DIFFUSION AND SOLUTION IN HIGH POLYMERS

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ABSTRACT

The results of a number of investigations have shown that the diffusion of vapours through high polymers does not conform to Fick's law. This thesis presents data on the diffusion of benzene vapour through films of rubber and of polythene together with a discussion of the deviations from Fick's law.

Rates of diffusion and permeation have been measured over a wide range of temperature and pressure. From the temperature variation the energies of diffusion and permeation have been calculated. The variation of these rates with pressure has been related to experimentally determined activities and it is shown that the deviations from Fick's law are due to:

(1) Non-linear dependence of activity upon concentration.

(2) Variation of mobility of the benzene in the polymer with concentration.

By making use of a suitably modified form of Fick's law these two factors have been measured, and they have each been examined in the light of approximate theories.

CHAPTER I

Fundamental Equations and Definitions

The molecular mixing of different substances or of distinguishable elements of the same substance is called diffusion. The theory of the process of diffusion in macroscopically homogeneous substances+ is treated by analogy with the theory of the conduction of heat in solids.

The fundamental hypothesis, due to Fick, upon which the theory is founded is the following:

The rate of flow of diffusing material, per unit time per unit area, across an infinitesimal surface normal to the direction of diffusion, called the flow and denoted by P, is equal to a quantity called the diffusion coefficient D multiplied by the gradient of concentration in the direction of flow, $-\frac{\partial c}{\partial x}$ across the surface. The equation

$$P = - D \frac{\partial c}{\partial x} \qquad \text{-----} \ 1$$

is called Fick's law by analogy with Fourier's law for the conduction of heat, $(f = - K \frac{\partial T}{\partial x})$. The concentration at a given point will be, in general, a function of the position of the point, the time, and the diffusion coefficient. It

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+ This excludes diffusion through macroscopic channels, tubes, and orifices which is sometimes more appropriately treated by the methods of Fluid Dynamics.

was assumed by Fick that the diffusion coefficient is independent of the concentration and position. With this assumption D becomes a true constant, and the concentration of diffusing substance at any given point, may be derived by considering the rate of accumulation of matter in an infinitesimal element of volume at the given point. In this way one obtains for the rate of change of concentration with time

$$\frac{\partial c}{\partial t} = D \nabla^2 c \qquad \text{-----} \; 2$$

In Cartesian co-ordinates this becomes, for diffusion in the x direction

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

Equation 2 is a second form of Fick's law. Its validity in this form is limited to diffusion in a single, isothermal, homogeneous phase in which the diffusion coefficient is independent of concentration and positional co-ordinates. In spite of these limitations it has been applied to a vast number of problems. The diffusion of gases in crystals, glasses, and high polymers, interdiffusion in many isotropic crystals and all isotopic systems (1), (2), are examples of processes which have been treated in terms of equation 2.

The Stationary and Non-Stationary States of Flow

When the concentration at any given point in a medium is independent of time equation 2 takes a particularly simple form, for $\partial c/\partial t = 0$ and therefore

$$0 = D\,\nabla^2 c \qquad \text{----- } 3$$

Systems satisfying equation 3 are said to be in the stationary state of flow. In the non-stationary state of flow the concentration at any point varies with time and equation 2 must be employed.

Solutions of equations 2 and 3 for many of the boundary conditions to be met with in practice are given by Barrer (1).

Variation of the Diffusion Coefficient with Concentration

If D is a function of concentration or, in the case of non-homogeneous media, of positional co-ordinates, then the equation $\frac{\partial c}{\partial t} = D\,\nabla^2 c$ does not apply. Such diverse systems as vapour and high polymer (3), vapour and zeolite (4), substitutional, and interstitial alloys (5), (6) all show variations of D with concentration. It is necessary, therefore, to reformulate the equations of diffusion in order to study these systems.

A complete phenomenological theory of diffusion may be based upon the fundamental hypothesis of equation 1 $P = -D\frac{\partial c}{\partial x}$, but equation 2, $\frac{\partial c}{\partial t} = D\,\nabla^2 c$, which involves the assumption that D is independent of c and x, y and z, must be replaced by the more general equation

$$\frac{\partial c}{\partial t} = \nabla . D \nabla c$$

$$= \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(D\frac{\partial c}{\partial z}\right) \qquad \text{----- } 4$$

This may be derived from equation 1 in the following way. Consider diffusion in the x direction only through two parallel planes at x and x + δx. The flow P_x at x is given by

$$P_x = - D \frac{\partial c}{\partial x}$$

and the flow $P_{x+\delta x}$ at x + δx given by

$$P_{x+\delta x} = P_x + \frac{\partial (P_x)}{\partial x} \delta x$$

The rate of accumulation of matter per unit area between the two planes is

$$\frac{\partial c}{\partial t} \delta x = P_x - P_{x+\delta x}$$

therefore

$$\frac{\partial c}{\partial t} = - \frac{\partial P_x}{\partial x}$$

and so

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right).$$

No general solution of this equation has so far been found. Resort must be made to either, numerical or graphical solutions, or to methods based on the stationary state of flow only. Some of these will now be discussed.

Numerical and Graphical Solutions

1. The method of Crank and Henry

Crank and Henry have shown (7) that the variation of D with C may be determined without recourse to the more general equation 4. They consider the absorption of gas or vapour by an infinite plane sheet of material for the boundary conditions.

$C = C_0$ for $x = -1$, $x = +1$, $t \geqslant 0$
$C = 0$ for $-1 < x < +1$, $t = 0$.

The solution of the equation $\frac{\partial c}{\partial t} = D_0 \frac{\partial^2 c}{\partial x^2}$ for these conditions is (ref. 1, p. 14, eq. 50).

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp - \frac{D_0 \pi^2 (n+\frac{1}{2})^2 t}{l^2} \qquad \text{-----} \ 5$$

where M_t is the amount absorbed at time t and M_∞ the amount sorbed when equilibrium has been reached. If D is constant then the value of D can be found by comparing the

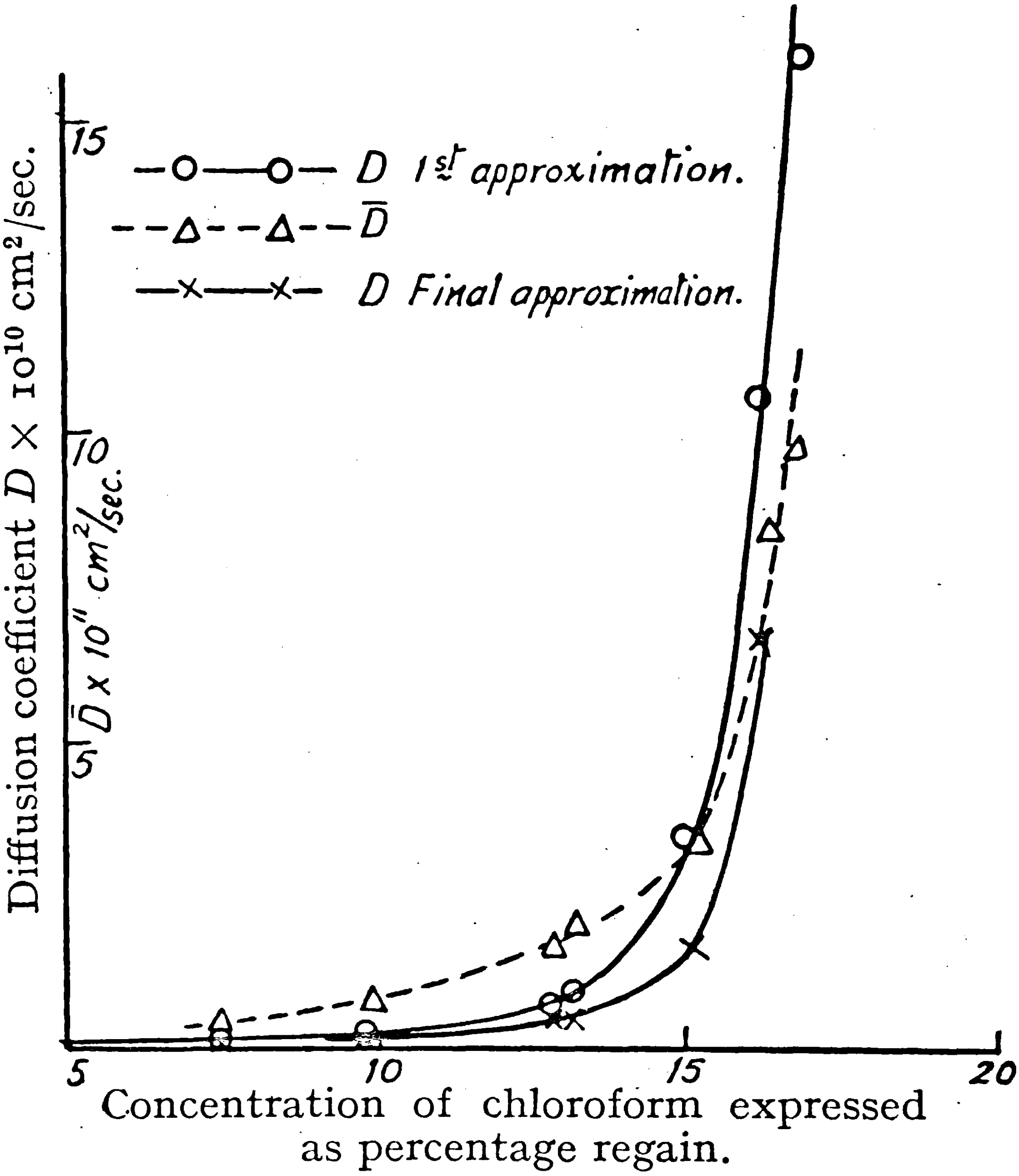

Fig. 1. Absorption of Chloroform by Polystyrene. Diffusion Coefficients by Method of Crank and Henry (8).

experimental curve with the one calculated using equation 5. If D is not constant, however, this comparison yields some mean value $\bar{D}$ whose value depends upon the way in which the comparison is made. Crank and Henry choose $\bar{D}$ such that at $M_t/M_\infty = 0.5$ the theoretical and experimental curves coincide. They assume that to a first approximation

$$\bar{D} = \frac{1}{C_o} \cdot \int_0^{C_o} D\,dc \qquad \text{-----} \; 6$$

(Graphical differentiation of $\bar{D}$ as a function of C_o gives D to a first approximation.) Curves of M_t/M_∞ can then be computed for each value of C_o using these D values. By comparison with the experimental curves new mean values $\bar{\bar{D}}$ are then found. Plotting the $\bar{\bar{D}}$ values calculated in this way against $\frac{1}{C_o} \int_0^{C_o} D\,dc$ using the $\bar{D}$ values obtained from the first approximation gives smoothed values of $\frac{1}{C_o} \int_0^{C_o} D\,dc$ for each value of $\bar{\bar{D}}$. Graphical differentiation of the smoothed $\bar{\bar{D}}$ values as a function of C_o then gives D to a second approximation. The process is repeated until two successive approximations agree to within the experimental accuracy of the measurements. Crank and Park (8) showed that in the case of the absorption of chloroform in polystyrene only three approximations were necessary. The results of these authors are shown in Fig. 1.

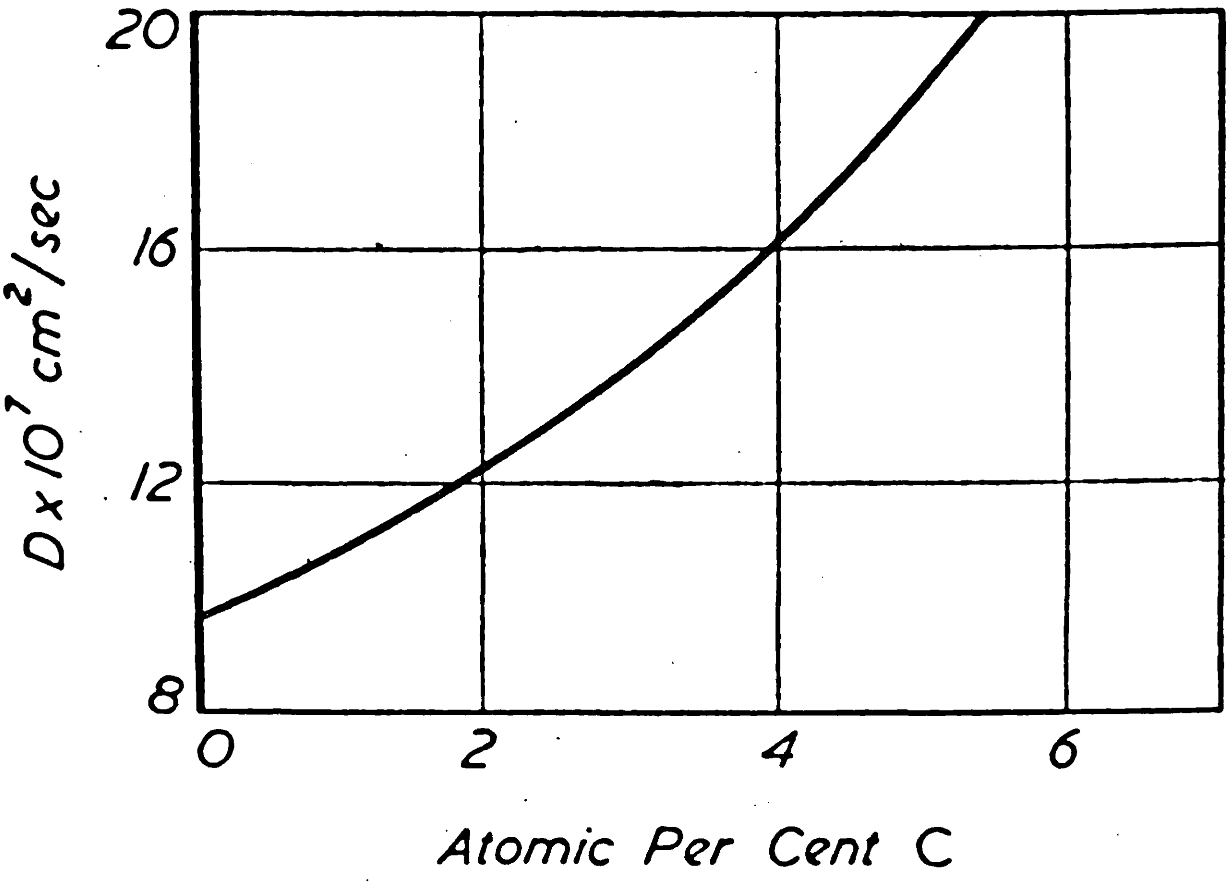

Fig. 2. Variation of D with C for the System Carbon-Austenite (10).

2. Methods based on Boltzmann's theorem

Boltzmann (9) showed that for the boundary conditions

$C = C_0$ for $0 < x < -\infty$ at $t = 0$.

$C = 0$ for $0 < x < \infty$ at $t = 0$.

Solutions of $\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}(D\frac{\partial c}{\partial x})$ will contain C as a function of a single variable λ, where

$$\lambda = \frac{x}{\sqrt{t}}$$

therefore

$$-\frac{\lambda}{2}\frac{\partial c}{\partial \lambda} = \frac{\partial}{\partial \lambda}(D\frac{\partial c}{\partial \lambda}) \qquad \text{-----}\ 7$$

In the initial stages of diffusion a numerical solution of this equation is possible using an iterative method (7). Alternatively equation 7 may be integrated to give

$$-\tfrac{1}{2}\int \lambda \; dc = D\frac{\partial c}{\partial \lambda}$$

$$D = -\frac{1}{2}\frac{\partial \lambda}{\partial c}\int \lambda\, dc = -\frac{1}{2t}\frac{\partial x}{\partial c}\cdot\int x\, dc \qquad \text{-----}\ 8$$

The experimental c - x curve is then plotted for a given time, and D evaluated as a function of concentration by graphical integration. This method is generally employed in alloy systems. Wells and Mehl (10) have determined the variation of D with C in the system carbon-austenite in this way. Their results are shown in Fig. 2.

3. Methods based on the Stationary State of Flow

The results presented in this thesis are based upon measurements of diffusion rates in the stationary state of flow. In such cases equation 4 reduces to the much simpler equation

$$0 = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D\frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(D\frac{\partial c}{\partial z}\right) \qquad \text{----- } 9$$

Barrer (11) has developed procedures for determining the variation of D with C or x, y, z, in such cases. The method will be illustrated by taking as an example the problem of diffusion through a plate of material of area A and thickness l where the boundary conditions are

$$C = C_1 \text{ for } x = 0,\ t \geqslant 0$$
$$C = C_2 \text{ for } x = l \quad t \geqslant 0,$$

and where D is a function of x only. Integration of equation 9 gives

$$D\frac{dc}{dx} = a \qquad \text{----- } 10$$

where a is a constant.

Now D may be written $D = D_0\,(1 + f(c))$ where f(c) is so defined that $D = D_0$ when $C \rightarrow 0$. Making this substitution in equation 10 and integrating, the distribution across the plate is found to be

$$D_0 \int (1 + f(c))\, dc = \int a dx + b \qquad \text{----- } 11$$

where b is a constant.

Making use of the boundary conditions this becomes on integration

$$\frac{C_1 + F(C_1) - (C + F(C))}{C_1 + F(C_1) - (C_2 + F(C_2))} = \frac{x}{l} \qquad \text{----- 12}$$

where F(C) has been written for $\int f(c)\,dc$. In the stationary state of flow the quantity of solute flowing through the plate in time t is

$$Q = A\int_0^t P\,dt \qquad \text{----- 13}$$

where P is the flow at x = l defined by

$$P = -D\frac{dc}{dx} \qquad \text{----- 14}$$

Differentiating 12, substituting into 14, and substituting the result into 13, one obtains finally

$$Q = \frac{D_oAt}{l}\left[C_1 + F(C_1) - (C_2 + F(C_2))\right] \qquad \text{----- 15}$$

When $C_1 \gg C_2$ equation 15 becomes

$$\frac{Ql}{At} = D_o[C_1 + F(C_1)] \qquad \text{----- 16}$$

the R.H.S. of which is then experimentally determined for several values of C_1. When C_1 is small D_o is given by

$$\frac{Ql}{AtC_1} = D_o \qquad \text{----- 17}$$

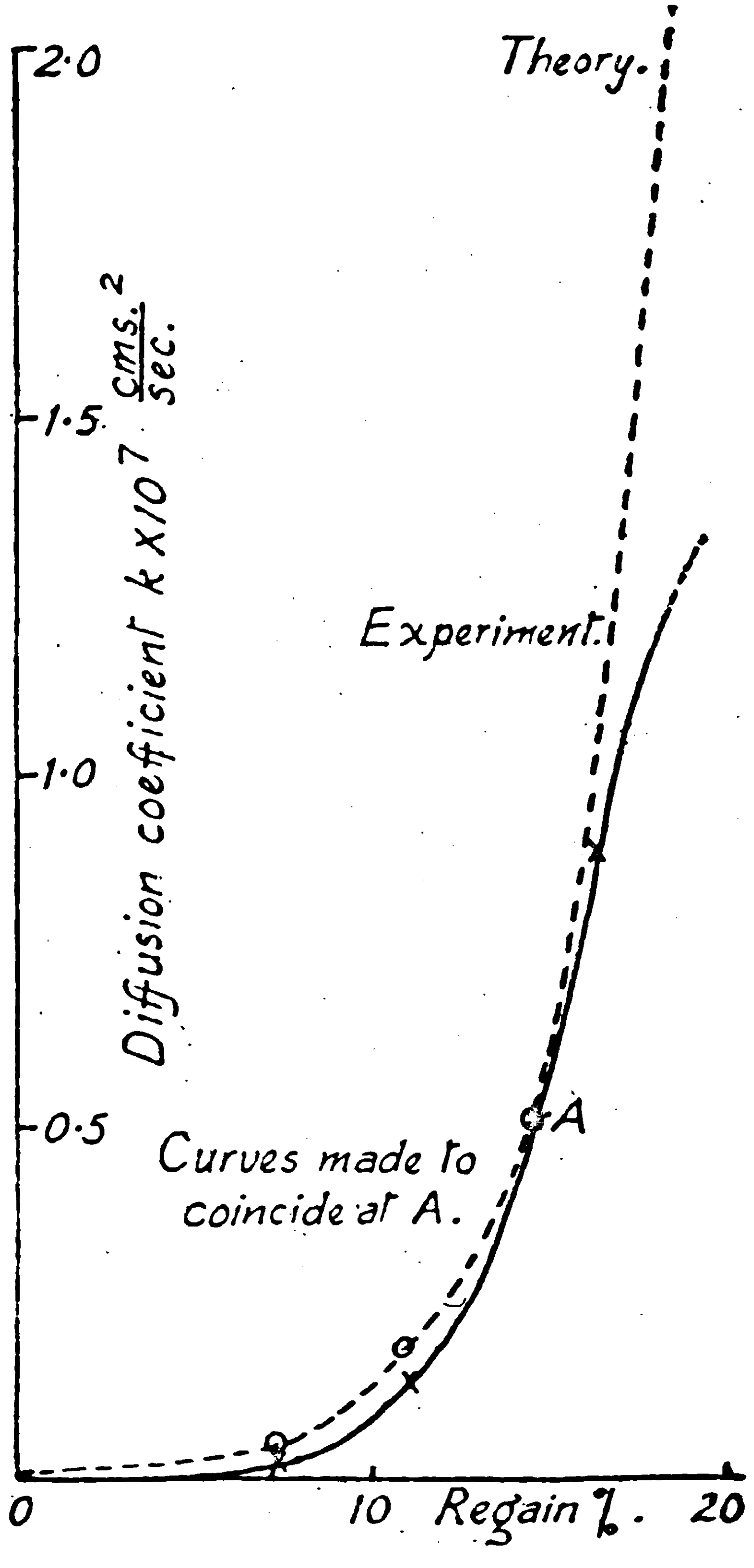

Fig. 3. Diffusion of Water Vapour through Horn Keratin (12).

hence $F(C_1)$ may be determined as a function of C_1. Differentiation then leads to $f(c)$, so that $D = D_0\ (1+f(c))$ can be found. King (12) has calculated the variation of the diffusion coefficient with concentration from measurements on the flow of water vapour through membranes of horn keratin by a method which, in its essentials, is very similar to the procedure here described. Fig. 3 shows the variation in diffusion coefficient he obtained.

The Thermodynamic Theory of Diffusion

The equations 1 and 4 although perfectly general serve merely as suitable mathematical equations to use in measuring the observable properties. They do not provide any explanation of the nature of the diffusion process and its relation to other properties of solutions. To do this it is necessary to analyse more fully the fundamental equation 1.

The first attempt in this direction was made by Nernst in 1888 (13). He approached the problem through the equality of the resistance to motion of a particle in a viscous medium and the driving force responsible for the motion. When the particle velocity v is constant the velocity and the frictional resistance f will be proportional to one another, so that one may write

$$v = Bf \qquad \text{-----} \ 18$$

where B, the factor of proportionality, is characteristic of the particle and medium through which it diffuses. The frictional work done by the particle in moving from x to x + δx is given by

$$dw = \frac{v}{B}\, dx \qquad \text{-----} \; 19$$

In moving from x to x + δx the particle passes from concentration C to concentration C − δC and in so doing does an amount of work

$$dw = -\, kT\, \frac{\delta c}{c} \qquad \text{-----} \; 20$$

If no other work is done then

$$\frac{v}{B}\, \delta x = -\, kT\, \frac{\delta c}{c} \qquad \text{-----} \; 21$$

If v is the average velocity of the diffusing particles then the flow as previously defined is given by

$$P = cv \qquad \text{-----} \; 22$$

combining 21 and 22 one obtains

$$P = -\, kTB\, \frac{\partial c}{\partial x} \qquad \text{-----} \; 23$$

Comparison with equation 1 shows that this is Fick's law with D replaced by kTB. The quantity B is called the mobility. It is important to note that this treatment does not assume that B and therefore D is constant. On the contrary it makes possible an analysis of variations of D in terms of the dependence of B, the particle mobility upon concentration.

The weakness of this derivation lies in the assumption that the work done by a particle in moving from concentration C to concentration $C - \delta C$ is equal to $- kT\,\delta C/C$. Although this amount of work is done in the reversible isothermal transfer of a particle when the solutions are in both cases ideal it is not necessarily the work done in diffusion which is essentially an irreversible process. For this reason the application of a thermodynamic treatment may not be valid. This difficulty is not confined to diffusion alone. Expressions for many other rate processes involve thermodynamic formulae. Rigorous theoretical investigations have shown (14) that in the case of irreversible processes occurring in gases (such as interdiffusion, viscosity, and chemical reaction) the application of equilibrium thermodynamic theory is justified. But because of their complexity no full investigation had yet been made in the case of condensed phases. Nevertheless approximate theories (the absolute reaction rate theory of Eyring, and Evans and Polanyi, and the electrolytic solution theory of Onsager 15, 16, 17) have achieved such notable successes that sufficient confidence can be placed in the above assumption. Assuming that one may use such a thermodynamic treatment it is apparent that the Nernst derivation will apply only to solutions which are ideal. In a non-ideal solution $- kT\,\delta a/a$ where a is the activity, will be the reversible work of transfer.

