

DIFFUSION AND SORPTION OF ISOMERIC HYDROCARBONS
IN SILICONE RUBBERS

by

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ABSTRACT

A study has been made of diffusion, permeability and solubility of isomeric hydrocarbons in unfilled and filled silicone rubbers. The study was undertaken in order to compare the diffusion and sorption processes of the unfilled rubbers with those of natural rubber and to investigate the role of filler particles on the transport and solution properties of elastomers.

The solubilities of the unfilled silicone rubbers were found to be similar to those of natural rubber. The free energies, heats and entropies of dilution compared well with those deduced from current polymer solution theory.

The solubilities were found to decrease as the filler content in the rubber was increased. In most cases the percentage difference of the solubility was found to correspond to the volume percentage of filler content. Simple models are proposed to relate solubilities to the volume fraction of rubber and filler. The results are interpreted in terms of both "independent sorption" and "zero sorption" of the vapour by the filler in the rubber.

Permeability coefficients for the unfilled rubbers were found to be 25 to 40 times higher than for natural rubber and diffusion coefficients were about 10 to 20 times higher. Compared with natural rubber, the activation energies of diffusion for silicone rubbers were about 3 times smaller and were less than the corresponding heats of solution so that

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the permeabilities decreased with increasing temperature. Interpretation of the ratios of the permeabilities of the isomeric hydrocarbons indicate that silicone rubbers give small fractionation factors than natural rubbers in the separation of gases, although this may be offset by the higher permeability.

Permeability coefficients and diffusion coefficients were found to decrease as the filler content was increased in the rubber. In general, percentage differences in the transient state of diffusion were found to be larger than in the corresponding steady state of flow. Models have been proposed to account for the observed permeation and diffusion behaviour. In this respect the distortion of flow lines around a spherical particle embedded in a medium of different conductivity is also considered.

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CHAPTER I

Introduction.

From investigations in the field of gas and vapour transport in polymer films, much useful information has been obtained about the factors controlling the diffusion and sorption processes in polymers. Much of this work has been reviewed by Barrer (1941, 1957), by Crank and Park (1951) and by Jost (1953). In particular, the effect of penetrant size, shape and cohesive energy density has been studied in a wide variety of polymer types. Recently, however, more attention has been centred on the nature of the bulk polymer, for example, whether amorphous, oriented, crystalline, above or below its glass transition etc. Besides elucidating further the mechanism of diffusion in polymer films, these investigations have often provided useful additional information regarding the microstructure of the polymer film itself. This is particularly true of recent studies of vapour diffusion in semicrystalline polymer films (Brandt - 1959a, 1959b, Thirion - 1954). where concurrent with the establishment of interrelations between gas permeability, gas solubility and degree of crystallinity, some useful deductions on crystallite size and distribution have also been made.

The diffusion of gases and vapours in filled rubbers in several aspects closely resembles the behaviour of semicrystalline films. The membrane with filler particles

incorporated in the polymer matrix presents a rather more formidable system. In most crystalline polymers sorption or diffusion of gas in the crystalline regions is small or negligible whereas filler particles may be porous and may sorb appreciable quantities of gas or vapour. One of the objects of this investigation was to investigate more fully the role of filler particles in the transport of gases or vapours in polymer membranes; and in particular to establish relationships between the filler content and both the vapour solubility and permeability. It is convenient at this point to review briefly previous work of this nature of both crystalline and filled membranes.

Semicrystalline membrane

A crystalline polymer constitutes a heterogeneous medium in that it may be regarded as an amorphous matrix in which are embedded numerous small crystallites impermeable to penetrant molecules. In the absence of an exact solution of the diffusion equation for such media, the customary procedure has been to adopt the equations of flow for the corresponding homogeneous systems and modify these accordingly by the introduction of suitable structure factors. Amongst other things, the structure factor allows for the fact that because of the crystallites the average diffusion path length is increased and the local directions of flow are in general, not normal to the geometrical cross-section of the membrane. Several expressions have

been deduced relating the structure factor to the volume of impermeable material for steady state flow (Maxwell-1873, Runge-1925, Fricke-1924, Meredith and Tobias-1960). Since however, the possibility arises that a fraction of the amorphous phase does not contribute significantly to the steady state of flow, the structure factor, in general, will not be identical for both steady and transient states of flow. An additional factor is introduced into the flow equation of the heterogeneous medium to account for any reduction imposed by the crystallites on the segmental motions of the amorphous phase.

Data for the diffusion and sorption of permanent gases in polyethylene (Michels and Parker-1959) of water in polyethylene (Klute-1959a, 1959b) and of hydrocarbon vapours in stretched crystalline rubbers (Platt-1959) have been interpreted in terms of the above model. These and other investigations support previous deductions that diffusion and sorption occur only in the amorphous regions of the polymer provided the penetrant concentration is not sufficiently high to cause melting of the crystallites. In polyethylene the mobility factor was small, whilst for stretched rubber it was practically non-existent. Since the dependence of the structure factor on volume of the dispersed phase is itself dependent to some extent on the shape of the impermeable particles, some deductions were also made in these studies as to the shapes of the crystallites.

Filled Membrane

There have been relatively few detailed studies in this aspect of the subject. The additional complicating factor of gas or vapour sorption by the filler particles is now encountered. Thus van Amerongen (1955) found that although the incorporation of carbon black into natural rubber reduced its permeability to permanent gases, the solubilities of the gases in the rubber were increased. This was attributed to sorption of the gas by the filler particles. In most studies of this nature the permeability has usually been found to decrease with increasing filler content (Carpenter and Twiss-1940, Thirion-1954, Melikhova, Reitlinger and Kuzina-1959). The possibility of diffusion of penetrant within the filler particles must not, however, be overlooked. The decrease in permeability for a given volume of filler depends markedly on the shape of the filler particles. In particular, the largest decreases are observed with the lamellar type of filler such as mica and graphite. Melikhova, Reitlinger and Kuzina (1959) concluded from their studies of nitrogen diffusion in rubbers containing different types of filler, that the permeability depends on many factors such as bond formation between filler and polymer; degree to which polymer wets filler particles; shape, size and orientation of the particles.

Silicone Rubbers

For the present investigation the system hydrocarbon vapour - filled silicone rubber was chosen. Apart from gaining further insight into the mechanism of the diffusion and sorption processes in such relatively complex media as filled rubbers in general, the unfilled silicone elastomer presents an interesting system in itself for comparison with the more common natural rubber.

Organosiloxanes, such as dimethylsiloxane, can be polymerised to yield linear polymers in which the backbone of the chain is constructed entirely of -Si - O - linkages. These polymers may then be crosslinked either by radiation or by the introduction of sufficient vinyl-benzene side groups which can then react with the 2:4 - dichlorobenzoyl peroxide type of crosslinking agent. The resultant elastomers are particularly resistant to high temperatures and retain the elasticity down to relatively low temperatures of incipient crystallization. The unfilled rubber has an extremely low tensile strength and tears easily. Incorporation of inorganic powders such as silica powders greatly enhances their tear resistance and tensile properties.

An interesting feature of the polysiloxanes is the -Si-O- linkage of the backbone which is believed to allow of rapid segmental rotation, which in turn endows the pendant methyl groups with unusual freedom of motion about these bonds. As a result, neighbouring molecules are unable to

approach close enough to enable intermolecular forces to become effective, which accounts for the low attraction observed between siloxane type molecules (Roth, Harker-1948, Scott-1946). The ease of segmental rotations should be reflected in the diffusion coefficients of gases and vapours in these polymers and in fact silicone rubbers exhibit extremely high permeabilities to gases and vapours (Kammermeyer-1957, Reitlinger, Masleninkova and Tarkho-1956). For this reason, it was decided to investigate this effect in more details and make a critical comparison of the data with similar results for the natural rubber system.

Present investigation

The diffusion of the isomeric hydrocarbon vapours, n- and iso-butane, n-, iso- and neo-pentane in natural rubber had been extensively characterised by Aitken and Barrer (1955) for regions of low penetrant concentration. The same gases have been chosen for this investigation with a view to comparing the diffusion and sorption data of these vapours in silicone rubbers with the data of Aitken and Barrer. This enables a comparison to be made of the relative effects of penetrant size and shape and degree of crosslinking in the two systems. The selectivities of the two types of membrane may be compared in particular, and also the relative magnitudes of diffusion coefficients and energies of activation for diffusion. Furthermore, by a comparison of the systems, filled and unfilled silicone rubber, the role of filler particles in the diffusion and sorption processes

may be more fully investigated.

There are two main experimental techniques employed in the measurement of diffusion coefficients in thin polymer films; these are,

- i. the measurement of the rate of uptake of vapour as a function of time as in the sorption - desorption kinetic approach, (Crank and Park - 1949, Prager and Long - 1951, and others). This method although experimentally simple involves successive approximations and mathematical complexity in deducing the diffusion coefficient.
- ii. the permeation rate method used extensively for polymer-penetrant systems (Barrer and Skirrow-1948, Aitken and Barrer-1955, Park-1952, etc.) involves the measurement of the amount of diffusing species through membranes at a constant pressure gradient on the two faces of the polymer film.

In the present investigation, the permeation rate method was chosen because of the low penetrant concentrations used and since this method also made possible analysis of the transient state data by the application of the time-lag analysis procedure developed by Barrer (1939). The experimental procedure was largely that employed by Aitken and Barrer (1955) and modified successively by Barrer, Barrie and Slater (1958) and Barrie and Platt (1959).

CHAPTER II

THEORETICAL

In this section general theoretical aspects of vapour diffusion and solution in polymer media are considered. However, firstly several quantities used in the analysis of the results are defined in terms of appropriate units as follows.

The Permeability Coefficient $\bar{P}$ is the volume of gas in cubic centimetres at N.T.P. which passes in one second in the steady state across one square centimetre of membrane, one centimetre thick when the pressure difference across the membrane is one centimetre mercury.

The Permeation rate P is the amount of gas, in cubic centimetres at N.T.P., which passes in one second across one square centimetre of a membrane.

The Solubility Coefficient σ is the volume of gas in cubic centimetres at N.T.P. which dissolves in one cubic centimetre of polymer, when the pressure of the gas is one centimetre mercury.

The Diffusion Coefficient D is the volume of gas in cubic centimetres at N.T.P. which passes in one second across one square centimetre of membrane when the concentration gradient of the section is unity. When the diffusion coefficient is independent of concentration it may be defined as the amount of gas which passes in one second in the steady state and under unit concentration gradient, through opposite faces

of a one centimetre cube.

By the above definition, the permeability coefficient is given by,

$$\bar{P} = \frac{V \cdot \ell}{t \cdot A(p_1 - p_2)} \quad \text{.....II.1}$$

where, V is the volume of gas (in cc. N.T.P.) passing through the membrane in t seconds,

ℓ is the thickness of membrane in centimetres,

A is the area of cross section of membrane in square centimetres,

p_1 and p_2 are respectively the pressures on the ingoing and outgoing sides of the membrane in cm.Hg.

The permeation rate becomes

$$P = \frac{V}{t \cdot A} \quad \text{.....II.2}$$

where the symbols have the same significance as for the permeability coefficient.

When D is independent of concentration one has

$$D = \frac{V \cdot \ell}{t \cdot A(c_1 - c_2)} \quad \text{.....II.3}$$

where c_1 and c_2 are the concentration of gas in the membrane at the two faces, expressed as cc. N.T.P./cc of polymer.

Now in the Henry's law region, the concentration of gas in the membrane is proportional to pressure, i.e.,

$$c_1 = p_1 \cdot \sigma \quad \text{and} \quad c_2 = p_2 \cdot \sigma$$

Hence, $\bar{P} = D \cdot \sigma \quad \text{.....II.4}$

When D is not independent of concentration, then equation II.4 is true only for $D_{c \rightarrow 0}$.

I. Fick's Law of Diffusion

According to Fick's laws, diffusion in an isotropic medium is governed by the following differential equations,

$$P = -D \frac{\partial c}{\partial x} \quad \text{.....II.5}$$

$$\text{and} \quad \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) \quad \text{.....II.6}$$

where D is the diffusion coefficient, P is the rate of transfer of gas per unit area of section normal to the direction of flow x, and c is the concentration of diffusing substance at x at time t.

When D is not dependent on concentration, equation II.6 reduces to,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{.....II.7}$$

If P and c are both expressed in the same units then D is independent of this unit and has the dimensions $(\text{length})^2 \cdot (\text{time})^{-1}$. Exact solutions are known for a wide variety of boundary conditions for constant D (Barrer-1941). No definite solution has yet been possible for equation II.6, and in general graphical and approximation methods must be employed for the evaluation of D.

Solutions for the diffusion equation may be subdivided into two groups, namely steady state and transient state systems.

A. Steady State of Diffusion

The steady state is defined by $\frac{\partial c}{\partial t} = 0$ and so equation II.6 reduces to,

$$\frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) = 0 \quad \dots\dots\dots \text{II.8}$$

and for constant D,

$$D \frac{\partial^2 c}{\partial x^2} = 0 \quad \dots\dots\dots \text{II.9}$$

For flow through a membrane with the following boundary conditions,

$$\begin{aligned} c &= 0, & 0 < x < l, & & t \leq 0 \\ c &= c_1, & x = 0, & & t \geq 0 \\ c &= c_2, & x = l, & & t \geq 0 \end{aligned} \quad \dots\dots\dots \text{II.10}$$

The solution of equation II.9 is

$$\frac{c - c_1}{c_2 - c_1} = \frac{x}{l} \quad \dots\dots\dots \text{II.11}$$

$$\text{and } P = -D \frac{\partial c}{\partial x} = -D \frac{(c_1 - c_2)}{l} \quad \dots\dots\dots \text{II.12}$$

The permeability coefficient $\bar{P}$ as defined previously is therefore,

$$\bar{P} = \frac{P \cdot l}{p_1 - p_2} \quad \dots\dots\dots \text{II.13}$$

where p_1 and p_2 are the pressures on either side of the membrane. In practice, p_1 is usually made much greater than p_2 so that equation II.13 becomes

$$\bar{P} = \frac{P \cdot l}{p_1} \quad \dots\dots\dots \text{II.14}$$

When D is a function of concentration equation II.6 becomes for the steady state of flow

$$\frac{\partial}{\partial x} \left(D \frac{dc}{\partial x} \right) = 0 \quad \dots\dots\dots \text{II.15}$$

Therefore equation II.5 is still valid and on integration between the limits, $x = 0, \quad c = c_1$ and $x = \ell, \quad c = 0$, this gives,

$$P = \frac{1}{\ell} \int_0^{c_1} D \cdot dc \quad \dots\dots\dots \text{II.16}$$

and hence

$$\frac{dP}{dc} = \frac{D_{c=0}}{\ell} \quad \dots\dots\dots \text{II.17}$$

B. Transient State of Flow

With the same boundary conditions (II.10) the transient state solution of equation II.7 gives as $t \rightarrow \infty$

$$\phi_t = \frac{D \cdot c_1}{\ell} \left(t - \frac{\ell^2}{6D} \right) \quad \dots\dots\dots \text{II.18}$$

Where ϕ_t is the amount of penetrant which has diffused through the membrane in time t. The intercept of this line on the time-scale gives,

$$L = \frac{\ell^2}{6D} \quad \dots\dots\dots \text{II.19}$$

where L is called the time-lag (Daynes-1920, Barrer-1939a). The expression therefore provides a useful means for calculation of the diffusion coefficient provided the latter is not a function of the concentration.

Since the present work is mainly concerned with a constant diffusion coefficient, the concentration dependence

of D is dealt with only briefly. In most polymer-penetrant systems, D has been found to vary with concentration of the diffusing molecules (Hayes and Park-1955, Prager and Long-1951). It has been shown by Aitken and Barrer (1955) that to a first approximation for the transient state of diffusion,

$$L = \frac{\ell^2}{6D_{c=0}} \left\{ \frac{1 + \frac{1}{4} \cdot a c_1}{1 + \frac{1}{2} \cdot a c_1} \right\} \dots\dots\dots \text{II.20}$$

for the stated boundary conditions. More recently Frisch (1957) has developed a procedure by which final solutions can be obtained without the necessity of solving equation II.6 provided the form of the concentration dependence is known. However, where D varies linearly with c, the exact Frisch solution extends that of Aitken and Barrer (1955), by including more terms.

In systems where the solubility of the gas is small (e.g. polymer-permanent gases) it is often convenient to use equations II.19 and II.20 to determine D by the time-lag method and hence calculate the solubility using equation II.4.

II. Significance of Diffusion Coefficients

In the measurement of diffusion coefficients it is necessary to define not only the units of P, C and x but also the frame of reference with respect to which the flux is measured. Hartley and Crank (1949) studied this aspect of diffusion in some detail and derived relationships between diffusion coefficients defined with respect to different

frames of reference.

Fixed volume section

The total volume of the system on either side of this section remains constant. The simplest system is that of interdiffusion of two liquids A and B in a closed volume and it is assumed there is no overall change in the total volume of the two liquids on mixing. The two diffusion coefficients D_A^V , D_B^V , one for each liquid are defined by the following relations:

$$P_A = -D_A^V \frac{\partial C_A^V}{\partial x} \dots\dots\dots \text{II.21}$$

and

$$P_B = -D_B^V \frac{\partial C_B^V}{\partial x} \dots\dots\dots \text{II.22}$$

where C_A and C_B are the concentrations of the two species A and B expressed per unit volume of the total solution. It can easily be shown that $D_A^V = D_B^V$ and the system may be represented by a single mutual diffusion coefficient D^V .

Fixed mass section

When the total volume of the system does not remain constant the volume fixed section is no longer satisfactory in that the side of the section on which the volume is to remain constant must be chosen arbitrarily. Hartley and Crank (1949) considered therefore alternative frames of reference fixed in particular with respect to mass. Thus for example, although the total volume of the system changes, the total mass will be conserved and a section may be defined such that the mass of the system on either side of it remains constant. For diffusion through a membrane a more convenient

frame of reference is one for which the mass of one component, say B, on either side of the section remains constant.

When a convention other than that of a constant volume on either side is used in defining the section the differential equation describing diffusion may no longer take the standard form of equation II.6. However, by modifying the linear scale of length, x , it is possible to bring it to the standard form. Thus if a scale of length is chosen, ξ_B , such that equal increments in ξ_B always include equal increments of amount of B then,

$$\frac{\partial C_A^B}{\partial t} = \frac{\partial}{\partial \xi_B} \left(D_A^B \frac{\partial C_A^B}{\partial \xi_B} \right) \dots\dots\dots \text{II.23}$$

provided that C_A^B , the concentration of component A, is defined as the amount of A per unit mass of B. In order that ξ_B have the dimensions of length and D the usual dimensions of $(\text{length})^2 \cdot (\text{time})^{-1}$ the mass of component B is multiplied by some arbitrary specific volume V_B^0 , the product being referred to as the 'basic volume' of that mass of B. The concentration C_A^B is now redefined as the amount of A per unit basic volume of B, and ξ_B by the relationship $d\xi_B = V_B^0 \cdot C_B^V \cdot dx$.

By similar procedures frames of reference can be obtained keeping the total mass of the system constant. Since in the case considered the section is fixed with respect to component B then $D_B^B = 0$, and hence again only one diffusion coefficient D_A^B is needed to describe the diffusion behaviour. It can also be shown that a single diffusion coefficient suffices in the case of a total mass fixed section (Crank-1956).

Thus the statement that the diffusion behaviour of a two component system can be described in terms of a single diffusion coefficient is valid, whether or not there is a change in volume of the whole system, provided that the appropriate frame of reference is used in defining the diffusion coefficient.

III. Intrinsic Diffusion Coefficients

From the point of view of interpreting diffusion coefficients in terms of molecular motions, the mutual diffusion coefficient D^V seems to be complicated by the presence of mass flow. Thus when the molecules A and B differ greatly in size and mass, as is the case in any polymer-penetrant system, the random molecular motion which brings about diffusion would result in a much lower rate of transport of a polymer molecule than of a small solvent molecule. The result of this great difference in the transfer rates of the two species therefore, is a build up of an appreciable hydrostatic pressure in the region rich in polymer, which is relieved by a compensating mass flow of the solution across the fixed section. Hartley and Crank have therefore, considered it desirable to define new diffusion coefficients, D_A, D_B in terms of the rate of transfer of A and B across a section fixed so that no mass flow occurs through it.

The rate of increase in total volume of solution denoted by $(\emptyset)$ on the side of x is given by,

$$(\emptyset) = V_A D_A \frac{\partial c_A^V}{\partial x} + V_B D_B \frac{\partial c_B^V}{\partial x} \dots\dots\dots \text{II.24}$$

($\emptyset$), thus defined is therefore equal to the rate of transport of total volume by mass flow across a volume fixed section. The two expressions for the net transfer of A across the volume fixed section is thus given by,

$$D^V \frac{\partial C_A^V}{\partial x} = D_A \frac{\partial C_A^V}{\partial x} - \emptyset C_A^V \quad \dots\dots\dots \text{II.25}$$

Thus for a system for which the total volume remains constant, the final form of the equation is,

$$D^V = V_A C_A^V (D_B - D_A) + D_A \quad \dots\dots\dots \text{II.26}$$

When the total volumes are no longer constant it is usually convenient to relate intrinsic diffusion coefficients to D_A^B . However, it is not considered necessary to include the resulting expressions further in this discussion.

Relations between D^V , D_A^B , D_A and D_B for polymer-penetrant Systems

From the definitions of the various sections involved it can be shown that for constant overall volume,

$$D_A^B = D^V (V_B C_B^V)^2 = D^V v_{2B}^2 \quad \dots\dots\dots \text{II.27}$$

where v_{2B} is the volume fraction of B = $V_B \cdot C_B^V$.

In the case of a polymer-penetrant mixture D_B can usually be assumed to be zero in comparison with D_A .

Equation II.26 can now be written as,

$$D^V = D_A (1 - V_A C_A^V) = D_A V_B C_B^V \quad \dots\dots\dots \text{II.28}$$

and hence using equation II.27,

$$D_A^B = D_A v_{2B}^3 \quad \dots\dots\dots \text{II.29}$$

Diffusion Coefficient Obtained in the Present Investigation

In the permeation rate method of measurement, the diffusion coefficient D_A^B is obtained provided that the concentration of vapour (component A) is expressed as amount of vapour per unit basic volume of the polymer membrane, and l is the unswollen thickness of the membrane. If there is no overall change of volume when the vapour enters the medium then D_A^B is related to D^V by equation II.27. It is clear from equations II.27, II.28 and II.29 that as the volume fraction of polymer tends to unity D_A^B , D^V and D_A tend to become equal.

In the remainder of this thesis, the measured diffusion coefficient D_A^B will be referred to simply as D since v_{2B} in all experiments is practically unity.

IV. Temperature Dependence of Diffusion Coefficients

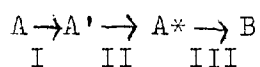
It was pointed out by Barrer (1937) that the temperature dependence of the diffusion coefficient can be represented by an Arrhenius type of equation

$$D = D_0 \exp \frac{-E_D}{RT} \quad \dots\dots\dots \text{II.30}$$

This suggested that in the diffusion of penetrant in a polymer the transfer of a molecule from one equilibrium position to another involves an activation energy E_D . In many cases it was found that a plot of $\log. D$ vs. $1/T$ was not quite linear indicating that both E_D and D_0 may be temperature dependent.

Two different methods of approach have been used to account for an equation of type II.30 and these are, the Transition State theory and the Kinetic Statistical theory both of which assume the existence of an activated state.

For a unimolecular reaction, say $A \rightarrow B$ which includes the passage of the system A over an energy barrier, the process may be divided into a number of steps which can be represented as,



where A and B represent the system in its initial and final positions respectively.

In step I the system A acquires the necessary energy of activation. An interval of time elapses during which this energy redistributes itself within the system to give state A^* . Finally in step III the system descends the energy barrier to its equilibrium position B. Step I is assumed to be very much faster than step II or step III. The fundamental difference between the two theories is that the rate controlling process in Transition State theory is step III while in the Kinetic Statistical theory it is step II.

The two theories are now dealt with separately.

The Transition State Theory

A significant development of the Transition State theory is based on the theory of absolute reaction rates first put forward by Glasstone, Laidler and Eyring (1941). The basic postulate of the theory is that before molecules possessing the requisite energy can react they must form an

'activated complex', which then passes down the energy barrier on the other side. This activated complex situated at the top of the potential energy barrier lying between the initial and final states is considered to pass over it at a definite rate. It is assumed that the activated complex is in thermodynamic equilibrium with the ordinary molecules. It is then possible to derive an equation for the specific reaction rate (k') of any process (Eyring-1935, Wynn-Jones and Eyring-1935). Hence,

$$k' = c \frac{kT k^*}{h} \dots\dots\dots \text{II.31}$$

where k and h are the Boltzman and Plank constants respectively, k^* is the equilibrium constant between the activated state and the reactants and c is the transmission coefficient representing the probability of the activated complex passing over the barrier and forming products.

The free energy of activation (ΔG^*) is given by,

$$\Delta G^* = -RT \ln k^* \text{ and } \Delta G^* = \Delta H^* - T \Delta S^*$$

where ΔH^* and ΔS^* are the corresponding heats and entropies of activation. Substituting in equation II.31,

$$k' = c \frac{kT}{h} \exp \left(-\frac{\Delta G^*}{RT} \right) \dots\dots\dots \text{II.32}$$

i.e.

$$k' = c \frac{kT}{h} \exp \left(\frac{\Delta S^*}{R} \right) \exp \left(-\frac{\Delta H^*}{RT} \right) \dots\dots\dots \text{II.33}$$

Since diffusion is a rate process we now endeavour to establish two relationships; (i) between the diffusion coefficient and the specific reaction rate k' and (ii) the

experimental activation energy (E_D) and the heat of activation (ΔH^*).

(i) Relationship between k' and D

Let (λ) be the jump distance between two successive equilibrium positions of the diffusing molecule. If 'c' is the concentration (moles/cc) in the initial state, then the concentration in the final state is $c + \lambda \frac{dc}{dx}$. Thus the number of molecules passing through a cross-section of one sq. cm. in one second in the forward direction is,

$$n_1 = N c k' \lambda \quad \text{molecules/sq.cm./second}$$

and N is the Avagadro's number.

The flow in the backward direction is given by,

$$n_2 = N k' \lambda \left(c + \lambda \frac{dc}{dx} \right)$$

and the resultant flow in the forward direction is therefore given by,

$$n = n_1 - n_2 = -N \lambda^2 k' \frac{dc}{dx} \quad \dots\dots\dots \text{II.34}$$

From Fick's law,

$$n = -ND \frac{dc}{dx} \quad \dots\dots\dots \text{II.35}$$

and so,

$$D = \lambda^2 k' \quad \dots\dots\dots \text{II.36}$$

(ii) Relationship between E_D and ΔH^*

From equation II.30 we have,

$$E_D = RT^2 \frac{d \ln D}{dT} \quad \dots\dots\dots \text{II.37}$$

and,

$$E_D = RT^2 \left(\frac{d \ln k'}{dT} \right) \quad \dots\dots\dots \text{II.38}$$

assuming (λ) to be independent of temperature, and combining equation II.38 with equation II.31, gives,

$$E_D = RT^2 \left(\frac{1}{T} + \frac{d \ln k^*}{dT} \right) \dots\dots\dots \text{II.39}$$

$$E_D = RT + \Delta E^* \text{ where,}$$

$$\Delta E^* = RT^2 \frac{d \ln k^*}{dT} ; \quad \text{this being the increase in}$$

the internal energy for activation. Now the van't Hoff equation can be written as,

$$\frac{d \ln k^*}{dT} = \frac{\Delta E^*}{RT^2} = \frac{\Delta H^* - p \cdot \Delta V^*}{RT^2} \dots\dots\dots \text{II.40}$$

where, ΔV^* , ΔH^* are the increase in the volume and heat of activation respectively. Compared with the other quantities ΔV^* will be nearly zero and hence from equations II.39 and II.40,

$$E_D = RT + \Delta H^* \dots\dots\dots \text{II.41}$$

and from equations II.33, II.36 and II.41, putting $c = 1$ for simplicity, the diffusion coefficient is,

$$D = e \lambda^2 \frac{kT}{h} \exp \frac{\Delta S^*}{R} \exp \frac{-E_D}{RT} \dots\dots\dots \text{II.42}$$

The activation energy (E_D) can be obtained from experimental data and if reasonable values are assumed for the jump distance λ , ΔS^* can be evaluated. The ΔS^* values so obtained for the polymer-penetrant systems were large and positive (Barrer-1939b, Park-1950, Aitken and Barrer-1955) and according to Glasstone, Laidler and Eyring (1941) these are due to the severing of bonds in the diffusion process. Barrer (1939b) advanced an alternative explanation that the high values of entropy are due to a considerable disturbance of the polymer matrix in the formation of the Transition State and this led to the

inception of the Kinetic Statistical theory.

Kinetic Statistical Theory

It has been postulated by Barrer (1939a, 1942, 1943) and Barrer and Skirrow (1948) that diffusion of gases through polymers be necessarily preceded by the formation of activated zones, i.e. co-operation of the medium through which diffusion takes place, resulting in the concentration of thermal energy in the regions surrounding the diffusing molecule. The kinetic theory is sometimes called the zone theory for this reason.

In a condensed medium such as a polymer, only internal vibrations and rotations are possible and in order to define the energy in each degree of freedom, two squared terms are necessary. The probability that an energy E or more shall be distributed among f degrees of freedom,

$$P = \frac{\exp\left(\frac{-E}{RT}\right) \cdot \left(\frac{E}{RT}\right)^{f-1}}{(f-1)!} \quad \text{.....II.43}$$

(Hinshelwood-1940). If now the polymer-penetrant mixture is divided into a number of small zones or quasi-molecules, the number of which N_r remains constant but the position and shape of which may change. If each quasi-molecule contains n degrees of freedom, then f in eq.43, may have any value between 1 to ∞ and hence the total number of activated regions is,

$$N = N_r \exp\left(\frac{-E}{RT}\right) \sum_{f=1}^{\infty} \frac{(E/RT)^{f-1}}{(f-1)!} \quad \text{.....II.44}$$

and n must be large enough to contain in every zone likely to contribute to diffusion but not so large that a quasi-molecule could contain more than one effective zone.

Since the interest is only in activated zones involving diffusing molecules, the number of zones N_r in the polymer can be replaced by the number of solute molecules N_s . The formation of an activated zone need not necessarily lead to a unit diffusion as synchronisation of molecular motion is also necessary. A new factor $\int_s$ which may be different for each act of libration is therefore introduced into eq.II.44. The probability of molecular place change taking place in the forward and backward direction is also included in the factor $\int_s$. If τ_0 is the period of a libration then the number of successful librations per zone per second is $\int_s/\tau_0$ and the total number involving N_s Molecules becomes,

$$N_1 = N_s \exp \left(\frac{-E}{RT} \right) \sum_{f=1}^n \frac{\int_s}{\tau_0} \left(\frac{E}{RT} \right)^{f-1} \frac{1}{(f-1)!} \quad \text{.....II.45}$$

By a procedure similar to that used in the derivation of equation II.36 in the Transition State theory, the expression for the diffusion coefficient is,

$$D = \lambda^2 \left(\frac{N_1}{N_s} \right) \quad \text{.....II.46}$$

and combining this with equation 45,

$$D = \lambda^2 \exp \left(\frac{-E}{RT} \right) \sum_{f=1}^n \frac{\int_s}{\tau_0} \left(\frac{E}{RT} \right)^{f-1} \frac{1}{(f-1)!} \quad \text{.....II.47}$$

A plot of the summation term,

$$\sum_{f=1}^n \left(\frac{E}{RT}\right)^{f-1} \cdot \frac{1}{(f-1)!}$$

against f for given values of $\frac{E}{RT}$ rises to a maximum, the locus of which can be shown to be, $E/RT = f_{\max}$ where $f_{\max}$ is the value of f at the maximum of the distribution. Barrer was then able to show that the important zones of activation were those intermediate in size between $f=1$ and $f=f_{\max}$ and that when f is not very large the summation term could be replaced by its maximum term. Thus,

$$D = \lambda^2 \frac{\int_0^s}{T_0} \exp\left(\frac{-E}{RT}\right) \cdot \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} \dots\dots\dots \text{II.48}$$

Since $D = D_0 \exp \frac{-E_D}{RT}$, where E_D is the experimental activation energy for diffusion combining with equation II.48 and assuming f to be independent of temperature gives,

$$E = E_D + (f-1) RT \dots\dots\dots \text{II.49}$$

By substituting equation II.49 for E in equation II.48,

$$D_0 = \frac{\int_0^s}{T_0} \lambda^2 \exp(1-f) \left(\frac{E_D + (f-1)RT}{RT}\right)^{f-1} \frac{1}{(f-1)!} \dots\dots\dots \text{II.50}$$

Taking logarithms and expanding the factorial by Stirling's approximation gives,

$$\ln D_0 = \ln\left(\lambda^2 \frac{\int_0^s}{T_0}\right) + (f-1) \ln\left(\frac{E_D + (f-1)RT}{RT}\right) - (f-1) \ln(f-1) + \frac{1}{2} \ln 2\pi(f-1) \dots\dots\dots \text{II.51}$$

Equations II.51 and II.49 afford two methods for calculating f . From the variation of E_D with temperature,

$$\frac{dE_D}{dT} = -(f-1)R \dots\dots\dots \text{II.52}$$

It is assumed here that f is independent of temperature, which is most unlikely. When E_D is not temperature dependent then equation II.52 will give the lower limiting value of f . An alternative method is to use reasonable values of p_s , τ_o and λ to calculate f from equation II.51.

Aitken and Barrer (1955) found for hydrocarbons in elastomers, values of f which varied between 20 and 180 by using equation II.52 and on the other hand by using equation II.51 they found values ranging from only 17 to 30. These discrepancies were ascribed to the uncertainties in the values chosen for p_s , τ_o and λ since the value of f was very sensitive to changes in these quantities.

Polymer Solution Theory

The measurement of the vapour pressure of polymer-penetrant mixtures at different temperatures affords a suitable method to evaluate the free energies, heats and entropies of dilution. The free energy of dilution is given by,

$$\Delta \bar{G} = RT \ln \frac{p_s}{p_o} \quad \text{.....II.53}$$

where p_s and p_o are the vapour pressures of the mixture and of the pure solvent respectively. $\Delta \bar{G}$ is thus the change in free energy of transferring, isothermally and reversibly one mole of liquid from the pure solvent to an infinite amount of mixture of a given composition, corresponding to the vapour pressure p_s . The heats and entropies of dilution can be derived using the following relations from values of $\Delta \bar{G}$ at

various temperatures,

$$\Delta \bar{H} = \left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial \left(\frac{1}{T} \right)} \right)_{p, n_0} \quad \dots\dots\dots \text{II.54}$$

$$\text{and } \Delta \bar{S} = - \left(\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right)_{p, n_0} \quad \dots\dots\dots \text{II.55}$$

where n_0 is the number of moles of liquid per unit volume of polymer and p is the hydrostatic pressure of the system ($=p_s$).

It is found for the solution of polymers in non-polar liquids that the values of $\Delta \bar{H}$ are small and positive whilst the $\Delta \bar{S}$ values are also positive but abnormally large. This deviation from the ideal solution theory was first explained by Meyer (1939) who attributed the large entropy of mixing to the large number of configurations possible in a mixture of small molecules and large flexible polymer molecules.

