

FURTHER INVESTIGATIONS INTO THE EFFECT OF HIGH
PRESSURE ON THE VISCOSITY OF LIQUIDS.

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by

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ABSTRACT.

A falling cylinder viscometer has been employed to measure the viscosity of heavy water, benzene, methanol, ethanol and four mixtures of ethanol and water at pressures up to $10,000 \text{ kg/cm}^2$ with an estimated accuracy between $+ 1.4\%$ and $- 1.0\%$ in the temperature range 10°C to 100°C . The viscometer and the associated high pressure system are described together with details of their calibration.

The viscosity-pressure behaviour of heavy water is similar to that of water. The temperature at which the initial viscosity-pressure coefficient is zero is estimated to be $34.0 \pm 0.5^\circ\text{C}$ compared with $33.0 \pm 0.5^\circ\text{C}$ for water. The heavy water data indicate that there is a large rotational contribution to momentum transfer in water which is independent of pressure but decreases with rising temperature. Theories of water structure are reviewed and the anomalous viscosity-pressure behaviour of water is interpreted in terms of a two species model.

The viscosity data for benzene, methanol and ethanol were obtained at 30°C , 50°C and 75°C . The data at 30°C and 75°C are in good agreement with those of Bridgman and are represented equally

well by the Arrhenius equation either at constant pressure or at constant volume.

The results for the ethanol-water system over a range of concentrations provide evidence of a shift in the viscosity maximum towards greater ethanol concentrations at high pressure. This effect is interpreted in terms of the bonded structures that exist in the mixtures.

The design and development of an unguided falling cylinder viscometer is described. The poor stability of the sinker make the instrument unsuitable for use at high pressures.

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CHAPTER I.

INTRODUCTION.

For a liquid moving in parallel layers, Newton postulated that the shearing stress at any point in the liquid is directly proportional to the velocity gradient perpendicular to the direction of flow at that point. This assumption is the basis of the definition for the viscosity, η , of a liquid and it is usually formulated as,

$$F = \eta \cdot \frac{dv}{dz} \quad \dots\dots(1-1)$$

where F is the viscous drag per unit area, and $\frac{dv}{dz}$ is the velocity gradient. It has been shown by experiment that the assumption implied in equation (1-1) is valid for gases and most liquids under steady flow conditions.

From a molecular concept of matter it may be shown that the viscous nature of a fluid is due to a transfer of momentum by the molecules down a velocity gradient. It is convenient at this stage to recognize two other fundamental transport processes in fluids; diffusion and thermal conductivity. Diffusion results from the transfer of mass down a concentration gradient, and thermal

conductivity from the transfer of energy down a temperature gradient. Since diffusion, viscosity, and thermal conductivity are all molecular processes, the object of any general theory of transport processes is to predict the transport coefficients in terms of the properties of the molecules.

An adequate description of the observed transport properties of gases has been provided by kinetic theory⁽⁵⁴⁾, on the basis of certain simple assumptions about the motion and interactions of the molecules. In the liquid state the problem is considerably more complex and no completely satisfactory theory has yet been proposed.

Any theory of transport processes requires detailed information on the structure of the liquid, the transport mechanisms, together with details of the shape and nature of the molecular interactions. This information is not available with the required accuracy because of the basic difficulty associated with a molecular description of liquid structure. The development of the subject is dependent primarily on the elaboration and modification of existing theories on the basis of additional information obtained from measurements of structure-dependent properties.

A change in the configuration or energy of the molecules in a liquid will generally result in a corresponding change in the viscosity. It is for this reason that experimental measurements of the viscosity of liquids as a function of pressure and temperature are a valuable source of information on molecular interactions.

Since both the molecular configuration and the molecular energy in a fluid are influenced by temperature and pressure changes, the viscosity of a liquid will, in general, be temperature and pressure dependent. Additional information on the molecular interactions and the mechanisms of viscous flow in liquids is provided from observations of the viscosity changes that result from systematic variation of the liquid structure (e. g. mixtures, homologous series, isotopic substitution).

Although there have been numerous investigations of the effects of temperature and structural changes on viscosity, experimental measurements at high pressures are limited. Pressure is an important variable, since it facilitates the analysis of results under conditions of theoretical significance; namely, constant volume and constant internal energy.

There is a general lack of accurate high pressure viscosity

data at pressures in excess of $1,000 \text{ kg/cm}^2$. The main source of data above this pressure is the notable paper of Bridgman⁽¹⁸⁾, published in 1926, which gives the results of viscosity measurements on 43 pure liquids at two temperatures, 30°C and 75°C , for pressures up to $12,000 \text{ kg/cm}^2$. However, some uncertainty exists as to the accuracy of these results, since his data for water are in poor agreement with recent measurements^{(9) (55)}.

Extensively hydrogen-bonded liquids, of which water and the lower aliphatic alcohols are typical examples, are viscous and have comparatively large viscosity-temperature and small viscosity-pressure coefficients. These properties are generally accepted to arise in some way from the association and the interactions of the molecules and changes in these with variations of temperature and pressure.

It is doubtful if any general theory of liquid viscosity will be applicable to liquids composed of complicated molecules, although a better understanding of the processes involved in viscous flow could lead to a method for estimating the temperature and pressure dependence of the viscosity of a liquid from a knowledge of its structure.

In addition to the information on molecular interactions that is provided by systematic viscosity measurements, there are numerous technological applications, such as bearing lubrication, where a knowledge of liquid viscosities at high pressure is required. In particular, a knowledge of the viscosity of heavy water under pressure is needed for the design of heavy water moderated nuclear reactors. Furthermore, the use of ethanol-water mixtures to remove the heat of reaction in high pressure tubular chemical reactors has been advocated, and for this application a knowledge of the viscosity-pressure characteristics is required.

This study is mainly concerned with the molecular processes that are involved in the transfer of momentum in complex hydrogen-bonded liquids.

CHAPTER II.

MOMENTUM TRANSPORT IN LIQUIDS

2.1 The Structure of Liquids.

Considerable information on the equilibrium structure of a liquid is required before any rigorous theory of viscous flow can be developed. Consequently, the developments of equilibrium and non-equilibrium theories of liquids are closely related. A brief review of the various approaches that have been made in developing an equilibrium theory of the liquid state is given in this section.

(a) Intermolecular Forces.

The spatial distribution of molecules in a dense phase will be determined by the nature and magnitude of the intermolecular forces and from elementary considerations it may be deduced that the intermolecular forces are attractive for large molecular separations and repulsive for small separations. The molecular interactions are conveniently expressed in terms of the potential, u , between a pair of molecules. It is usually assumed that the various contributions to u are additive in order that the final

potential may be expressed as the sum of an attractive and a repulsive term.

The simplest liquid is one of which the molecules are monatomic, spherically-symmetric, non-polar and have a completed outer electron shell. The attractive forces between such molecules are solely due to the mutual polarization of the atoms (London-forces), and the repulsive forces arise from the interaction of the positive nuclei and the electron cloud of one molecule with those of neighbouring molecules. London⁽⁶⁹⁾ showed that the pair potential for these molecules is given quite closely by

$$u(r) = Ae^{-Cr} - Br^{-6} \quad \dots\dots(2-1)$$

where A, B, and C are constants and r is the intermolecular separation. Equation (2-1) is rarely employed in liquid theories on account of the complexity that is introduced by the exponential term. Consequently, calculations are usually made with simplified potentials, such as the rigid-sphere, square well, or Lennard-Jones (n, m) potentials.

The pair potential for the molecules of most liquids is complicated by the additional forces that arise from the asymmetry

and permanent dipole moments of molecules, and by other more specific molecular interactions, (e. g. hydrogen bonding).

(b) Statistical Theories.

The kinetic theory of the 19th century was remarkably successful in predicting the properties of gases: assuming the molecules to be in random motion with long mean free paths, and acting as rigid spheres. Statistical theories of liquids seek to extend these methods by assuming that a liquid is a highly compressed gas and by introducing more realistic intermolecular potentials.

Hence, if a liquid is considered as a closed system of N identical interacting particles, then under equilibrium conditions the usual equations of statistical mechanics will be applicable. The partition function, Z , for this system is given by,⁽⁵⁴⁾

$$Z = \frac{1}{N! h^{3N}} \int \dots \int e^{-\frac{H}{kT}} \cdot dr_1 \dots dr_N \cdot dp_1 \dots dp_N \dots (2-2)$$

where H is the Hamiltonian for the system. Thermodynamic parameters are related directly to the partition function, (e. g. Helmholtz free energy $A = -kT \ln Z$), and therefore evaluation of Z provides an immediate comparison between theory and experiment.

A rigorous evaluation of the partition function is totally impracticable, and statistical theories are based on the pair distribution function, $n^{(2)}$. This function is defined as the probability of finding two molecules simultaneously at a particular separation. The pressure, p , and mean configurational energy, U' , of a system are related to the pair distribution function and the pair potential by ⁽⁹⁴⁾

$$p = \frac{NkT}{V} - \frac{1}{6} \int_0^{\infty} \frac{du(r)}{dr} \cdot n^{(2)}(r) \cdot 4\pi r^2 \cdot dr \quad \dots (2-3)$$

and

$$U' = \frac{V}{2} \int_0^{\infty} u(r) \cdot n^{(2)}(r) \cdot 4\pi r^2 \cdot dr \quad \dots (2-4)$$

Exact integral equations for the pair distribution function may be derived, but as these include higher order distribution functions some approximation is required in order to evaluate $n^{(2)}$. Recently Rowlinson⁽⁹⁵⁾ has reviewed the approximations by which the statistical equations may be solved, and compared the solutions with direct calculations for model systems and with the properties of real systems.

(c) Lattice Theories.

These theories of the liquid state assume a model for the liquid which enables the partition function for the system to be evaluated. They are conveniently subdivided into two classes: 'cell' theories and 'hole' or 'free-volume' theories.

In the cell model each molecule of the liquid is confined by its neighbours for long periods to a restricted region. The local environment of the molecule is not very different from that in a solid, but there is no long range order. If it is assumed that each cell has a volume V/N and contains one molecule, and that the molecules move independently but are chosen so that they form a regular lattice, the model may be formulated mathematically. Lennard-Jones and Devonshire⁽⁶⁵⁾ were first to make these assumptions and evaluate the partition function for a liquid. This approach has proved to be an excellent basis for the theory of solids, and it remains of fundamental importance in liquid theory since much progress has resulted from attempts to justify or improve the model.

The hole or free-volume theories of liquids have been developed from the cell model by taking account of the vacant

lattice sites that exist in liquids. The admission of empty cells in the model is essentially a generalisation of the cell theory which leads to an adjustable coordination number. This refinement gives better agreement with experimental data, particularly at the lower densities.

A review of lattice theories of the liquid state has been given by Barker⁽⁵⁾. Many of the calculations based on lattice models have been quite successful, but they have yet to provide a completely satisfactory description of the liquid state.

2.2 Theories of Transport Processes in Liquids.

The first test of any formal theory of transport processes in fluids is a direct comparison of the transport coefficients and their predicted temperature dependence with experimental data. Viscosity, diffusion and thermal conductivity are known to increase with increasing temperature in gases, but in liquids their temperature dependence is less uniform. The coefficients of viscosity and thermal conductivity in a liquid generally decrease with increasing temperature, while the diffusion coefficient increases. These observations indicate that the mechanism of momentum and energy

transfer in liquids is fundamentally different from that in gases.

An additional test of transport theories is provided by certain relationships that exist between the various coefficients. One of the most important of these relations is the ratio $\frac{m\lambda}{k\eta}$, which has a temperature-independent value of $\frac{15}{4}$ for the inert gases, and for many simple liquids, a value of approximately $\frac{5}{2}$.

Although some distortion of the molecular structure from the equilibrium arrangement is inevitable when the transport processes are operative, formal transport theories are based on the same models that are employed for general liquid theory and are classified accordingly.

(a) Enskog's Theory.

The fundamental assumption of elementary kinetic theory is that the mean free path between molecular collisions is much greater than the molecular diameter. This assumption implies that the transfer of mass, momentum or energy in a gas is a purely convective mechanism and, although this is a valid assumption for dilute gases, it is not true for compressed gases or liquids. The kinetic model of smooth rigid spherical molecules has been extended to the dense gas region by Enskog⁽²⁷⁾. In this theory the frequency

of molecular collisions in a gas changes on compression owing to molecular shielding effects and the reduced mean free path. The instantaneous transfer of momentum and energy between the centres of molecules on collision becomes of increasing importance as a gas is compressed and the intermolecular distances are reduced. Taking account of the change in collision frequency with density, Enskog showed that the increasing importance of the collisional mechanism relative to the convective mechanism leads to the observed minimum of the viscosity and thermal conductivity of a gas on compression. The diffusion coefficient continues to decrease with increasing density, since only a convective mechanism occurs in this process. The importance of the Enskog theory lies in its prediction of the correct temperature dependence of the transport coefficients for dilute and for dense systems, and, although it is derived for rigid spherical molecules, it may be employed with little modification to predict the transport properties of real gases over a wide range of densities. It remains essentially a gas theory rather than a liquid theory because of the grossly over-simplified intermolecular potential that is assumed.

(b) Distribution Function Theories.

A rigorous theory of transport processes in fluids may be developed on the basis of the Liouville equation. The non-equilibrium distribution functions, $n^{(h)}(r)$, for a system of N identical interacting particles must satisfy the Liouville equation,

$$\frac{\partial n^{(h)}}{\partial t} = - \frac{1}{m} \cdot p \cdot \frac{\partial n^{(h)}}{\partial r} + \frac{\partial u}{\partial r} \cdot \frac{\partial n^{(h)}}{\partial p} \dots\dots (2-5)$$

From this equation and the general equation for the expectation of a time-independent variable, expressions may be derived for the transport flux vectors, and hence the transport coefficients, in terms of the non-equilibrium pair distribution function, $n^{(2)}(r)$, and the intermolecular potential, $u(r)$. The solution of these equations is dependent on the evaluation of $n^{(2)}(r)$, and although this is theoretically possible via the Liouville equation or via the equations that inter-relate the lower order distribution functions, because of the complexity of the equations these methods are intractable.

Kirkwood et al⁽¹¹⁶⁾ have attempted to solve the equations from a consideration of the irreversibility in a transport process. This approach leads to a Brownian Motion type of equation which

may be solved by assuming a 'friction factor'. The resulting expressions for the viscosity and the thermal conductivity are the sum of two terms; a convective term and a collisional term. In dense systems, the convective term is sufficiently small to be neglected.

Although comparisons between theory and experiment are few, some success has been obtained with these statistical methods.

(c) Eyring's Theory.

This theory⁽⁴⁴⁾ assumes a lattice model of the liquid state and the transport coefficients are calculated by a rate process technique. The fundamental rate process is assumed to be the transfer of activated molecules to adjacent 'holes' in the lattice. The shape of the potential barrier in the region of a cell is distorted under the influence of a shearing force and the probability of a molecule moving into an adjacent cell is increased.

Momentum transfer in the liquid is considered to be solely due to the movement of molecules into vacant sites. The rigorous theory gives a non-Newtonian expression for the viscosity, but for most simple liquids an approximation is possible giving,

$$\eta = \frac{N}{V} \cdot (v_f)^{1/3} \cdot (2\pi mkT)^{1/2} \exp\left(\frac{E_{act}}{RT}\right) \dots\dots (2-6)$$

where v_f is the free volume, and E_{act} is the additional energy required by a molecule to engage in momentum transfer. Inserting the known values of N and R , expressing the free volume as a function of the molar energy of vaporization, ΔE_{vap} , and assuming cubic packing, equation (2-6) reduces to,

$$\eta = 1.09 \times 10^{-3} \cdot \frac{(MT^3)^{\frac{1}{2}}}{v^{2/3} \Delta E_{vap}} \cdot \exp \left(\frac{E_{act}}{RT} \right) \dots\dots (2-7)$$

If
$$E_{act} = \frac{\Delta E_{vap}}{n} + \frac{pV}{n^f}$$

where n , n^f are empirical constants then,

$$\eta = 1.09 \times 10^{-3} \cdot \frac{(MT^3)^{\frac{1}{2}}}{v^{2/3} \Delta E_{vap}} \cdot \exp \left(\frac{\Delta E_{vap}}{nRT} + \frac{pV}{n^f RT} \right) \dots\dots (2-8)$$

Equation (2-8) has been employed to predict the temperature and pressure dependence of the viscosity of several liquids with fair accuracy. It must be noted, however, that the fitting of data is normally empirical, requiring appropriate adjustment of the energies of activation, and that the theory makes no specific assumptions about the nature of the lattice structure in the liquid.

(d) Vibrational Theories.

The most successful of the early theories of viscous flow was

due to Andrade⁽²⁾, who obtained an expression for the viscosity of a monatomic liquid at its melting point, by postulating that the essential difference between a solid and a liquid at the melting point is the amplitude of the molecular vibrations. The resistance to flow is thought to arise from the transfer of momentum which takes place when the molecules collide at the extremities of their oscillations. The total momentum transferred per unit area per second is given by,

$$\frac{4}{3} \cdot \frac{m \gamma}{a} \cdot \frac{dv}{dz} = \eta \cdot \frac{dv}{dz} \quad \dots\dots (2-9)$$

where m is the mass of a molecule, γ the vibrational frequency and a the intermolecular separation,

Equation (2-9) has been applied to metals by Andrade, who considered that the intermolecular forces in the liquid and the solid must be similar at the melting point since their specific volumes and heat capacities are approximately equal. From the Lindemann expression for γ in a metal and assuming that

$$a^3 = \frac{V}{N}$$

the viscosity at the melting point is given by,

$$\eta_m = \frac{4}{3} \cdot C \cdot \frac{(AT_m)^{\frac{1}{2}}}{(NV)^{2/3}} \quad \dots\dots(2-10)$$

where C is a constant and A the atomic weight. Inserting the known values of C and N leads to,

$$\eta_m = 5.1 \times 10^{-4} \cdot \frac{(AT_m)^{\frac{1}{2}}}{v^{2/3}} \quad \dots\dots(2-11)$$

No specific molecular force field or lattice structure is assumed in deriving equation (2-9) and development of this theory has been continued by using alternative methods for the calculation of η . Barrer⁽⁷⁾ has calculated these frequencies from entropy considerations, while Horrocks and McLaughlin⁽⁵⁶⁾ employed the cell model of liquids assuming a face-centred cubic structure with the molecules interacting according to a Lennard-Jones (12 : 6) potential.

2.3 The Temperature and Pressure Dependence of Viscosity.

(a) Temperature Dependence.

In contrast to the behaviour of dilute gases, the viscosity of liquids decrease with rising temperature. The first quantitative experiments on the temperature variation of the viscosity of liquids were conducted by Poiseuille, who proposed that,

$$\eta_T = \frac{\eta_0}{(1 + aT + bT^2)} \quad \dots\dots (2-12)$$

where η_0 , a , and b are constants for a particular liquid. Numerous other empirical equations have been suggested to represent the viscosity-temperature behaviour of liquids at atmospheric pressure, but it is generally accepted that the most satisfactory is,

$$\eta_T = A_p \exp\left(\frac{E_p}{RT}\right) \quad \dots\dots (2-13)$$

where A_p and E_p are constants, and R the gas constant. This equation is variously known as the Arrhenius, de Guzman, or Andrade equation. Extensive experimental measurements on many liquids have revealed that equation (2-13) provides a reasonable description of the viscosity over a wide range of temperatures, but is generally unsatisfactory near the melting point.

In the regions of non-Arrhenius behaviour, Doolittle⁽³⁴⁾ showed that the viscosity is related to the free volume of the liquid by,

$$\eta = A \exp\left(\frac{B}{f}\right) \quad \dots\dots (2-14)$$

where A , B are constants and f is the fractional free volume. Subsequently, Cohen and Turnbull⁽²⁸⁾ derived this relation from considerations of molecular mobility in liquids. Barlow et al⁽⁶⁾

have shown that a modified free-volume equation,

$$\ln \eta = A' + \frac{B'}{T - T_0} \quad \dots\dots (2-15)$$

where A' , B' and T_0 are constants, provides an accurate description of the viscosity-temperature behaviour of supercooled liquids.

It is of interest to compare equation (2-13) with the equations that are generally employed to represent the temperature dependence of diffusion and thermal conductivity in liquids,

$$D = D_0 \exp \left(- \frac{b}{T} \right) \quad \dots\dots (2-16)$$

$$\text{and} \quad \lambda = \lambda_0 - cT \quad \dots\dots (2-17)$$

where D_0 , λ_0 , b and c are constants. From these equations it is evident that the factors influencing the mechanisms of mass, momentum and energy transfer in liquids are essentially different.

(b) Pressure Dependence.

The viscosity of all pure liquids increases with pressure at constant temperature, with the notable exception of water and heavy water at low temperatures. Warburg and Sachs⁽¹⁰⁸⁾ were amongst the first workers to make viscosity measurements at high pressures,

and they found that their results up to 150 kg/cm^2 for a few simple liquids were satisfied by the following equation,

$$\eta_p = \eta_o (1 + Ap) \quad \dots\dots(2-18)$$

where η_o and A are constants for a particular liquid. The description of the pressure dependence of viscosity represented by equation (2-18) was shown to be totally inadequate by the subsequent improvement of experimental techniques and extensions of the pressure range.

A more satisfactory description of the viscosity-pressure behaviour of liquids at constant temperature is provided by the exponential relation,

$$\eta_p = \eta_o \exp (Bp) \quad \dots\dots(2-19)$$

Although this equation is approximately obeyed for a large number of liquids, detailed examination of the viscosity data over a large pressure range shows marked departures from exponential behaviour.

Since pressure and temperature changes invariably lead to corresponding changes in the internal energy, volume, and transport mechanisms, it is more reasonable to consider viscosity under

constant volume conditions, than at constant pressure or at constant temperature, as implied by the empirical equations (2-13) and (2-19). It may be fortuitous that equation (2-13) fits the viscosity-temperature data of liquids at constant pressure so well, since it has been shown^{(57) (58)} that the viscosity of a number of liquids under constant volume conditions are equally well described by,

$$\eta = A_v \exp \left(\frac{E_v}{RT} \right) \quad \dots (2-20)$$

If equations (2-13) and (2-20) are compared with Eyring's model, E_p and E_v may be considered as the activation energies that a molecule must possess in order to engage in momentum transport, under constant pressure and constant volume conditions, respectively.

Recently, Matheson⁽⁷³⁾ has shown that the viscosity-pressure behaviour of several liquids is closely predicted by the free volume theory of liquid viscosities, provided the temperature and pressure dependence of the limiting specific volumes are taken into consideration.

2.4 The Structural Dependence of Viscosity.

(a) Simple Liquids.

These liquids are generally considered to be monatomic or

composed of small spherically symmetric molecules and they include the liquid metals, the liquefied inert gases, and liquids such as carbon tetrachloride. In order to simplify theories of the liquid state and of viscosity it is usually assumed that liquids are composed of spherically symmetric molecules. Consequently experimental data on these liquids, excluding the liquid metals in which the molecular interactions are complicated by free electrons, provide a direct comparison with theories.

Measurements of the viscosity of these liquids indicate that the viscosity variation is described approximately by the exponential equations (2-13), (2-19) and (2-20).

The Andrade equation, (Eqn. (2-11)) for the viscosity of metals at the melting point is in good agreement with experimental data⁽²⁾. The effect of temperature and pressure on the viscosity of liquid metals is small in comparison with most other liquids on account of the strong free-electron bonding.

(b) Polyatomic Liquids.

Since polyatomic molecules will, in general, lack spherical symmetry and have permanent dipole moments, the intermolecular pair potential will be complex compared to the pair potential in

simple liquids. Additional factors, which are difficult to incorporate in viscosity theory, result from the shielding of the atoms at the centre of the molecule by outer atoms and the flexibility of the chemical bonds in the molecule. Each of these factors increases in importance as the molecules become more complicated, and may eventually determine the mechanisms of viscous flow.

Although it is possible to make a number of generalizations concerning the viscosity of polyatomic non-associating liquids and their temperature and pressure dependence, these cannot as yet be defined quantitatively. In general the viscosity, viscosity-temperature, and viscosity-pressure coefficients of liquids,

- (i) tend to increase with increasing molecular complexity.
- (ii) are approximately equal for molecules of approximately the same size and shape.
- (iii) are greater for rigid molecules than for more flexible molecules.

The marked structural dependence of viscosity may be contrasted with the small influence of increasing molecular complexity on thermal conductivity. This can be explained qualitatively by the severing of intermolecular forces during viscous flow; such a

process is not essential for heat conduction through a liquid.

(c) Isotopic Liquids.

The viscosity of a liquid depends on the mass of the molecules. A comparison of viscosity data for liquids of isotopic species with the predicted mass dependence provides an important link between theory and experiment. Isotopic substitution has practically no effect on the pair potential for spherical molecules and, if the subscript i refers to the isotopic species, the relation between the viscosity, η , and the mass, m , is simply⁽⁷⁰⁾,

$$\eta_i = \eta \cdot \left(\frac{m_i}{m} \right)^{\frac{1}{2}} \quad \dots\dots (2-21)$$

This equation is not valid for liquids if the intermolecular forces are non-central, or where rotational momentum transfer is significant. If momentum transfer is by molecular rotation, then the moments of inertia, I , of the species must be considered, and,

$$\eta_i = \eta \cdot \left(\frac{I_i}{I} \right)^{\frac{1}{2}} \quad \dots\dots (2-22)$$

Experimental viscosity data are available for very few isotopically substituted systems, but the data for methane and cyclohexane and

their corresponding deuterio-substituted compounds are in good agreement with equation (2-21).

(d) Associated Liquids.

These liquids, like liquid metals and ionic melts, have chemical forces in addition to Van der Waal's attractive forces, and the effects of these are to increase the normal molecular interactions in the liquid. The viscosities of associated liquids are greater than those of similar non-associated liquids because of the additional molecular energy that is required to overcome the potential barriers.

The influence of temperature and pressure on the viscosity of an associated liquid is complicated by changes in the degree of association of the liquid. The degree of association generally decreases with rising temperature, and it is for this reason that associated liquids have large viscosity-temperature coefficients.

(e) Mixtures.

The viscosities of mixtures are measured in an attempt to deduce a general relation between the viscosity of a mixture, the mixture composition, and the viscosities of the components, or to relate structural changes in a mixture with details of the viscosity-

composition curves. Numerous empirical equations have been proposed to represent the viscosity of a liquid mixture, but no one equation has been recognised as satisfactory. Viscosity-concentration curves under constant pressure and temperature conditions may exhibit maxima or even minima, i. e. the viscosity of a mixture may be greater or less than the viscosity of either of its components. This behaviour is explained by structural changes in the mixture due to increased or decreased association, or to complex formation.

The fundamental problem in extending the theories of viscosity to mixtures is the formulation of a pair potential for the binary system.

CHAPTER III

THE STRUCTURE OF WATER AND LIQUID ALCOHOLS

3.1 Introduction.

(a) Some Physical Properties of Water.

Water, the most common of all liquids, is one of the most complex and many of its physical properties are unique. It is well known that the density of ice at 0°C is 0.917 gm/cm^3 , whereas the density of water at the same temperature is 1.000 gm/cm^3 . The melting of the normal solid form of water to a more dense liquid state is an unusual property that is shared by few other substances. Further, after melting at 0°C , the density of water continues to increase with rising temperature for a few degrees and passes through a maximum at 3.98°C .

In comparison with other liquids, the compressibility of water is abnormally small and at low temperatures it decreases with increasing temperature, passing through a minimum at 50°C . The anomalous behaviour of the density and compressibility is alone sufficient to indicate a fundamental difference in structure between water and most other liquids.

It is generally observed that the properties of liquids within an homologous series vary regularly with increasing molecular weight. Water is a member of two homologous series; (1) the hydrides of the sixth main group of elements in the periodic table:- H_2O , H_2S , H_2Se , H_2Te , and (2) the hydrides of the second period of elements from boron:- BH_3 , CH_4 , NH_3 , H_2O , HF . In contrast with the other compounds in these series, the properties of water are anomalous. In particular, the melting and boiling temperatures of water, together with its heat of fusion, heat of vaporization, critical temperature, viscosity and surface tension, are all much greater than predicted from the corresponding values of these properties for the other compounds in the series.

The specific heat of water is unusually high and in contrast with other liquids its temperature variation exhibits a minimum at 35°C . The excellence of water as a solvent is explained by a high dielectric constant. It is found that many of the properties of a dilute aqueous solution of a polar solute are similar to those of pure water at a higher temperature and, for a non-polar solute, the properties are similar to those of the pure solvent at a lower temperature.

The main details of the actual physical structure of water have been provided by the radial distribution function. This function is a measure of the molecular spacing within the liquid and may be calculated from the results of X-ray or neutron diffraction experiments. Morgan and Warren⁽⁷⁹⁾ have determined the radial distribution function for water at several temperatures using an X-ray diffraction technique and their results show that there is a gradual increase of the average coordination number for water from 4.4 at 1.5°C to 4.9 at 83°C. These values are to be compared with the average coordination number for ice at 0°C of 4.0, and the overall decrease in density over the same temperature range. The success of any model or theory of water structure depends upon the extent to which it is able to predict or explain its anomalous properties. At the same time, however, it must be in agreement with the experimentally observed details of water structure.

(b) Coupling Interactions of Water Molecules.

It has been generally accepted that the anomalous properties of water are due to very strong molecular interactions and association of the water molecules⁽⁸¹⁾. The interactions are considered to

consist mainly of hydrogen bonding between the water molecules; additional cohesive forces being provided by strong dipole-dipole interactions. Before considering the various theories that have been proposed for the structure of water, it is necessary to consider the nature of these interactions.

The hydrogen bond may be explained on the basis of electrostatic forces due to charge separations, although the complete explanation for the formation of the bond is more complex. The two hydrogen atoms of the water molecule are situated to one side of the oxygen atom; this results in a partial charge separation within the molecule. In this simple model the hydrogen bond is thought to arise from an electrostatic attraction between the partial positive charge of one of the hydrogen atoms in a water molecule, and the negative charge concentration of a lone pair of electrons belonging to an oxygen atom in a neighbouring molecule. Thus, one water molecule is able to participate in four hydrogen bonds; two of them involving the two hydrogens of the molecule, and two the lone pairs of electrons of the oxygen with the hydrogens of two neighbouring molecules. This is the arrangement in the crystal structure of ice, where the water molecules are tetrahedrally-

oriented with extensive hydrogen bonding. Coulson⁽³¹⁾, and Frank and Wen^{(39) (41)} have emphasized the inadequacies of this simple electrostatic model and the importance of the contributions to the bond energy from exchange forces due to electron overlap. These exchange forces are highly directional and they introduce a co-valent character to the hydrogen bond. In effect, the formation of the initial hydrogen bond between two single water molecules promotes the formation of extensive hydrogen-bonding through a three dimensional array comprised of many molecules.

The hydrogen bond is intermediate in strength between the strong ionic bonds and the weak Van der Waal's attractions which occur, even in electrically-neutral molecules, due to charge fluctuations. Because of its marked asymmetry the water molecule has a large dipole moment and hence strong dipole-dipole interactions create additional cohesive forces between the molecules. Because the water molecule is so highly polarizable, London forces provide a further contribution to the cohesive energy of the molecules.

Many estimates have been made of the energy required for breaking one hydrogen bond in liquid water⁽⁸⁸⁾. The various

estimates range from about 1.3 to 6.8 kcal per mole depending on whether or not a correction is made for the dipole interactions. Pauling⁽⁸⁶⁾, on the basis of analogies with other compounds, has estimated the energy of the hydrogen bond in water to be 4.5 kcal/mole, a value quoted and utilized widely. The various dipole interactions provide relatively weak coupling forces between the molecules compared to the cohesive energy provided by the hydrogen bonds.

3.2 Theories of Water Structure.

Since no exact theory of liquid water has been developed to account for all of its properties, a brief review of the various models is given with particular reference to the more recent theories.

(a) Early Theories.

It has long been recognised that water is an associated liquid and many of the early theories postulated the existence of polymeric species of the form $(\text{H}_2\text{O})_n$, (where n is a positive integer greater than unity), to explain its anomalous properties. However, many of the observed properties of water were not

explained satisfactorily by these theories and, since there has not been any experimental evidence to support polymerization of water molecules, they have been superseded.

In 1933, Bernal and Fowler⁽⁸⁾ initiated the current belief that extensive hydrogen bonded regions are present in liquid water, and that these are responsible for many of its anomalous properties. Their model assumed that on melting ice changed from the tetrahedrally bonded tridymite structure to a more dense tetrahedrally bonded quartz-like structure, in addition to which the unbonded water molecules adopt a close packed structure characteristic of normal liquids. The degree of hydrogen bonding was assumed to decrease gradually with increasing temperature.

Although the theory accounted for the density anomalies of water, it was unable to account for the high specific heat of water compared to that of ice. This model was superseded because of its apparent rigidity. However, the existence of extensive hydrogen bonding and its gradual reduction with increasing temperature has been generally accepted and incorporated in most subsequent models.

(b) The Bending Bond Model.

The majority of recent theories of water structure assume

that liquid water consists of a mixture of two distinct molecular species. The most important of the non-mixture models was presented by Lennard-Jones and Pople⁽⁶⁶⁾ ⁽⁸⁹⁾ in 1951. Employing Pauling's estimate of the energy of the hydrogen bond, (i. e. 4.5 kcal/mole), they concluded that very few hydrogen bonds are actually broken when ice at 0°C melts to water at the same temperature. They postulated that the hydrogen bonds are gradually bent with increasing temperature, until at a certain stage this process leads to a breakdown of long range order which corresponds to fusion. Since the hydrogen bonds in the liquid are less rigid, the molecules are free to move to regions within the lattice that were not formerly occupied and hence this may lead to an overall diminution in volume. Further, with increasing temperature the model predicts a gradual smoothing out of the radial distribution function.

Pople⁽⁸⁹⁾ derived an expression for the energy of bending of the hydrogen bonds as a function of temperature using statistical thermodynamics. He obtained satisfactory quantitative explanations of the observed radial distribution function, the discontinuity in density associated with melting, and the observed temperature

dependence of the dielectric constant of water.

The main objections to this theory have been based on the highly directional nature of the hydrogen bond⁽⁴¹⁾ which would preclude bending. The model has not been employed to explain the other anomalous properties of water and, in particular, it is very difficult to see how it can be adapted to explain the behaviour of aqueous solutions.

(c) The Hydrate Model.

In a model for the structure of water proposed by Pauling⁽⁸⁷⁾, water molecules are assumed to form hydrate structures similar to those that are known to be formed with inert gases, halogens, and low molecular weight hydrocarbons. These hydrates consist of tetrahedrally bonded water molecules in a cage network, within which a gas molecule may be trapped. Assuming the basic structural unit to be the pentagonal dodecahedron and the trapped molecules to be non hydrogen bonded water molecules, Pauling was able to show that such a structure would have a density of 0.98 gm/cm^3 .

A quantitative examination of Pauling's model has been given by Frank and Quist⁽⁴⁰⁾. They calculated the equilibrium of water molecules between the network and interstitial sites and showed,

with the aid of simple assumptions, that the model represents the P-V-T properties of water from 0°C to about 30°C satisfactorily. However, the model was less successful in predicting the heat capacity of water or the partial molar properties of non-polar solutes. Frank and Quist suggested that it might be improved by assuming the existence of a third state in which the water molecules are neither trapped in the hydrate lattice nor participating in the lattice, but represent the broken down structures.

(d) The Flickering Clusters Model.

Frank and Wen^{(39) (41)} have postulated that water consists of two distinct species, which are designated $\text{H}_2\text{O}^{\text{I}}$, (ice-like) and $\text{H}_2\text{O}^{\text{II}}$, (water-like). $\text{H}_2\text{O}^{\text{I}}$ is assumed to consist of clusters of molecules which are hydrogen bonded into a tetrahedral ice-like structure with little or no bending of the bonds. $\text{H}_2\text{O}^{\text{II}}$ consists of unbonded molecules, closer packed than $\text{H}_2\text{O}^{\text{I}}$, with large dipole-dipole interactions. On the macroscopic scale an equilibrium is established between the two species, but on the molecular scale, the $\text{H}_2\text{O}^{\text{I}}$ clusters are continually breaking up and reforming as a consequence of local energy fluctuations. The half-life of a cluster is estimated to be of the order 10^{-10} to 10^{-11} seconds, (i. e. about

10^2 to 10^3 times longer than the period of a molecular vibration). The effect of increasing the temperature and pressure is to shift the equilibrium in favour of the unbonded species. This model is frequently referred to as the 'flickering clusters' model.

Qualitative explanations of many of the anomalous properties of water are possible with this model. For instance, the thermodynamic properties of aqueous solutions may be explained by the tendency of non-polar solutes to stabilize clusters, whereas polar solutes tend to break them up. The anomalous density behaviour at low temperatures is explained by a rapid equilibrium shift to the more dense $\text{H}_2\text{O}^{\text{II}}$ species, resulting in a reduction in molecular volume greater than the increase due to 'normal' thermal expansion. The minima in the specific heat and compressibility curves as a function of temperature are both explained by the shift in the equilibrium towards the $\text{H}_2\text{O}^{\text{II}}$ species with increasing temperature.

Employing Frank and Wen's flickering clusters model, Némethy and Scheraga^{(81) (82)} have calculated the energy of the hydrogen bond, the temperature variation of cluster size, the degree of hydrogen bonding, and the values of several thermodynamic functions for water and heavy water. Recognising that any water

molecule may participate in any number of hydrogen bonds from zero to four, they derived expressions for the partition function and the mole fractions of the various species. The energy of the hydrogen bond and the molecular free-volume of the unbonded species were introduced as adjustable parameters.

The average number of molecules in an $\text{H}_2\text{O}^{\text{I}}$ cluster was estimated to decrease from 91 at 0°C to 21 at 100°C , and the fraction of unbroken hydrogen bonds decreased from 0.528 to 0.325 over the same range of temperature. Values of the internal energy, Helmholtz free energy, and entropy, agreed with experimental values to within 3% for water, and 6% for heavy water. Agreement with specific heat data was poor, although the calculated radial distribution curve was in excellent agreement with the experimental results of Morgan and Warren⁽⁷⁹⁾.

Further direct experimental evidence has been published in support of Némethy and Scheraga's interpretation of the flickering clusters model. Buijs and Choppin⁽²⁴⁾ have measured the absorption bands for water in the near infra-red region, (1.1 - 1.3 μ). They calculated that the fraction of unbroken hydrogen bonds after melting was 54%, a value in excellent agreement with the 52.8%

predicted by Némethy and Scheraga⁽⁸¹⁾.

Lately, the theory of Némethy and Scheraga has been examined in the light of Buijs and Choppin's experimental results and the two have been shown to be inconsistent⁽¹⁰⁴⁾. Vand and Senior⁽¹⁰⁵⁾ modified the model of Némethy and Scheraga from five to three species, replaced the distinct equally spaced energy levels with energy bands, and recalculated the partition function over the range 0° - 100°C. Re-evaluation of the Helmholtz free energy, internal energy, entropy, and specific heat showed them to be in agreement with experimental values over the whole temperature range to better than 1%.

(e) The Theory of Marchi and Eyring.

Some thermodynamic calculations on a variant of the mixture model of water have been given by Marchi and Eyring⁽⁷¹⁾. The assumed model considered water to be composed of two species: a non-rotating, hydrogen bonded, 'ice-like' species and an unbonded freely-rotating monomer. The monomeric component of the mixture could pack more closely than the ice-like species, which packed in a bulky manner with voids and interstitial sites. The vacancies were large enough to be occupied by the rotating

monomer molecules. It was postulated that as the temperature is increased there is an equilibrium shift towards the monomer. Also, more water molecules move into the interstitial sites thus decreasing the overall volume, but at the same time further fluidised vacancies are being created.

Applying their 'significant structure' theory to this model, Marchi and Eyring⁽⁷¹⁾ calculated the partition function for water. The computed values of the Helmholtz free energy and the entropy of water agreed reasonably well with experimental values, but the behaviour of the molar volume was in poor agreement with accepted data and failed to exhibit a minimum at 4°C.

(f) The Theory of Davis and Litovitz.

Yet a further model with a specific description of the structured regions in liquid water, was proposed in 1965 by Davis and Litovitz⁽³³⁾. In this model puckered hexagonal rings similar to those that are known to make up the structure of ice, were assumed to exist. Further, these rings were considered to co-exist in two forms: an open packed ice-like structure which favours the formation of hydrogen bonds between rings, and a close packed structure in which the molecules occupy a nearly complete body-

centred cubic structure. Employing this model, Davis and Litovitz⁽³³⁾ estimated that only 18% of the hydrogen bonds in ice are broken on melting, a value which is claimed to be in good agreement with estimates obtained from the Raman spectra and dielectric constant of water. The calculated radial distribution function was shown to be in agreement with the results of Morgan and Warren⁽⁷⁹⁾.

(g) Other Theories.

In addition to the models described above, several other partially successful two-state models and theories of water structure have been proposed. These theories have been mainly concerned with explaining the anomalous density behaviour of water.

A review of a two species thermodynamic approach to the structure of water, first suggested by Hall⁽⁴⁹⁾, has been given by Lawson and Hughes⁽⁶³⁾. In this theory it is postulated that there are two states in water differing in Gibb's free energy,

ΔG , entropy, ΔS , internal energy, ΔU , and volume Δv .

The distribution between the two states is governed by the usual Boltzmann statistics of activated processes. The consistent application of thermodynamics leads to the conclusion that as

well as the anticipated contribution to the compressibility from the 'ice-like' species, there are also structural effects in the thermal expansion and the specific heat. Hall⁽⁴⁹⁾ made estimates of ΔG , on the basis of sound absorption data, and was able to explain not only the minimum in compressibility, but the minimum in the specific heat and the maximum density. Fair agreement for several other properties of water was obtained using substantially the same values of ΔG , ΔH , and Δv . Hall concluded that the energy difference between the two states was due to the breaking of a hydrogen bond, but this is unlikely since ΔH was only one half the usually accepted value of 4.5 kcal/mole⁽⁸⁶⁾.

Eucken⁽³⁷⁾ proposed a model for water in which clusters of two, four and eight molecules existed with the monomer. By adjusting the concentrations of the clusters he was able to reproduce accurately the experimental compressibility and thermal expansion data of water.

Liquid water was also assumed to be a mixture of an 'ice-like' species and a 'water-like' species by Grjotheim and Krogh-Moe⁽⁴⁷⁾. The densities of the two species were estimated by extrapolation of the densities of water at high temperatures and

by extrapolation of the densities of ice at different temperatures. The fraction of hydrogen bonds as a function of temperature was calculated from the extrapolated densities and the known density of water. Qualitative agreement with Morgan and Warren's⁽⁷⁹⁾ radial distribution curves were obtained.

Taking the experimental density data as a basis, Wada⁽¹⁰⁷⁾ has calculated several thermodynamic quantities for water using a two species model. Haggis et al⁽⁴⁸⁾ have employed an equilibrium treatment to account for the dielectric properties of aqueous solutions.

3.3 Structure of Liquid Alcohols.

A comparison of the physical properties of alcohols with those of 'normal' liquids leads to the conclusion that there is some association of the molecules. This molecular association is explained by the ease with which the co-valent -OH group forms hydrogen bonds⁽⁸⁸⁾. Alternatively, by regarding water with its extensive hydrogen bonding as the 'zero'th' member of the aliphatic alcohol series, (H-OH, CH₃-OH, C₂H₅-OH, etc.), one might also expect a degree of hydrogen bonding in the other

members of the series. Further, since water has essentially two co-valent -OH groups, one would anticipate a lesser degree of association and this is in fact the case. The alcohols have received limited theoretical attention in comparison with normal (non-associated) liquids and with (highly associated) water. Formal thermodynamic methods have been developed for associated liquids⁽⁹⁰⁾, and in certain cases these methods may be applied to the alcohols.

Theoretically it is possible for the alcohols to form three hydrogen bonds, (c.f. four for water), since the oxygen atom has only one 'active' hydrogen in addition to its two lone-pair electrons. Radial distribution curves⁽⁵²⁾ (112) and dielectric constant⁽⁸⁵⁾ measurements indicate, however, that not more than two hydrogen bonds per molecule are formed. This limitation, which precludes three dimensional association of the molecules, results from a combination of the essentially co-operative nature of hydrogen bonding and the unfavorable steric effect of the bulky organic group. As in the case of water precise details of the structure of the associated groups is lacking but some generalisations are possible from experimental observations of structure dependent

properties.

Radial distribution curves⁽⁵²⁾ (112), obtained by X-ray scattering techniques, indicate the existence of linear polymer chains in alcohols. It is known also that liquid alcohols, in contrast to water, exhibit a range of relaxation times⁽⁴³⁾ and these may be associated with the various modes of vibration of the polymer chains. Further evidence in support of these structures has been provided by Oster and Kirkwood⁽⁶⁹⁾, who employed a linear chain model to predict, with fair agreement, the dielectric constants of the lower alcohols.

The dielectric constants of octan- 1-, 2-, 3-, and 4-ols and of 4 - methylheptan - 4 - ol are 9.8, 7.7, 6.8, 5.0 and 2.9⁽⁴³⁾ respectively; these data suggest that the degree of hydrogen bonding in the liquid alcohols is subject to strong steric limitations. This is in agreement with results from infra-red spectroscopy which indicate that, in general, association of alcohols decreases with increasing molecular weight. In the isomeric forms, there is decreasing association in the sequence primary, secondary, tertiary.

The generally accepted model of the alcohols assumes that

short-lived linear chains of variable, but restricted length ($n_{\text{max}} \sim 6$), are in dynamic equilibrium with unbonded molecules. Although water and the alcohols are similar in their tendency to exhibit hydrogen bonding, their structures, and hence their structure dependent properties, are very different.

CHAPTER IV.

DESCRIPTION OF THE HIGH PRESSURE VISCOSITY APPARATUS.

4.1 Features of the Design.

(a) Type of Viscometer.

The falling-weight or Lawaczeck viscometer is frequently used for relative viscosity measurements. The instrument consists of a weight falling vertically in a tube of slightly larger diameter. The fluid flow past the sinker is essentially that through an annulus, and for laminar conditions, theory predicts that the terminal velocity of the weight is inversely proportional to the fluid viscosity. (Appendix I). Falling-weight viscometers may be subdivided into those using a guided sinker and those using an unguided sinker.

The viscometer employed in this investigation was of the guided sinker type. The design and initial development of this viscometer, (designated Mark I), and that of the high pressure system has been described in detail by Cappi⁽²⁵⁾. Provision was made in the design of the high pressure system for possible conversion to an unguided sinker or rolling ball viscometer. An

attempt has been made during the development of a Mark II viscometer to assess the relative merits of the guided and unguided sinker systems for high pressure viscometers (Chapter VII).

(b) Principle of Sinker Timing System.

Practical and theoretical studies of the falling cylinder viscometer have shown that the sinker reaches its terminal velocity from rest in less than 1 cm. of travel⁽⁹⁶⁾. Consequently, the terminal velocity of a sinker is readily measured by observing the time of fall of the sinker between fixed points along the tube.

The principle of the system employed for measuring the sinker fall time in the Mk. I. viscometer is illustrated in Figure (4-1). A pair of coils wound externally on the viscometer tube form one arm of an A. C. bridge; the other arm is used to balance the bridge so that the output voltage displayed on an oscilloscope is zero. When a ferromagnetic sinker approaches the coils, the bridge balance is upset and the output voltage increases, since the inductance of the first coil is increased to a greater extent than that of the second coil. When the sinker is 'midway' between the coils the inductance of each coil is increased by an identical amount

FIG. 4-1. Sinker Detection System.

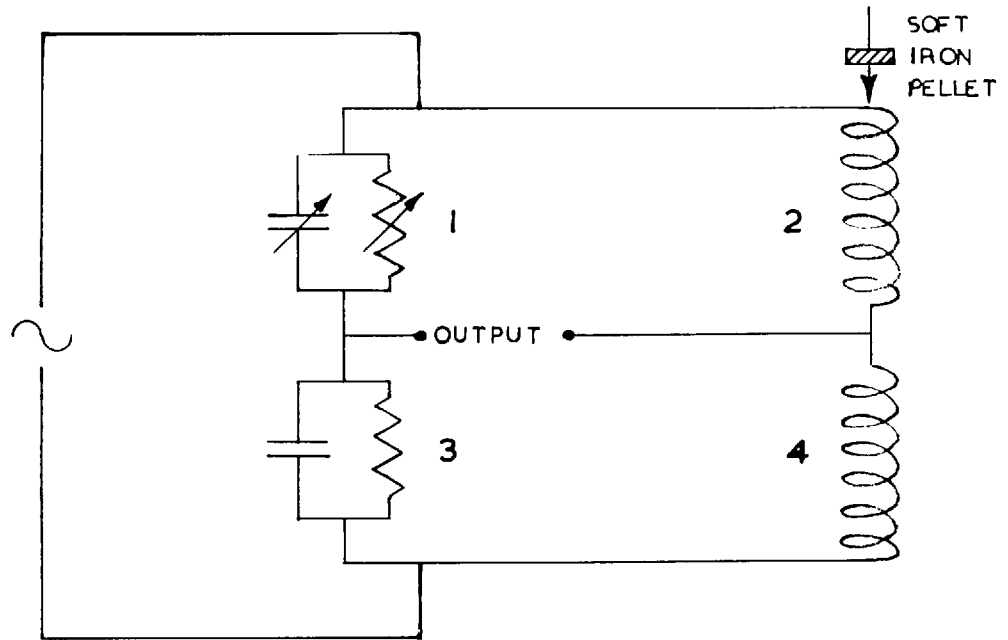
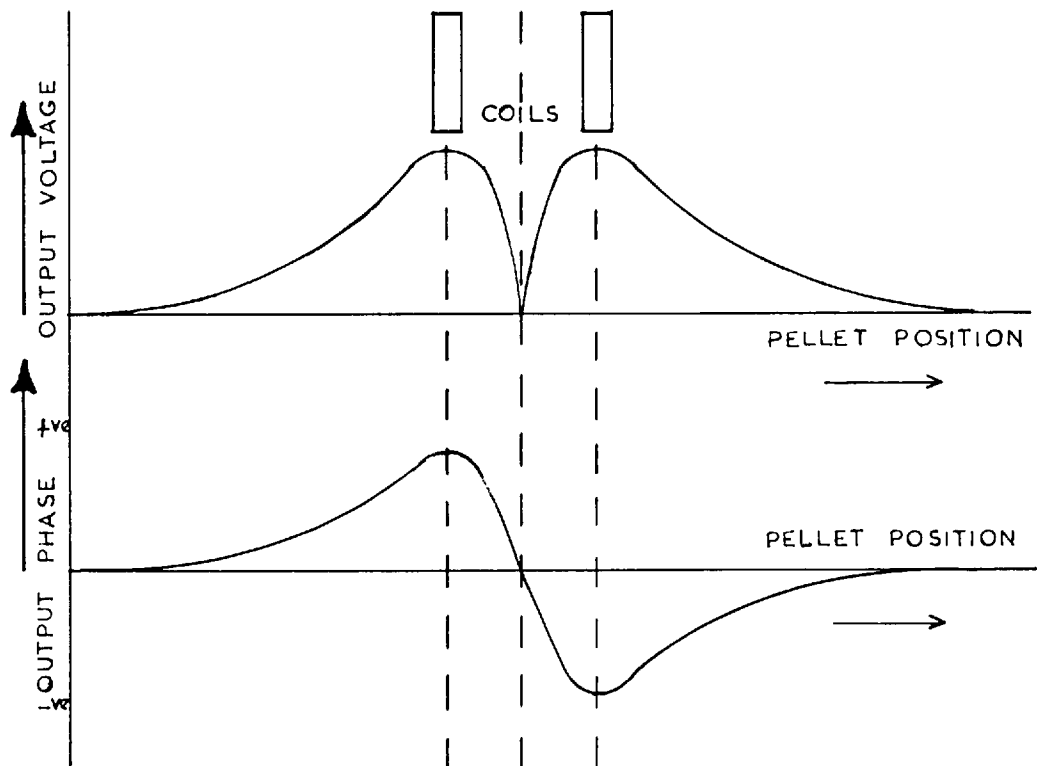


FIG. 4-2. Bridge Output Signal.



and hence the bridge balance is restored. As the sinker passes through the second coil the bridge is unbalanced again and the output signal increases, but in the reverse phase.

The variation of the bridge output voltage and phase as a sinker passes through the detection coils is illustrated in Figure (4-2).

(c) Density Measurement.

A knowledge of the density variation of the test fluid with pressure is required in order that buoyancy corrections may be applied to the observed fall times.

A technique using a viscometer with two sinkers of the same size, but different mass, to measure both the viscosity and the density of a liquid was first proposed by Jobling and Lawrence⁽⁵⁷⁾ and has been employed subsequently by Gordon et al⁽⁴⁶⁾. When compressibility data for the test fluid are not available, the Mk. I. viscometer can be used with a high density and a low density sinker, to enable an estimate of the fluid density to be made with sufficient accuracy for the calculation of buoyancy corrections.

4.2 The Mark I Viscometer.

For maximum sensitivity of the ferromagnetic timing system, it is essential that the detection coils are wound on a non-magnetic tube and that the sinker is made of a magnetic material. However, corrections due to dimension changes are simplified if the tube and sinker are constructed of the same material. A compromise is reached in the sinker design, by setting small pellets of soft iron inside a non-magnetic shell machined from the same material as the viscometer tube.

(Numbers in the following description refer to Drawing 1(a)).

(a) The Tube.

The Mk. I. viscometer tube, shown in Drawing 1(a), is $14\frac{1}{2}$ inches long and has an overall diameter of $15/16$ inch.

The tube (1), made from an austenitic stainless steel, (EN specification 58 JM), has good machining and excellent corrosion resisting characteristics. Its bore has been measured for uniformity of diameter, straightness and surface finish by the Standards Division of the National Physical Laboratory. The bore diameter of $0.3028(5) \pm .0003$ inches is maintained over its length of 8 inches. It is straight to $\pm .002$ inches and has a Centre-Line-

Average (C. L. A.) value for surface roughness of 4 microinches.

The transducer coils for the timer are wound externally in grooves (2) machined near the ends of the tube and as close to the bore as possible. The coils consist of 500 turns each of 46 S.W.G. double silk covered copper wire.

Stainless steel components (3), (4) are screwed to both ends of the tube and seat on gaskets of .004 inch thick annealed copper foil. Pockets are machined in parts (3) and (4) such that the two sinkers, by appropriate rotation of the pressure vessel, can be made to fall individually in the tube. The pockets in the two components are located in the same plane by means of a brass locking ring (5). A bursting disc of .0005 inch silver foil designed to burst under a differential pressure of 10 kg/cm^2 is soft soldered to end pocket (3).

The stainless steel end cap (6) sealed to pocket (3) with a copper gasket makes with a spigot machined to the pressure vessel closure so as to maintain axial alignment of the viscometer tube. A filling hole for the viscometer is provided in the end cap and this is sealed by a disc of copper foil and a grub screw. The top of the viscometer is free to accommodate minor strains due

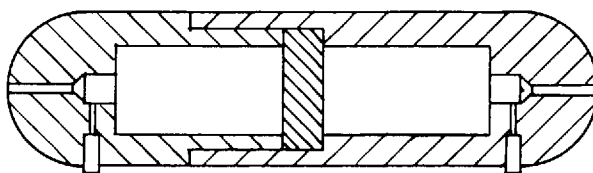
to temperature and pressure changes, while a small spring bearing against the vessel closure prevents free movement of the viscometer in the vessel.

The lower end of the viscometer is closed with a bellows unit (7) which accommodates volume changes of the test fluid. The bellows are covered by a brass sleeve (8) which is a push fit on end pocket (4). Numerous holes are drilled in the sleeve to provide adequate ventilation of the bellows. A moulded 'Araldite' electrical plug (9) is secured to a brass component (10) which is free to rotate relative to the sleeve (8). A miniature socket fixed to the bottom closure of the pressure vessel mates with (9) and a locating tongue on (10) so as to provide axial location at the lower end of the viscometer tube and fix the orientation of the sinker pockets relative to the pressure vessel.

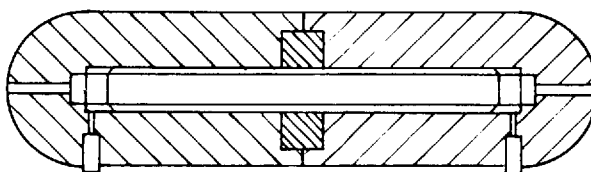
(b) The Sinkers.

Drawings of the two guided sinkers employed with the Mk. I viscometer are shown in Figure (4-3); the design of the high density stainless steel sinker is shown in Figure (4-3(a)) and that for the low density aluminium alloy sinker in Figure (4-3(b)). The aim in the design of the former was to keep the total sinker weight

FIG. 4-3. Sinkers for Mark I Viscometer.



a) Stainless Steel Sinker.



b) Aluminium Alloy Sinker.

small whereas the aluminium alloy sinker was designed to have as small a mean density as practicable.

A soft iron pellet is located centrally in each of the sinkers to actuate the timing system. The stainless steel sinker is a push fit assembly and the aluminium alloy sinker is assembled on a stud. The sinkers are guided by pins located at the ends and formed by forcing wire into radial holes.

4.3 The High Pressure System.

(a) General Arrangement.

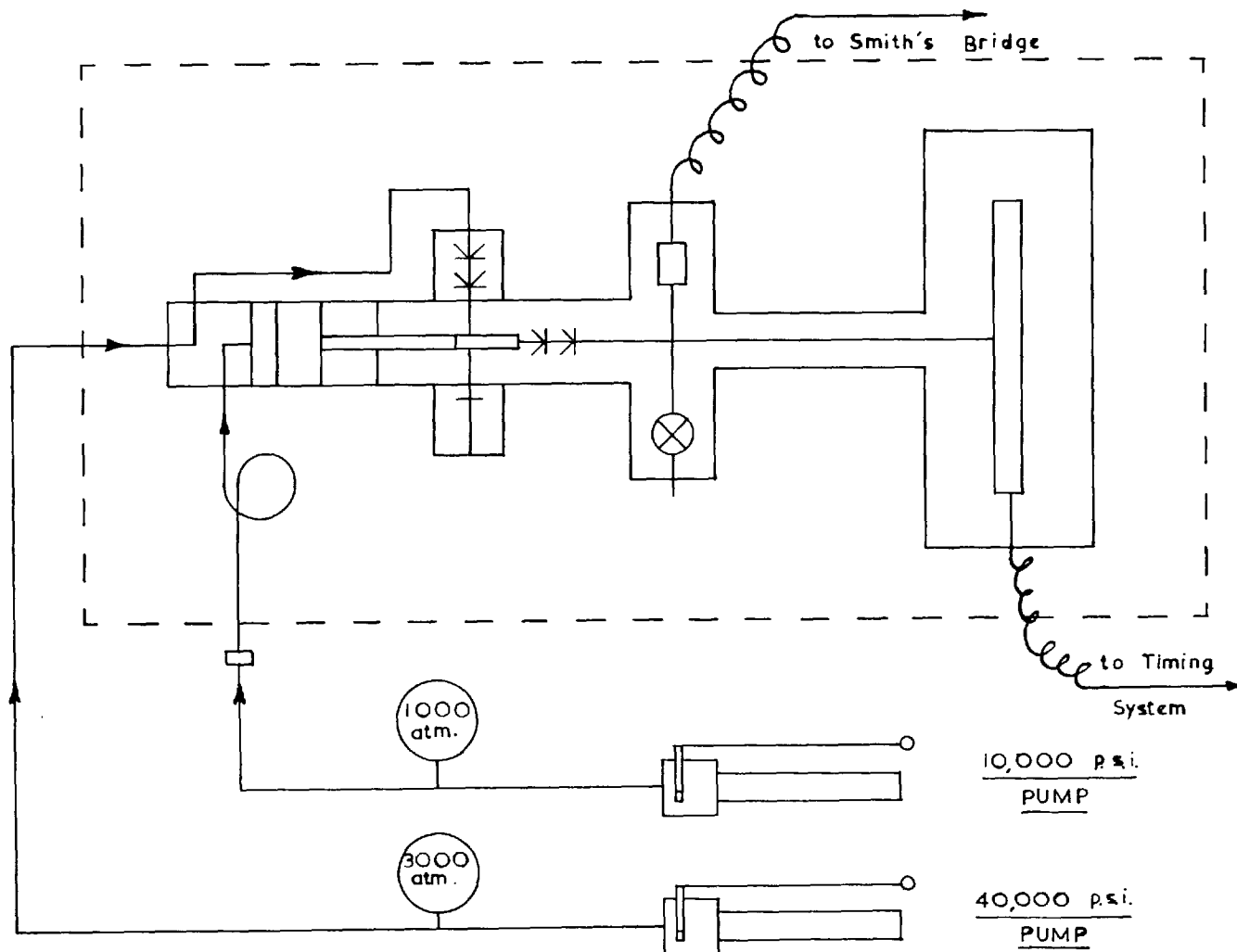
The general arrangement of the high pressure system is illustrated in detail in Drawing 2, and the complete high pressure system is shown schematically in Figure (4-4). To facilitate description of the high pressure apparatus it is convenient to divide it into the intensifier, the valve and gauge block, the pressure vessel, and the auxiliary pressure system.

(Numbers in the following descriptions refer to Drawing 2.)

(i) The Intensifier.

The intensifier is a small multi-stroke unit with suction and delivery valves and has a theoretical intensification ratio of

FIG. 4-4. Schematic Drawing of High Pressure System.



21.8 : 1. It comprises a low pressure piston and cylinder coupled and aligned with a high pressure piston and cylinder assembly.

The low pressure piston (1) is sealed with a moving Bridgman-type seal. The low pressure fluid to the intensifier is supplied through a flexible hose connected to a coupling (2) sealed in the cylinder.

The high pressure cylinder has a radius ratio of 7.6 and is closed at the delivery end by ball valves (3) located by a screwed spigot on the valve and gauge block. Two diametrically opposed cross-bores are situated near the delivery end of the cylinder. Pressure transmitting fluid is supplied through one of these holes to the high pressure system, via inlet ball valves (4), while the other hole, (which may be used for an alternative supply of high pressure fluid), is generally blanked off.

The high pressure piston (5) is a hardened cylinder bearing directly on the low pressure piston in a well-radiused counterbore. The high pressure piston seal is made by a pair of O rings supported on a phosphor-bronze carrier. The positions of both pistons may be observed through large diametrically opposed spy holes (6).

The collar (7) houses the inlet valves (4) and has an identical

housing for additional inlet valves should these be required. The housings are arranged to line up with the cross-bores in the high pressure cylinder.

The suction and delivery valves consist of $1/8$ inch diameter steel balls which plug $1/16$ inch diameter holes by virtue of the pressure difference across the ball. Twin balls are incorporated in each valve to reduce the likelihood of leakage due to particles of dirt adhering to the valve seatings.

(ii) The Valve and Gauge Block.

The valve and gauge block (8) houses the pressure gauge (9) and the pressure release valve (10) and provides a connection between the intensifier and the pipe (11) leading to the pressure vessel. The block itself has a main bore of $1/8$ inch diameter, and cross-bores leading to the pressure gauge chamber and the pressure release valve.

A manganin wire resistance gauge is employed to measure the pressure in the apparatus. The gauge consists of a coil of manganin wire wound loosely, as a single layer coil, on a hollow brass former. The gauge is mounted on closure (12) which provides four electrical connections to the gauge by means of three insulated leads and a 'ground' connection. A threaded plug (13) and an O ring complete

the sealing arrangements for the pressure gauge chamber. A copper-constantan thermocouple junction is situated close to the manganin coil on the low pressure side of one of the insulated electrodes.

A renewable valve seat (14) for the pressure release valve (10) is sealed against the valve and gauge block with an O ring and supported by the valve body (15). The conical tip of the valve spindle seats in a 1/16 inch diameter hole in item (14). The spindle is attached to a non-rotating piston and is controlled by a threaded spindle passing through the valve cover (16).

(iii) The Pressure Vessel

The pressure vessel (17) has external dimensions of 22 inches by $7\frac{1}{2}$ inches diameter with a bore of 1 inch. The vessel is connected to the high pressure system by the pressure pipe (11) and fluid enters the vessel by a small cross-bore. Bearing trunnions (18) are secured centrally to the vessel and the entire high pressure system may be rotated by means of a shaft and handwheel bolted to one of the trunnions, (not shown in Drawing 2). The top of the vessel is closed by a plug (19) backed up by a screw ring (20) containing cap screws which bear on a washer behind the plug. The

other end of the vessel is closed by an electrical connections plug (21) supported by a threaded member (22). Six electrical connections are provided by three twin 'Thermocoax' mineral insulated wires hard soldered into (21).

(iv) Auxiliary Pressure System.

The high pressure system is completed by the low and high pressure fluid supplies to the intensifier as shown in Figure (4-4).

