VOLUMETRIC COMPRESSIBILITY MEASUREMENT OF N-PENTANE, ISOPENTANE AND THEIR EQUIVOLUMETRIC MIXTURE AT HIGH PRESSURES

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ABSTRACT

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VOLUMETRIC COMPRESSIBILITY MEASUREMENT OF N-PENTANE, ISOPENTANE AND THEIR EQUIVOLUMETRIC MIXTURE AT HIGH PRESSURES

Compressibility measurements were made on three liquids: n-pentane, isopentane and their equivolumetric mixture, from 300 to 8,000 bar at room temperature using a volumetric method.

A new method of analysis of the experimental data was developed which does not require an experimental measurement of V_o, the volume of the liquid at atmospheric pressure. Experimental results are expressed in terms of L and C, the two characteristic constants of a liquid in Tait's equation. The compression, $k = (V - V_o)/V_o$, was calculated using Tait's equation.

The values of C and L found in this work are in agreement with published results, within the estimated experimental error. This indicates that the new method of analysis is valid.

The advantages of the method developed in this work are simplicity of experimental apparatus and measurement technique. Some improvements are suggested which would increase the accuracy of the results.

RESUME

PAUL CARLE

MESURE VOLUMETRIQUE DE LA COMPRESSIBILITE DU N-PENTANE, DE L'ISOPENTANE ET DE LEUR MELANGE EQUIVOLUMETRIQUE A HAUTE PRESSION

Des mesures de compressibilité ont été effectuées à l'aide d'une méthode volumétrique sur trois liquides: le n-pentane, l'isopentane et leur mélange équivolumétrique, de 300 à 8,000 bar, à la température de la pièce.

Une nouvelle méthode d'analyse des données expérimentales a été mise au point; cette méthode ne requiert par la mesure expérimentale de V_o, le volume du liquide étudié à pression atmosphérique. Les résultats expérimentaux sont exprimés en fonction de L et C, les deux constantes caractéristiques de l'équation de Tait. Les valeurs de la compression, $k = (V - V_o)/V_o$, ont été calculées à l'aide de l'équation de Tait.

Les valeurs de C et L trouvées dans ce travail sont en accord avec les résultats publiés sur ces liquides, à l'intérieur des limites d'erreur expérimentale. Ceci implique donc que cette nouvelle méthode d'analyse est valable.

Les avantages de la méthode mise au point dans ce travail sont la simplicité de l'appareillage expérimental et des techniques de mesures. Des améliorations qui pourraient accroître la précision des résultats sont suggérées.

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INTRODUCTION

The compressibility of a substance is a measure of the amount of volume decrease caused by an increase in pressure. Experimentally, compressibility is found from the measurement of compression as a function of pressure. Compression, k, is defined as the relative volume decrease that is,

$$k = \frac{-(V - V_o)}{V_o}$$

where V_o is the initial volume (usually at atmospheric pressure) and V is the volume at pressure P.

The isothermal compressibility, β, is defined as

$$\beta = -\frac{1}{V_o}\left(\frac{\partial V}{\partial P}\right)_T$$

where the subscript T denotes that the temperature is constant. By comparing the definitions of β and k it is seen that β is the slope of a plot of k vs P. The symbols for compression and compressibility are those used by Andersson (1963).

Compressibility measurements that started during the last century are still today of major importance for many reasons. Isothermal compressibility plays a major

role in thermodynamics; its knowledge permits the establishment of the isothermal equation of state, and the evaluation of useful parameters like intermolecular forces. The pressure range of these measurements is always increasing and permits new developments in the theory of equations of state.

Perkins in 1819 made the first true compressibility measurements on liquids; by sinking a cannon to different depths in the sea, he developed pressures up to 200 kg /cm^2 (kg in this usage means 1 kilogram weight which equals 9.80665 Newtons).

Parrot and Lenz (1833) while observing the application of Boyle's law to air, measured pressure effects on some liquids up to 100 bars.[1]

Amagat (1893) was first to use the piezometric method to measure compressibilities; he analysed gases and liquids up to 3000 kg /cm^2. Tammann (1903) measured compressibility, expansivity, specific heat and electrical conductivity of solutions up to 3000 kg /cm^2. Lussana (1904, 1910) published data on thermal properties of solids and liquids under pressure, after improving the design of the piezometers. Other important measurements were made by T.W. Richards (1912) on organic liquids.

---

[1] One kbar = 1000 bar = 1.0 x 10^9 dynes/cm^2 = 986.92 atm = 1.0197 x 10^3 kg /cm^2.

Precise results only started being available with the work of Bridgman (1932, 1933, 1949) on the compressibility of liquids. He is responsible for the major developments of high pressure technology in the twentieth century. Bridgman expressed his results of volume change under pressure in quadratic form, that is,

$$\frac{V - V_o}{V_o} = AP - BP^2$$

where P is the gauge pressure, V_o is the volume at atmospheric pressure (P = 0), V is the volume at pressure P and A and B are constants. This form of isothermal equation of state is still used, for example, by Holder and Whalley (1962).

Experimental methods

Three major methods are used to measure liquid compressibilities: piezometric, ultrasonic and volumetric.

The piezometric method, used by Bridgman in all of his work on liquids, is experimentally the simplest. Variations of volume are measured by an electrical micrometer in the pressure chamber (liquids are usually maintained in a pyrex tube equipped with microcontacts that give an electrical signal when certain volumes are attained). This method requires correction for the

compressibility of pyrex. Details of the method can be found in papers by Bridgman (1949) and Anderson (1963).

The ultrasonic method consists of sending sound pulses through a known distance of the liquid under study. The speed of sound recorded is directly related to the adiabatic compressibility. The isothermal compressibility is found from the relation :

Adiabatic compressibility/isothermal compressibility = C_v/C_p

where C_v and C_p are the specific heats at constant volume and pressure, respectively. The factor C_v/C_p is slightly pressure dependent and a certain amount of uncertainty is to be expected in the results, unless theoretical corrections are applied. A description of the ultrasonic method can be found in Heydemann (1970) and Boule (1972).

The volumetric method which is the method used for the work presented in this paper, is based on a straightforward relation between the measurable geometry of the high pressure apparatus and the change of volume under pressure. Severe conditions are imposed on the apparatus; no leakage of the liquid must occur during the experiment (in high pressure technology, leaking is certainly the major problem). A description of such a method is given by H.W. Schamp (1965). This method gives

good compressibility results in a short time with a minimum of electronic instrumentation.

Materials

The liquids studied were n-pentane, $CH_3(CH_2)_3CH_3$, iso-pentane, $(CH_3)_2CHCH_2CH_3$, and an equivolumetric mixture of the two. These liquids were choosen for study because mixtures of n-pentane and iso-pentane are widely used as pressure transmitting media, and not much information is available about their compressibility. A precise konwledge of the compressibility of these liquids could be of great help in high pressure research.

CHAPTER I

EXPERIMENTAL PROCEDURE

1.1 High Pressure Apparatus

The high pressure apparatus used for this experiment is shown in Figure 1. It is custom-made by Basset-Bretagne-Loire in France.

1.1.1 Press.

The press is a four-column press with a total thrust of 300 tons. The primary piston has a diameter of 250 mm (cross-sectional area of 490.6 cm^2). The maximum pressure in the primary pot (low pressure chamber) is of the order of 200 bars. The elongation under pressure of the columns was found to be 0.009 mm/kbar.

1.1.2 Pressure pumps.

In order to be able to vary the range of pressures and pressure rates by large amounts, a two-pump design was chosen. Both pumps are hydraulic and can be used independently. The low pressure pump, with a large flow for fast compressions, is used mainly to settle the teflon joints. The teflon undergoes a phase transition around 3 kbar and in order to avoid any leaks, because of the sudden change of volume of the joints, it was found

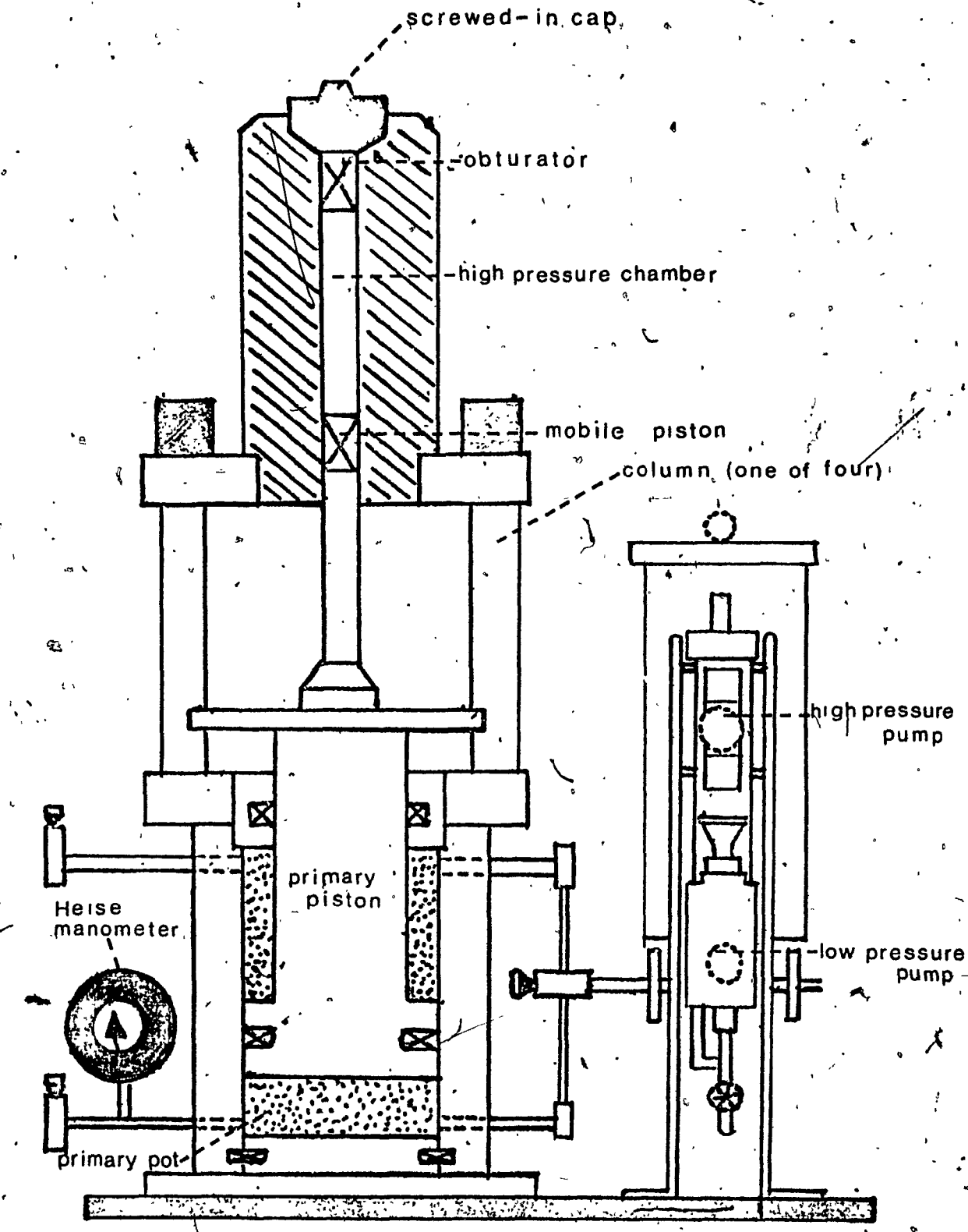


FIGURE 1

HIGH PRESSURE INSTRUMENT

necessary to pass over this 3 kbar point very fast. The high pressure pump with fine regulation of flow permitted compressions at small controlled rates.

1.1.3 Measurement of primary pressure.

A manometer of range of 500 bar, manufactured by Heise, is connected directly to the primary pot. The precision of the measurement of this primary pressure is better than 1%. This measurement is necessary to evaluate the friction of the joints during the experiment.

1.1.4 High pressure chamber.

This chamber is attached to the top of the press. The body of the chamber itself is of the multi-layer type. The inside cylinder is made of Vascomax 385 steel which is finely polished. The cylinder must be periodically polished with an alumina powder (maximum grain size of 0.03 micron) to reduce friction and therefore minimize wear of the interior surface. The interior diameter of the chamber is 19.96 mm (area is 3.13 cm^2) at atmospheric pressure. Therefore the maximum pressure in the high pressure chamber is 32kbar, the ratio of the area of low and high pressure chambers times the maximum pressure in the low pressure chamber. Using Lamé's equation, it is shown in Appendix A that the dilatation of this diameter is of the order of 0.006 mm/kbar. The

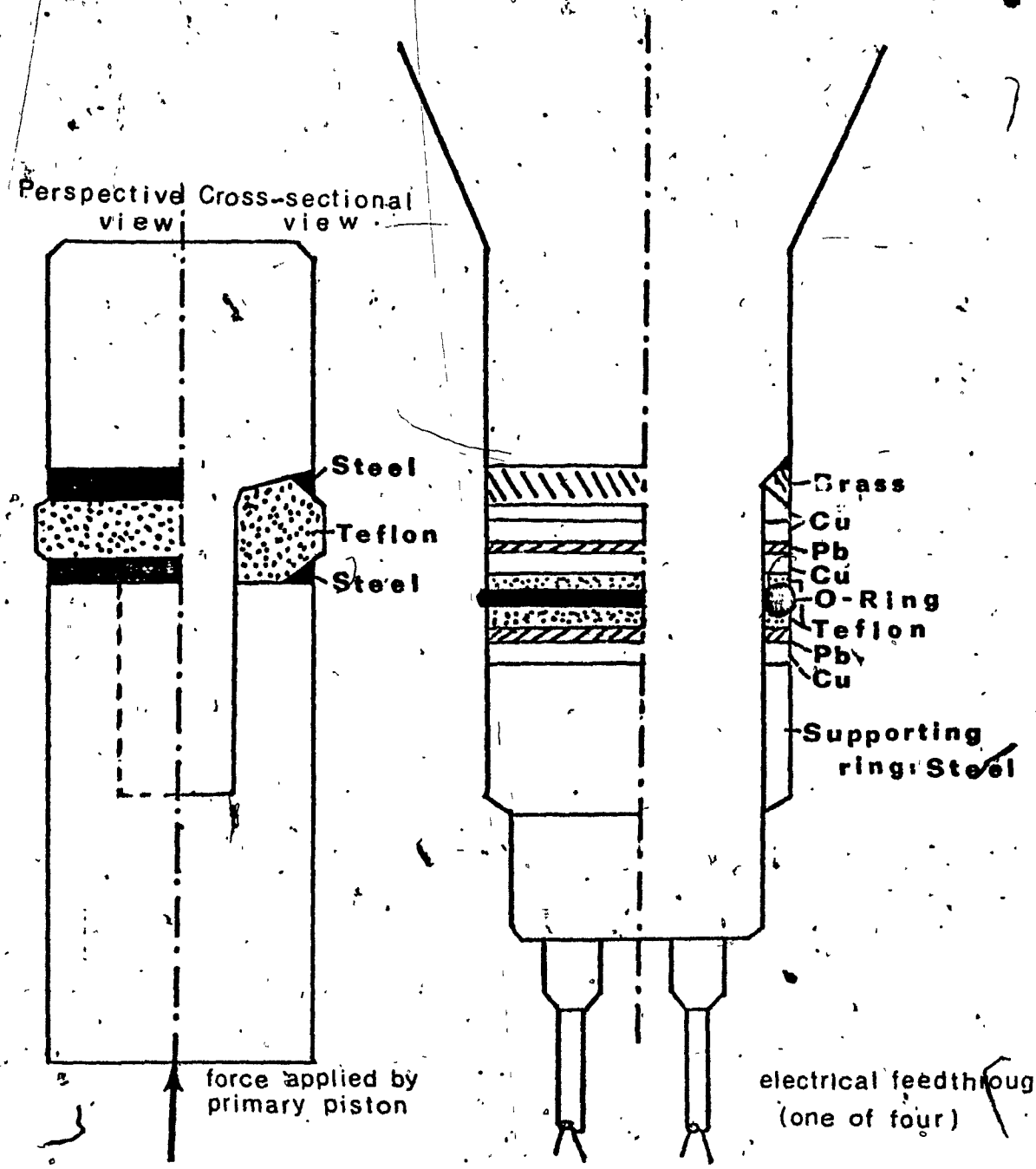


FIGURE 2

HIGH PRESSURE SEALS ON MOBILE PISTON AND OBTURATOR

pressure chamber is closed on top by an obturator, and by a mobile piston at the bottom. The maximum useful volume is of the order of 60 cm^3.

1.1.5 Mobile piston.

A force of friction is exerted on the mobile piston by the walls of the pressure chamber. To minimize this friction, the system shown in Figure 2(a) is used: a teflon O-ring with an unsupported area of the order of 20% and two steel anti-extrusion rings (rings are of 819B steel treated at 110 kgf/cm^2). Before the experiment, the rings are covered with a molybdenum disulfide grease that permits an easy displacement of the rings in the chamber. The weakness of the steel rings ensures a minimum degradation of the interior polish of the chamber.

1.1.6 Obturator.

The obturator shown in Figure 2(b) has a rubber O-ring held in place by two teflon rings and two lead rings which flow out towards the chamber walls under pressure and thus form a leak-proof seal. The piling order shown in Figure 2(b) is found experimentally to permit a better deformation of the rubber and lead and to permit a better tightening of the obturator at the beginning of the experiment.