Lattice Theory and its Limitations

Flory (1942) and Huggins (1942) independently dealt with the problem of calculating the number of possible configurations in a polymer-solvent system in order to evaluate the entropy of athermal mixing of the two species. Their treatment consists of counting the number of distinct ways in which n_1 solvent molecules and n_2 polymer molecules each containing x segments can be arranged on a hypothetical lattice of $n_1 + n_2$ cells. Each cell in the lattice may be occupied by a chain segment of the polymer or by a solvent molecule. The number of configurations was then related to

the entropy of mixing by the Boltzmann equation. The following relationship was obtained,

$$\Delta S^* = -k(n_1 \ln v_1 + n_2 \ln v_2) \quad \text{.....II.56}$$

where the asterisk indicates a configurational entropy, k is the Boltzmann constant and v_1 and v_2 are the volume fractions of the solvent and polymer respectively defined by,

$$v_1 = \frac{n_1}{n_1 + xn_2} \quad \text{and} \quad v_2 = \frac{xn_2}{n + xn_2} \quad \text{.....II.57}$$

Differentiating II.56 with respect to n and multiplying by Avogadro's number gives the entropy of dilution,

$$\Delta \bar{S} = -R \left\{ \ln(1-v_2) + \left(1 - \frac{1}{x}\right) v_2 \right\} \quad \text{.....II.58}$$

Huggins (1942) using a method similar to that of Flory but with some refinements obtained,

$$\Delta \bar{S} = -R \left\{ \ln(1-v_2) - \frac{1}{2}z\left(1 - \frac{1}{x}\right) \ln\left(1 - \frac{2v_2}{z}\right) \right\} \quad \text{.....II.59}$$

where z is the co-ordination number of the hypothetical lattice.

Free Energies and Heats of Mixing

The free energy change in the case of athermal mixing is given simply by, $\Delta G^* = -T\Delta S^*$. In most cases of polymer-liquid mixtures, however, there is a definite, though frequently small heat of mixing arising out of intermolecular interactions, which may introduce a certain degree of ordering.

Using the lattice model, Flory (1953) obtained

the following equation, for the heat of mixing,

$$\Delta H^* = kT n_1 v_2 \chi_1 \quad \dots\dots\dots \text{II.60}$$

where χ_1 , the interaction parameter is given by,

$$\chi_1 = \frac{z \Delta W_{12}}{kT} \quad \dots\dots\dots \text{II.61}$$

and

$$\Delta W_{12} = W_{12} - \frac{1}{2} (W_{11} + W_{22}) \quad \dots\dots\dots \text{II.62}$$

where the W's represent the energies associated with the respective contact pairs. e.g. W_{12} is the energy associated with a solvent polymer bond. χ_1 is a dimensionless quantity which can be regarded as characterising the interaction energy per solvent molecule.

The equation for the free energy can then be obtained if it can be assumed that the entropy of mixing arises solely from the configurational entropy resulting from random mixing (equation II.56)

$$\Delta \bar{G}^* = kT(n_1 \ln v_1 + n_2 \ln v_2 + \chi_1 n_1 v_2) \quad \dots\dots\dots \text{II.63}$$

Guggenheim (1944) has pointed out that there is no justification for dismissing the possibility of an entropy term arising from first neighbour interactions. Here, ΔW_{12} may therefore be regarded as a free energy rather than a heat change. The free energy is still given by equation II.63 but the expressions for the heat of mixing and entropy are now obtained by the application of equations II.54, II.55.

$$\Delta S^* = -k \left\{ n_1 \ln v_1 + n_2 \ln v_2 + \frac{d(\chi_1)}{dT} n_1 v_2 \right\} \quad \dots\dots\dots \text{II.64}$$

$$\Delta H^* = -kT^2 \left(\frac{\partial \chi_1}{\partial T} \right) n_1 v_2 \quad \dots\dots\dots \text{II.65}$$

The free energy, heat and entropy of dilution are now found by differentiating equations II.63, II.60 and II.56 with respect to the number of moles of solvent,

$$\Delta \bar{G} = RT \left\{ \ln(1-v_2) + \left(1 - \frac{1}{x}\right) v_2 + \chi_1 v_2^2 \right\} \dots\dots\dots \text{II.66}$$

$$\Delta \bar{H} = RT v_2^2 \chi_1 \dots\dots\dots \text{II.67}$$

$$\Delta \bar{S} = -R \left\{ \ln(1-v_2) + \left(1 - \frac{1}{x}\right) v_2 \right\} \dots\dots\dots \text{II.68}$$

where x is the number of segments per polymer molecule. When the interaction parameter is regarded as free energy rather than an energy parameter the heat and entropy terms become respectively,

$$\Delta \bar{H} = -RT \left\{ \frac{\partial \chi_1}{\partial T} \right\} v_2^2 \dots\dots\dots \text{II.69}$$

and

$$\Delta \bar{S} = -R \left\{ \ln(1-v_2) + \left(1 - \frac{1}{x}\right) v_2 + \frac{\partial (\chi_1 T)}{\partial T} \right\} \dots\dots\dots \text{II.70}$$

The heat of dilution can also be related to the cohesive energy densities of the two interacting species. Thus Hildebrand and Scott (1950) have shown that for the case of polymer-liquid mixtures, the expression is,

$$\Delta \bar{H} = v_1 \left[\left(\frac{E_1}{v_1} \right)^{\frac{1}{2}} - \left(\frac{E_2}{v_2} \right)^{\frac{1}{2}} \right]^2 v_2^2 \dots\dots\dots \text{II.71}$$

where v_1 is the molar volume of the monomeric liquid and

$\frac{E_1}{v_1}$ and $\frac{E_2}{v_2}$ are the cohesive energy densities of liquid and polymer respectively. The expression is not always

quantitatively accurate and in practice it is assumed that

$\Delta \bar{H}$ is proportional to v_2^2 .

Marked deviations from the lattice theory have been found for most polymer solutions, the only exception being the rubber-benzene system. The free energy equations serve as better working models between theory and experiment than do the corresponding heat and entropy expressions. This is largely due to a cancellation of errors which arise in the expressions for the heat and entropy of mixing.

Many attempts have been made to calculate more accurately the number of configurations of the polymer chain on the lattice (Orr-1944, Guggenheim-1944 and Miller-1943) but the expressions obtained show little better agreement with the theory and are considerably more complicated. For dilute polymer solutions however, the theory is completely inadequate and a new approach has been devised by Flory (1953) for such media. Bueche and Krigbaum (1955) have pointed out that the objection to the lattice theory on the basis of its assumption that the solvent and polymer molecules are identical in shape and size is largely unfounded and suggest that a more valid objection is that the lattice treatment corresponds to a hard sphere approximation.

Swelling of Polymer Networks

A cross linked polymer placed in a non-polar liquid is capable of absorbing a large amount of the liquid and may swell to many times its original volume. Complete solution of the polymer is rendered impossible because of the three dimensional network structure formed by crosslinking. The tendency of the network to swell is opposed by a retractive

force similar to the elastic retractive force in rubber and as swelling proceeds, a state of equilibrium swelling is reached in which these two forces are in balance.

Flory and Rehner (1943) derived an expression for the elastic contribution to the free energy and obtained for the final expression,

$$\Delta \bar{G}_c = RT \left\{ \ln(1-v_2) + v_2 + \chi_1 v_2^2 + \left(\rho \frac{V_1}{M_c} \right)^{\frac{1}{3}} v_2 \right\} \dots\dots\dots \text{II.72}$$

where the subscript in the free energy symbol indicates a crosslinked network, M_c is the molecular weight between crosslinks, ρ is the density of the swollen polymer and V_1 is the molar volume of the solvent.

An important application of equation II.72 is in the calculation of M_c and this is usually done by swelling the polymer in a suitable solvent and since $\Delta \bar{G}$ is then zero,

$$M_c = - \frac{\int V_1 v_2^{\frac{2}{3}}}{\ln(1-v_{2m}) + v_{2m} + \chi_1 v_{2m}^2} \dots\dots\dots \text{II.73}$$

where v_{2m} is the volume fraction of the polymer at equilibrium swelling. Using a more exact expression for the entropy of elastic deformation Flory (1950) obtained,

$$M_c = \frac{1}{2} \left\{ \frac{v_{2m} \int V_1 - 2 \int V_1 v_{2m}^{\frac{1}{3}}}{\ln(1-v_{2m}) + v_{2m} + \chi_1 v_{2m}^2} \right\} \dots\dots\dots \text{II.74}$$

CHAPTER III

FILLER PHENOMENA IN ELASTOMERS

Interaction between polymers and fillers

The reinforcing action of fillers can improve markedly the tensile properties of many elastomers. Whether or not the filler has a reinforcing effect on the polymer will depend largely on the interaction of the chain segments with the surface of the filler particles. In general, the polymer would be expected to wet and adhere strongly to the surface of a reinforcing type of filler. This feature of filler action is of interest in considering vapour diffusion in filled rubbers. In particular, if the polymer were to wet the filler completely then adsorption of the vapour by the filler would be much less than that observed on the loose powder.

It is, in fact, generally agreed that in many cases the polymer is bonded to the surface of an effective filler (Blanchard and Parkinson-1952, Rehner-1951; Stearns and Johnson-1951, 1956). The nature of the bond is somewhat more obscure and depending on the polymer and filler types may be a result of physical adsorption or chemical bonding. The unvulcanised natural rubber when compounded with carbon black can be rendered insoluble in gasoline. Several authors (Weiss-1942, Guth and Gold-1938, Guth-1945, Smallwood-1944, Rehner-1943) have attempted to relate the tensile strength to the number of polymer-filler attachments.

Bueche (1957) obtained such a relationship and deduced from it that when the number of filler-polymer contacts was zero then the tension on the sample at a given elongation would decrease as the filler content is increased. Bueche also concluded that the relatively non-porous fillers were more efficient in their reinforcing action than the porous type.

Another feature of interest arises in the dispersion of the filler particles throughout the rubber phase. Thus Dannenberg (1952) considered three possibilities as to the mode of dispersion of the filler in the rubber matrix.

- a) Each particle is separated from any other by a film of rubber. This is considered to be most unlikely since such an ideal dispersion of particles is extremely difficult to effect.
- b) Aggregates of the particles are present in the elastomer and their size is proportional to the size of the individual particles.
- c) A third possibility is that the dominant factor in reinforcement is the extent of interfacial surface developed between the filler and the rubber phase. In this case, a highly aggregated and flocculated condition of the filler is compatible with extensive development of interfacial surface. The correlation between particle size and reinforcement would be due to the direct relation between surface area and particle size.

The presence of particle aggregates could have a significant effect on the transport of vapour through the polymer. Thus (Melikhova, Reitlinger and Kuzina-1959) observed that the permeability of several filled rubber membranes first decreased and then increased as the filler content was increased. This increase with filler content at high values of the latter they attributed to the presence of air gaps between filler particles.

Finally, since the rubbers in this investigation are polysiloxane gums reinforced with silica filler, these are considered in some more detail. Fine particle hydrated silica shows a capacity to reinforce silicone rubbers similar to that of HAF blacks in natural rubber. The role of surface groups appears to be of great importance and the blocking of SiOH structures may markedly alter the strength of the polymer-filler bond. The effect of surface composition is apparent on treating a given silica with a very small amount of gaseous ammonia when the tensile strength drops to a quarter of its value with the untreated silica. The amount of polymer bound to the polymer surface can be estimated by flooding the mix with excess of solvent. The amount of polymer not removed from the filler is termed "bound" polymer. Before milling, silicas have a high bound polymer level but after milling the effect is reduced considerably. It has been suggested (Warrick and Lauterbrun-1955) that structure can be introduced into a fine silica by ball

milling. Apparently small particles become welded together to form large porous aggregates. This structure does not seem to be destroyed on milling the filler with the rubber and as a result the reinforcing effect of the filler is reduced. The chemical nature of the filler surface is of considerable importance and the more inert fillers seem to be most beneficial suggesting that the principal function of the filler must be something other than providing temporary bonding between polymer molecules.

CHAPTER IV

EXPERIMENTAL

Silicone Rubbers

The silicone rubber samples were supplied by the Imperial Chemical Industries Limited, and were in sheets with approximate dimensions, 15 x 15 x 0.2 cm. from which portions were used for the experiments. Two of the sheets were without filler while five sheets contained a range of filler contents.

The unfilled samples were designated Si.R-I and Si.R-H and contained 0.1 mol.% and 1 mol.% of vinyl groups respectively. They were crosslinked using "Cadox" paste (2:4 - dichloro benzoyl peroxide in silicone oil) and after pressing were given an oven cure of 1 hour at 150°C. The samples Si.R-A, Si.R-B, Si.R-C, Si.R-D and Si.R-E contained respectively 0, 10, 20, 30 and 40 parts by weight of filler to 100 parts of polymer. These samples contained 0.1 mol.% of vinyl groups. The filler used in the rubber was "Santocel CS" (silica) a relatively porous amorphous form of silica. The polysiloxane chains become attached to the filler surface but the precise nature of this bonding is not known. The filled sheets were cured with di-tert-butyl peroxide (2%) by pressing at 170°C for ten minutes followed by an oven cure (air circulated) at 150°C for 1 hour. The method of crosslinking is a peroxide induced free radical mechanism and the degree of crosslinking is proportional to the vinyl content.

The silicone rubbers show little tendency to oxidise in the temperature range used in the experiments and the only foreign materials present were slight traces of catalyst decomposition products. The degree of reinforcement of filler depends very much on the particle size of filler (Warrick and Lauterbrur-1955, Blanchard and Parkinson-1952). A number of aromatic hydrocarbons and chlorinated solvents cause severe swelling of silicone rubbers but the properties of the elastomer are retained once the solvents are removed from contact.

Before using the rubbers in the experiments, they were extracted with acetone in a soxhlet apparatus for about three hours to remove impurities. The samples were then dried in an oven at about 50°C and outgassed in the high vacuum apparatus at a pressure of 10^{-6} cm. Hg. for at least two days.

The thicknesses of the membranes used in the permeability experiments were measured with a micrometer screw gauge. Since the thickness was not perfectly uniform at all points an average value was used in the calculation of permeabilities.

The densities of the polymer samples were determined by the water displacement method. Since the density of the unfilled samples was less than 1 gm/cc, a sinker was attached to the sample by a thin lead wire.

Gas samples

The hydrocarbons, n-butane, iso-butane, n-pentane and neo-pentane were Research Grade products supplied by the

Chemical Research Laboratories, Teddington, in sealed glass containers. High purity nitrogen was supplied by the British Oxygen Company, in one litre glass bulbs. The purity of the hydrocarbons were stated as follows by the suppliers:

n-butane	-	99.99 mole percent
iso-butane	-	99.90 moles percent
n-pentane	-	99.95 moles percent
neo-pentane	-	99.83 moles percent

No further purification was attempted.

General description of the apparatus

The apparatus was constructed entirely by pyrex glass and consisted of three main sections, namely, pumping, permeation and solubility systems.

Pumping System

A diagram of this part of the apparatus is shown in Figure II.1. A pumping pressure of 10^{-6} cm. Hg. could be obtained using a two-stage mercury diffusion pump backed with an Edwards speedivac rotary oil pump. A buffer volume (B) between the rotary pump and the diffusion pump enabled the diffusion pump to operate while the rotary pump was otherwise engaged. A cold trap (E) prevented hydrocarbon vapours from entering the rotary pump. A by-pass (not shown in the Figure) was constructed to avoid switching off the mercury diffusion pump each time air was admitted to the system. In the event of breakdown of the rotary pump a large bulb (T) served as a safety reservoir in

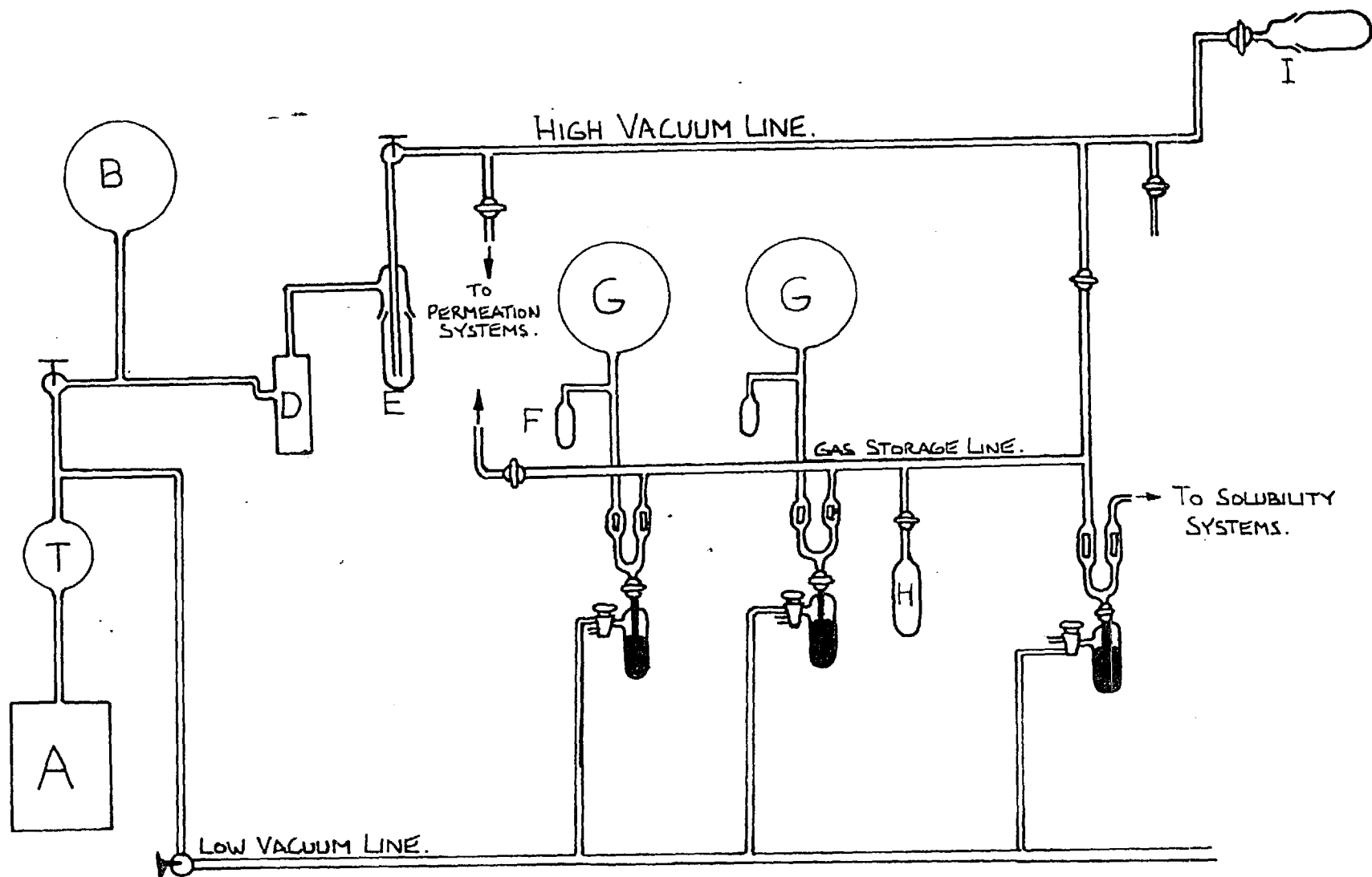


FIG. IV.1

preventing oil from being sucked back into the system.

The hydrocarbons were stored in glass bulbs (G, G) and connected to the gas line via mercury cut-offs. The limbs (F, F) were used to freeze out the hydrocarbons before the mercury cut-offs were lowered to transfer the vapour to other parts of the system. Nitrogen gas contained in a glass bulb (H) was connected to the gas line through a tap. The storage cylinder (I) was used to store refluxed rubber gaskets which were used in the diffusion cell.

All taps in the apparatus were lubricated with "Apiezon N" grease. Triple distilled mercury was used in the different parts of the system. Parts of the permeability and solubility systems where accurate low pressure measurements were made were isolated by mercury cut-offs.

The permeation system

The permeation system is diagrammatically shown in Figure II.2. Two such systems were actually used. Each consisted of a McLeod gauge (P), two buffer volumes (N, Q), a diffusion cell (O), a manometer (M) and a mercury cut-off (U). With tap (S) closed the gas was admitted from the gas line to the ingoing side of the diffusion cell by opening tap (K). Values of the ingoing pressure were read-off (M) with a silver mirrored scale. A two litre buffer volume was attached to (M) to prevent any appreciable reduction in the ingoing pressure. The manometer (M) was made from pyrex glass tube of internal diameter 1 cm. and was connected to

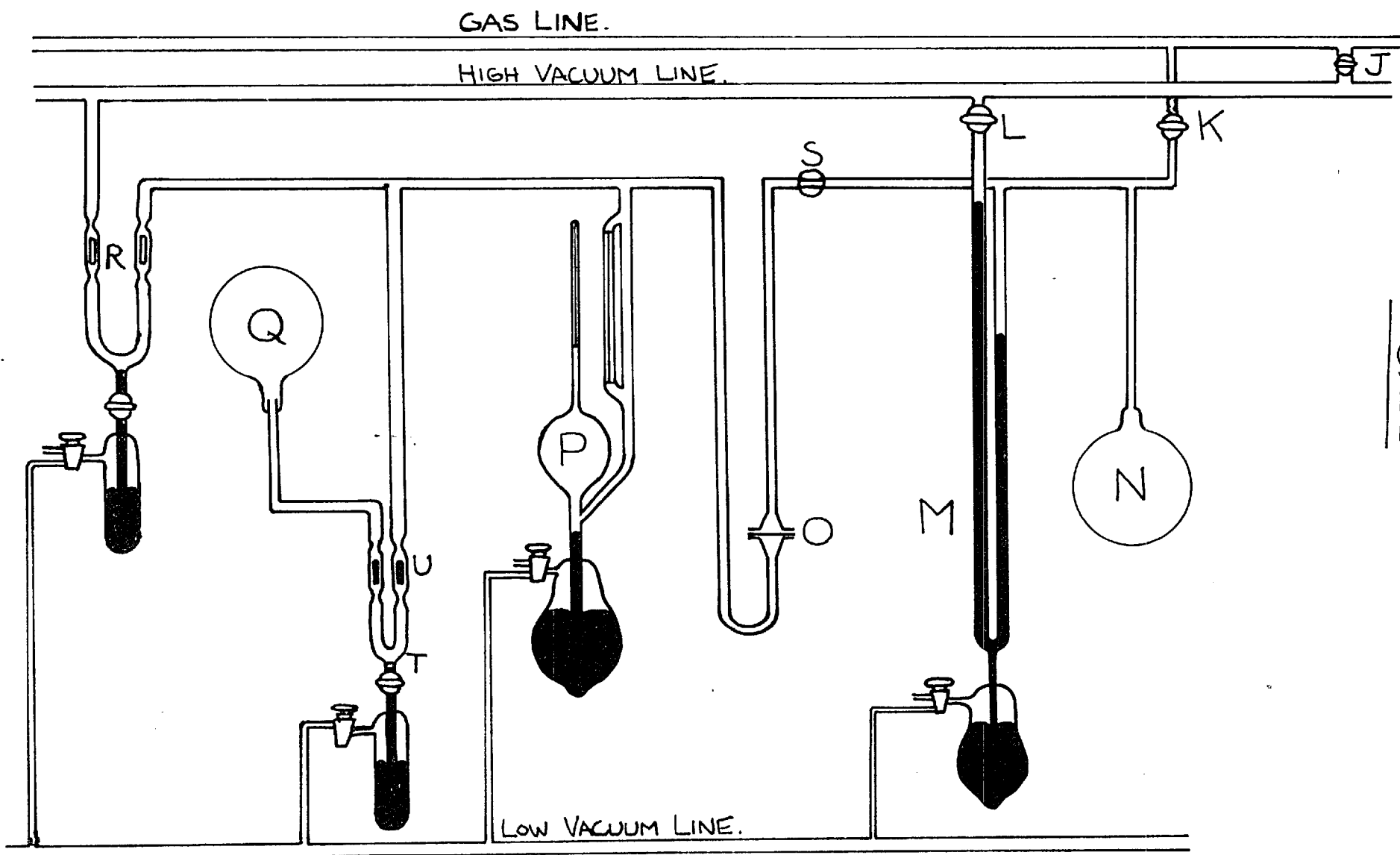


FIG. IV.2

the Hyvac line through tap (L) and to the diffusion cell through tap (S). When high permeation rates were encountered it was necessary to add an additional 1 litre buffer volume (Q) in order to keep the outgoing pressure in the range of the McLeod gauge.

The McLeod gauges

The capillary stem of the gauges were made from "Veridia" tubing of 2 mm. diameter. Fixed reference marks were etched on the closed capillary stem and the volumes between the marks were accurately calibrated by measuring the lengths of known weights of mercury in the capillary. The volume of the bulb was obtained by filling it with distilled water from an accurate burette. A linear scale was employed to measure the pressure so that $p = \frac{v \cdot h}{V}$ where V is the total volume of the gauge, h the difference in the mercury menisci in the two capillary limbs and v is the volume of gas enclosed by the mercury meniscus in the closed capillary stem. The v/V ratios for the two gauges employed were as follows:

	V for Gauge I - 192.9 ccs.		V for Gauge II - 191 ccs.		
Mark No.	I	II	III	IV	V
v/V (I)	9.66×10^{-5}	18.4×10^{-5}	5.07×10^{-4}	14.69×10^{-4}	40.62×10^{-4}
v/V (II)	9.89×10^{-5}	16.59×10^{-5}	5.00×10^{-4}	14.74×10^{-4}	41.14×10^{-4}

where the Roman numerals represent the fixed reference marks starting from the closed end of the capillary. The volume of the low pressure side of the diffusion system was obtained by application of the gas laws by a series of low pressure

expansion measurements using nitrogen gas.

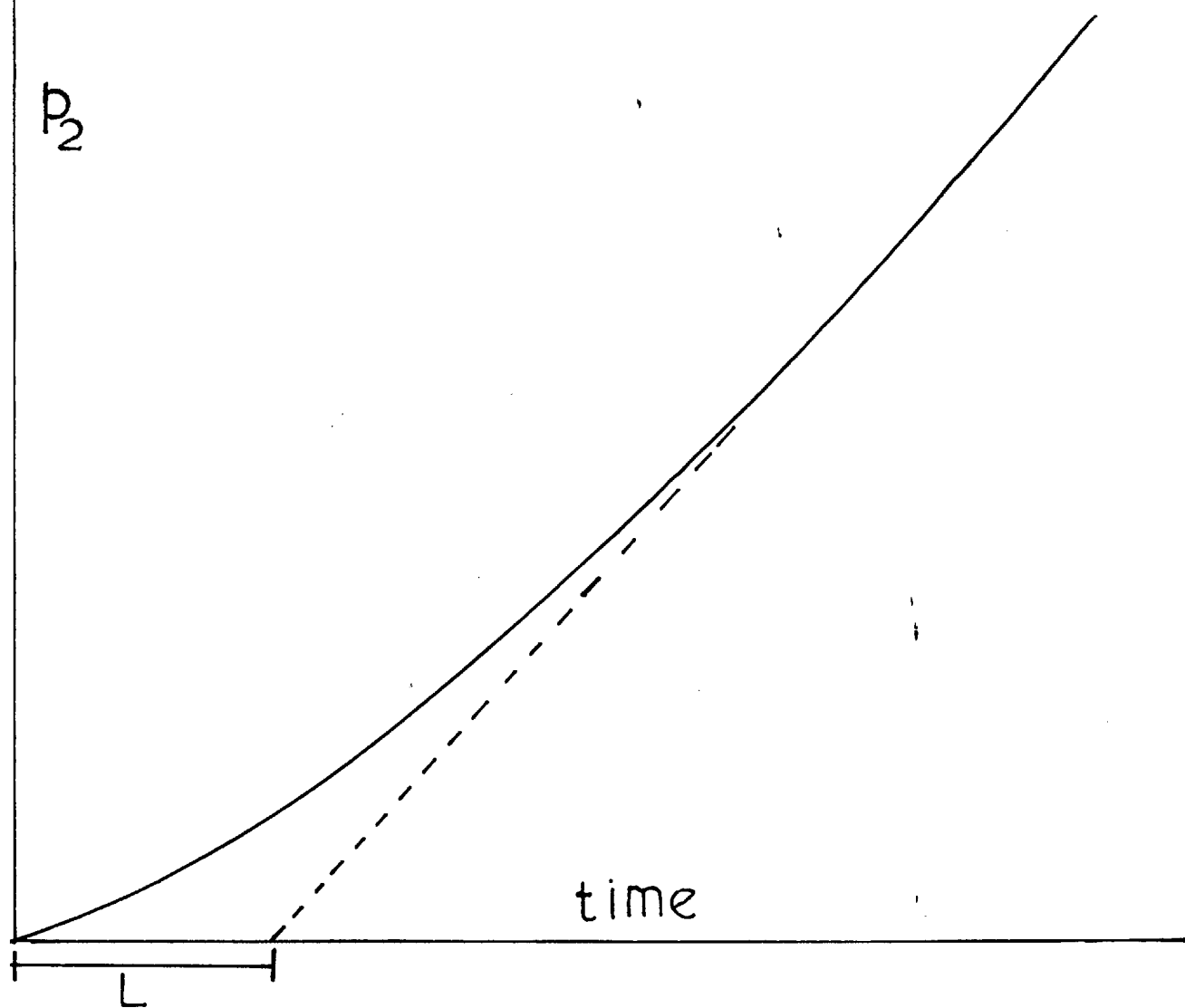
The diffusion cell (O) was placed in a copper cylinder loosely packed with cotton wool to prevent convection currents. The copper cylinder was placed in a water thermostat the temperature of which was controlled by a "Sunvic" relay to within 0.05°C . Permeation runs were made at fixed temperatures of 30, 40, 50, 60 and 70°C . The temperature of the thermostat was always maintained at a temperature higher than that of the room to prevent mercury condensing on the membrane.

Method of operation

Before a run was made, the membrane was thoroughly outgassed at a high temperature. Then with tap (S) closed a charge of gas was admitted through tap (K) to the ingoing side of the system and the pressure read off on the manometer (M). Next, tap (S) was opened and a stop watch started. The pressure of the diffused gas was measured on the McLeod gauge at suitable intervals. Before each diffusion run was made the membrane was thoroughly outgassed.

Time-lags were obtained by plotting the outgoing pressure (p_2) against the time in minutes. A typical plot p_2 vs. time is shown in Figure II.3. The intercept on the time axis of the steady state curve gives the time-lag (L) while the permeability coefficients ($\bar{P}$) and the permeation rate (P) were calculated from the slope of the linear portion of the plot using the following equations.

FIG. IV.3



$$\bar{P} = \frac{V_o \times \ell \times 273}{p_1 \times A \times (273 + T_R) \times 76} \times \frac{dp_2}{dt} \quad \dots \text{IV.1}$$

$$P = \frac{V_o \times 273}{A \times (273 + T_R) \times 76} \times \frac{dp_2}{dt} \quad \dots \text{IV.2}$$

where,

V_o - volume of the low pressure side, cc.

p_1 - the ingoing pressure in cm. H_g.

ℓ - thickness of membrane, cm.

A - area of the membrane exposed to the gas, cm²

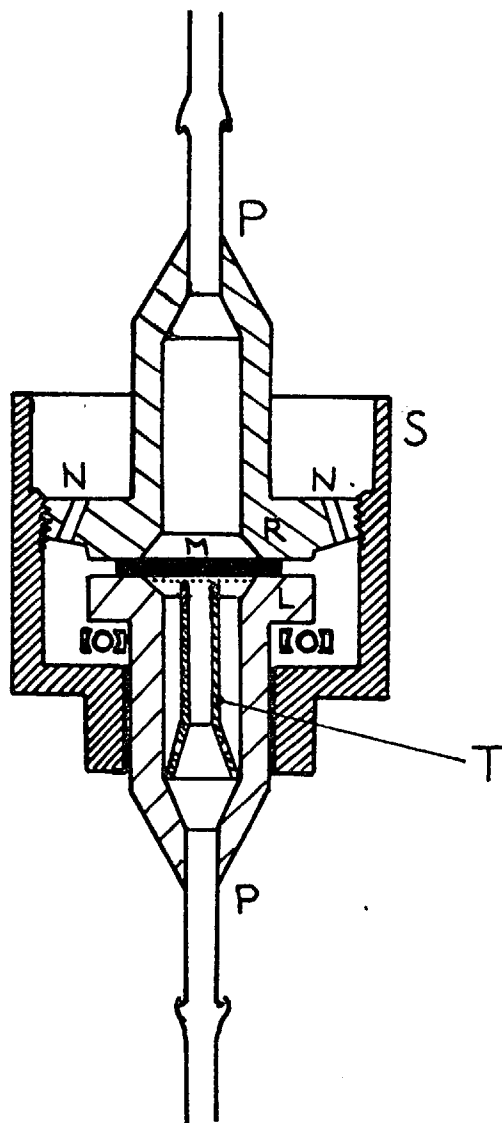
T_R - room temperature, °C

$\frac{dp_2}{dt}$ - slope of the linear portion of the pressure vs. time plot, cm.H_g/min.

The Diffusion Cell

A diagram of the cell which is based on that of Schumacher and Ferguscn (1927) is shown in Figure II.4. It was made of stainless steel and was circular in cross-section. The membrane was clamped in a membrane holder (M) and held between two circular flanges R and L and screwed together by means of the outer cup (S), to make gas tight fit. This was achieved by holding the two flanges steady whilst screwing the cup (S) by hand. The ball race under the lower flange (L) prevented irregular screwing of the flanges. The bottom half of the cell (L) was a mercury tight fit in (S) and the annular space was filled with mercury, admitted through a number of holes (N, N). The cell was connected to the permeation system through copper-pyrex glass seals (P), the copper tube being silver soldered to the stainless steel at points (P, P).

FIG. IV.4



The membrane holder

If the membrane was introduced directly between the faces of the diffusion cell, then on tightening the latter, compression effects resulted in pronounced bulging of the membrane. To minimise this effect a modified method of clamping was adopted (Platt-1959). The membrane (O) was clamped between a pair of circular stainless steel plates (Figure II.5) which were joined together by a series of screws (S'). Care was taken to avoid tight screwing as this invariably resulted in the membrane bulging in the central ^{screwed} hole. A second series of screws (S'') were/through the top plate until they came in contact with the bottom plate to prevent changes in the distance of separation of the two plates once the membrane was clamped. A copper gauze (indicated by broken line) was supported by a steel disc (D) which was screwed in the central hole of the bottom plate. The gauze served to support the membrane under larger pressure gradients. The thickness of the membrane was always measured once it was clamped in the holder. The upper plate had flanges (F, F) which reduced the tendency of the membrane to buckle. The unit was then placed between the faces of the diffusion cell and a pair of rubber gaskets (G, G) inserted between the flanges and the plates ensured a mercury tight-seal. The diameter of the apertures of the inner faces of the steel plates were measured with a cathetometer from which the area of the membrane exposed to diffusion was obtained.

