

DIFFUSION AND SOLUTION IN SILICONE ELASTOMERS

by

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ABSTRACT

Permeability, diffusion and solubility coefficients for inert gases, permanent gases and n-butane in silicone elastomers have been measured over the temperature range 0°C to -78°C. The time lag apparatus and techniques have been used in these determinations which employed two different forms of diffusion system - the plane sheet membrane and the hollow cylindrical membrane.

For all gas-silicone elastomer pairs investigated, a linear plot of the logarithm of the diffusion or permeability coefficients vs. the reciprocal Kelvin temperature is observed, indicating that activated diffusion occurs. As the experimental temperature was lowered from -48°C to -55°C, the sudden drop in the flow rate of the penetrant indicates that crystallization of the elastomer has set in. In so far as the selectivity of these gases by means of silicone elastomer is concerned, it appears from steady state investigations that no striking improvement is achieved by lowering the working temperature. The results of the temperature coefficients of diffusion have been interpreted in terms of the transition state theory and the zone theory. Both treatments indicate that only a small zone of activation is required in order for a unit diffusion process to take place. A functional relationship is observed when in the Arrhenius equation $D = D_0 \exp(-\frac{E_D}{RT})$, one plots $\log D_0$ vs. $\frac{E_D}{T}$.

Between 0°C and -40°C, the order of magnitudes of the solubility coefficients agrees with that of the solubilities of these gases in various organic solvents. The critical temperature, boiling temperature and the Lennard-Jones (6-12) force constants have been used to correlate the solubility data. The free energy, heat and entropy of solution were compared with those of the same gases dissolving in some monomeric solvents. The free energy, heat and entropy of dilution agree reasonably with those deduced from the theory of polymer solution. Below the transition temperature, the anomalous behaviour of the temperature coefficients of the solubility data indicates the extreme heterogeneity of the silicone elastomer.

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PART I
INTRODUCTION AND LITERATURE SURVEY . .

1.1 INTRODUCTION

Transport and equilibrium phenomena in high polymeric membranes have been studied by many workers¹⁻¹⁸ because, aside from the technical interest of the resulting data, there exist certain correlations among diffusion parameters and the known molecular structure parameters. Thus, investigations of permeation, diffusion and solution of gases or vapours in high polymeric membranes enable one to characterise these membranes as barriers to gases or vapours. Furthermore, valuable information may be obtained on the mechanism of diffusion process and the micro-structure of the polymer.

While some work, especially on the flow of gas through a natural rubber membrane, was published by Graham¹⁹, the majority of systematic investigations and references date back to the work of Barrer¹ in 1939, and of van Amerongen⁴ in 1946. It appears to be generally accepted at present that permeation of gas or vapour through a high polymeric membrane is a complex phenomenon involving the following sequence of processes: (i) sorption of the gas at one interface of the barrier; (ii) solution of the gas into, and diffusion in and through the barrier; and (iii) evaporation at the opposite interface. Of these physical processes, diffusion is usually the slowest and therefore constitutes the rate determining step.

According to Fick's law, the rate of permeation per unit area is the product of the diffusion coefficient and the concentration gradient within the membrane. This rate of permeation will therefore be governed by factors which affect both the diffusion coefficient and the solubility of the penetrant. These factors, which will be described in the following sections may include at least the temperature, the size and shape of the diffusing molecule, the cross-linking of the polymer, the crystallinity of the polymer, the nature and the amount of the filler particles in the polymer, the concentration of the diffusing species, and sometimes, the previous history of the polymer.

There have been relatively few systematic investigations of diffusion and solution of gases or vapours in silicone elastomers. All investigators^{3,16,18} do agree, however, that as a result of high chain flexibility, silicone elastomers are very much more permeable to gases and vapours than any other membranes reported so far. In view of the completeness of the data presented by Barrer et al¹⁶ it is worthwhile to summarise their findings relating hydrocarbon vapour - silicone elastomer systems as compared with natural rubber, as follows: (i) solubility data are very similar to those of natural rubber, and solubility decreases with increasing filler content; (ii) permeability data are 25 to 40 times larger, and diffusion data 10 to 20 times larger than the corresponding data for natural rubber; (iii) the activation energies for diffusion are only about one-third those in natural rubber; (iv) the permeability coefficient P decreases with increasing temperature; (v) the permeability and

the diffusion coefficients decrease with increasing filler content; (vi) diffusion in silicone rubber is less sensitive to size and shape of the penetrant molecules, so that silicone rubber is less selective than natural rubber as a separation medium.

However, as silicone elastomers can withstand higher and lower temperatures than many other organic membranes, they may constitute quite promising barriers for gas and vapour separation.

The object of this work is an attempt to present systematic data of permeation, diffusion and solution of gases at low temperatures with a view to characterising silicone elastomer as barrier to gases. Inert gases are chosen to act as "probes", for they represent a family of gases changing systematically in size and other physical properties. To cover a wider field, permanent gases and n-butane are also employed. It has been reported¹⁸ that, within 30° to 70°C, the selectivity of silicone membranes for isomeric hydrocarbon vapours (C₄ and C₅) is slightly inferior to natural rubber, although Kammermeyer¹⁸ claimed that, within 0° to 40°C, its selectivity towards permanent gases is as good as any other membrane then available. It is hoped, therefore, that by working at temperatures below 0°C more favourable conditions with respect to its selectivity towards gases may be established. It is also hoped that from this method of investigation at low temperatures some information may be gained as regards the morphology of the silicone elastomer.

1.2 EFFECT OF TEMPERATURE

It has been shown that the temperature coefficient of the permeation rate is independent of the pressure difference and the thickness of the membrane. Correlation of experimental data indicates that over a moderate temperature range the permeability coefficient $\bar{P}$ can be expressed by equation

$$\bar{P} = P_0 \exp \left(- \frac{E_p}{RT} \right) \quad (1.1)$$

where P_0 is constant, and E_p the apparent activation energy of the permeation process - a relation first demonstrated by Barrer¹. Barrer^{1,20} also showed that $\bar{P}$ can be resolved into the product of diffusion coefficient D and the solubility coefficient σ , i.e.

$$\bar{P} = D\sigma \quad (1.2)$$

Satisfactory agreement exists between the values of σ or D calculated from (1.2) and the values found by direct measurement, at least in the case of a good number of penetrant-polymer systems.

Barrer¹ pointed out that D and σ vary exponentially with temperature according to

$$D = D_0 \exp \left(- \frac{E_D}{RT} \right) \quad (1.3)$$

$$\sigma = \sigma_0 \exp \left(- \frac{\Delta H^0}{RT} \right) \quad (1.4)$$

where D_0 and σ_0 are constants, E_D is the activation energy for diffusion, and ΔH^0 is the heat of solution of the gas in the membrane. In fact, the temperature coefficient of $\bar{P}$ represented by (1.1) is the direct outcome of the activated diffusion process according

to (1.3) and the solubility following a comparable law represented by (1.4). It follows from (1.1), (1.3) and (1.4) that the relation between the three energy terms is

$$E_P = E_D + \Delta \bar{H}^0 \quad (1.5)$$

According to (1.3), a linear plot of $\log D$ vs $\frac{1}{T}$ is expected. However, over a wider range of temperature, a slight curvature may sometimes be observed^{5,21,22} so that in (1.3) both D_0 and E_D can be temperature dependent, each becoming smaller as temperature rises. An explanation of this follows from Barrer's zone theory²³, and an interpretation is also possible in terms of Eyring's treatment of rate processes²⁴.

1.3 EFFECT OF SIZE AND SHAPE OF DIFFUSING MOLECULE

The effect of molecular size on diffusion coefficient has been investigated by many workers^{4,9,15,20,21}. As expected, the measured diffusion coefficient decreases and the activation energy increases with increasing molecular size of the diffusant. Barrer et al²¹ pointed out that the size of the diffusing molecule has in elastomers a much smaller influence than would be inferred from analogous experiments on diffusion through a rigid membrane such as silica glass^{75,74}.

The effect of shape of the penetrant has also been considered^{25,26,22}. Prager and Long²⁵ conclude that adding a CH_3 side-chain reduces D in polyisobutylene rubber by a larger amount than does

an increase of chain length by one carbon atom. It is therefore inferred that diffusion occurs preferentially along the direction of greatest length of the molecule. This view is also supported by Aitken and Barrer²². The influence of molecular weight (i.e. number of carbon atoms) of the penetrant upon $\bar{P}$, D , and σ is also very striking²¹.

1.4 EFFECT OF CROSS-LINKING

Barrer and Skirrow²¹ have demonstrated the marked effect which cross-linking of rubber (up to 13% of combined sulphur) can have upon $\bar{P}$ and D of nitrogen and of C_1 to C_4 paraffins. In contrast, the solubility coefficients were not greatly influenced by this degree of vulcanisation. Aitken and Barrer²² observed similar relation in rubber cross-linked by t-butyl peroxide; in particular, they found that the diffusion coefficient falls linearly with the reciprocal of the average molecular weight between cross-links, i.e. proportionally to the number of cross-links.

1.5 EFFECT OF CRYSTALLINITY

The effect of crystallinity on transport and equilibrium properties of gases in microcrystalline polymer, polyethylene, has been thoroughly investigated by Michaels and co-workers¹¹⁻¹³. From their observations it was concluded that the solubility of gases in, and their flow through, crystallites of polyethylene

are negligible, and that since isotropic diffusion was also shown to be occurring, crystallites must be randomly distributed in the amorphous phase with respect to the macroscopic dimensions of the polymer samples; and also that amorphous fractions of polyethylene can be treated as a homogeneous liquid-like material with characteristic thermodynamic properties which are independent of the level of crystallinity. It appears, therefore, that the relationships for the solubility, diffusion and permeability coefficients are valid only in partially or wholly amorphous systems, and might be corrected for the fraction of the system existing as crystallites. The observed value of the permeability coefficient has however obvious practical value in describing transport process, even though the degree of crystallinity may not be known with any degree of accuracy.

Michaels et al^{11,12} have shown that the solubility coefficients of gases in crystalline polyethylene determined by the equilibrium (static) and time-lag (dynamic) methods were found to agree within the limit of accuracy, thus confirming the applicability of the transient state diffusion equation to essentially isotropic crystalline polymer. Furthermore, the solubility coefficients for a particular gas in a variety of polyethylene samples were found to be proportional to the volume fraction of the amorphous material, when the polymer was treated as a simple two-phase mixture of crystalline and amorphous polymer each with a characteristic specific volume. With this model of crystalline-amorphous matrix, several authors have attempted to apply to the diffusion of

of gases in polyethylene the concept of impedance to flow as it has been used in the flow of gases through particulate porous media, or flow of electrical current through composite media consisting of non-conducting phase dispersed in a conducting phase. Thus as the flow of gas in a porous medium is impeded as it traverses irregularly shaped , elongated pores, and likewise as the flow of current is confined to similarly constricted regions of conducting phase in a composite medium, gas diffusion in a microcrystalline polymer must also be impeded in the irregularly shaped regions of interconnected amorphous polymer bounded by impenetrable crystallites.

Myers et al²⁷ have shown that considering the crystalline phase to be a homogeneous dispersion of spheres is an underestimate of the restriction to flow in polyethylene. Klute²⁸, also considering a spherical geometry for crystallites, has concluded that experimental impedances determined from electrical conductivity measurements in beds of spheres of different sizes in varying proportions may be a better approximation of resistance to flow encountered by gases diffusing in polyethylene. Although possibly more realistic, this model still predicts impedances which are lower than those observed experimentally.

Michaels et al^{11,13} have studied a more complete series of polyethylenes, both with respect to mode of polymerisation and range of amorphous fraction. They have proposed that two impedance factors are operating to reduce the diffusion coefficients in semi-crystalline polyethylene below the

value anticipated in the completely amorphous polymer. The diffusion coefficient is formulated as $D = \frac{D^*}{\tau\beta}$, where D^* is the diffusion coefficient in completely amorphous polyethylene, and τ is a geometric impedance factor accounting for the reduction in diffusion coefficient due to the necessity of molecules to bypass crystallites and move through amorphous regions of non-uniform cross-sectional area. β is a chain immobilisation factor which takes into account the reduction in amorphous chain segment mobility due to the proximity of crystallites. Since activated diffusion was observed, and the most realistic model for this process involves the cooperative movement of amorphous chain segments and diffusing molecules, restricting the mobility of polymer chains by the cross-linking action of crystallites must reduce the diffusion coefficient. Myers et al²⁷ recognised this latter factor but found no way of determining it. Michaels et al^{11,13}, by what appear to be suitable assumptions, have been able to estimate values of D^* , τ and β . The resulting values of τ showed a marked dependence on mode of polymerisation and were of such magnitude that the authors concluded that crystallites in polyethylene must be highly anisotropic.

Michaels et al¹⁴ extended the above investigations in gas-polyethylene terephthalate system to cover not only rubbery crystalline polymer but also glassy amorphous as well as glassy plus crystalline polymer. Meares^{6,7} also studied diffusion and solution of gases in polyvinyl acetate over a temperature range between 4° to 44°C, enabling him to determine two transition temperatures. It is clear that

an important aspect of these investigations is the insight into polymer morphology gained by the analysis of the diffusion process. Use of diffusing gases as molecular "probes" tends to supplement data from other sources such as X-ray analysis, electron microscopy, and light scattering.

1.6 EFFECT OF FILLER PARTICLES

A dispersion of filler particles in the polymer matrix constitutes a complex heterogeneous medium for which no rigorous treatment of diffusion has so far been successfully developed. In most investigations of this nature, however, it has generally been demonstrated that permeability decreases as the filler content increases^{16,17,29,30}. Moreover, Melikhova et al³⁰ found that mica fillers, among others, were more effective in reducing the flow of N₂ through rubber vulcanizates, and concluded that the permeability depends on many factors, such as the size, shape and orientation of the filler particles, the degree to which polymer wets the filler particles, and bond formation between the filler and polymer. Van Amerongen³¹ found that although the incorporation of carbon black in natural rubber reduced its permeabilities to gases, the solubilities of the gases in the rubber were increased - thus implying sorption of the gas by the filler.

In the absence of an exact solution of the diffusion equation for such a complex heterogeneous medium, the usual approach is to modify the corres-

ponding equation for flow through a homogeneous medium by introducing suitable structural parameter, as in the case of semicrystalline polymer previously discussed in section 1.5. Recently, the role of the filler particles in the process of diffusion and solution was thoroughly investigated^{16,17}. The experimental data were interpreted in terms of two reference models, namely (i) the filler and polymer phases act independently as sorbents, and (ii) the filler is regarded as completely wetted by the polymer and is thus a non-sorbent. Although some aspects of the behaviour can be explained, the findings are not fully in agreement with either model, and the behaviour of the heterogeneous membranes are complex.

1.7 EFFECT OF CONCENTRATION OF PENETRANT

The way in which diffusion coefficients change with penetrant concentration has been investigated for a number of penetrant-polymer systems. Crank and Park³², Park³³, Prager and Long²⁵ suggested that over a fairly wide range of concentration the diffusion coefficient, D , can be represented as exponential functions of penetrant concentration, or on expanding the exponential, D varies linearly with concentration in dilute solution, as has been shown by Aitken and Barrer²². Many of these investigations refer to hydrocarbon in polyvinyl acetate, cellulose acetate, cellulose nitrate and polystyrene as diffusion media, and therefore time components may enter the diffusion coefficient, and the concentration dependence

may be incorrectly deduced. However, data of Prager and Long²⁵ for hydrocarbon-polyisobutylene systems (systems which should give correct concentration dependence of the diffusion coefficient since polyisobutylene is an elastomer) still follow the exponential expression. As a corrective to any tendency to read undue significance into an exponential relation, one notes that Fujita³⁴ was just as successful in representing the concentration dependence of D for CHCl_3 diffusing in polystyrene by means of the relation $D = D_0 (1 - bc)^{-2}$ (where b is constant and c is the penetrant concentration) as Crank and Park³² had previously been with exponential relation. Barrer, Barrie and Slater³⁵ in their studies of diffusion in ethyl cellulose in which time-dependent effects were eliminated have come to the same conclusion.

1.8 SEPARATION OF GASES BY MEANS OF PERMEABLE MEMBRANE

Since polymeric membranes have a much higher permeability towards some gases than towards others, they should be quite effective as a means of gas separation. The economics of large scale separations of air into N_2 and O_2 , and also of He from natural gas, have been investigated by Weller and Steiner^{36,37}. Although the process is not yet commercially feasible as compared to the cryogenic process, it is suggested that improvement of the membrane may perhaps bring about conditions which may be more favourable. Whilst many investigations do not touch upon the subject of gas separation specifically, the findings contribute

much to the basic knowledge required for the study of gas separation by means of such membranes.