1.1.7 Electrical feedthroughs.

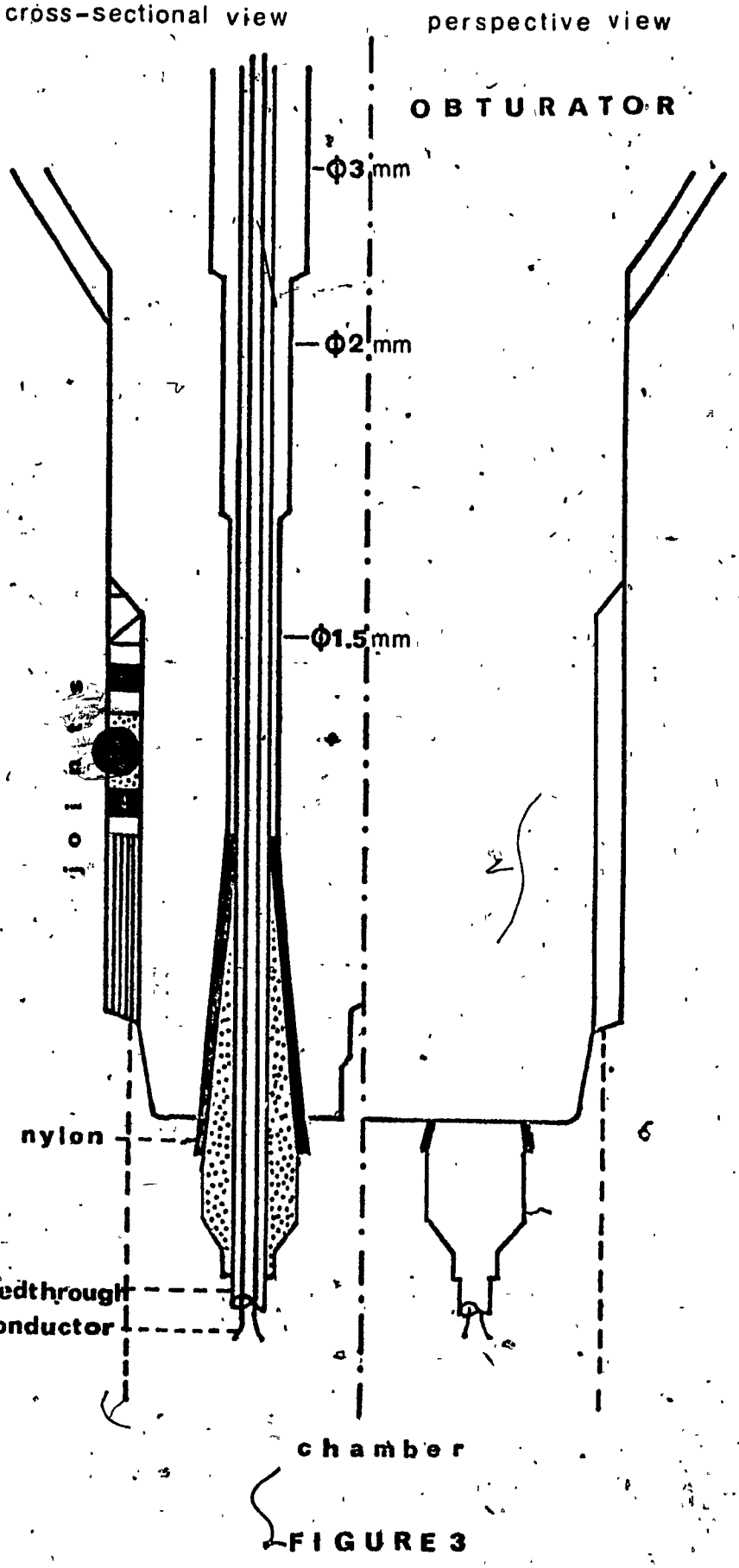


FIGURE 3

OBTURATOR

The obturator has four electrical feedthroughs as shown in Figure 3. Each feedthrough consists of two conductors inside a stainless steel tube packed with magnesia. If the magnesia powder is dry, an insulation resistance of the order of 5 megohms is obtained. The resistance of each conductor is 0.02 ohms/cm.

The feedthroughs are Thermocoax 2CzCzAC10, manufactured by Sodern. During the experiment the obturator is held in place by a screwed-in cap, shown in Figure 1, that also protects the electrical entries against mechanical damage.

1.1.8 Holder.

The holder shown in Figure 4 has been designed to ensure good stability of the electrical contacts in the high pressure chamber (the conductors are 0.18 mm in diameter and also very brittle). The manganin coils are placed inside the holder for protection against mechanical damage during the preparation of the experiment. Electrical conections on the holder are isolated from one another by a teflon ring.

1.2 Friction

Pressure inside the chamber depends on the ratio of the cross-sectional area of the primary and mobile pistons and also on the friction between the joints of the mobile piston and the walls of the chamber. If p is the

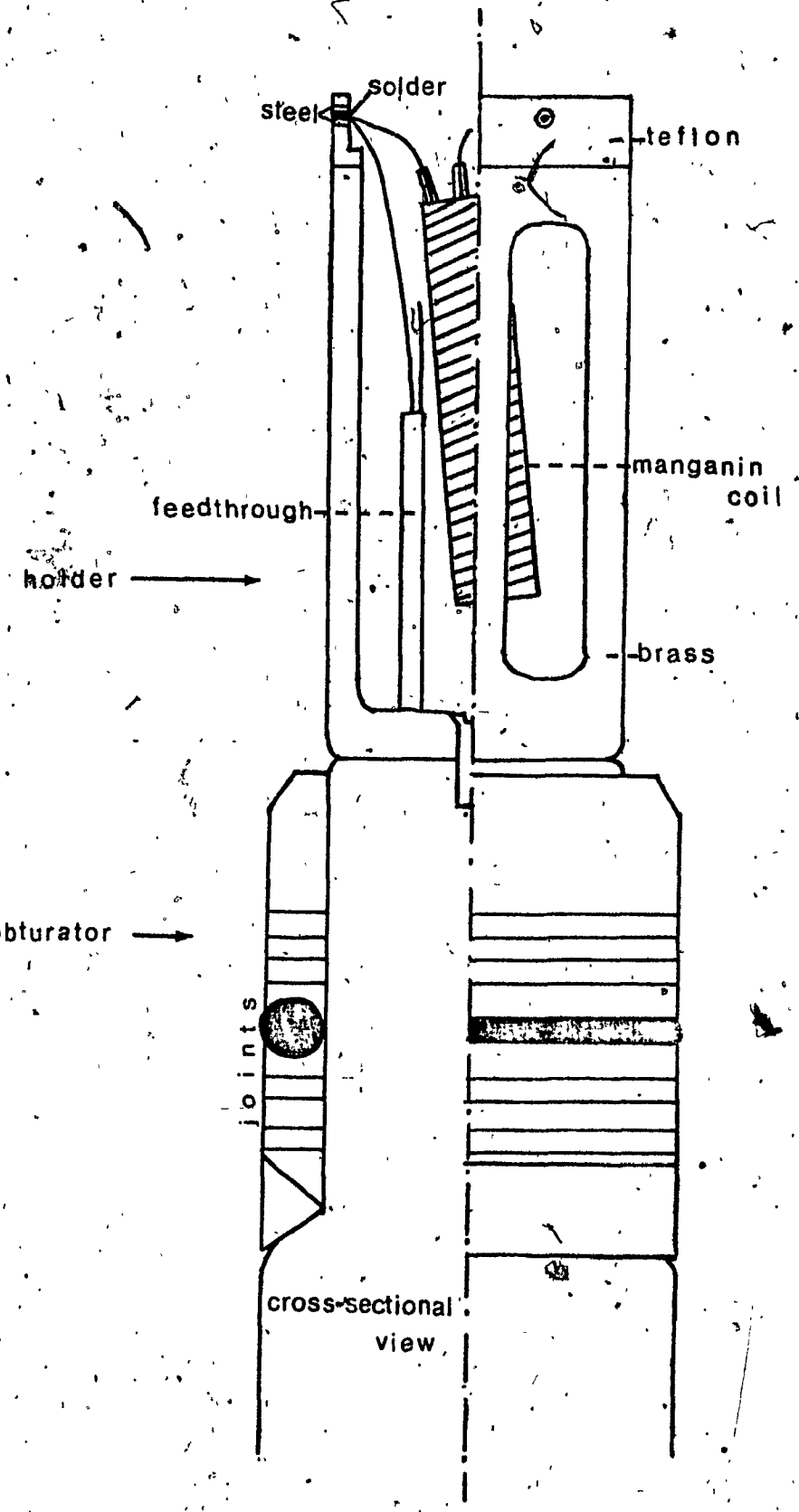


FIGURE 4

HOLDER

pressure read on the Heise manometer in the primary pot, and if P is the pressure in the high pressure chamber

$$P = \frac{S}{s} p + f(p), \qquad (1\text{-}1)$$

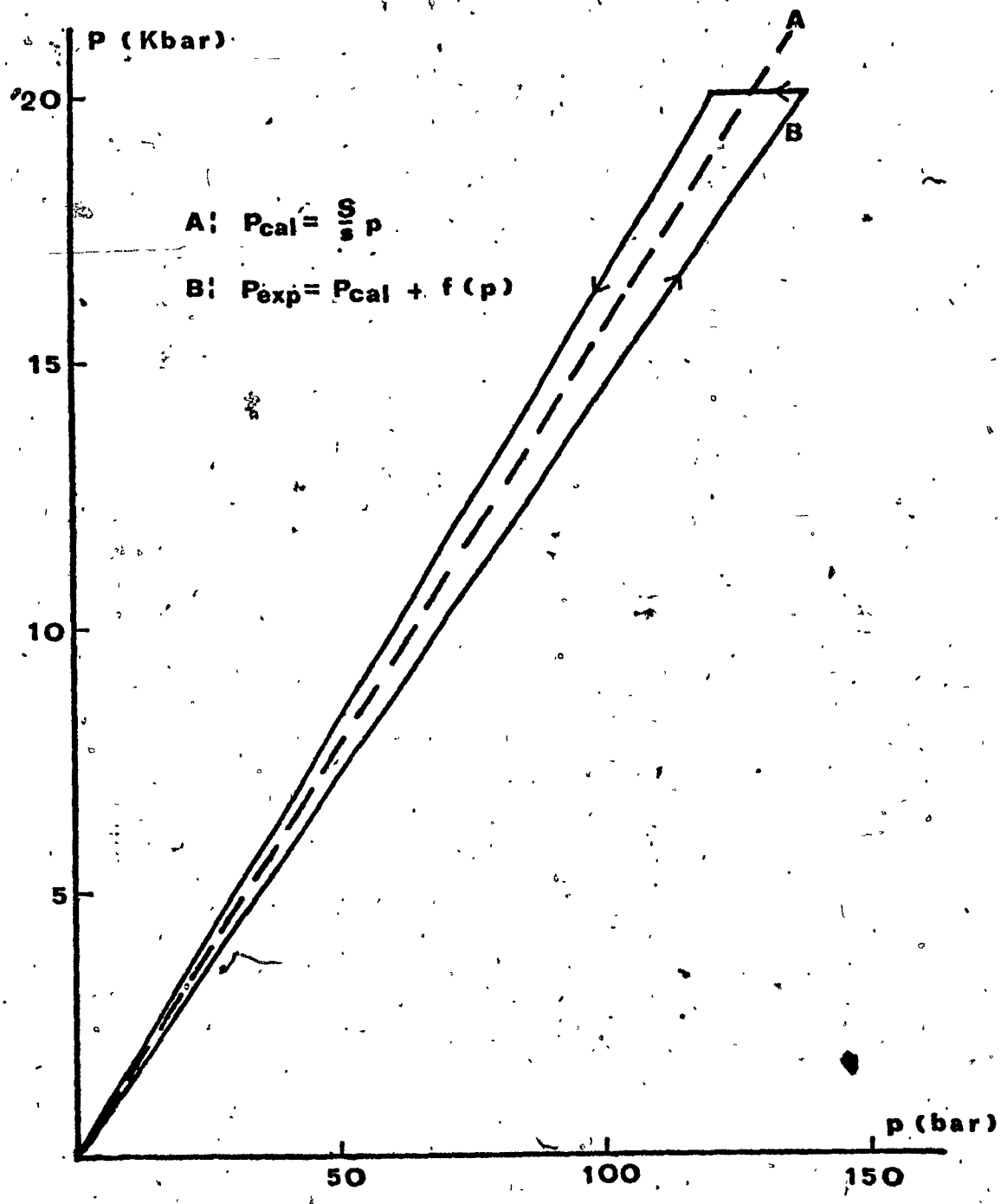
where S is the cross-sectional area of the primary piston and s the cross-sectional area of the mobile piston. The function of pressure, f(p), depends on the frictional forces.

On the upstroke, $f(p) < 0$, and $f(p) > 0$ on the downstroke. In this experiment, S= 490.6 cm^2, s= 3.13cm^2. The pressure p is measured by the Heise manometer, and P by the manganin coil in the high pressure chamber. Figure 5 shows an experimental plot of P vs p. Up to P= 10 kbar, f(p)/Pcal, where Pcal= (S/s)p, is about 0.08, that is frictional forces inside the high pressure chamber are about 8% of the force acting on the mobile piston.

1.3 Pressure Measurements

1.3.1. Manganin gauges.

The manganin wire, which is covered with silk, is wound non-inductively on a paper support. The total resistance of the coils is of the order of 120 ohms at atmospheric pressure. The gauges are seasoned by a special treatment consisting of temperings from 140°C to liquid nitrogen temperature (-196°C) and then a compression to



Experimental determination of friction

FIGURE 5

25 kbar at room temperature.

Manganin gauges are widely used because of their large resistance variation with pressure and small resistance variation with temperature. The temperature coefficient is the change of resistance due to a temperature change of 1°C divided by the initial resistance. From the experimental data used to plot Figure 6, the resistance changes by 10 parts per million as the temperature changes from 17°C to 25°C. Therefore the temperature coefficient is about 1 part per million per °C. The change of resistance with pressure is linear up to 40kbar and is reproducible as demonstrated by Bridgman (1952), Newhall (1962) and Ivanova (1965).

1.3.2 Calibration of the manganin coils.

The coils used in this experiment have been calibrated at "Le Laboratoire des Interactions Moléculaires et des Hautes Pressions du C.N.R.S." in Bellevue, (Paris), France, in a free piston instrument. Pressure was measured with an accuracy better than 0.1% and up to 8 kbar. A Kelvin bridge was used to measure the resistance of the coil with a precision of the order of 0.05%

The change of resistance of the manganin coils, ΔR, due to change of pressure, $P - P_o$ is given by

$$\Delta R/R_o = \gamma (P-P_o),$$

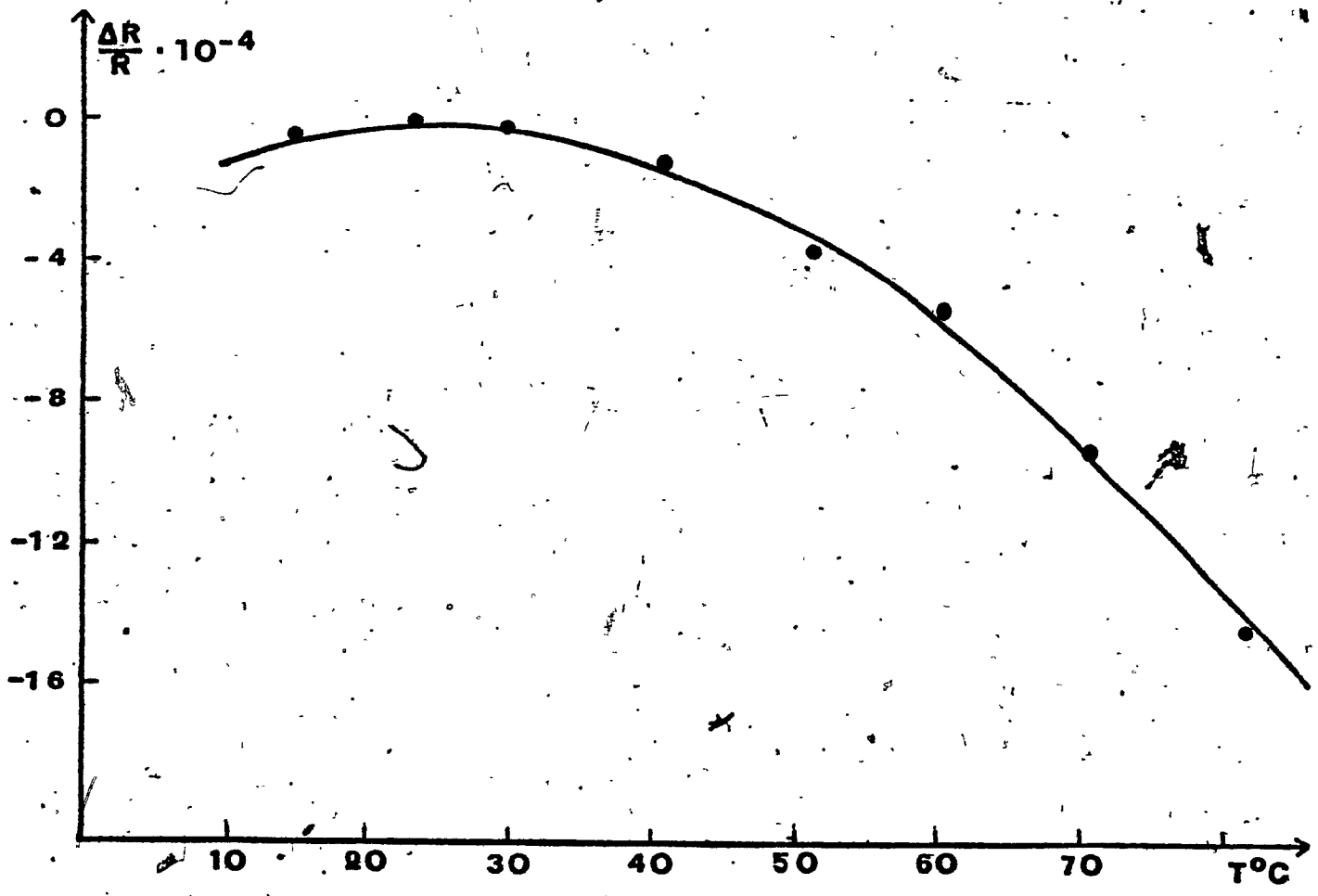


FIGURE 6

TEMPERATURE COEFFICIENT OF MANGANIN WIRE

where R_o is the resistance of the coil at atmospheric pressure, P_o. The constant γ is called the pressure coefficient. It was found to very slightly with pressure as described below.

The least square method was applied to the different values obtained and the results are shown in Table 1. The correlation coefficient is a measure of goodness of fit of the straight line with the experimental points. The deviation from the straight line, between 0 and 7.5 kbar is of the order of 5 bars from Figure 7. The pressure coefficient $\Delta R/R_o P$, neglecting P_o, is plotted in Figure 8 where R_o= resistance value at atmospheric pressure, P is the pressure in the chamber and ΔR is the change of resistance caused by pressure P. A correction equation has been established using a reference point at 5 kbar, and the equation of the line in Figure 8. Letting P_m be the pressure calculated using the mean coefficient,

$$P = (0.2779\ P_m)/(0.2789 - 0.0002\ P_m) \qquad (1\text{-}2)$$

where the pressures are in kbar.