Equation 21 can therefore be rewritten as

$$\frac{v}{B}\,\delta x = -\,kT\,\frac{\delta a}{a} \qquad \text{----- } 24$$

Making the substitution $\gamma = a/c$, where γ is the activity coefficient one obtains

$$P = -\,kTB\left(1 + \frac{\partial \ln\gamma}{\partial \ln c}\right)\frac{\partial c}{\partial x} \qquad \text{----- } 25$$

The diffusion coefficient in Fick's law now becomes

$$D = kTB\left(1 + \frac{\partial \ln\gamma}{\partial \ln c}\right) \qquad \text{----- } 26$$

A thermodynamic treatment of diffusion applicable to non-ideal systems was first given by Hartley (18), and discussed in relation to diffusion through rubber by Daynes (19).[+] Equation 26 can be of great value in studying diffusion in those systems for which D is a function of concentration insofar as it permits the deviations from ideal solution behaviour to be separated out of the diffusion coefficient. This has been recognised for some time by those concerned with diffusion in electrolyte solutions (17), (18) and in metals (20). It has not been widely applied to diffusion studies in other systems.

(+) Daynes suggested the equation $\frac{\partial h}{\partial t}\cdot\frac{\partial c}{\partial h} = D'\,\frac{\partial^2 h}{\partial x^2}$, where h is the relative humidity. This equation, though it may reduce variations in D, if these arise out of non-ideal behaviour, is not strictly speaking a thermodynamic diffusion equation. See the discussion, especially Hartley's remarks, following a paper by Barrer, Soc. Dyers and Colourists; Symposium on Fibrous Proteins, p. 108 (1946).

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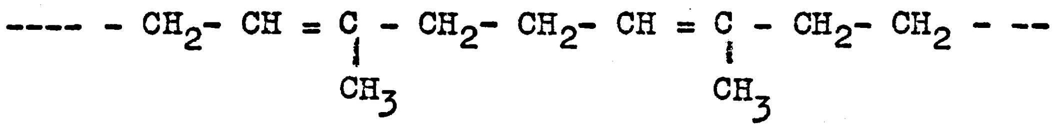
CHAPTER II

In the previous chapter there has been given an account of the fundamental theory of diffusion. General methods by means of which diffusion coefficients may be determined have been outlined. In the present chapter attention is focussed on diffusion with particular reference to high polymers. A brief account of the structure of high polymers is followed by a review of some of the investigations made into the processes of diffusion and solubility in these materials, together with an account of the units and dimensions for diffusion, solubility, and permeability.

The Structure of High Polymers

The term high polymer is used to connote a class of substances whose molecules consist of a large number of identical atomic groups, called monomer units, joined together by covalent bonds. Typical high polymers are:

Natural Rubber

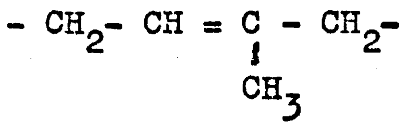


$$---- - CH_2 - CH = \underset{\substack{| \\ CH_3}}{C} - CH_2 - CH_2 - CH = \underset{\substack{| \\ CH_3}}{C} - CH_2 - CH_2 - --$$

and Polythene (polyethylene)

$$--- - CH_2 - CH_2 - CH_2 - CH_2 - ---$$

The monomer unit in the first case is the isoprene group



$$- CH_2 - CH = \underset{\substack{| \\ CH_3}}{C} - CH_2 -$$

and in the second case, the methylene group

$$- CH_2 -$$

High Polymers differ markedly from simple low molecular weight solids and liquids. Three factors are chiefly responsible for the differences:-

i) The chemical structure of the monomer
ii) The degree of polymerisation (D.P.)
iii) The extent of cross-linking or chain-branching.

The chemical structure of the monomer unit greatly influences the physical state of the high polymer: polymers consisting of small or highly polar monomer units are generally found to be fairly rigid and crystalline, in contrast those polymers made up of bulky or weakly polar monomer units are more often amorphous and plastic. Many polymers are only partially crystalline, that is, they contain micro-crystalline regions, in which the monomer units are arranged and oriented in regular fashion, interspersed among amorphous regions. The extent of crystallinity is governed by both the degree of polymerisation and the extent of cross-linking. A high D.P. and much cross-linking bestow on a polymer an entangled network like structure in which complete crystallisation is impossible; within certain regions however, the structure may be sufficiently free from entanglements to allow the monomer units to take up an ordered crystalline arrangement.

By comparing the effect of temperature on high polymers and low molecular weight compounds the differences between the two classes are exemplified; and may be elucidated in terms of the three afore mentioned factors.

At a sufficiently low temperature, because of large Van der Waal's forces, compounds in both classes exist as solid substances, able to sustain external forces and having high tensible strengths. In the case of a low molecular weight compound the molecules will, in general, vibrate about fixed lattice points; a long-range order, manifested by sharp X-ray diffraction bands, will exist and impart to the compound a regular crystalline form. In a high polymer, by contrast, long range entanglements of the molecular chains, extensive cross-linking, and bulky monomer units which do not easily pack together - all tend to give the material a disordered amorphous structure. Crystallinity, if it exists at all, is never complete. For this reason the X-ray bands are much broader than those of a crystalline solid and more nearly resemble those of a liquid. The effect of heat on a low molecular weight solid is discontinuous. The amplitude of molecular vibrations about fixed points gradually increases until it is of the order of the mean intermolecular distance. Further heating causes an abrupt change. The solid is converted into a liquid and the temperature stays constant until no solid remains. The molecules are then no longer located about fixed points but are able to move throughout the entire volume occupied by the liquid. Because of this, the resistance to external forces disappears and the material is a fluid of low viscosity. In solid high polymers there is no discontinuous change on heating. The Van der Waal's attractive forces become less influential, any crystallinity which is present disappears, gradually, the monomer units become more mobile. But by contrast with a simple liquid, they are prevented from attaining high degree of mobility by cross-linking and entanglements. The substance becomes highly viscous and elastic and is said to be rubber-like. At still higher temperatures, and even in the presence of cross-linking, the rubber-like state changes over continuously to a state more resembling that of a true liquid. The molecular chains become freely mobile and able to move past one another. The elasticity disappears and the viscosity falls until its magnitude approaches that of a true liquid. In highly cross-linked polymers these changes are accompanied by the rupture of covalent bonds.

Early Investigations into Diffusion in High Polymers

Thomas Graham (1) laid the original foundations. He measured the rates of permeation of several gases through rubber membranes. From his results he concluded that "a film of rubber appears to have no porosity and to resemble a film of liquid in its relation to gases - differing entirely in this respect from a thin sheet of paper, graphite, or even gutta-percha. These last all appear to be pervaded by open channels or pores sufficiently wide to allow gases to be projected through by their own proper molecular movement of diffusion." How then does transport through the rubber membrane take place? Graham supposed that "the first absorption of the gas by the rubber depends upon a chemical affinity between the two analogous to that attraction admitted to exist between a soluble body and its solvent, conducing to solution -- the rubber being 'wetted through' by the liquefied gas, the latter -- reappears as gas on the other side of the membrane." Graham's theory, in particular the hypothesis that three stages, absorption, diffusion, and evaporation, are involved in the transmission of a gas through a polymer, forms a firm basis for all subsequent work.

Within a few years of Graham's original investigations, in 1879, Wroblewski (2) published measurements made on the permeation rates of several gases through rubber and found that these rates were governed by Fick's law. This confirmed Graham's views and showed that neither absorption or evaporation, but diffusion within the rubber is the rate-determining step.

Units and Dimensions

It is worthwhile saying something about units and dimensions before proceeding to the discussion of more recent work. Many of the values for the diffusion rates of gases and vapours in high polymers have been calculated from measurements of the permeability of thin films or membranes. This is partly on account of the relative simplicity of this procedure - a steady state one, but also because, from a practical viewpoint, it is the permeability, the flow rate under a unit pressure gradient, that is the most important consideration. For both permeability and diffusion rates a formidable diversity of units and dimensions have been used. Logical definitions that are mutually consistent have been provided by Barrer (3) and are given here.

The Diffusion Coefficient D is defined by equation 1 of chapter I and is a measure of the rate of flow of diffusing material through unit area under a unit gradient of concentration. When the concentration is measured per unit volume it has the dimensions (c.g.s.) $cm^2 sec^{-1}$.

The unit of Permeability, denoted by P, is defined as the number of cubic centimetres of gas, measured at N.T.P., flowing per second through an area of one square centimetre and thickness one millimetre across which is a pressure difference of one centimetre of mercury.

It is evident that the diffusion coefficient, defined in terms of a concentration gradient, and the permeability, defined in terms of a pressure gradient are related to each other through the solubility, at least for homogenous systems in which the diffusion process occurs without hysteresis.

By defining a solubility coefficient this relationship takes a particularly simple form in ideal cases. Barrer (4) defined the solubility coefficient S as the number of cubic centimetres of gas, measured at N.T.P., that will dissolve in one cubic centimetre of a substance when the pressure of the gas is one centimetre of mercury.

If both Fick's law+ and Henry's law are obeyed by a system then D and S are constants at constant temperature so that

$$P = 10\,DS \qquad \text{-----}\ 1$$

Equation 1 can readily be tested in two ways:

i) Measure P and S separately, a rate and an equilibrium experiment, over a range of pressures. If both are independent of pressure equation 1 is valid and can be used to calculate D.

ii) Measure P and D over a range of pressures. If both are independent of pressure equation 1 is valid and can be used to calculate S.

Both P and D can be obtained from a single rate experiment, by a method introduced by Daynes (5) and later generalised by Barrer (6), accordingly method ii) has greater experimental simplicity and is to be preferred. Of

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+ $\partial c/\partial t = D\nabla^2 c$, constant D.

course the value of S obtained in this way may advantageously be compared with the value derived from equilibrium experiments.

Polymer-gas and polymer-vapour diffusion systems may be divided into two classes: those which obey the equation $P = 10\ DS$ and those which do not (i.e. those for which both Henry's law and Fick's law hold and those for which one or the other or both fail).+

Systems which obey the equation $P = 10\ DS$

These include most gas-polymer systems that have been studied. The earlier investigations were mainly devoted to the study of the permeation of hydrogen, helium, and the atmospheric gases through rubber and rubber-coated membranes (7), (8).

Barrer (8) greatly extended these observations by measuring permeation rates through synthetic rubbers and other high polymers such as Bakelite, Cellophane, and Polythene. The gases used included He, H_2, Ne, and N_2. Two important trends were shown by his results:

\+ This classification is slightly different from that of Barrer, who divided systems into those which do, and those which do not, obey Fick's law (assuming a constant diffusion coefficient), the reason for the more restrictive classification given here is that the validity of Fick's law is not a sufficient condition for the validity of Hnery's law. Even although (as eq. 26, ch. I shows) the most general diffusion equation takes account of variations in the solubility coefficient these may happento be exactly cancelled by opposing variations in the mobility, leaving D constant. This is the case in certain gas-zeolite systems (7).

i) The more 'permanent' gases have lower permeabilities by virtue of smaller solubilities.

ii) The magnitude of the diffusion coefficient varies inversely with the size of the diffusing gas molecules.

Barrer was able to show in addition that the diffusion process in these systems is an activated one. The logarithm of the diffusion coefficient or permeability is proportional to the reciprocal of the absolute temperature. Values of the energy of activation for diffusion and permeation were derived and analysed in the light of molecular theories for the diffusion process.

Van Amerongen (9) has investigated similar systems. In general his results confirm those of Barrer. He has reached, in addition, two important conclusions.

i) The solubility of a gas in a polymer can be expressed quantitatively in terms of its critical temperature T_c (a measure of its 'permanent' character) by an equation of the form $\log S = a+bT_c$, where a and b are independent of the gas.

ii) Over wide ranges of temperature there are slight but definite departures from the relationships $D = D_0 \exp - E_D/RT$ and $P = P_0 \exp - E_P/RT$ found to hold by Barrer.

Barrer and Skirrow (10) ha~~s~~ measured the permeability, diffusion, and solubility of N_2, methane, ethane, propane and butane in rubber membranes having different amounts of combined sulphur. They found:

i) The diffusion constant falls as the % vulcanisation increases

ii) The diffusion constant falls as the molecular size of the diffusing molecule increases.

iii) The energies of activation for diffusion and permeation increase as the % vulcanisation increases.

iv) The conclusions i) and ii) of van Amerongen apply to these systems also.

Systems which do not obey the equation $P = 10 DS$

These are not only extremely numerous but also diverse. Attention is confined here to vapour-polymer systems.

In the vapour-polymer systems studied there are large deviations from Fick and Henry's laws. The results obtained are briefly reviewed.

Taylor, Hermann and Kemp (11) measured the permeability of rubber membranes to water vapour. They calculated the concentration gradient, in the steady state, across the membrane and found it to be far from linear. About the same time Daynes (12) on the basis of his own work, and that of Lowry and Kohman (13) on the same system, found the same thing. Daynes suggested that an osmotic gradient, viz. a gradient of the relative humidity, should replace the concentration gradient used to calculate the diffusion coefficient. He showed that the principal predictions based on this suggestion were borne out by the available evidence; and he noted the desirability of measuring the diffusion coefficient over a wide range of pressures.

Since the war King has made a careful study of the absorption of water, methyl alcohol, and ethyl alcohol, by wool and horn keratin (14) and of the permeability of horn keratin membranes to water vapour (15). From the latter observations he determined the variation of D with concentration. In none of the systems King investigated was the variation of activity with concentration - determined from equilibrium absorption isotherms - sufficiently large to account for the variation of diffusion coefficient with concentration.

The diffusion of water vapour through films of nylon and polythene has been investigated by Rouse (16) using the steady state methods developed by King (15) and Barrer (17) (see chap. I). For the diffusion through nylon he found that the diffusion coefficient increased with concentration. This, he suggested, was due to the greater ease of mobility of the diffusing molecules as the degree of swelling is increased. King's explanation (15) of this same phenomenon was that at higher concentrations the water molecules are held on sites of lower energy because the high energy sites are first occupied. For the water-vapour polythene system Rouse found that the diffusion coefficient decreased with increasing concentration and the permeation behaviour was similar to that observed by Lowry and Kohman in the rubber-H_2O system. Rouse concluded that the same mechanism operates in these two systems.

More recently Crank and Park (18) have measured the rates of absorption and desorption of chloroform by polystyrene. The diffusion coefficient was found to increase rapidly with concentration. Making use of the Crank and Hartley procedure, described in Chap. I, the diffusion coefficient-concentration relationship was derived from the sorption-time curves. Over the range studied D varied almost 300-fold.

Duffusion into highly polar oriented polymers has been studied by Hartley (19). Such systems exhibit distinctive and, as far as this investigation is concerned, anomalous features which lie outside the scope of this thesis.

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CHAPTER III

It is clear that in order to understand the reasons for the deviations from Fick and Henry's laws described in the last chapter it is very necessary to know what kind of deviations to expect for the equilibrium solubility. These deviations can be most pronounced for high polymer solution, even at low concentrations. Fortunately, in the last two decades, gifted experimental and theoretical investigators have accounted in a large measure for these deviations, and have presented equations by which their magnitude may be calculated. These topics are now reviewed.

The Distinction between Ideal and Non-Ideal Solutions

A solution is called ideal if it obeys Raoult's law. If, that is, there is a direct proportionality between the partial vapour pressure and the mole fraction for all species in solution.

Thus, for an ideal solution $p_i/p_i^o = N_i$ for all i. Since p_i/p_i^o, or more strictly f_i/f_i^o where f is the fugacity, is equal to the activity a_i of species i it follows that $a_i = N_i$ for an ideal solution. In a solution which is not ideal one can write

$$a_i = \gamma_i N_i \qquad \text{-----} \ 1$$

where γ_i is called the activity coefficient.

It can be shown from thermodynamics (1) that there is no change in volume, nor emission or absorption of heat in changing the concentration of an ideal solution. Statistical mechanics indicates a further condition necessary for ideality. That is, the size of the molecules should not differ greatly.

The quasi-crystalline lattice model

The conditions for ideality described above are not fulfilled by solutions of monomeric solutes in high polymers. Accordingly such solutions show departures from Raoult's law. Many of the theoretical equations that such solutions do ~~apply~~ obey have been derived by the use of the quasi-crystalline lattice model. In this model it is supposed that the molecules of the solution are arranged at random and close together in the points of a crystalline lattice such that, although the system is not completely ordered, the degree of randomness is much less than that of the molecules in a gas. If the molecules, species 1 and 2, are so arranged on a lattice it can be shown that the entropy increase on mixing n_1 molecules of species 1 with n_2 molecules of species 2 is given by

$$\Delta s^m = -k(n_1 \ln N_1 + n_2 \ln N_2) \qquad \text{-----}\ 2$$

Where $N_1 = 1 - N_2 = \frac{n_1}{n_1 + n_2}$; and k is the Boltzmann constant. Equation 2 implies that there is no heat or volume change on mixing. It is valid for ideal binary systems of molecules having approximately equal size.

The Flory-Huggins Equation

In making use of the quasi-crystalline lattice model for solutions of high polymers the foregoing treatment cannot apply for the size of the polymer molecules greatly exceeds that of the solvent. It is possible however to regard the polymer as consisting of a large number of segments, corresponding generally to the monomeric units of which it consists. These units can then be assigned singly to the lattice sites and the entropy calculated by enumerating the possible number of ways in which these segments can be arranged. Such calculations have been made by Flory (2) and Huggins (3) using slightly different methods of approach.

Consider the successive additions of polymer molecules to the bare lattice. Let the fraction of sites occupied by the first n_i polymer molecules be given by

$$i = \frac{xn_i}{n_1 + xn_2} \qquad \text{------ } 3$$

where x is the number of segments per polymer molecule, and $n_1 + xn_2$ is the total number of lattice sites. The number available for the first segment of the next polymer molecule is $(1 - i)(n_1 + xn_2)$, and $z(1 - i)$ will be available for the second if z is the co-ordination number of the lattice. $(z - 1)(1 - i)$ are then available for the third segment. At this stage the distinction between the Flory and Huggins treatment arises. Flory neglects complications arising out of the possibility of the polymer molecules being so arranged that the sites available to segments of any one polymer molecule are reduced because of some sites are already occupied by segments of the same molecule. For succeeding polymer segments he takes the number of available sites to be $(z - 1)(1 - i)$.

The number of possible configurations ν_i of the $(n_i + 1)$ polymer is thus found to be

$$\nu_i \simeq \tfrac{1}{2} \cdot (1 - i)^x (n_1 + xn_2)(z - 1)^{x-1} \quad \text{---- } 4$$

and the total number of configurations of the system is given by

$$W = \frac{1}{(n_1 + xn_2)!} \prod_{n_i = 0}^{n_2 - 1} \nu_i \quad \text{---- } 5$$

The entropy is given by $S = k\ln W$. Making use of Stirling's approximation $\ln N! = N\ln N - N$ one finds

$$-\Delta S = k\left(n_2 \ln \frac{n_1}{n_1 + xn_2} + n_2 \ln \frac{n_2}{n_1 + xn_2}\right)$$

$$+ k(x - 1)n_2 \left\{\ln(Z - 1) - 1\right\} - kn_2 \ln n_2 \qquad \text{-----} \; 6$$

correcting for the configurational entropy of the polymer alone this reduces to

$$-\Delta S^m/k = n_1 \ln v_1 + n_2 \ln v_2 \qquad \text{-----} \; 7$$

Where v_1 and v_2 are the volume fractions of solvent and polymer respectively. From equation 7 the partial molar entropies of mixing - the entropies of dilution - can be found by differentiation.

$$\Delta \bar{S}_1 = R\left[\ln \frac{1}{v_1} - v_2\left(1 - \frac{1}{x}\right)\right] \qquad \text{-----} \; 8$$

$$\Delta \bar{S}_2 = R\left[\ln \frac{1}{v_2} + v_1 (x - 1)\right]$$

In the analysis of Huggins the corresponding expression for ΔS_1 is given by

$$\Delta \bar{S}_1 = R \ln \frac{1}{v_1} + \frac{1}{2} Z'\left(1 - \frac{1}{x}\right) \ln\left(1 - \frac{2v_2}{Z'}\right) \qquad \text{-----} \; 9$$

where $Z' \simeq Z$.

The Calculation of the Heat and Free energy of Mixing

No account has been taken, in the derivation just described, of the interaction energies between solvent and polymer:, which, if they exist, will lead to preferred non-random configurations on the lattice sites. Calculations of the configurational entropy in such cases have been made by Orr (4), and also by Guggenheim (5). The corrections introduced by this, much more complicated, procedure are not large in practice for non-polar systems. They can be considered as an entropy contribution to the heat of mixing expression now to be derived.

Let w_{11}, w_{22} and w_{12} represent the energies per molecular pair of solvent-solvent, polymer-segment-polymer segment, and solvent-polymer-segment respectively.

The energy increase in making a 1-2 contact is

$$\Delta w_{12} = w_{12} - \tfrac{1}{2}(w_{11} + w_{22}) \qquad \text{-----} \ 10$$

The heat of mixing will be given by

$$\Delta H^m = \Delta w_{12} P_{12} \qquad \text{-----} \ 11$$

where P_{12} is the number of 1-2 contacts in solution. The total number of contacts per polymer molecule will be $(Z - 2)x$ plus 2 additional ones for the ends. Approximately $(Z - 2)\,x + 2 = Zx$ and hence the total number of 1-2 contacts in solution is $Zx.n_2v_1 \equiv Zn_1v_2$ so that the heat of mixing becomes

$$\Delta H^m = Z\Delta w_{12} n_1 v_2 \qquad \text{-----}\ 12$$

Because the heat of mixing is required to take account of the deviations from random configurations due to the interactions equation 12 may be written more generally as

$$\Delta H^m = kT\mu n_1 v_2 \qquad \text{-----}\ 13$$

where $\mu = \frac{Z\Delta w_{12} x_1}{kT}$ if these deviations are ignored.

The Free energy of mixing is obtained from equations 13 and 7 as

$$\Delta G^m = kT[n_1 \ln v_1 + n_2 \ln v_2 + \mu\, n_1 v_2] \qquad \text{-----}14$$

Differentiation of this equation with respect to n_1 leads to the partial molar free energy of mixing - the free energy of dilution.

$$\Delta \bar{G}_1 = \mu_1 - \mu_1^o = RT[\ln(1-v_2)+(1-\tfrac{1}{x})v_2 + \mu v_2^2] \qquad \text{-----}\ 15$$

This expression is referred to as the Flory-Huggins equation. From it one can derive the vapour pressure equation of the system.

$$\frac{\Delta \bar{G}_1}{RT} = \ln a_1 \simeq \ln \frac{p_1^m}{p_1^0} \simeq \ln(1-v_2)+(1-\frac{1}{x})v_2 + \mu v_2^2 \qquad \text{-----}\ 16$$

For large values of x and at low solvent concentrations this equation reduces to

$$a_1 \simeq \frac{\overset{m}{p_1}}{p_1^{o}} \simeq v_1 \exp(1+\mu) \qquad \text{-----} \; 17$$

$$\text{or} \quad \frac{a_1}{v_1} = \gamma_1 = \exp(1+\mu)$$

where γ is the activity coefficient, and $\exp(1+\mu)$ is the limiting Henry's law constant in volume fraction units.

Comparison of Experiment with Theory

The solubilities of the permanent gases in high polymers are very small, and so are the heats of dilution. Henry's law is obeyed and equation 17 is valid (6).+

Experimental determinations of the thermodynamic properties of polymer-liquid and polymer-vapour systems are numerous. Free energies of dilution have been calculated from vapour pressure, swelling pressure, and osmotic pressure measurements. Heats of dilution have been calculated from the effect of temperature on these characteristics, and also from direct calorimetric measurements.

A complete test of the theory has only been made for the system natural rubber-benzene, studied comprehensively by Gee and his collaborators Treloar and Orr (7), (8). For

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\+ With modifications appropriate to conditions under which measurements are made. Above the critical temperature p_1^{o} loses its meaning.

