A STUDY OF THERMAL CONDUCTIVITY
AND VELOCITY OF SOUNDS IN LIQUIDS

by

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ABSTRACT

The theories of thermal conductivity of gases, solids and liquids are reviewed. Equations which relate the thermal conductivity of liquids to velocity of sound in that medium are discussed in detail.

A simple and accurate method of determining the velocity of sound in liquids is presented. The velocity of sound was measured in five organic liquids covering a temperature range of 40 °C to 140 °C with an estimated accuracy of ± 0.5 per cent. These data, some of which have not been previously reported, were used, in conjunction with the most reliable values of the thermal conductivity for the specific liquids, to study the theoretical equation developed by P. W. Bridgman for predicting the thermal conductivity of liquids. A modification of the equation, which considerably improves the agreement between the calculated and experimental values, is proposed.

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NOMENCLATURE

C_v - molar heat capacity at constant volume

c - velocity of sound

c_p - specific heat at constant pressure

c_v - specific heat at constant volume

f - frequency of the sound wave

K - Boltzman constant

k - thermal conductivity

L - distance between adjacent molecular surfaces

L_d - acoustic path length of the delay line

L_w - acoustic path length of the interferometer

l - mean free path of the molecules

M - molecular weight

N - Avogadro number

n - pure number related to energy

Q - energy per mole

q - energy transfer per unit time per unit area

q' - energy drop per molecule along a row of molecules

R - universal gas constant

R' - Rao constant or molecular sound velocity

T - temperature or absolute temperature

T_{abs} - absolute temperature

T_c - critical temperature

t - time flight of sound pulse in the delay line

t_w - time flight of sound pulse in the interferometer

u - mean molecular velocity of gas

V - velocity of sound in liquids

$V_{m,g}$ - mean molecular velocity of ideal gas

$V_{s,g}$ - velocity of sound in ideal gas

$V_{s,l}$ - velocity of sound in liquids

V_w - velocity of sound in water

v - molar volume

v_f - free volume

w - velocity of propagation of elastic wave

Greek Symbols

β_s - adiabatic compressibility

β_t - isothermal compressibility

γ - ratio of specific heat at constant pressure to that at constant volume

ΔS - entropy of vaporization at normal boiling point

δ - mean distance of separation of centers of molecules under the assumption that the molecules of liquid are in cubical array

ε - multiplying factor that varies with temperature

ϵ - numerical parameter

λ - average distance of effect of the thermoelastic wave, or the distance which wave travels before its intensity is reduced to 1/e of its initial value

λ' - wavelength of the sound wave

μ - viscosity

ρ - density

ϕ - parameter which depend upon the structural or position contribution of the molecules

I. INTRODUCTION

The thermal conductivity of liquids is an important physical property in technological applications. The need for additional and reliable data on the thermal conductivity of liquids is obvious from the increasing use of various liquids as heat transfer media in many industrial processes, especially in the development of nuclear reactors.

Presently, the theories of thermal conductivity of liquids are less advanced than those which have been used to describe the mechanism of heat conduction in gases and solids, mainly because the structure of liquids is not well understood. Thus it is necessary to employ experimental methods to determine this property and many difficulties exist as noted from the fact that the experimental results by different workers rarely agree within ± 6 per cent. Considerable effort has been expended in many different experimental techniques; numerous geometrical arrangements for steady state test cells and transient hot-wire cells have been developed but little progress has been made toward developing a standard apparatus that yields dependable results. The major difficulties usually lie in the prevention of unwanted heat losses and avoiding free convection in the test cells.

Numerous correlations, both theoretical and empirical, relating the thermal conductivity to other physical properties have been proposed. They have met with extremely limited success. One of the promising theories of heat conduction in liquids assumes heat transfer is by longitudinal vibrations similar to the propagation of elastic waves or sound in a medium. The earliest attempts to derive an expression for the thermal conductivity of liquids based on this assumption were made by Brillouin [1] and Paschki [2]. Independent of them, Bridgman [3] derived a simple equation in which the thermal conductivity of liquid is directly proportional to the velocity of sound in that liquid and is inversely proportional to the square of inter-molecular center to center distance, assuming the liquid molecules are arranged in a simple cubical array. Other equations for predicting the thermal conductivity of liquids which involved the velocity of sound were derived by Kardos [4], Kincaid and Eyring [5], and Sakiadis and Coates[6]. Their equation is discussed in detail in the thesis.

The lack of data relating the velocity of sound to other properties such as the density and temperature contributed a major difficulty in verifying the equations proposed. Therefore the purpose of this study was to develop a simple and accurate method for determining the velocity of sound in liquids at various temperatures and to investigate the validity of some of the theoretical and empirical equations between the sonic velocity and the most reliable data available on thermal conductivity. Bridgman's equation proved to be of particular interest and a modified version which improves the correlations of experimental results is proposed.

II THEORIES OF THERMAL CONDUCTIVITY

2.1 Introduction

The modern theory of heat is closely associated with the internal energy of matter which in thermodynamics is referred to as the energy connected to the physical and chemical state of the body, i.e., the configuration and motion of the molecules and atoms within the body. Following this consideration, the transfer of heat by conduction must be strictly related to the translational, rotational and vibrational motions of the molecules, atoms and their components. Analysis of the various thermal conductivity data shows that a close relationship does, in fact, exist between the thermal conductivity and structure of matter. Therefore, all the phenomena connected with thermal conductivity must be explained by a combined theory of the nature of heat and structure of matter.

In accordance with the theories of heat and structure of matter, the conduction of heat in gases, amorphous solids and liquids is considered as the result of direct transfer of molecular (or atomic) motions from molecule to molecule at the contact areas. This type of heat transfer is usually referred to as a process of heat diffusion. In the substances which have a more organized structure, for example in crystals, the atomic motions are converted into a vibratory motions of the whole crystal lattice. The lattice waves that are produced by these atomic motions are the mechanism of heat conduction in non-metallic solids.

In the study of thermal conductivity of liquids, it is necessary to review the thermal conduction processes in both gases and solids. In any theory of the liquid state, it is possible to begin with a concept of the liquid, either as a disordered solid, or as a compressed gas where the free volume available for translational motion is more restricted.

2.2 Thermal Conductivity of Gases

A gas is assumed to consist of molecules in motion which exert no forces of attraction or repulsion on each other and which are distributed with complete randomness. The molecules behave as elastic spheres and are negligibly small in comparison with the mean free path. With these assumptions, all the properties and behavior of gases can be adequately explained in terms of the kinetic theory of gases . In other words, the conduction of heat in gases may be visualized as a process of diffusion, characterized by the movement of molecules from hotter to colder regions and vice versa, and by the exchange of kinetic energy in the collision of the molecules. The kinetic theory of gases leads to the following expression for the thermal conductivity:

$$k = \frac{1}{3} c_v l \, u \, \rho \quad \ldots\ldots\ldots\ldots\ldots \quad (2-1)$$

where ρ = density of the gas

c_v = specific heat at constant volume

l = mean free path of the molecules

u = mean molecular velocity

For a given temperature, the mean molecular velocity is constant, and the mean free path is inversely proportional to the density. The thermal conductivity should therefore be independent of the density or pressure. This surprising fact is in good agreement with experiments except at very low pressure; it approaches zero with pressure because eventually no molecules are available for the transportation of energy. With increasing temperature, the molecules will have higher velocity and, therefore, the thermal conductivity will increase, again agreeing with experiments .

Considering the exchange of momentum among molecules, the kinetic theory of gases gives the coefficient of viscosity as

$$\mu = 1/3 \rho l u \quad \ldots\ldots\ldots\ldots\ldots\ldots (2 - 2)$$

Combining Eq. (2 - 1) and Eq. (2 - 2), results in

$$k = c_v \mu \quad \ldots\ldots\ldots\ldots\ldots\ldots (2 - 3)$$

which is the well-known relation between the thermal conductivity and viscosity of gases. However, the analysis which led to the expressions given above, is not rigorous. Experiments show that thermal conductivity of gases is greater than that calculated from Eq. (2 - 3) and should be expressed by a modified relation of the form

$$k = \epsilon c_v \mu \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2-4)$$

where ϵ is a numerical constant which is greater than unity. The evaluation of ϵ is a complex problem and a generally valid expression has not been obtained. For monoatomic gases (of spherical molecules), it was found that ϵ has the highest value of 2.5. With an increasing number of atoms in a molecule, ϵ approaches the value 1. Although the significance of ϵ is not fully understood, it is believed to be connected with the rate of exchange of the various forms of molecular energies during the collisions of molecules[8]. A well known empirical relation for ϵ was suggested by Eucken[9]:

$$\epsilon = \frac{9\gamma - 5}{4} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2-5)$$

where γ is the ratio of the specific heat at constant pressure to that at constant volume. Thus, except for a few individual gases, the thermal conductivity may be written as:

$$k = \frac{9\gamma - 5}{12} c_v \mu \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2-6)$$

or

$$k = \frac{9\gamma - 5}{12} \rho c_v l u \quad \ldots\ldots\ldots\ldots\ldots \quad (2-7)$$

2.3 Thermal Conductivity of Solids

The present theory of heat conduction in solids makes a clear distinction between dielectric (non-metallic) and metallic substances. In the dielectric solids, the conduction of heat is accomplished by means of lattice waves produced by the atomic motions. It is generally accepted that these motions assume the form of thermal vibration which in turn can be regarded as a superposition of thermoelastic (acoustic) waves. In metals or other solid electrical conductors the heat is transferred by the lattice waves and the free electrons. In fairly pure metals nearly all the heat is, in fact, carried by the electrons and very little by the lattice waves.

The concept of the lattice wave as a heat conducting mechanism in solids and the concept of thermal resistance due to scattering of the lattice waves by themselves and other obstacles in their paths were first introduced by Debye [10]. In his theory of lattice conductivity, the solid is assumed to be a continuous elastic medium. If one end is heated then this may be considered as the introduction of an oscillatory disturbance at that end. The disturbance will be propagated in a manner analogous to an elastic (acoustic) wave propagated in a medium. The propagation of displacement waves through a medium is governed by its density and elastic modulus. As long as the density and modulus of elasticity are homogeneous, a displacement wave can propagate itself through a medium without loss of energy. This would imply an infinite conductivity which is not observed in practice. In order for the thermal conductivity to be finite, some mechanism for scattering the lattice waves must exist.

Debye suggested that this scattering is produced by the interaction of a particular wave with all the other waves which are present in the medium and whose frequency and amplitude will be dependent on the specimen temperature. No interaction will occur, however, if the wave motion is perfectly harmonic. Any interaction between the waves is due to the anharmonicity in their motions. From such arguments, Debye arrived at the following theoretical formula for the thermal conductivity of solids:

$$k = \frac{1}{4} \rho c_V w \lambda \qquad (2 - 8)$$

where ρ = density of solids

c_V = specific heat at constant volume

λ = average distance of effect of the thermoelastic wave, or the distance which wave travels before its amplitude is reduced to 1/e of its initial value (where e = 2.718)

w = average velocity of propagation of the elastic wave

The meaning of ρ , c_V and w are obvious; λ , the distance which the lattice wave travels before its amplitude is reduced to 1/e of its original value, is therefore dependent upon the scattering of the lattice waves by various scattering processes and may be considered as a parameter characteristic of the scattering processes. If λ is large such that the waves can travel a relatively long distance without being scattered, the thermal conductivity will be high; if λ is small, the waves will be scattered and the thermal conductivity will be low. Debye showed that λ is almost proportional to the inverse value of absolute temperature as found experimentally by Eucken.[11] In other words, the thermal conductivity of dielectric solids, according to Debye's equation, will decrease with increasing temperature as found experimentally.

A considerable advance on Debye's theory of thermal conductivity was made by Peierls.[12] Debye considered the atomic vibrations in solids as a collection of thermoelastic waves in a continuum while Peierls treated the individual atomic motion and quantized the thermoelastic wave into a quanta of vibration which is called the "phonon" by analogy with the photon in the theory of electromagnetic radiation. A phonon is therefore a quantum of energy in the form of a thermoelastic wave of a fixed frequency. By regarding the lattice waves to be equivalent to a "phonon gas", the modified Debye's theory leads to the following equation for the thermal conductivity of solids:

$$k = \frac{1}{3} \rho c_v l w \quad \ldots\ldots\ldots\ldots \quad (2-9)$$

which is formally identical with that derived for gases from the kinetic theory. Where ρ is the density of solids; c_v is the specific heat at constant volume; ℓ is the mean free path of phonons, defined in the same manner as λ in Eq. (2 - 8); and w is the velocity of phonons (lattice waves). A general discussion of the Eq. (2 - 9) was given by Kowalczyk[8], and for detailed treatment of Peirls' theory, one may refer to Ziman.[13]

2.4 Thermal Conductivity of Liquids

Presently, the theory of the liquid state is far from satisfactory as compared to that of gaseous and solid states. The fact that liquids flow and diffuse readily led in the past to a general belief that the structure of liquids is close to that of gases. The only difference is that liquids have smaller average distance and therefore distinctive attractive forces among molecules. However, in the vicinity of the melting point, the density of liquid is close to that of a solid and, hence, there is little possibility of free movement of the molecules within liquids. For this reason, the modern theory of liquid state assumed that structurally liquids are closer to solids than to gases. This point of view is supported by the X-ray diffraction studies of liquids.

However, it is generally accepted that in liquids, as in gases, the conduction of heat is due to the movement of the molecules and atoms. A number of theoretical equations, derived from assumed liquid models and heat transfer mechanism, have been proposed for predicting the thermal conductivity of liquids. Those which involved velocity of sound as a principle property are discussed as follows:

(1) Bridgman's Equation

Bridgman [3], in 1923, suggested the following theoretical equation for the thermal conductivity of liquids:

$$k = n K \frac{V}{\delta^2} \quad \ldots\ldots\ldots\ldots\ldots \quad (2-10)$$

where n = pure number related to energy

K = Boltzman constant

V = velocity of sound in liquids

δ = mean distance of separation of centers of molecules, under the assumption that the molecules of liquid are in cubical array and, hence, may be calculated by

$$\delta = \left(\frac{M}{\rho N}\right)^{1/3}$$

, where M is the molecular weight; N is Avogadro's number; and ρ is the density of liquids.

The formula may be derived in terms of the following simple physical picture. Assume the molecules of liquid to be in cubical array, the distance between molecular centers being δ. The total energy of a molecule is nKT (half potential and half kinetic) and, hence the energy difference between molecules in the adjoining plane along the temperature gradient is $nK \frac{dT}{dx}\delta$. This energy difference is assumed to be propagated along a row of molecules with the velocity of sound v cm/sec. Hence the energy passing a fixed point in a molecular row in unit time is $nK \frac{dT}{dx}\delta\frac{V}{\delta}$. Since there are $1/\delta^2$ rows in unit cross-sectional area, the total energy transfer is therefore $nK \frac{dT}{dx} \frac{V}{\delta^2}$ per unit area per unit time. This transfer, by definition, is equal to $k \frac{dT}{dx}$. Hence, identifying the coefficients, Eq. (3 - 10) results.

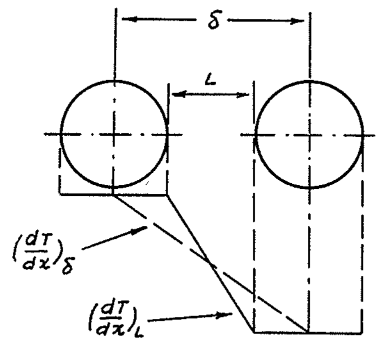
The formula, except for the numerical coefficient, as pointed out by Bridgman, is the same as Debye's equation (eg. 3 - 8) for the thermal conductivity of solids, provided Debye's quantities take the proper values in liquid.

When Bridgman took n = 2, the calculated thermal conductivities were found to be consistantly lower than the observed values obtained by Bridgman, Riedel and Fillipov.[14] By taking n = 3, Sakiadis and Coates[6] found, for 28 liquids, an average and maximum deviation of ± 15 per cent and 40 per cent respectively. However, in view of the simplicity of the relation, this agreement is surprising; it is not numerically correct but it is of the correct order of magnitude and the sign of the temperature coefficient of thermal conductivity is correct. In most organic liquids, both V and $\frac{1}{\delta^2}$ decrease with increasing temperature, giving a negative temperature coefficient of thermal conductivity as found experimentally. For water, V increases with increasing temperature at a rate which is sufficient to more than offset the decrease of $\frac{1}{\delta^2}$, so that the net effect is an increase of thermal conductivity, again agreeing with experiments.

Bridgman found the thermal conductivity of all liquids increase with increasing pressure as would be expected from the formula, since both V and $\frac{1}{\delta^2}$ increase with pressure. But the calculated values increase rather more rapidly than the observed ones. The reason for this, according to Bridgman, is that pressure produces some change in the structure of the liquid which interferes the transfer of energy and the formula does not account for this effect.

(2) Kardos' Equation

Kardos [4] modified Bridgman's theory by introducing the distance L between the surface of adjacent molecules instead of the distance δ between their centers, and considered the energy drop across it. Thus the temperature gradient, as illustrated is increased from $\left(\frac{dT}{dx}\right)_\delta$ to $\left(\frac{dT}{dx}\right)_L$.



By reasoning similar to that of Bridgman, Kardos arrived at the following equation for the thermal conductivity of liquids:

$$k = \rho \, c_p \, L \, v \quad \ldots\ldots\ldots\ldots\ldots \quad (2 - 11)$$

where ρ = density of liquid

c_p = specific heat at constant pressure

L = distance between adjacent molecular surfaces

V = velocity of sound in liquid

The difficulty in using this equation lies in the finding proper values for L. As a first approximation, Kardos considered that L would not differ much for various liquids and assumed it be constant and equal to 0.95×10^{-8} cm. Using this value of L, Smith[15] found, for 29 liquids, the average and maximum error to be ± 23.4 and 104 per cent respectively. It appears that the assumption of constancy of L is not justified. However, the equation was interpreted later by Sakiadis and Coates [6] on the basis of more recent development which will be discussed later.