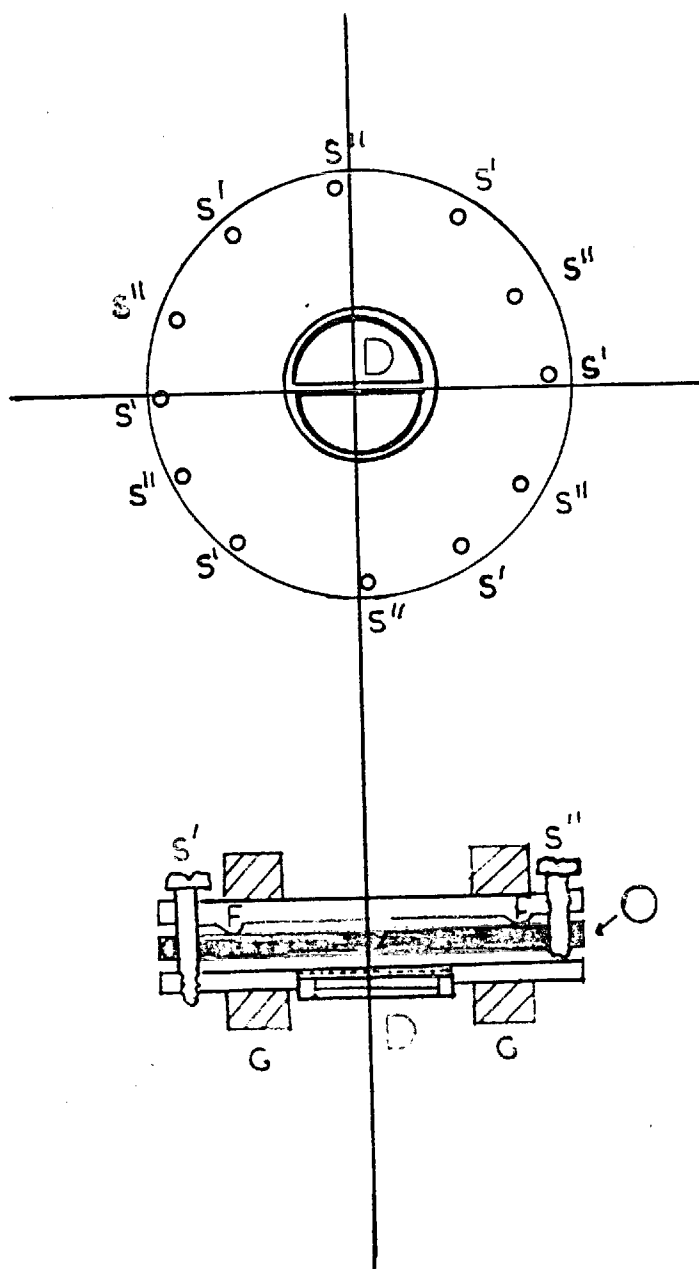


FIG. IV.5

The solubility system

In Figure II.6 is shown a diagram of the solubility system. It consisted of two main parts, a doser volume enclosed by the mercury cut-offs (B) and (E_1) and a sorption volume enclosed by (E_1) and the manometer (M_2).

The doser system consisted of a wide-bore U-tube manometer (M_1) of internal diameter 1.cm., a gas burette (D) and a mercury cut-off (B). The volume enclosed by the fixed marks (V_1) and (V_4) of the burette had been determined, using mercury, before assembly of the system.

The sorption system consisted of a cut-off (E_1), a U-tube manometer (M_2), constructed of 'Veridia' uniform bore tubing, internal diameter 0.6 cm., and a sample tube (S). The two sorption systems were immersed in separate water thermostats, controlled to $\pm 0.05^\circ\text{C}$ by a Sunvic control. Each thermostat had two plate-glass windows at opposite sides to enable the pressure in the system to be read-off (M_2) with a cathetometer.

The freezing-out bulbs (C) and (F) were used in transferring the hydrocarbon vapours to and from the systems.

Calibration of doser volume

The mercury in manometer (M_1) was raised and with cut-off (E_1) closed, a charge of nitrogen was introduced into the system with the mercury level in the gas burette at mark (V_1) and with cut-off (B) closed. The pressure (P_1) was recorded along with the distance of the mercury meniscus (h_1) from reference mark 'a' and M_1 . By raising

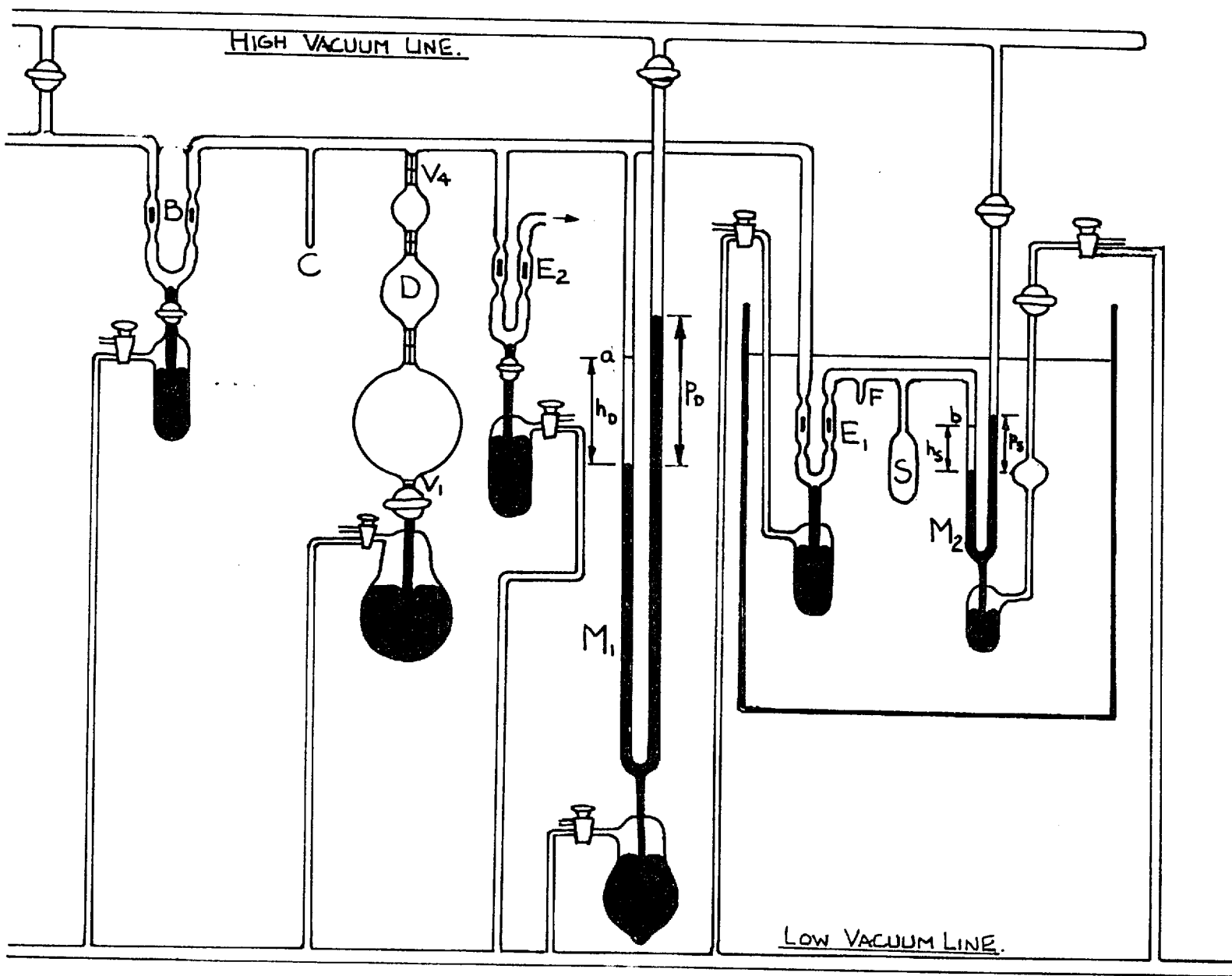


FIG. IV/6

the level of mercury in (D) to mark (V_4) the new (P_2) and (h) were obtained. From these the doser volume was² calculated by the application of gas laws.

Calibration of sorption volume

With cut-off (E_1) open, a charge of nitrogen was admitted to both the sorption and doser volumes and (E_1) closed. The corresponding pressures were measured in the two manometers (M_1) and (M_2). Cut-off (E_1) was then lowered and the mercury level in (D) raised to the mark (V_4). The new pressures were recorded in both volumes after closing (E_1) and the sorption volume calculated by the application of gas laws. A series of measurements were made and an average value obtained.

Method of operation

Before a charge was admitted into the sorption system, the polymer samples were thoroughly outgassed at about 70°C for at least a day. The thermostat was emptied and the system allowed to reach room temperature. With cut-off (E_1) closed a charge of hydrocarbon was admitted to the doser system and its volume pressure and temperature measured. The vapour was now frozen in the limb (C) and (E_1) lowered. Next the refrigerant was removed from (C) and placed around (F) and the charge was transferred to the sorption system. Cut-off (E_1) was now closed and the system brought to the required temperature. No residual pressure was observed in the doser volume for any of the hydrocarbons once (E_1) was closed. The equilibrium pressure and the distance of mercury meniscus below (b) were measured at fixed temperatures of 30, 40, 50,

60 and 70°C once the temperature was regulated. When measurements were completed for a charge, the hydrocarbon was returned to its reservoir by operating the appropriate cut-offs and the sample outgassed before a new charge was admitted.

The volume of gas (V_D) in the doser system was obtained using the equation:

$$V_D = (V' + h_D A_D) \times \frac{273 \times P_D}{76 \times (273 + T_R)} \quad \text{c.c. N.T.P. IV.3}$$

where, V' is the volume of the doser dead space, h_D the distance of mercury meniscus from the reference mark 'a', A_D is the area of cross-section of manometer (M_1), cm^2 , T_R is the room temperature and P_D the pressure of gas in the doser system.

The volume of the undissolved gas (V) in the sorption system was given by:

$$V = (V'' + h_S A_S) \times \frac{273 \times P_S}{76 \times (273 + T_S)} \quad \text{.....IV.4}$$

where V'' is the volume of the sorption system and the subscript 'S' in the other symbols represent sorption system and have the same significance as for the doser system. The volume of gas sorbed (V_S) was then given by,

$$V_S = V_D - V \quad \text{c.c. N.T.P. IV.5}$$

and the solubility coefficient by,

$$\sigma = \frac{V_S}{P_S \times v} \quad \text{.....IV.6}$$

where 'v' is the volume of the polymer sample.

From a series of equilibrium pressure/temperature measurements with different charges, isotherms were constructed and the solubility coefficients obtained from the linear plots of V_S vs. P_S .

Accuracy of Results

Permeability measurements

- a. Membrane thickness: The thickness of the membrane was measured with an accurate micrometer screw gauge and the error in the measurement estimated to be less than 1.5%
- b. Area of the membrane: This measurement was extremely accurate and any error should be negligible.
- c. Room temperature variations: No appreciable variation in the room temperature was observed when runs were made. This error should therefore be very small.
- d. McLeod gauge readings: All readings were taken at fixed reference marks which were accurately calibrated. The scatter in the points of pressure/time plots were always less than 1% and this error was further reduced by drawing the best straight line through them in the steady state of flow.
- e. Ingoing pressure: The measurement was made with a silver mirrored scale and the error was less than 1%. A drop in the pressure due to diffusion and solution in the membrane was of course unavoidable but this did not introduce any appreciable error

due to the large buffer volume on the ingoing side and also because steady state conditions were reached in a comparatively short time for silicone rubbers.

- f. Gauze effect: The copper gauze used to support the membrane on the outgoing side requires consideration. In many cases the membranes after use were examined and were found to contain an imprint of the pattern of the gauze. This area of contact can be expected to increase with pressure on the ingoing side resulting in a reduction of the permeabilities due to metal rubber contact preventing desorption of gas. In some cases the reduction in the permeabilities at higher ingoing pressures was as high as 4% although there was good agreement in time-lags at different pressures.

Total error: From the above, the maximum error in the permeability is estimated to be about $\pm 4\%$ although the reproducibility of $\bar{P}$ for a given membrane was much less, about $\pm 1\%$.

Solubility measurements

The following are the sources of error in the solubility measurements:

- a. Doser volume: From a series of measurements values reproducible to within $\pm 1\%$ were obtained and an average value used.

- b. Sorption volume: Since measurement of sorption volume also involved the doser volume the estimated error is at the most $\pm 2\%$. The average of at least six measurements was taken.
- c. Volume of the polymer sample: The main error in this is the determination of density of the sample. There should be no error in the weight of the sample which was obtained with a high accuracy balance but since the density determinations were made on a different portion of the same sheet, slight non-uniformity should be expected. The density determinations were accurate to within $\pm 2\%$.

Total error: The total error in the solubility is estimated to be $\pm 2\%$ obtained from the reproducibility of the solubility isotherms.

CHAPTER V.

The solubility results are given in the following pages.

Explanation of symbols in the tables:

- P_D pressure of gas in cm.Hg. in the doser system.
- h_D distance of mercury meniscus in cm. from fixed reference mark 'a' in manometer M_1 .
- V_D volume of gas charge in the doser system.
- T_D temperature of the doser system, $^{\circ}K$.
- P_S pressure of gas in cm.Hg. in the sorption system.
- h_S distance of mercury mensicus from fixed reference mark 'b' in manometer M_2 .
- V_S volume of gas in cc. N.T.P. sorbed by the polymer.
- T_S temperature of the sorption system, $^{\circ}K$.

The sample No., weight, density and volume content of filler are shown in Table V.1.

TABLE V.1.

Sample No.	Weight (g.)	Density (g./cc.)	Filler content (parts per 100 parts by weight of rubber)
Si.R-I	2.127	0.958	-
Si.R-H	2.508	0.977	-
Si.R-A	2.369	0.974	-
Si.R-B	2.744	1.009	10
Si.R-C	2.621	1.065	20
Si.R-D	3.385	1.096	30
Si.R-E	2.819	1.148	40

TABLE V.2

Sample No. Si.R-I : n-butane				<u>1st Charge</u>
($P_D = 2.777$	$h_D = 0.423$	$V_D = 2.910$	$T_D = 297.3$)	
P_S	h_S	V_S	T_S	
3.185	0.278	1.982	303	
3.744	0.162	1.851	313	
4.560	0.100	1.657	323	
5.280	0.300	1.501	333	
5.982	0.507	1.355	343	
				<u>2nd Charge</u>
($P_D = 5.442$	$h_D = 3.100$	$V_D = 5.820$	$T_D = 293.6$)	
6.347	0.875	3.936	303	
7.693	1.546	3.608	313	
9.126	3.078	3.229	323	
10.526	3.838	2.905	333	
11.938	4.582	2.574	343	
				<u>3rd Charge</u>
($P_D = 3.987$	$h_D = 1.437$	$V_D = 4.177$	$T_D = 299.8$)	
4.527	1.155	2.838	303	
5.450	1.533	2.607	313	
6.482	1.990	2.358	323	
7.464	2.419	2.135	333	
8.476	2.861	1.925	343	
				<u>4th Charge</u>
($P_D = 7.415$	$h_D = 4.612$	$V_D = 8.158$	$T_D = 294$)	
8.782	2.140	5.519	303	
10.617	4.000	5.030	313	
12.578	5.220	4.511	323	

TABLE V.3

Sample No. Si.R-I : iso-butane				<u>1st Charge</u>
($P_D = 2.590$	$h_D = 0.128$	$V_D = 2.739$	$T_D = 293.3$	
P_S	h_S	V_S	T_S	
3.690	0.178	1.664	303	
4.285	0.045	1.526	313	
4.945	0.072	1.383	323	
5.576	0.210	1.252	333	
6.183	0.293	1.137		

TABLE V.3 (continued)

				<u>2nd Charge</u>
($P_D = 4.875$	$h_D = 3.300$	$V_D = 5.187$	$T_D = 298)$	
P_S	h_S	V_S	T_S	
7.355	1.310	3.008	303	
8.530	2.590	2.705	313	
9.835	3.227	2.398	323	
11.010	3.797	2.146	333	
12.114	5.122	1.880	343	

				<u>3rd Charge</u>
($P_D = 3.440$	$h_D = 2.129$	$V_D = 3.745$	$T_D = 291.5)$	
5.240	2.129	2.177	303	
6.110	2.060	1.976	313	
6.940	2.400	1.795	323	
7.902	2.812	1.573	333	
8.750	3.130	1.405	343	

TABLE V.4

Sample No. Si.R-I : n-Pentane				<u>1st Charge</u>
($P_D = 2.218$	$h_D = 0.200$	$V_D = 2.340$	$T_D = 292.5)$	
P_S	h_S	V_S	T_S	
1.145	1.130	1.975	303	
1.500	3.750	1.914	313	
1.925	3.875	1.796	323	
2.390	4.040	1.684	333	
2.935	4.250	1.537	343	

				<u>2nd Charge</u>
($P_D = 5.650$	$h_D = 3.625$	$V_D = 6.141$	$T_D = 294.3)$	
2.880	4.325	5.255	303	
3.850	4.880	4.982	313	
4.938	5.558	4.721	323	
6.320	3.555	4.393	333	
7.635	4.310	4.079	343	

TABLE V.4 (continued)

<u>3rd Charge</u>			
(P _D = 7.000	h _D = 5.300	V _D = 7.825	T _D = 290.4)
P _S	h _S	V _S	T _S
3.712	3.912	6.688	303
4.765	4.575	6.398	313
6.230	5.525	6.007	323
7.980	3.855	5.606	333
9.655	4.905	5.190	343

<u>4th Charge</u>			
(P _D = 8.830	h _D = 6.730	V _D = 9.876	T _D = 292.9)
4.585	4.760	8.471	303
6.230	3.220	8.046	313
7.945	4.280	7.601	323
9.940	5.590	7.077	333
12.145	5.280	6.564	343

TABLE V.5

Sample No. Si.R-I : neo-pentane

<u>1st Charge</u>			
(P _D = 5.010	h _D = 3.195	V _D = 5.375	T _D = 292)
P _S	h _S	V _S	T _S
5.287	2.285	3.752	303
6.485	2.910	3.485	313
7.750	3.610	3.182	323
9.055	4.350	2.847	333
10.368	5.065	2.548	343

<u>2nd Charge</u>			
(P _D = 2.822	h _D = 2.922	V _D = 3.052	T _D = 290.2)
3.040	0.330	2.167	303
3.720	0.515	1.991	313
4.500	0.765	1.811	323
5.197	2.405	1.638	333
5.965	2.730	1.472	343

<u>3rd Charge</u>			
(P _D = 5.860	h _D = 3.460	V _D = 6.413	T _D = 295.7)
6.150	3.415	4.528	303
7.510	4.205	4.180	313
9.018	5.103	3.764	323
10.525	6.000	3.385	333
12.040	5.895	3.100	343

TABLE V.5 (continued)

<u>4th Charge</u>			
($P_D = 7.315$	$h_D = 5.135$	$V_D = 8.067$	$T_D = 293.5$)
P_S	h_S	V_S	T_S
7.750	2.295	5.765	303
9.455	4.065	5.274	313
11.335	4.495	4.800	323
13.184	6.379	4.310	333

TABLE V.6

<u>1st Charge</u>			
Sample No. Si.R-H : n-butane			
($P_D = 2.992$	$h_D = 1.012$	$V_D = 3.200$	$T_D = 292.6$)
P_S	h_S	V_S	T_S
3.072	0.130	0.892	303
3.808	0.403	1.074	313
4.567	0.670	1.252	323
5.377	0.960	1.437	333
6.165	1.245	1.605	343

<u>2nd Charge</u>			
($P_D = 4.116$	$h_D = 2.688$	$V_D = 4.518$	$T_D = 288.6$)
4.366	3.317	1.305	303
5.318	3.818	1.559	313
6.477	1.767	1.796	323
7.515	2.275	2.042	333
8.577	2.807	2.256	343

<u>3rd Charge</u>			
($P_D = 5.817$	$h_D = 6.083$	$V_D = 6.475$	$T_D = 293$)
6.312	0.816	1.848	303
7.758	1.596	2.220	313
9.250	3.566	2.631	323
10.730	4.421	2.978	333
12.251	5.311	3.334	343

<u>4th Charge</u>			
($P_D = 7.045$	$h_D = 5.887$	$V_D = 7.830$	$T_D = 294$)
7.456	2.199	2.216	303
9.151	3.195	2.577	313
10.921	4.257	3.107	323
12.698	5.344	3.563	333

TABLE V.7

Sample No. Si.R-H : iso-butane				<u>1st Charge</u>
($P_D = 3.350$	$h_D = 1.425$	$V_D = 3.584$	$T_D = 292$)	
P_S	h_S	V_S	T_S	
4.415	1.725	1.305	303	
5.310	2.110	1.511	313	
6.162	2.445	1.725	323	
6.985	2.780	1.908	333	
7.814	3.125	2.062	343	
				<u>2nd Charge</u>
($P_D = 4.696$	$h_D = 1.377$	$V_D = 5.049$	$T_D = 291$)	
6.303	2.967	1.891	303	
7.469	3.576	2.185	313	
8.660	4.219	2.549	323	
9.828	4.819	2.737	333	
10.962	5.382	2.984	343	
				<u>3rd Charge</u>
($P_D = 6.217$	$h_D = 6.267$	$V_D = 6.938$	$T_D = 293.5$)	
8.584	3.905	2.605	303	
10.179	4.860	3.024	313	
11.802	5.797	3.425	323	
13.355	6.697	3.810	333	
14.898	7.530	4.156	343	
				<u>4th Charge</u>
($P_D = 7.012$	$h_D = 7.089$	$V_D = 7.873$	$T_D = 292.5$)	
9.732	4.061	2.956	303	
11.521	5.129	3.441	313	
13.333	6.204	3.884	323	

TABLE V.8

Sample No. Si.R-H : n-pentane				<u>1st Charge</u>
($P_D = 5.673$	$h_D = 3.860$	$V_D = 6.136$	$T_D = 296.5$)	
P_S	h_S	V_S	T_S	
2.520	0.783	0.739	303	
3.397	1.198	0.966	313	
4.420	1.705	1.227	323	
5.610	2.353	1.523	333	
6.865	3.060	1.824	343	

TABLE V.8 (continued)

				<u>2nd Charge</u>
($P_D = 7.544$	$h_D = 8.771$	$V_D = 9.856$	$T_D = 294.5)$	
P_S	h_S	V_S	T_S	
4.030	0.855	1.181	303	
5.431	1.669	1.964	313	
7.064	2.652	1.964	323	
8.923	3.848	2.456	333	
10.990	5.222	2.979	343	

				<u>3rd Charge</u>
($P_D = 10.450$	$h_D = 9.650$	$V_D = 12.114$	$T_D = 291.5)$	
4.900	2.210	1.457	303	
6.585	3.280	1.921	313	
8.605	4.620	2.465	323	
10.829	6.132	3.056	333	
13.360	6.305	3.662	343	

				<u>4th Charge</u>
($P_D = 6.000$	$h_D = 5.955$	$V_D = 6.675$	$T_D = 292.4)$	
2.772	2.052	0.822	303	
3.720	2.550	1.086	313	
4.842	3.170	1.367	323	
6.157	3.960	1.702	333	
7.560	4.820	2.047	343	

TABLE V.9

Sample No. Si.R-H : neo-pentane				<u>1st Charge</u>
($P_D = 2.453$	$h_D = 0.118$	$V_D = 2.594$	$T_D = 293)$	
P_S	h_S	V_S	T_S	
2.305	0.185	0.670	303	
2.858	0.315	0.820	313	
3.458	1.792	0.962	323	
4.057	1.967	1.098	333	
4.698	2.162	1.236	343	

				<u>2nd Charge</u>
($P_D = 4.700$	$h_D = 3.050$	$V_D = 5.104$	$T_D = 292.3)$	
4.448	1.006	1.305	303	
5.535	1.523	1.583	313	
6.718	2.131	1.874	323	
7.927	2.770	2.157	333	
9.167	3.405	2.453	343	

TABLE V.9 (continued)

<u>3rd Charge</u>			
($P_D = 6.250$	$h_D = 5.160$	$V_D = 6.983$	$T_D = 291.5$)
P_S	h_S	V_S	T_S
5.975	1.162	1.757	303
7.417	1.943	2.130	313
8.967	4.257	2.542	323
10.557	5.215	2.940	333
12.146	6.188	3.323	343

<u>4th Charge</u>			
($P_D = 9.070$	$h_D = 7.650$	$V_D = 10.098$	$T_D = 297$)
8.557	2.800	2.550	303
10.657	4.113	3.134	313
12.760	7.023	3.739	323

TABLE V.10

Sample No. Si.R-A : n-butane

<u>1st Charge</u>			
($P_D = 2.906$	$h_D = 0.557$	$V_D = 3.049$	$T_D = 297.4$)
P_S	h_S	V_S	T_S
2.968	3.425	2.153	303
3.632	3.615	1.986	313
4.338	3.840	1.815	323
5.076	4.075	1.644	333
5.800	4.340	1.487	343

<u>2nd Charge</u>			
($P_D = 3.188$	$h_D = 0.655$	$V_D = 3.318$	$T_D = 299.8$)
3.235	3.341	2.343	303
3.930	3.553	2.169	313
4.735	3.823	1.972	323
5.445	4.071	1.813	333
6.188	4.333	1.652	343

<u>3rd Charge</u>			
($P_D = 5.386$	$h_D = 3.065$	$V_D = 5.848$	$T_D = 293.5$)
5.702	4.771	4.104	303
7.035	5.469	3.737	313
8.345	6.555	3.400	323
9.598	7.255	3.106	333
10.930	8.405	2.790	343

TABLE V.10 (continued)

<u>4th Charge</u>			
($P_D = 6.865$	$h_D = 4.612$	$V_D = 7.531$	$T_D = 294$)
P_S	h_S	V_S	T_S
7.305	5.196	5.288	303
8.928	7.230	4.824	313
10.528	8.224	4.404	323

TABLE V.11

Sample No. Si.R-A: iso-butane

<u>1st Charge</u>			
($P_D = 2.860$	$h_D = 0.515$	$V_D = 3.031$	$T_D = 293.4$)
P_S	h_S	V_S	T_S
3.851	3.550	1.875	303
4.546	3.752	1.699	313
5.203	4.265	1.546	323
5.828	4.450	1.414	333
6.485	4.625	1.279	343

<u>2nd Charge</u>			
($P_D = 4.820$	$h_D = 2.570$	$V_D = 5.201$	$T_D = 294.5$)
6.549	4.821	3.198	303
7.711	5.391	2.910	313
8.835	6.682	2.615	323
9.935	7.612	2.339	333
11.046	8.565	2.095	343

<u>3rd Charge</u>			
($P_D = 3.960$	$h_D = 2.406$	$V_D = 4.186$	$T_D = 299.0$)
5.390	4.081	2.550	303
6.335	4.826	2.308	313
7.312	5.252	2.075	323
8.220	5.650	1.816	333
9.095	6.790	1.684	343

<u>4th Charge</u>			
($P_D = 6.870$	$h_D = 4.830$	$V_D = 7.566$	$T_D = 294$)
9.470	7.100	4.609	303
11.75	8.795	4.131	313

TABLE V.12

Sample No. Si.R-A : n-pentane				<u>1st Charge</u>
(P _D = 2.400	h _D = 0.350	V _D = 2.498	T _D = 292.5)	
P _S	h _S	V _S	T _S	
1.104	1.876	2.160	303	
1.505	5.515	2.112	313	
1.905	5.595	1.947	323	
2.380	5.740	1.834	333	
2.920	5.940	1.706	343	
				<u>2nd Charge</u>
(P _D = 4.675	h _D = 2.650	V _D = 5.021	T _D = 294.3)	
2.135	7.705	4.349	303	
2.880	8.100	4.134	313	
3.735	8.605	3.906	323	
4.660	7.495	3.690	333	
5.690	8.080	3.423	343	
				<u>3rd Charge</u>
(P _D = 5.900	h _D = 4.200	V _D = 6.489	T _D = 290.6	
2.775	5.050	5.626	303	
3.735	5.535	5.376	313	
4.730	6.150	5.115	323	
5.985	6.845	4.777	333	
7.370	7.690	4.430	343	
				<u>4th Charge</u>
(P _D = 8.340	h _D = 6.220	V _D = 9.242	T _D = 293	
3.900	4.835	8.055	303	
5.320	5.685	7.649	313	
6.805	6.600	7.260	323	
8.580	7.765	6.791	333	
10.415	8.020	6.324	343	

TABLE V.13

Sample No. Si.R-A : neo-pentane				<u>1st Charge</u>
(P _D = 4.300	h _D = 2.305	V _D = 4.597	T _D = 292)	
P _S	h _S	V _S	T _S	
3.900	5.615	3.400	303	
4.815	6.040	3.158	313	
5.795	6.525	2.906	323	
6.780	7.065	2.664	333	
7.625	7.565	2.478	343	

TABLE V.13 (continued)

				<u>2nd Charge</u>
($P_D = 3.678$	$h_D = 3.655$	$V_D = 3.984$	$T_D = 290)$	
P_S	h_S	V_S	T_S	
3.500	5.800	2.902	303	
4.520	6.170	2.635	313	
5.185	6.575	2.410	323	
6.065	7.040	2.269	333	
6.990	7.510	1.866	343	
				<u>3rd Charge</u>
($P_D = 9.000$	$h_D = 6.795$	$V_D = 9.944$	$T_D = 293.5)$	
8.705	7.275	7.620	303	
10.735	8.605	7.034	313	
				<u>4th Charge</u>
($P_D = 6.255$	$h_D = 3.860$	$V_D = 6.985$	$T_D = 296.3$	
5.950	5.755	5.152	303	
7.332	6.545	4.780	313	
8.815	7.410	4.402	323	
10.300	8.305	4.014	333	
11.800	9.195	3.643	343	

TABLE V.14

Sample No. Si.R-B : n-butane

				<u>1st Charge</u>
($P_D = 2.595$	$h_D = 0.177$	$V_D = 2.748$	$T_D = 292.8)$	
P_S	h_S	V_S	T_S	
2.558	4.086	1.930	303	
3.156	4.286	1.744	313	
3.778	4.508	1.607	323	
4.435	4.720	1.446	333	
5.107	4.944	1.289	343	
				<u>2nd Charge</u>
($P_D = 3.900$	$h_D = 2.415$	$V_D = 4.282$	$T_D = 288.6)$	
3.987	4.412	3.012	303	
4.860	4.860	2.764	313	
5.767	5.201	2.530	323	
6.712	5.640	2.292	333	
7.652	6.185	2.063	343	

TABLE V.14 (continued)

<u>3rd Charge</u>			
($P_D = 6.090$	$h_D = 5.728$	$V_D = 6.756$	$T_D = 293$)
P_S	h_S	V_S	T_S
6.282	5.090	4.715	303
7.684	5.873	4.329	313
9.095	7.060	3.952	323
10.585	8.312	3.537	333
12.024	9.599	3.158	343

<u>4th Charge</u>			
($P_D = 7.405$	$h_D = 6.255$	$V_D = 8.261$	$T_D = 294$)
7.609	6.640	5.762	303
9.300	7.698	5.368	313
11.103	8.833	4.783	323
12.895	9.990	4.282	333

TABLE V.15

Sample No. Si.R-B : iso-butane

<u>1st Charge</u>			
($P_D = 3.066$	$h_D = 1.145$	$V_D = 3.251$	$T_D = 293$)
P_S	h_S	V_S	T_S
3.979	3.518	1.993	303
4.780	3.796	1.770	313
5.487	4.010	1.607	323
6.187	5.960	1.410	333
6.900	6.228	1.248	343

<u>2nd Charge</u>			
($P_D = 4.914$	$h_D = 1.591$	$V_D = 5.303$	$T_D = 291$)
6.300	6.229	3.242	303
7.514	6.878	2.905	313
8.730	7.552	3.604	323
9.838	8.127	2.321	333

<u>3rd Charge</u>			
($P_D = 4.001$	$h_D = 4.155$	$V_D = 4.284$	$T_D = 292.5$)
5.314	4.678	2.672	303
6.302	5.134	2.407	313
7.315	5.599	2.151	323
8.263	6.914	1.895	333
9.203	7.334	1.691	343

TABLE V.15 (continued)

				<u>4th Charge</u>
($P_D = 6.387$	$h_D = 6.437$	$V_D = 7.135$	$T_D = 292.5$	)
P_S	h_S	V_S	T_S	
8.486	7.190	4.320	303	
10.093	8.152	3.865	313	
11.605	9.427	3.443	323	

TABLE V.16

Sample No. Si.R-B : n-pentane

				<u>1st Charge</u>
($P_D = 6.208$	$h_D = 4.383$	$V_D = 6.670$	$T_D = 295$	)
P_S	h_S	V_S	T_S	
2.768	4.875	5.777	303	
3.635	5.360	5.528	313	
4.705	5.975	5.227	323	
5.829	6.701	4.925	333	
7.383	7.565	4.521	343	
				<u>2nd Charge</u>
($P_D = 9.070$	$h_D = 7.910$	$V_D = 10.229$	$T_D = 294.5$	)
4.045	4.313	8.936	303	
5.525	5.183	8.497	313	
7.141	6.197	8.036	323	
8.992	7.420	7.521	333	
11.018	8.813	6.976	343	
				<u>3rd Charge</u>
($P_D = 11.805$	$h_D = 11.040$	$V_D = 13.807$	$T_D = 291.5$	)
5.443	5.837	12.032	303	
7.340	7.105	11.459	313	
9.527	7.382	10.852	323	
11.979	9.832	10.092	333	
				<u>4th Charge</u>
($P_D = 7.990$	$h_D = 7.900$	$V_D = 9.025$	$T_D = 292.4$	)
3.555	4.890	7.879	303	
4.911	6.177	7.468	313	
6.315	7.080	7.069	323	
7.983	8.173	6.597	333	
9.785	9.385	6.117	343	

TABLE V.17

Sample No. Si.R-B : neo-pentane				<u>1st Charge</u>
($P_D = 2.706$	$h_D = 0.333$	$V_D = 2.873$	$T_D = 293$)	
P_S	h_S	V_S	T_S	
2.395	3.367	0.763	303	
3.000	3.517	0.940	313	
3.607	3.670	1.113	323	
4.245	3.872	1.298	333	
4.901	4.071	1.386	343	
				<u>2nd Charge</u>
($P_D = 4.396$	$h_D = 3.231$	$V_D = 4.781$	$T_D = 292.5$)	
4.009	4.194	1.284	303	
4.989	4.659	1.556	313	
5.990	5.147	1.821	323	
7.076	5.705	2.097	333	
8.109	6.979	2.351	343	
				<u>3rd Charge</u>
($P_D = 5.200$	$h_D = 4.120$	$V_D = 5.761$	$T_D = 292.7$)	
4.795	4.655	1.543	303	
5.950	5.260	1.867	313	
7.144	6.580	2.204	323	
8.374	7.287	2.521	333	
9.645	8.010	2.824	343	
				<u>4th Charge</u>
($P_D = 7.743$	$h_D = 6.318$	$V_D = 8.478$	$T_D = 297$)	
7.066	5.761	2.303	303	
8.785	6.845	2.790	313	
10.477	9.022	3.317	323	