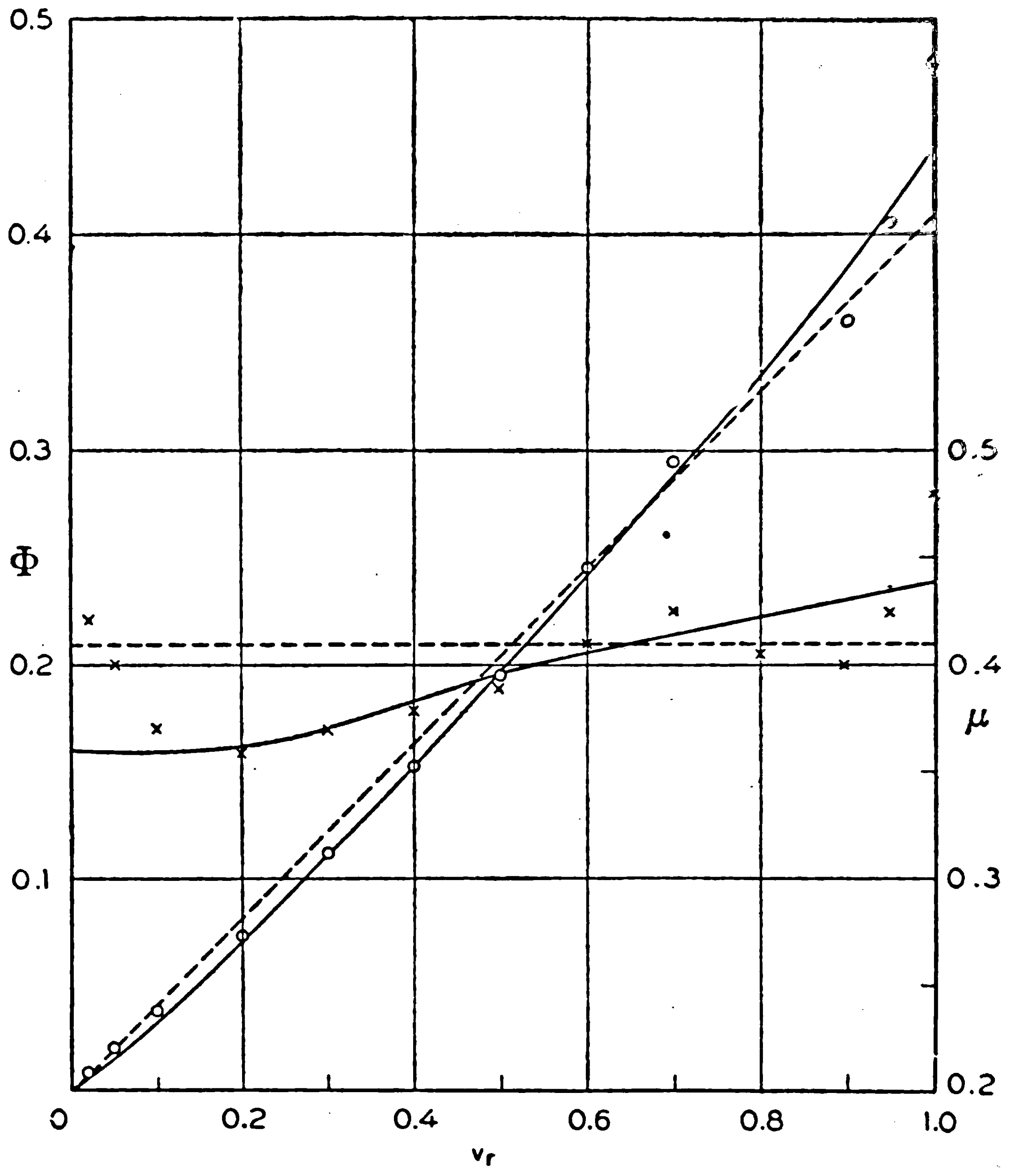

Fig. 1. Application of the Flory-Huggins Equation to the System Benzene-Rubber (7).

this system, in which there is a negligible volume change and emission of heat on mixing, the theory has been notably successful. The parameter μ of equation **15** scarcely varies at all over the entire concentration range (see Fig. 1). This constancy is better even than could be expected for, as Gee has pointed out (9), the agreement between theory and experiment for the heats of dilution are less satisfactory. The success of the Flory-Huggins equation arises out of a compensation of errors in $\Delta \bar{S}_1$ and $\Delta \bar{H}_1$.

For other systems experimental measurements have been less detailed, and there are larger discrepancies between experiment and theory. Nevertheless the latter is fairly successful for non-polar systems and μ varies little with concentration - except at high solvent concentrations. Within these limitations the theory of high polymer solutions described in this chapter has been of considerable utility in understanding polymer-solvent interactions.

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CHAPTER IV

The diffusion coefficient and the mobility are related in this chapter to parameters necessitated by the conception of the diffusion process in terms of random molecular motions. The means by which particular molecular diffusion mechanisms may be interpreted are outlined. Models for the diffusion process in high polymers are described and used to illustrate these means.

Diffusion as a molecular process

The thermodynamic interpretation of the diffusion coefficient given in chapter I is not completely satisfactory, because it relates diffusion to the individual motions of the molecules through the use of the idealised concepts of a driving force and a frictional force experienced by a molecule. The average velocity per molecule is equated to the product of the driving force and the velocity per unit frictional force, or mobility

$$v = -\frac{1}{N}\frac{\partial \mu}{\partial x} \cdot B \qquad \text{----- } 1$$

so that the flow, $P = vc$, is given by

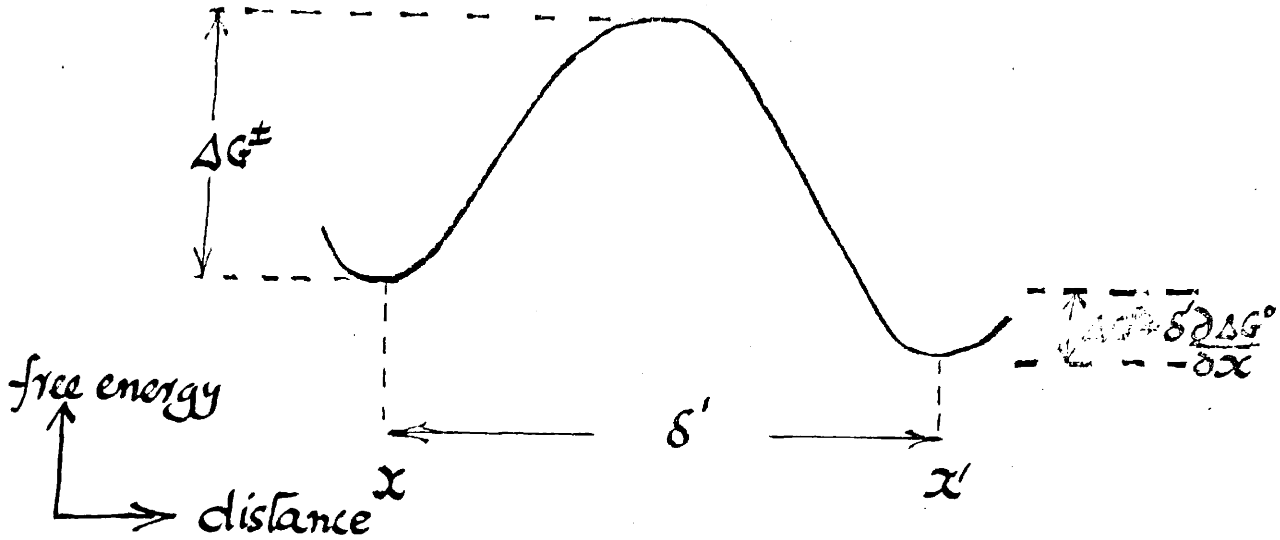
$$P = -D\frac{\partial c}{\partial x} = -kTB\left(1 + \frac{\partial \ln\gamma}{\partial \ln c}\right)\frac{\partial c}{\partial x} \qquad \text{----- } 2$$

How is the mobility to be interpreted? In the molecular kinetic interpretation diffusion is supposed to occur as the result of random jumps of the molecules. These jumps are specified by the values the jump length δ and frequency $1/\tau$.

In a gas the jumps correspond to the mean free paths of the gas molecules between collisions, and the frequency of collisions is given directly by the ratio of the mean path length to the mean molecular velocity. In a simplified treatment the molecules are hard spheres moving outside of any force field.

In solids and liquids the molecules are so close together that such a simplification is out of the question. However the frictional resistance to molecular motion is to be comprehended in the molecular force fields in which displacements occur: these forces are exerted over short ranges, and they are discontinuous; and, rather than try to define a mean molecular mobility in terms of them and the mean displacement lengths and frequencies, it is more convenient to abandon the concept of mobility for the present and to treat diffusion in terms of the parameters themselves.

1. Ideal Systems (1)



Consider the flow of molecules between x and x' a distance δ' apart between which there is an energy barrier arising out of the intermolecular forces. Let δ be defined as the x component of the root mean square jump length, and $1/\tau$ the mean frequency of such jumps.

The net flow across the energy barrier is the difference between the flows in the positive and negative directions, and is given by

$$J = \frac{\delta c}{2\tau} - \frac{\delta c'}{2\tau} \qquad ----- 3$$

where c and c' are the average concentrations at x and x' and the factor 2 is on account of the fact that, on the average, half the molecules will jump to the right and half to the left.

Now because δ is small

$$c' = c + \delta \frac{\partial c}{\partial x} \qquad \text{----- } 4$$

so that

$$J = - \frac{\delta^2}{2\tau} \frac{\partial c}{\partial x} \qquad \text{----- } 5$$

A comparison with Fick's law shows that

$$D = \delta^2/2\tau \qquad \text{----- } 6$$

2. Non-ideal systems

In the derivation just given the mean velocity $\delta/2\tau$ has been assumed to be independent of concentration. This is an obviously undesirable restriction for non-ideal systems.

Referring to the diagram one sees that if this restriction is removed one must take account of the different values of τ at x and x'. δ may also of course be dependent on concentration, so that its value will vary with x. In the derivation to be given the value of δ is plausibly assumed to be the same for positive displacements from x, as it is for negative displacements from x'.[+]

[+] Ogston (2) has derived an equation for the diffusion coefficient in which the variation of the mean displacement length δ with concentration leads to a term $\frac{\partial \ln \delta}{\partial \ln c}$, in addition to one accounting for the variation of $1/\tau$ with concentration. This additional term has no analogue in the thermodynamic derivation.

Accordingly one may write for the net flow across the energy barrier

$$J = \frac{\delta}{2\tau_{+}} c - \frac{\delta}{2\tau'_{-}} c' \qquad \text{----- } 7$$

where τ_{+} is the mean positive jump frequency from x, and τ'_{-} is the mean negative jump frequency from x'. Since $c' = c + \delta\frac{\partial c}{\partial x}$, and $\frac{1}{\tau'} = \frac{1}{\tau} + \delta\frac{\partial 1/\tau}{\partial x}$

$$J = -\frac{\delta c}{2\tau}\left(\frac{\partial \ln c}{\partial x} + \frac{\partial \ln 1/\tau}{\partial x}\right) \qquad \text{----- } 8$$

$$= -\frac{\delta^2}{2\tau}\left(1 + \frac{\partial \ln 1/\tau}{\partial \ln c}\right)\frac{\partial c}{\partial x} \qquad \text{----- } 9$$

From equation 9 it is apparent that

$$D = \frac{\delta^2}{2\tau}\left(1 + \frac{\partial \ln 1/\tau}{\partial \ln c}\right)$$

which is to be compared with the corresponding thermodynamic equation

$$D = BkT\left(1 + \frac{\partial \ln \gamma}{\partial \ln c}\right) \qquad \text{----- } 10a$$

That there is a correspondence between the terms $\frac{\partial \ln 1/\tau}{\partial \ln c}$ and $\frac{\partial \ln \gamma}{\partial \ln c}$ may be shown by use of the absolute reaction rate theory (see later) to calculate $1/\tau_{+}$ and $1/\tau'_{-}$. Using this theory it may be shown (2) that $\partial \ln 1/\tau / \partial x = \frac{1}{RT}\frac{\partial G^{\circ}}{\partial x}$ Where G° is the Gibb's free energy in the standard state at unit concentrations; so that $\frac{1}{RT}\frac{\partial G^{\circ}}{\partial x} = \frac{\partial \ln \gamma}{\partial \ln x}$.

Hence $\frac{\partial \ln \gamma}{\partial \ln c} = \frac{\partial \ln 1/\tau}{\partial \ln c}$.

The Effect of Temperature on the Diffusion Coefficient

The frequency, $1/\tau$, is clearly going to be temperature-dependent and will contain an exponential energy term, since only molecules which have acquired an activation energy can be expected to jump to a new position.

Let $$1/\tau = \frac{kT}{h} \exp \Delta G^{\pm}/RT \qquad \text{----- 11}$$

$$= \frac{kT}{h} \exp^{-} \frac{\Delta H^{\pm}}{RT} \exp + \Delta S^{\pm}/R \qquad \text{----- 12}$$

Then

$$D = \frac{\delta^2}{2}\frac{kT}{h} \exp - \Delta H^{\pm}/RT \exp \Delta S^{\pm}/R. \qquad \text{----- 13}$$

where $\Delta S^{\pm}$, $\Delta H^{\pm}$, and $\Delta G^{\pm}$ are called respectively the entropy, enthalpy, and free energy of activation. (3)

It is an experimentally known fact that for many diffusion systems the effect of temperature on the diffusion coefficient obeys, to a high degree of approximation, the equation $D = D_0 \exp - E_a/RT$, Where D_0 is a constant and E_A is called the energy of activation. Identifying this experimental energy of activation with $\Delta H^{\pm}$ in equations 12 and 13 provides a method whereby the entropy of activation may be calculated. This latter quantity is useful in arriving at the diffusion mechanism.

Barrer (4) has calculated the entropy increase for the diffusion of inert gases into several synthetic rubbers assuming plausible values for δ . He obtained values much greater than would correspond to the entropies of solution; and he therefore concluded that the medium must share in the entropy change. This is consistent with the 'hole' theory of diffusion in polymers, in which it is supposed that the diffusing molecules pass through the medium via holes which arise out of spontaneous thermal fluctuations of the polymer segments among the points of a quasi-crystalline lattice (chapter III). The movement of these 'holes' will require a considerable loosening of the quasi-crystalline structure and so lead to large, positive, entropies of activation.

The Absolute Reaction Rate Theory (3)

In this theory diffusion is assumed to be the result of a large number of unit diffusion steps in which the unit molecule, 'hole', or group of molecules, jumps from one position to the next on acquiring an energy, $\Delta H^{\ddagger}$ in a single vibrational co-ordinate lying along the direction of the jump.

Having acquired this energy, vibration in this co-ordinate is converted into translation. The quantity

$\exp \Delta G^{\ddagger}/RT$ represents the ratio of the partition functions of the unit diffusion systems with this vibrational frequency missing in the activated state (hence the factor kT/h in equations 11-13) to the partition function in the ground state.

The Zone Theory of Diffusion (5)

This is an alternative description to the absolute reaction rate theory. Instead of requiring the energy of activation for the unit diffusion step to be concentrated, at least formally, in a single degree of freedom; it is assumed to be distributed among several degrees of freedom within the microscopic region constituting the diffusion zone. The rate determining process in this theory is the rate at which these zones become activated.

Let the total system be divided into N_Z regions potentially capable of becoming diffusion zones, and let n denote the number of degrees of freedom in each of these zones. If the energy of activation E_a must be distributed among f degrees of freedom for the diffusion step to occur, then the chance that any one zone is activated is given by

$$\frac{\sum N}{N_Z} = \exp - E_a/RT . \sum_{f=1}^{f=n} \left(\frac{E_a}{RT}\right)^{f-1} \frac{1}{(f-1)!} \qquad \text{----- } 14$$

where $\sum N$ is the number of activated zones.

The frequency for the unit diffusion process is obtained by multiplying the quantity $\sum N$ by $1/T_0$, tthe vibrational frequency of the diffusion unit, since at all times this is located within one of the N_z regions. The summation in equation 14 may be replaced by its largest term, a simplification that is justified when $E_a \gg fRT$, which is the case for the 'hot' zones which alone contribute to the diffusion process. Hence the expression for the frequency of the unit diffusion process is

$$1/\tau = 1/\tau_0 \exp - E_a/RT \left(\frac{E_a}{RT}\right)^{f-1} \frac{1}{(f-1)!} \qquad \text{----- } 15$$

τ is related to D through the equation

$$D = \delta^2/2\tau \qquad \text{----- } 16$$

A value for the vibrational frequency of the diffusing unit is generally taken as equal to the mean vibrational frequency of the diffusing molecules.

For certain diffusion models (4), e.g. those involving Schottky or Frenkel defect mechanisms, the R.H.S. of equation 14 and 15 are to be multiplied by a quantity which measures the probability that the diffusing species is in a microscopic environment appropriate to the particular mechanism. This probability is unity for direct substitution, and at low solute concentrations, zeolitic and interstitial solution mechanisms. For Schottky and Frenkel processes it is the ratio of the number of defects to the total number of molecules in the system.

Barrer, who developed the zone theory of diffusion has applied it to gas-polymer systems to calculate the number of degrees of freedom necessary to give values of δ of expected molecular magnitude - assuming a reasonable value for the vibrational frequency of the diffusing molecules (7).

Skirrow (6) has also applied this same procedure to his results on the diffusion of hydrocarbon gases through vulcanised rubbers. In his experiments, as noted in chapter II, the equation $D = D_0 \exp - E_a/RT$ was found not to be obeyed. This is to be expected on the basis of the zone theory whenever the number of zones taking part in the unit process is greater than one; and it enables one to calculate f from the variation of E_a with temperature. The values for f calculated by Skirrow in this way were in fair agreement with those calculated by the previously mentioned method. This agreement lends weight therefore to the guessed values assigned to δ and $1/T_0$ in Barrer's original method. In all of these experiments of Barrer and Skirrow on polymer diffusion, values of f between about 10 and 40 were obtained. One may conclude that a zone of considerable size is required for diffusion; a conclusion in harmony with that based upon an absolute reaction rate theory treatment, and in conformity with the 'hole' theory of diffusion in polymers.

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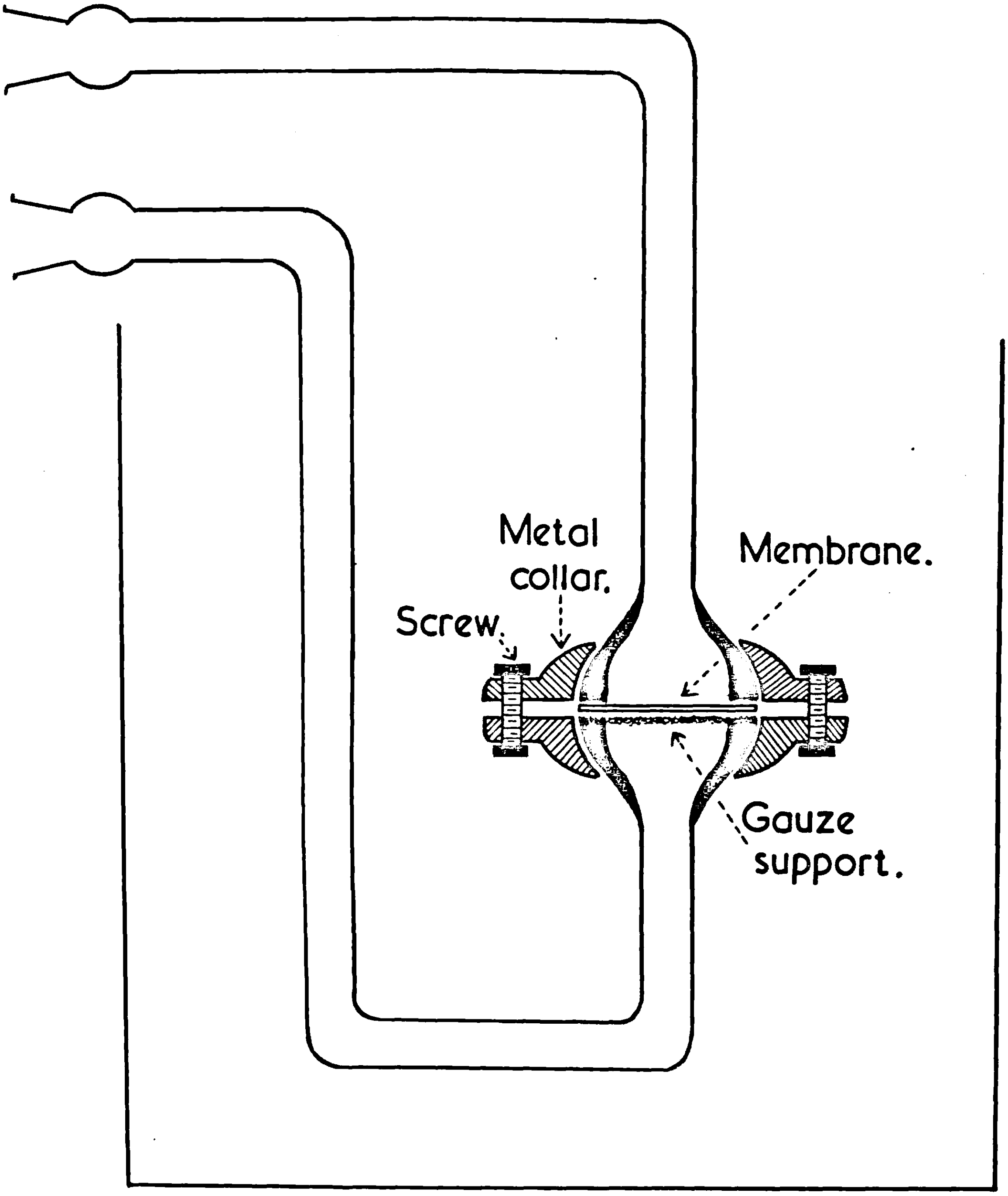

Fig. 1. Diffusion Cell

CHAPTER V

In this chapter are described, the experimental techniques used in this investigation to measure the permeation rates of benzene vapour through films of natural rubber and of polythene, the methods employed to measure the equilibrium amounts of benzene absorbed by these same materials over a range of pressures,and finally the sources and description of the polymers, and the purification procedures and physical properties of the benzene used.

Measurement of Permeation Rates

The Diffusion Cell

This is illustrated in fig. 1 and consisted of the polymer membrane placed across the interface separating two Pyrex pipeline joints securely clamped together by means of flanged metal collars. The membrane was supported on the low pressure side by a metal gauze disc to prevent distortion. The entire diffusion cell was placed in a deep cylindrical copper vessel just wide enough to contain it and this was immersed in a thermostatically controlled water bath. The cell was connected to the rest of the apparatus by ground glass joints so that it could easily be dismantled.

Benzene vapour was admitted to the ingoing side of the

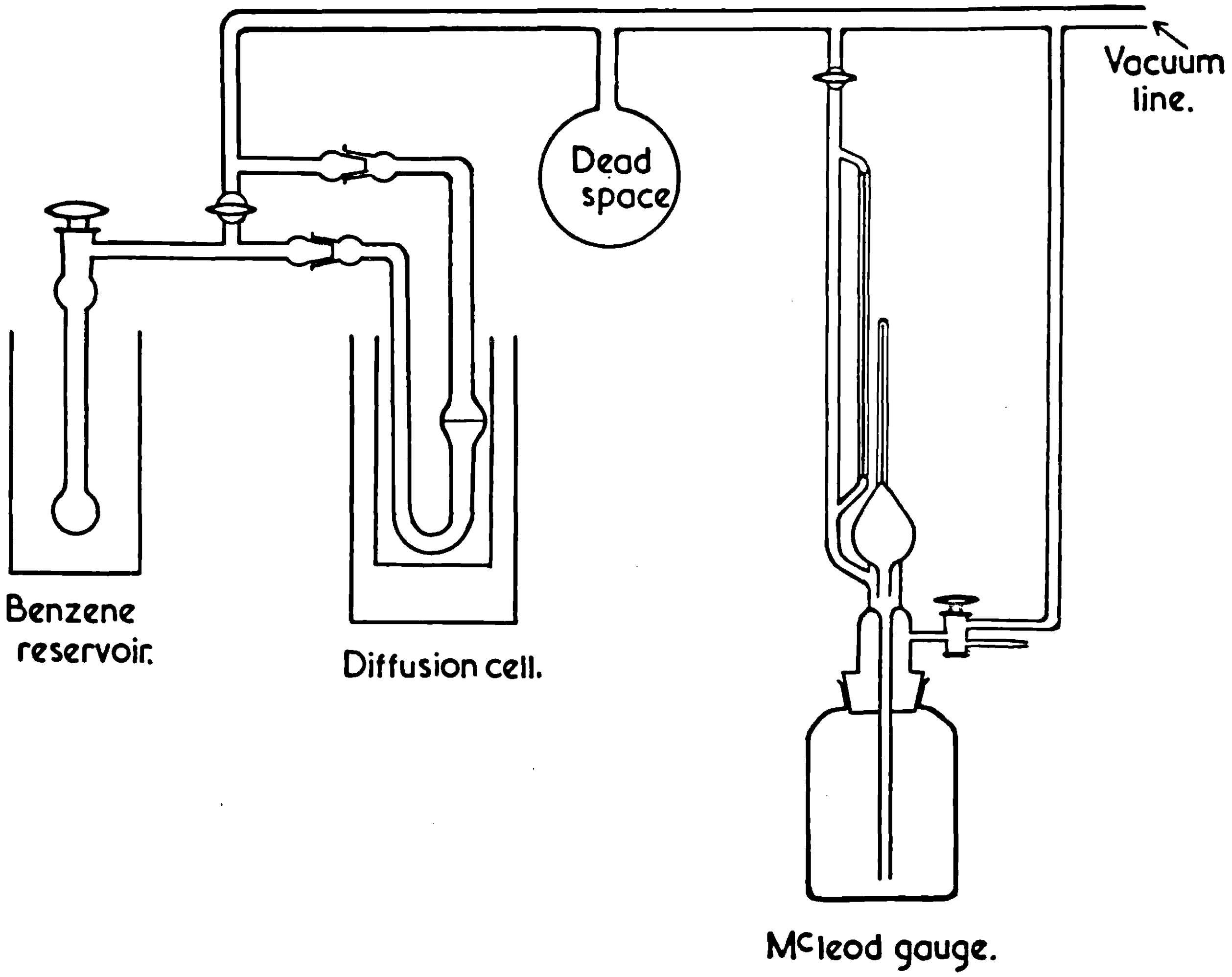

Fig. 2. Complete Diffusion Apparatus

membrane from a small reservoir of liquid benzene. This was immersed in a thermostat so that the vapour pressure of the liquid remained constant. The pressure of the vapour which diffused through was measured as a function of time. The volume of the outgoing side was made large compared with the flow rate so that at all times the pressure across the membrane was determined only by the vapour pressure of the benzene in the reservoir. The complete apparatus is illustrated in fig. 2.

