8 \right\} \right]^{\frac{1}{2}} C_v \sqrt{2(1 - n_h/N)/a}, \quad (14)$$

where  $C_v$  is the specific heat per molecule.

#### (b) THE CONVECTIVE CONTRIBUTION

According to the convective mechanism the frequency of convective movement  $k$  in the liquid is the same as that which is operative in self-diffusion at the same temperature. This frequency is given by eqn. (6) where for a liquid composed of spherically symmetric molecules interacting according to eqn. (11),

$$\nu_f = 2\pi\sqrt{2GV/N}. \quad (15)$$

$G$  is a tabulated function <sup>7</sup> of  $kT/\varepsilon$  and  $V/V_0$ , where  $V_0 = N\sigma^3$ . The activation energy  $e_0$  is given by \*

$$e_0 = \frac{\Phi_0 \omega}{N} \approx z\varepsilon \left\{ 1.2045 \left( \frac{V_0}{V} \right)^2 - 0.5055 \left( \frac{V_0}{V} \right)^4 \right\} / 3, \quad (16)$$

where  $\Phi_0$  is the lattice energy of the liquid and  $z$  is the co-ordination number. In the previous theory it was shown that at present no adequate expression exists for determining the number of holes in the liquid and in the frequency factor  $k$  this was taken care of by using an approximate expression and then fixing  $\omega$  in eqn. (16) with reference to the experimental data for argon.  $\omega$  was found to be a third in the first approximation so that the factor  $z/3$  can be replaced by 4 for a f.c.c. lattice. The final expression for the convective contribution given by eqn. (8) is therefore

$$\lambda_{\text{conv.}} = \frac{n_h}{N} \left( \frac{kT}{2\pi m} \right)^{\frac{1}{2}} \frac{C_v}{v_f^{\frac{1}{2}}} \frac{\sqrt{2}}{a} (1 - n_h/N) \exp(-e_0/kT). \quad (17)$$

#### COMPARISON OF THEORY WITH EXPERIMENT

In the application of eqn. (14) and (17) to the liquid state, comparison of the relative magnitude of the respective contributions is of interest.

For the convective contribution the frequency of movement  $k$  is the same as that operative in self-diffusion and this term would be expected to become important only in the critical region. In the present theory the values of  $k$  calculated using the molar volumes and force constants  $\varepsilon/k$  and  $\sigma$  for argon, nitrogen, carbon monoxide, methane, benzene and carbon tetrachloride listed in ref. (1) are the same as those which give satisfactory calculated values of the self-diffusion coefficient. Using these values and neglecting the contribution of the internal degrees of freedom by assuming  $C_v$  as  $3k$  per molecule, the convective contribution to the thermal conductivity from eqn. (17) turns out to be small. For argon at its boiling point at atmospheric pressure  $\lambda_{\text{conv.}} = 54 \text{ erg cm}^{-1} \text{ sec}^{-1} \text{ deg.}^{-1}$ .

To calculate the vibrational contribution it can be assumed that the vibrational frequency is unaffected by holes and that

$$(1 - n_h/N) \approx 1$$

as  $n_h/N$  is in reality small. In addition,  $C_v$  can be taken as  $3k$  per molecule and in the absence of particular knowledge of  $P$  it can be set equal to unity. For argon at its boiling point,  $\lambda_{\text{vib.}}$  is then given by (14) as  $9.28 \times 10^3 \text{ erg cm}^{-1} \text{ sec}^{-1} \text{ deg.}^{-1}$ . This indicates that for simple liquids up to their boiling points the thermal conductivity arises almost entirely from the vibrational contribution and that the convective contributions can be neglected, i.e.,

$$\lambda = \lambda_{\text{vib.}} + \lambda_{\text{conv.}} \approx \lambda_{\text{vib.}}$$

Table 1 gives values of the calculated (vibrational) and experimental thermal conductivities of the series of molecules listed above, over a range of temperature for which calculations of the other transport coefficients have been made. Included in this table are values obtained from the Bridgman equation,<sup>8</sup>

$$\lambda = 3ku_e \left( \frac{N}{V} \right)^{\frac{1}{3}}, \quad (18)$$

where  $u_e$  is the velocity of sound in the liquid. On this model the energy difference between successive layers of molecules in the liquid is considered to be passed on with

\* In ref. (1), eqn. (24) should read as (16) above, the first exponential in eqn. (23) should be positive and eqn. (29) should be divided by  $N^{\frac{1}{2}}$ .

the velocity of sound. The sonic data for argon nitrogen and methane were taken from van Itterbeek <sup>9</sup> *et al.* and for carbon tetrachloride and benzene from Lagemann, McMillan and Woolf.<sup>10</sup> No data could be found for carbon monoxide.