(3) Kincaid and Eyring's Equation

Kincaid and Eyring [5] treated the molecule moving in its free volume in the liquid as equivalent to the molecule moving in the total volume in the gas phase. Following this consideration, certain kinetic theory formulae for gases can be modified in such a way as to make them applicable in liquids. A more detailed treatment is as follows. The velocity of sound in an ideal gas $V_{s,g}$ and the mean molecular velocity in an ideal gas $V_{m,g}$ are given by the equations:

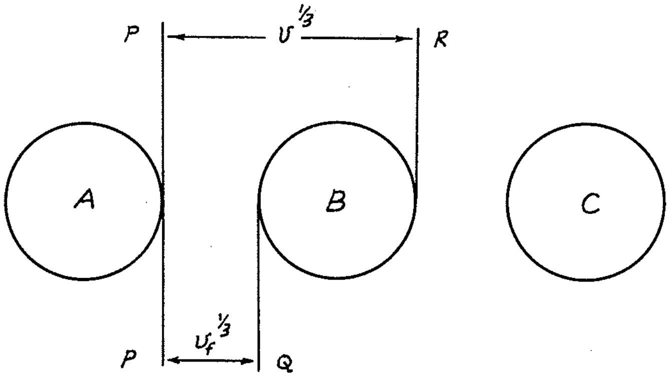
$$V_{s,g} = \left(\frac{\gamma RT}{M}\right)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2 - 11)$$

$$V_{m,g} = \left(\frac{8\ RT}{M\ \pi}\right)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2 - 13)$$

where γ is the ratio of specific heat at constant pressure to that at constant volume; R is the universal gas constant; T is the absolute temperature; and M is the molecular weight. Combining Eq. (2 - 12) and Eq. (2 - 13), gives

$$V_{s,g} = \left(\frac{\pi\gamma}{8}\right)^{1/2} V_{m,g} \quad \ldots\ldots\ldots\ldots \quad (2 - 14)$$

It can be seen that $V_{s,g}$ is always slightly smaller than $V_{m,g}$, since the factor $\left(\frac{\pi\gamma}{8}\right)^{1/2}$ is always smaller than unity. This would reasonably expected from the fact that a wave propagated by matter could hardly travel faster than the molecules which carry it. However, in liquids, where the finite size of the molecules can not be ignored, the velocity of sound was found to be greater by a factor of 5 to 10 when compared to velocity of molecules as obtained by the kinetic theory. The reason for this, according to Kincaid and Eyring, can be visualized as follows:



For a sound wave to be transmitted from P to R, i.e., from the edge of the molecule A to the adjacent edge of molecule B, it need only travel a distance PQ. Since the signal is transmitted across molecule B almost instantaneously. PR is proportional to the cube root of the molar volume, and PQ to the cube root of the free volume. Therefore the velocity of sound in liquid $V_{s,l}$, in terms of the intermolecular distances, should be written:

$$V_{s,l} = V_{s,g} \left(\frac{v}{v_f}\right)^{1/3} \quad \ldots\ldots\ldots\ldots \quad (2 - 15)$$

or

$$V_{s,l} = \left(\frac{\gamma RT}{M}\right)^{1/2} \left(\frac{v}{v_f}\right)^{1/3} \quad \ldots\ldots\ldots\ldots \quad (2 - 16)$$

Similarly, the mean molecular velocity in liquid can be written:

$$V_{m,l} = V_{m,g} \left(\frac{v}{v_f}\right)^{1/3} \quad \ldots\ldots\ldots\ldots \quad (2 - 17)$$

or

$$V_{m,l} = \left(\frac{8RT}{M\pi}\right)^{1/2} \left(\frac{v}{v_f}\right)^{1/3} \quad \ldots\ldots\ldots\ldots \quad (2 - 18)$$

Hence, Eq. (2 - 16) and Eq. (2 - 18), result in

$$V_{m,l} = \left(\frac{8}{\pi\gamma}\right)^{1/2} V_{s,l} \quad \ldots\ldots\ldots\ldots \quad (2 - 19)$$

which is analogous to the Eq. (2 - 14).

An acceptable empirical expression for the thermal conductivity of gases, as indicated previously, is given by

$$k = \frac{9\gamma - 5}{12} \rho c_v l u$$

This equation, according to Kincaid and Eyring, should apply to liquids, provided that the mean free path is represented by $\left(\frac{V}{N}\right)$ and the mean molecular velocity by Eq. (2 - 19). The resulting formula is

$$k = \frac{9\gamma - 5}{12} \frac{C_v}{v} \left(\frac{v}{v_f}\right)^{1/3} \left(\frac{8}{\pi\gamma}\right)^{1/2} V_{s,1}$$

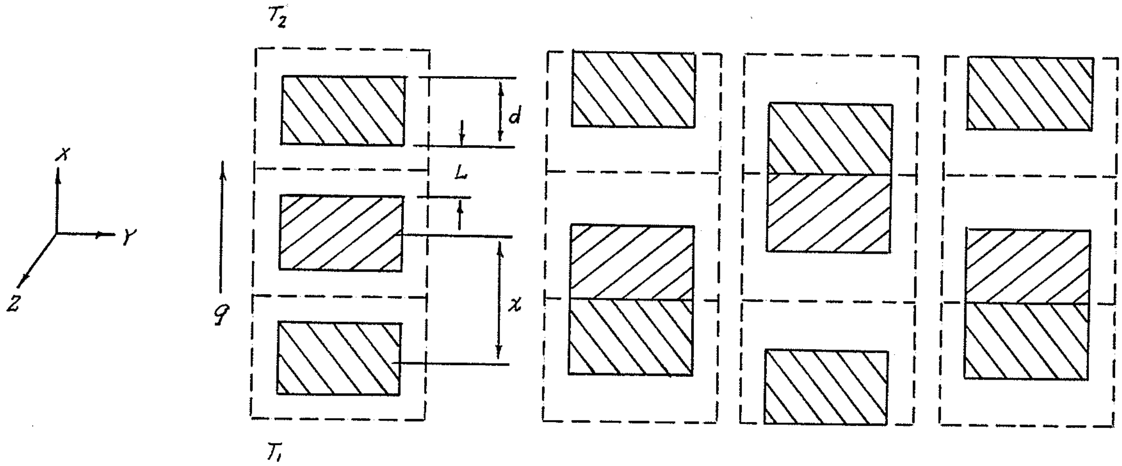
where C_v is the molar heat capacity at constant volume and can be written as nR, n is a pure number and R is the gas constant. The formula reduces to

$$k = \frac{9\gamma - 5}{12} \left(\frac{8}{\pi\gamma}\right)^{1/2} n\,K \quad \frac{V_{s,1}}{\left(\frac{v}{N}\right)^{2/3}} \quad \ldots\ldots \quad (2 - 20)$$

where $K = \frac{R}{N}$ is the Boltzman constant. It can be seen that the equation, except for the numerical factor $\frac{9\gamma - 5}{12}\left(\frac{8}{\pi\gamma}\right)^{\frac{1}{2}}$, is exactly identical with Bridgman's equation. Kincaid and Eyring supposed that only the translational and rotational degree of freedom are effective in transfering energy, so that the proper value to use for γ in the Eucken correction is 4/3. With $n = 3$, and γ values from direct measurement of specific heats, Kincaid and Eyring calculated the thermal conductivities of 11 liquids at 30 °C. It was found that the deviations of the calculated from the observed values are roughly symmetrical with the average and maximum error of ± 9.6 and 20.4 per cent respectively. However, the scatter of the calculated values is not appreciably smaller than that which would be obtained by the much simpler Bridgman's equation using a slightly higher value of n. Equation (2 - 20), as Bridgman's equation, gives the right sign for the temperature coefficient of thermal conductivity but does not predict the pressure effect correctly.

(4) Sakiadis and Coates' Equation

By using a model of the liquid state which originated from the results of X-ray diffraction studies of liquids, and an assumption of a mechanism of heat conduction, Sakiadis and Coates [6] derived an equation for the thermal conductivity of liquid which is exactly identical with Kardos' equation.



The figure above shows the assumed liquid model and the heat transfer mechanism. The cross-sectional area of the molecule is represented as a rectangle merely for the purpose of calculation. According to Sakiadis and Coates, the molecule (of organic liquids) appears like a rod with rough edges if the atom is visualized as distribution of charges in space rather than a point mass. The space occupied by one molecule represents the minimum molecular volume at absolute zero and the dotted lines represent the molar volume at a certain temperature. In other words, the empty space, within which the molecules move, is the difference between the molar volume at a certain temperature and that at absolute zero. The process of heat conduction may be visualized as shown on the diagram. Each molecule vibrates and collides alternately with adjacent molecules in the direction of heat flow, receiving energy when it collides with the hotter molecule and passing it to the colder molecule in the successive collision. It is thus obvious that the significant intermolecular distance, according to the assumed mechanism of heat conduction, is the distance between the molecular surface L. The energy drop per molecule in the direction of heat flow can be written

$$q' = -\frac{d\left(\frac{Q}{N}\right)}{dx} L \qquad \ldots\ldots\ldots\ldots\ldots \quad (2 - 21)$$

$$q' = -\frac{L}{N}\frac{dQ}{dT}\frac{dT}{dx} \qquad \ldots\ldots\ldots\ldots\ldots \quad (2 - 22)$$

where Q is the energy per mole; N is the Avogadro number; L is the mean surface to surface distance between molecules; and x is the direction of heat flow and may be considered equal to (d+L), where d is the molecular diameter. If the energy is transmitted with the speed of sound V in that medium, the total energy per unit time passing a fixed point in a row of molecules is $-\frac{L}{N}\frac{dQ}{dT}\frac{dT}{dx}\frac{V}{x}$, where $\frac{V}{x}$ is the number of steps contained in a row V units long.

The energy transfer per unit area yz per unit time is then

$$\frac{q}{A} = -\frac{L}{N}\frac{dQ}{dT}\frac{dT}{dx}\frac{V}{x}\frac{1}{yz} \quad \ldots\ldots\ldots\ldots \quad (2 - 23)$$

By definition, the energy transfer per unit area per unit time is also k $\frac{dT}{dx}$. Hence, identifying the coefficient yields

$$k = \frac{L}{N}\frac{dQ}{dT}\frac{V}{xyz} \quad \ldots\ldots\ldots\ldots \quad (2 - 24)$$

Also by definitions,

$$\frac{dQ}{dT} = M c_p \quad \ldots\ldots\ldots\ldots \quad (2 - 25)$$

$$xyz = v = \frac{M}{N\rho} \quad \ldots\ldots\ldots\ldots \quad (2 - 26)$$

where M is the molecular weight; c_p is the specific heat at constant pressure; v is the molecular volume; and ρ is the density of liquid. Substituting Eq. (2 - 25) and Eq. (2 - 26) into Eq. (2 - 24) results in

$$k = \rho c_p L V \quad \ldots\ldots\ldots\ldots \quad (2 - 27)$$

which is exactly identical with Kardos' equation.

Sakiadis and Coates emphasized that the value of L will vary from liquid to liquid and is a function of temperature, becoming zero at the absolute zero, while Kardos erroneously assigned a constant value to it. Although a method of obtaining the value of L was also given by Sakiadis and Coates, it is an extremely complex procedure. On the other hand, additional experimental data are required to carry out the calculations. According to the calculations done by Sakiadis and Coates on 42 liquids, the average deviation from the observed values was found to be ± 2.6 per cent. But comparison given by Reid and Sherwood [16] shows the average deviation to be ± 16 per cent and errors as large as 61 per cent are noted.

The discussion above was limited to the equations of thermal conductivity of liquids which involves the velocity of sound as a principle property. Except for the Kincaid and Eyring's equation, they were all basically following Bridgman's consideration for the transfer of energy. Hence, Bridgman's equation are studied more thoroughly later.

III DETERMINATION OF ULTRASONIC VELOCITY IN LIQUIDS

3.1 Generation of Ultrasonic Waves

Sound wave is an alteration in pressure, stress, particle displacement, or particle velocity, which is propagated in an elastic material or the superposition of such propagated vibrations. In other words, sound waves are produced as a result of a mechanical disturbance taking place in a material medium. The term "ultrasonic" is used to describe sound waves having frequencies higher than those which the human ear can respond; it generally embraces all frequencies above approximately 20 KHz/sec. The generation of ultrasound in fluids can be affected through excitation by a solid vibrator, one face of which is put in contact with the fluid and produces ultrasonic waves in it. This method is commonly employed for measurements of velocity or attenuation in both liquids and gases. Electromechanical tranducers are by far the most convenient vibrators to use. There are several types of electromechanical tranducers which can be used to generate ultrasonic waves, but the most commonly used are magnetostrictive and piezoelectric types.

Some metals and alloys, notably nickel, will change in dimension when subjected to a magnetizing force. This effect, which is nonlinear, is known as magnetostriction. Magnetostrictive elements are usually only useful up to a frequency of 100 KH_z/sec. They are widely used for underwater signaling and agitation systems.

A solid is said to be piezoelectric if electric charges are liberated on it when it is subjected to a mechanical stress. The magnitude of the charge density is directly proportional to the applied stress. When the sign of the stress is reversed, the polarity of the electric charges is also reversed. This phenomenon is called the "direct piezoelectric effect". Conversely, when electric force is applied to a material possessing the piezoelectric property its size is altered, the amount of change being proportional to the intensity of the applied electric force. Piezoelectric elements are composed of sections cut from the crystals and are identified by the axis perpendicular to the largest face of the cut. Thus, if a slab is cut with its major faces perpendicular to the X crystallographic axis, it is known as an "X-cut". Depending on the type of crystal and the orientation of cut, a single plate can exhibit one of thickness shear, thickness expansion, face shear, or transverse expansion. The mode most widely used in ultrasonics is the thickness expansion mode.

The piezoelectric effects are prominent in crystals such as quartz, Rochelle salt, tourmaline, and lithium sulphate. A natural quartz crystal, which has exclusively been used in ultrasonic research work, is an extremely stable material, both chemically and physically, and very hard. It is also capable of withstanding reasonably high temperatures (it has a Curie temperature of 573 °C). An X-cut quartz crystal resonates at approximately 2870/t KH_z/sec; where t is the thickness of the quartz crystal in mm. It is capable of producing frequencies up to about 15 Mc/sec when operating in the fundamental mode. Beyond this, it becomes so thin that it has a tendency toward mechanical failure. However, a very much higher frequency can be obtained by operating at one of its harmonics.

3.2 Methods of Determining Sound Velocity in Liquids

The determination of the velocity of sound in liquids has been carried out by many investigators using various techniques. The following methods are most commonly used for measurement in liquids:

1. Optical methods
2. The acoustic interferometer
3. The pulse technique

The optical methods include the striation and optical diffraction method. They depend on the variation of refractive indices brought about by periodic changes in density due to ultrasonic waves passing through transparent media. This phenomena is known as Debye-Sear effect. However, it was concluded by Vigoureux [17] that the optical methods do not seem to be capable of yielding results as accurately as the other two methods. Therefore only the interferometer method and the pulse method are described.

3.2.1 Acoustical Interferometer

The interferometer method depends on the formation of standing waves between the tranducer and a flat reflector. The reflector is positioned coaxial with and parallel to the tranducer, and at a distance which can be varied at will by means of a micrometer screw. The tranducer is connected to an oscillating circuit. When the position of the reflector is changed, periodic variations of the current through the tranducer are obtained; sharp maxima appear for the positions of the reflector at which the liquid column vibrates in resonance. Resonance occurs only when the reflected waves build up in the same phase with those transmitted, i.e., when the distance between the transducer and the reflector is an integral number of one-half wavelengths. Thus, the distance between adjacent resonance positions for the reflector, which are indicated by sharp increases in transducer current, is an one-half wavelength.

The velocity may be obtained from the relationship $c = \lambda' f$; where c is the velocity, λ' is the wavelength, and f is the frequency. The interferometer's accuracy depends upon the care with which it is mechanically designed and constructed. An accuracy of one part in a thousand has been reported for the interferometer measurement of velocity in liquids.[18]

3.2.2 The Pulse Technique

The pulse technique consists of sending short trains of ultrasonic waves through the medium to a receiver. The velocity of sound is obtained by measuring the time required for a sound pulse to travel a known distance between the source and the receiver. This is known as transmission method. For the echo method a reversible transducer serves as both source and receiver, a reflector being used to return the pulse.

The pulse technique is especially suited for measurement of ultrasonic propagation in liquids due to their relatively small absorption coefficients and high characteristic impedances. It was first employed by Pellam and Galt[19] (1946) for velocity and absorption measurements at 15 megacycles.

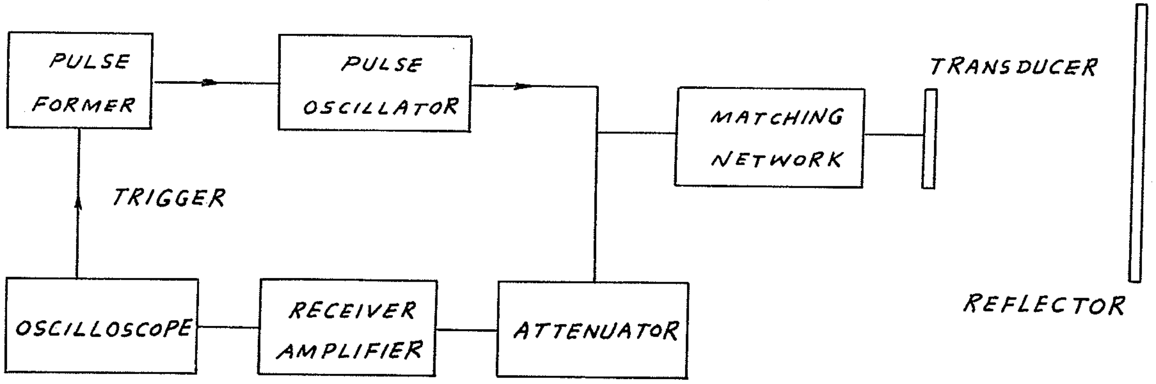


Fig. 3.1 Block diagram of Pellam and Galt's pulse circuit for measuring velocity and absorption in liquids.

Fig. 3.1 shows a block diagram of the circuit used by Pellam and Galt. A crystal-controlled circuit in the oscilloscope starts the time base and simultaneously triggers the pulse generator. The pulse formed by the generator is used to excite the crystal transducer which radiates ultrasonic pulse into liquid. The reflected ultrasonic pulses are picked up and converted back to electrical signals by transducer which is reversible. The signal is fed to the oscilloscope which, in addition to triggering the pulse generator and starting the time base, provides marker pips spaced accurately along the time base. The attenuator is used to keep the receiver input signal constant. The acoustic path length is made variable by mounting the transducer on a movable support. Velocity is then obtained directly from the slope of distance travelled plotted against pulse delay. The method depends for its accuracy on the precision of the micrometer screw which is used to move the transducer support and on the electronic time measuring devices. Pellam and Galt estimated that their results for velocity were accurate to about one part in a thousand.