The M^{c}Leod Gauge

In its usual form the M^{c}Leod Gauge is unsuitable for the measurement of vapour pressures because of their non-ideal behaviour on compression. In the modification used here this difficulty was overcome by heating the capillary in which compression takes place to a temperature at which the non-ideality becomes negligible. From the nomograms of Lewis (1) it is evident that, at the pressures used, 100°C is a sufficiently high temperature. It was obtained electrically by surrounding the capillary with a narrow glass cylinder on which was wound nichrome wire. The exact temperature obtained with this device varied from day to day depending on the room temperature. A small thermometer within the cylinder provided a means of determining the temperature accurately so that corrections could be made.

Careful calibration of the gauge used this way showed that the method gave accurate results.

Thermostat Temperature Control

Both thermostats consisted of insulated cylindrical copper tanks filled with water and heated by electric elements clamped to their base. The water was stirred by electrically driven motors, and the temperature regulated by 'Sunvic' bimetallic relays. Regulation was to within 0.1°C.

Method of Operation

The membrane and the benzene were first completely degassed. The former by evacuating both sides of the diffusion cell, with the water in the thermostat at a temperature of 80-90°C; and the latter by repeatedly connecting the limb containing the benzene to the vacuum pump, after freezing the benzene with a solid carbon dioxide-acetone mixture, then closing the stopcock and allowing the benzene to melt.

The system was checked for freedom from leaks, benzene vapour was then admitted to the ingoing side of the membrane and the time noted. The pressure on the outgoing side was measured by means of the M^cLeod gauge at suitable time intervals. Initially the flow rate is a function of time, but when the steady state is reached the flow rate

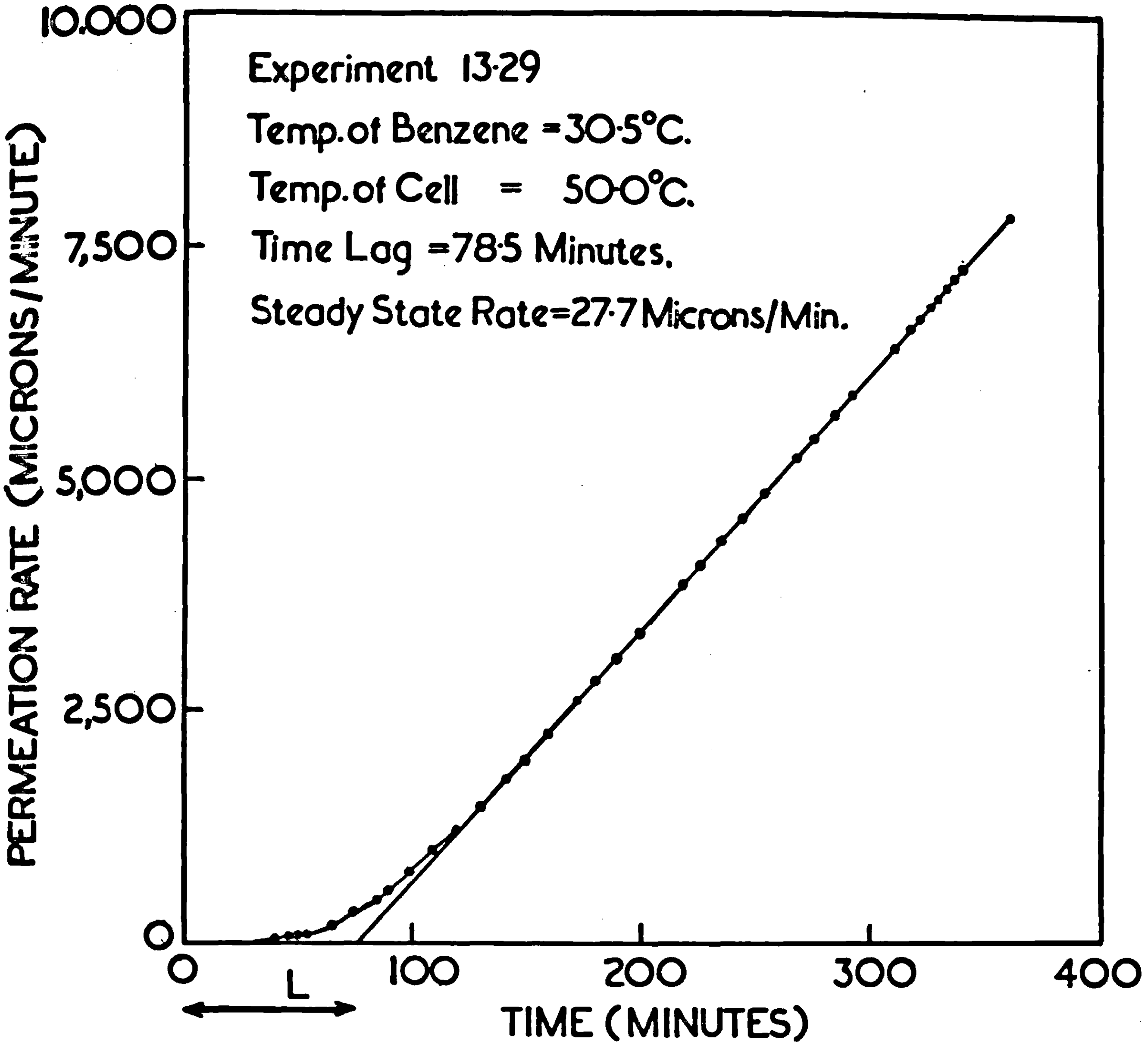

Fig. 3. Permeation Rate Curve

becomes constant.

Fig. 3 shows a typical permeation rate curve. The steady state Permeation Rate (S.S.R.) - the slope of the linear portion of the curve, and the Time Lag (L) - the intercept on the time axis of the linear portion, provided the experimental data from which calculations have been made.

The Measurement of the Equilibrium Vapour Pressures of Vapour-Polymer Mixtures

The apparatus designed and used for this purpose was a modified version of that used by Gee and Treloar (2). It consisted (see fig. 4) of a bulb containing the polymer connected by an antisplash head (which prevents mercury from getting into the bulb) to a manometric device, which was in turn connected to a tube containing liquid benzene and also to a vacuum line.

The whole apparatus was immersed in a large, water filled, insulated copper tank. The inside of the tank was painted white and brightly illuminated. In one side was a window, making it possible to see the positions of the menisci in the manometer tubes and the benzene meniscus in the benzene reservoir tube. The tubing used was 'Veridia' constant bore capillary of internal diameter 4 mm. The heights of the menisci were measured with the aid of a cathetometer. The water in the tank was stirred and heated electrically, and the temperature was controlled to within

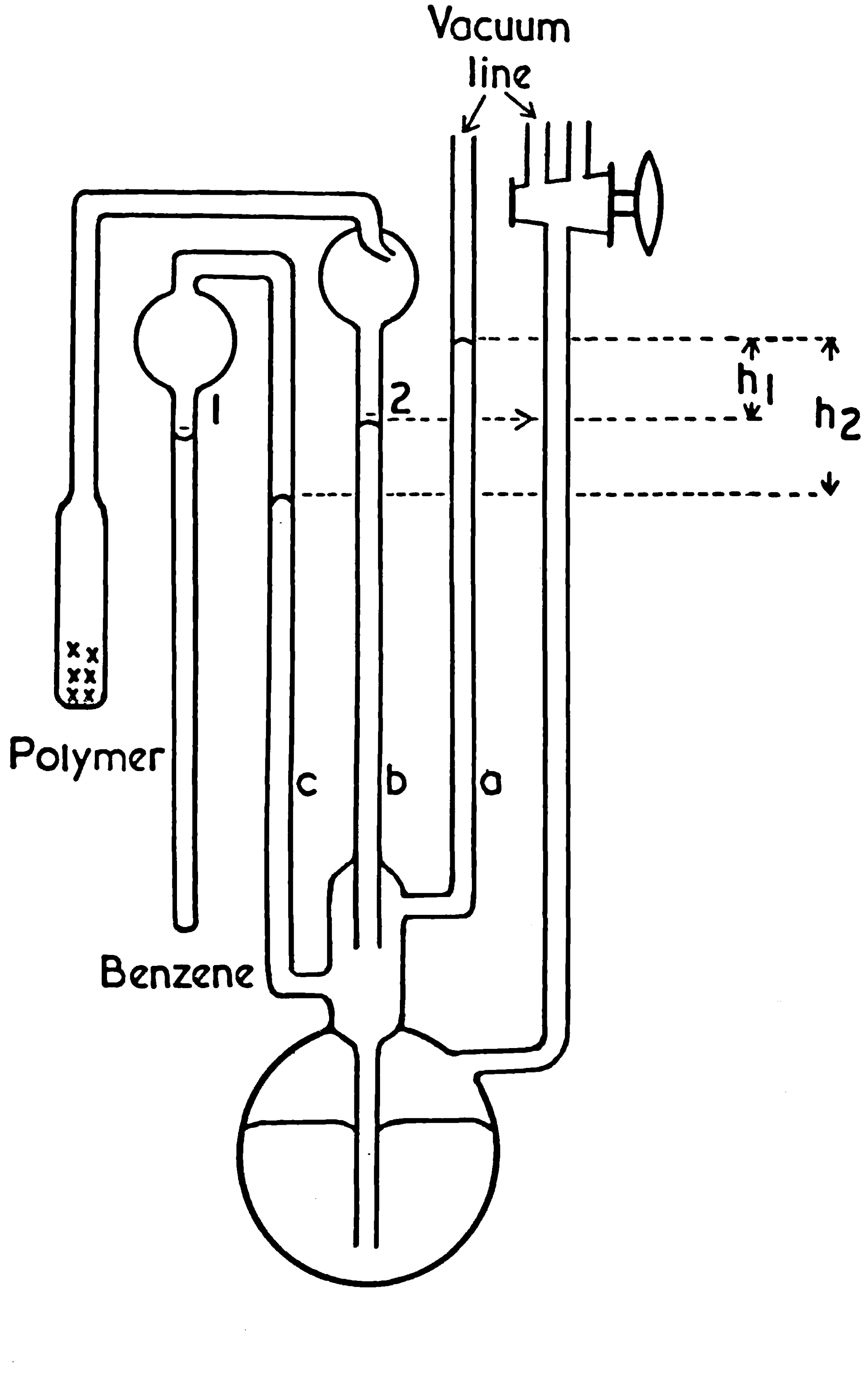

Fig. 4. Equilibrium Vapour Pressure Apparatus

0.1°C of a specified value by a mercury-toluene thermoregulator.

Method of Operation

Thorough degassing procedures, as described for the permeation apparatus with appropriate modifications, were first carried out. With the mercury at arbitrary levels in columns a, b, and c, the vapour pressure of the benzene was determined from the measured difference in heights of the menisci in columns b and c. That the polymer was completely degassed was checked by comparing the mercury levels in columns a and b.

Next the height of the benzene meniscus relative to fixed mark (1) was measured with the benzene at 10°C, done by immersing this limb only in a beaker of water at 10°, so that all the benzene was in the reservoir and none floating on top of the mercury in column c. During this measurement the mercury in column c was kept at a height corresponding to mark (2). After this measurement the benzene was frozen, by immersion of the tube in a freezing mixture, and the mercury columns a, b, and c lowered to below the cut-off.

The mercury was kept in this position until sufficient vapour had been absorbed by the polymer. The length of time required for this absorption depended on the temperature of the freezing mixture, and the amount already absorbed. In the early stages the process was very hit and miss; but experience later made it possible to predict satisfactorily a suitable transfer time. When the required amount of benzene had been transferred the mercury was raised into the manometer until the mercury in column c was at a height corresponding to mark (2) and the new benzene level determined as before. Finally the relative heights h_1 and h_2 were determined with, this time, the mercury in column b at mark (2).

Such a sequence of operations constitutes a single transfer; succeeding transfers - absorption and desorption - were made in an identical manner. From the results, after correction for the amount of benzene vapour in the gas space, the vapour-pressure concentration curves were obtained.

Materials .

1) Polymers.

a) Rubber. The rubber used was from rubber sheet provided by the Research Association of British Rubber Manufacturers, to whom I am indebted. The recipe of the sample c used in this research is given below.

Smoked sheet	100
Sulphur	4
Accelerator A.3	0.5
Stearic acid	0.5
Zinc Oxide	3.

The combined sulphur was stated to be 3.6%. The density measured at 18°C was found to be 0.958 gms/ml. Membranes were cut from uniformly thick regions of the sheet. The thickness was measured with a micrometer screw gauge, by placing the sheet between a sandwich of mica strips.

b) Polythene. I am grateful to Imperial Chemical Industries, Plastics Division, for gifts of polythene film. The material used was described as '"Alkathene" Grade 20 Standard' and was stated to have a nominal molecular weight of 16,500, based on the melt viscosity. The density of the polythene was measured and found to be 0.920 gms/ml at 18°C.

2) Benzene.

The benzene used in the experiments was purified in the following way. Onelitre of reagent grade benzene was shaken for two hours with mercury, washed twice with water, filtered, and distilled. It was then fractionally crystallized twice, and dried over fresh sodium wire. The purity was not all that could be desired. In particular the vapour pressures, one of the most sensitive indicators, were greater than that found by others for highly purified benzene.

Below are listed some of the important physical properties.

a) Freezing point 5.48°C (corrected); Glasgow, Murphy, Willingham, and Rossini (3) obtained 5.509°C (actual at 1 atm.) 5.533 ± 0.01°C (calculated for zero impurity).

b) Refractive Index $n_D^{20} = 1.5009 \pm 0.00005$ (VS H_2O at 20°C $n_D^{20} = 1.3330$). Forziati, Glasgow, Willingham and Rossini (4) obtained $n_D^{20} = 1.50110 \pm 0.00005$.

c) Density. This was not measured. The value $D_4^{25} = 0.8733$ gms/ml quoted by Tompa (5) was used.

d) Vapour pressures. In the rubber-benzene equilibrium experiments the vapour pressure at 25.0°C was found to be 10.00 ± 0.07 cms. Hg. This value is 3% greater than that calculated from the accurate data of Smith (6), whose vapour pressure equation was used to calculate the vapour pressures at other temperatures. In the benzene-polythene equilibrium experiments the vapour pressure at 25°C gradually decreased over fourteen transfers from 10.00 cms. Hg. to 9.87 cms. Hg.

References

(1) Lewis. Indust. Eng. Chem. 257 28 (1936).

(2) Gee and Treloar. Trans. Faraday Soc. 147 38 (1942).

(3) Glasgow, Murphy, Willingham and Rossini.
J. Res. Nat. Bur. Stands. 141 37 (1946).

(4) Forziati, Glasgow, Willingham and Rossini.
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(5) Tompa, J. Chem. Phys. 302 16 (1948).

(6) Smith. J. Res. Nat. Bur. Stands. 129 26 (1941).

CHAPTER VI

This chapter contains all the important experimental results; and the methods and results of the calculations leading to the activities, and diffusion coefficients. The assumptions made and the additional information used are noted and, where necessary, examined.

The Calculations of the Permeability coefficient and the Permeation Rate

The permeability coefficient already defined is the volume of gas measured at N.T.P., flowing per second through an area of one square centimetre and a thickness of one millimetre, under a pressure difference of one centimetre of mercury.

$$P = \frac{l}{p_1 a} \left(\frac{dV}{dt}\right)_{N.T.P.}$$

The permeation rate will be defined as the product of the pressure difference and the permeability coefficient, and denoted by P', so that

$$P' = p_1 P = \frac{l}{a} \cdot \left(\frac{dV}{dt}\right)_{N.T.P.} \qquad \text{-----} \quad 1$$

These two quantities are to be derived from the measured values of the steady state rate (S.S.R.) of increase of pressure on the outgoing side of the membrane. Let $\Delta p/\Delta t$

denote the S.S.R. measured in microns/minute. The relationship between this quantity and P and P' is derived below.

The equation of state for benzene vapour may be written

$$pV = n(RT + Bp) \qquad \text{-----}\ 2$$

Where B is the second virial coefficient. Differentiating, with respect to p at constant V, and V at constant p, one obtains

$$V\frac{dp}{dt} = nB\frac{dp}{dt} + \frac{dn}{dt}(RT + Bp) \qquad \text{-----}\ 3$$

and $$\frac{pdV}{dt} = (RT + Bp)\frac{dn}{dt} \qquad \text{-----}\ 4$$

combining equations 3 and 4.

$$\frac{pdV}{dt} = \frac{Vdp}{dt} - \frac{nBdp}{dt}$$

$$= V\frac{dp}{dt} - \frac{pVB}{RT+Bp} \cdot \frac{dp}{dt}$$

or $$\frac{dV}{dt} = \frac{V}{p}\frac{dp}{dt} \cdot \frac{1}{(1+Bp/RT)} \qquad \text{-----}\ 5$$

$\frac{dV}{dt}$ in cm.^{3} at N.T.P. is given by

$$\left(\frac{dV}{dt}\right)_{N.T.P.} = V\frac{dp}{dt}\left(\frac{1}{1+B/273R}\right) \qquad \text{-----}\ 6$$

If volume V - the volume of the outgoing side - is at temperature T_R, where T_R denotes the room temperature, then

$$\left(\frac{dV}{dt}\right)_{N.T.P.} = \frac{273}{T_R} \cdot V \frac{dp}{dt} \left(\frac{1}{1 + B/273R}\right) \qquad \text{----- } 7$$

When the rate of change of pressure is measured in microns/minute equation 7 becomes

$$\left(\frac{dV}{dt}\right)_{N.T.P.} = \frac{273}{T_R} \cdot \frac{V}{76 \times 60 \times 10^{+4}} \cdot \frac{1}{(1+B/273R)} \cdot \Delta p/\Delta t \qquad \text{----- } 8$$

substituting equation 8 into 1

$$P' = p_1 P = \frac{l}{a} \cdot \frac{273}{T_R} \frac{V}{76 \times 60 \times 10^{+4}} \cdot \frac{1}{(1+B/273R)} \cdot \Delta p/\Delta t \qquad \text{----- } 9$$

Results.

Values obtained for P' and P by the use of equation 9 are tabulated below. In every case a is 5.07 sq. cms., R is 82.05 $cm.^3$ atm/mole degree, and B is 1200 $cm.^3$ The value of V was changed several times depending on the permeation rate. Values between 500 and 2,500 $cm.^3$ were used.

Table I gives the values of P for the diffusion of benzene through rubber, over a range of cell temperatures, for a constant value of p_1, the vapour pressure of solid benzene at 0°C. The value for p_1 was taken from the International Critical Tables (2.472 cms Hg.). The membrane thickness l was 0.767 mm. At this low pressure the membrane swelling is negligible.

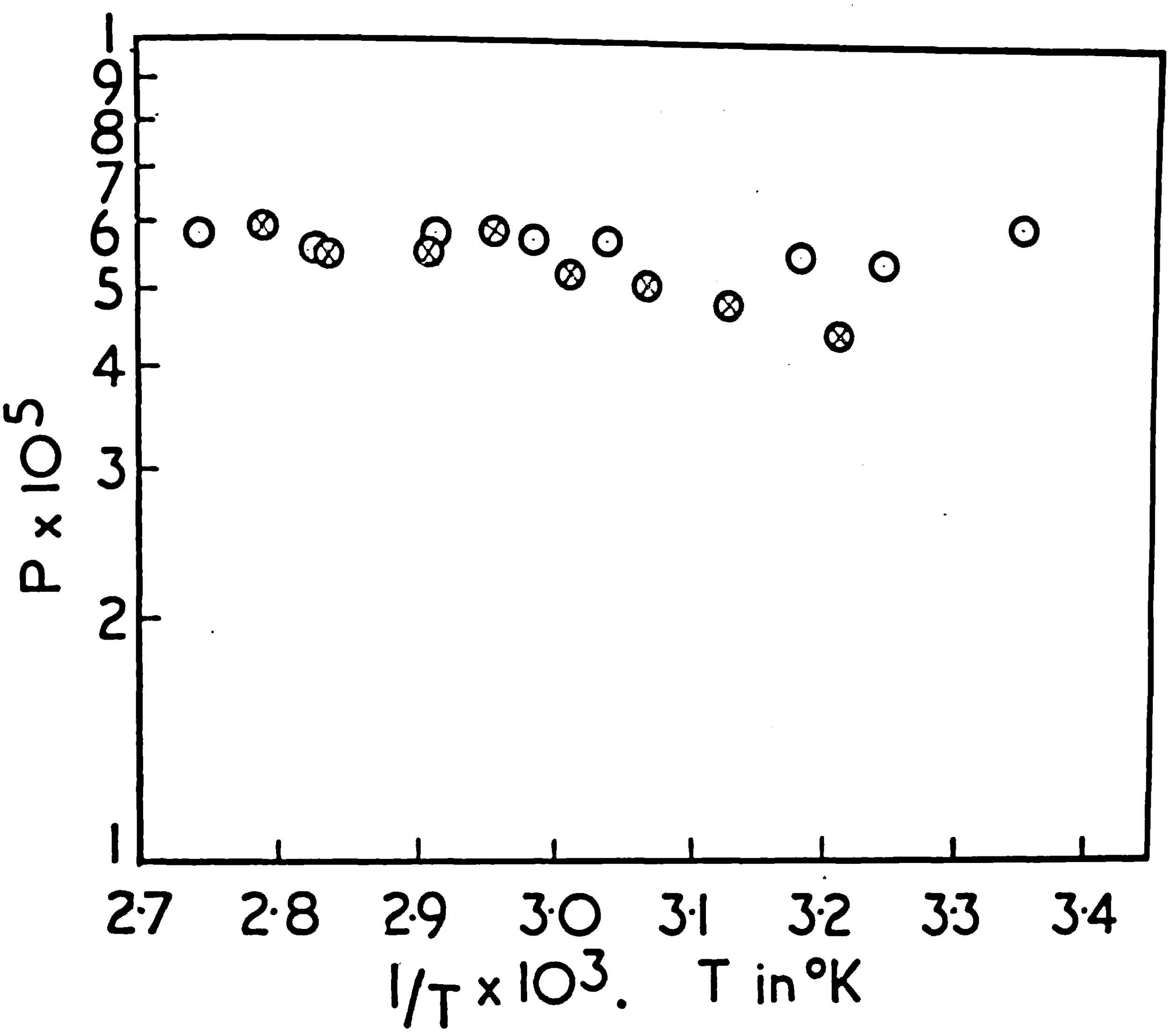

Fig. 1. Permeability of Rubber to Benzene at Different Temperatures (P_1 = 2·47 cm.Hg)

Table I

Permeability Coefficient in Rubber at Different Temperatures

(p_1 = 2.472 cms Hg.)