TABLE 1.—COMPARISON OF THEORETICAL AND EXPERIMENTAL RESULTS

| liquid               | temp., °K | $\lambda \times 10^{-3}$ erg cm <sup>-1</sup> sec <sup>-1</sup> deg. <sup>-1</sup> |         |          | $u_e$ m. sec <sup>-1</sup> |
|----------------------|-----------|------------------------------------------------------------------------------------|---------|----------|----------------------------|
|                      |           | expt.                                                                              | present | Bridgman |                            |
| argon                | 84.2      | 12.60                                                                              | 9.92    | 27.77    | 872.4                      |
|                      | 87.3      | 12.16                                                                              | 9.28    | 26.71    | 847.6                      |
| nitrogen             | 69.1      | 15.11                                                                              | 10.28   | 27.33    | 953.5                      |
|                      | 71.4      | 14.80                                                                              | 9.77    | 26.40    | 928.5                      |
|                      | 77.3      | 13.96                                                                              | 8.49    | 23.94    | 860.7                      |
| carbon monoxide      | 72.0      | 15.89                                                                              | 7.70    |          |                            |
|                      | 77.7      | 15.05                                                                              | 6.59    |          |                            |
|                      | 80.8      | 14.21                                                                              | 5.96    |          |                            |
| methane              | 93.2      | 21.53                                                                              | 17.24   | 42.50    | 1558                       |
|                      | 103.2     | 20.27                                                                              | 15.27   | 39.68    | 1483                       |
|                      | 108.2     | 19.64                                                                              | 14.36   | 38.77    | 1463                       |
| benzene              | 288.2     | 14.94                                                                              | 12.26   | 20.11    | 1350                       |
|                      | 298.2     | 14.63                                                                              | 11.71   | 19.26    | 1303                       |
|                      | 308.2     | 14.24                                                                              | 11.24   | 18.43    | 1257                       |
|                      | 318.2     | 13.89                                                                              | 10.78   | 17.56    | 1209                       |
| carbon tetrachloride | 298.2     | 10.64                                                                              | 10.18   | 12.90    | 922.4                      |
|                      | 308.2     | 10.51                                                                              | 9.77    | 12.37    | 891.5                      |
|                      | 318.2     | 10.39                                                                              | 9.42    | 11.85    | 860.7                      |

References for experimental thermal conductivities A, 11; N<sub>2</sub>, 12; CO, 13; CH<sub>4</sub>, 13; C<sub>6</sub>H<sub>6</sub>, 14; CCl<sub>4</sub>, 15.

It is seen from table 1 that calculated values of  $\lambda$  agree on average within 20 % of experimental values compared with values from Bridgman's formula which are within about 35 %. However, some of the velocity of sound data are at pressures slightly less than atmospheric pressure. In addition the present theory gives the correct temperature dependence of thermal conductivity.

#### THE RATIO $m\lambda/k\eta$

According to the model of Longuet-Higgins and Pople<sup>16</sup> the ratio  $m\lambda/k\eta$ , where  $\eta$  is the coefficient of viscosity, should be 5/2 and independent of temperature. On the basis of Enskog's<sup>17</sup> theory this ratio is 3.75 independent of temperature if the ratio of the quadratic terms is taken as unity. Fig. 1 shows a plot of experimental and theoretical values for these theories and the present work as a function of  $T/T_c$ , where  $T_c$  is the critical temperature. It is seen that the theory of Longuet-Higgins and Pople gives about the correct average value of the ratio  $m\lambda/k\eta$  but does not give the correct temperature dependence. This may arise because it is assumed that both momentum and energy are transferred by the same mechanism and have both the same temperature dependence.

On the present theory where viscosities have been calculated according to approximation 2 of ref. (1), the theoretical and experimental curves for each individual substance are approximately parallel giving the correct temperature dependence. The ratio is, however, in general lower at an average value of about 1.5. In this second approximation for calculating the coefficient of viscosity  $\eta$  from the frequency of molecular hopping (eqn. (6)) the constant co-ordination number  $z$  in the activation energy  $e_0$  (eqn. (16)) is replaced by one which varies with temperature.

The present model therefore suggests that for liquids, as distinct from condensed gases, the mechanism of momentum transfer may be mainly convective and the mechanism of heat transfer vibrational.

## THE THERMAL CONDUCTIVITY OF SOLIDS

As the model for the liquid state proposed is quasi-crystalline it might be expected that the theory could be applied to solids of materials like the inert gases. Few data are at present available except for argon. At 77°K at an unspecified pressure Uhler gives a value for the thermal conductivity of solid argon of  $17.56 \times 10^3 \text{ erg cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$  and Ziebland and Burton<sup>18</sup> a value of  $17.85 \times 10^3 \text{ erg cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$  at 83.6°K and 120 atm. Calculated values on the present theory assuming only vibrational contributions are  $16.77 \times 10^3$  and  $16.45 \times 10^3 \text{ erg cm}^{-1} \text{ sec}^{-1} \text{ deg}^{-1}$  respectively. The theory thus predicts about the correct increase in  $\lambda$  on passing to the solid state. The only data at lower temperatures are those of White and Woods<sup>19</sup> which according to Dobbs and Jones<sup>20</sup> extrapolated to the melting point give solid argon about three times the thermal conductivity of liquid argon whereas the data quoted above give an increase by a factor of about  $1\frac{1}{2}$ .