1.3.3 Measurement of resistance changes.

A few authors, particularily Yamamoto (1972), have noted a shift of R_o, the resistance of the manganin

pressure coefficient as established in free piston gauge in pressure range 0 to 8 kbar

	Manganin gauge №1 Ro = 117.9721	Manganin gauge №2 Ro = 118.8029
mean pressure coefficient	$2.390 \times 10^{-6} \Omega/\Omega/\text{bar}$	$2.391 \times 10^{-6} \Omega/\Omega/\text{bar}$
Correlation coefficient	0.99999612	0.99999767
deviation from straight line	16×10^{-4} bar	13×10^{-4} bar

TABLE 1

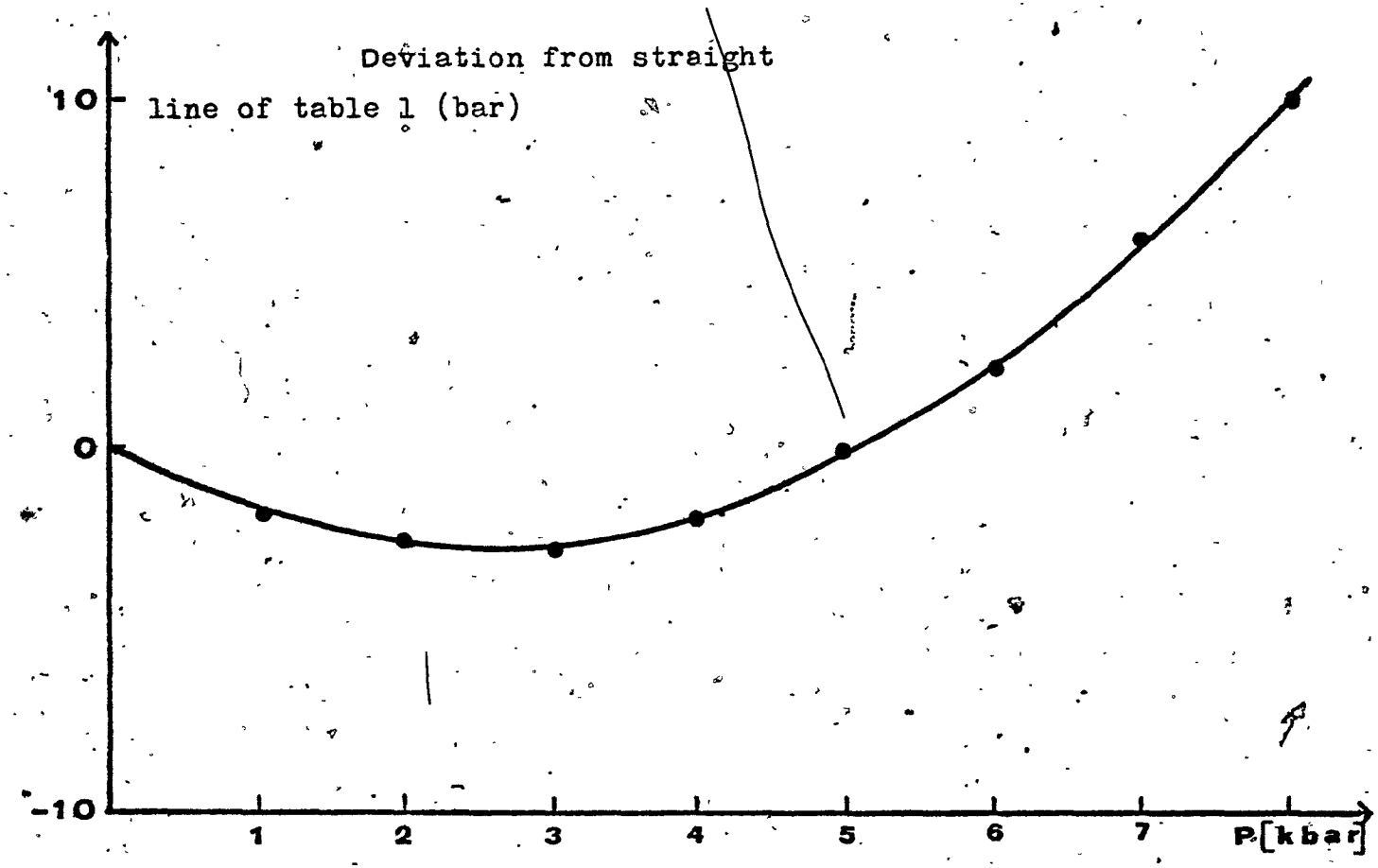


FIGURE 7

NON-LINEARITY CORRECTION OF PRESSURE COEFFICIENT

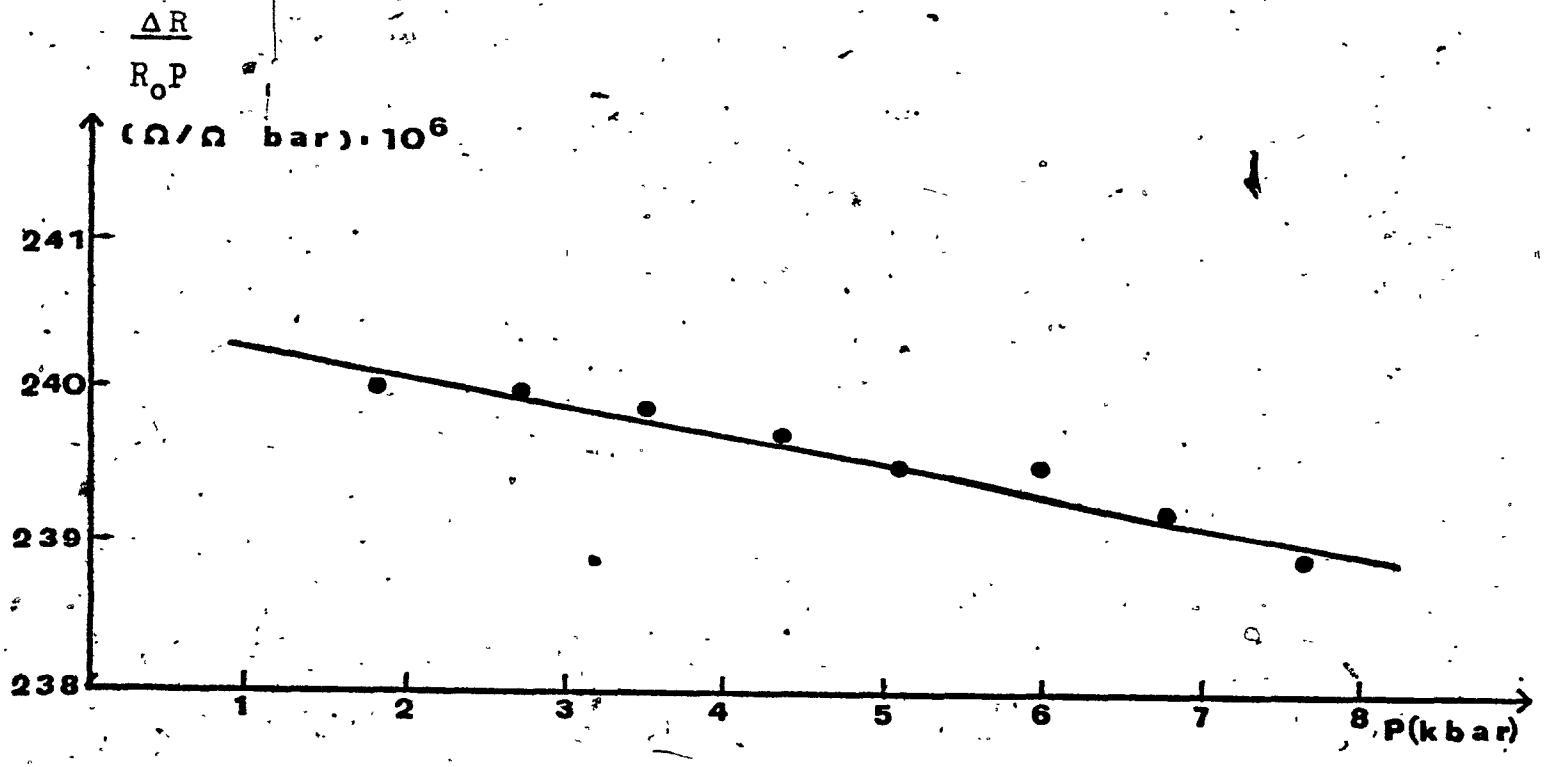


FIGURE 8

PRESSURE COEFFICIENT OF MANGANIN WIRE

gauge at atmospheric pressure, with time. The gauges used for this experiment have been used for five years of experimentation with only slight changes of R_o of the order of 0.001%. This constancy of R_o has also been observed by Boren (1965) and Atanov (1971). A Kelvin bridge was used to measure the R_o of the gauges before each experiment with a precision of 0.001%.

Figure 9 shows the electrical measurement method. As the pressure is varied, a Tekelec digital ohmmeter was used to measure the absolute resistance of one of the manganin gauges with a precision of $\pm$ 0.002 ohms, corresponding to an uncertainty of $\pm$ 10 bar in pressure. The change of resistance of the other manganin gauge was observed by a Kelvin bridge and displayed on a voltage-versus-time recorder. The Kelvin bridge is manufactured by Electro Scientific Industries, with a claimed precision of one part per million.

The comparison of the two pressure readings indicates leak in the chamber and malfunction of the electrical circuits. If both readings decrease with time when the pressure is expected to be constant, it is likely that there is a leak in the high pressure chamber . If one reading changes while the other remains constant this may indicate that the circuit producing the changing reading is faulty.

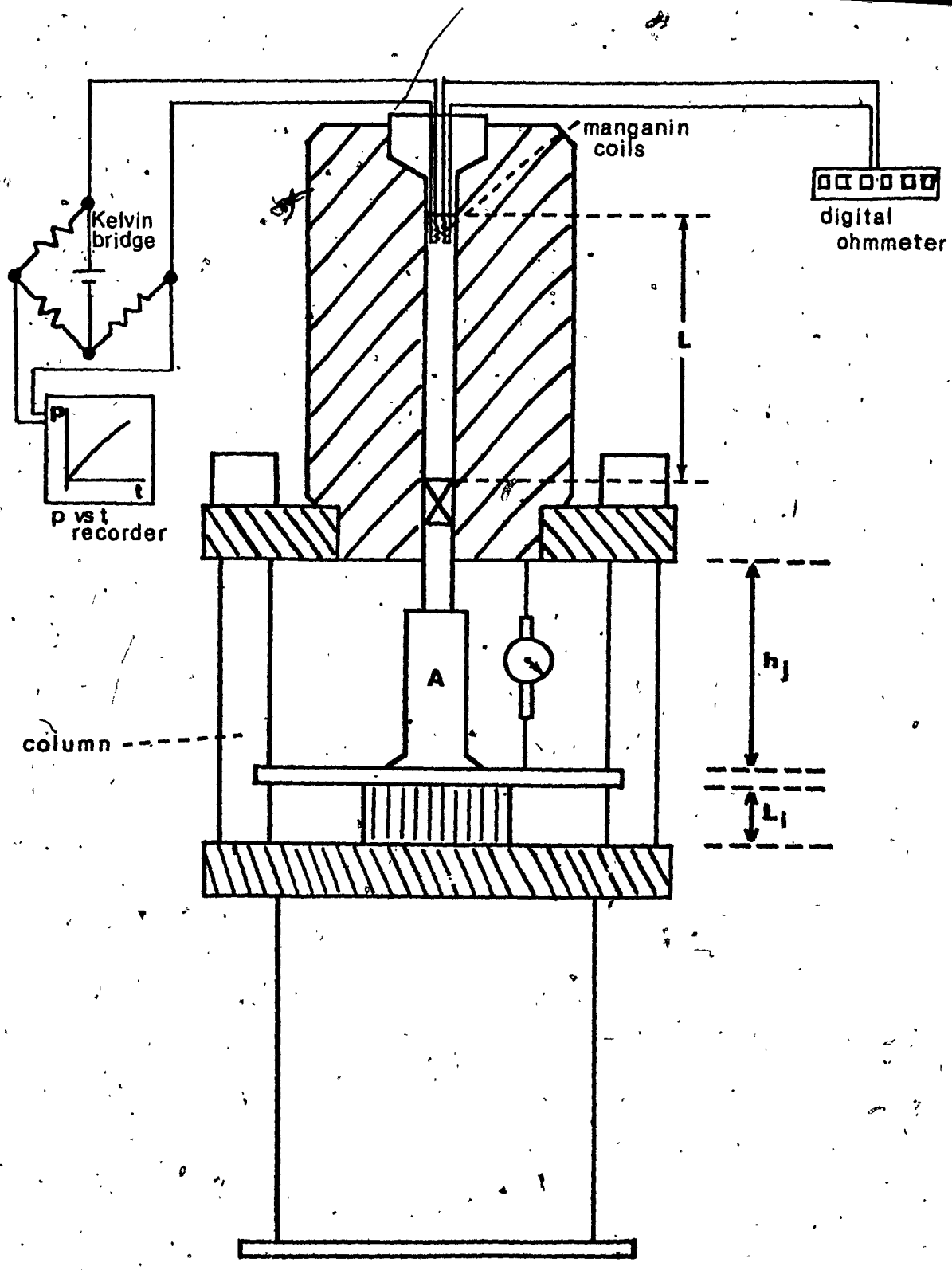


FIGURE 9

ELECTRICAL AND VOLUMETRIC MEASUREMENT METHOD

1.4 Volumetric Measurement

The change of length of the cylindrical volume under pressure is measured by two methods, as shown in Figure 9. The change of distance h_j, Δh_j, is measured with a micrometer giving a precision of 0.01 mm; L_i is measured with a calliper square giving an absolute precision of 0.02 mm.

Because the steel cylinder A did not show any deformation under pressure, and because the elongation of the columns was easily evaluated (0.009 mm/kbar), the absolute value of L_i was taken as the reference length for the calculation of change of volume of the liquid in the high pressure chamber. Δh_j was used as a verification of the variation of L_i. The total precision in the measurement of L_i is of the order of 0.002%.

The measure of L_o, the initial length of the cylindrical volume of liquid in the high pressure chamber will be discussed in the chapter on data analysis.

1.5 Liquids Studied

The liquids studied were "technical" grade n-pentane and isopentane and an equivolumetric mixture of each. These liquids are not pure. The n-pentane is 95% pure, of relative density 0.63 and of molecular weight 72.15; the isopentane is 98% pure, of relative

density 0.62 and of molecular weight 72.15. Both products were used without any special treatment.

The n-pentane and isopentane were obtained from Prolabo, in France.

CHAPTER II

THEORY OF THE LIQUID STATE AND TAIT'S EQUATION

The theory developed in this chapter is based on the work of Ginell, (1955a, b, 1961a, b, c, d). The notation used is summarized at the end of this chapter.

The equation of state for liquids which is presented in this chapter, was first derived empirically by Tait. It describes the isothermal behaviour of liquids. Without any reference to the structure of liquids, this equation was successfully applied to many liquids including water, alcohols, acetone, benzene and aqueous solutions. Hirschfelder, Curtiss and Bird (1954) regard it as the best empirical representation of the equation of state of liquids. A theoretical derivation of this equation will be given here with a discussion on the structure of liquids. The derivation is based on association theory and starts with the assumption that the same equation of state describes both gases and liquids. This assumption is not new and was first made by Van der Waals (1873).

First, a word about a term used frequently in this chapter: a cluster or i-mer is defined as a particle consisting of i molecules without any concern about its physical shape. A single molecule for example is called a 1-mer. More recent terminology for i-mer and 1-mer is polymer and monomer, respectivily.

For a collection of i-mers for i = 1 to m, the ideal gas law is

$$PV/T \sum_{i}^{m} n_i = R \qquad (2\text{-}1)$$

where $\sum_{i}^{m} n_i$. is the number of moles, that is, the total number of particles present divided by Avogadro's number, n_i being the number of moles of particles of size i (i-mer). P is pressure in bars, V is volume in m^3, T is temperature in ^{o}K and the universal gas constant, $R = 8.314 \times 10^{-5}$ bar $m^3\ {}^{o}K^{-1}$ mole^{-1}. The number of moles of molecules in the system is

$$\sum_{i}^{m} i n_i = W/W_o \qquad (2\text{-}2)$$

where W is the weight of material in the system, W_o is the weight of Avogadro's number (1 mole) of molecules (1-mers). The implicit assumption in the use of these equations is that the law of partial pressures hold, that is the total

pressure, P, is

$$P = \sum_{j}^{N} p_j = \sum_{i}^{m} N_i p_i \qquad (2\text{-}3)$$

where p_i is the pressure exerted by all particles of size i, N_i is the number of particles of size i, p_j is the pressure exerted by one particle and N is the total number of particles. The subscript j labels one of the particles.

Consider a cube of side H, containing a gas at equilibrium. In the gas, there are N_1 1-mers, N_2 2-mers, ...N_i i-mers ... N_m m-mers and therefore $N = \sum_{i}^{m} N_i$ particles.

When particle j strikes the wall of the box, it undergoes a collision and exerts pressure on the wall; its change in momentum is $2m_j u_j$, where m_j is its mass and u_j its velocity component normal to the wall. The time between two successive collisions, from the definition of velocity, is $(H - D_j)/u_j$ where D_j is the diameter of particle j. The change in this component of momentum/unit time, using Newton's second law, is the force F_j given by

$$F_j = \frac{2m_j u_j^2}{H - D_j} \qquad (2\text{-}4)$$

The area of the two opposite walls against which the particle can strike is $2(H-D_j)^2$. Hence the pressure exerted by

particle j on the walls is

$$p_j = m_j \cdot u_j^2 / (H - D_j)^3 \qquad (2\text{-}5)$$

The total pressure using Dalton's law, (2-3) is

$$P = \sum_i^m \frac{N_i \cdot m_i \langle u_i^2 \rangle_{av}}{(H - D_i)^3} = \sum_j^N \frac{m_j \cdot u_j^2}{(H-D_j)^3} \qquad (2\text{-}6)$$

where N_i is the number of particles of mass m_i, and $\langle u_i^2 \rangle_{av}$ is the average of the squares of the u-components of the velocity of the particles of size i.