Expt. No.	T °C	P x 10^5
12.7	25.5	6.00
12.8	35.0	5.41
12.9	41.0	5.51
.10	55.9	5.78
.11	62.0	5.80
.12	70.0	5.88
.13	80.8	5.59
.14	91.3	5.82
.15	85.4	5.99
.16	79.7	5.50
.17	70.8	5.53
.18	65.4	5.99
.19	58.7^5	5.29
.20	52.6	5.12
.21	46.5	4.84
.21	38.1	4.42

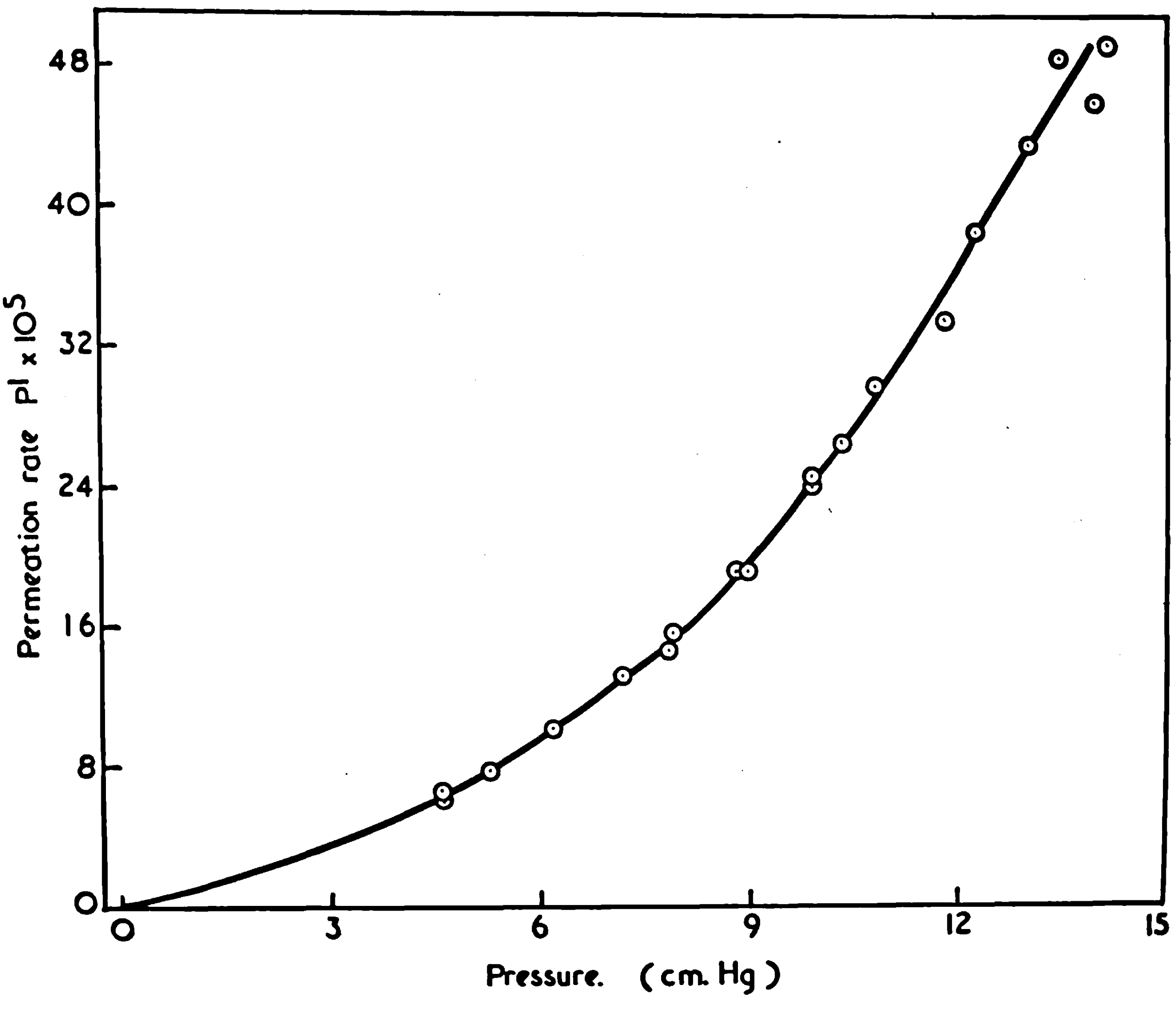

Fig. 2. Permeation of Benzene in Rubber at Different Pressures (50°C)

Table II

Values of P and P' for the Diffusion of Benzene in Rubber at 50°C

Expt. No.	p_1 mm.Hg.	P' x 10^5	P x 10^5
13.11	45.81	6.653	1.45
13.12	"	6.273	1.37
13.13	"	6.340	1.38
.14	"	6.413	1.40
.15	52.72	7.880	1.49
.16	61.66	10.27	1.69
.17	71.60	13.26	1.85
.18	78.95	15.73	1.99
.19	87.80	19.28	2.20
.20	-	-	-
.21	98.70	24.75	2.51
.22	"	24.28	2.46
.23	"	24.41	2.47
.24	89.50	19.23	2.15
.25	78.20	14.73	1.88
.26	102.8	26.59	2.59
.27	107.7	29.83	2.77
.28	117.6	33.67	2.86
.29	122.3	38.70	3.16
.30	130.0	43.71	3.36
.31	134.5	48.64	3.62
.32	141.4	49.39	3.49
.33	139.7	46.08	3.30

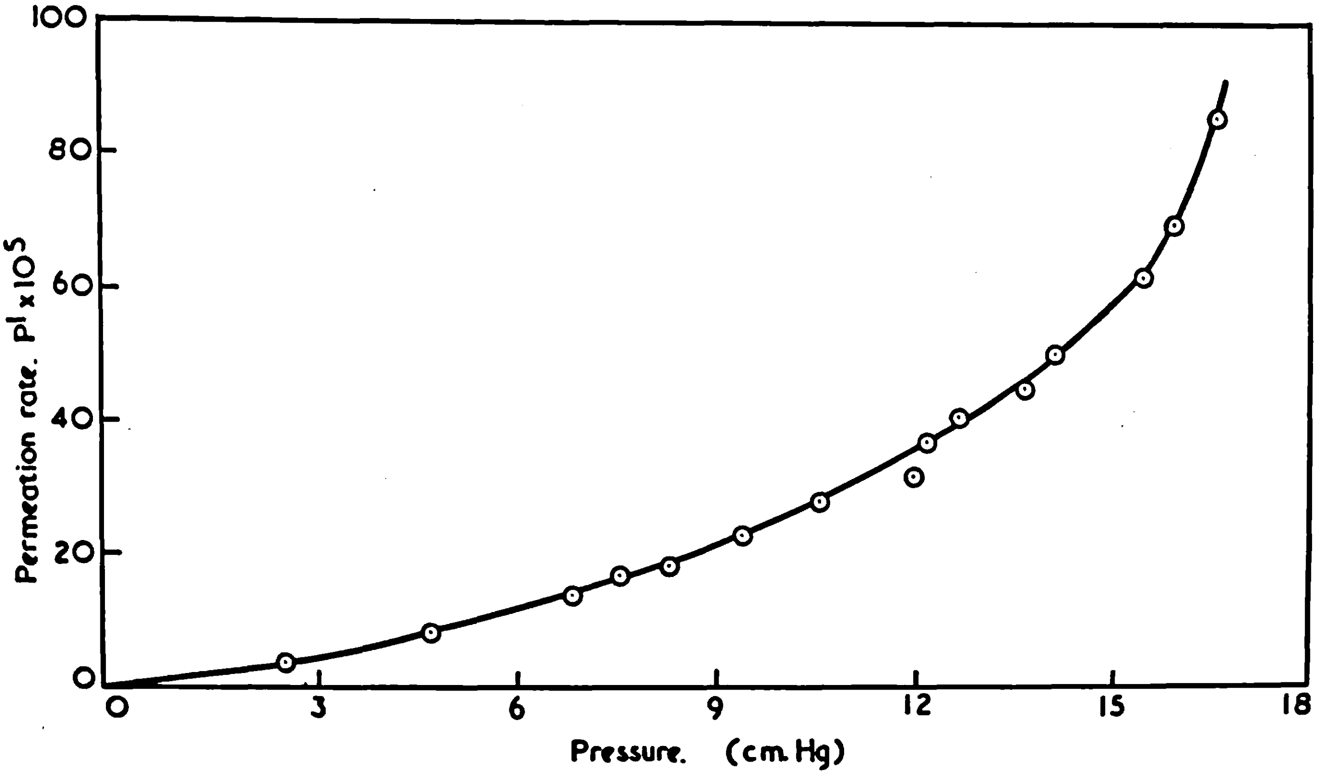

Fig. 3. Permeation of Benzene in Polythene at Different Pressures (50°C)

Table III

Values of P and P' for the Diffusion of Benzene in Polythene at 50°C

Expt. No.	p_1 mm.Hg.	P' x 10^5	P x 10^6
P.11	82.30	1.801	2.188
P.12	93.65	2.283	2.438
P.13	105.3	2.762	2.623
.14	154.3	6.184	4.007
.15	119.4	3.170	2.654
.16	121.2	3.680	3.036
.17	126.2	4.019	3.184
.18	136.2	4.496	3.301
.19	159.0	6.958	4.376
.20	140.9	5.007	3.555
.21	165.5	8.588	5.189
.22	75.20	1.666	2.216
.23	67.93	1.384	2.036
.24	46.84	0.8070	1.723
.25	24.72	0.3579	1.447

Table II gives the values of P and P' for the diffusion of benzene through rubber, at 50°C, over a range of ingoing pressures. The initial membrane thickness was 1.14 mm. For these experiments the swelling is not negligible. The correction for swelling is dealt with later. The results are given in terms of the initial membrane thickness.

Table III gives the values of P and P' for the diffusion of benzene through polythene at 50°C over a range of ingoing pressures. The initial thickness of the membrane was 0.57 mm. These data also are given in terms of the unswollen thickness and the correction applied later.

The data of Tables I, II, and III, are plotted in figs. 1, 2 and 3.

The Calculation of the Diffusion Coefficient from the Time Lag

In cases where the diffusion coefficient is constant it can be calculated from a measurement of the time to set up the steady state by a method due to Daynes. As applied to diffusion through a membrane by the present technique the boundary conditions for the solution of Fick's equation $\partial c/\partial t = D\partial^2 c/\partial x^2$ are:

$$C = C_1 \text{ at } x = l \text{ for all } t,$$

$$C = 0 \text{ at } x = 0 \text{ for all } t,$$

and $$C = 0 \text{ at } t = 0 \text{ for } 0 < x < l.$$

The solution is

$$C = \frac{C_1 x}{l} + \frac{2}{\pi} \sum_{1}^{\infty} \frac{C_1 \cos n\pi}{n} \cdot \frac{\sin n x \pi}{l} \exp - Dn^2\pi^2 t/l^2 \qquad \text{-----} \; 1$$

By differentiation with respect to x one can show that $(\partial C/\partial x)_{x=0}$ is given by

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{C_1}{l} + \frac{2}{l} \sum_{1}^{\infty} C_1 \cos n\pi \exp - \frac{Dn^2\pi^2 t}{l^2} \qquad \text{-----} \; 2$$

If the vapour flows into a volume V, then the flow is given by $V \frac{dC_g}{dt} = D\left(\frac{\partial C}{\partial x}\right)_{x=0}$ ----- 3

Substituting 3 into 2 and integrating between 0 and t one obtains:

$$C_g = \frac{DC_1 t}{lV} + \frac{2}{\pi^2} \sum_{1}^{\infty} C_1 \frac{\cos n\pi}{n^2} \left(1 - \exp - \frac{Dn^2\pi^2 t}{l^2}\right) \qquad \text{-----} \; 4$$

When t tends to infinity equation 4 approaches the line

$$C_g = \frac{D}{lV}\left[C_1 t - \frac{C_1 l^2}{6D}\right] \qquad \text{-----} \; 5$$

Had there been no time lag the stationary state would have been given by

$$C_g = \frac{DC_1 t}{lV} \qquad \text{-----} \; 6$$

So that the time lag (L), the intercept of the steady state permeation rate on the time axis, is related to the diffusion coefficient by the equation

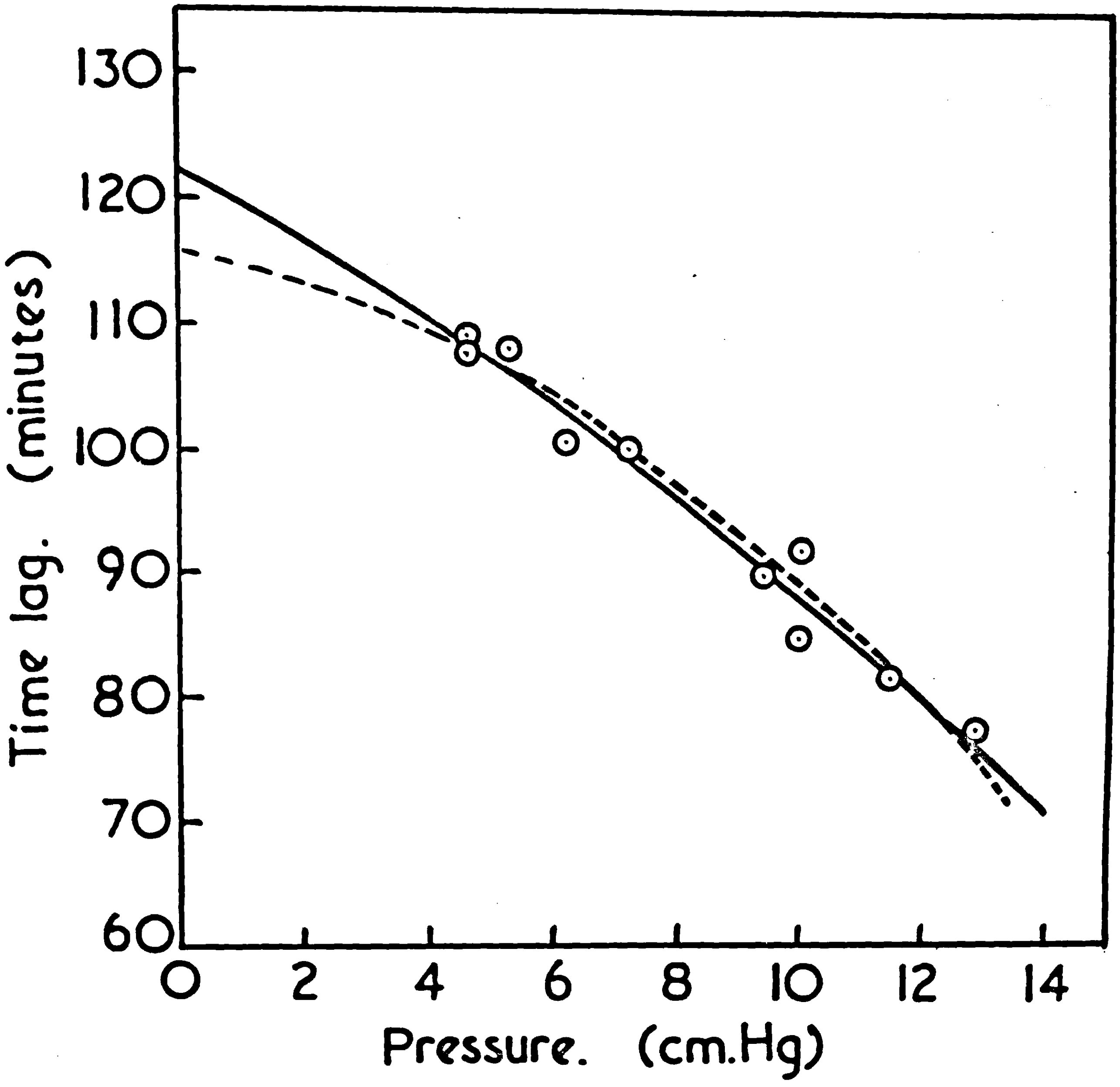

Fig. 4. Time Lag to set up Steady-State Diffusion of Benzene in Rubber (50°C)

$$L = \frac{l^2}{6D} \qquad \text{----- 7}$$

This very simple method of calculating D is not permissible if D is a function of concentration. It has been used directly to calculate D for the experiments in Table IV.

Table IV

The Diffusion Coefficients of Benzene in Rubber from the Time Lags at Low Pressures p_1 = 2·472 cm.Hg.

Expt.No.	1/T°K	L minutes	D x 10^7 cm^2 sec^{-1}
12·7	3.348	115	1.42
12.8	3.245	75.0	2.17
12.9	3.183	56.5	2.89
.10	3.039	28.5	5.74
.11	2.983	21.8	7.50
.12	2.913	16.5	9.90
.13	2.825	10.7^5	15.2
.14	2.743	9.0	18.1
.15	2.788	10.9	15.0
.16	2.834	11.3	13.6
.17	2.907	17.9	9.13
.18	2.954	23.5	6.94
.19	3.013	27.8	5.88
.20	3.068	38.7	4.23
.21	3.128	48.0	3.40
.22	3.212	73.9	2.21

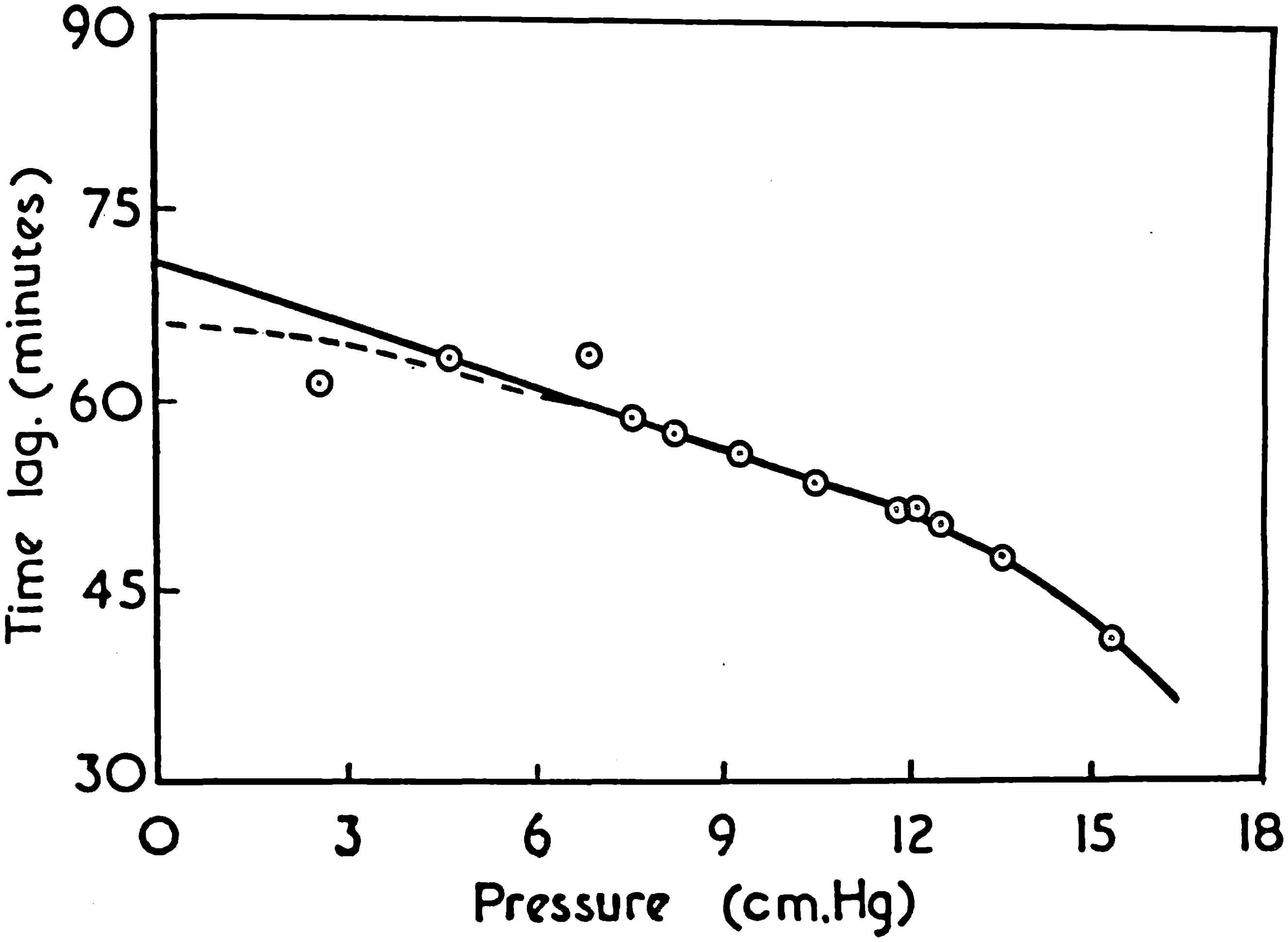

Fig. 5. Time Lag to set up Steady-State Diffusion of Benzene in Polythene (50°C)

Equation 7 has also been used to calculate, by extrapolation, the value of D at zero concentration of benzene. Figs. 4 and 5 show the results for the diffusion of benzene in rubber and polythene at 50°C.

Extrapolated values of L, D, and P, denoted by L^o, D^o and P^o, for benzene in rubber and polythene are listed in Table V.

Table V

Values of P^o, L^o, and D^o, for Benzene in Rubber and Polythene at 50°C. Calculated by extrapolation to zero pressure

	Benzene-Rubber	Benzene-Polythene
P^o	$1{\cdot}14 \times 10^{-5}$	$1{\cdot}27 \times 10^{-6}$
L^o(minutes)	116	64·9
D^o(cm.^{2}sec.$^{-1}$)	$3{\cdot}84 \times 10^{-7}$	$1{\cdot}39 \times 10^{-7}$

Temperature Dependence of D and P in Rubber

From the measurements made on rubber at a low ingoing pressure and over a range of cell temperatures the energies of activation for diffusion and permeation have been calculated. Both P and D obey simple exponential relations; $P = P_o \exp - Ep/RT$, and $D = D_o \exp - E_D/RT$. The values are recorded in Table VI and figs. 6 and 7.

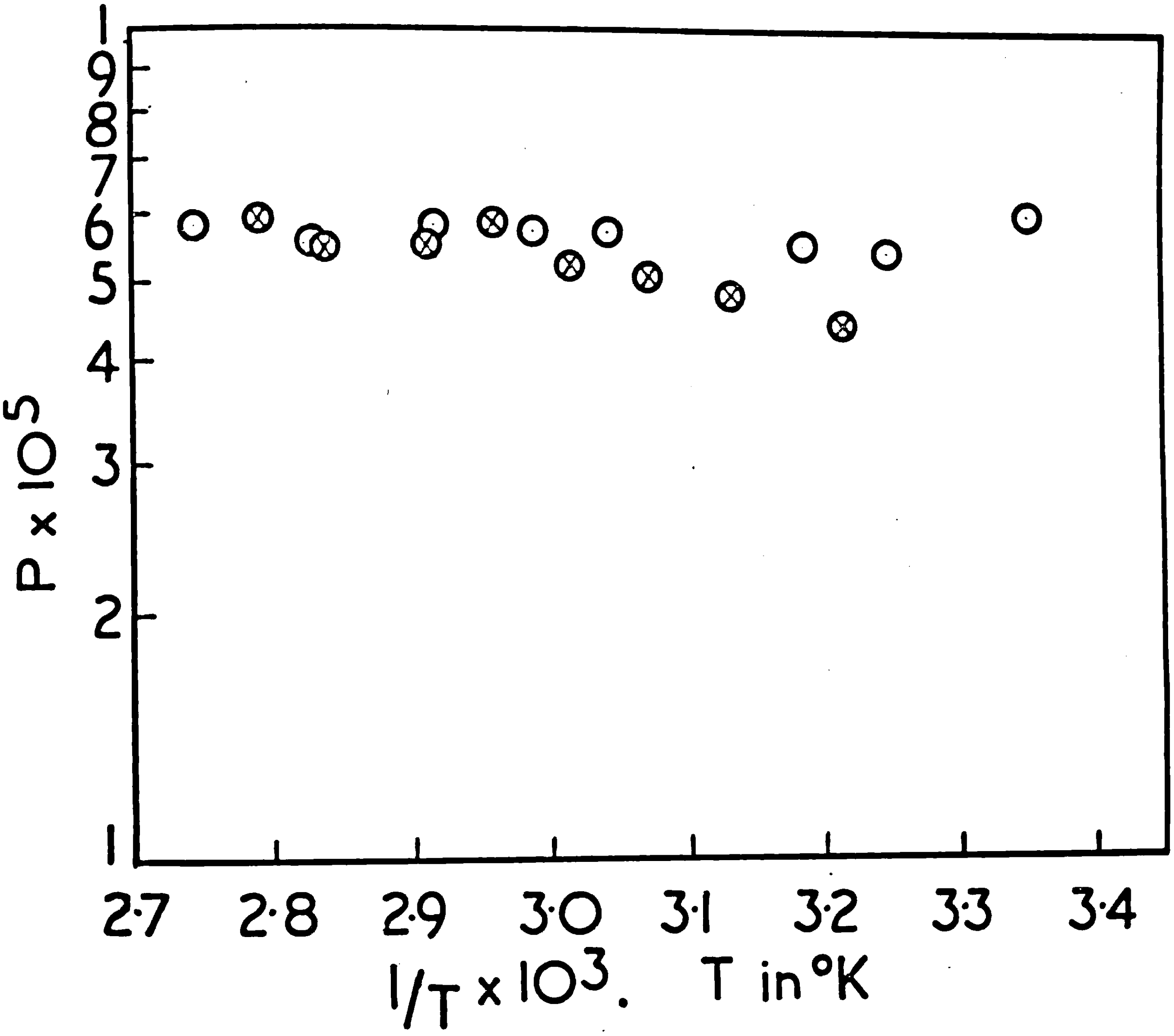

Fig. 6. Arrhenius Plot of Permeability Coefficient.
Rubber-Benzene.

Table VI

Values of D_o. E_p, and E_D, calculated for Benzene in Rubber from the Temperature Dependence of P and D at low pressures p_1 = 2.472 cms. Hg.

D_o(cm^2 sec^{-1})	E_p cals/mol. x 10^{-3}	E_D cals/mol. x 10^{-3}
0.526	0.58 ± 0.5	9.03 ± 0.3

There is a slight, but distinct, difference between the absolute magnitudes of the 'up' and the 'down' points in fig. 6. This does not affect the value of E_p, calculated from the slope. The distinctions between P^o and P_o and D^o and D_o are to be noted. P^o and D^o represent the values to which P and D tend in the limit of zero benzene concentration, whereas P_o and D_o represent the temperature insensitive parts of P and D.

The Conversion of the Concentration Units for P and P'

The derived values for P and P' will be used to calculate diffusion coefficients at different concentrations of benzene in the polymers. The unit to be employed for the concentration of benzene in the polymer is the volume fraction, defined by the equation

$$v_1 = V_1/(V_1 + V_2)$$

Where V_1 and V_2 are the volumes of liquid benzene and polymer respectively. Accordingly the values of P and P' have to be converted to the units of volume of liquid benzene (cm^3) in order that the units of D are cm^2 sec^{-1}.