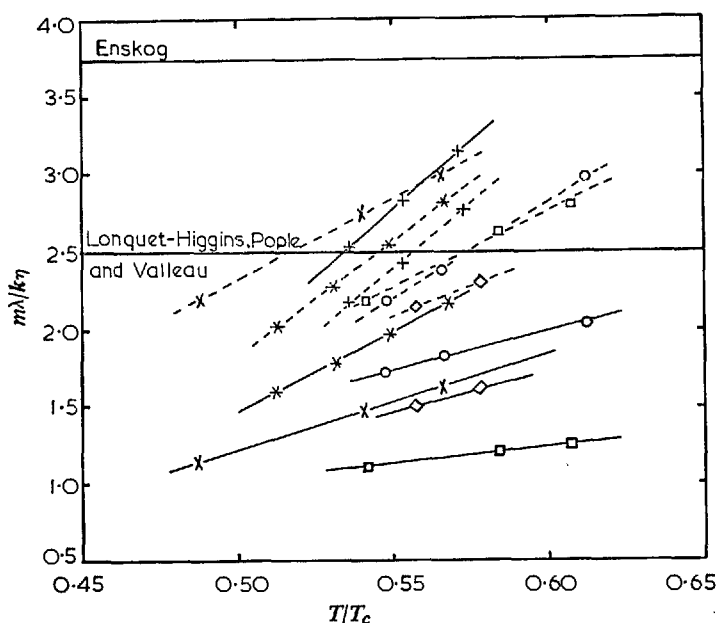


FIG. 1.—The ratio  $m\lambda/k\eta$  as a function of  $T/T_c$ . The dash lines indicate experimental results and the full lines theoretical values for argon  $\diamond$ , nitrogen  $\circ$ , methane  $\times$ , benzene  $*$ , carbon monoxide  $\square$  and carbon tetrachloride  $+$ .

Examination of eqn. (14) shows that because  $a$  tends to a constant as  $T$  tends to zero the controlling term in  $\lambda$  is  $C_v$ . This makes the coefficient of thermal conductivity tend to zero approximately as  $T^3$  simply as a consequence of the third law of thermodynamics and the Debye theory of specific heats. In the intermediate range  $\lambda$  as a function of  $T$  passes through a broad maximum. However, the experimental data of White and Woods from 2 to 25°K differ markedly from the present theory. Reasons for these departures at lower temperatures can be found in the phonon theory of thermal conductivity of solids.<sup>21</sup> This theory shows that at temperatures high compared with  $\Theta$ , anharmonicity accounts for most of the thermal resistance as in the present case. However, as the temperature is lowered, a thermal resistance due to Umklapp processes which dies away as  $\exp(-\Theta/2T)$  causes the thermal conductivity to rise exponentially. In addition, while the above calculations are referred to an infinite crystal it is known that, at the lowest temperatures,

phonon scattering at the crystal boundaries introduces a size effect which controls the thermal conductivity, the measured thermal conductivity being dependent on the grain size.

Thanks are due to Prof. A. R. Ubbelohde, F.R.S. and Prof. H. C. Longuet-Higgins, F.R.S., for helpful comments on this work. One of us (J. K. H.) wishes to thank the National Coal Board for a grant.

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## Transport Properties of Binary Regular Solutions

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Received 6th November, 1961

From the theoretical expressions for the transport properties of binary regular solutions, as developed by Bearman, the complete set of relationships between the different transport coefficients is given. The resulting equations are then tested with available experimental results on the viscosity, thermal conductivity and diffusion coefficients of various mixtures, together with new viscosity and thermal conductivity data on the ethyl iodide + n-butyl iodide system.

In general, for simple mixtures, the behaviour of the viscosity and diffusion coefficients conforms better with theoretical predictions than thermal conductivity. For ethyl iodide + n-butyl iodide mixtures, calculated self-diffusion and viscosity coefficients agree with experimental data within about 2 % in contrast with the thermal conductivity where deviations up to 50 % occur. The calculated values of the mutual diffusion coefficient of the system carbon tetrachloride + cyclohexane agree with experiment within  $\frac{1}{2}$  %, on average, over the complete composition range.