A 10,000 p. s. i. handpump is used to supply hydraulic fluid (specification D. T. D. 585), employed in the low pressure circuit, the pressure being estimated by means of a 0 - 1000 atmosphere dial gauge. The pressure transmitting fluid used in the high pressure cylinder is a mixture of petroleum ether (boiling range 100°C - 120°C) with 10% hydraulic oil (D. T. D. 585), supplied from a 40,000 p. s. i. handpump.

(b) Mounting of the High Pressure System.

The high pressure system is supported on a rigidly constructed framework of mild steel angle and an insulated thermostat tank is bolted at its base to the main structure. The pressure vessel is supported by a steel sub-frame suspended in the tank from the main framework. The rotating high pressure system is carried on self-

aligning ball bearings as shown in Drawing 2. These bearings are mounted horizontally in special housings, which are supported on channel sections welded to the sub-frame.

A mechanism for locating the pressure vessel in a vertical plane is provided by a wheel which is attached to a loaded piston and which engages a V-shaped slot in a steel ramp. The piston-cylinder assembly is bolted to the sub-frame, and the ramps are bolted to the ends of the pressure vessel. The stop is disengaged manually by a small lever attached to the piston.

(c) Assembly and Operation.

(i) Assembly.

At all stages of the assembly of the high pressure apparatus care is taken to ensure that dirt is excluded from the system, since dust particles would impair the sealing characteristics of the ball valves and the O rings.

Before assembling the O ring seals, the seating surfaces are polished, cleaned and inspected for dirt or scratches. The condition of the O ring is inspected and the surfaces are lightly covered with oil to assist assembly. All the load bearing threads are cleaned and smeared with a molybdenum disulphide grease, and

the seal is completed by tightening the closure and compressing the O ring. The pre-loading necessary to prevent leakage of the seals at $10,000 \text{ kg/cm}^2$ depends on the diameter of the O ring. The closures of the pressure vessel and the pressure gauge chamber require special attention, but adequate loading of the remaining seals is effected by hand tightening the closures with standard spanners. For satisfactory sealing of the pressure vessel at $10,000 \text{ kg/cm}^2$ it is necessary to sledge the cap screws in the top closure and to tighten the electrical connections plug with a hydraulic spanner. The pressure gauge seal, the least satisfactory of all the seals, is loaded by sledging a long reach spanner. It is probable that leaks from this seal may be eliminated if a hydraulic spanner is used to tighten the closure.

(ii) Operation.

After the apparatus is assembled, the intensifier pistons are accurately aligned by pumping the low pressure piston to the end of its stroke. In this position the two pistons lie naturally in their cylinders and their relative position is retained on subsequent strokes by the friction in the seals. With the pistons in this position, the high pressure region is filled with filtered and dried pressure

transmitting fluid from the reservoir of the 40,000 p. s. i. handpump. The pressure release valve is closed and further pumping raises the pressure in the apparatus until at about 600 kg/cm² the pressure is sufficient to force the intensifier pistons back to the beginning of their stroke. A priming pressure of 2000 kg/cm² is reached in the apparatus by continued pumping. The pressure is further increased by transferring the charge of fluid in the high pressure cylinder past the delivery valves. The intensifier pistons are forced to the end of their stroke by raising the pressure in the low pressure cylinder with the 10,000 p. s. i. pump, and this pressure is then quickly released to assist the seating of the delivery ball valves. Once the delivery valves are seated, the high pressure cylinder is recharged with fluid, and the pistons are forced back to the beginning of their stroke by renewed pumping with the 40,000 p. s. i. pump. The desired pressure in the apparatus is attained by successively priming the high pressure cylinder to 2,000 kg/cm² and transferring the fluid to the high pressure section, as described above.

At low pressures with the viscometer tube in the pressure vessel, one stroke of the intensifier will raise the pressure in the system by about 1,000 kg/cm². To prevent seizure or scuffing,

the pistons in the intensifier are frequently lubricated with penetrating oil containing colloidal graphite.

The pressure in the system is reduced by slowly unscrewing the spindle of the pressure release valve with a hand key. The excess fluid escapes past the spindle and runs to waste through a hole in the valve body.

(d) Performance.

The overall performance of the high pressure system is satisfactory, although minor improvements to the delivery ball valves and the pressure release valve could be effected.

The pressure required to seat the delivery valves employing the low viscosity pressure transmitting fluid, is about $2,500 \text{ kg/cm}^2$. However, once seated the valves will continue to seal at pressures down to 500 kg/cm^2 . The delivery valves were subjected to an autofrettage pressure of $13,500 \text{ kg/cm}^2$ and this pressure undoubtedly deformed the ball seats. It is thought that the performance of the valves could be improved by completely renewing these units.

The 40,000 p. s. i. handpump operates satisfactorily with the low viscosity pressure transmitted fluid, provided the delivery valve seats in the pump are polished regularly.

Although the pressure release valve can be used for steady pressure reductions in the apparatus, (e. g. $10,000 \text{ kg/cm}^2$ in 4 hours), one complete turn of the key after the pressure has commenced to fall is sufficient for the complete release of pressure in the system. Steady pressure reductions are achieved by gently tapping the valve key with a hammer. The pressure release valve originally employed a spindle of 60° included cone angle, but the spindle was prone to stick in its seat, and pressure reduction was erratic. To reduce the likelihood of sticking, the valve is now used with a spindle of 90° included cone angle. Although sticking of the valve spindle has been eliminated, the sensitivity of pressure let down has been reduced. Finer control during pressure reduction could be provided by replacing the valve bonnet and controlling spindle.

The majority of the seals in the high pressure system are O rings of polyurethane (E. M. 1093) or low nitrile rubber (A. M. 90); both materials are supplied by Dowty Seals Ltd. Both square-section rings and normal circular section rings of 1/16 inch thickness are employed.

With the exception of the high pressure piston seals the polyurethane O rings in the equipment have very long lives. After

approximately 100 strokes of the intensifier, the high pressure piston is dismantled and the seals on the phosphor bronze carrier replaced. In view of the exceptionally good mechanical strength and sealing properties of the polyurethane O rings, it is unfortunate that pitting of the sealing surfaces results from extended use of the rings. The low nitrile, (A. M. 90), rubber seals have a limited life and need replacing periodically. These rings lose their flexibility after a time and become quite stiff. This is believed to be due to a continuation of the curing processes in the rubber, promoted by high pressures and temperatures.

4.4 Ancillary Equipment.

(a) The Sinker Timing System.

The principle of operation of the sinker timing system has been described earlier, (section 4.1(b)).

The central balance of the bridge provides a fixed point for timing the fall of a sinker. This point is detected by a semi-automatic system and used to trigger an electronic timer. The fall time of a sinker is measured by means of two independent triggering circuits connected to the coils on the viscometer tube and coupled to the

appropriate start or stop facility of the timer. A timing range of 10^{-4} seconds to 10 seconds is obtained on decatron counters, and this range is extended to 10^4 seconds by coupling these to a mechanical register.

A block diagram of the timing system is given in Figure (4-5). The whole arrangement, with the exception of the signal generator and timer is transistorised and battery supplied to reduce noise.

(b) The Pressure Measuring Equipment.

The resistance of the manganin coil is measured on a Smith's Difference Bridge in conjunction with a 'Pye' D. C. microvoltmeter, employed as a null-point galvanometer. The bridge is oil filled and the oil is circulated through the bridge by an external pump. A water cooler is employed in the circuit to regulate the temperature of the bridge. The e. m. f. of the pressure gauge thermocouple is measured on a 'Pye' Universal Potentiometer.

The principle of operation of the Smith's Difference Bridge is illustrated in Figure (4-6). If the resistance of the manganin gauge is S ohms, then it may be shown that S is given by,

$$S = \frac{(X_1 + X_2)}{2} - \frac{(X_3 + X_4)}{2} \quad \dots\dots (4-1)$$

FIG. 4-5. Block Diagram of Timing System.

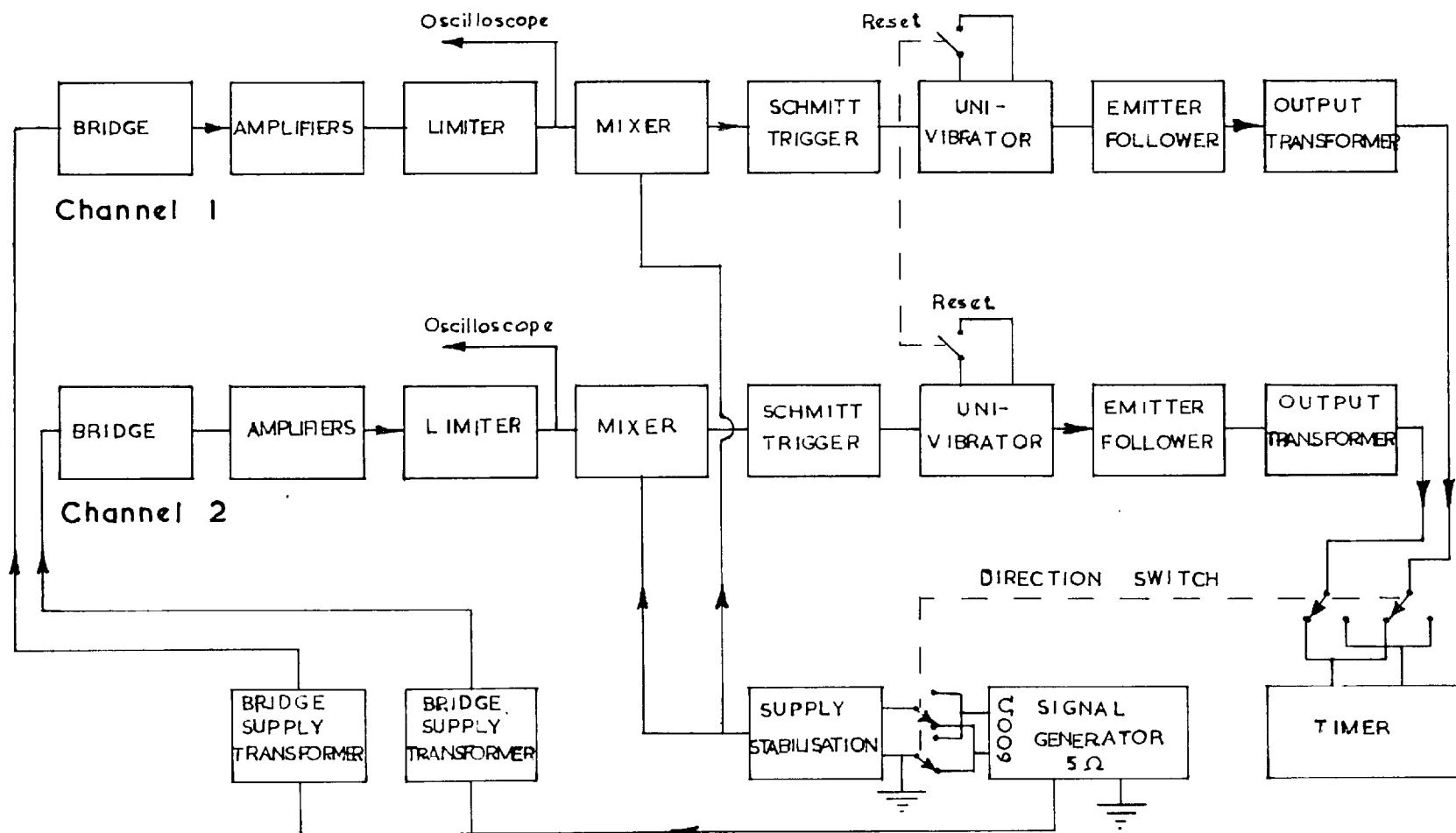
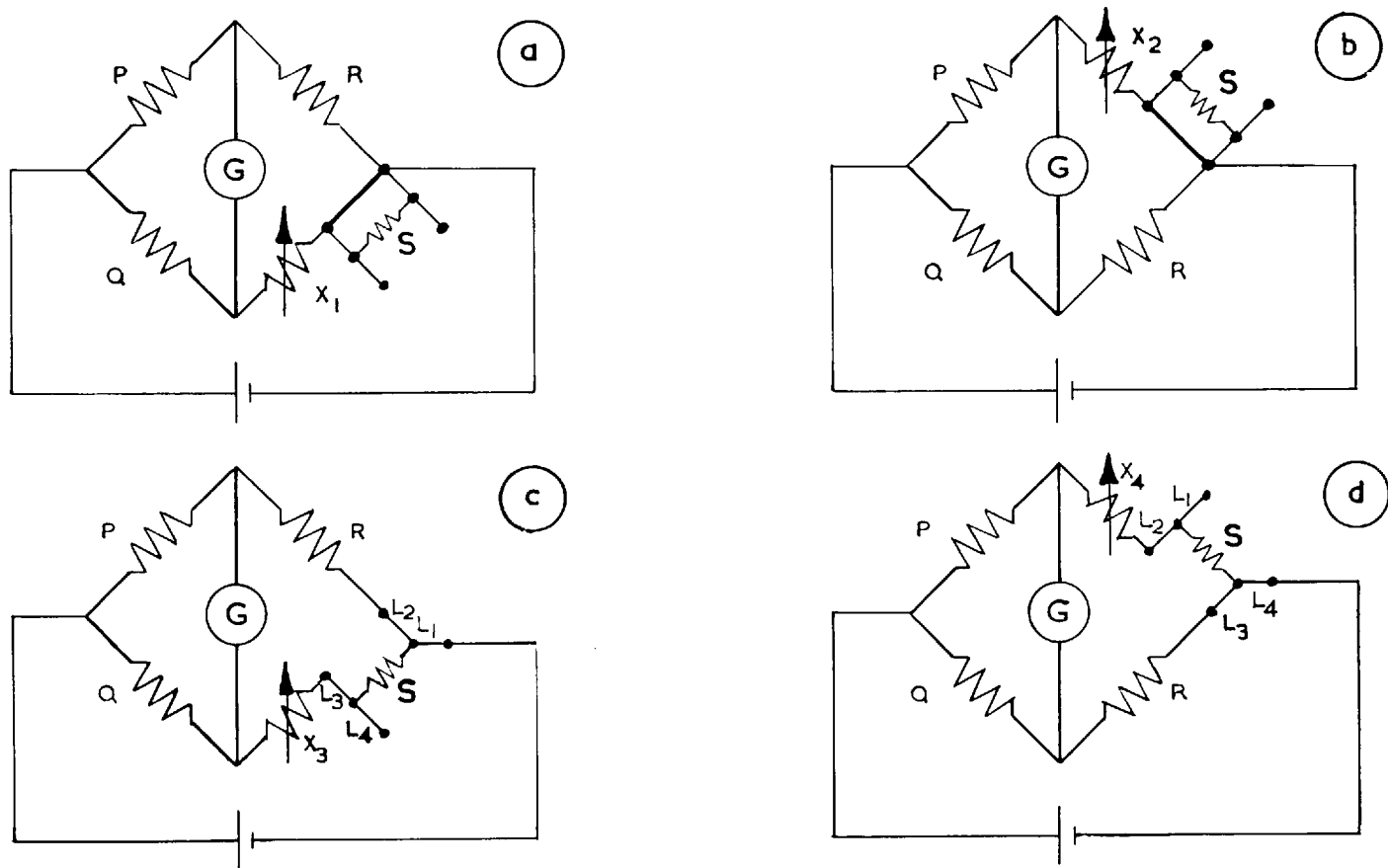


FIG. 4 -6. Principle of Operation of Smith's Bridge.



where X_1 , X_2 , X_3 , X_4 are the values of the variable arm of the bridge at balance.

The bridge is provided with two switches which permit the circuit to be connected in the sequence shown in Figure (4-6).

The resistance of the coil is calculated using the appropriate values of X_1 , X_2 , X_3 , X_4 required to balance the bridge. The temperature of the Smith's Bridge and the e.m.f. of the coil thermocouple are noted at the time of each resistance measurement.

(c) Temperature Control of Pressure Vessel.

The temperature of the pressure vessel and viscometer tube is controlled by circulating and regulating the temperature of the thermostating fluid in the tank surrounding the vessel. The fluid is drawn from the top of the tank by an externally mounted turbine pump, circulated through a heat exchanger, and returned to the bottom of the tank through two distributor pipes. The heat exchanger is used as a water cooler, or coupled to a refrigeration unit when low temperatures are required. Shell 'Tellus 23' oil is used as the thermostating fluid above 20°C; below this temperature kerosene is employed.

The bath is heated by two $1\frac{1}{2}$ kilowatt heaters with three heat

control. The bath is equipped with two thermostatic controllers; a mercury contact thermometer employed during 'warm-up' periods, and a toluene regulator fitted with a proportioning head for accurate temperature control.

The gradients and cyclic variations of temperature in the tank have been measured by means of a thermocouple. When the toluene regulator is employed for thermostatic control, cyclic variations are less than 0.005°C . However, the adjustment of the proportioning head varies with ambient temperature, and over an extended period the mean temperature of the bath may drift by 0.05°C . This long term variation is easily corrected, and the drift during an experimental measurement is negligible. The maximum deviation from the mean temperature within the tank is $\pm 0.02^{\circ}\text{C}$.

The temperature of the viscometer is assumed to be equal to the mean bath temperature and is measured with calibrated mercury-in-glass thermometers appropriately situated in the tank. It is estimated that the measured mean temperature of the viscometer is accurate to $\pm .02^{\circ}\text{C}$.

CHAPTER V.

CALIBRATION AND PERFORMANCE OF MARK I VISCOMETER.

5.1 Characteristic Behaviour of Falling Cylinder Viscometers.

(a) Theory.

Under laminar flow conditions the terminal velocity of a symmetric body falling through a liquid in a direction parallel to its axis of symmetry is inversely proportional to the viscosity of the liquid and proportional to some function of its shape. Although in general the equations of motion of a falling body cannot be solved exactly, the shape factor can be evaluated for spheres and cylinders. The method of measuring viscosity with a falling body viscometer is based on an assumed linear relationship between the terminal velocity and the viscosity; such viscometers generally employ a spherical or a cylindrical sinker.

The terminal velocity of a sinker is measured experimentally by determining the fall time between two fiducial marks on the viscometer tube. If the observed fall time of the sinker is t , and the distance between the timing stations is L , then the terminal velocity v is equal to L/t . For a given viscometer the sinker fall

time is directly proportional to the viscosity, and relative viscosity measurements are obtained from the ratio of fall times provided the constant of proportionality remains unchanged. Since the constant of proportionality is dependent on the dimensions of the viscometer and the densities of the sinker and the liquids under investigation, a theoretical analysis of the viscometer is essential in order to predict the effect on the fall time of changes in these variables.

For the purposes of mathematical analysis the falling cylinder viscometer is assumed to consist of a perfect cylinder of radius r_1 and length l , falling vertically along its axis in a perfectly round and straight tube of radius r_2 . It is further assumed that the cylinder falls concentrically in the tube and that all fluid flow is laminar.

At its terminal velocity the forces acting on the cylinder are,

- (i) The gravitational force, numerically equal to the bouyancy corrected weight of the cylinder.
- (ii) The viscous drag on the sides of the cylinder, caused by the relative motion of the sinker and tube.
- (iii) A pressure gradient across the ends of the sinker, associated with the fluid flow through the annulus between the cylinder and the

tube.

(iv) A drag on the ends of the sinker, due to the formation of stream lines at the entrance and at the exit of the annulus.

The contribution of the force (iv) is very difficult to calculate and, since its importance may be minimised by employing long cylinders with small radial clearances, it is usually neglected. The pressure gradient (iii) is assumed to be uniform across the ends of the cylinder and the surrounding annulus.

Using this simple model and neglecting the force on the cylinder arising from (iv) the following equation is derived in Appendix I,

$$\eta = \frac{w'}{2\pi L} \left\{ \ln\left(\frac{r_2}{r_1}\right) - \frac{(r_2^2 - r_1^2)}{(r_2^2 + r_1^2)} \right\} \cdot t \quad \dots\dots (5-1)$$

For a perfect cylinder equation (5-1) may be rewritten in the form,

$$\eta = k'(\rho_s - \rho_f)t \quad \dots\dots (5-2)$$

where

$$k' = \frac{r_1^2 g}{2L} \cdot \left\{ \ln\left(\frac{r_2}{r_1}\right) - \frac{(r_2^2 - r_1^2)}{(r_2^2 + r_1^2)} \right\} \quad \dots\dots (5-2A)$$

and ρ_s, ρ_f are the sinker and fluid densities respectively. By

substituting $r_2 = r_1 + c$ in equation (5-2A) and assuming that the radial clearance of the sinker, c , is small, it is shown in Appendix I that,

$$k' = \frac{c^3 g}{6Lr_1} \quad \dots\dots (5-2B)$$

Lohrenz, Swift and Kurata⁽⁶⁷⁾ have obtained similar expressions.

In one of the first theoretical studies of the falling cylinder viscometer, Lawaczeck⁽⁶³⁾ obtained equation (5-2B) by considering the fluid flow through the annulus to be similar to that between moving parallel plates.

Another expression relating viscosity to the dimensions of the falling cylinder viscometer is given in the A. S. M. E. Pressure-Viscosity Report⁽³⁾ as,

$$\eta = \frac{c^3 g}{6Lr_2} \left\{ 1 - \frac{1}{2} \left(\frac{c}{r_2} \right) - \frac{13}{20} \left(\frac{c}{r_2} \right)^2 - \frac{13}{40} \left(\frac{c}{r_2} \right)^3 \right\} (\rho_s - \rho_f) t$$

The model and assumptions used in deriving this relation are not given, but for the case where $c \ll r_2$ it reduces to Lawaczeck's approximation.

In a detailed theoretical and practical study of the falling cylinder viscometer, Scott⁽⁹⁶⁾ derived the following equation,

$$\eta = A(\rho_s - \rho_f)t - \frac{B\rho_f}{t} \quad \dots\dots (5-3)$$

where A and B are constants.

A is given by,

$$A = \frac{c^3 g}{6Lr_1 F}$$

where

$$F = \left\{ 1 + \frac{3}{2} \left(\frac{c}{r_1} \right) + \frac{7}{5} \left(\frac{c}{r_1} \right)^2 + \frac{4}{5} \left(\frac{c}{r_1} \right)^3 + \dots \right\}$$

The first term reduces to Lawaczeck's approximation if $c \ll r_1$.

The second term is a correction term which makes allowance for the kinetic energy losses due to turbulence and for the development of fluid flow in the annulus. These factors are combined in the constant B, which is given by,

$$B = \frac{9}{280} \cdot \frac{cLr_1}{1F} \left\{ 1 - \frac{1}{3} \left(\frac{c}{r_1} \right) + \frac{353}{540} \left(\frac{c}{r_1} \right)^2 + \dots\dots \right\} \cdot f'$$

and

$$f' = 1.056 \left\{ 1 - 0.11 \left(\frac{c}{r_1} \right) + \dots \right\}$$

(b) Stability of Falling Cylinders.

Some general observations on the nature and speed of fall of simple cylinders falling in a closed tube are required to ascertain

the extent to which the assumptions made in the previous section are satisfied by practical viscometers. The work of Scott⁽⁹⁶⁾, verified in the development of an improved viscometer (Chapter VII), indicates that there is a well defined range of terminal velocities for a cylinder within which the fall is both stable and reproducible.

Within the range of terminal velocities for steady fall, Scott observed the fluid flow past the cylinders to be parallel to the axes of the cylinders and evenly distributed around them, but for low terminal velocities the behaviour of the cylinders was erratic and fall times inconsistent. At high velocities a slight oscillation about a middle diameter of the sinker occurred which increased in amplitude with increasing fall velocity until eventually the cylinder collided with the walls of the tube.

The existence of centralising forces maintaining concentric and coaxial fall of the cylinders is demonstrated by releasing the cylinder from the side of the tube. On commencing to fall the sinker rapidly moves from the wall to a position concentric with the tube. The tendency of a sinker to centre itself is accounted for partly by the radial pressure effects of fluid entering and leaving

the annulus, and partly by the flow along the body of the sinker. The centralizing forces are dependent on the sinker velocity and will increase with decreasing fall time.

Small variations in the radial clearance between the sinker and the tube, which are unavoidable, will lead to an uneven shear stress distribution on the sinker. Since the terminal velocity is proportional to the cube of the radial clearance, it follows that the shape and surface finish of the components are very important in minimising any asymmetric forces. The self-centring forces on a sinker decrease with decreasing fall velocity until they become comparable with the forces due to asymmetry. At this stage the sinker is displaced from the axis and falls eccentrically and erratically. At short fall times the sinker becomes unstable due to the effects of turbulence in the flow past the cylinder. Scott⁽⁹⁶⁾, Lohrenz et al⁽⁶⁷⁾, and Lohrenz and Kurata⁽⁶⁸⁾ have shown that the fall time of the sinker may be correlated with the Reynold's Number in the annulus over this range.

At $10,000 \text{ kg/cm}^2$ the viscosity of a pure liquid is typically a factor of 10^2 or 10^3 times greater than its value at atmospheric pressure. Therefore, a viscometer for use over this pressure

range should be capable of measuring viscosity increases of this order without changing sinkers. The literature does not give a clear indication of the useful viscosity range of a simple unguided cylinder.

Sinker stability at low velocities is improved by fitting guiding or stabilizing pins as in the instruments of Bridgman⁽¹⁸⁾, A. S. M. E. ⁽³⁾, and Lohrenz et al⁽⁶⁷⁾⁽⁶⁸⁾.

Although guiding pins considerably reduce the limits of eccentric fall, they complicate the sinker design, are difficult to make accurately, and provide additional drag.

The effect of various end shapes on the stability of cylinders has not been fully investigated. It is doubtful if the low velocity performance of a sinker can be improved by this means, although at short fall times some streamlining may lead to better stability and reduced turbulence.

(c) Calibration of Viscometers.

The bouyancy corrected weight of a sinker w' , may be written in terms of the fluid and sinker densities as,

$$w' = V(\rho_s - \rho_f)g \quad \dots\dots (5-4)$$

where V is the volume of the sinker. Hence the viscometer constant k' of equation (5-2) is given by,

$$k' = \frac{Vg}{2\pi L} \left\{ \ln \frac{r_2}{r_1} - \frac{(r_2^2 - r_1^2)}{(r_2^2 + r_1^2)} \right\} \dots\dots (5-5)$$

In the derivation of equation (5-2) the frictional forces on the sinker are assumed to be solely due to the viscous drag on the cylindrical portion of the sinker. The other contributions to the total drag on the sinker include,

- (i) The drag caused by kinetic energy losses due to turbulence.
- (ii) The drag due to flow effects at the ends of the annulus.
- (iii) The drag arising from fluid flow past the guiding pins.

If additional contributions to the total viscous drag are negligible then the viscometer may be employed for absolute viscosity measurements using equations (5-2) and (5-5). Lohrenz et al⁽⁶⁷⁾ have noted that the sinker and tube diameters must be measured with an accuracy of 1 part in 10^9 in order to compute k' to four significant figures. On account of the difficulties involved in machining and measuring to this order of accuracy the falling cylinder viscometer cannot be used for absolute measurements.

In the case where additional drag is not negligible compared

with that on the cylindrical surface of the sinker, the fall time can be represented by equation (5-2) provided the additional contributions are substantially laminar effects. The viscometer constant k' is not given exactly by equation (5-5) and must therefore be experimentally determined by calibration against liquids of known viscosity and density. Guided sinkers have been calibrated by Lohrenz et al⁽⁶⁷⁾ ⁽⁶⁸⁾ according to equation (5-2) and they have shown that the experimental determinations of k' are as much as 35% lower than the theoretical values calculated from equation (5-5).

Falling cylinder viscometers have been widely calibrated by assuming the proportionality between the viscosity and time-density difference product expressed in equation (5-2), (Bridgman⁽¹⁸⁾, Mason⁽⁷²⁾, Jobling and Lawrence⁽⁵⁷⁾, and A. S. M. E.⁽³⁾). However, it has been shown that this proportionality is not valid at short fall times⁽⁶⁷⁾ ⁽⁹¹⁾, on account of increased energy losses due to turbulence. Scott⁽⁹⁶⁾ added a correction term of the form $\frac{B\rho_f}{t}$ to equation (5-2) to take account of these turbulence losses. Her theoretical equation (5-3) yielded absolute viscosities to about 2%, when the correction term was small.

For sinkers that are not perfectly cylindrical, it is more convenient to express the bouyancy corrected weight of the sinker as,

$$w' = mg \frac{(\rho_s - \rho_f)}{\rho_s}$$

where m is the mass of the sinker.

From equation (5-1) it follows that,

$$\eta = k \frac{(\rho_s - \rho_f)}{\rho_s} \cdot t \quad \dots\dots (5-6)$$

where

$$k = \frac{mg}{2\pi lL} \left\{ \ln\left(\frac{r_2}{r_1}\right) - \frac{(r_2^2 - r_1^2)}{(r_2^2 + r_1^2)} \right\} \quad \dots\dots (5-6A)$$

Theoretical expressions such as those in equations (5-6) and (5-6A) are useful in that they permit the effect of temperature and pressure changes on the proportionality of η and t to be estimated. Since the radius ratio (r_2/r_1) is independent of temperature and pressure for a sinker and tube constructed of the same type of material, changes in the viscometer constant k are dependent only on the changes of l and L provided that the material is isotropic. If the coefficient of thermal expansion of

the viscometer material is α and the compressibility coefficient is β , then the correction factor for a temperature change ΔT and a pressure change ΔP , is given by,

$$\left(1 + \frac{\Delta k}{k}\right) = \frac{1}{(1 + \alpha \Delta T)^2 (1 - \beta \Delta P)^2} \quad \dots (5-7)$$

and

$$t^* = t \left(1 + \frac{\Delta k}{k}\right)$$

where t^* is the corrected fall time.

Using equation (5-6A) Lohrenz and Kurata⁽⁶⁸⁾ have shown that changes of as much as 60% in the viscometer constant may be predicted with an accuracy of 5%. If the tube and sinker are not manufactured from the same type of material, the pressure and temperature dependence of (r_2/r_1) and hence that of the correction factor may be calculated with the aid of equations (5-6) and (5-6A).

The object of calibrating a viscometer is to check the range of velocities for which the sinker fall time satisfies equation (5-6). The fall time is determined in a series of liquids of known viscosity and density and the product $\frac{t^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$ evaluated. It is essential that every tube and sinker assembly is calibrated over its entire viscosity range since the relative magnitudes of the various

contributions to the total viscous drag will vary from sinker to sinker. Although the general form of the calibration curves will remain constant for a particular sinker design the detail will vary.

5.2 Additional Factors Influencing Sinker Fall Time.

(a) Introduction.

The sinkers employed with the Mk. I. viscometer are guided cylinders with hemispherical ends as shown in Figures (4-3(a) and(b)). Two sinkers have been employed with this viscometer tube, one of stainless steel and the other of aluminium alloy. The shell of the high density sinker was made from steel (E N 58 J M) similar to that used for the viscometer tube. The low density sinker was machined from an aluminium alloy (R R . 77). The thermal expansion and compressibility coefficients of R R . 77 differ appreciably from those of E N . 58 J M .

It is assumed that (r_2/r_1) is independent of temperature and pressure for the stainless steel sinker, and that equation (5-7) can be used for the calculation of changes in k . However, for the aluminium sinker (r_2/r_1) is not constant and changes in the viscometer constant are calculated by computing the changes of

$$\frac{1}{1L} \left\{ \begin{array}{l} \ln\left(\frac{r_2}{r_1}\right) - \frac{(r_2^2 - r_1^2)}{(r_2^2 + r_1^2)} \end{array} \right\}$$

At 20°C and 1 atmosphere the stainless steel and aluminium alloy sinkers have radial clearances of .004" and .0045" and mean densities of 7.9556 gm/cc and 3.1997 gm/cc respectively. The minimum fall time of either sinker is taken as 10 seconds, because this is the shortest acceptable limit for the time taken to rotate the vessel and operate the timing system. This fall time corresponds to a lower viscosity limit of 0.2 centipoise for both sinkers.

In addition to the dependence of the fall time on the fluid flow conditions, it is essential to consider the effects of the following factors.

(b) Eccentric Fall.

Since the terminal velocity of a sinker is proportional to the cube of the radial clearance, it is obvious that deviations from concentric fall will be reflected in the fall time. Further, since the volume flow rate of a fluid through an annular tube, in which the inner core touches the outer pipe, is 2.5 times that through a concentric annular tube⁽³⁶⁾, the terminal velocity of a sinker which is eccentric relative to the tube will increase. Cappi⁽²⁵⁾ has

obtained an approximate expression for the terminal velocity of an eccentrically falling sinker and his calculations show that the variation of the terminal velocity with the displacement of the tube and sinker axes is of the form shown in Figure (5-1). It may be seen that for small displacements the increase in fall velocity is approximately proportional to the square of the displacement.

In common with other inversion type falling cylinder viscometers^{(3) (18)} both the stainless steel and aluminium alloy sinkers exhibit a directional effect, i. e. their terminal velocity is dependent on the direction of fall. Because of this effect the sinkers are always orientated in the same direction relative to the tube. If the blank end is denoted as 'end 1' and the bellows end as 'end 2', then the fall times of both sinkers starting from end 2 are shorter than the corresponding fall times from end 1. The discrepancy being approximately 1% for the stainless steel sinker and 0.1% for the aluminium alloy sinker. These effects were demonstrated to be properties of the sinkers rather than the tube by reversing the orientation of the sinkers relative to the tube, when the effect was shown to be reversed. The directional effect is constant over a range of fall times, from 10 seconds to an upper

FIG. 5-1. Effect of Eccentricity on Fall Time.

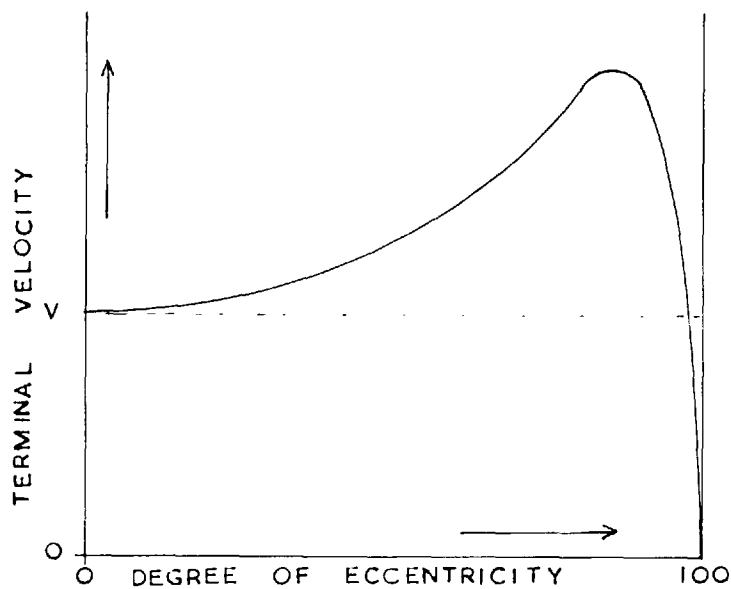
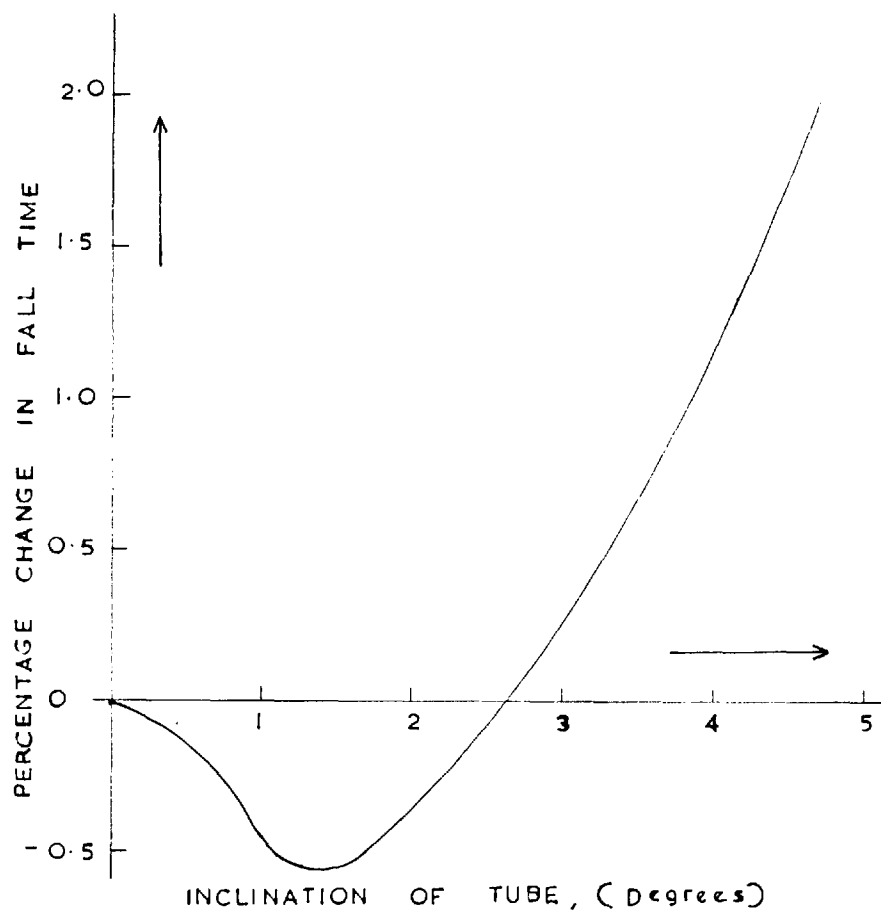


FIG. 5-2. Effect of Inclination on Fall Time.



limit, which for the stainless steel sinker is approximately 70 seconds. At this limit the scatter of fall times from end 2 increases and the mean fall time from this end becomes 6% - 8% less than that from end 1. The aluminium alloy sinker maintains a constant directional effect for fall times from end 2. The fall time at which the sinkers begin to fall eccentrically from end 1 is greater than 340 seconds for the stainless steel sinker, and greater than 450 seconds for the aluminium alloy sinker.

The self-centring forces acting on a falling cylinder have already been mentioned, together with the tendency of a sinker to fall eccentrically when the forces due to asymmetry become comparable with them. The directional effects observed with the stainless steel and aluminium alloy sinkers may be explained if the sinkers fall with a greater degree of eccentricity from end 2. The asymmetric forces causing the sinkers to tilt and fall eccentrically are most probably due to the stabilizing pins being of slightly different lengths, although out of roundness and an uneven mass distribution could be important. The inferior directional performance of the stainless steel sinker may be explained by its smaller radial clearance, thus making surface imperfections more significant, and

by the asymmetrically placed joint in its shell.

At short fall times a high degree of turbulence may cause the sinker to snake and fall eccentrically. Turbulence increases the fall time, in contrast to the decrease caused by eccentric fall. These effects are combined in the calibration curve and the fall time may increase or decrease depending on their relative magnitude. Eccentricity of the falling sinker may also be caused by a non-vertical viscometer tube.

(c) Non-Vertical Viscometer Tube.

When an unguided sinker is falling in a slightly inclined tube it falls eccentrically with its axis tilted relative to the bore of the tube. While the tilting of the sinker provides hydrodynamic lift it also tends to increase the viscous drag and consequently the fall time. However, it has been shown that eccentricity of a sinker leads to an increase in its terminal velocity, so that the fall time may initially increase or decrease on inclining the viscometer tube, depending on the relative magnitudes of the effects. For guided sinkers a further increase in the angle of inclination quickly introduces frictional resistance when the stabilizing pins touch the tube walls. At large inclinations therefore the fall time increases

rapidly.

Scott⁽⁹⁶⁾ observed both an increase and a decrease in fall time on inclining the tube, whereas Awbery and Griffith⁽⁴⁾ found an initial decrease with their instrument.

The results in Figure (5-2) obtained by Cappi⁽²⁵⁾ for a .006" clearance sinker in the Mk. I viscometer indicate the errors incurred if the viscometer tube is not vertical.

(d) Terminal Velocity Effects.

It can be shown that the distance, S , travelled by a cylinder falling vertically in a closed tube from rest to $E\%$ of its terminal velocity is given by,

$$S = \frac{(\rho_s - \rho_f) \rho_s g c^6}{36 \eta^2 r_1^2} \cdot \{ 3.605 - \ln E \} \quad \dots (5-8)$$

Equation (5-8) is derived for a simple cylinder and assumes that (c/r_1) and E are small.

When an inversion system is employed for sinker recovery, simple theory is complicated by the finite time taken in rotating and locking the system. With such a system the sinker commences to fall before the viscometer is vertical, and may travel some distance before its true terminal velocity is attained. In the Mk. I viscometer

the sinker travels about 3 cm. from rest before reaching the first triggering position. Assuming that the sinker falls at its final velocity over the whole of this distance, then for a total fall time of 10 seconds the time taken from rest to the triggering position is about $\frac{1}{2}$ second. At very short fall times it is doubtful if the sinker is falling at its final velocity when timing commences, but for fall times greater than 20 seconds it is probable that the terminal velocity has been reached.

(e) Contamination.

During preliminary experiments with the viscometer it was observed that the sinker fall time was very sensitive to contamination of the test liquid. The effect of contamination was to increase the overall scatter of the results and the fall of the sinker became erratic. Generally, the mean fall time was increased by the presence of a second liquid phase.

Contamination of the test liquid by solid particles was guarded against by filtering all liquids entering the viscometer and by careful cleaning and inspection of parts during assembly.

The seals of the Mk. I. instrument are not entirely satisfactory since slight leaks occur during rapid pressure reductions.

The effect was first observed when it was found that the mean fall time of the sinker in water at atmospheric pressure increased slightly after pressurisation of the viscometer. Since it has been shown that the viscosity of water is independent of pressure cycling⁽⁶¹⁾, it was concluded that the observed increase was due to contamination of the water by the pressure transmitting fluid. The levels of contamination involved were very small since with test liquids that were completely miscible with the pressure transmitting fluid, no significant increase in fall time was observed.

5.3 Calibration of Mk. I. Viscometer.

(a) Stainless Steel Sinker ($c = .004''$)

The .004" clearance sinker was calibrated by determining the mean fall time of the sinker at atmospheric pressure in a wide range of liquids of known viscosity and density. As the measurements were not made at the same temperature it was necessary to correct the times for changes of the viscometer constant with temperature. For calibration purposes the fall time was taken as the arithmetic mean of at least four, and usually eight, readings in both directions. An arbitrary reference temperature of 25°C was taken and fall times

were corrected to this temperature by dividing them by

$$(1 + 2 \times 1.6 \cdot (T - 25) \cdot 10^{-5})$$

where T was the viscometer temperature in $^{\circ}\text{C}$.

During the early stages of experimental work it was observed that on reassembling the viscometer the mean fall times for samples of the same liquid at identical temperatures often differed by as much as $\frac{1}{2}\%$. This difference was attributed to either, (or both), of the following possibilities,

- (i) A contamination film on the sinker and tube surfaces of variable thickness, dependent on the amount of cleaning and exposure.
- (ii) Asymmetry of the sinker and tube, which could influence the fall time depending on the angular orientation of the sinker relative to the tube.

Variations in (i) and (ii) during an experimental run were demonstrated to be negligible by the excellent agreement of successive relative viscosity determinations under the same conditions. This is not unexpected since the thickness of the contamination layer is unlikely to vary during an experiment and it has been demonstrated that falling cylinders do not rotate about their axes⁽⁹⁶⁾.

A large number of points are required for an accurate calibration curve because of the uncertainty in a single determination of the viscometer constant. The density and viscosity data employed for the calibration were taken directly, or by interpolation, from published values for the pure liquids. Where compounds of low purity were used the values were obtained by standard techniques. The sinker density was calculated at each temperature from the weights and densities of its component parts, as shown in Appendix III.

The complete calibration curve is plotted as

$$\frac{t^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$$

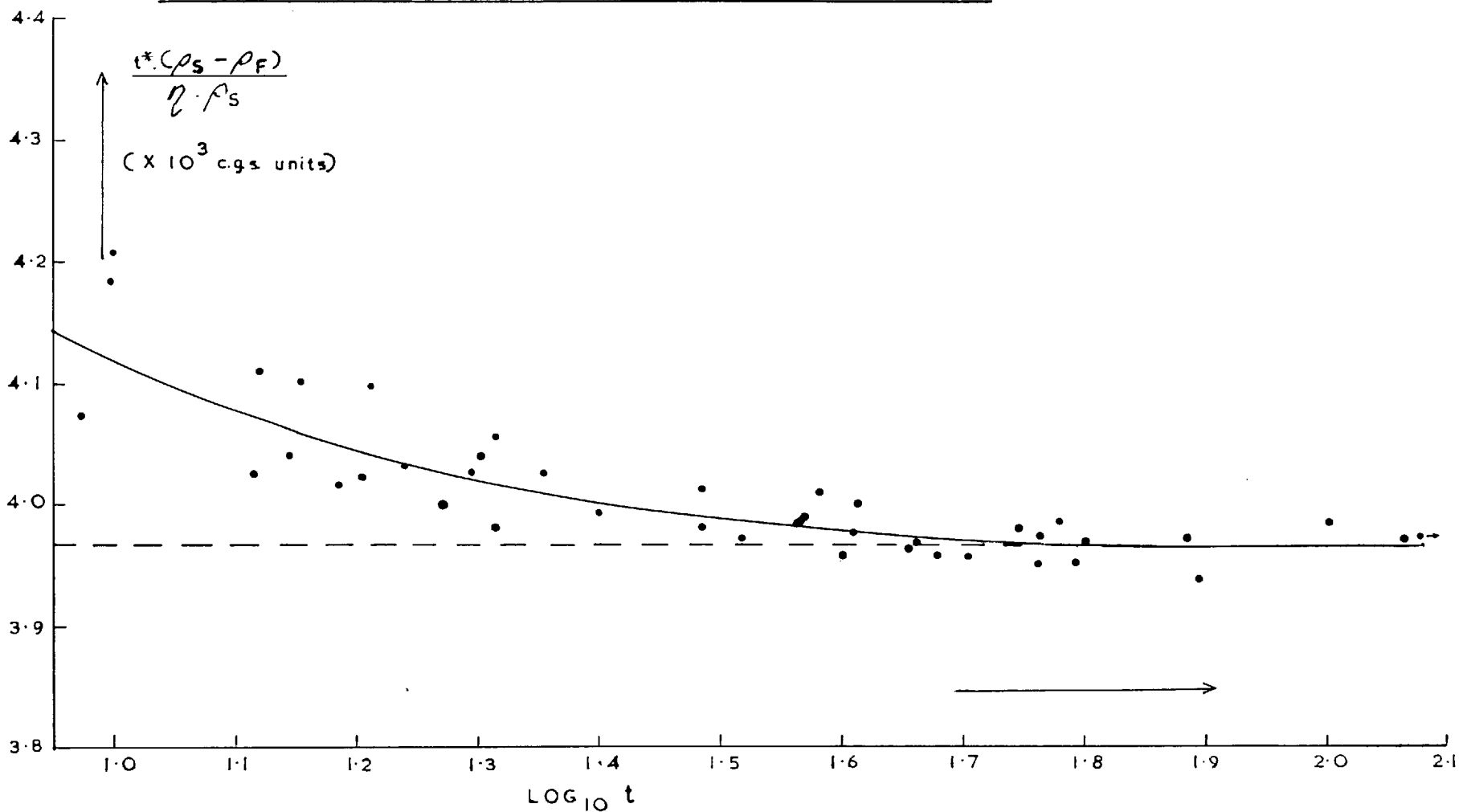
against $\log_{10} t$ in Figure (5-3); the data are tabulated in Appendix II.

From the calibration equation (5-6),

$$\frac{t^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s} = \frac{1}{k}$$

The calibration points in Figure (5-3) lie close to a smooth curve, although the scatter is much larger at the shorter fall times. The data have been fitted with a polynomial 'least squares'

FIG. 5-3. Calibration Curve for Stainless Steel Sinkers.



program on a digital computer, giving,

$$\frac{t^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s} = 5.0988 \cdot 10^3 - 1.6319 \cdot 10^3 \cdot (\log_{10} t) \\ + 7.743 \cdot 10^2 \cdot (\log_{10} t)^2 - 1.205 \cdot 10^2 \cdot (\log_{10} t)^3$$

The value of

$$\frac{t^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$$

is not a constant independent of the terminal velocity as predicted by the calibration equation (5-6), but decreases with increasing fall time to attain a steady value of $3.96 \cdot 10^3$ c. g. s. units at fall times greater than 65 seconds. At these fall times the effects of non-laminar flow are negligible and, if the experimental value of the viscometer constant is denoted by k_{expt} ,

$$k_{\text{expt}} = \frac{1}{3.96 \cdot 10^3} = 2.52 \cdot 10^{-4} \text{ c. g. s. units.}$$

This may be compared with the theoretical value of the viscometer constant for the stainless steel sinker: $3.51 \cdot 10^{-4}$ c. g. s. units, which is given by the application of equation (5-6A). Thus additional drag effects reduce the viscometer constant to 72% of its theoretical

value for a simple cylinder of similar length and diameter.

Lohrenz, Swift and Kurata⁽⁶⁷⁾ found that laminar flow conditions for guided sinkers prevail at Reynond's Numbers, N_{RE} , less than 0.1 to 0.2, where N_{RE} is defined by,

$$N_{RE} = \frac{\rho_f v}{\eta} \cdot r_1 \sqrt{\frac{\ln\left(\frac{r_2}{r_1}\right) - \frac{(r_2^2 - r_1^2)}{(r_2^2 + r_1^2)}}{1}}$$

For the stainless steel sinker it can be shown from Figure (5-3) that laminar flow prevails when N_{RE} is less than 0.15.

In an uninterrupted sinker annulus, Lohrenz and Kurata⁽⁶⁸⁾ showed that k was independent of fall time for N_{RE} less than 10, although Scott⁽⁹⁶⁾ contends that the flow conditions are never completely laminar. The turbulence correction curve Figure (5-4) was constructed from the calibration data and k_{expt} by calculating the percentage of the fall time, ($x\%$), to be subtracted from t^* such that,

$$\frac{t^* (1 - x/100)}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s} = \frac{1}{k_{expt}} = 3.96 \cdot 10^3 \text{ c. g. s. units}$$

The correction curve is given within the range of fall times from 10 seconds to 65 seconds by,

$$x = 26.649 - 38.006 (\log_{10} t) + 17.830 (\log_{10} t)^2 - 2.743 (\log_{10} t)^3 \quad \dots (5-9)$$

FIG. 5-4. Sinkers Turbulence Corrections.

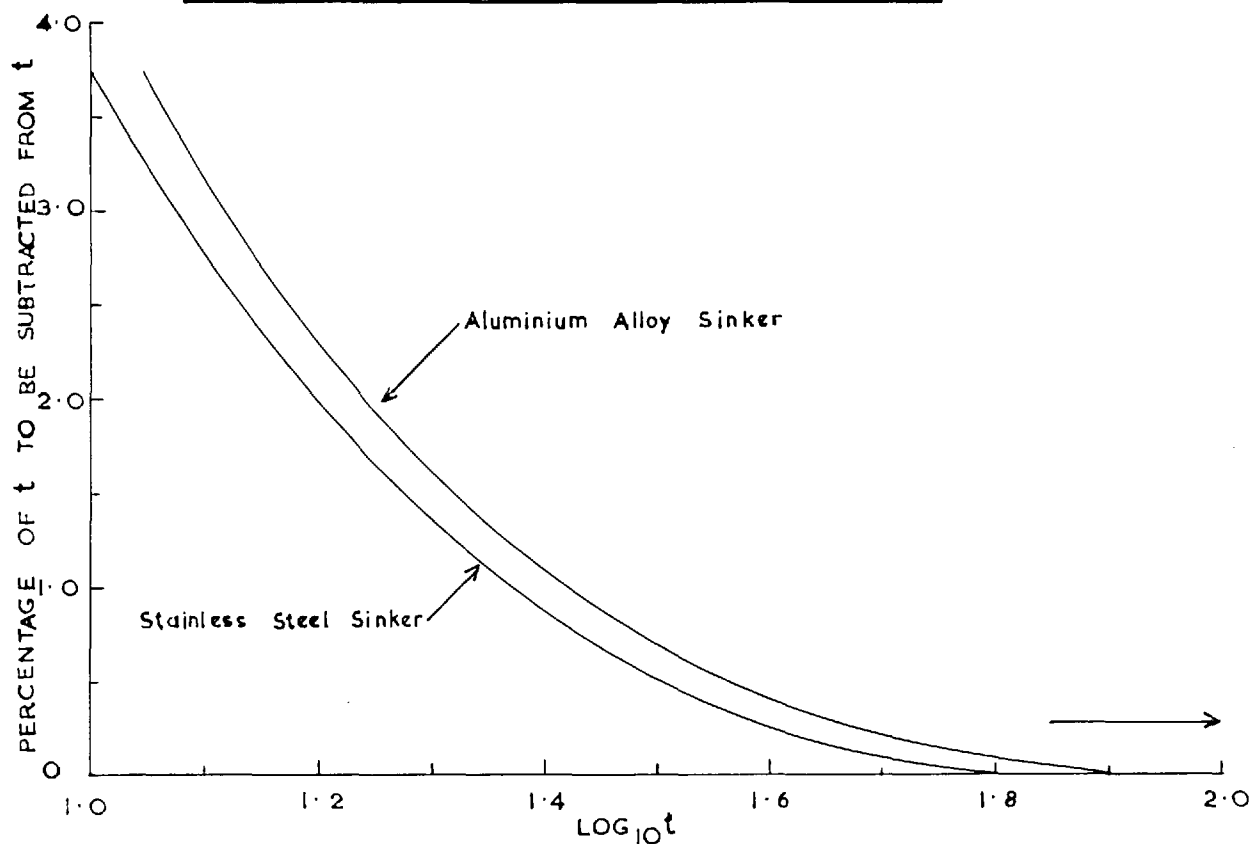
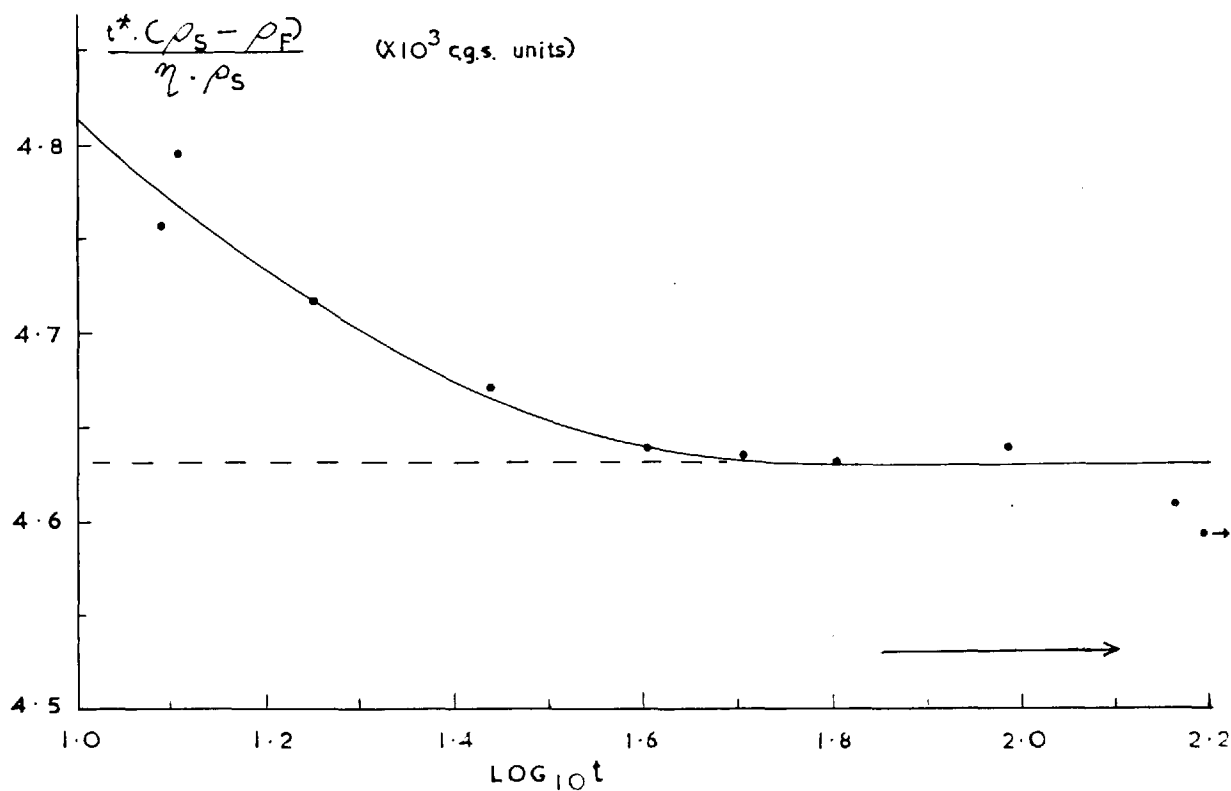


FIG. 5-5. Calibration Curve for Aluminium Alloy Sinkers.



For fall times less than 65 seconds, the turbulence correction, x , is calculated directly from equation (5-9) and for fall times greater than 65 seconds it is taken as zero. It may be seen from Figure (5-4) that the correction is 3.73% for a fall time of 10 seconds but this decreases rapidly to 1% at 23.5 seconds and is zero at 65 seconds.

(b) Calibration of Aluminium Alloy Sinker.

Since sufficiently accurate compressibility data were available for the majority of fluids studied it was not necessary to calibrate the aluminium alloy sinker to the same accuracy as the stainless steel sinker. The calibration data for the aluminium alloy sinker were obtained in the same manner as those for the stainless steel sinker and these are tabulated in Appendix II. The calibration data is plotted as $\frac{t^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$ against $\log_{10} t$ and is shown in Figure (5-5).

The turbulence correction curve was calculated from a smooth curve drawn through the calibration points assuming $k_{\text{expt}} = 1/4.625 \cdot 10^3 = 2.16 \times 10^{-4}$ c. g. s. units. For comparison this curve is given with that for the stainless steel sinker in Figure (5-4). The correction is calculated in the range

from 10 seconds to 80 seconds from equation (5-10).

$$x = 80.536 - 18.491(\log_{10}t) + 167.61(\log_{10}t)^2 \\ - 70.017(\log_{10}t)^3 + 11.203(\log_{10}t)^4 \quad \dots (5-10)$$

The calibration and correction curves are of the same general shape as for the stainless steel sinker, but the corrections at the same fall times are always greater for the low density sinker. This is not unexpected since, other factors being constant, the Reynold's Number in the annulus increases with clearance. The calibration points in Figure (5-5) appear to be less scattered than those in Figure (5-3). The reason for this is that any asymmetry of the sinker and/or contamination becomes less significant with increasing sinker clearance.

5.4 Performance of Mk. I. Viscometer.

(a) Timing System.

The timing system and the principle on which it operates have been described in Chapter IV. In addition to the various factors already considered the stability of the time period counter and the reproducibility of the triggering positions are of importance

in assessing the accuracy of the sinker fall time. As the pairs of coils on the tube are not perfectly matched, the balance of the coils is pressure and temperature dependent, and this introduces a further uncertainty as to whether or not rebalancing shifts the triggering positions.

The experimental procedure for the adjustment of the timing system prior to operation is as follows,

- (i) The bridge circuits for each timing station are balanced with the sinker(s) away from the transducer coils, by adjusting the variable resistance and capacitance arms of the bridge until its output is zero.
- (ii) After setting the trigger units on each circuit, the reference signal voltage and the triggering voltages are adjusted until both circuits just trigger at the same reference level.
- (iii) The reference voltage is reduced by 1 volt.
- (iv) The adjustments are finally checked by putting the bridge out of balance with the variable resistance arm and observing the size of the signal that is required to trigger the timer.

The reproducibility of the triggering positions has been investigated at room temperature and atmospheric pressure by

moving the stainless steel sinker through the tube and noting the various triggering positions⁽²⁵⁾. The sinker was rigidly attached to the slide of a cathetometer by means of a non-magnetic rod. The bridges were rebalanced several times and the triggering positions were found to be reproducible to $\pm .001$ cm. The separation of the triggering positions for the forward and reverse directions was .015 cm. and the mean distance of sinker travel between the triggering points was approximately 17.4 cm.

A different procedure was adopted to check the reproducibility of the triggering positions under variable temperature and pressure conditions.

A special stainless steel sinker was employed for this check, with two soft iron pellets located on rods screwed into the ends of the sinker. The positions of the soft iron pellets were adjusted so that the timer was started by one of the pellets and stopped shortly afterwards by the pellet at the other end of the sinker. The sinker fall time was determined at a series of temperatures and pressures in the ranges $0^{\circ}\text{C} - 100^{\circ}\text{C}$ and $0 - 10,000 \text{ kg/cm}^2$ respectively. The object of the experiment was to detect small changes in the triggering positions by observing

a significant variation in the fall times as compared with the known viscosity variation of water. Changes in the overall length of the fall distance due to thermal expansion and compressibility effects are exactly compensated by an identical change in the length of the sinker. From these experiments it was concluded that except for the thermal and compressibility changes the distance between the triggering positions is constant, to 0.1%.

On the basis of the manufacturer's specification the stability of the time period counter is assumed to be $\pm .02\%$ in the temperature range from -10°C to $+70^{\circ}\text{C}$.

The resolution of the triggering circuits is one half of the operating frequency of 500 c. p. s. Hence, the error involved in starting and stopping the timer is .002 seconds and the maximum uncertainty in the fall time is .02%.

(b) Viscosity Measurement.

From the viscometer calibration equation (5-6) it follows that,

$$\frac{\eta_p}{\eta_o} = \frac{k_p}{k_o} \cdot \frac{(\rho_{sp} - \rho_{fp})}{\rho_{sp}} \cdot \frac{\rho_{so}}{(\rho_{so} - \rho_{fo})} \cdot \frac{t_p}{t_o} \quad \dots\dots (5-11)$$

where the subscripts p and o refer to the values of the variables

at pressure, p , and atmospheric pressure respectively. Provided the variation of k , ρ_s and ρ_f with pressure is known or can be estimated, then equation (5-11) enables the relative viscosity of a liquid $\frac{\eta_p}{\eta_o}$ to be calculated from the ratio $\frac{t_p}{t_o}$. The errors in a relative viscosity determination are dependent on the magnitude and accuracy of the buoyancy correction and the k factor correction as well as the errors in t_p and t_o .

The maximum correction for the stainless steel sinker due to changes of k with pressure is 0.4% at 10,000 kg/cm². This correction is assumed, from Lohrenz and Kurata's work⁽⁶⁸⁾, to be accurate to 5%. The maximum error in the fall time ratio after corrections for dimensional changes is therefore .02%.

The buoyancy correction is also a maximum at 10,000 kg/cm², when it is about 4% of the fall time. It is assumed that the error in the buoyancy correction factor

$$\frac{(\rho_{sp} - \rho_{fp})}{\rho_{fp}} \cdot \frac{\rho_{so}}{(\rho_{so} - \rho_{fo})}$$

is due entirely to the errors in ρ_{sp} and ρ_{fp} . The error in ρ_{sp} is 2%, (see Appendix III) and the error in ρ_{fp} is assumed to be 5%. Hence, for the stainless steel sinker the correction factor

is accurate to 3% and the maximum uncertainty in the fall time ratio after buoyancy corrections is 0.12%.

If the stability of the time period counter is $\pm .02\%$ and the resolution of the timing system is .002 seconds, then there is a maximum uncertainty of .02% in the minimum fall time of 10 seconds. The triggering positions are reproducible to $\pm .001$ cm. in 17.4 cm., which implies an uncertainty of .01% in the fall distance. Since the fall time is taken as the mean of several determinations the uncertainty in a relative viscosity measurement on account of errors in the timing system is $\pm .05\%$.

It is estimated that the axis of the viscometer tube is always within 2 minutes of arc from the vertical. From Figure (5-2), the maximum error in the fall time due to a non-vertical viscometer is .01%.

It has been noted that the fall time is strongly influenced by imperfections in the viscometer components and by contamination of the test fluid. Random variations of the fall time occur principally as a result of the former, whilst the latter effect leads to an increase in the mean fall time with greater scatter in individual readings. Normally, the overall scatter of 6 - 8 falls for the stainless steel

sinker in direction 1 or direction 2 is within 0.2%. The presence of a high level of contamination is immediately obvious, but it is estimated that the maximum level of contamination which could remain undetected would lead to an increase of 0.3% in the mean fall time. The maximum uncertainties arising from these causes are -0.1% and $+0.4\%$.

Consideration of the scatter of the calibration data for the stainless steel sinker leads to an estimated accuracy of $\pm 15\%$ for turbulence corrections calculated from equation (5-9). The maximum turbulence correction at a 10 second fall time being 3.7%, the maximum error in a fall time after turbulence corrections is 15% of 3.7%, i.e. 0.56%. This leads to an error of $\pm 0.80\%$ in the relative viscosity. At long fall times the turbulence correction is zero and the inaccuracy of the relative viscosity measurement as a consequence of turbulence corrections is governed by the error in the base fall time. Any errors in the fall time due to terminal velocity effects will be included in the calibration curve.

From a consideration of all the various sources of error in the corrected fall time it is estimated that the maximum error in a relative viscosity measurement is within the range -1.0% to

+ 1.4%.