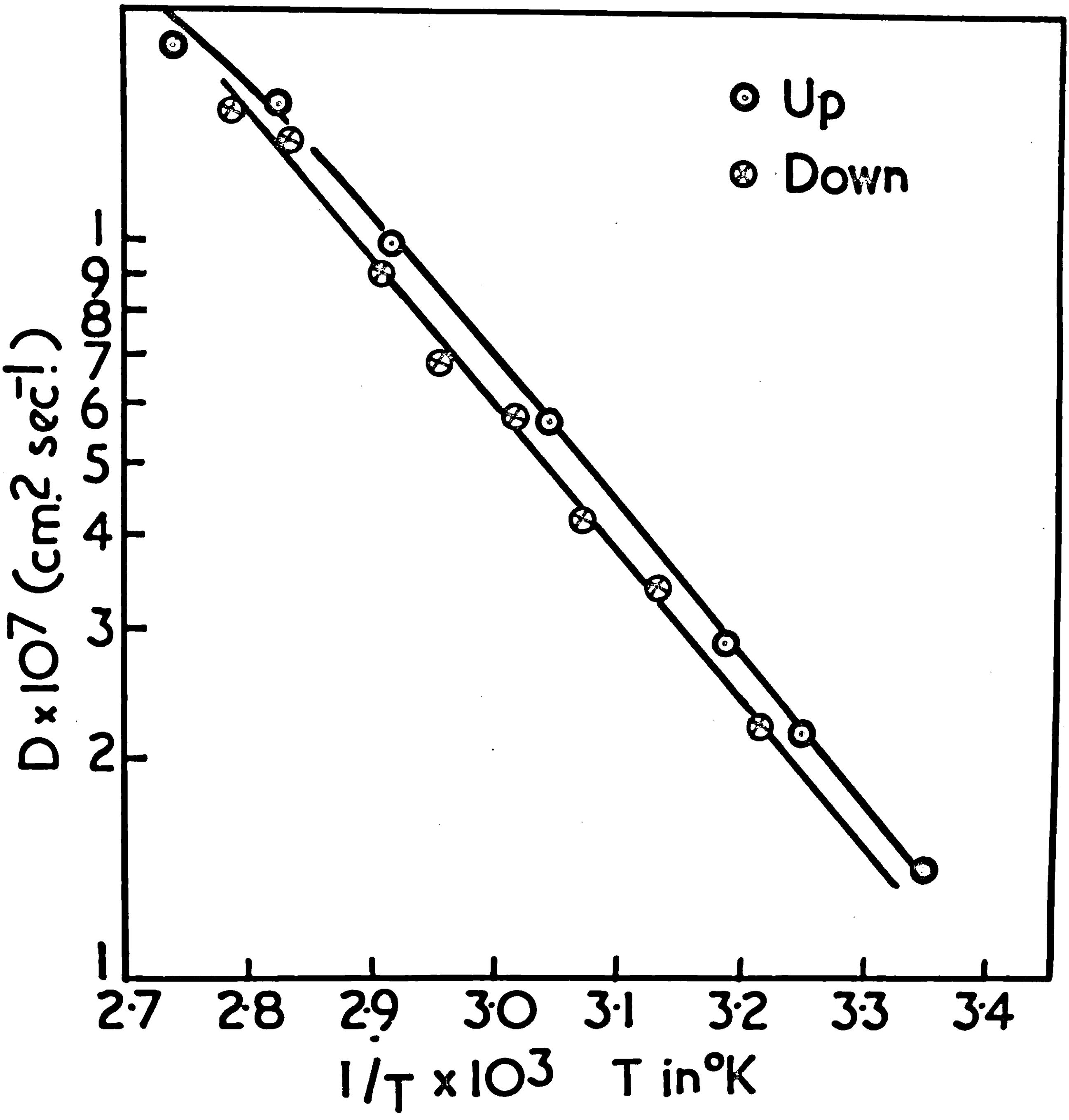

Fig. 7. Arrhenius Plot of Diffusion Coefficient.
Rubber-Benzene.

The flow, in cm^3 of benzene vapour at N.T.P. under one centimetre of mercury pressure difference for a membrane of one millimetre thickness, is given by P. Hence the flow, in moles of benzene under one centimetre of mercury pressure difference for a membrane of one centimetre thickness, is given by $\frac{P}{10} \frac{1}{(273R + B)}$.

The flow, in cubic centimetres of liquid benzene at temperature T for a membrane of one centimetre thickness, is therefore given by $Pp_1 \frac{M}{10 \rho_T} \frac{1}{(273R + B)} = P' \frac{M}{10 \rho_T} \frac{1}{(273R + B)}$.

Where M the molecular weight of benzene is 78.01, ρ_T the density of liquid benzene at temperature T is 0.842 g/ml at 50°C (extrapolated from the data of Forziati and Rossini (1)), and B the virial correction at 273°C is taken to be 1200 cm^3.

Introducing these values the flow of vapour calculated as cm^3 liquid benzene, under a pressure gradient of one centimetre of mercury, for a membrane of one centimetre thickness, at a temperature of 50°C is given by

$$\mathcal{P} = 4{\cdot}37 \times 10^{-4} P' \qquad \text{-----} \ 8$$

It is now appropriate to consider the effect of swelling on the choice of concentration units. Because the vapour flowing across the membrane dissolves in it and causes it to swell the initial thickness used to calculate P and P' is not the true thickness. Let l_1 denote the true thickness for the ingoing pressure p_1. By defining P and P' in terms of

l_1 the concentration unit is converted from cm^3 benzene/cm^3 polymer (c_1) to cm^3 benzene/cm^3 total volume (v_1); for of necessity the swelling can only increase the membrane thickness. It follows that the permeation rate appropriate to volume fraction concentration units is $\mathcal{P} l_1/l$. At the lowest concentrations the swelling is negligible, so that $l \simeq l_1$, and $c_1 \simeq v_1$.

The Calculation of the Diffusion Coefficient from the Permeation Rate

Case I: Assuming the membrane does not swell.

The general theory of the procedure has been outlined in Chapter I. As applied to these results it is as follows.

Let $D = D^{o} . [1 + f(v_1)]$.

Where v_1 is the concentration of benzene in the polymer in units of volume fractions (equivalent, in the case of no swelling, to cm^3 benzene/cm^3 polymer). In the steady state

$$\partial v_1/\partial t = \frac{\partial D(\partial v_1/\partial x)}{\partial x} = 0$$

Therefore $D^{o} \int_0^{v_1} [1 + f(v_1)] \, dv_1 = Ax + B$ ----- 1

let $v_1 = v_1^{o}$, when $x = 0$, $v_1 = 0$ when $x = l$,

and $\int_0^{v_1} [1 + f(v_1)] \, dv_1 = F(v_1)$.

Introducing these boundary conditions, and making the above substitution for $\int_0^{v_1} [1 + f(v_1) \, dv_1$, one gets

$$\frac{F(v_1^o) - F(v_1)}{F(v_1^o)} = \frac{x}{l} \qquad \text{----- 2}$$

so that $- \frac{\partial F(v_1)}{\partial x} = \frac{F(v_1^o)}{l}$ ----- 3

by definition $\frac{\partial F(v_1)}{\partial v_1} = [1 + f(v_1)$ ----- 4

Substituting equations 3 and 4 into the identity

$$\frac{\partial v_1}{\partial x} = \frac{\partial v_1}{\partial F(v_1)} \cdot \frac{\partial F(v_1)}{\partial x}$$

one obtains $- \frac{\partial v_1}{\partial x} = \frac{1}{l} \frac{F(v_1)}{[1 + f(v_1)]}$ ----- 5

Fick's equation for the flow may be written

$$J = - D\partial c/\partial x = - D\partial v_1 \partial x$$

(where the flow is denoted by J rather than P to avoid confusion with the permeability coefficient.)

$$J = - D\partial c_1/\partial x = - D\partial v_1/\partial x.$$

Substituting into this equation the value of $\partial v_1/\partial x$ given by equation 5, and writing $D = D^o[1 + f(v_1)]$, leads to

$$J = \frac{D^o F(v_1)}{l} \qquad \text{----- 6}$$

Let Q denote the quantity of benzene (cm.^{3} liquid) permeating through ~~unit~~ area a (cm.^{2}) in time t (sec.). Then

$$Q = a\int_0^t J_{x=l} \; dt$$

so that in the steady state

$$\mathcal{P} = \frac{Ql}{at} = D^{o}F(v_1^{o}) = D^{o}\int_{0}^{v_1^{o}} [1 + f(v_1)]\, dv \quad \text{-------} \; 7$$

D^{o} may be calculated from equation 7 by extrapolation to the limit $v_1^{o} \rightarrow 0$, when $\mathcal{P} \rightarrow D^{o}$. Then $D = D^{o}[1+f(v_1)]$ can be determined by differentiation of $\mathcal{P}$ with respect to v_1^{o}.

Case II: Making allowance for the swelling of the membrane.

It will be assumed that there is no net volume change on mixing benzene and polymer. This is an assumption but there are no indications that it is not approximately correct. Provided it is valid the true membrane thickness l_1 is given by the equation

$$l_1 = l + \int_{0}^{l_1} v_1\, dx \quad \text{-----} \; 8$$

and the diffusion coefficient can be calculated in the following way. Substitute for dx in equation 8 using equation 2. Differentiate the result with respect to v_1. Integrate by parts and replace, by the equation for l_1 so obtained, the value of l in equation 6. Finally integrate with respect to time as before.

However, there exists a much neater way of obtaining the same result. Consider a modified scale of length ξ, on which the thickness remains constant and equal to its unswollen value (2). On this scale

$$l = \int_0^{l_1} d\xi$$

and from 8

$$l = \int_0^{l_1} dx - \int_0^{l_1} v_1 dx.$$

so that $\frac{\partial \xi}{\partial x} = 1 - v_1.$

Now $J = - D \frac{\partial v_1}{\partial x}$

$$= - D \frac{\partial v_1}{\partial \xi} \frac{\partial \xi}{\partial x} = -D(1 - v_1) \frac{\partial v_1}{\partial \xi} .$$

From which it follows, by analogy with the preceding treatment, that the flow rate in the steady state is given by

$$\mathcal{P} = D^{o} \int_0^{v_1^{o}} (1 - v_1)[1 + f(v_1)] \, dv_1 \qquad \text{----- } 9$$

As before the diffusion coefficient is obtained by differentiation.

$$\frac{d\mathcal{P}}{dv_1} = D^{o}[1 + f(v_1)] \, (1 - v_1) = D(1 - v_1) \qquad \text{----- } 10$$

Equation 10 is only applicable when there is no net volume change on mixing and when the concentration is measured in terms of the ratio of the amount of the diffusing species to the total amount of every species.

If the assumption is made that the net motion of the benzene molecules alone contribute to the diffusion process, and this is indeed plausible for the polymer molecules are so much larger and are cross-linked and intertwined, then the diffusion coefficients obtained by the above treatment of the permeation data are what Hartley and Crank (2) have called 'intrinsic diffusion coefficients' for the solvent species.

The Equilibrium Vapour Pressure Measurements

The results of these measurements, for benzene-rubber, and benzene-polythene at 25°C are recorded in tables VII and VIII and figs. 8 and 9.

In the tables: Column 1 gives the volumes of benzene transferred.

Column 2 gives the correction for the volume of benzene in the vapour phase, calculated using $B = -1400$ cm.^{3} for the second virial coefficient.

Column 3 gives the volume fractions of the benzene in the polymer, v_1.

Column 4 gives the corresponding vapour pressure, p_1^m (cms.Hg.).

Column 5 gives the activity, a_1 (25°C), calculated using the relationships

$$a_1 = f_1^m / f_1^o$$

and $$\ln f = \ln p + Bp/RT.$$

Where f is the fugacity and B the second virial coefficient.

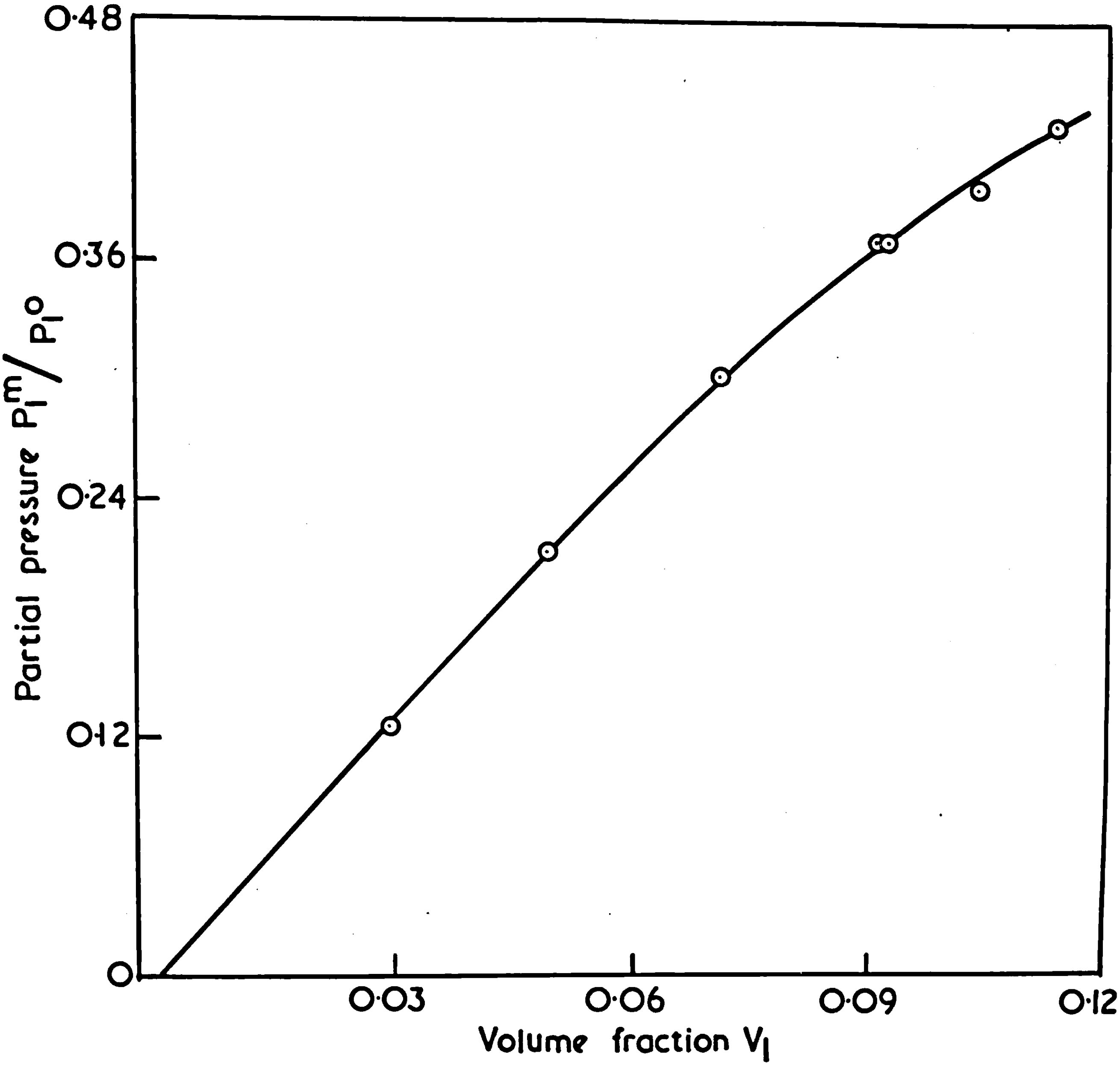

Fig. 8. Equilibrium Vapour Pressure Data. Benzene-Rubber (25°C.)

Table VII

Benzene-Rubber Vapour Pressure Measurements at 25°C

Col. No.	1	2	3	4	5
			v_1	p_1^m(cms.Hg.)	a_1 (25)
1	0·0138	0·0025	0·0292	1.275	0.1280
2	0.0245	0.0052	0.0488	2.120	0.2133
3	0.0358	0.0073	0.0705	3.005	0.3020
4	0.04$\overset{65}{\overline{71}}$	0.0090	0.09$\overset{07}{\overline{20}}$	3.747	0.3767
5	0.0528	0.0095	0.1033	4.000	0.4020
6	0.0584	0.0104	0.1132	4.290	0.4312

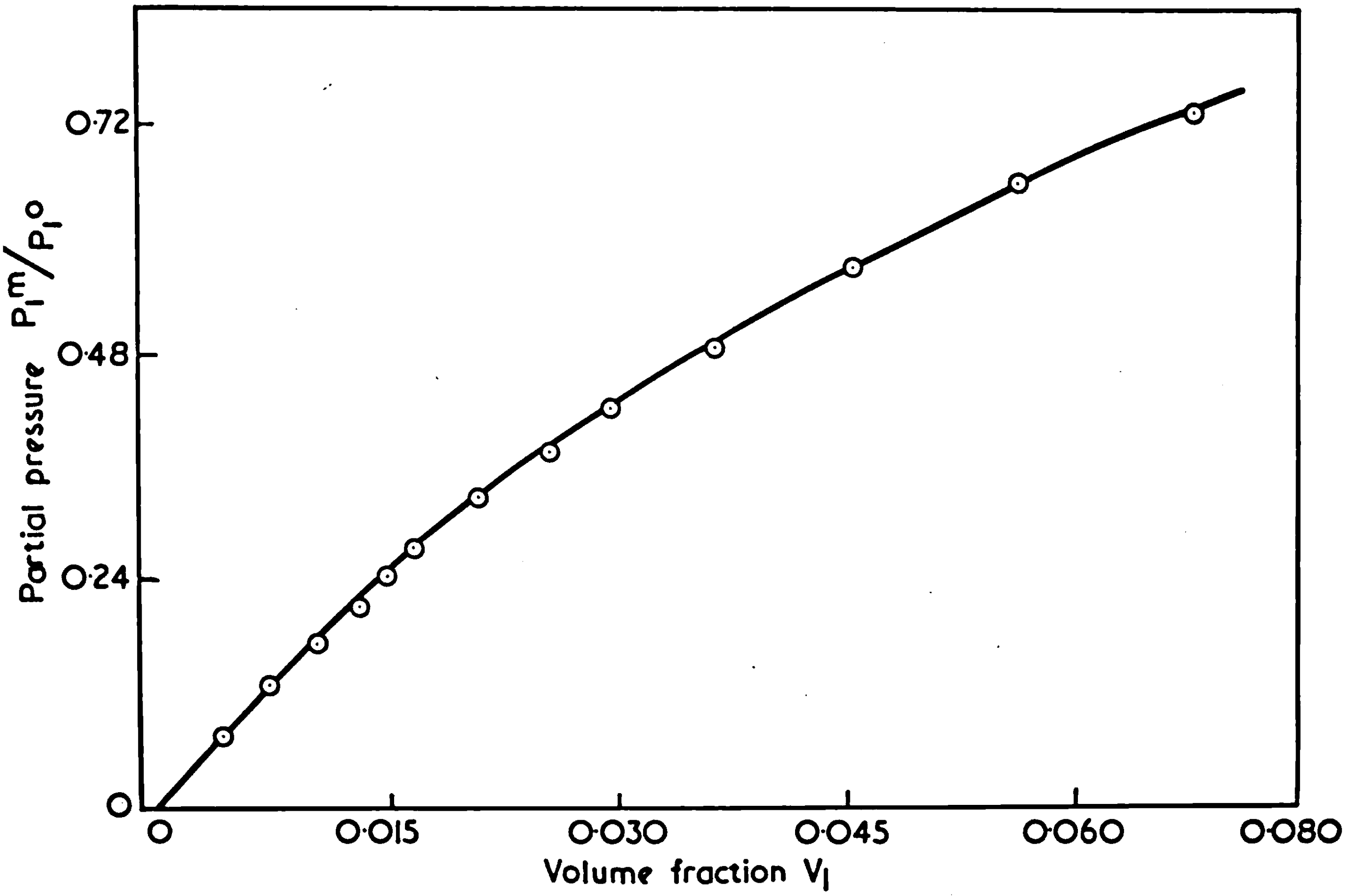

Fig. 9. Equilibrium Vapour Pressure Data.
Benzene-Polythene (25°C)

Table VIII

Benzene-Polythene Vapour Pressure Measurements at 25°C

Col.

No.	1	2	3	4	5
			v_1	p_1^m(cms.Hg.)	$a_1(25)$
1	0.00902	0.0019	0.004216	0.7866	0.07866
2	0.01546	0.0032	0.007238	1.310	0.1318
3	0.02171	0.00425	0.01028	1.740	0.1750
4	0.02771	0.00520	0.01321	2.121	0.2134
5	0.03139	0.00595	0.01490	2.442	0.2460
6	0.03536	0.00675	0.01672	2.758	0.2773
7	0.04406	0.00800	0.02099	3.285	0.3303
8	0.05339	0.00915	0.02564	3.750	0.3785
9	0.06167	0.01025	0.02968	4.200	0.4237
10	0.07516	0.01170	0.03637	4.824	0.4862
11	0.09412	0.01375	0.04561	5.659	0.5714
12	0.1163	0.01585	0.05636	6.460	0.6592
13	0.1404	0.01765	0.06801	7.240	0.7348

Because the rate measurements were made at a temperature of 50°C and the activities measured at 25°C, the latter have been converted to activities at 50°C.

By definition $\Delta\bar{H}_1 = \frac{\partial\Delta(\bar{G}_1/T)}{\partial 1/T} = -RT^2\frac{\partial \ln a_1}{\partial T}$

and $\int_{T_2}^{T_1}\frac{\Delta\bar{H}}{RT^2}dT = \ln a(T_2) - \ln a(T_1)$

If the heat of dilution is independent of temperature

then $$\frac{\Delta\bar{H}_1}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \ln a(T_2) - \ln a(T_1)$$

The values of $\Delta\bar{H}_1$ used for the rubber-benzene system have been taken from the results of Gee and Orr (3) for the same system. It is to be noted that $\Delta\bar{H}_1$ is very small, less than 300 cals/mole. Between the temperatures 25 and 50°C its influence, relative to the experimental precision, is only barely discernible. The results are given in Table IX.

Table IX

The Activities for Benzene in Rubber at 50°C

No.	$a_1(25)$	$\bar{H}$(cals/mol)	$a_1(50)$	$p_1^m(50)$
1	0.1285	290	0.1237	3.306
2	0.2133	277	0.2057	5.504
3	0.3020	263	0.2918	7.820
4	0.3767	255	0.3643	9.774
5	0.4020	243	0.3894	10.45
6	0.4312	237	0.4181	11.23

The heat of dilution has not been measured for the benzene-polythene system. Raine, Richards and Ryder (4) have suggested that, by analogy with the heat of mixing of heptane and medicinal paraffin with xylene, the heat of mixing of 'liquid' (i.e. non-crystalline) polythene and xylene is about -5 calories/gm. polythene. Accepting such a value as a reasonable one for the benzene-polythene system, it follows that the heat of solution of polythene in benzene cannot be more than 5 calories/gm. more negative than the heat of fusion of cyrstalline polythene at the same temperature.

The heat of fusion of one gram of polythene is approximately 56.5 cals. (4), and the degrees of crystallinity at 25 and 50°C are 0.82 and 0.76 respectively (5). So the heats of fusion are 46.3 and 42.9 cals./gm., corresponding to maximal values - all the crystalline regions melting - of 51 and 48 cals./gm. for the heats of solution.

A value of 50 cals. corresponds to a value of 700 cals/mole for the heat of dilution of benzene, taking 14 as the molecular weight of a polythene segment. This assumes that the addition of onemole of benzene to an infinite amount of polythene completely melts one mole (14 gms.) of polythene segments initially crystalline. The results using 400 cals./mol. for the heat of dilution are given in Table X.

Table X

The activities for Benzene in Polythene at 50°C, assuming $a(50) = 0.95\ a(25)$.

No.	$p_1^m(50)$
1	2.033
2	3.407
3	4.524
4	5.517
5	6.356
6	7.166
7	8.537
8	9.783
9	10.95
10	12.57
11	14.77
12	17.04
13	19.00

Even if the heat of dilution is twice this value the difference between $a_1(25)$ and $a_1(50)$ is less than 10%. Because of the uncertainty in $\Delta\bar{H}_1$ the small fugacity correction has not been made.

The Combination of the Rate and Equilibrium Data

The results in tables IX and X and I and II have been plotted on large scale and the best smooth curves drawn through the points. From these plots $\mathscr{P}$ as a function of v_1^o has been found. The values are given in tables XI and XII. They have been fitted to polynomial expressions of the form

$$\mathscr{P} = Av_1 + Bv_1^2 + Cv_1^3 + Dv_1^4 \qquad \text{-----} \; 11$$

The values of the constants so obtained are recorded in table XIII.