TABLE V.18

Sample No. Si.R-C : n-butane				<u>1st Charge</u>
($P_D = 3.340$	$h_D = 2.210$	$V_D = 3.600$	$T_D = 293.5$)	
P_S	h_S	V_S	T_S	
3.792	1.461	1.079	303	
4.620	1.776	1.278	313	
5.486	2.162	1.478	323	
6.426	2.548	1.689	333	
7.287	2.907	1.867	343	

TABLE V.18 (continued)

				<u>2nd Charge</u>
(P _D = 4.990	h _D = 3.540	V _D = 5.417	T _D = 293.7)	
P _S	h _S	V _S	T _S	
5.770	0.728	1.629	303	
6.980	1.998	1.938	313	
8.297	2.688	2.248	323	
9.680	3.428	2.564	333	
11.011	4.123	2.845	343	

				<u>3rd Charge</u>
(P _D = 6.585	h _D = 4.190	V _D = 7.205	T _D = 294)	
7.495	2.920	2.172	303	
9.123	3.880	2.590	313	
10.846	4.881	3.003	323	
12.538	5.880	3.404	333	
14.178	7.677	3.823	343	

				<u>4th Charge</u>
(P _D = 7.770	h _D = 5.440	V _D = 8.593	T _D = 293)	
8.976	3.849	2.627	303	
10.937	5.092	3.151	313	
12.992	6.360	3.677	323	

TABLE V.19

Sample No. Si.R-C : n-pentane

				<u>1st Charge</u>
(P _D = 4.150	h _D = 3.120	V _D = 4.512	T _D = 292.6)	
P _S	h _S	V _S	T _S	
2.128	0.468	0.599	303	
2.850	0.728	0.780	313	
3.693	1.058	0.981	323	
4.645	1.513	1.206	333	
5.710	2.046	1.448	343	

				<u>2nd Charge</u>
(P _D = 6.650	h _D = 4.400	V _D = 7.309	T _D = 294.8)	
3.386	0.958	0.958	303	
4.491	1.565	1.240	313	
5.825	2.330	1.573	323	
7.374	3.284	1.955	333	
9.010	4.265	2.335	343	

TABLE V.19 (continued)

				<u>3rd Charge</u>
($P_D = 9.235$	$h_D = 7.290$	$V_D = 10.349$	$T_D = 293$	)
P_S	h_S	V_S	T_S	
1.726	3.889	1.386	303	
6.315	4.955	1.815	313	
8.239	3.627	2.252	323	
10.345	5.015	2.796	333	
12.626	6.558	3.370	343	

				<u>4th Charge</u>
($P_D = 10.972$	$h_D = 10.197$	$V_D = 12.539$	$T_D = 295$	)
5.700	4.645	1.685	303	
7.670	3.535	2.149	313	
9.965	5.055	2.776	323	
12.505	6.810	3.440	333	

TABLE V.20

Sample No. Si-R-C : iso-butane

				<u>1st Charge</u>
($P_D = 2.450$	$h_D = 1.040$	$V_D = 2.600$	$T_D = 293$	)
P_S	h_S	V_S	T_S	
3.569	3.439	1.039	303	
4.230	3.685	1.197	313	
4.895	3.930	1.348	323	
5.530	4.135	1.480	333	
6.184	4.379	1.613	343	

				<u>2nd Charge</u>
($P_D = 4.653$	$h_D = 3.648$	$V_D = 5.069$	$T_D = 294$	)
6.775	3.980	1.987	303	
8.010	4.640	2.286	313	
9.215	5.288	2.571	323	
10.395	5.939	2.825	333	
11.550	6.510	3.078	343	

				<u>3rd Charge</u>
($P_D = 6.093$	$h_D = 4.268$	$V_D = 6.675$	$T_D = 294$	)
8.865	5.683	2.660	303	
10.385	6.613	3.049	313	
12.090	5.218	3.376	323	
13.510	6.830	3.734	333	
15.036	7.669	4.069	343	

TABLE V.20 (continued)

<u>4th Charge</u>			
($P_D = 8.325$	$h_D = 6.665$	$V_D = 9.276$	$T_D = 292.7$)
P_S	h_S	V_S	T_S
12.325	7.590	3.760	303
14.536	7.502	4.293	313

TABLE V.21

Sample No. Si.R-C : neo pentane

<u>1st Charge</u>			
($P_D = 2.645$	$h_D = 1.325$	$V_D = 2.849$	$T_D = 293.7$)
P_S	h_S	V_D	T_S
2.720	2.310	0.784	303
3.320	2.530	0.934	313
4.020	2.817	1.093	323
4.747	3.090	1.245	333
5.440	3.350	1.402	343

<u>2nd Charge</u>			
($P_D = 5.720$	$h_D = 4.550$	$V_D = 6.272$	$T_D = 291$)
5.675	1.198	1.872	303
7.380	3.360	2.081	313
8.920	4.310	2.459	323
10.400	5.180	2.822	333
11.965	6.085	3.171	343

<u>3rd Charge</u>			
($P_D = 2.200$	$h_D = \text{Nil}$	$V_D = 8.606$	$T_D = 293.5$)
8.075	4.120	2.367	303
10.010	5.335	2.896	313
12.028	6.610	3.407	323
13.985	7.635	3.894	333

<u>4th Charge</u>			
($P_D = 3.735$	$h_D = 2.950$	$V_D = 4.043$	$T_D = 292.5$)
3.930	0.347	1.105	303
4.840	0.712	1.323	313
5.820	3.217	1.588	323
6.797	3.699	1.811	333
7.805	4.102	2.015	343

TABLE V.22

Sample No. Si.R-D : n-butane				<u>1st Charge</u>
($P_D = 4.800$	$h_D = 3.150$	$V_D = 5.216$	$T_D = 293.7$)	
P_S	h_S	V_S	T_S	
4.846	4.309	1.511	303	
5.990	4.858	1.822	313	
7.120	5.468	2.111	323	
8.345	6.113	2.424	333	
9.495	7.468	2.690	343	
<u>2nd Charge</u>				
($P_D = 2.400$	$h_D = 0.985$	$V_D = 2.554$	$T_D = 293.8$)	
2.358	2.842	0.724	303	
2.859	2.882	0.851	313	
3.480	3.030	1.004	323	
4.066	3.171	1.142	333	
4.588	3.313	1.246	343	
<u>3rd Charge</u>				
($P_D = 6.625$	$h_D = 4.240$	$V_D = 7.209$	$T_D = 294$)	
6.688	4.334	2.089	303	
8.227	5.912	2.525	313	
9.826	6.835	2.952	323	
11.380	8.515	3.367	333	
12.926	9.885	3.781	343	
<u>4th Charge</u>				
($P_D = 7.850$	$h_D = 5.500$	$V_D = 8.682$	$T_D = 293$)	
7.997	6.072	2.538	303	
9.837	7.595	3.070	313	
11.664	9.469	3.597	323	

TABLE V.23

Sample No. Si.R-D' : n-pentane				<u>1st Charge</u>
($P_D = 4.215$	$h_D = 3.04$	$V_D = 4.575$	$T_D = 292.6$)	
P_S	h_S	V_S	T_S	
1.830	0.765	0.548	303	
2.486	0.895	0.724	313	
3.221	4.429	0.946	323	
4.113	4.879	1.177	333	
5.032	5.345	1.405	343	

TABLE V.23 (continued)

<u>2nd Charge</u>			
($P_D = 6.55$	$h_D = 4.275$	$V_D = 7.192$	$T_D = 295$)
P_S	h_S	V_S	T_S
2.850	4.225	0.889	303
3.838	4.743	1.166	313
4.963	5.375	1.471	323
6.298	6.178	1.826	333
7.738	7.035	2.181	343

<u>3rd Charge</u>			
($P_D = 8.630$	$h_D = 7.310$	$V_D = 9.666$	$T_D = 293$)
3.801	5.367	1.200	303
5.142	6.184	1.585	313
6.645	7.162	1.929	323
8.433	8.357	2.504	333
10.4	8.307	2.976	343

<u>4th Charge</u>			
($P_D = 11.950$	$h_D = 11.125$	$V_D = 13.846$	$T_D = 294.4$)
5.388	5.843	1.708	303
7.265	7.108	2.264	313
9.400	7.295	2.851	323
11.960	9.075	3.568	333

TABLE V.24

Sample No. Si.R-D : iso-butane				<u>1st Charge</u>
($P_D = 2.580$	$h_D = 1.160$	$V_D = 2.738$	$T_D = 293$)	
P_S	h_S	V_S	T_S	
3.365	6.057	1.071	303	
3.945	6.282	1.218	313	
4.580	6.517	1.381	323	
5.230	6.757	1.526	333	
5.865	6.987	1.664	343	

<u>2nd Charge</u>			
($P_D = 4.450$	$h_D = 3.470$	$V_D = 4.838$	$T_D = 294$)
5.733	6.923	1.839	303
6.785	7.477	2.123	313
7.885	8.055	2.387	323
8.980	8.650	2.670	333
9.993	9.165	2.892	343

TABLE V.24 (continued)

				<u>3rd Charge</u>
($P_D = 7.125$	$h_D = 5.380$	$V_D = 7.915$	$T_D = 292.7)$	
P_S	h_S	V_S	T_S	
9.345	7.945	3.032	303	
11.090	9.035	3.527	313	
				<u>4th Charge</u>
($P_D = 6.025$	$h_D = 4.200$	$V_D = 6.563$	$T_D = 294.4)$	
7.805	7.283	2.497	303	
9.237	8.137	2.896	313	
10.670	8.983	3.275	323	
12.100	9.813	3.640	333	
13.500	10.666	3.968	343	

TABLE V.25

Sample No. Si.R-D : neo-pentane				<u>1st Charge</u>
($P_D = 3.050$	$h_D = 1.768$	$V_D = 3.268$	$T_D = 293.8)$	
P_S	h_S	V_S	T_S	
2.735	2.220	0.833	303	
3.394	5.404	1.040	313	
4.075	5.690	1.209	323	
4.807	5.982	1.393	333	
5.562	6.317	1.569	343	
				<u>2nd Charge</u>
($P_D = 4.045$	$h_D = 2.435$	$V_D = 4.371$	$T_D = 292.7)$	
3.720	3.445	1.012	303	
4.670	3.845	1.404	313	
5.605	5.285	1.661	323	
6.610	5.765	1.910	333	
7.688	6.310	2.169	343	
				<u>3rd Charge</u>
($P_D = 7.050$	$h_D = 5.895$	$V_D = 7.839$	$T_D = 291.1)$	
6.521	6.009	2.078	303	
8.130	7.003	2.507	313	
9.790	8.083	2.967	323	
11.540	9.193	3.458	333	
13.200	10.805	3.906	343	

TABLE V.26

Sample No. Si.R-E : n-butane				<u>1st Charge</u>
(P _D = 2.770	h _D = 2.815	V _D = 2.967	T _D = 291)	
P _S	h _S	V _S	T _S	
3.585	0.645	0.934	303	
4.347	2.747	1.126	313	
5.143	3.068	1.297	323	
5.989	3.385	1.471	333	
6.803	3.715	1.628	343	
				<u>2nd Charge</u>
(P _D = 4.690	h _D = 4.400	V _D = 5.153	T _D = 291.8)	
6.003	1.560	1.582	303	
7.310	2.260	1.879	313	
8.683	2.970	2.181	323	
10.035	3.690	2.473	333	
				<u>3rd Charge</u>
(P _D = 2.065	h _D = 2.780	V _D = 7.368	T _D = 294.5)	
8.540	2.230	2.262	303	
10.405	3.365	2.699	313	
12.245	6.110	3.201	323	
14.068	7.223	3.618	333	
				<u>4th Charge</u>
(P _D = 4.470	h _D = 3.850	V _D = 4.889	T _D = 293.5)	
5.652	1.341	1.483	303	
6.875	1.956	1.755	313	
8.160	2.656	2.039	323	
9.475	3.311	2.312	333	
10.690	5.531	2.623	343	

TABLE V.27

Sample No. Si.R-E : n-pentane				<u>1st Charge</u>
(P _D = 3.780	h _D = 2.860	V _D = 4.098	T _D = 292)	
P _S	h _S	V _S	T _S	
2.110	0.385	0.546	303	
2.843	0.645	0.717	313	
3.732	1.025	0.917	323	
4.660	1.425	1.116	333	
5.735	1.985	1.335	343	

TABLE V.27 (continued)

<u>2nd Charge</u>			
(P _D = 6.075	h _D = 5.740	V _D = 6.756	T _D = 293)
P _S	h _S	V _S	T _S
3.440	1.075	0.901	303
4.592	1.672	1.166	313
5.949	2.422	1.488	323
7.476	3.348	1.836	333
9.125	4.345	2.200	343

<u>3rd Charge</u>			
(P _D = 11.140	h _D = 9.710	V _D = 12.664	T _D = 295)
6.240	1.815	1.649	303
8.410	3.235	2.199	313
13.650	6.810	3.483	333

<u>4th Charge</u>			
(P _D = 1.650	h _D = 2.040	V _D = 14.441	T _D = 292.7)
7.072	3.175	1.900	303
9.535	4.840	2.526	313
12.785	7.280	3.388	323

TABLE V.28

<u>1st Charge</u>			
Sample No. Si.R-E : neo-pentane			
(P _D = 3.040	h _D = 2.515	V _D = 3.289	T _D = 292)
P _S	h _S	V _S	T _S
3.500	0.135	0.904	303
4.323	0.423	1.086	313
5.205	0.740	1.274	323
6.095	1.095	1.451	333
7.020	1.470	1.633	343

<u>2nd Charge</u>			
(P _D = 1.930	h _D = 0.165	V _D = 5.336	T _D = 292.5)
5.565	1.590	1.466	303
6.880	2.295	1.772	313
8.227	3.030	2.068	323
9.645	3.795	2.364	333
10.997	4.542	2.647	343

TABLE V.28 (continued)

<u>3rd Charge</u>			
$(P_D = 2.030$	$h_D = 1.230$	$V_D = 7.507$	$T_D = 291.5)$
P_S	h_S	V_S	T_S
9.575	4.535	2.517	313
11.857	6.197	3.105	323
13.247	6.865	3.408	333
14.998	7.908	3.770	343
<u>4th Charge</u>			
$(P_D = 1.890$	$h_D = 1.550$	$V_D = 9.529$	$T_D = 290.5)$
9.722	4.290	2.652	303
14.260	7.230	3.789	323

SOLUBILITY COEFFICIENTS

Sample No. Si.R-I

TABLE V.29

	30°C	40°C	50°C	60°C	70°C
n-butane	0.281	0.214	0.165	0.120	0.100
iso-butane	0.186	0.145	0.109	0.087	0.069
n-pentane	0.819	0.589	0.432	0.315	0.243
neo-pentane	0.322	0.243	0.187	0.144	0.113

Sample No. Si.R-H

TABLE V.30

n-butane	0.288	0.218	0.163	0.128	0.101
iso-butane	0.198	0.150	0.115	0.092	0.074
n-pentane	0.839	0.597	0.437	0.320	0.247
neo-pentane	0.339	0.253	0.194	0.147	0.116

Sample No. Si.R-A

TABLE V.31

n-butane	0.295	0.227	0.171	0.135	0.107
iso-butane	0.199	0.153	0.119	0.093	0.770
n-pentane	0.836	0.585	0.436	0.324	0.246
neo-pentane	0.364	0.269	0.209	0.158	0.129

Sample No. Si.R-B

TABLE V.32

n-butane	0.277	0.207	0.159	0.125	0.097
iso-butane	0.187	0.141	0.109	0.085	0.066
n-pentane	0.809	0.576	0.417	0.306	0.229
neo-pentane	0.320	0.234	0.181	0.141	0.111

Sample No. Si.R-C

TABLE V.33

n-butane	0.266	0.203	0.156	0.122	0.096
iso-butane	0.182	0.140	0.109	0.087	0.069
n-pentane	0.751	0.544	0.397	0.292	0.223
neo-pentane	0.312	0.232	0.174	0.173	0.107

Sample No. Si.R-D

TABLE V.34

n-butane	0.247	0.183	0.141	0.110	0.087
iso-butane	0.168	0.127	0.099	0.078	0.063
n-pentane	0.723	0.509	0.374	0.272	0.209
neo-pentane	0.290	0.214	0.161	0.123	0.097

SOLUBILITY COEFFICIENTS (cont'd)

Sample No. Si.R-E

TABLE V.35

	30°C	40°C	50°C	60°C	70°C
n-butane	0.243	0.190	0.138	0.109	0.086
n-pentane	0.716	0.505	0.364	0.271	0.201
neo-pentane	0.285	0.212	0.159	0.126	0.099

II PERMEATION RESULTS

The measured permeabilities of the hydrocarbons are given in the following pages. The sample No. and the thickness of the membranes used in this study are given in Table V.36

TABLE V.36

Sample No:	Si.R-I	Si.R-H	Si.R-A	Si.R-B	Si.R-C	Si.R-D	Si.R-E
Thickness(cm)	0.217	0.215	0.223	0.221	0.253	0.297	0.313

EXPLANATION OF SYMBOLS

- T = Temperature of the experiment in $^{\circ}\text{K}$.
- p_1 = Ingoing pressure in cm.Hg.
- $\bar{P}$ = The permeability
- L = Time-lag in minutes
- D_L = Transient state diffusion coefficient.

TABLE V.37

n-butane		Sample No. Si.R-I		
T	P ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.90	1.529	5.23	25.00
313	1.95	1.462	6.51	20.10
323	2.10	1.401	8.02	16.3
333	2.70	1.346	9.64	13.6
343	2.70	1.294	11.89	11.0

TABLE V.38

i so-butane		Sample No. Si.R-I		
T	P ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.00	0.896	3.83	34.2
313	2.40	0.868	4.73	27.7
323	2.50	0.841	5.78	22.6
333	2.70	0.818	6.97	18.8
343	2.50	0.795	8.38	15.6

TABLE V.39

n-pentane		Sample No. Si.R-I		
T	P ₁	$P \times 10^6$	$D_L \times 10^6$	L
303	2.70	3.67	4.36	30.0
313	2.60	3.33	5.58	23.4
323	2.45	2.99	7.03	18.6
333	2.70	2.67	8.78	14.9
343	2.80	2.48	10.90	12.0

TABLE V.40

neo-pentane		Sample No. Si.R-I		
T	P ₁	$P \times 10^6$	$D_L \times 10^6$	L
303	2.45	0.910	2.49	52.5
313	2.45	0.867	3.06	42.7
323	2.45	0.807	3.72	35.2
333	3.10	0.766	4.43	29.5
343	2.60	0.723	5.95	22.0

TABLE 41

n-butane

Sample No. Si.R-H

T	P_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.45	1.620	5.13	25.0
313	2.95	1.521	6.14	20.8
323	3.05	1.380	7.31	17.5
333	3.40	1.260	8.55	15.0
343	2.50	1.153	10.69	12.0

TABLE 42

iso-butane

Sample No. Si.R-H

T	P_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.90	0.856	3.77	34.00
313	2.30	0.836	4.79	26.8
323	2.20	0.818	6.03	21.3
333	1.70	0.800	7.44	17.2
343	1.70	0.771	9.17	14.0

TABLE V.43

n-pentane

Sample No. Si.R-H

T	P_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	1.55	3.95	4.71	29.3
313	1.60	3.51	5.87	23.4
323	1.80	3.12	7.14	18.8
333	1.65	2.80	8.75	15.9
343	1.95	2.51	10.16	13.1

TABLE V.44

neo-pentane

Sample No. Si.R-H

T	P_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.30	0.944	2.62	50.0
313	2.25	0.910	3.11	42.1
323	1.90	0.847	3.77	34.7
333	2.50	0.809	4.64	28.1
343	2.70	0.773	5.68	23.0

TABLE V.45

n-butane		Sample No. Si.R-A		
T	p ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.00	2.053	6.52	20.4
313	1.95	1.956	7.94	17.4
323	2.10	1.866	10.22	13.5
333	2.70	1.788	12.17	11.3
343	2.70	1.714	15.34	9.0

TABLE V.46

iso-butane		Sample No. Si.R-A		
T	p ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.10	1.137	5.11	27.0
313	2.95	1.120	6.45	21.4
323	2.50	1.09	8.02	17.2
333	2.65	1.059	9.82	14.0
343	2.95	1.051	12.00	11.5

TABLE V.47

n-pentane		Sample No. Si.R-A		
T	p ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.10	5.41	5.31	26.0
313	2.65	4.73	6.71	20.6
323	2.55	4.17	8.35	16.5
333	2.80	3.70	10.28	13.4
343	2.90	3.29	12.55	11.0

TABLE V.48

neo-pentane		Sample No. Si.R-A		
T	p ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.50	1.334	2.79	49.5
313	2.55	1.274	3.56	38.8
323	2.00	1.221	4.48	30.8
333	3.20	1.170	5.58	24.7
343	2.65	1.130	6.90	20.0

TABLE V.49

n-butane		Sample No. Si.R-B		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.00	1.81	5.21	26.0
313	3.00	1.675	5.89	23.0
323	3.00	1.568	6.78	20.0
333	3.30	1.468	8.17	16.5
343	3.75	1.381	9.68	14.0

TABLE V.50

iso-butane		Sample No. Si.R-B		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	1.5	0.966	3.66	37.0
313	2.3	0.943	4.11	33.0
323	2.2	0.913	5.09	26.6
333	1.7	0.825	6.28	21.6
343	3.3	0.788	7.75	17.5

TABLE V.51

n-pentane		Sample No. Si.R-B		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.40	4.365	4.49	30.2
313	2.50	3.720	5.51	24.6
323	1.80	3.236	6.69	20.2
333	1.80	2.880	8.04	16.8
343	1.95	2.480	9.68	14.0

TABLE V.52

neo-pentane		Sample No. Si.R-B		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.30	0.928	2.49	54.4
313	2.25	0.895	2.92	46.4
323	1.90	0.856	3.43	39.5
333	2.50	0.834	3.92	34.5
343	1.65	0.805	5.17	26.2

TABLE V.53

n-butane		Sample No. Si.R-C		
T	p ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.50	1.456	5.05	35.2
313	2.10	1.339	-	-
323	6.25	1.230	-	-
333	6.00	1.134	9.61	18.5
343	2.25	1.058	10.97	17.0

TABLE V.54

iso-butane		Sample No. Si.R-C		
T	p ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.10	0.736	3.55	50.1
313	2.50	0.710	-	-
323	1.90	0.689	-	-
333	2.30	0.663	6.03	29.5
343	2.10	0.645	7.11	25.0

TABLE V.55

n-pentane		Sample No. Si.R-C		
T	p ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.50	3.408	4.40	40
313	2.40	2.903	5.08	35
323	2.00	2.612	5.79	30.7
333	1.85	2.323	6.58	27
343	2.90	2.077	7.43	23.9

TABLE V.56

neo-pentane		Sample No. Si.R-C		
T	p ₁	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.0	0.777	2.37	75
313	3.80	0.738	3.24	54.6
323	2.30	0.705	4.04	44
333	3.65	0.673	4.84	36.7
343	2.35	0.604	5.85	30.4

TABLE V.57

n-butane		Sample No. Si.R-D		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.95	1.338	4.41	55.5
313	2.10	1.181	5.31	46.1
323	3.15	1.094	6.46	37.9
333	6.00	1.023	7.24	33.8
343	2.25	0.912	8.16	30.0

TABLE V.58

n-pentane		Sample No. Si.R-D		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.50	3.285	3.04	80.6
313	2.40	2.884	4.17	58.7
323	2.00	2.407	5.10	48.0
333	1.85	2.06	5.84	42.0
343	2.90	1.803	6.58	37.2

TABLE V.59

i so-butane		Sample No. Si.R-D		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.40	0.728	2.70	90.8
313	2.10	0.687	3.71	66.0
323	4.80	0.646	4.55	53.8
333	4.90	0.602	5.21	47.0
343	4.30	0.579	5.83	42.0

TABLE V.60

neo-pentane		Sample No. Si.R-D		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	1.95	0.719	1.87	131
313	3.80	0.682	2.13	115
323	2.30	0.654	2.49	99
333	3.55	0.617	2.72	90
343	2.35	0.584	3.23	76.0

TABLE V.61

n-butane		Sample No. Si.R-E		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	2.50	1.247	4.46	61.0
313	3.00	1.123	5.26	52.0
323	4.20	1.042	5.65	48.0
333	3.0	0.970	6.81	40.0
343	3.20	0.902	7.35	37.0

TABLE V.62

n-pentane		Sample No. Si.R-E		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.25	3.216	3.20	85.0
313	3.70	2.776	3.49	78.0
323	3.80	2.394	3.89	70.0
333	3.40	2.063	4.12	66.0
343	4.50	1.795	4.94	55.0

TABLE V.63

neo-pentane		Sample No. Si.R-E		
T	p_1	$\bar{P} \times 10^6$	$D_L \times 10^6$	L
303	3.45	0.718	1.68	150
313	4.75	0.653	2.16	126
323	3.35	0.606	2.42	112.5
333	4.60	0.554	-	-
343	4.60	0.511	-	-

CHAPTER VI

Before discussing the results for the filled rubbers it is necessary to determine the density of the silica filler and the sorption of vapour by the bulk filler.

The density of the filler

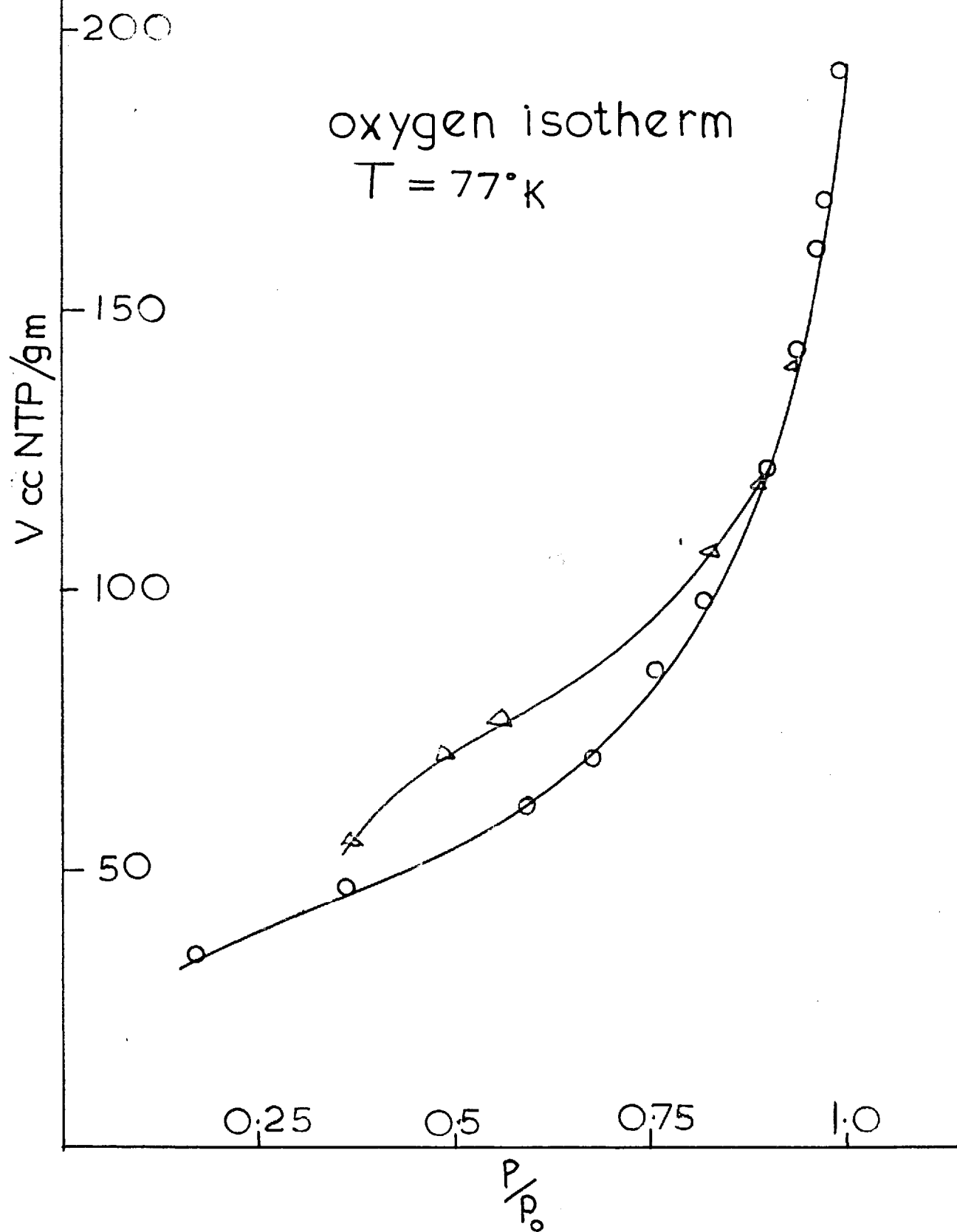
The silica filler was believed to be porous and this was confirmed by the B.E.T. surface area obtained from a nitrogen isotherm at 90°K. The value of 114 m²/g is consistent with an appreciable internal surface.

To estimate the porosity of the powder an oxygen isotherm at 77°K was constructed, the higher pressure region of which is shown in Figure VI.1. For $p/p_0 > 0.8$ no hysteresis was observed and presumably any inter-particle spaces responsible for capillary-type sorption were too large to give rise to any appreciable hysteresis. In a desorption loop of this nature it is not possible to separate completely intra-particle from inter-particle capillary sorption and so fix precisely the point at which intra-capillary desorption commences. However, an average value of 75 has been taken for the amount sorbed at this point which corresponds to 0.089 cc of liquid oxygen per gm. of powder. Using a value of 2.22 for the density of silica this leads to a value of 1.5 for the density of the porous filler.

An alternative procedure adopted to obtain an estimate of the filler density was the following. A known weight of the filler was subjected to rapid pumping for a

FIG. VII.1

oxygen isotherm
 $T = 77^\circ\text{K}$



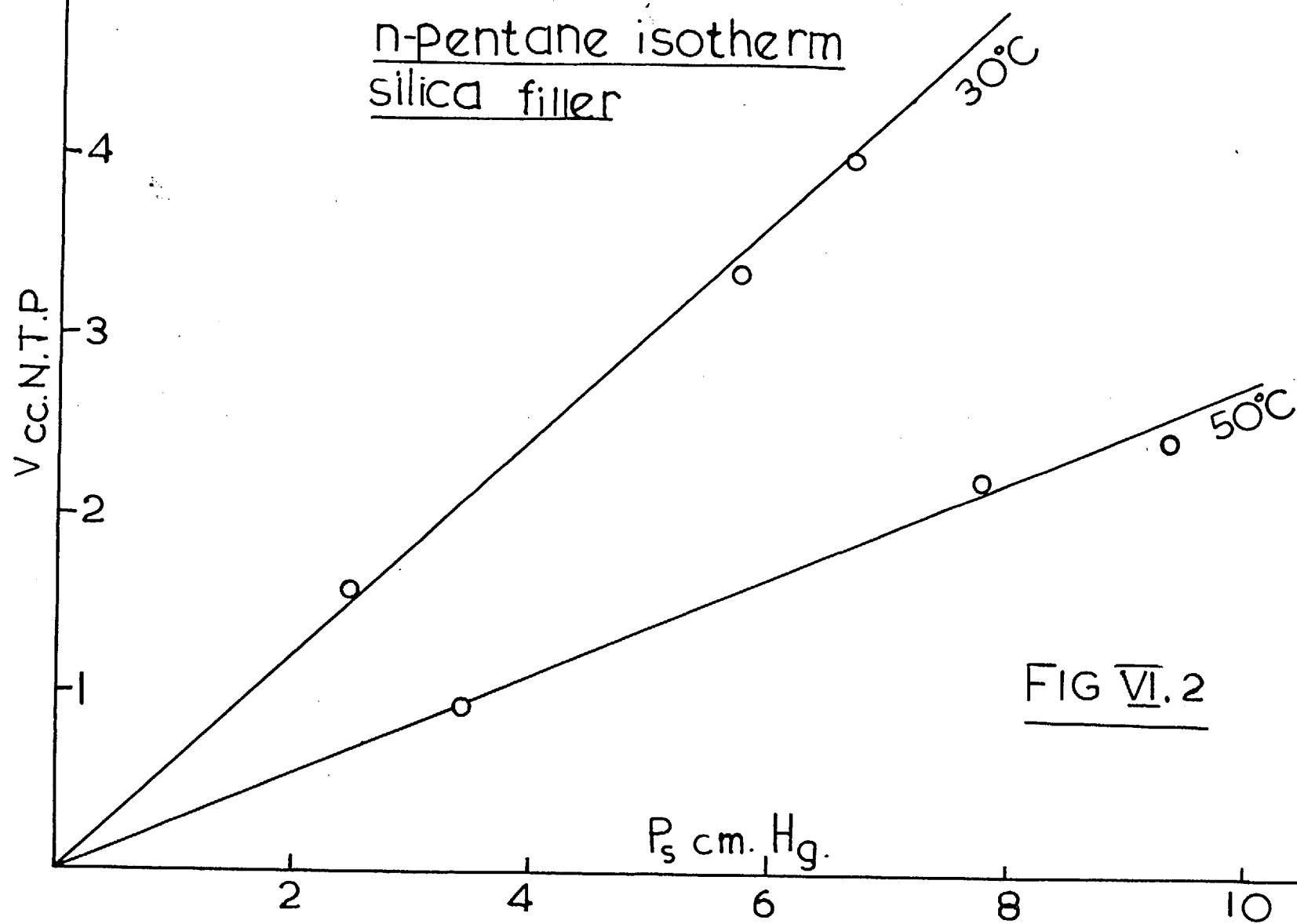


FIG VI. 2

short period so as to remove all air from the sample without causing appreciable desorption of the water from the capillaries. Water was then admitted to the evacuated bulb, the volume of which was known and the volume of water displaced was then obtained. The average of two determinations in one of which the sample was held at 273°K during the preliminary outgassing, gave a value of 1.66 g/cc for the density of the filler. Since before immersion, the capillaries will not be completely filled with water at room temperature this value is probably too high. As a check on the method a sample was completely outgassed at 100°C and the procedure repeated to give a density of 2.22, in good agreement with the literature value of 2.1 - 2.4.

Assuming additivity of volumes of filler and rubber phases then, from the filler contents of the sheets (Table V.1) the rubber and filler volume fractions, λ_r and λ_f respectively are easily calculated. The values are recorded in Table VI.1 and were obtained using the value of 1.66 for the density of the filler.

Table: VI.1

Volume fractions of rubber (λ_r) and filler (λ_f)				
	Si.R-B	Si.R-C	Si.R-D	Si.R-E
λ_r	0.944	0.894	0.851	0.809
λ_f	0.056	0.106	0.149	0.191

Sorption of vapour by the filler

To further the analysis of the sorption and diffusion results for the filled rubber, it is necessary to determine

the sorption of the hydrocarbons in the filler itself. Some examples of the sorption isotherms are shown in Figure VI.2

Sorption coefficients (cc NTP per cc of filler per cm Hg.) were calculated from the slopes of the linear regions of the isotherms. The n-butane and neo-pentane isotherms had slight curvature at higher pressures. The sorption coefficients in these cases were obtained from the linear portions at lower concentration regions. The values obtained at 30°C and 50°C for n-butane, n-pentane and neo-pentane are given in Table VI.2. The partial molar standard heat of sorption, $\Delta \bar{H}_f^\circ$ in the filler, was then obtained from the sorption coefficients at 30°C and 50°C. These values are also included in Table VI.2.