At equilibrium if $\langle c_i^2 \rangle_{av}$ is the mean square velocity of the particles of size i, the average kinetic energy of each mer is the same, that is

$$\frac{1}{2} m_2 \langle c_2^2 \rangle_{av} = \frac{1}{2} m_1 \langle c_1^2 \rangle_{av} = \frac{1}{2} m_i \langle c_i^2 \rangle_{av} \qquad (2\text{-}7)$$

Since by definition $m_i = i.m_1$, from (2-7)

$$\langle c_i^2 \rangle_{av} = \frac{\langle c_1^2 \rangle_{av}}{i} \qquad (2\text{-}8)$$

and since the component velocities along the three axis in space are equal,

$$\langle u_i^2 \rangle_{av} = \frac{\langle c_i^2 \rangle_{av}}{3} = \frac{\langle c_1^2 \rangle_{av}}{3_i}$$

Hence

$$m_i \langle u_i^2 \rangle_{av} = \frac{m_1 \langle c_1^2 \rangle_{av}}{3} \qquad (2\text{-}9)$$

and substituting (2-9) into (2-6)

$$P = \frac{m_1 \langle c_1^2 \rangle_{av}}{3} \sum_i^m \frac{N_i}{(H-D_i)^3}$$

By the law of equipartition of energy,

$$\frac{m_1 \langle c_1^2 \rangle_{av}}{3} = k\,T$$

where k is Boltzmann's constant.

Hence

$$P = k\,T \sum_i^m \frac{N_i}{(H-D_i)^3}$$

Letting n_i be the number of moles of particles of size i, since $N_i = n_i N_o$, where N_o is Avogadro's number, and $R = kN_o$

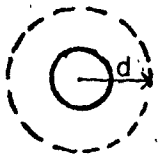
$$P = R\,T \sum_i^m \frac{n_i}{(H-D_i)^3} \qquad (2\text{-}10)$$

The derivation of (2-10) followed the classical kinetic derivation of the ideal gas law.

Consider a large number of particles in the box and that collisions with the wall are not instantaneous. The distance particle j would have to travel to exert pressure, is less by the average thickness of particles between it and the wall; on the average this distance, H, will be $H = (V-b)^{1/3}$, where V is the actual volume of the box and b the excluded volume of all particles. Thus (V-b) is the equivalent cube of free space of the particle,

the total volume of the box minus the total volume of particles in the box.

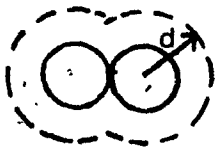
The excluded volume is a rather complex function. It is not, as one may expect, the total number of molecules, $\sum_1 iN_i$ times the excluded volume of one molecule, a 1-mer. This can be shown by the following calculation based on assumptions indicated in the figures below. The solid line represents the boundary of the 1-mer excluding the valence electrons and the dashed line represents the highest occupied orbital of the 1-mer.



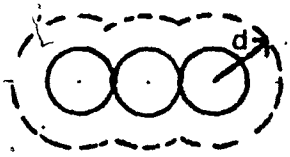
Assuming the 1-mer is a sphere of radius d, than its volume, b_1, is

$$b_1 = \frac{4}{3}\pi d^3$$

similarly, for the 2-mer, and for the linear 3-mer, assuming no shrinkage occurs,



$$b_2 = \frac{9}{4}\pi d^3$$



$$b_3 = \frac{38}{12}\pi d^3$$

and generally, for a linear chain of i molecules (linear i-mer)

$$b_i = (11i + 5)\frac{\pi d^3}{12} = i\left(\frac{4}{3}\pi d^3\right) - (2i-2)\left(\frac{5}{24}\pi d^3\right) \quad (2\text{-}11)$$

Using the concept of excluded volume, the equation of state, (2-10), becomes

$$\frac{P}{RT} = \sum_i^m \frac{n_i}{\left[(V-b)^{1/3} - D_i\right]^3}$$

or

$$\frac{PV}{RT} = \sum_i^m \frac{n_i}{\left[\left(1-\frac{b}{V}\right)^{1/3} - \frac{D_i}{V^{1/3}}\right]^3} \qquad (2\text{-}12)$$

where the excluded volume, b, is

$$b = \sum_\alpha \sum_i^m b_i^\alpha \, N_i^\alpha \qquad (2\text{-}13)$$

where α denotes the type of packing of the i-mer. For example if there are two types of packing, linear and closed packed, then α is summed from 1 to 2.

If the volume that the liquid occupies is comparatively large, than $V^{1/3}$ is large compared to D_i. Equation (2-12) becomes

$$\frac{PV}{RT} = \sum_i^m \frac{n_i}{\left[1 - \frac{b}{V}\right]} \qquad (2\text{-}14)$$

Letting $C_i = n_i/V$, the concentration (moles per unit volume) of i-mer present in the liquid solution, (2-14) is

$$\frac{P}{RT} = \sum_i^m \frac{C_i}{\left[1 - \frac{b}{V}\right]} \qquad (2\text{-}15)$$

Differentiating (2-15) with respect to volume at constant temperature, rearranging and substituting equation (2-15) in the result, one obtains

$$\frac{dV}{dP} = \frac{1 - \frac{b}{V}}{RT \frac{d}{dV} \sum_i C_i + P \frac{d}{dV} \left[\frac{b}{V}\right]} \qquad (2\text{-}16)$$

To evaluate the derivative of C_i in the denominator, a relation from association theory has to be introduced, namely

$$K_i = \frac{C_i}{(C_1)^i} \qquad (2\text{-}17)$$

where K_i is called the equilibrium constant of the i-mer, or the equilibrium constant for the formation of a cluster of i molecules from i 1-mers.

Therefore

$$\sum_i^m C_i = \sum_i^m K_i C_1^i \qquad (2\text{-}18)$$

This finite series can be inverted into an infinite series,

$$C_1 = \sum_{x=1}^{\infty} d_x \left(\sum_i i C_i\right)^x \qquad (2\text{-}19)$$

provided all the coefficients greater than K_m, that is, K_{m+1}, K_{m+2}, etc. are equal to zero. The d_x are functions

of the equilibrium constants as follows

$$d_1 = 1$$
$$d_2 = -2K_2$$
$$d_3 = 8K_2^2 - 3K_3$$
$$d_4 = -40K_2^3 + 30K_2K_3 - 4K_4$$
$$\vdots$$

Hence the derivative of C_i in (2-16) is, using (2-18) and (2-17),

$$\frac{d}{dV}\sum_i C_i = \frac{d}{dV}\sum_i K_i C_1^i = \sum_i \frac{iC_i}{C_1}\frac{d}{dV}C_1 \qquad (2\text{-}20)$$

and therefore

$$\frac{d}{dV}C_1 = \sum_x xd_x \left(\sum_i iC_i\right)^{x-1} \frac{d}{dV}\left(\sum_i iC_i\right)$$
$$= \left[-\sum_x xd_x \left(\sum_i iC_i\right)^x / V\right]$$

using (2-2) with $n_i = C_i V$,

$$\sum_i iC_i = w / w_o V, \qquad (2\text{-}21)$$

Hence equation (2-20) becomes

$$\frac{d}{dV}\sum_i C_i = \frac{-\sum_i iC_i}{C_1}\left(\frac{\sum_x xd_x \left(\sum_i iC_i\right)^x}{V}\right) \qquad (2\text{-}22)$$

Using equation (2-19) and (2-21), equation (2-22) becomes

$$\frac{d}{dV}\sum_i C_i = -\left[\frac{W}{W_o V}\right] V^{-1}\left[\sum_x x d_x \left(\sum_i i C_i\right)^x\right] \Bigg/ \left[\sum_x d_x \left(\sum_i i C_i\right)^x\right]$$

$$= -\left[\frac{W}{W_o V}\right] \frac{1}{V} \sum_x S_x \left(\frac{1}{V}\right)^{x-1}$$

$$= -\left[\frac{W}{W_o V}\right] \sum_x S_x \left(\frac{1}{V}\right)^x \qquad (2\text{-}23)$$

where the S_x's are given by the relation

$$S_x = x g_x (W/W_o)^{x-1} \qquad (2\text{-}24)$$

and the g_x are functions of the equilibrium constants

$$\begin{aligned} g_1 &= 1 \\ g_2 &= -K_2 \\ g_3 &= 4K_2^2 - 2K_3 \\ g_4 &= -20K_2^3 + 18K_2K_3 - 3K_4 \\ &\vdots \end{aligned} \qquad (2\text{-}25)$$

The other derivative in the denominator of (2-16) is computed using (2-13) assuming all i-mers are identical, that is,

$$\frac{d}{dV}\left(\frac{b}{V}\right) = \frac{d}{dV}\sum_i b_i C_i$$

using definition of C_i

$$\frac{d}{dV}\left(\frac{b}{V}\right) = \sum_i' ib_i K_i C_1^{i-1} \frac{d}{dV} C_1$$

and using (2-17)

$$= \sum_i \left(ib_i C_i / C_1 \right) \left(\frac{d}{dV} C_1 \right) \qquad (2\text{-}26)$$

The same method as used to obtain (2-23) from (2-20) gives the following result

$$\frac{d}{dV}\left(\frac{b}{V}\right) = - \sum_i ib_i C_i \sum_x S_x \left(\frac{1}{V}\right)^x \qquad (2\text{-}27)$$

Substituting equations (2-27) and (2-23) in equation (2-16),

$$-\frac{dV}{dP} = \left[\frac{1 - b/V}{\sum_i ib_i C_i \sum_x S_x (1/V)^x} \right] \Bigg/ \left[\frac{(RTW/W_o V) \sum_x S_x (1/V)^x}{\sum_i ib_i C_i \sum_x S_x (1/V)^x} + P \right] \qquad (2\text{-}28)$$

or

$$-\frac{dV}{dP} = \left[\frac{V-b}{\sum_i ib_i n_i \sum_x S_x (1/V)^x} \right] \Bigg/ \left[\frac{RTW}{W_o \sum_i ib_i n_i} + P \right] \qquad (2\text{-}29)$$

Putting

$$J \equiv (V-b) / \sum_i ib_i n_i \sum_x S_x (1/V)^x \qquad (2\text{-}30)$$

and

$$L \equiv \frac{RTW}{W_o} \left[\frac{1}{\sum_i ib_i n_i} \right] \qquad (2\text{-}31)$$

(2-29) becomes

$$-\frac{dV'}{dP} = J / L + P \qquad (2\text{-}32)$$

This last equation after integration yields Tait's empirical equation

$$- V = J \log (L + P).$$

The initial conditions are P = 1 atm, $V = V_o$, and therefore

$$- V_o = J \log (L + 1)$$

the final form of Tait's equation is

$$V_o - V = J \log \left[\frac{L + P}{L + 1}\right] \qquad (2\text{-}33)$$

which is used to analyse compressibility data. The meaning of the two constants, J and L will now be discussed.

Meaning of L

Equation (2-31) is the definition of L, where T is temperature and R is the gas constant, W is the weight of the sample, W_o is the molecular weight of the 1-mer, n_i is the number of moles of particles of size i in the sample and b_i the excluded volume of a particle of size i.

L is found experimentally to be constant with

pressure under isothermal conditions by Gibson and Loeffler (1949). Therefore, $\sum_i i b_i n_i$ must then be constant within experimental error. This term is the sum of the excluded volumes for each mer $b_i N_i$, divided by Avogadro's Number N_o (since $n_i = N_i/N_o$), multiplied by i the number of molecules in the mer.

It is expected that this sum should not vary too much with pressure at constant temperature. However L does vary with temperature (Wohl, 1921) since the sizes of the mers change with temperature. It should be noted that the quantity $\sum_i i b_i n_i$ is heavily weighted towards the larger particles. This means that if the liquid consists of large particles connected by small particles, the value of L depends mainly on the size of the large particles.

Meaning of J

There has not been as much discussion in the literature about the nature of the quantity, J. It can be shown, Ginell (1961), that

$$\frac{1}{J} = \left\{ \frac{\partial}{\partial V} \ln\left[1 - \frac{b}{V}\right] \right\}_T \qquad (2\text{-}34)$$

Thus J is the reciprocal of the change of the logarithm of the fraction of space unoccupied by the molecules

with respect to a change in volume at constant temperature. Since this fraction does not change greatly with pressure, the logarithm of this quantity changes still less. J was found experimentally to be constant with pressure, but not with temperature, by Gibson and Loeffler (1949). Rearranging (2-33),

$$\frac{V_o - V}{V_o} = \frac{\Delta V}{V_o} = C \log \left[\frac{L-P}{L-1}\right] \qquad (2\text{-}35)$$

where $C = J/V_o$. C was found experimentally to be constant with temperature by Gibson and Loeffler (1939). C is found to have the same value for related groupe of substances, for example, benzene and benzene derivatives; water and concentrated aqueous solutions.

Summary of Notation

W - weight of the material

P - total pressure

V - total volume

R - universal gas constant = 8.314×10^{-5} bar m^3 $^oK^{-1}$ $mole^{-1}$

k - Boltzmann's constant

N_o - Avogadro's number

T - Temperature

W_o - weight of Avogadro's number of 1-mer

N - total number of particles

b - excluded volume of all particles

i - subscript labelling the size of a mer

j - subscript labelling the particle

γ - superscript labelling the type of packing

n_i - number of moles of particle of size i (i-mer)

N_i - number of particles of size i (i-mer)

m_i - mass of particle of size i (i-mer)

u_i - velocity component of particle of size i (i-mer)

c_i - total velocity of particle of size i (i-mer)

D_i - diameter of particle of size i (i-mer)

P_i - pressure exerted by i-th particle

b_o - excluded volume of particle of size i (i-mer)

C_i - concentration of i-mer present in the liquid

K_i - equilibrium constant of a i-mer

m_j - mass of any particle

u_j - velocity component of any particle

CHAPTER III

DATA ANALYSIS

3.1 Transformation of Tait's Equation.

It was shown in the preceding chapter, that Tait's equation has the form given by (2-35), that is,

$$V_o - V_i = V_o C \log \left[\frac{L + P_i}{L + 1}\right],$$

where P_i is the absolute pressure in atmospheres. Note that when P_i = 1 atm, the right side is zero and $V_i = V_o$.

Tait's equation is expressed in terms of measureable quantities as follows. With reference to Figure 10,

$$L_o^o = L_t - L_p$$

$$L_{oi}^o = L_{ti} - L_p$$

Letting A be the cross-sectional area and V_o the volume of the high pressure chamber at P = 1 atm, and A_i the corresponding area and V_i the corresponding volume at $P = P_i$, then

$$V_o = A\,(L_o^o - L_o)$$

$$V_i = A_i(L_{oi}^o - L_i)$$

Tait's equation, (2-35), then becomes

$$A\,(L_o^o - L_o) - A_i\,(L_{oi}^o - L_i) = A(L_o^o - L_o)C \log \left[\frac{L + P_i}{L + 1}\right] \quad (3\text{-}1)$$

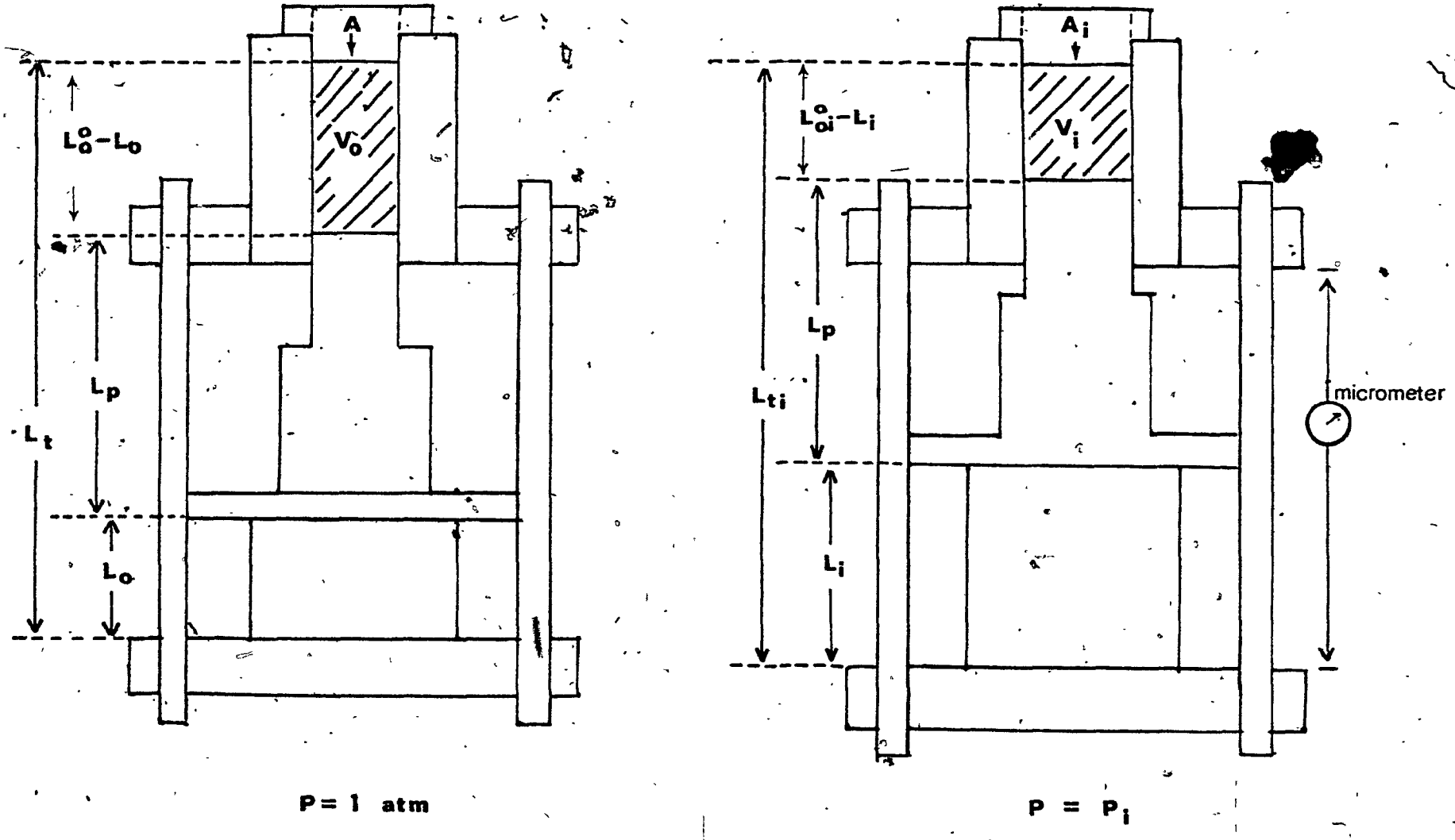


FIGURE 10

SCHEMATIC VIEW OF HIGH PRESSURE APPARATUS AT P=1 AT. AND P=P_i

By definition,

$$X = \frac{A_i}{A} \qquad \text{and} \qquad Y = \frac{L^o_{oi}}{L^o_o}$$

where X is the dilatation coefficient of the high pressure chamber and Y is the elongation coefficient of the columns of the press. Using these definitions, (3-1) becomes

$$L^o_o (1-XY) + XL_i = L_o + (L^o_o - L_o) C \log\left[\frac{L + P_i}{L + 1}\right] \qquad (3\text{-}2)$$

Equation (3-2) is used to experimentally determine the properties of the liquid, C and L. The value of X is determined theoretically in Appendix A. The quantities L_i, P_i, L^o_o and Y are measured directly. The measurements of the constants L^o_o and Y are discussed below. The length L_i is measured as a function of pressure P_i during the experiment. L_o is determined from the analysis of the data.