Table XI

$\mathscr{P}$ as a function of v_1^o at 50°C for Benzene-Rubber

$(K = 10^9/4.37)$

No.	v_1^o	$\mathscr{P}$ x K(curve)	$\mathscr{P}$ x K(eq.)
0	0	0	0.003
1	0.015	1.98	4.366
2	0.030	4.33	4.366
3	0.045	7.53	7.526
4	0.060	11.74	11.625
5	0.075	16.51	16.649
6	0.090	22.43	22.401
7	0.105	28.53	28.498
8	0.120	34.36	34.374

Table XII

$\mathcal{P}$ as a function of v_1° at 50°C for Benzene-Polythene

$(K = 10^9/4.37)$

No.	v_1°	$\mathcal{P} \times K$ (curve)	$\mathcal{P} \times K$ (equation)
0	0	0	0.011
1	0.009	0.630	0.662
2	0.018	1.600	-
3	0.027	2.617	-
4	0.036	3.807	-
5	0.045	5.390	5.435
6	0.054	8.540	-

Table XIII

Values of the Coefficients in the Approximating Polynomials

$$\mathcal{P} = Av_1^{\circ} + Bv_1^{\circ 2} + Cv_1^{\circ 3} + Dv_1^{\circ 4}$$

Coefficient x $4.37/10^9$	Benzene-Rubber	Benzene-Polythene	
		4 terms	3 terms
A	1.2905×10^2	1.3783×10	-2.1823×10^2
B	-2.4561×10^2	7.6935×10^3	-2.5018×10^3
C	3.1178×10^4	-2.4603×10^5	5.9937×10^4
D	-1.5166×10^5	2.8334×10^6	——

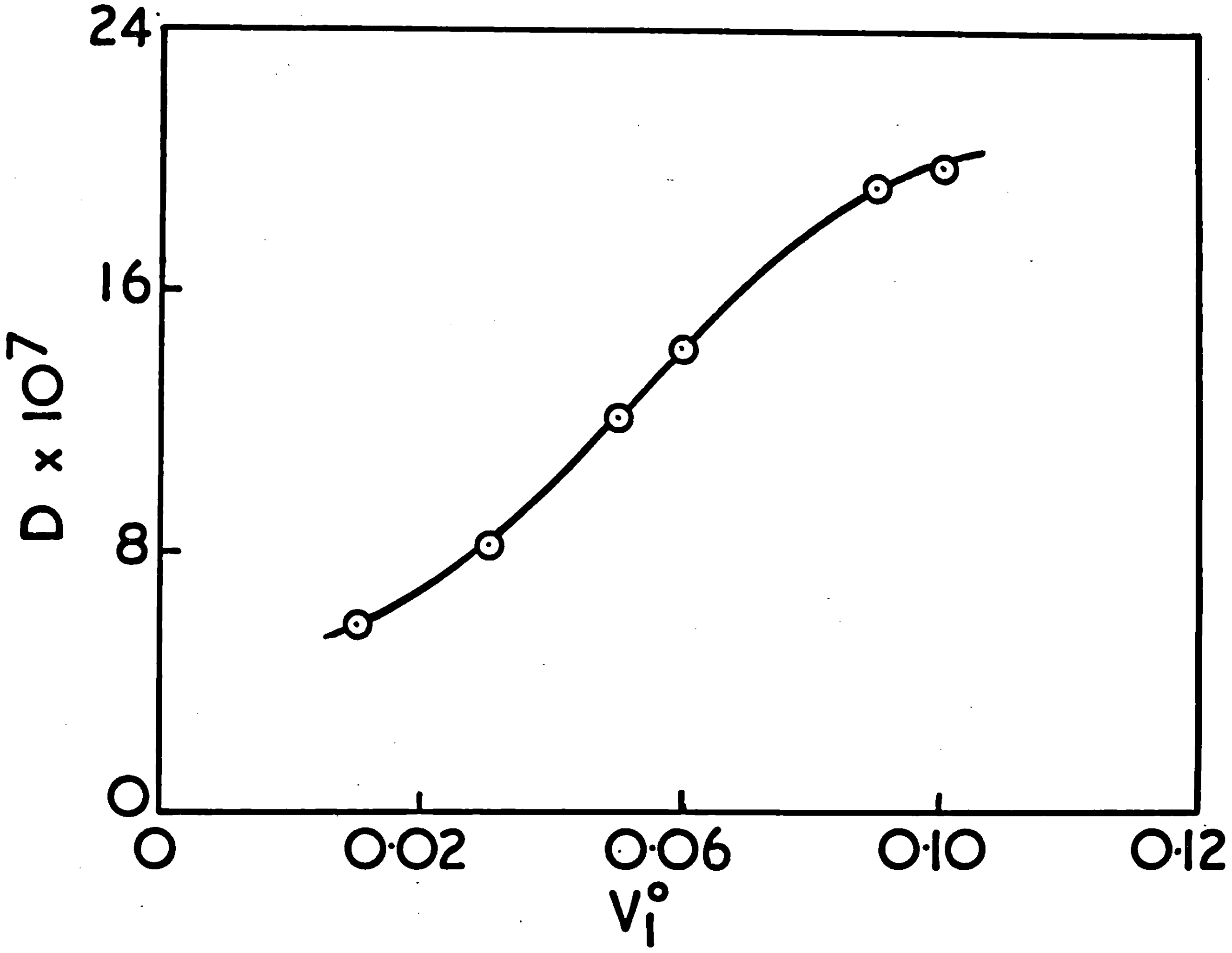

Fig. 10. Diffusion Coefficient against Volume Fraction.
Benzene-Rubber (50°C)

A number of simpler empirical expressions have been considered but have not been found to represent the data satisfactorily. Equation 11 is the lowest degree polynomial which gives the best fit to the smoothed data for the benzene-rubber system.

For benzene-polythene both a fourth degree polynomial and a cubic equation give a good representation of the data over the range of experimental measurements. Within this range the fourth degree polynomial is slightly better and has been used. But at concentrations less than those for which permeation rates have been measured there is a marked divergence between the two polynomials. The reason for this is not hard to see. It arises out of the hazards of extrapolation; there is a pronounced curvature of the benzene-polythene plots at low concentrations.

From equation 11 the diffusion coefficients have been calculated by differentiation

$$\frac{d\mathcal{P}}{dv_1} = D(1 - v_1) = A + 2Bv_1 + 3Cv_1^2 + 4Dv_1^3 \qquad \text{-----} \; 12$$

The results of this treatment of the experimental data are presented in tables XIV and XV and figs. 10 and 11.

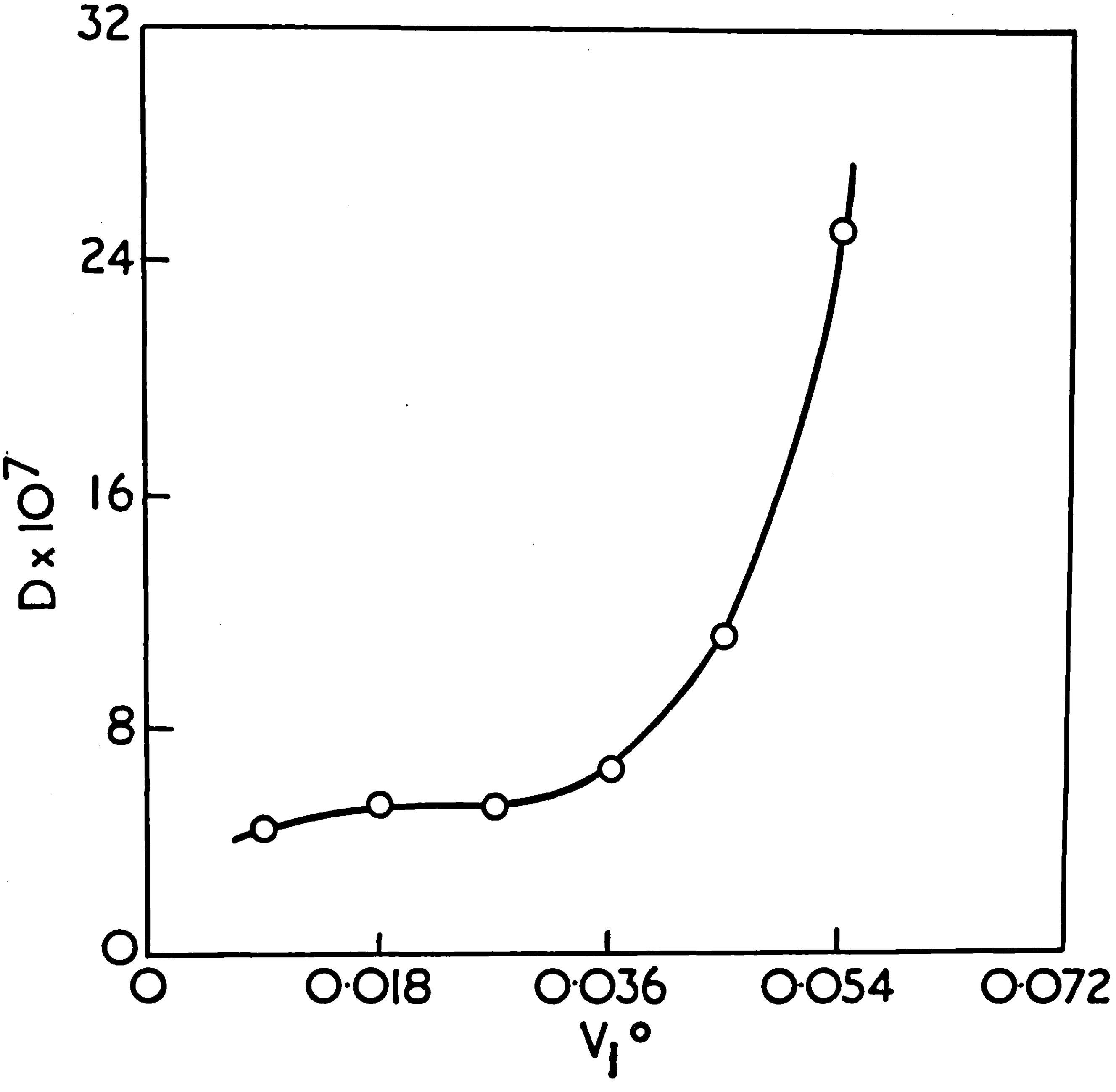

Fig. 11. Diffusion Coefficient against Volume Fraction.
Benzene-Polythene (50°).

Table XIV

Benzene-Rubber. Diffusion Coefficients at 50°C

v_1^o	$1 - v_1^o$	$D \times 10^7$
0.01	0.99	5.87
0.03	0.97	8.21
0.05	0.95	12.11
0.06	0.94	14.20
0.09	0.91	19.23
0.10	0.90	19.86

Table XV

Benzene-Polythene. Diffusion Coefficients at 50°C.

v_1^o	$1 - v_1^o$	$D \times 10^7$
0.009	0.991	4.44
0.018	0.982	5.23
0.027	0.973	5.12
0.036	0.964	6.50
0.045	0.955	11.17
0.054	0.946	25.10

Inspection of equation 12 shows that D^{o} , the diffusion coefficient extrapolated to zero concentration is equal to the coefficient A in the polynomial.

$$\left(\frac{d\mathcal{P}}{dv_1}\right)_{v_1 \rightarrow 0} = A.$$

Values of D^{o} so determined are not very accurate, particularly for the benzene-polythene system, because of the extrapolation difficulties already mentioned; and also because there exist the possibility that the error in A, the first coefficient, is larger than the net error in all the coefficients.

There are two other ways to calculate D^{o}.

(1) By graphical extrapolation to zero concentration of the time lags. See figs. 4 and 5.

(2) By a combination of graphical extrapolation to zero concentration, of the permeability as a function of pressure, and the equilibrium vapour pressure data.

One has $D^{o} = \left(\frac{\mathcal{P}}{v_1{}^{o}}\right)_{v_1{}^{o} \rightarrow 0} = 4.37 \times 10^{-4} \left(\frac{P'}{v_1{}^{o}}\right)_{v_1{}^{o} \rightarrow 0}$

$$= 4.37 \times 10^{-4} \cdot \left(\frac{P'}{p_1}\right)_{p_1 \rightarrow 0} \cdot \left(\frac{p_1{}^{m}}{v_1{}^{o}}\right)_{p_1{}^{m} \rightarrow 0}$$

Table XVI gives the values of D^{o} calculated by the different methods.

Table XVI

Values for D^o determined by Different Methods

Method	Time Lag	Polynomial	Graphical Extrapolation of P and $\frac{p_1^m}{v_1^o}$
<u>Rubber-Benzene</u>. 50°C			
	$3{\cdot}11 \times 10^{-7}$	$5{\cdot}64 \times 10^{-7}$	$5{\cdot}52 \times 10^{-7}$
<u>Polythene-Benzene</u>. 50°C			
	1.39×10^{-7}	0.60×10^{-7} (3rd degree) 5.64×10^{-7} (4th degree)	2.85×10^{-7}

References

(1) Forziati and Rossini. J. Res. Nat. Bur. Stds. 473 43 (1949).

(2) Hartley and Crank. Trans. Faraday Soc. 801 45 (1949).

(3) Gee and Orr. ibid. 507 42 (1946).

(4) Raine, Richards and Ryder, ibid 56 41 (1945).

(5) Price. J. Chem. Phys. 973 19 (1951).

CHAPTER VII

The experimental results of the equilibrium vapour pressures, the variation of diffusion coefficients and mobility with concentration, and the effect of temperature on the diffusion process are discussed in this chapter; from both the theoretical standpoint and in relation to the work of other investigators.

The Comparison between Theoretical and Experimental Equilibrium Vapour Pressures.

1. Benzene-Rubber.

The experimentally determined values of $p_1{}^m/p_1{}^o$ are plotted against v_1 in fig. 1. The full line is obtained from the Flory-Huggins equation (Ch. III) with $\mu = 0.58$. The agreement is seen to be good over the whole range of measured values. The agreement with the results of Gee and Orr (1) and Gee and Treloar (2) is not quite as satisfactory. Their results at 25°C are consistent with a value of $\mu = 0.43$. A likely explanation for the discrepancy is to be found in the difference between the rubber used in the experiments. Gee and his collaborators used highly purified and fractionated rubber of intermediate molecular weight. The experiments described in this thesis were made on unfractionated vulcanisate

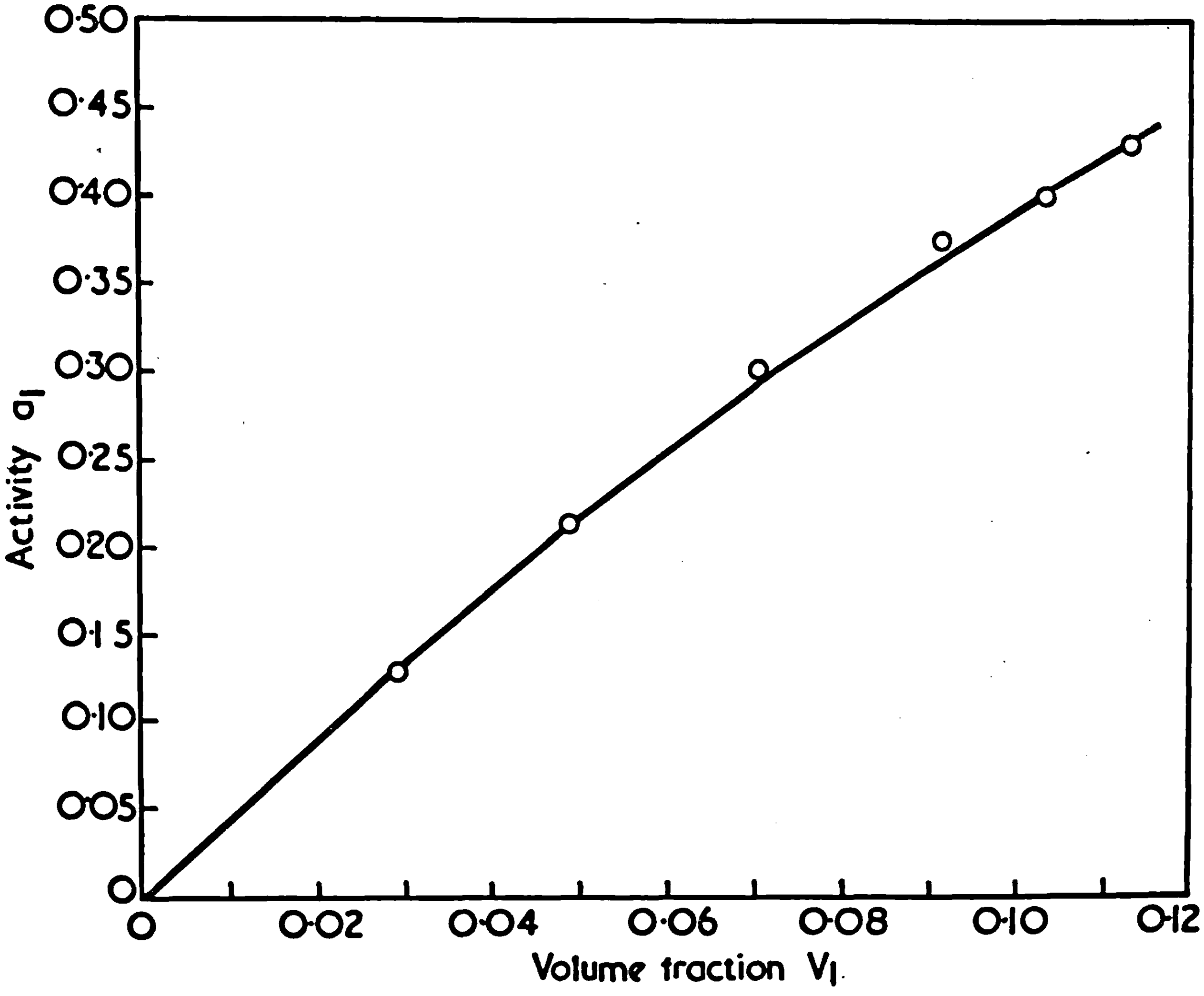

Fig. 1. Agreement between Experiment and Flory-Huggins Theory for Equilibrium Vapour Pressures. Benzene-Rubber.

containing accelerator, anti-oxidant, and filler (ZnO). If the volume fractions used to calculate μ are adjusted to take account of these additives, which comprise 8% of the total amount, then the value of μ falls to 0.48 and the agreement between the present work and that of Gee and his collaborators is considerably improved.

2. Benzene-Polythene.

The Flory-Huggins equation gives an unsatisfactory representation of the data. Table I shows the calculated values of μ.

Table I

Values of μ Calculated from the Flory-Huggins Equation for the Benzene-Polythene System

v_1	0.00423	0.00724	0.0149	0.0297	0.0564
μ	1.93	1.92	1.83	1.74	1.54

They are seen to be extraordinarily large and also a function of concentration. Clearly the partial cyrstallinity of the polythene must play a significant part in any theory of the interaction between this polymer and solvent. van der Waals and Hermans (3) have shown that vapour pressure measurements on the system n-heptane-polythene at 108.9°C are consistent with a value of $\mu = 0.34$. At 108.9°C polythene is completely melted so that one might hope to use the Flory-Huggins treatment to predict the equilibrium vapour pressures at temperatures below the melting point provided one could account for the effect of the crystallisation.

Raine, Richards and Ryder (4) have derived an equation which is applicable to the interaction between solvent and polymers which like polythene can exist in partially crystallised form. The data recorded in this thesis are not sufficiently comprehensive to afford a proper test of this equation for it involves several parameters which, in the absence of detailed experimental results, can only be assigned arbitrary values. As an alternative one might examine the data in the following cruder and more empirical way. Let it be assumed that the Flory-Huggins equation is applicable only to the interaction between the solvent and that fraction of the polymer which is not crystalline; and that there is no interaction at all between the solvent and the fraction of polymer initially crystalline. With these assumptions the volume fraction of benzene to be used will be less than the true volume fraction by an amount which will be determined by the degree of crystallinity of the polymer. Table 2 and fig. 2 give the results calculated in this way. The degree of crystallinity at 50°C is taken from the data of Price (5).

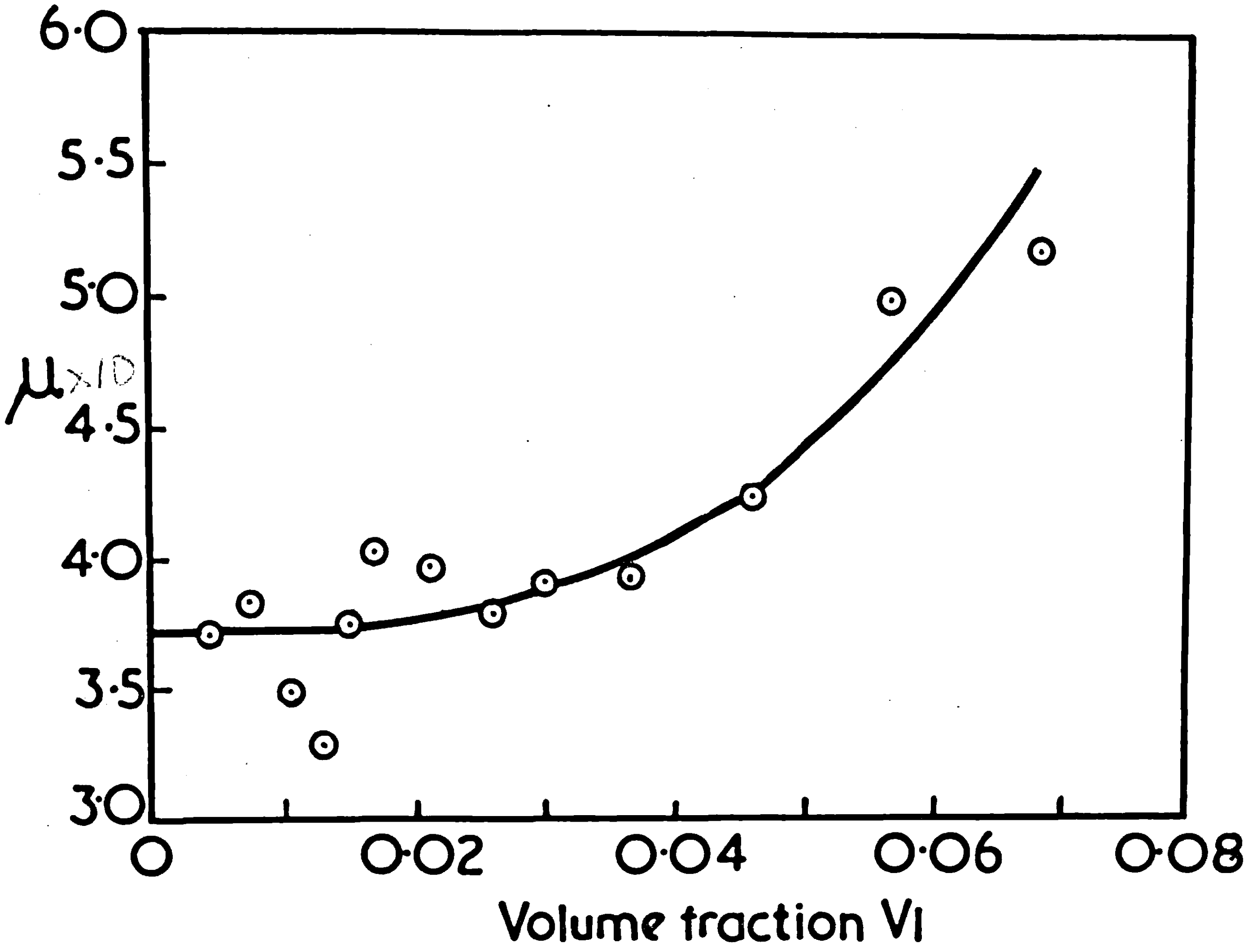

Fig. 2. Agreement between Experiment and Modified Flory-Huggins Theory for Equilibrium Vapour Pressures. Benzene-Polytene.

Table II

Values of μ Calculated from the Flory-Huggins Equation for the Benzene-Polythene System Making Allowance for the Effect of Crystallinity

Expt. No.	1	3	5	7	9	11	13
v_1	0.00422	0.0103	0.0149	0.0210	0.0297	0.0456	0.0680
μ	0.370	0.348	0.375	0.396	0.391	0.424	0.518
	Mean value of μ for points 1-9 inclusive (nine points) 0.372 ± 0.010						

Inspection of the curves in fig. 2 shows that for low benzene concentrations this treatment leads to a value of μ of the order of magnitude to be expected for non-crystallised polymers, a value moreover which is very close to that found by van der Waals and Hermans for the n-heptane-polythene system at 108.9°C. As the concentration of benzene increases so does the value of μ. This is understandable since it is undoubtedly true that the solution of benzene will lead to a progressive melting of the crystallised fraction of the polymer. The complex nature of the Raine, Richards and Ryder equation noted previously arises out of an attempt to allow for this melting.

The Effect of Changes in Activity on the Diffusion Coefficients

From the equilibrium vapour pressure measurements the quantity $d\ln a_1/d\ln v_1$ has been calculated in order that the mobility can be determined from the diffusion coefficient by the use of the previously derived equation

$$D = d\ln a_1/d\ln v_1 \cdot BkT \qquad \text{-----} \ 1$$

where

$$d\ln a_1/d\ln v_1 = (1 + d\ln\gamma_1/d\ln v_1)$$

For the benzene-rubber system $d\ln a_1/d\ln v_1$ has been calculated from the Flory-Huggins equation

$$\ln a_1 = \ln v_1 + (1 - v_1) + \mu(1 - v_1)^2$$

whence

$$d\ln a_1/d\ln v_1 = (1 - v_1)(1 - 2\mu v_1) \qquad \text{-----} \ 2$$

The heat of mixing parameter μ should be inversely proportional to the absolute temperature (Ch. III eq. 13) so that if $\mu = 0.58$ at 25°C it takes the value 0.53 at 50°C (in fact the values of $d\ln a_1/d\ln v_1$ are almost the same for both values of μ). Table III gives the values of $d\ln a_1/d\ln v_1$ calculated by the use of equation 2 with $\mu \doteq 0.53$.

Table III

v_1	0.01	0.03	0.05	0.06	0.09	0.10
$d\ln a_1/d\ln v_1$	0.979	0.939	0.900	0.880	0.823	0.805

It is not justifiable to calculate $d\ln a_1/d\ln v_1$, for the benzene-polythene data from equation 2 because μ is not constant for this system. $d\ln a_1/d\ln v_1$ has been obtained by differentiation of an empirical equation which fits the data. This equation is of the form

$$a_1 = A + Bv_1 + Cv_1 2 + Dv_1^3 \qquad ----- 3$$

whence

$$d\ln a_1/d\ln v_1 = \frac{Bv_1 + 2Cv_1 2 + 3DV_1^3}{A + Bv_1 + Cv_1^2 + Dv_1^3} \qquad ----- 4$$

Table IV gives the results.