The principal source of error associated with the Mk. I. viscometer is the large uncertainty in turbulence corrections. As has been mentioned, the prime cause of the large turbulence corrections and the uncertainty in this correction is the difficulty involved in manufacturing a truly symmetric composite guided sinker. The magnitude of the turbulence correction is easily reduced by removing the stabilizing pins from the region of maximum fluid flow in the sinker annulus as is shown in Chapter VII.

(c) Density Measurement.

In order that the buoyancy correction factor,

$$\frac{(\rho_{sp} - \rho_{fp}) \cdot \rho_{so}}{\rho_{sp} \cdot (\rho_{sp} - \rho_{fo})}$$

may be evaluated, the density of the sinker and the fluid must be known within the experimental range of pressures and temperatures. In estimating the effects of errors in the densities on viscosity measurements it is assumed that the uncertainty in ρ_{so} and ρ_{fo} is negligible. If the calculated value of ρ_{sp} is accurate to 2% and ρ_{fp} is known to 5%, say, then the maximum error from an

inaccurate buoyancy correction is $\pm 0.1\%$.

The following expression is obtained in Appendix I for ρ_{fp} as a function of the fall times of the high and low density sinkers,

$$\rho_{fp} = \frac{c_{so} \left(\frac{t_{sp}}{t_{so}} \right)^* - c_{ao} \left(\frac{t_{ap}}{t_{ao}} \right)^*}{\frac{c_{so} \left(\frac{t_{sp}}{t_{so}} \right)^*}{\rho_{sp} \left(\frac{t_{sp}}{t_{so}} \right)^*} - \frac{c_{ao} \left(\frac{t_{ap}}{t_{ao}} \right)^*}{\rho_{ap} \left(\frac{t_{ap}}{t_{ao}} \right)^*}} \quad \dots (5-12)$$

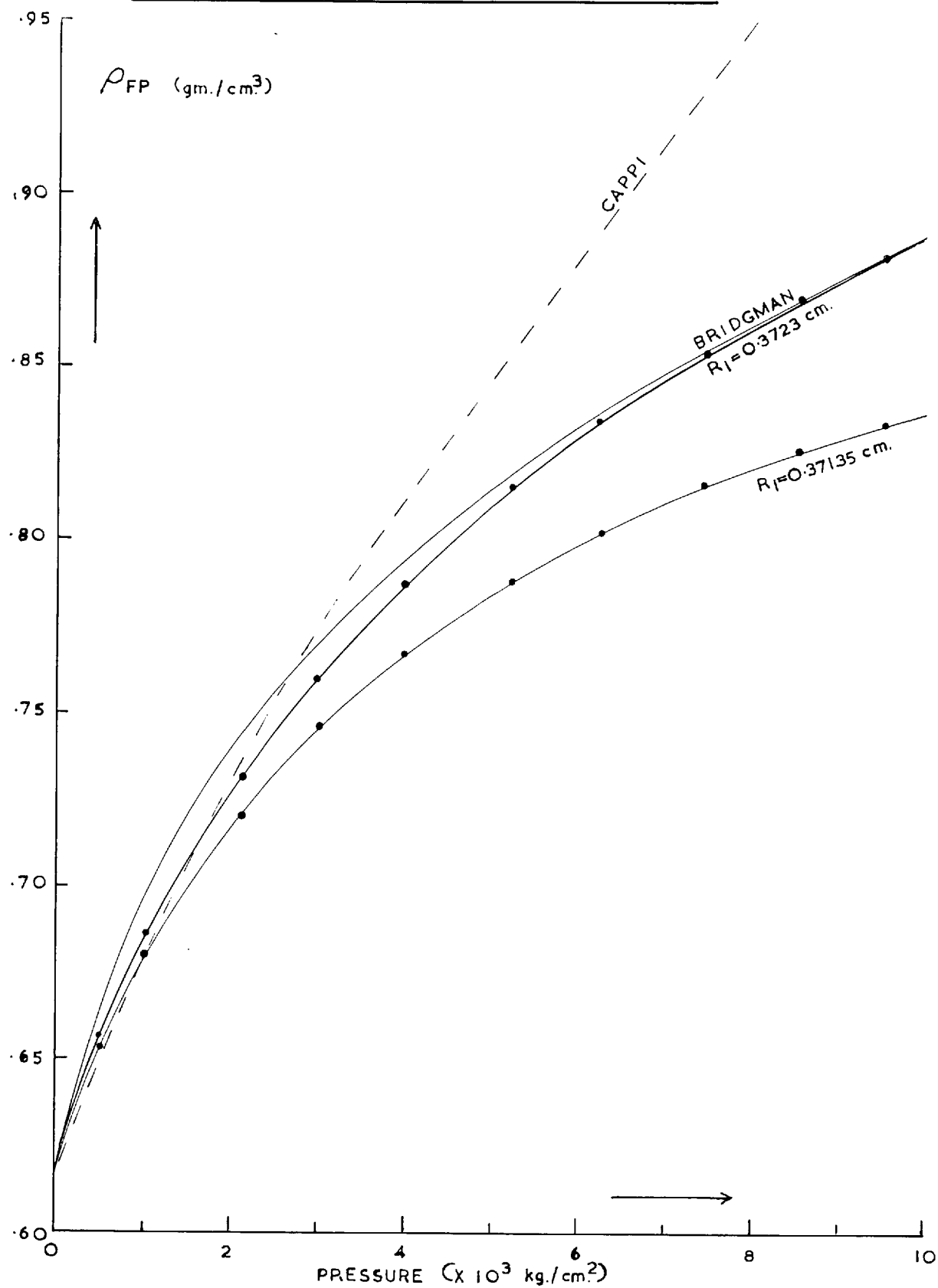
where

$$c_{so} = \frac{\rho_{so}}{\rho_{so} - \rho_{fo}} \quad \text{and} \quad c_{ao} = \frac{\rho_{ao}}{\rho_{ao} - \rho_{fo}} \quad \text{and} \quad \left(\frac{t_{sp}}{t_{so}} \right)^* \quad \text{and} \quad \left(\frac{t_{ap}}{t_{ao}} \right)^*$$

are the fall time ratios corrected for changes of the viscometer constant with pressure.

The Mk. I. viscometer has been employed with pentane at 30°C using the stainless steel and aluminium alloy sinkers by Cappi⁽²⁵⁾ to assess the practicability of the two sinker method for density estimation. His results are compared with those of Bridgman⁽²²⁾ in Figure (5-6) and although at low pressures they are in fair agreement, above $3,000 \text{ kg/cm}^2$ they diverge rapidly until the difference at $10,000 \text{ kg/cm}^2$ is $13\frac{1}{2}\%$.

FIG. 5-6. Density of N-Pentane at 30°C.



The results obtained by Cappi for the mean times in direction 1, the temperature and pressure of each observation, together with the calculated densities of the sinkers are given in Table(5-1.)

TABLE(5-1)

Fall time $t_{sp}(\text{sec})$	Fall time $t_{ap}(\text{sec})$	Temperature ($^{\circ}\text{C}$)	Pressure (kg/cm^2)	ρ_{sp} (gm/cm^3)	ρ_{ap} (gm/cm^3)
9.359	12.504	29.88	0.0	7.9499	3.1978
14.357	19.284	29.86	513.9	7.9524	3.1999
19.795	26.553	29.86	1051.3	7.9550	3.2020
32.208	42.771	29.86	2096.4	7.9602	3.2062
46.142	60.491	29.86	3032.5	7.9648	3.2100
65.007	83.951	29.86	4035.7	7.9698	3.2140
95.142	120.614	29.86	5257.9	7.9758	3.2189
127.480	160.019	29.86	6258.2	7.9808	3.2230
178.021	219.162	29.88	7448.9	7.9867	3.2278
241.733	292.299	29.90	8574.3	7.9923	3.2324
316.271	374.210	29.90	9574.7	7.9973	3.2364

These results have been used to compute ρ_{fp} taking account of an error in ρ_{ap} as calculated by Cappi, and using the improved calibration curve for the stainless steel sinker. The fall times

were corrected initially to 30°C by assuming a constant viscosity-temperature coefficient of 0.98×10^{-2} per °C at this temperature. They were then corrected for turbulence using the calibration equations (5-9) and (5-10) and finally for dimensional changes by calculating the ratios of $\frac{k_{sp}}{k_{so}}$ and $\frac{k_{ap}}{k_{ao}}$ at each pressure. The density of pentane was calculated at each pressure assuming that the atmospheric pressure density is 0.616 gm/cm³ at 30°C, and finally smoothed using a polynomial 'least squares' routine.

ρ_{fp} was first calculated following the procedure outlined above with $r_2 = 0.3846$ cm. and the aluminium sinker radius, $r_1 = 0.37135$ cm. (r_1 and r_2 were obtained from the measured diameters of the sinker and tube respectively at room temperature and atmospheric pressure.) The results of this calculation are summarised in the lowest curve in Figure (5-6). The dimensional correction factor at the highest pressure was 19.7%. To ascertain the effects of a small error in the measured radii on the correction factor and ρ_{fp} the results were recomputed with r_1 slightly changed. It was found that Bridgman's curve was fitted to within 2% over the complete pressure range with $r_1 = 0.3723$ cm. In this case the correction factor at the highest pressure was 21.4%.

Lohrenz and Kurata⁽⁵⁸⁾ showed that equation(5-6A) predicts large changes in k from the properties of the sinker and tube materials to only 5%. At the highest pressure (k_{ap}/k_{a0}) changes by about 8% for a change of 0.00095 cm. in r_1 . Since the theory ignores the effect of dimension changes on the non-ideal viscous drag terms an 'effective' sinker radius of 0.3723 cm. and the 8% discrepancy in the calculation of the correction factor are reasonable.

The excellent agreement of the recalculated results with Bridgman's curve may be fortuitous, since the scatter of the experimental points about the smoothed curve is quite large. The large turbulence corrections required for the fall times of both sinkers at the low pressures is probably the main source of this scatter.

Where dimensional corrections are large, it is considered that the two sinker method may be employed to estimate densities to within 5%, if an 'effective' sinker radius is deduced from a comparison of the calculated density of a liquid and its known compressibility. Additionally the accuracy of the method may be improved by using a more suitable material for the low density sinker. A material like beryllium would be better than aluminium

since it combines both a lower density and smaller dimensional corrections. In all cases the region of large turbulence corrections must be avoided and greater accuracy in the sinker calibration curves would be beneficial.

CHAPTER VI.

CALIBRATION AND PERFORMANCE OF PRESSURE MEASURING SYSTEM.

6.1 Calibration Requirements.

The pressure in the apparatus is determined by measuring the resistance of a manganin coil gauge as described in Chapter IV. The measured resistance of the manganin coil will be a function of the following variables,

- (i) The pressure of the fluid surrounding the coil.
- (ii) The temperature of the coil.
- (iii) The temperature of the Smith's bridge.

In order to calculate the resistance change of a fixed length of manganin wire due solely to pressure, corrections must be applied for any change of resistance caused by fluctuations of (ii) and (iii). These corrections are calculated from calibrations of the coil and the Smith's bridge at different temperatures.

The manganin gauge is a secondary pressure gauge and consequently requires calibration. Ideally, the coil should be calibrated against a primary pressure gauge over its complete

pressure range. The absolute accuracy of the gauge resistance measurements are not important, provided the coil is calibrated directly against the Smith's bridge, and the bridge is self-consistent within the range of resistance measurements.

6.2 Calibration of the Smith's Bridge.

(a) Internal Consistency.

The Smith's Difference Bridge, employed for all gauge resistance measurements in this work, is over 30 years old and it is assumed that its resistors are stable with time. The internal consistency of the bridge was checked at a bridge temperature of 25.0°C and it was found that the resistors corresponding to the maximum variation of the coil resistance were equal to their nominal values to within the sensitivity limits of the bridge balance ($\pm .00005$ ohm). The resistances of the bridge ratio arms are stated to be 195.009 ohms and 195.019 ohms at 25.0°C in an N. P. L. calibration certificate, dated 1935. Any changes in the resistance of these arms are assumed to be sufficiently similar for equation (4-1) to remain valid.

(b) Temperature Dependence.

The temperature dependence of the bridge was determined.

by evaluating equation (4-1) at different bridge temperatures in the range $23^{\circ} - 27^{\circ}\text{C}$ when measuring a constant external resistance. The external resistance employed was the manganin gauge, immersed in a constant temperature bath.

Figure (6-1) shows the graph of the measured coil resistance, S ohms, as a function of the bridge temperature, $t_B^{\circ}\text{C}$. The experimental points were fitted to a second degree polynomial in t_B with a 'least squares' program on a digital computer giving,

$$S = 44.593983 - 0.271858 \cdot 10^{-2} \cdot t_B + 0.406745 \cdot 10^{-4} \cdot t_B^2$$

Since the temperature of the bridge is maintained in the range $24.7^{\circ} - 25.3^{\circ}\text{C}$ during resistance measurements, a bridge temperature of 25.0°C is taken as datum. All coil resistance measurements are corrected to this temperature by addition of the following term,

$$C_B = 0.2718158 \cdot 10^{-2} (t_B - 25.0) - 0.406745 \cdot 10^{-4} (t_B^2 - 25.0^2) \quad \dots (6-1)$$

where $t_B^{\circ}\text{C}$ is the temperature of the bridge at the time of the

FIG. 6-1. Smith's Bridge - Temperature Calibration.

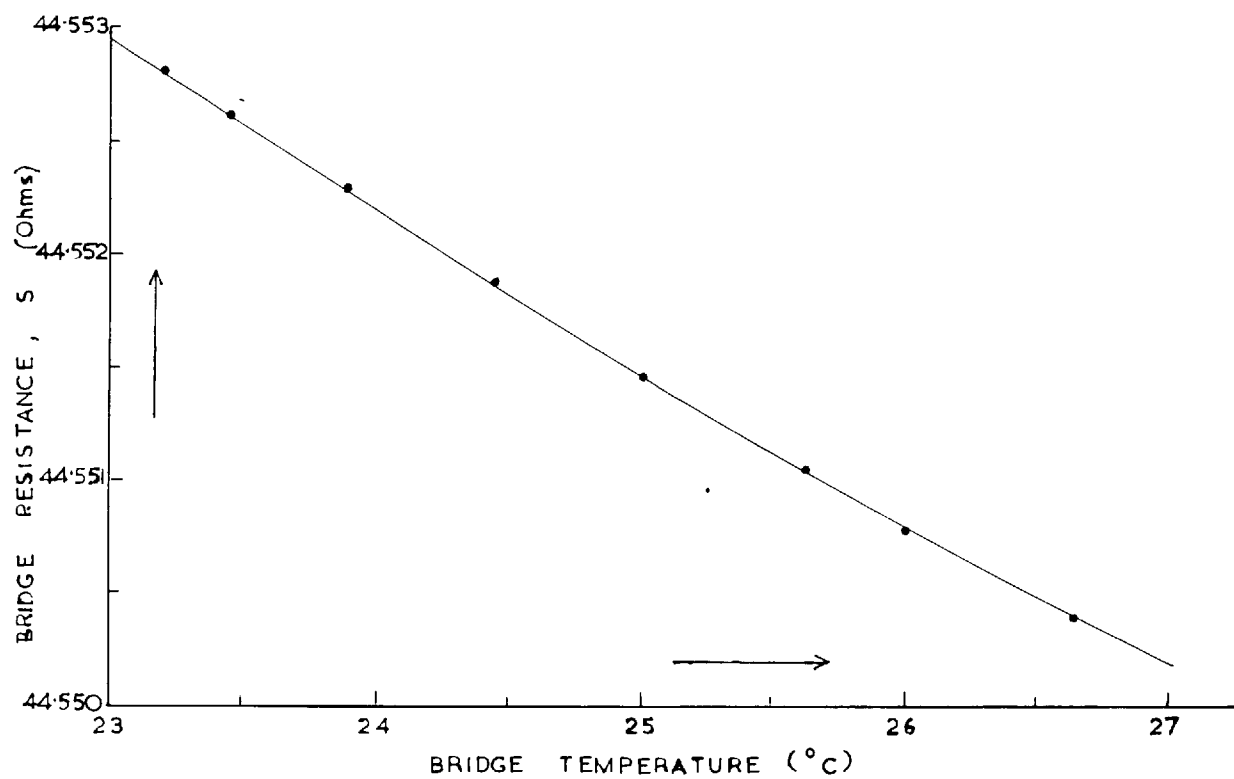
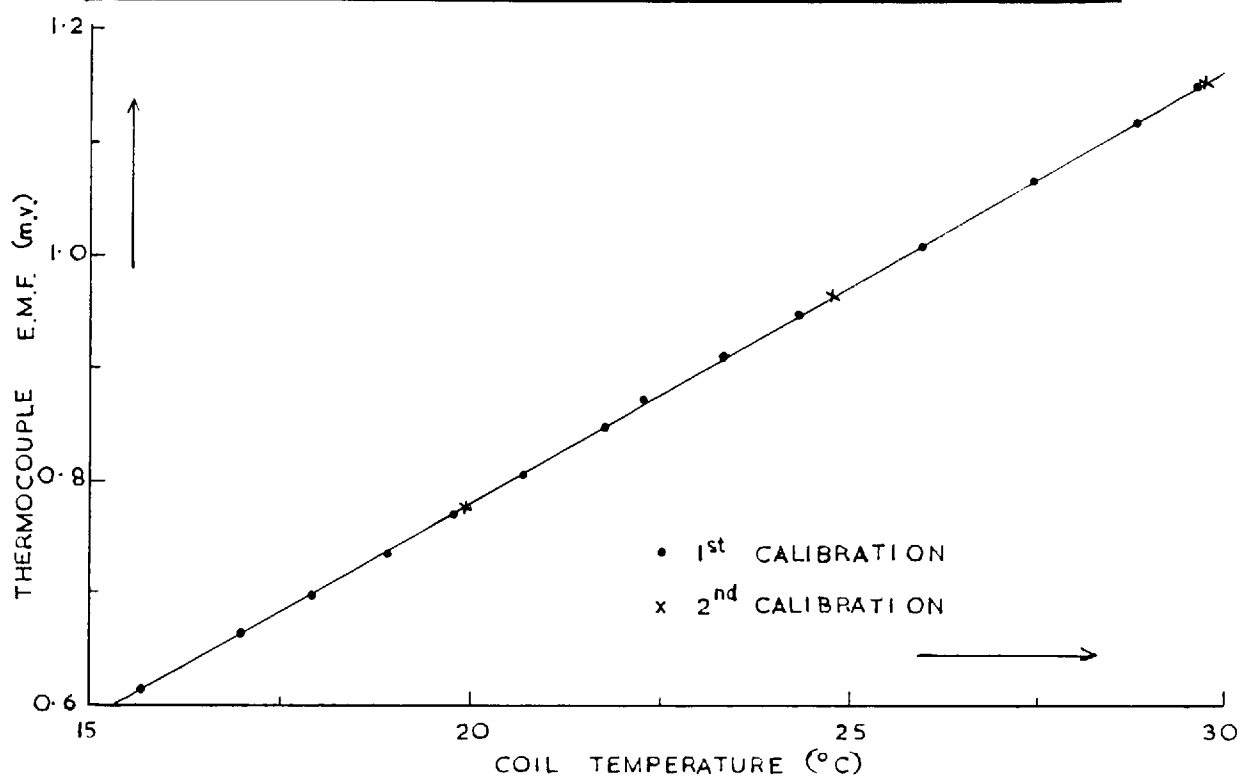


FIG. 6-2. Gauge Thermocouple - Temperature Calibration.



resistance measurement. Since the bridge is equipped with a thermometer graduated in divisions of $.05^{\circ}\text{C}$, t_B can be estimated to $\pm .01^{\circ}\text{C}$. The maximum variation of the bridge temperature from 25.0°C during experimental measurements was $.03^{\circ}\text{C}$; this corresponds to a resistance correction equivalent to $\pm 2 \text{ kg/cm}^2$.

The correction given by equation (6-1), will only be accurate when the resistance being measured is the same as that of the coil, i. e. 44.55146 ohms . When the external resistance differs from this value by δ , where δ is small compared with 44.55146 , then a secondary correction given by $\frac{\delta}{44.55146} \times C_B$ should be added.

In this work the external resistance measured was always the coil itself, and the maximum change of resistance was approximately 1 ohm , i. e. $\delta \leq 1$. Since the maximum value of the primary correction was about 2 kg/cm^2 , the secondary correction was negligible compared with other errors.

6.3 Resistance Gauge - Temperature Calibration.

(a) Gauge Thermocouple.

The temperature of the manganin resistance gauge is measured by an adjacent copper-constantan thermocouple.

The pressure gauge thermocouple was calibrated between 15° and 30°C by immersing the whole pressure gauge unit in a constant temperature bath. Figure (6-2) shows the measured thermocouple e. m. f. 's as a function of the coil temperature for two independent calibrations. These calibrations agree with each other and with the literature values for copper-constantan thermocouples to $\pm .003$ millivolts.

The plugs and sockets in the thermocouple circuit were broken and reconnected several times and it was confirmed that the thermocouple e. m. f. remained constant to within the sensitivity of the readings ($\pm .001$ millivolt).

As a consequence of these experiments it is assumed that no significant variation of the thermocouple e. m. f. 's occurred during the course of this work.

(b) Resistance Gauge.

The temperature calibration curve for the pressure gauge was obtained, using the experimental arrangement described in the previous section, by measuring the resistance of the gauge and noting the coil temperature as measured by the adjacent thermocouple. The coil resistance readings were corrected to the bridge reference

temperature using equation (6-1). Figure (6-3) shows calibration curves for the coil resistance, S ohms, plotted against the corresponding coil temperature, t_C millivolts, obtained at the beginning and at the end of the experimental work. A 'least squares' polynomial fit to the 2nd power of the experimental points in the first calibration curve gives,

$$S = 44.516612 + 0.0533308 \cdot t_C - 0.0162227 \cdot t_C^2$$

An arbitrary coil temperature of 0.850 mV is taken as datum and all gauge resistance measurements are corrected to this temperature by addition of the following term,

$$C_C = 0.0533308 (.850 - t_C) - 0.0162227 (.850^2 - t_C^2) \\ \dots\dots (6-2)$$

The two calibration curves shown in Figure (6-3) are separated by a constant difference and consequently corrections calculated from the second curve are identical with those given by equation (6-2). Since the e. m. f. of the thermocouple remained constant during the entire experimental work, the difference between the calibration curves is due solely to a drift in the coil resistance.

FIG. 6 - 3. Gauge - Temperature Calibration.

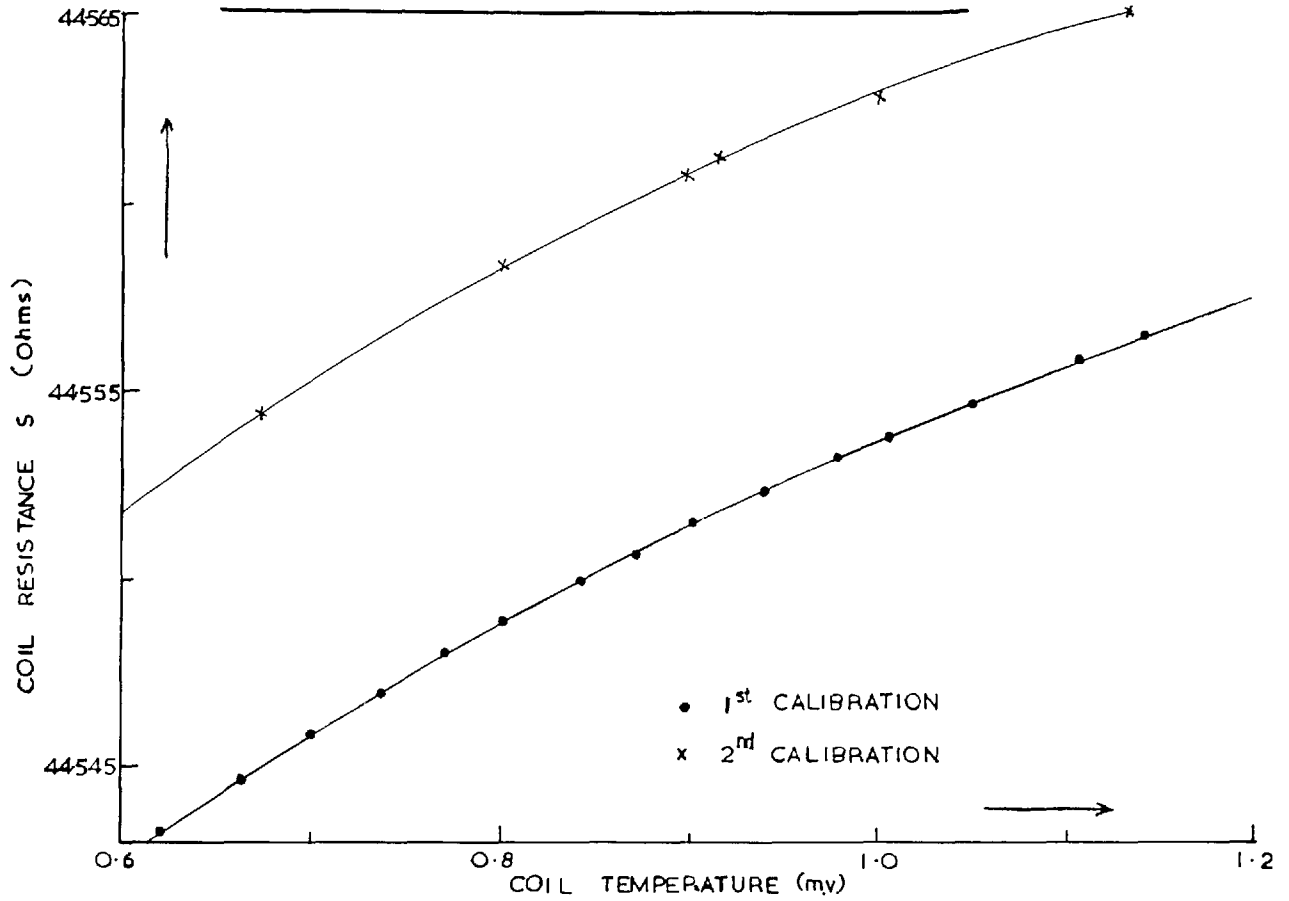
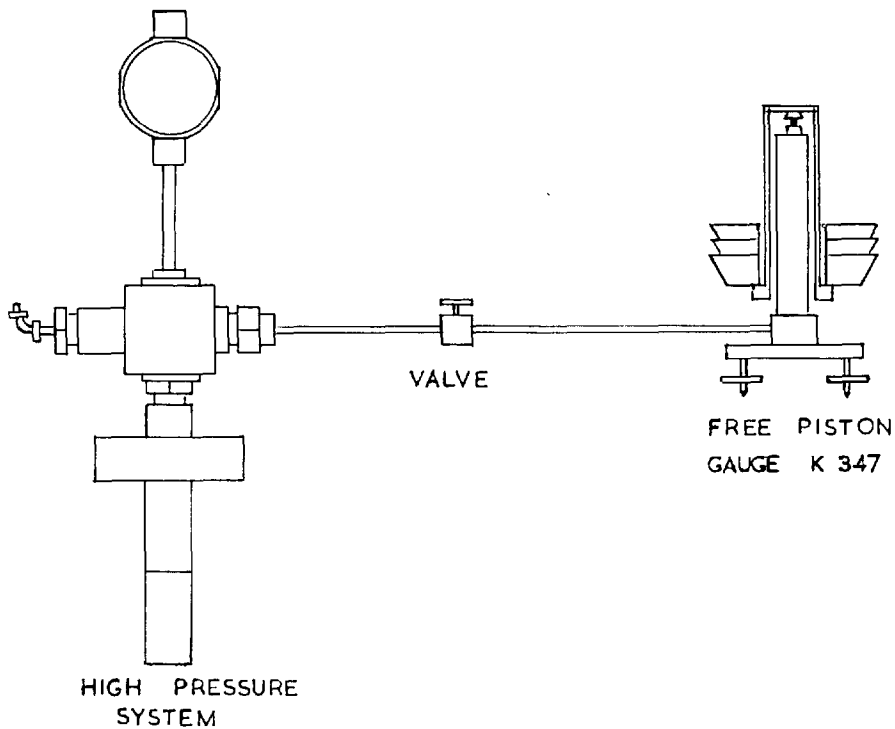


FIG. 6 - 4, Gauge - Calibration against K 347.



It is assumed that the resistance-temperature characteristics of the gauge are not changed by pressure, and hence the corrections calculated from equation (6-2) remain valid at all pressures. The agreement, within experimental error, of several resistance-pressure calibration curves (see following section) at different gauge temperatures suggests that any errors introduced as a consequence of this assumption are small. While the maximum temperature correction to the gauge resistance, C_C , may be equivalent to 60 kg/cm^2 , the variation of C_C during an experiment is generally less than 10 kg/cm^2 .

6.4 Resistance Gauge - Pressure Calibration.

Initially the manganin coil was calibrated at several pressures up to $3,000 \text{ kg/cm}^2$ against a free piston gauge and at 7718.5 kg/cm^2 , the freezing pressure of mercury at 0°C . The calibration curve was completed by interpolating and extrapolating over the remainder of the range. A free piston gauge was designed and constructed to facilitate continuous pressure calibrations to $6,000 \text{ kg/cm}^2$ and was employed to check the calibration curve to this pressure.

(a) Calibration to $3,000 \text{ kg/cm}^2$ - K347.

The 'Budenberg' free-piston gauge employed for this calibration,

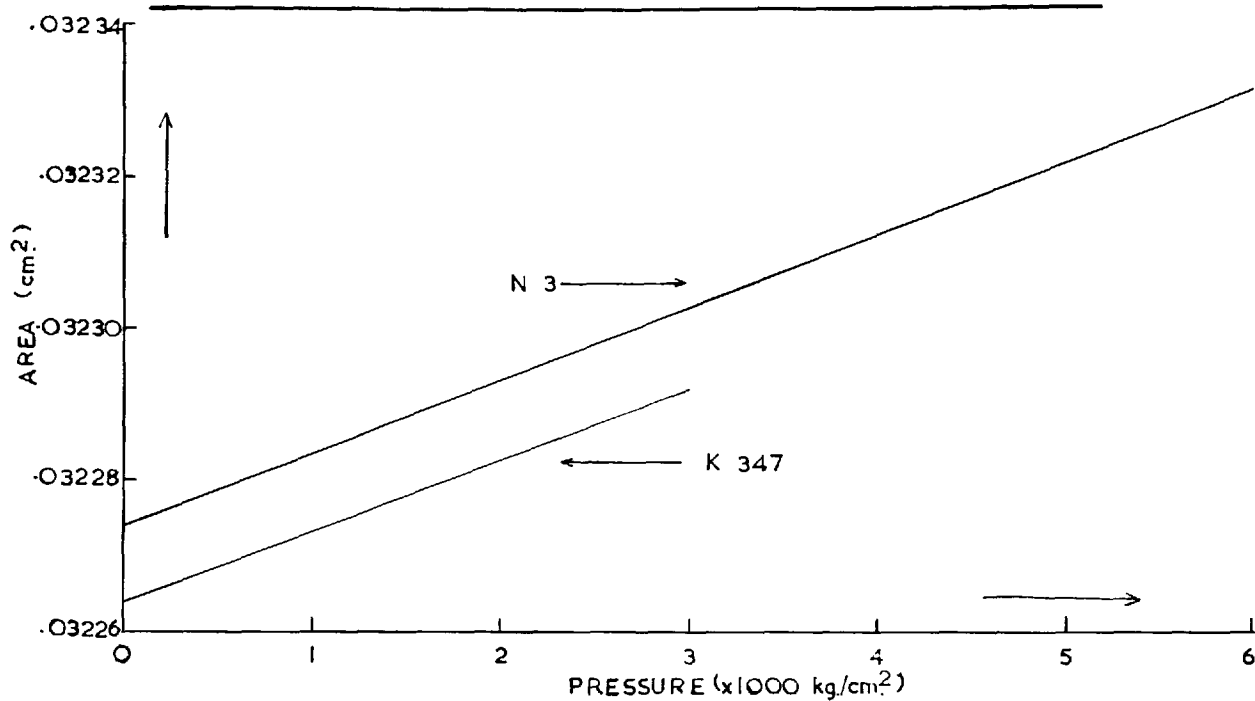
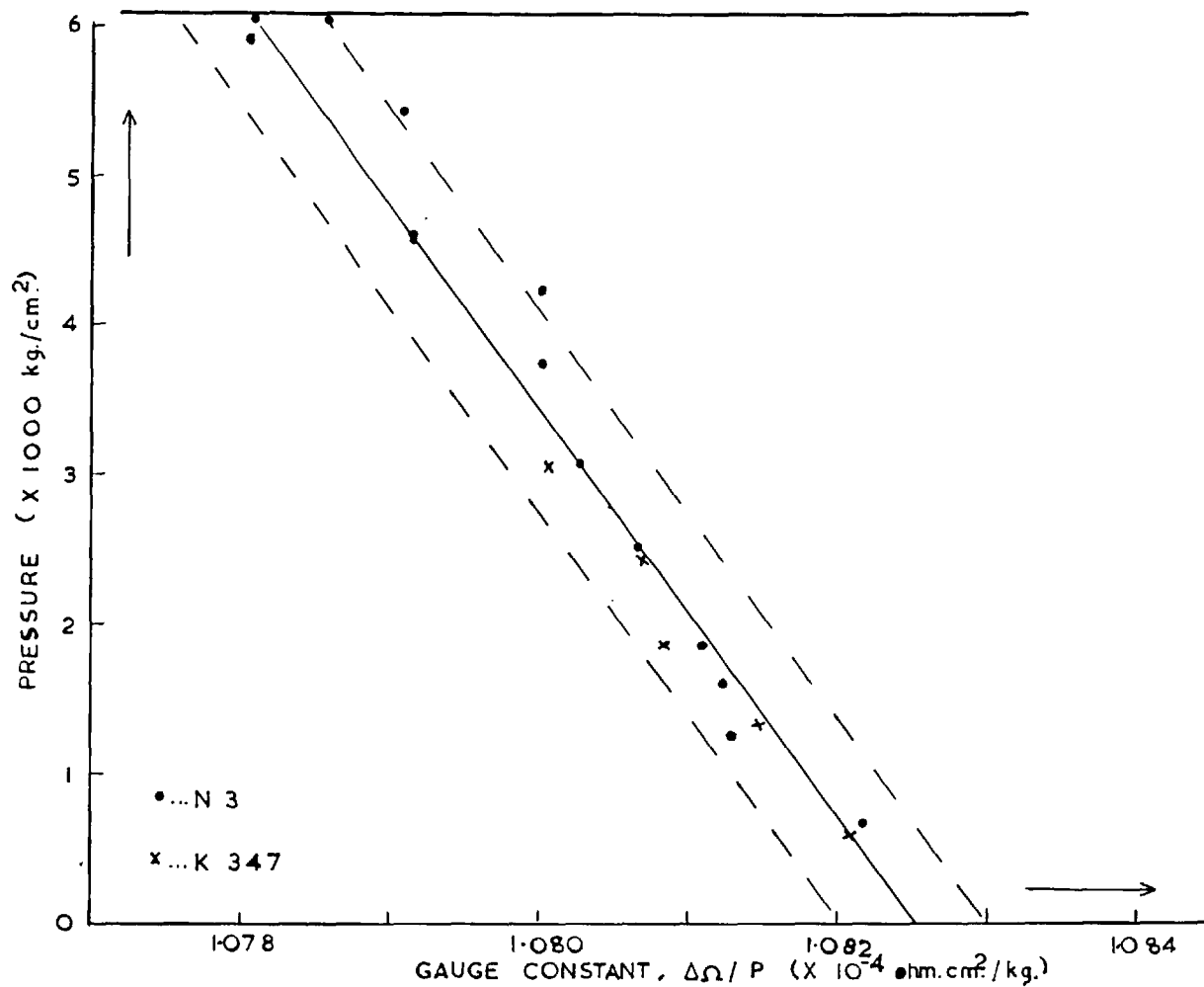
K347, had a nominal area of 0.005 in^2 . It was connected to the high pressure system, via a 100,000 p.s.i. handvalve, through the pressure release valve as shown in Figure (6-4). The three-way hand valve, with one limb blanked off, was employed both as a screw ram injector for fine pressure adjustment, and as a let-down valve. A mixture of 3 parts liquid paraffin and 1 part D. T. D. 585 was used as the pressure transmitting fluid.

The manganin coil was calibrated against the free-piston gauge at a series of pressures up to $3,000 \text{ kg/cm}^2$. Measurements were made by adjusting the screw injector and the weights on the load carrier until the freely rotating piston was balanced. When pressure and temperature equilibrium were reached the resistance of the gauge was measured and the total load on the piston noted.

The mass of the weight carrier and each of the weights was determined to $\pm 0.01 \text{ gm.}$, by weighing them against standardised analytical weights on a 10 kg. balance. The effective area of piston and cylinder assembly K347, shown in Figure (6-5) as a function of pressure, was determined by calibrating it directly against a similar assembly of N. P. L. certified effective area.

Included in the calibration curve shown in Figure (6-6) are

FIG. 6-5. Areas of Free Piston Gauges K 347 & N 3.

FIG. 6-6. Gauge - Calibration to 6,000 kg/cm²

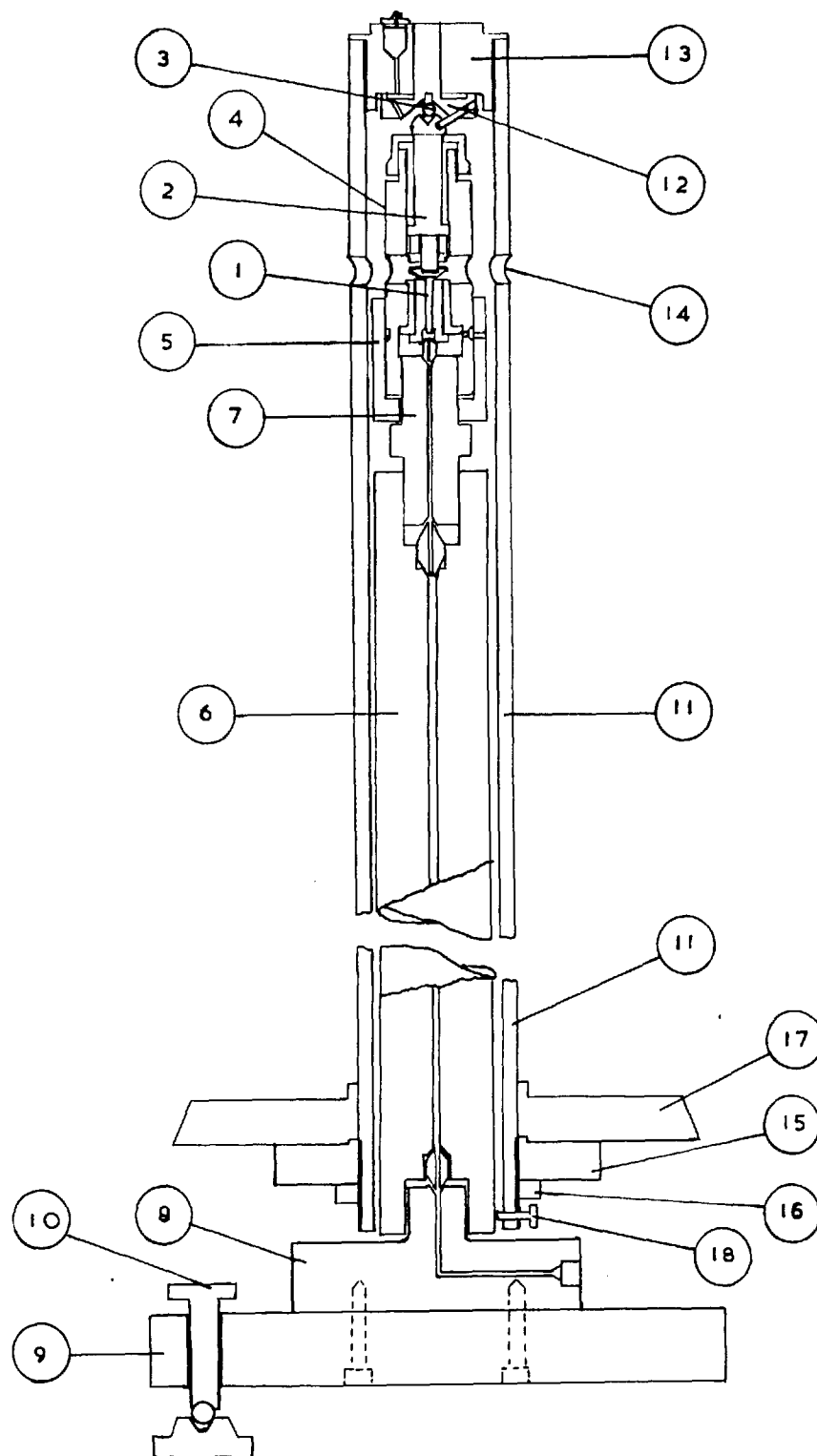
the results of the calibration against K347, expressed as p against $\Delta\Omega/p$, where p is the applied pressure and $\Delta\Omega$ is the corresponding change in resistance of the gauge. The errors associated with each calibration point arise mainly from the resistance measurements and the applied temperature corrections.

(b) Calibration to 6,000 kg/cm² - N3.

The free-piston gauge constructed for pressure calibrations up to 6,000 kg/cm² is shown diagrammatically in Figure (6-7). The design of the pressure balance was based on the availability of a 'Budenberg' piston and cylinder assembly suitable for use at pressures up to 100,000 p. s. i.

This assembly, number N3, is of nominal area 0.005 in², and consists of a steel piston (1) about 1½ inches long lapped into a steel cylinder about 2 inches long. The load is balanced on the top of the piston through an auxiliary piston (2) and steel ball (3). The cylinder and auxiliary assembly are fitted into a steel housing (4) terminated in a threaded section. The assembly is supported externally by a stainless steel sleeve (5) and is connected to a vertical column (6) by means of a coupling unit (7) of EN26 steel. The column is 39 inches long with internal and external diameters

FIG.6-7. Free Piston Gauge for 6,000 kg./cm.²



of $\frac{3}{8}$ inch and $2\frac{1}{2}$ inches respectively. At its lower end it is sealed with a coned olive to a connecting block (8) and the whole arrangement is mounted on a heavy circular base (9) fitted with levelling screws (10). The high pressure fluid supply to the balance is made through a connection in the side of the connecting block.

To minimise weight variations due to wear and corrosion the load carrier (11), with the exception of the central EN26 load bearing support (12), is constructed of stainless steel. The main body of the carrier weighs 16.8 kg. and has internal and external diameters of $2\frac{3}{4}$ inches and $3\frac{1}{2}$ inches respectively. Since the largest available balance had a maximum load rating of 10 kg. , the body was split centrally and the two sections screw together. To facilitate lubrication of the auxiliary piston a small oil well and channels are machined in the head assembly (13) of the carrier. The height of the main piston is observed through four diametrically opposed 1 inch diameter viewing ports (14). A plate (15) backed up by a locking ring (16) screws on the lower end of the carrier and supports the cast-iron weights (17). The weights are oil blackened to prevent corrosion and weigh approximately 9.6 kg. each. Mating locations are machined in items (15) and (17) to

maintain a symmetric mass distribution in the assembled load. Three small ball-ended screws (18) at the lower end of the carrier constrain the axis of rotation of the load.

Before the pressure balance was assembled, the balance weights, the components of the load carrier, the auxiliary piston, the main piston and all attachments were accurately weighed. Since particles of dust rapidly promote wear in the piston and cylinder, precautions were taken during the assembly of the pressure balance to exclude dirt from the system. Prolonged application of the instrument at high pressures was avoided since the rate of wear of a piston and cylinder assembly increases rapidly with increased pressure.

The experimental arrangement and procedure employed for the calibration of the resistance gauge with N3 was identical to that described in section 6.4(a). However, for this calibration the pressure transmitting fluid used was oil to specification D. T. D. 822A (Esso Univis P38). The effective area of N3 has been determined at the National Physical Laboratory to 1 part in 25,000 with the same pressure transmitting fluid, and its variation with applied pressure is shown graphically in Figure (6-5).

The results of the manganin resistance gauge calibration to 6,000 kg/cm² are included in Figure (6-6).

(c) Calibration at 7718.5 kg/cm².

The results of a number of determinations of the freezing pressure of mercury at 0°C made against free-piston gauges are given in Table (6-1).

TABLE(6-1)

Date	Worker(s)	Reference	Freezing Pressure
1911	Bridgman	(15)	7640 $\pm$ 30 kg/cm ²
1953	Johnson and Newhall	(59)	7717.0 $\pm$ 53 kg/cm ²
1955	Zhokovskii	(113)	7715.0 kg/cm ²
1963	Newhall, Abbot and Dunn	(83)	7715.6 $\pm$ 4 kg/cm ²
1965	Dadson and Greig	(32)	7718.5 $\pm$ 1.2 kg/cm ²

The technique employed for the calibration of the manganin coil against the freezing pressure of mercury at 0°C is based on the

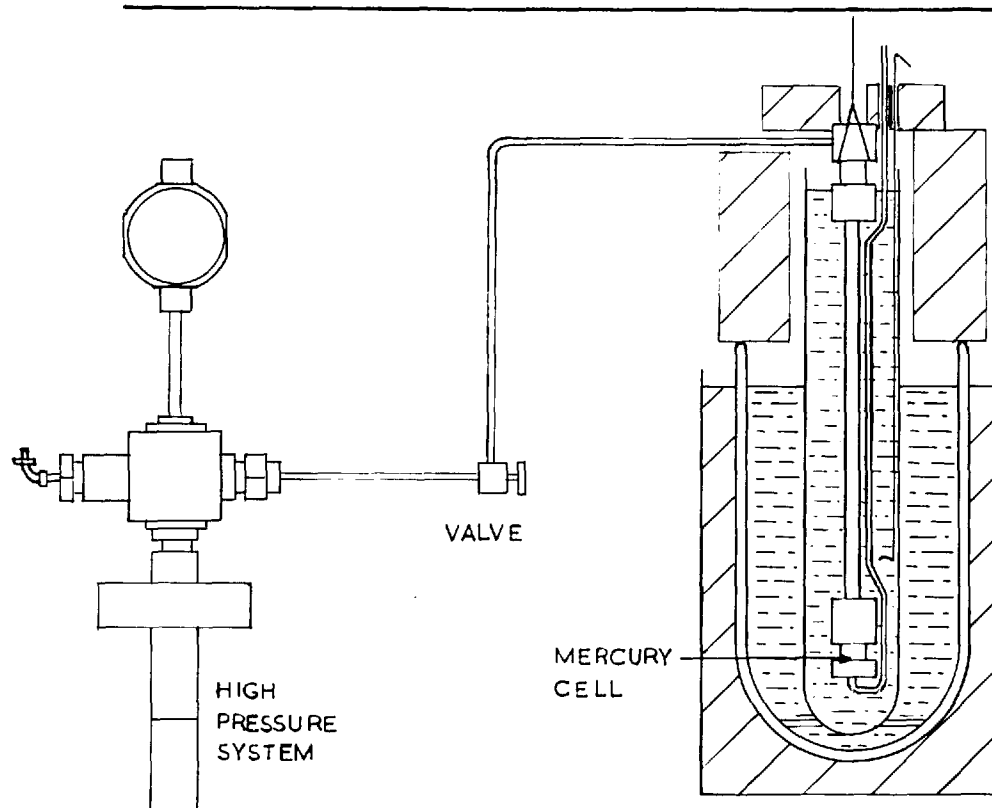
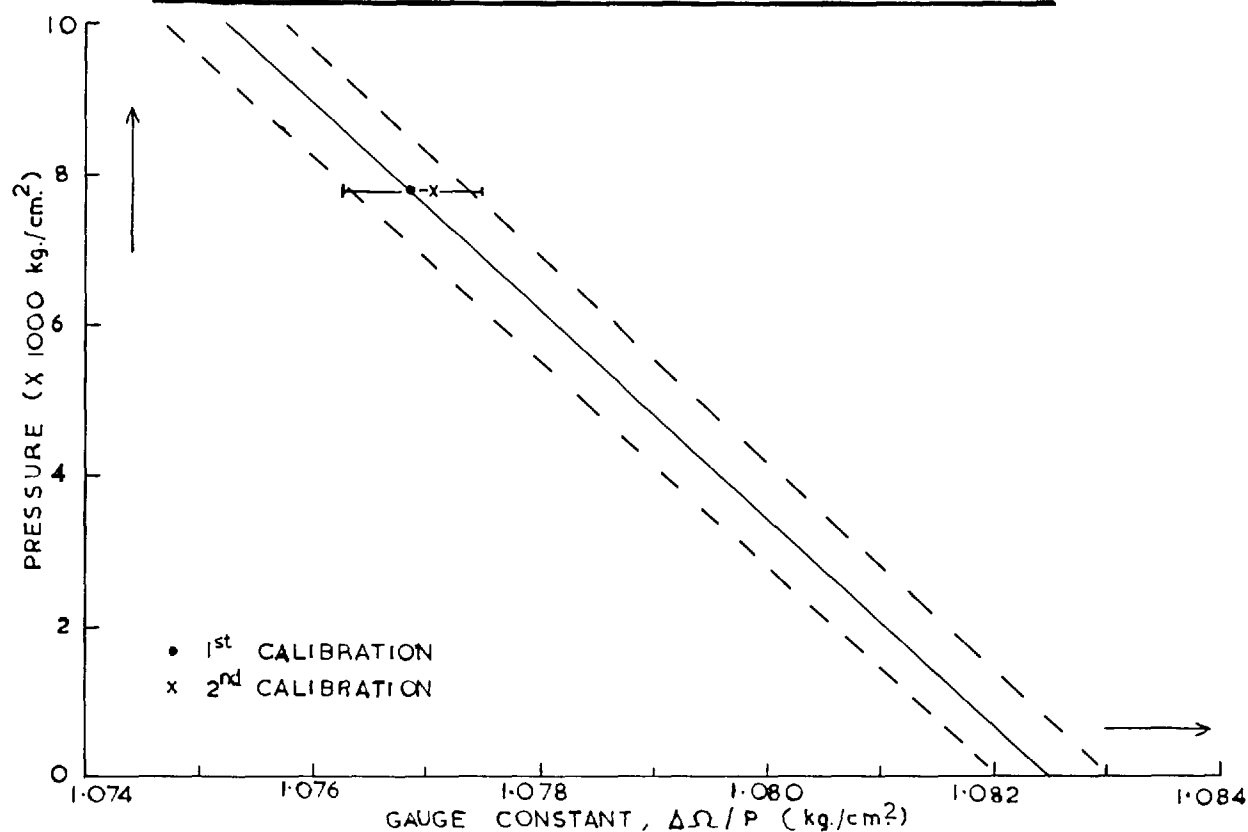
75% increase in resistivity of mercury on melting. The experimental arrangement used is shown diagrammatically in Figure (6-8).

The mercury cell consists of a thread of pure mercury in a U-tube of P. T. F. E. sleeving contained in the 1/16 inch bore of a length of high pressure tubing. The tube is sealed at the top end with an elbow and at the bottom end with a blank plug containing a single electrode. Connections are made to the mercury thread by means of two .006 inch diameter nichrome wires, one of which is connected to the bottom electrode and the other directly to the pressure tubing.

The mercury cell was connected to the high pressure system through a 100,000 p. s. i. handvalve in a similar manner to the arrangement employed for the calibrations with the free piston gauges. The resistance of the mercury cell was measured with a Wheatstone resistance box and the cell temperature was maintained at 0°C by filling the glass tube and the outer dewar arrangement with melting ice. The handvalve was used for pressure release from the system and fine adjustment of the pressure was obtained by regulating the temperature of the pressure vessel.

The following procedure was adopted to adjust the pressure

FIG. 6-8. Gauge - Calibration against Mercury Cell.

FIG. 6-9. Gauge - Calibration to 10,000 kg./cm².

in the system exactly to the mercury freezing pressure. Initially the pressure in the whole system was raised to approximately $7,750 \text{ kg/cm}^2$ and the mercury cell was cooled by introducing a freezing mixture of alcohol and crushed dry ice into the outer dewar. The resistance of the mercury cell decreased on freezing from about 50 ohms to 44 ohms. When the mercury thread was completely frozen, i. e. the cell resistance remained steady at 44 ohms, the freezing mixture was quickly replaced by melting ice and the inner glass tube was filled with small cubes of ice prepared from distilled water. The pressure in the system was then gradually reduced by slowly lowering the temperature of the pressure vessel, and the resistance of the mercury cell was monitored to detect the onset of melting. After the melting point had been approximately located relative to the resistance of the manganin coil, it was possible to reduce the pressure in the system sufficiently slowly for the complete melting of the mercury thread, as measured on the Wheatstone bridge, to take more than an hour. No change in the resistance of the manganin gauge was apparent during this period. The melting ice surrounding the mercury cell was frequently stirred.

Calibrations of the resistance gauge against the freezing

pressure of mercury were made at the beginning and at the end of the project. The increase in resistance of the gauge $\Delta\Omega$, corrected to the bridge and coil reference temperatures was 0.83102 ohms for the first calibration and 0.83119 ohms for the final calibration. Assuming a freezing pressure of 7718.5 kg/cm² the corresponding values of $\Delta\Omega/p$ are 1.0768×10^{-4} and 1.0770×10^{-4} ohms per kg/cm².

6.5 Performance of the Pressure Measuring System.

(a) Accuracy of Measurements.

In estimating the accuracy of a pressure measurement it is necessary to consider both the accuracy of the pressure resistance calibration curve for the gauge and the accuracy of the gauge resistance determinations.

The resistance of the manganin gauge, S ohms, is determined using equation (4-1), i. e.

$$S = \frac{(X_1 + X_2)}{2} - \frac{(X_3 + X_4)}{2}$$

where X_1, X_2, X_3, X_4 are the values of the variable arm of the bridge required for successive bridge balances. The error associated with

For each balance is estimated to be $\pm .00005$ ohm and hence the corresponding error in calculating S will be $\pm .0001$ ohm⁽¹⁰²⁾. It is assumed that the total error in S after applying the bridge and coil temperature corrections is $\pm .0002$ ohm.

The increase in resistance, $\Delta\Omega$, of the gauge is given by,

$$\Delta\Omega = S_p - S_0$$

if S_p is the gauge resistance at pressure p and S_0 is the resistance at atmospheric pressure. Thus the total error associated with the determination of $\Delta\Omega$ will be $\sqrt{2} \times .0002 = \pm .0003$ ohm. This corresponds to an uncertainty of ± 3 kg/cm² in the pressure.

In estimating the accuracy of the resistance calibration of the gauge, it is convenient to begin by considering the accuracy of the freezing pressure of mercury calibrations. The change in resistance of the gauge at the freezing pressure is assumed, from the considerations set out previously, to be accurate to $\pm .0003$ ohm. Since the temperature dependence of the freezing pressure is very sensitive, (.005°C per kg/cm²), an additional uncertainty of $\pm .0001$ ohm is added to allow for possible error in the temperature control of the mercury cell. The freezing pressure of mercury at 0°C is

taken from Dadson and Greig's recent work⁽³²⁾ as 7718.5 ± 1.2 kg/cm². This value, the mean result of 74 determinations, is in good agreement with the smoothed value for 0°C, 7719 kg/cm² obtained by Zhokovskii et al⁽¹¹⁴⁾ from their experimental data for the freezing pressure of mercury as a function of temperature up to 25,000 kg/cm². By compounding the errors in $\Delta\Omega$ and the freezing pressure, it is estimated that $\Delta\Omega/p$ is accurate to $\pm 0.05\%$ at this calibration point.

The complete calibration curve is shown in Figure (6-9) with the maximum estimated errors indicated by dotted lines. At any pressure p , the calibration factor is given by,

$$\frac{\Delta\Omega}{p} = 1.0825 \times 10^{-4} - 0.720 \times 10^{-10} p \quad \dots (6-3)$$

with an uncertainty of $\pm .0005 \times 10^{-4}$ ohms per kg/cm².

As a consequence of the inaccuracies inherent in the gauge calibration curve and in the resistance measurements of the gauge, it is considered that the total error associated with a pressure measurement, in the absence of pressure leaks, increases steadily from ± 3 kg/cm² at low pressures to ± 9 kg/cm² at 10,000 kg/cm².

A computer program has been written for calculating the

pressure in the apparatus from the experimentally observed variables t_B , t_C and S , using equations (6-1), (6-2) and (6-3).

(b) General Behaviour.

Contrary to the findings of Bridgman⁽¹⁴⁾ and Adams et al⁽¹⁾, who in their studies of the manganin resistance gauge concluded that a properly prepared gauge was linear to 10 kbar, the resistance variation of the manganin coil is not truly linear with pressure. From Figure (6-9) the non-linearity of this gauge is about 0.07% per 1,000 kg/cm². With similar gauges, Michels and Lenssen⁽⁷⁵⁾ and Boren, Babb and Scott⁽¹³⁾ encountered non-linearities of 0.25% and 0.13% respectively. Boren et al⁽¹³⁾ produced several resistance gauges of different dimensions from the same grade of manganin wire and found that the non-linearity terms of the gauges were consistent to better than 1%. It seems likely, therefore, that the more closely linear behaviour of this coil is due to the grade of manganin wire employed rather than to the method of winding the coil.

In contrast to the behaviour of gold-chromium gauges⁽¹³⁾, no hysteresis effects were detectable in the pressure-resistance characteristics of the manganin gauge. After correcting for any

temperature changes which occurred during a pressure cycle, the gauge recovered its atmospheric pressure resistance to within the sensitivity of the readings.

The biggest disadvantage of the manganin gauge is the drift of the atmospheric pressure resistance with time. Over a period of 30 months the resistance of the gauge at 0.850 mV has increased from 44.5463 ohms to 44.5593 ohms. This drift in resistance is equivalent to a pressure increase of about 130 kg/cm^2 and has occurred at a rate which is apparently independent of the number of pressure excursions.

Although the principal errors in using the high pressure viscometer are associated with viscosity measurement rather than with pressure measurement, an improvement in the accuracy of pressure determinations is desirable. This can be achieved by using a more sensitive galvanometer for detecting the Smith's bridge balance point, and by reducing or eliminating the temperature corrections of the manganin coil.

CHAPTER VII.

THE MARK II VISCOMETER.

7.1 Design of Viscometer.

(a) Introduction.

A brief review of the limitations of the Mk. I. viscometer precedes the description of the improved design.

The worst feature in the Mk. I. viscometer is the sinker design because the composite construction and the short guiding pins make the production of a sinker with the required symmetry of shape and mass very difficult. The sinker turbulence corrections are large for short fall times and because of the inaccuracies in the turbulence correction curve, there is a significant error in calculated viscosities.

The bore of the Mk. I. viscometer tube has been examined by the National Physical Laboratory for uniformity of diameter, circularity, straightness and surface finish. With the exception of the regions around the ends of the bore, where some bell-mouthing was introduced during manufacture, the maximum variations from the nominal diameter of the bore are ± 0.0003 inches. The

Centre-Line-Average value of surface roughness is 4 micro-inches. The maximum departure from circularity is 0.00004 inches. The axis of the bore is straight to within ± 0.002 inches over the 8 inches of its length.

Small variations in the circularity and uniformity of diameter of the sinker and tube lead to large variations in the radial clearance and hence to erratic and eccentric fall of the sinker. Any improvements, therefore, in the shape of the tube and sinker would be beneficial in improving the accuracy of viscosity measurements.

The Mk. I. viscometer was designed with O ring seals, but these were later modified to compression seals, since a 'swell-pumping' effect was observed with the former⁽²⁵⁾. The modified sealing arrangement is satisfactory for rising or steady pressures, but slight leakages occur during rapid pressure reductions.

The falling cylinder viscometer has been widely employed for viscosity measurements at high pressures, but since few workers have given detailed accounts of the useful viscosity ranges and conditions of use of their instruments, the design remains completely unstandardized. The main differences in design are in the sinkers, where both guided and unguided sinkers having a variety of end shapes

are employed. The Mk. II. viscometer was designed primarily to assess the practicability of the unguided sinker for viscosity measurements over a wide range of pressures. However, in the event of unguided sinkers being unsuitable, the design allowed for the use of the viscometer with guided sinkers.

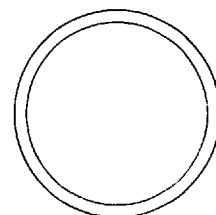
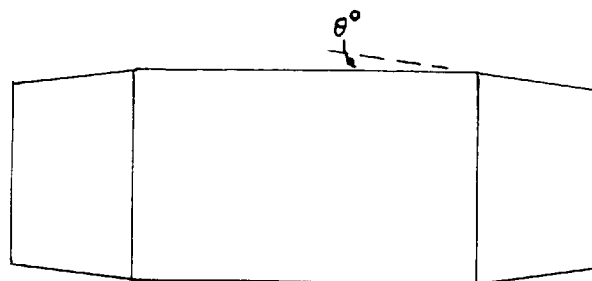
(b) Sinkers.

Three sinker designs have been tested in the Mk. II. viscometer, and these are shown diagrammatically in Figure (7-1).

The composite construction of sinkers was abandoned in favour of solid sinkers, since this feature facilitates their manufacture and reduces the likelihood of an asymmetric mass distribution. However, because the tube was machined from a non-magnetic stainless steel, and because it was essential that the sinker and tube be constructed from similar materials, some modification of the timing system was required.

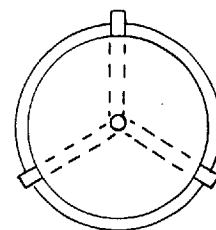
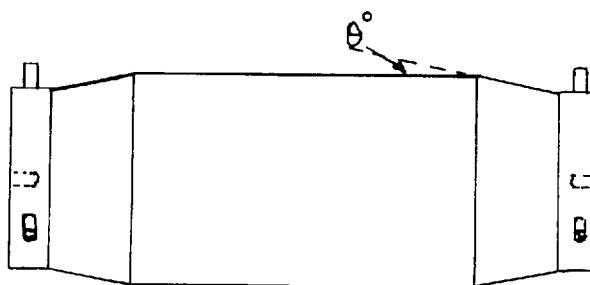
Viscometers with unguided falling cylinders have been employed by Van Wijk and Van der Veen⁽¹⁰⁶⁾, Boelhoefer and Toneman⁽¹²⁾, Jobling and Lawrence⁽⁵⁷⁾, and Scott⁽⁹⁶⁾. The instruments of Van Wijk and Van der Veen, and Boelhoefer and Toneman used an unguided needle-shaped body falling in a pressurised

FIG. 7-1. Sinkers for Mark II Viscometer.



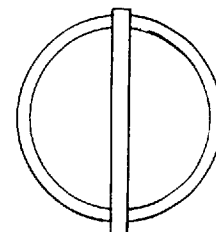
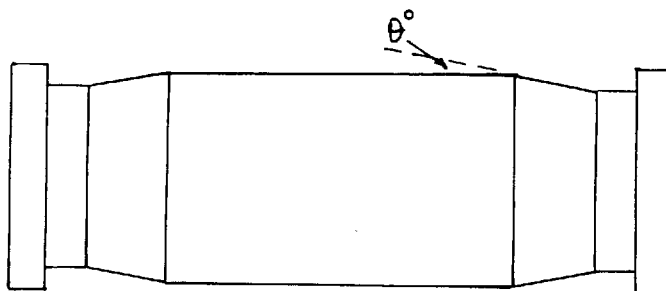
(a)

UNGUIDED SINKER



(b)

GUIDED SINKER - TYPE A



(c)

GUIDED SINKER - TYPE B

capillary, whereas Jobling and Lawrence employed a hollow weighted cylinder with hemispherical ends which was guided over the initial stages of its fall. Although Scott's experiments were mainly conducted with square-ended cylinders, the same general behaviour was observed with sinkers having hemispherical ends or 90° coned ends; these observations are not unexpected because,

- (i) the same widely divergent conditions exist for the fluid flow at the annulus exit with these end-shapes and the onset of instability due to turbulent fluid flow will occur at the same Reynold's Numbers.
- (ii) At low terminal velocities the centralizing forces on an unguided sinker are determined more by the radial pressure effects on the sinker body than by the flow forces at the entrance and exit of the sinker annulus.

The design adopted for the investigation of unguided sinkers in the new viscometer tube is shown in Figure (7-1(a)). The overall length of a sinker is 0.750 inches and the length of the cylindrical part is 0.450 inches. The sinker shape was adopted mainly because of its simplicity, but also because it was considered that the slightly tapered ends would reduce kinetic energy losses and turbulence corrections.

The guided sinker designs, shown in Figure (7-1(b)) and (7-1(c)), were based on the design adopted for the unguided sinker. The large turbulence corrections in the Mk. I. viscometer are attributed to the location of the sinker guiding pins in the region of maximum fluid velocity. To reduce turbulence corrections the guiding pins in both designs are sited at the ends of the sinkers. The cone angle, θ , is chosen so that the fluid velocity at the end of a sinker is reduced to one-tenth of its maximum value in the annulus. Typically, this makes $\theta = 10^\circ$ for a sinker of .004 inches radial clearance.