Table: VI.2

Sorption coefficients (cc/g) and $\Delta \bar{H}_f^\circ$

	30°C	50°C	$\Delta \bar{H}_f^\circ$
n-butane	0.216	0.102	-7263
n-pentane	0.535	0.242	-7663
neo-pentane	0.343	0.165	-7066

CHAPTER VII.

DISCUSSION OF SOLUBILITY

It is convenient to deal with the solubility results for the filled and unfilled rubbers separately. Firstly, the solubilities of the isomeric hydrocarbon vapours in unfilled silicone rubber are analysed in terms of polymer solution theory and compared with the corresponding data for the natural rubber. The solubilities for the filled rubbers are then presented and the effect of filler on the solubility is investigated.

1. Unfilled Silicone Rubber

The sorption isotherms

Isotherms were determined at temperatures of 30, 40, 50, 60, and 70°C., and at least three points were obtained on each isotherm in the pressure range 0-15 cm.Hg. In all cases a plot of the volume of hydrocarbon sorbed V_S (cc.N.T.P.) against the equilibrium gas phase pressure P_S (cm.Hg.) resulted in a straight line which passed through the origin Figure VII.1. With a few isotherms the equilibrium pressure was approached from higher and lower temperatures and hysteresis effects were shown to be absent. The Henry's law solubility coefficients (p. 53) were calculated from the slopes of the isotherms and are given in Tables V. 29 to VI 31.

The temperature dependence of the solubility

Several workers (Doty-1945, Barrer and Skirrow-1948b van Amerongen-1950) have shown that the temperature

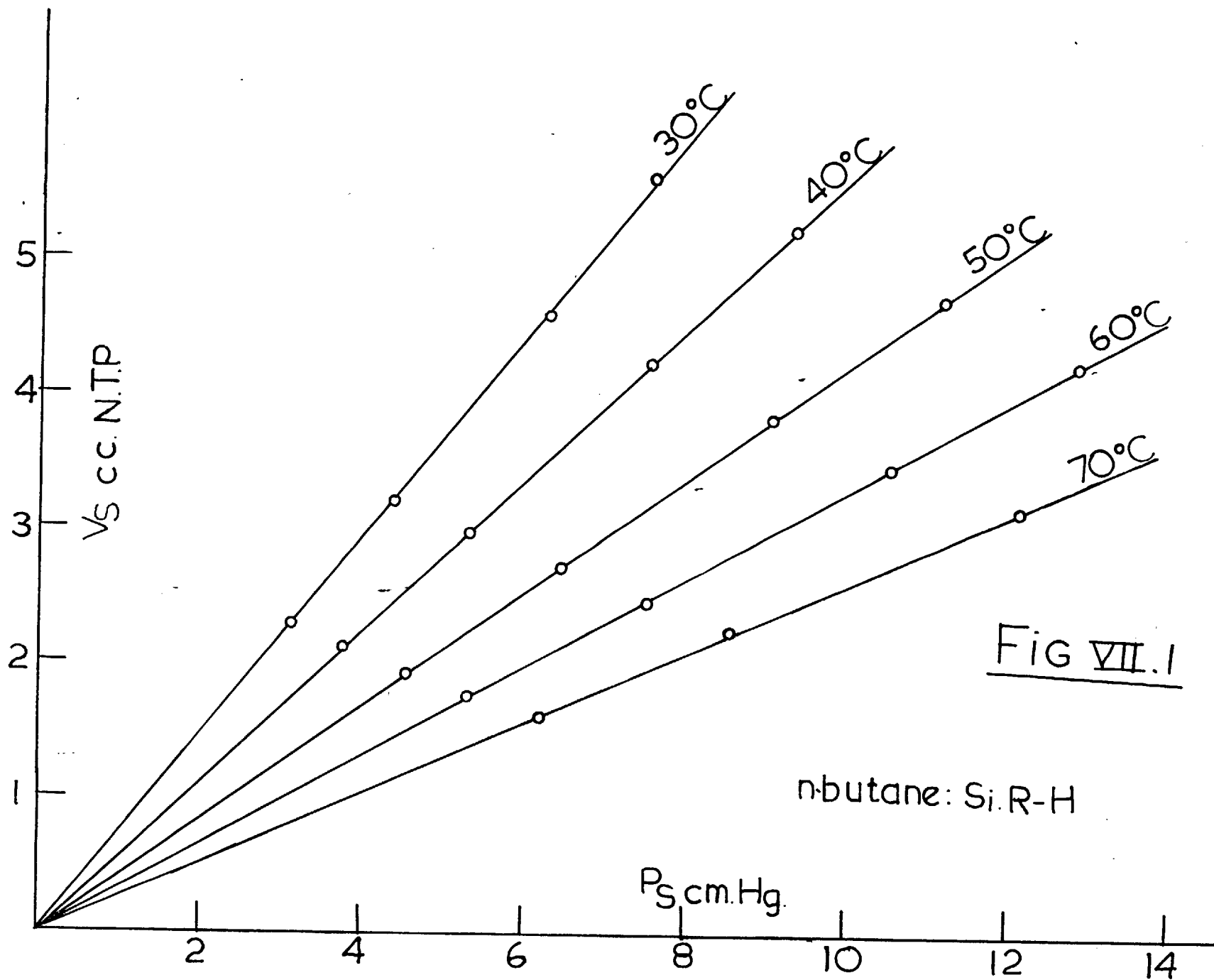


Fig VII.1

n-butane: Si.R-H

RUBBER: Si.R-I

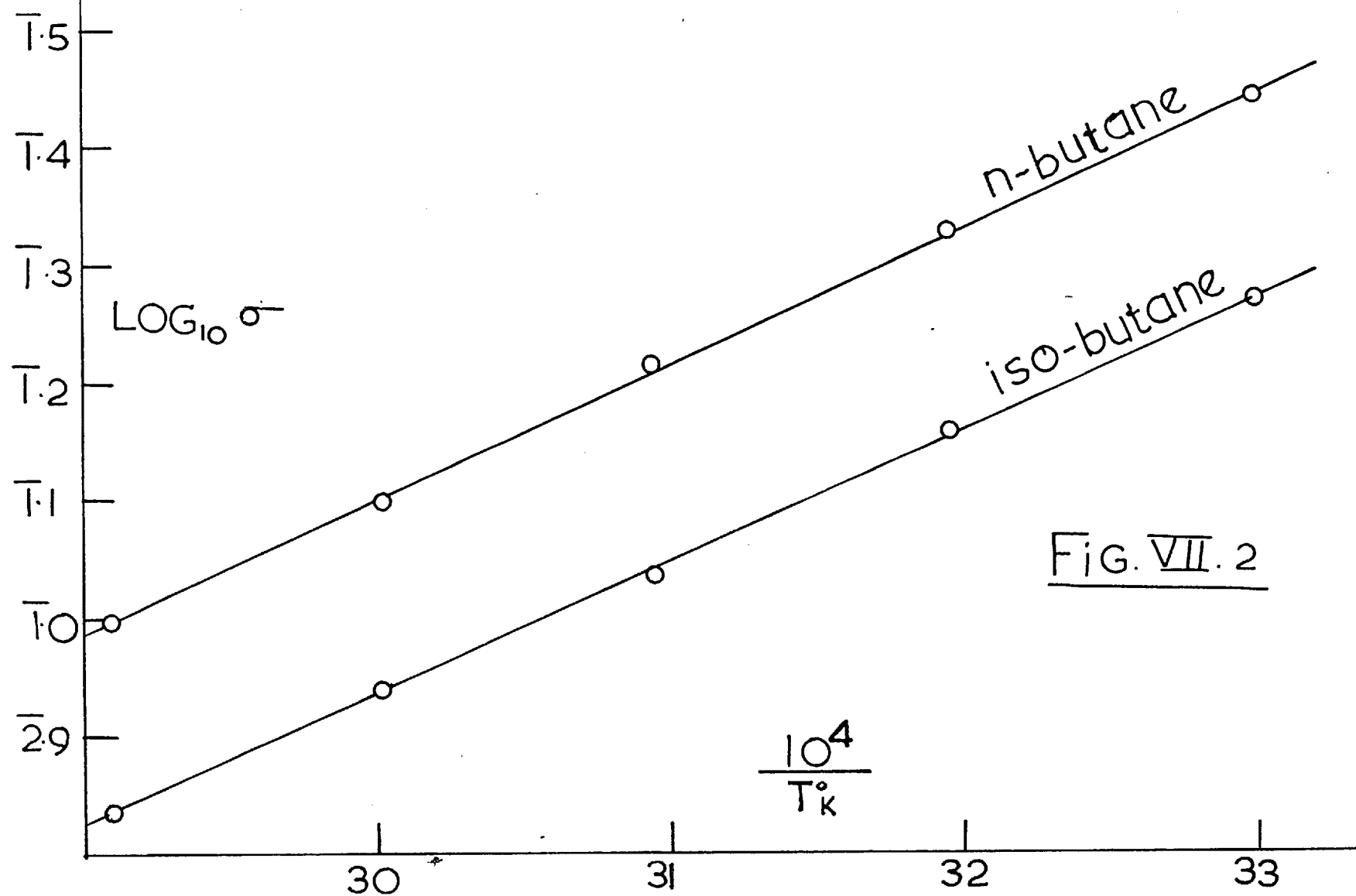


Fig. VII. 2

coefficient of the solubility of a gas in an elastomer is well represented by an equation of the form,

$$\bar{\sigma} = \bar{\sigma}_0 \exp \left(- \frac{\Delta \bar{H}^0}{RT} \right) \quad \text{.....VII.1}$$

where $\bar{\sigma}_0$ is a constant, T is the absolute temperature and $\Delta \bar{H}^0$ is the partial molar standard heat of solution. Some typical $\log \bar{\sigma}$ vs $1/T$ plots for the hydrocarbon-silicone rubber system are shown in Figure (VII.2). The values of $\Delta \bar{H}^0$ calculated from the slopes of these straight lines are given in Table (VII.1). The samples Si.R-I and Si.R-H were prepared from the same stock but contained respectively 0.1 and 1 mole percent of the crosslinking agent. Apparently this difference in degree of crosslinking has no significant effect on the solubility.

Table: VII.1

Partial molar standard heat of solution, $\Delta \bar{H}^0$ cal. mole⁻¹

	Si.R-I	Si.R-H	Si.R-A
n-butane	-5270	-5361	-5045
iso-butane	-5186	-5305	-5144
n-pentane	-6258	-6257	-6326
neo-pentane	-5361	-5500	-5397

In Table (VII.2) are given solubilities for the same hydrocarbons in natural rubber with two different degrees of crosslinking.

Table VII.2

Solubility coefficients (cc.N.T.P./ cc polymer/cm.Hg.) for natural rubber (Aitken and Barrer - 1955)

	Rubber A			Rubber I		
	30°C.	40°C.	50°C.	30°C.	40°C.	50°C.
n-butane	0.232	0.178	0.138	0.238	0.183	0.143
iso-butane	0.156	0.123	0.099	0.152	0.120	0.097
n-pentane	0.713	0.511	0.372	0.686	0.484	0.350
neo-pentane	0.260	0.198	0.153	0.250	0.193	0.151

It is clear that the solubility of these vapours in silicone rubber is similar to that in natural rubber and if anything perhaps slightly greater. In both rubbers $\Delta \bar{H}^{\circ}$ is greatest for n-pentane. As the number of carbon atoms in the hydrocarbon chain is increased one would perhaps expect greater heats of solution. The fact that the $\Delta \bar{H}^{\circ}$ values for the other hydrocarbons are apparently identical is probably a result of steric factors which reduce the effective contribution to $\Delta \bar{H}^{\circ}$ from an additional CH_2 group.

To facilitate comparison of the results with those of Aitken and Barrer (1955) we define a solubility $\sigma^{\circ} = 76$. used by these authors. The partial molar standard free energy of solution $\Delta \bar{G}^{\circ}$ is given by,

$$\Delta \bar{G}^{\circ} = - RT \ln \sigma^{\circ} \quad \text{.....VII.2}$$

and represents the free energy change in transferring isothermally and reversibly one mole of gas from the gas phase (76 cm.Hg.) to an infinite amount of the solution phase in equilibrium with vapour at pressure P_S . The partial molar standard entropy of

solution is then obtained from,

$$\Delta \bar{G}^{\circ} = \Delta \bar{H}^{\circ} - T \Delta \bar{S}^{\circ} \quad \text{.....VII.3}$$

Values of $\Delta \bar{G}^{\circ}$ and $\Delta \bar{S}^{\circ}$ are listed in Table VII.3. Not surprisingly the $\Delta \bar{S}^{\circ}$ values for n-pentane are again greater than for the other vapours. The increase in solubility on addition of a CH_2 group to the n-butane backbone is a result of additional contributions from this group to both $\Delta \bar{H}^{\circ}$ and $\Delta \bar{S}^{\circ}$. For comparison, the $\Delta \bar{G}^{\circ}$, $\Delta \bar{H}^{\circ}$ and $\Delta \bar{S}^{\circ}$ values for the two natural rubbers of Table (VII.2) are given in Table (VII.4)

Table:VII.3

Partial molar standard free energies ($\Delta \bar{G}^{\circ}$) at 30°C and entropies ($\Delta \bar{S}^{\circ}$)

	Si.R-I		Si.R-H		Si.R-A	
	$\Delta \bar{G}^{\circ}$	$\Delta \bar{S}^{\circ}$	$\Delta \bar{G}^{\circ}$	$\Delta \bar{S}^{\circ}$	$\Delta \bar{G}^{\circ}$	$\Delta \bar{S}^{\circ}$
n-butane	-1846	-11.30	-1861	-11.74	-1875	-10.46
iso-butane	-1597	-11.84	-1635	-12.11	-1638	-11.57
n-pentane	-2491	-12.43	-2506	-12.38	-2504	-12.61
neo-pentane	-1928	-11.33	-1959	-11.68	-2002	-11.20

Table:VII.4

Free energies, heats and entropies of solution for natural rubber (30°C)

	Rubber A			Rubber I		
	$\Delta \bar{G}^{\circ}$	$\Delta \bar{H}^{\circ}$	$\Delta \bar{S}^{\circ}$	$\Delta \bar{G}^{\circ}$	$\Delta \bar{H}^{\circ}$	$\Delta \bar{S}^{\circ}$
n-butane	-1416	-5050	-11.6	-1435	-4960	-11.6
iso-butane	-1210	-4430	-10.6	-1126	-4340	-10.6
n-pentane	-2007	-6340	-14.3	-1970	-6540	-15.1
neo-pentane	-1482	-5120	-12.0	-1473	-4910	-11.5

It can be seen from Tables VII.3 and VII.4 that $\Delta\bar{G}^0$ for natural rubber is consistently less negative.

The free energy, heat and entropy of dilution

For a comparison of the data with polymer solution theory the free energy, heat and entropy of dilution (p.26,27) are more suitable and were obtained using equations II.53, II.54 and II.55. These quantities were calculated at a constant weight fraction $w_1 = 0.01$ for the vapour chosen since this weight fraction lies in the Henry's law region of sorption and since the same quantities have been calculated for the same weight fraction for natural rubber (Aitken and Barrer-1955). The p_s/p_o ratio for the vapour was given by,

$$p_s/p_o = \frac{0.01 \times 22414 \times \int_r}{G \times M \times p_o} \dots\dots\dots \text{VII.4}$$

where p_s and p_o denote respectively the experimental equilibrium gas phase pressure for a vapour weight fraction of 0.01 and the saturated vapour pressure (cm.Hg.) of the hydrocarbon at the temperature of the experiment. M and $\int_r$ are respectively the molecular weight of the hydrocarbon and density of the polymer. The values of p_o for n-butane, iso-butane and n-pentane were obtained directly or interpolated from the data of Timmermans (1950) and the neo-pentane values from Beattie, Douslin and Levine (1951). Within the experimental error plots of $\Delta\bar{G}$ vs. T and $\Delta\bar{G}/T$ vs. $\frac{1}{T}$ (equations II.54 and II.55 respectively) were linear. The $\Delta\bar{G}$, $\Delta\bar{H}$ and $\Delta\bar{S}$ values are given in Table VII.5 and Table VII.6 and the corresponding data for the natural rubber system is presented in Table VII.7.

Table: VII.5

Free energies of dilution (ΔG) cal.mole⁻¹ at different temperatures, °C.

	30	40	50	60	70
Si.R-I					
n-butane	-1798	-1848	-1895	-1943	-1990
iso-butane	-1637	-1693	-1750	-1807	-1864
n-pentane	-1710	-1770	-1824	-1888	-1947
neo-pentane	-1682	-1744	-1812	-1870	-1928
Si.R-H					
n-butane	-1800	-1842	-1885	-1929	-1972
iso-butane	-1655	-1703	-1774	-1834	-1894
n-pentane	-1705	-1765	-1825	-1885	-1945
neo-pentane	-1701	-1756	-1816	-1870	-1932
Si.R-A					
n-butane	-1818	-1868	-1913	-1966	-2014
iso-butane	-1668	-1727	-1787	-1847	-1908
n-pentane	-1705	-1765	-1826	-1886	-1946
neo-pentane	-1740	-1803	-1829	-1867	-1995

Table V.II.6

Heats and entropies of dilution

	Si.R-I		Si.R-H		Si.R-A	
	$\Delta \bar{H}$	$\Delta \bar{S}$	$\Delta \bar{H}$	$\Delta \bar{S}$	$\Delta \bar{H}$	$\Delta \bar{S}$
n-butane	-339	4.80	-497	4.30	-350	4.85
iso-butane	92	5.68	160	5.95	146	6.00
n-pentane	83	5.93	110	6.00	120	6.18
neo-pentane	181	6.15	56	5.80	177	6.38

Table: VII.7

Data of $\Delta\bar{G}$ at 50°C, $\Delta\bar{H}$ and $\Delta\bar{S}$ for natural rubber

	Rubber A			Rubber I		
	$\Delta\bar{G}$	$\Delta\bar{H}$	$\Delta\bar{S}$	$\Delta\bar{G}$	$\Delta\bar{H}$	$\Delta\bar{S}$
n-butane	-1810	0	5.60	-1830	0	5.70
iso-butane	-1700	700	7.40	-1690	770	7.60
n-pentane	-1760	0	5.50	-1720	-190	4.70
neo-pentane	-1710	290	6.20	-1770	510	6.80

As for natural rubber $\Delta\bar{S}$ values are positive and large. The values of $\Delta\bar{H}$ are small and positive except for n-butane which is negative. Prager, Bagley and Long (1953) and Aitken and Barrer (1955) also found small values of $\Delta\bar{H}$ for these vapours in polyisobutylene and natural rubber respectively.

Comparison with polymer solution theory

To compare the results with Flory's theory for concentrated polymer solutions the weight fraction w_1 is converted to volume fraction v_1 using the relation,

$$v_1 = \frac{w_1 \rho_r}{\rho_o} \quad \text{.....VII.5}$$

where ρ_r and ρ_o are the densities of rubber and liquid penetrant respectively. Equation VII.5 is only valid for low concentrations of penetrant in the rubber when swelling is negligible. The densities of the liquid hydrocarbons n- and iso-butane at 50°C were interpolated from the data of Kay (1940) and Kretchmer and Wiebe (1951) and n-pentane from

Timmermans (1950). The value for neo-pentane at 50°C was estimated from the value at 20°C quoted by Doss (1943) assuming the coefficient of expansion was equal to that of iso-pentane. With the values of v_1 calculated from equation VII.5 the corresponding values for the volume fraction of rubber were obtained, viz. $v_2 = 1 - v_1$.

In Table VII.8 the experimental entropies of dilution for the rubber Si.R-A are compared with the calculated values obtained using the Flory expression (equation II.68). Aitken and Barrer (1955) showed that at these low penetrant concentrations the effect of crosslinking as introduced in the Flory-Rehner treatment (equation II.72) is negligible. Except for n-butane, the agreement between calculated and experimental values is good considering the simplicity of the theoretical model. For all the silicone rubbers investigated the $\Delta \bar{S}$ values for n-butane were always lower than for the other hydrocarbons whilst a similar effect was found by Aitken and Barrer with natural rubber.

Table: VII.8

Theoretical and Experimental Entropies for Si.R-A

	$\Delta \bar{S}$ (theoretical)	$\Delta \bar{S}$ (experimental)	v_1
n-butane	6.05	4.85	0.0179
iso-butane	5.96	6.00	0.0188
n-pentane	6.24	6.18	0.0163
neo-pentane	6.12	6.38	0.0173

Using equation II.66 values of the Flory-Huggins interaction parameter χ_1 were calculated and are given in Table VII.9. Also included in this table are the corresponding values for natural rubber. In general the values are lower for the silicone rubbers and are less than 0.5 which would indicate that these penetrants are solvents for the uncrosslinked rubber. However, values of 0.62 and 0.82 have been obtained for n-pentane and iso-pentane respectively in polyisobutylene in spite of the fact that these hydrocarbons are solvents for this rubber (Prager, Bagley and Long-1953). Similarly Baughan (1946) obtained values of $\chi_1 > 0.5$ for polystyrene-liquid systems, where the liquids were solvents for polystyrene.

Table: VII.9

Values of the interaction parameter χ_1 for silicone and natural rubber

	silicone rubber	natural rubber
n-butane	0.061	0.29
iso-butane	0.220	0.42
n-pentane	0.298	0.46
neo-pentane	0.176	0.48

The experimental $\Delta \bar{H}$ values are compared with those calculated from the Hildebrand-Scott (1950) expression for the internal energy of dilution,

$$\Delta \bar{E} = v_1 \left[\left(\frac{E_1}{V_1} \right)^{\frac{1}{2}} - \left(\frac{E_2}{V_2} \right)^{\frac{1}{2}} \right]^2 v_2^2 \dots\dots\dots \text{VII.6}$$

where V_1 and V_2 are respectively the molar volumes of penetrant and polymer and E_1 and E_2 are the corresponding energies of vaporization per mole of component. The energy of vaporization is related to the latent heat of Vaporization L by $E_1 = L + RT$, and values of L were obtained from the following sources; n-butane, iso-butane and n-pentane from Holcomb and Brown (1942) and neo-pentane from vapour pressure data of Beattie, Douslin and Levine (1951). The ratio E/V has been termed the cohesive energy density and is related to the so called solubility parameter by $\delta = (\frac{E}{V})^{\frac{1}{2}}$. No accurate data were available for the cohesive energy densities of silicone rubbers. However, an approximate value of 30.3 was given by Small (1953) for silicones and it is assumed that the same value will apply to silicone rubbers. The experimental and calculated $\Delta\bar{H}$ values are given in Table VII.10. Except for n-butane which gave a negative experimental $\Delta\bar{H}$, the agreement between the two sets of results can be regarded as satisfactory.

Table: VII.10

Experimental and calculated entropies of dilution for Si.R-A

	E_1	$\Delta\bar{H}$ (equation II.71)	$\Delta\bar{H}$ (experimental)
n-butane	3980	37	-350
iso-butane	3470	0	146
n-pentane	5270	138	120
neo-pentane	4910	59	177

On the whole the silicone rubbers differ but little from natural rubber in their solution properties and as for natural rubber thermodynamic functions calculated from current concentrated polymer solution theory compare favourably with the experimental values.

2. Filled Silicone Rubber

As with the unfilled rubbers Henry's law sorption isotherms were obtained for all filled rubbers at temperatures of 30, 40, 50, 60 and 70°C (Figure VII.3). The solubilities calculated from the isotherms are presented in Tables V.32 to 35. Again straight line plots of $\log \bar{S}$ vs $1/T$ were obtained (Figure VII.4) and as with the unfilled rubbers, values of $\Delta \bar{G}^\circ$, $\Delta \bar{H}^\circ$ and $\Delta \bar{S}^\circ$ were calculated and are given in Tables VII.10 and VII.11. In Tables VII.12 and VII.13 values of the corresponding dilution quantities $\Delta \bar{G}$, $\Delta \bar{H}$, $\Delta \bar{S}$ at a weight fraction of $w_1 = 0.01$ are tabulated. The weight fraction w_1 for the filled rubbers is referred to unit weight of filled sheet.

Table: VII.10.

Partial molar standard heats of solution $\Delta \bar{H}^\circ$

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
n-butane	-5391	-5374	-5378	-5729
iso-butane	-5305	-4963	-4881	-
n-pentane	-6392	-6210	-6350	-6499
neo-pentane	-5444	-5175	-5642	-5409

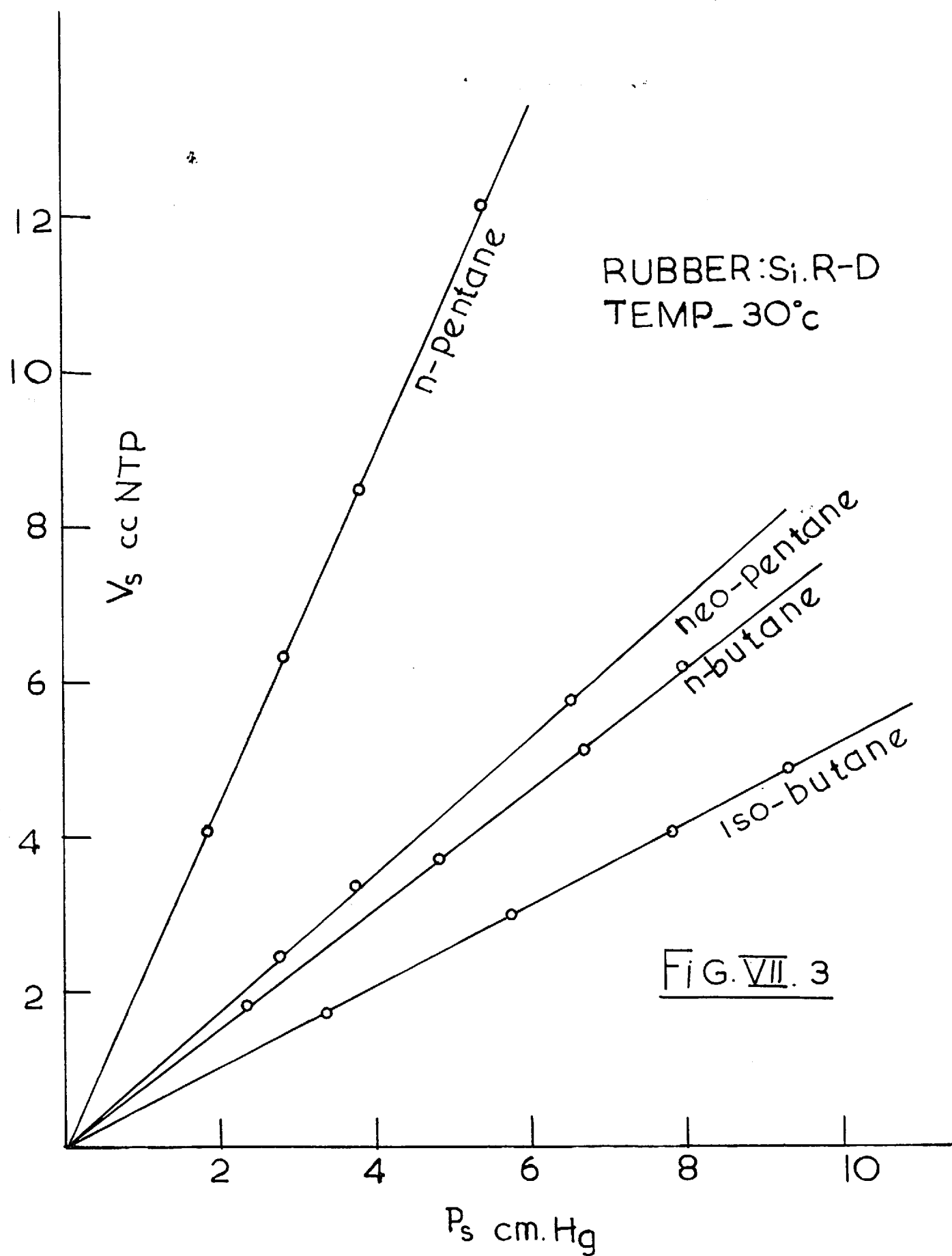


FIG. VII. 3

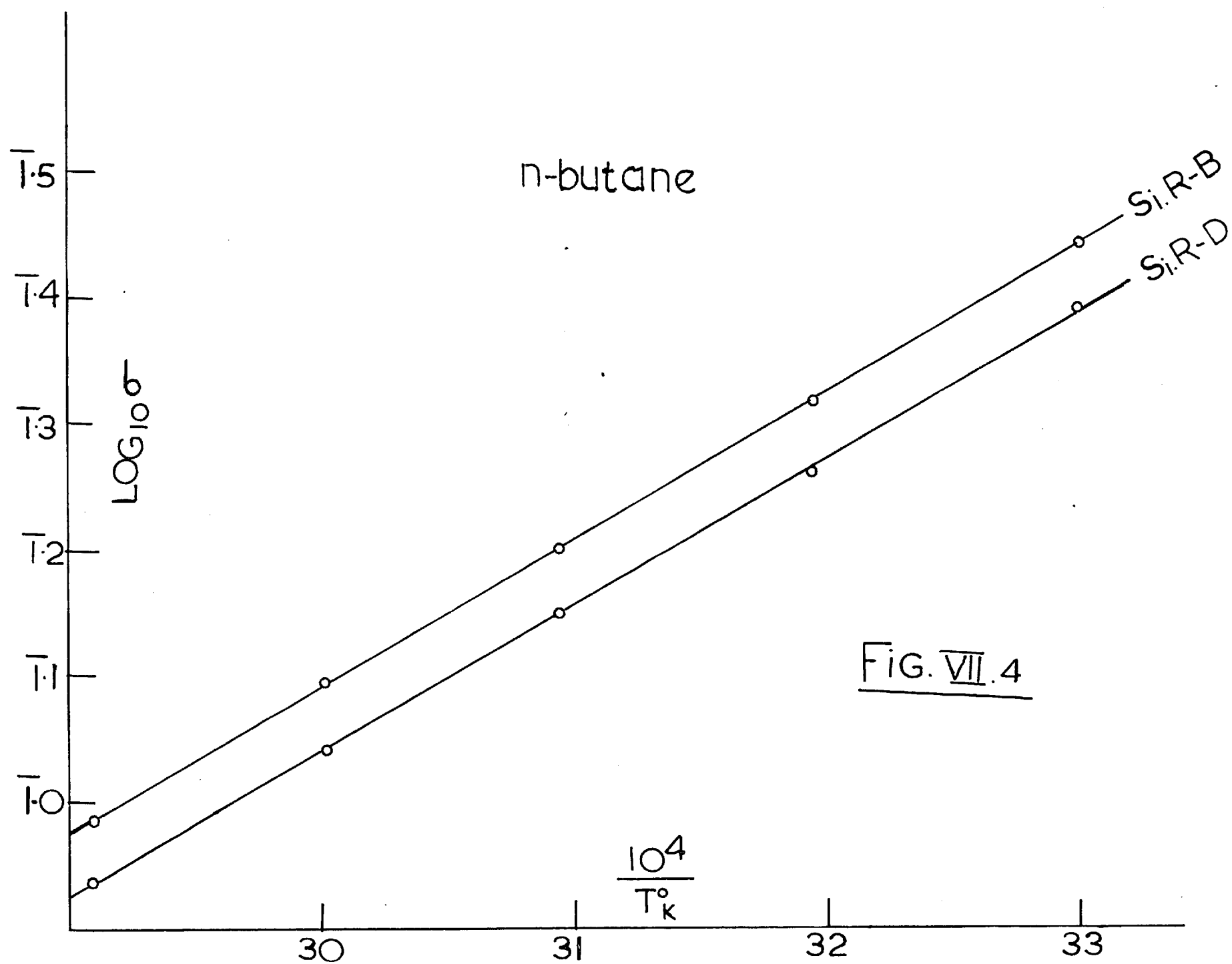


Table VII.11

Partial molar standard free energies and entropies of solution.

	$\Delta\bar{G}^\circ$	$\Delta\bar{S}^\circ$	$\Delta\bar{G}^\circ$	$\Delta\bar{S}^\circ$	$\Delta\bar{G}^\circ$	$\Delta\bar{S}^\circ$	$\Delta\bar{G}^\circ$	$\Delta\bar{S}^\circ$
	<u>Si.R-B</u>		<u>Si.R-C</u>		<u>Si.R-D</u>		<u>Si.R-E</u>	
n-butane	-1837	-11.73	-1813	-11.75	-1768	-11.91	-1759	-13.10
iso-butane	-1601	-12.22	-1957	-9.92	-1536	-11.04	--	--
n-pentane	-2484	-12.89	-2439	-12.44	-2416	-12.98	-2410	-13.49
neo-pentane	-1925	-11.61	-1909	-11.77	-1865	-12.46	-1855	-11.72

Table VII.12

Free energies of dilution ($\Delta\bar{G}$) Cal.mole⁻¹ at different temperatures, °C.

	30	40	50	60	70
<u>Si.R-B</u>					
n-butane	-1755	-1800	-1837	-1883	-1937
iso-butane	-1608	-1657	-1709-	-1760	-1810
n-pentane	-1680	-1729	-1777	-1824	-1870
neo-pentane	-1635	-1696	-1758	-1821	-1880
<u>Si.R-C</u>					
n-butane	-1712	-1753	-1796	-1837	-1880
iso-butane	-1559	-1619	-1674	-1734	-1791
n-pentane	-1610	-1660	-1711	-1757	-1815
neo-pentane	-1591	-1648	-1698	-1766	-1818
<u>Si.R-D</u>					
n-butane	-1636	-1670	-1713	-1752	-1792
iso-butane	-1485	-1541	-1594	-1652	-1709
n-pentane	-1546	-1600	-1654	-1708	-1762
neo-pentane	-1530	-1580	-1629	-1685	-1731

Table: VII.12 (cont'd)

	30	40	50	60	70
<u>Si.R-E</u>					
n-butane	-1601	-1637	-1669	-1715	-1748
iso-butane	---	---	---	---	---
n-pentane	-1512	-1558	-1607	-1658	-1700
neo-pentane	-1499	-1549	-1592	-1661	-1713

Table VII.13

Heats and entropies of dilution.