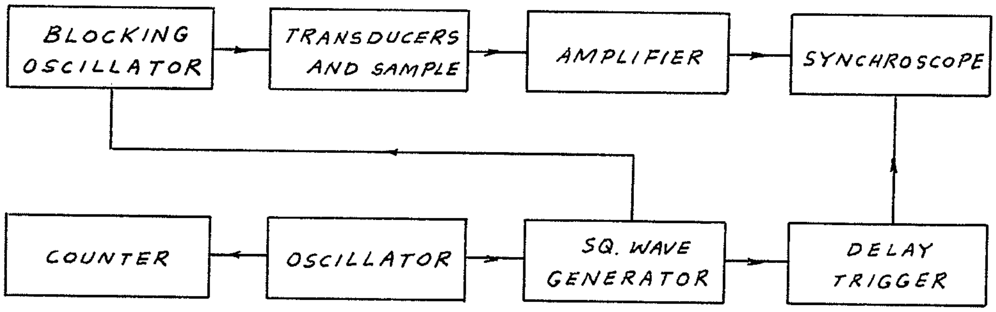


Fig. 3.2 Block diagram of the apparatus used by Greenspan and Tschiegg for sound velocity measurements.

A more accurate and sophisticated pulse method for velocity measurement in liquids has been developed by M. Greenspan and C. Tschiegg.[20] It basically uses the same principle of measuring the time elapses, only a more accurate indirect method is used.

The apparatus consists of a known length hollow cylinder, which is usually called a delay line, with a piezoelectric transducer attached to each end, and an electronic system to excite the transmitting transducer and display the received signals. The specimen of the liquid being tested is contained within the bore of the cylinder. Fig. 3.2 shows the block diagram of the apparatus used by Greenspan and Tschiegg. When a pulse is applied to the transmitter, a wave train is propagated through the liquid and is reflected back and forth between the two transducers. The pulse repetition frequency, which is controlled by a sine-wave oscillator, is adjusted so that a new pulse is initiated each time the reflected wave returns to the transmitter. In this manner, all wave trains move in phase through the liquid. It is indicated on the oscilloscope by the superimposing of the wave trains. The electronic counter, which is connected to the oscillator, measures the pulse repetition frequency. Thus, the reciprocal of the frequency determines the time required for the sound pulse to travel twice the length of the delay line. The velocity may then be obtained from the relationship $c = 2\,l\,f$; where c is the velocity, l is the length of delay line, and f is the pulse repetition frequency.

The method was employed for the measurement of sound velocity in distilled water over a temperature range of 0° to 100 °C. Accuracy was estimated to be better than one part in 30,000. It is believed that the pulse method is inherently capable of yielding high accuracy for the velocity measurements.

3.2.3 Method Employed

In this study, the measurement of sound velocity was carried out by a comparison method rather than an absolute one. The apparatus consisted of three basic parts: a delay line which is a hollow cylinder of known length with a quartz crystal attached at one end and a fixed reflector at the other end, (Fig. 3.5) an acoustic interferometer (Fig. 3.6) to provide comparison path length, and an ultrasonic flaw detector, (Fig. 3.4) which basically consists of a pulse generator and a cathod-ray tube, to excite the crystal and display the received signals.

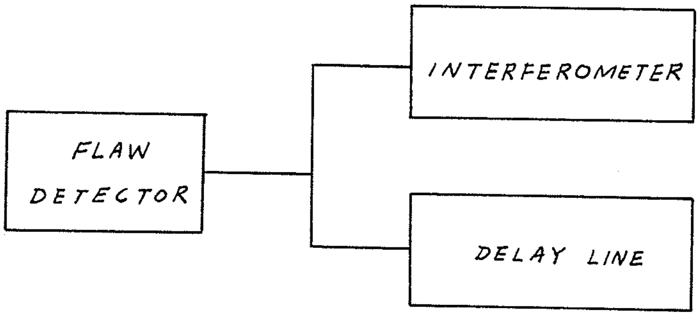
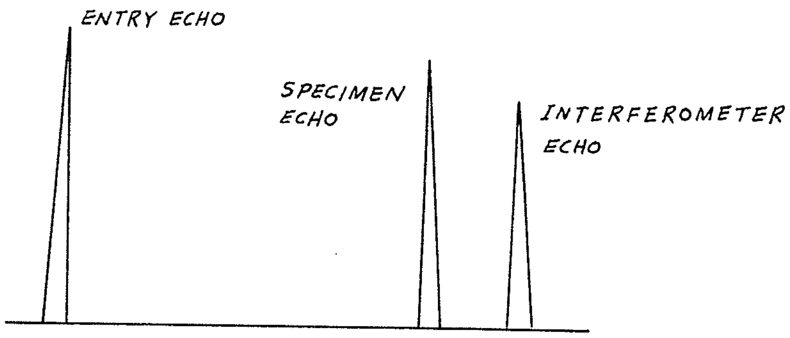


Fig. 3.3a

(a) Schematic arrangement of the apparatus



(b) Schematic diagram of the echoes

Fig. 3.3 b

The schematic arrangement of the apparatus is shown in Fig. 3.3 (a). Distilled water was used for the reference fluid in the interferometer and the liquid to be tested was placed in the delay line. A pulse was sent out simultaneously from the flaw detector to both the interferometer and the delay line, and the echoes from both reflectors were picked up and displayed on the screen of the flaw detector as shown schematically in Fig. 3.3 (b). The interferometer echo is then made to coincide with the specimen echo. This is done by adjusting the acoustic path length of the interferometer by means of the micrometer adjustment on the reflector.

The coincidence of the echoes implies that the travel time of each sound pulse in the delay line is equal to that in the interferometer, or

$$\frac{L}{v} = \frac{L_W}{v_W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3 - 1)$$

where L = acoustic path length of the delay line

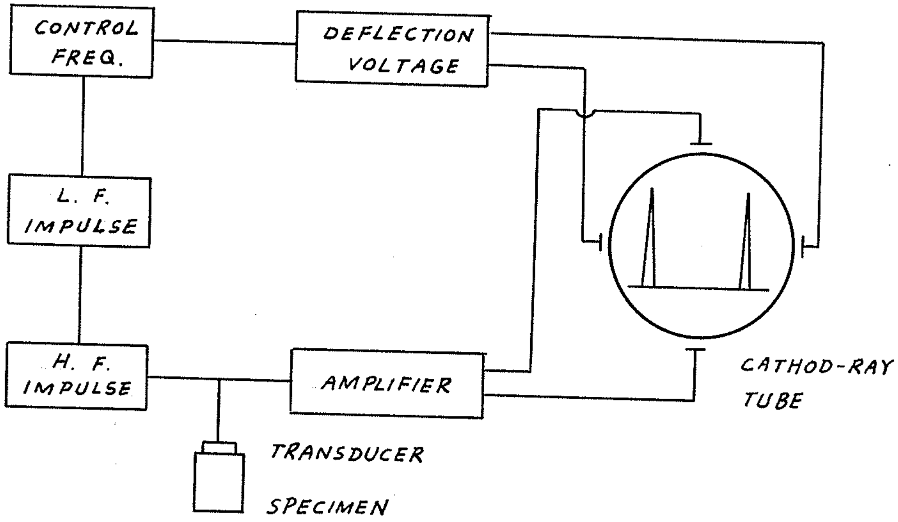
v = sound velocity in the liquid tested

L_W = acoustic path length of the interferometer

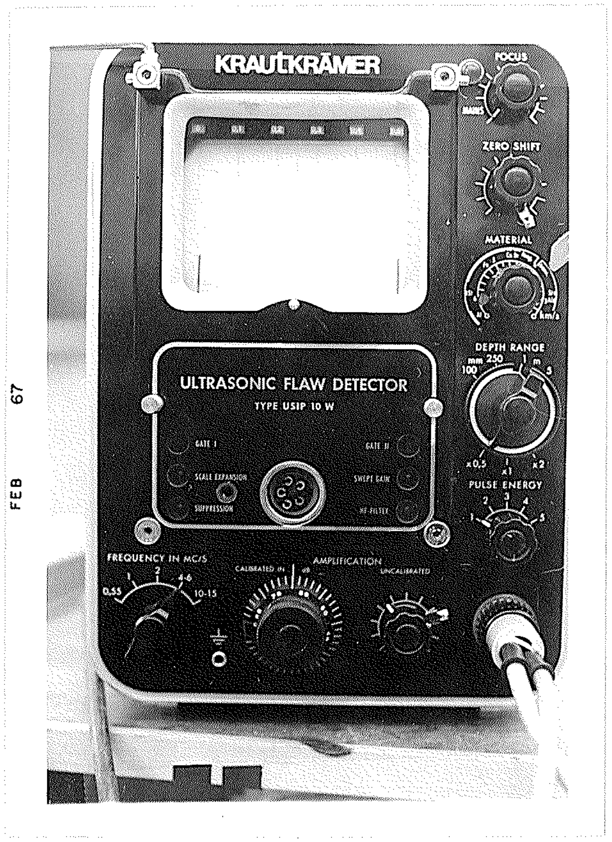
v_W = sound velocity in water

The path length of the interferometer can be read directly from its scale and the sound velocity in the liquid tested calculated from Eq. (3 - 1).

The use of the electrical transmitting pulse as a reference point presents one basic source of error to all ultrasonic time measurement by the pulse method. Mainly because piezoelectric crystals have a certain mass, the start of the mechanical vibration of the crystal is somewhat later than the start of the electrical pulse. A measurement of this delay for a particular crystal is very complex and difficult. However, this source of error was eliminated in the present work by first bringing the interferometer echo in coincidence with the first specimen echo and then with the second one. The difference between the two readings on the scale of the interferometer gives the path length L_W which does not involve error by the difference in delay in the interferometer and specimen crystals. Another advantage is that the distance between the interferometer probe and reflector does not enter into measurement and the values of L_w obtained in this manner are free from errors due to mechanical construction and assembly of the interferometer. The details of the method and procedure of the experiment are presented later.



(a) Schematic arrangement of the flaw detector



(b) Front panel of the flaw detector

Fig. 3.4

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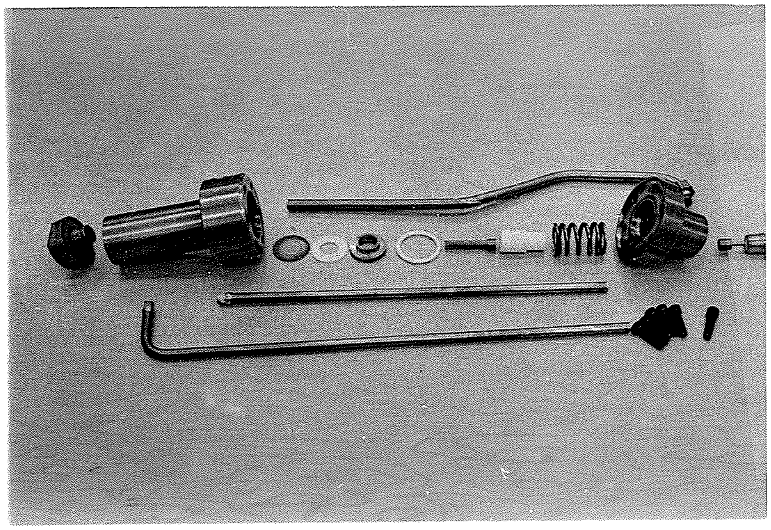

Fig. 3.5 Delay line and accessories

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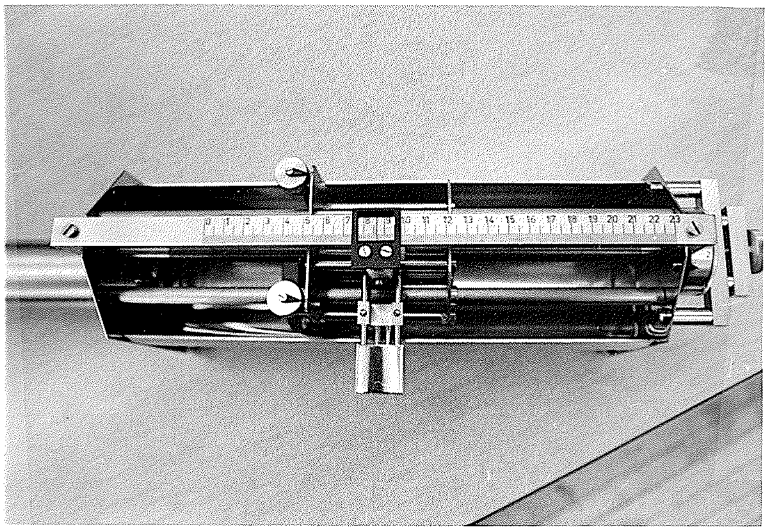


Fig. 3.6 The acoustic interferometer

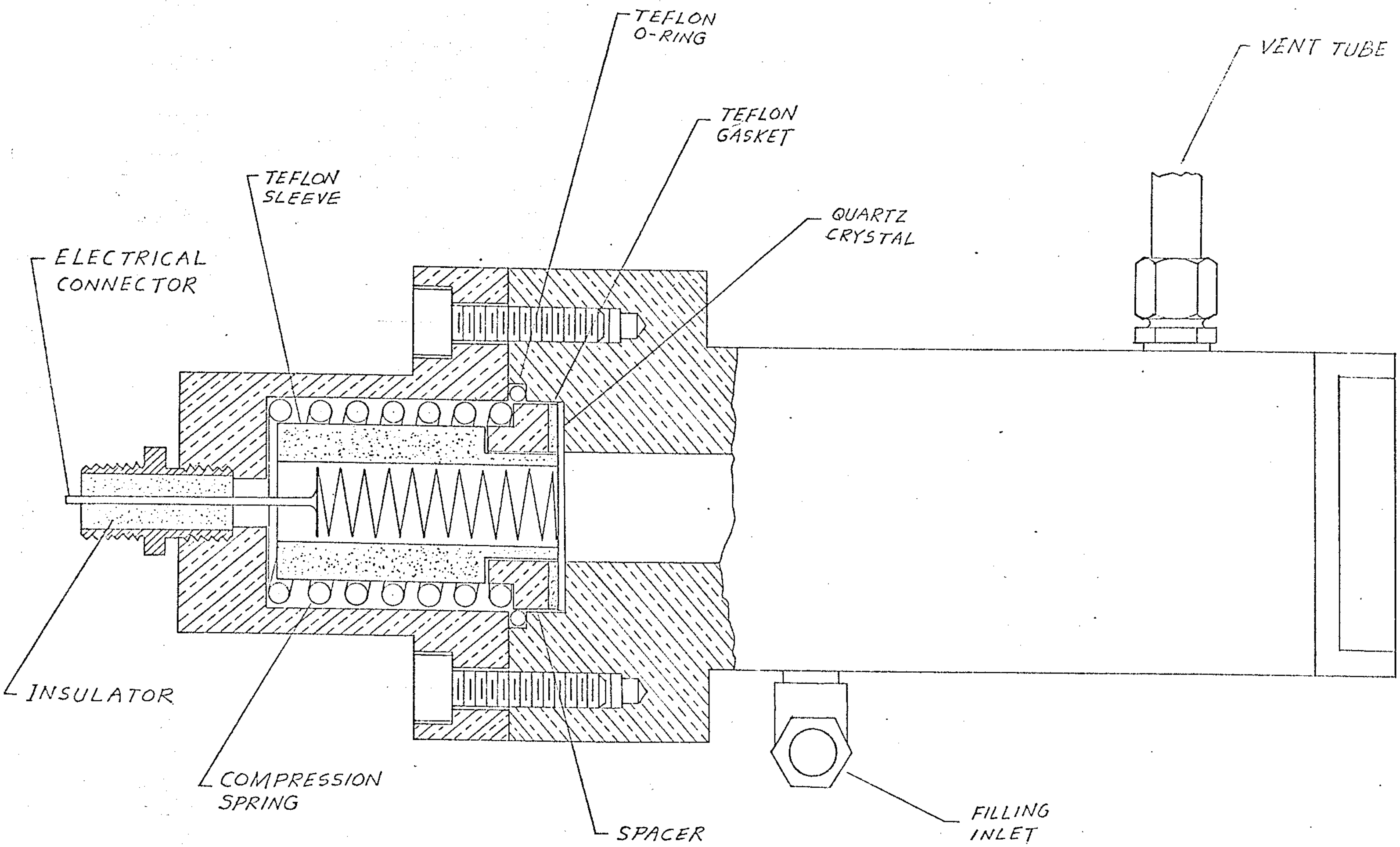
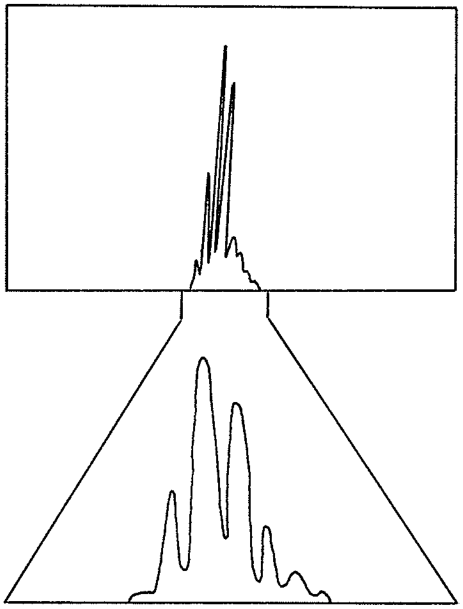


Fig. 3.7 Delay line assembly

3.3 Description of Equipment

3.3.1 Ultrasonic Flaw Detector - The unit was manufactured by Dr. J. U. H. Krautkramer Gesellschaft fur Electrophysik, Cologne, Germany. It employs the principle of the reflection of ultrasonic waves in the frequency range from 0.5 to 15 MH_z/sec. Fig. 3.4 (a) shows the schematic arrangement of the unit. The transmitted pulses and reflected echoes appear as peaks on the fluorescent screen of the cathod-ray tube. The distance between the peaks is a measure of the time of travel of a sound pulse in certain medium. Fig. 3.4 (b) shows picture of the front panel of the unit.



The unit had rectified vedio presentation with a four position filter. One of these positions gives rectified RF without any filtering and the individual high frequency cycles, each of which corresponds to one oscillation of the ultrasonic pulse, are clearly presented. Any particular portion of the screen can be expanded, as shown schematically, by means of the scale expansion.

By means of the scale expansion, one cycle of the 4 megacycle wave train, or 0.25 microseconds, is approximately displayed over 10 mm on the screen when the lowest range is used. The combination of the two features mentioned above permits the exact coincidence of the pulses or echoes to be obtained.

3.3.2 Delay line - The delay line is a hollow cylinder made from brass. One end serves for the mounting of the crystal and the other end is a fixed plane reflector which is parallel to the crystal when they are assembled. The diameter of the bore is 5/8 in. and the acoustic path length is 3.999 ± 0.001 ins. as measured at 22 °C. The test liquid is contained within the bore of the cylinder. The whole assembly is immersed in a constant temperature oil bath during the test. Two small tubes open into the bore of the cylinder; one for pressure release and the other one for filling up with the test liquid which may evaporate. It is important to have the delay line full with liquid during the test.