Aitken and Barrer²² defined the separation factor S through permeation as $S = Q_1 C_2 / Q_2 C_1$, where Q_1 and Q_2 are the amount of gaseous species 1 and 2 diffusing through the membrane in time t , and C_1 and C_2 are the respective concentrations at the ingoing surface of the membrane. S can, in the steady state, be estimated to a first approximation from the ratio of individual permeabilities, since, at least in the regions where Henry's law is valid and solubility rather small, interference effects are not likely to be very large. Barrer³⁸ has pointed out that in the transient state of flow, this separation factor may be very large indeed; the faster moving component may reach the outgoing surface of the membrane long before the slower moving component. Calculated data for separation of n-butane and iso-butane in the transient state have been given by Barrer² and theoretical limitations of separation discussed^{38, 22}.

1.9 EXPERIMENTAL METHODS OF MEASUREMENT

The accurate and rapid measurement of permeability coefficients of membranes and plastic films to gases is important to the packaging industry (especially for food packaging), the construction industry, and potentially in the separation of gases by selective permeation. Of the various methods of measuring gas permeabilities described in the literature, three have received particular attention. These three

methods may, for convenience, be described as the variable pressure, the variable volume, and the variable concentration methods.

The variable pressure method: this method usually requires that the membrane be initially out-gassed. A constant gas pressure is then applied on one side of the membrane, and the increase in the pressure of the permeating gas is measured on the opposite side of the membrane. This method has been used by many investigators; for instance, Barrer¹ has, in 1939, developed a research apparatus for the simultaneous determination of permeability, diffusion and solubility coefficients, while Heilmann et al³⁹ and Brown et al⁴⁰ have also designed permeability cells for the same and routine purpose.

The variable volume method: according to this method, a conveniently high gas pressure is applied on one side of the membrane and the permeating gas is allowed to expand on the opposite side against some low constant pressure, usually atmospheric. The change in the volume on the outgoing side is then measured as a function of time by following, for example, the displacement of a short column of liquid in a capillary. This method has been employed by Brubaker and Kammermeyer^{41,42}, and recently by Stern et al⁴³.

The variable concentration method: according to this method, two different gases are allowed to contact the opposite side of the membrane and the gas composition is monitored as a function of time on either

side of the membrane. The measurements are conducted under zero total pressure differential. This method has been used by Landrock and Proctor⁴⁴.

Of the three methods described above, the first two have proved to be more popular as they do not require costly analytical apparatus. The variable pressure method, in particular, is widely used nowadays, and has been adopted as a standard by the American Society for Testing Materials⁴⁵. This variable pressure method was employed throughout this work.

1.10 SILICONE ELASTOMERS

1.10.1 General

Silicone elastomers are based on high molecular weight silicone "gum" which is predominantly a methyl polysiloxane. The characteristic elastic properties are produced as a result of intermolecular cross-linking in the presence of an oxidising curing agent, whilst mechanical strength is imparted by the addition of a suitable inorganic filler.

Silicone rubbers are normally cured by the action of organic peroxides though vulcanisation can also be effected by high energy radiation⁴⁶. Highly reactive peroxides, such as benzoyl peroxide, 2,4-dichlorobenzoyl peroxide, and t-butylperbenzoate, are necessary for curing saturated polysiloxane, whereas less active peroxides, such as di-t-butyl peroxide, dicumyl peroxide, and t-butyl peracetate, will bring about a satisfactory cure when methyl and vinyl groups are present in the gum.

Fillers for silicone elastomers must fulfil two main criteria: (i) they must be stable under the environmental conditions which the rubber will encounter in use; (ii) they must be chemically inert toward other rubber components. (This latter condition should not be taken to exclude any possible interaction between filler and polymer which leads to the reinforcement of physical properties). These criteria limit the useful fillers to various types of silica, certain inorganic oxides and salts. The factor common to all reinforcing fillers is high specific area, though whether this is the only, or even the principal, requirement for reinforcement has not yet been demonstrated with certainty. It has been established for silicone elastomers that reinforcing power increases rapidly when filler particle size falls below $500 \text{ \AA}$. The best and most widely used of the fillers is the group of artificially prepared silicas with particle size lying in the region of $30\text{--}300 \text{ \AA}$, and with specific surface of up to 400 sq.m/g . Typical members of the group are the aerogel (SANTOCEL), the fumed silica (AEROSIL), and the precipitated silica (HI-SIL). Fillers of the order of $10,000 \text{ \AA}$ in particle size are semi-reinforcing.

1.10.2 Physical properties of methyl polysiloxane

Much attention has been given to explaining one of the most important properties of methyl polysiloxane (the basic polymer for silicone elastomer), namely, the small change in viscosity with temperature.

This property appears to be associated with the presence of $\text{Si}-\text{O}-\text{Si}$ linkages rather than the presence of Si atoms. This relatively small temperature coefficient of viscosity has been recognised as a result of low intermolecular forces in organopolysiloxanes⁴⁸⁻⁵². If intermolecular cohesions are weak, then the activation energy of viscous flow and hence the temperature coefficient of viscosity will be low. The weakness of the intermolecular cohesions might arise from the unusually large freedom of motion within the siloxane molecule which causes the molecule to occupy a large volume, so that forces between adjacent molecules are weak^{53,54}. The motion may include free rotation of CH_3 groups attached to Si atoms, free rotation about $\text{Si}-\text{O}-\text{Si}$ bonds, and flexing of the readily deformed $\text{Si}-\text{O}-\text{Si}$ angles. The random motions of siloxane molecules in stretched methyl silicone rubber even at low temperature are such as would normally be associated with the liquid state⁵³. This hypothesis of weak intermolecular cohesion has the great advantage of explaining physical properties of methyl polysiloxanes.

The small temperature coefficient of viscosity has also been explained in terms of a coiling action at low temperatures and uncoiling as temperature is raised⁵⁵. This coiling and uncoiling explanation is attractive because of its simplicity, but a more careful examination of its implications reveals difficulties⁵³.

Nuclear magnetic resonance studies on methyl silicone rubber show that there is unusual freedom of

rotation of the methyl group even at -196°C ⁵³. This property of free rotation of the methyl group at very low temperatures is also found in some other silicon compounds, e.g. the halides, and may be associated with the large size of the Si atom; but at higher temperatures there is additional motion in the siloxane molecules which may originate in flexing of the $\text{Si}-\text{O}-\text{Si}$ bonds. Indeed above -109°C there is, in silicone rubber, much motion not restricted to any particular axis or plane - the type of random motion, in fact, which is usually associated with the liquid state ⁵³.

Silicone rubber, on cooling, and particularly on extension at low temperatures, tends to crystallise and also to undergo a second order transition (glass temperature). Interferometric measurements ⁵⁶ of the dimensions of a cube of silicone gum and silicone rubber showed that crystallisation occurred at temperatures between -60° and -67°C , and a second order transition at -123°C .

Crystallisation at low temperatures has also been studied by the X-ray method ⁵⁷ using methyl silicone elastomer containing about 17% by volume of fine silica filler. It was shown that a relatively large amount of crystallising materials forms within the narrow temperature range -50° to -60°C , and that crystallinity increases with further decrease of temperature. Further studies ⁵⁸ of crystallisation of the same silicone rubber were made by other physical methods, e.g. density measurements revealed that the sharp change in volume between -54° and -56°C for the unstretched sample is accompanied by a rapid attainment

of equilibrium. There is some evidence⁵⁷ that crystals which form on cooling do so at the same orientation as the amorphous segments from which they were derived. Moreover, because of the relatively low viscosity, the crystals form quickly and equilibrium is achieved in a matter of minutes. Both X-ray and physical methods yield good evidence that crystallisation of silicone rubber produces tension rise, the opposite effect to that observed in natural rubber. Moreover, the nature of crystallisation differs in that while natural rubber forms crystallites oriented almost exclusively in the direction of stress, silicone rubber seems to be able to crystallise chain segments at all orientations in space. This is said to be due to the greater chain segment mobility of the silicone rubber, so that stretching can bring together chains over a much wider range of angles than is usual.

The introduction of fillers into silicone gums affects their properties by polymer-filler interactions. Thus non-Newtonian flow characteristics are introduced⁵⁹ and measured cross-linking is increased⁴⁷. Such interactions have been studied by measuring bound polymers which cannot be removed from a filler by washing with solvent. More conveniently, the number of cross-links can be measured either by swelling experiments or by measuring the modulus of elasticity at low elongations.

PART 2. THEORETICAL

2.1 FUNDAMENTAL LAWS OF DIFFUSION

Diffusion is a process by which matter is transferred from one part of the system to another as a result of random molecular motion. Thus, the laws of diffusion connect the rate of flow of the diffusing substance with the concentration gradient responsible for this flow.

2.1.1 Diffusion in a plane sheet membrane

If x be the co-ordinate chosen perpendicular to the reference surface, and C the concentration of the diffusing substance given as the amount of substance per unit volume (in the same units as that chosen for the rate of transfer, P , per unit area of the section), then the diffusion coefficient D is defined by

$$P = -D \frac{\partial C}{\partial x} \quad (2.1)$$

D is, in effect, a measure of the rate at which diffusion occurs. The negative sign in (2.1) is used merely to indicate that diffusion occurs in the direction opposite to that of increasing concentration. Dimensional analysis shows that D has dimension $[\frac{L^2}{T}]$, independent of the unit of amount of substance diffusing. From (2.1) the condition of conservation of mass yields for constant D

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2.2)$$

(2.1) and (2.2) are sometimes known as Fick's first and second law of diffusion respectively.

2.1.2 Diffusion in a hollow cylindrical membrane

In the case of diffusion in a cylinder, the corresponding expression is given, for constant D , by:

$$\frac{\partial C}{\partial t} = \frac{D}{r} \left[\frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) + \frac{\partial}{\partial \theta} \left(\frac{1}{r} \frac{\partial C}{\partial \theta} \right) + \frac{\partial}{\partial z} \left(r \frac{\partial C}{\partial z} \right) \right] \quad (2.3)$$

It is derived by the use of cylindrical polar co-ordinates with the following transformation equations: $x = r \cos \theta$, $y = r \sin \theta$. In particular, where diffusion is considered to be everywhere radial, the concentration C is then a function of radius r and time t only. It follows from (2.3) that

$$\frac{\partial C}{\partial t} = \frac{D}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C}{\partial r} \right) \quad (2.4)$$

2.2 SOLUTIONS OF DIFFUSION EQUATIONS (for constant D only)

The following solutions apply to diffusion in a membrane so thin that all the diffusant enters through the membrane surface and a negligible amount through the edges. Only the one dimensional problem with constant D will be considered.

The general boundary conditions for diffusion in a membrane with unswollen thickness, l , are:

$$\begin{aligned} C &= 0 & \text{at } 0 < x < l & \text{for } t = 0 \\ C &= C_1 & \text{at } x=0 & \text{for } t \geq 0 \\ C &= C_2 & \text{at } x=l & \text{for } t \geq 0. \end{aligned}$$

In particular, by putting $C = C_1 = 0$ (or rather $C_2 \gg C_1$), the above becomes exactly the boundary conditions relevant to the experimental arrangements in all this work. Solutions are required for both steady and transient state of flow.

2.2.1 Plane sheet membrane

(a) Steady state diffusion

When steady state is reached, in which concentration remains constant at all points of the membrane, $\frac{\partial C}{\partial t} = 0$. It follows from (2.2) that

$$D \frac{\partial^2 C}{\partial x^2} = 0 \quad (2.5)$$

Integrating (2.5) twice w.r.t. x , and putting the general boundary conditions at $x = 0$ and $x = \ell$, we have

$$C = C_1 + (C_2 - C_1) \frac{x}{\ell} \quad (2.6)$$

Now, the rate at which gas emerges from unit area of the face $x = 0$ of the membrane is $-D(\frac{\partial C}{\partial x})_{x=0}$, or P as defined in (2.1), so that we have from (2.6)

$$P = -D(\frac{\partial C}{\partial x})_{x=0} = D \frac{C_2 - C_1}{\ell} \quad (2.7)$$

In this work the experimentally determined quantities are the ingoing (p_2) and the outgoing (p_1) gas pressures, not the respective concentrations C_2 and C_1 stated above. Thus, the rate of transfer of diffusing substance per unit area in the steady state is

$$P = \bar{P} \frac{(p_2 - p_1)}{\ell} \quad (2.8)$$

where $\bar{P}$ is the permeability coefficient defined as the volume (cm^3) of gas at N.T.P. passing per second through unit area (cm^2) of the surface of the membrane 1 cm thick, when the pressure difference across the membrane is 1 cm Hg. In practice, $p_2 \gg p_1$, so that

$$\bar{P} = P \frac{l}{p_2} \quad (2.9)$$

While $\bar{P}$ is a useful index of the barrier properties of the membrane, it is a much less fundamental quantity than the diffusion coefficient D , particularly when different workers used different units. If now the sorption isotherm is linear, i.e. Henry's law is obeyed, and D is constant, then (2.7) and (2.8) are equivalent, but not otherwise. The linear isotherm may be written

$$C = \sigma p \quad (2.10)$$

where C is the concentration of the gas within the membrane in equilibrium with an external gas pressure, p , and σ is the Henry's law solubility coefficient. It follows from (2.7), (2.8) and (2.10) that

$$\bar{P} = D\sigma \quad (2.11)$$

where D is expressed in $\text{cm}^2\text{sec}^{-1}$ and σ in cm^3 N.T.P. per cm^3 of membrane when the pressure is 1 cm Hg. Hence, the conditions for (2.11) to be valid are $C = \sigma p$ and $D = \text{constant}$.

Denoting the flow rate per unit area, i.e. P , by $\frac{V_0}{A} \frac{dp_1}{dt}$ where V_0 is the outgoing volume, A the area of the membrane, and p_1 the outgoing pressure, (2.7) becomes

$$\frac{V_0}{A} \frac{dp_1}{dt} = D \frac{C_2}{l} \quad \text{if } C_2 \gg C_1$$

$$\text{or } \bar{P} = \frac{V_0 l}{p_2 A} \frac{dp_1}{dt} \quad \text{since } C_2 = \sigma p_2 \text{ and } \bar{P} = D\sigma,$$

or, with the volume of gas expressed in cm^3 at N.T.P.,

$$\bar{P} = \frac{\text{Vol}}{p_2 A} \frac{273.16}{273.16 + T_R} \frac{1}{76} \frac{dp_1}{dt} \quad (2.9a)$$

(2.9a) is equivalent to (2.9).

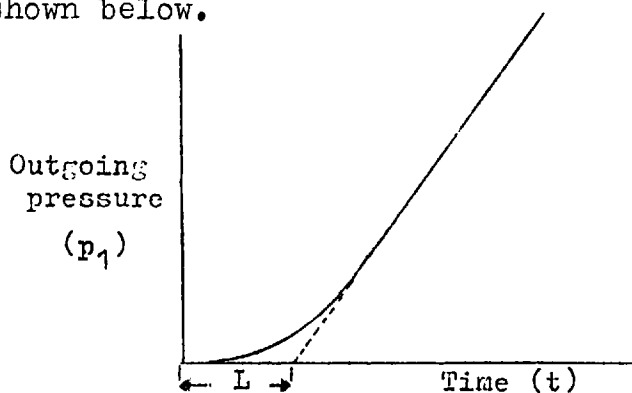
Now, if $\bar{P}$ is determined from the steady state flow rate (2.9a) and σ is determined independently, e.g. by the equilibrium (static) method, the diffusion coefficient deduced from (2.11) is called the steady state diffusion coefficient, denoted by D_S , whilst the solubility coefficient so determined is called static solubility coefficient, denoted by σ_S .

(b) Transient state diffusion

The transient state diffusion equation can be determined from the time-lag method first introduced by Daynes⁶⁰, extended by Barrer¹, and used extensively by many workers. For the boundary conditions applicable to the present experiment, the transient state diffusion coefficient, D_L , is obtained from

$$D_L = \frac{l^2}{6L} \quad (2.12)$$

(see ref. 1 for derivation) where l (in cm) is the unswollen thickness of the membrane and L (in secs) is called the time lag which is the intercept on the t -axis shown below.



Thus, from the determination of L , D_L can be deduced. Moreover, from the steady state flow rate, the permeability coefficient $\bar{P}$ can be obtained from (2.9a), and hence the solubility coefficient deduced from (2.11). Solubility coefficients determined in this way are called dynamic solubility coefficients, denoted by σ_D . With this simple and versatile method, D_L , $\bar{P}$ and σ_D can be determined simultaneously in one and the same experiment.

(c) The "early approximation method"

When the time lag is inconveniently long, this so-called "early approximation method" can be used to save time and to avoid fluctuation in temperature control and other experimental parameters. It is sufficient to indicate here that the principle is based on the inversion of time, t , in the exponential terms that appear in the general solution of the diffusion equation; that is to say, the flow rate is a function of $e^{-\frac{A}{t}}$ in this case, as contrast to $e^{-A't}$ in the other case. The expression, after suitable rearrangement is (see ref. 61):

$$\ln\left(t^{\frac{1}{2}} \frac{dp_1}{dt}\right) = \ln\left[\frac{2A}{V_c} \sigma p_2 \left(\frac{D}{\pi}\right)^{\frac{1}{2}}\right] - \frac{l^2}{4Dt} \quad (2.13)$$

This method has been used mainly in the glass industry⁶¹⁻⁶³ for reasons mentioned above. Moreover, the gas flow rate can be determined directly by a mass spectrometer. Diffusion coefficients obtained in the manner will be denoted by D_E .