In a recent series of papers<sup>1</sup> the theory, initially proposed by Bearman and Kirkwood,<sup>2</sup> has been developed for the transport properties of mixtures. For viscosity and thermal conductivity the resulting expressions reduce, in the limit, to the equations of Kirkwood, Buff and Green<sup>3</sup> and Irving and Kirkwood<sup>4</sup> for a pure substance.

The equations are complex, but undergo considerable reduction for binary regular solutions with spherically symmetric force fields, where<sup>20</sup> the radial distribution function is independent of composition and no volume change on mixing occurs. Under these conditions the following relationships were derived.

### (i) DIFFUSION

$$D_1/D_2 = v_2/v_1, \quad (1)$$

$$\lim_{c_1 \rightarrow 0} D = D_1^\infty,$$

$$\lim_{c_1 \rightarrow 0} D = D_2^\infty, \quad (2)$$

$$D = D_1[\partial \ln a_1 / \partial \ln c_1]. \quad (3)$$

### (ii) VISCOSITY

$$\frac{x_1}{x_2} v_1^2 [D_1 \eta - D_1^\infty \eta_1] + 2v_1 v_2 D_1 \eta + \frac{x_2}{x_1} v_2^2 [D_1 \eta - D_1^\infty \eta_2] = A_{12}. \quad (4)$$

### (iii) THERMAL CONDUCTIVITY

$$\frac{x_1}{x_2} v_1^2 \left[ \frac{\lambda}{D_1} - \frac{\lambda_1}{D_1^\infty} \right] + 2v_1 v_2 \frac{\lambda}{D_1} + \frac{x_2}{x_1} v_2^2 \left[ \frac{\lambda}{D_1} - \frac{\lambda_2}{D_1^\infty} \right] = B_{12}. \quad (5)$$

$D_1$  and  $D_2$  are respectively the coefficients of self-diffusion of species 1 and 2 in the mixture,  $D$  the mutual diffusion coefficient,  $v_1$  and  $v_2$  the molecular volumes,  $v$  the mean molecular volume, and  $a_1$  and  $c_1$  the activity and concentration (molecules

per unit volume) of species 1.  $D_1^\infty$  and  $D_2^\infty$  are the coefficients of self-diffusion of species 1 and 2 at infinite dilution, and  $D_1^\circ$  and  $D_2^\circ$  the self-diffusion coefficients in the pure state. The viscosities and thermal conductivities of mixtures of species 1 and 2 are  $\eta$  and  $\lambda$  respectively, with coefficients in the pure state of  $\eta_1$ ,  $\eta_2$ ,  $\lambda_1$  and  $\lambda_2$ . At a fixed temperature and pressure,  $A_{12}$  and  $B_{12}$  are constants independent of the mole fraction  $x_i$ .

Eqn. (1) shows that  $D_1/D_2$  is a constant and in addition Bearman has shown from eqn. (4) and (5) that  $D_1\eta$  and  $\lambda\eta$  are also constants. The values of the last two constants and the complete set of relationships between the transport coefficients may be derived as follows.

Eqn. (4) and (5) can be arranged in the form

$$v^2 = x_1^2 v_1^2 \frac{\eta_1 D_1^\circ}{\eta D_1} + x_1 x_2 \frac{A_{12}}{\eta D_1} + x_2^2 v_2^2 \frac{\eta_2 D_1^\circ}{\eta D_1}, \quad (6)$$

$$v^2 = x_1^2 v_1^2 \frac{\lambda_1 D_1}{\lambda D_1^\circ} + x_1 x_2 \frac{B_{12} D_1}{\lambda} + x_2^2 v_2^2 \frac{\lambda_2 D_1}{\lambda D_1^\circ}, \quad (7)$$

as  $v$  is defined by  $v = x_1 v_1 + x_2 v_2$ . Expanding eqn. (6) in the variable  $x_1$  yields

$$\begin{aligned} x_1^2 [v_1^2 - 2v_1 v_2 + v_2^2] + x_1 [2v_1 v_2 - 2v_2^2] + [v_2^2] = \frac{1}{\eta D_1} [x_1^2 \{\eta_1 v_1^2 D_1^\circ + A_{12} + \eta_2 v_2^2 D_1^\circ\} + \\ x_1 \{A_{12} - 2\eta_2 v_2^2 D_1^\circ\} + \{\eta_2 v_2^2 D_1^\circ\}] \end{aligned} \quad (8)$$