The crystal for the delay line was a disc type X-cut quartz with a diamter of 1.25 in. and a thickness of 0.0029 in. It has a fundamental frequency of 4.0±1% KH_z/sec when operating in thickness mode of vibration. Both faces of the disc are fine-ground and plated with chromium and gold, completely over one face, and 5/8 in. diameter spot centered on the other. When the cap of the delay line is bolted on, the crystal is held against the end of the delay line by means of a compression spring. The fully plated surface of the crystal is then in good electrical contact with the grounded delay line. A coaxial cable passes through a seal in the cap, and the center conductor makes electrical contact with the spot plated electrode of the crystal through a light spring. Fig. 3.5 shows the delay line and accessories and Fig. 3.7 shows the assembly of delay line.

3.3.3 Acoustic Interferometer - The Unit, as shown in Fig. 3.6 was supplied by Krautkramer Ultrasonic Inc. It consists of the following basic components: a nickel sheet tank with provision to mount a normal probe at one end, a reflector which can be adjusted exactly at right angles to the sound beam in the liquid path, a lead screw with backlash-free nut to transport the reflector, and a measuring system for the reflector positions.

In normal use, the quartz crystal probe is clamped to the tank by means of a clasp on one side. It is necessary that the frequency of the probe be the same as that used in the delay line. An attenuator is connected in series with the probe. It serves to adjust the amplitude of the echoes from the interferometer independently of the other conditions of test.

The total scale length in the interferometer is 230 mm, but the reflector can move a distance of only 194 mm. Using the method described above for the velocity measurement in this study, it can only measure specimen equivalent to 92 mm of water. The delay line is approximately 102 mm in length and the velocities to be measured cover the range which is much lower than the velocity of sound in water. It is thus obvious that the original liquid column of the interferometer is not long enough to permit the adjustment of the reflector such that two successive coincidences with the specimen echoes are obtained. Therefore, a modification had been made to lengthen the liquid column of the interferometer. This was done by adding an extension which can be varied continuously. Since the distance between the interferometer probe and reflector does not enter into measurement, no accuracy requirement is imposed on the length of the extension. By making the extension sufficiently long, the usable range of the interferometer can be doubled, permitting measurement of specimen up to 194 mm water equivalent which covered the entire velocity range to be measured.

As mentioned previously, the liquid column was filled with water (distilled) in which the velocity of sound has been accurately determined. Since the temperature coefficient of the velocity of sound in water at room temperature of 20 °C is approximately 2.5 m/sec °C, and the room temperature fluctuates by ± 1 °C, accurate temperature measurement of the water in the interferometer was required during the tests. A precision mercury thermometer was used for this purpose.

3.4 Temperature Control and Measurement System

In order to control the temperature of the test liquid, the whole delay line assembly was submerged in a oil-filled constant temperature bath. The bath, designed in the Department of Mechanical Engineering, University of Manitoba, had one 4 Kilowatt heater and two separately connected 600 Watt heaters. The 4 Kilowatt heater, controlled by an on-off switch, was used only for rapid heating. The two 600 Watt heaters were connected in parallel to a temperature controller. The oil in the bath was kept in continuous motion by two motor-driven propellers to ensure temperature equilibrium for the entire bath. The controller had three control nodes; on-off proportional, and proportional with reset. It uses a nickel resistance thermometer sensing element as the variable arm in an A.C. Wheatstone bridge circuit which is operated at balance by means of an adjustable ratio arm which selects the temperature setting.

The temperature of the oil bath, or at equilibrium, the temperature of the test liquid, was measured by a precision, four lead, platinum resistance thermometer calibrated by National Research

Council, Ottawa. The resistance of the platinum resistance thermometer was determined by a Mueller Bridge which reads to 0.0001 Ohm with a mercury commutator to nullify the effect of the unequal lead resistances. An electronic D-C null detector was used to ascertain the balance of the Mueller bridge.

The procedure of controlling the oil bath temperature during the test is as follows: The resistance of the platinum resistance thermometer corresponding to the required temperature was preset on the Mueller bridge. The temperature controller was then set to the approximate required temperature according to the calibration curve provided. The bath was allowed to reach a steady state condition and the D-C null detector indicated when the bath temperature attained the approximate preset value. A trial and error adjustment of the setting of the temperature controller was then made to attain the desired temperature as indicated by a zero deflection of the null detector. The bath was assumed to have reached a steady state when the temperature did not vary by more than $\pm 0.003\ ^{o}C$.

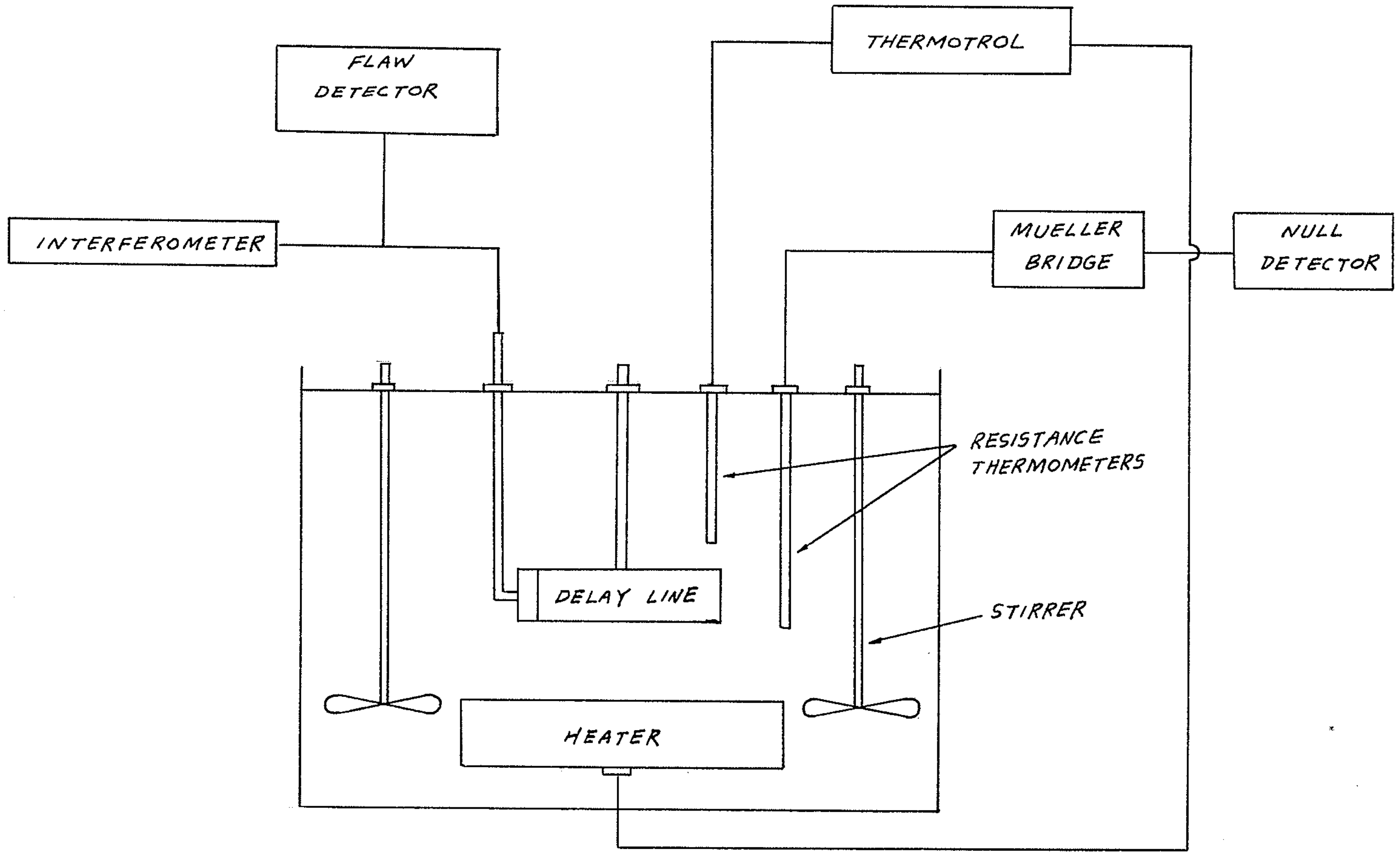


Fig. 3.8 Schematic arrangement of the experimental system

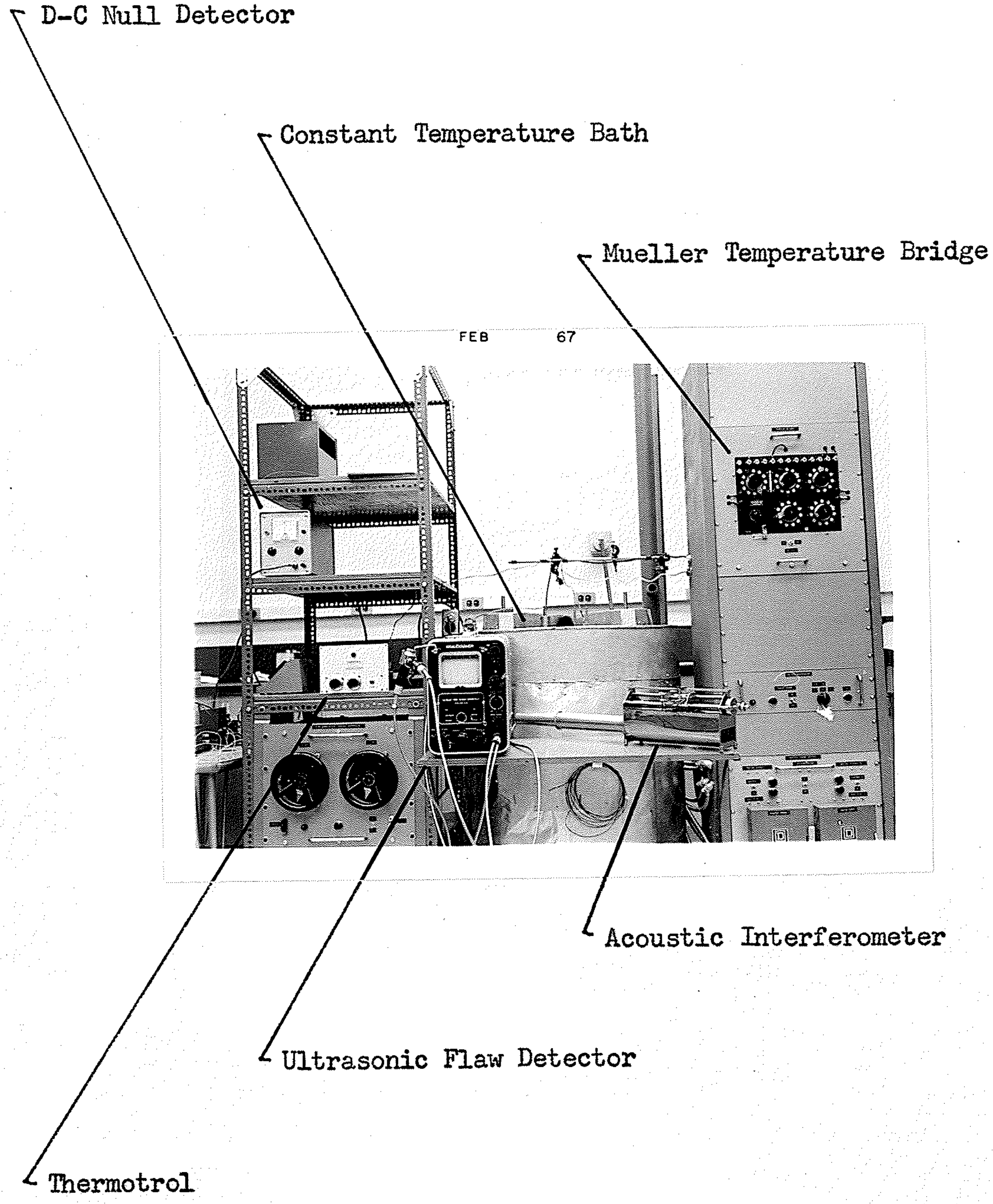


Fig. 3.9 The experimental system

3.5 Experimental Techniques

Before filling, the delay line was thoroughly cleaned with solvents, using the test liquid for the final rinse and, after filling, was suspended in the oil bath. The oil bath was then heated to the required temperature and controlled to within ± 0.003 °C by the method previously described. Fig. 3.8 shows a schematic arrangement of all instruments employed.

The reflector of the acoustic interferometer is spring mounted at three points, two of which are eccentric and adjustable by means of a knurled knob. After adjustment the eccentrics must not be re-adjusted, since the multiple echoes from the reflector are very sensitive to the adjustment. The variable path extension was adjusted to such a position that the first concidence occurred when the reflector was approximately at the beginning of the useful range of the interferometer.

The range of the fluorescent screen on the flaw detector was selected to display two echoes from the delay line. The pulse energy was set at different levels depending on the liquid samples. For highly absorptive liquids, for example benzene and carbon tetrachloride, a high pulse energy was required. The high-frequency filter was set so that high frequency cycles of the pulse, which corresponded to the original ultrasonic vibrations, could be viewed clearly on the screen. The amplifier threshold control was used to eliminate all the noise signals from the screen trace.

The interferometer echo was brought close to the first echo from the delay line by adjusting the reflector of the interferometer and that particular portion of the screen was then expanded using scale expansion. The position of the superimposed echoes on the screen did not, in any way, affect the accuracy. Any high-frequency node on the rising flank of the echoes could have been used as the reference point for setting the coincidences, but preferably the strongest cycle, because it was easier to identify. Before bringing the echoes into an exact coincidence, the echo from the delay line was first adjusted by the gain control to about half of the screen height, and the echo from the interferometer was also adjusted by means of the attenuator to about the same height. In this case, the exact coincidence of the strongest cycle of each echo brought the echo to the full height of the screen. This "tunning" was very sharp and there was no doubt as to the exact point. A reading on the interferometer scale was taken at this position. The second reading was obtained when the interferometer echo coincided with the second delay line echo on the corresponding node. Procedure for setting the second coincidence was same as for the first one. The interferometer spindle was always brought into reading position from the same direction in order to eliminate backlash.

For each temperature the measurement was repeated three times. The average of the three readings was used to calculate the velocity of sound in the test liquid by Eq. (3 - 1).

Fig. 3.10 (a) shows the first and second echoes from both delay line and interferometer. Fig. 3.10 (b) shows the first echoes from both delay and interferometer with scale expansion. Fig 3.10 (c) shows the best achievable coincidence of the two echoes. Fig. 3.10 (d) shows the coincident echo when it was slightly less exact.

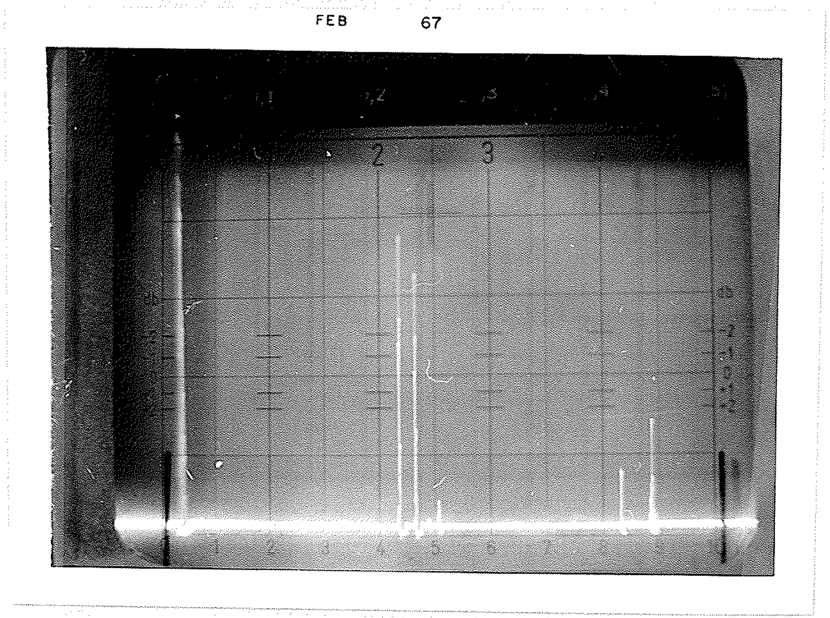


Fig. 3.10 (a) First and second echoes from delay line and interferometer.

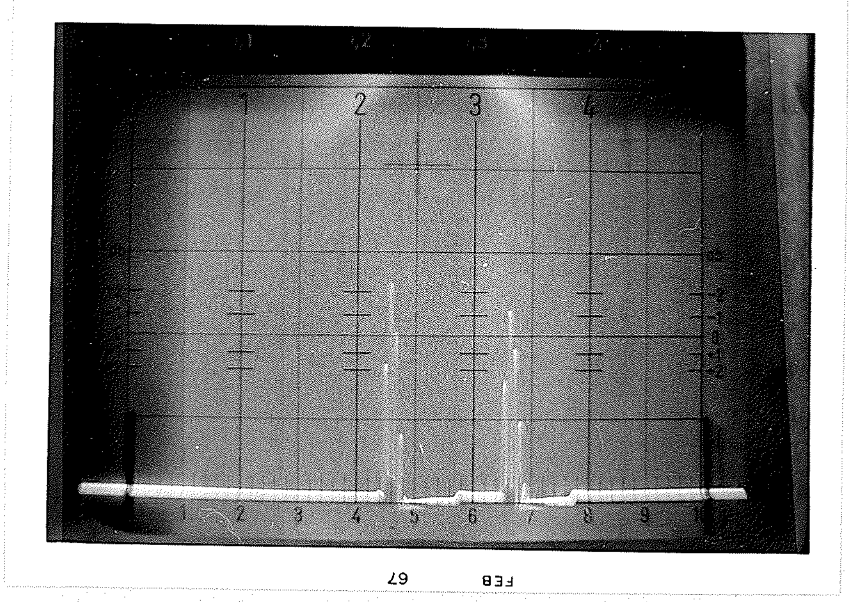


Fig. 3.10 (b) The first echoes from delay line and interferometer with scale expansion.