2.2.2 Hollow cylindrical membrane

(a) Steady state diffusion

Consider a hollow cylindrical membrane having internal radius a , and external radius b . Then, for constant D , the diffusion equation describing the steady state condition, $\frac{\partial C}{\partial t} = 0$, is from (2.4)

$$\frac{\partial}{\partial r}(r \frac{\partial C}{\partial r}) = 0, \quad a < r < b \quad (2.14)$$

The general solution of this is

$$C = A + B \ln r \quad (2.15)$$

where A and B are constants to be determined from the boundary conditions at $r = a$ and $r = b$. Using the same boundary conditions as those in the plane sheet membrane, namely the surface $r = a$ is kept at concentration C_1 , and $r = b$ at $C = C_2$, then

$$C = \frac{C_1 \ln \frac{b}{r} + C_2 \ln \frac{r}{a}}{\ln \frac{b}{a}} \quad (2.16)$$

It follows that the quantity Q_t of the diffusant which passes radially through the cylinder in time t is

$$Q_t = \frac{2\pi h D t (C_2 - C_1)}{\ln \frac{b}{a}} \quad (2.17)$$

where h is the length of the membrane. As in the plane sheet membrane, we can measure the rate of change of outgoing gas pressure p_1 as the quantity which diffuses out at face $r = a$ into an outgoing volume V_o . Then

$$\frac{d}{dt} Q_t = V_o \frac{dp_1}{dt} = \frac{2\pi h D (C_2 - C_1)}{\ln \frac{b}{a}} \quad (2.18)$$

Using the same boundary conditions relevant to the experimental arrangement of this work, i.e. keeping $C = C_2 = \text{const.}$ at $r = b$, and $C = C_1 \rightarrow 0$ (i.e. $C_2 \gg C_1$) at $r = a$, and using the relationship $C_2 = \sigma p_2$ and $\bar{P} = D\sigma$, (2.18) becomes on rearrangement

$$\bar{P} = \frac{V_0 \ln \frac{b}{a}}{p_2 2\pi h} \frac{dp_1}{dt} \quad (2.19)$$

or, expressing the outgoing volume of gas in cm^3 at N.T.P.,

$$\bar{P} = \frac{V_0 \ln \frac{b}{a}}{p_2 2\pi h} \frac{273.16}{273.16 + T_R} \frac{1}{76} \frac{dp_1}{dt} \quad (2.20)$$

(b) Transient state diffusion

As in the plane sheet membrane, the transient diffusion coefficient, D_L , can be obtained by the time-lag method. The expression for the time lag, L , has been given, for our boundary conditions, by Jaeger⁶⁴ as

$$L = \frac{a^2 - b^2 + (b^2 + a^2) \ln \frac{b}{a}}{4D \ln \frac{b}{a}} \quad (2.21)$$

where a = internal radius, and b = external radius. Rogers et al⁶¹ have also derived an expression for radial diffusion from which the time lag L can be deduced. The intercept on the time axis (i.e. the time lag) of outgoing pressure vs time plot has been given as

$$\frac{l^2}{6D} Z(R) \quad (2.22)$$

where $R = \frac{b}{a}$ and $Z(R) = \frac{\frac{3}{2}[(R^2+1)\ln R + 1 - R^2]}{(R-1)^2 \ln R}$.

When (2.22) is expanded term by term, the same expression for the time lag, L , as that of Jaeger, equation (2.21), is obtained.

Thus, from the determination of L , the transient state diffusion coefficient D_L can be calculated from (2.21) for hollow cylindrical membrane. (NOTE: Crank⁶⁵ deduced on p. 78 that the time lag L , corresponding to (2.21), is $L = \frac{(b-a)^2}{6D}$, the same as diffusion in spherical system. Confusion might have arisen here).

(c) The "early approximation method"

In this early approximation method, the solution of radial flow in hollow cylindrical membrane is identical with that in the plane sheet membrane. Thus the method of obtaining the diffusion coefficient is the same, except that in eq. (2.13) the surface area A is to be evaluated from the geometric mean radius $(ab)^{\frac{1}{2}}$.

2.3 TYPES OF DIFFUSION COEFFICIENT IN A BINARY MIXTURE AND THEIR INTER-RELATIONSHIPS

Hartley and Crank⁶⁶ and Carman and Stein⁶⁷ have discussed the physical significance of diffusion coefficients measured under different conditions. Any binary mixture of species 1 and 2 (gas, liquid or

solid) can, according to the frame of reference, be characterised by five diffusion coefficients, namely, two intrinsic diffusion coefficients D_1 and D_2 , one mutual diffusion coefficient $D_{12}(\equiv D_{21})$, and two self diffusion coefficients, D_1^* and D_2^* .

2.3.1 Intrinsic diffusion coefficients

Intrinsic diffusion coefficients, D_1 and D_2 , are defined in terms of the rate of transfer of species 1 and 2 respectively across a section fixed so that no mass flow occurs through it; in other words, they refer to pure diffusion. If we consider pure diffusion of species 1 and 2 along the x-coordinate, then the origin of the x-coordinate is in a plane normal to the flow and moves in such a way that there is no mass flow across it. Such a section may be impossible to determine in practice. Denoting the flow densities of 1 and 2 by P_1 and P_2 respectively, the flows in the x-direction normal to the section are

$$P_1 = -D_1 \frac{\partial C_1}{\partial x} \quad \text{and} \quad P_2 = -D_2 \frac{\partial C_2}{\partial x} \quad (2.23)$$

where D_1 , D_2 , C_1 and C_2 are respectively the intrinsic diffusion coefficients and concentrations of species 1 and 2.

2.3.2 Mutual diffusion coefficients

The mutual diffusion coefficients D_{12} and D_{21} are those which measure the rate of transfer of the

species across a section defined by the condition that the total volume on either side of it remains constant as diffusion proceeds. They describe, in effect, the combination of mass flow and pure diffusion. Consider a binary mixture which undergoes no overall volume change on mixing at constant pressure, and which fills a constant volume vessel. If now transport were to take place through unit cross-section normal to the x-coordinate and fixed with respect to the walls of the vessel, then a compensating mass flow must occur to maintain uniform pressure throughout the diffusion volume, since in general the flow rates of species 1 and 2 are not equal. Now the total volume transfer of species 1 and 2 per unit time across unit area of the section defined (due to mass flow and pure diffusion) are:

$$P_1' = -D_{12}V_1\frac{\partial C_1}{\partial x} \quad \text{and} \quad P_2' = -D_{21}V_2\frac{\partial C_2}{\partial x} \quad (2.24)$$

where V_1 and V_2 are respectively the specific volumes of species 1 and 2. By definition of the section as one across which there is no net transfer of volume, then

$$D_{12}V_1\frac{\partial C_1}{\partial x} + D_{21}V_2\frac{\partial C_2}{\partial x} = 0 \quad (2.25)$$

Since for unit volume of solution,

$$V_1C_1 + V_2C_2 = 1 \quad (2.26)$$

then

$$V_1\frac{\partial C_1}{\partial x} + V_2\frac{\partial C_2}{\partial x} = 0 \quad (2.27)$$

In general, V_1 and V_2 are not equal to zero. Therefore, in order that (2.25) and (2.27) shall both be satisfied, it follows that $D_{12} \equiv D_{21}$. Hence, only one mutual diffusion coefficient is required to describe the combination of mass flow and pure diffusion.

2.3.3 Self-diffusion coefficients

The last two are the self-diffusion coefficients D_1^* and D_2^* . The rate of diffusion of one component can be measured directly by using radioactively-labelled molecules. Suppose a mixture consists of $(n_1+n_1^*)$ molecules of species 1 ($*$ denotes the labelled molecules), and n_2 molecules of species 2. In solution we have $\frac{dn_2}{dx}=0$ and $\frac{d(n_1+n_1^*)}{dx}=0$. If however $\frac{dn_1^*}{dx}$ and so $\frac{dn_1}{dx}$ are not zero, the pure diffusion flux given by $P_1^* = -D_1^* \frac{\partial C_1^*}{\partial x}$ can be measured, and D_1^* evaluated. D_2^* may be obtained in a similar manner.

2.3.4 Inter-relationships of the diffusion coefficients

The five diffusion coefficients described above are related to one another by the following expressions, the assumption being that no overall volume change takes place on mixing. The relations are merely quoted^{2,65,67} here without proof.

The equations relating mutual and intrinsic diffusion coefficients are

$$D_{12} = V_1 C_1 D_2 + V_2 C_2 D_1 \quad (2.28)$$

or when $V_1 = V_2$,

$$D_{12} = N_1 D_2 + N_2 D_1 \quad (2.29)$$

where N_1 and N_2 are respectively the mole fraction of species 1 and 2.

The equations relating intrinsic and self-diffusion coefficients are

$$D_1 = D_1^* \frac{d \ln a_1}{d \ln C_1} \quad \text{and} \quad D_2 = D_2^* \frac{d \ln a_2}{d \ln C_2} \quad (2.30)$$

where a_1 and a_2 are respectively the activities of species 1 and 2.

The equation relating mutual and self-diffusion coefficients is

$$D_{12}(\equiv D_{21}) = [N_2 D_1^* + N_1 D_2^*] \frac{d \ln a_1}{d \ln N_1} \quad (2.31)$$

2.4 MEASUREMENT OF DIFFUSION COEFFICIENTS

Crank⁶⁵ has summarised the methods of measurement of diffusion coefficients under different conditions. It suffices to point out here how the five diffusion coefficients mentioned previously can be determined.

For two interdiffusing liquids, mutual diffusion coefficient D_{12} and self-diffusion coefficients D_1^* and D_2^* can be determined directly, but not the intrinsic diffusion coefficients D_1 and D_2 . This is the case because in liquids no method of separating mass flow and intrinsic diffusion rate has been devised. However, from a knowledge of $\frac{d \ln a_1}{d \ln C_1}$ and $\frac{d \ln a_2}{d \ln C_2}$, D_1 and D_2 can be calculated from D_1^* and D_2^* by equation (2.30).

For two solids, e.g. Ag-Au, mass flow accompanying diffusion may be measured by placing markers at the Ag-Au interface and observing the rate at which the markers move (the Kirkendall⁶⁸ effect). Indeed for one composition of Ag-Au alloy (50-50 atomic %) all five diffusion coefficients have been separately determined⁶⁹.

When liquid, gas or vapour diffuses in a polymer (species 2, say) it may be assumed that $D_2 \sim 0$, so that its effect may be neglected. Also, over nearly all the composition range eq. (2.28) then reduces to

$$D_1 = \frac{D_{12}}{V_2 C_2} \quad (2.32)$$

Finally, in the case of steady state permeation rate through a membrane of unswollen thickness, ℓ , it can be shown⁶⁶ that

$$P_1 = \frac{1}{\ell} \int_0^{C_1} D_1 (V_2 C_2)^3 dC_1$$

so that

$$\begin{aligned} \ell \frac{dP_1}{dC_1} &= D_1 (V_2 C_2)^3 \\ &= D_{12} (V_2 C_2)^2 \text{ by virtue of (2.32).} \end{aligned} \quad (2.33)$$

Hence the slope of P_1 vs C_1 plot serves to measure D_1 .

Also, the self-diffusion coefficient D_1^* may be measured in a polymer just as in the case of liquids.

2.5 CLASSIFICATION OF POLYMER-PENETRANT SYSTEMS

Barrer², from his extensive researches on diffusion and solution of gases and vapours in polymeric membranes, has been able to classify such systems into four main categories, as follows:

$$(a) \quad \frac{\partial C_1}{\partial t} = D_{12} \frac{\partial^2 C_1}{\partial x^2}, \quad C_1 = \sigma p_1 \text{ (i.e. Henry's law is obeyed)}$$

This category is exemplified by the diffusion and solution of permanent and inert gases in natural

rubber, synthetic elastomers, and probably in many harder polymers. Since V_2C_2 (= volume fraction of elastomer) is approximately unity, and $D_1 \gg D_2$, it is clear from (2.28) that all measurements of D_{12} are in fact measurements of D_1 . Moreover, at equilibrium $\frac{d \ln a_1}{d \ln C_1} = \frac{d \ln p_1}{d \ln C_1} = 1$, and so from (2.30), $D_1 = D_1^*$.

$$(b) \quad \frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left(D_{12} \frac{\partial C_1}{\partial x} \right), \quad D_{12} = f(C_1) \text{ and } C_1 = \sigma p_1$$

Examples of this are well represented by C_4 and C_5 paraffin diffusing and dissolving in rubber²². D_{12} is no longer independent of concentration C_1 , but Henry's law is still obeyed. Thus

$$D_{12} = V_2 C_2 D_1 \quad \text{and} \quad D_1 = D_1^*$$

$$(c) \quad \frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left(D_{12} \frac{\partial C_1}{\partial x} \right), \quad D_{12} = f(C_1) \text{ and } C_1 = F(p_1)$$

i.e. D_{12} is a function of concentration C_1 , and Henry's law is no longer valid. Examples of this are given by the diffusion and solution of heavier hydrocarbon vapours^{70, 71, 72} (e.g. benzene, toluene, heptane) in rubber or rubbers with high chain mobility and short relaxation times. Normally, the relationship $D_1 \gg D_2$ and so from (2.28) $D_{12} \doteq V_2 C_2 D_1$ still holds.

$$(d) \quad \frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left(D_{12} \frac{\partial C_1}{\partial x} \right), \quad D_{12} = f(t, C_1) \\ \text{or } D_{12} = f'(t) \times f''(C_1), \quad C_1 = F(p_1)$$

i.e. D_{12} is not only a function of concentration, but also time-dependent; and the isotherm is no longer linear. Examples are given by the diffusion and solution of methylene chloride in polystyrene, and cellulose acetate; acetone in cellulose acetate, polyvinyl acetate, cellulose nitrate, and generally

in more rigid and internally viscous polymers with long relaxation times. This category includes the group of "anomalous" diffusions (see ref. 24 and 25 in Barrer's article²), in which it is likely that time components enter the diffusion coefficients in the transient state flow.

Although the above comprise the four main categories of polymer-penetrant systems, they are not the only possible cases. When there is a steady thermal gradient across a membrane (as in thermal-diffusion⁷³), or where a membrane consists of laminae of different polymers, the following cases may be concerned:

$$(e) \quad \frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left(D_{12} \frac{\partial C_1}{\partial x} \right), \quad D_{12} = f(x) \text{ and } C_1 = \sigma p_1$$

$$(f) \quad \frac{\partial C_1}{\partial t} = \frac{\partial}{\partial x} \left(D_{12} \frac{\partial C_1}{\partial x} \right), \quad D_{12} = f(x, C_1) \text{ and } C_1 = F(p_1).$$

Moreover, when thermal transients are combined with material diffusion, D_{12} in (e) and (f) may also be complicated by time dependency.

(D_{12} will henceforth be written simply as D)

2.6 TEMPERATURE AND DIFFUSION COEFFICIENT

As previously noted, the diffusion coefficient in elastomers depends exponentially upon temperature T , according to the Arrhenius type of equation¹

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad (2.34)$$

Diffusion is therefore an activated process in which

the transfer of penetrant molecule in the elastomer from one equilibrium position to another involves an activation energy E_D . E_D may be pictured as the energy required for completion of a unit diffusion process, and presumably it involves the work of separation of the polymer chains, whilst D_0 , according to the zone theory, is a measure of the zone size. Both E_D and D_0 may therefore throw light upon the nature of the diffusion process^{1,4,5,21,23,74,75}. The magnitudes of D_0 in elastomers are far above those usually observed in diffusion processes.

When in the Arrhenius equation (2.34) one plots $\log D_0$ vs $\frac{E_D}{T}$, a functional relationship of the type

$$\log D_0 = A + B \frac{E_D}{T} \quad (2.34a)$$

is found^{1,4,5,21,74,76}. The significance of this relationship is as follows. From the Arrhenius equation $\log D = \log D_0 - 0.22 \frac{E_D}{T}$ and if the range in values of $\log D$ is small compared with that of $0.22 \frac{E_D}{T}$, then to a first approximation $\log D$ is constant ($=A$). Accordingly

$$\log D_0 = A + 0.22 \frac{E_D}{T} \quad (2.34b)$$

which has the form of (2.34a). In fact it is always found that the range in $\log D$ is less than that in $0.22 \frac{E_D}{T}$, either due to experimental limitations of measurements, or because of a fundamental property of rate processes in condensed phases.