As this equation holds for all  $x_1$ , it is seen that  $\eta D_1$  is constant, therefore equating coefficients of the powers of  $x_1$  gives

$$\eta D_1 = \eta_1 D_1^\circ = \eta_2 D_1^\circ. \quad (9)$$

Similarly, from eqn. (7),  $\lambda/D_1$  is a constant given by

$$\lambda/D_1 = \lambda_1/D_1^\circ = \lambda_2/D_1^\circ, \quad (10)$$

hence

$$\lambda\eta = \lambda_1\eta_1 = \lambda_2\eta_2. \quad (11)$$

In addition expressions (9) and (10) must also be true when the species numbers are interchanged so that

$$\eta D_2 = \eta_2 D_2^\circ = \eta_1 D_2^\circ, \quad (12)$$

and

$$\lambda/D_2 = \lambda_2/D_2^\circ = \lambda_1/D_2^\circ, \quad (13)$$

hence

$$D_1/D_2 = D_1^\circ/D_2^\circ = D_1^\circ/D_2^\circ, \quad (14)$$

and

$$A_{12} = 2v_1 v_2 D_1^\circ \eta_2 = 2v_1 v_2 D_1^\circ \eta_1, \quad (15)$$

$$B_{12} = 2v_1 v_2 \lambda_2/D_1^\circ = 2v_1 v_2 \lambda_1/D_1^\circ. \quad (16)$$

The set of equations (9) to (14) which contains the various possible relationships between the transport coefficients are implicit in Bearman's papers and can be checked directly by comparison with experimental data.

## EXPERIMENTAL

There is no simple binary mixture for which all the necessary transport and thermodynamic data are available to test the equations of the previous section. Carman and

Stein<sup>5</sup> have, however, recently measured the self-diffusion coefficients for the system ethyl iodide+n-butyl iodide at 19.35°C, and these measurements have been supplemented with the necessary viscosity and thermal conductivity data.

Ethyl iodide and n-butyl iodide (Hopkin and Williams) were treated<sup>6</sup> carefully with sodium to remove free hydrogen iodide and water. They were then fractionated in a column containing copper turnings at the top and stored in the dark over calcium in an atmosphere of oxygen-free nitrogen. Fractionation was repeated before each mixture was made up. Properties of the purified materials were ethyl iodide  $n_{25}^D$  1.5104, b.p.  $72.6 \pm 0.2^\circ\text{C}$  at 770 mm; n-butyl iodide  $n_{25}^D$  1.4967, b.p.  $130.8 \pm 0.2^\circ\text{C}$  at 770 mm. Viscosities at 19.35°C were determined relative to water in the apparatus previously described.<sup>7</sup> With this technique it is not necessary to know the density accurately. Carman and Stein also measured the viscosities of this system using an Ostwald-type viscometer, but assumed there was no volume change on mixing to calculate the density. This assumption is sufficient to mask the non-linear dependence of viscosity on composition. Results are given in table 1.

Thermal conductivities were determined using a non-steady state method, details of which are in course of publication.

TABLE 1.—EXPERIMENTAL VISCOSITY AND THERMAL CONDUCTIVITY DATA OF MIXTURES OF ETHYL IODIDE (1) AND n-BUTYL IODIDE AT 19.35°C

| mole fraction<br>$x_1$ | Viscosity $\eta \times 10^3$<br>poise | mole fraction<br>$x_1$ | thermal conductivity $\lambda \times 10^{-3}$<br>erg cm <sup>-1</sup> sec <sup>-1</sup> deg. <sup>-1</sup> |
|------------------------|---------------------------------------|------------------------|------------------------------------------------------------------------------------------------------------|
| 0.000                  | 8.82                                  | 0.000                  | 8.90                                                                                                       |
| 0.212                  | 8.21                                  | 0.183                  | 8.80                                                                                                       |
| 0.397                  | 7.74                                  | 0.336                  | 8.75                                                                                                       |
| 0.589                  | 7.12                                  | 0.589                  | 8.60                                                                                                       |
| 0.628                  | 7.04                                  | 0.835                  | 8.58                                                                                                       |
| 0.796                  | 6.55                                  | 1.000                  | 8.57                                                                                                       |
| 1.000                  | 5.89                                  |                        |                                                                                                            |

## DISCUSSION

To obtain some indication of the general validity of eqn. (9)-(14), it is only necessary to check the experimental values of the ratios  $D_1^\infty/D_1^\circ$ ,  $D_2^\infty/D_2^\circ$ ,  $\eta_1/\eta_2$  and  $\lambda_2/\lambda_1$  which should, according to the theory, all be equal. Table 2 gives the transport coefficients and their ratios for various binary systems at 25°C, and table 3 the coefficients in the pure state at the same temperature.