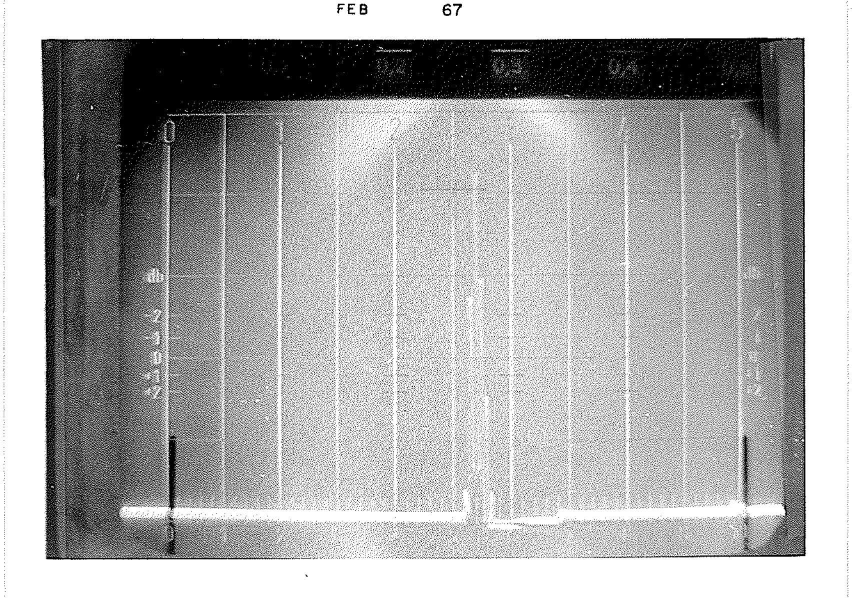


Fig. 3.10 (c) The best achievable coincidence of two echoes.

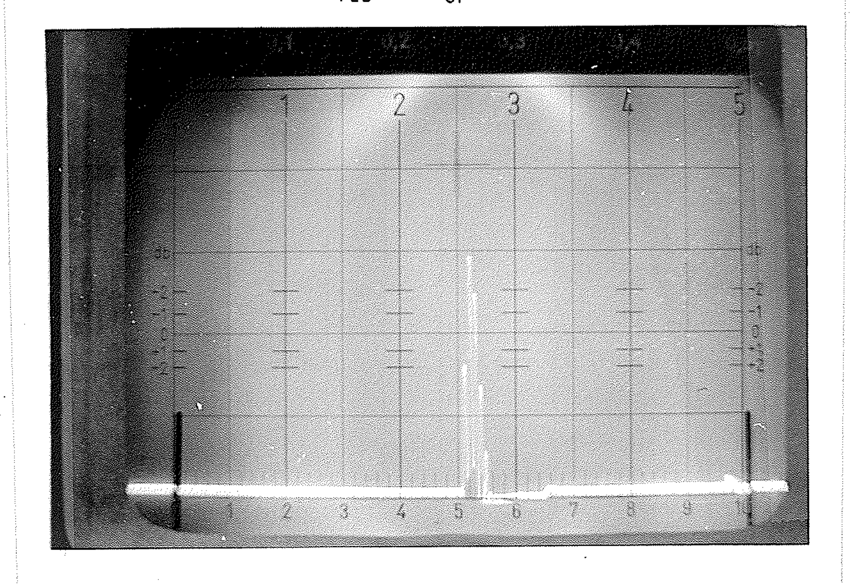


Fig. 3.10 (d) The coincident echo when it was slightly less exact.

IV PRESENTATION AND DISCUSSION OF THE EXPERIMENTAL RESULTS

The measurements were made on the following five organic liquid samples at five degree centigrade increments:

Benzene	40°C - - - 75°C
Toluene	40°C - - - 105°C
Xylene	40°C - - - 135°C
Carbontetrachloride	40°C - - - 70°C
Biphenyl	90°C - - - 140°C

Benzene, toluene, xylene and carbon tetrachloride were obtained from Fisher Scientific Company and biphenyl from Eastman Organic Chemicals. No attempt was made to purify the liquid samples. The velocities of sound were calculated according to the equation:

$$V = \frac{L_d}{L_w} V_w$$

The experimental results thus evaluated are plotted against temperature on Fig. 4.1 to Fig. 4.5.

The errors in the measurement of each quantity entering the above equation contribute toward the total experimental inaccuracy. Estimates of the upper limits of these errors are given in the following.

4.1 Discussion of Errors

Length of the delay line (L_d) - The length of the delay line as stated previously was 3.999 ± 0.001 in. at 22 °C. The uncertainty is therefore ± 0.025 per cent. The increase in path length due to thermal expansion in the brass wall of the delay line was calculated in the usual manner assuming a linear expansion coefficient of 0.000019/ °C. The maximum error introduced by this was estimated to be within ± 0.025 per cent. The variation of the bath temperature did not contribute any significant error to the path length. Therefore, the maximum possible error in the length of the delay line was ±0.05 per cent.

Path length of the interferometer (L_w) - There are two possible errors affecting the path length of the interferometer; the error in obtaining the exact coincidence of the echoes and the error in reading the scale of the interferometer. Each measurement was repeated three times as described previously, it was found that the readings did not deviate by more than ± 0.04 mm from the average. The L_w varied from 115 mm to 193 mm depending on the liquid sample and the temperature. The maximum error in L_w was therefore not more than ± 0.035 per cent.

The velocity of sound in water (V_w) - The temperature of the water in the interferometer was measured with a mercury thermometer. For each interferometer path length reading, a temperature reading of the water was taken at the same time. The corresponding values of the sound velocity in water were obtained by interpolation from the table given by Greenspan and Tschiegg. The linear interpolations were performed in the manner suggested, and accordingly the error was estimated to be not more than ±0.05 m/sec for each velocity interpolated. The temperature of the water could be measured to within ± 0.2 °C. With a temperature coefficient of 2.5 m/sec °C, the absolute error amounted to ± 0.5 m/sec. Therefore the maximum error in the velocity of sound in water, which is roughly 1480 m/sec, was not more than ± 0.038 per cent.

Apart from the errors discussed above, there were also errors in obtaining the desired temperatures. The Mueller bridge with which the resistance of the platinum resistance thermometer was measured has an accuracy of ± 0.02 per cent of readings from one ohm to 81.111 ohms. At the highest temperature of measurement the error amounts to about ± 0.008 ohm which was equivalent to about ± 0.08 °C. The variation of the bath temperature, which was controlled to within ± 0.003 °C, did not introduce significant error especially when thermal lag exists between the heat sink and the test liquids. The error in the calibration of the platinum resistance thermometer itself is negligible. The error in the resulting velocities due to temperature measurement differed from liquid to liquid depending on the temperature, the temperature coefficient of the velocity and the absolute magnitude of the velocities. However, the largest error did not exceed ± 0.036 per cent.

4.2 Accuracy of Results

Combining all the known errors in the foregoing discussion, the maximum error in the velocity of sound was estimated to be about ±0.16 per cent. Allowing for some unknown errors, eg., purity of water and liquid samples used, assembly of the delay line, precision of the interferometer, etc., it is felt that the overall accuracy of this work was better than ±0.2 per cent.

The data that are available are mainly from older works. However, some of the data for benzene, toluene, and carbon tetrachloride obtained by Lagemann, and by McMillan, Jr. and Woolf[18] and by Freyer, Hubbard and Andrews[21] are plotted on the graphs showing the results of this work. (Fig. 4.1, Fig. 4.2 and Fig. 4.4). It can be seen that the results of this work was consistently lower, and the largest deviation, that of benzene, was found to be 0.65 per cent from the value of Lagemann and co-worker. However, their data was found to be slightly higher. Comparison with the data of Freyer, Hubbard and Andrews shows the largest deviation from their work is -0.44 per cent for toluene. However, there is no reason to suspect the accuracy of ±0.2 per cent calculated for these results.

As a check on the reliability of the method and apparatus of the present work, determination of the velocity of sound in pure water was made. Water was chosen because it is the only liquid for which accurate data of sound velocity have been recently determined by several different investigators. The results for water as shown in Fig. 4.6 agree within the estimated error with the data of Greenspan and Tschiegg[20] which has an accuracy of one part in 30,000.

In an attempt to find out the causes for the discrepancy, the following had been observed: For water, because of its higher velocity, a smaller range on the fluorescent screen was used, and therefore, when using scale expansion, the high-frequency cycles of the pulse train were larger and more clear. Water is much less absorptive and consequently the second echo from the delay line is still quite strong. In setting the second coincidences, little amplification was needed. For the organic liquids tested a larger range had to be used due to their lower velocity and hence pulse trains were not as large and clear as those for water. More important, the second echoes from the delay line were rather weak due to their high absorptivity, especially for benzene and carbon tetrachloride. In bringing into coincidence they were first amplified considerably. By doing so the general shape of the pulse train usually changes. The high-frequency nodes, which were used as reference points for setting the coincidences, were displaced slightly or some other high-frequency cycle appeared to be the strongest one. For this reason, it was believed the discrepancy resulted. This speculation was reasonably supported by the fact that the deviations were unidirectional.

In spite of the drawback discussed above, the presented results of this work were believed to be good within ±0.5 per cent.

4.3 Suggestions for Improvement

The crystal in the delay line was found to be unsufficiently damped and produces long pulse trains. It was clamped around the circumference for a width approximately equal to $\frac{1}{4}$ of its diameter. This would reduce the effective area of the crystal and tend to make it resonate at a higher frequency than it was cut for. For better performance of the experimental set up, the following modifications are suggested:

(1) The crystal should be clamped around the circumference for not more than 1/16 in. and its damping be greatly increased.

(2) The delay line should be made shorter than the existing one. This would result in a considerably stronger second echo due to a shorter path length and permit the use of a smaller range on the fluorescent screen. A shorter path length would also greatly increase the velocity range that can be measured.

(3) The temperature control and measurement system, which was found to be inconvenient and time-consuming, should be improved.

(4) The temperatures of the oil bath and water in the interferometer, which had contributed significant errors in the present work, should be determined more accurately.

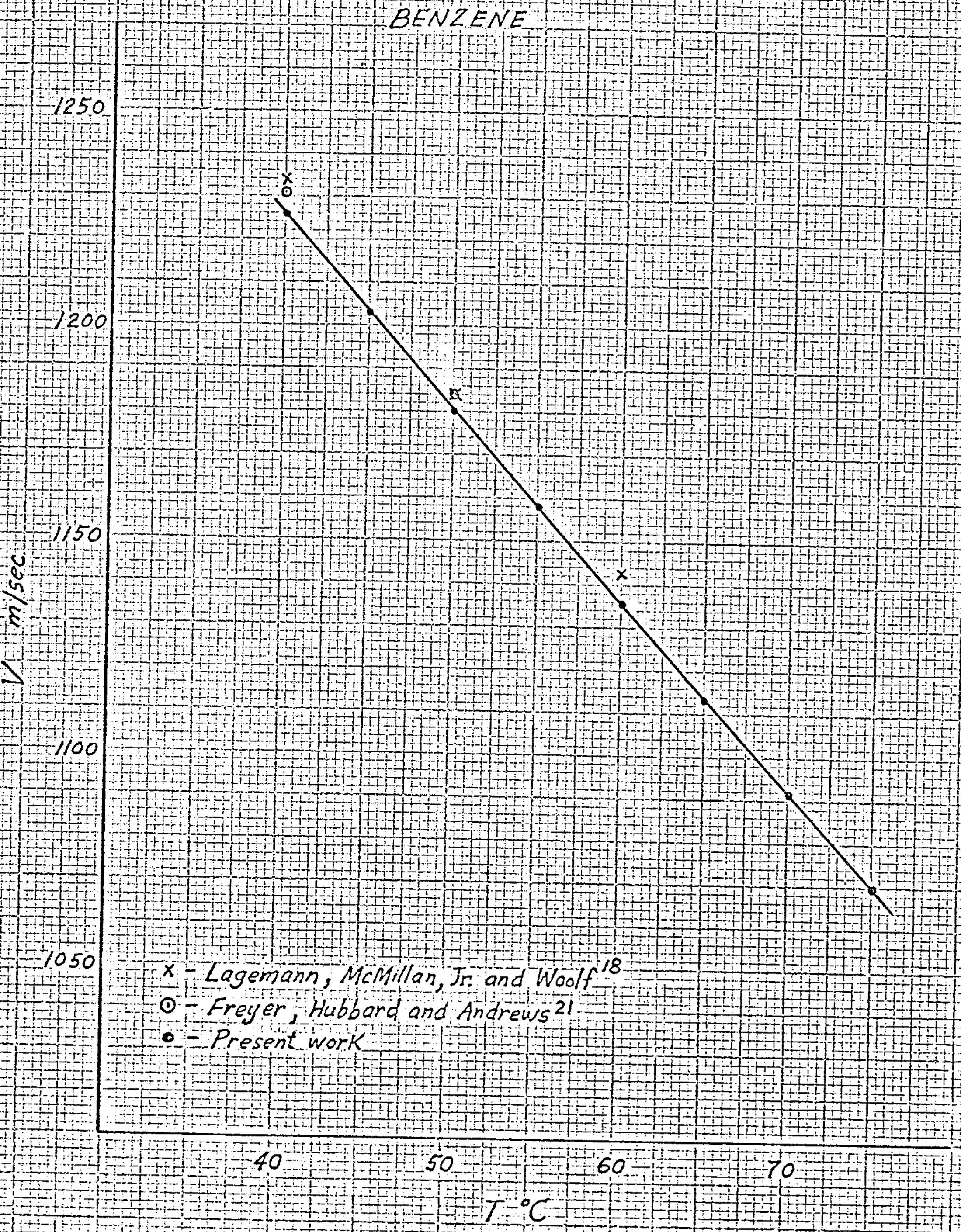


Fig. 4.1 Plot of Velocity VS Temperature for Benzene

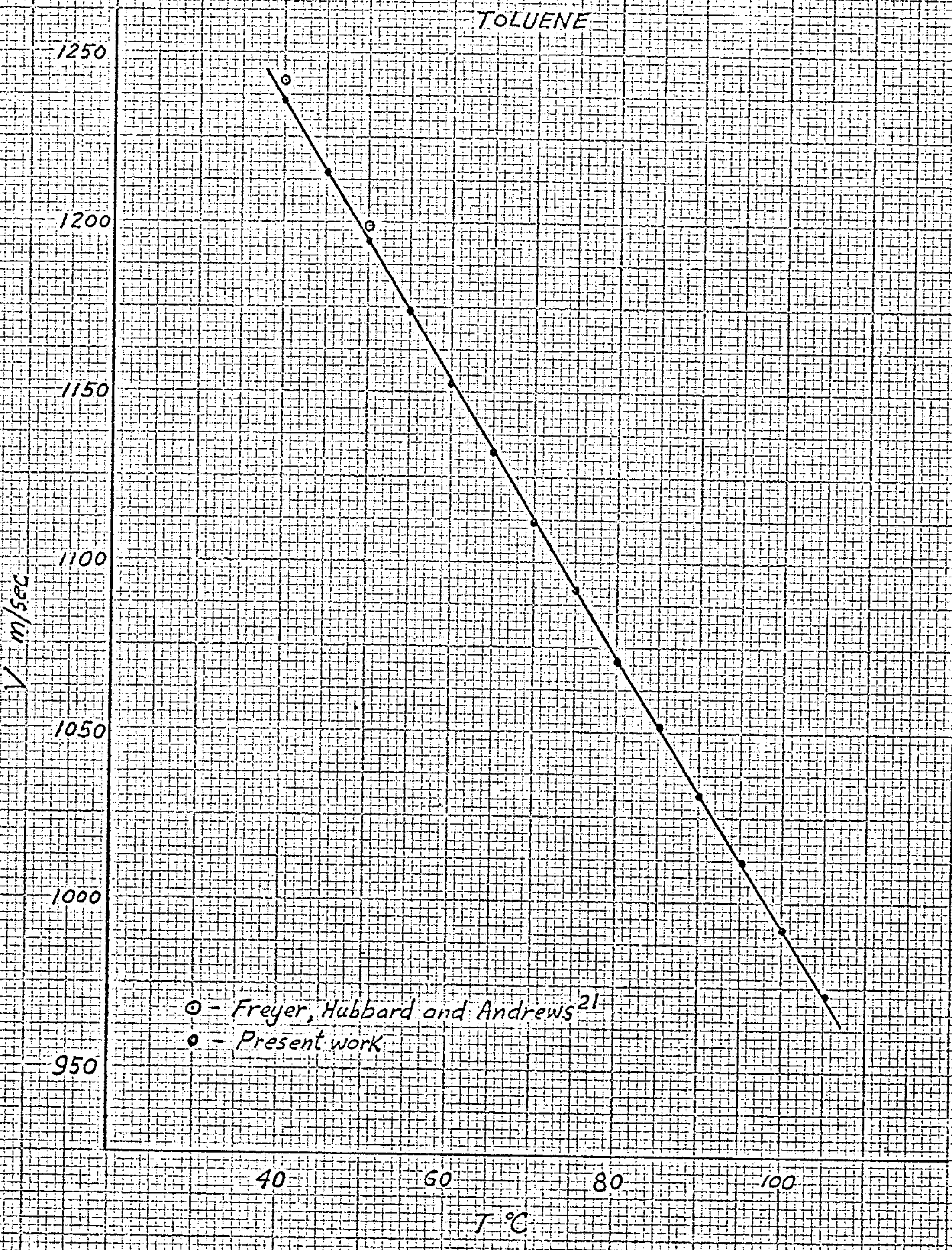


Fig. 4.2 Plot of Velocity VS. Temperature For Toluene.