In the design shown in Figure (7-1(b)), designated type A, three equally spaced guiding pins are located at each end. The design shown in Figure (7-1(c)) is designated type B and is based on a design proposed by Lohrenz and Kurata⁽⁶⁸⁾, who demonstrated that a double pin of the type shown was satisfactory in stabilizing the fall of a sinker at low terminal velocities.

(c) Timing System.

The principle of the new timing system is based on the decrease of inductance in a coil when approached by a metallic sinker, due to the setting up of eddy currents in the sinker. In principle the original

system may be employed operating at a higher frequency, provided the eddy current signal is sufficiently large to give a reasonable sensitivity about the central balance point.

The sensitivity of the eddy current system is increased by winding the transducer coils such that their mean separation is equal to the sinker length, and by increasing the eddy current signal. The latter effect is obtained by increasing the frequency of the applied signal and by further amplification of the bridge output. Since the principle of the original timing system is based on an increase in coil inductance on the passage of a sinker, the inductance decrease due to eddy currents requires that the phase of the reference signal be reversed in order to obtain the correct triggering positions.

(d) The Tube.

The Mk. II. viscometer is shown as an assembled unit in Drawing 1(b). Since this instrument was intended for use in the same pressure vessel as the Mk. I. viscometer many of the features of the two instruments are identical.

The viscometer tube was machined from stainless steel (EN specification 58 JM.), and has an overall length of 7.25 inches with

a nominal bore of 0.285 inches. The bore of the tube was measured for uniformity of diameter, circularity, straightness, and surface finish by the Standards Division of the National Physical Laboratory. The diameter of the bore is $0.2856 \pm \begin{smallmatrix} .0001 \\ .0002 \end{smallmatrix}$ inches and the error in straightness of its axis is 0.0004 inches. The maximum departure from circularity in the bore is 60 micro-inches and the Centre-Line-Average value of surface roughness is between 36 and 48 micro-inches.

Four identical transducer coils are wound in grooves machined near the ends of the tube. Because of the eddy current timing system, the separation of the coil centres of each pair are 0.750 inches. The details of the coil windings are identical with those described earlier in connection with the Mk. I. viscometer. Ventilation of the coil windings is provided by radial slots in the walls of the grooves. The ends of the tube are counterbored concentric with the bore to a depth of 0.425 inches. Interchangeable guiding sleeves with an internal diameter slightly smaller than the bore are located in the counterbores. These sleeves are used to steady an unguided sinker during the initial stages of its fall. 'Dummy' sleeves of the same diameter as the tube are employed with guided sinkers.

End pockets are sealed to both ends of the tube with compression type seals. These pockets enable the tube to accommodate two sinkers when density measurements are required. The pockets are attached to the tube in a similar manner to that used in the Mk. I. viscometer. The top pocket is orientated relative to the bottom pocket with a swivel nut arrangement. The pockets in these units are machined with square-ended profiles to accommodate the improved sinkers. The seals are designed specifically for compression type gaskets with a groove and mating tongue configuration and strong threads. The $3/16$ inches engaged thread length of 40 T. P. I. used in the Mk. I. viscometer is increased to $5/16$ inches and the thread pitch to 32 T. P. I. for the new instrument. The locking ring for the top pocket unit is made from stainless steel to enable the seals to be subjected to a greater preload than is possible in the original instrument. The viscometer is sealed with an end cap and a bellows unit in a similar manner to the Mk. I. viscometer, although the seals are of the compression type using a groove and tongue arrangement.

Other details of the Mk. II. viscometer design are identical with those given previously in connection with the Mk. I. instrument.

7.2 Development of the Eddy Current Timing System.

In order to convert the original timing system to operate on the eddy current principle it is necessary that,

- (i) the frequency be increased as much as possible, since the eddy current signal is frequency dependent.
- (ii) the phase of the reference voltage be reversed to obtain the correct triggering positions.
- (iii) the separation of the transducer coils be equal to the length of the sinker for maximum sensitivity at the central balance point.

Most of the development work for the eddy current timing system was concerned with adapting the electronic equipment for satisfactory operation at the higher frequencies.

A simple cylinder of EN 58 JM, 0.750 inches in length with a radial clearance of .004 inches, was used for the initial testing. Starting at 500 c.p.s., the bridge circuits were balanced and the system tested. Satisfactory operation of the system was observed, but it was noted that this was due to a ferromagnetic effect rather than to an anticipated eddy current effect. On increasing the frequency, a range of frequencies was found where the triggering positions for the two timing stations were opposite, until at 4 kc/s

the system again functioned satisfactorily, but because of a ferromagnetic signal.

It was observed at this stage that the 'magnetic' properties of the tube and sinker were different; the sinker was attracted by a powerful magnet whereas the tube was not. Analysis of samples of the two materials by X-ray spectrometry revealed that they were both within the specification of EN 58 JM, but the nickel and chromium contents of the 'non-magnetic' specimen were respectively 1.5% and 1% greater than in the 'magnetic' specimen. The specification for EN 58 JM permits the nickel and chromium concentrations to vary within the ranges 8% - 12% and 17% - 20% respectively, and the magnetic permeability to vary between 1.005 and 1.03.

From the complex behaviour of the triggering positions on increasing the frequency, it was concluded that the stainless steel sinkers were slightly ferromagnetic and that the output signal would be dependent on the relative magnitudes of the ferromagnetic and the eddy current effects. To a first approximation the ferromagnetic signal for a particular sinker is independent of frequency. Consequently, if the frequency is increased sufficiently the eddy

current signal will become dominant and the system will function as intended.

A new cylinder was machined from a 'non-magnetic' sample of EN 58 JM and tested in the viscometer at 6 kc/s with an identical cylinder machined from aluminium alloy. It was found that the aluminium sinker triggered the timer correctly, but from the observations on the stainless steel sinker, it was obvious that at this frequency the ferromagnetic and eddy current signals were comparable. The minimum frequency for the satisfactory operation of the timing system on the eddy current principle with the stainless steel sinker was found to be 6.5 kc/s.

Operation of the timing equipment at higher frequencies led to four major problems,

- (i) The pulse output from one channel of the timing equipment was insufficient to operate the timer at frequencies over 6 kc/s. It was found that increasing the power supply to the unit from 12 v. to $13\frac{1}{2}$ v. was sufficient to raise the limit of satisfactory operation of the circuit to 7.5 kc/s.
- (ii) On changing the direction of fall switch, (i. e. reversing the phase of the reference voltage), the balance of the bridge circuits

in both channels was disturbed. This disturbance was reduced to a negligible level by attenuating the reference signal.

(iii) The bistable multivibrator circuits of both channels oscillated at the higher frequencies and triggered the time period counter.

The oscillations were prevented by increasing the bias to both circuits from $1\frac{1}{2}$ v. to 3 v.

(iv) Pick-up from the thermostatic controller was sufficient to cause premature triggering of the timing circuits over a wide range of frequencies. Several attempts were made to solve this problem by better screening but without success, and it was necessary at all times to guard against premature triggering of the timer by this means. It is suggested that this problem could be overcome by replacing the toluene regulator and relay with a proportional temperature controller.

As a result of the development work on the new system, it was concluded that the eddy current principle is a feasible alternative to the ferromagnetic principle. The behaviour of the electronic trigger units at the higher frequencies made it impossible to gauge the sensitivity of the new system accurately.

A new electronic triggering unit should be built along similar

lines to that employed for the original system but designed to operate at a frequency of 10 kc/s or preferably higher. The output signal from a non-magnetic sinker, (e.g. aluminium), at this frequency would be appreciable, and that from a stainless steel sinker should be adequate. It is considered that under these conditions the sensitivity of the eddy current system would be as good as that of the former system.

7.3 Sinker Calibrations.

(a) Unguided Sinkers.

Three unguided sinkers of the type shown in Figure (7-1(a)) with cone angles θ of 3° , 5° and 7° were tested in the improved viscometer tube. The sinkers were manufactured from a 'magnetic' sample of stainless steel before the large variation of magnetic permittivity for steels of the same specification was discovered. The timing system was operated at 500 c. p. s. using the ferromagnetic principle. Each of the three sinkers was calibrated by measuring its time of fall in liquids of known viscosity and density.

The general behaviour of these sinkers is very similar in that for each sinker there exists a well defined range of fall times

for which the function

$$\frac{\bar{t}^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$$

is independent of the terminal velocity. A summary of the calibration data obtained for the 5° and 7° sinkers is given in Figures (7-2(a)) and (7-2(b)) respectively. The curves show the variation of

$$\frac{\bar{t}^*}{\eta} \cdot \frac{\rho_s - \rho_f}{\rho_s}$$

(i. e. the reciprocal of the viscometer constant k), as a function of the mean fall time $\bar{t}$. These results suggest that for both sinkers k is independent of fall time within the range of fall times from 11 seconds to 50 seconds. However, outside these limits

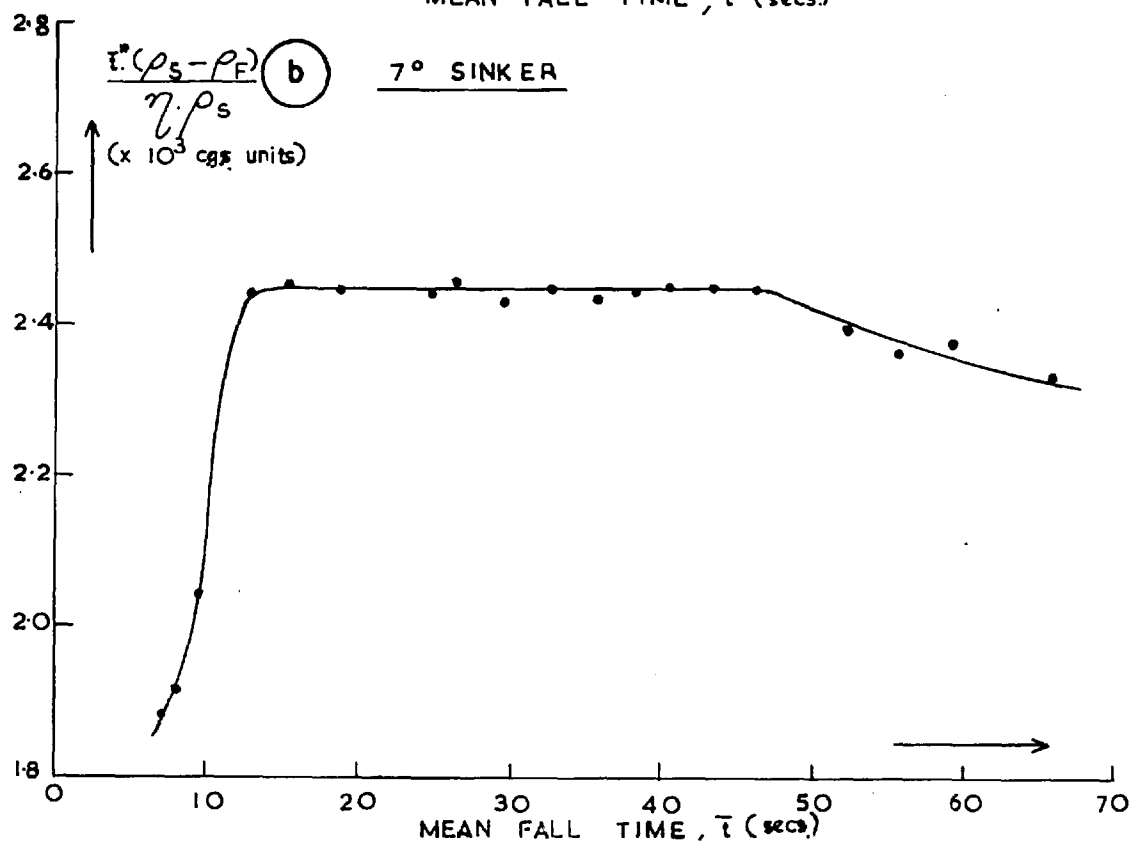
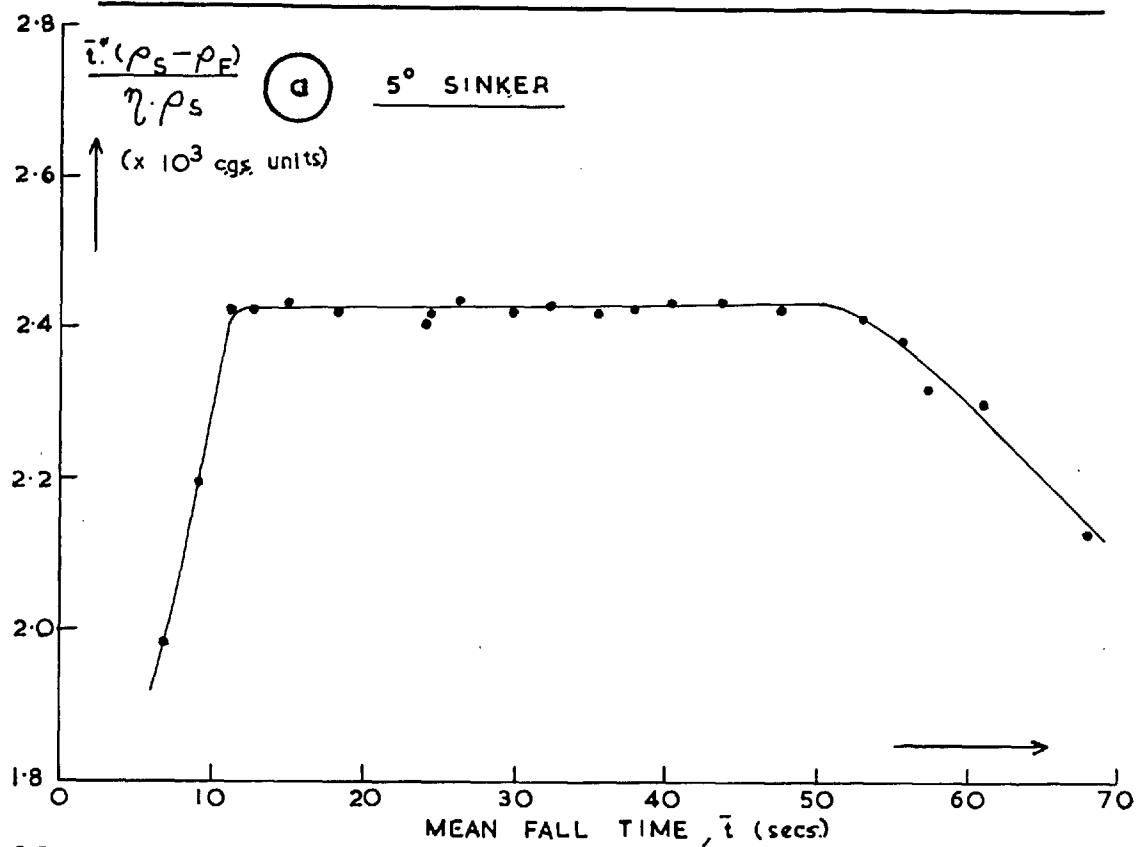
$$\frac{\bar{t}^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$$

decreases rapidly as the sinkers fall eccentrically in one or both directions. If the scatter of the mean fall time in a particular direction is defined as

$$\frac{t_{\max} - t_{\min}}{t_{\text{mean}}} \times 100$$

where $t_{\max}$, $t_{\min}$ and t_{mean} refer to the maximum, minimum and

FIG. 7-2. Calibration Curves for Unguided Sinkers.



mean fall times respectively in that direction, then the scatter of the fall times increase rapidly at both limits of steady fall.

The directional effects of the 5° and 7° sinkers are constant over the range of steady fall and equal to 0.15% and 0.12% respectively. The experimental scatter for both sinkers is generally much less than 0.1%. The 5° sinker starts to fall eccentrically in one direction at about 50 seconds but remains concentric in the other direction to at least 75 seconds, by which time the scatter has increased to about 2% in that direction, and the overall directional effect to 9%. The 7° sinker starts to fall eccentrically in both directions at fall times of about 50 seconds.

A complete calibration curve was not constructed for the 3° sinker. Its general behaviour is similar to that of the 5° and 7° sinkers, but its performance is inferior. The directional effect is fall time dependent, even in the range of steady fall, and decreases from 0.7% to 0.1% over the range of fall times between 10 seconds and 27 seconds. The scatter of the fall times is 0.2% and the upper limits of steady fall are 28 seconds and 45 seconds.

Measurements of the surface finish and departures from circularity of the cylindrical sections of the 3° and 7° sinkers

confirmed that the latter sinker is superior in both respects. The C. L. A. values of surface roughness for these sinkers are 16 and 4 micro-inches, and the maximum departures from circularity are .00150 inches and .00005 inches. No measurements of shape were made of the 5° sinker, but it may be concluded from the calibration data that it is not less symmetric than the 7° sinker.

(b) Guided Sinkers.

Incomplete calibration curves have been obtained for two type A guided sinkers. The results for the high terminal velocity region are summarised in Figure (7-3), where

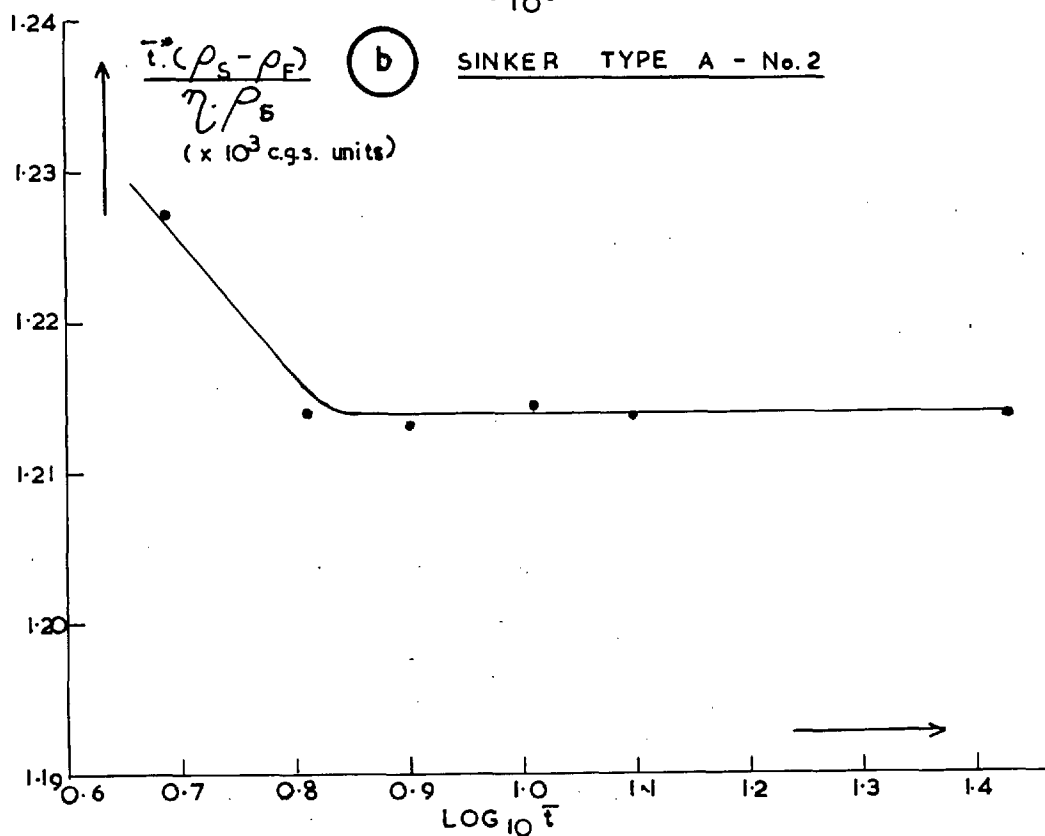
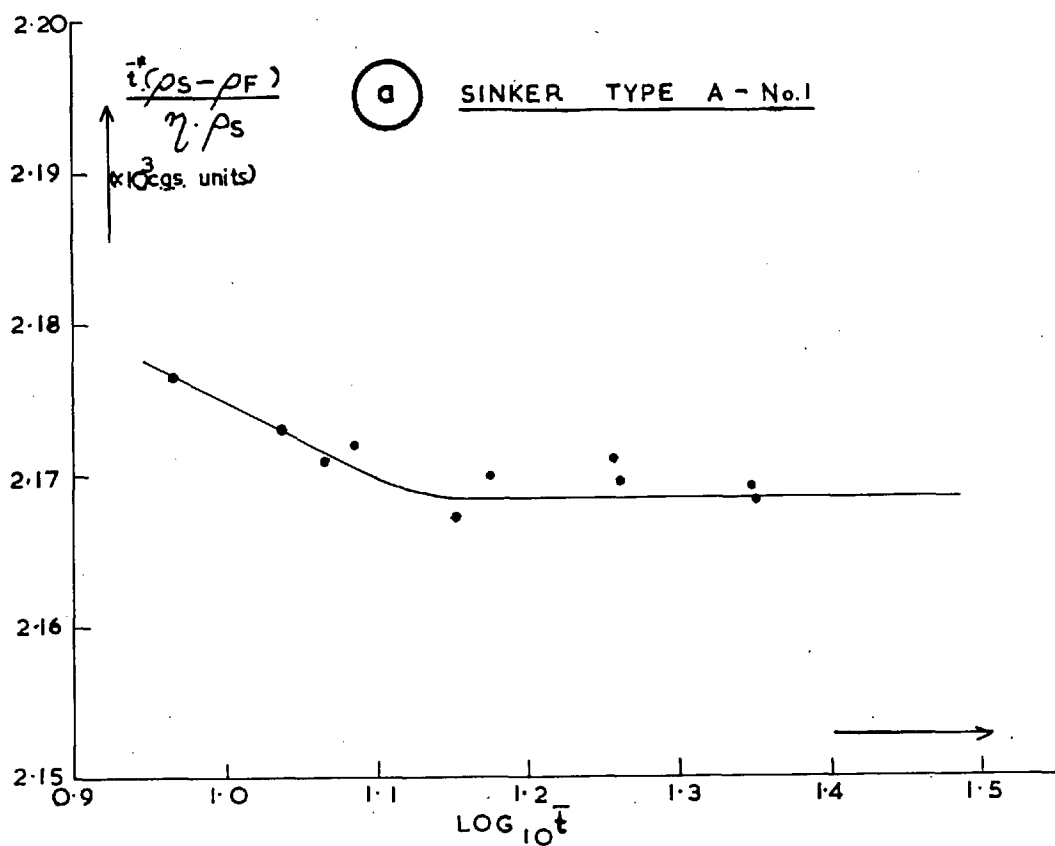
$$\frac{\bar{t}^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$$

is shown as a function of $\log_{10} \bar{t}$.

The sinkers, designated A1 and A2, were machined from 'non-magnetic' stainless steel, and have radial clearances of 0.0041 inches and 0.0050 inches respectively. The fall times of the sinkers were measured in liquids of known viscosity and density, operating the timing equipment on the eddy current principle at 7 kc/s.

The experimental scatter of the fall times for each sinker is between 0.1% and 0.2%, except for one fall direction of sinker A1

FIG. 7 - 3. Calibration Curves for Guided Sinkers.



where the scatter is consistently near 1%. The directional behaviour of sinker A1 is superior to that of A2, remaining constant at 1% of the mean fall time up to 580 seconds. The directional effect of A2 increases from 2.1% to 3.3% within the range of fall times from 10 seconds to 60 seconds.

The form of the calibration curves are quite similar, with

$$\frac{t^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$$

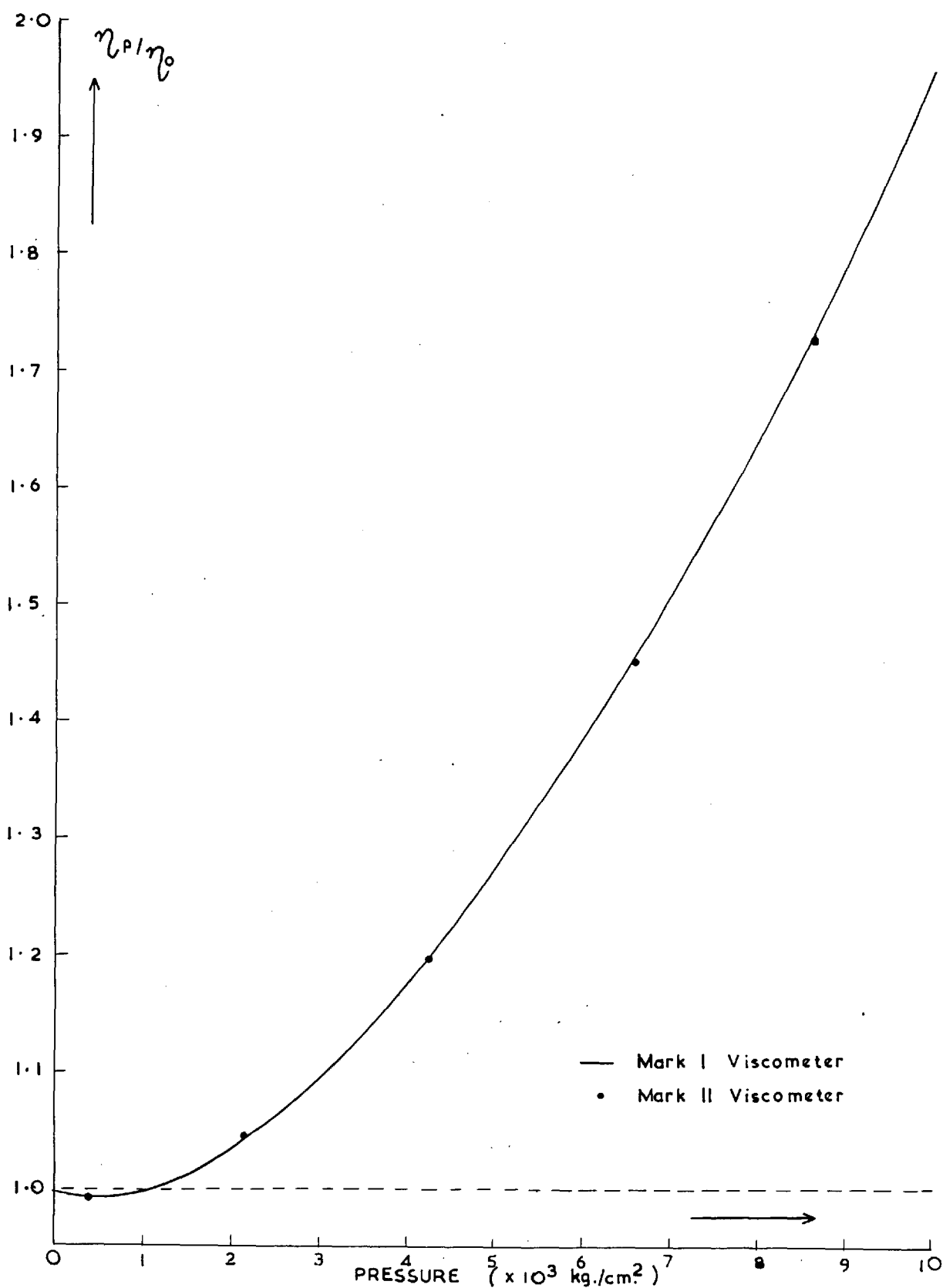
increasing rapidly at the shorter fall times. The deviations of the experimental points from a smooth curve are greater than the deviations of the data employed in constructing the calibration curves for the unguided sinkers. One of the reasons for this is that the shape and mass symmetry of the unguided sinker is better than that of the guided sinker. Another factor may be due to the reduced stability and sensitivity of the eddy current system compared with the ferromagnetic system.

Five stainless steel sinkers of type B were produced and tested in the viscometer. However, not one of these sinkers falls consistently in both directions and the minimum directional effect of any of them at low velocities is about 3.7%. Another sinker, although

it has a large directional effect, does fall consistently in one direction. This sinker was tested over the range of fall times between 10 seconds and 40 seconds. The experimental scatter in the good fall direction is less than 0.1% in this range, but in the reverse direction the fall is very inconsistent. Within the tested range, the viscometer constant is independent of the fall time to better than 1%.

7.4 General Conclusions.

The performance of the Mk. II. viscometer at high pressures was tested by determining the viscosity of water at 25°C and at pressures up to 8,500 kg/cm². The guided sinker A1 was employed for this experiment. The minimum sinker fall time was approximately 15 seconds. The experimental results are shown in Figure(7-4), together with the curve for water at the same temperature obtained with the Mk. I. viscometer. The results were calculated by the method described in Appendix III taking account of the different sinker density, and assuming that turbulence corrections were negligible. The maximum deviation of the experimental results from the smooth curve is about 1%. This may be compared with the estimated accuracy of the curves, $\pm 1.0\%$ and a similar uncertainty in the results with

FIG. 7-4. Viscosity of Water at 25°C.

the Mk. II. instrument.

The errors in the experimental points arise mainly from the assumption that the turbulence corrections are equal and negligible within the range of the measurements. It is probable that the scatter of points along the calibration curve is sufficiently large to hide a small increase in

$$\frac{\bar{t}^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$$

from its base value, (say, 0.1% - 0.2% for a 15 seconds fall time). Additional errors in the results arise from random variations of the fall time, contamination, errors in the bouyancy correction, and errors in the dimensional corrections. These uncertainties are of the same order as are incurred with the Mk. I. viscometer.

The chief limitation in improving the accuracy of viscosity measurements with the falling cylinder viscometer is the accuracy of the calibration curve. From the operational experience gained with both viscometers it is concluded that calibration data are more consistent if obtained at different temperatures with the same liquid, than with many liquids at the same temperature. Using this technique errors in the data due to contamination films are eliminated

for a particular filling, and the accuracy of the points is dependent on the accuracy of the viscosity and density data employed.

The surface finish of the sinker and the tube bore should be as good as possible to facilitate cleaning, inspection and assembly of an instrument with the minimum level of contamination. The surface roughness of the bore in the Mk. II viscometer is between 36 and 48 micro-inches; it is recommended that this be improved by honing to at least 5 micro-inches. This operation is possible without adverse changes in the uniformity of diameter, straightness and circularity of the bore, but after this operation it would be necessary to make new guided sinkers.

From the experiments with unguided sinkers it is concluded that the maximum relative viscosity increase for which the unguided sinker principle is feasible is 10 : 1. The symmetry of mass and shape required to extend this range are not easily obtained and for this reason the unguided falling cylinder viscometer is of limited use at high pressures.

No definite conclusions can be reached concerning the effect of tapered ends on stabilizing the fall of a cylinder, since variations in the shape and surface finish of the sinkers are too large. At high

velocities where the tapered ends were specifically intended to reduce turbulent flow and improve stability, the onset of erratic fall for each of the sinkers is around 11 seconds. Hence, it seems likely that the improvement in stability due to tapering the sinker ends is small, and it may well be that asymmetry introduced as a consequence of the more complex shape reduces stability at low velocities.

The calibration curves obtained for the various sinkers in the Mk. II. viscometer are not sufficiently accurate for the construction of turbulence correction curves. The accuracy of the calibration curves for the 5° and 7° sinkers is about 0.5% and it may be concluded that the maximum turbulence correction is not greater than this figure.

Since the asymmetry of shape and mass are the most important factors in determining the stability of an unguided sinker, it is suggested that where this principle is employed the most practical shape for the sinker is the simple cylinder. The disadvantages of this shape from flow considerations are outweighed by the greater symmetry that can be maintained during machining.

In the discussions on the behaviour of unguided sinkers it is assumed that falling cylinders do not rotate about their principal axis.

Because rotation of a body about its principal axis leads to increased stability, an investigation into the effects of inducing a falling sinker to rotate would be interesting. It is envisaged that rotation of such a sinker could be induced by small flutes.

The difficulties involved in the production of a guided sinker that falls consistently with a small and constant directional effect are so great as to be decisive in choosing between the suggested designs. The 'type A' sinker is chosen as the best design for future work because the manufacture of the body is simpler than for 'type B' and more important, the stabilizing pins may be renewed.

Although the new viscometer has not been tested extensively at high pressures the indications are that the leakage problems associated with the Mk. I. viscometer have been eliminated. Some difficulty was experienced with the seal between the tube and the pocket component at end 1, and the locking ring for this seal was appreciably deformed after making and breaking the seal several times. Since the mechanical strength of the locking ring is not easily improved it is recommended that in another instrument the tube and end pockets should be machined as a single component. This complicates the manufacture of a tube, but it is considered that this

disadvantage is offset by the reduction in the number of seals.

The eddy current timing system is a practical alternative to the ferromagnetic system. Neither the stability nor the sensitivity of the eddy current system has been gauged accurately, but the results of the preliminary testing are sufficiently encouraging to warrant the manufacture of a new electronic timing system designed to operate at 10 kc/s.

CHAPTER VIII.

EXPERIMENTAL PROCEDURE AND RESULTS.

8.1 Experimental Procedure.

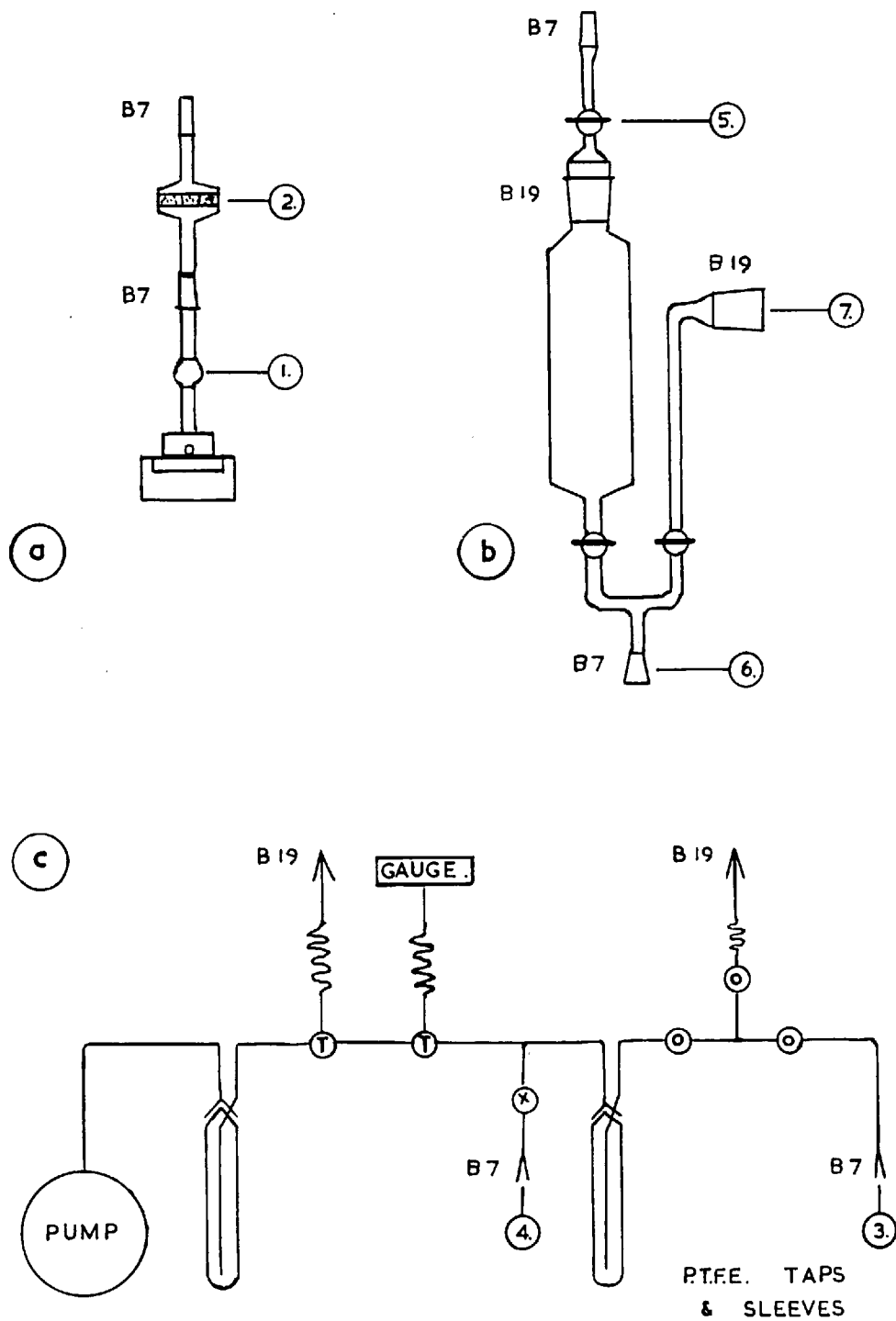
(a) Assembly of Viscometer.

It was noted earlier, (Chapter V), that the accuracy of viscosity measurements is adversely affected even by a relatively small level of contamination in the viscometer. Considerable care is taken, therefore, at all stages of the assembly and filling of the instrument, to ensure that the level of contamination in the test liquids is kept as small as possible. The final assembly of the viscometer is completed from four separate pre-assembled units consisting of the bellows, the sinker, the filling connection (shown in Figure (8-1(a)) and the tube with end pockets attached.

The procedure adopted for the assembly of the viscometer is as follows:

The end pockets are sealed to the viscometer tube with 0.004 inches thick annealed copper gaskets. A brass filling tube (1) is screwed into the top of the viscometer, sealing with an O ring. At its other end the brass tube, cemented with 'Araldite' to a ground

FIG. 8-1. Equipment for Filling Viscometer.



glass 'B7' cone, mates with a filter unit. The filter (2) is of grade 3X sintered glass with a 'B7' cone and socket.

The assembled units are washed several times in filtered benzene and, with the exception of the filling connection which is allowed to dry at room temperature, they are dried in a vacuum oven at 60°C. After drying, the assembled tube unit is removed from the oven and inspected for any remaining dirt, which is removed by forcing plugs of cotton wool through the tube. Finally, this unit is washed in a stream of filtered distilled water and dried again in the vacuum oven. After a final inspection, the assembly of the units is completed as quickly as possible with a smear of a molybdenum disulphide grease on the threads to prevent seizure.

At all stages during the assembly of the viscometer the components are kept under glass or wrapped in clean aluminium foil to protect them from dust in the atmosphere. Particular attention is taken during the assembly of the seals to avoid dirt or scratches on the gaskets or sealing surfaces.

When the viscometer has been assembled it is tested for leaks by immersion in a tube containing petroleum ether. Nitrogen gas is supplied to the viscometer via the filter and filling tube up to a pressure

of 25 p. s. i. g. Any leaks in the region of the seals, bellows or bursting disc are indicated by the appearance of bubbles.

When the viscometer is leak tight, the electrical connections sleeve covering the bellows is fitted and secured. The assembly is completed by plugging in the connections to the coils and binding the leads to the outside of the tube with cotton.

(b) Filling the Viscometer.

All the liquids on which pressure-viscosity measurements have been made were first deaerated and then introduced into the viscometer under vacuum. As two filling systems are available, the exact procedure adopted for filling the viscometer is governed by the nature of the test liquid. One of the filling systems is completely grease-free with P. T. F. E. stopcocks and P. T. F. E. sleeved joints, while the other is a conventional system with silicone-greased joints and stopcocks. The filling vessel is shown diagrammatically in Figure (8-1(b)) and the complete vacuum system in Figure (8-1(c)). The grease-free filling system is employed when the viscometer is filled with organic liquids. Non-pure liquids which were employed for some preliminary calibrations were not deaerated, since this might have changed their composition.

The appropriate filling vessel is washed, cleaned, and thoroughly dried before being filled with the liquid to be studied. The filling vessel is connected to the vacuum system at (3) or (4), depending on whether the normal or grease-free system is being used. The liquid is completely deaerated. It is possible to reduce the pressure in the filling vessel to about 1 mm. Hg. with the normal system, and to about 5 mm. Hg. with the grease-free system.

This procedure was modified slightly in the case of the ~~ethanol~~-water mixtures which were made up from samples of pure ethanol and pure water that had been deaerated separately prior to mixing. This procedure reduced the time required for deaeration of the mixture, and enabled the final concentration to be more closely controlled.

After complete deaeration of the liquid sample, stopcock (5) is closed. The viscometer is connected to the filling vessel at (6), which is itself recoupled to the vacuum system at (7) by a flexible connection. The bellows of the viscometer are supported by a screwed rod and locking nut arrangement to prevent them collapsing. The viscometer tube is evacuated for about half an hour until it is completely dry. At the end of this period the stopcock to the vacuum

system is closed, and the liquid allowed to drain from the filling vessel into the viscometer. The transfer of liquid is assisted by gently warming the filling vessel, and the bellows are flexed to ensure that no bubbles remain in the viscometer. The bellows are almost fully extended and the filling tube and vessel are disconnected. The O ring is replaced by an annealed copper disc and the viscometer is sealed with a stainless steel grub screw. Finally, the bellows are released completely and the screwed rod removed, leaving the viscometer ready for insertion in the pressure vessel.

After each experiment a sample of the liquid from the filling vessel is retained in a sealed ampoule together with a sample from the viscometer. The refractive indices of these samples are subsequently measured to give an indication of the purity and to provide a check on any increase of contamination during an experiment.

(c) Viscosity Determinations.

After the viscometer has been filled, it is loaded into the pressure vessel. The vessel is inverted several times to ensure that the sinker is falling freely and that the timing system is operating satisfactorily. The locking arrangements of the vessel are checked for alignment and the bath filled with thermostating fluid. The

toluene regulator and heaters are adjusted to maintain the required operating temperature.

A minimum period of three hours is allowed for the viscometer to attain thermal equilibrium. Before commencing measurements, the temperature of the Smith's Bridge is regulated to 25°C , and the cold junction of the coil thermocouple is surrounded by pure ice and distilled water. The potentiometer is standardised against a Weston Cell, and the timing system is balanced and adjusted. Throughout the period of the experiment, the last two adjustments are checked from time to time.

The viscosity measurements are made at fixed temperatures within the pressure range 1 to $10,000 \text{ kg/cm}^2$. The determination of the viscosity involves measuring the fall time of the sinker under known conditions of temperature and pressure. The steps followed in making a measurement are,

- (i) Measure pressure in system.
- (ii) Measure temperature of viscometer.
- (iii) Determine sinker fall time.
- (iv) Check temperature.
- (v) Check pressure.

After these measurements, the pressure is altered and, when the viscometer has regained thermal equilibrium, steps (i) to (v) are repeated.

The methods used to raise and lower the pressure in the apparatus have been described in Chapter IV. Six readings are required to measure the resistance of the manganin coil and calculate the pressure. Four of these readings are the resistance of the variable arm in the Smith's Bridge required for the balances shown in Figure (4-6). The remaining readings are the temperature of the resistors in the Smith's Bridge and the e. m. f. of the coil thermocouple.

The temperature of the viscometer is measured by calibrated mercury-in-glass thermometers, graduated in 0.01°C and immersed in the thermostating liquid.

After the bridge circuits have been balanced and the reference voltage adjusted, the fall time of the sinker is determined in the following manner:

Commencing with the sinker at end 1, the direction of fall switch, the trigger circuit and the time period counter are set appropriately, and the vessel inverted. The time period counter is started by the sinker falling through the first pair of coils, and is

stopped at end 2 by setting the trigger circuit on the approach of the sinker. After noting the fall time of the sinker, the procedure is reversed and the fall time from end 2 is found. These measurements are repeated until about six results have been obtained in each direction.

The initial and final measurements of a run are always made at atmospheric pressure with special care. The importance of these results is that they are used as base measurements and values of viscosity under pressure, η_p , are calculated from the relative viscosity, η_p/η_o , and the known value of η_o . If t_p and t_o are the fall times (buoyancy and dimensionally corrected) corresponding to η_p and η_o , then

$$\frac{\eta_p}{\eta_o} = \frac{t_p}{t_o}$$

For convenience the reference of base values η_o and t_o are taken at atmospheric pressure.

The pressure is calculated from the change in resistance of the manganin coil, and the error in the base resistance measurement is important in that it determines the accuracy of the pressure measurements in a particular experiment.

In this study viscosity measurements have been made at various temperatures using several different liquids. Curves have been obtained for the relative viscosity as a function of pressure as follows:

(i) Heavy Water, (Deuterium Oxide).

Isotherms at 10°C, 20°C, 25°C, 30°C, 50°C, 75°C,
100°C.

(ii) Benzene.

Isotherms at 30°C, 50°C, 75°C.

(iii) Methanol.

Isotherms at 30°C, 50°C, 75°C.

(iv) Ethanol.

Isotherms at 30°C, 50°C, 75°C.

(v) Four binary mixtures of ethanol and water.

Isotherms at 30°C, 50°C, 75°C.

The pressure range for all the systems studied was 1 - 10,000 kg/cm², with the exception of benzene where the maximum pressure was restricted by the freezing pressure of benzene at that temperature. All the measurements reported in this thesis, were obtained using the Mk. I. viscometer and the stainless steel sinker. The experimental results are tabulated in full in Appendix III together with some

recalculated results for water.

8.2 Heavy Water.

The experimental results for heavy water are summarised in Figures (8-2) to (8-8), where the relative viscosity is shown as a function of pressure at each of the experimental temperatures.

Also included in these graphs are the recalculated data for water at the same temperature. The original results for water obtained using the same viscometer and sinker^{(9) (25)} have been recomputed from the more consistent fall times from end 1 and the improved calibration curve of the stainless steel sinker. The difference between the original results and the recomputed values is negligible at low temperatures, but at higher temperatures the difference is more significant, although still less than 1%.

A comparison of the curves for water and heavy water shows that their relative viscosities vary in a similar manner, although η_p / η_o for heavy water is mostly less than that for water at the same temperature and pressure. This difference is greatest for the isotherm at 10°C, but decreases with increasing temperature until at 100°C the curves are indistinguishable.

FIG. 8-2. Viscosity of Water & Heavy Water - 10°C.

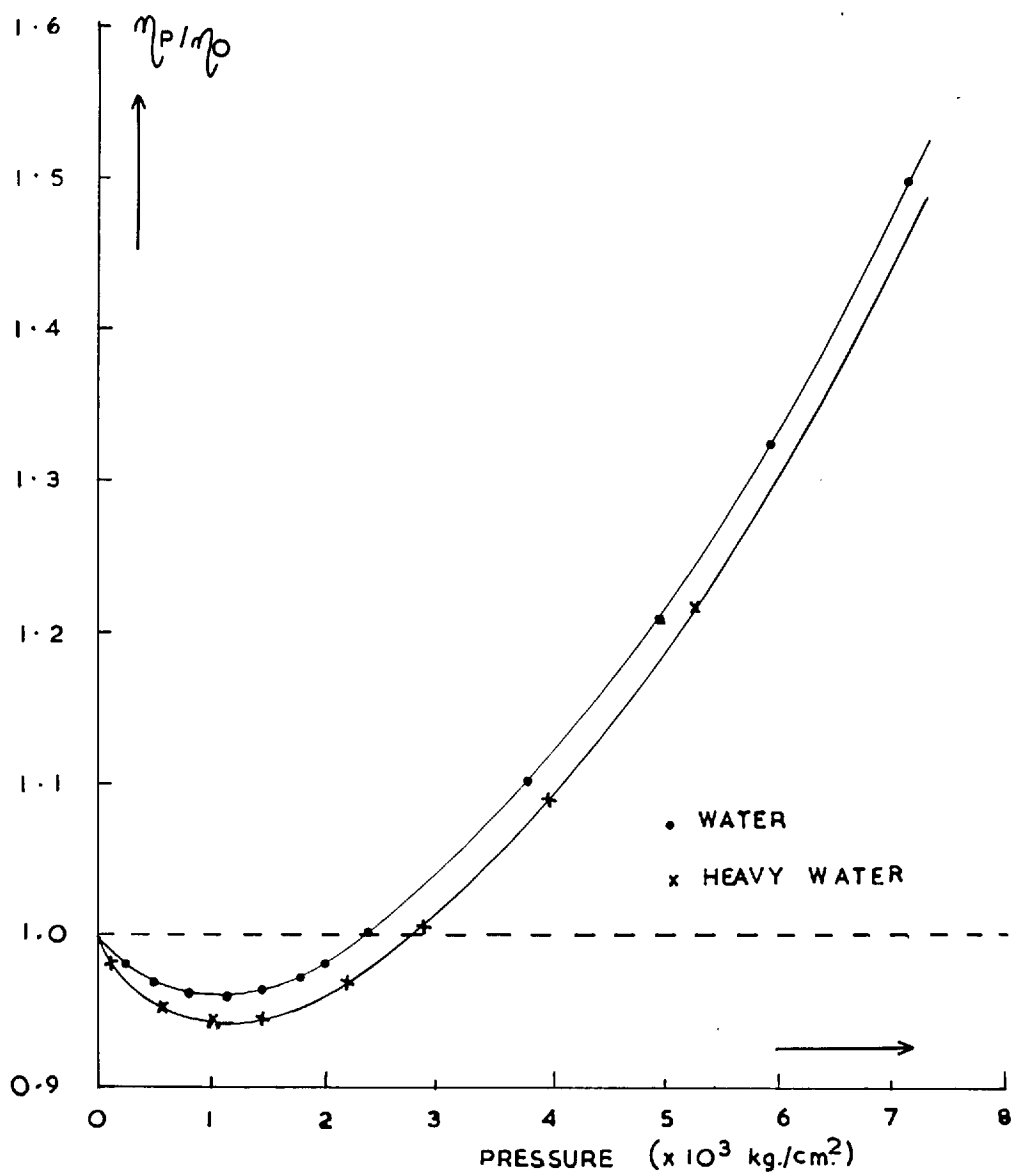


FIG. 8-3. Viscosity of Water & Heavy Water - 20°C.

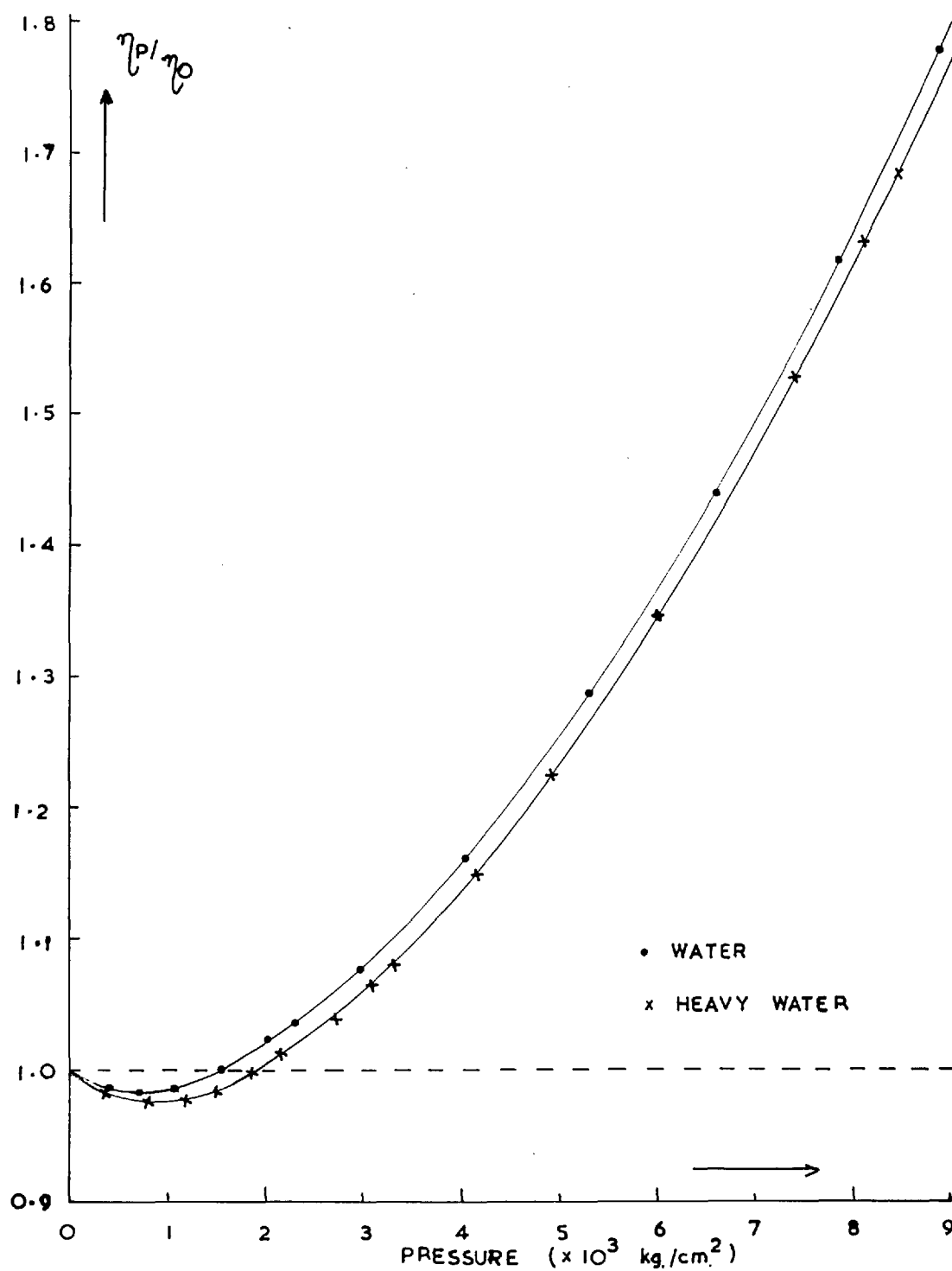


FIG. 8-4. Viscosity of Water & Heavy Water - 25°C.

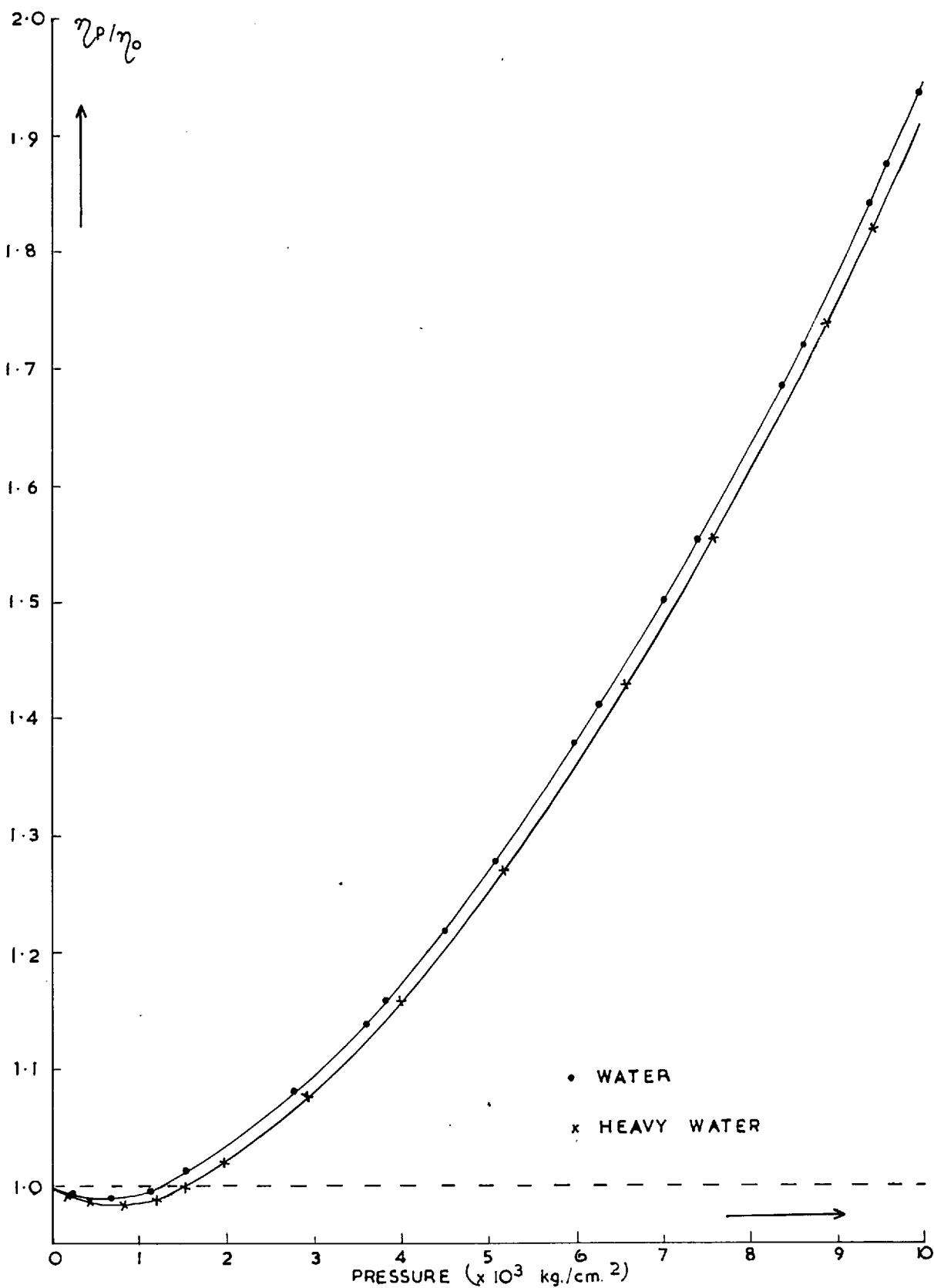


FIG. 8-5. Viscosity of Water & Heavy Water - 30°C.

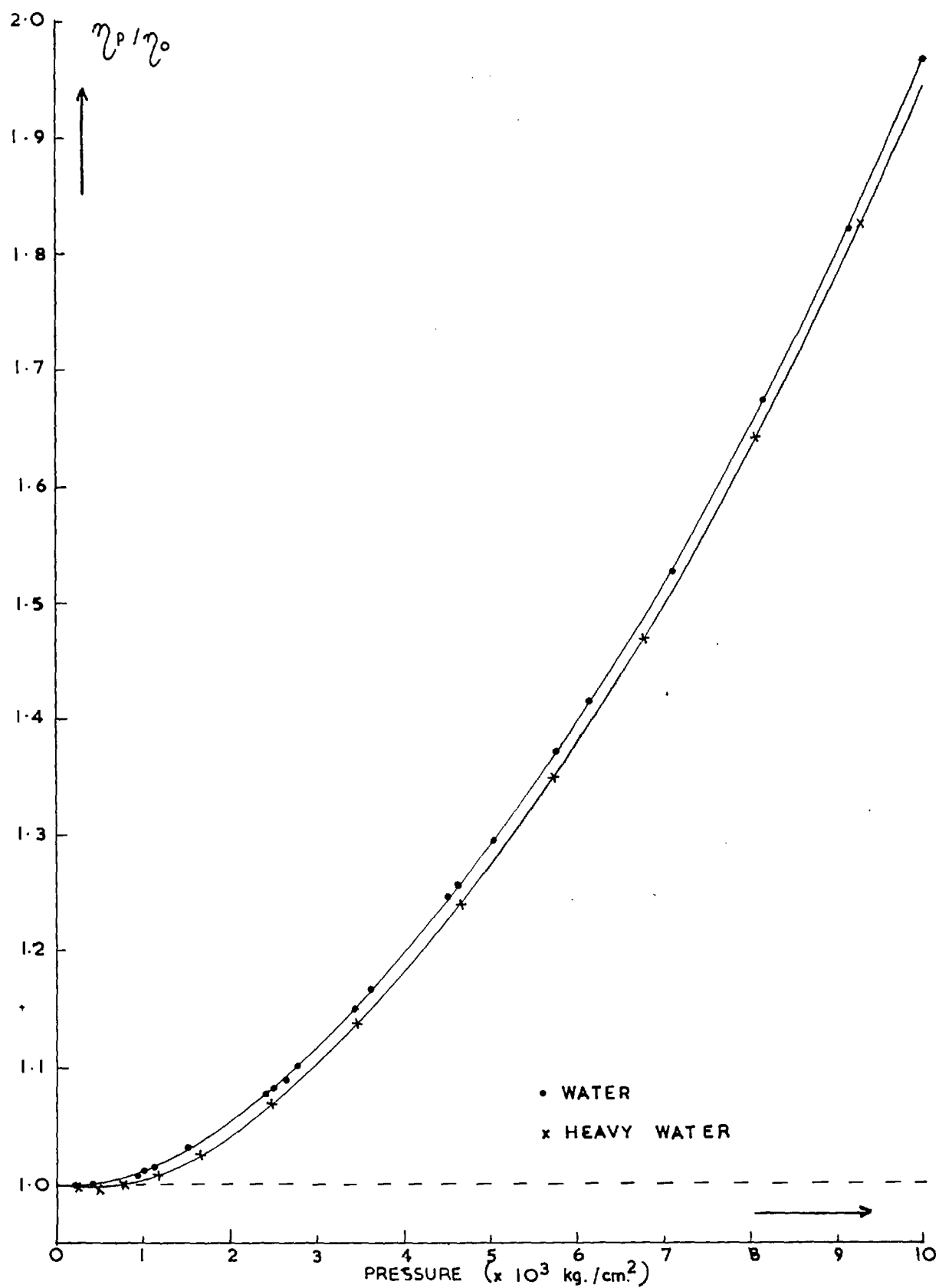


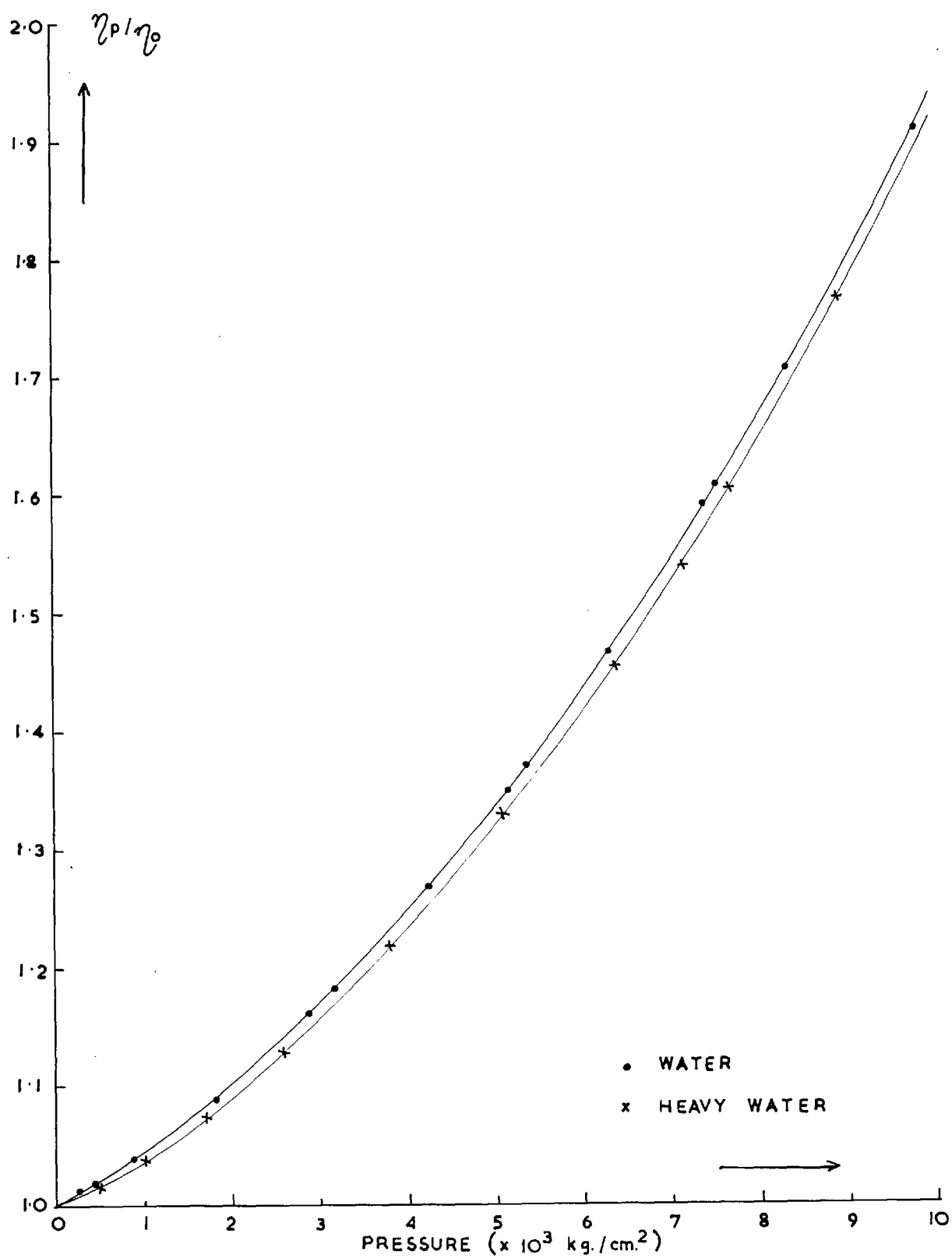
FIG. 8-6. Viscosity of Water & Heavy Water - 50°C.

FIG. 8-7. Viscosity of Water & Heavy Water - 75°C.