	Si.R-B		Si.R-C		Si.R-D		Si.R-E	
	$\Delta\bar{H}$	$\Delta\bar{S}$	$\Delta\bar{H}$	$\Delta\bar{S}$	$\Delta\bar{H}$	$\Delta\bar{S}$	$\Delta\bar{H}$	$\Delta\bar{S}$
n-butane	-372	4.85	-423	4.20	-461	3.90	-482	3.90
iso-butane	- 77	5.05	196	5.90	209	5.60	-	-
n-pentane	-240	4.75	56	5.13	90	5.40	- 87	4.70
neo-pentane	218	6.10	126	5.67	0	5.00	120	5.35

Reference model for sorption in a filled rubber

Before considering in more detail the solubility results for the filled rubbers it is of interest to examine the role of the filler particles in the sorption process. In the reference model the sorptive capacity of the rubber phase is identified with the solubility of the unfilled rubber and the sorptive capacity of the filler phase with the solubility of the filler powder in bulk. One may then write,

$$\sigma = \lambda_r \sigma_r + \lambda_f \sigma_f \quad \text{.....VII.7}$$

where σ_r and σ_f denote respectively the solubilities in one cm³ of unfilled rubber and of bulk filler, and λ_r and λ_f are the corresponding volume fractions of the two phases. For the special case where the polymer wets completely all of the available filler surface then σ_f is effectively zero and equation VII.7 reduces to,

$$\sigma = \lambda_r \sigma_r \quad \text{.....VII.8}$$

If the polymer only partially wets the available filler surface then σ_f will have a value somewhere in the range of 0 to its value for the bulk powder. Plots of the solubility of the filled rubber vs λ_r (Table VI.1) are shown in Figure VII.5 to VII.7. Also included are the two reference lines calculated from equations VII.8 and VII.7 assuming $\sigma_f = 0$ and equal to its value for the bulk powder respectively.

Role of filler on solubility

A convenient method of comparing the solubility results of the filled and unfilled rubbers lies in the calculation of ∇_σ which is given by

$$\nabla_\sigma = (1 - \frac{\sigma}{\sigma_r})100 \quad \text{.....VII.9}$$

where σ and σ_r are the measured solubilities in the filled and unfilled rubbers respectively. The reference unfilled sample is again Si.R-A and in Table VII.4 are collected values of ∇_σ for the various filled rubbers. The accuracy of ∇_σ is estimated at approximately ± 3 and the following points are noted from Table VII.14.

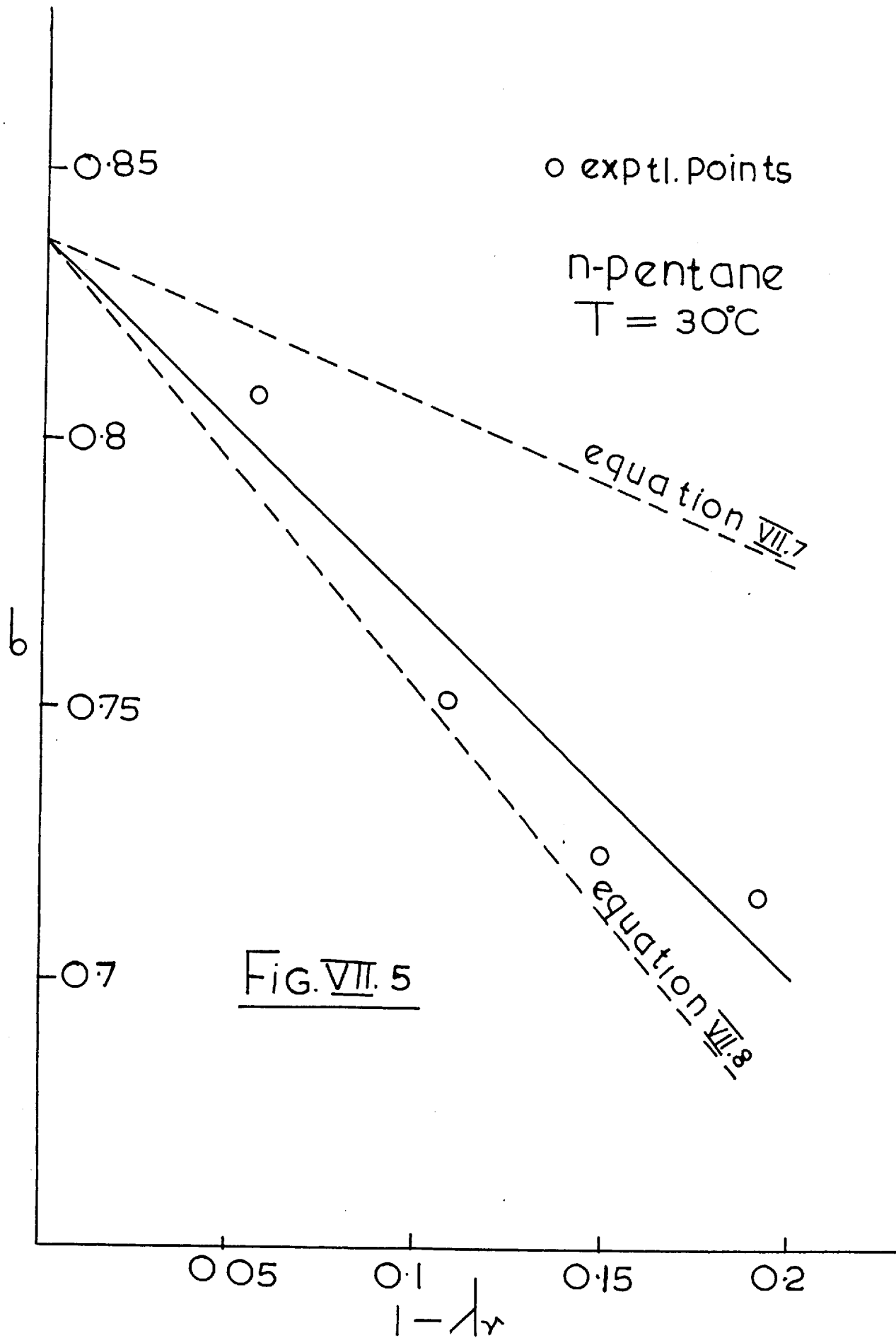


FIG. VII. 6

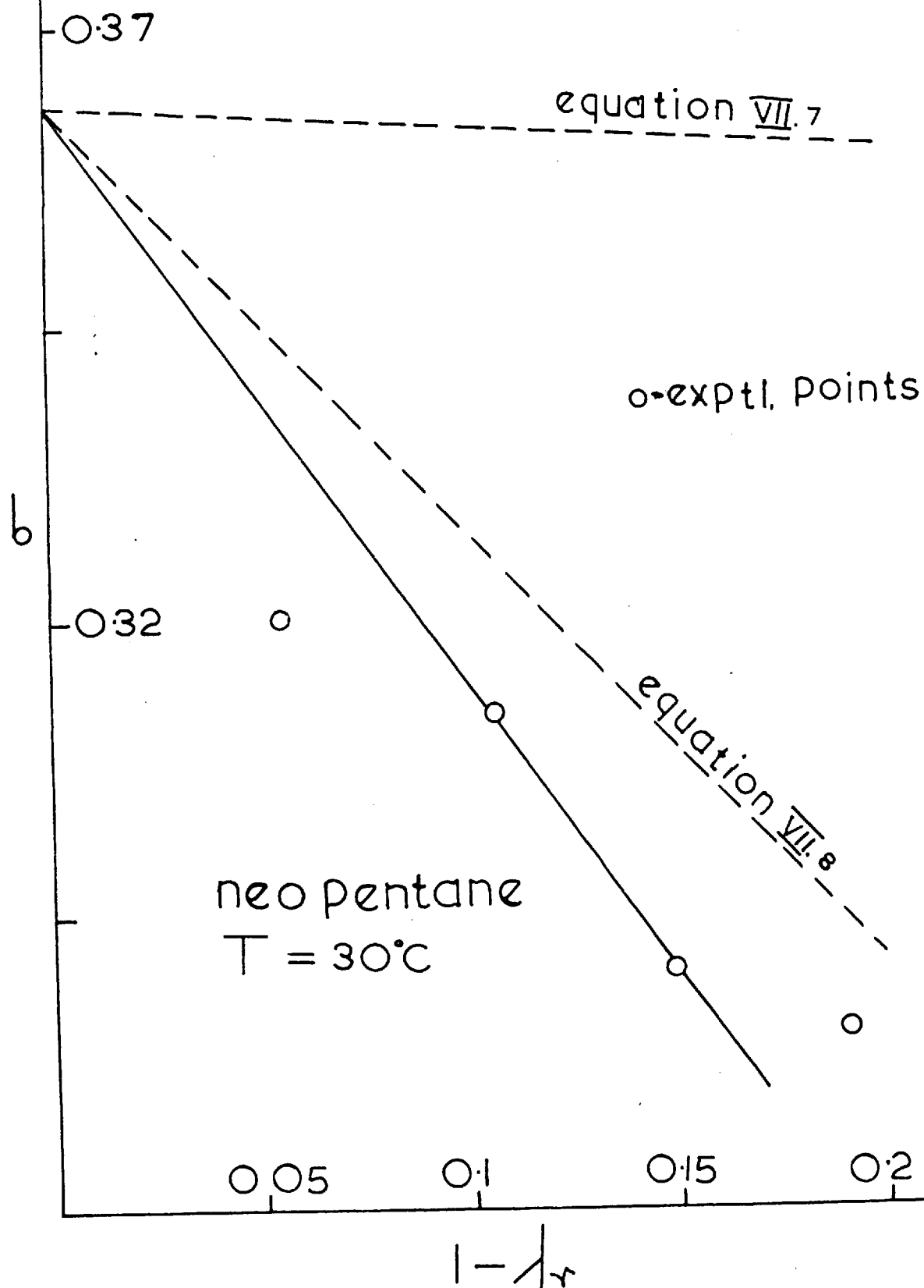
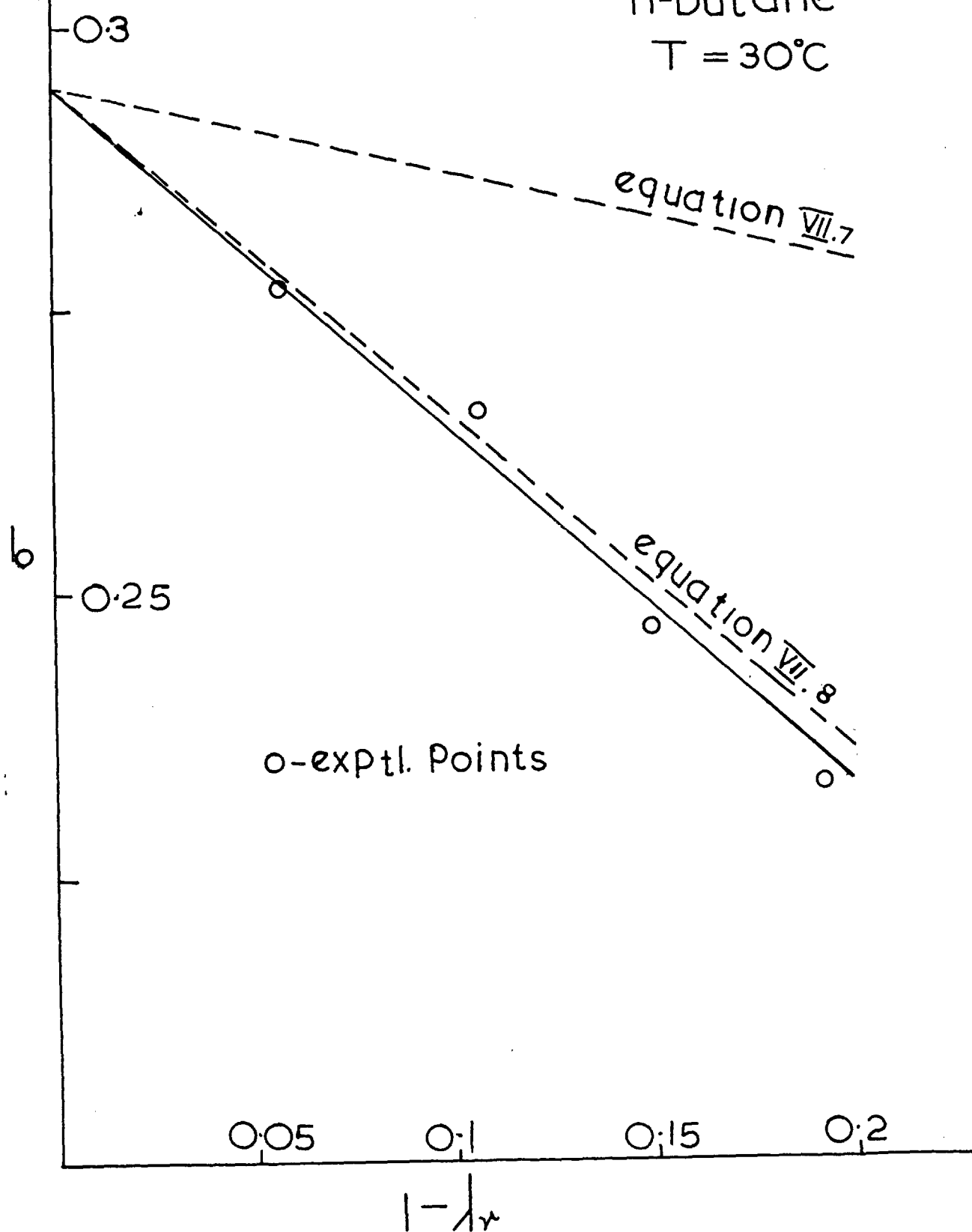


FIG. VII. 7

n-butane

$T = 30^{\circ}\text{C}$



1. There is a general tendency for ∇_{σ} to increase with temperature.
2. Values for neo-pentane are always slightly higher than for n-butane, iso-butane and n-pentane.

In terms of the reference models (equations VII.7 and VII.8) by substituting for σ in equation VII.9 we have,

$$\nabla_{\sigma} = (1 - \lambda_r) \left(1 - \frac{\sigma_f}{\sigma_r}\right) \cdot 100 \quad \text{.....VII.10}$$

and when $\sigma_f = 0$ we may write,

$$\nabla_{\sigma} = (1 - \lambda_r) 100 \quad \text{.....VII.11}$$

From equation VII.10 it is seen that if there were no sorption of the hydrocarbons by the filler particles in the rubber ($\sigma_f = 0$) then according to equation VII.11 ∇_{σ} should be the same as the volume percentage of filler irrespective of the vapour or temperature. Except for neo-pentane the data on the whole are in reasonable agreement with the no-sorption model. However features (1) and (2) of the data cannot be accounted for in terms of this simple model unless sorption on the filler is introduced. Since the value of σ_f in the filled rubber is not known one may for simplicity assume independent sorption by the filler and rubber phase so that σ_f will have its value for the bulk filler. Even so the ratio $\frac{\sigma_f}{\sigma_r}$ is less than unity and values of ∇_{σ} calculated from equation VII.10.

Table VII.14

∇_{σ} from equation VII.9

T°C	30	40	50	60	70
<u>Si.R-B</u>					
n-butane	6.1	8.8	7.0	7.4	9.4
iso-butane	6.0	7.8	8.4	9.0	--
n-pentane	3.2	1.5	4.4	5.6	6.9
neo-pentane	12.3	13.0	13.4	10.8	14.0
<u>Si.R-C</u>					
n-butane	9.8	10.6	8.8	9.7	10.3
iso-butane	8.6	8.5	8.5	6.5	10.4
n-pentane	10.2	8.9	9.0	9.9	9.4
neo-pentane	14.3	13.8	16.7	13.3	17.1
<u>Si.R-D</u>					
n-butane	16.3	19.4	17.6	18.6	18.7
iso-butane	15.6	17.0	16.8	16.1	18.2
n-pentane	13.6	13.0	14.3	16.1	15.0
neo-pentane	20.3	20.5	23.0	22.2	24.9
<u>Si.R-E</u>					
n-butane	17.6	16.3	19.3	19.3	20.0
iso-butane	14.4	13.7	16.5	16.4	18.3
n-pentane	14.4	13.7	16.5	16.4	18.3
neo-pentane	21.8	21.2	24.0	20.3	23.3

are given in Table VII.15 for temperatures of 30°C and 50°C. The data show that ∇_{σ} does in fact increase with temperature although the agreement with the experimental values of ∇_{σ}

is now very poor. This is not surprising as σ_f in the rubber will in all probability be much less than its value for the bulk filler. If the $\frac{\sigma_f}{\sigma_r}$ ratio varied with the penetrant then $\bar{V}_f$ also should be dependent on the latter. Thus the higher values of $\bar{V}_f$ obtained with neo-pentane would indicate that this vapour is sorbed to a negligible extent by the filler in the rubber. The accuracy of the data do not allow one definitely to establish sorption of the penetrant by the filler in the rubber and are perhaps satisfactorily represented within experimental error by the no-sorption model.

Table: VII.15

	Si.R-B		Si.R-C		Si.R-D		Si.R-E	
T°C	30	50	30	50	30	50	30	50
n-butane	1.5	2.3	2.8	4.3	4.0	6.0	5.1	7.7
n-pentane	2.0	2.5	3.8	4.7	5.4	6.7	6.9	8.5
neo-pentane	0.32	1.2	0.6	2.2	0.9	3.1	1.1	4.0

Effect of filler on the thermodynamic functions of solution and dilution

Solution functions

For the unfilled rubber we may write,

$$\Delta \bar{G}_u^o = -RT \log \sigma_r^o \quad \dots\dots\dots \text{VII.12}$$

$$\Delta \bar{H}_u^o = -R \frac{d \log \sigma_r^o}{d 1/T} \quad \dots\dots\dots \text{VII.13}$$

$$\text{and} \quad \Delta \bar{S}_u^o = R \log \sigma_r^o + RT \frac{d \log \sigma_r^o}{dT} \quad \dots\dots\dots \text{VII.14}$$

The corresponding quantities for the filled rubber have σ_r^o replaced by σ^o , and substituting for σ in terms of equation VII.7 gives,

$$\Delta G^o = -RT \log (\lambda_r \sigma_r^o + \lambda_f \sigma_f^o) \quad \text{.....VII.15}$$

$$\Delta H^o = -R \frac{d \log}{d 1/T} (\lambda_r \sigma_r^o + \lambda_f \sigma_f^o) \quad \text{.....VII.16}$$

and

$$\Delta S^o = R \log (\lambda_r \sigma_r^o + \lambda_f \sigma_f^o) + RT \frac{d \log (\lambda_r \sigma_r^o + \lambda_f \sigma_f^o)}{dT} \quad \text{.....VII.17}$$

Thus one has,

$$\Delta G^o - \Delta G_u^o = -RT \log \left(\lambda_r + \lambda_f \frac{\sigma_f^o}{\sigma_r^o} \right) \quad \text{.....VII.18}$$

$$\Delta H^o - \Delta H_u^o = -R \frac{d \log}{d 1/T} \left(\lambda_r + \lambda_f \frac{\sigma_f^o}{\sigma_r^o} \right) \quad \text{.....VII.19}$$

and

$$\Delta S^o - \Delta S_u^o = R \log \left(\lambda_r + \lambda_f \frac{\sigma_f^o}{\sigma_r^o} \right) + RT \frac{d \log}{dT} \left(\lambda_r + \lambda_f \frac{\sigma_f^o}{\sigma_r^o} \right) \quad \text{....VII.20}$$

Even assuming independent sorption by filler and rubber phases the data of Table VI.2 show that the ratio $\frac{\sigma_f^o}{\sigma_r^o}$ is always

less than unity, and bearing in mind that $\lambda_r + \lambda_f = 1$ then the term $\log \left(\lambda_r + \lambda_f \frac{\sigma_f^o}{\sigma_r^o} \right)$ will be negative. Further, for $\frac{\sigma_f^o}{\sigma_r^o}$ we may write $\text{const. exp } \frac{-(\Delta H_f^o - \Delta H_u^o)}{RT}$ where

ΔH_f^o denotes the heat of solution in bulk filler. For

$\Delta H_f^o < \Delta H_u^o$ it follows that the log term will increase with

$1/T$. For our system then it is expected that the free energy difference will be positive, the heat difference negative and the entropy difference either negative or positive depending

on the relative magnitudes of the two terms involved; for zero sorption it would be negative. Values of these differences for the various rubbers are given in Tables VII.16 to VII.18. In Tables VII.19 to VII.21 are given the corresponding differences for the dilution functions. It can be shown that the same equations (VII.18, 19, 20) hold for these differences with very little error.

Table: VII.16

$$\Delta \overline{G}^{\circ} - \Delta \overline{G}_u^{\circ}$$

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
n-butane	38	62	107	116
iso-butane	37	-319	102	---
n-pentane	20	65	88	94
neo-pentane	77	91	137	47

Table VII.17

$$\Delta \overline{S}^{\circ} - \Delta \overline{S}_u^{\circ}$$

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
n-butane	-1.27	-1.29	-1.45	-1.65
iso-butane	-0.65	1.65	0.53	---
n-pentane	-0.28	0.17	-0.37	-0.88
neo-pentane	-0.41	-1.57	-1.26	-0.52

Table VII.18

$$\Delta \overline{H}^{\circ} - \Delta \overline{H}_u^{\circ}$$

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
n-butane	-346	-329	-333	-684
iso-butane	-161	181	263	---
n-pentane	- 66	-116	- 24	-173
neo-pentane	- 47	- 78	-245	- 12

Table: VII.19

$$\Delta \overline{H} - \Delta \overline{H}_u$$

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
n-butane	- 22	- 73	-111	-132
iso-butane	-223	50	63	---
n-pentane	-360	- 64	- 30	-207
neo-pentane	41	- 51	-177	- 57

Table: VII.20

$$\Delta \overline{S} - \Delta \overline{S}_u$$

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
n-butane	0	-0.65	-0.95	-0.95
iso-butane	-0.95	-0.10	-0.40	---
n-pentane	-1.43	-1.05	-0.78	-1.48
neo-pentane	-0.28	-0.71	-1.38	-1.03

Table: VII.21

$(\Delta \overline{G} - \Delta \overline{G}_u)$

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
n-butane	63	106	182	217
iso-butane	60	109	183	---
n-pentane	25	95	159	193
neo-pentane	105	149	210	241

CHAPTER VIII

DISCUSSION OF PERMEABILITY

First the results for the unfilled rubbers are discussed and then those for the filled samples.

1. Unfilled Silicone Rubbers

The permeability $\bar{P}$ (p. 9) was determined at several ingoing pressures in the range 0-6 cm. Hg. for each of the samples Si.R-I, Si.R-H and Si.R-A. With all membranes $\bar{P}$ decreased slightly with the ^{higher} ingoing pressure. The maximum decrease observed was about 4% over a pressure range 0-6 cm. Hg. This effect may have been due to the effective area of the outgoing side of the membrane being reduced by contact with the gauze, particularly at higher ingoing pressures. To minimise any such errors measurements were made only at the lower ingoing pressures so that the values of $\bar{P}$ recorded are effectively permeabilities at zero concentration. The values of $\bar{P}$ for each of the unfilled membranes at temperatures of 30, 40, 50, 60 and 70°C are given in Tables V.37 to V. 48. Comparison of the data for samples Si.R-I and Si.R-H indicate that the difference in degree of crosslinking between the samples has little effect on the permeability. The rubber Si.R-A was prepared from a different gum stock and has a decidedly larger permeability. It may have been a gum of lower molecular weight and as such would contain a proportionally larger number of end groups, the presence of which would facilitate the diffusion process. It is also noted in this respect that the solubilities for this sample were slightly

larger than those for the two other samples. (p. 80)

Steady state and transient state diffusion coefficients were calculated respectively from the relationships, (p. 9 and 12)

$$D_S = \frac{\bar{P}}{\delta}$$

and

$$D_L = \frac{l^2}{6L}$$

Values of the two coefficients are given in Table VIII.1. For a given temperature the diffusion coefficients generally decrease in the following order,

n-butane > n-pentane > iso-butane > neo-pentane

The addition of a CH_2 group as a side branch has a more marked effect on the diffusion coefficient than its addition to the main chain. The order of the above series has also been observed for the diffusion of the same hydrocarbons in natural rubber (Aitken and Barrer-1955). As with the permeabilities, comparison of the Si.R-H and Si.R-I rubbers reveal no obvious dependence of the diffusion coefficient on the degree of crosslinking.

The agreement between steady state and transient state diffusion coefficients is not as good as may be expected, the values for D_S being in general greater than the corresponding D_L values. This feature of the data is by no means uncommon and has been observed by several workers (Aitken and Barrer-1955, Platt-1959) with the same hydrocarbons in natural rubber. Failure to attain the true steady state of flow would lead to values of D_L greater

than D_S for the steady state. Similar effects are found for homogeneous polymer media where slow relaxation effects occur simultaneously with the diffusion process. The time taken to establish the true steady state of flow is determined mainly by the relaxation process and as a result long time-lags and correspondingly short values of D_L are obtained. With highly elastic materials such as the silicone rubbers slow relaxation effects of this nature are, however, not easily accounted for. The design of the diffusion cell has been considered with respect to this problem by Rogers (1961). Thus the portion of membrane clamped between the faces of the diffusion cell are assumed to play no part in the diffusion process. Consideration of this overlap region indicates increased time-lags since for the true steady state of flow to be established equilibrium must also obtain between the overlap and unclamped portions of the membrane.

Table V.III.1

Transient and Steady State Diffusion Coefficients in
cm.².sec⁻¹ (x 10⁶)

		30°C	40°C	50°C	60°C	70°C
<u>Si.R-I</u>						
n-butane	D_L	5.23	6.51	8.02	9.64	11.89
	D_S	5.44	6.83	8.49	10.68	12.94
iso-butane	D_L	3.83	4.75	5.78	6.97	8.38
	D_S	4.81	5.98	7.71	9.40	11.52
n-pentane	D_L	4.36	5.58	7.03	8.78	10.90
	D_S	4.48	5.65	6.92	8.48	10.21

		30°C	40°C	50°C	60°C	70°C
<u>Si.R-I (cont'd)</u>						
neo-pentane	D _L	2.49	3.06	3.72	4.43	5.95
	D _S	2.83	3.53	4.32	5.32	6.40
<u>Si.R-H</u>						
n-butane	D _L	5.13	5.89	6.78	8.17	9.68
	D _S	6.53	8.09	9.42	11.74	14.24
iso-butane	D _L	3.77	4.79	6.03	7.44	9.17
	D _S	4.32	5.57	7.11	8.71	10.48
n-pentane	D _L	4.38	5.58	6.83	8.22	9.98
	D _S	4.71	5.87	7.14	8.75	10.16
neo-pentane	D _L	2.62	3.11	3.77	4.64	5.68
	D _S	2.78	3.50	4.36	5.50	6.66
<u>Si.R-A</u>						
n-butane	D _L	6.52	7.94	10.22	12.17	15.34
	D _S	6.96	8.62	10.91	13.24	16.02
iso-butane	D _L	5.11	6.45	8.02	9.82	12.00
	D _S	5.71	7.32	9.15	11.39	13.65
n-pentane	D _L	5.31	6.71	8.35	10.28	12.55
	D _S	6.47	8.09	9.56	11.42	13.37
neo-pentane	D _L	2.79	3.56	4.48	5.58	6.90
	D _S	3.66	4.74	5.84	7.40	8.76

Temperature coefficients of Diffusion and Permeation

Plots of $\log D_S$ vs $1/T$ were practically linear with only very slight curvature. Typical plots are shown in Figure VIII.1 and in Table VIII.2 are given the values

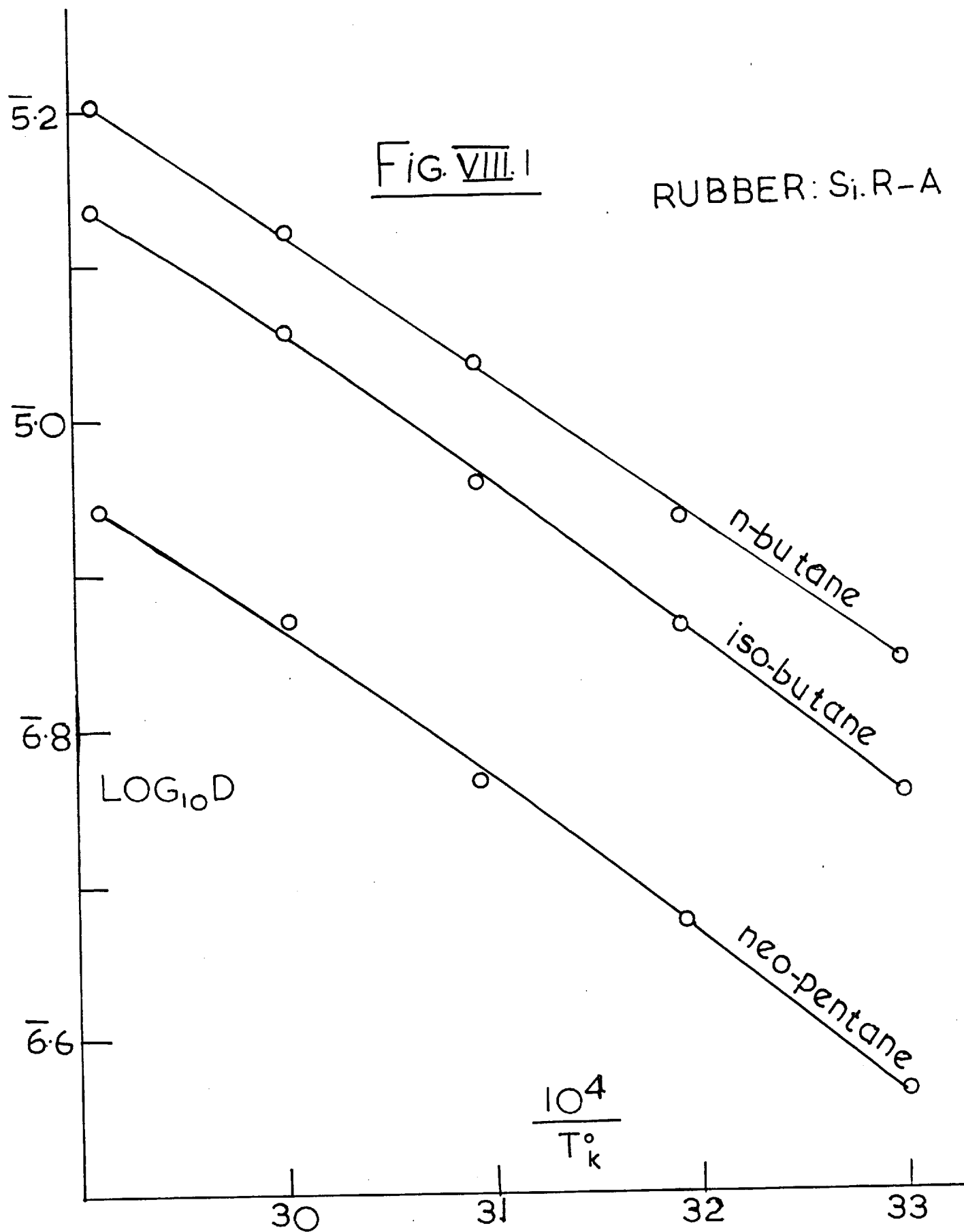
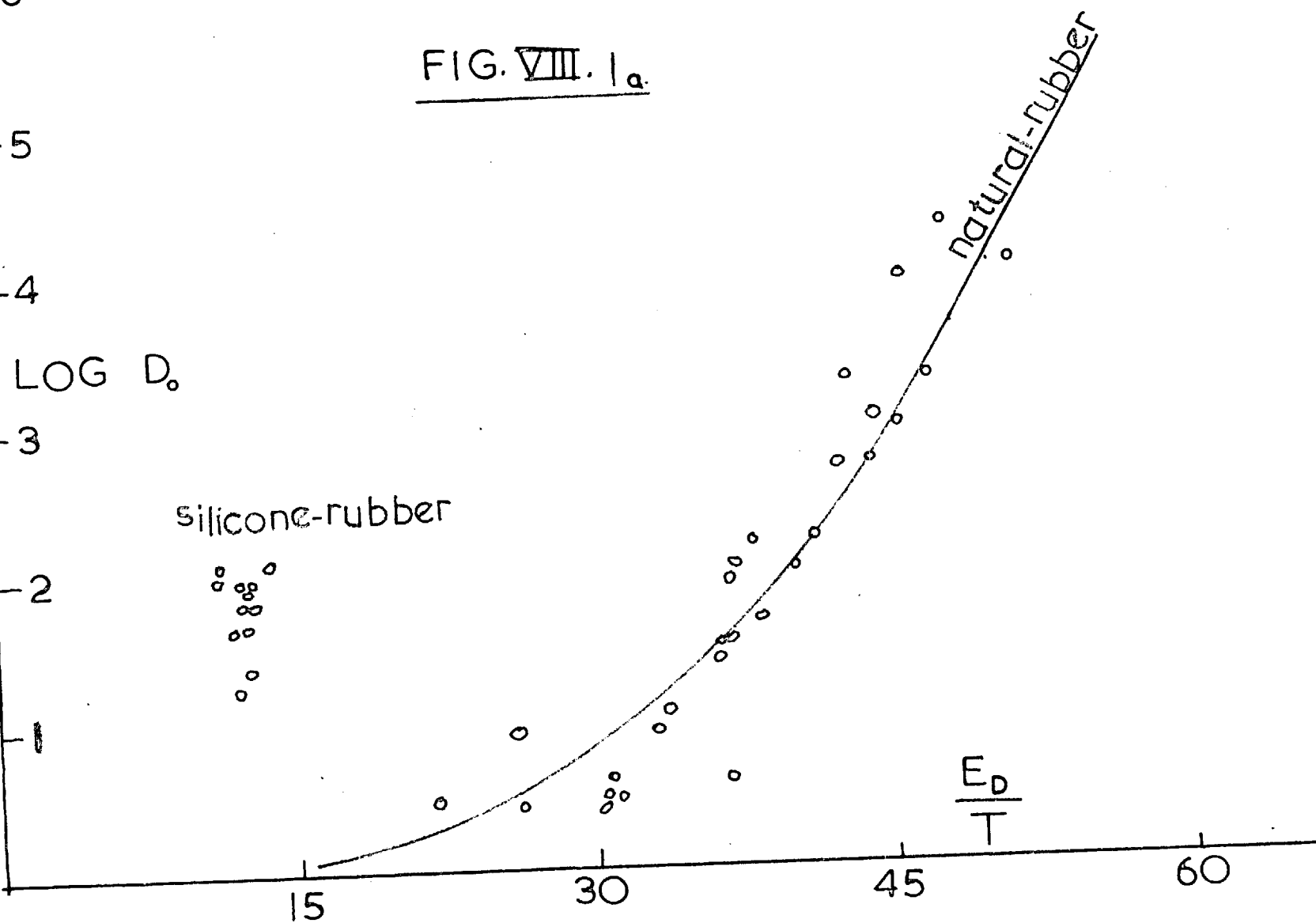


FIG. VIII. 1_a.



of the E_D and D_0 parameters of the Arrhenius type equation,

$$D = D_0 \exp \left(\frac{-E_D}{RT} \right) \quad (\text{p.18})$$

The values of the activation energy for diffusion are accurate to within 12% whilst the D_0 values may be in error by as much as a factor of 5.