TABLE 2.—VALUES OF THE TRANSPORT COEFFICIENTS AND THEIR RATIOS FOR VARIOUS BINARY SYSTEMS AT 25°C

| SYSTEM               |                  | $D_1^\infty \times 10^5$          | $D_2^\infty \times 10^5$ | ref. | $D_1^\infty/D_1^\circ$ | $D_2^\infty/D_2^\circ$ | $\eta_1/\eta_2$ | $\lambda_2/\lambda_1$ |
|----------------------|------------------|-----------------------------------|--------------------------|------|------------------------|------------------------|-----------------|-----------------------|
| species 1            | species 2        | cm <sup>2</sup> sec <sup>-1</sup> |                          |      |                        |                        |                 |                       |
| carbon tetrachloride | cyclohexane      | 1.486                             | 1.265                    | 8    | 1.05                   | 1.09                   | 1.00            | 1.17                  |
| carbon tetrachloride | benzene          | 1.922                             | 1.408                    | 15   | 1.36                   | 1.53                   | 1.51            | 1.38                  |
| ethyl iodide         | n-butyl iodide * | 1.482                             | 2.062                    | 5    | 0.67                   | 0.66                   | 0.67            | 1.04                  |

\* temp. (19.35°C)

It is seen from table 2 that, for the first two simple systems, agreement of the ratios is within about 5 %, on average, while for the third system the thermal conductivity ratio differs by about 50 % from the other three ratios which are almost identical.

Following this initial comparison it is necessary to examine the variation of the transport expressions over the whole mole fraction range.

#### VISCOSITY OF A BINARY MIXTURE

By eqn. (9) and (12) the viscosity of a binary mixture is

$$\eta = \eta_1 D_1^\circ / D_1 = \eta_2 D_1^\circ / D_1 = \eta_2 D_2^\circ / D_2 = \eta_1 D_2^\circ / D_2. \quad (17)$$

Tables 2 and 3 show that  $\eta_1 D_1^\circ = \eta_2 D_1^\circ$  and  $\eta_2 D_2^\circ = \eta_1 D_2^\circ$ , as predicted, with values  $13.07 \pm 0.05$  and  $12.11 \pm 0.08$  respectively, so that, using the known experimental values of  $D_1$  and  $D_2$ , the viscosities of the mixtures can be calculated. These are compared in table 4 with experimental values and agree within 2 %. It follows, therefore, that  $D_1 \eta$  and  $D_2 \eta$  are constant, to 2 %, as predicted by theory.

TABLE 3.—TRANSPORT COEFFICIENTS OF PURE COMPONENTS AT 25°C

| substance            | $\eta_i \times 10^3$<br>poise | ref. | $\lambda_i \times 10^3$<br>erg/cm <sup>2</sup> sec <sup>-1</sup> deg. <sup>-1</sup> | ref. | $D_i^\circ \times 10^4$<br>cm <sup>2</sup> sec <sup>-1</sup> | ref. |
|----------------------|-------------------------------|------|-------------------------------------------------------------------------------------|------|--------------------------------------------------------------|------|
| carbon tetrachloride | 9.04                          | 8    | 10.64                                                                               | 13   | 1.41                                                         | 10   |
| benzene              | 6.00                          | 9    | 14.63                                                                               | 14   | 2.15                                                         | 11   |
| cyclohexane          | 9.00                          | 8    | 12.47 (20°)                                                                         | 14   | 1.38                                                         | 12   |
| ethyl iodide *       | 5.91 †                        |      | 8.58 †                                                                              |      | 2.22                                                         | 5    |
| n-butyl iodide *     | 8.78 †                        |      | 8.91 †                                                                              |      | 1.37                                                         | 5    |

\* temp. (19–35°C). † end-values of quadratic curve fitted to experimental results in table 1.

According to eqn. (11), it is also possible to calculate the viscosity of a mixture from the thermal conductivity if the viscosity and thermal conductivity of either pure component is known. The lack of agreement, which results for the ethyl iodide + n-butyl iodide system, is reflected in the inverse calculations of the thermal conductivities given below.

#### THERMAL CONDUCTIVITY OF A BINARY MIXTURE

The thermal conductivity may be obtained from eqn. (10), (11) or (13), using either diffusion or viscosity data. Table 4 compares experimental thermal conductivities with values calculated from eqn. (11). It is seen that discrepancies of up to 50 % occur.

While Bearman has shown, for the system benzene + carbon tetrachloride, that  $\eta \lambda$  is constant within about 2 % over the mole fraction range, examination of the viscosities and thermal conductivities of a series of closely related simple molecules<sup>16</sup> shows that  $\eta \lambda$  for the pure state, at a fixed temperature, is not constant.

It has, however, recently been pointed out by Bearman (private communication) that for the theory to hold, an additional restriction not previously stated is implied. This is, that the ratio of the thermal expansion and isothermal compressibility coefficients be independent of composition. No data are available to check this for the present system.

#### THE SELF-DIFFUSION COEFFICIENTS OF A BINARY MIXTURE

Inverting the calculations yields the self-diffusion coefficients for binary mixtures. From table 4, however, it is seen that the use of experimental viscosities gives agreement within 2 % whereas the use of thermal conductivities gives errors of up to 50 %.