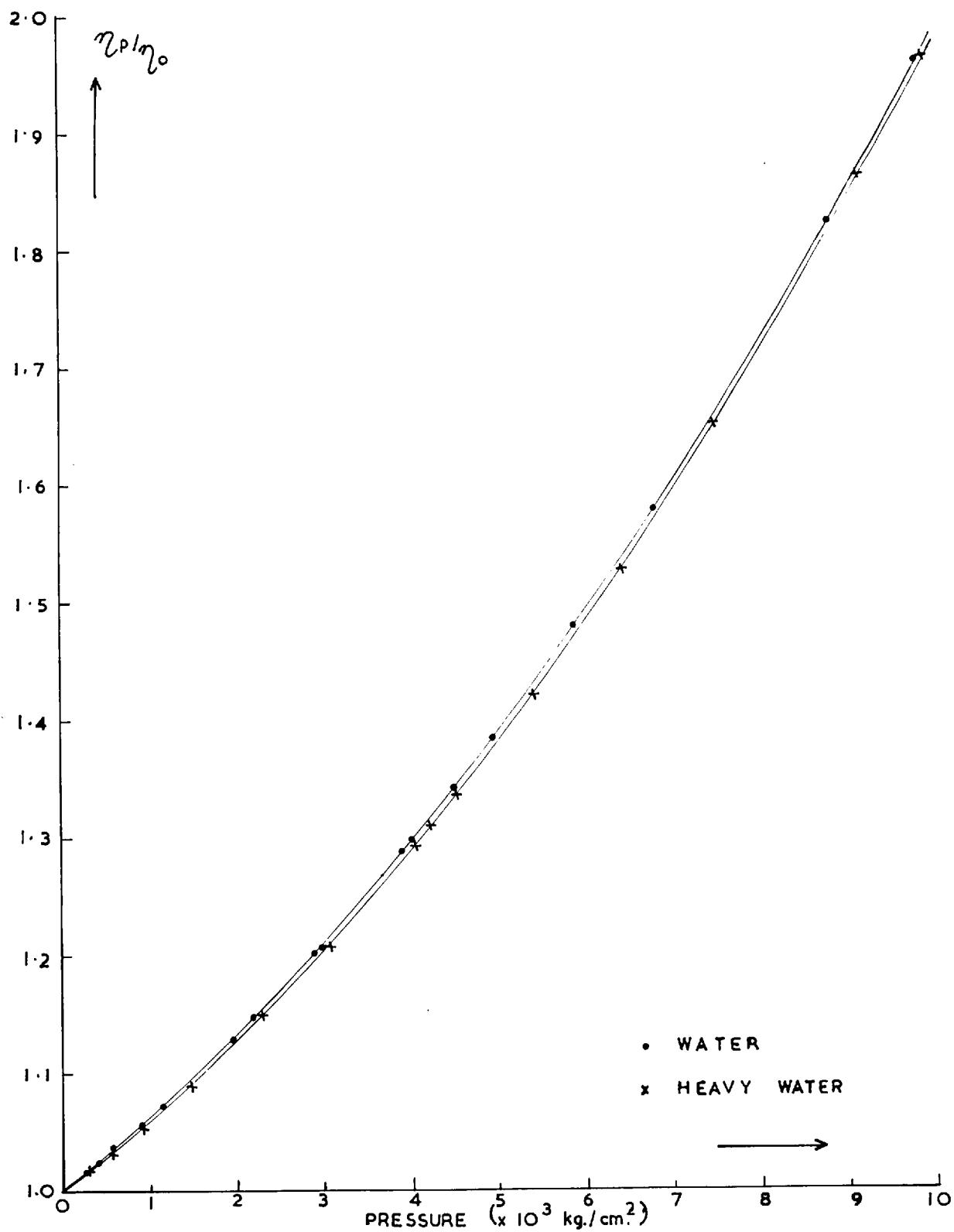
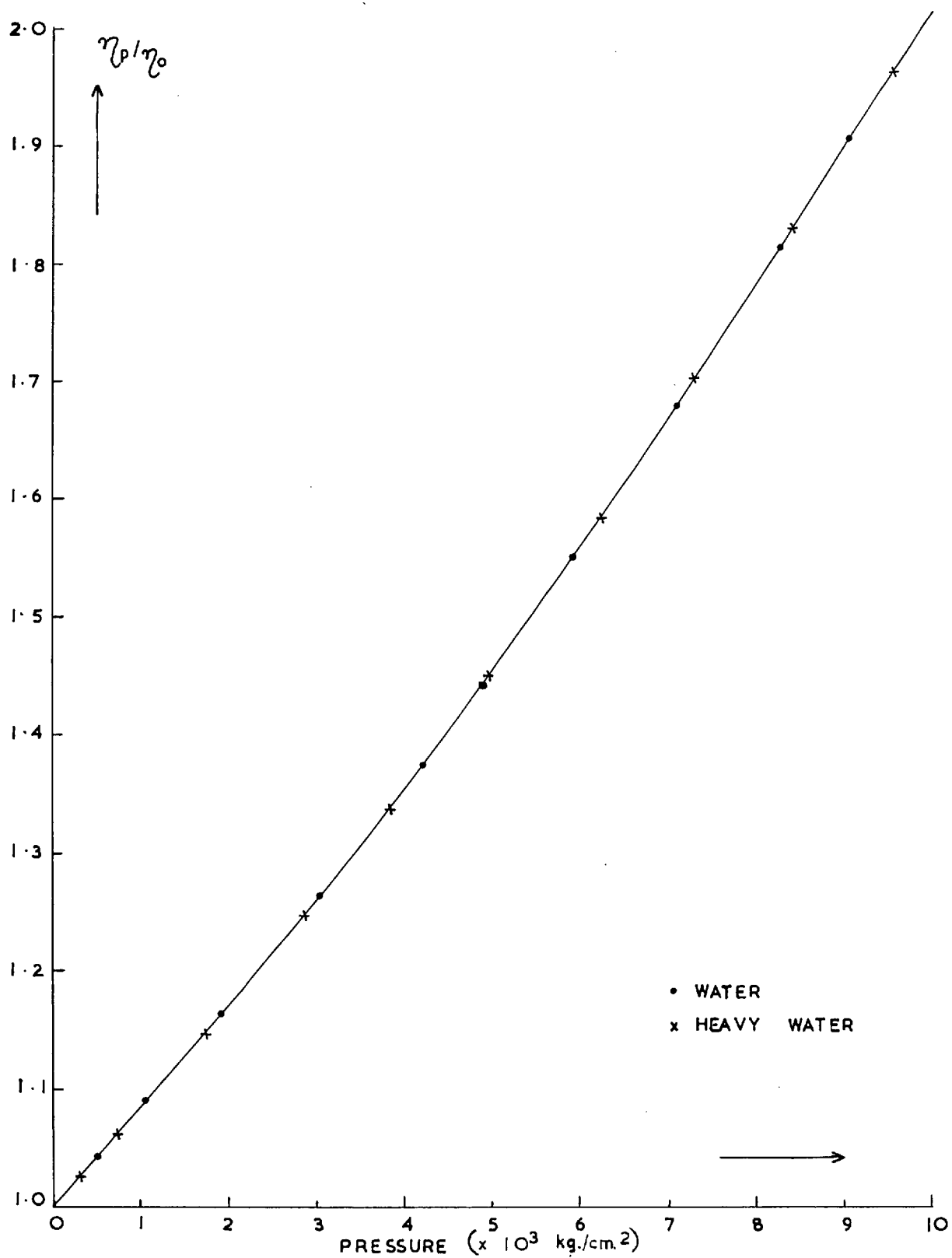


FIG. 8-8. Viscosity of Water & Heavy Water — 100°C.



Values of η_p have been calculated from the measured relative viscosities and the atmospheric pressure viscosity data of Bingham and Jackson⁽¹⁰⁾, and Hardy and Cottingham⁽⁵¹⁾. In Figure (8-9) η_p for heavy water is shown as a function of pressure for each of the temperatures studied. The experimental data have been fitted with a polynomial 'least squares' computer program and smoothed values of η_p/η_o regenerated at fixed pressures. Isobars of $\text{Log } \eta_p$ for D_2O are shown as a continuous function of temperature in Figure (8-10).

It may be seen from Figures (8-2) to (8-5) that at low temperatures both water and heavy water exhibit an initial decrease in viscosity. This initial reduction in viscosity on the application of pressure becomes smaller with rising temperature and eventually disappears. The value of η_p/η_o at the minimum is shown as a function of temperature in Figure (8-11). The pressure at which the relative viscosity is a minimum and the pressure at which the relative viscosity regains its initial value of unity are plotted against temperature in Figures (8-12) and (8-13) respectively. The temperature at which the initial pressure-viscosity coefficient is zero is deduced from the intercepts of the curves in Figures(8-11),

FIG.8-9. Viscosity - Pressure Behaviour of Heavy Water.

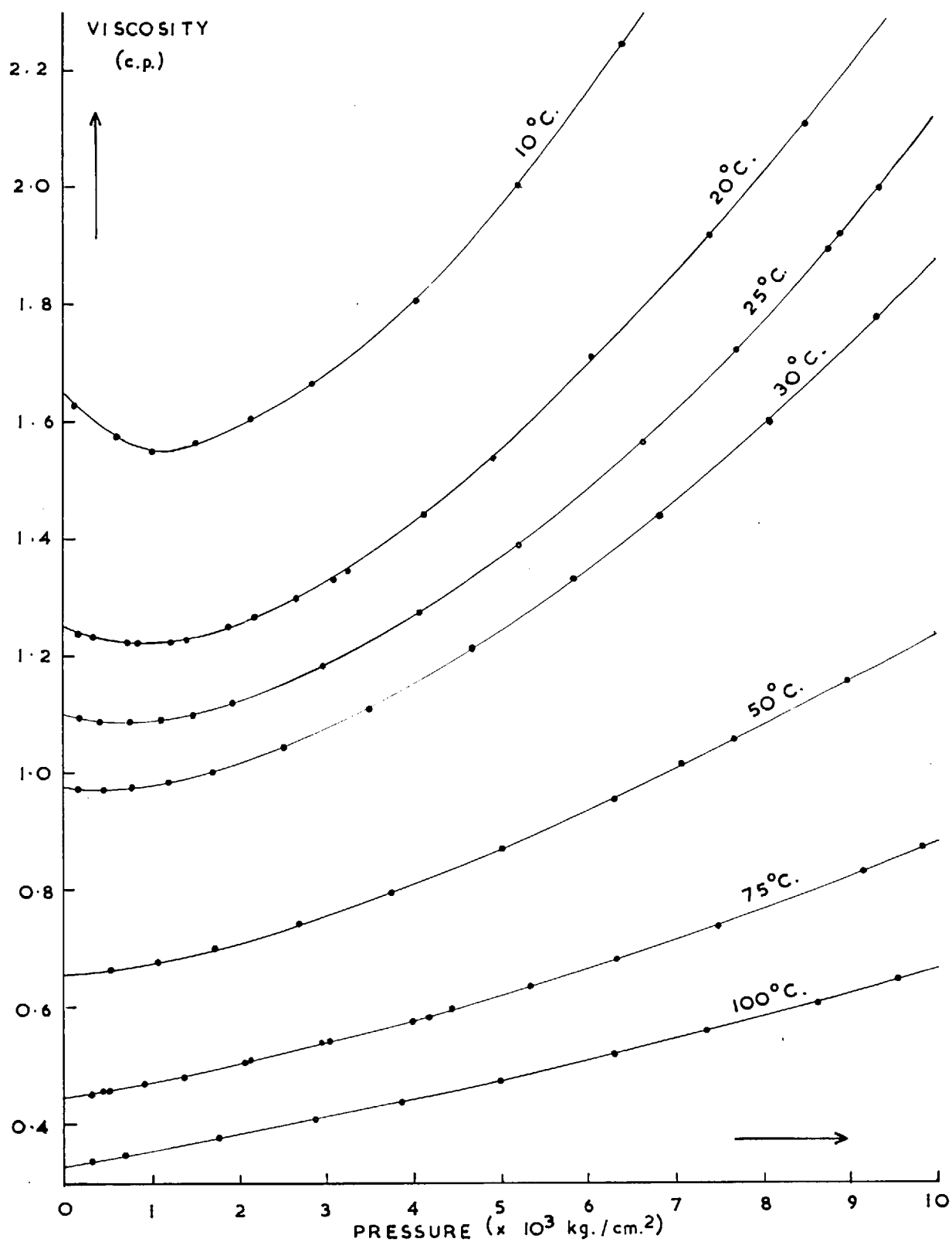
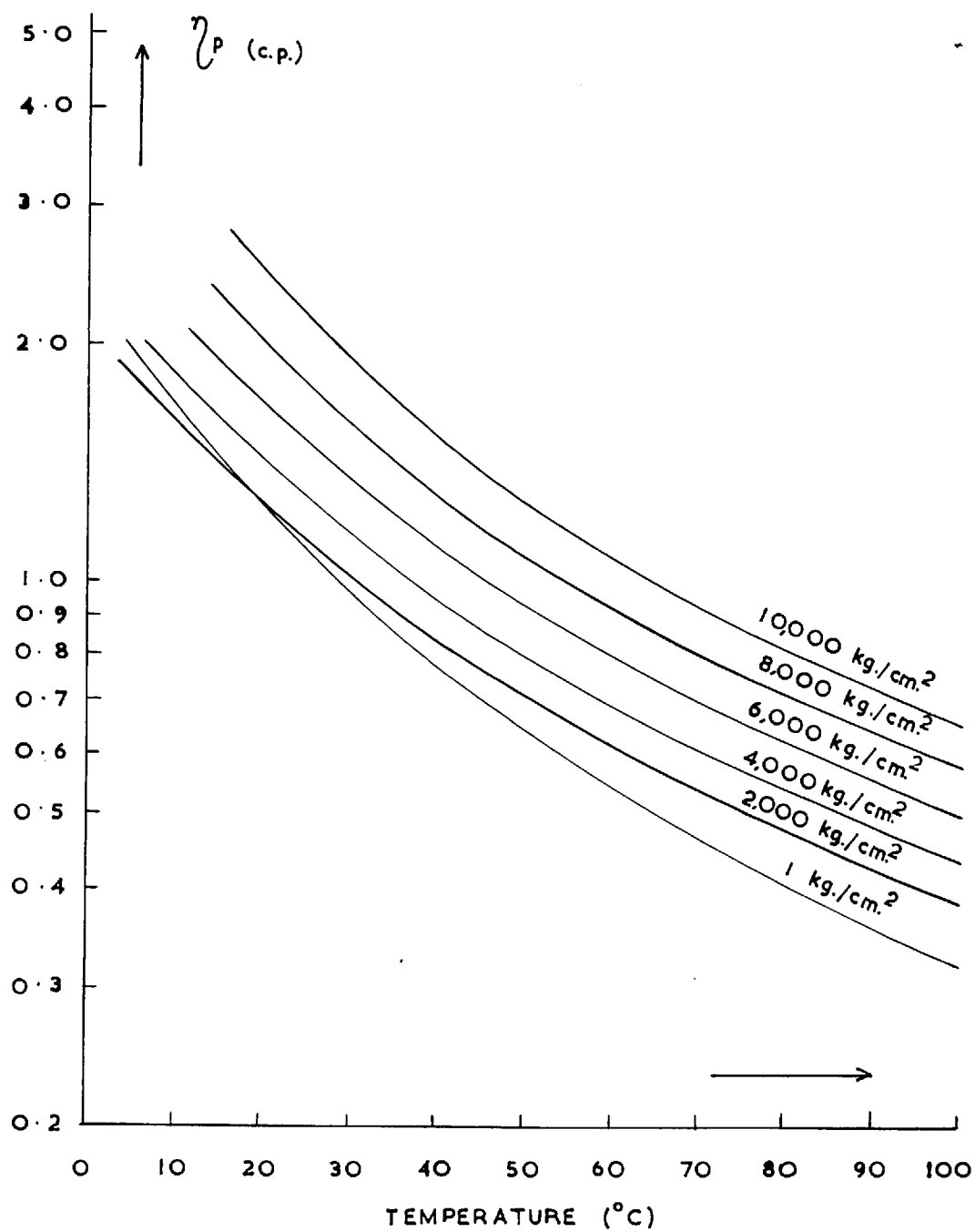
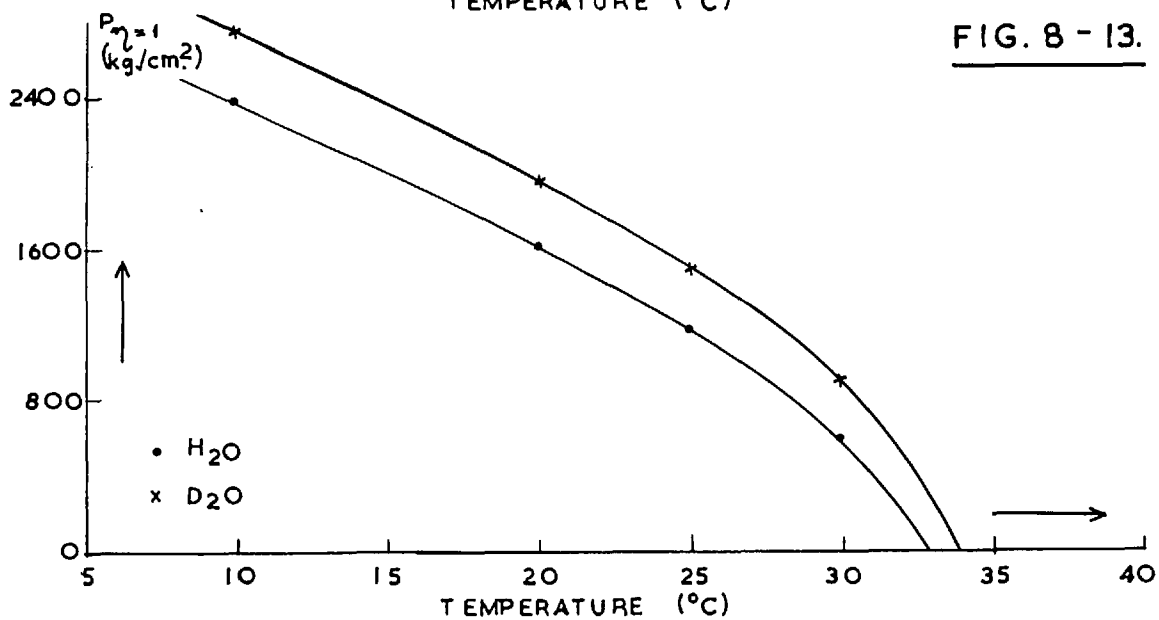
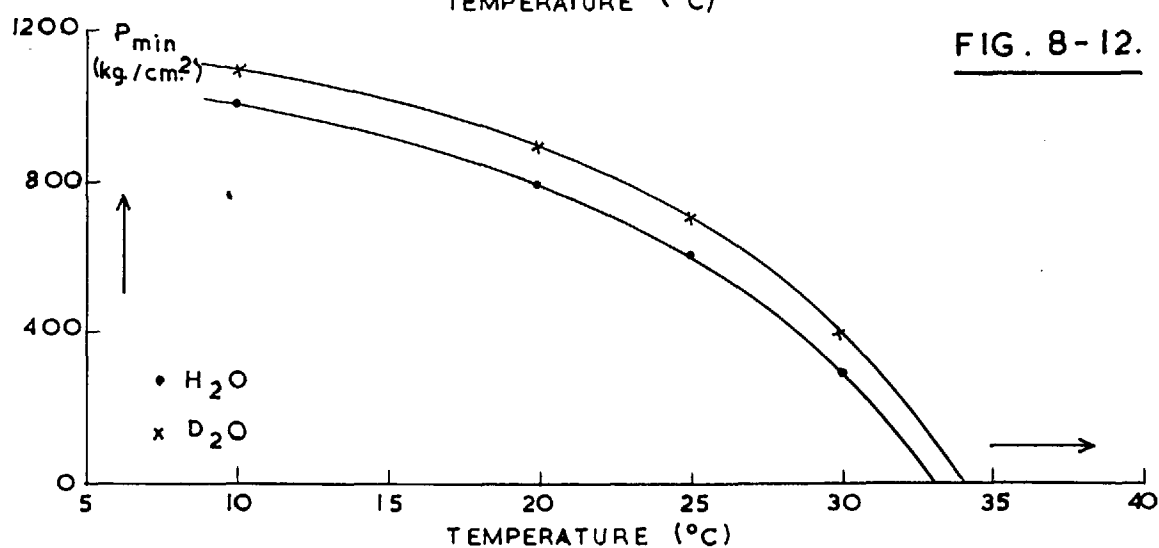
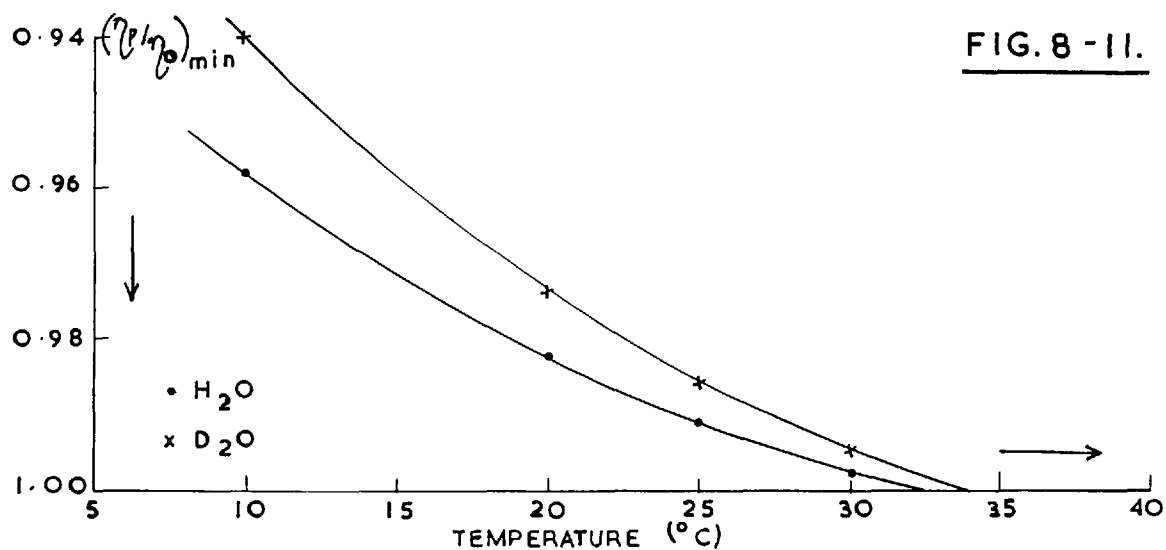


FIG.8 -10. Isobaric Viscosity Behaviour of
Heavy Water.



Viscosity Minima for Water & Heavy Water.



(8-12) and (8-13) to be $33.0 \pm 0.5^{\circ}\text{C}$ for H_2O and $34.0 \pm 0.5^{\circ}\text{C}$ for D_2O . The sources of error that arise in a viscosity measurement have been outlined, (Chapter V), and it is concluded that the maximum uncertainties with the Mk. I. viscometer are $+ 1.4\%$ and $- 1.0\%$ respectively. Since the maximum turbulence correction for the D_2O measurements is only 2.1% , the uncertainty in (η_p/η_o) arising from this correction is $\pm 0.5\%$. If the remaining errors are assumed to be unchanged, the overall accuracy of the D_2O results is $+ 1.1\%$
 $- 0.7\%$.

The experimental data for water and heavy water are tabulated in Appendix III.

8.3 Benzene.

The experimental results for benzene are shown graphically in Figures (8-14) and (8-15). To avoid freezing, the maximum pressure for each of the isotherms at 30°C , 50°C , 75°C was restricted to 900 kg/cm^2 , 1650 kg/cm^2 , and 2750 kg/cm^2 respectively.

The logarithmic variation of η_p/η_o with pressure is shown in Figure (8-14). The experimental results for all three temperatures

FIG. 8-14. Viscosity Behaviour of Benzene.

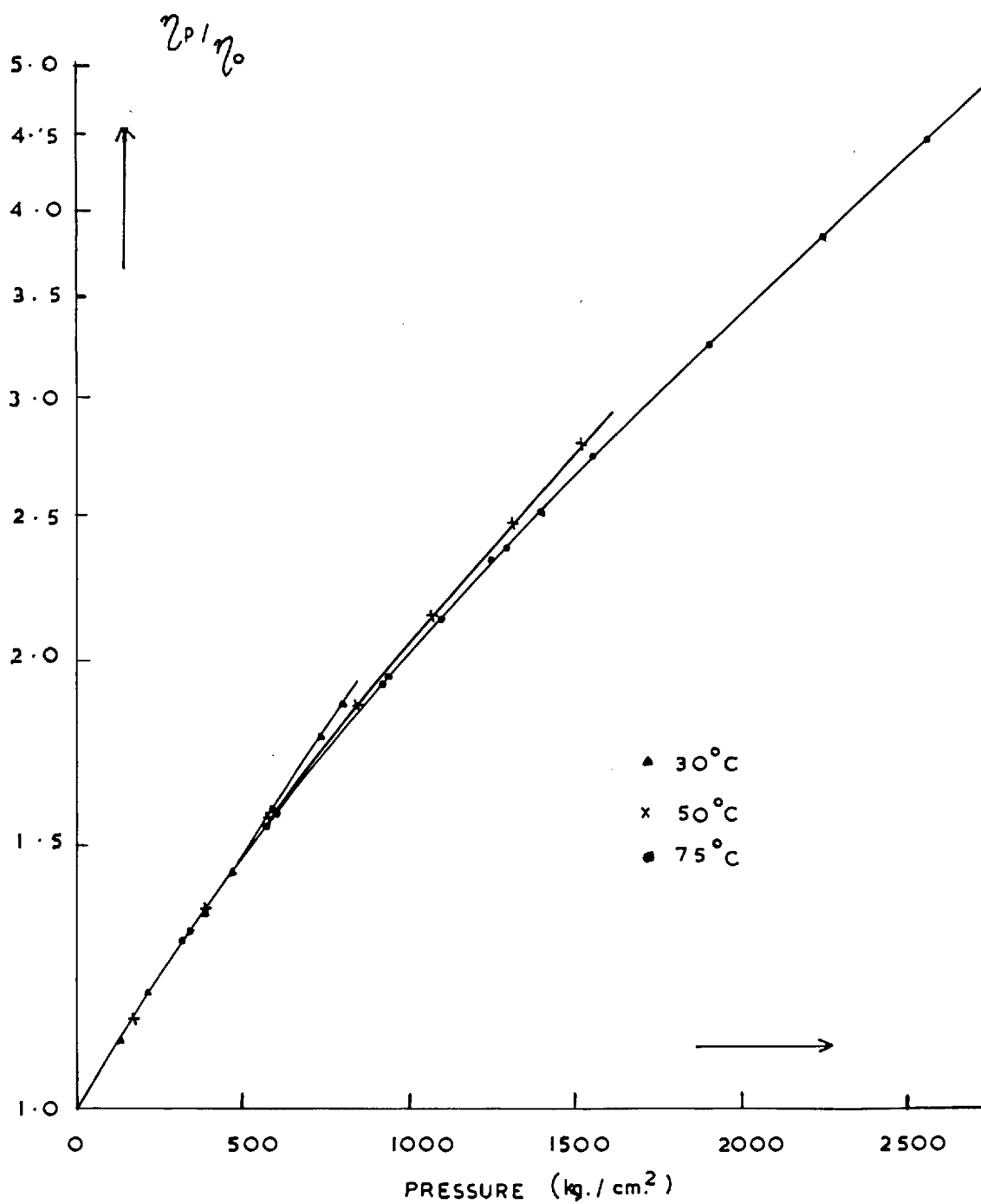


FIG. 8-15. Viscosity of Benzene under Pressure.

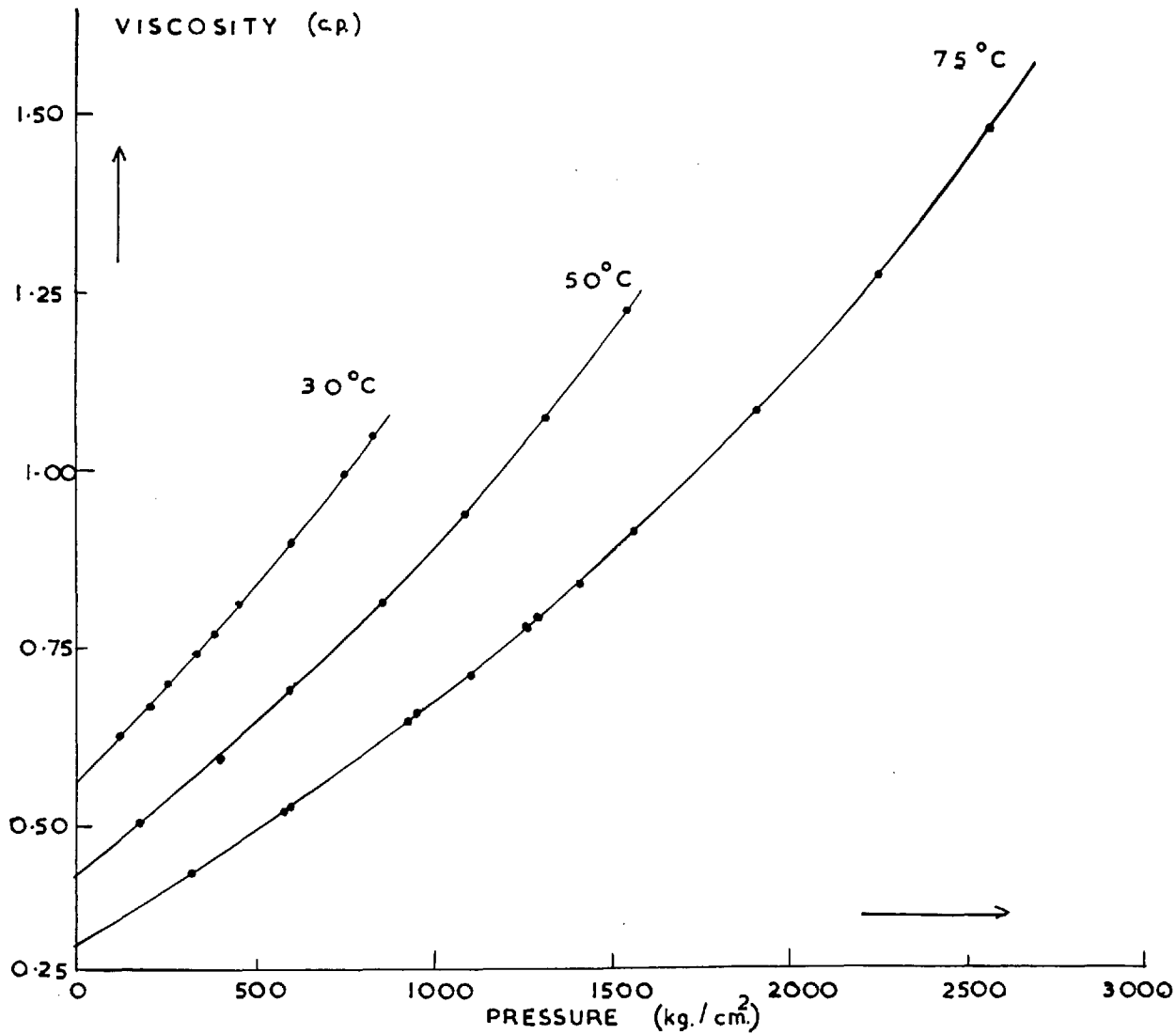
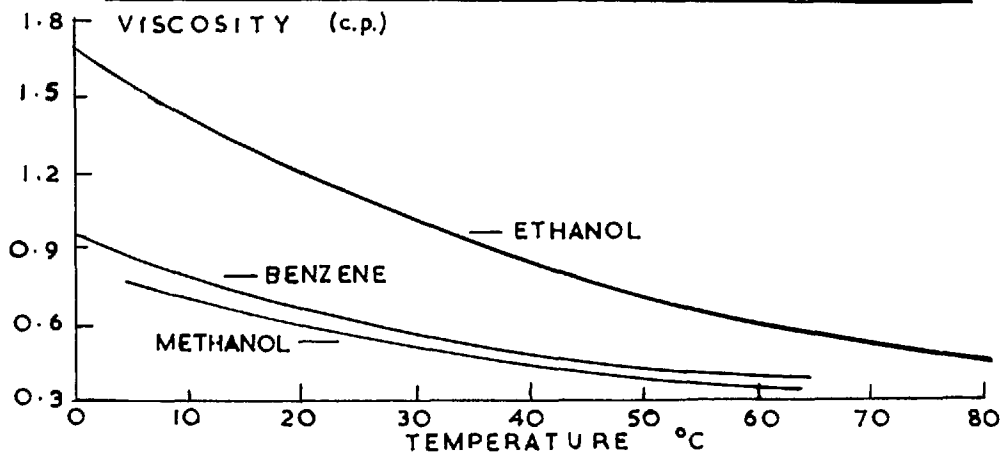


FIG. 8-16. Atmospheric Pressure Viscosities.



lie on a single smooth curve at all pressures up to 500 kg/cm². At higher pressures the relative viscosity increases slightly less rapidly with increasing temperature.

Figure (8-15) shows the variation of η_p as a function of pressure. This curve was plotted using the viscosity-temperature data for benzene at atmospheric pressure given in Figure (8-16)⁽⁶⁰⁾.

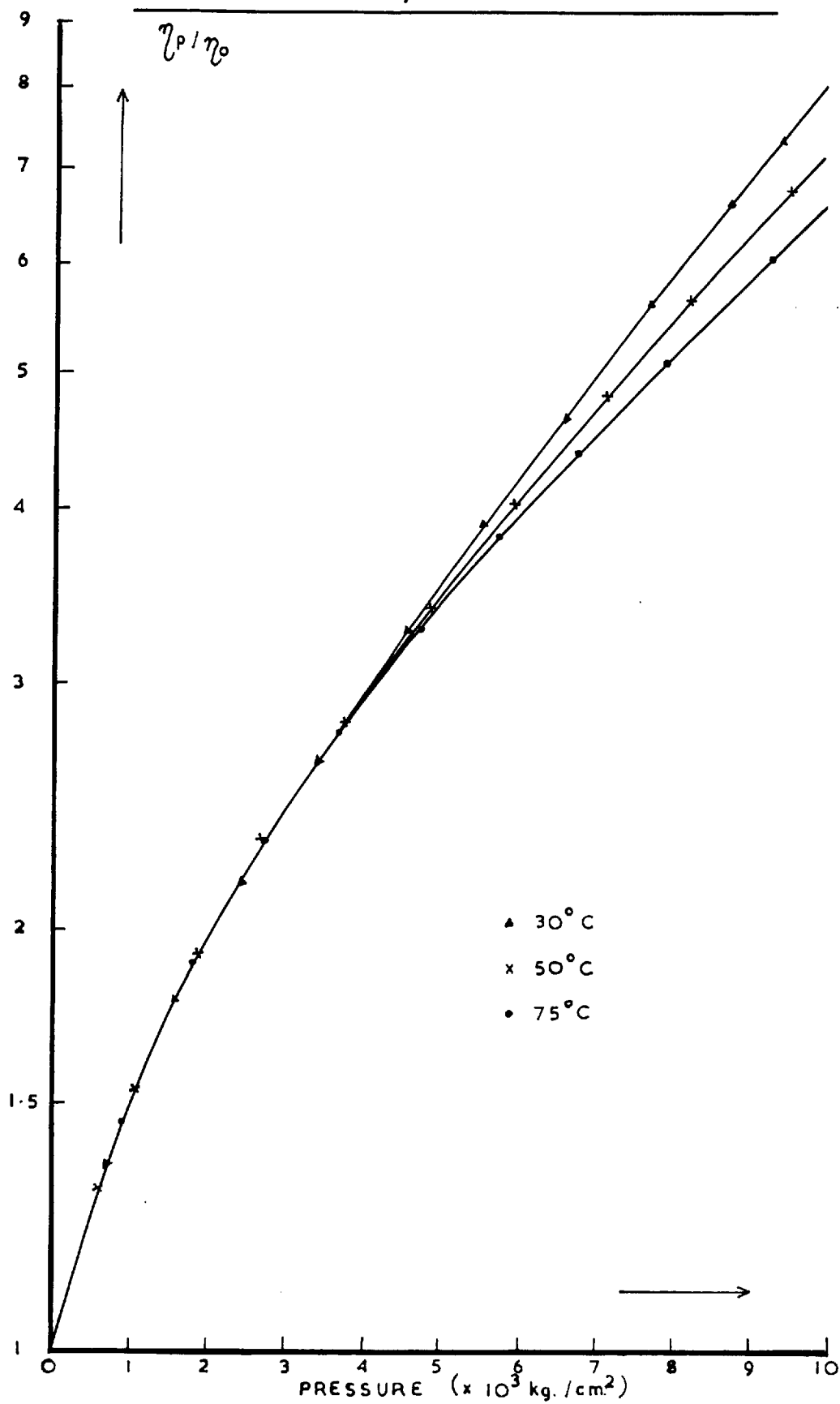
The accuracy of the experimental data is estimated to be $\pm 1\%$.

8.4 Methanol

The relative viscosity of methanol is found to exhibit a similar variation with pressure and temperature to that of benzene. The experimental results for methanol are shown as $\text{Log } \eta_p / \eta_o$ against p in Figure (8-17). The experimental points for 30°C, 50°C and 75°C lie on a single smooth curve from atmospheric pressure to 3,500 kg/cm². Above this pressure the curves diverge since the rate of viscosity increase is lower at the higher temperatures.

The absolute viscosity, η_p , was calculated from η_p / η_o by interpolation and extrapolation of the viscosity-temperature data for methanol at atmospheric pressure⁽⁶⁰⁾ given in Figure (8-16).

FIG.8-17. Viscosity Behaviour of Methanol. 192.



η_p is illustrated as a function of pressure in Figure (8-18).

The accuracy of the relative viscosity measurements for methanol is $\pm 1\%$.

8.5 Ethanol.

In Figures (8-19) and (8-20) the variation of $\text{Log } \eta_p / \eta_o$ and of η_p is shown as a function of pressure at 30°C , 50°C and 75°C . The values of η_p were calculated from the relative viscosities using values of η_o interpolated from Figure (8-16).

The variation of $\text{Log } \eta_p / \eta_o$ with pressure is of the same form as that exhibited by methanol, although as one would expect, η_p / η_o increases more rapidly for the more complex molecule. At low pressures η_p / η_o is not independent of temperature as found for methanol. It can be seen from Figure (8-19) that in the low pressure region η_p / η_o has a larger value for the 75°C isotherm than for the 30°C isotherm. The curves appear to cross at $3,500 \text{ kg/cm}^2$, and diverge with further increase in pressure.

The accuracy of the ethanol data is estimated to be $\pm 1\%$, with the exception of the three results at the highest pressures at 30°C , and one value at the highest pressure on the 50°C isotherm.

FIG. 8 - 18. Viscosity of Methanol under Pressure.

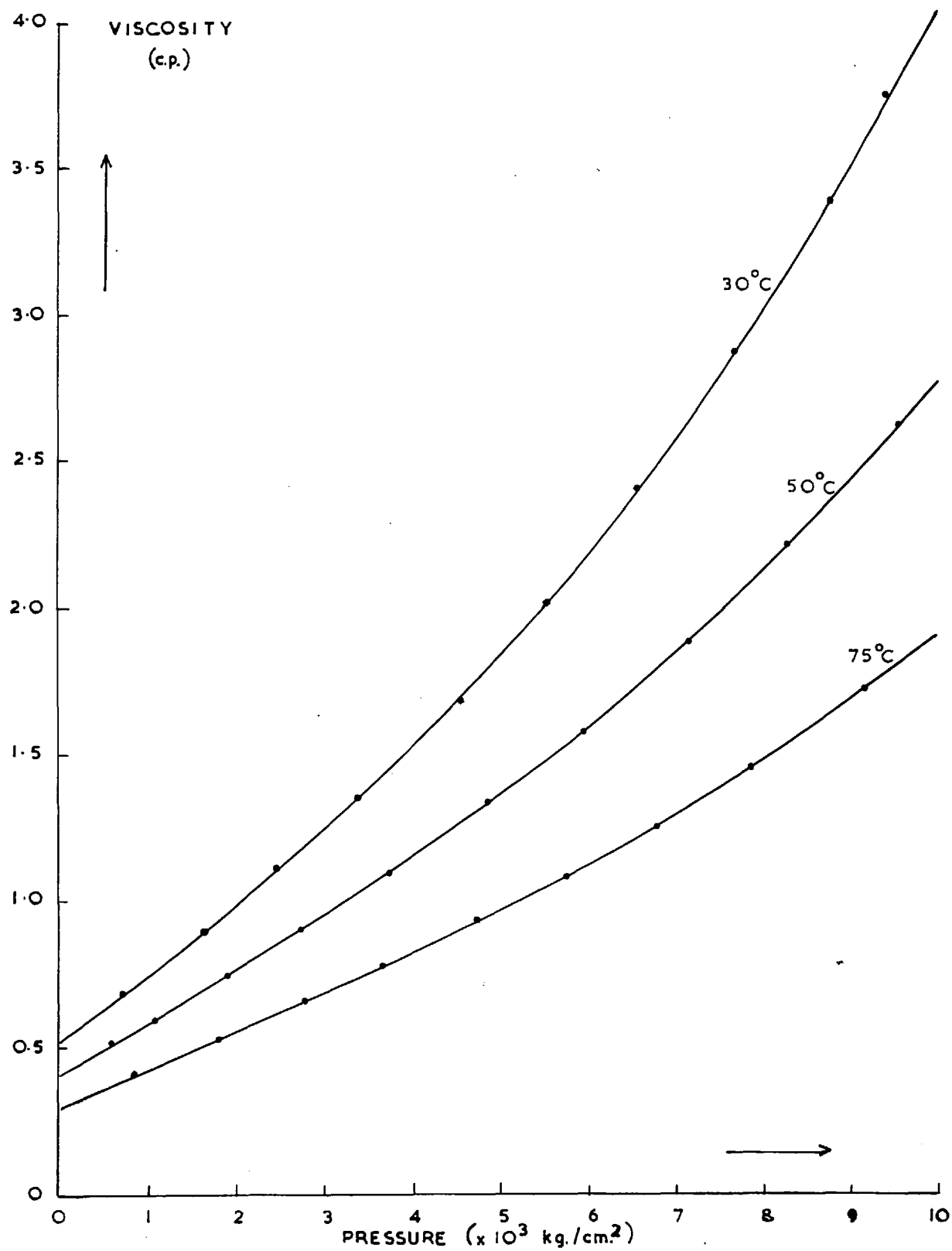


FIG. 8-19. Viscosity Behaviour of Ethanol.

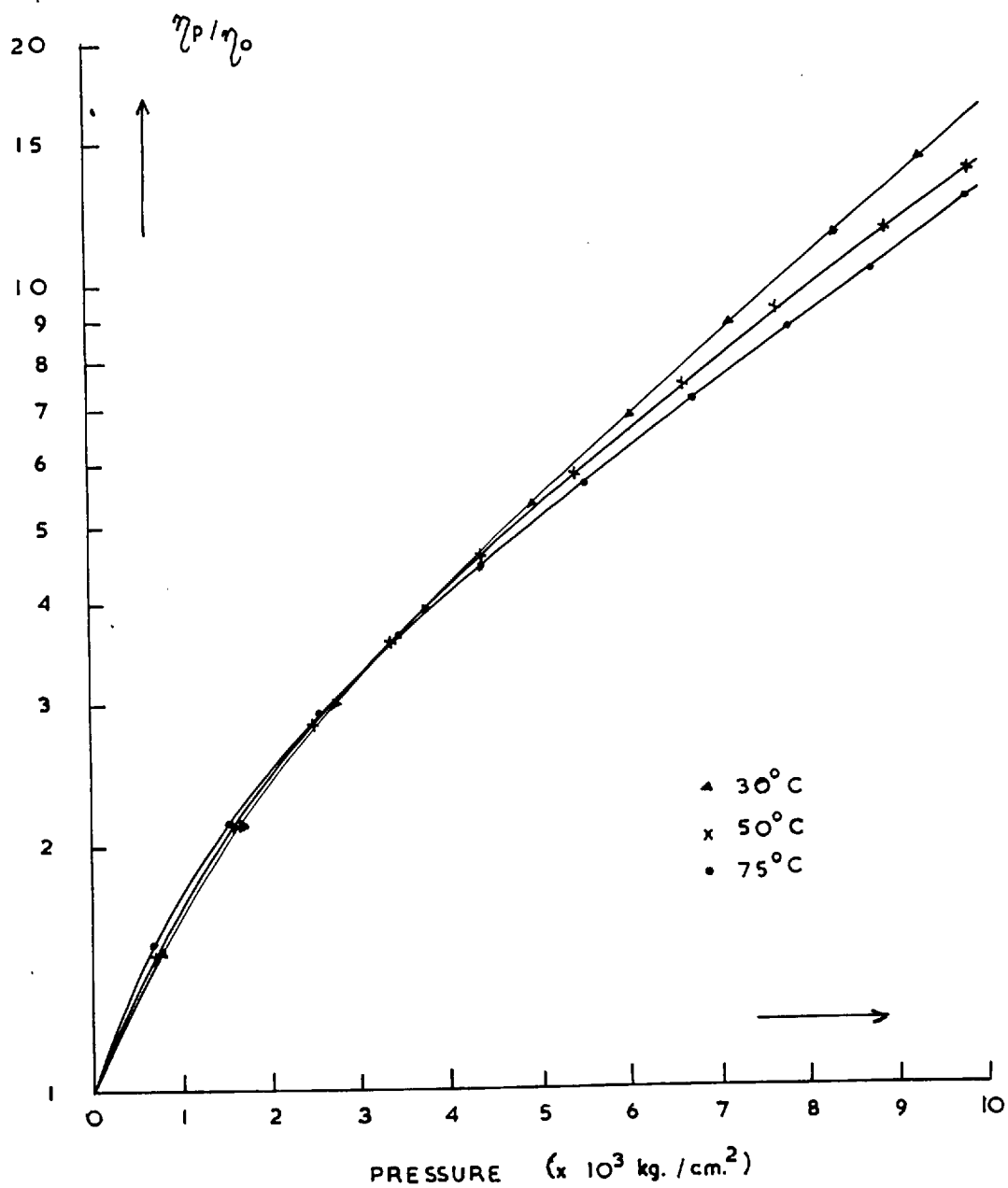
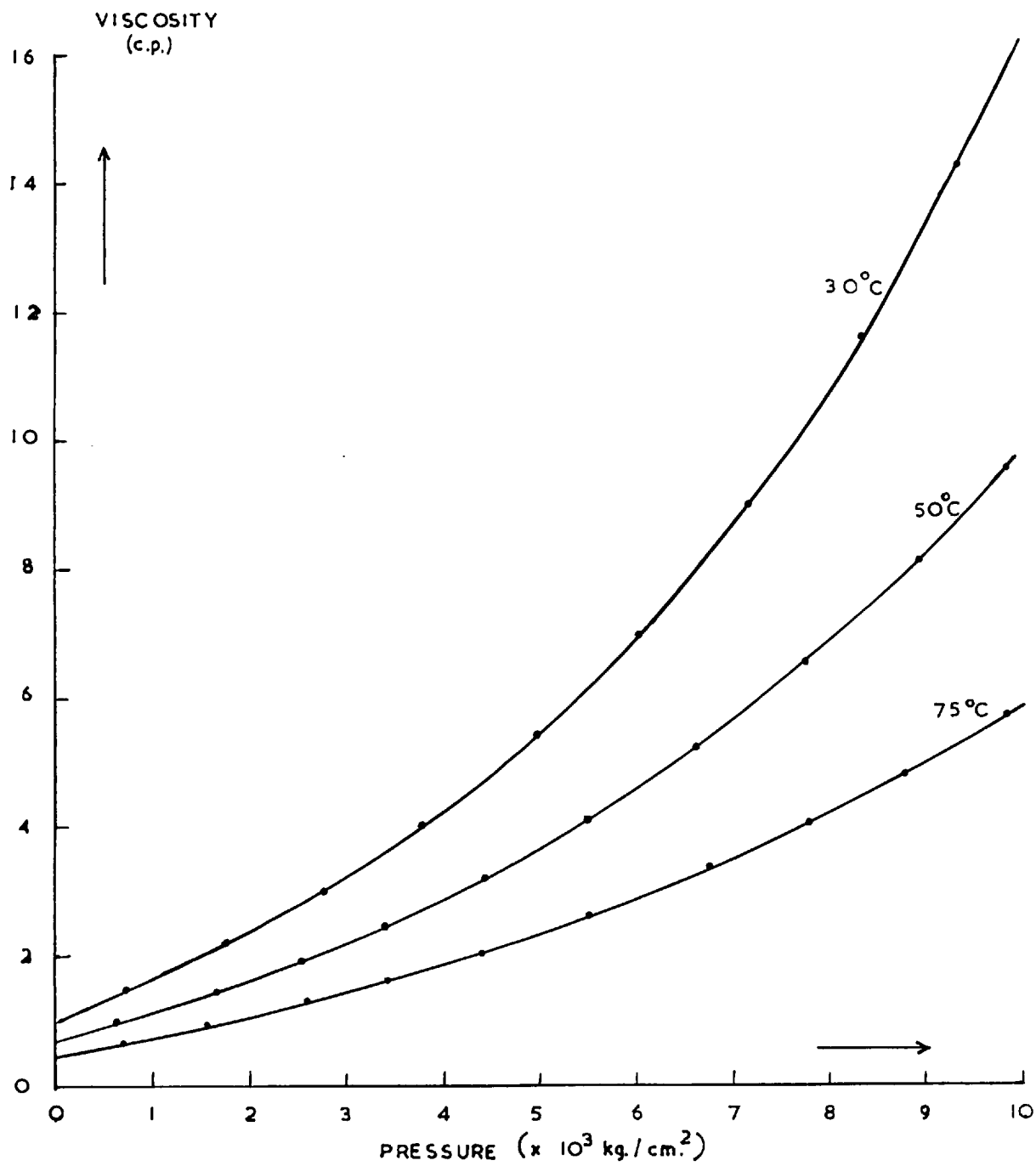


FIG. 8-20. Viscosity of Ethanol under Pressure.



The calibration curve was not checked at the fall times of these measurements and to take account of inconsistent or erratic sinker behaviour, the error in these particular results is estimated to be $\pm 3\%$.

8.6 Ethanol-Water Mixtures.

The concentrations of the ethanol-water mixtures were determined by measuring their relative densities at 25°C and interpolating the tabulated data⁽⁵⁰⁾ for this system. These are given in weight % Ethanol and mole % Ethanol in Table (8-1).

TABLE (8-1)

Mixture	Ethanol Weight %	Concentration Mole %
I	16.3 %	6.8 %
II A	41.3 %	20.9 %
II B	45.2 %	23.6 %
III	69.2 %	45.7 %
IV	86.1 %	69.7 %

From a consideration of the range of interpolation and the accuracy of the relative density measurements, it is estimated that the errors in the given concentrations are less than $\pm 0.15\%$ by weight for mixture I and less than $\pm 0.10\%$ by weight for the other mixtures.

Two concentrations are given for mixture II because it was necessary to fill the viscometer twice to complete these measurements. The isotherms at 30°C and 50°C were obtained for mixture II A , whereas the results at 75°C were obtained for mixture II B.

The experimental results for each of the mixtures are tabulated in Appendix III and are shown graphically in Figures (8-21), (8-22) and (8-23). The data is plotted in the form $\log \eta_p / \eta_o$ against pressure for the four mixtures at 30°C , 50°C and 75°C . Also included in these graphs are the results for water and pure ethanol at the same temperature.

The absolute viscosities at atmospheric pressure of the mixtures studied were determined at 30°C and 75°C using an Ostwald viscometer. The data are presented in Figure (8-24) together with those of Bingham et al⁽¹¹⁾. It proved to be difficult

FIG. 8-21. Viscosity of Ethanol-Water Mixtures at 30° C.

199.

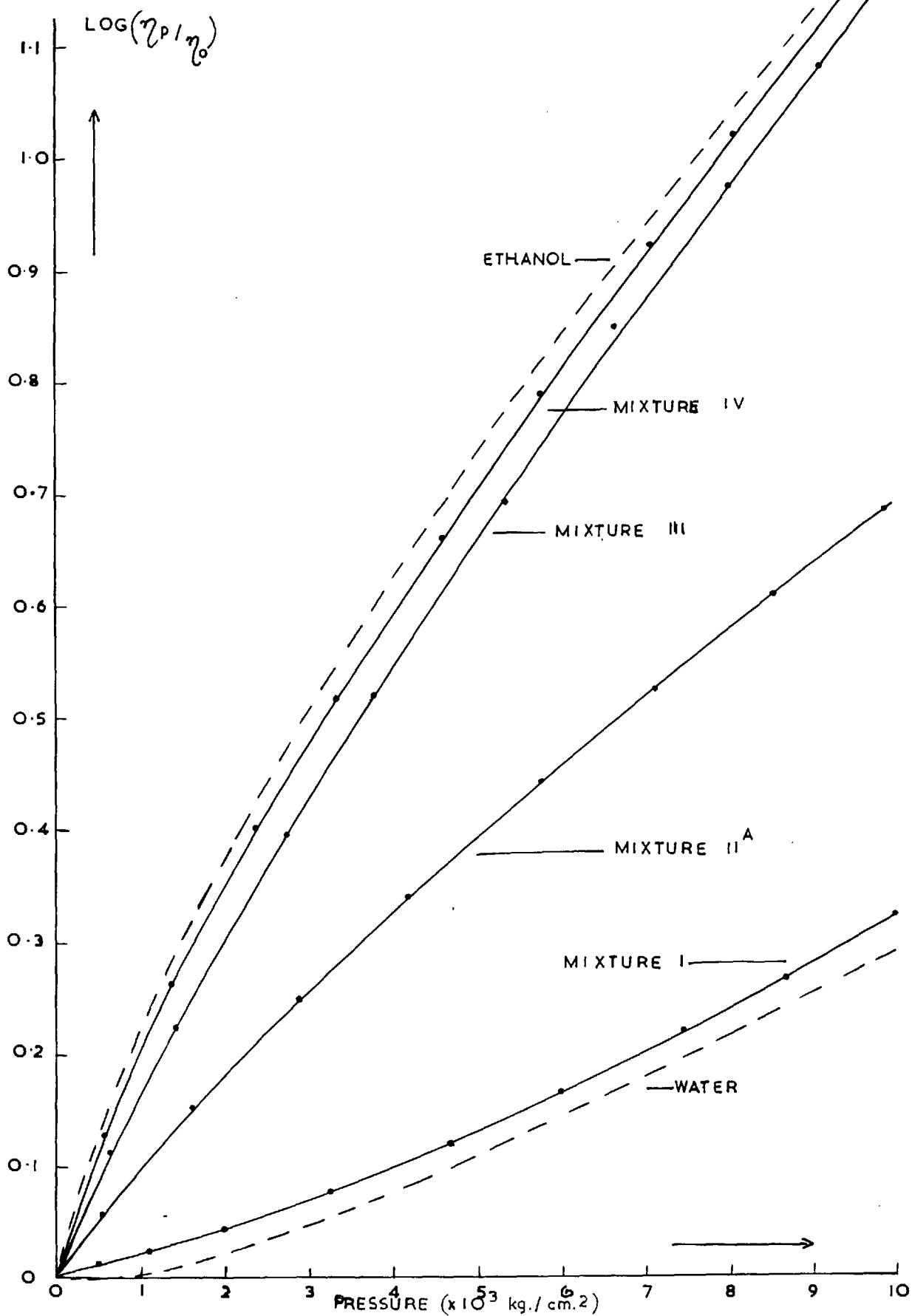


FIG.8-22. Viscosity of Ethanol-Water Mixtures at 50°C.^{200.}

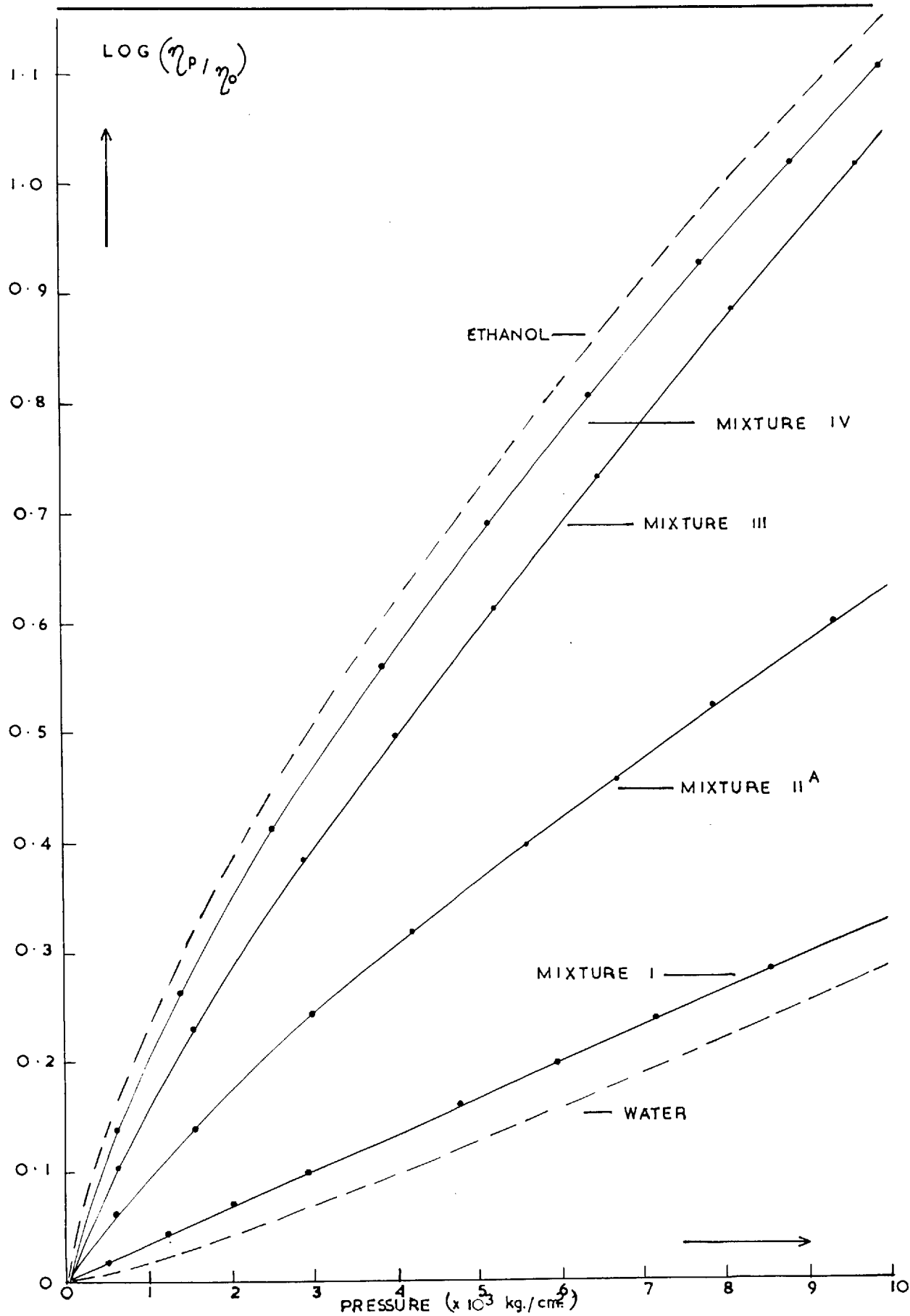


FIG. 8-23. Viscosity of Ethanol-Water Mixtures at 75°C.

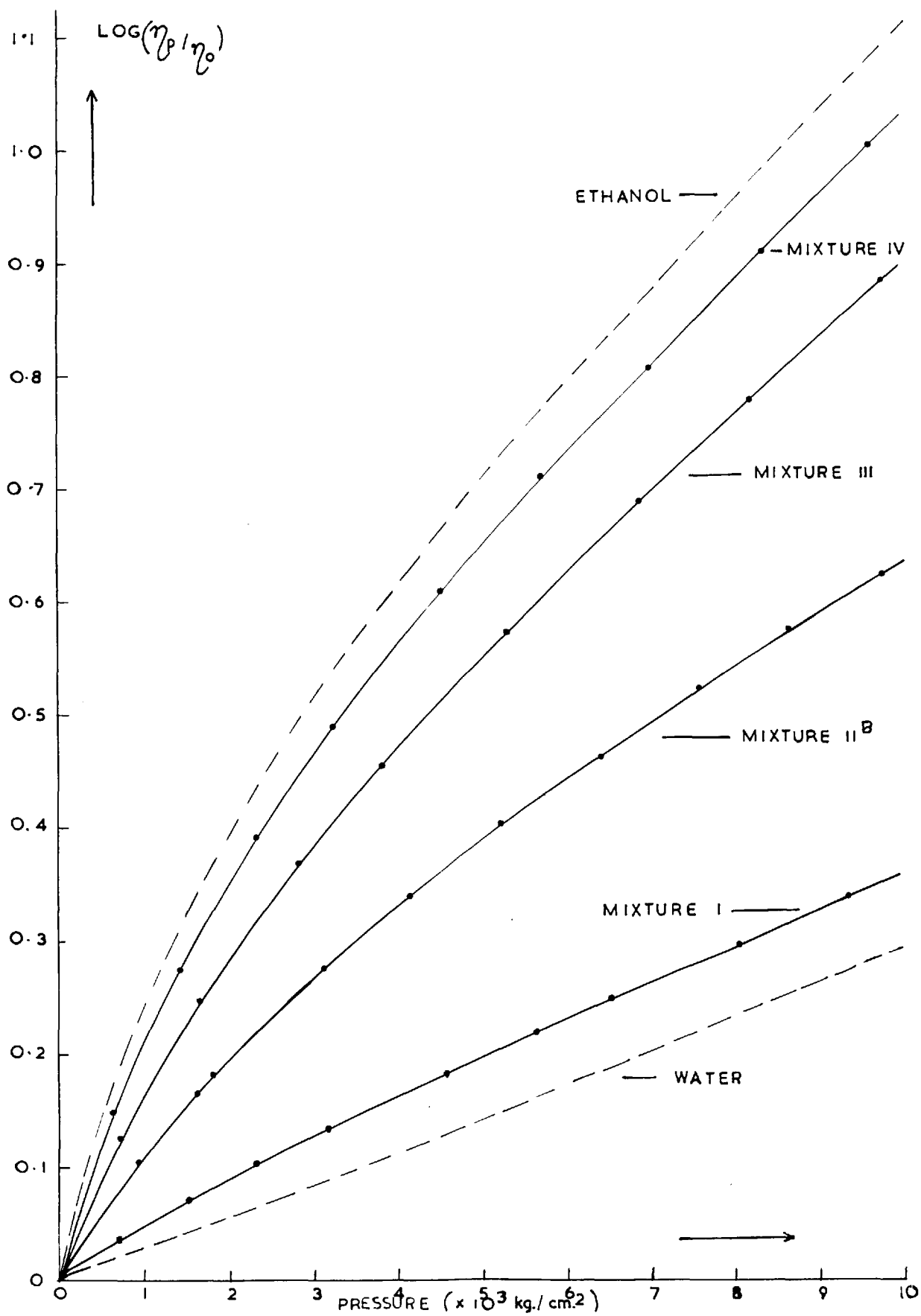
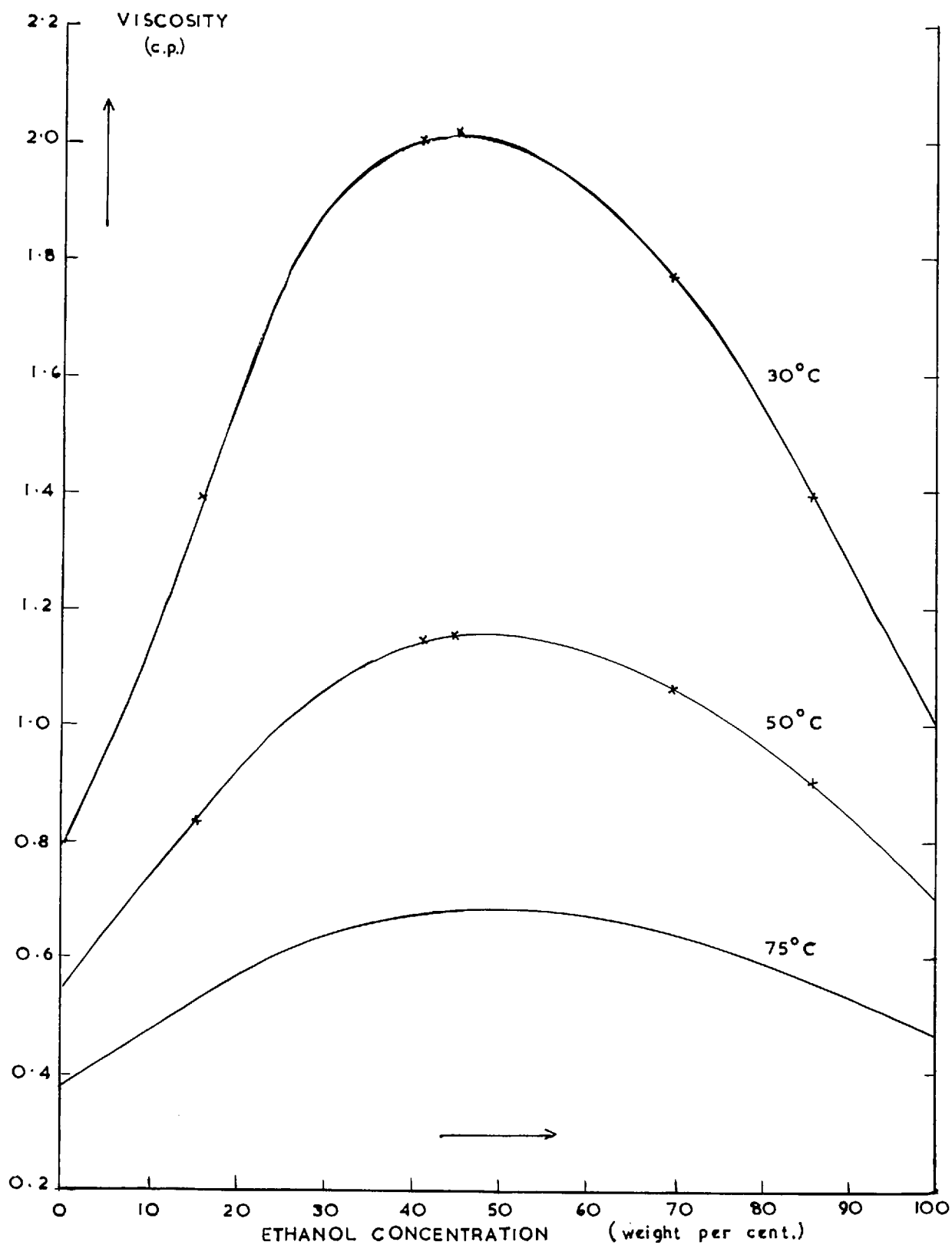


FIG.8 -24. Atmospheric Pressure Viscosities of Mixtures.



to measure the viscosities of the mixtures at 75°C using the Ostwald viscometer, and the viscosities at that temperature were estimated from the data in Figure(8-24). The viscosities at atmospheric pressure, η_o , of the mixtures are listed in Table (8-2).