The striking feature of the data in Table VIII.2 are the extremely low values of E_D as compared with the values obtained for the same vapours in natural rubber, which are given in Table VIII.3. The values for natural rubbers are in fact almost 3 times those in silicone rubber. McCall, Anderson and Huggins (1961), obtained values of the activation energy for self-diffusion of several polydimethylsiloxanes containing from 1 to 9 dimethylsiloxane groups. The values of E_D reached a limit of approximately 4 k. cals. as the length of the chain was increased, in good agreement with the values of Table VIII.2. The values of E_D do not show any marked dependence on the nature of the penetrant. The low energies of activation for diffusion in silicone rubbers are a reflection of the relative ease of rotation about the Si - O linkage as compared with say the C - C linkage, and the relatively weak interaction forces believed to exist between neighbouring siloxane segments (Roth, Harker - 1948, Scott - 1946)

TABLE VIII.2

Activation Energies for Diffusion, E_D , cal. mole⁻¹ and D_0 , cm.².sec⁻¹

	Si.R-I		Si.R-H		Si.R-A	
	E_D	D_0	E_D	D_0	E_D	D_0
n-butane	4205	49.30	3758	131	4265	82.3
iso-butane	4005	16.8	4548	131	4365	88.5
n-pentane	4313	63.7	3932	42.6	3714	105
neo-pentane	4175	23.7	3958	72.2	4465	92.9

TABLE VIII.3

E_D cal. mole⁻¹ and D_0 cm.².sec⁻¹ at 30°C (natural rubber)

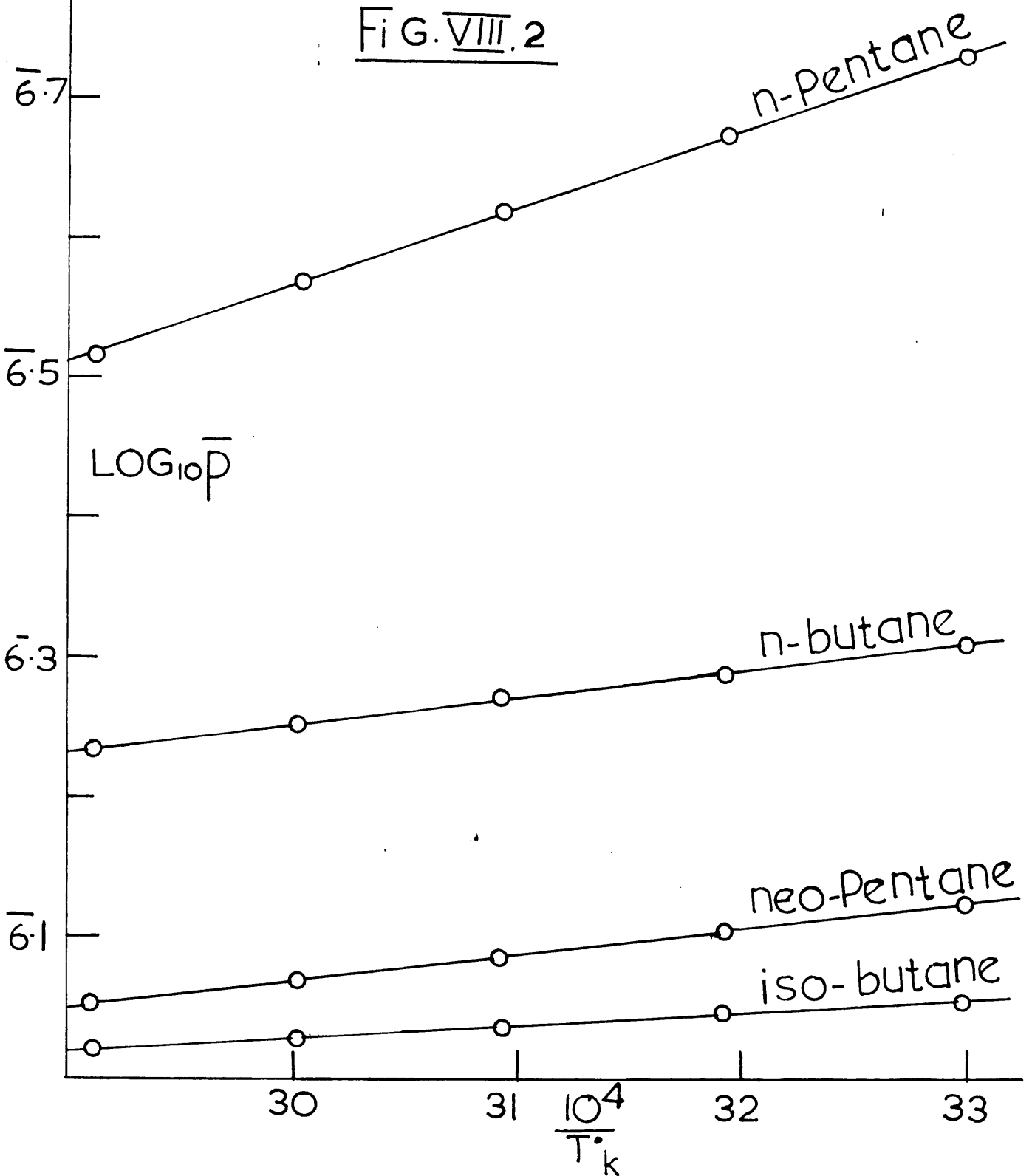
	Rubber A		Rubber I	
	E_D	D_0	E_D	D_0
n-butane	12970	5.03×10^2	13500	1.05×10^3
iso-butane	12500	1.62×10^2	13400	5.61×10^2
n-pentane	14700	8.77×10^3	19780	2.43×10^7
neo-pentane	---	----	15700	1.17×10^4

The low energy of activation for E_D leads to another interesting difference between the hydrocarbon diffusion processes in silicone and natural rubbers. Thus, whereas the permeabilities of the hydrocarbons in natural rubber increase with temperature, in the silicone rubbers they decrease as the temperature is increased. Plots of $\log \bar{P}$ vs $1/T$ were linear, for example, Figure (VIII.2), and so one can write,

$$\bar{P} = P_0 \exp \left(-\frac{E_D}{RT} \right) \quad \text{.....VIII.1}$$

RUBBER: Si. R-A

FIG. VIII.2



Values of the temperature coefficient E_p are given in Table VIII.5. Since by equation (II.4), $\bar{P} = D \cdot \sigma$ then,

$$P_o \exp\left(-\frac{E_p}{RT}\right) = D_o \exp\left(-\frac{E_D}{RT}\right) \times \sigma_o \exp\left(-\frac{\Delta \bar{H}^o}{RT}\right) \dots\dots\dots \text{VIII.2}$$

and so

$$E_p = E_D + \Delta \bar{H}^o \dots\dots\dots \text{VIII.3}$$

$\Delta \bar{H}^o$ is a negative quantity whilst E_D is positive. Accordingly when $\Delta \bar{H}^o$ is numerically larger than E_D , as is the case with silicone rubbers, then E_p will be negative and the permeability decreases as the temperature is increased. With natural rubber E_D is numerically larger than $\Delta \bar{H}^o$, E_p is positive and therefore the permeability increases with temperature. The E_p values for n-pentane are generally more negative than those for the other hydrocarbons since the E_D values for all the hydrocarbons are similar and $\Delta \bar{H}^o$ for n-pentane is numerically larger than for the other hydrocarbons.

Separation of gases

The separation of gases of similar boiling points but differing in molecular shape by fractional permeation through polymer membranes is of technical importance. Economically, this process if widely employed could compete with the low temperature process that is in common use. Long (1944) suggested that rubber membranes could be used to fractionate hydrocarbons and Robertson (1949) in a patent claimed the separation of straight chain and branched chain hydrocarbons by diffusion of the liquids through synthetic rubber. Aitken and Barrer (1955), showed that more marked fractionation could occur in the transient state of diffusion.

In order to obtain some information on the use of silicone rubber membranes as a fractionation medium, ratios of the permeabilities for n-butane/iso-butane and n-pentane/neo-pentane were calculated for rubber Si.R-A at 30, 40, 50 and 60°C. For comparison similar data are presented for natural rubber and the values are collected in Table VIII.4. The higher values of the ratios in natural rubber indicate that this polymer is more effective as a medium for fractional permeation than silicone rubber. This is perhaps not very surprising in view of the relative ease of the diffusion process in the silicone rubbers where the unit diffusion will not be so markedly influenced by the size of the penetrant.

TABLE VIII.4

Separation factors for silicone and natural rubbers

T°C	30	40	50	60
<u>n-butane/iso-butane</u>				
$\frac{P_{n-p}}{P_{iso-b}}$	1.8	1.7	1.7	1.7
	(2.3)	(2.2)	(2.2)	(2.1)
<u>n-pentane/neo-pentane</u>				
$\frac{P_{n-p}}{P_{neo-p}}$	4.1	3.7	3.4	3.2
	(8.7)	(7.8)	(6.5)	(5.4)

Values for natural rubber are shown in brackets

Comparison of D_0 values for silicone and natural rubbers

From Tables VIII.2 and VIII.3 it is seen that D_0 values for natural rubber are larger than for silicone rubbers. Although the accuracy of these values is very low the general trend seems to suggest that D_0 in effect is

is smaller for silicone rubbers. Interpretation of D_o by the zone theory (Barrer-1939a, 1942 etc.) reveal that D_o values are dependent, among other factors, on the activation energy for diffusion, E_D and the jump distance (λ) of the penetrant molecule (equation II.50). It is thus possible that in the case of penetrant diffusion in silicone rubbers lower values of one or both of E_D and λ , could considerably reduce the overall values of D_o . Since our E_D values are about three times lower than for natural rubbers it is possible that this factor accounts for lower values of D_o .

A plot of $\log D_o$ vs. $\frac{E_D}{T}$ is shown in Figure VIII. 1a. For comparison, the data of natural rubber are also plotted in Figure VIII. 1a. It is clear from the figure that the points for silicone rubbers lie above the curve for natural rubbers, thus suggesting that silicone rubbers are more rubbery in character.

To conclude this section a comparison is presented of the diffusion data for the hydrocarbon vapours in silicone and natural rubbers.

- a) Permeability coefficients are about 25 to 40 times higher for the silicone rubbers.
- b) Diffusion coefficients are approximately 20 times larger at 30°C and the ratio reduces to about 10 at 70°C. Presumably as the temperature increases natural rubber approaches more closely the ideal network with unhindered C - C rotation and low interchain forces.

- c) The ease of backbone chain rotations and the strength of interchain interactions is reflected in the values of the energies of activation for diffusion for the two rubbers. E_D values for natural rubber are approximately 3 times larger than those for silicone rubbers. The D_0 values are lower for silicone rubbers.
- d) Because with the silicone rubbers $\Delta \bar{H}^0$, the partial molar standard heat of solution, is numerically larger than E_D , the energy of activation for diffusion, the permeabilities decrease with increasing temperature. The converse holds for natural rubber.
- e) Calculations of the $\bar{P}$ ratios for the hydrocarbons differing in molecular shape reveal that silicone rubbers are less effective as a medium for fractional separation of gases in comparison with natural rubbers.

Table VIII.5

E_p values for various rubbers and hydrocarbons

	Si.R-I	Si.R-H	Si.R-A
n-butane	-851	-1736	-924
iso-butane	-611	- 535	-401
n-pentane	-2005	-2319	-2544
neo-pentane	-1177	-1022	- 848

2. Filled Silicone Rubbers

The results for the filled membranes, Si.R-B, Si.R-C, Si.R-D and Si.R-E with filler volume fractions of 0.056, 0.106, 0.149 and 0.191 (Table VI.1) respectively are now

considered. Permeabilities were obtained as a function of the ingoing pressure in the range 0-8 cm. Hg. As was observed with the unfilled samples (p.123) the permeability decreased slightly when the ingoing pressure was increased. For this reason the values of $\bar{P}$ given in Tables V.49 to V.63 are those for the lowest ingoing pressures and correspond in effect to the permeabilities at zero concentration.

Steady state and transient state diffusion coefficients were calculated using equations II.4 and II.19 respectively, and the values tabulated in Table VIII.6. The order of the series for decreasing diffusion coefficients is again,

n-butane > n-pentane > iso-butane > neo-pentane
(cf. p 124) and is apparently not affected by the presence of filler.

Plots of $\log D_S$ vs $1/T$ were linear, for example, Figure (VIII.3), and values of the activation energy for diffusion E_D are given in Table VIII.7. Within experimental error the filler does not appear to have any marked effect on the values of E_D . (cf. Table VIII.2 for unfilled rubbers).

Similarly, from linear plots of $\log \bar{P}$ vs $1/T$ values of the temperature coefficient E_p were obtained and are given in Table VIII.8. Comparison of the data with Table VIII.5 again reveal no significant variation in E_p with the introduction of filler into the rubber.

RUBBER: Si. R-C

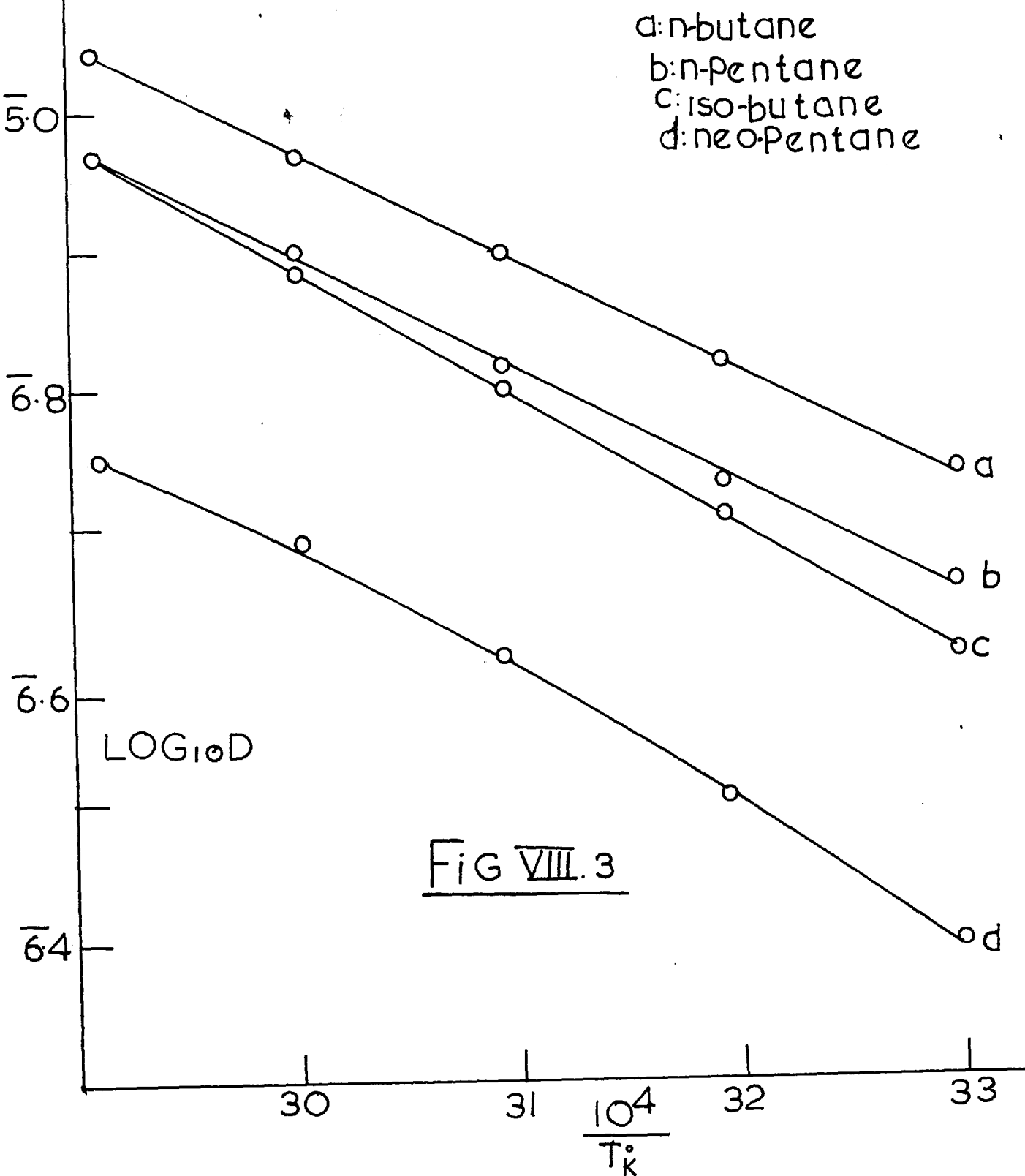


Table VIII.6

Steady and transient state diffusion coefficients,
cm.² . sec⁻¹ (x 10⁶)

Temp. °C		30	40	50	60	70
<u>Si.R-B</u>						
n-butane	D _L	5.21	5.89	6.78	8.17	9.68
	D _S	6.53	8.09	9.42	11.74	14.24
iso-butane	D _L	3.66	4.11	5.09	6.28	7.75
	D _S	5.34	6.68	8.37	9.74	11.88
n-pentane	D _L	4.49	5.51	6.69	8.04	9.68
	D _S	5.39	6.46	7.76	9.41	10.82
neo-pentane	D _L	2.49	2.92	--	--	5.17
	D _S	2.90	3.82	4.72	5.92	7.25
<u>Si.R-C</u>						
n-butane	D _L	5.05				
	D _S	5.47	6.60	7.88	9.29	11.04
iso-butane	D _L	3.55			6.03	7.11
	D _S	4.04	5.07	6.32	7.66	9.34
n-pentane	D _L	4.40	5.08	5.79	6.58	7.43
	D _S	4.53	5.34	6.57	7.95	9.31
neo-pentane	D _L	2.37				
	D _S	2.49	3.18	4.05	4.91	5.64
<u>Si.R-D</u>						
n-butane	D _L	4.41	5.31	6.46	7.24	8.16
	D _S	5.40	6.45	7.81	9.15	10.48
iso-butane	D _L	2.70	3.71	4.55	5.21	5.83
	D _S	4.33	5.41	6.53	7.72	9.19
n-pentane	D _L	3.04	4.17	5.10	5.84	6.56
	D _S	4.54	5.67	6.43	7.57	8.63

Temp. °C.		30	40	50	60	70
<u>Si.R-D (cont'd)</u>						
neo-pentane	D _L	1.88	2.13	2.49	2.72	3.23
	D _S	2.47	3.18	4.06	5.01	6.02
<u>Si.R-E</u>						
n-butane	D _L	4.46	5.26	5.65	6.81	7.35
	D _S	5.93	5.91	7.55	8.90	10.55
n-pentane	D _L	3.20	3.49	3.89	4.12	4.94
	D _S	4.49	5.48	6.57	7.61	8.93
neo-pentane	D _L	1.68	2.16	2.42	--	--
	D _S	2.52	3.08	3.81	4.39	5.16

Table VIII.7

Activation energies for diffusion, E_D cal.mole⁻¹

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
n-butane	3989	3686	3391	3689
iso-butane	4093	4287	3850	--
n-pentane	3931	3685	3946	3520
neo-pentane	4684	4183	4556	3666

Table VIII.8

E_p for the filled rubbers

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
n-butane	-1384	-1630	-1961	-1656
iso-butane	-1040	- 907	-1169	--
n-pentane	-2892	-2530	-3066	-2979
neo-pentane	- 729	-1290	-1063	-1736

The Effect of the Filler

To facilitate a comparison of the diffusion data for the filled and unfilled rubbers we define a percentage difference in the same way as for the solubility (p. 112) for example, for the permeability,

$$\nabla \bar{P} = \left(1 - \frac{\bar{P}}{\bar{P}_A} \right) \cdot 100 \quad \text{..... VIII.4}$$

where the subscript A denotes the unfilled rubber, Si.R-A. Similarly percentage differences may be defined for the diffusion coefficients, D_S and D_L . Values of these quantities for the various filled rubbers are given in Tables VIII.9 to VIII.12. The error in $\nabla \bar{P}$ is estimated at ± 5 and for ∇D_S and ∇D_L is about ± 8 . Inspection of the data reveals the following points:

- a) There is in general a tendency for $\nabla \bar{P}$ at a given temperature to increase with the size of the penetrant. A similar but less marked trend appears in the ∇D_S and ∇D_L data.
- b) For a given penetrant $\nabla \bar{P}$ and ∇D_S tend to increase with temperature.
- c) $\nabla \bar{P}$ values are always larger than the corresponding ∇D_S values.
- d) ∇D_L is usually slightly larger than ∇D_S .

Table V.III.9

Percentage differences in permeabilities and diffusion coefficients.

Temp. °C	$\nabla \bar{P}$	∇D_S	∇D_L
<u>Si.R-B - n-butane</u>			
30	11.9	6.2	20.1
40	14.4	7.8	25.8
50	16.0	-	33.7
60	17.9	3.5	38.1
70	19.5	7.2	36.9
<u>Iso-butane</u>			
30	15.1	6.5	28.4
40	15.8	8.7	36.3
50	16.3	8.5	41.8
60	22.1	14.5	36.0
70	25.0	13.0	35.4
<u>n-pentane</u>			
30	19.4	16.0	15.5
40	21.4	20.1	17.9
50	22.4	18.8	19.9
60	22.2	17.6	21.8
70	24.6	19.1	22.9
<u>neo-pentane</u>			
30	30.5	20.8	13.3
40	29.8	19.5	19.1
50	29.1	19.2	23.5
60	28.8	20.0	29.8
70	28.8	17.3	31.6

Table VIII.10

Si,R-C

Temp. °C	$\nabla \bar{P}$	∇D_S	∇D_L
<u>n-butane</u>			
30	29.1	21.5	22.6
40	31.6	23.5	--
50	34.1	27.8	--
60	36.6	29.9	--
70	38.3	31.1	--
<u>iso-butane</u>			
30	35.3	29.3	30.5
40	36.6	30.7	--
50	36.8	30.9	--
60	37.4	32.8	38.6
70	38.6	31.6	40.8
<u>n-pentane</u>			
30	37.1	30.0	--
40	38.6	34.0	--
50	37.4	31.3	30.7
60	37.3	30.4	36.0
70	36.9	30.4	40.8
<u>neo-pentane</u>			
30	41.8	32.0	--
40	42.1	32.9	--
50	42.3	30.7	--
60	42.5	33.7	--
70	46.6	35.7	--

Table VIII.11

Si.R-D

Temp. °C	∇P	∇D_S	∇D_L
<u>n-butane</u>			
30	34.9	22.5	32.4
40	39.7	25.2	33.2
50	41.4	28.4	36.8
60	42.8	30.9	40.6
70	46.8	34.6	46.8
<u>iso-butane</u>			
30	36.0	24.2	47.2
40	38.7	26.1	42.5
50	40.8	28.6	43.3
60	43.2	32.2	47.0
70	38.6	32.7	51.5
<u>n-pentane</u>			
30	39.3	29.9	42.7
40	39.0	30.0	37.8
50	42.3	32.8	38.8
60	44.4	33.7	43.2
70	45.2	35.5	47.7
<u>neo-pentane</u>			
30	46.2	32.5	33.0
40	46.5	33.0	40.2
50	46.4	30.5	44.5
60	47.3	32.3	51.3
70	48.3	31.3	53.2

Table VIII.12

Si.R-E

Temp. °C	$\nabla \bar{P}$	∇D_S	∇D_L
<u>n-butane</u>			
30	39.3	26.3	31.6
40	42.6	31.5	34.2
50	45.8	30.2	44.7
60	45.8	32.8	44.1
70	47.4	34.2	52.1
<u>n-pentane</u>			
30	40.6	30.6	39.8
40	41.4	32.3	48.0
50	42.6	31.3	53.4
60	44.3	33.4	60.0
70	45.5	33.2	60.6
<u>neo-pentane</u>			
30	46.2	31.2	40.0
40	48.8	35.1	39.4
50	50.4	34.8	46.0
60	52.7	40.7	--
70	54.8	41.1	--

Model for diffusion in filled rubbers

In the absence of an exact solution of Fick's diffusion equation for flow in heterogeneous media the customary procedure has been to adopt the equations of flow for the corresponding homogeneous systems and modify these by the introduction of suitable structure factors

(Klute-1959, Klute and Franklin-1958, Barrer-1953, Barrer and Barrie-1952, Barrer and Gabor-1959). Thus for the filled rubber we may write for the flux per unit area of the geometrical cross-section,

$$J = -D_A \cdot \lambda_r \cdot K \frac{\partial C_r}{\partial x} \dots\dots\dots \text{VIII.5}$$

where D_A is the diffusion coefficient in the rubber phase and is assumed to be equal to that for the unfilled rubber. The concentration of penetrant in rubber phase is C_r , and λ_r the volume fraction of rubber is also equal to the fraction of geometrical cross-section occupied by this phase. The model as presented assumes that there is no contribution to the flux other than that through the rubber phase. Thus surface fluxes on the filler and gas phase fluxes through capillary structures in filler particles are presumed to be absent. Accordingly we consider only two cases, the one representing zero sorption by the filler, the other immobile sorption of vapour by the filler. The structure factor allows, amongst other things, for the fact that because of the filler particles the average diffusion path length is increased and the localized direction of flow is in general not normal to the geometrical cross-section of the membrane.

With C the concentration of penetrant referred to unit volume of the filled rubber and D_S the diffusion coefficient measured experimentally then,

$$D_S \frac{\partial C}{\partial x} = D_A \cdot \lambda_r \cdot K \cdot \frac{\partial C_r}{\partial x} \dots\dots\dots \text{VIII.6}$$

Assuming independent sorption of vapour by the rubber and filler phases the concentration C can be related to the concentration C_r by,

$$C = \lambda_r \cdot C_r + \lambda_f \cdot C_f \quad \text{.....VIII.7}$$

where C_f is the concentration of vapour referred to unit volume of filler and so,

$$C = (\lambda_r + \lambda_f \frac{\sigma_f}{\sigma_r}) C_r \quad \text{.....VIII.8}$$

since, $C_f = \sigma_f \cdot p$ and $C_r = \sigma_r \cdot p$

It follows therefore that

$$D_S = K \cdot D_A \frac{\lambda_r}{(\lambda_r + \lambda_f \frac{\sigma_f}{\sigma_r})} \quad \text{.....VIII.9}$$

and for zero sorption $\sigma_f = 0$, and so

$$D_S = K \cdot D_A \quad \text{.....VIII.10}$$

Equations VIII.9 and VIII.10 also hold for transient state flow with D_S replaced by D_L . In general, the structure factor for steady and transient states of flow will differ and the possibility exists of part of the rubber phase not contributing to the steady state of flow. This fraction may be termed the 'dead volume'. It must, however, contribute to the establishment of the steady state of flow in that equilibrium must be set up between the main flow space and the dead volume. In this respect therefore the structure factor for transient state of flow will be less than for the steady state.

The quantity $(D_A \cdot \frac{\partial C_r}{\partial x})$ on the right hand side of equation VIII.5 represents $-J_A$, where J_A is the flux per unit area of unfilled rubber. Hence it follows that

$$\bar{P} = K \lambda_r \cdot \bar{P}_A \quad \text{.....VIII.11}$$

irrespective of whether or not the gas is sorbed by the filler phase provided that if sorption does occur the molecules are immobile on the filler surface.

The corresponding expressions for the percentage differences follow from equations VIII.11 and VIII.9 and are,

$$\nabla \bar{F} = (1 - K \cdot \lambda_r) \cdot 100 \quad \dots\dots\dots \text{VIII.12}$$

$$(\text{immobile sorption}) \quad \nabla D_S = \left[1 - \frac{K \lambda_r}{\lambda_r + \lambda_f \cdot \frac{\sigma_f}{\sigma_r}} \right] \cdot 100 \quad \dots \text{VIII.13}$$

$$\text{and zero sorption} \quad \nabla D_S = (1 - K) \cdot 100 \quad \dots\dots\dots \text{VIII.14}$$

The structure factor

Several attempts have been made to relate the conductivity of heterogeneous conductors, consisting of dispersions of small particles in a medium of different conductivity, to the conductivity of the homogeneous continuous phase (Rayleigh - 1892, Fricke - 1924, Cornell and Katz - 1953) . These problems are analogous to gas or vapour flow in heterogeneous media such as filled polymers and the expressions for the structure factors obtained for the electrical problems may be carried over to the diffusion field without alteration in any way.

Thus Maxwell (1873) obtained an expression for the conductivity of a heterogeneous medium consisting of a random dispersion of small spheres in a phase of different conductivity in terms of the volume fraction of the dispersed phase. For non-conducting spheres this expression can be written in terms of our structure factor as,

$$K = \frac{2}{3 - \lambda_r} \quad \dots\dots\dots \text{VIII.15}$$

where λ_r as before denotes the volume fraction of the rubber phase. Maxwell's treatment, however, only applies for dilute dispersions where interference effects between neighbouring spheres are negligible. This limitation must also be placed on the use of expressions obtained by Fricke (1924) for dispersions of oblate and prolate spheroids. Rayleigh (1892) attempted to allow for interference effects between neighbouring spheres and deduced expressions for cubic arrays of uniform spheres and of uniform cylinders in a medium of different conductivity. Runge (1925) and Meredith and Tobias (1960) using Rayleigh's approach obtained modified expressions. The expressions deduced by Rayleigh and the other workers are given below in terms of the structure factor K and the volume fraction of the filler λ_f for the special case when the dispersed particles are non-conducting.

Rayleigh (spheres)

$$K = \frac{1}{\lambda_r} \left[\frac{2 - 2\lambda_f - 0.394\lambda_f^{\frac{10}{3}}}{2 + \lambda_f - 0.394\lambda_f^{\frac{10}{3}}} \right] \dots\dots\dots \text{VIII.16}$$

Rayleigh (cylinders)

$$K = \frac{1}{\lambda_r} \left[1 - \frac{2\lambda_f}{2 + \lambda_f - 0.306\lambda_f^4 - 0.0134\lambda_f^8} \right] \dots\dots \text{VIII.17}$$

Meredith and Tobias (spheres)

$$K = \frac{1}{\lambda_r} \left[\frac{2 - 2\lambda_f + 0.613\lambda_f^{\frac{7}{3}} - 1.599\lambda_f^{\frac{10}{3}}}{2 + \lambda_f + 0.613\lambda_f^{\frac{7}{3}} - 0.6795\lambda_f^{\frac{10}{3}}} \right]$$

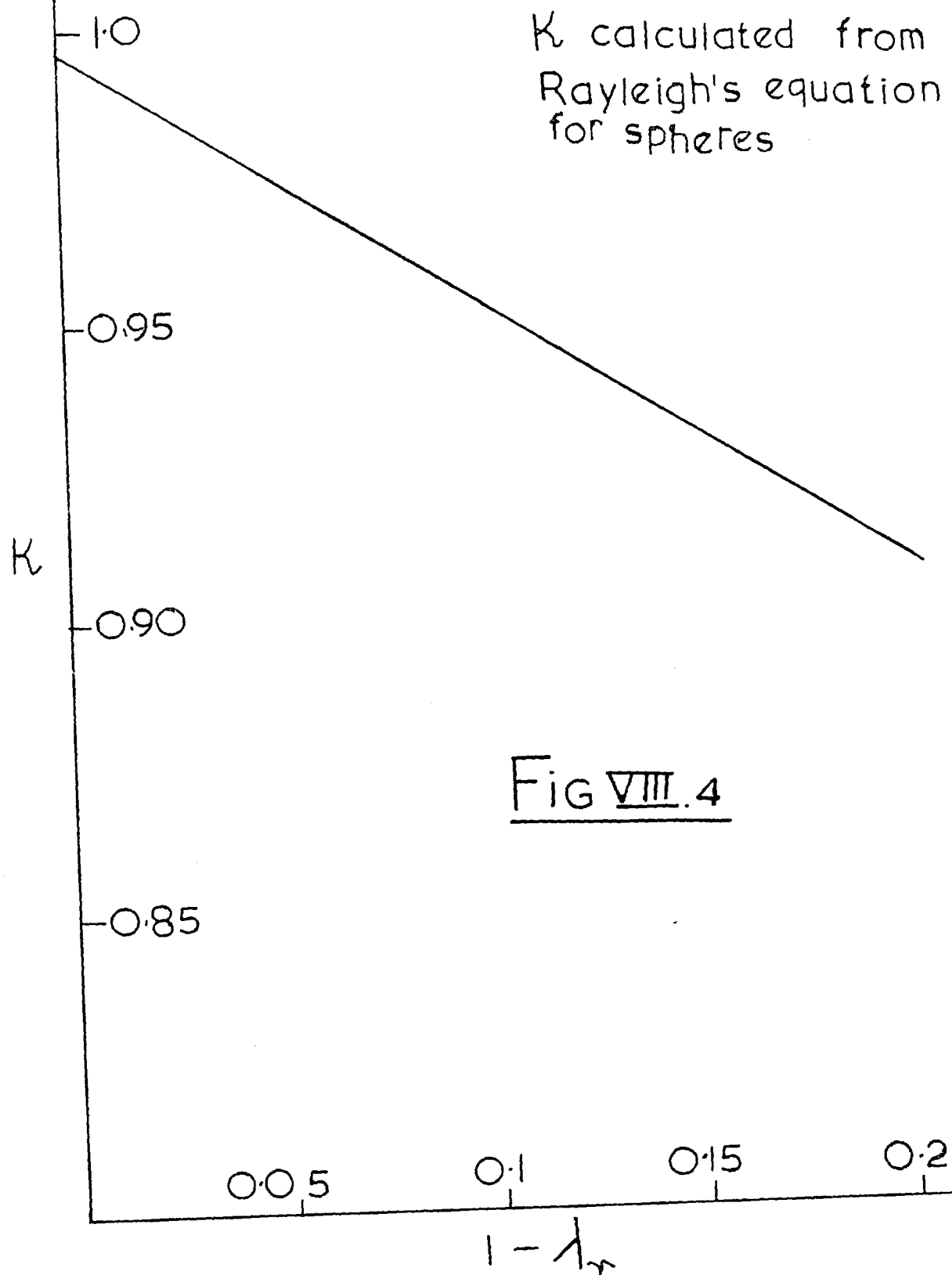
Equations VIII.16 and VIII.17 include a numerical correction introduced by Runge (1925). These expressions agree closely with each other at lower volume fractions of dispersed phase and at very low values of the latter Rayleigh's expressions for spheres reduces to that obtained by Maxwell. Meredith and Tobias (1960) have shown by plotting the volume fraction of the dispersed phase against the structure factor that for lower values of λ_f (upto about 0.2) Rayleigh's, Maxwell's and their own expressions give similar values of K . For the range of filler volume fractions covered by the silicone rubber samples the Rayleigh expression for spheres probably represents the structure factor as closely as any of the other expressions and we shall use it only in the following analysis. Values of K calculated from equation VIII.16 at volume fractions corresponding to the rubber phases in the different rubbers are given in Table VIII.13 and a plot of K vs. $(1 - \lambda_r)$ is shown in Figure VIII.4.