3.2 Measurement of L^o_o

The length L_t and L_p were measured directly. The volume of the assembly in the high pressure chamber, that is, the holder, electrical connections and a manganin gauge was also measured and then the length of the high pressure chamber corresponding to this volume, L_a, was computed. The value of L^o_o corrected for the assembly volume is $L^o_o = L_t - L_p - L_a$. The result is $L^o_o = 279.5 \pm 3$ mm.

The error in L_o^o is due to the uncertainty in the measurement of L_t, L_p, L_a; the change of volume of the high pressure chamber due to the deformation of teflon joints and change in volume of assembly under pressure is included in the error in L_o^o.

3.3 Measurement of Y

A micrometer with a relative precision of better than 0.01 mm was placed between the upper and lower plates supporting the columns as shown in Figure 10. The change of length was measured as a function of pressure and found to be 0.009 mm/kbar.

Using $L_o^o = 279.5$ mm,

$$Y = 1 + 3.2 \times 10^{-8} P_i$$

where P_i is in bars.

3.4 Data Analysis

Calculations were done on a Pallas Computer. Programming was done in fortran and is given in Appendix B.

Input data consists of L_i, length defined by Fig. 10, and R_i and R_o the resistance values of the manganin gauge. With the calibration curves of the gauges, resistance values R_i are transformed into pressure values P_i. The resistance R_o is the resistance

of the gauge at P = 1 atm. Using equation (3-2), three quantities must be determined: L, L_o and C.

An iteration method is used first to evaluate L. Equation (3-2) behaves like a straight line

$$y = L_o + Qx \qquad (3-3)$$

where $y = XL_i + L_o^o (1 - XY)$, $x = \log \left[\frac{L + P_i}{L + 1}\right]$

$$Q = C (L_o^o - L_o)$$

L can be considered as an internal pressure, and Tait's equation, (2-35) as a relation between volume and total pressure. Figure 11 shows descriptive curves of P_i and L_i and certain values of L. This graph presents two characteristics. First for a particular value of L, L', (L' = 650 bar in Figure 11) equation (3-2) is a straight line. Secondly there is a change of sign of the second degree coefficient of the curves, when L goes from a value $L<L'$ to a value $L>L'$. The iteration process then consists in assuming an equation of the type

$$y = L_o + Q\ x\ +\ R\ x^2 \qquad (3-4)$$

and looking for the value of L for which R = 0.

Table II shows the evolution of such a calculation as it appears at the output of the computer. For values of L' around 650 bar, the error introduced by the iteration process and the calculations performed

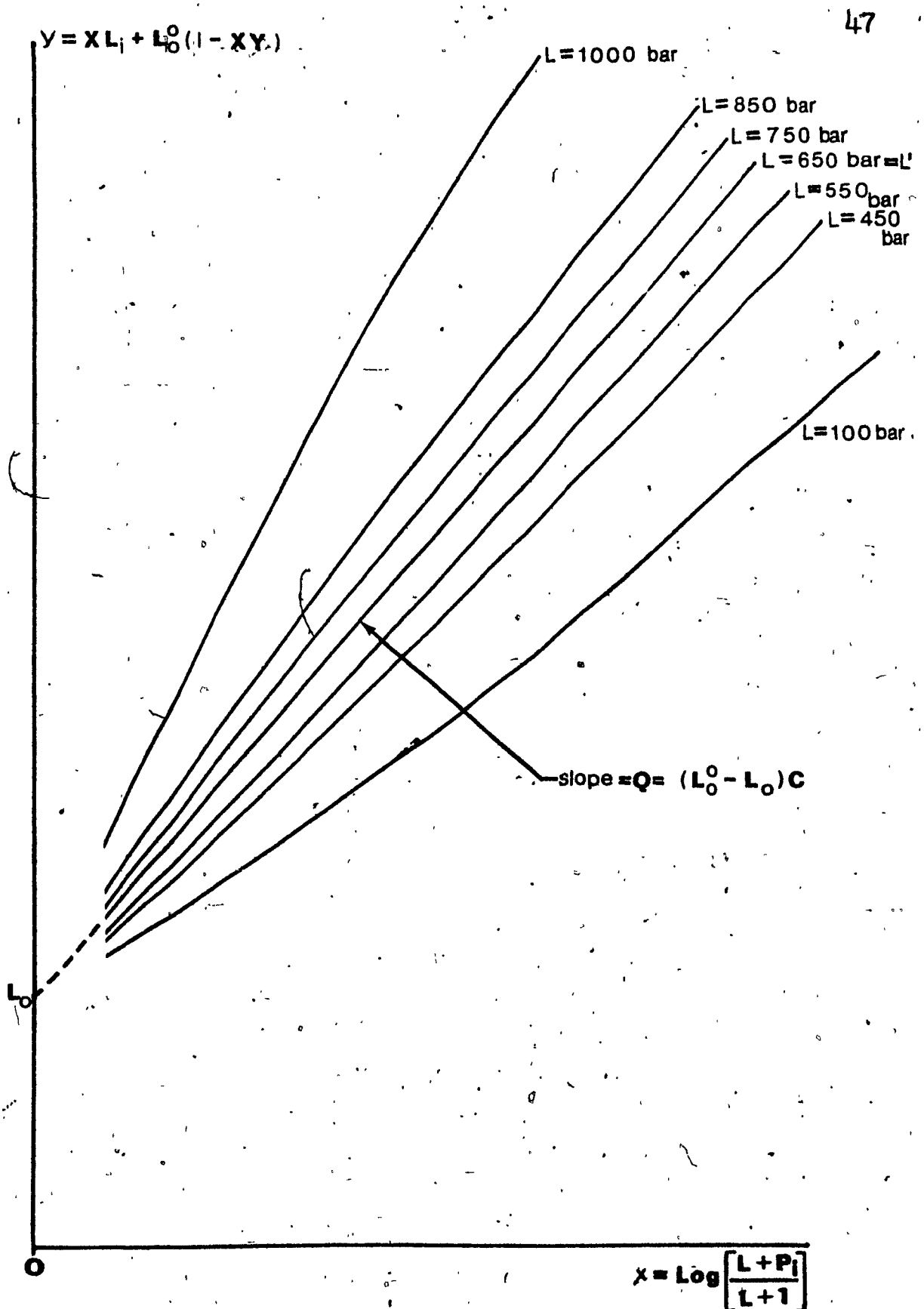


FIGURE 11

DESCRIPTIVE PLOT OF (3-4) FOR DIFFERENT VALUES OF L

in the program is of the order of 0.1% since L' is found to the nearest bar. For this case L' = 656 $\pm$ 1 bar. When the value of L' is found equation (3-3) is satisfied.

The other two quantities, L_o and C, are found after L = L' is found by using the values of L_o and Q determined by the program. As shown in Figure 11, L_o is the intercept obtained by extrapolation and Q is the slope of the straight line (curve for which L = L'). Using the definition of Q which follows equation (3-3) C is found.

3.5 Polynomial Expression of Tait's Equation

Using equation (2-35) and assuming that $L \gg 1$, by successive transformations a polynomial expression of Tait's equation is obtained which is used by other workers.

$$\frac{V_o - V_i}{V_o} = C \log \left[\frac{L + P_i}{L}\right]$$

$$= C \left[\log e\right] \ln \left[1 + \frac{P_i}{L}\right]$$

$$= C \log e \left[\frac{P_i}{L} - \frac{1}{2}\frac{P_1^2}{L^2} + \frac{1}{3}\frac{P_1^3}{L_1^3} - \cdots\right]$$

$$= \left[\frac{C \log e}{L}\right] P_i - \left[\frac{C \log e}{2L^2}\right] P_i^2 + \left[\frac{C \log e}{3L^3}\right] P_i^3 - \cdots$$

$$= A'P_i + B'P_i^2 + C'P_i^3$$

where the coefficients are given by

L (bar)	R
1000	- 0.15059
900	- 0.10434
800	- 0.05999
700	- 0.01765
600	+ 0.02256
700	- 0.01765
690	- 0.01354
680	- 0.00944
670	- 0.00535
660	- 0.00131
650	+ 0.00271
660	- 0.00131
659	- 0.00091
658	- 0.00047
657	- 0.00008
656	+ 0.00027
L' = 656	

TABLE II

STEPS IN THE ITERATION PROCEDURE
FOR THE EVALUATION OF L'

$$A' = \frac{C \log e}{L}$$

$$B' = -\frac{C \log e}{2L^2}$$

$$C' = \frac{C \log e}{3L^3}$$

These transformation coefficients permit a comparison between the results expressed in terms of L and C, and other results published in polynomial form notably by Schamp (1965).

3.6 Error Analysis

The maximum error in L and C was found using the same analysis as in section 3.4. The maximum and minimum values of L and C were calculated using the appropriate maximum and minimum values of the four measured quantities L_o^o, Y, L_i and R_i and the one theoretically computed quantity, X. The reported values of L and C are the mean of the maximum and minimum values and the maximum error is $\pm \frac{1}{2}$ the difference between the maximum and minimum values.

The following quantities where used to find the mean values of L and C and their maximum errors:

Quantity	Reference
$L_o^o = 279 \pm 3$ mm	Section 3.2

Quantity	Reference
$Y = 1 + 3.2 \times 10^{-8} P_i \pm .4 \times 10^{-8} P_i$	Section 3.3.
$L_i = L_i$ (measured) $\pm$ 0.02 mm	Section 1.4
$R_i = R_i$ (measured) $\pm$ 0.002 ohm	Section 1.3.3
$X = 1 + 1.1 \times 10^{-6} P_i \pm .6 \times 10^{-6} P_i$	Appendix A

The relation between R_i and P_i is given in Section 1.3.2.

The results below are mean values of L and C and their errors found as described above for one set of experimental data

$$L = 646 \pm 39 \text{ bar}$$

$$C = 0.2495 \pm 0.0080$$

The error in L is 7% and in C, 3%.

The main source of the errors in L and C is the error in X which in turn is due to the uncertainty in Young's Modulus of the steel in the high pressure chamber.

CHAPTER IV

INTERPRETATION OF RESULTS

Volumetric measurements were made on three liquids: n-pentane, isopentane and their equivolumetric mixture.

4.1 Results and Data Analysis

All raw data are given in Appendix C. Eight repeated experiments were done for each of the three liquids, a total of 24 experiments in all.

Table 3 shows the results for one of the experiments on the equivolumetric mixture of n-pentane and isopentane. Figure 12 is a plot of these experimental points. The method does not permit an experimental determination of L_o and hence of V_o. The volume V_o is nevertheless required for the computation of compression, k, defined as

$$k = -\frac{(V_i - V_o)}{V_o}$$

In the preceding chapter, a method has been developed using a form of Tait's equation of state, which permits the successive evaluation of L, V_o and C where L and C are the coefficients in Tait's equation. Two

For R_o = 115.914 ohms

L_i	R_i
9.472	115.944
10.476	116.063
11.478	116.273
12.182	116.498
12.686	116.714
13.188	116.985
13.689	117.321
13.991	117.558
14.494	118.016

TABLE 3

EXEMPLE OF EXPERIMENTAL DATA FOR EQUIVOLUMETRIC MIXTURE

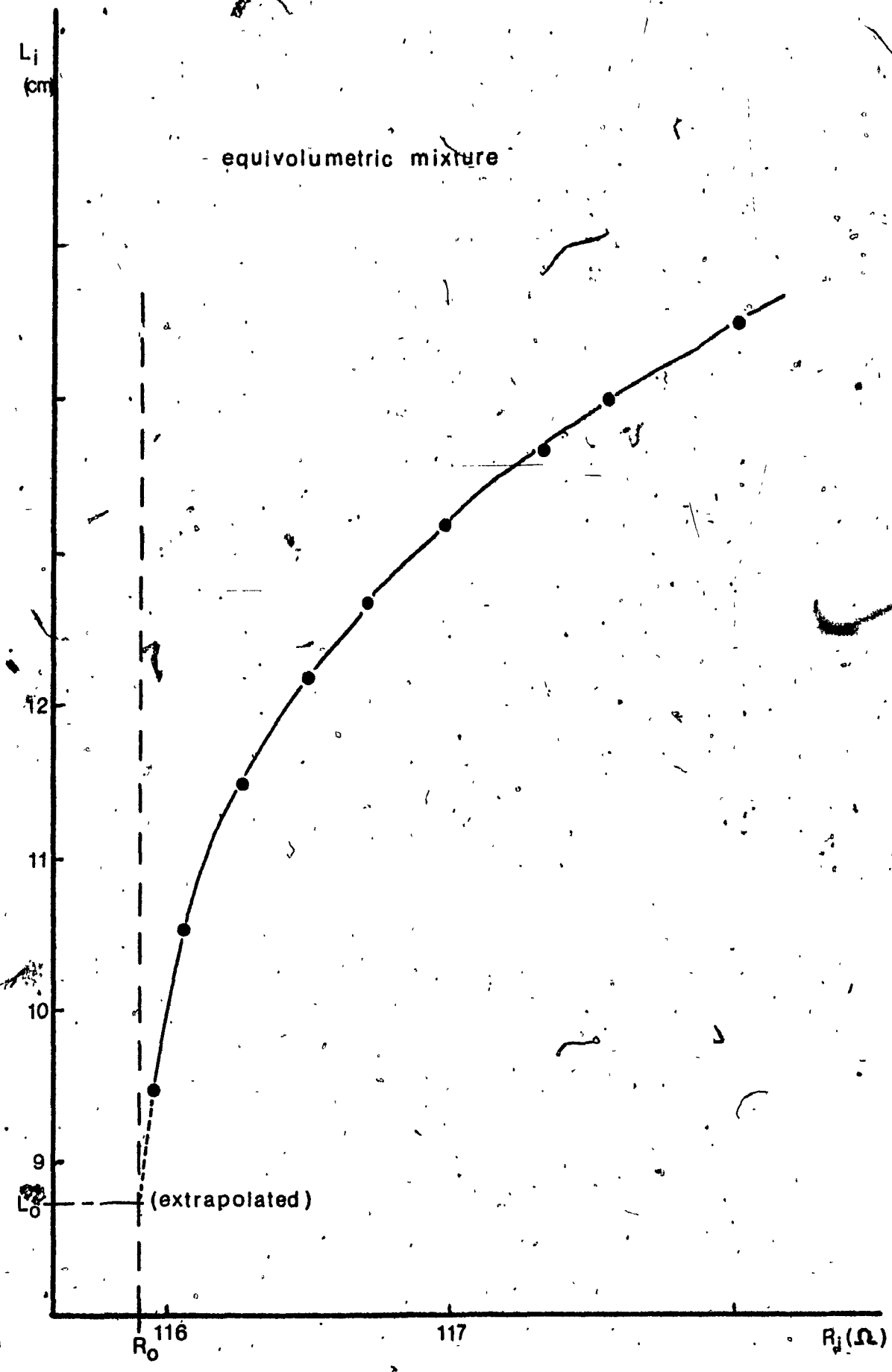


FIGURE 12

PLOT OF EXPERIMENTAL DATA OF TABLE 3

other methods were examined in order to evaluate V_o from experimental data L_i : polynomial extrapolation and graphical extrapolation.

The polynomial extrapolation of L_o is done by fitting a polynomial of degree n to the experimental points. One condition for this procedure to be acceptable is that the series converge in the pressure interval considered. Using a least square method, polynomials up to the 15th degree were fitted to the experimental points, without any evidence of convergence in the series. This fact is not surprising: the polynomial equation (3-5) converges only for $P < L$ and L is of the order of 600 bar. Since two or three experimental points available in the convergence interval ($0 < P < 600$ bar) were too few, the polynomial method of extrapolation was abandoned.

Graphical extrapolation permits an evaluation of V_o. Table 4 shows the average values of k obtained from 24 experiments (8 per liquid studied), after graphical extrapolation to find L_o. Graphical interpolation was used to obtain values of k at multiples of 10^3 bar. The mean deviation between values obtained is large (of the order of 10%). This fact can be understood by examining Figure 12. At zero pressure, the L_i vs R_i curve becomes

P(bar)	n-Pentane k(average)	Δk	isopentane k(average)	Δk	50-50 mixture k(average)	Δk
0	0.0000	-	0.0000	-	0.0000	-
1000	0.0994	0.0090	0.1035	0.0105	0.1002	0.0110
2000	0.1485	0.0130	0.1535	0.0160	0.1495	0.0150
3000	0.1835	0.0135	0.1865	0.0165	0.1835	0.0165
4000	0.2085	0.0110	0.2125	0.0220	0.2105	0.0230
5000	0.2305	0.0165	0.2330	0.0180	0.2320	0.0190
6000	0.2465	0.0180	0.2470	0.0230	0.2470	0.0370
7000	0.2595	0.0210	0.2625	0.0310	0.2620	0.0310
8000	0.2730	0.0240	0.2745	0.0285	0.2740	0.0280

$$k(\text{average}) = \sum_{i=1}^{8} k_i / 8 \quad ; \Delta k = \sum_{i=1}^{8} |k_i - k(\text{average})| / 8$$

TABLE 4

COMPRESSION DATA OBTAINED BY GRAPHICAL EXTRAPOLATION OF V_o

nearly tangent to the L_i axis, so that extrapolation is inaccurate.

Tait's equation was used to analyse the experimental data as described in Chapter 3, due to the disadvantages of the polynomial and graphical methods described above. The mathematical method permits the evaluation of L without a knowledge of V_o, and hence does not introduce an extrapolation error in its evaluation. V_o and C are then found simultaneously using equation (3-4). Table 5 shows the results of this work for n-pentane, isopentane and their equivolumetric (50-50) mixture. Figure 13 shows the compression curves of the three substances. The values of k were computed from Tait's equation (2-35) using the average values of L and C in Table 5. The temperature effect is presented in terms of $\Delta L/\Delta T$, as done by Eduljee, Newitt and Weale (1951).