TABLE (8-2)

Mixture	30°C	50°C	75°C
I	1.401 c. p.	0.838 c. p.	0.525 c. p.
II A	2.029 c. p.	1.143 c. p.	-
II B	-	-	0.676 c. p.
III	1.795 c. p.	1.073 c. p.	0.642 c. p.
IV	1.410 c. p.	0.903 c. p.	0.565 c. p.

Absolute viscosities were calculated at 1, 2,000, 4,000, 6,000, 8,000, and 10,000 kg/cm² for each of the experimental temperatures employing smoothed values of η_p/η_o and values of η_o from Table (8-2). The results are summarised in Figures (8-25), (8-26) and (8-27).

FIG. 8-25. Viscosity Isobars for the Ethanol-Water System

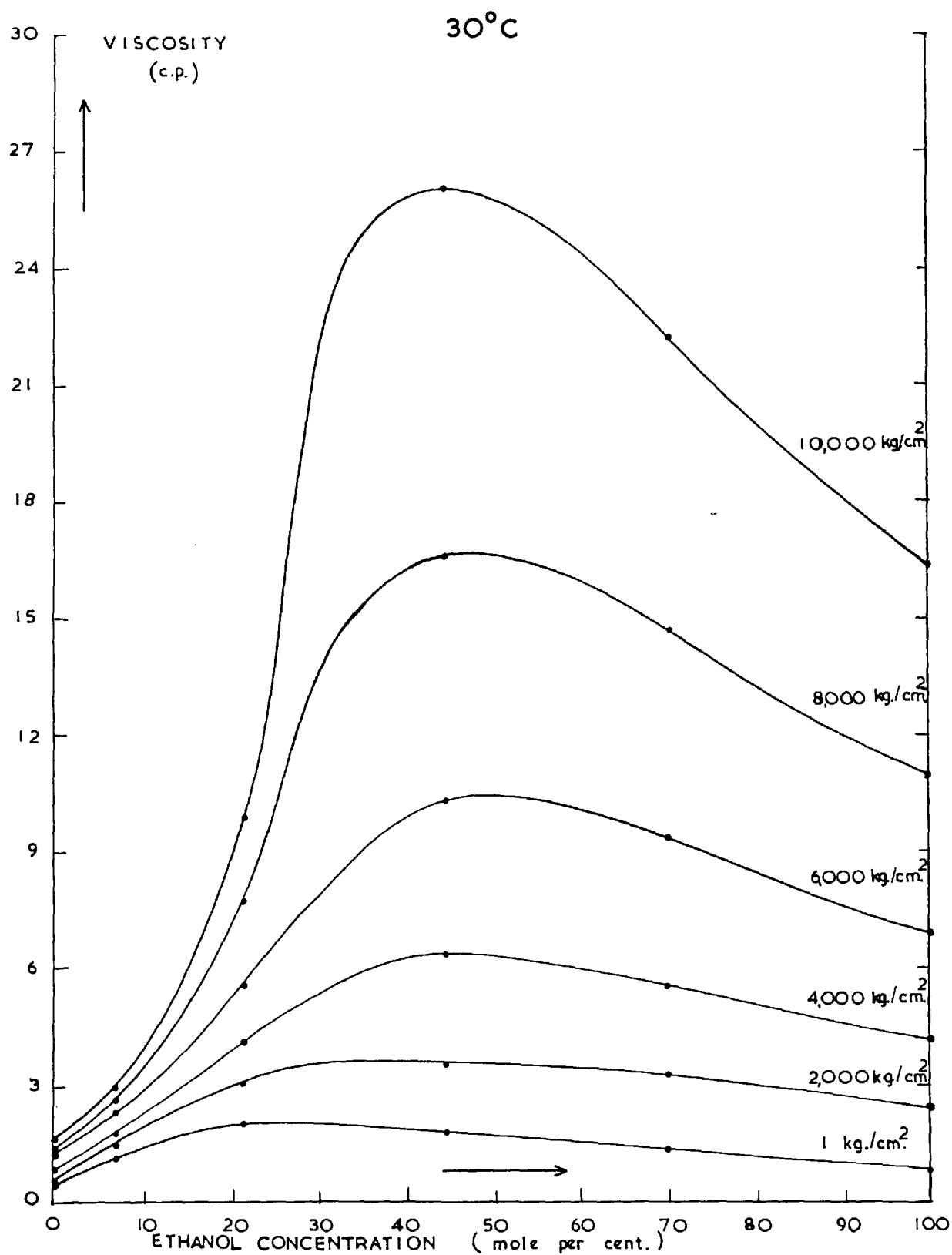


FIG. 8-26. Viscosity Isobars for the Ethanol-Water System

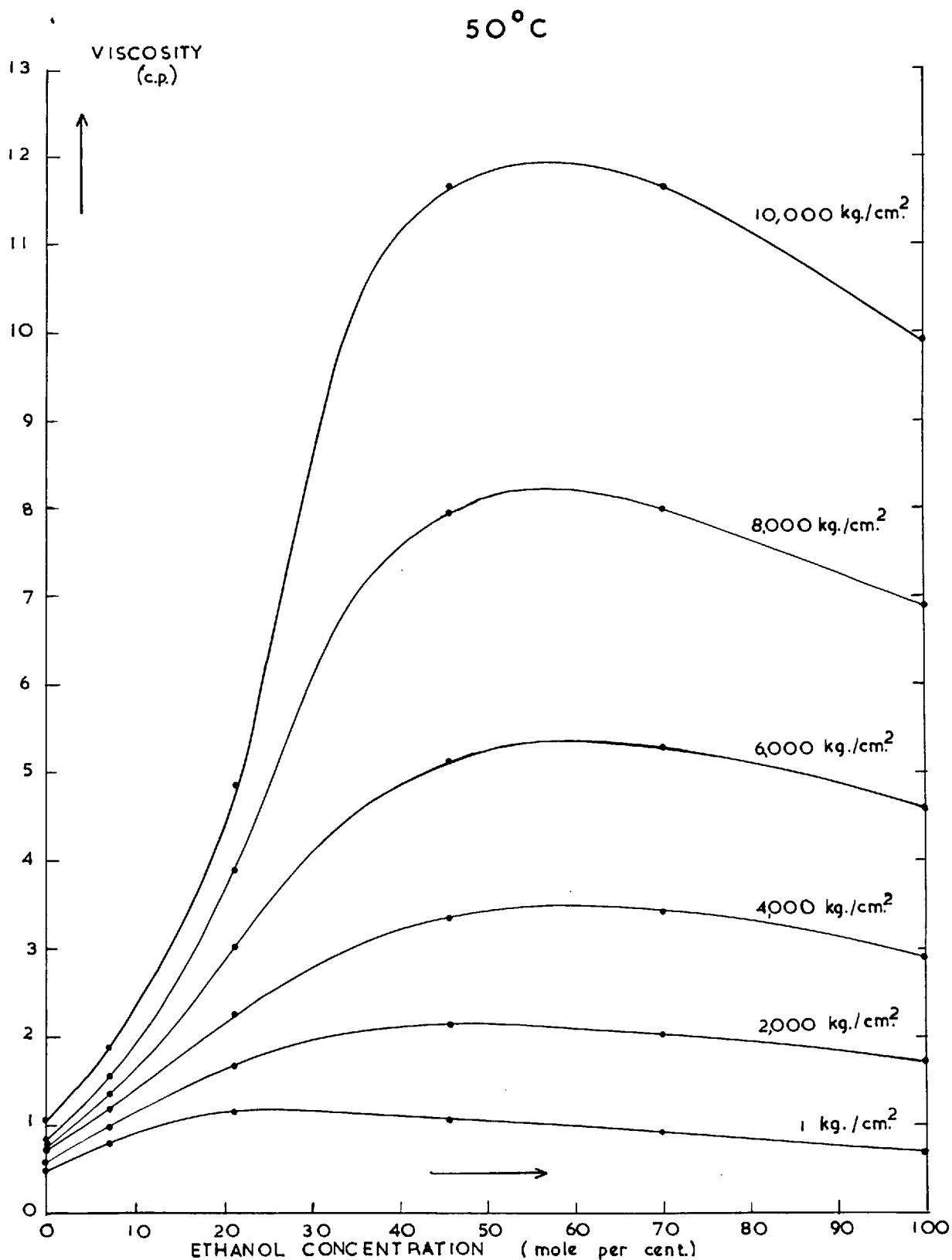
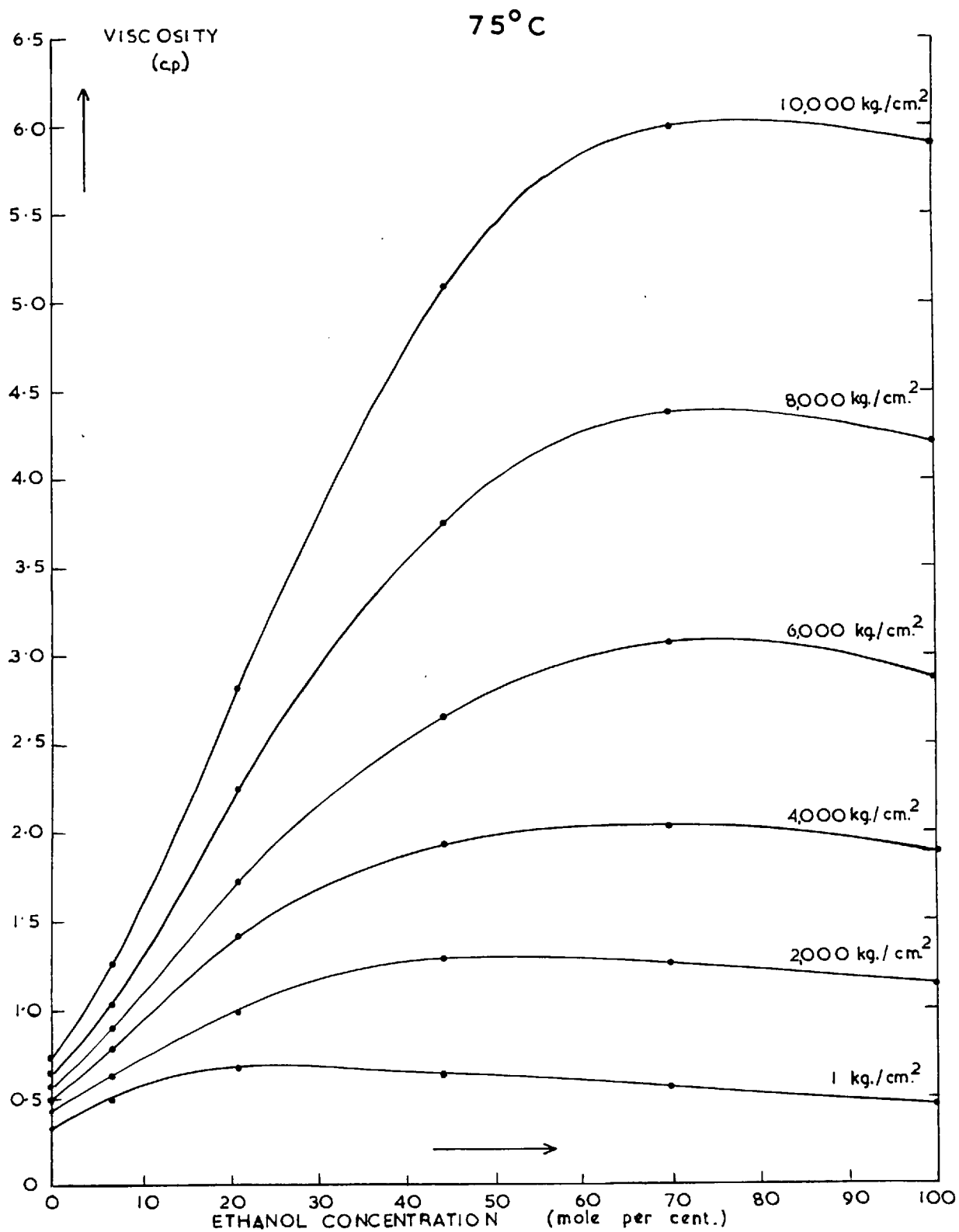


FIG.8-27. Viscosity Isobars for the Ethanol-Water System



CHAPTER IX.

DISCUSSION

9.1 Comparison of Results.

(a) Water.

The viscosity of water has been measured extensively at high pressures within the temperature range 0°C - 100°C . A list of some of the investigations, together with the range of temperature and pressure covered and the type of viscometer employed, are given in Table (9-1).

A detailed comparison of the viscosity results for water obtained with the Mk. I. viscometer and the work quoted in Table (9-1) has been given by Cappi⁽²⁵⁾. The measurements of Roentgen⁽⁹²⁾, and Warburg and Sachs⁽¹⁰⁸⁾ are of historical interest only, but the other low pressure determinations of Cohen⁽²⁹⁾, Hauser⁽⁵³⁾, Moszynski⁽⁸⁰⁾ and Weber⁽¹¹⁰⁾ are in overall agreement with the results from the Mk. I. viscometer to better than $\pm 1\%$. The results obtained by Bridgman⁽¹⁸⁾, the only data to cover the same range of pressures as this work, are in very poor agreement, the discrepancy being as large as 25% at 75°C and $10,000 \text{ kg/cm}^2$.

TABLE (9-1)

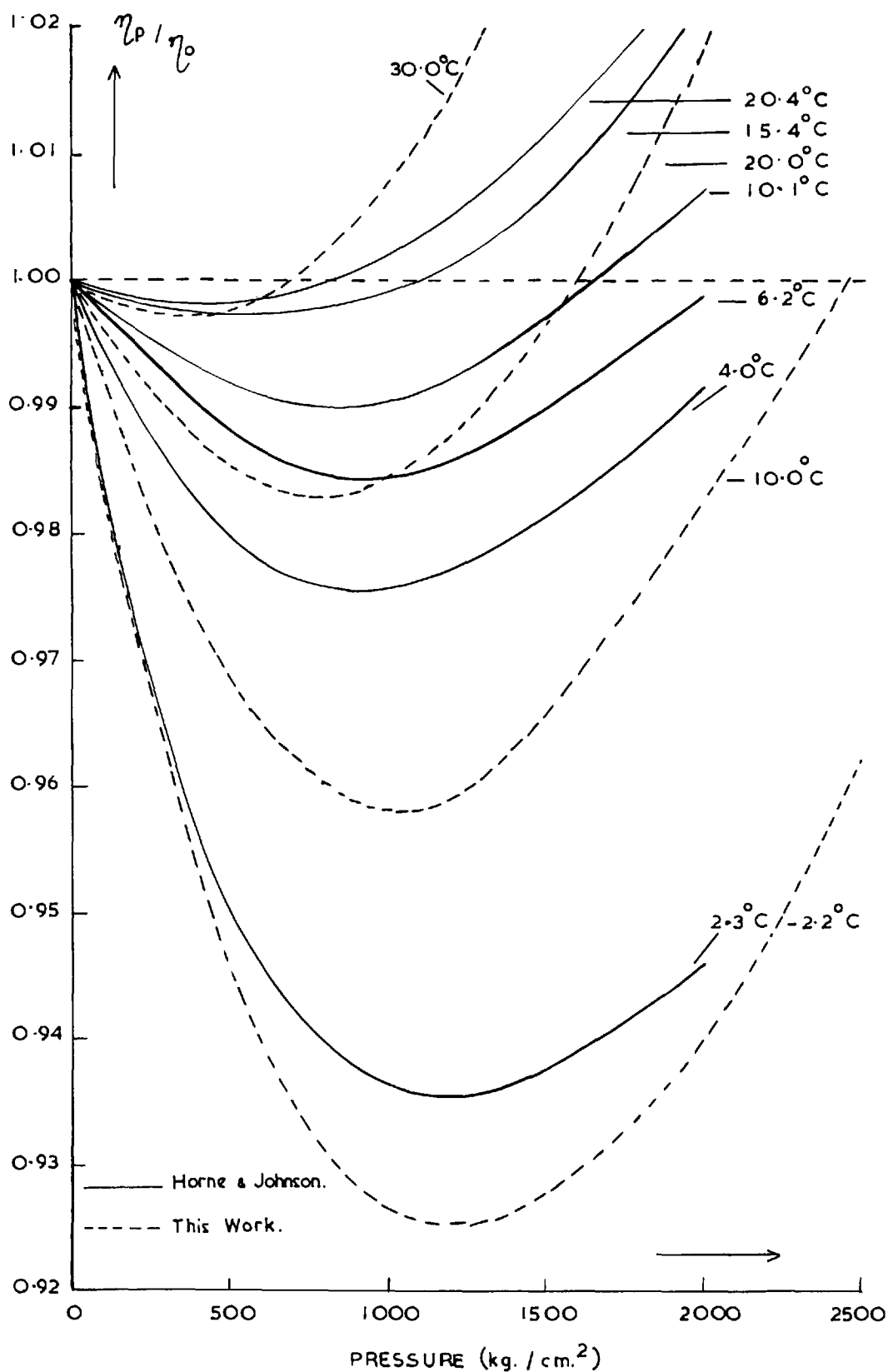
Author(s)	Year	Pressure Range	Temperature Range	Viscometer
Roentgen ⁽⁹²⁾	1884	1 - 20 kg/cm ²	5° - 11°C	Capillary
Warburg and Sachs ⁽¹⁰⁸⁾	1884	1 - 150 kg/cm ²	20°C	Capillary
Cohen ⁽²⁹⁾	1892	1 - 900 kg/cm ²	1° - 23°C	Capillary
Hauser ⁽⁵³⁾	1901	1 - 400 kg/cm ²	18° - 100°C	Capillary
Bridgman ⁽¹⁸⁾	1926	1 - 11,000 kg/cm ²	0° - 75°C	Falling Cylinder
Moszynski ⁽⁸⁰⁾	1961	1 - 340 kg/cm ²	20° - 186°C	Oscillating Sphere
Weber ⁽¹¹⁰⁾	1963	1 - 500 kg/cm ²	20° - 160°C	Rolling Ball

Additional data for the viscosity of water at high pressures and low temperatures have been obtained recently by Horne and Johnson⁽⁵⁵⁾. They employed a rolling ball viscometer and operated over a pressure range from 1 - 2,000 kg/cm² at temperatures in the range 2.3°C to 20.4°C. Their results are compared graphically

with the isotherms at 2.2°C, 10°C, 20°C, and 30°C obtained with the Mk. I. viscometer in Figure (9-1). Although both sets of curves exhibit a viscosity minimum which decreases with increasing temperature, the quantitative agreement is poor. Their values of relative viscosity are in general greater than those of the present work, with a maximum difference of approximately $3\frac{1}{2}\%$ at 10°C and 1,000 kg/cm². If their results are plotted isobarically against temperature, an abrupt change of slope is observed near 4°C. This change they attribute to a very rapid break-up of the clustered regions in water at temperatures below 4°C.

Horne and Johnson have not estimated the accuracy of their measurements, but in view of temperature fluctuations of $\pm 0.2^\circ\text{C}$ from the nominal temperature, and the large $\eta - T$ coefficient of water in this region, errors from temperature fluctuations alone may be appreciable. Although the dimensional changes of their instrument were small, no attempt was made to correct the roll time for these changes. Additional uncertainty about the accuracy of their results must arise from their prediction that the activation energy of viscous flow at 1,000 kg/cm² changes from 2.0 kcal/mole to 3.8 kcal/mole for a temperature change of 1.7°C between 2.3°C and 4.0°C.

FIG. 9-1. Viscosity of Water - Horne & Johnson.



(b) Heavy Water.

The only published results on the viscosity of heavy water as a function of pressure and temperature are those of Timrot and Shuiskaia⁽¹⁰¹⁾. These workers employed a capillary viscometer and measured the viscosity of pure D₂O between 20°C and 283°C in the pressure range 45 - 325 kg/cm² with an estimated accuracy of $\pm 2\%$. They concluded that to within this accuracy the relative viscosity of heavy water varies with pressure in the same way as the relative viscosity of water. A direct comparison of the results of Timrot and Shuiskaia⁽¹⁰¹⁾ with those of the present work is not possible, since their measurements were made at many temperatures and pressures within the specified ranges.

From the present work, (Figures (8-2) to (8-8)), it is observed that the difference between the relative viscosity of D₂O, and that of H₂O at the same temperature and pressure, is less than 2%, even for the low temperature isotherms where the differences are greatest.

The differences between η_p / η_o for water and heavy water are shown from Figures (8-2) to (8-8) to be very small and less than the estimated accuracy of the results, i.e. $\pm 1.4\%$ - 1.0% . However, in

view of the excellent consistency of the two series of results and the qualitative agreement with Timrot and Shuiskala, it is probable that the increasing similarity of viscosity behaviour of water and heavy water under pressure with rising temperature is real.

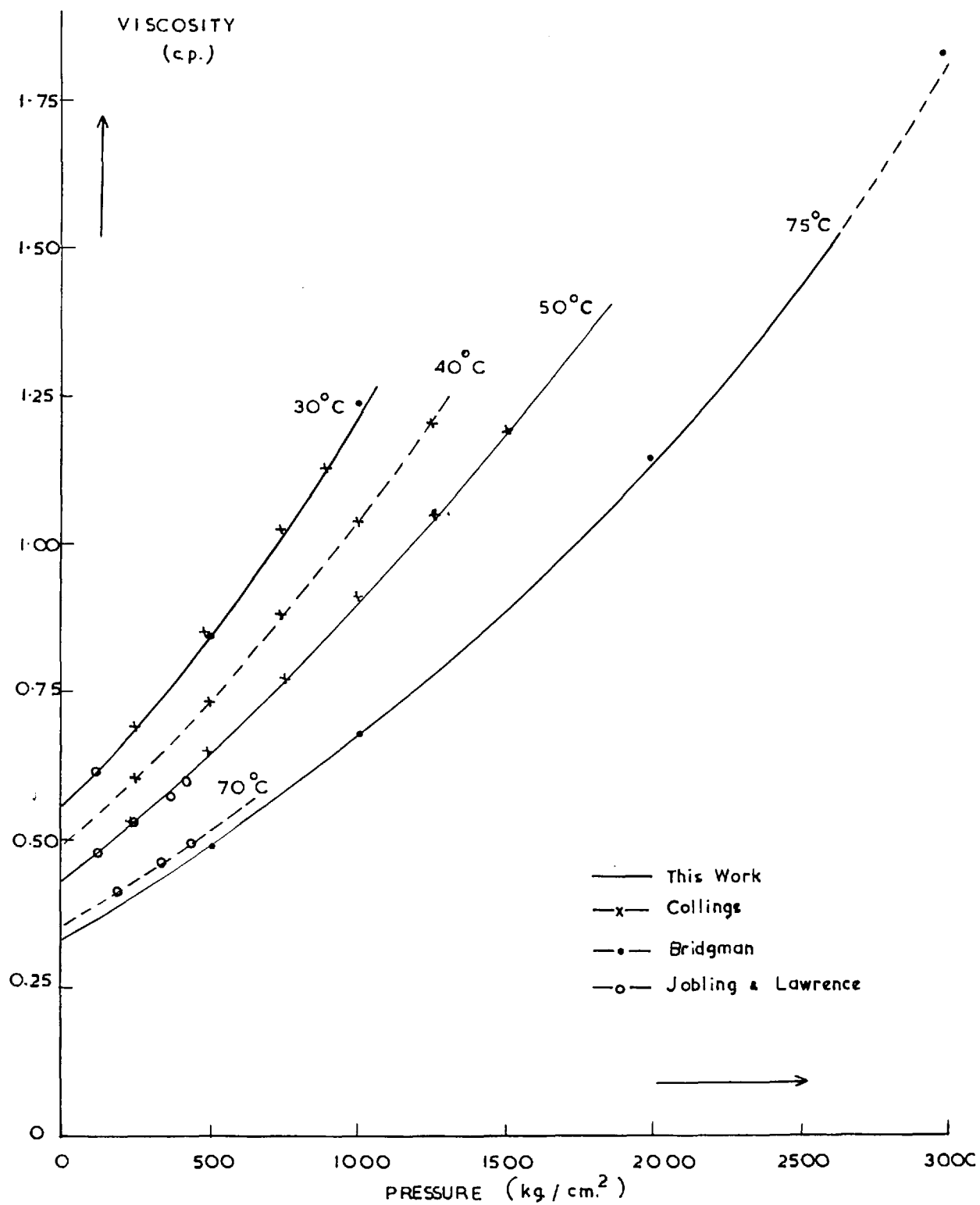
(c) Benzene.

A list of previous investigations into the pressure-viscosity behaviour of benzene is given in Table (9-2) and a comparison of the data of Bridgman, Jobling and Lawrence, and Collings is presented graphically in Figure (9-2).

TABLE (9-2)

Author(s)	Year	Temperature Range	Viscometer
Bridgman ⁽¹⁸⁾	1926	30° - 75°C	Falling Cylinder
Jobling and Lawrence ⁽⁵⁷⁾	1951	30° - 90°C	Falling Cylinder
Kuss ⁽⁶²⁾	1955	25° - 80°C	Falling Sphere
Collings ⁽³⁰⁾	1966	30° - 50°C	Oscillating Crystal

FIG. 9- 2. Comparison of Results for Benzene.



The results of Kuss have not been included in Figure (9-2) because they are of low accuracy and are in poor agreement with the other data.

The data of Bridgman⁽¹⁸⁾ at 30°C and 75°C are in excellent agreement with the results of the present work at low pressures, but the results differ by about 2% at high pressures.

The mean deviation from the smooth curves of the single result at 30°C and the four results at 50°C of Jobling and Lawrence⁽⁵⁷⁾ is 1%.

The isotherms of Collings⁽³⁰⁾ at 30°C and 50°C are straighter and tend to lie above the corresponding curves from this work. The maximum deviation at 30°C is 3% and occurs at a pressure of about 750 kg/cm², whereas at 50°C the maximum deviation is about 1.5% and occurs at 1,000 kg/cm².

The results for benzene at 30°C, 50°C and 75°C are self-consistent and in good agreement with published data.

(d) Methanol.

The most important data on the viscosity of methanol at high pressures are due to Bridgman⁽¹⁸⁾ (21). His results to 12,000 kg/cm² (18) were obtained at two temperatures, 30°C and 75°C, with a falling cylinder viscometer, and these are compared with the

curves from this work in Figure (9-3). Within the limits of experimental error the results are in agreement, although Bridgman's data are 2% lower. Bridgman has extended his viscosity measurements with methanol to $30,000 \text{ kg/cm}^2$ by employing a falling-vane viscometer⁽²¹⁾. These results are of lower accuracy, and were made at one temperature, 23.5°C , only.

(e) Ethanol.

The viscosity of ethanol has been measured up to pressures of $12,000 \text{ kg/cm}^2$ by Bridgman⁽¹⁸⁾, up to $10,000 \text{ kg/cm}^2$ by Zolotykh⁽¹¹⁵⁾ and up to $3,000 \text{ kg/cm}^2$ by Faust⁽³⁸⁾.

Faust's results were obtained at four temperatures, (0°C , 1.5°C , 30°C and 53.5°C), employing a capillary viscometer. His data are not included in the comparison of results given in Figure (9-4), because they are inconsistent and differ by as much as 20% from the other data.

Zolotykh⁽¹¹⁵⁾ has measured the viscosity of ethyl alcohol at 15°C , 20°C and 30°C at pressures up to $10,000 \text{ kg/cm}^2$, in connection with a study of the viscosity of pressure transmitting fluids. At 30°C , his results only extend over the upper part of the pressure range from $4,600 \text{ kg/cm}^2$ to $10,000 \text{ kg/cm}^2$. Although his data are

FIG. 9-3. Comparison of Results for Methanol.

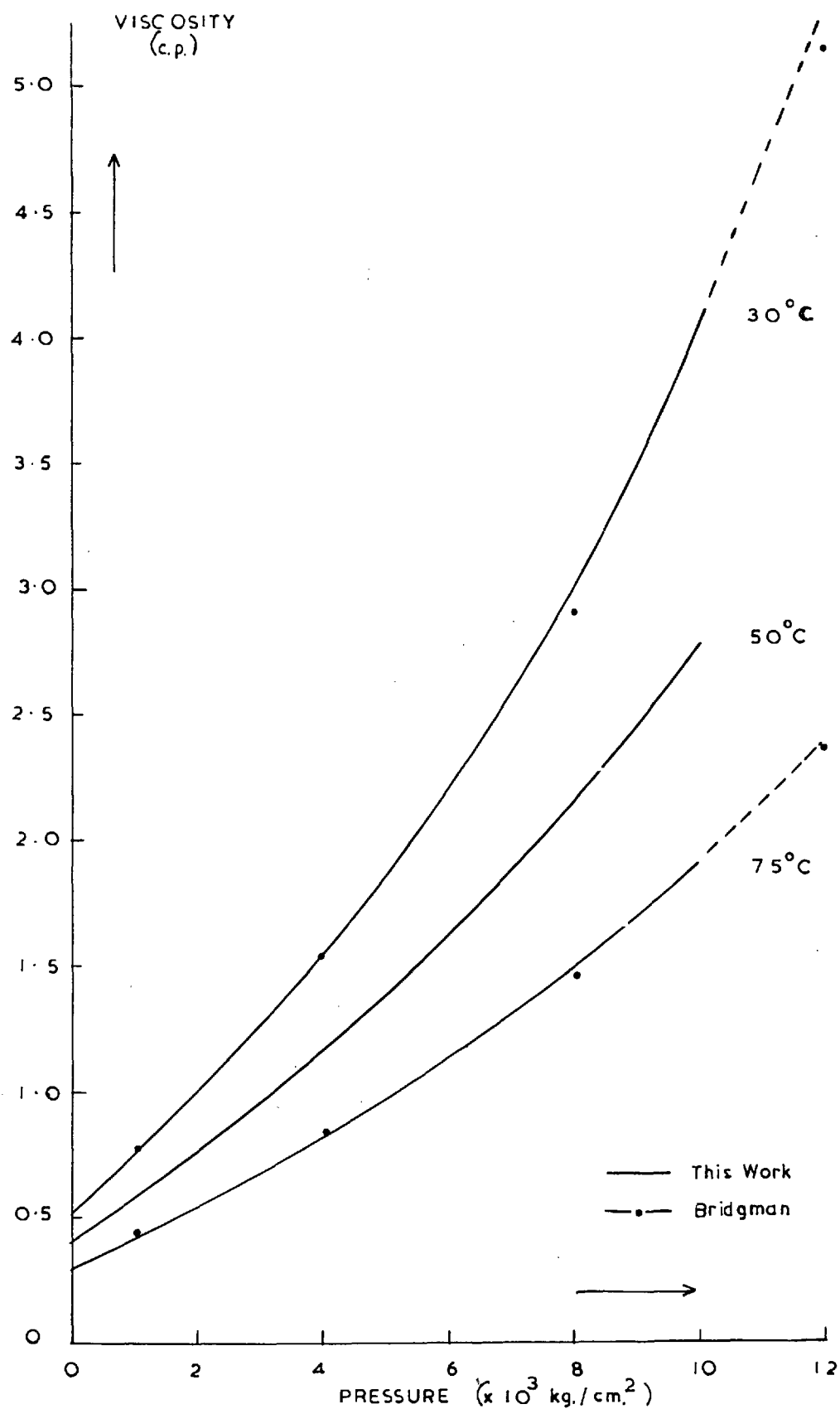
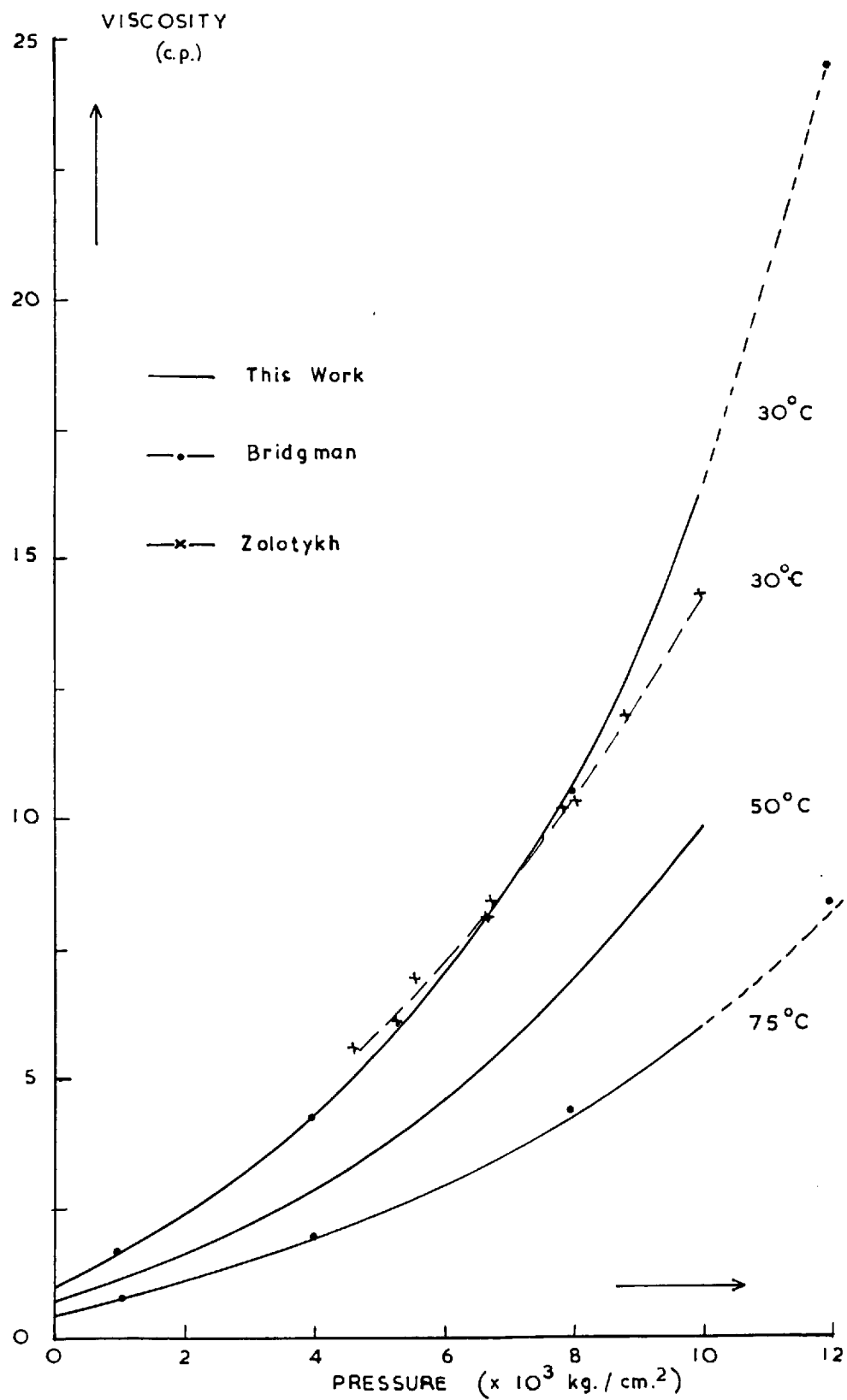


FIG.9-4. Comparison of Results for Ethanol.



in broad agreement with those of this work and those of Bridgman⁽¹⁸⁾, smaller viscosity-pressure coefficients are indicated over this pressure range. Zolotych states that the initial purity of his ethanol sample was only 93%, and reports that it was contaminated during the experiment. Thus the deviations of his results from those of this work may be due to impurities.

Bridgman's results⁽¹⁸⁾ are in good agreement but tend to be lower by about $2\frac{1}{2}\%$ at 30°C and higher by about 2% at 75°C .

It is likely that Bridgman's viscosity results for water⁽¹⁸⁾ are in error because of the particular experimental difficulties he encountered when he used his viscometer to investigate water. This conclusion is supported by the good agreement of the new measurements on benzene, methanol and ethanol at 30°C and 75°C with his data for these liquids⁽¹⁸⁾.

(f) Ethanol-Water Mixtures.

No previous measurements have been reported of the effect of pressure on the viscosity of this system.

9.2 Water and Heavy Water.

(a) Abnormal viscosity behaviour.

In common with most of their other properties, the viscosity

behaviour of water and heavy water is anomalous. It has been noted previously that water is a member of two homologous series, and that its viscosity is much higher than would be predicted from consideration of the viscosities of the other members in these series. Further, the temperature and pressure dependence of its viscosity does not conform to the general pattern of liquid behaviour.

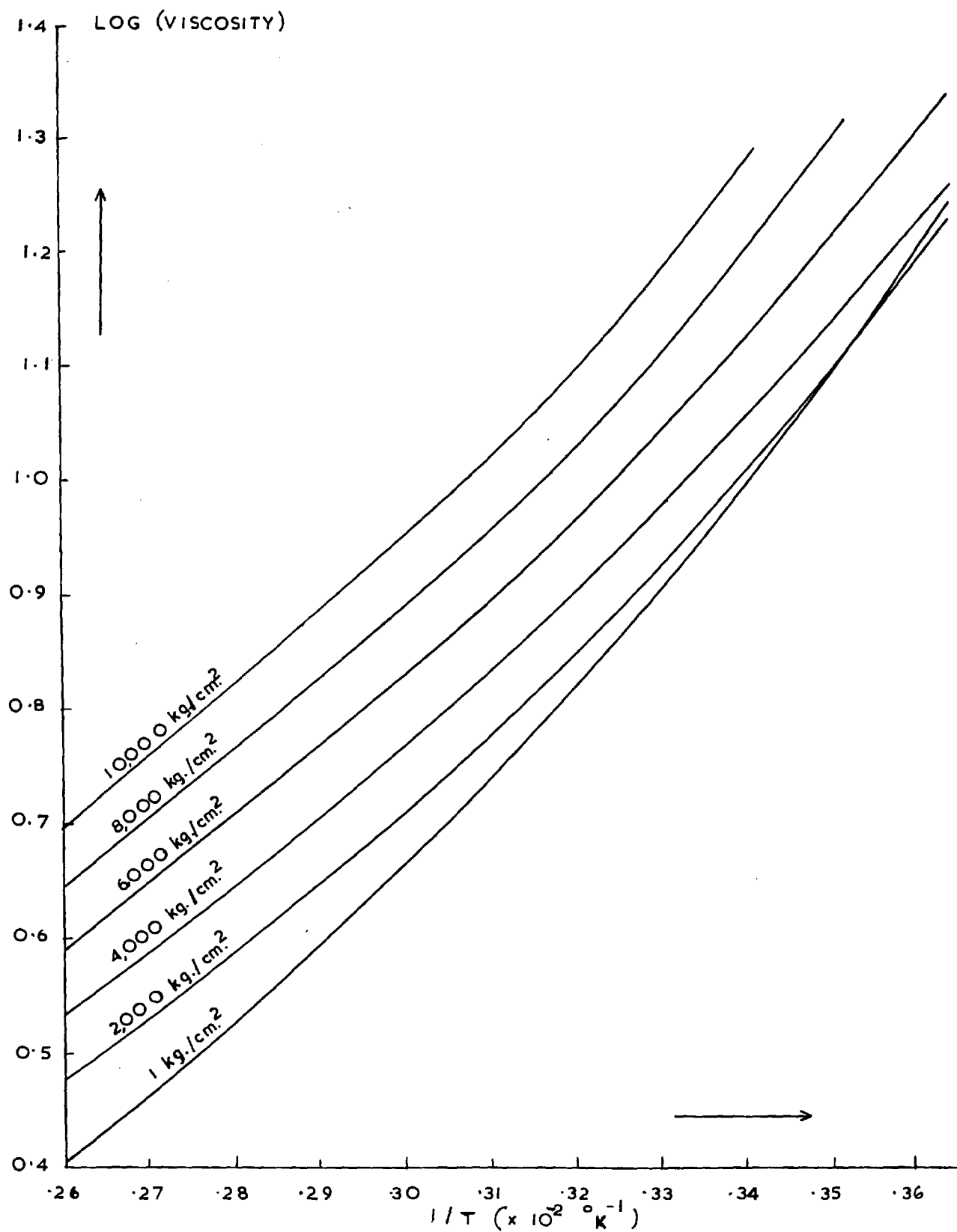
The viscosity of many liquids under constant pressure is well described by the Arrhenius equation,

$$\eta = A_p \exp. \frac{E_p}{RT} \quad \dots\dots (9-1)$$

where A_p is a constant, R is the gas constant, T is the absolute temperature, and E_p is the isobaric activation energy for viscous flow. Smoothed viscosity data for water are plotted in Figure (9-5) as $\log \eta$ against $1/T$ for constant pressures of 1, 2,000, 4,000, 6,000, 8,000, 10,000 kg/cm². Although these isobars do not conform to the straight line behaviour predicted by equation (9-1), it may be observed that the departures from linearity are least at high pressures and high temperatures.

The viscosity-pressure dependence of water is abnormal in two respects. Firstly, water exhibits a negative viscosity-pressure

FIG. 9-5. Isobaric Arrhenius Plot for Water.



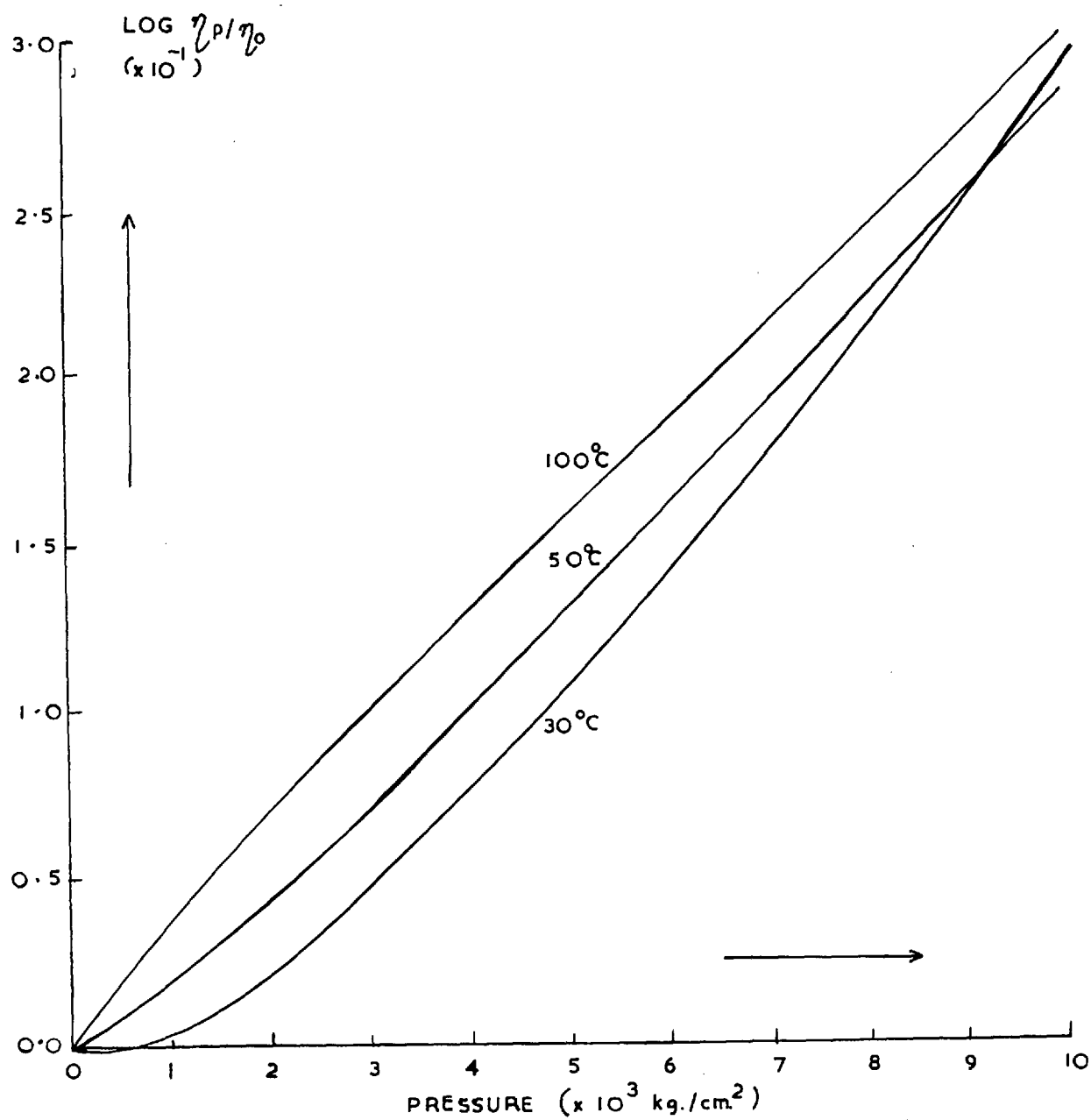
coefficient, and secondly, with the exception of liquid metals, the coefficient is much less than for other liquids. In Figure (9-6) smoothed relative-viscosity data for water are presented in the form of $\log (\eta_p / \eta_o)$ against pressure. Comparison of these curves with the more typical behaviour of benzene, methanol or ethanol (Figures (8-14), (8-17), (8-19)) provides a good illustration of the abnormal viscosity-pressure behaviour of water.

(b) Mechanism of Viscous Flow.

The anomalous viscosity behaviour of water may be explained qualitatively in terms of Frank and Wen's 'flickering clusters' model⁽⁴¹⁾. The dynamic equilibrium between the 'icelike', H_2O_I , species and the unbonded, H_2O_{II} , species is displaced in the direction of the H_2O_{II} phase by increasing pressure and temperature. Since the activation energy of viscous flow and the energy of the hydrogen bond in water are approximately equal, (~ 4.5 kcal/mole), Frank and Wen falsely concluded that momentum transfer takes place mainly in the H_2O_I phase.

However, Miller⁽⁷⁶⁾ has employed a modified Arrhenius equation to make an empirical correlation between free volume and the viscosity of water at atmospheric pressure. The calculated free

FIG.9 - 6. Logarithmic Plot of Water Viscosity.



volume fractions were found to agree with the volume fractions of unbonded molecules as estimated by Némethy and Scheraga⁽⁸¹⁾ on the basis of the 'flickering clusters' model. Further, since the energy to separate molecules in the unbonded state is less than in the 'icelike' state, it is now generally recognised that momentum transport occurs predominantly in the $\text{H}_2\text{O}_{\text{II}}$ phase.

When viscous flow occurs in water, a velocity gradient is set up in the unbonded molecules, and momentum transport takes place between adjacent layers of molecules principally by overcoming the dipole-dipole interactions and forcing the molecules to roll in the direction of flow. Both the strong dipole-dipole interactions, and the fact that momentum transport involves only a fraction of the total number of molecules, contribute to the high viscosity of water.

Since the fraction of unbonded molecules increases at higher temperatures, this increases the number of molecules available for momentum transport. Thus, in addition to the normal decrease in viscosity due to increased intermolecular distances and internal energy of the molecules, there is an additional reduction in viscosity with increasing temperature arising from the equilibrium shift to the unbonded state. The large viscosity-temperature coefficient of water,

and its failure to follow the usual Arrhenius behaviour, arise directly from this structural effect.

The explanation of the anomalous viscosity-pressure behaviour of water is based on the increasing number of unbonded molecules that are able to participate in momentum transfer at high pressures.

The equilibrium shift $\text{H}_2\text{O}_\text{I} \rightarrow \text{H}_2\text{O}_\text{II}$ with pressure is greatest at low temperatures as evidenced by the initial viscosity-pressure coefficient being negative below 33°C , (34°C for D_2O). At higher temperatures the viscosity-pressure coefficient is always positive since the effects of the equilibrium shift on viscosity are less significant than the decreasing intermolecular distances. Figure (9-6) shows that at 100°C the viscosity of water closely follows the pressure variation of normal liquids.

Since nearly all the modern theories of water involve the 'flickering clusters' mechanism of molecular association, the model of Frank and Wen is not unique in its ability to account for the anomalous viscosity behaviour. However, the explanation of this behaviour in terms of a two species model, lends considerable support to the current 'mixture' theories of water structure.

Although the viscosity of a liquid is influenced by strong

molecular interactions and association of the molecules, viscosity measurements cannot provide detailed information on the structure of a liquid. Consequently, qualitative considerations of water's viscosity behaviour do not permit any conclusions to be drawn concerning the merits of the various mixture models.

(c) Viscosity-Temperature Dependence.

If, as appears likely, the effect of temperature and pressure on viscosity is due to the combination of the normal viscosity variation of the unbonded species, and a contribution arising from an equilibrium shift between the two species, then the actual viscosity, η , may be expressed as,

$$\eta(P, T) = \eta_o(P, T) \cdot f'(\Phi) \quad \dots\dots (9-2)$$

where η_o is the intrinsic viscosity of the H_2O_{II} molecules, and $f'(\Phi)$ is the structural factor arising from a volume concentration, Φ , of H_2O_I molecules. Since Φ is, in general, a function of temperature and pressure, equation (9-2) may be written as,

$$\eta(P, T) = \eta_o(P, T) \cdot f(P, T) \quad \dots\dots (9-3)$$

where $f'(\Phi) = f(P, T)$

In the absence of detailed information on the concentration and shape of the bonded structures and a general theory of viscosity in liquids, equation (9-3) cannot be used to calculate η . However, the equation provides a link between theory and experiment, if experimental viscosity data are employed with estimates of η_0 or f . From Figure (9-8) it can be seen that at atmospheric pressure, the viscosity of water is given quite closely over the temperature range from 30°C to 100°C by,

$$\eta = A \exp \left\{ \frac{1}{T} \left\{ B + \frac{C}{T} \right\} \right\} \quad \dots\dots (9-4)$$

where $A = 1.0 \times 10^{-1}$ c. p.

$$B = - 652^\circ\text{K}$$

$$C = 388,300 (\text{°K})^2$$

The concentration of bonded molecules in water is decreased at elevated temperatures and pressures and it may be seen from Figures (9-5) and (9-7) that under these conditions the viscosity tends to the normal Arrhenius behaviour. It is suggested, therefore, that at a constant pressure the temperature dependence of the unbonded viscosity is of the form,

$$\eta_0 = a \exp \left(\frac{b}{T} \right) \quad \dots\dots (9-5)$$

FIG.9-7. Limiting Viscosity Behaviour of Water.

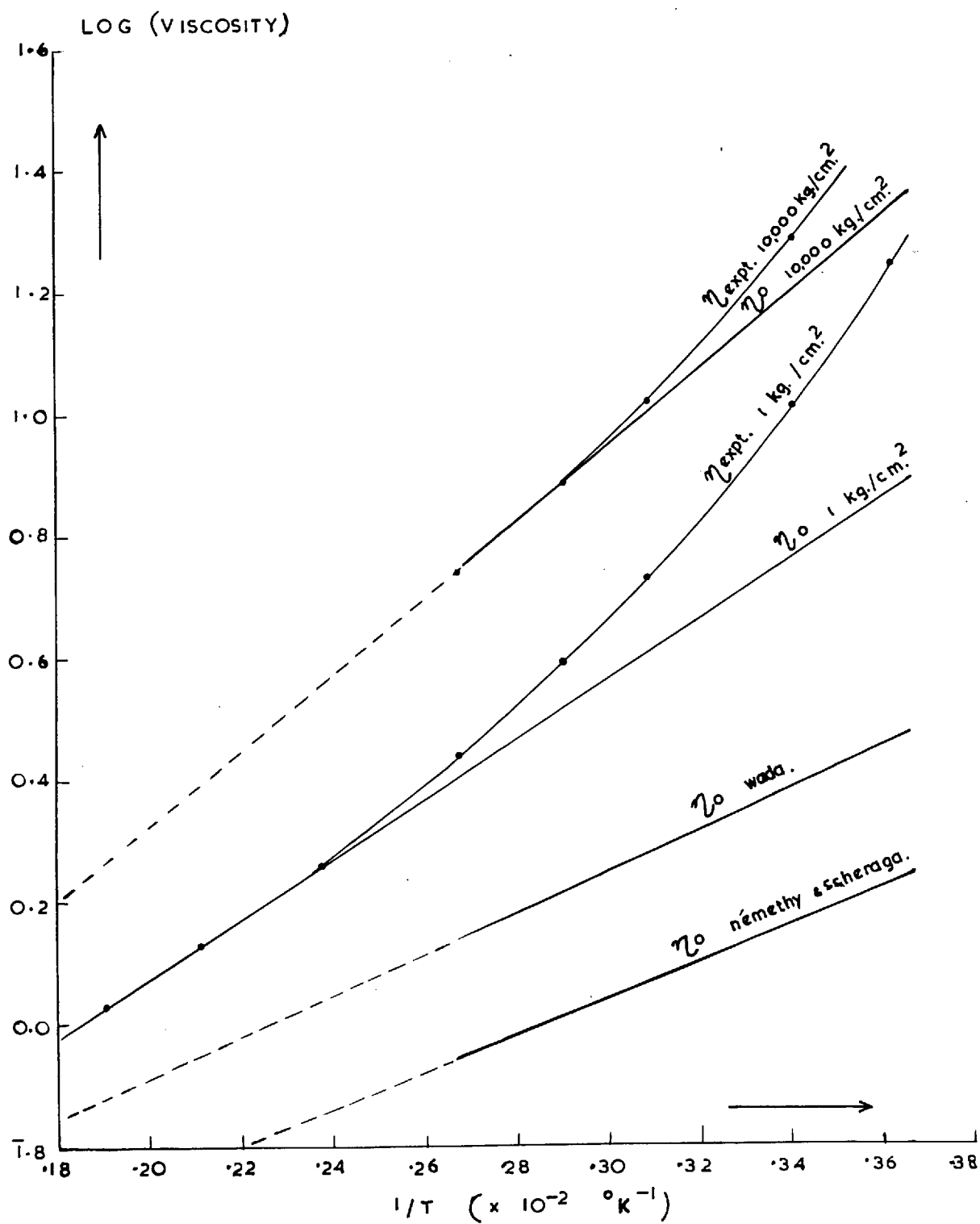


FIG. 9-8. Temperature Dependence of η at 1 kg./cm.²

228.

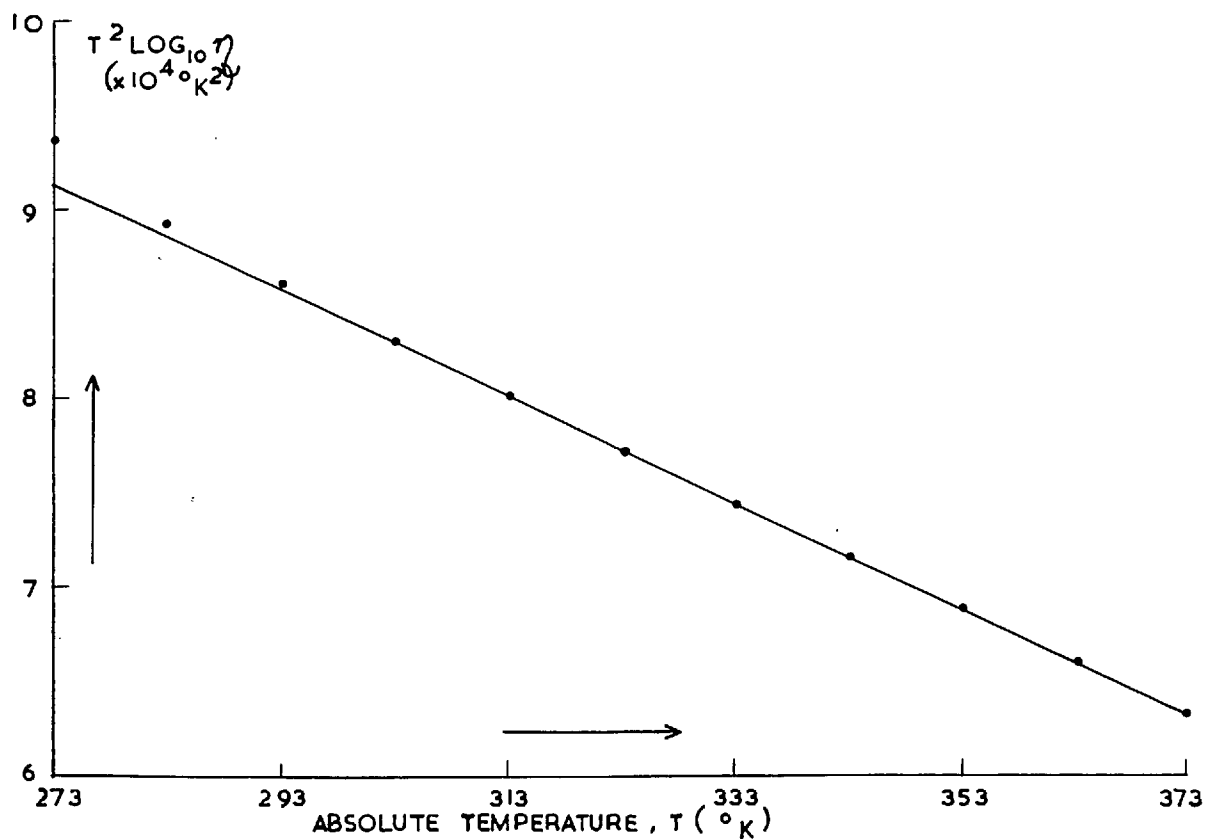
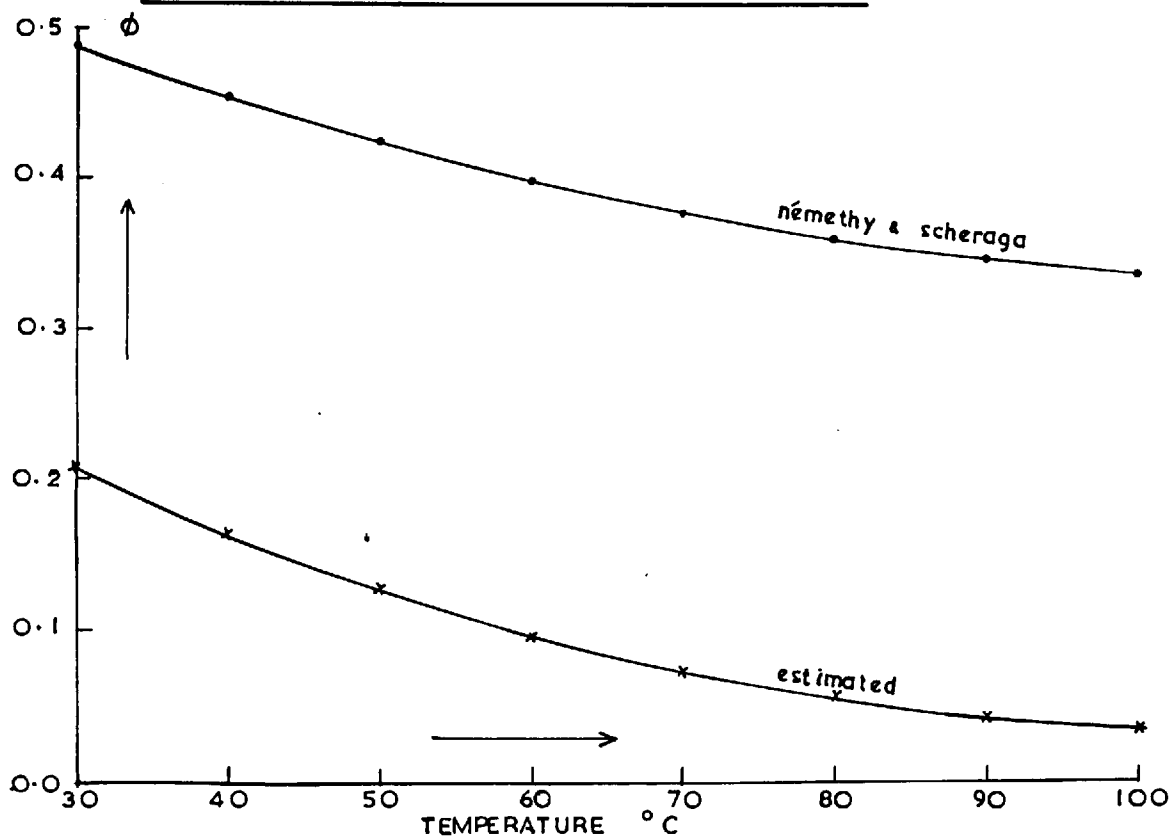


FIG. 9-9. Temperature Dependence of ϕ .



where a and b are constants.

Thus, combining (9-4) and (9-5),

$$f(T) = \frac{A}{a} \cdot \exp \left\{ \frac{1}{T} \left\{ (B - b) + \frac{C}{T} \right\} \right\} \dots\dots (9-6)$$

for $303 < T < 373^\circ\text{K}$.

The constants a and b in equation (9-5) may be estimated from Figure (9-7), if it is assumed that ϕ is zero when the viscosity follows the Arrhenius pattern. The estimated values of a and b at one atmosphere are,

$$a = 1.26 \times 10^{-2} \text{ c.p.}$$

$$b = 1133^\circ\text{K}$$

For simplicity the bonded molecules are assumed to form spherical incompressible clusters of molecules, so that water may be considered as a suspension of spheres in a dipolar fluid. The viscosity of a concentrated suspension of hard spheres is given approximately by⁽¹⁰³⁾,

$$\eta = \eta_0 (1 + 2.5 \phi + 7.17 \phi^2 + 16.2 \phi^3) \dots\dots (9-7)$$

where ϕ is the volume fraction of the spheres. Comparison of equations (9-2) and (9-7) gives,

$$f(\phi) = 1 + 2.5 \phi + 7.17 \phi^2 + 16.2 \phi^3 \quad \dots\dots(9-8)$$

Equations (9-6) and (9-8) have been used to calculate ϕ as a function of temperature at atmospheric pressure in the range 30°C to 100°C. The results are presented graphically in Figure (9-9), and ϕ is seen to decrease quite steadily with increasing temperature.