Table VIII.13

Sample No.	Si.R-B	Si.R-C	Si.R-D	Si.R-E
λ_r	0.944	0.894	0.851	0.809
K	0.972	0.949	0.931	0.913

The percentage differences in the diffusion coefficients and permeabilities

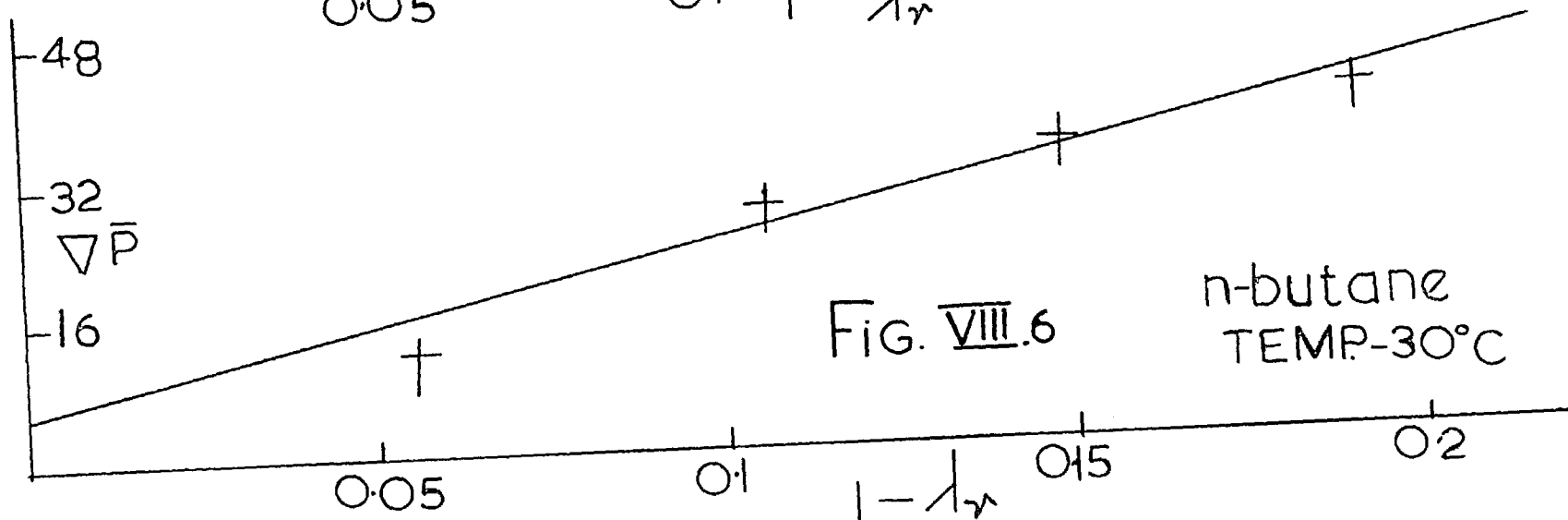
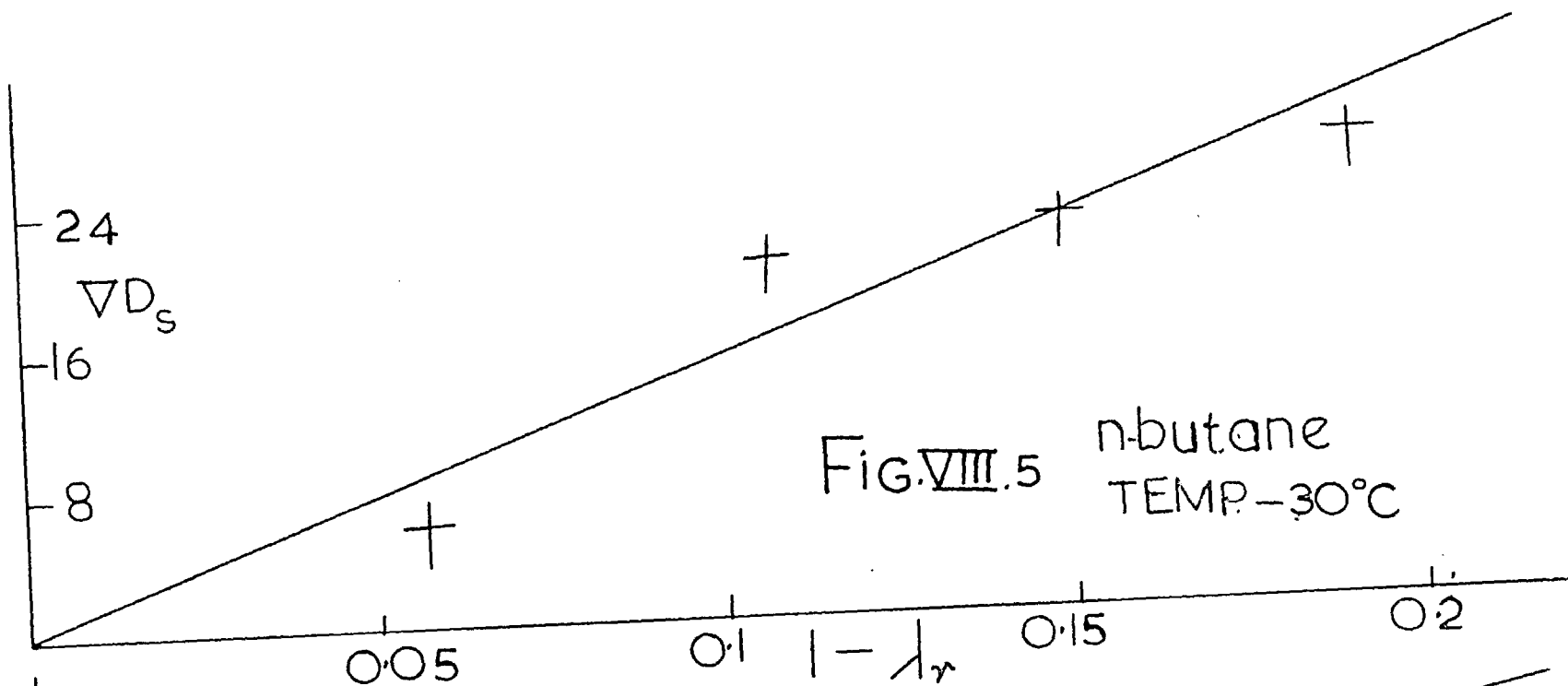
Since the expressions for ∇D_S and ∇D_L in terms of the simple reference models chosen for diffusion are identical the fact that ∇D_L is generally greater than ∇D_S



is probably an indication that the structure factors for the two states of flow are different. In particular K in equation VIII.13 or VIII.14 will be less for the transient state and as a result ∇D_S will be less than ∇D_L .

In Table VIII.14 are given values of $(1 - K)100$ at various volume fractions calculated from Rayleigh's expression for spheres, equation VIII.16. Although there is a considerable error in the values of ∇D_S it is clear that the percentage differences are considerably greater than the corresponding values of $(1 - K)100$. It can be seen from equation VIII.13 that immobile sorption of vapour by the filler will in fact lead to increased values of ∇D_S . Thus for the case where $\frac{\sigma_f}{\sigma_r} = 1$ then $\nabla D_S = (1 - K\lambda_r)100$ and becomes equal to $\nabla \bar{P}$. Values of $(1 - K\lambda_r)100$ are also included in Table VII.14 and are seen to be much closer to the ∇D_S values. However, the solubility data (p.117) are certainly not consistent with independent sorption by filler and rubber phases. Plots of $\nabla \bar{P}$ and ∇D_S vs. $(1 - \lambda_r)$ are shown in Figures VIII.5 and VIII.6.

Provided diffusion occurs in the rubber phase only then irrespective of whether or not the gas is sorbed by the filler $\nabla \bar{P}$ is related to the volume fraction λ_r by equation VIII.12. Comparison of the $\nabla \bar{P}$ values of Tables VIII.8 - VIII.11 with $(1 - K\lambda_r)100$ of Table VIII.14 shows that the $\nabla \bar{P}$ values are definitely larger. These differences between the experimental and theoretical results would indicate that either the models presented do not adequately



represent the filled rubber or else the theoretical expressions developed for K is dependent on the shape of the particle and in particular becomes smaller for lamellar type fillers. This has already been illustrated by Melikhova, Reitlinger and Kuzina (1959) who found that the shape factor was of considerable importance in the flow of nitrogen through rubber vulcanisates. When fillers with lamellar shapes (e.g. aluminium powder, mica) were arranged for the most part perpendicular to the flow of gas relatively low permeabilities were obtained. A lower structure factor for the silicone rubbers would in fact account for the differences between the experimental and calculated ∇D_S and $\nabla \bar{P}$ values.

Even allowing for a lower value for the structure factor neither the immobile sorption or zero sorption models can account for the variation of $\nabla \bar{P}$ and ∇D_S with temperature and penetrant size. According to equation VIII.12 $\nabla \bar{P}$ should be independent of both. Further the temperature dependence of ∇D_S will reside in the term $\frac{\sigma_f}{\sigma_r}$ which we may write as $\text{const.} \exp \frac{-(\Delta \bar{H}_f^0 - \Delta \bar{H}_r^0)}{RT}$. Since $\Delta \bar{H}_f^0 < \Delta \bar{H}_r^0$ the model would in fact indicate a decrease in ∇D_S with temperature contrary to the trend of the values shown in Tables VIII.9 VIII.12. The possibility of complex surface and gas phase fluxes within the filler particles cannot be ruled out but it is difficult to account for these in a qualitative manner. However, another possibility arises in that K may indeed be determined to a certain extent by the diffusion rate of penetrant in the medium. The data would suggest in this

respect that K decreases with increase of temperature or with increase in penetrant size, both of which correspond to a decrease in flow rate.

From the discussion of the data it appears that the permeation and diffusion processes in the filled silica rubbers are probably more complex than is indicated by the simple models for diffusion presented above. Finally to gain some more insight into the effect of the dispersed phase on the flow lines of the continuous phase we consider in the next section diffusion around a sphere embedded in an otherwise homogeneous body.

Table VIII.14

	Si.R-B	Si.R-C	Si.R-D	Si.R-E
$(1 - K)100$	2.8	5.1	6.9	8.7
$(1 - K\lambda_r)100$	8.2	15.2	20.8	26.1

Flow round a spherical particle

Although an exact solution of the diffusion equation for heterogeneous media consisting of dispersions of one phase in another would be a formidable task and so far is not forthcoming, steady state solutions for a single particle in a homogeneous medium are available. Thus Carslaw and Jaeger (1959) consider disturbances of a steady linear flow of heat in a uniform medium by a sphere of different conductivity embedded in it. They consider a sphere of radius 'a' and conductivity K' embedded in a medium of conductivity K and

obtain for v the temperature in the region outside of the sphere;

$$v = V \cdot r \cos \Theta + \frac{V a^3 (K - K') \cos \Theta}{r^2 (2K + K')} \dots\dots\dots \text{VIII.19}$$

where V is the constant gradient of temperature at large distances from the sphere in the direction of the z axis ($z = r \cos \Theta$). The same equation is also valid for diffusion by replacing v by concentration c and the thermal conductivity K by the diffusion constant D . Plots of lines of constant temperature (concentration) around the region of the sphere were constructed by plotting v/V as a function of r and Θ for various ratios of K/K' . It is clear from Figures VIII.7 - VIII.10 that the lines of constant temperature suffer considerable distortion in the region close to the sphere, and the effect becomes negligible only at distances of 2 - 3 times the diameter of the sphere.

The lines of constant flow will be at right angles to the lines of constant temperature. The equation for the family of curves at right angles to equation VIII.19 is shown in the appendix to be,

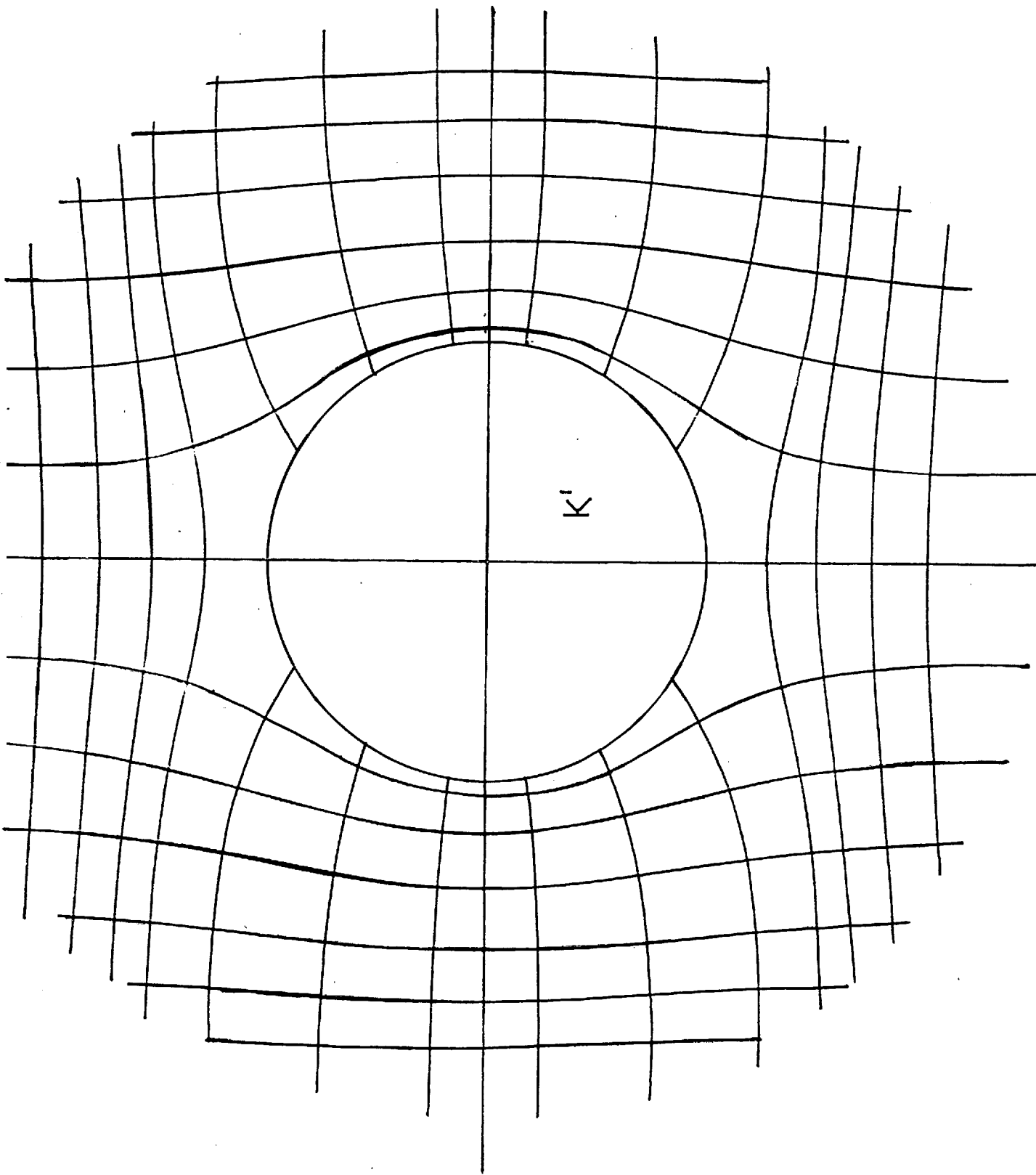
$$A' = r^2 \cos^2 \Theta - \frac{2a^3 (K-K') \cos^2 \Theta}{r (2K + K')} \dots\dots\dots \text{VIII.20}$$

Plots of the constant flow lines were constructed by fixing values for A' and plotting A' as a function of r and Θ . These lines are also found in Figures VIII.7 - VIII.10. The shadow effect of a non-conducting particle is apparent from these plots, the effective volume of the particle being somewhat greater than its geometric volume. The distortion of the flow line pattern varies with the ratio K/K' . This

ratio, if the filler particles are permeable, could thus vary in the material diffusion problem from one penetrant to another with consequent modifications to the structure factors for these penetrants.

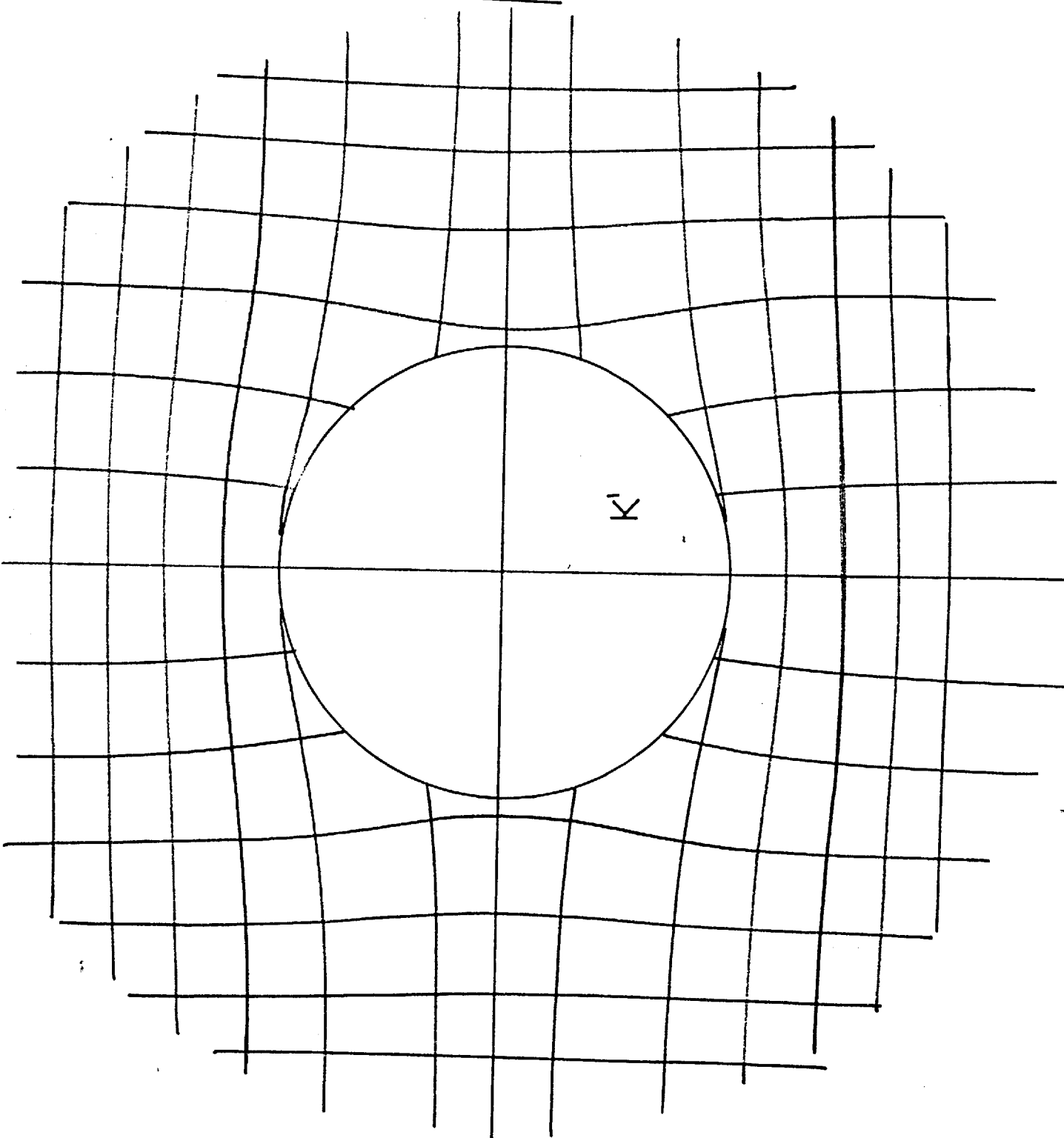
$K' \rightarrow O$

Fig. VIII. 7



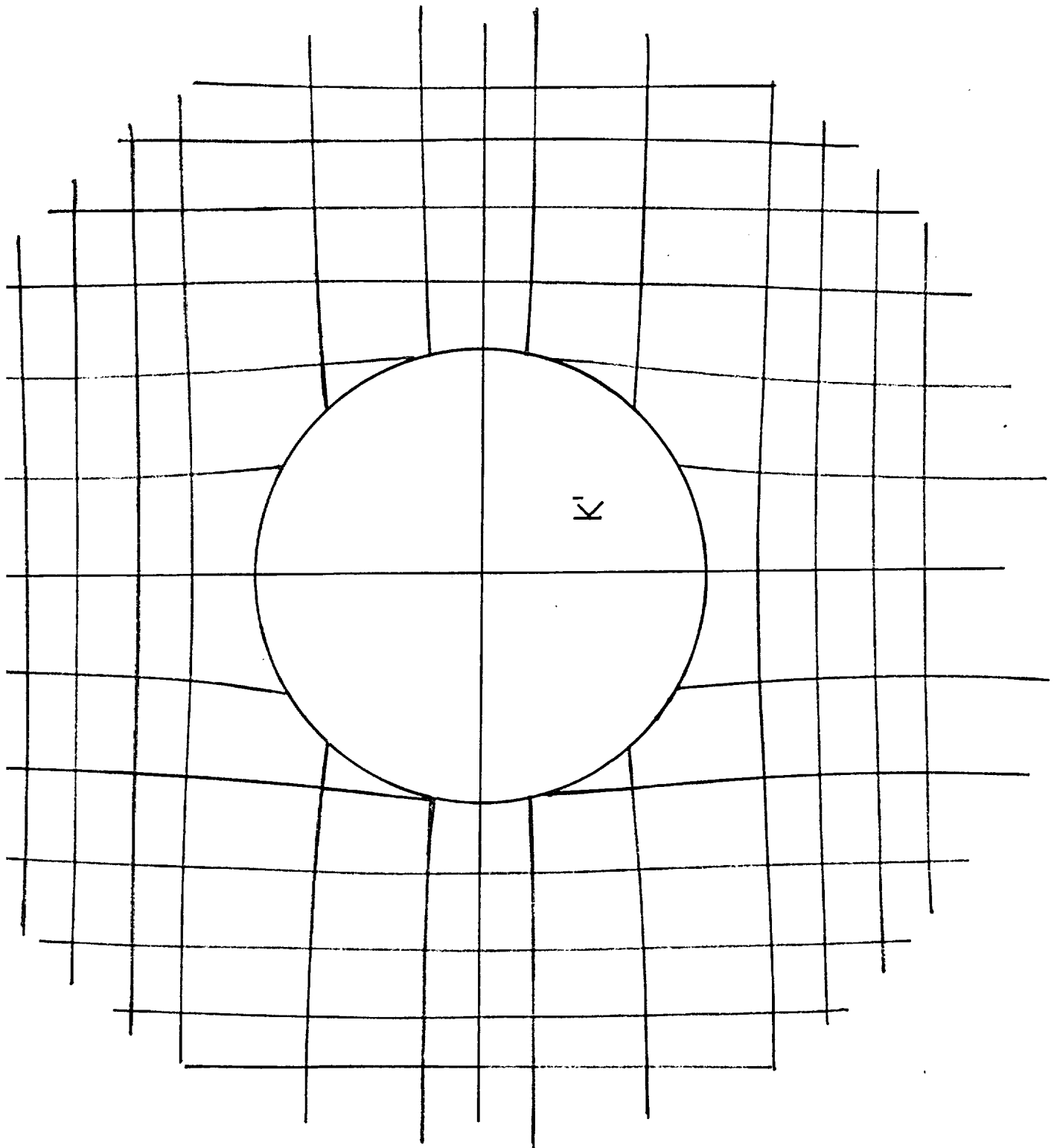
$$\frac{K}{K'} = 0.5$$

Fig. VIII. 8



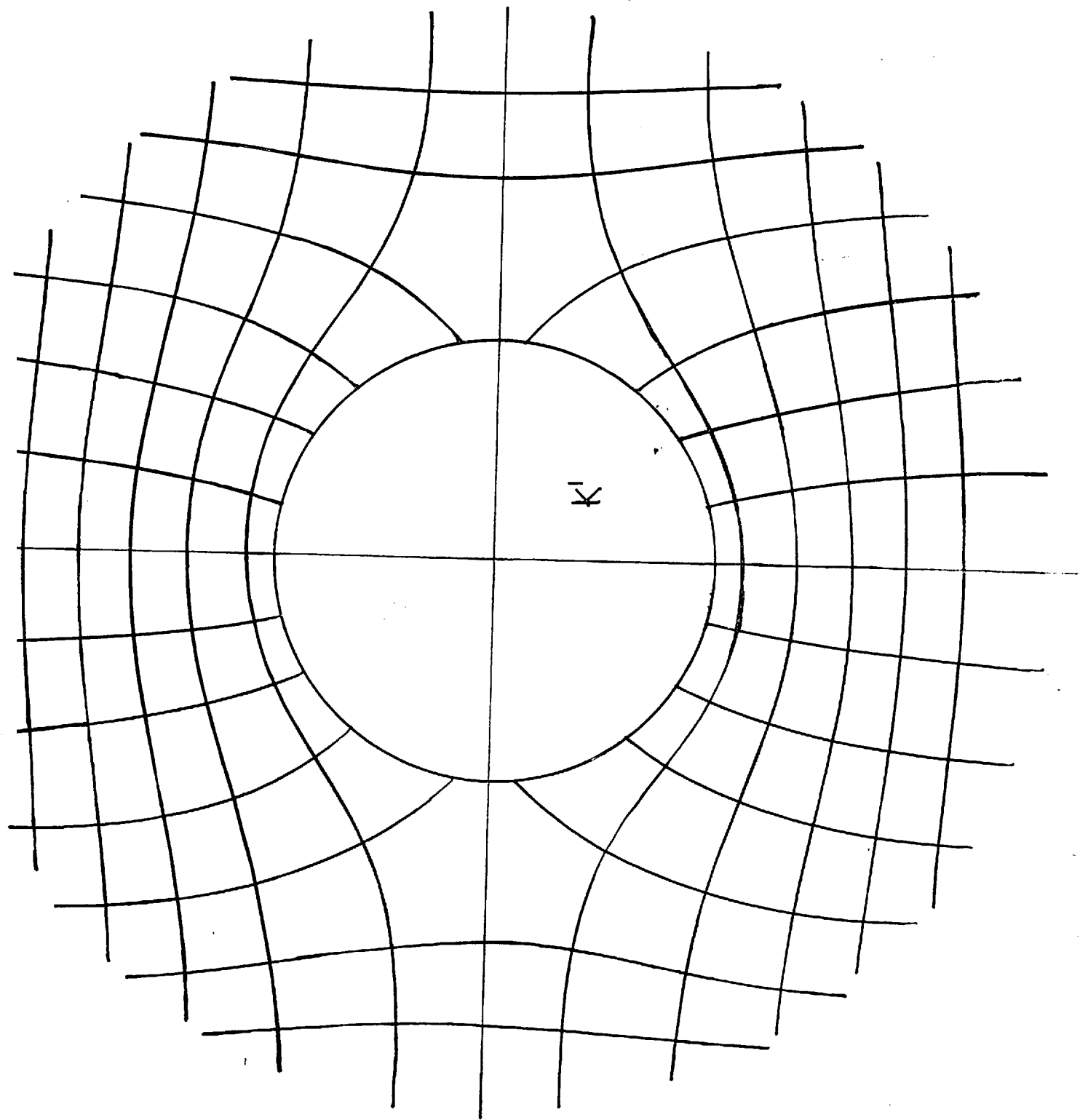
$$\frac{K}{K'} = 1.5$$

FIG. VIII, 9



$$K' \rightarrow \infty$$

FIG. VIII, 10



SUMMARY

The diffusion and sorption of the isomeric pairs of hydrocarbons n-butane, iso-butane, n-pentane and neo-pentane in unfilled and filled silicone rubbers has been investigated. A comparison has been made of the permeability, solubility and diffusion data of the unfilled silicone rubbers with those of natural rubber. The role of the filler particles in the transport and solution processes has been investigated in some detail. The following are the main points arising from the previous discussion on solubility and permeability.

1. Solubility

a. Unfilled samples

In all cases solubility isotherms in the pressure range 0 - 15 cm.Hg. were linear thus implying that Henry's law is obeyed. The solubility coefficients were about 20% higher than those for natural rubber. The values of free energy, heat and entropy of dilution compared satisfactorily with those deduced from current polymer solution theory. The effect of cross-linking in the range investigated was found to be negligible.

b. Filled samples

Henry's law was again obeyed for all the samples containing respectively, 5.6%, 10.6%, 14.9% and 19.1% by volume of silica filler. The solubility coefficients were found to decrease as the filler content of the rubber increased. In analysing the solubility results for the filled rubbers, two reference models are presented

(equations VII.7 and VII.8) relating the solubility coefficients (σ) to the volume fractions of rubber and filler (λ_r, λ_f) and their corresponding solubilities (σ_r, σ_f),

$$\begin{aligned}\sigma &= \lambda_r \sigma_r + \lambda_f \sigma_f \\ \sigma &= \lambda_r \sigma_r \quad (\text{for } \sigma_f = 0)\end{aligned}$$

If the rubber and filler sorb vapour independently then the values of the solubility coefficients would be represented by the first model while if there were no sorption by the filler then the measured solubilities in the filled rubbers should correspond to the second model. The values of the solubility coefficients obtained in the present investigation were found to be closer to the second model and it is therefore considered likely that sorption of vapour by the filler in the rubber was negligible.

The effect of filler on the thermodynamic functions of solution and dilution are investigated and models are presented relating the free energy, heat and entropy terms to the volume fractions of rubber and filler. The agreement of the experimental results with the theoretical models is satisfactory.

2. Permeability

a. Unfilled samples

The main points of interest in the permeability results of the unfilled rubbers are the following.

1. By comparison with natural rubbers, the permeability coefficients of the hydrocarbons in silicone rubbers were found to be 25 to 40 times higher.

2. Diffusion coefficients were independent of concentration of the penetrant with the dilute range studied and about 10 to 20 times higher, the lower values of the ratios being at the higher temperatures. The diffusion coefficients generally decreased in the order,

n-butane > iso-butane > n-pentane > neo-pentane

3. The values of the activation energies for diffusion, E_D were about 3 times lower in silicone rubbers and E_p values were negative and small. The permeability coefficients decreased with increasing temperature.
4. Similar to solubility results, the effect of cross-linking was found to be negligible on both permeability and diffusion coefficients.
5. A comparison of the D_0 values for silicone and natural rubbers has been made by plotting $\log D_0$ vs. E_D/T . Interpretation of the data in terms of the zone theory of activation indicate that silicone rubbers are the more rubbery in character.
6. The effective use of silicone rubbers as a medium for fractional separation of vapours differing in molecular shape has been considered and the results show that fractionation factors in these rubbers are smaller than for natural rubbers.

b. Filled samples

Similar to unfilled rubbers, the permeability and diffusion coefficients were found to be independent of concentration of vapour. The activation energies for diffusion, and E_p values, were again similar within experimental errors, to the values of these quantities in the unfilled rubbers.

Permeability and diffusion coefficients were found to decrease as the filler content was increased. The differences in the results of the unfilled and filled samples are compared by calculating the percentage differences which is defined for any given parameter X by,

$$\nabla X = \left\{ 1 - \frac{X_{\text{filled}}}{X_{\text{unfilled}}} \right\} \times 100$$

X in this case can denote the permeability ($\nabla \bar{P}$) or the transient state (∇D_L) or steady state (∇D_S) diffusion coefficients. In general, ∇D_L values were found to be larger than ∇D_S values. Differences in the structure factor (K) between ∇D_L and ∇D_S quantities are considered to be the reason for larger ∇D_L values. Thus the possibility exists of part of the rubber phase not contributing to the steady state flow but becoming significant in the transient state of diffusion. Similar comparison of $\nabla \bar{P}$ and ∇D_S values suggest that the former is always larger. Models are therefore proposed to relate $\nabla \bar{P}$ and ∇D_S with the structure factor and the volume fraction of the rubber and these are,

$$\nabla \bar{P} = (1 - K_r \lambda_r) 100$$

$$\nabla D_S = (1 - K_v) 100$$

It is shown that while $\nabla \bar{P}$ is dependent on both the structure factor K and volume fraction of rubber λ_r , ∇D_s is dependent only on the structure factor.

The problem of diffusion of gas around a particle is similar to the flow of heat around a non-conducting sphere embedded in a medium of a different conductivity. Flow patterns are therefore presented to show the distortion of flow lines as they approach the sphere for different K/K' ratios where K and K' are the conductivities of the medium and sphere respectively.

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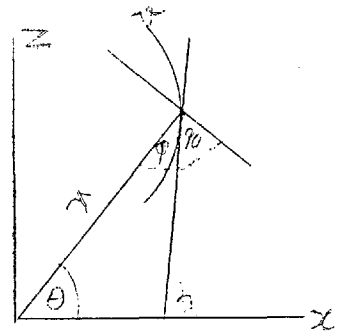
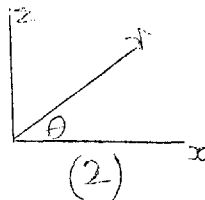
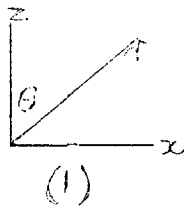
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APPENDIX

For the condition of $K' \rightarrow \infty$

$$v = V.r \cos \theta - \frac{V.a^3}{r^2} \cos \theta \dots\dots\dots (1)$$

$$\text{or } v = V.r \sin \theta - \frac{V.a^3}{r^2} \sin \theta \dots\dots\dots (2)$$

$$\sin \theta = \frac{v.r^2}{V.r^3 - V.a^3}$$



Differentiating with respect to r,

$$\begin{aligned} \cos \theta \frac{d\theta}{dr} &= \frac{v}{V} \cdot \frac{dr^2/r^3 - a^3}{dr} \\ &= \frac{v}{V} \cdot \left[\frac{2r}{r^3 - a^3} - \frac{r^2 \cdot 3r^2}{(r^3 - a^3)^2} \right] \\ &= - \frac{v}{V} \cdot \frac{r^4 + 2ra^3}{(r^3 - a^3)^2} \end{aligned}$$

If ϕ is the angle made by the tangent to the curve with the r co-ordinate then,

$$\tan \phi = r \frac{d\theta}{dr} = - \frac{vr}{V \cos \theta} \left[\frac{r^4 + 2ra^3}{(r^3 - a^3)^2} \right]$$

Then $(90 + \phi)$ is the angle between the normal to the curve and the r coordinate and

$$\tan(90 + \phi) = \frac{\tan 90 + \tan \phi}{1 - \tan 90 \tan \phi}$$

$$= \frac{1 + \frac{\tan \theta}{\tan 90}}{\frac{1}{\tan 90} - \tan \phi} = -\frac{1}{\tan \phi}$$

$$\therefore \frac{r d\theta}{dr} = \tan(90 + \phi) = -\frac{1}{\tan \phi}$$

$$= \frac{V \cos \theta}{V \sin \theta} \cdot \frac{r}{(r^3 - a^3)} \left[\frac{(r^3 - a^3)^2}{r^4 + 2ra^3} \right]$$

$$\frac{d\theta}{dr} = \frac{1}{\tan \theta} \left[\frac{r^3 - a^3}{r^4 + 2ra^3} \right]$$

The equation for the family of curves at right angles to equation (1) is then obtained as follows,

$$\int \tan \theta d\theta = \frac{(r^3 - a^3) \cdot dr}{r(r^3 + 2a^3)}$$

$$- \log \cos \theta = \frac{1}{2} \log(r^3 + 2a^3) - \frac{1}{2} \log r + \frac{1}{2} \log A$$

(where A is the constant of integration)

$$\therefore \cos \theta (r^3 + 2a^3)^{\frac{1}{2}} A^{\frac{1}{2}} = r^{\frac{1}{2}}$$

If we denote A' as the right-angle function then,

$$A' = r^2 \cos^2 \theta + \frac{2a^3 \cos^2 \theta}{r}$$

$$\text{or } A' = r^2 \sin^2 \theta + \frac{2a^2 \sin^2 \theta}{r} \dots \dots \dots (3)$$