TABLE 4.—COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF THE TRANSPORT COEFFICIENTS FOR THE SYSTEM ETHYL IODIDE (1)+n-BUTYL IODIDE (2) AT 19.35°C

| $x_1$ | $\eta$ (exp) | $\eta$ (calc.)                           | $\eta$ (calc.)                                           | $D_1$ (exp)t                                | $D_2$ (expt.) | $\lambda$ (expt.)                                                       | $\lambda$ (calc.)                         |
|-------|--------------|------------------------------------------|----------------------------------------------------------|---------------------------------------------|---------------|-------------------------------------------------------------------------|-------------------------------------------|
|       |              | $\eta_1 D_1^\infty + \eta_2 D_1^\infty$  | $\eta_1 D_2^\infty + \eta_2 D_2^\infty$                  |                                             |               |                                                                         | $\lambda = \frac{\lambda_1 \eta_1}{\eta}$ |
|       |              | $\frac{2D_1}{\times 10^3 \text{ poise}}$ | $\frac{2D_2}{\times 10^5 \text{ cm}^2 \text{ sec}^{-1}}$ | $\times 10^5 \text{ cm}^2 \text{ sec}^{-1}$ |               | $\times 10^{-3} \text{ erg cm}^{-1} \text{ sec}^{-1} \text{ deg.}^{-1}$ |                                           |
| 0     | 8.78         | 8.84                                     | 8.84                                                     | 1.48                                        | 1.37          | 8.91                                                                    | 5.78                                      |
| 0.1   | 8.52         | 8.43                                     | 8.65                                                     | 1.55                                        | 1.40          | 8.85                                                                    | 5.95                                      |
| 0.2   | 8.25         | 8.07                                     | 8.35                                                     | 1.62                                        | 1.45          | 8.79                                                                    | 6.15                                      |
| 0.3   | 7.98         | 7.73                                     | 8.07                                                     | 1.69                                        | 1.50          | 8.74                                                                    | 6.35                                      |
| 0.4   | 7.70         | 7.43                                     | 7.76                                                     | 1.76                                        | 1.56          | 8.70                                                                    | 6.59                                      |
| 0.5   | 7.42         | 7.14                                     | 7.47                                                     | 1.83                                        | 1.62          | 8.66                                                                    | 6.83                                      |
| 0.6   | 7.13         | 6.84                                     | 7.12                                                     | 1.91                                        | 1.70          | 8.63                                                                    | 7.11                                      |
| 0.7   | 6.83         | 6.60                                     | 6.80                                                     | 1.98                                        | 1.78          | 8.61                                                                    | 7.42                                      |
| 0.8   | 6.53         | 6.34                                     | 6.51                                                     | 2.06                                        | 1.86          | 8.59                                                                    | 7.77                                      |
| 0.9   | 6.23         | 6.11                                     | 6.18                                                     | 2.14                                        | 1.96          | 8.58                                                                    | 8.14                                      |
| 1.0   | 5.91         | 5.89                                     | 5.88                                                     | 2.22                                        | 2.06          | 8.58                                                                    | 8.58                                      |

## THE MUTUAL DIFFUSION COEFFICIENT

The expression for the mutual diffusion coefficient in terms of the self-diffusion coefficients in the mixture  $D_1$  and  $D_2$  can be derived as follows. As  $c_1 = x_1/(x_1v_1 + x_2v_2)$ , no volume change on mixing being assumed, then

$$\frac{\partial \ln a_1}{\partial \ln c_1} = \frac{\partial \ln a_1}{\partial \ln x_1} \left( \frac{x_1 v_1 + x_2 v_2}{v_2} \right). \quad (18)$$

Substituting eqn. (18) in eqn. (3) gives

$$D = \left( \frac{\partial \ln a_1}{\partial \ln x_1} \right) \left[ D_1 \left\{ x_1 \frac{v_1}{v_2} + x_2 \right\} \right] \quad (19)$$

$$= \left( \frac{\partial \ln a_1}{\partial \ln x_1} \right) [x_1 D_2 + x_2 D_1] \quad (20)$$

after using eqn. (1). Eqn. (20) formally resembles that previously proposed by Hartley and Crank<sup>17</sup> and this similarity has been discussed by Bearman.<sup>18</sup>

For the purpose of calculating the mutual diffusion coefficient in terms of more readily available experimental data, it is better to use eqn. (19) after substituting for  $D_1$  in terms of either viscosities or thermal conductivities using eqn. (9), (10), (12) or (13). For example, in terms of viscosities, the resulting expressions are

$$D = \frac{\eta_1 D_1^\infty}{\eta} \left( \frac{\partial \ln a_1}{\partial \ln x_1} \right) \left[ x_1 \frac{v_1}{v_2} + x_2 \right], \quad (21)$$

$$D = \frac{\eta_2 D_1^\infty}{\eta} \left( \frac{\partial \ln a_1}{\partial \ln x_1} \right) \left[ x_1 \frac{v_1}{v_2} + x_2 \right]. \quad (22)$$

Eqn. (22) involves the use of  $D_1^\infty$  rather than  $D_1^\circ$  and hence makes  $D$  exact initially.