2.7 DIFFUSION COEFFICIENT ACCORDING TO THE TRANSITION STATE THEORY

Diffusion as a rate process is amenable to treatment by the transition state theory, also known as the theory of Absolute Reaction Rates⁷⁷. It is based on the assumption that in order for any rate process to occur it is necessary for the reactants to approach one another to form an activated complex. This complex is regarded as being situated at the top of an energy barrier lying between the initial and final states, and the rate of the reaction is controlled by the rate by which these complexes travel over the top of the barrier. According to Eyring's formulation, this activated complex is to be regarded as an ordinary molecule possessing all the usual thermodynamic properties, and that the activated complexes are assumed to be in equilibrium with the reactants even when the reactants and the products are not. With these assumptions, it is possible to derive⁷⁸ the rate constant k' of any process in terms of the equilibrium constant K^* between the activated complex and the reactants, i.e.,

$$k' = \frac{kT}{h} K^* \quad (2.35)$$

$$\text{Since } \Delta G^* = -RT \ln K^* \quad (2.36)$$

$$(2.35) \text{ becomes } k' = \frac{kT}{h} \exp\left(-\frac{\Delta G^*}{RT}\right) \quad (2.37)$$

$$\text{or } k' = \frac{kT}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (2.38)$$

by virtue of $\Delta G^* = \Delta H^* - T\Delta S^*$, where ΔG^* , ΔH^* and ΔS^* refer respectively to the free energy, heat content and entropy of activation with activated

complexes and reactants in their standard state. It has been shown⁷⁸, (p. 519), that

$$D = \lambda^2 k' \quad (2.39)$$

where λ is the jump between successive equilibrium positions, so that from (2.38) and (2.39), the diffusion coefficient D may be expressed as

$$D = \lambda^2 \frac{kT}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (2.40)$$

Taking logarithms and differentiating w.r.t. T , (2.40) becomes

$$\frac{d \ln D}{dT} = \frac{1}{T} + \frac{\Delta H^\ddagger}{RT^2} \quad (2.41)$$

Similarly from (2.34),

$$\frac{d \ln D}{dT} = \frac{E_D}{RT^2} \quad (2.42)$$

Comparing (2.41) and (2.42) we have

$$E_D = RT + \Delta H^\ddagger \quad (2.43)$$

as a relationship between the energy of activation E_D and the heat of activation $\Delta H^\ddagger$. Also equating (2.40) and (2.34) and using (2.43),

$$D_0 = e \frac{kT}{h} \lambda^2 \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (2.44)$$

Hence, $\Delta S^\ddagger$, $\Delta H^\ddagger$ and $\Delta G^\ddagger$ can all be calculated from the experimentally determined quantities E_D and D_0 , e.g. Barrer and Skirrow²¹. (NOTE: Eqs.(4) and (5) of this paper must be corrected. 2.72 (=e) should appear in the numerator, not in the denominator. The values of $\Delta S^\ddagger$ and $\Delta G^\ddagger$ in Table V must accordingly be corrected, though no major upset of the treatment is caused.)

Values of $\Delta S^\ddagger$ so obtained for polymer-hydrocarbon systems are usually large and positive^{21,33,75}. According to Glasstone et al⁷⁸ these high values are

attributed to the severing of bonds in the diffusion process. To explain this phenomenon, Barrer⁷⁵ suggested that there is a considerable disturbance in the polymer matrix surrounding the penetrant in the formation of transition state, and this leads to Barrer's postulation of Kinetic-Statistical Theory, best known as the theory of Zone of Activation.

2.8 DIFFUSION COEFFICIENT ACCORDING TO KINETIC STATISTICAL THEORY (BARRER'S THEORY OF ZONE OF ACTIVATION)

Barrer^{23,76,79} proposed the application to membranes of Wheeler's concept⁸⁰ of a zone of activation of f degrees of freedom which must acquire an energy $\geq E$ before a jump step can occur. The underlying idea of this theory is that for a unit diffusion process to take place in any region of the polymer, an activation energy must first appear in that region as a result of thermal energy fluctuations. The probability that there is a total energy $\geq E$ in a small region surrounding the penetrant molecule and which, including the penetrant molecule, contains n degrees of freedom, is

$$\begin{aligned}
 P &= \sum_{f=1}^{f=n} \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} \exp\left(-\frac{E}{RT}\right) \\
 &= \sum_{f=1}^n P_f \exp\left(-\frac{E}{RT}\right)
 \end{aligned} \tag{2.45}$$

where
$$P_f = \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} .$$

Expression (2.45) is based on the assumption that the components of the polymer chains may be treated as classical vibrators. If for any value of $\frac{E}{RT}$, P_f is plotted against f , a family of curve (see ref. 79, p. 238, Fig. 1) with maxima is obtained. The locus of the maxima corresponds to $E = \bar{U} = fRT$, where $\bar{U}$ is the average energy in any f degrees of freedom. This most probable distribution does not however define the important distribution for transport processes, for this would mean that these processes occurred with no apparent or Arrhenius energy of activation E_D at all, since $E_D = E - \bar{U} = 0$ which is contrary to experience. Certainly then the value of n in the region need not exceed $f_{\max}$ to include all energy distributions likely to contribute to a successful unit transport process, for we may exclude all "colder" than average distributions. Thus only the "hot" distribution ($E > \bar{U}$ and $E_D > 0$) are to be considered. The important "hot" distributions are decided by two balancing conditions: (1) $E_D = E - \bar{U}$ must be as concentrated as possible to give the most energised zone compatible with (2) below; (2) there must be an "a priori" probability P_f which is as large as possible, bearing (1) in mind. This means the optimum zone of activation will have values of f lying between 1 and $f_{\max}$ ($f_{\max} = \frac{E}{RT}$). Furthermore, there will normally be need for cooperation or synchronisation between segmental rotations and intermolecular vibrations within the zone of activation if a successful unit transport process is to occur within the lifetime of the important energy fluctuations defined by conditions (1) and (2) above. For example, if each of p groups must simultaneously move in one of m directions, the probability of this is $(\frac{1}{m})^p$, and

since various cooperations may be successful, the total probability of all individual possible chances of cooperation is the sum of all individual chances ρ_f . ρ_f will be expected to depend on f , and is less than unity. In general a spectrum of terms $\rho_f \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} \exp\left(-\frac{E}{RT}\right)$ for different values of f may contribute to the probability of a successful unit transport process. Barrer's theory of zone activation then gives for the diffusion coefficient

$$D = v\lambda^2 \sum_{f=1}^n \rho_f \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} \exp\left(-\frac{E}{RT}\right) \quad (2.46)$$

where f is the number of degrees of freedom among which the total energy of activation E is shared in any zone, the summation being taken up to n . n is the number of degrees of freedom in the largest, i.e. the most diffuse zone of activation contributing appreciably to D ; v is the mean vibration frequency of the diffusing molecule relative to its environment; λ is the mean distance moved in a unit diffusion process; and ρ_f has the form $\sum \left(\frac{1}{m}\right)^p$ as explained previously, for instance, $\rho_f = \frac{1}{6}$ when Schottky defects or holes move in a cubic lattice. It may be assumed that only one term of the summation in (2.46) is important (most nearly true if $E \gg (f-1)RT$). Then (2.46) becomes

$$D = \rho_f v\lambda^2 \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} \exp\left(-\frac{E}{RT}\right) \quad (2.47)$$

Comparing (2.47) with

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \quad (2.41)$$

we find that

$$D_0 = \rho_f v\lambda^2 \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} \exp(1-f) \quad (2.48)$$

$$\text{and } E_D = E - (f-1)RT \quad (2.49)$$

It is seen that E may be regarded as the effective activation energy at absolute zero temperature. So far it has been assumed that E is independent of temperature, but no such assumption has been made about E_D and D_0 . If f is independent of temperature, it follows from (2.48), by taking logarithms and differentiating w.r.t. T , that

$$RT \frac{d \ln D_0}{dT} = -(f-1)R \quad (2.50)$$

and from (2.49) that

$$\frac{dE_D}{dT} = -(f-1)R \quad (2.51)$$

Eqs. (2.50) and (2.51) provide means of measuring f , as has been done by Barrer and Skirrow²¹ and by van Amerongen⁵. f so deduced would be an upper limitation.

An alternative method, used by Barrer and Skirrow²¹, for measuring f is to take the logarithm of (2.48), using Stirling's approximation for factorial, and to substitute for E by (2.49), giving

$$\ln D_0 = \ln(\rho_f v \lambda^2) + (f-1) \ln \left[\frac{E_D + (f-1)RT}{RT} \right] - (f-1) \ln(f-1) - \frac{1}{2} \ln[2\pi(f-1)] \quad (2.52)$$

Then by first plotting the r.h.s. of (2.52) against f for various values of f one may then read off from the curve the value of f required to give any experimental value of $\ln D_0$, assuming suitable values to ρ_f , v and λ .

It is clear from (2.51) that E_D has a negative temperature coefficient according to this zone theory. On the other ^{hand} ~~and~~ the transition state theory predicts a positive temperature coefficient of E_D whenever ΔS^* is positive as seen from

$$E_D = RT + \Delta H^* \quad (2.43)$$

$$\text{i.e. } \frac{dE_D}{dT} = R + \Delta C_v^*$$

where $\Delta C_v^* = \frac{\partial \Delta H^*}{\partial T}$ is the change in specific heat in passing to the transition state.

2.9 THERMODYNAMICS OF POLYMER SOLUTIONS

2.9.1 General

The Gibbs' free energy, heat and entropy of dilution are important thermodynamic quantities used to describe the equilibrium properties of polymer solutions. If we consider the isothermal transfer of one mole of liquid from a mass of pure liquid of vapour pressure p_1^0 to an infinite amount of solution above which the vapour pressure of the liquid is p_1 , the resultant changes in the Gibbs free energy, heat content and entropy are termed respectively the Gibbs free energy of dilution ($\Delta \bar{G}_1$), the heat of dilution ($\Delta \bar{H}_1$), and the entropy of dilution ($\Delta \bar{S}_1$). Since these thermodynamic quantities are related to one another by $\Delta \bar{G}_1 = \Delta \bar{H}_1 - T\Delta \bar{S}_1$, and because also

$$\Delta \bar{G}_1 = RT \ln \frac{p_1}{p_1^0} \quad (2.53) \quad \text{and} \quad \Delta \bar{H}_1 = \left[\frac{\partial \left(\frac{\Delta \bar{G}_1}{T} \right)}{\partial \frac{1}{T}} \right] = -T^2 \left[\frac{\partial \left(\frac{\Delta \bar{G}_1}{T} \right)}{\partial T} \right] \quad (2.54)$$

measurements of vapour pressures of polymer-penetrant mixtures at various temperatures enable one to obtain $\Delta \bar{G}_1$, $\Delta \bar{H}_1$ and hence $\Delta \bar{S}_1$. $\Delta \bar{S}_1$ may also be obtained from:

$$\Delta \bar{S}_1 = - \left[\frac{\partial \Delta \bar{G}_1}{\partial T} \right] \quad (2.55)$$

With polymer solutions, values of $\Delta\bar{H}_1$ are usually small and positive, whilst $\Delta\bar{S}_1$ values are positive and abnormally large. Deviations from ideal solution behaviour may be due to the heat of dilution not being zero, and/or the entropy of dilution not being given by the ideal value. It is now accepted that the deviation is largely due to the entropy change rather than to the occurrence of a non-zero heat of dilution.

2.9.2 Entropy of mixing (ΔS_m) and entropy of dilution (ΔS_1)

An abnormally large entropy change can be a consequence of the large differences in size between molecules of a solvent and of a chain polymer, and of the flexibility of the latter. Thermodynamic treatments of polymer-liquid systems aim at the theoretical interpretation of the values of $\Delta\bar{S}_1$ and $\Delta\bar{H}_1$, and the expression of these and of $\Delta\bar{G}_1$ in terms of concentration and other measurable quantities. Two of the numerous treatments which were developed independently are those due to Flory^{81,82} and Huggins^{83,84,85}. They followed Meyer's suggestion^{86,87} that, by using an idealised lattice model, the entropy of mixing long chain molecules with small molecules could be made by computing the number of ways of arranging a flexible chain on an array of lattice points such that each site could be occupied either by a solvent molecule, or by a segment of the polymer molecule having a size approximately equal to that of the solvent. Both analyses lead to similar equations for the configurational entropy of mixing ΔS_m . That given by Flory is:

$$\Delta S_m = -k[n_1 \ln v_1 + n_2 \ln v_2] \quad (2.56)$$

where n_1 and n_2 are respectively the number of molecules of solvent and polymer; v_1 and v_2 the volume fractions of solvent and polymer defined by

$$v_1 = \frac{n_1}{n_1 + x n_2} \quad v_2 = \frac{x n_2}{n_1 + x n_2} \quad (2.57)$$

x is the number of segments per polymer molecule, or the ratio of molar volumes of polymer and solvent. It follows from (2.56) that the partial molar entropy of dilution is

$$\Delta \bar{S}_1 = -R[\ln(1-v_2) + (1-\frac{1}{x})v_2] \quad (2.58)$$

More rigorous treatments give an expression which includes the coordination number z , as in Huggin's expression:

$$\Delta \bar{S}_1 = -R[\ln(1-v_2) - (1-\frac{1}{x})^{\frac{z}{2}} \ln(1 - \frac{2v_2}{z})] \quad (2.59)$$

Miller^{88,89} by a different approach to the calculations, arrived at a similar expression for $\Delta \bar{S}_1$ which is

$$\Delta \bar{S}_1 = -R[\ln(1-v_2) - \frac{z}{2} \ln\{1 - \frac{2v_2}{z}(1-\frac{1}{x})\}] \quad (2.60)$$

When x is large, in particular, Flory's, Huggin's and Miller's equations reduce to the same expression given by

$$\Delta \bar{S}_1 = -R[\ln(1-v_2) + v_2] \quad (2.61)$$

an expression free from any molecular parameter. Thus according to this theory, the entropy of dilution of any polymer by any liquid should be the same.

2.9.3 Heat and free energy of mixing

In view of the interaction of molecules in solution, the heat of mixing may be considered to originate in the replacement of some of the contacts between like species in the pure liquids with contacts between the unlike species in the solution. According to the lattice model, the heat of mixing of the process represented by stoichiometric equation:

$$\frac{1}{2}[1,1] + \frac{1}{2}[2,2] = [1,2] \quad (2.62)$$

is given by⁹⁰:

$$\Delta H_m = kTn_1v_2\chi_1 \quad (2.63)$$

where

$$\chi_1 = \frac{z\Delta w_{12}}{kT} \quad (2.64)$$

$$\text{and} \quad \Delta w_{12} = w_{12} - \frac{1}{2}(w_{11} + w_{22}) \quad (2.64a)$$

w being the energies associated with respective contact pairs. Thus χ_1 , known as the interaction parameter, is a dimensionless quantity characterising the interaction energy per solvent molecule divided by kT ; whilst $kT\chi_1$ represents the difference between the energy of a solvent molecule surrounded by pure polymer molecules and that surrounded by molecules of its own kind, i.e. in the pure solvent.

The free energy of mixing, ΔG_m , is then obtained by combining (2.56) and (2.63) in

$$\begin{aligned} \Delta G_m &= \Delta H_m - T\Delta S_m^{\text{Total}} \\ &= \Delta H_m - T\Delta S_m \\ &= kT[n_1\ln v_1 + n_2\ln v_2 + \chi_1 n_1 v_2] \end{aligned} \quad (2.65)$$

The effect of putting the configurational entropy of mixing ΔS_m equal to the total, or effective, entropy of mixing $\Delta S_m^{\text{Total}}$ is to neglect the possible contribution

which may arise from specific interactions between neighbouring components.

Guggenheim⁹¹ pointed out, however, that there is no justification in not considering the entropy contribution as a result of interactions between near neighbours. Writing

$$\Delta\omega_{12} = \Delta\omega_h + T\Delta\omega_s \quad (2.66)$$

where $\Delta\omega_h$ is the heat contribution, and $T\Delta\omega_s$ the entropy contribution both for process of type (2.62), $\Delta\omega_{12}$ then acquires the character of the standard state free energy. Consequently χ_1 defined by (2.64) will contain an entropy term divided by k in addition to the heat of mixing term divided by kT ; the quantity $kTn_1v_2\chi_1(=\Delta H_m)$ in (2.63) being regarded as the standard state free energy change rather than the heat of mixing only. In the light of the above refinements, the free energy of mixing is still given by equation (2.65), i.e.

$$\Delta G_m = kT[n_1 \ln v_1 + n_2 \ln v_2 + \chi_1 n_1 v_2]$$

but the heat and the entropy of mixing are now given by

$$\Delta H_m = -T^2 \left[\frac{\partial \left(\frac{\Delta G_m}{T} \right)}{\partial T} \right] = -kT^2 \left(\frac{\partial \chi_1}{\partial T} \right) n_1 v_2 \quad (2.67)$$

and

$$\Delta S_m^{\text{Total}} = - \left[\frac{\partial \Delta G_m}{\partial T} \right] = -k[n_1 \ln v_1 + n_2 \ln v_2 + \frac{\partial (\chi_1 T)}{\partial T} n_1 v_2] \quad (2.68)$$

Hence, if $\Delta\omega_{12}$ is independent of temperature, i.e. if $\Delta\omega_{12}$ contributes no entropy term, χ_1 will be inversely proportional to T by (2.64). Then $\frac{\partial (\chi_1 T)}{\partial T}$ in (2.68) is zero, and $\Delta S_m^{\text{Total}} = \Delta S_m$. Also, since $\chi_1 = -T \frac{\partial \chi_1}{\partial T}$ ΔH_m in (2.67) reduces to the previous equation (2.63).