Table IV

$$p_1^m = A^1 + B^1 v_1 + C^1 v_1^2 + D^1 v_1^3$$

$$\frac{d\ln a_1}{d\ln v_1} \cong \frac{d\ln p_1^m}{d\ln v_1} \quad \text{if } a_1 = p_1^m/p_1^o \text{ and } p_1^o \text{ constant}$$

$A^1 = -0.01606$ $B^1 = 504.8266$ $C^1 = -5{,}809.63$ $D^1 = 39{,}323.3$

No.	v_1	p_1^m(expt.curve)	p_1^m(polynom.)	$d\ln a_1/d\ln v_1$
0	0	0	-0.016	-
1	0.009	4.020	4.085	0.903
2	0.018	7.525	7.418	0.810
3	0.027	10.120	10.153	0.737
4	0.036	12.465	12.463	0.692
5	0.045	14.590	14.520	0.684
6	0.054	16.540	16.496	0.724

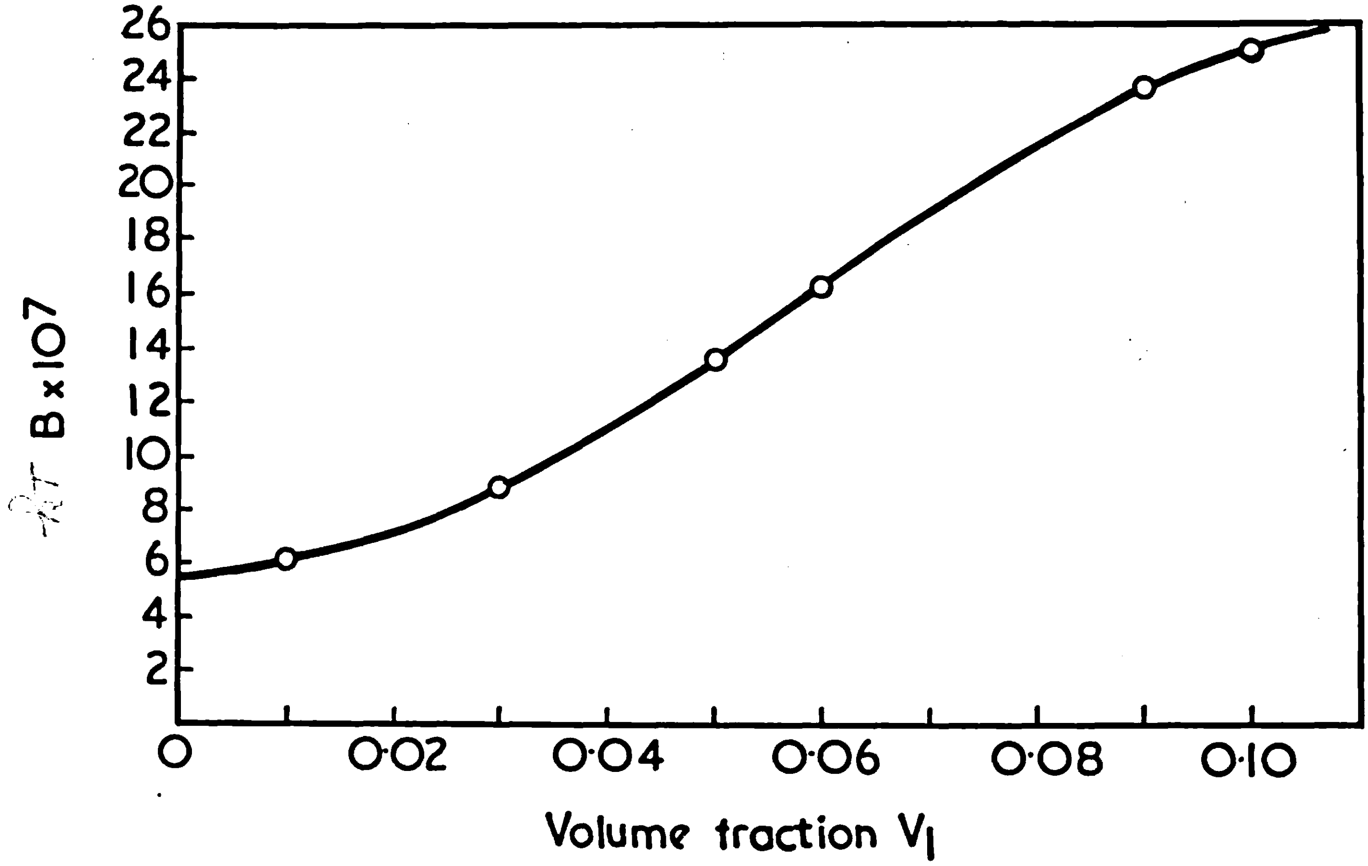

Fig. 3. Variation of the Mobility with Concentration.
Benzene-Rubber (50°C.)

The variation of the mobility with concentration, derived from these results combined with the diffusion coefficients listed in tables XIV and XV of the previous chapter, are given in figs. 3 and 4. For both systems $d\ln a_1/d\ln v_1$ is less than unity and decreases with increasing solvent concentration, so that the variation of B with concentration must be greater than that of D. Variations in the activity cannot therefore provide the full explanation for the increase in the magnitude of the diffusion coefficients in these systems as the solvent concentration is increased.

The Variation of the Mobility with Concentration

The mobility is markedly concentration dependent (figs. 3 and 4). If some theory could be adduced which would embrace such a variation then, in conjunction with the theories for the variation of the activity, one could in principle explain completely the dependence of the diffusion coefficient on concentration.

It has been previously noted (Ch. IV) that the mobility is to be understood on a kinetic microscopic scale in terms of the frequency of the unit molecular jumps and of the jump distance. The following simple theory leads to a means of allowing for the dependence of the frequency of unit diffusion jumps upon concentration.

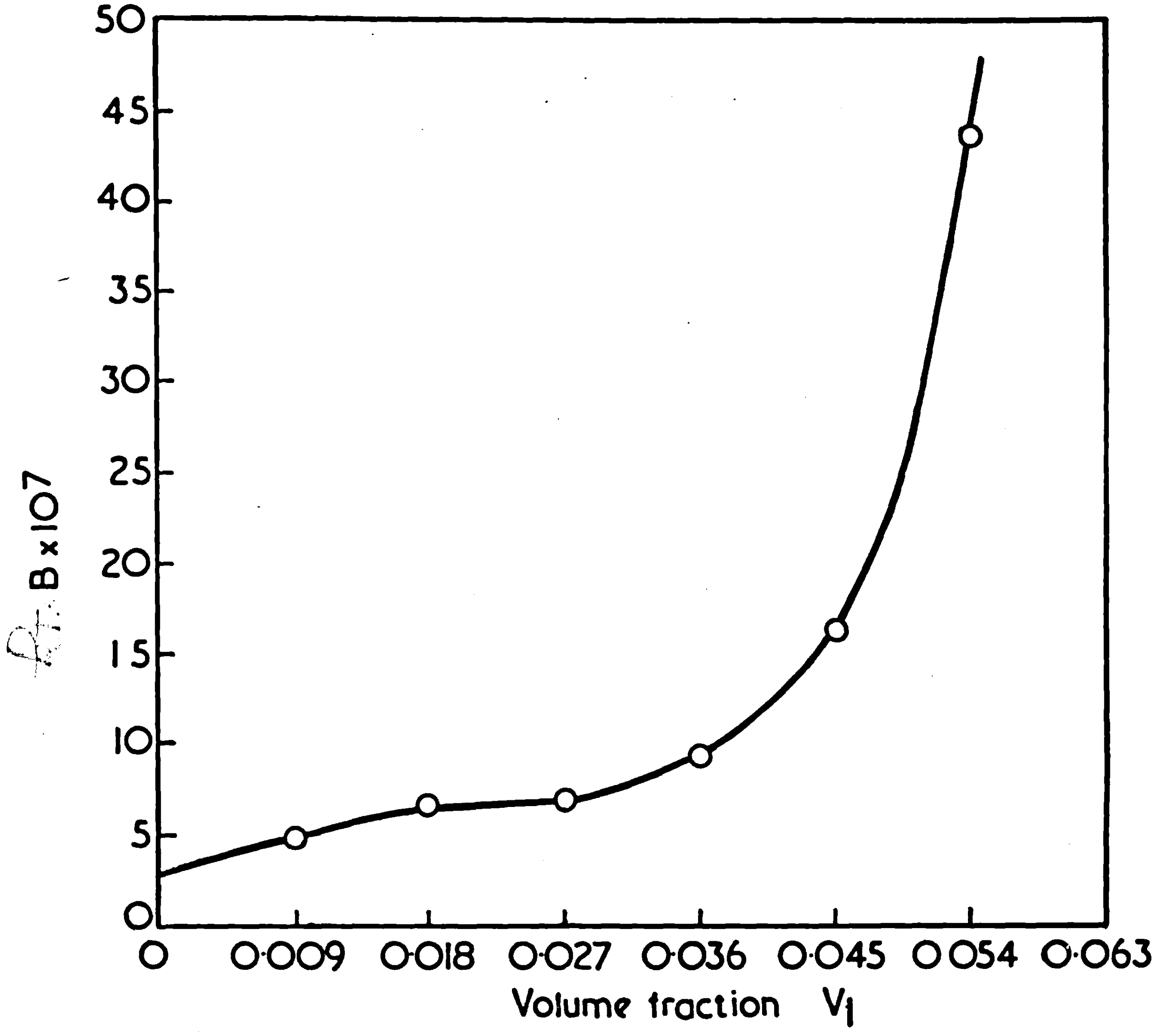

Fig. 4. Variation of the Mobility with Concentration.
Polythene (50°C.)

Consider a binary system composed of species A and B. Let the concentrations in mol fractions be N_A and N_B. Suppose that before a molecule of species A can make a unit diffusion jump it is necessary for there to be a synchronised outward displacement of several of those molecules which are its nearest neighbours. Let Z denote the number which must be displaced outwards simultaneously, and P_A and P_B the individual probabilities for the correct displacements of species A and B; Z, P_A and P_B are assumed to possess fixed values independent of concentration. The probability of getting a particles of species A and b particles of species B in a group Z in a system of composition N_A and N_B will be the coefficient of $t_A^{\,a}\ t_B^{\,b}$ in the expansion of the equation $(N_A t_A + N_B t_B)^Z$, for the A and B molecules in the group Z will be distributed binomially. The probability that a A molecules and bB molecules in an arbitrarily chosen group Z (= a + b) will move apart simultaneously will be given by the summation

$$\sum_{\text{all possible particles}} (\text{Probability of getting } \underline{a}\text{ A's and } \underline{b}\text{ B's}) \times \text{probability that they will move apart.}$$

$$= \sum P_A^{\,a} P_B^{\,b} \times \text{the coefficient of } t_A^{\,a} t_B^{\,b} \text{ in the expansion of } (N_A t_A + N_B t_B)^Z$$

$$= (N_A P_A + N_B P_B)^Z \qquad \text{----- } 5$$

The variation of the mobility of benzene in rubber may be directly interpreted by the use of this model if it is assumed that the whole of the variation is to be accounted for by the model. Provided this is so one has

$$(P_A)^z/(P_B)^z = \frac{\text{mobility of benzene in pure benzene}}{\text{mobility of benzene at infinite dilution in rubber}}$$

since the mobility of self diffusion of benzene will be proportional to $(P_A)^z$, and the mobility at infinite dilution of benzene in rubber will be proportional to $(P_B)^z$. For the rubber benzene system at 50°C this ratio is given very approximately by

$$(P_A/P_B)^z = \frac{4 \times 10^{-5}}{2 \times 10^{-7}}$$

$$\text{so that } (P_A/P_B) \doteq \sqrt[z]{200} \qquad \text{-----} \; 6$$

In a system of composition N_A and N_B the mobility B will be given by

$$B = K(N_AP_A + N_BP_B)^z$$

where K is a constant of proportionality. Using volume fractions this equation may be written

$$B = KP_B^z\,[v_A \sqrt[z]{200} + (1 - v_A)]^z \qquad \text{-----} \; 7$$

Equation 7 predicts a smaller variation of B with concentration than has been found experimentally if values of z between 3 and 6 are chosen. If the value for $(P_A/P_B)^z$ is increased the equation may be made to give a better fit. Table V gives the agreement between experiment and theory for a value of $(P_A/P_B)^z = 560$, and $z = 3{\cdot}5$.

Table V

Comparison between Theoretical and Experimental Mobility Coefficients. Rubber-Benzene

v_1	0	0.01	0.03	0.05	0.06	0.08	0.10	0.12
10^7 B calc.	(5.70)	6.78	9.38	12.6	14.5	18.9	24.2	30.3
10^7 B expt.	5.70	6.01	8.77	13.5	16.2	21.2	25.0	26.0

It is evident that this treatment is capable of explaining the dependence of the mobility on concentration for the systems studied using values for P_A/P_B and Z which are not implausible. Of course the fact that such a procedure is successful in these instances affords no guarantee that it is correct.

It might be argued that the assumptions on which the theory is based are unreal, that the probabilities P_A and P_B must be related to molecular vibrations that cannot possibly be independent of concentration; but if thisis so a more refined approach along similar lines may correctly describe the physical situation. More experiments and alternative theoretical interpretations are needed. Some of the latter are outlined later.

The Effect of Temperature on the Diffusion Process

The magnitude of the energy of activition for the diffusion of benzene in rubber (9·03 Kcal) is very close to the values found by Skirrow (6) for the diffusion of methane, ethane, ethylene, propane, and butane in lightly vulcanised rubber (8.2 - 8.9 Kcal for rubber containing 1.7% S).
It is interesting to note that the value for the energy of activation for the diffusion of benzene in rubber is also close to those values measured by Barrer (7) for the diffusion of much smaller molecules (H_2, N_2, Ar) through several synthetic rubbers. If as Barrer has suggested the diffusing species is accommodated within holes in the rubber set up by fluctuations in thermal energy then here would be an explanation for these similarities. Moreover this suggestion would imply, as Barrer has noted (7), that the energies of activation for diffusion should be of comparable magnitude to the energies for viscous polymer flow because this process also will depend in the same way on a Frenkel 'hole' mechanism.
The temperature coefficient for the bulk viscosity of rubber is about 10 Kcal (8), a value whose magnitude is in harmony with this point of view.

The energies of activation for the diffusion of some halomethanes in polystyrene that have been measured by Park (9) are far larger (14 - 26 Kcal) than those just discussed, and they show a marked dependence on concentration. The energies of activation for the diffusion in highly vulcanised rubber of inert gases and low molecular weight hydrocarbons that Skirrow measured (6) are also large. He considered this as being due to the high energy barriers to viscous flow in rigid polymers, an explanation that is also applicable to the measurements of Park.

The hypothesis that the diffusion process occurs by a 'hole' mechanism which is intimately linked to the process of viscous flow is an attractive one not only for the reasons adduced above but because it leads to an interpretation of the dependence of the diffusion coefficients on concentration. An interpretation which is both conceptually simple and invulnerable to the criticisms which have been levelled against that described in the previous section. If the 'hole' mechanism is correct then the diffusion rate will be determined by the number of 'holes' within the polymer. This number Frenkel (10) has shown to be related to the energy E_h required to create a 'hole' by an equation of the form

$$n = n_o \exp - E_h/2RT$$

where n is the number of 'holes'

It follows that the diffusion coefficient will vary with temperature according to an equation of the form

$$D = D_o \exp - (E_h + 2E_1)/2RT$$

in which E_1 is the activation energy requires for a 'hole' containing a diffusing molecule to surmount the energy barrier between one quasi-equilibrium position and the next. Both E_h and E_1 may be expected to be functions of concentration, particularly so for the diffusion of liquids in polymers where there is a large difference between the viscosities of liquid and polymer. The exact form of this functional relationship is not easily seen, but it seems reasonable to suppose that, at least to a first approximation, E_h the energy required to form a 'hole' will be directly proportional to the concentration of the diffusing species (Ch. III eq. 12)*. If $E_h = E_h^1(1 + \alpha v_1)$ than the diffusion coefficient will vary with temperature according to the equation

$$D = D_o \exp-(E_h^1(1 + \alpha v_1) + 2E_1]/2RT \qquad \text{-----}\ 8$$

Such an equation, with a negative value for the constant α, leads to an increase in the diffusion coefficient with concentration, as is found experimentally. It will moreover account for the linearity of the Arrhenius plots of the diffusion coefficientsprovided E_h^1, E_1 and α are independent of or vary little with temperature.

(*) Compare the discussion of the viscosity of liquid mixtures by Glasstone, Laidler and Eyring (11). These authors have proposed that the free energy of activation for viscous flow in a mixture, which they relate to the energy required to make a 'hole' in the liquid, will be given by the average value $N_1\Delta G_1^* + N_2\Delta G_2^*$, where N_1 and N_2 are the mole fractions, and ΔG_1^* and ΔG_2^* are the free energies of activation for viscous flow for the pure components.

The absolute magnitude of the constant D_o in the Arrhenius equation for the diffusion of benzene in rubber is 0.526. From D_o one may calculate ΔS^{*}, the entropy of activation for diffusion, provided the jump length δ is known (the method is described in Ch. IV). In the absence of any accurate knowledge of this quantity it is impossible to assign an exact value to ΔS^{*}. The jump length is certainly of the order of magnitude of the intermolecular distance. Skirrow has used the value $\sqrt{10} \times 10^{-8}$ cm. With this value ΔS^{*} for the rubber-benzene system is 10.5 e.u., the same value as that found by Skirrow for the diffusion of butane in rubber containing 1.7% sulphur. A value of δ of 1×10^{-8} cm. would reduce this by about 3 e.u. Even so ΔS^{*} would still be considerably larger than the values calculated by Barrer (12) for diffusion in unassociated liquids. One concludes that the diffusion process in the rubber-benzene system follows the same pattern as the diffusion process in other polymer-gas and polymer-liquid systems in that, unlike the diffusion process in liquids, the motion of a single diffusing molecule involves a profound disturbance of its environment.

One final remark concerning the effect of temperature on the diffusion process. The experiments here reported for the rubber-benzene system show that the permeability coefficient scarcely varies between 25 and 90°C. Surprising though this seems the theoretical significance is trivial. Because of the negligibly small heat of solution of benzene in rubber and the fortuitous cancellation of the energy of vaporisation of benzene ($\sim$8 Kcal) by the energy of activation for diffusion ($\sim$9 Kcal) the activation energy term in the permeability coefficient is virtually zero.

Recent Investigations into the Diffusion of Vapours through High Polymers by Others

Since the experimental work here described was performed there have been published several papers the contents of which bear closely on the experimental results and conclusions of this thesis. These are now considered. In England these papers are the work of Park, Crank and Hayes and in the United States Prager, Long, Kokes and their collaborators. Both groups have investigated the diffusion of vapours in high polymers, mostly by measuring absorption and desorption rates from which diffusion coefficients have been derived by the method of Crank and Henry described earlier. Park and Crank have measured diffusion coefficients for the transmission of halomethanes through polystyrene (9)(3). Hayes and Park have investigated the rubber-benzene system (14). Kokes, Long and Hoard have studied the diffusion of acetone in polyvinyl acetate (15), and Prager, Bagley and Long the diffusion of several aliphatic hydrocarbons in polyisobutylene (16).

Excepting the measurements on the benzene-rubber system (14) to be described later, and the diffusion of acetone through PVA below the second order transition temperature, for which the diffusion process is influenced by factors other than concentration - with these exceptions, all the above investigations have shown that there is (i) an exponential dependence fo the diffusion coefficient on concentration of the form

$$D = D^{o} \exp Ac \qquad \text{-----} \; (9)$$

(ii) an exponential dependence of the diffusion coefficient on temperature, at a fixed concentration, in conformity with the Arrhenius equation.

$$D = D_{o} \exp - E/RT$$

Table VI summarises the values found in the different systems for the constants in these equations.

Both groups of workers have put forward theories to account for the form of the equations. Parks (9) has interpreted the variation of the diffusion coefficient for the diffusion of halomethanes in polystyrene in the light of the absolute reaction rate equation for the diffusion coefficient

$$D = \delta^{2}\frac{kT}{h} \exp - \Delta G^{\pm}/RT$$

by supposing that $\Delta G^{\pm}$ is a measure of the widening of the channels, through which the molecules diffuse, with dilution of the polymer, or as a lowering of the interaction between channel wall and penetrant. In terms of a diffusion theory

Table VI

System		Reference	$D^o cm^2 sec^{-1}$ (25°C)	$D_o cm^2 sec^{-1}$*	A (25°C)	EKcal.*
Acetone-PVA		(15)	1.3×10^{-10} (30°C)		28 (30°C)	39
Propyl Alcohol-PVA		(16)	-	-	-	41
Benzene-PVA		"	-	-	-	37
n-Butane-Polyisobutylene		"	1.17×10^{-9}	2,500	28	16.7
iso-Butene-	"	"	0.53×10^{-9}	32	28.8	17.5
n-Pentane-	"	"	1.08×10^{-9}	400	25.8	16.0
iso-Pentane-	"	"	0.47×10^{-9}	20	26.6	18.1
neo-Pentane-	"	"	0.20×10^{-9}	4	17.2	18.0
CH_2Cl_2-Polystyrene		9(c)	121×10^{-12}	-	60	-
"	"	9(a)	19×10^{-12}	-	56.3	14 (15-25°C) 18 (25-35°C)
CH_31 -	"	"	4.6×10^{-12}	-	57.7	-
CH_2Br_2-	"	"	2.5×10^{-12}	-	57.7	12
$CHCl_3$ -	"	"	0.58×10^{-12}	-	52.0	-
CH_2Cl-CH_2Cl-	"	9(b)	50×10^{-14}	-	76	-
CH_3-$CHCl_2$-	"	"	41×10^{-14}	-	52	-
$CH_3(CH_2)_2Cl$-	"	"	35×10^{-14}	-	83	-
$CH_3(CH_2)_3Cl$-	"	"	41×10^{-14}	-	54	-
CH_21_2-	"	"	69×10^{-14}	-	47	-
C_6H_6-	"	"	9×10^{-14}	-	52	-
CCl_2=$CHCl$-	"	"	28×10^{-14}	-	76	-
Benzene-Rubber		(14)	7.1×10^{-7} (55°C)		-	8(50°C)
"	"	This work	5.6×10^{-7} (50°C)	0.53(25-90°C)	-	9.0 (50°C)

* At zero concentration of penetrant

requiring 'hole' formation he has suggested that $\Delta G^{\pm}$ is a measure of the loosening of the polymer structure and that this is related to the change in plasticity or viscosity as the penetrant concentration increases. Prager and Long in discussing their results for the diffusion of aliphatic hydrocarbon vapours through polyisobutylene (17) have pointed out that if the polymer-hydrocarbon bonds are weaker than those between the polymer chains then the energy required to form a 'hole' of a certain size will decrease linearly with increasing hydrocarbon concentration, consequently the number of 'holes' big enough to permit diffusion should increase exponentially with hydrocarbon concentration, and would lead to an equation for the variation of the diffusion coefficient with concentration of the form found empirically. Prager, Bagley and Long (16) have summarised the results for the energies of activation in PVA, polystyrene and polyisobutylene and noted that they show the expected relative order of magnitude when one considers the relative viscous and polar properties of these polymers.

In the work discussed in the previous paragraph the energies of activation and the reciprocal diffusion coefficients are large and the dependence of the diffusion coefficients on concentration is great. These factors constitute essential points of distinction between these systems and the rubber-benzene system. Hayes and Park (14) have tentatively concluded that the much larger values of D^o in rubber, and to a lesser degree polyisobutylene, are to be ascribed to a much greater similarity between these polymers and ordinary liquids than is the case with the other polymers. The writer concurs with this view and suggests that not only the larger D^o values but also the other essential distinctions noted above can be explained, in the light of the previous section, on the same terms.

The results of Hayes and Park on the rubber-benzene system are in good agreement with those here described. The diffusion coefficients, their variation with concentration, and the energies of activation are concordant. But there is one point of conflict. Hayes and Park found the Arrhenius energies for diffusion to be temperature dependent at constant concentration, in agreement with the findings of Skirrow, and also van Amerongen for the diffusion of small hydrocarbon and inert gas molecules through natural and synthetic rubber, whereas no such dependence was observed by the writer. The reason for this difference is uncertain. Certainly the departures from linearity exhibited in Hayes and Park's Arrhenius plots are consistent and cannot be due to chance experimental deviations. The temperature range covered by them (0 - 100°C) was greater than that of the present work (20 - 90°C) and it may be that if measurements had been made over a wider temperature range by the writer, then deviations from the Arrhenius equation would have appeared.* Hayes and Park's results are more extensive than those here described not only by virtue of the wider temperature range but also because they have made measurements on samples of rubber of several different degrees of vulcanisation. Their results agree with those of Skirrow, previously described, in that vulcanisation is found to decrease the value of the diffusion coefficients; in addition it is found by ~~Park~~ them to make the diffusion of benzene more dependent on concentration.

(*) The curvature of Hayes and Park's Arrhenius plots increases as the temperature falls and is scarcely detectable, at low benzene concentrations, above 25°C. There is the possibility that the onset of crystallisation of the rubber is largely responsible for this change. Unstretched rubber crystallises at about -25°C, but the onset of crystallisation can occur at temperatures as high as 15°C (18).

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