4.2 Relative Values of Compression for the Three Substances Studied

It has been found in the preceding chapter that the maximum error in the evaluation of L is 7%, and 3% in the evaluation of C. This error is due to both reproducibility errors and systematic errors. To discuss the validity of the relative values of L and C for n-pentane, isopentane and their equivolumetric mixture, the reproduci-

	n-Pentane			Isopentane			50-50 mixture		
	L(bar)	C	T(°C)	L(bar)	C	T(°C)	L(bar)	C	T(°C)
Results of eight experiments on each liquid	584	0.2291	18.5	551	0.2332	21	546	0.2282	19
	636	0.2361	18	558	0.2295	19	563	0.2310	22
	621	0.2349	21	585	0.2320	18.8	578	0.2326	20
	609	0.2319	23.5	539	0.2268	22	581	0.2327	21.5
	590	0.2333	22	560	0.2275	21	587	0.2350	19.2
	677	0.2366	22.5	567	0.2275	19	585	0.2345	19.3
	621	0.2367	23	558	0.2318	21	622	0.2360	16.3
	628	0.2373	22.8	582	0.2339	18.5	607	0.2360	18.1
Average	614	0.2344		563	0.2302		584	0.2332	
Root mean square deviation	18	0.0027		15	0.0027		22	0.0025	

TABLE 5

EXPERIMENTAL RESULTS IN TERMS OF THE CONSTANTS OF TAIT'S EQUATION

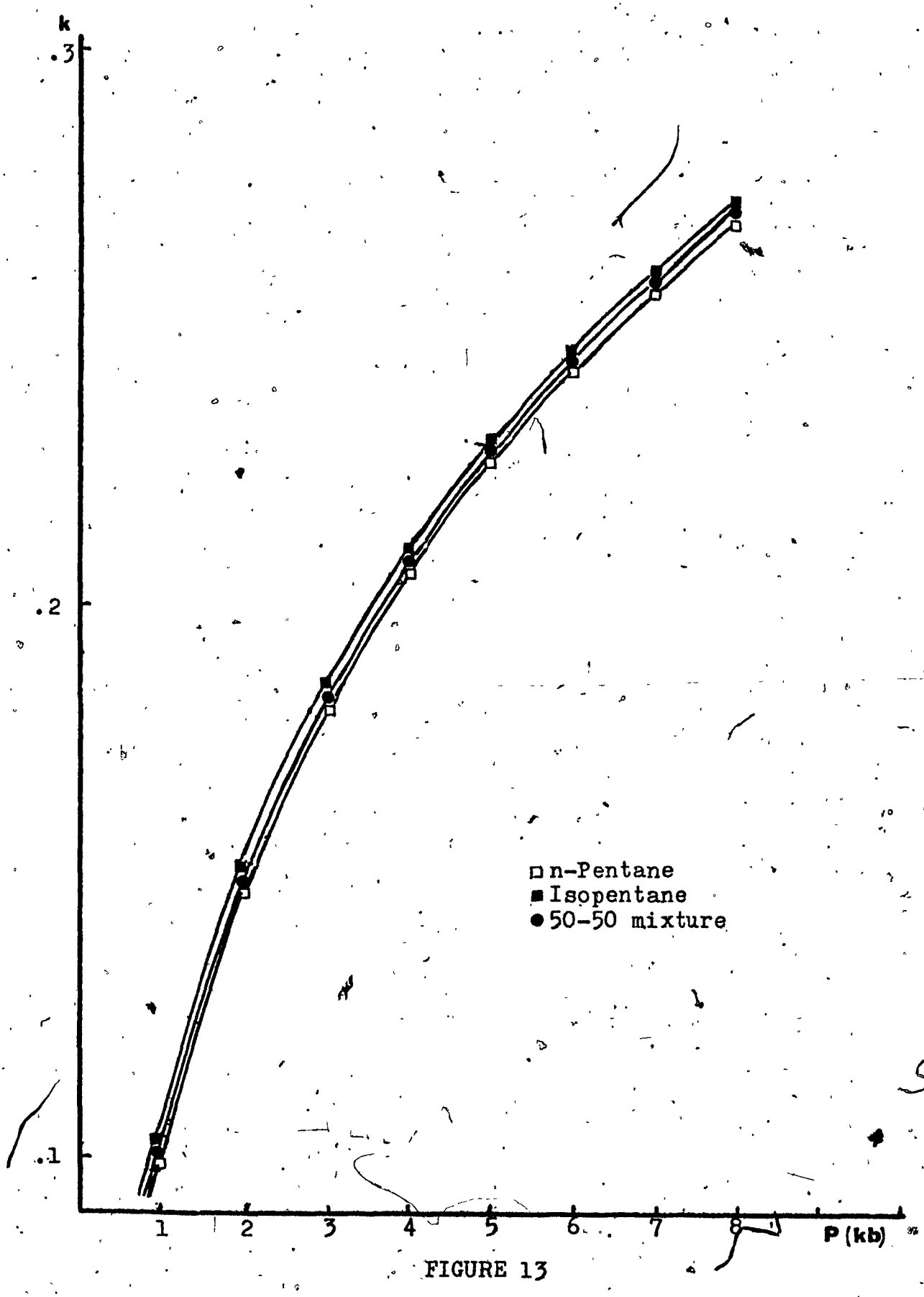


FIGURE 13

EXPERIMENTAL COMPRESSION CURVES FOUND USING TAIT'S EQUATION

bility errors must be evaluated.

The dilatation of the high pressure chamber, the elongation of the columns, the linearity of the measuring apparatus are phenomena common to all experiments and hence do not affect the relative values of L and C found for the three substances studied. These are sources of systematic errors. On the contrary, the temperature, the purity of the materials, and the use of the measuring apparatus are phenomena which differ from one experiment to the next and contribute to the reproducibility errors.

The purity of the material is different for each experiment: the greases used to ensure a minimum friction of the joints in the chamber, come in contact with the liquid under study in an unpredictable fashion. The fact that the liquids used were of technical grade and from different batches also contributes to the error in the relative measure of L and C. Since no chemical analysis was done either before or after the experiments, the effect of purity is difficult to evaluate and probably not negligible.

The temperature effect will be analysed in the next section. It plays an important role in the determination of L. However, temperature has no noticeable effect

on the experimental value of C .

The precision of the measuring apparatus as discussed in the chapter on instrumentation, can only account for an error of 1% or less in the reproducibility of the experiments.

From Table 5 the reproducibility error in C is about 1%. Since the values of C for each liquid are different by less than 1% from Table 5, C can be considered to be the same for all three liquids.

4.3 Temperature Effect

Figure 14 shows the values of L obtained for each experiment plotted against the ambient temperature, T, at which each of these experiments was performed (data from Table 5). The method of least squares was used to find the straight line of best fit passing throught these points. The following equations were found assuming a linear relation between L and T, for T in ^{o}C,

$$L = 694 - 3.4\ T \quad \text{for n-pentane,}$$
$$L = 737 - 8.7\ T \quad \text{for isopentane,} \qquad (4\text{-}1)$$
$$L = 790 - 10.4\ T \quad \text{for the equivolumetric mixture.}$$

The temperature dependence is non nigligible; $\Delta L/\Delta T$ is of the order of 7 bar/^{o}C. For temperature

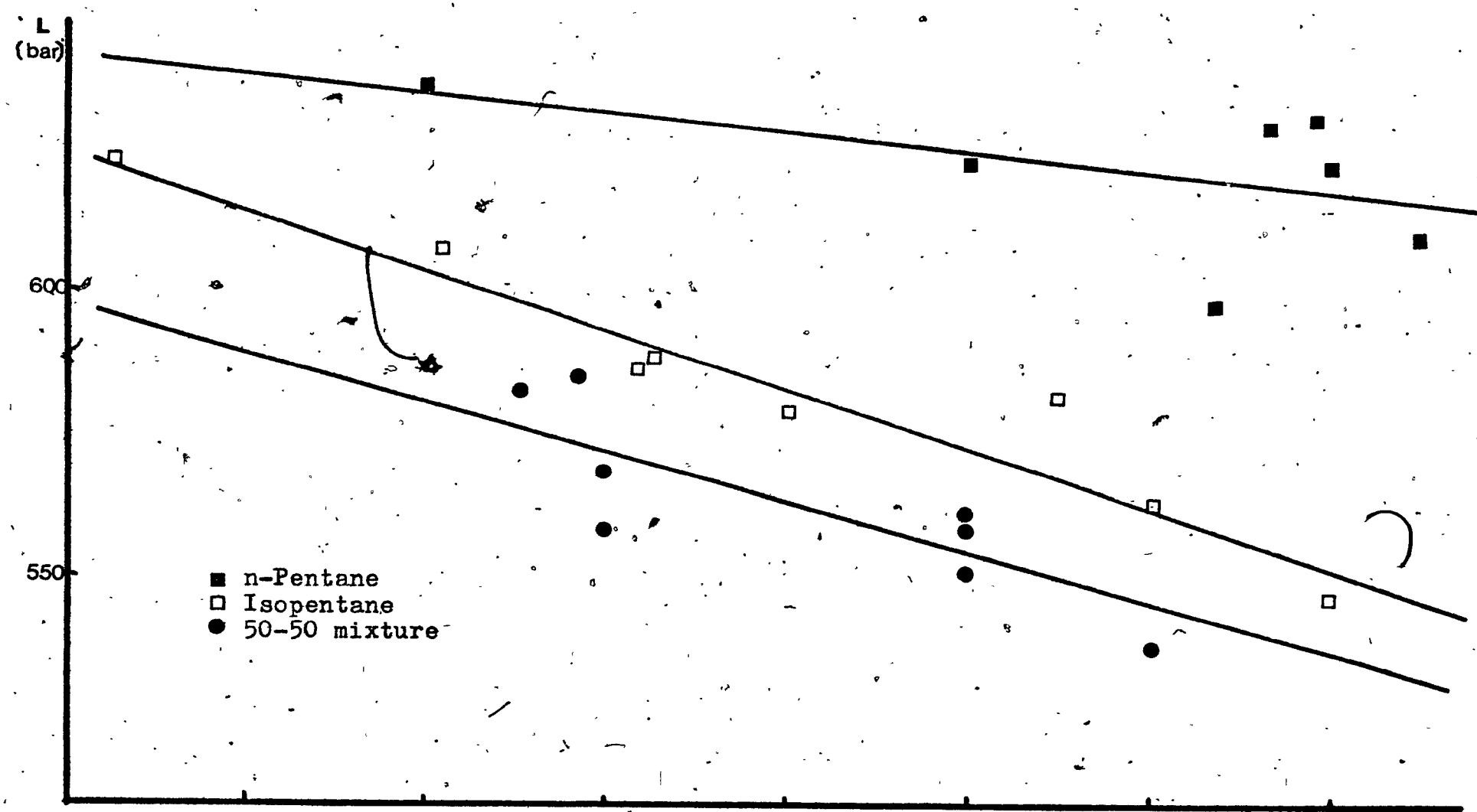


FIGURE 14

EXPERIMENTAL CURVES OF L VERSUS T

differences between the experiments, the effect of T on the average values of L is of the order of 3%.

This temperature effect can be compared to other work. Eduljee, Newitt and Weale (1951) have studied the variation of L with T for n-octane, n-heptane and n-hexane. Table 9 shows their results, obtained by the piezometric method. The coefficient $\Delta L/\Delta T$ is almost the same for n-octane, n-heptane and n-hexane, and should then roughly apply to n-pentane. They found a variation of the order of 7 bar/°C in the temperature region around 20°C. This coefficient is of the same magnitude as that observed in this work.

Using equations (4-1), values of L in Table 5 are corrected according to the temperature observed during each experiment. This correction narrows the root mean square deviation of the results. The values of L at 20°C are

$$\begin{aligned} L &= 625 \pm 7 && \text{for n-pentane,} \\ L &= 589 \pm 5 && \text{for equivolumetric mixture,} \\ L &= 564 \pm 7 && \text{for isopentane} \end{aligned} \qquad (4\text{-}2)$$

Temperature variations between the beginning and the end of each experiment also introduce uncertainties in the results. These variations were kept minimum by working

during certain "isothermal" hours of the day. Nevertheless variations of 0.2 to 0.5°C during each experiment were inevitable. Their effect is hard to evaluate without a knowledge of the variation of the thermal expansion under pressure. These variations should introduce less than a 1% error on L.

4.4 Comparison with Bridgman's Results.

Tables 6 and 7, together with Figures 15 and 16 show Bridgman's compression data (1931) for n-pentane and isopentane at 0°C, 50°C and 95°C. With a second degree polynomial, this data was interpolated to 20°C. Results of this interpolation, together with the results of the present work at 20°C are also shown in Tables 6 and 7 and Figures 15 and 16.

The precision claimed by Bridgman is of the order of 0.2% on isopentane and of 0.1% on n-pentane. The difference between Bridgman's results and the results of the present work is 5 to 7%, Bridgman's results being larger (see Figures 15 and 16). This corresponds to the maximum error of the method as evaluated in the preceeding chapter.

Bridgman also found that n-pentane is more compres-

P (kgf/cm^2)	k (0°C) Bridgman (1952)	k (50°C) Bridgman (1952)	k (95°C) Bridgman (1952)	k (20°C) Extrapolated from Bridgman	k (20°C) This work
0	0.0000	0.0000	0.0000	0.0000	0.0000
1000	0.0979	0.1331	0.1771	0.1102	0.0995
2000	0.1454	0.1862	0.2352	0.1600	0.1488
3000	0.1771	0.2199	0.2695	0.1926	0.1819
4000	0.2003	0.2440	0.2948	0.2161	0.2069
5000	0.2189	0.2632	0.3155	0.2348	0.2269
6000	0.2353	0.2796	0.3317	0.2513	0.2436
7000	0.2494	0.2934	0.3450	0.2653	0.2580
8000	0.2619	0.3061	0.3[illegible]	0.2781	0.2705
9000	0.2719	0.3164	0.3659	—	—
10000	0.2808	0.3249	0.3738	—	—

TABLE 6

COMPRESSION DATA FOR N-PENTANE

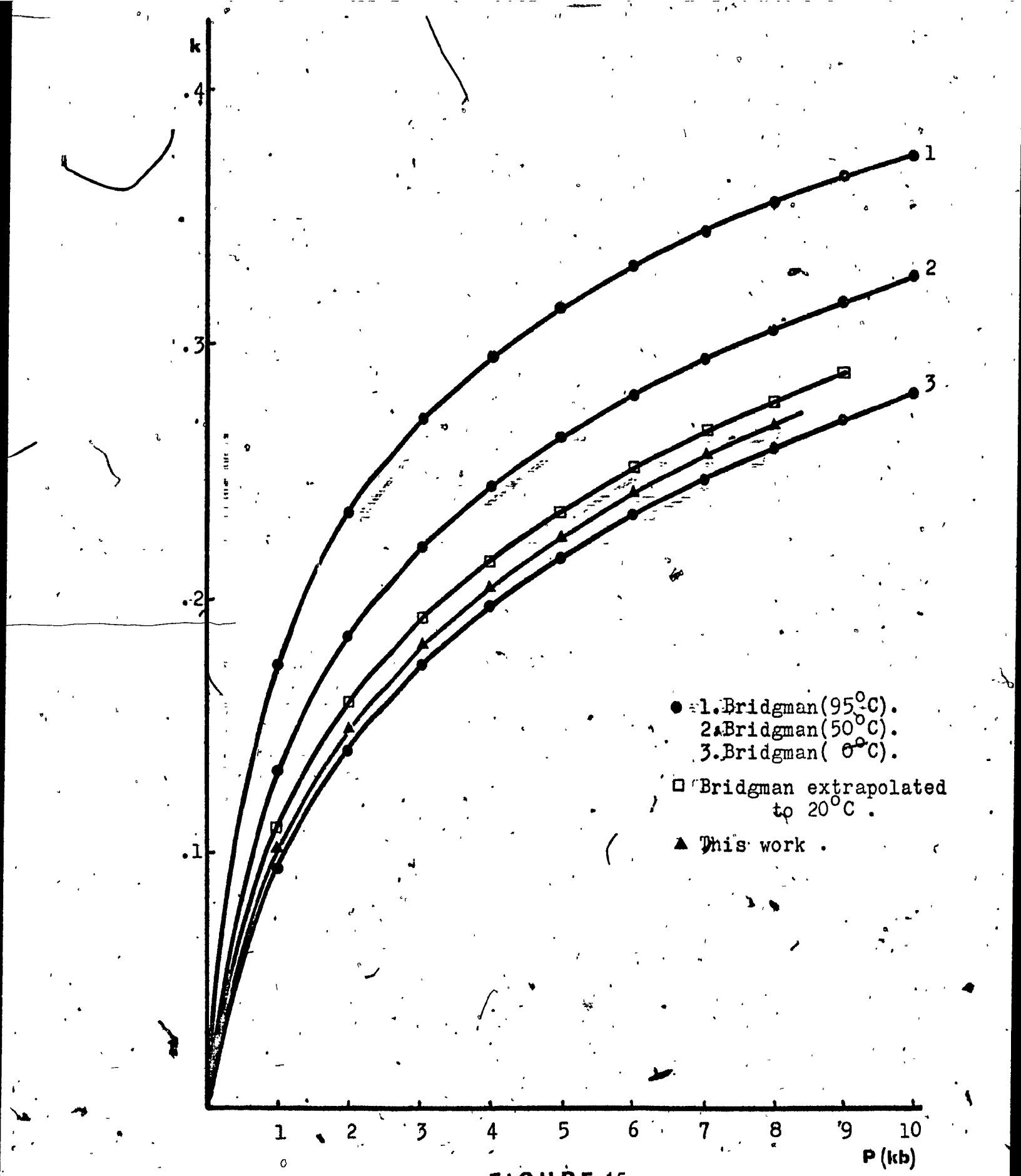


FIGURE 15

COMPRESSION DATA FOR N-PENTANE FROM DATA IN TABLE 6

P (kgf/cm^2)	k (0°C) Bridgman (1952)	k (50°C) Bridgman (1952)	k (95°C) Bridgman (1952)	k (20°C) Extrapolated from Bridgman	k (20°C) This work
0	0.0000	0.0000	0.0000	0.0000	0.0000
1000	0.0972	0.1317	0.1646	0.1108	0.1032
2000	0.1429	0.1842	0.2233	0.1591	0.1529
3000	0.1736	0.2170	0.2579	0.1907	0.1860
4000	0.1975	0.2417	0.2843	0.2148	0.2108
5000	0.2170	0.2609	0.3035	0.2341	0.2306
6000	0.2330	0.2760	0.3184	0.2497	0.2472
7000	0.2466	0.2871	0.3303	0.2618	0.2614
8000	–	0.2998	0.3437	–	0.2738
9000	–	0.3107	–	–	–