No mutual diffusion results are available for the system ethyl iodide + n-butyl iodide for comparison, but all the necessary data are available for the carbon tetrachloride + cyclohexane system. These data show<sup>8</sup> that a plot of  $D\eta/(\partial \ln a_1/\partial \ln x_1)$  is not linear in  $x_1$ , as predicted by the present theory. This can be seen by rearranging eqn. (22) in the form

$$D\eta / \left( \frac{\partial \ln a_1}{\partial \ln x_1} \right) = D_1^\infty \eta_2 \left[ x_1 \frac{v_1}{v_2} + x_2 \right]. \quad (23)$$

As the system does exhibit a volume change on mixing, an alternative assumption has been made, viz., that in such a case, the theory is unaltered except for the replacement of molecular volumes by partial molecular volumes  $\bar{v}_1$  and  $\bar{v}_2$ . The values are given in table 5,  $D$  (calc.) (I). In addition, values of  $D$  calculated assuming no volume change on mixing are given for comparison  $D$  (calc.) (II). The  $D_1^\infty$ ,  $\eta$  and  $(\partial \ln a_1 / \partial \ln x_1)$  data are given by Hammond and Stokes.<sup>8</sup> Partial molar volumes were calculated from the specific excess volumes of Barker and Brown.<sup>19</sup>

Agreement between the experimental and calculated values, assuming the volume change on mixing modification, is on average within  $\frac{1}{2}\%$ . This is consistently better than the values calculated assuming no volume change on mixing. The improvement which is small may be more significant in systems where larger volume changes occur.

TABLE 5.—COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF THE MUTUAL DIFFUSION COEFFICIENT FOR THE SYSTEM CARBON TETRACHLORIDE+CYCLOHEXANE AT 25°C

| $x_1$<br>mole<br>fract. CCl <sub>4</sub> | $\eta_2 D_1^\infty$<br>$\eta$ | $\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)$ | $\left[x_1 \frac{\bar{v}_1}{\bar{v}_2} + x_2\right]$ | $D$ calc. (I) | $D$ expt.<br>$\times 10^5 \text{ cm}^2 \text{ sec}^{-1}$ | $D$ calc. (II) |
|------------------------------------------|-------------------------------|----------------------------------------------------------|------------------------------------------------------|---------------|----------------------------------------------------------|----------------|
| 0                                        | 1.486                         | 1                                                        | 1                                                    | 1.486         | 1.486                                                    | 1.486          |
| 0.1                                      | 1.516                         | 0.982                                                    | 0.9897                                               | 1.473         | 1.474                                                    | 1.473          |
| 0.2                                      | 1.539                         | 0.967                                                    | 0.9792                                               | 1.457         | 1.460                                                    | 1.456          |
| 0.3                                      | 1.549                         | 0.956                                                    | 0.9686                                               | 1.434         | 1.444                                                    | 1.433          |
| 0.4                                      | 1.558                         | 0.948                                                    | 0.9577                                               | 1.415         | 1.426                                                    | 1.413          |
| 0.5                                      | 1.562                         | 0.944                                                    | 0.9447                                               | 1.393         | 1.405                                                    | 1.395          |
| 0.6                                      | 1.555                         | 0.944                                                    | 0.9353                                               | 1.373         | 1.382                                                    | 1.373          |
| 0.7                                      | 1.547                         | 0.950                                                    | 0.9238                                               | 1.358         | 1.357                                                    | 1.360          |
| 0.8                                      | 1.535                         | 0.960                                                    | 0.9121                                               | 1.344         | 1.329                                                    | 1.348          |
| 0.9                                      | 1.509                         | 0.977                                                    | 0.9002                                               | 1.327         | 1.298                                                    | 1.332          |
| 1.0                                      | 1.479                         | 1                                                        | 0.8883                                               | 1.314         | 1.265                                                    | 1.321          |

Finally, it may be said that while the predictions of the theory, with the exception of thermal conductivity, are encouraging, further experimental results on self-diffusion coefficients in simple binary mixtures are necessary for more comprehensive tests of the theory.

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<sup>18</sup> Bearman, *J. Physic. Chem.*, 1961, **65**, 1961.

<sup>19</sup> Barker and Brown, *Austral. J. Sci. Res. A*, 1950, **3**, 306.

<sup>20</sup> Hildebrand and Scott, *The Solubility of Non-Electrolytes* (Reinhold Publishing Corp., New York, 1950).