Franks and Good⁽⁴²⁾ have used the estimated volume fractions of bonded molecules from the theories of both Némethy and Scheraga⁽⁸¹⁾ and of Wada⁽¹⁰⁷⁾, together with equations (9-2) and (9-8), to calculate the temperature dependence of η_o at atmospheric pressure. They showed that η_o followed the usual exponential behaviour above about 40°C. The unbonded viscosity calculated from both models is included in Figure (9-7) for comparison with the experimental data. The values of the constants a and b in equation (9-5) predicted by the two theories are,

$$(1) \text{ Némethy and Scheraga, } a = 1.3 \times 10^{-2} \text{ c. p. ,}$$

$$b = 700^\circ\text{K}$$

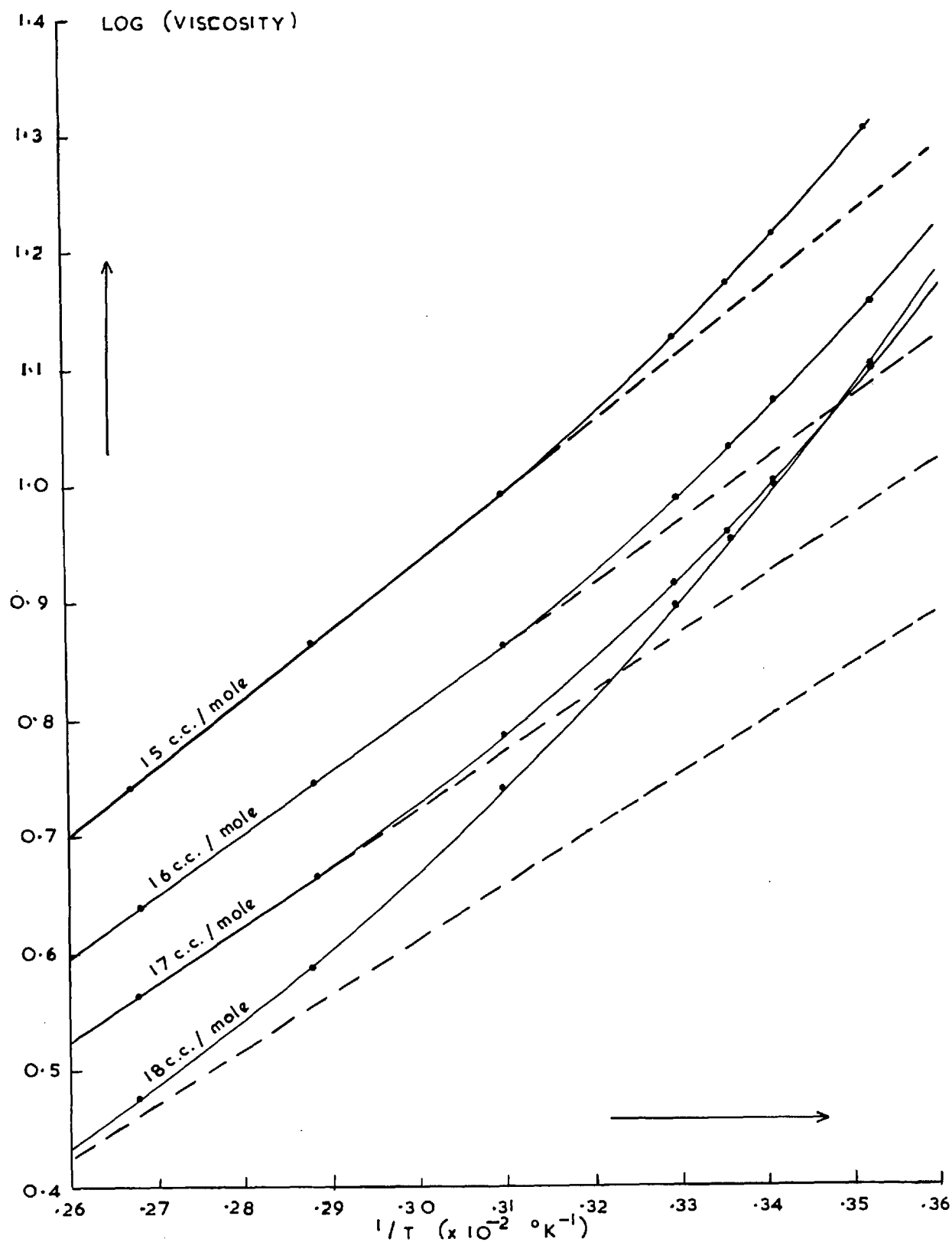
$$(2) \text{ Wada, } a = 1.7 \times 10^{-2} \text{ c. p. , } b = 780^\circ\text{K}$$

Values of ϕ between 30°C and 100°C as calculated from the theory of Némethy and Scheraga are given in Figure (9-9). Although

the actual magnitude of the volume fractions calculated from this theory are in poor agreement with the previously estimated values, the temperature dependence of ϕ is shown to be very similar. It is suggested that the large discrepancy between the two estimates of ϕ occurs for two main reasons. Firstly, molecules on the surface of clusters engage in momentum transfer providing an 'effective' volume fraction of bonded molecules that is smaller than the calculated volume fraction, and secondly, the factor, $f(\phi)$, approaches Arrhenius behaviour at high temperatures thus making the estimates of the constants a and b inaccurate. Both of these factors tend to reduce the value of ϕ that is estimated from the asymptotic behaviour of the experimental data.

The viscosity of water at 15, 16, 17, and 18 cc/mole, calculated from the viscosity data of this work and the density data of Bridgman⁽²⁰⁾ is presented in Figure (9-10) in the form of $\log \eta$ against $1/T$. The general pattern of behaviour is similar to that shown by the isobars in Figure (9-5), with an approximately linear relationship being exhibited at small volumes and high temperatures, and with increasing departures from linearity at lower temperatures and larger volumes. The interpretation of this behaviour is essentially

FIG.9-10. Isochoric Arrhenius Plot for Water.



the same as that given previously for the isobaric curves.

Activation energies of viscous flow in water at constant pressure, E_p , and at constant volume, E_v , have been estimated from the limiting viscosity behaviour at high temperatures, and these are listed in Table (9-3).

TABLE (9-3)

P kg/cm ²	E_p kcal/mole	V cc/mole	E_v kcal/mole
1	2.25	18	2.10
2,000	2.45	17	2.24
4,000	2.59	16	2.40
6,000	2.68	15	2.65
8,000	2.79		
10,000	2.87		

E_p and E_v are approximately equal and rise steadily with increasing pressure, (i.e. decreasing volume). It is interesting to compare the estimated value of E_p at atmospheric pressure, i.e. 2.25 kcal/mole, with the calculated values of 1.39 kcal/mole from Némethy and Scheraga's theory and of 1.55 kcal/mole from Wada's theory. A comparison of E_v with its value for simple non-associated

liquids, like pentane or benzene for example, shows that E_v is greater at low pressures, but does not change so rapidly with increasing pressure. This small volume dependence arises because the attractive forces between water molecules are so strong that the additional energy required by a molecule to engage in momentum transfer is quite small.

(d) The Rotational Contribution to Momentum Transfer.

Viscosity data for isotopically substituted liquids can provide information on the molecular mechanisms of transport where momentum transfer involves only vibration and/or convection of the molecules,

$$\frac{\eta_i}{\eta} = \left(\frac{m_i}{m} \right)^{\frac{1}{2}} \quad \dots\dots (9-9)$$

whereas for rotational momentum transfer,

$$\frac{\eta_i}{\eta} = \left(\frac{I_i}{I} \right)^{\frac{1}{2}} \quad \dots\dots (9-10)$$

The molecular weight of water and that of deuterium oxide are such that,

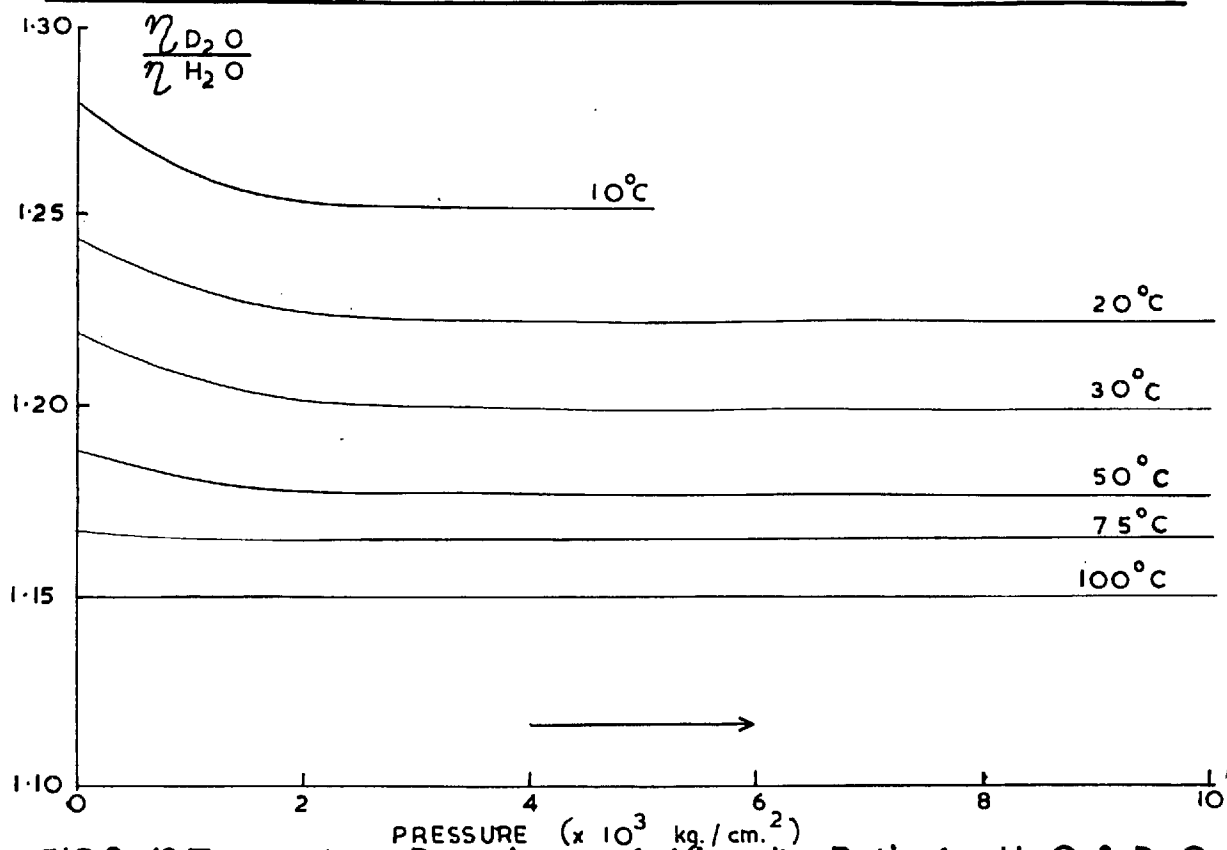
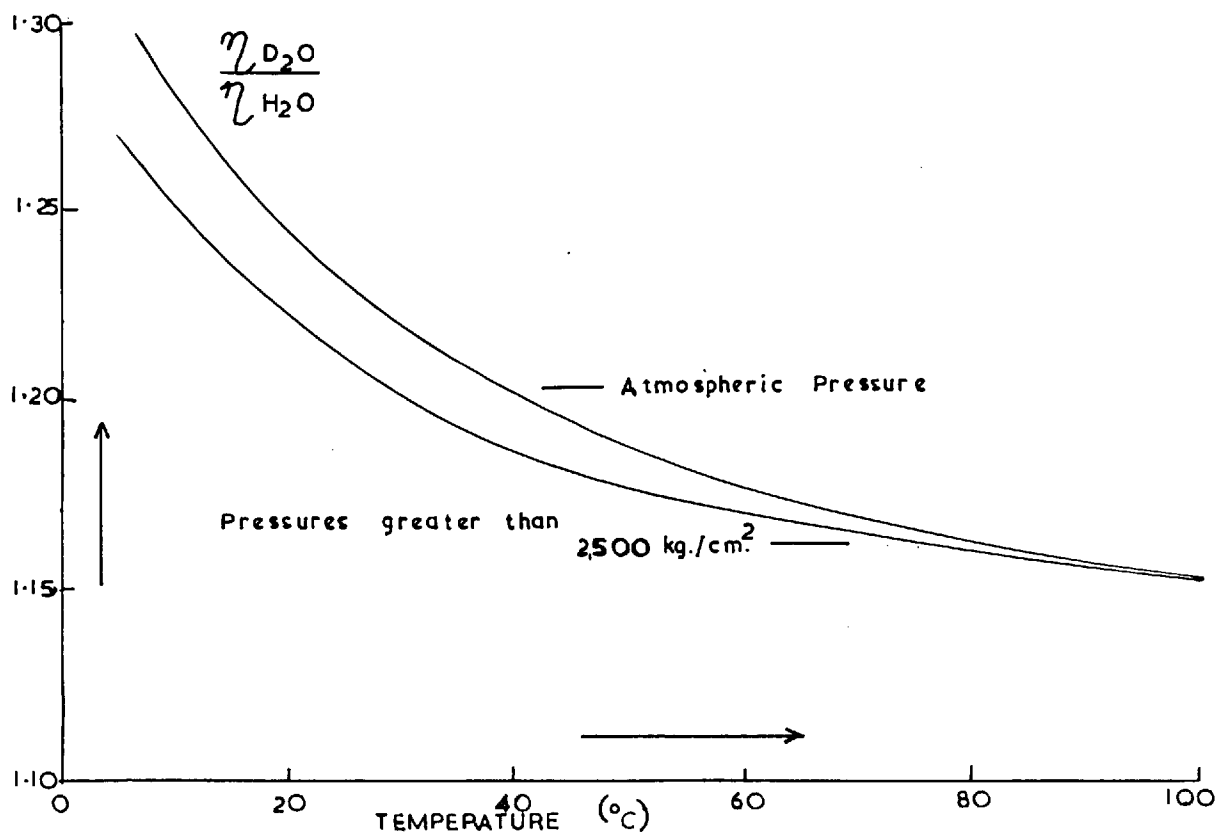
$$\left(\frac{m_i}{m} \right)^{\frac{1}{2}} = 1.054$$

and their moments of inertia in the three principal directions are such that,

$$\left(\frac{I_1}{I} \right)_A^{\frac{1}{2}} = 1.341; \left(\frac{I_1}{I} \right)_B^{\frac{1}{2}} = 1.411; \left(\frac{I_1}{I} \right)_C^{\frac{1}{2}} = 1.389$$

The ratio of η_{D_2O}/η_{H_2O} has been calculated as a function of temperature and pressure from the smoothed relative viscosity data given in Figures (8-2) to (8-8) and from the data for η_{D_2O}/η_{H_2O} at atmospheric pressure from Hardy and Cottingham⁽⁵⁷⁾. The results presented graphically, are plotted isothermally against pressure in Figure (9-11), and are plotted isobarically against temperature in Figure (9-12). It may be seen from these graphs that for the range of temperatures and pressures studied, the ratio η_{D_2O}/η_{H_2O} remains within the limits defined by the values of $(m_j/m)^{\frac{1}{2}}$ and $(I_1/I)^{\frac{1}{2}}$, implying that in water, molecular rotation plays an important role in momentum transfer.

Figure (9-11) shows that η_{D_2O}/η_{H_2O} tends to decrease with increasing pressure for the first 2,000 kg/cm² or so, until it reaches a steady value which is independent of further pressure increase. The difference between the steady value of η_{D_2O}/η_{H_2O} and its value at atmospheric pressure is greatest at 10°C, but becomes smaller as the

FIG.9-11. Pressure Dependence of Viscosity Ratio for H₂O & D₂O.FIG.9-12. Temperature Dependence of Viscosity Ratio for H₂O & D₂O.

temperature rises, until at 100°C no decrease is observed. This effect is also illustrated by Figure (9-12), where the limiting high pressure value of η_{D_2O}/η_{H_2O} and its value at atmospheric pressure are plotted separately against temperature. Both curves show a gradual reduction in the rotational contribution to momentum transfer with rising temperature, but the initial rate of decrease is larger at atmospheric pressure and the curves converge at high temperatures.

The interpretation of Figures (9-11) and (9-12) is complicated by small differences in the degree of H-bonding in H_2O and D_2O . At low temperatures, it is generally recognised that there is more structural order in liquid deuterium oxide than in water⁽¹¹¹⁾. However, since both appear to have similar degrees of order at high temperatures, the rate of dissociation of D_2O at low temperatures must be faster than that of H_2O . The initial decrease in η_{D_2O}/η_{H_2O} with increasing pressure is assumed to arise solely from the small differences in the cluster concentrations in the two liquids.

On the basis of this assumption, the results show that, in water, the rotational contribution to momentum transfer is large, independent of pressure, and decreases with rising temperature.

The large rotational contribution to momentum transfer is

explained if the shearing of adjacent layers of unbonded molecules occurs mainly by overcoming the strong dipole-dipole forces, and forcing molecules to roll in the direction of flow. Unfortunately accurate compressibility data for H_2O and D_2O are not available at high pressures but a comparison of many of their properties at high temperatures suggests that their molecular volumes and compressibilities are similar at high pressures. On this assumption, the variation of $\eta_{\text{D}_2\text{O}}/\eta_{\text{H}_2\text{O}}$ at constant volume is given by the limiting high pressure curve in Figure (9-12).

As the temperature of a liquid is raised at constant volume, the internal energy of the molecules is increased and since this increases the probability of a molecule possessing sufficient energy to engage in convective or rotational momentum transfer, the viscosity of the liquid decreases. Conversely, however, the viscosity of the liquid will increase for rising pressures (i. e. decreasing volume) at constant temperature, because both convective and rotational momentum transfer are restricted by reduced intermolecular distances.

It should be observed that the agreement of experimental viscosity data with equation (9-9) does not distinguish between purely convective or purely rotational momentum transfer.

On account of the very strong attractive forces between molecules in liquid water, the convective contribution to momentum transport and any changes in this contribution arising from temperature or pressure variation, will be small.

On the basis of the foregoing assumptions, Figure (9-11) shows that the rotational contribution to momentum transfer in water is independent of the molecular volume. If momentum transfer by convection in water is assumed to be unimportant, then Figure (9-11) implies that the molecular volume dependence of the rotational and the vibrational contribution is identical. Applying similar reasoning, it follows from Figure (9-12) that the temperature dependence of the vibrational contribution must be greater than the temperature dependence of the rotational contribution.

It is interesting to contrast the viscosity behaviour of liquid water and heavy water with that of their vapours. The ratio of the viscosities of their vapours are consistent with equation (9-9)⁽⁹³⁾ indicating that in the vapour phase rotational momentum transfer is insignificant.

If energy transfer by molecular rotation is negligible, it may be shown⁽⁷⁰⁾ that the coefficients of thermal conductivity in isotopically

substituted liquids are related by,

$$\frac{\lambda}{\lambda_i} = \left(\frac{m_i}{m} \right)^{\frac{1}{2}} \quad \dots\dots (9-11)$$

Challoner and Powell⁽²⁶⁾ have measured the thermal conductivity of liquid D₂O over a range of temperatures at atmospheric pressure and obtained good agreement with equation (9-11). The contrasting effects of isotopic substitution on the viscosity and thermal conductivity of water provides a good indication of the importance of rotation in the viscous flow of molecules with highly directional inter-molecular potentials.

9.3 Benzene, Methanol and Ethanol.

(a) Activation Energies of Viscous Flow.

Arrhenius plots at constant pressure have been made from the smoothed viscosity data for benzene, methanol and ethanol given in Figures (8-15), (8-18), and (8-20). Although measurements were made at only three temperatures the results satisfy equation (9-1) over the entire range of experimental pressures. Activation energies at constant pressure, E_p , calculated from the plots are presented in Table (9-4).

TABLE (9-4)

BENZENE		METHANOL		ETHANOL	
p kg/cm ²	E_p kcal/mole	p kg/cm ²	E_p kcal/mole	p kg/cm ²	E_p kcal/mole
1	2.52	1	2.88	1	3.70
400	2.59	2,000	2.61	2,000	3.45
800	2.69	4,000	2.88	4,000	3.58
1,200	2.77	6,000	3.07	6,000	4.11
		8,000	3.27	8,000	4.31
		10,000	3.99	10,000	4.74

Arrhenius plots have also been made at constant volume for benzene, methanol and ethanol using smoothed viscosity data from this work and the density data of Bridgman⁽¹⁶⁾ (19). The data was found to satisfy the Arrhenius equation at constant volume,

$$\eta = A_v \exp\left(\frac{E_v}{RT}\right) \quad \text{.....(9-12)}$$

over the complete range of volumes studied. Values of E_v , the activation energy at constant volume, are given in Table (9-5).

TABLE (9-5)

BENZENE		METHANOL		ETHANOL	
Mol. Vol.	E_v	Mol. Vol.	E_v	Mol. Vol.	E_v
c. c.	kcal/mole	c. c.	kcal/mole	c. c.	kcal/mole
91	0.475	41	1.68	59	2.44
89	0.511	39	1.68	56	2.53
87	0.550	37	1.93	53	2.35
85	0.610	35	2.14	50	2.72
		33	2.39	47	3.19
				44.5	3.65

The Arrhenius plots for methanol at constant pressure and at constant volume are presented in Figures (9-13) and (9-14) respectively.

An empirical viscosity-free volume correlation for benzene has been given by Miller⁽⁷⁷⁾ using Bridgman's viscosity data and the Doolittle free volume equation, (equation (2-15))

(b) Comparison of Viscosity-Pressure Behaviour.

The relative viscosities of benzene, methanol and ethanol at 75°C are compared in Figure (9-15). This graph shows the rate at which the viscosity of each of these liquids increases with pressure.

The relative viscosity of benzene is about 4.33 at 2,500 kg/cm².

FIG.9-13. Isobaric Arrhenius Plot for Methanol.

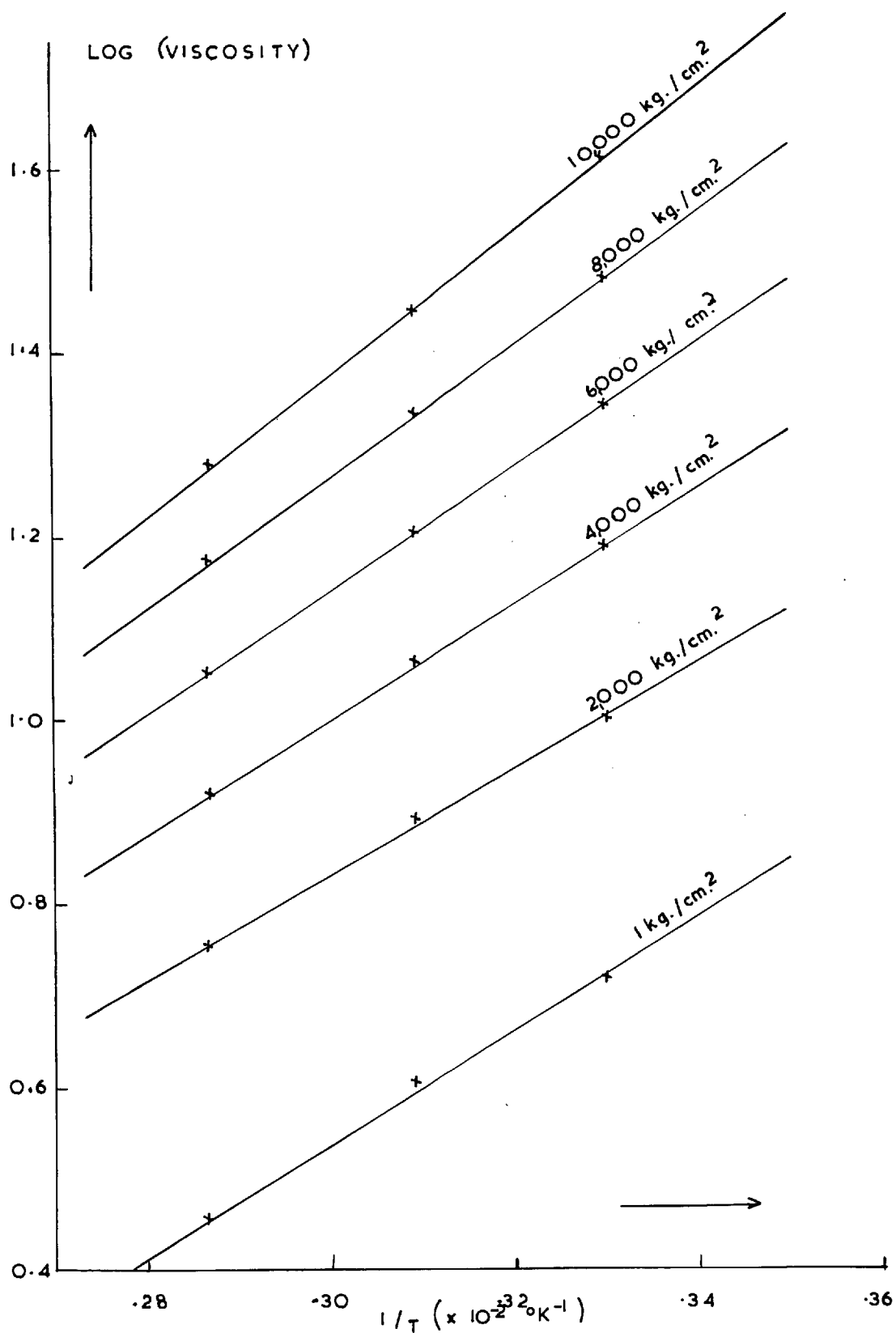


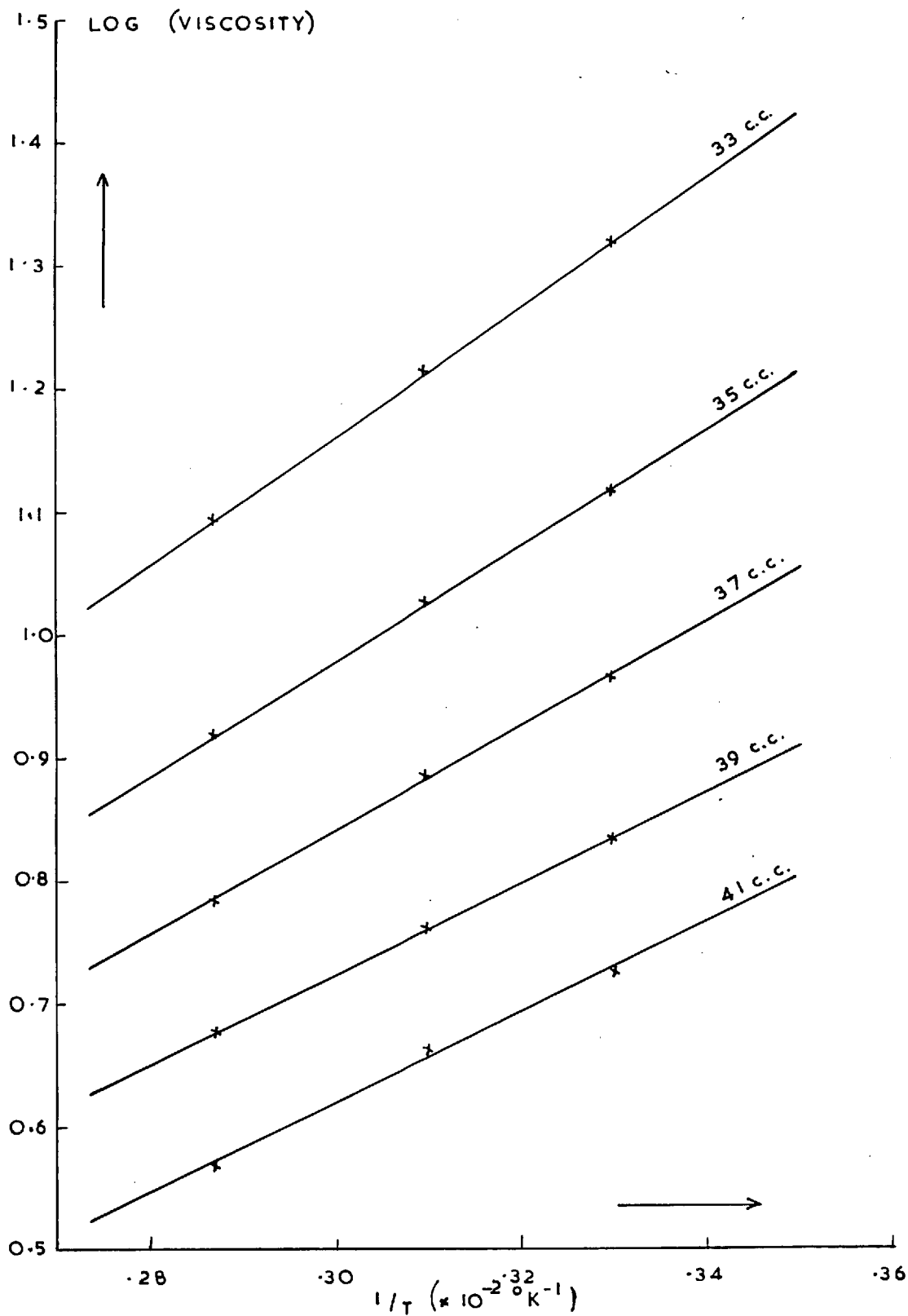
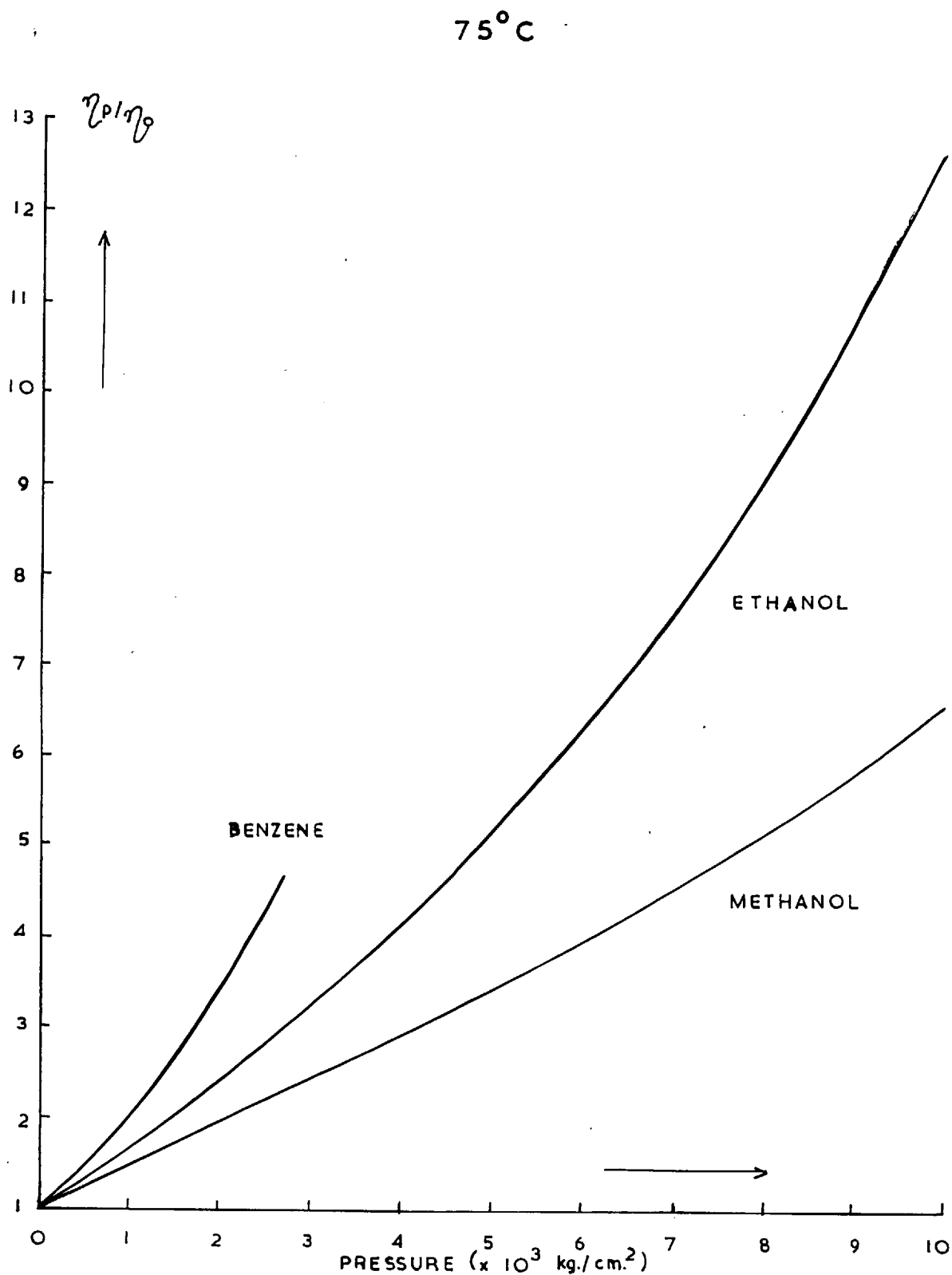
FIG.9-14. Isochoric Arrhenius Plot for Methanol.

FIG.9-15. Viscosity Behaviour of Benzene, Methanol & Ethanol.



This increase in η_p/η_o is $1\frac{1}{2}$ times the increase for ethanol and nearly twice that of methanol at the same pressure. The relative viscosity of ethanol remains greater than that of methanol over the complete pressure range and at $10,000 \text{ kg/cm}^2$ the ratio of their relative viscosities is about 2 : 1.

A comparison of the activation energies given in Tables (9-4) and (9-5) emphasises the differences in the viscosity-pressure behaviour of benzene and that of the alcohols. For benzene, E_p increases steadily with rising pressure, whereas for methanol and ethanol, it exhibits a pronounced minimum at about $2,000 \text{ kg/cm}^2$. Under constant volume conditions it is found that E_v is much smaller than E_p for benzene, but again it increases steadily with decreasing volume. The minima of E_p exhibited by methanol and ethanol is not repeated by E_v . However, the activation energy at constant volume appears to be independent of volume for small decreases in volume. (Jobling and Lawrence⁽⁵⁸⁾ reported that E_v passed through a minimum for ethanol, but not for methanol).

Benzene and the lower aliphatic alcohols have quite different structures. Benzene is a non-associated liquid with near spherical molecules, whereas methanol and ethanol are associated liquids with

extensive H-bonding and highly directional intermolecular potentials. In view of these structural differences it is surprising to find that the viscosity-pressure behaviour of benzene, methanol and ethanol are well represented over a wide range of pressures by the same equations. It has been mentioned previously that equation (9-1) is an empirical equation without theoretical justification, whereas equation (9-12) is very similar to the theoretical equations proposed by Andrade⁽²⁾ and by Eyring⁽⁴⁴⁾. However, since it is often more convenient to consider viscosity under constant pressure conditions rather than under constant volume conditions, equation (9-1) provides a useful basis for the correlation of viscosity data at high pressures.

Spectroscopic measurements have shown that the effect of raising the pressure on alcohols is to increase the degree of H-bonding⁽⁹⁸⁾. This behaviour may be contrasted with that of water, for which increasing pressure decreases the degree of association. The solid phases of water, methanol and ethanol have extensive H-bonded structures. However, ice is less dense than water and has an open structure, whereas solid methanol and solid ethanol have more close packed structures with long chains of bonded molecules⁽⁸⁸⁾. The differing effects of pressure on the degree of association in these liquids

is considered to arise from such differences in the packing of the bonded structures.

Compared with other pure liquids, the viscosity behaviour of water, methanol and ethanol is similar in that they each have high viscosities, large viscosity-temperature coefficients and small viscosity-pressure coefficients. The high viscosity and the large viscosity-temperature coefficient arises from the association of the molecules and the breaking-down of this association with rising temperature. The reason for the similarity in the viscosity-pressure dependence is not apparent. In contrast to water, the structural contribution to the viscosity in methanol and ethanol increases with rising pressure and it would seem likely therefore, that this contribution changes very little with pressure. Factors which may lead to the small viscosity-pressure effect in methanol and ethanol are strong intermolecular forces and a large rotational contribution to momentum transfer that is insensitive to pressure change. The rotational contribution to momentum transfer and its pressure dependence should be investigated experimentally by comparing the viscosities of methanol and ethanol with those of their isotopically substituted derivatives.

9.4 Ethanol-Water Mixtures.

Although there have been numerous studies of the effects of temperature and structural changes on the viscosities of binary liquid mixtures, few results are available at high pressures.

The first investigation of the effect of pressure on the viscosities of binary mixtures was by Dow⁽³⁵⁾ in 1935, who studied six systems over the entire concentration range at 30°C and 75°C and at pressures extending to 12,000 kg/cm². He found that the isobaric log viscosity against concentration curves were linear for two systems, but for the remainder the corresponding viscosity isobars exhibited marked irregularities which varied with temperature and pressure. The irregularities were considered to arise from structural differences of the component molecules and complex temperature and pressure sensitive molecular interlocking effects.

Another example of irregular relative viscosity behaviour of a mixture at high pressures has been investigated by Zolotykh⁽¹¹⁵⁾. His measurements at pressures up to 10,000 kg/cm² on the system glycerine-ethylene glycol revealed that although the viscosity-concentration isobars are smooth curves, the relative viscosity-concentration curves are irregular.

Webb, Griest and Schiessler⁽¹⁰⁹⁾ measured the viscosities of binary mixtures of pure hydrocarbons at several temperatures and at pressures up to $3,400 \text{ kg/cm}^2$. They found that to an accuracy of 5% the mixtures exhibit the same viscosity-pressure behaviour that is predicted for a pure liquid of similar molecular structure and equivalent molecular weight.

The only other published data on the viscosities of binary liquid mixtures at high pressures are the recent measurements of Gonikberg and Shakovskoi⁽⁴⁵⁾ on the systems nitrobenzene - n methylaniline and nitrobenzene - pyridine. The effect of increasing pressure was to shift the viscosity-concentration curves towards higher viscosities with no appreciable change in shape.

It may be seen from Figure (8-24) that at atmospheric pressure the viscosity-composition curve for the ethanol-water system exhibits a large maximum at about 45% by weight EtOH or 25 mole % EtOH.

With rising temperature the maximum is shifted slightly towards higher ethanol concentrations, and becomes less marked. Figures (8-25), (8-26) and (8-27) show that the mixtures continue to exhibit viscosity maxima at high pressures, but that the maxima are shifted towards larger ethanol concentrations. At $10,000 \text{ kg/cm}^2$ the

magnitude of the shift is much larger than the shift with temperature at atmospheric pressure. Comparison of Figures (8-25), (8-26) and (8-27) shows that the maxima shift increases with rising temperature and is greatest at 75°C.

Since Dow⁽³⁵⁾ and Zolotikh⁽¹¹⁵⁾ found irregularities in the relative viscosity behaviour of liquid mixtures with strong inter-component forces, it might be expected that the relative viscosity behaviour of the ethanol-water mixtures would be irregular. Log relative viscosities at 50°C are plotted isobarically against composition in Figure (9-16) and log relative viscosities at 5,000 kg/cm² are plotted against composition at 30°C, 50°C and 75°C in Figure (9-17). Although only four mixtures were studied there does not appear to be any marked irregularities in the isobaric relative viscosity-concentration behaviour at high pressures. The high pressure relative viscosity curves at 30°C and 75°C are similar to Figure (9-16). The isotherms in Figure (9-17) intersect for a mixture of approximately 18 mole % ethanol. This point of intersection arises because at 5,000 kg/cm² the relative viscosity of water increases between 30°C and 75°C, whereas for ethanol it decreases.

FIG.9-16. Isobaric Viscosity Behaviour of the Ethanol-Water System.

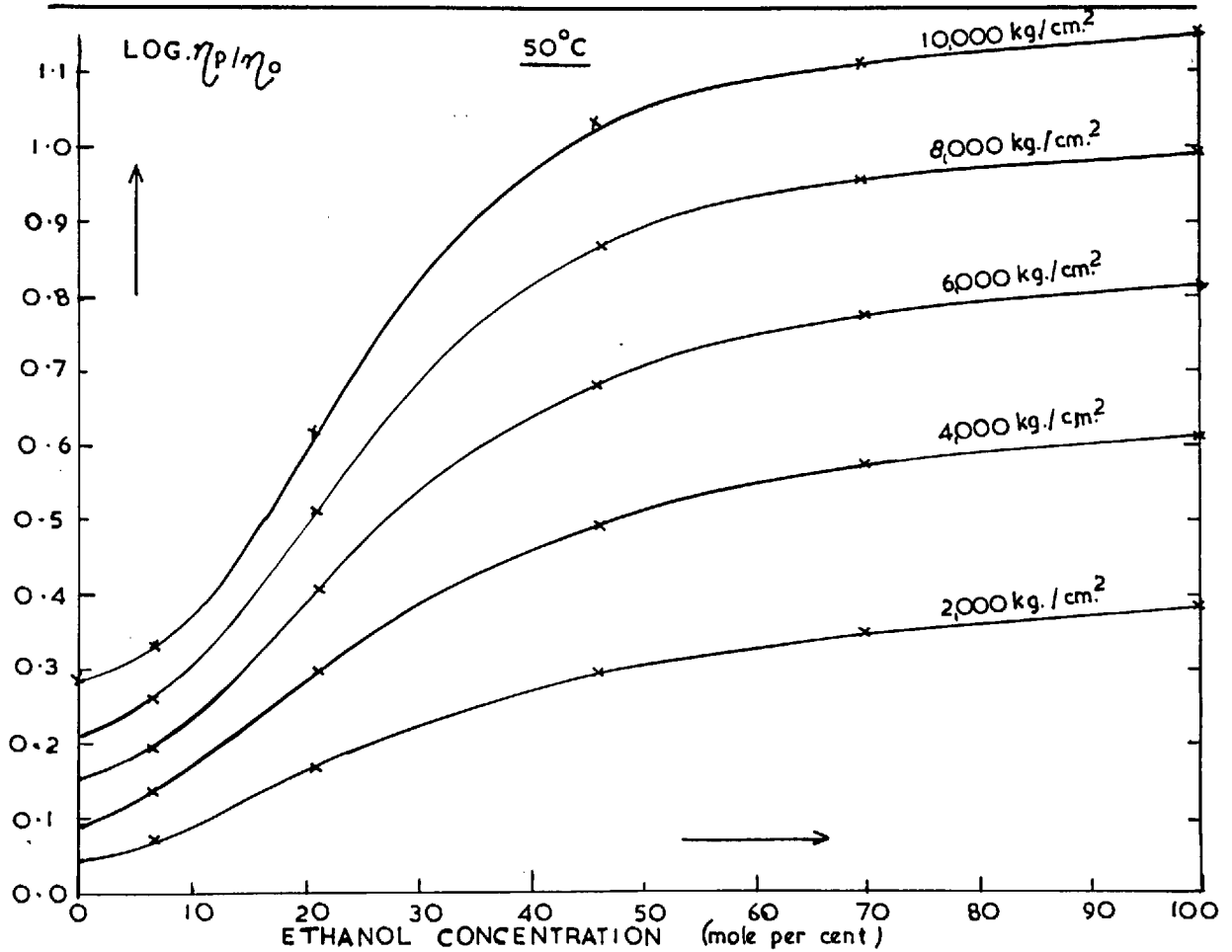
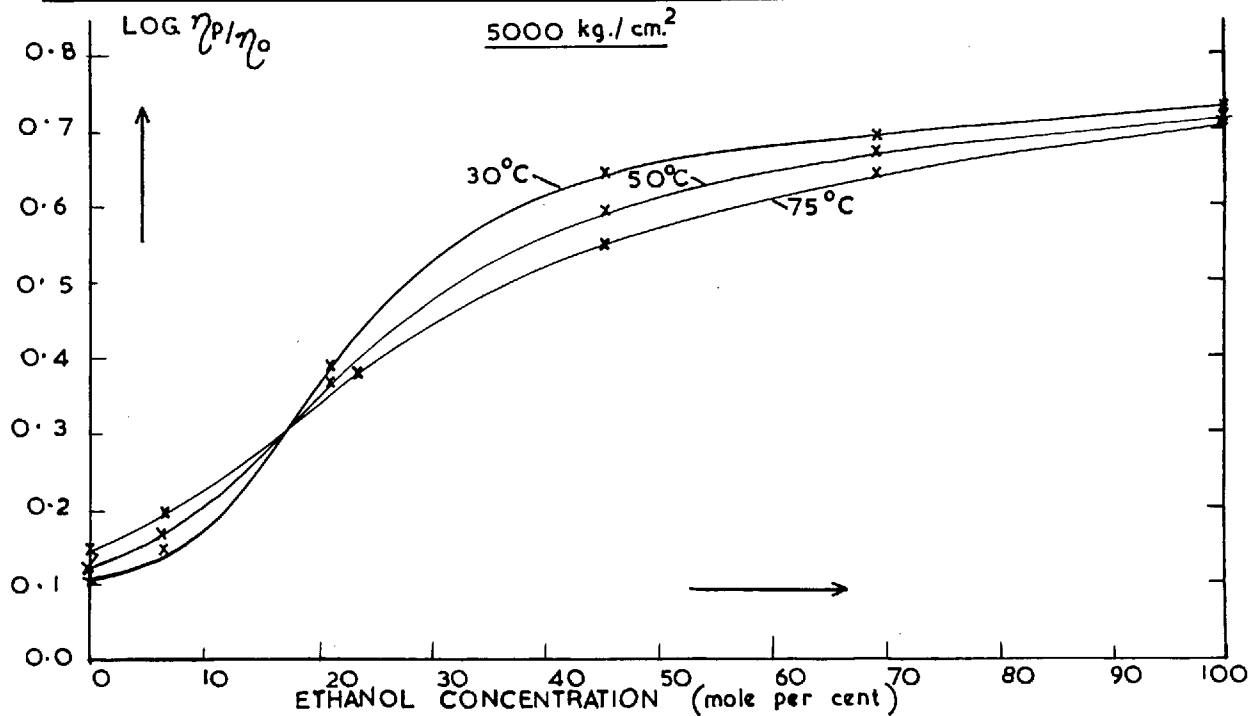


FIG.9-17. Isothermal Viscosity Behaviour of Ethanol-Water System.



There is a large contraction in volume on mixing ethanol and water that reflects the strong interaction between the molecules and the rearrangement of the H-bonded structures that exist in the pure components. Although infra-red spectroscopy has been of value in the study of the structure of water and ethanol, it provides little information about the binary mixture, since only broad unresolvable absorption bands are obtained⁽⁴³⁾.

In a recent review of the structural properties of alcohol-water mixtures⁽⁴³⁾ it is suggested that the range of concentrations are conveniently subdivided into an 'essentially aqueous' region and an 'alcohol-rich' region. At low temperatures the structure of the essentially aqueous region will depend on the interaction of the ethanol and water molecules and on the type of bonded structure that exists in pure water.

The large contraction in volume on mixing ethanol and water supports the hydrate model of water structure, (section 3.2(c)), since it is considered that ethanol molecules may be interstitially dissolved within the clustered networks without interacting with the networks. In addition to the maxima in the viscosity of the ethanol-water system, maxima are also shown in the 'essentially aqueous' region by velocity

of sound and sound absorption data. It is difficult to see how these effects can arise from interstitially dissolved ethanol molecules, and it is considered that they are better explained if the ethanol molecules form hydrogen bonds to the water molecules at the surface of the clusters. These structures are pictured as 'hairy' clusters with a core of tetrahedrally-bonded H_2O molecules and with EtOH molecules hydrogen bonded to surface molecules.

Thermodynamic excess functions indicate that during the preparation of 'alcohol-rich' mixtures there is dissociation of one component and strong intercomponent attractions⁽⁴³⁾. There is strong evidence that in this region the water molecules act as centres of association. The bonded structures are thought to consist of four linear hydrogen bonded ethanol chains attached by hydrogen bonds to a water molecule.

The viscosity behaviour of the ethanol-water system may be explained in a qualitative manner on the basis of the proposed structures. If an excess viscosity, η^E is defined by,

$$\eta^E = \eta - (1 - x)\eta_{\text{H}_2\text{O}} - x\eta_{\text{EtOH}}$$

where x is the molar concentration of ethanol in the mixture, then for

the ethanol-water system, η^E is always positive. It is suggested that these positive deviations arise partly because of increased association of the molecules and partly because of the increased complexity of shape of the bonded structures. The maxima in the viscosity-composition curve is considered to arise when the interaction between the different bonded structures is largest. It is doubtful if the structural changes with composition will be . . sharp, and more probably there will be a gradual transition with increasing EtOH concentration from 'hairy' clusters and interstitial association, to the water-centred structures.

The effect of increasing temperature is known to decrease the degree of H-bonding in both water and ethanol. It is considered that there is a similar breakdown of the bonded structures in the mixtures and that the slight shift of the maximum with increasing temperature arises from a small difference in rate of breakdown for the various structures.

The effect of raising the pressure is to cause some breakdown of the bonded structures in the 'essentially aqueous' region and an increase in the water-centred associated structures. These opposing effects will lead to a shift in the relative concentrations of the various

structures for a particular mixture at a constant temperature and hence to a pressure dependent change in the viscosity maxima.

The smaller shift at low temperatures probably arises from differences in the rates of structure formation and structure breakdown with temperature.

9.5 Conclusions.

- (i) There exists a range of velocities for an unguided cylinder falling in a tube within which the fall of the cylinder is stable and reproducible. This range corresponds to a relative viscosity change of about 10 for instruments similar to the one described.
- (ii) The performance of falling cylinder viscometers is improved by employing an eddy current timing system and by the removal of sinker guiding pins from the regions of maximum fluid flow.
- (iii) At high pressures the relative viscosity of heavy water is generally less than that of water at the same temperature, the difference being greatest at low temperatures. This effect is considered to arise from small differences in the degree of association in the liquids.
- (iv) There is a large rotational contribution to momentum transfer

in water which is independent of pressure but decreases with rising temperature.

(v) New measurements have been made of the viscosity of benzene, methanol and ethanol up to $10,000 \text{ kg/cm}^2$ at 30°C , 50°C and 75°C . These data are in agreement within experimental error with the results of Bridgman at 30°C and 75°C .

(vi) Viscosity data have been obtained for the ethanol-water system at 30°C , 50°C and 75°C for a range of concentrations and at pressures up to $10,000 \text{ kg/cm}^2$. The results indicate a shift in the viscosity maxima at high pressures towards greater ethanol concentrations.

APPENDIX I.

THEORY OF THE FALLING CYLINDER VISCOMETER.

1A.1 Viscosity Measurement.

In deriving an expression for the terminal velocity of the sinker in a falling cylinder viscometer the following assumptions are made,

- (i) The sinker is a simple cylinder of radius r_1 and length l falling axially at its terminal velocity v through a fluid of viscosity η contained in a closed vertical tube of internal radius r_2 .
- (ii) The fluid is Newtonian, homogeneous and incompressible.
- (iii) Flow conditions are perfectly laminar in all regions around the sinker.
- (iv) A constant pressure difference ΔP is maintained across the ends of the sinker and across the ends of the fluid annulus surrounding the sinker.
- (v) The forces on the cylinder due to the development of fluid flow at the entrance and at the exit of the fluid annulus are negligible.

When the cylinder is falling at its terminal velocity through the fluid, then the resultant force acting on the cylinder must be

zero, i.e.

$$-\pi r_1^2 \cdot \Delta P - 2\pi r_1 l \eta \left(\frac{du}{dr} \right)_{r=r_1} + w' = 0 \quad \dots (1A-1)$$

where w' is the buoyancy corrected weight of the sinker.

Considering the forces acting on an incremental annulus of fluid between the sinker and the tube, under steady flow conditions:-

$$\begin{aligned} & \pi \left((r + \delta r)^2 - r^2 \right) \cdot \Delta P + 2\pi(r + \delta r)l \left(\frac{du}{dr} + \frac{d^2u}{dr^2} \cdot \delta r \right) \\ & - 2\pi r l \eta \frac{du}{dr} = 0 \quad \dots (1A-2) \end{aligned}$$

where r = radius of the annulus

δr = thickness of the annulus

u = the velocity of the fluid at radius r relative to the tube.

In the limit as δr approaches zero, equation (1A-2) reduces to,

$$\frac{d}{dr} \left(r \cdot \frac{du}{dr} \right) = - \frac{\Delta P}{\eta l} \cdot r \quad \dots (1A-3)$$

Integrating equation (1A-3):

$$r \cdot \frac{du}{dr} = - \frac{\Delta P}{2\eta l} \cdot r^2 + A \quad \dots (1A-4)$$

where A is the constant of integration.

From equation (1A-4),

$$\left(\frac{du}{dr} \right)_{r=r_1} = - \frac{\Delta P}{2\eta l} r_1 + \frac{A}{r_1} \quad \dots\dots(1A-5)$$

Substituting (1A-5) in (1A-1) leads to

$$A = \frac{w'}{2\kappa l \eta}$$

thus from (1A-4),

$$\frac{du}{dr} = - \frac{\Delta P}{2\eta l} \cdot r + \frac{w'}{2\kappa l \eta} \cdot \frac{1}{r}$$

and on further integration,

$$u = - \frac{\Delta P}{4\eta l} \cdot r^2 + \frac{w'}{2\kappa l \eta} \cdot \ln r + B \quad \dots\dots(1A-6)$$

where B is the constant of integration.

Provided no slipping occurs at the liquid-solid interfaces,
then the following boundary conditions must be satisfied :-

$$(a) \quad u = 0, \quad r = r_2$$

$$(b) \quad u = -v, \quad r = r_1$$

which when substituted into equation (1A-6) leads to,

$$0 = - \frac{\Delta P}{4\eta l} \cdot r_2^2 + \frac{w'}{2\pi l\eta} \cdot \ln r_2 + B \quad \dots\dots(1A-7)$$

and

$$-v = - \frac{\Delta P}{4\eta l} \cdot r_1^2 + \frac{w'}{2\pi l\eta} \cdot \ln r_1 + B \quad \dots\dots(1A-8)$$

These equations are satisfied if:-

$$\Delta P = \frac{2w'}{\pi} \cdot \frac{\ln(r_2/r_1)}{(r_2^2 - r_1^2)} - \frac{4\eta l}{(r_2^2 - r_1^2)} \cdot v$$

and

$$B = \frac{w'}{2\pi l\eta} \left(\frac{r_2^2 \ln(r_2/r_1)}{(r_2^2 - r_1^2)} - \ln r_2 \right) - \frac{r_2^2 v}{(r_2^2 - r_1^2)}$$

Hence from equation (1A-6)

$$u = \frac{w'}{2\pi l\eta} \cdot \frac{(r_2^2 - r^2) \ln(r_2/r_1)}{(r_2^2 - r_1^2)} + \frac{w'}{2\pi l\eta} \cdot \ln(r/r_2) - \frac{(r_2^2 - r^2)v}{(r_2^2 - r_1^2)} \quad \dots\dots(1A-9)$$

The velocity of the fluid relative to the sinker is $(u + v)$, and thus the total volume of fluid flowing through the sinker annulus per unit time, Q , equals

$$2\pi \int_{r_1}^{r_2} r \cdot (u + v) \cdot dr$$

but $Q = \pi r_2^2 v$

since the terminal velocity of the sinker is v , and so,

$$\pi r_2^2 v = 2\pi \int_{r_1}^{r_2} r \cdot (u + v) \cdot dr \quad \dots\dots (1A-10)$$

Substituting for u from equation (1A-9), integrating and rearranging leads to,

$$\eta = \frac{w'}{2\pi l} \left(\ln(r_2/r_1) - \frac{(r_2^2 - r_1^2)}{(r_2^2 + r_1^2)} \right) \cdot \frac{1}{v}$$

If the terminal velocity of the sinker is determined by measuring the time of fall of the sinker, t , over a distance L , then,

$$v = \frac{L}{t}$$

and consequently,

$$\eta = \frac{w'}{2\pi lL} \cdot \left(\ln(r_2/r_1) - \frac{(r_2^2 - r_1^2)}{(r_2^2 + r_1^2)} \right) \cdot t \quad \dots\dots (1A-11)$$

For a perfect cylinder,

$$w' = \pi r_1^2 l (\rho_s - \rho_f) \cdot g$$

Hence

$$\eta = k' \cdot (\rho_s - \rho_f) \cdot t$$

where

$$k' = \frac{r_1^2 g}{2L} \cdot \left(\begin{array}{c} \ln(r_2/r_1) - \frac{(r_2^2 - r_1^2)}{(r_2^2 + r_1^2)} \end{array} \right)$$

Substituting for the tube radius in terms of the sinker radius and radial clearance c , since

$$r_2 = r_1 + c$$

$$k' = \frac{r_1^2 g}{2L} \cdot \left(\begin{array}{c} \ln\left(\frac{r_1 + c}{r_1}\right) - \frac{((r_1 + c)^2 - r_1^2)}{((r_1 + c)^2 + r_1^2)} \end{array} \right)$$

which may be rewritten,

$$k' = \frac{r_1^2 g}{2L} \cdot \left(\begin{array}{c} \ln\left(1 + \frac{c}{r_1}\right) - \frac{\left(\frac{c}{r_1}\right) \cdot \left(1 + \frac{1}{2} \cdot \frac{c}{r_1}\right)}{\left(1 + \frac{c}{r_1} + \frac{1}{2} \cdot \frac{c^2}{r_1^2}\right)} \end{array} \right)$$

expanding in terms of c/r_1 , since $c/r_1 \ll 1$, it follows that,

$$k' = \frac{r_1^2 g}{2L} \cdot \left(\begin{array}{c} \frac{1}{3} \cdot \left(\frac{c}{r_1}\right)^3 - \frac{1}{2} \left(\frac{c}{r_1}\right)^4 + \dots \end{array} \right)$$

and hence to a first approximation,

$$\eta = \frac{(\rho_s - \rho_f) g}{6L} \cdot \frac{c^3}{r_1} \cdot t \quad \dots\dots(1A-12)$$

1A.2 Density Estimation.

The object of employing two sinkers in a viscometer is to measure liquid densities at high pressures with sufficient accuracy for buoyancy corrections to be applied to sinker fall times. If the fall times of a high density and a low density sinker are t_{so} and t_{ao} at atmospheric pressure in a liquid viscosity η_o , then from equation (5-6),

$$\eta_o = k_{so} \cdot \frac{(\rho_{so} - \rho_{fo})}{\rho_{so}} \cdot t_{so} = k_{ao} \cdot \frac{(\rho_{ao} - \rho_{fo})}{\rho_{ao}} \cdot t_{ao} \quad \dots\dots(1A-13)$$

Similarly if the corresponding fall times at a constant pressure p are t_{sp} and t_{ap} then,

$$\eta_p = k_{sp} \cdot \frac{(\rho_{sp} - \rho_{fp})}{\rho_{sp}} \cdot t_{sp} = k_{ap} \cdot \frac{(\rho_{ap} - \rho_{fp})}{\rho_{ap}} \cdot t_{ap} \quad \dots\dots(1A-14)$$

Dividing (1A-14) by (1A-13),

$$\frac{\eta_p}{\eta_o} = \frac{k_{sp}}{k_{so}} \cdot \frac{(\rho_{sp} - \rho_{fp})}{(\rho_{so} - \rho_{fo})} \cdot \frac{\rho_{so}}{\rho_{sp}} \cdot \frac{t_{sp}}{t_{so}}$$

$$= \frac{k_{ap}}{k_{ao}} \cdot \frac{(\rho_{ap} - \rho_{fp})}{(\rho_{ao} - \rho_{fo})} \cdot \frac{\rho_{ao}}{\rho_{ap}} \cdot \frac{t_{ap}}{t_{ao}} \quad \dots\dots(1A-15)$$

The ratios

$$\frac{k_{sp}}{k_{so}} \quad \text{and} \quad \frac{k_{ap}}{k_{ao}}$$

may be calculated from the sinker and tube dimensions using equation (5-6A). The k-corrected time ratios are denoted by

$$(t_{sp}/t_{so})^* \quad \text{and} \quad (t_{ap}/t_{ao})^*.$$

Also, rewriting the atmospheric density ratios,

$$\frac{\rho_{so}}{\rho_{so} - \rho_{fo}} = c_{so}; \quad \frac{\rho_{ao}}{\rho_{ao} - \rho_{fo}} = c_{ao}$$

Equation (1A-15) simplifies to,

$$\frac{(\rho_{sp} - \rho_{fp})}{\rho_{sp}} \cdot \left(\frac{t_{sp}}{t_{so}} \right)^* \cdot c_{so} = \frac{(\rho_{ap} - \rho_{fp})}{\rho_{ap}}$$

$$\cdot \left(\frac{t_{ap}}{t_{ao}} \right)^* \cdot c_{ao} \quad \dots\dots(1A-16)$$

Equation (1A-16) rearranged gives,

$$\rho_{fp} = \frac{\left(c_{so} \cdot \left(\frac{t_{sp}}{t_{so}} \right)^* - c_{ao} \cdot \left(\frac{t_{ap}}{t_{ao}} \right)^* \right)}{\left(\frac{c_{so}}{\rho_{sp}} \cdot \left(\frac{t_{sp}}{t_{so}} \right)^* - \frac{c_{ao}}{\rho_{ap}} \cdot \left(\frac{t_{ap}}{t_{ao}} \right)^* \right)} \quad \dots\dots(1A-17)$$

from which, knowing the fall times of two sinkers of different density, the fluid density may be calculated.

APPENDIX II.CALIBRATION DATA - Mk. I. VISCOMETER.2A.1 Stainless Steel Sinker.

Temp. °C	Liquid	Viscosity (c. p.)	Density ρ
99.88	H ₂ O	0.2842	0.9584
34.96	H ₂ O	0.7225	0.9941
19.99	H ₂ O	1.0050	0.9982
9.95	H ₂ O	1.3080	0.9997
25.06	H ₂ O	0.8937	0.9971
29.98	H ₂ O	0.8007	0.9957
25.04	D ₂ O	1.1000	1.1044
30.00	C ₅ H ₁₂	0.2118	0.6162
49.94	H ₂ O	0.5494	0.9881
50.02	D ₂ O	0.6531	1.0963
30.01	D ₂ O	0.9767	1.1030
75.03	D ₂ O	0.4434	1.0820
100.09	D ₂ O	0.3279	1.0650
20.00	D ₂ O	1.2514	1.1053
20.02	D ₂ O	1.2512	1.1052
50.00	H ₂ O	0.5494	0.9881
81.85	H ₂ O	0.3486	0.9710
94.58	H ₂ O	0.3008	0.9622
69.95	H ₂ O	0.4061	0.9778
29.98	H ₂ O	0.8007	0.9957
29.98	C ₇ H ₁₆	0.3619	0.6744
29.98	C ₁₅ H ₃₂	2.2597	0.7614
74.96	H ₂ O	0.3799	0.9749
30.01	H ₂ O	0.8007	0.9957
24.92	H ₂ O	0.8937	0.9971
10.10	D ₂ O	1.6761	1.1060

Sinker Density, ρ_s	Fall Time t	$\text{Log}_{10} t$	$\frac{t^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$
7.9256	13.098	1.117	40.41
7.9498	32.819	1.516	39.73
7.9556	45.620	1.659	39.71
7.9592	59.598	1.775	39.86
7.9535	40.624	1.609	39.76
7.9517	36.523	1.562	39.89
7.9535	50.528	1.703	39.56
7.9517	9.347	0.971	40.70
7.9443	25.062	1.399	39.91
7.9443	30.407	1.483	40.10
7.9517	44.967	1.653	39.64
7.9351	20.449	1.311	39.77
7.9256	15.228	1.183	40.10
7.9556	57.411	1.759	39.51
7.9556	57.756	1.762	39.75
7.9443	25.055	1.399	39.90
7.9325	15.994	1.204	40.19
7.9277	13.850	1.141	40.36
7.9368	18.547	1.268	39.99
7.9517	36.462	1.562	39.83
7.9517	16.199	1.209	40.96
7.9517	99.583	1.998	39.84
7.9351	17.484	1.243	40.31
7.9517	36.485	1.562	39.85
7.9535	40.867	1.611	40.00
7.9592	77.301	1.888	39.73

2A.1 Stainless Steel Sinker - continued.

Temp. °C	Liquid	Viscosity (c. p.)	Density ρ_f
74.98	Me OH	0.288	0.7332
74.98	EtOH	0.460	0.7420
50.00	EtOH	0.700	0.7635
49.97	C ₆ H ₆	0.435	0.8470
74.92	C ₆ H ₆	0.333	0.8190
30.01	H ₂ O-EtOH	1.395	0.9686
49.97	H ₂ O-EtOH	1.066	0.8437
30.02	H ₂ O-EtOH	1.780	0.8603
30.00	H ₂ O-EtOH	1.398	0.8197
50.00	H ₂ O-EtOH	0.899	0.8016
25.01	C ₅ H ₁₂	0.217	0.6203
25.01	C ₆ H ₁₄	0.316	0.6697
24.97	C ₇ H ₁₆	0.450	0.7097
24.98	C ₈ H ₁₈	0.509	0.6995
25.01	C ₁₀ H ₂₂	0.855	0.7259
24.99	C ₅ H ₁₁ OH	1.236	0.8484
24.96	C ₄ H ₉ OH	2.603	0.8058
25.00	C ₈ H ₁₇ OH	7.666	0.8219

Sinker Density, ρ_s	Fall Time t	$\text{Log}_{10} t$	$\frac{t^* \cdot (\rho_s - \rho_f)}{\eta}$
7.9351	13.055	1.116	41.08
7.9351	20.555	1.313	40.51
7.9443	30.845	1.489	39.80
7.9443	19.609	1.292	40.24
7.9351	15.055	1.178	40.48
7.9517	63.061	1.800	39.69
7.9443	47.237	1.674	39.56
7.9517	78.597	1.895	39.37
7.9517	61.652	1.790	39.53
7.9443	39.566	1.597	39.56
7.9535	9.905	0.996	42.07
7.9535	14.152	1.151	41.00
7.9535	19.975	1.301	40.40
7.9535	22.492	1.352	40.25
7.9535	37.752	1.577	40.10
7.9535	55.063	1.741	39.80
7.9535	114.957	2.061	39.69
7.9535	339.789	2.531	39.74

2A.2 Aluminium Alloy Sinker.