TABLE 7

COMPRESSION DATA FOR ISOPENTANE

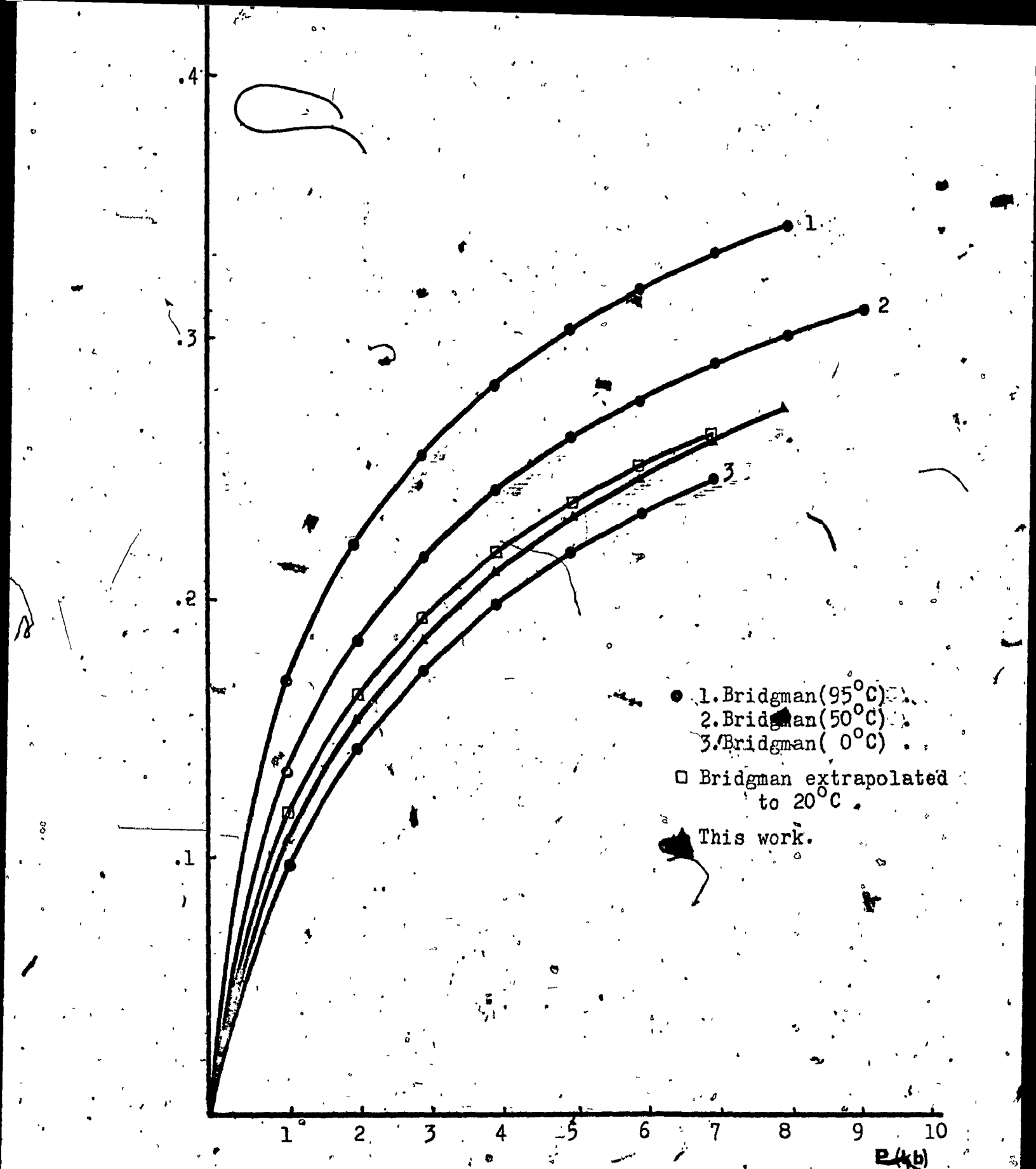


FIGURE 16

COMPRESSION DATA FOR ISOPENTANE FROM DATA IN TABLE 7

sible than isopentane; this difference between the two compressibilities is of the order of 1%. In the present work, isopentane is found to be 2% more compressible than n-pentane. This relative difference in the results can be explained by the degree of purity of the materials used. The n-pentane used by Bridgman was more than 99% pure; the n-pentane used in this work is claimed to be 95% pure and subjected to contact with grease in the high pressure chamber. Also the resolution power of the present method is less than the 1% difference in compressibility observed by Bridgman. A comparison of both sets of results is then not possible.

4.5 Comparison with Other Work on Hydrocarbons

Tables 8 and 9 and Figure 17 show compression results obtained by Eduljee, Newitt and Weale (1951) on hydrocarbons. Results of Table 9 are given in terms of Tait's coefficient L. These authors report results for n-octane, n-heptane, n-hexane and found that the values of L were proportional to the density of the liquids. Therefore an extrapolation in terms of density is justified to n-pentane at 20°C. The results of this extrapolation together with the results of this work are shown in Table 9. The data of Table 8 and Table 9 show a difference of the order of 3% between the results obtained from Eduljee, Newitt and Weale (1951) and the results of this work.

P (atm.)	P, (bar)	k (25°C) OCTANE* $CH_3(CH_2)_6CH_3$	k (25°C) HEPTANE* $CH_3(CH_2)_5CH_3$	k (25°C) HEXANE* $CH_3(CH_2)_4CH_3$	k (20°C) PENTANE** $CH_3(CH_2)_3CH_3$
0	0	0.0000	0.0000	0.0000	0.0000
1000	1013	0.0779	0.0875	0.0945	0.0990
2000	2026	0.1201	0.1321	0.1407	0.1483
3000	3039	0.1490	0.1621	0.1716	0.1814
4000	4053	0.1711	0.1850	0.1950	0.2060
5000	5066	0.1892	0.2034	0.2135	0.2263
6000	6079	—	—	—	0.2430
7000	7092	—	—	—	0.2574
8000	8105	—	—	—	0.2699

*Data from Eduljee, Newitt and Weale (1951)

**Data from this work .

TABLE 8

COMPRESSION DATA FOR LIQUID HYDROCARBONS

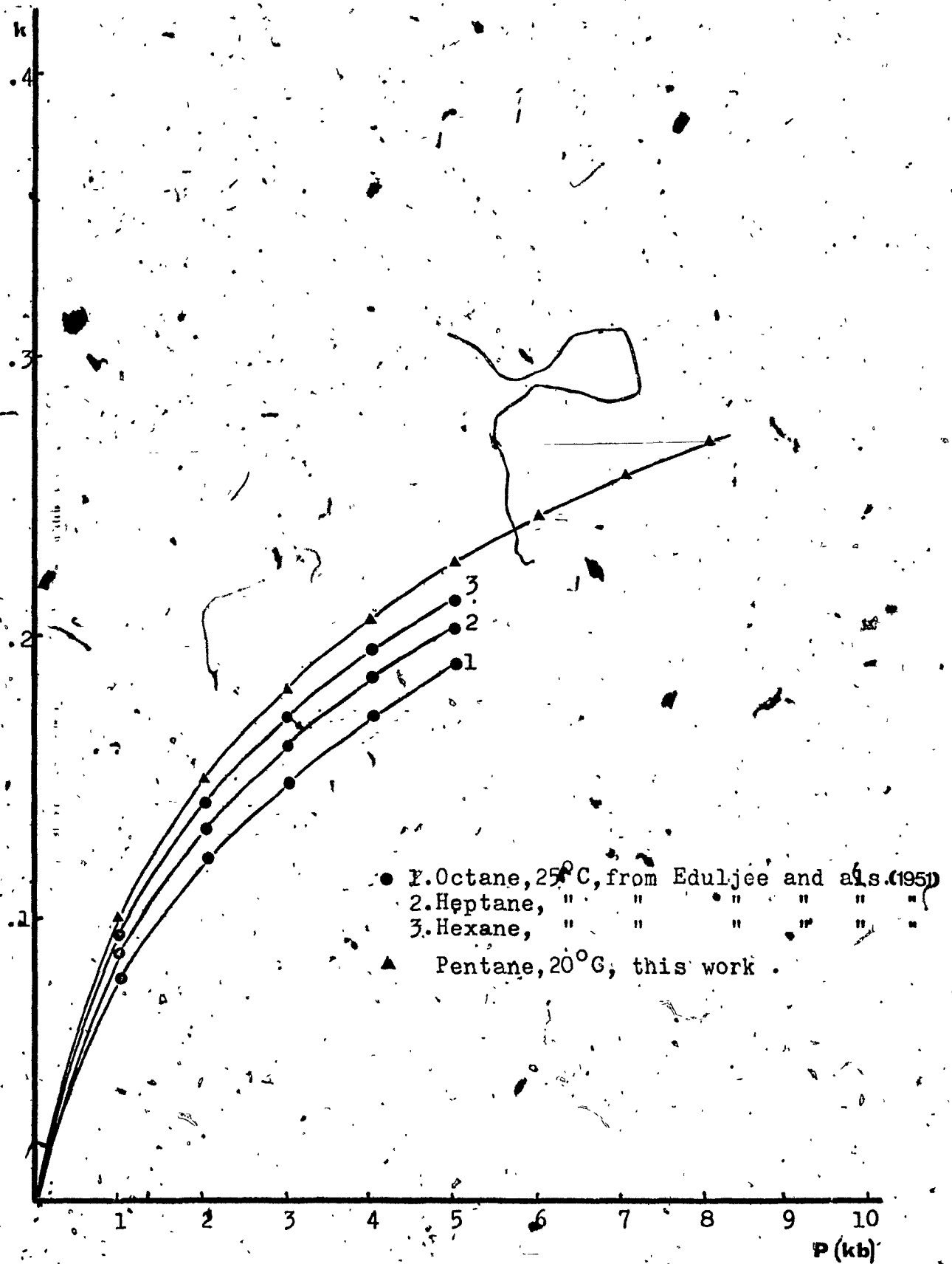


FIGURE 17.

COMPRESSION DATA FOR HYDROCARBONS. FROM DATA IN TABLE 8

N-Hydrocarbons	L (0°C)	L(25°C)	L (40°C)	L (60°C)	L (20°C) Extrapolated*
Octane**	944	787	706	607	817 (841-799)
Heptane**	799	662	591	505	688 (709-672)
Hexane**	723	587	515	430	612 (633-597)
Pentane (extrapolated)	716	562	477	382	589*** (614-572)

* Values in parenthisis indicate a variation of L between 16° and 23°C
** C = constant = 0.2172
*** Value found in this work, L= 614

TABLE 9

DATA FROM EDULJEE, NEWITT AND WHEALE (1951) FOR N-OCTANE, N-HEPTANE AND N-HEXANE, EXTRAPOLATED TO N-PENTANE

CONCLUSIONS

Volumetric compressibility measurements were done on three liquids: n-pentane, isopentane and their equivolumetric mixture. Eight repeated experiments were done on each of the three liquids. Three physical quantities were measured: L_i, R_i and T. L_i is defined as the displacement of the primary piston (displacement from about 100 mm at atmospheric pressure to about 150 mm at the highest pressure). R_i is the resistance of the manganin gauge for pressure variations from 300 bar to 8 kbar. T is the ambient temperature which was constant to within 0.5°C for each experiment but varied from 16°C to 23°C for the series of experiments.

A new method of analysis was developed which does not require an experimental determination of V_o, the volume of liquid in the high pressure apparatus at atmospheric pressure. First, L, one of the two characteristic constants of a liquid in Tait's equation, was found by fitting experimental data L_i and R_i to Tait's equation. Next, L_o, the length of the cylinder of liquid in the high pressure apparatus at atmospheric pressure, and then C, the second characteristic constant in Tait's equation, are found. The compression, $k = (V - V_o)/V_o$, as a function of pressure was calculated from Tait's equation using the value of L and C found in the analysis.

For all liquids C was found to be constant within experimental error, C = 0.233 ± 0.0026, which is the mean of the three values given in Table 5. C was found to be independent of the temperature in each experiment. The final values of L for each liquid are given in equation (4-2). The errors in C given above and on L in equation (4-1) are reproducibility errors. The maximum error in C was estimated to be 3% and in L, 7%. These maximum errors are mainly due to the uncertainty in the dilatation of the high pressure chamber.

The independence of C with temperature together with the estimated temperature dependence of L agree with published work. Values obtained for L and C in this experiment agree with those in the literature within maximum experimental error. This indicates that new method used to analyse the results is valid.

Three main improvements could be made to this experimental method. The ambient temperature varied during each experiment. Temperature control could be improved to ensure isothermal conditions. Secondly, the theoretical corrections which were made for the dilatation of the high pressure chamber were relatively imprecise. An experimental study of the dilatation of the chamber is required for a precise evaluation of X, the dilatation coefficient.

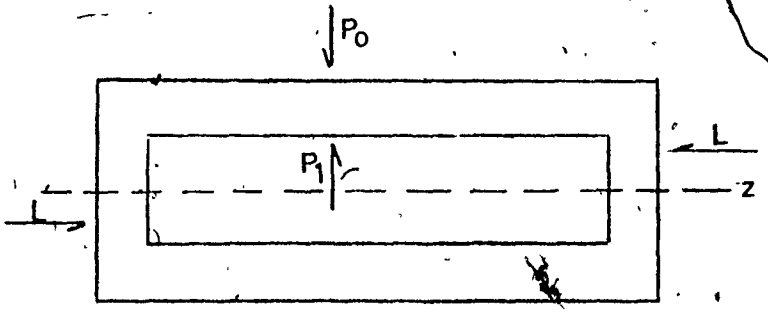
Thirdly, the purity of the materials studied was assumed to be the nominal value, 95%, claimed by the supplier of the materials. Chemical analysis of the liquids before and after the experiments would improve the precision of the method.

The advantages of the method developed in this work lie in the simplicity of measurements and the little time required for each experiment. The measuring instruments required are few: an ohmmeter, calliper square, manganin gauge and micrometer. With the improvements described above, precision of the order of 1% or less could be easily attainable.

APPENDIX A

DILATATION OF HIGH PRESSURE CHAMBER

Consider a cylinder with internal radius, a, and external radius, b, submitted to internal pressure p_1 and external pressure p_o, and submitted to equal and opposite compressive forces on its two ends, acting parallel to its axis.



Using cylindrical coordinates r, θ, and z, the elements of the stress tensor are

$$\sigma_r , \sigma_\theta , \sigma_z ; \tau_{r\theta} , \tau_{rz} , \tau_{\theta z} .$$

Calling u, v, and w, displacements of a unit volume in the cylinder along the r, θ, and z axis, the expansion coefficients become:

$$\varepsilon_r = \frac{u}{r} \qquad \varepsilon_\theta = \frac{u}{r} + \frac{1}{r}\frac{\partial v}{\partial \theta} \qquad \varepsilon_z = \frac{\partial w}{\partial z}$$

$$\gamma_{r\theta} = \frac{1}{r}\frac{\partial u}{\partial \theta} + \frac{\partial v}{\partial r} - \frac{v}{r} \qquad \gamma_{rz} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial r}$$

$$\gamma_z = \frac{1}{r}\frac{\partial w}{\partial \theta} + \frac{\partial v}{\partial z}$$

Because of symmetry around the z axis, $v \equiv 0$, and

$$\frac{\partial v}{\partial r} = \frac{\partial v}{\partial \theta_r} = \frac{\partial v}{\partial z} = 0 \quad .$$

Because of orthogonality,

$$\frac{\partial u}{\partial \theta} = \frac{\partial w}{\partial \theta} = 0 \quad .$$

Since the cylinder is long enough, u is independent of z

$$\frac{\partial u}{\partial z} = 0 \quad .$$

If any section of the cylinder perpendicular to z is flat initially, it will remain flat under deformation

$$\frac{\partial w}{\partial r} = 0 \quad .$$

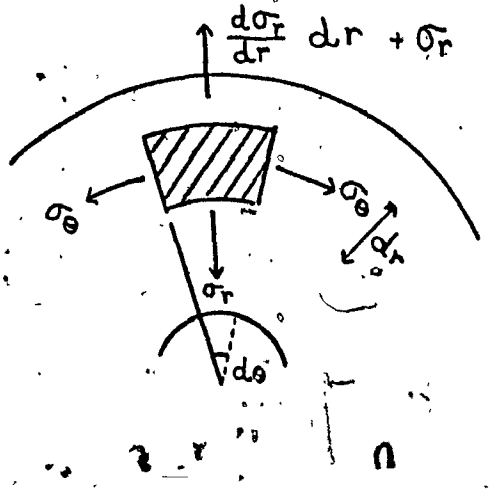
If pressure is applied uniformly over the z axis

$$\varepsilon_z = \frac{\partial w}{\partial z} = \text{constant} \quad .$$

Under these conditions there are no torsion forces acting on the unit volume in the cylinder, hence

$$\gamma_{z\theta} = \gamma_{rz} = \gamma_{r\theta} = 0 \quad ,$$

$$\varepsilon_r = \frac{\partial u}{\partial r} \quad , \quad \varepsilon_\theta = \frac{u}{r} \quad , \quad \varepsilon_z = \frac{\partial w}{\partial z} = \text{cst.} \qquad (A-1)$$



Equilibrium condition of a unit volume in the cylinder is such that -

$$r \cdot \frac{d\sigma_r}{dr} + \sigma_r = \sigma_\theta \qquad (A-2)$$

Hooke's law gives the relation between stress and deformation as

$$\sigma_r = \frac{\nu E}{(1+\nu)(1-2\nu)}\left[\varepsilon_r + \varepsilon_\theta + \varepsilon_z\right] + \frac{E}{(1+\nu)}\cdot\varepsilon_r$$

$$\sigma_\theta = \frac{\nu E}{(1+\nu)(1-2\nu)}\left[\varepsilon_r + \varepsilon_\theta + \varepsilon_z\right] + \frac{E}{(1+\nu)}\cdot\varepsilon_\theta$$

$$\sigma_z = \frac{\nu E}{(1+\nu)(1-2\nu)}\left[\varepsilon_r + \varepsilon_\theta + \varepsilon_z\right] + \frac{E}{(1+\nu)}\cdot\varepsilon_z , \qquad (A-3)$$

where E is Young's Modulus and ν is Poisson's ratio.