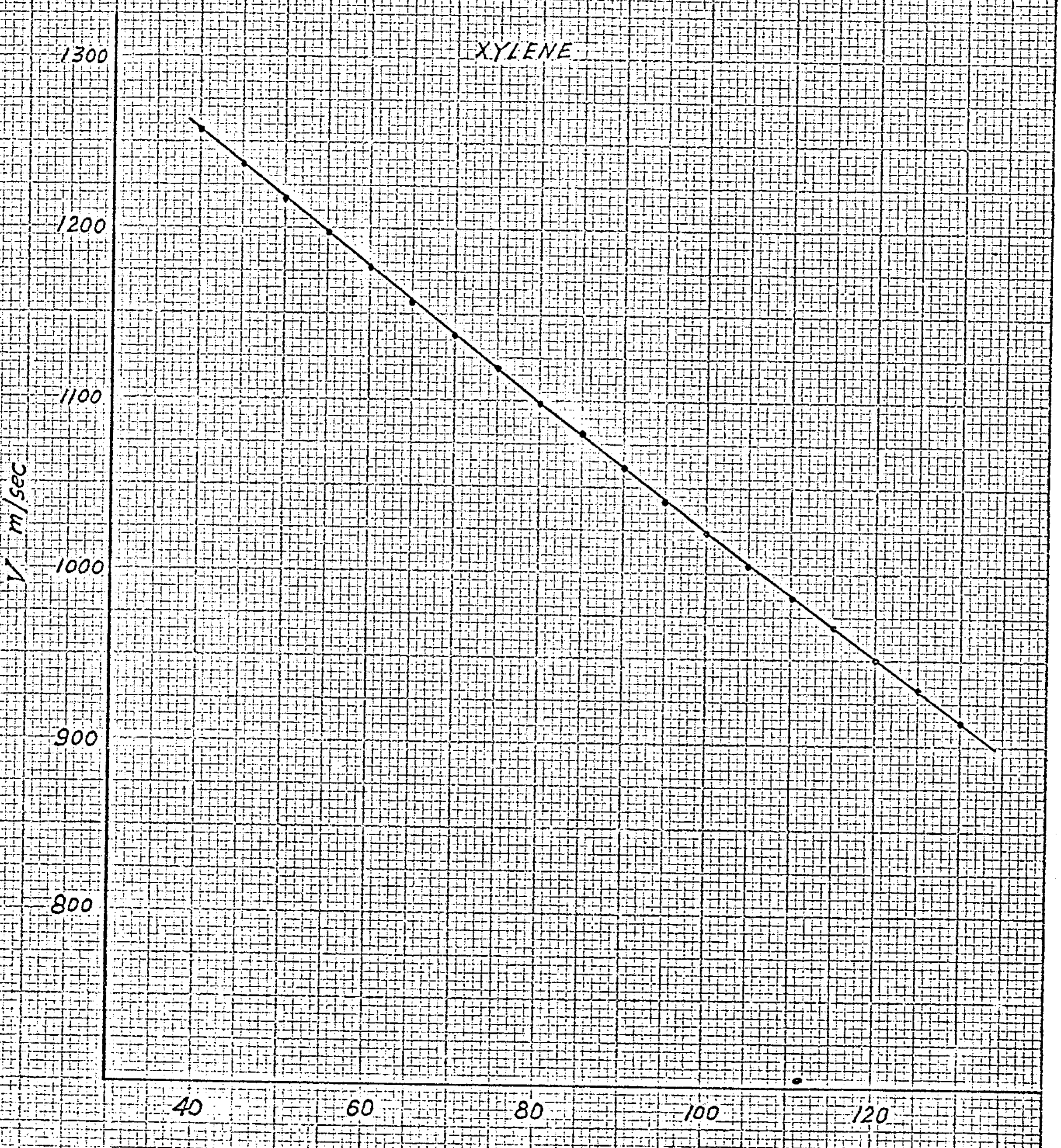


Fig. 4.3 Plot of Velocity VS Temperature for Xylene

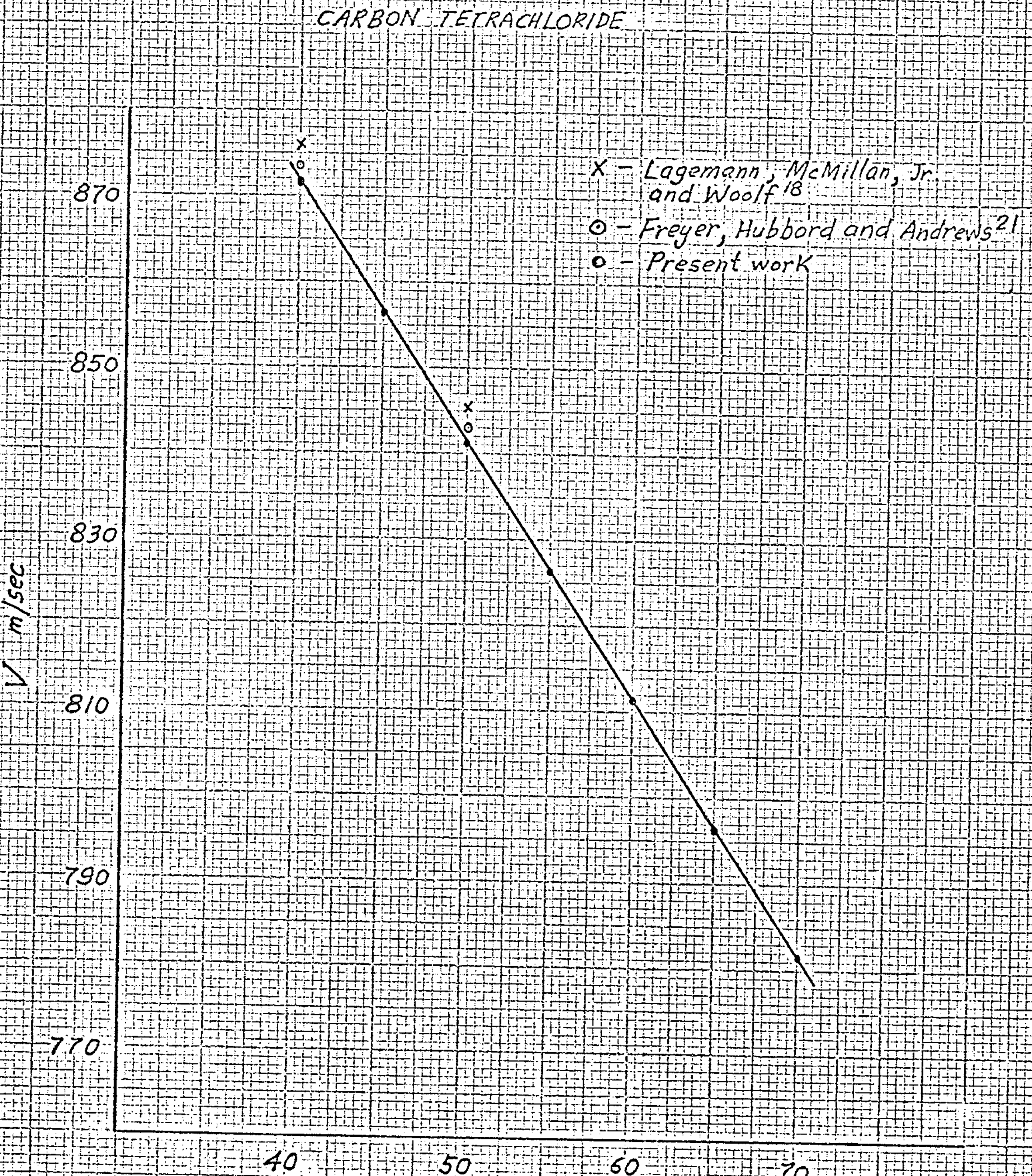


Fig. 4.4 Plot of Velocity VS Temperature For Carbon Tetrachloride

Fig 4.5 Plot of Velocity Vs Temperature For Biphenyl

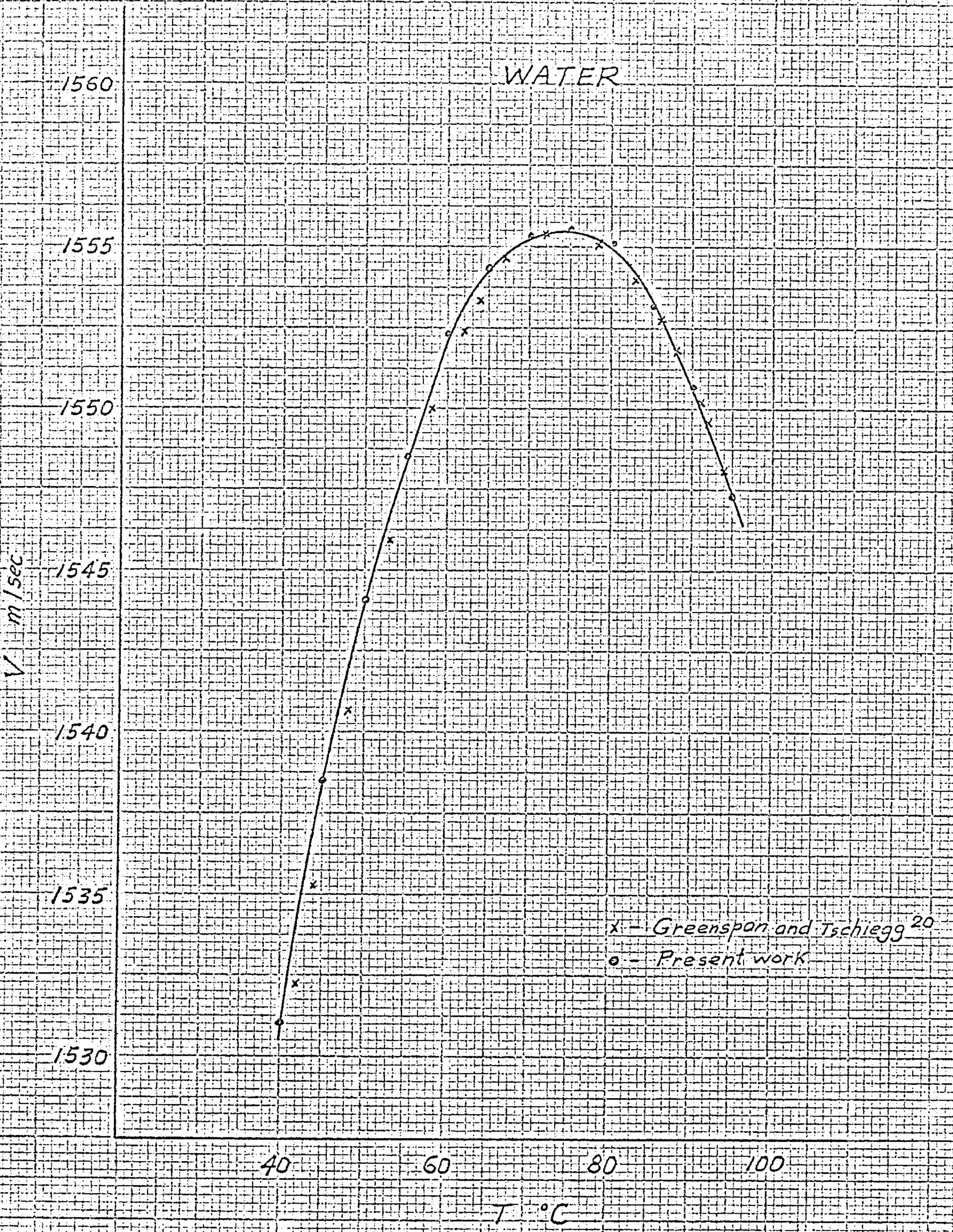


Fig. 4.6 Plot of Velocity VS Temperature For Water

V DISCUSSION ON THERMAL CONDUCTIVITY AND VELOCITY OF SOUND IN LIQUIDS AND THEIR CORRELATION

The velocity of sound in fluids is given by the general hydrodynamic formula as:

$$V = \left(\frac{\partial P}{\partial \rho}\right)_s^{1/2} = \left(\frac{\gamma}{\rho \beta_t}\right)^{1/2} = \left(\frac{1}{\rho \beta_s}\right)^{1/2} \quad \ldots\ldots \quad (5-1)$$

where P is the pressure; ρ is the density of fluid, γ is the ratio of specific heat at constant pressure to that at constant volume; β_t is the isothermal compressibility; and β_s is the adiabatic compressibility. The data of adiabatic compressibilities and γ's are usually more difficult to obtain than the velocity of sound. Hence, in the past, measurement of velocity of sound was mainly used for determination of the adiabatic compressibility from which the ratio of the specific heats may be found provided the isothermal compressibility is known. However, for organic liquids, Rao [22] found that the temperature coefficient of the velocity of sound is about three times the temperature coefficient of the density, or

$$\frac{1}{V}\frac{dV}{dT} = 3\,\frac{1}{\rho}\frac{d\rho}{dT}$$

integrating, $\dfrac{V^{\frac{1}{3}}}{\rho}$ = constant multiplying both sides by the molecular weight M, results in

$$V \frac{M}{\rho} = R \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (5 - 2)$$

where R', which is known as Rao's constant or molecular sound velocity, is substantially independent of temperature, and is an additive function of the molecular structure. The molecular structural contributions for estimating R were given by Sakiadis and Coates[6]. However, Eq. (5 - 2) can not be used if accurate velocity data are required.

The effect of temperature on the velocity of sound in liquids has been studied extensively by many workers. For most organic liquids the relationship is essentially linear, the velocity decreasing with increasing temperature, as found experimentally in this work. However, close examination of the present data shows that the numerical magnitude of the temperature coefficient has a tendency to decrease slightly at higher temperature where no data has been reported previously. In other words, the velocity of sound deviates slightly from linear relationship with temperature when approaching the boiling point. There was no indication that free convection might affect the propagation of sound waves. Besides the measurements were carried out under the steady state conditions. Non-linearity of velocity with temperature at very low temperature has also been reported[23]. Considerable work has been done in finding a relation between the temperature coefficient of the sonic velocity and other physical properties. Lagemann, McMillan, Jr. and Woolf[18] pointed out that there is a general tendency for the numerical value of the temperature coefficient of the sonic velocity to decrease with an increase in molecular weight of the liquids, and found the following empirical relation connecting them:

$$\left|\frac{\Delta V}{\Delta T}\right| M^{\frac{1}{2}} \approx 39 \quad \ldots\ldots\ldots\ldots\ldots \quad (5-3)$$

The relationship does not hold for highly associated liquids, and the general agreement is only considered fair.

The relationships between the velocity of sound and other physical properties such as van der Waal's b, boiling and critical points, etc., has also been investigated by Lagemann and Dunbar.[24] It was hoped that all these efforts would lead to better understanding of the liquid state. However, Lagemann[25] concluded later that there appeared to be no generalized theory relating the sonic velocity to molecular structure.

With regard to the thermal conductivity of liquids, the situation is even less satisfactory. Although it is generally accepted that in liquids, as in gases, the thermal conduction is due to the movement of the molecules and atoms, but the behavior of their thermal conductivity shows a clear distinction. The thermal conductivity of most organic liquids decreases with increasing temperature similar to that of dielectric solids. This is in contrast to the thermal conductivity of gases which increases with rising temperature. The same is true for viscosity which decreases with a rising temperature for liquids and increases for gases. Therefore, the theoretical relation between the thermal conductivity and viscosity of gases does not hold for liquids. The viscosity of liquids is much more sensitive to temperature than is their thermal conductivity. For most organic liquids, the variation of thermal conductivity with temperature is essentially a linear one. Riedel[26] found that it could be represented empirically by the equation

$$\frac{k}{k_c} = 1 + 6.7 \left(1 - \frac{T}{T_c} \right)^{2/3} \quad \ldots\ldots\ldots\ldots \quad (5 - 4)$$

where T_c is the critical temperature and k_c is an empirical parameter which has formal significance of the thermal conductivity at the critical temperature. Eq. (5 - 4) may be used to estimate the value of k at a certain temperature if one experimental value is known.

The existence of many variables, of which the thermal conductivity appears to be a function, has made its prediction difficult. Molecular weight has long been considered to be one of the most important properties and the thermal conductivity usually decreases with increasing molecular weight. However, there are many exceptions; a plot of thermal conductivity vs molecular weight for a series of compounds showed a succession of sharp minima and maxima[27] indicating that more than molecular weight is involved. The early attempt to correlate the thermal conductivity of liquids to other data was made by Weber[28]. He first suggested that $\frac{k}{c_p}$ is constant for liquids, and later modified it to

$$k = A \rho c_p \left(\frac{\rho}{M}\right)^{1/3} \quad \dots\dots\dots\dots\dots\dots \quad (5 - 5)$$

where A is a constant; ρ is the density of liquids, c_p is the specific heat at constant pressure; and M is the molecular weight. The equation tends to give high values for associated liquids and low ones for normal liquids. More extensive experimental data revealed that A is not, in fact, a universal constant, it differs for different classes of substances and is a function of temperature. The equation was modified by Palmer[29] to take account for the effect of association by introducing the entropy of vaporization at normal boiling point ΔS. The equation becomes

$$k = A \rho c_p \left(\frac{\rho}{M}\right)^{\frac{1}{3}} \frac{21}{\Delta S} \quad \ldots\ldots\ldots \quad (5-6)$$

where 21 is known as the Trouton constant. A comparison of values obtained by the use of Weber's and Palmer's equation with experimental values, compiled from more recent references, was given by Reid and Sherwood.[16] The agreements were far from satisfactory. Weber's equation had a smaller average error of ± 13 per cent, but errors as large as 49 per cent were found. Palmer's equation, which usually yielded much larger values of k than were found experimentally, had an average error of ± 18 per cent. There appears to be no sound theoretical basis for this type of relationship. However, it has served as a starting point for other empirical correlations.

A further modification of Weber's equation has recently been proposed by Krishnaumurthy and Venart.[30] The modified equation is

$$k = \phi \left(\frac{T_c}{T}\right)^N \rho \quad c_p \left(\frac{\rho}{M}\right)^{\frac{1}{3}} \quad \frac{21}{\Delta S} \quad \ldots \quad (5-7)$$

where ϕ is a parameter, the value of which depend upon the structural contribution or position contribution of the molecules;

$\left(\frac{T_c}{T}\right)^N$ is a reduced temperature term to account for the temperature effect, the value of N varies according to the density of liquids and has a value of 0.95 for straight chain hydrocarbons. The modification was made from the fact that A in the Weber's equation is not a universal constant; it differs for various liquids and is a function of temperature. Therefore, the modification appears to be quite logical. A comparison of values obtained by the use of Eq. (5 - 7) with experimental values for 200 liquids gave an average deviation of ± 3.5 per cent. The agreement is remarkable.

The foregoing discussion showed that the empirical relations proposed, either give unsatisfactory results, or are very complex and require more empirical and experimental data. While Bridgman's equation, which has a certain theoretical basis, is much simpler and, as discussed previously, proved to be more interesting and practical than other theoretical equations which originated from the same consideration of energy transfer. In Bridgman's equation, the sonic velocity and density are the only variables for which experimental values must be known. For this reason, Bridgman's equation is studied in this work thoroughly.

Bridgman's equation with Boltzman constant equal to 1.38×10^{-23} Joule/C, can be written as

$$k = 0.9845 \times 10^{-7} \, n \, V \left(\frac{\rho}{M}\right)^{\frac{2}{3}}$$

The thermal conductivities of the liquids in which the velocities of sound were determined in this study are plotted against $V \left(\frac{\rho}{M}\right)^{\frac{2}{3}}$ in Fig. 5.1. The values of thermal conductivities were obtained from Riedel [26,31], Horrocks and McLaughlin [32], and Challoner and Powell [33]. The availability of these accurate thermal conductivity values was the reason for selecting the specific liquids tested. Bridgman's equation gives a much higher numerical value of temperature coefficient. The points show a considerable scatter, and differences in slopes for some liquids were noted. The points for biphenyl are considerably apart from the line of benzine. This was mainly due to its high molecular weight. Therefore, larger deviation would be expected for terphenyls (polyphenyls), since the thermal conductivity and sonic velocity do not change appreciably with the chain length. A plot of k vs. $V \left(\frac{\rho}{M}\right)^{\frac{1}{3}}$ for the same liquids showed the scatter is larger and the author could see little prospect of reducing the scatter by modifying the exponent of $\left(\frac{\rho}{M}\right)$. The high temperature coefficient given by Bridgman's equation is obviously due to a too sensitive change of sound velocity with temperature. This fact suggests that more than velocity of sound is involved for a correct temperature coefficient of thermal conductivity. However, it is remarkable that the unusual variation of thermal conductivity of water with temperature, which is a parabolical one, is also exhibited by the velocity of sound in water. Thus, Bridgman's equation provides, so far, the most convincing argument as to the behavior of thermal conductivity of water. However, glaring exceptions were noted. Glycerine, for example, which has a positive temperature coefficient of thermal conductivity, has a negative temperature coefficient of velocity. A satisfactory explanation of the phenomena has not yet been found.