2.9.4 Heat and free energy of dilution

If the interaction parameter χ_1 is inversely proportional to temperature T , i.e. if the interaction contributes an energy only, the heat and the free energy of dilutions are obtained simply from (2.63) and (2.65) by differentiating w.r.t. n_1 and multiplying the results by Avogadro's number to give respectively

$$\Delta \bar{H}_1 = RTv_2^2\chi_1 \quad (2.69)$$

$$\Delta \bar{G}_1 = RT[\ln(1-v_2) + (1-\frac{1}{X})v_2 + \chi_1 v_2^2] \quad (2.70)$$

If χ_1 contains an entropy contribution, the form of $\Delta \bar{G}_1$ is unaltered given by (2.70), but the heat of dilution becomes

$$\Delta \bar{H}_1 = -RT(\frac{\partial \chi_1}{\partial T})v_2^2 \quad (2.71)$$

It follows that the entropy of dilution is

$$\Delta \bar{S}_1 = -R[\ln(1-v_2) + (1-\frac{1}{X})v_2 + \frac{\partial(\chi_1 T)}{\partial T}v_2^2] \quad (2.72)$$

2.9.5. Hildebrand's treatment for the heat of dilution

Neglecting all but the dispersion forces, Hildebrand⁹² expressed the heat of dilution $\Delta \bar{H}_1$ in terms of the cohesive energy densities ($\frac{E}{V}$) of the components as:

$$\Delta \bar{H}_1 = [(\frac{E_1}{V_1})^{\frac{1}{2}} - (\frac{E_2}{V_2})^{\frac{1}{2}}]^2 V_1 v_2^2 \quad (2.73)$$

where V_1 is the molar volume of component 1 (solvent). The cohesive energy density (CED) is defined as the molar energy of vaporisation divided by its molar

volume. It is thus a measure of the cohesion per unit volume and is related to the solubility parameter δ by $\delta = (\frac{E}{V})^{\frac{1}{2}}$. Hildebrand applied this method to liquid mixtures, and Gee⁹³ has used it for polymer-liquid systems, in which the CED of polymer ($\frac{E_2}{V_2}$) or δ_2^2 was deduced from the swelling of a non-linked polymer. This deduction is based on the assumption that (2.73) is valid, or at least that $\Delta\bar{H}_1 = 0$ when $\delta_1 = \delta_2$. In general, the expression (2.73) is not quantitatively accurate for liquid mixtures, and in most discussions of polymer-liquid mixtures, it has simply been assumed that $\Delta\bar{H}_1 \propto v_2^2$ where v_2 is the volume fraction of the polymer.

2.9.6 Limitation of the Flory-Huggin's treatment

Because of the assumptions made in deriving equations for the entropy of dilution $\Delta\bar{S}_1$ and heat of dilution $\Delta\bar{H}_1$, the Flory-Huggin treatment is not exact, and agreement with experiments is often only approximate. The lattice model on which the treatment is based is physically unreal. Mixing is assumed to be random, although this cannot strictly be so, unless $\Delta\bar{H}_1 = 0$. Solvent molecules and polymer segments are assumed to be of the same size; this is improbable though allowance can be made for differences in size. Polymer segments are assumed to be distributed randomly throughout the lattice, an assumption unlikely to be correct for very dilute solutions. Expressions involving interaction energy are only true if the forces between polymer and solvent are dispersion forces. If the polymer is crystalline, the free energy change

involved in dissolution of the crystalline region must be taken into account. Equation (2.73) predicts $\frac{\Delta\bar{H}_1}{v_2^2}$ is constant, and equation (2.70) predicts χ_1 is independent of concentration; neither of which is usually found to hold over a wide range of concentration. It is to be noted, however, that the deviations of $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ from theory are to some extent mutually compensating, and the expression for $\Delta\bar{G}_1$ is often a good working approximation. In spite of the limitations, the treatment successfully accounts for the very large deviations from ideality shown by polymer solutions, and provides at least a useful guide to the interpretation and understanding of many aspects of polymer-solvent interaction.

2.10 SOLUBILITY OF GASES IN ELASTOMERS

The theory of the solubility of gases in elastomers has been developed by Barrer⁹⁴ using the statistical thermodynamics of random mixing of monomer-polymer mixtures. Two cases were considered.

(1) The resultant interaction energy, w , between the gas and the elastomer is zero. Using Miller's⁹⁸ expression for the partial molar configurational free energy of mixing, $\Delta\bar{G}_1$, the sorption isotherm for gas-elastomer system was derived; and this leads as a special case to the vapour-elastomer system.

(2) w is no longer negligible, in which case Orr's⁹⁵ more elaborate expression for $\Delta\bar{G}_1$ was used to obtain the expression for the sorption-isotherm.

2.10.1 Barrer's sorption isotherm for negligible interaction energy ($w=0$)

The process of sorption of gas in elastomers may be considered to occur in two steps, namely, condensation of the gas (physically unnatural process involving an increase in Gibbs' free energy) and then mixing of the hypothetical condensed gas in the elastomer. At equilibrium, the tendency of the sorbed molecules to dissolve is exactly counteracted by the tendency of the molecules to evaporate. Thus Barrer⁹⁴ obtained for the sorption isotherm of a freely rotating gas in an elastomer:

$$\frac{v_1}{\left\{1 - \left(1 - \frac{1}{x}\right) \frac{2v_2}{z}\right\}^{\frac{z}{2}} n_1} = K = \left(\frac{kT}{2\pi m}\right)^{\frac{3}{2}} \frac{1}{\bar{v}^3} \exp\left(\frac{X}{RT}\right) \quad (2.75)$$

where v_1 and v_2 = the volume fractions of the gas and polymer molecules respectively

x = the number of segments per polymer molecule

z = co-ordination number of the lattice site

n_1 = number of molecules per cm^3

K = solubility constant.

m = mass of the gas molecule

$\bar{v}$ = mean vibration frequency for the gas molecule in the polymer matrix

X = the least energy required to remove a mole of gas from the mixture to the gas phase corresponding to the assumed lattice structure of the mixture.

$$\text{Now, with } \Delta U \text{ defined by } \frac{\partial \ln K}{\partial T} = \frac{\Delta U}{RT} \quad (2.76)$$

one finds by comparing (2.76) with the logarithm of

the r.h.s. of (2.75) that

$$X = -\Delta U + \frac{3}{2}RT \quad (2.77)$$

It follows from (2.75) and (2.77) that

$$\frac{v_1}{[1 - (1 - \frac{1}{x})\frac{2v_2}{z}]^{\frac{z}{2}} n_1} = K = \left(\frac{kT}{2\pi m}\right)^{\frac{3}{2}} \frac{1}{\bar{v}^3} \exp\left(\frac{-\Delta U + \frac{3}{2}RT}{RT}\right) \quad (2.78)$$

When gases are sorbed by an elastomer at low pressures, the solution is usually very dilute, so that $v_1 \ll 1$ and $v_2 \rightarrow 1$. Together with x very large, (2.78) becomes:

$$\frac{v_1}{(1 - \frac{2}{z})^{\frac{z}{2}} n_1} = K = \left(\frac{kT}{2\pi m}\right)^{\frac{3}{2}} \frac{1}{\bar{v}^3} \exp\left(\frac{-\Delta U + \frac{3}{2}RT}{RT}\right) \quad (2.79)$$

and the gas-elastomer system then obeys Henry's law.

In the case of constant pressure, substitution of $p = n_1 kT$ and $\Delta U = \Delta H + RT$ in (2.78) gives for large x

$$\frac{v_1}{(1 - \frac{2v_2}{z})^{\frac{z}{2}} p} = K = \frac{1}{kT} \left(\frac{kT}{2\pi m}\right)^{\frac{3}{2}} \frac{1}{\bar{v}^3} \exp\left(\frac{-\Delta H + \frac{1}{2}RT}{RT}\right) \quad (2.80)$$

As a special case when vapour is sorbed by an elastomer, (2.80) simplifies, because as $p \rightarrow p_s$, $v_1 \rightarrow 1$, and $v_2 \rightarrow 0$, then

$$K = \frac{1}{p_s} \quad (2.81)$$

From (2.80) and (2.81) then

$$\frac{p}{p_s} = \frac{v_1}{(1 - \frac{2v_2}{z})^{\frac{z}{2}}} \quad (2.82)$$

for a vapour-elastomer system.

Since $\bar{v}$ is not known independently, the best test of equation (2.80) is to determine the value of $\bar{v}$ for which experimental and calculated v_1 agrees; for $\bar{v}$, the mean vibration frequency corresponding to the weak van der Waals interaction between sorbed molecule and its environment, should be in the infra-red region

($\sim 10^{+12} \text{ sec}^{-1}$). Moreover, the term $(1 - \frac{z}{Z})^{\frac{Z}{2}}$ does not vary very greatly for values of z between 4 and 6.

2.10.2 Barrer's sorption isotherm for non-zero interaction energy ($w \neq 0$)

Barrer extended the previous treatment to include the case of non-zero interaction energy for monomer-polymer mixtures. The final expression for the isotherm is

$$\frac{p}{p_s} = \frac{v_1(\beta+1-2y)^{\frac{Z}{2}}}{[(1-\frac{2v_2}{Z})(\beta+1)(1-y)]^{\frac{Z}{2}}} \quad (2.83)$$

where β is a function of w , and y a function of z , v_1 and v_2 , as embodied in Orr's expression for the partial molar configurational free energy. Partial miscibility of vapour in elastomer often signifies non-zero interaction energy. Data for testing (2.83) are seldom complete or very accurate.

PART 3. EXPERIMENTAL
MATERIALS, APPARATUS AND EXPERIMENTAL TECHNIQUES

3.1 SILICONE ELASTOMERS

3.1.1 Plane sheet membrane (designated as SiR-I)

This silicone membrane was supplied by the Nobel Division of I.C.I. Ltd. It was reported to contain 100 parts by weight of methyl polymer gum containing 0.1 mole % vinyl groups (average density 0.974 g/cc) and 10 parts by weight of Santocel CS filler (average density 1.66 g/cc). It was cured with di-tert-butyl peroxide (2%) by pressing at 170°C for 10 minutes, followed by an oven cure (air circulated) at 150°C for 1 hour. Other details which were measured or calculated are:

volume fraction of filler	= 55.42×10^{-3}
avg. thickness of membrane (ℓ)	= 0.207 (cm)
avg. density of membrane	= 1.009 (g/cc).

3.1.2 Hollow cylindrical membrane (designated as SiR-M)

This silicone elastomer was obtained from Midland Silicones Ltd. In view of the difficulty of getting smooth extrusion of silicone rubber tubing with a composition similar to that of the plane sheet membrane, this hollow cylindrical membrane was prepared from the Midland Silicones Ltd. silicone rubber ref. no. TS 5095, and was formulated as having 100 parts by weight of methyl/vinyl gum (average density 0.98 g/cc),

50 parts by weight of Aerosil K3 silica filler (average density 2.20 g/cc) and 25 parts by weight of 40% concentrated paste of 2:4-dichlorobenzoyl peroxide in silicone fluid. The tube was cured 5 min. at 200°C followed by 4 hr. at 250°C in an air circulating oven. Other details calculated or measured include:

volume fraction of filler = 182.15×10^{-3}
average internal radius (a) = 0.349₇ (cm)
average external radius (b) = 0.573₆ (cm)
average density of membrane = 1.19₅ (g/cc).

3.2 GAS SAMPLES

3.2.1 Inert gases

Helium, neon, argon, krypton and xenon were used for permeation work. They were each supplied in a litre glass cylinder, equipped with a break-seal, from the British Oxygen Co. Ltd. The purity specifications were reported to be as follows:

He, Ne and Ar: spectrally pure
Kr: 99-100% (Balance Xe)
Xe: 99-100% (Balance Kr).

3.2.2 Permanent gases

Hydrogen, nitrogen and oxygen were employed for permeation work. Like the inert gases, each was contained in a litre glass cylinder and supplied by the British Oxygen Co. Ltd. They were all reported to be pure.

3.2.3 n-Butane

This n-butane sample was a Research Grade product supplied by the Chemical Research Laboratories, Teddington, in 500-ml glass cylinder. Its purity was stated to be 99.99 mole per cent. n-Butane was used not only for permeation experiments, but also for direct solubility measurement.

3.3 GENERAL DESCRIPTION OF APPARATUS

The apparatus for permeation work, and for direct solubility measurements (the latter being used for n-butane only), shown diagrammatically in Fig. 3-1, was made up of three main sections, namely, the pumping system, the permeation system, and the solubility system. All glass equipment was constructed from pyrex glass, and all taps were lubricated with Apiezon N high vacuum grease.

3.3.1 The pumping system

The pumping system is shown in the left hand side of Fig. 3-1. By means of a two-stage mercury diffusion pump backed with Edwards' Speedivac high vacuum rotary oil pump, the apparatus can be evacuated to better than 10^{-6} cm of Hg. The oil trap prevents oil from being sucked back into the system in the event of power failure. The cold trap, a dewar flask filled with liquid oxygen or nitrogen, serves to prevent any

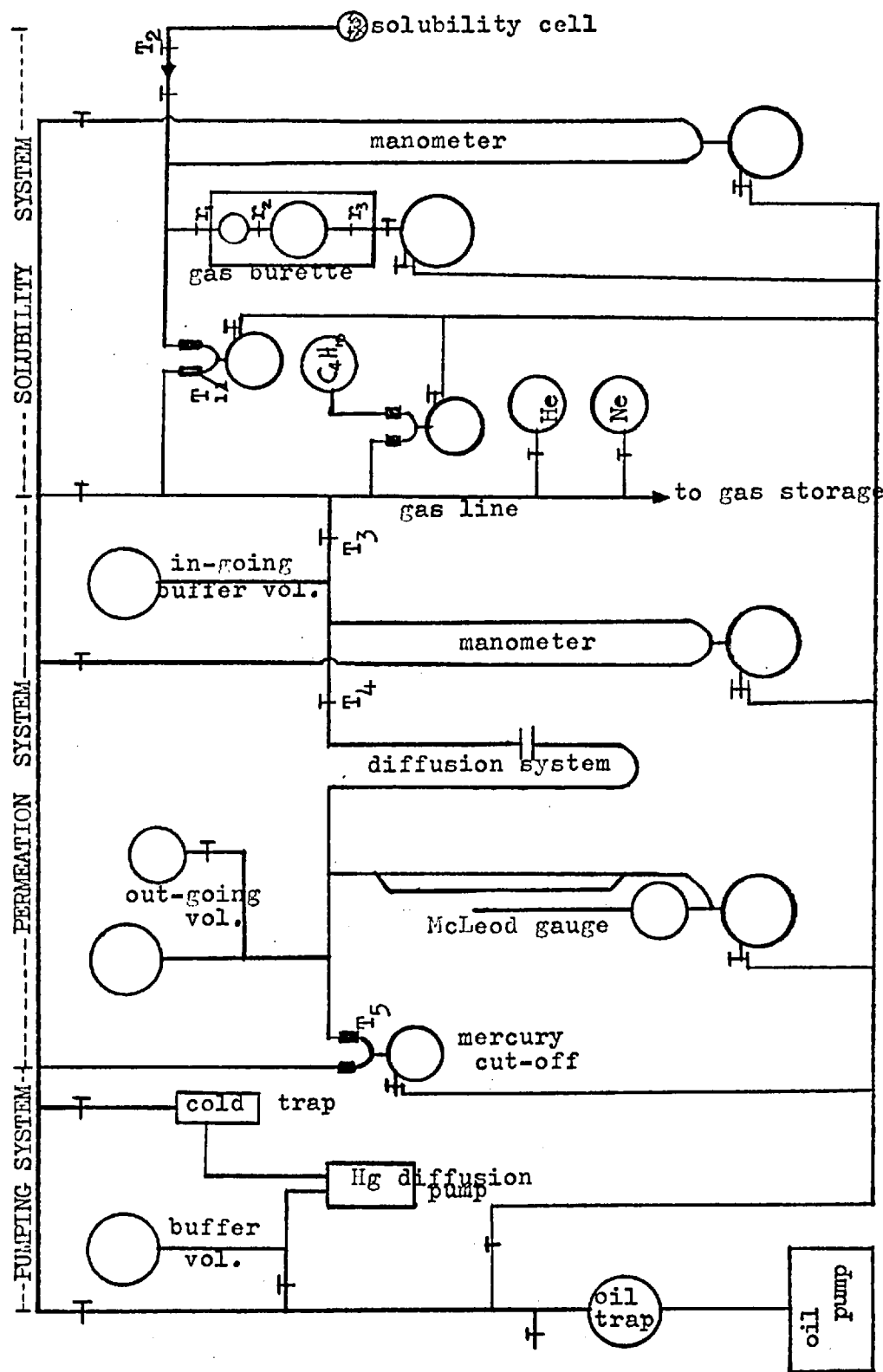


Fig. 3-1 The PUMPING, PERMEATION and SOLUBILITY SYSTEMS.

condensable materials from contaminating the mercury and oil pumps; and also to prevent the uncondensed mercury vapour from the mercury diffusion pump getting into the high vacuum line and other parts of the apparatus. The buffer volume between the oil pump and the mercury diffusion pump enables the latter to operate while the oil pump is otherwise engaged. A by-pass was also constructed to avoid switching off the mercury diffusion pump each time air was being admitted to the main system.