Substituting (1) in (3) and substituting the σ's in (2), we obtain the differential equation governing the displacement of the unit volume in the r-direction:

$$r\cdot\frac{d^2u}{dr^2} + \frac{du}{dr} - \frac{u}{r} = 0 , \qquad (A-4)$$

whose solutions are of the form

$$u = Ar + B/r \qquad (A-5)$$

Substituting (5) in (1) yields

$$\varepsilon_r = A - B/r^2 , \qquad \varepsilon_\theta = A + B/r^2 , \qquad (A-6)$$

and:

$$\frac{(1+\nu)(1-2\nu)}{E}\cdot\sigma_r = A - \frac{B}{r^2}(1-2\nu) + \nu\cdot\varepsilon_z$$

$$\frac{(1+\nu)(1-2\nu)}{E}\cdot\sigma_\theta = A + \frac{B}{r^2}(1-2\nu) + \nu\cdot\varepsilon_z$$

$$\frac{(1+\nu)(1-2\nu)}{E}\cdot\sigma_z = 2\nu A + (1-\nu)\varepsilon_z \qquad (A-7)$$

The boundary conditions are the following

$$(\sigma_r)_{r=a} = -p_o \quad \text{and} \quad (\sigma_r)_{r=b} = -p_1$$

Applying these conditions, constants A and B are determined, and we obtain Lamé's equation

$$\sigma_r = \frac{p_o a^2 - p_1 b^2}{b^2 - a^2} - \frac{1}{r^2} \cdot \frac{a^2 b^2}{b^2 - a^2} \cdot (p_o - p_1)$$

$$\sigma_\theta = \frac{p_o a^2 - p_1 b^2}{b^2 - a^2} + \frac{1}{r^2} \cdot \frac{a^2 b^2}{b^2 - a^2} \cdot (p_o - p_1)$$

$$\sigma_z = \frac{p_o a^2 - p_1 b^2}{b^2 - a^2} \cdot 2\nu + E \cdot \varepsilon_z \qquad (A-8)$$

As expected σ_θ and σ_r are independent of z, and σ_z is independent of r. The cylinder is only submitted to interior pressure ($p_1 = o$), and the forces acting on the ends, L, are given by

$$L = \pi a^2 p_o$$

Hence

$$\sigma_z = \frac{L}{\pi (b^2 - a^2)}$$

Then from (8)

$$\sigma_z = p_o \cdot \frac{a^2}{b^2 - a^2}$$

$$\varepsilon_z = p_o \cdot \frac{a^2 (1-2\nu)}{E(b^2 - a^2)}$$

Substituting in (7), (6), and (5), we obtain an expression for the radial dilatation u

$$u = p_o \cdot \frac{a^2}{E(b^2-a^2)} \left[(1-2\nu) r + (1+\nu) \frac{b^2}{r} \right]$$

This formula is directly applicable to our dilatation pro-

blem, provided E and ν are known for the type of steel used in the construction of the high pressure vessel. Both factors are dependent on the composition and the exact treatment that was given to the vessel, so that rough figures are available from the manufacturer. Nevertheless, the volume dilatation at 10 Kbar is of the order of 1% and should be accounted for.

Values used for Vascomax 385 steel were

$$E = 3 \times 10^7 \text{ psi} = 2 \times 10^3 \text{ Kbar}$$

$$\nu = 0.3 \quad ,$$

giving a radial dilatation for r = a = 9.98mm and b = 139mm,

$$u = 6 \times 10^{-3} \text{ mm/kbar}$$

The volume correction curve is plotted on Figure 18, and the correction equation for P in kbar is

$$V_{true} = V_{measured} (1 + 0.0011 P_i) \quad .$$

The definition of the dilatation coefficient, X, is $X = A_i/A$ where A and A_i are defined in Figure 10. Since $A_i/A = V_{true} / V_{measured}$,

$$X = 1 + 1.1 \times 10^{-6} P_i$$

where P_i is in bar.

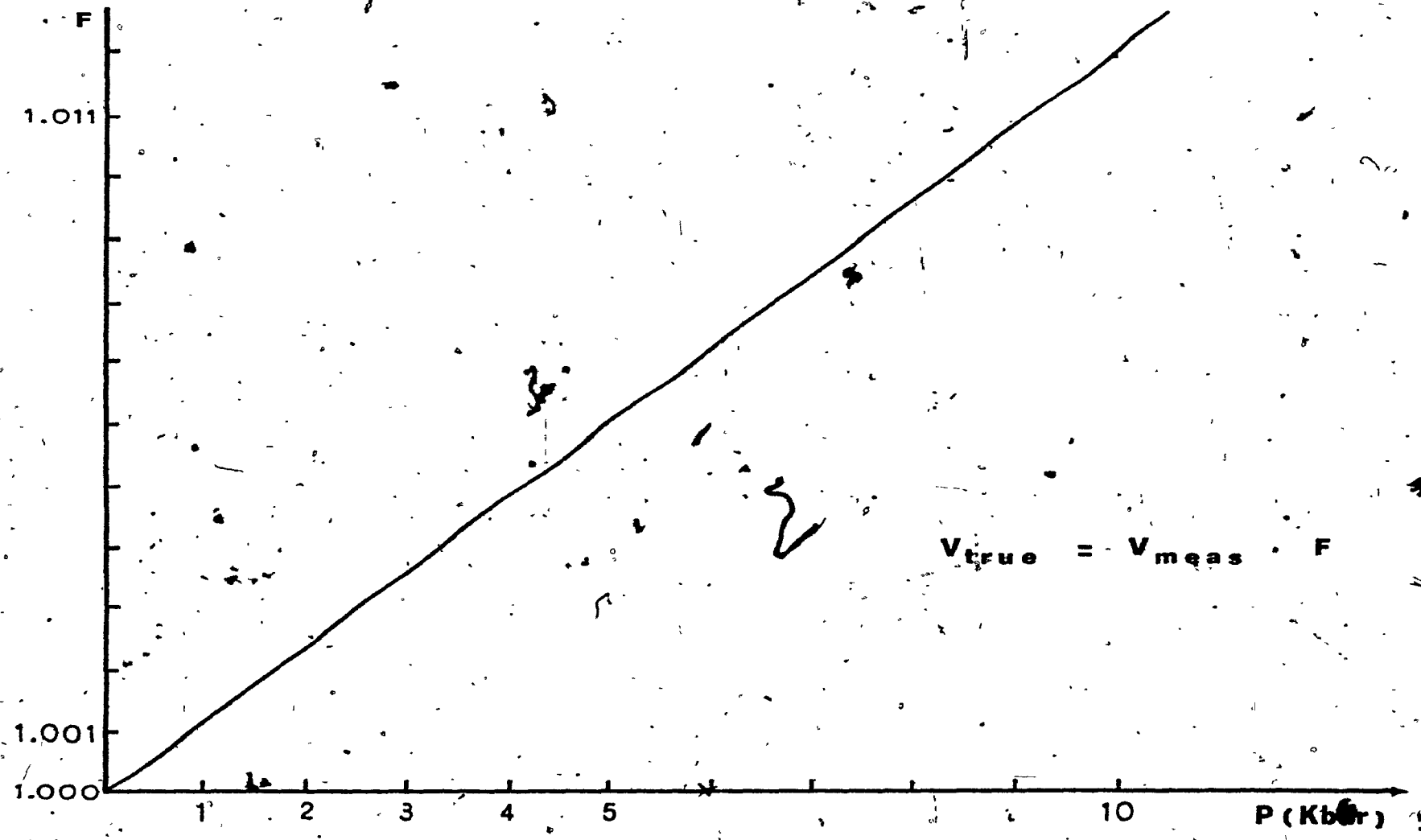


FIGURE 18

Volume correction factor F

APPENDIX B

PROGRAM FOR DATA PROCESSING

List of symbols used and their definition

LT = L_o^o

GF = Pressure coefficient of manganin gauge

n = Number of experimental data for one experiment

R = Initial value of resistance of manganin coil

VCF= Volume correction for dilatation of high pressure vessel

LCF= Length correction for dilatation of columns

B = L (coefficient in Tait's equation)

SX = $\sum x$

SY = $\sum y$

SXS= $\sum x^2$

SXC= $\sum x^3$

SXF= $\sum x^4$

SXY= $\sum xy$

SXSY= $\sum x^2 y$

A = L_o

TC = C (coefficient in Tait's equation)

```
      DIMENSION X(50),Y(50),P(50),PR(50),PL(50),TX(50),TXS(50)
    1 FORMAT(I2,F8.3)
    2 FORMAT(F6.3,F8.3)
    3 FORMAT(/2E20.8)
    4 FORMAT(//3E20.8//)
      LT=27.94
      GF=0.0002779
      READ(20,1)N,R
      DO 10 I=1,N
   10 READ(20,2)X(I),Y(I)
      DO 11 I=1,N
      P(I)=(Y(I)-R)/GF
      PR(I)=(0.2779*P(I))/(0.2789-0.0000002*P(I))
      VCF=(10000.+(.011*PR(I)))/10000.
      LCF=(100000.+(.032*PR(I)))/100000.
      TCF=((VCF*LCF)-1.)*LT
   11 X(I)=(VCF*X(I))-TCF
      J=1
      B=100.
      FN=N
   13 SX=0.
      SY=0.
      SXS=0.
      SXC=0.
      SXF=0.
      SXY=0.
      SXSY=0.
      DO 12 I=1,N
      PL(I)=(B+PR(I))/(B+1.0132)
      TX(I)=ALOG(PL(I))
      TXS(I)=TX(I)*TX(I)
      SX=SX+TX(I)
      SXS=SXS+TXS(I)
      SXC=SXC+TXS(I)*TX(I)
      SXF=SXF+TXS(I)*TXS(I)
      SXY=SXY+TX(I)*X(I)
      SY=SY+X(I)
```

```
   12 SXSY=SXSY+TXS(I)*X(I)
      D1=FN*(SXS*SXF-SXC*SXC)-SX*(SX*SXF-SXC*SXS)+SXS*(SX*SXC-SXS*SXS)
      D4=FN*(SXS*SXSY-SXY*SXC)-SX*(SX*SXSY-SXY*SXS)+SY*(SX*SXC-SXS*SXS)
      D=D4/D1
      WRITE(60,3)B,D
      IF(B.LT.999.9) GO TO 14
      A1=D
      B=B-100.0
      GO TO 13
   14 A2=A1-D
      A3=ABS(A2)
      A4=ABS(A1)
      IF(A3.GT.A4) GO TO 15
      IF(A1.LT.0.) GO TO 16
      IF(A2.LT.0.) GO TO 20
      GO TO (17,18,19),J
   16 IF(A2.GT.0.) GO TO 20
      GO TO (17,18,19),J
   15 GO TO (21,22,23),J
   21 J=2
      B=B+100.0
      GO TO 13
   22 J=3
      B=B+10.0
      GO TO 13
   17 B=B-100.0
      GO TO 13
   18 B=B-10.0
      GO TO 13
   19 B=B-1.0
      GO TO 13
   23 D2=SY*(SXS*SXF-SXC*SXC)-SX*(SXY*SXF-SXC*SXSY)+SXS*(SXY*SXC-SXS*SXSY)
      A=D2/D1
      D3=FN*(SXY*SXF-SXC*SXSY)-SY*(SX*SXF-SXC*SXS)+SXS*(SX*SXSY-SXY*SXS)
      C=D3/D1
      C1=C/A
      ZR=(27.94/A)-1.0000
      TC=(C1/ZR)*2.302585
      WRITE(60,4)A,TC,B
   20 END
```

Output format:

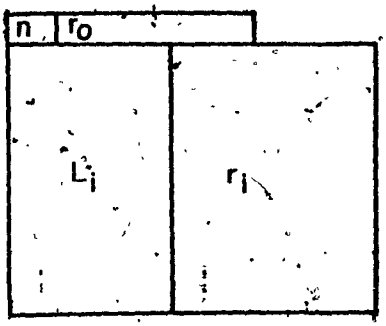
1.0000000E 03	-2.0200735E-01
9.0000000E 02	-1.4546933E-01
8.0000000E 02	-9.1266168E-02
7.0000000E 02	-3.9540960E-02
6.0000000E 02	9.4215956E-03
7.0000000E 02	-3.9540960E-02
6.9000000E 02	-3.4542119E-02
6.8000000E 02	-2.9543865E-02
6.7000000E 02	-2.4576887E-02
6.6000000E 02	-1.9607175E-02
6.5000000E 02	-1.4724721E-02
6.4000000E 02	-9.8319808E-03
6.3000000E 02	-4.9649220E-03
6.2000000E 02	-1.3875762E-04
6.1000000E 02	4.6628399E-03
6.2000000E 02	-1.3875762E-04
6.1900000E 02	3.6105540E-04

L_o= 1.0011561E 01 C= 2.4285370E-01 L = 6.1900000E 02

APPENDIX C

EXPERIMENTAL DATA

input format;



(A) PENTANE

8 116.755	
14.890 116.796	
15.444 116.897	
15.837 117.002	
16.588 117.299	
17.096 117.601	
17.481 117.905	
17.798 118.209	
17.938 118.359	
.A.	

8 115.933	
11.242 115.974	
12.244 116.127	
13.246 116.402	
13.980 116.720	
14.482 117.016	
14.984 117.392	
15.488 117.854	
15.890 118.298	
.B.	

8 116.755	
10.853 116.790	
11.647 116.900	
12.157 117.000	
13.144 117.299	
13.791 117.598	
14.319 117.920	
14.695 118.203	
14.878 118.357	
.C.	

8 115.933	
11.278 115.980	
12.279 116.135	
13.281 116.434	
13.982 116.720	
14.482 117.015	
14.987 117.391	
15.490 117.850	
15.893 118.292	
.D.	

7 116.755
15.686 116.797
16.218 116.902
16.573 117.001
17.292 117.305
17.762 117.605
18.125 117.903
18.288 118.062

E.

8 115.933
11.384 115.979
12.386 116.137
13.392 116.420
14.094 116.732
14.596 117.034
15.098 117.416
15.611 117.895
16.004 118.336

F.

8 116.755
17.642 118.051
17.296 117.750
16.834 117.432
16.254 117.147
15.978 117.046
15.655 116.949
15.204 116.848
14.890 116.796

G.

8 115.933
11.022 115.963
12.024 116.102
13.026 116.353
13.734 116.633
14.238 116.904
14.738 117.246
15.266 117.698
15.740 118.189

H.

(B) EQUIVOLUMETRIC MIXTURE :

9 115.932
10.801 115.961
11.504 116.045
12.204 116.175
12.906 116.369
13.610 116.648
14.113 116.918
14.614 117.260
15.118 117.686
15.599 118.177

A.

9 115.914
9.472 115.944
10.476 116.063
11.478 116.273
12.182 116.498
12.686 116.714
13.188 116.985
13.689 117.321
13.991 117.558
14.494 118.016

B.

9 115.932
10.860 115.956
11.562 116.039
12.264 116.168
12.967 116.359
13.671 116.638
14.173 116.907
14.676 117.249
15.180 117.676
15.682 118.192

C.

8 115.914
9.889 115.947
10.890 116.068
11.890 116.285
12.594 116.518
13.100 116.743
13.602 117.027
14.102 117.380
14.610 117.814

D.

12 116.021	
12.246 116.061	
12.889 116.165	
13.364 116.268	
13.728 116.368	
14.531 116.672	
15.128 117.005	
15.549 117.306	
15.919 117.631	
16.222 117.936	
16.554 118.314	
16.719 118.523	
16.946 118.841	
E.	
12 116.028	
9.236 116.055	
10.088 116.166	
10.624 116.266	
11.122 116.385	
12.012 116.687	
12.650 116.991	
13.170 117.308	
13.582 117.615	
13.932 117.914	
14.254 118.225	
14.530 118.524	
14.815 118.868	
F.	
8 115.919	
9.889 115.947	
10.890 116.068	
11.890 116.285	
12.594 116.518	
13.100 116.743	
13.602 117.027	
14.102 117.380	
14.610 117.814	
G.	
8 115.918	
9.778 115.952	
10.780 116.079	
11.782 116.300	
12.584 116.576	
13.085 116.811	
13.589 117.109	
14.090 117.479	
14.596 117.925	
H.	

(C) ISOPENTANE

10 115.931	
13.344 115.972	
13.914 116.051	
14.400 116.152	
14.804 116.265	
15.526 116.553	
16.059 116.860	
16.454 117.155	
16.793 117.454	
17.084 117.753	
17.218 117.905	
A.	
10 115.931	
12.982 115.945	
13.744 116.048	
14.228 116.149	
14.598 116.251	
15.396 116.572	
15.878 116.853	
16.288 117.157	
16.617 117.455	
16.903 117.752	
17.040 117.902	
B.	
9 115.931	
11.030 115.998	
11.726 116.099	
12.430 116.253	
13.137 116.480	
13.839 116.803	
14.344 117.115	
14.846 117.505	
15.350 117.983	
15.520 118.165	
C.	
9 115.931	
10.805 115.983	
11.516 116.078	
12.219 116.218	
12.920 116.425	
13.621 116.723	
14.124 117.010	
14.626 117.371	
15.128 117.815	
15.456 118.155	
D.	

10	115.904
10.200	115.926
11.198	116.048
11.734	116.150
12.145	116.251
13.018	116.552
13.648	116.867
14.089	117.151
14.481	117.456
14.810	117.752
14.966	117.905

.E.

10	115.921
12.982	115.945
13.744	116.048
14.228	116.149
14.598	116.251
15.396	116.572
15.878	116.853
16.288	117.157
16.617	117.455
16.903	117.752
17.040	117.902

.F.

10	115.904
9.979	115.904
10.877	115.999
11.469	116.099
11.926	116.201
12.849	116.498
13.480	116.796
13.981	117.103
14.378	117.402
14.718	117.702
14.880	117.856

.G.

10	115.931
12.988	115.953
13.675	116.050
14.160	116.153
14.528	116.254
15.272	116.549
15.800	116.852
16.212	117.155
16.544	117.451
16.838	117.752
16.976	117.907

.H.

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