In Fig. 5.1 the lines of benzene, toluene, and xylene, which belong to the same family of aromatic hydrocarbons, lie close to each other and have essentially the same slope. It was therefore possible to obtain an expression of the form $k = A + B\,V\left(\frac{\rho}{M}\right)^{\frac{2}{3}}$, where A and B are constant, which would well represent the thermal conductivity and their variation with temperature for benzene hydrocarbons. An estimation, with proper choice of A and B, indicates that the agreement is within ±3 per cent. Therefore, it is felt that works on some other series of liquids would be valuable. They could lead to a further understanding of the relation between the thermal conductivity and the sonic velocity and verify whether the case of benzene hydrocarbons is just coincidental.

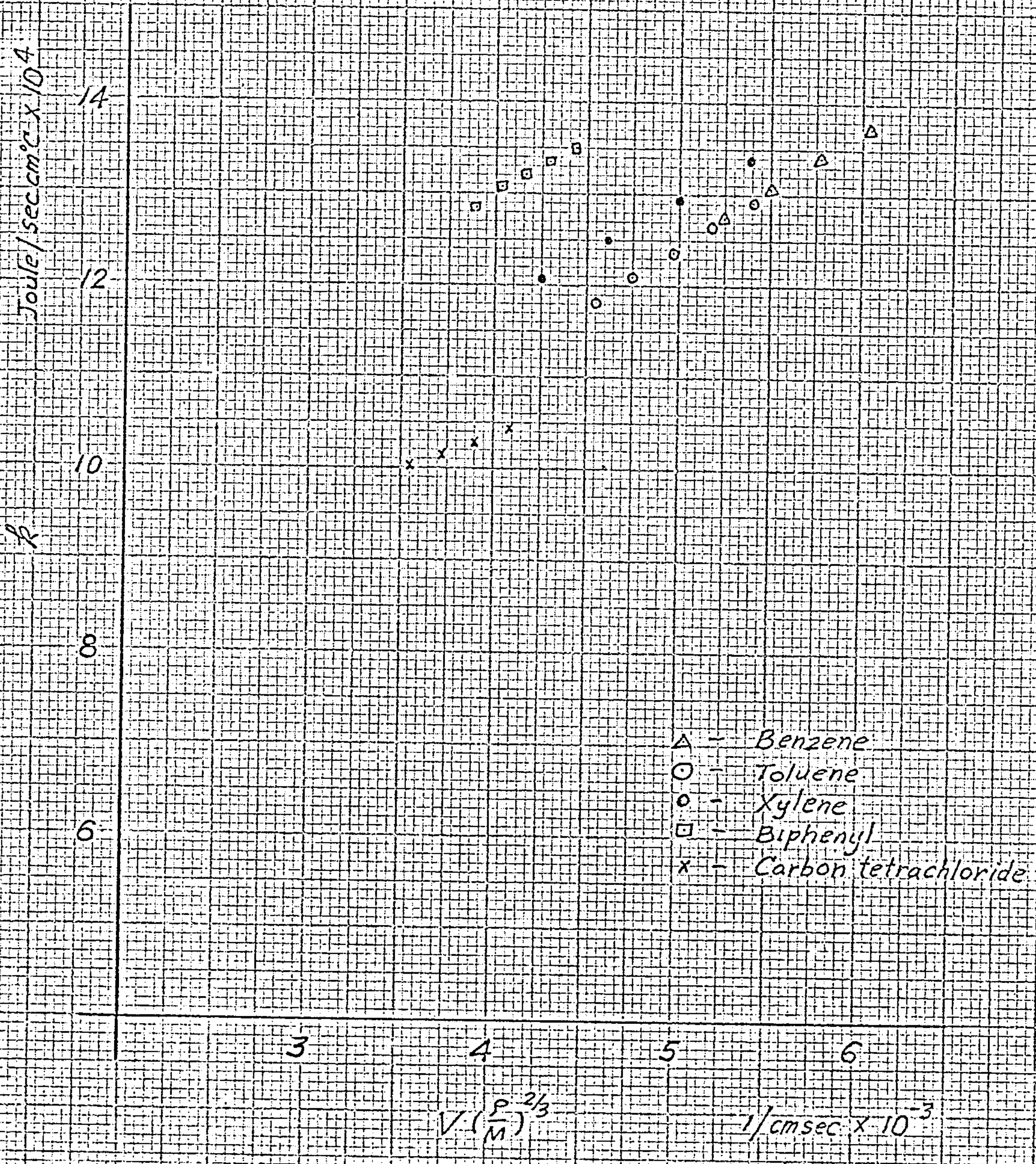


Fig 5.1 Plot of k vs $V\left(\frac{\rho}{M}\right)^{2/3}$

The previous check of Bridgman's equation by Tyrrell[14] was arbitrarily made at 30 °C. Since Bridgman's equation does not give the correct temperature coefficient, the agreement between the calculated and experimental values are different at various temperatures. Figs. 5.2, 5.3 and 5.4 show comparison of experimental values with that calculated by Bridgman's equation using $n = 2$ at 0 °C, 20°C and 40°C respectively. Four more liquids (methyl alcohol, acetone, chlorobenzene and bromobenzene), for which reliable data on both thermal conductivity and the sonic velocity were available at these temperatures were added for comparison. It can be seen that the calculated values were consistantly lower than the experimental values, and the deviations increase considerably with temperature. The average errors were found to be - 9.4 per cent, - 12.93 per cent and - 17.6 per cent at 0 °C, 20 °C and 40 °C respectively. With $n = 3$, the check was repeated at 20 °C as shown on Fig. 5.5. The calculated values are now consistantly much higher than experimental ones with average deviation of + 30.9 per cent. Comparison made by Sakiadis and Coates [6] with $n = 3$, at unspecified temperature, gave an average error of ± 15 per cent for 28 liquids. Although the temperature at which the comparison is made is essential, the large discrepancy shown above is probably due to the lack of reliable values of thermal conductivity. Data of Sakiadis and Coates on thermal conductivity of liquids, as pointed out by Challoner and Powell,[33] are usually higher than those

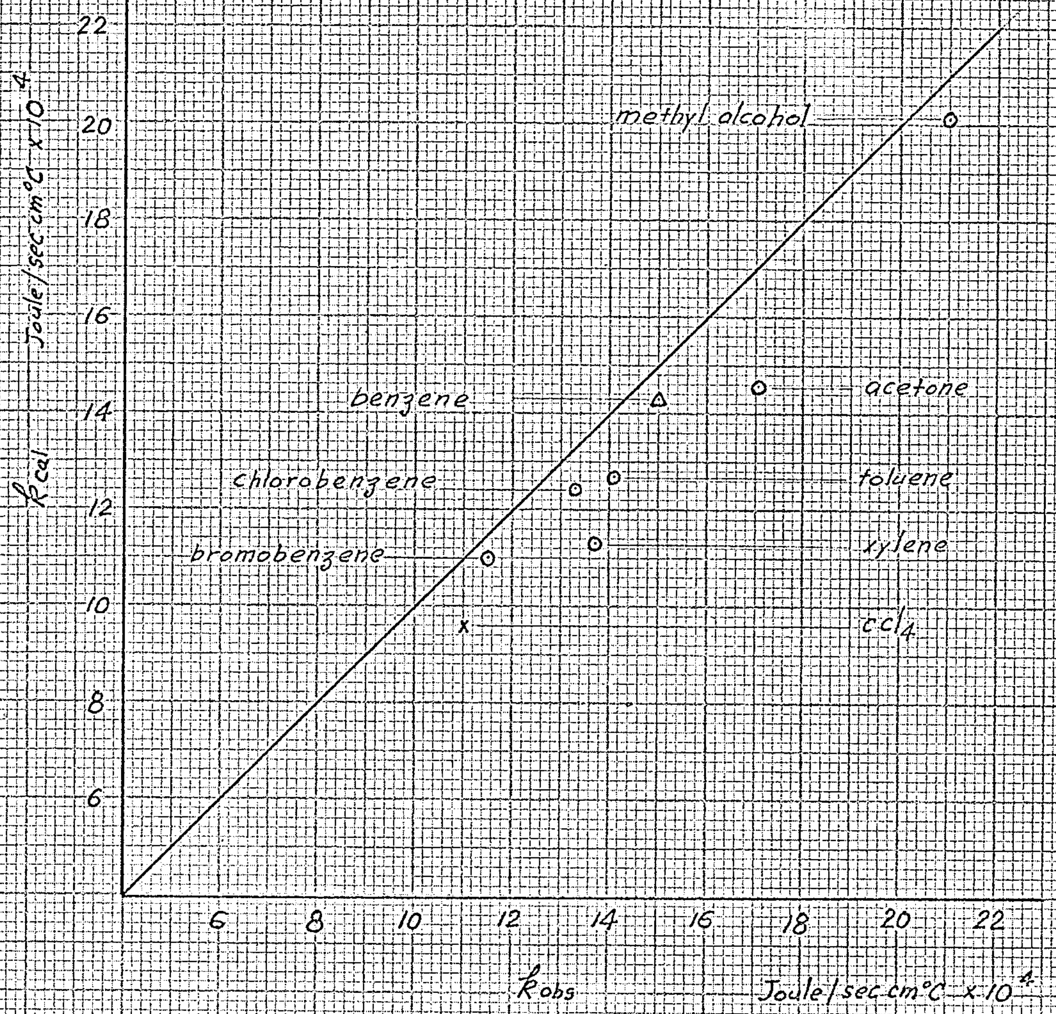


Fig. 5.2 Test of Bridgman's equation with n=2 at 0°C

⊙ - Riedel[26,31]
Δ - Horrocks and McLaughlin[33]
x - Challoner and Powell[32]

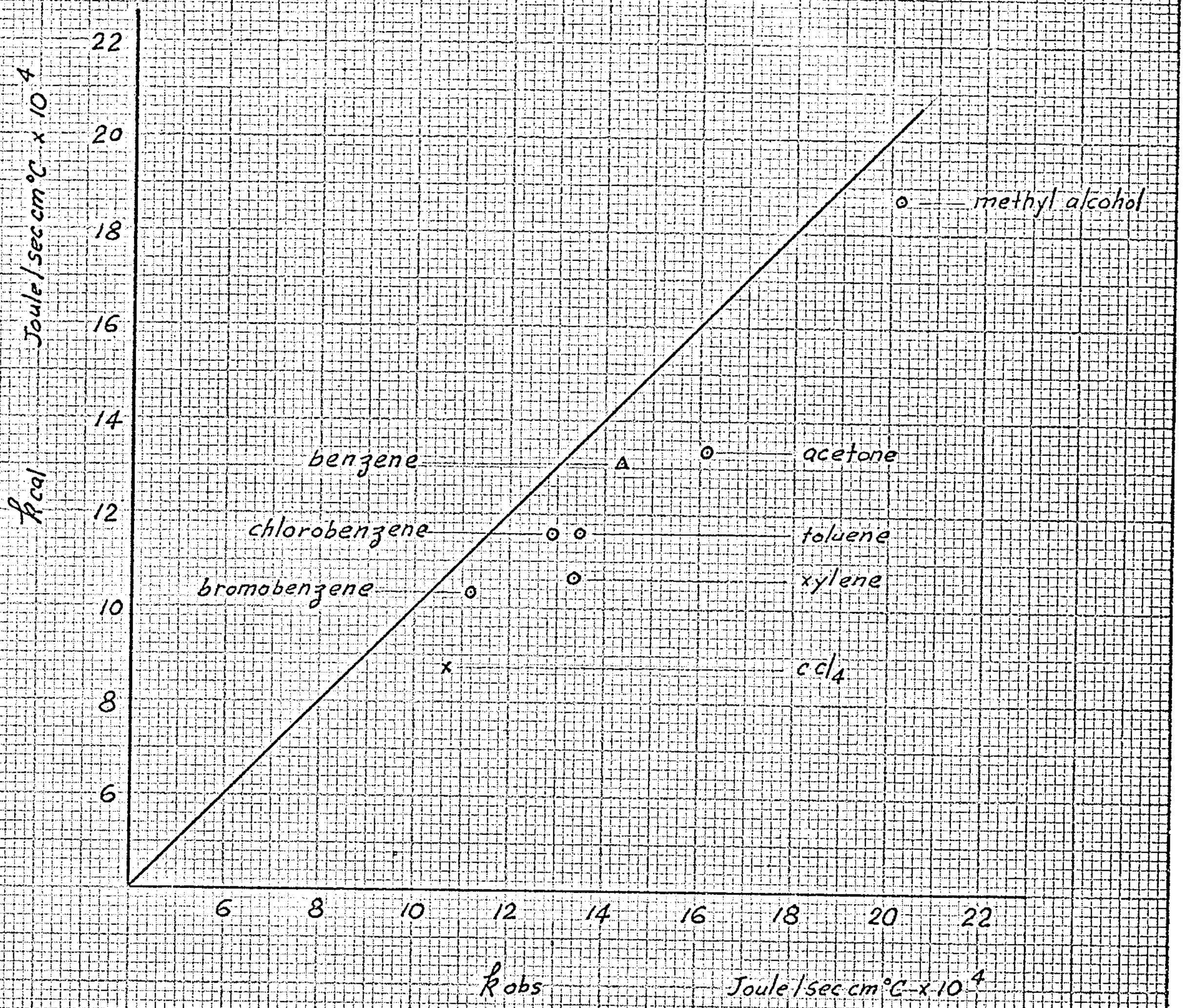


Fig. 5.3 Test of Bridgman's equation with n = 2 at 20 °C

○ - Riedel[26,31]
△ - Horrocks and McLaughlin[33]
× - Challoner and Powell[32]

Fig. 5.4 Test of Bridgman's equation with n=2 at 40 °C

○ - Riedel[26,31]
△ - Horrocks and McLaughlin[33]
x - Challoner and Powell[32]

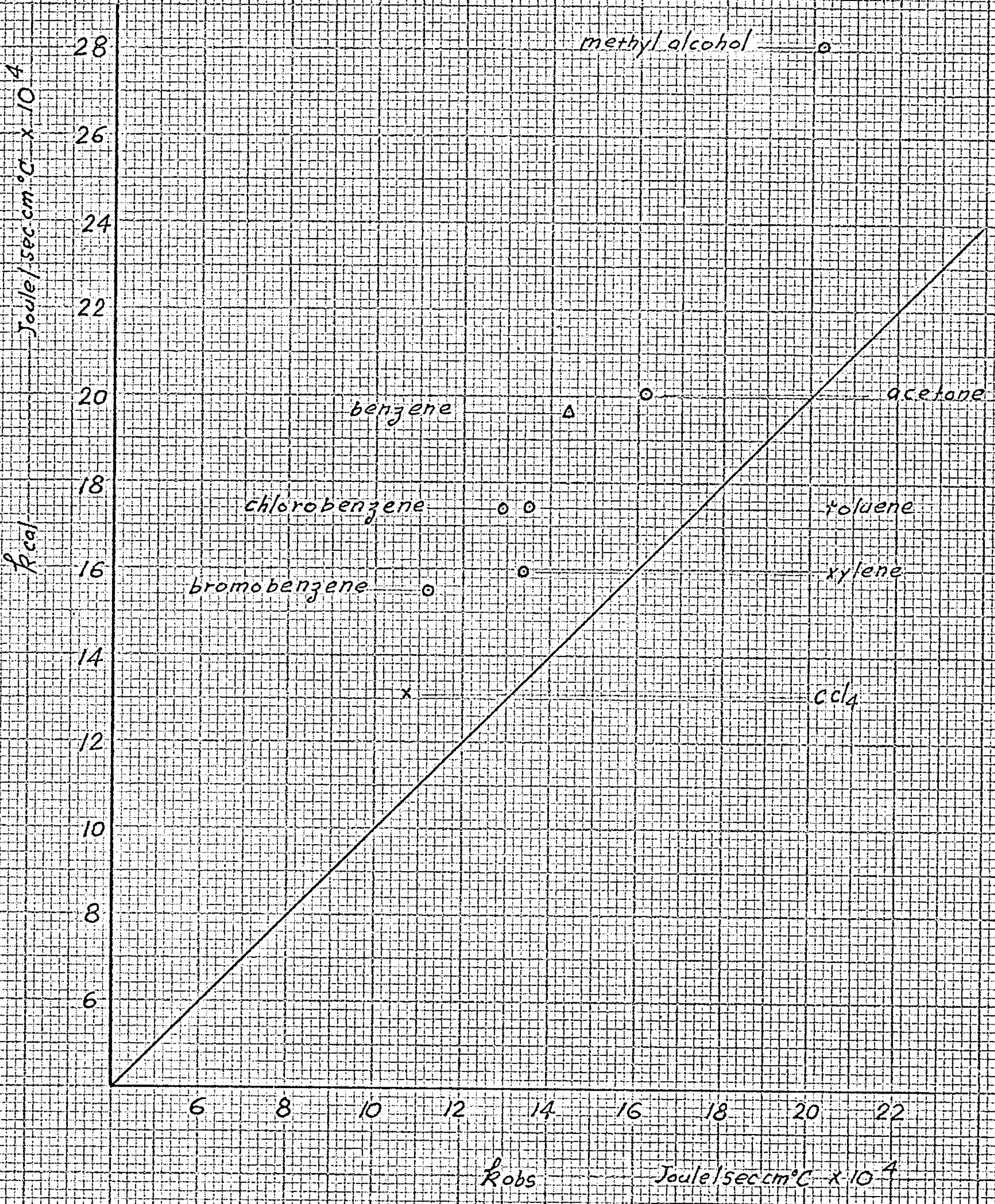


Fig. 5.5 Test of Bridgman's equation with n=3 at 20 °C

○ - Riedel[26, 31]
△ - Horrocks and McLaughlin[33]
x - Challoner and Powell[32]

which are considered most reliable. Their comparison between the calculated and experimental values would therefore give somewhat smaller average error.