3.3.2 The permeation system

The permeation system is shown in the central part of Fig. 3-1. It consists of an ingoing buffer volume of 2-litre capacity, a manometer, a diffusion system (embodying the diffusion cell and the membrane) immersed in a thermostat, a McLeod gauge, and a variable out-going volume.

(a) The Diffusion System

1. Plane sheet membrane

The arrangement of the diffusion system used for investigating gas permeation through a plane sheet membrane is shown in Fig. 3-2. It is basically identical to that used by Barrer¹, and later on by many other workers in this field. It is made of stainless steel and is circular in cross-section. This diffusion system is made up of the membrane holder and the diffusion cell described below.

(i) The membrane holder

The membrane holder and the manner in which the membrane M was held between them is shown in Fig. 3-3.

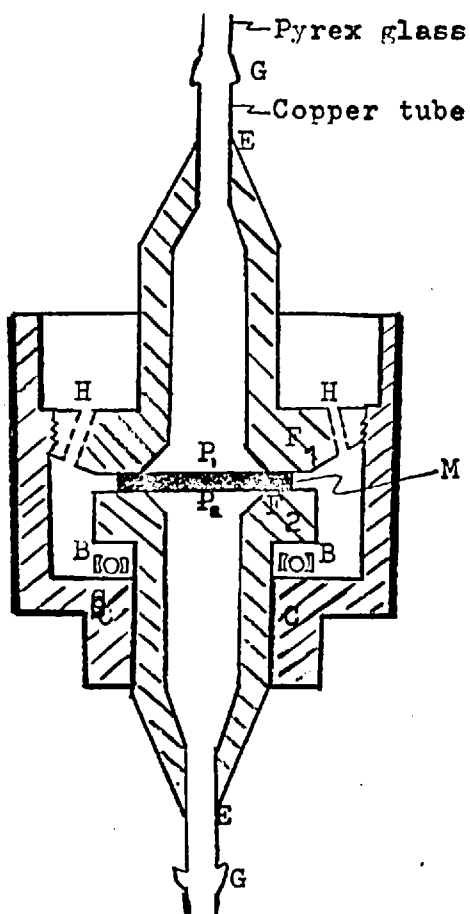


Fig. 3-2.

The Diffusion System.

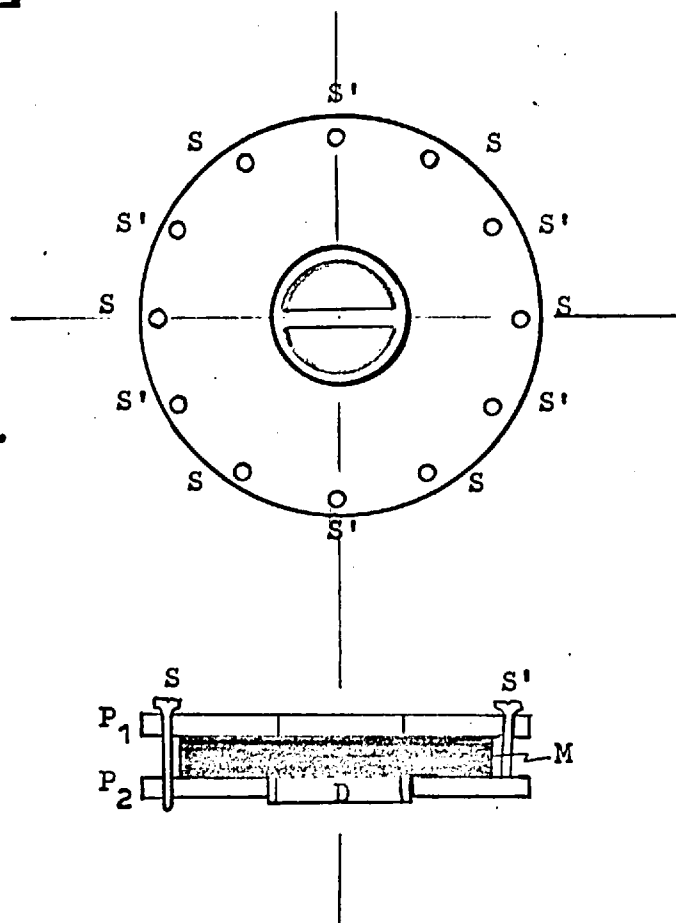


Fig. 3-3. The Membrane Holder.

In order to minimise the effect of bulging, the membrane was clamped between a pair of circular steel plates, P_1 , P_2 , which were joined together by a series of screws S . Care was taken to avoid excessive tightening, as this might distort the membrane in the central hole. A second series of screws S' , positioned between those of the first series was screwed through the top plate P_1 until the bottom plate P_2 was reached lightly; thus preventing any change in the distance of separation of the plates once the membrane had been clamped. When a higher ingoing pressure was introduced, further distortion of the membrane could be prevented by supporting it on the outgoing side (lower side in Fig. 3.3) by a piece of copper-gauze held horizontally by a steel disc D . Two silicone rubber (I.C.I. low temperature performance rubber DP54, stiffening temperature -90°C) O-rings were mounted between the plates P_1P_2 and the flanges F_1F_2 of the diffusion cell so as to ensure a mercury-tight seal. The area of the membrane exposed to permeation was in effect the area bounded by the aperture of the plates P_1 and P_2 of the membrane holder, the diameter of which was measured by means of a travelling microscope.

(ii) The diffusion cell

The diffusion cell consists of four detachable parts, namely the outer cup C , the upper flange F_1 , the lower flange F_2 , and a set of steel ball bearings B fixed loosely on a steel ring. The overall arrangement, complete with the membrane M clamped in its holder P_1P_2 , is presented in Fig. 3-2. The membrane clamped by the holder as described previously

and placed between the flanges F_1 and F_2 , was then assembled by screwing the casing C until it was sufficiently tight. The ball bearings B so placed under the lower flange F_2 provided a regular and balanced tightening of the flanges. A gas-tight seal was then effected by pouring into the holes H some mercury which occupied the annular space below the upper flange as well as the cup above the holes. It was found that this mercury-seal made permeation experiments at temperatures below the freezing point of mercury (-38.87°C) practically impossible. The diffusion system so set up was then lowered into a 7 cm diameter glass tube and allowed to rest firmly on a supporter consisting of cork rings. This was finally immersed into a low temperature thermostat and connected to the permeation system through copper-pyrex glass seals G, the copper tube being silver-soldered to the cell at E.

2. Hollow cylindrical membrane

For permeation experiments at temperatures below the freezing point of the sealing agent, mercury, the diffusion system described previously can no longer be employed. It was found that when mercury solidified, gas leakage developed. Such difficulty was overcome by the use of a hollow cylindrical membrane (tubing). Two such arrangements are shown in Fig. 3-4. Owing to the thickness of the membrane used and the low incoming pressure (under 5 cm Hg) introduced in the experiments, no support inside the tube was necessary. In both cases, flow of gas proceeded inward as shown by the arrow. The height of the hollow cylindrical membrane exposed to the gas

was determined from the average of a number of measurements recorded by a cathetometer.

(i) Type I: In Fig. 3-4(a), araldite was used as a sealing agent. The membrane was mounted on to glass tubes of suitable diameter with the closed end at the bottom and the open end at the top. To obtain a reasonably sharp boundary between the membrane and the araldite cellotape was wrapped around the membrane along CD and araldite applied over the portion above CD, thus making a seal between the membrane and the glass tubing. The araldite was allowed to soften in front of a radiator and the unit rotated slowly to obtain an even distribution of the seal. The cellotape was removed before the araldite hardened. This procedure was repeated on the lower end AB. The seal was finally allowed to set in front of a radiator ($\sim 30^{\circ}\text{C}$) for at least 24 hours. Such a diffusion system was found not reliable. For instance, at -55°C the araldite was found to crack at times. It seemed therefore that -55°C was the lower temperature limit for its use.

(ii) Type II: In Fig. 3-4(b), Apiezon N high vacuum grease was used as sealing agent. This arrangement is similar to that described in Fig. 3-4(a). In this case, however, a glass tubing, which fitted nicely on to the membrane, was used as a jacket. Indeed this much simpler design was found to be applicable for low temperature work.

(b) The McLeod Gauge

The McLeod gauge used in measuring the outgoing pressure has a pressure range of better than

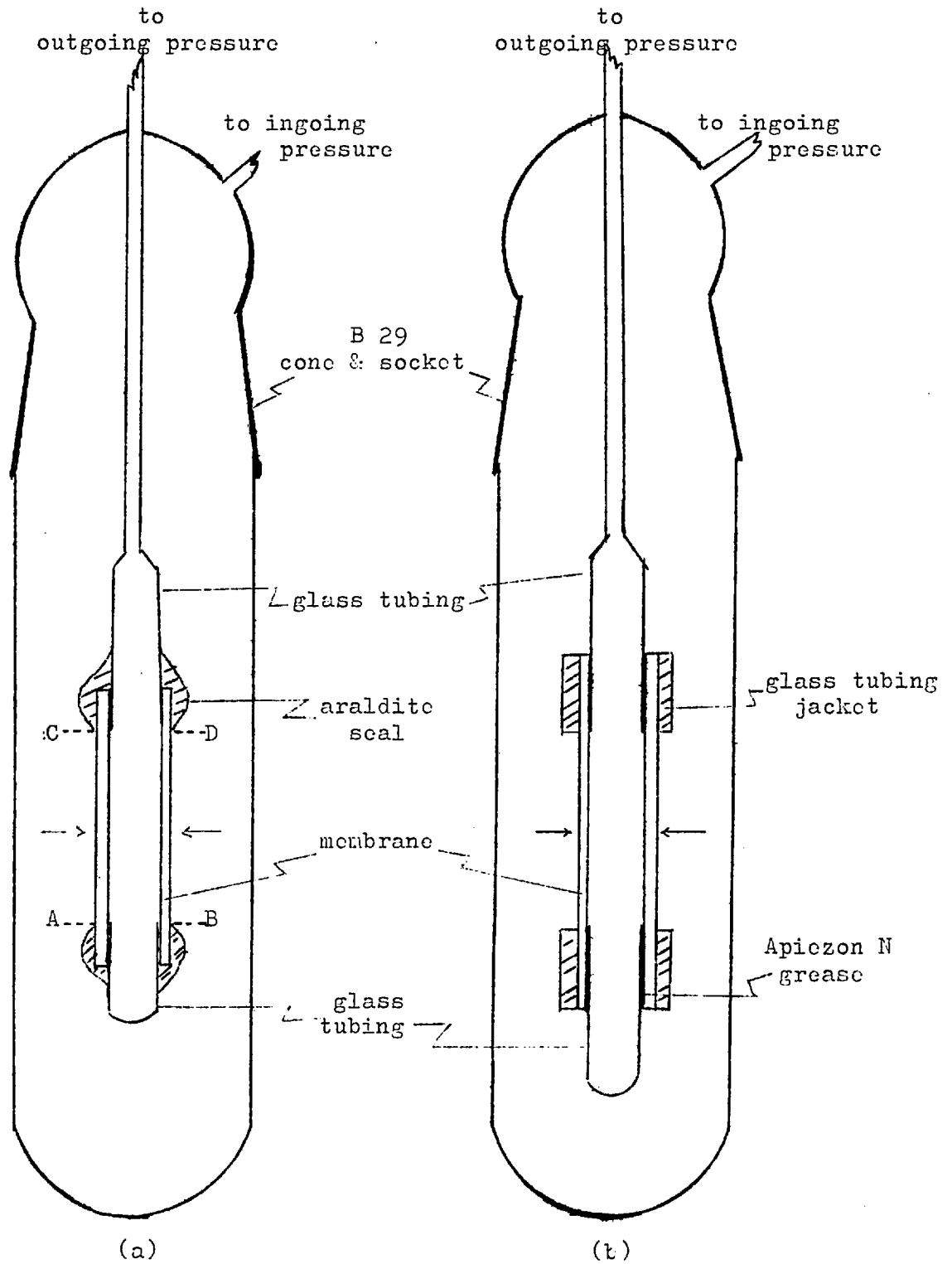


Fig3-4 The Diffusion System for Hollow Cylindrical Membrane

1×10^{-6} cm Hg to about 0.17 cm Hg. In the experiments, an upper limit of about 10^{-2} cm Hg was actually measured for n-butane, though for inert and permanent gases a much lower upper limit was involved.

The capillary stems of the gauge were made from "Veridia" tubings of 2 mm diameter. Fixed reference marks were etched on the closed stem and the volumes between the marks were calibrated using known weights of mercury. The outgoing pressure p_1 was then given by $p_1 = \frac{V}{V}h$ where v is the volume of gas enclosed between the mercury meniscus and the closed end, V the total volume of the gauge, and h the difference in mercury heights in the two capillary stems. The calibration was that made by Raman⁹⁶, and was reported to have the following details:

Total volume $V = 191 \text{ cm}^3$

Reference mark from close end	I	II	III	IV	V
$\frac{v}{V}$ ratio	0.0989	0.1659	0.5	1.474	4.114
	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$

3.3.3 The solubility system

The solubility system is shown on the right hand side of Fig. 3-1, and is shown again in Fig. 3-5 with more detailed explanations of the various parts. It consists of a gas burette, the volume of which had been calibrated before use, a manometer of 1 cm diameter, and the sorption cell. This solubility system was used only for the measurement of the static solubility coefficient of n-butane as sorbate and SiRI as sorbent.

3.3.4 Thermostat

The "Minus Seventy Thermostat Bath, Toluol Regulator Model" (manufacturer, Townson and Mercer, Ltd.) was employed for work requiring temperatures between 0°C and -70°C.

The bath consists of a large cylindrical Dewar vessel (7 $\frac{3}{4}$ inch diameter and 14 $\frac{1}{2}$ inch height) with unsilvered strips on opposite sides so that objects in the bath can be observed through the viewing windows in the casing. A second identical Dewar vessel holds the heat exchanger and the supply of solid CO₂ in petroleum ether (100/120 fraction). The pumping and control mechanism is mounted on the centre cover plate which can be removed by lifting. The lead from the top is connected to the amplifier valve relay box and the control is by a toluol regulator. During operation, the immersion pump circulates the contents of the bath with one pump. The other pump on the same spindle has an adjustable valve on one side, and on the other a flap valve operated by a solenoid. This solenoid is controlled by a relay operated by the thermionic valve and the grid of which is switched by the toluol regulator. When the valve is open, the second pump by-passes part of the bath contents through the heat exchanger in the second Dewar vessel. At relatively high temperatures the adjustable valve is set so that, even with the flap valve open, only a small quantity of bath liquid traverses the heat exchanger. When running at lower temperatures, practically the whole of the pump output comes directly through the heat exchanger.

Although the performance of this thermostat was found to be not very consistent (many disappointments were indeed encountered!) it served quite satisfactorily once it functioned overnight. Its sensitivity tended to decrease with decreasing temperature, due probably to evaporation of bath liquid and clogging with ice particles especially over long periods of operation. Successful runs at about -65°C had, however, been continued for four days. Experience showed that routine drying and oiling of the unit were necessary for successful operation.

3.3.5 Thermometers

(a) Mercury-thallium filled thermometer (Griffin and George Ltd.). This thermometer was used to measure all thermostat temperatures in the range 0°C - -55°C . The specification is as follows:

Range:	-55°C to $+20^{\circ}\text{C}$
Scale division:	0.2°C
Total length:	40 cm
Type:	Total immersion
Max. error:	0.4°C .

Comparison with the ammonia vapour pressure thermometer at -55°C gave very good agreement.

(b) Ammonia vapour pressure thermometer was used for temperatures about -65°C .

(c) Carbon dioxide vapour pressure thermometer was used for temperature of petroleum ether - cardice mixture.