Temp. °C	Liquid	Viscosity (c. p.)	Density ρ_f
30.0	C ₅ H ₁₂	0.212	0.6162
25.0	C ₈ H ₁₇ OH	7.666	0.8219
25.0	C ₄ H ₇ OH	2.603	0.8058
25.0	C ₁₀ H ₂₂	0.855	0.7259
25.0	C ₇ H ₁₆	0.450	0.7097
25.0	C ₅ H ₁₂	0.217	0.6203
25.0	C ₆ H ₁₄	0.301	0.6815
25.0	C ₉ H ₂₀	0.660	0.7166
25.0	C ₅ H ₁₁ OH	1.182	0.8376
30.0	H ₂ O-EtOH	1.395	0.9686

Sinker Density, ρ_s	Fall Time t	$\text{Log}_{10} t$	$\frac{t^*}{\eta} \cdot \frac{(\rho_s - \rho_f)}{\rho_s}$
3.1978	12.501	1.097	47.65
3.1988	475.025	2.677	46.04
3.1988	159.659	2.203	45.89
3.1988	51.278	1.701	46.34
3.1988	27.023	1.432	46.69
3.1988	12.909	1.111	47.94
3.1988	18.075	1.257	47.24
3.1988	39.390	1.595	76.31
3.1988	70.994	1.851	46.21
3.1978	92.820	1.968	46.38

APPENDIX III.

RESULTS.

3A.1 Specification of Test Liquids.

(a) Water.

Distilled water from a Manesty laboratory still was deionized with a Deeminac ion-exchange filter before use. Its refractive index was measured with an Abbé refractometer and found to be,

$$n_D^{25.0} = 1.3327 \pm .0001$$

as compared with the accepted value⁽⁵⁰⁾,

$$n_D^{25.0} = 1.33287$$

(b) Heavy Water (Deuterium Oxide).

Deuterium oxide of purity not less than 99.7 gm. D₂O per 100 gm. and density,

$$\rho_{D_2O}^{20} = 1.10515$$

was supplied by Imperial Chemical Industries Limited.

The refractive index was,

$$n_D^{25.0} = 1.3281$$

compared with⁽⁵⁰⁾,

$$n_D^{20.0} = 1.32844$$

(c) Benzene.

The purest commercially available grade, 'Benzene-Special for M. W. determinations', (freezing temperature not less than 5.4°C), was supplied by The British Drug Houses Limited (B. D. H.)

The experimental value of,

$$n_D^{25.0} = 1.4980$$

is in agreement with two recent results^{(23) (99)} which give,

$$n_D^{25.0} = 1.49792$$

(d) Methanol.

'Methanol-Special for Spectroscopy' was used as supplied by B. D. H.

The refractive index was,

$$n_D^{25.0} = 1.3270$$

(e) Ethanol.

'Ethanol absolute-Special for Spectroscopy' was supplied by B. D. H.

Because of ethanol's hygroscopic nature, the filling vessel was charged with liquid in an airtight dry box. The measured refractive index was,

$$n_D^{25.0} = 1.3593$$

This single value is in excellent agreement with the results of Scott⁽⁹⁷⁾ for concentrated ethanol-water mixtures,

$$99.73\% \text{ (by weight) EtOH} \quad n_D^{25.0} = 1.35923$$

$$99.53\% \text{ (by weight) EtOH} \quad n_D^{25.0} = 1.35926$$

$$98.94\% \text{ (by weight) EtOH} \quad n_D^{25.0} = 1.35958$$

It is concluded that the purity of ethanol used was greater than 99.0% and probably better than 99.3%.

(f) Ethanol-Water Mixtures.

The mixtures were prepared directly from the pure components. The refractive indices of the mixtures were measured at the conclusion of the measurements, and the results are given in Table (3A-1).

TABLE (3A-1)

Mixture	Refractive Index $n_D^{25.0}$	Estimated EtOH concentration in mixture
I	1.3435	16.4% $\pm$ 0.2%
II A	1.3569	41.5% $\pm$ 0.4%
II B	1.3581	45.1% $\pm$ 0.4%
III	1.3628	72.5% $\pm$ 1.0%
IV	1.3629	80.0% $\pm$ 1.0%

Scott's data⁽⁹⁷⁾ for $n_D^{25.0}$ against concentration in ethanol-water mixtures were used to estimate the mixture compositions quoted in the Table (3A-1). These values may be compared with the concentrations obtained from the relative density measurements which are given in Chapter VIII. The agreement is good for mixtures I and II, but not so good for mixtures III and IV. Scott's results show that $n_D^{25.0}$ goes through a point of inflection within the range of EtOH concentrations from 75% to 80%, and that in this region changes in $n_D^{25.0}$ are small. Consequently, the accuracy of the estimated concentrations is lower in this range assuming the error in $n_D^{25.0}$ remains constant.

3A.2 Density of Sinkers.

The density of the composite sinkers employed with the Mk. I viscometer are calculated from the densities and weights of the component parts. Denoting the densities of the components as ρ_a and ρ_b and the corresponding weights as w_a and w_b , then the density of the assembled sinker is,

$$\rho_s = \frac{w_a + w_b}{\left(\frac{w_a}{\rho_a} + \frac{w_b}{\rho_b}\right)} \quad \dots\dots (3A-1)$$

For the stainless steel sinker,

Weight of EN 58 JM in sinker	= 3.6164 g.
Weight of soft iron in sinker	= 0.5230 g.
Density of EN 58 JM at 20°C (Measured)	= 7.9652 g/cm ³
Density of soft iron at 20°C ⁽⁷⁴⁾	= 7.8740 g/cm ³

and for the aluminium alloy sinker,

Weight of RR 77 in sinker	= 1.9522 g.
Weight of soft iron in sinker	= 0.4886 g.
Density of RR 77 at 20°C (Measured)	= 2.7858 g/cm ³
Density of soft iron at 20°C	= 7.8740 g/cm ³

From equation (3A-1) and the above data, the densities of the stainless steel and aluminium alloy sinkers at 20°C and atmospheric pressure are 7.9556 g/cm³ and 3.1997 g/cm³ respectively.

The densities of the sinkers were calculated at other temperatures and pressures from the above data and the volume compressibility and linear expansion coefficients of the component parts. The initial volume compressibilities (β_{SS} and β_{AL}) of EN 58 JM and RR 77 were calculated from values of Young's modulus, E , and Poisson's ratio, σ , which had been determined at the National Physical Laboratory on samples of the materials using an ultrasonic technique. The results of these measurements were,

EN 58 JM	$E = 19.55 \cdot 10^{11}$ dynes/cm ² , $\sigma = 2.92$
RR 77	$E = 7.22 \cdot 10^{11}$ dynes/cm ² , $\sigma = 3.40$

β_{SS} and β_{AL} were calculated from E and σ ⁽⁸⁴⁾ giving,

$$\begin{array}{ll} \text{EN 58 JM} & \beta_{SS} = 6.26 \cdot 10^{-7} / \text{kg/cm}^2 \\ \text{RR 77} & \beta_{AL} = 13.04 \cdot 10^{-7} / \text{kg/cm}^2 \end{array}$$

For soft iron⁽¹⁷⁾,

$$\beta_{SI} = 5.80 \cdot 10^{-7} / \text{kg/cm}^2$$

Coefficient of linear expansion,

$$\begin{array}{ll} \text{EN 58 JM}^{(74)} & \alpha_{SS} = 1.60 \cdot 10^{-5} / ^\circ\text{C} \\ \text{RR 77 (supplier's figure)} & \alpha_{AL} = 2.00 \cdot 10^{-5} / ^\circ\text{C} \\ \text{Soft iron}^{(74)} & \alpha_{SI} = 1.26 \cdot 10^{-5} / ^\circ\text{C} \end{array}$$

The density of EN 58 JM at temperature, T°C and pressure, p, kg/cm² is given by,

$$\rho_{SS} = \frac{7.9652}{(1 + 3 \times 1.6 \times 10^{-5}(T - 20))(1 - 6.26 \times 10^{-7}p)} \quad \dots\dots (3A-2)$$

RR 77,

$$\rho_{AL} = \frac{2.7858}{(1 + 3 \times 2.0 \times 10^{-5}(T - 20))(1 - 13.04 \times 10^{-7}p)} \quad \dots\dots (3A-3)$$

Soft iron,

$$\rho_{SI} = \frac{7.8740}{(1 + 3 \times 1.26 \times 10^{-5}(T - 20))(1 - 5.80 \times 10^{-7}p)} \quad \dots\dots (3A-4)$$

The density of a sinker at any temperature and pressure is

calculated from equations (3A-2), (3A-3) and (3A-4) in conjunction with equation (3A-1).

Errors in calculated densities may arise from errors in the compressibility data for two reasons. Firstly the coefficient of compressibility is calculated from the elastic constants, and secondly it is assumed to be constant over the entire pressure range. Bridgman⁽¹⁷⁾ found that the coefficient of volume compressibility decreases with increasing pressure and his data for iron and aluminium show that at $10,000 \text{ kg/cm}^2$ the correction is about 3.8%.

The maximum error in the calculated sinker densities is estimated to be $\pm 2\%$.

3A.3 Density and Compressibility of Test Liquids.

In order that the buoyancy correction may be evaluated at each pressure, the density and compressibility of the liquids studied must be known.

(a) Water and Deuterium Oxide.

The density data for water and heavy water are summarised in Figures (3A-1) and (3A-2). These curves were constructed by interpolation of Bridgman's⁽²⁰⁾ results for water and heavy water over

FIG. 3A -1. Density of Water.

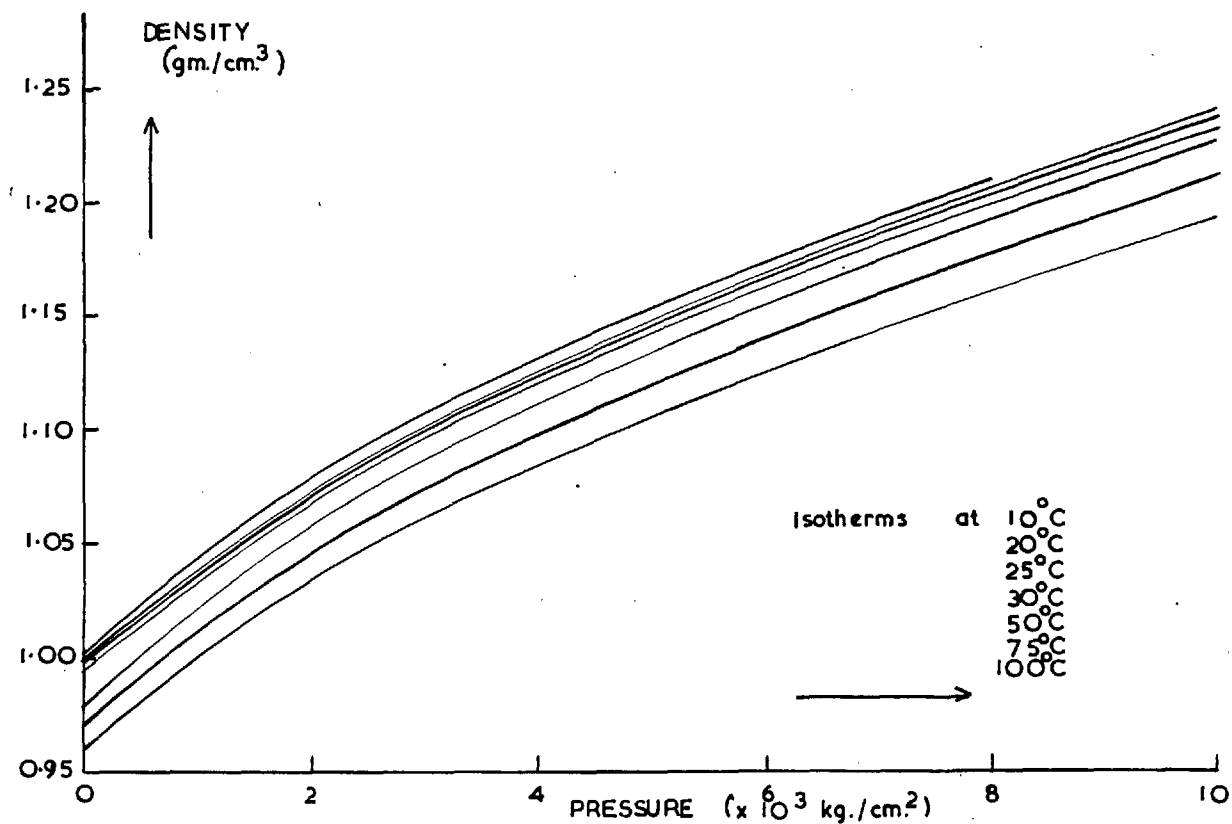
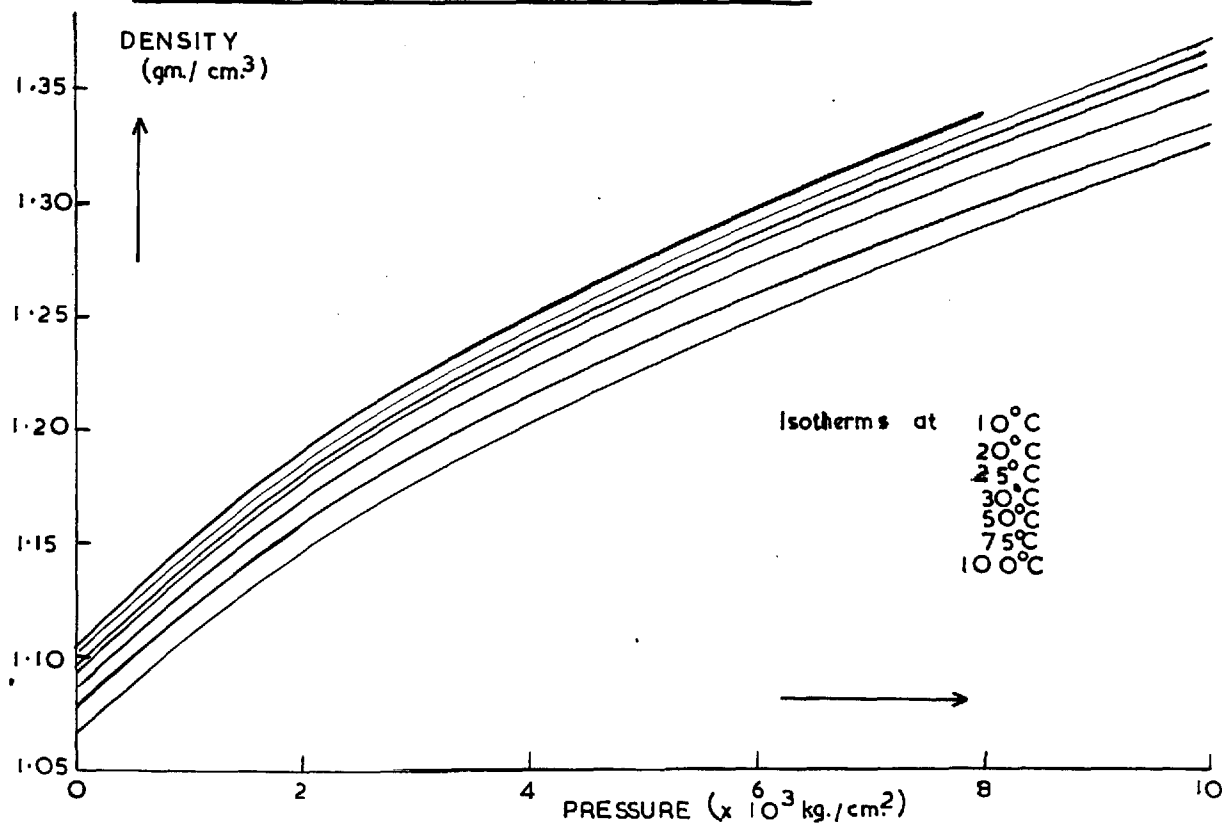


FIG. 3A -2. Density of Heavy Water.



the entire liquid range and up to 12,000 atmospheres.

(b) Benzene.

Bridgman⁽¹⁹⁾ has measured the density of benzene up to its freezing pressure at 50°C and 95°C. His results for 50°C are given in Figure (3A-3) together with assumed density curves at 30°C and 75°C.

(c) Methanol and Ethanol.

Bridgman⁽¹⁶⁾ has also measured the densities of methanol and ethanol at a number of temperatures, and his results have been interpolated to obtain the curves given in Figures (3A-4) and (3A-5).

(d) Ethanol-Water Mixtures.

The densities of the four binary mixtures at atmospheric pressure were determined at 30°C and 50°C, using standard techniques. The mixture densities at 75°C were estimated by interpolating the results of Schwers (1909), as quoted by Timmermans⁽¹⁰⁰⁾. Curves for 30°C, 50°C and 75°C are shown in Figure (3A-6) together with the measured densities at 30°C and 50°C.

Since the density of ethanol-water mixtures have not been measured above 1,500 atmospheres, the compressibility of the mixtures was assumed to vary linearly with composition. The

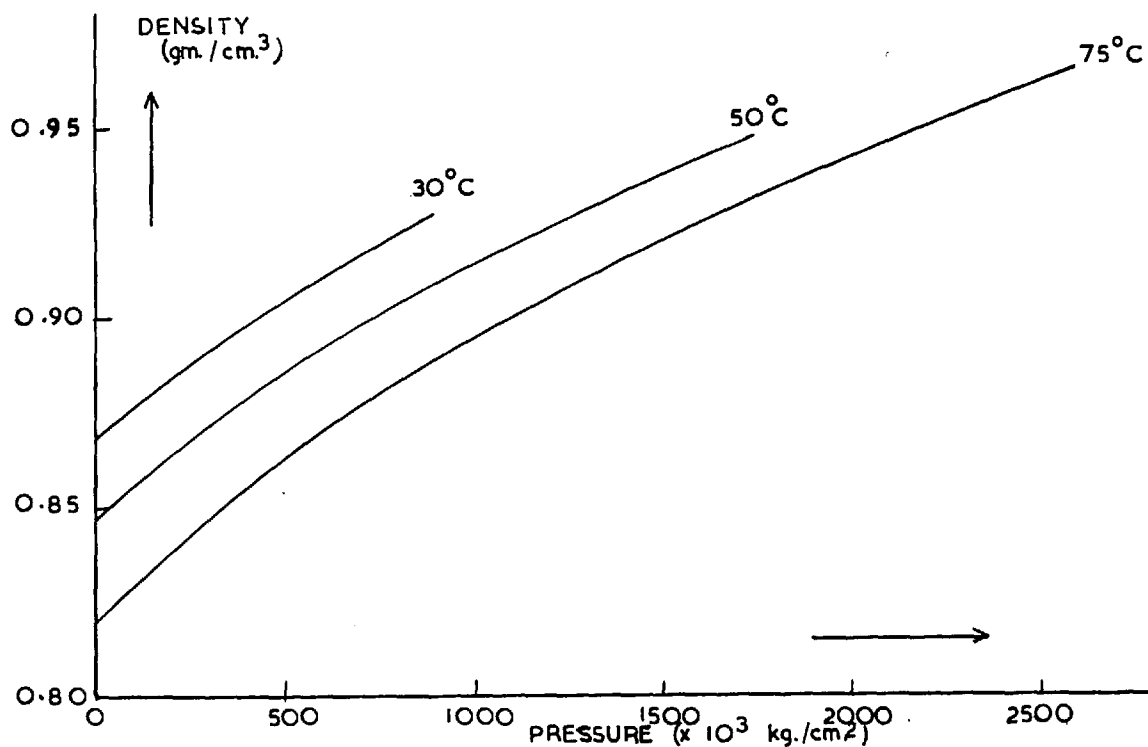
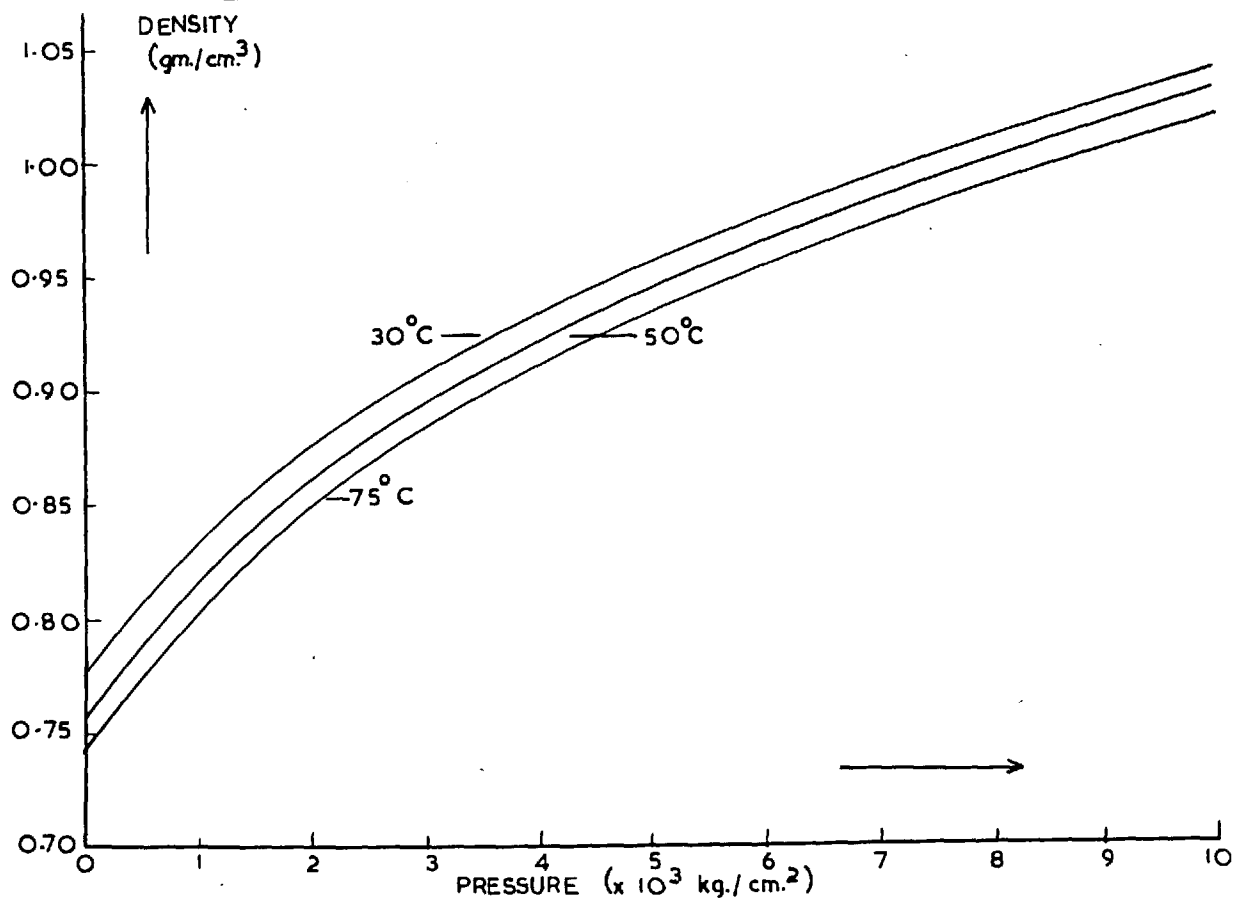
FIG. 3A-3. Density of Benzene.FIG. 3A-4. Density of Methanol.

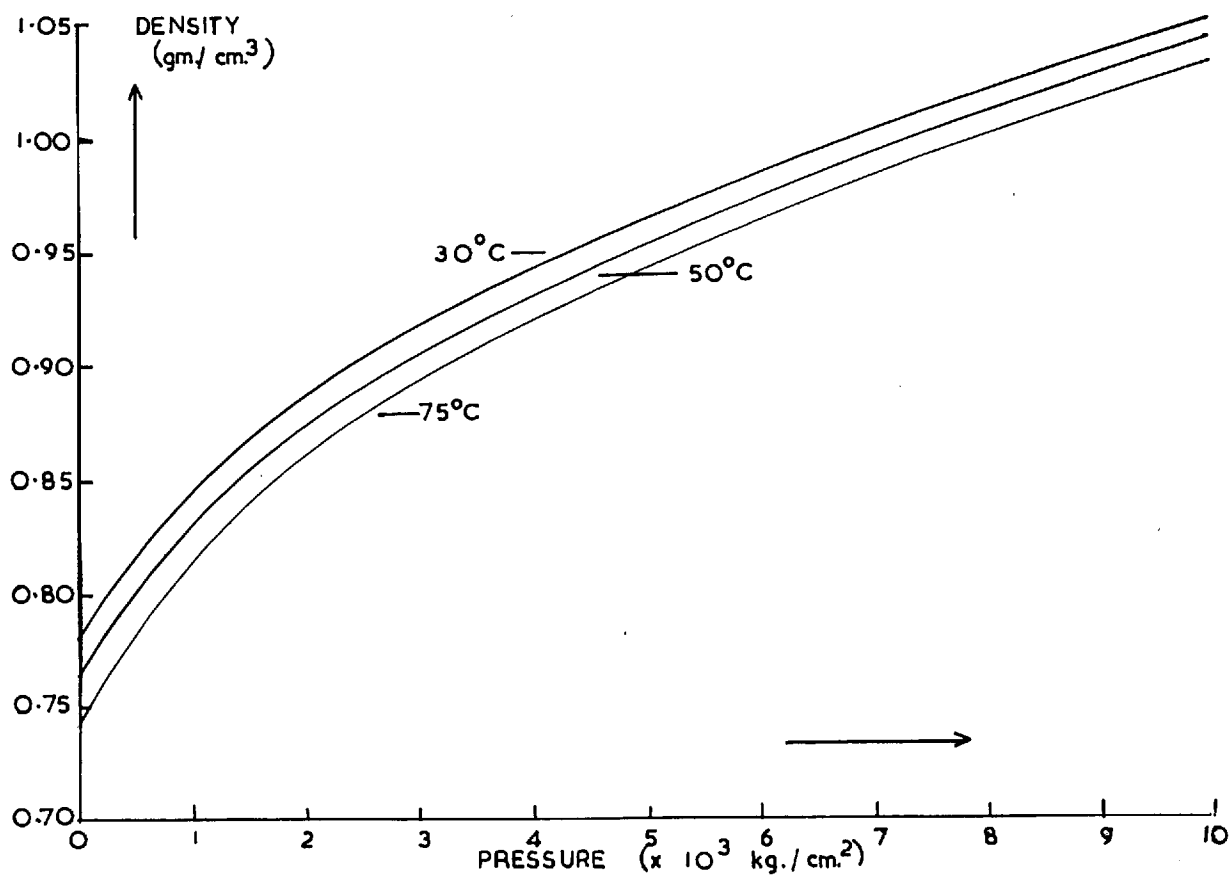
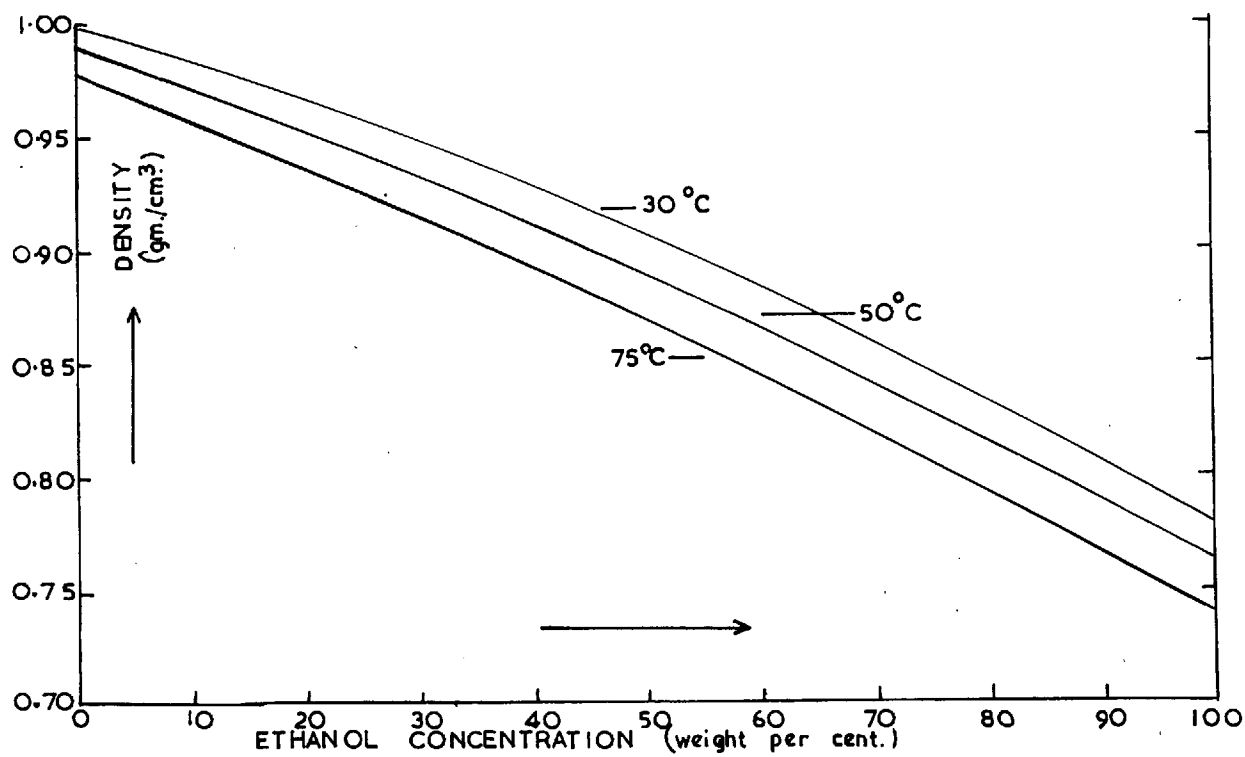
FIG. 3A-5. Density of Ethanol.**FIG. 3A-6. Density of Ethanol-Water Mixtures.**

FIG. 3A-7. Density of Ethanol - Water Mixtures - 30°C

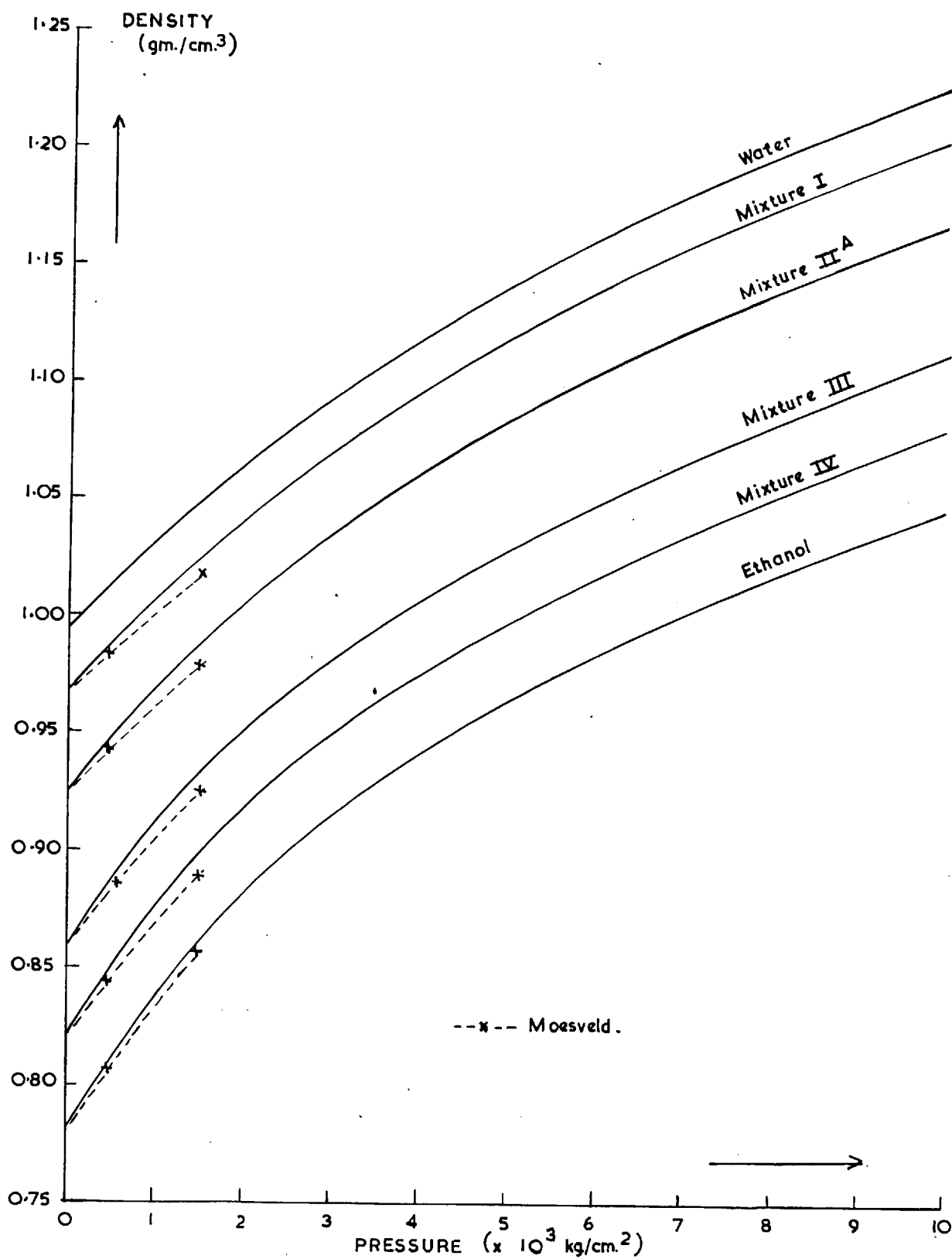


FIG. 3A-8. Density of Ethanol-Water Mixtures - 50°C. ²⁸²

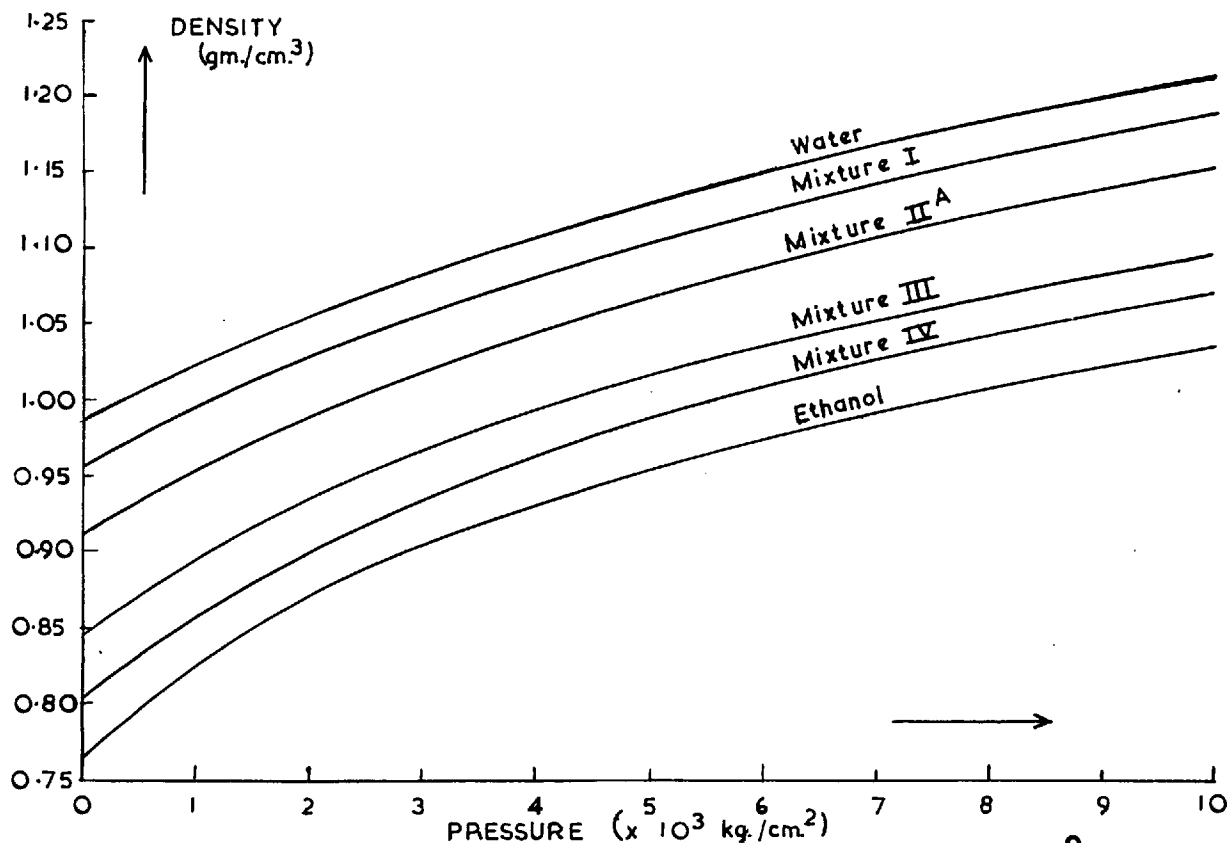
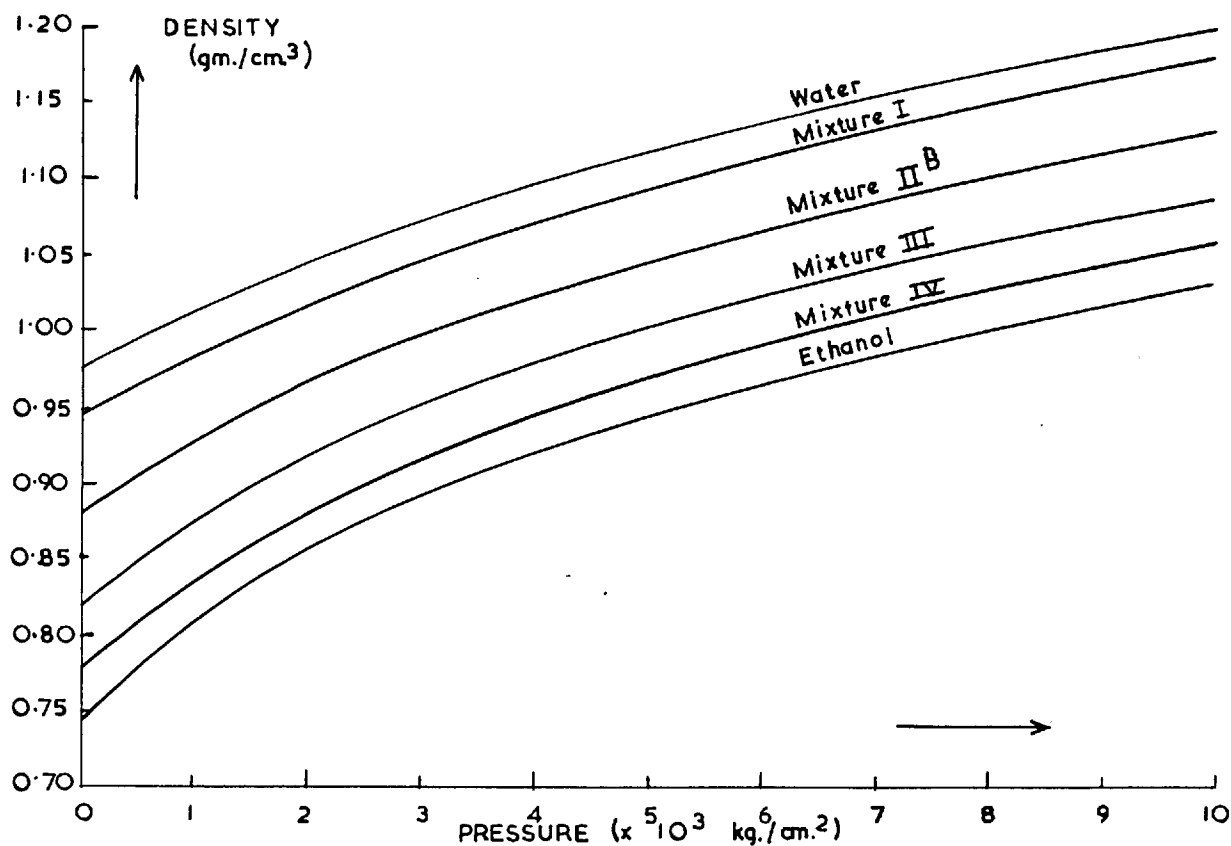


FIG. 3A-9. Density of Ethanol-Water Mixtures - 75°C.



buoyancy correction factors were calculated from the density curves shown in Figures (3A-7), (3A-8), and (3A-9).

The results of Moesveld⁽⁷⁸⁾ at 25°C, and up to 1,500 atmospheres, interpolated for each mixture, are compared in Figure (3A-7) with the assumed density variations at 30°C. Although these densities are lower than the assumed values, by about 1% at 1,500 kg/cm², it is unlikely that the difference exceeds 5% at 10,000 kg/cm². (The error in η_p/η_o as a result of a 5% error in ρ_{fp} was shown in Chapter V to be 0.12%). Moesveld's results show that the compressibility does not vary linearly with concentration, but passes through a minimum. Thus densities calculated from these results will be less than the assumed densities.

3A.4 Calculation of Results.

Full details of the procedure for making a viscosity determination are given in Chapter V III, together with notes on the actual measurements required. A typical set of experimental results are given in Table (3A-2). The results were obtained for heavy water at 100°C; for brevity the individual readings required for the calculation of the coil resistance and the mean fall times are not included. The

TABLE (3A-2)

1	2	3	4
Bridge Temp. °C	Coil Temp. (mV)	Coil Resistance (Ω)	Computed Pressure (kg/cm ²)
24.97 25.12	1.157 1.158	44.561500 44.561250	1.0
24.98 24.90	1.173 1.173	44.594175 44.593925	299.0
24.88 24.96	1.190 1.193	44.636000 44.635825	682.9
24.96 24.92	1.200 1.194	44.749250 44.749200	1731.2
25.09 25.07	1.182 1.178	44.867875 44.867825	2333.8
24.99 24.98	1.177 1.176	44.975300 44.975250	3830.2
25.12 25.12	1.156 1.159	45.097375 45.097475	4968.9

5	6	7	8	9
Temp. Viscometer (°C)	Mean Time 1 (secs)	Mean Time 2 (secs)	$\frac{(\eta_p)}{(\eta_o)_1}$ Computed	$\frac{(\eta_p)}{(\eta_o)_2}$ Computed
100.09	15.228	15.034	1.0000	1.0000
100.10	15.657	15.431	1.0264	1.0246
100.10	16.212	15.950	1.0622	1.0592
100.10	17.604	17.346	1.1498	1.1476
100.12	19.153	18.852	1.2482	1.2444
100.10	20.578	20.250	1.3383	1.3340
100.10	22.302	21.961	1.4479	1.4443

TABLE (3A-2) - continued

1	2	3	4
Bridge Temp. °C	Coil Temp. (mV)	Coil Resistance (Ω)	Computed Pressures (kg/cm ²)
25.08	1.157	45.236375	6262.2
25.11	1.157	45.236375	
25.16	1.167	45.351400	7333.1
25.18	1.165	45.351300	
25.05	1.168	45.470425	8443.4
25.10	1.166	45.470275	
24.94	1.178	45.583525	9497.9
24.96	1.176	45.583250	
25.15	1.107	44.560100	1.0
25.35	1.105	44.559850	

5	6	7	8	9
Temp. Viscometer (°C)	Mean Time 1 (secs)	Mean Time 2 (secs)	$\frac{(\eta_p)}{(\eta_o)_1}$ Computed	$\frac{(\eta_p)}{(\eta_o)_2}$ Computed
100.08	24.410	24.091	1.5817	1.5813
100.08	26.255	26.863	1.6990	1.6956
100.08	28.296	27.804	1.8286	1.8402
100.10	30.308	29.963	1.9570	1.9590
100.07	15.270	15.075	1.0000	1.0000

computed values of pressure and relative viscosity for each observation are given in columns 4 and 9 respectively.

The results were calculated on a digital computer using for convenience two programs, one to calculate the pressure and the other the relative viscosities. Both programs are written in the 'Fortran IV' programming language.

(a) Pressure Computation.

The pressure computation program may be outlined as follows;

The input data for this program are the measurements of bridge temperature, coil temperature, and coil resistance. Corresponding to each pressure, there are two sets of readings obtained before and after the fall time measurements. The coil resistances are corrected to the bridge reference temperature of 25°C and the coil reference temperature of 0.850 mV using the corrections given by equations (6-1) and (6-2) respectively. The mean of each pair of the corrected coil resistance is calculated, and the base resistance of the coil is taken as the mean of the temperature corrected resistances obtained at atmospheric pressure. After the change in resistance, $\Delta\Omega$, has been calculated for each set of observations, the approximate pressures are computed assuming that $\Delta\Omega/p$ is independent of pressure and equal

to 1.08×10^{-4} ohm/kg/cm². Accurate values of the factor $\Delta\Omega/p$ are determined by substituting for the approximate pressures in equation (6-3) and final pressures are obtained by dividing the $\Delta\Omega$'s by the accurate values of $\Delta\Omega/p$.

(b) Relative Viscosity Computation.

The relative viscosity, η_p / η_o , is calculated with the aid of the known pressures and a second program. The input data for this program are the experimental values of temperature and the mean fall times, together with the estimated fluid density and the calculated pressures for each observation. The fall times are initially corrected to the nominal temperature of the isotherm. The dimensional correction factor is calculated for each pressure and applied, (equations (5-6) and (5-7)). The buoyancy correction factor,

$$\frac{(\rho_{sp} - \rho_{fp})}{\rho_{sp}} \cdot \frac{\rho_{so}}{(\rho_{so} - \rho_{fo})}$$

is evaluated for each pressure. ρ_{sp} and ρ_{so} are calculated as indicated in section 3 A.2 while ρ_{fp} and ρ_{fo} are obtained from the input data. After the buoyancy correction has been applied, the fall times are corrected for turbulence by computing the percentage correction directly from the sinker calibration equation (equation (5-9)).

Values of η_p / η_o are determined for each direction of fall by evaluating the fully corrected fall time ratio, t_p / t_o . The more reliable values of η_p / η_o obtained from end 1 fall times are then used to calculate absolute viscosities η_p , from the known atmospheric viscosity, η_o , at that temperature.

3A.5 Tabulated Results.(a) Water.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
2.2°C		
1	1.000	1.662
343	0.958	1.593
659	0.936	1.556
1042	0.925	1.538
1304	0.925	1.537
1657	0.930	1.545
2051	0.942	1.565
2448	0.959	1.594
2924	0.987	1.641
3552	1.033	1.716
4450	1.114	1.851
5424	1.221	2.030
10°C		
1	1.000	1.308
294	0.978	1.280
561	0.967	1.264
838	0.960	1.255
1125	0.960	1.256
1386	0.963	1.260
1723	0.973	1.272
2039	0.984	1.287
2442	1.004	1.313

Water - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
10°C		
3018	1.040	1.360
3832	1.102	1.441
4951	1.208	1.580
5947	1.322	1.729
7189	1.493	1.952
20°C		
1	1.000	1.005
299	0.989	0.994
706	0.985	0.989
1103	0.987	0.992
1583	1.003	1.008
2348	1.039	1.044
2945	1.078	1.083
4060	1.160	1.166
5316	1.284	1.290
6688	1.441	1.448
7941	1.613	1.621
8930	1.770	1.779
25°C		
1	1.000	0.894
230	0.996	0.890
635	0.991	0.885

Water - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
25°C		
1009	0.996	0.890
1543	1.012	0.905
2788	1.078	0.963
3573	1.136	1.015
3867	1.158	1.035
4510	1.218	1.088
5044	1.271	1.136
6005	1.367	1.221
6317	1.413	1.263
7391	1.552	1.387
8320	1.689	1.509
8585	1.712	1.530
9299	1.843	1.647
9562	1.869	1.670
9955	1.939	1.733
30°C		
1	1.000	0.801
252	0.999	0.800
462	0.999	0.800
556	1.001	0.801
922	1.007	0.806
1119	1.013	0.811
1559	1.027	0.822
2404	1.075	0.861
2404	1.077	0.862
2472	1.078	0.863

Water - continued.

Pressure (kg/ cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
2597	1.087	0.871
2762	1.103	0.883
3431	1.150	0.921
3608	1.166	0.934
4572	1.252	1.002
4687	1.258	1.007
5040	1.287	1.030
5835	1.373	1.099
6156	1.415	1.133
7084	1.525	1.221
8193	1.672	1.339
9188	1.829	1.464
9244	1.826	1.462
10077	1.982	1.587
35°C		
1	1.000	0.722
193	1.001	0.723
418	1.004	0.725
655	1.007	0.727
1415	1.037	0.749
2719	1.112	0.803
3790	1.192	0.861

Water - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
50°C		
1	1.000	0.549
366	1.012	0.556
464	1.018	0.559
871	1.039	0.571
1810	1.093	0.600
2941	1.162	0.638
3133	1.185	0.651
4181	1.270	0.698
5146	1.350	0.742
5337	1.372	0.754
6266	1.464	0.804
7395	1.589	0.873
7511	1.605	0.882
8333	1.702	0.935
9817	1.918	1.054
75°C		
1	1.000	0.380
385	1.030	0.391
691	1.047	0.398
1112	1.072	0.407
1885	1.129	0.429
2756	1.202	0.456
3849	1.288	0.489
4894	1.385	0.526
5891	1.479	0.562
6817	1.581	0.601
8799	1.824	0.693
9817	1.949	0.740

Water - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
100°C		
1	1.000	0.284
453	1.041	0.295
1033	1.088	0.309
1889	1.161	0.330
2991	1.259	0.357
4195	1.368	0.388
4870	1.435	0.407
5815	1.539	0.437
7062	1.672	0.475
8276	1.806	0.513
9019	1.892	0.537

(b) Deuterium Oxide.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
10°C		
1	1.000	1.650
142	0.985	1.625
612	0.952	1.570
1005	0.941	1.553
1565	0.946	1.560

Deuterium Oxide - continued.

Pressure (kg/ cm ²)	Relative Viscosity	Viscosity (c. p.)
10°C		
2157	0.972	1.603
2864	1.009	1.664
4019	1.094	1.805
5227	1.214	2.003
6382	1.361	2.245
20°C		
1	1.000	1.251
186	0.989	1.238
353	0.983	1.230
728	0.974	1.219
835	0.973	1.218
1205	0.978	1.224
1444	0.981	1.227
1875	0.997	1.248
2201	1.008	1.262
2699	1.040	1.301
3071	1.059	1.326
3278	1.076	1.347
4107	1.147	1.436
4912	1.227	1.535
6038	1.363	1.706
7460	1.529	1.913
8147	1.635	2.046
8506	1.679	2.102

Deuterium Oxide - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
25°C		
1	1.000	1.100
195	0.994	1.093
405	0.989	1.088
766	0.986	1.085
1087	0.990	1.089
1448	0.999	1.100
1919	1.016	1.118
2936	1.073	1.180
4063	1.157	1.273
5194	1.260	1.386
6625	1.418	1.561
7671	1.553	1.709
8756	1.713	1.885
8916	1.742	1.917
9394	1.817	1.999
30°C		
1	1.000	0.977
179	0.997	0.974
494	0.995	0.972
779	0.997	0.974
1179	1.006	0.982
1715	1.026	1.002
2495	1.067	1.043
3493	1.136	1.110
4694	1.238	1.210
5846	1.356	1.325
6812	1.468	1.434
8118	1.640	1.602
9311	1.820	1.777

Deuterium Oxide - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
50°C		
1	1.000	0.653
548	1.017	0.664
1080	1.040	0.679
1741	1.076	0.703
2690	1.134	0.741
3775	1.219	0.796
5022	1.327	0.867
6292	1.454	0.950
7075	1.535	1.002
7647	1.602	1.046
8940	1.764	1.152
75°C		
1	1.000	0.443
298	1.019	0.452
462	1.031	0.457
513	1.033	0.458
927	1.062	0.471
1375	1.091	0.484
2068	1.145	0.508
2177	1.151	0.510
2919	1.212	0.537
3036	1.219	0.541
3966	1.301	0.577
4167	1.316	0.583
4490	1.343	0.595
5326	1.424	0.631

Deuterium Oxide - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
75°C		
6354	1.533	0.680
7430	1.655	0.734
9117	1.863	0.826
9833	1.963	0.870
100°C		
1	1.000	0.327
300	1.026	0.336
684	1.062	0.348
1732	1.150	0.377
2835	1.248	0.409
3831	1.338	0.438
4970	1.448	0.474
6263	1.582	0.518
7334	1.699	0.556
8444	1.829	0.599
9499	1.957	0.641

(c) Benzene.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
1	1.000	0.560
129	1.115	0.625

Benzene - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
217	1.198	0.671
332	1.312	0.735
383	1.364	0.764
458	1.438	0.805
589	1.588	0.889
594	1.589	0.890
745	1.764	0.988
816	1.860	1.042
50°C		
1	1.000	0.435
174	1.156	0.503
391	1.364	0.593
587	1.575	0.685
849	1.859	0.808
1083	2.145	0.933
1309	2.450	1.066
1540	2.790	1.214
75°C		
1	1.000	0.333
326	1.301	0.433
577	1.548	0.516
604	1.575	0.524

Benzene - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
75°C		
926	1.925	0.641
948	1.948	0.649
1101	2.128	0.709
1252	2.319	0.772
1292	2.362	0.787
1403	2.501	0.833
1564	2.734	0.910
1909	3.232	1.076
2247	3.802	1.266
2572	4.418	1.471

(d) Methanol.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
1	1.000	0.515
692	1.355	0.698
1600	1.773	0.913
2440	2.168	1.116
3407	2.653	1.366
4564	3.294	1.696
5519	3.904	2.010
6590	4.667	2.404
7690	5.578	2.873
8744	6.589	3.393
9395	7.307	3.763

Methanol - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
50°C		
1	1.000	0.395
584	1.309	0.517
1071	1.538	0.607
1908	1.923	0.759
2766	2.315	0.915
3723	2.778	1.097
4852	3.374	1.333
5949	4.013	1.585
7159	4.805	1.898
8257	5.617	2.219
9535	6.667	2.663
75°C		
1	1.000	0.287
854	1.463	0.420
1799	1.899	0.545
2745	2.326	0.667
3676	2.758	0.791
4746	3.285	0.943
5750	3.814	1.094
6742	4.379	1.257
7868	5.068	1.454
9232	6.018	1.727

(e) Ethanol.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
1	1.000	1.000
687	1.456	1.456
1712	2.158	2.158
2748	2.994	2.994
3766	3.979	3.979
4967	5.393	5.393
6018	6.916	6.916
7164	8.947	8.947
8347	11.552	11.552
9335	14.232	14.232
50°C		
1	1.000	0.700
612	1.434	1.004
1583	2.102	1.472
2524	2.810	1.967
3376	3.517	2.462
4421	4.580	3.206
5471	5.842	4.090
6619	7.433	5.203
7769	9.337	6.536
8905	11.576	8.103
9820	13.691	9.584

Ethanol - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
75°C		
1	1.000	0.460
684	1.520	0.669
1567	2.154	0.991
2583	2.922	1.344
3405	3.603	1.657
4378	4.495	2.068
5530	5.697	2.620
6789	7.231	3.326
7815	8.769	4.034
8775	10.481	4.821
9856	12.519	5.759

(f) Ethanol-Water Mixtures.Mixture I.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
1	1.000	1.395
514	1.025	1.430
1126	1.056	1.474
1965	1.106	1.542
3243	1.194	1.666

Mixture I - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
4670	1.321	1.843
6002	1.474	2.056
7450	1.667	2.326
8657	1.853	2.586
10036	2.107	2.939
50°C		
1	1.000	0.837
589	1.051	0.880
1255	1.106	0.925
2019	1.170	0.979
2978	1.256	1.051
4802	1.438	1.203
5987	1.574	1.317
7181	1.726	1.444
8561	1.918	1.605
75°C		
1	1.000	0.525
653	1.086	0.570
1515	1.178	0.619
2323	1.272	0.668
4560	1.516	0.796
5623	1.653	0.868
6499	1.760	0.924
8018	1.979	1.039
9336	2.185	1.147

Mixture II^A.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
1	1.000	2.011
529	1.141	2.296
1543	1.409	2.834
2874	1.780	3.579
4195	2.188	4.401
5800	2.759	5.549
7135	3.361	6.760
8560	4.080	8.206
9886	4.868	9.791
50°C		
1	1.000	1.136
610	1.154	1.311
1504	1.380	1.567
2967	1.751	1.989
4198	2.089	2.373
5587	2.504	2.845
6679	2.865	3.255
7911	3.317	3.769
9379	3.979	4.521

Mixture I^B.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
75°C		
1	1.000	0.676
918	1.275	0.862
1672	1.460	0.987
1819	1.523	1.029
3161	1.889	1.277
4151	2.168	1.466
5244	2.508	1.695
6408	2.896	1.958
7549	3.328	2.250
8644	3.738	2.527
9737	4.202	2.841

Mixture III.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
1	1.000	1.780
635	1.296	2.307
1411	1.682	2.993
2735	2.460	4.377
3795	3.319	5.907
5286	4.946	8.804
6609	7.139	12.707
8053	9.389	16.711
9144	12.094	21.524

Mixture I I I - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
50°C		
1	1.000	1.066
591	1.271	1.355
1509	1.702	1.815
2894	2.422	2.583
4079	3.152	3.361
5252	4.061	4.330
6511	5.362	5.718
8100	7.729	8.242
9648	10.341	11.027
75°C		
1	1.000	0.642
711	1.336	0.858
1628	1.760	1.130
2825	2.338	1.501
3820	2.845	1.826
5292	3.742	2.403
6856	4.845	3.111
8165	5.965	3.830
9720	7.654	4.914

Mixture IV.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
30°C		
1	1.000	1.398
575	1.336	1.868
1365	1.822	2.547
2382	2.528	3.536
3299	3.281	4.589
4548	4.570	6.392
5776	6.119	8.557
7086	8.308	11.619
8103	10.428	14.584
9465	13.995	19.572
50°C		
1	1.000	0.898
609	1.365	1.227
1378	1.829	1.643
2497	2.584	2.322
3820	3.602	3.237
5138	4.861	4.367
6401	6.341	5.698
7766	8.368	7.518
8858	10.295	9.250
9944	12.701	11.412

Mixture IV - continued.

Pressure (kg/cm ²)	Relative Viscosity	Viscosity (c. p.)
75°C		
1	1.000	0.565
638	1.407	0.795
1428	1.883	1.064
2337	2.459	1.390
3245	3.083	1.742
4487	4.051	2.289
5673	5.118	2.891
6925	6.437	3.637
8292	8.142	4.600
9632	10.180	5.752

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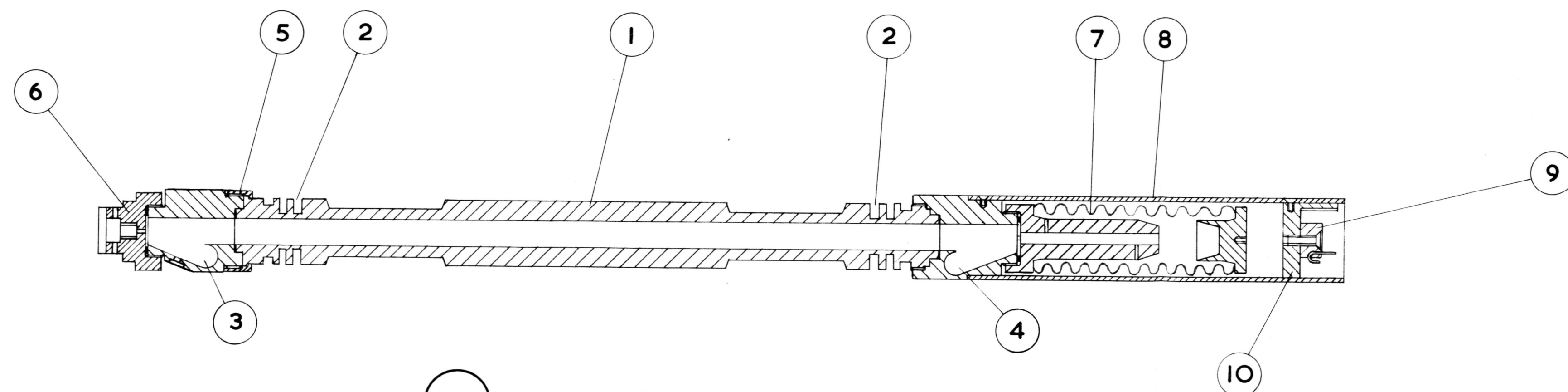
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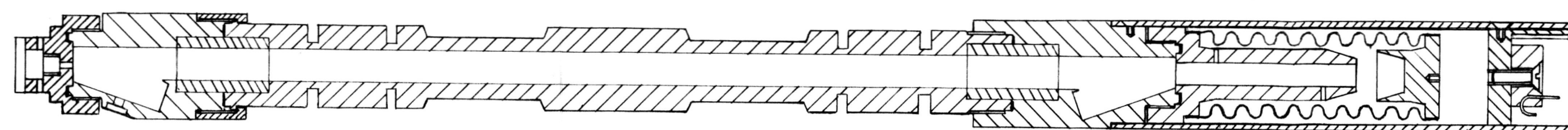
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a MARK I VISCOMETER



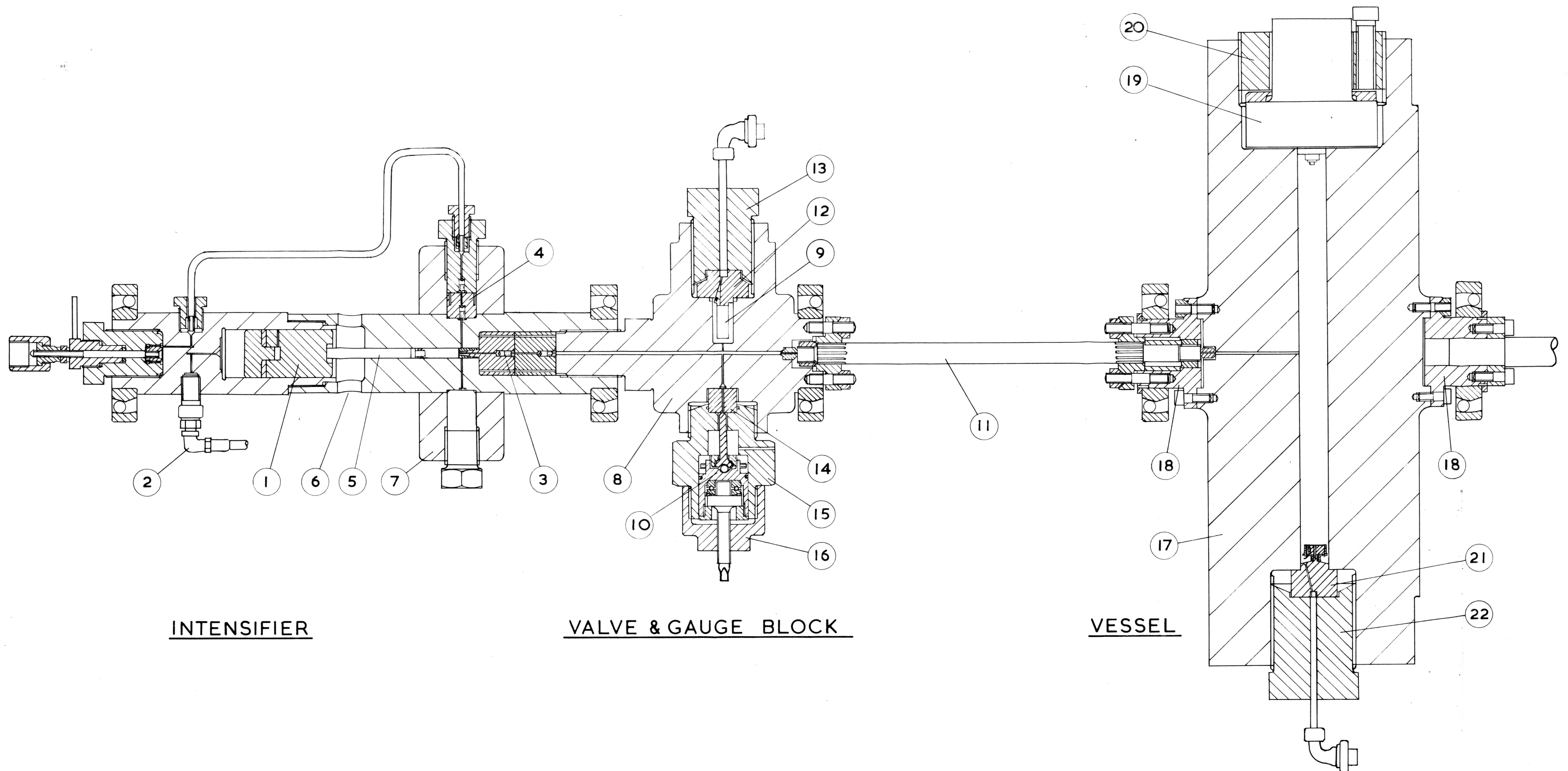
b MARK II VISCOMETER

VISCOMETER ASSEMBLIES

SCALE - FULL SIZE

A. HARLOW

DRAWING 2.



THE HIGH PRESSURE SYSTEM

SCALE~ HALF FULL SIZE

A. HARLOW