Although the molar heat capacities of liquids near the melting point are approximately equal to 3R, which implies that n should be about 3, but comparison above showed that n = 2 gives much better agreement. It was found that the best agreement at 0 °C, 20 °C, and 40 °C would be obtained when using a corresponding n values of approximately 2.18, 2.269 and 2.398 respectively. However, it is both unlikely that n has a non-integer value and varies with temperature. Therefore, for better agreement, Bridgman's equation with n = 2 should be written as

$$k = 1.969 \times 10^{-7} \mathcal{E} V \left(\frac{\rho}{M}\right)^{\frac{2}{3}} \quad \ldots\ldots \quad (5-8)$$

where $\mathcal{E}$ is a multiplying parameter that varies with temperature. The problem becomes one of finding the proper value for $\mathcal{E}$. For a first approximation, it may be represented by $\left(\frac{T_{abs}}{235}\right)^{\frac{2}{3}}$, where T_{abs} is the absolute temperature of the liquids. The modified equation thus becomes

$$k = 5.17 \times 10^{-9} V \left(\frac{\rho T_{abs}}{M}\right)^{\frac{2}{3}} \quad \ldots\ldots \quad (5-9)$$

The relations of values of k calculated by Eq. (5 - 9) to the experimental values are shown in Figs. 5.6, 5.7, and 5.8 for 0 °C, 20 °C and 40 °C. The deviations of calculated values from the experimental ones are now roughly symmetrical, and the average deviations are respectively ±4.9 per cent, ±5.2 per cent and ± 5.0 per cent. Agreements are obviously much better than that obtained by the original Bridgman's equation. Further tests of the modified equation are necessary, and would require much more reliable thermal conductivity data which presently are scarce.

Conclusion - - Bridgman's equation is not, in it's original form, practical for estimating the thermal conductivity of liquids. While there are still many questions with regard to the theory which offer scope for further investigation, the present work strengthens the ground for considering the velocity of sound as an acceptable property in predicting, at least empirically, the thermal conductivity of liquids.

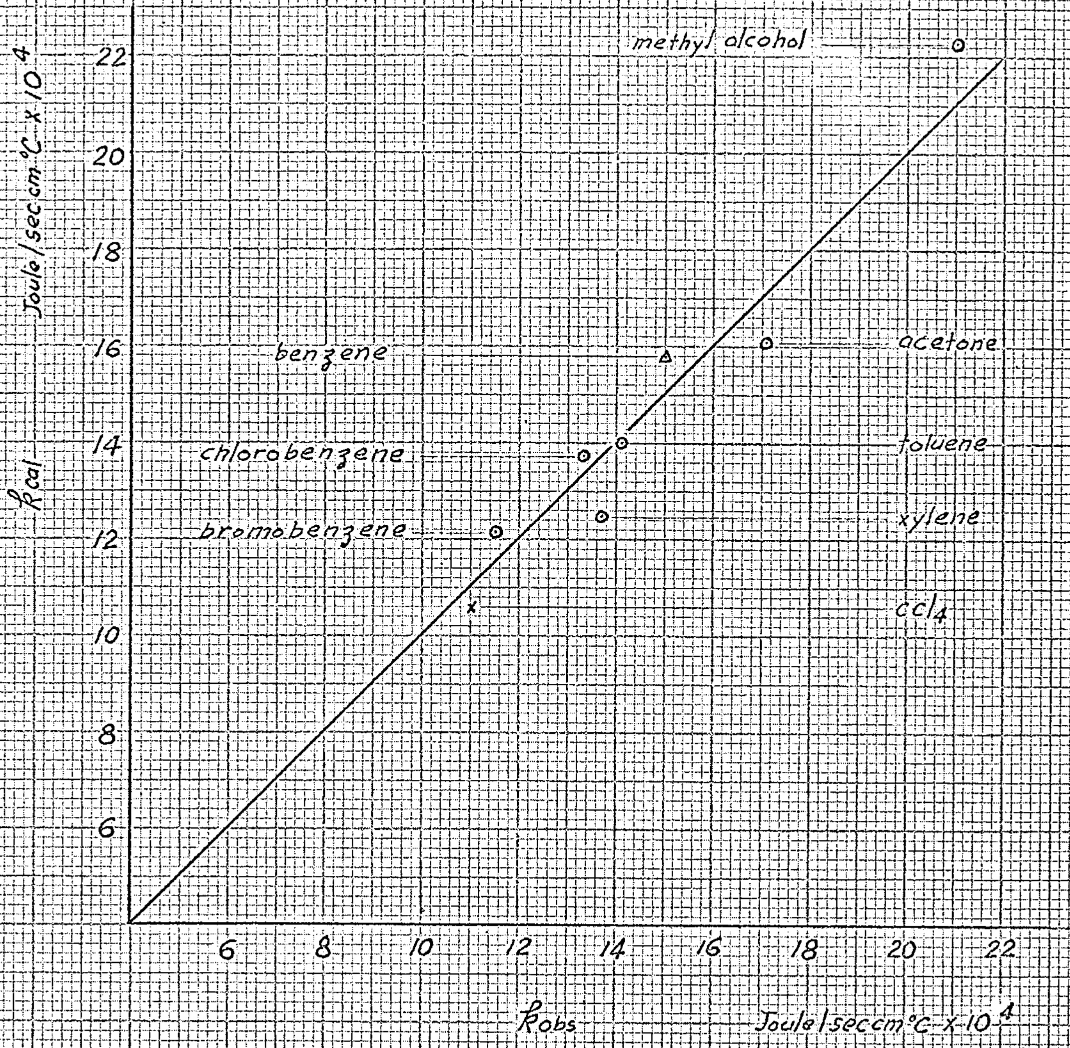


Fig. 5.6 Test of modified Bridgman's equation at 0 °C

⊙ – Riedel[26,31]
△ – Horrocks and McLaughlin[33]
x – Challoner and Powell[32]

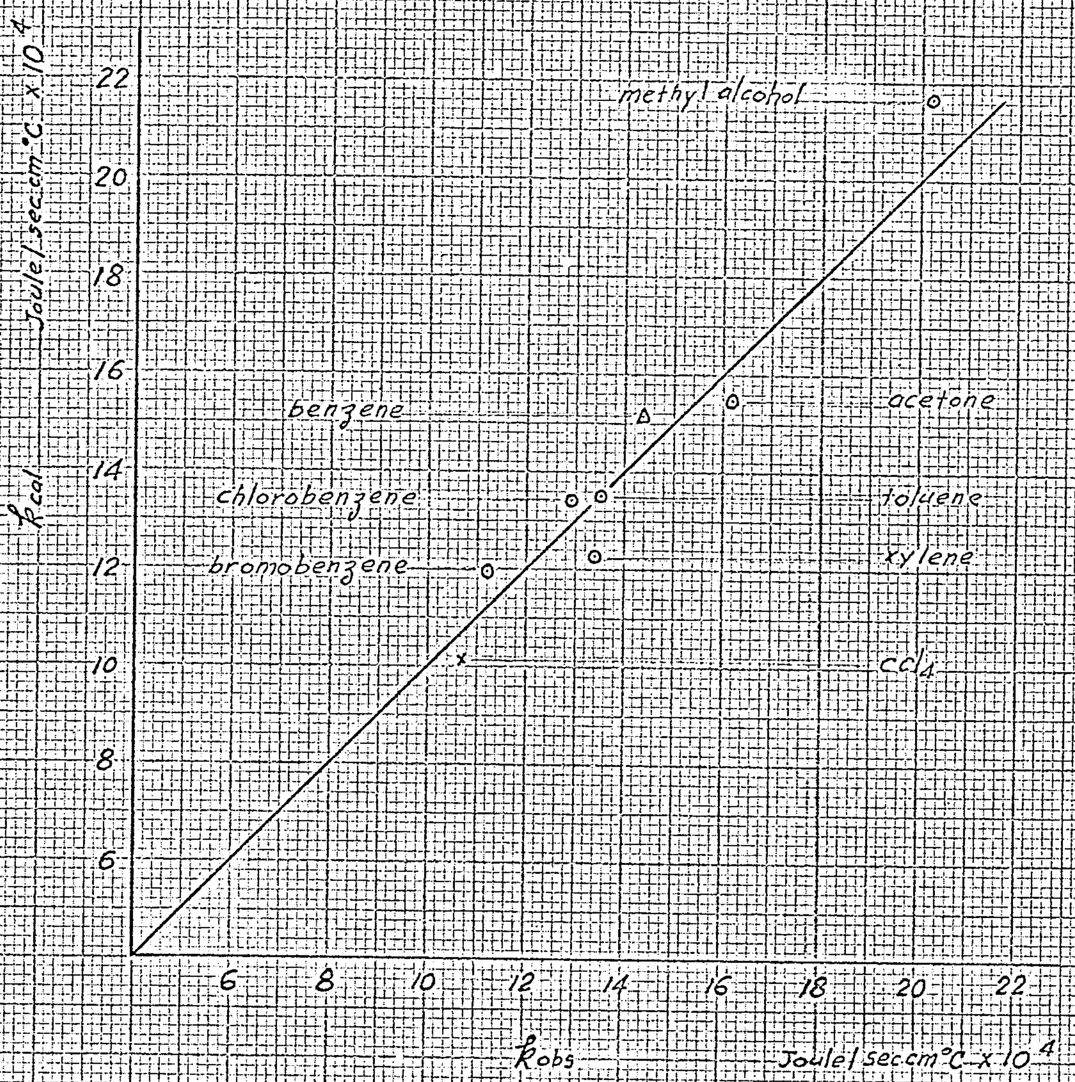


Fig. 5.7 Test of modified Bridgman's equation at 20 °C

⊙ — Riedel[26,31]
△ — Horrocks and McLoughlin[33]
x — Challoner and Powell[32]

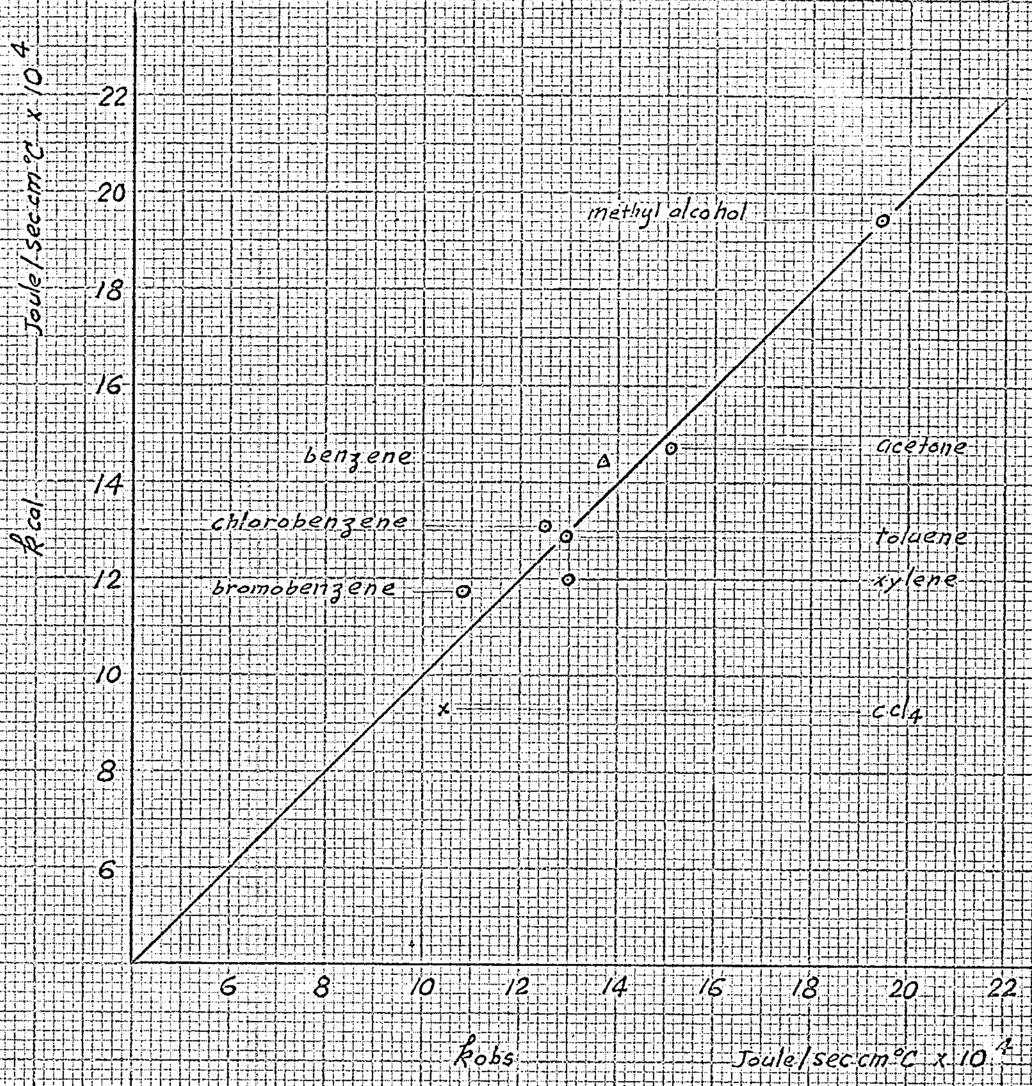


Fig. 5.8 Test of modified Bridgman's equation at 40 °C

APPENDIX

List of Equipment

Acoustical Interferometer: Krautkramer Ultrasonics Inc.

Constant Temperature Bath

Delay Line and Accessories

Mercury Commutator: Leeds and Northrup, Model 8067

Mueller Bridge: Leeds and Northrup, Model 8067, Type G-1

Null Detector: Leeds and Northrup, Catalog No. 9834

Platinum Resistance Thermometer: Leeds and Northrup, Model 8163

Thermotrol: Hallikainen Instruments, Model 1053A

Ultrasonic Flaw Detector: Krautkramer Ultrasonics Inc., Type USIP 10W

REFERENCES

1 Brillouin, L., Comptes Rendus, 159: 27; 1914.

2 Paschki, Journal of Russian Chemical Society, p 276; 1915.

3 Bridgman, P.W., "The Thermal Conductivity of Liquids under Pressure". Proc. Am. Acad. Arts and Sci., 59: 141; 1923.

4 Kardos, A., Forsch. Gebiete Ingenieurw., 5: 14; 1934.

5 Kincaid, J.F.; and Eyring, H., "Free Volumes and Free Angle Ratios of Molecules in Liquids". J. Chem. Phys., 6 : 620; 1938.

6 Sakiadis, B.C; and Coates, J., "Studies of Thermal Conductivity of Liquids". J.A.I.Ch.E., 1: No. 3; 275; 1955.

7 Loeb, L.B., "Kinetic Theory of Gases". McGraw-Hill, New York, 1927.

8 Kowalczyk, L.S., "Thermal Conductivity and Its Variability With Temperature and Pressure". Trans. A.S.M.E., 77: 1021; 1955.

9 Eucken, A., Physik. Z., 12: 1101; 1911 and 14: 324; 1913.

10 Debye, P., "Vortrage über der Kinetische Theorie der Materie und der Electrizitat" Teubner, Berlin, Germany, 1941.

11 Eucken, A., Forsch. Gebiete Ingenieurw., 11: 6; 1940.

12 Peirls, R., Ann. Phys., Lpz; 3: 1055; 1929

13 Ziman, J.M., "Electrons and Phonons; The Theory of Transport Phenomena in Solids". Clarendon Press, Oxford, 1960.

14 Tyrrell, H.J.V., "Diffusion and Heat Flow in Liquids" Butterworths, London, 1961.

15 Smith, J.F.D., "The Thermal Conductivity of Liquids" Trans. A.S.M.E., 58: 719; 1936.

16 Reid, R.C., and Sherwood, T.K., "The Properties of Gases and Liquids". McGraw-Hill, New York, 1958.

17 Vigoureux, P. "Ultrasonics" John Wiley & Son Inc., New York, 1951.

18 Lagemann, R.T., McMillan, D. R. Jr.; and Woolf, W.E., "Temperature Variation of Ultrasonic Velocity in Liquids". J. Chem. Phys. 17: No. 4: 369; 1949.

19 Pellam, J.R.; and Galt, J.K. "Ultrasonic Propagation in Liquids: I. Application of Pulse Technique to Velocity and Absorption Measurements at 15 Megacycles". J. Chem. Phys., 14: No. 10 : 608; 1946.

20 Greenspan, M.; and Tschiegg, C.E., "Speed of Sound in Water by a Direct Method". J. Research of the National Bureau of Standards, 59: No. 4: 249; 1957

21 Freyer, E.B.; Hubbard, J.C.; and Andrews, D.H., "Sonic Study of the Physical Properties of Liquids. I. The Sonic Interferometer. The Velocity of Sound in Some Organic Liquids and Their Compressibilities". J. Am. Chem. Soc., 51: 759; 1929.

22 Rao, M.R., Ind. J. Phys., 14: 109; 1940

23 Padmini, P.R.K.L.; Seshagiri Rao, M.G.; Ramachandra Rao, B., "Study of Temperature Variation of Ultrasonic Velocity in Liquids at Low Temperature". J. Phys. Soc. Japan, 18: No. 6: 871; 1963.

24 Lagemann, R.T.; and Dunbar, W.S., "Relationships Between the Velocity of Sound and Other Physical Properties of Liquids". J. Phys. Chem., 49: 428; 1945

25 Lagemann, R.T., Abstracts, Office of Naval Research Symposium on Acoustics and Chemistry, Western Reserve University, May 1952.

26 Riedel, L., Chem. Ing. Tech., 23: 321; 1951.

27 Gambill, W.R., Chem. Eng., 64: 237; 1957

28 Weber, H.F., Ann. Phys., Lpz., 10: 304; 1880 and 11: 345; 1880.

29 Palmer, G., "Thermal Conductivity of Liquids", Ind. Eng. Chem., 49: 89; 1948

30 Krishnamurthy, C.; and Venart, J.E., "The Thermal Conductivity of Organic Liquids". Reports, Dept. of Mech. Eng., Univ. of Calgary, Alberta. July 1966.

31 Riedel, L., Chem. Ing. Tech., 23: 465; 1951

32 Horrocks, J.K. and McLaughlin, E., "Non-steady-state measurements of the thermal conductivities of liquid polyphenyls". Proc. Roy. Soc. A 273: 259; 1963.

33 Challoner, A.R.; and Powell, R.W., "Thermal conductivity of liquids: new determinations for seven liquids and appraisal of existing values". Proc. Roy. Soc. A 238: 90; 1956.

34 Ziebland, H.; and Burton, J. T. A., J. Chem. Eng. Data, 6: 879; 1961.