3.4 CALIBRATION OF APPARATUS

3.4.1 The permeation system

Calibration of the outgoing volume, V_o :-
The outgoing volume, V_o , on the low pressure side of the permeation system, as defined in Fig. 3-1 by the volume enclosed between the mercury cut-off T_5 and the diffusion cell, was calibrated using N_2 gas by pressure drop on expansion measurements against the standard volume of the McLeod gauge. The probable error due to the escape of gas by permeation through the membrane within such a short period between two successive pressure readings was considered negligible. Variation of the "effective volume" of this outgoing system with thermostat temperature was too small to be significant.

3.4.2 The solubility system

(a) Calibration of the volume of doser dead space, V_d :-

V_d is defined (see Fig. 3-5) as the volume enclosed between the mercury cut-off T_1 , the reference mark r_3 on the gas burette, the reference mark a on the manometer, and the tap T_2 . V_d can then be deduced from

$$[V_d + V_g + h_D A_D] p_D' = [V_d + h_D'' A_D] p_D''$$

where V_g is the known volume of the gas burette, A_D the area of the manometer tube deduced from its known diameter, h_D the displacement of mercury level from reference mark a , and p_D the corresponding pressure measured as the difference in height of the mercury levels. The procedure was to introduce a suitable

amount of nitrogen gas while T_2 was closed and the mercury level in the gas burette was at r_1 . With T_1 closed, h_D^I and p_D^I were measured with a cathetometer. Then the mercury level in the gas burette was raised to r_3 and the corresponding values of h_D^{II} and p_D^{II} were measured.

(b) Calibration of the sorption cell:- The required volumes V_x , V_y and V_z , as defined in the self-explanatory Fig. 3-6, were calibrated in the following manner:

V_z : by adding a known weight of mercury to the empty cell before joining it to the main system; the volume of the silicone rubber being deduced from its known weight and density.

V_x : by the gas expansion method.

V_y : this is then given by $V_x - V_z$.

3.5 EXPERIMENTAL TECHNIQUES

3.5.1 Permeation experiment

(a) Plane sheet membrane (SiRI): The membrane was thoroughly outgassed before each permeation run at a temperature not exceeding 40°C , though mainly at room temperature. It was also allowed to remain in the thermostat at the required experimental temperature for a period of not less than 12 hours. With T_4 and T_5 closed (see Fig. 3-1) a change of gas was introduced via T_3 into the ingoing side of the permeation system. The 2-litre buffer volume served to

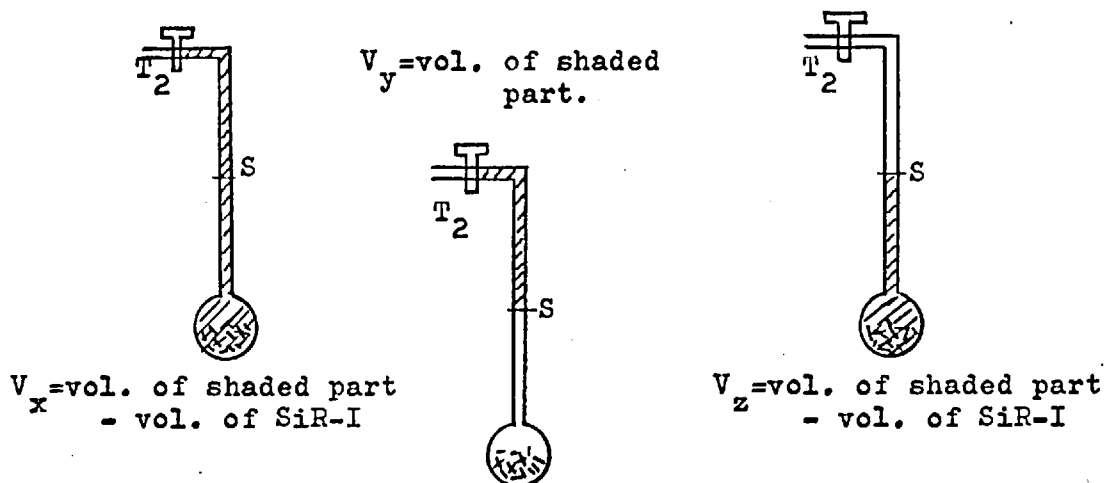


Fig. 3-6. Calibration of sorption cell.

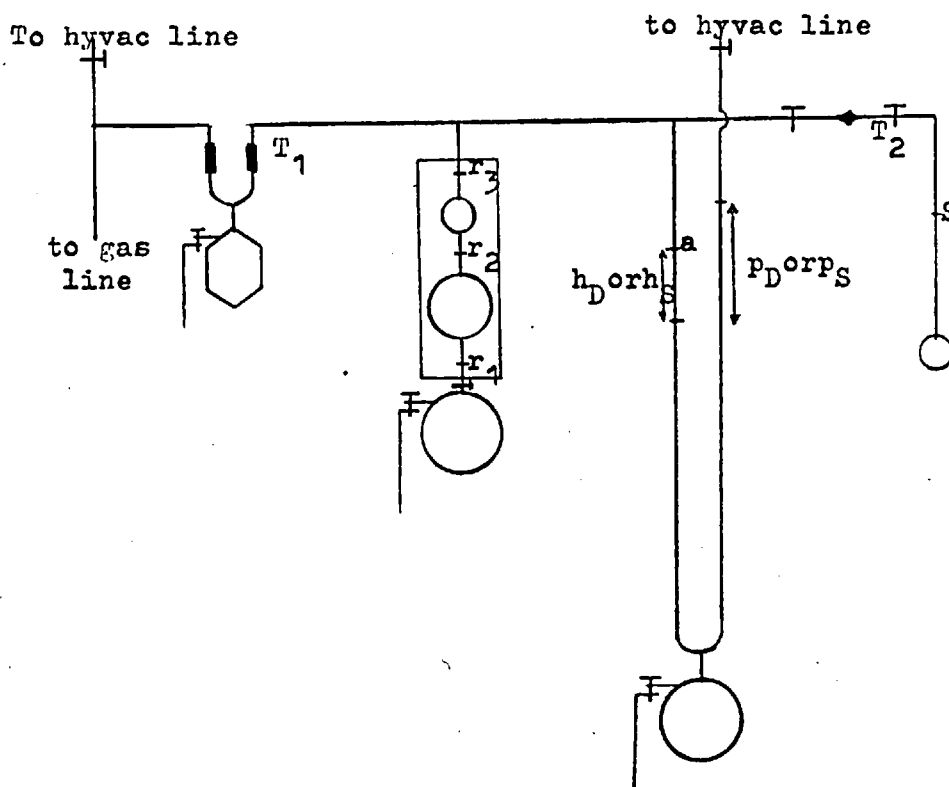


Fig. 3-5 The Solubility System.

avoid fluctuations in the ingoing pressure p_2 . Using a stop-watch to record the time, a permeation experiment was started by opening T_4 . The outgoing pressure p_1 was recorded at suitable time intervals by the McLeod gauge. A plot of outgoing pressure p_1 vs time t gave, as explained in section 2.2.1(a) and (b), the time lag L , and the steady-state rate of increase of outgoing pressure $\frac{dp_1}{dt}$. Ideally, L and $\frac{dp_1}{dt}$ should be obtained by application of the method of least squares to the p_1 - t data. It follows that the transient-state diffusion coefficient D_L , the permeability coefficient $\bar{P}$, and the dynamic solubility coefficient σ_D were deduced from one and the same experiment using equations (2.12), (2.9a) and (2.11) respectively. p_2 was the average value of the ingoing pressure measured with a cathetometer, and T_R was the average room temperature in $^{\circ}\text{C}$, both taken over a regular interval during the permeation experiment.

(b) Hollow cylindrical membrane (SiR-M): The same experimental procedure as that described above was used. The expressions for D_L and $\bar{P}$ are now given by equations (2.21) and (2.20) respectively.

The dynamic solubility coefficient σ_D was again deduced from (2.11).

(c) Analysis of the permeation data by the "early approximation method": In both cases (i.e., plane sheet and hollow cylindrical membranes) the transient state data of outgoing pressure p_1 vs time t could be treated by the early approximation method, provided the time lag was sufficiently long and enough data in the

transient state obtained. As explained in sections 2.2.1(c) and 2.2.2(c), the required expression was given by equation (2.13) so that when $\log(t^{\frac{1}{2}} \frac{dp_1}{dt})$ was plotted against $\frac{1}{t}$, a straight line was obtained, the slope of which was given by $\frac{l^2}{2.302 \times 4 \times D}$. Hence the diffusion coefficient, denoted by D_E , was deduced. $\frac{dp_1}{dt}$ values were obtained either from the tangents at various t of p_1 - t data, or by dividing the difference between two successive p_1 readings by the time interval, t being the mean of the time interval.

3.5.2. Equilibrium solubility experiment (for SiR-I: n-butane only)

Silicone rubber (SiR-I), cut into small pieces and placed in the sorption cell, was thoroughly outgassed before experiment. With T_2 closed and mercury level in the gas burette at r_1 (see Fig. 3-5), a charge of n-butane was introduced into the solubility system. Measuring h_D and p_D and noting the room temperature $T_R(^{\circ}\text{C})$, the volume (NTP) V_D of n-butane used in this experiment was then calculated from

$$V_D = [V_d + V_g + h_D A_D] \frac{273.16}{273.16 + T_R} \frac{1}{76} p_D$$

Next, T_2 was opened. After equilibrium had been attained at the thermostat temperature $T_S(^{\circ}\text{C})$ the corresponding h_S and p_S were measured and room temperature was noted. Then the volume (NTP) V'_c of n-butane above mark s was given by

$$V'_c = [V_d + V_g + V_y + h_S A_D] \frac{273.16}{273.16 + T_R} \frac{1}{76} p_S$$

Also, the volume (NTP) V''_0 of n-butane remaining in the

sorption cell below mark s was given by

$$V_o'' = V_z \frac{273.16}{273.16 + T_s} \frac{1}{76} p_s$$

Thus the total volume (NTP) of n-butane not sorbed = $(V_s' + V_o'')$, and the volume (NTP) V_s of n-butane sorbed at thermostat temperature = $[V_D - (V_o' + V_o'')]$. The static solubility coefficient σ_s was then given by $\sigma_s = \frac{V_s}{p_s V}$ where V is the volume of the sample. Still using the same charge of n-butane, V_D , the thermostat was set to other temperatures required and the procedures repeated. Thus a series of V_s and p_s measurements was obtained for various temperatures.

The above procedure was repeated using different charges of n-butane. Finally, isotherms $\frac{V_s}{V}$ vs p_s were drawn, and the average static solubility coefficient σ_s at various temperatures was deduced from the slope of the isotherms.

3.6 ACCURACY OF MEASUREMENTS

In order to compute the diffusion and permeability coefficients, it is necessary to measure the following basic variables with the accuracy stated. Absolute accuracy is, however, difficult to determine.

(a) Dimensions of the membrane:

(1) Plane sheet membrane: The thickness was measured with a micro-meter screw gauge reading to 0.001 cm. The mean value used in the calculation was for 12 measurements and was found to have a maximum spread of $\pm 1\%$. The area of the membrane was assumed

to be the same as that of the opening of the membrane holder. A cathetometer was used to measure the diameter of the opening. The error in this diameter was estimated to be better than 0.5%.

(2) Hollow cylindrical membrane: The internal and external radii, and the length of the exposed area were average values determined with a cathetometer. The maximum error was approximately $\pm 3\%$ for the radii and $\pm 1\%$ for the length.

(b) McLeod gauge:

The spread of points giving the outgoing pressures in the plots of pressure vs. time was reasonably good.

(c) Outgoing volume:

This was calibrated by pressure drop on expansion measurements against the volume of the McLeod gauge. The reproducibility was about $\pm 1\%$. Variation of the "effective volume" with the thermostat temperature was too small to be significant.

(d) Ingoing pressure:

The average value was used. This was recorded to better than 0.01 cm by observing a wide bore mercury manometer with a cathetometer. The maximum variation of the ingoing pressure was less than 1%.

(e) Room temperature:

The average value was used. With longer runs especially late at night and in the early morning during the summer, temperature fluctuations as much as 4% were noted.

No account has been taken for the coefficient of thermal expansion of the membrane. In conclusion, it may be stated that the accuracy of the reported data is of the order of $\pm 5\%$.

PART 4. RESULTS AND DISCUSSIONS

4.1 PERMEABILITY, DIFFUSION AND SOLUBILITY COEFFICIENTS

The experimental data for permeation, diffusion and solution are tabulated and presented in this section (4-1). This section is further subdivided into two, one for the plane sheet membrane (SiR-I) and the other for the hollow cylindrical membrane (SiR-M). Explanations of the symbols used are as follows:

- T = temperature of permeation experiment.
- p₂ = ingoing pressure in cm of Hg
- L = time lag in minutes
- D_L = transient-state diffusion coefficient in cm²sec⁻¹
- D_s = steady-state diffusion coefficient in cm²sec⁻¹
- D_E = transient-state diffusion coefficient deduced by the "early approximation method"
- $\bar{P}$ = permeability coefficient in cc NTP/sec/cm² area/cm thickness/cm Hg
- σ_D = dynamic solubility coefficient in cm³ NTP per cm³ of the actual silicone elastomer when the pressure of the gas is 1 atm.

$$(\sigma_D = \frac{\bar{P}}{D_L} \times 76)$$

continued.

σ_D^* = the above σ_D converted to cm^3 NTP per cm^3 of silicone elastomer without filler when the pressure of the gas is 1 atm.

Since the volume fractions of the filler are 55.42×10^{-3} for SiR-I, and 182.15×10^{-3} for SiR-M, σ_D is converted to σ_D^* by the following relationships:

$$\sigma_D^* = \frac{\sigma_D}{0.94458} \quad (\text{for SiR-I}), \quad \text{and}$$

$$\sigma_D^* = \frac{\sigma_D}{0.81785} \quad (\text{for SiR-M})$$

σ_S and σ_S^* = static solubility coefficients expressed in the same units as those of σ_D and σ_D^* respectively

T_S = temperature of static solubility experiment

p_S = equilibrium pressure of the gas in cm of Hg (static measurements)

$\frac{V_S}{V}$ = volume (NTP) of gas sorbed per unit volume of the actual silicone elastomer at the equilibrium pressure p_S

4.1.1 Experimental data for the plane sheet membrane (SiR-I)

TABLE 4-1

SiR-I: He

T	p_2	L	$D_L \times 10^6$	$\bar{P}_x \times 10^8$	σ_D	σ_D^*
0	4.259	2.9	41.04	2.332	0.0432	0.0457
-5	3.842	3.3	36.07	2.097	0.0442	0.0468
-10	4.216	3.5	34.01	1.878	0.0420	0.0444
-20	4.402	4.0	29.76	1.456	0.0372	0.0394
-24	3.623	4.3	27.68	1.247	0.0342	0.0362
-30.5	3.543	4.6	25.88	1.026	0.0304	0.0322
-37	4.350	5.2	22.89	0.870	0.0289	0.0306

TABLE 4-2

SiR-I: Ne

T	p_2	L	$D_L \times 10^6$	$\bar{P}_x \times 10^8$	σ_D	σ_D^*
0	3.847	7.4	16.08	1.914	0.0904	0.0957
-10	3.468	8.6	13.96	1.507	0.082	0.0868
-20	3.238	10.0	11.90	1.218	0.0778	0.0823
-30	3.865	11.8	10.08	0.913	0.0688	0.0728
-37	3.759	13.1	9.09	0.746	0.0624	0.0661

TABLE 4-3

SiR-I: Ar

T	p_2	L	$D_L \times 10^6$	$D_E \times 10^6$	$\bar{P}_x \times 10^8$	σ_D	σ_D^*
0	2.50	9.7	12.23	12.12	5.509	0.342	0.362
-10	2.65	11.6	10.29	8.81	4.722	0.349	0.369
-20	2.54	13.6	8.73	8.70	4.052	0.352	0.374
-30	2.60	17.0	7.01	6.33	3.313	0.359	0.380
-37	2.62	19.9	5.98	6.86	2.863	0.364	0.385

TABLE 4-4

SiR-I: Kr

T	p_2	L	$D_L \times 10^6$	$\bar{P}_x \times 10^8$	σ_D	σ_D^*
0	3.704	14.9	7.97	10.229	0.975	1.032
-10	3.527	18.6	6.40	9.21	1.094	1.159
-20	3.759	23.0	5.19	8.225	1.205	1.276
-30	3.666	28.7	4.15	7.276	1.332	1.410
-37	3.726	35.1	3.39	6.55	1.467	1.553

TABLE 4-5

SiR-I: Xe

T	p_2	L	$D_L \times 10^6$	$D_E \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	2.56	24.6	4.84	5.17	25.51	4.002	4.237
-10	3.05	31.4	3.79	4.5	24.58	4.924	5.213
-20	2.85	40.3	2.95	3.75	23.29	5.993	6.345
-30	2.66	52.3	2.28	2.29	21.52	7.183	7.604
-37	2.84	64.9	1.83	1.75	20.52	8.499	8.997

TABLE 4-6

SiR-I: H₂

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	4.289	2.5	47.61	4.64	0.0741	0.0784
-10	4.403	3.0	39.68	3.65	0.0699	0.074
-15	3.974	3.3	36.07	3.242	0.0683	0.0723
-20	3.690	3.6	33.06	2.837	0.0652	0.069
-30	3.632	4.2	28.34	2.195	0.0589	0.0623
-37	3.375	4.8	24.80	1.799	0.0551	0.0584

TABLE 4-7

SiR-I: N₂

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	4.386	14	8.50	2.271	0.2031	0.215
-10	4.393	16.6	7.17	1.925	0.204	0.216
-20	4.489	20.5	5.81	1.56	0.2042	0.2162
-30	4.250	25.6	4.67	1.262	0.2055	0.2176
-37	4.535	30.3	3.93	1.077	0.2081	0.2203

TABLE 4-8 (Interpolated values)

SiR-I: O₂

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	4.908	10	11.95	4.888	0.3109	0.3291
-10	4.648	11.6	10.28	4.227	0.3125	0.3308
-20	4.913	13.6	8.73	3.614	0.3146	0.3331
-30	4.551	16.3	7.32	3.052	0.3169	0.3355
-37	4.501	18.6	6.41	2.686	0.3185	0.3372

TABLE 4-9

SiR-I: n-Butane

T	p_2	L	$D_L \times 10^6$	$D_E \times 10^6$	$\bar{P} \times 10^6$	σ_D
0	3.10	49.5	2.40	2.29	1.94	61.56
-10	3.00	60	1.98	1.97	2.26	86.64
-20	3.00	78	1.53	1.40	2.69	133.76
-30	2.60	103	1.16	0.93	3.20	209.76
-37.4	2.55	123	0.97	0.70	3.87	303.24

σ_D^*	σ_S	σ_S^*	$D_S (= \frac{P_{76}}{\sigma_S}) \times 10^6$
65.17	57.76	61.15	2.55
91.72	84.28	89.22	2.07
141.61	131.48	139.19	1.55
222.07	208.24	220.45	1.17
321.03	302.48	320.23	0.97

TABLE 4-10 Data from static solubility experiments.

SiR-I: n-Butane

$T_s = 0^\circ\text{C}$	$\frac{p_s}{V_s}$	1.918	2.151	2.650	2.935	3.650	4.845
	$\frac{1}{V}$	1.445	1.600	2.001	2.238	2.755	3.718
$T_s = -10^\circ\text{C}$	$\frac{p_s}{V_s}$	1.543	1.721	2.157	2.250	2.836	3.742
	$\frac{1}{V}$	1.708	1.902	2.347	2.465	3.175	4.293
$T_s = -20^\circ\text{C}$	$\frac{p_s}{V_s}$	1.160	1.285	1.610	1.626	2.057	2.723
	$\frac{1}{V}$	1.974	2.20	2.731	2.844	3.572	4.819
$T_s = -32.2^\circ\text{C}$	$\frac{p_s}{V_s}$	0.753	0.840	1.035	1.079	1.321	1.732
	$\frac{1}{V}$	2.257	2.519	3.132	3.096	3.945	5.322
$T_s = -40^\circ\text{C}$	$\frac{p_s}{V_s}$	0.540	0.606	0.724	0.745	0.912	1.205
	$\frac{1}{V}$	2.404	2.680	3.359	3.249	4.153	5.594
$T_s = -52.2^\circ\text{C}$	$\frac{p_s}{V_s}$	0.301	0.336	0.369	0.411	0.507	0.735
	$\frac{1}{V}$	2.570	2.870	3.422	3.571	4.359	5.829
$T_s = -63^\circ\text{C}$	$\frac{p_s}{V_s}$	0.238	0.270	0.297	0.330	0.411	0.532
	$\frac{1}{V}$	2.612	2.916	3.454	3.626	4.403	5.933

From the experimental data in Table 4-10, isotherms were drawn and the static solubility coefficients deduced (Table 4-10A).

TABLE 4-10A

T_s ($^\circ\text{C}$)	0	-10	-20	-32.2	-40	-52.2	-63
σ_s (=slope $\times 76$)	57.76	84.28	131.48	227.24	354.16	652.84	832.2

4.1.2 Experimental data for the hollow cylindrical membrane (SiR-M)

TABLE 4-11

SiR-M: He

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	3.840	3.2	43.57	1.766	0.0308	0.0377
-10	3.528	4.0	34.85	1.366	0.0298	0.0364
-20	3.418	5.0	24.88	1.038	0.0283	0.0346
-30	3.190	6.5	21.45	0.7591	0.0269	0.0329
-40	3.641	8.5	16.40	0.5565	0.0258	0.0315
-48	4.435	10.5	13.28	0.4389	0.0251	0.0307
-55	3.952	22	6.337	0.0892	0.0107	0.0131
-55	3.929	22	6.337	0.0897	0.0107 ₆	0.0131 ₅
-64.3	4.182	40	3.485	0.0535	0.0117	0.0143
-64.3	4.390	42	3.319	0.0509	0.0116 ₅	0.0142
-78	4.226	118.8	1.173	0.0199	0.0129	0.0158
-78	4.367	114	1.223	0.0215	0.0134	0.0163
-78	4.130	123	1.133	0.0198	0.0133	0.0163

TABLE 4-12

SiR-M: Ne

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	2.950	6.7	20.81	1.484	0.0542	0.0663
-10	2.700	8.25	16.90	1.147	0.0516	0.0631
-20	2.866	10.5	13.28	0.8929	0.0511	0.0625
-30	2.620	13.5	10.33	0.6619	0.0487	0.0596
-40	3.032	18.0	7.745	0.4656	0.0457	0.0559
-48	2.892	22.5	6.196	0.3419	0.0419	0.0513
-55	2.881	84.9	1.641	0.0702	0.0325	0.0397
-55	3.474	87	1.602	0.0672	0.0319	0.0390
-64.3	4.109	168	0.830	0.0356	0.0326	0.0399
-64.3	4.072	168	0.830	0.0358	0.0328	0.0402
-78	3.667	477	0.292	0.0124	0.0322	0.0394
-78	4.714	468	0.298	0.0134	0.0343	0.0419

TABLE 4-13

SiR-M: Ar

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	2.750	13.7	10.18	4.274	0.3192	0.3903
-10	2.843	17.5	7.966	3.646	0.3479	0.4254
-19.8	2.586	22.5	6.196	3.008	0.3690	0.4512
-30	2.696	30	4.647	2.437	0.3986	0.4874
-38.5	2.912	39	3.575	1.975	0.4198	0.5134
-40	2.926	41	3.40	1.943	0.4342	0.5309
-55	3.166	245.4	0.5681	0.2353	0.3147	0.3848
-59.5	3.005	390	0.3575	0.1717	0.365	0.4463
-64.3	3.565	618	0.2256	0.1119	0.3770	0.4609
-64.3	3.123	618	0.2256	0.1242	0.4185	0.5117
-78	3.209	2976	0.0469	0.0421	0.6837	0.8359

($D_E = 0.0468$)

TABLE 4-14

SiR-M: Kr

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	2.833	21	6.639	8.399	0.9616	1.176
-10	2.757	26.8	5.202	7.577	1.107	1.354
-20	2.843	37	3.768	6.422	1.295	1.584
-30	2.806	50	2.788	5.653	1.541	1.884
-44	3.289	75	1.859	4.867	1.990	2.433
-44.5	2.850	88.5	1.575	4.454	2.149	2.628
-55.2	2.989	577.3	0.2415	0.6469	2.036	2.489

($D_E = 0.298$)

TABLE 4-15

SiR-M: Xe

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	2.980	33	4.225	19.15	3.445	4.212
-10	2.788	45	3.098	17.72	4.348	5.316
-19.6	2.660	61.3	2.274	16.60	5.546	6.781
-30	2.540	88	1.584	15.29	7.335	8.969
-36.6	2.261	115	1.212	14.32	8.978	10.98

TABLE 4-16

SiR-M: H_2

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	3.031	4.9	28.45	3.507	0.0937	0.1145
-10	3.215	6.0	23.24	2.801	0.0916	0.112
-20	3.072	7.5	18.59	2.208	0.0903	0.1104
-30	2.958	9.75	14.30	1.657	0.0881	0.1077
-40	3.232	12.5	11.15	1.253	0.0854	0.1044
-55	3.441	63	2.213	0.1816	0.0624	0.0762
-55.5	3.235	67.5	2.065	0.17	0.0626	0.0765
-64.3	3.460	129	1.081	0.1068	0.0751	0.0918
-64.3	3.893	126	1.106	0.108	0.0742	0.0907
-78	3.980	406	0.3432	0.0413	0.0915	0.1118

TABLE 4-17

SiR-M: N_2

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
-0.8	3.296	18.3	7.606	1.668	0.1667	0.2038
-10	3.645	22.6	6.169	1.363	0.1679	0.2053
-20	3.558	29	4.807	1.069	0.1690	0.2066
-30	3.536	38	3.669	0.8195	0.1698	0.2076
-40	3.515	51.6	2.702	0.6036	0.1698	0.2076

TABLE 4-18

SiR-M: O_2

T	p_2	L	$D_L \times 10^6$	$\bar{P} \times 10^8$	σ_D	σ_D^*
0	3.117	13.2	10.56	3.848	0.2769	0.3386
-10	3.162	16.2	8.606	3.213	0.2838	0.3470
-20	2.558	20.4	6.834	2.671	0.2971	0.3632
-30	2.866	26.4	5.281	2.162	0.3111	0.3804
-40	2.579	34.5	4.041	1.685	0.3169	0.3875

4.2 KINETIC PHENOMENA

4.2.1 Permeability and diffusion coefficients

Plane sheet membrane (SiR-I): The permeability coefficients $\bar{P}$ and the transient-state diffusion coefficients D_L for the plane sheet membrane have been measured at a number of temperatures between 0°C and -37.4°C. The experimental data were presented in Section 4.1.1 (Tables 4.1 to 4.9). Since static solubility measurements were made for SiR-I:n-butane system, the steady-state diffusion coefficients D_S were also listed in Table 4.9. For Ar, Xe and n-butane as penetrants, the transient-state diffusion coefficients deduced by the "early approximation" method, D_E , were also given in Tables 4.3, 4.5 and 4.9. Since the time lag, e.g. for Ar, is short, the accuracy of D_E tends to be rather poor. Fig. 4.1 shows the typical plot from which D_E was deduced. In this case, data of $\frac{dp_1}{dt}$ were obtained by drawing tangents at various times, t , to the curve of outgoing pressure vs time.

Hollow cylindrical membrane (SiR-M): The corresponding experimental data of $\bar{P}$ and D_L determined in the temperature range between 0°C and -78°C were given in Section 4.1.2 (Table 4.11 to 4.18). D_E for Ar at -78°C and for Kr at -55.2°C were also included. For Ar, in particular, when the time lag is so large (49.6 hours) and hence sufficient data of the outgoing pressure p_1 were actually obtained during the transient state of the diffusion process, analysis by the early approximation method becomes more appropriate. With $\frac{dp_1}{dt}$ now obtained by dividing the difference of two

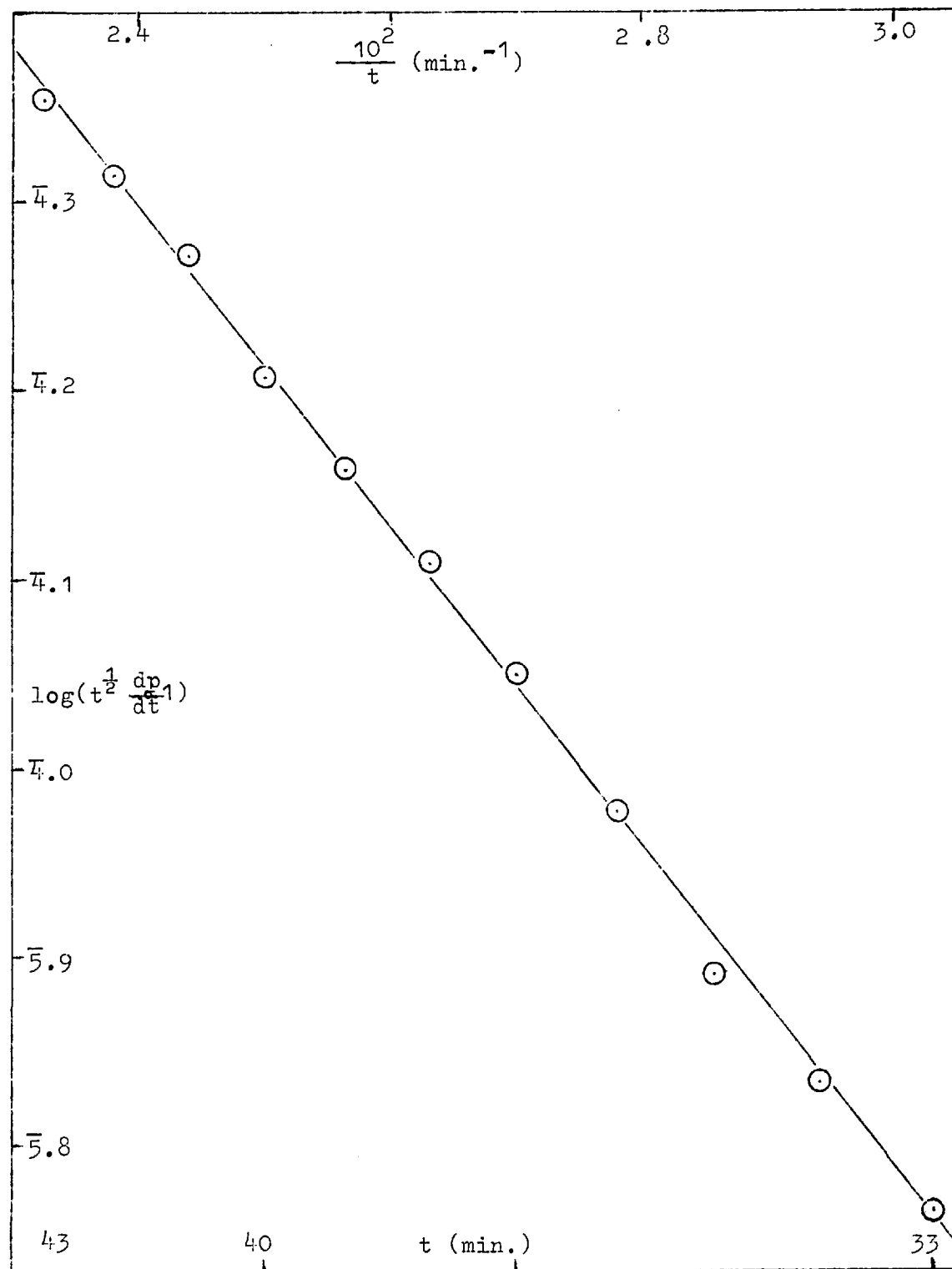


Fig.4-1 The "early approximation" analysis
for SiR-I : n-butane at -30°C.

successive readings in p_1 by the corresponding time difference, the typical plot is shown in Fig. 4.2.

Comparison of the magnitudes of $\bar{P}$ and D_L in these two silicone elastomers reveals that between 0°C and -37.4°C , where comparison is permitted,

$$\bar{P}(\text{SiR-I}) > \bar{P}(\text{SiR-M}) \text{ and } D_L(\text{SiR-I}) > D_L(\text{SiR-M})$$

with the exception of D_L values for He and Ne for which the order is rather uncertain. These conclusions are to be expected since SiR-I contains less filler than SiR-M. Indirectly, results for $\bar{P}$ and D_L also show that the experimental technique for the hollow cylindrical membrane (tubing) is as reliable as the more conventional method using the plane sheet form. Moreover, with the simplicity of the arrangement of the diffusion system and the ready availability of polymer tubing, this technique of measuring $\bar{P}$, D_L and σ_D using hollow cylindrical membranes may be useful.

For both membranes, SiR-I and SiR-M, the order of magnitude of the permeability coefficients at 0°C is

$$\bar{P}(\text{Ne}) < \bar{P}(\text{N}_2) < \bar{P}(\text{He}) < \bar{P}(\text{H}_2) < \bar{P}(\text{O}_2) < \bar{P}(\text{Ar}) < \bar{P}(\text{Kr}) < \bar{P}(\text{Xe}).$$

This order is maintained at temperatures between -5°C and -40°C except that below -5°C $\bar{P}(\text{He}) < \bar{P}(\text{N}_2)$ (see Fig. 4.3 and Fig. 4.4). In a study of thermal diffusion, Bearman⁹⁸ has determined the permeability at 34.5°C of natural rubber to inert gases. The order of magnitude of $\bar{P}$ is:

$$\bar{P}(\text{Ne}) < \bar{P}(\text{Ar}) < \bar{P}(\text{He}) < \bar{P}(\text{Kr}) < \bar{P}(\text{Xe}).$$

If permeability data of van Amerongen⁵ for H_2 , N_2 and O_2 through natural rubber at 25°C are combined with

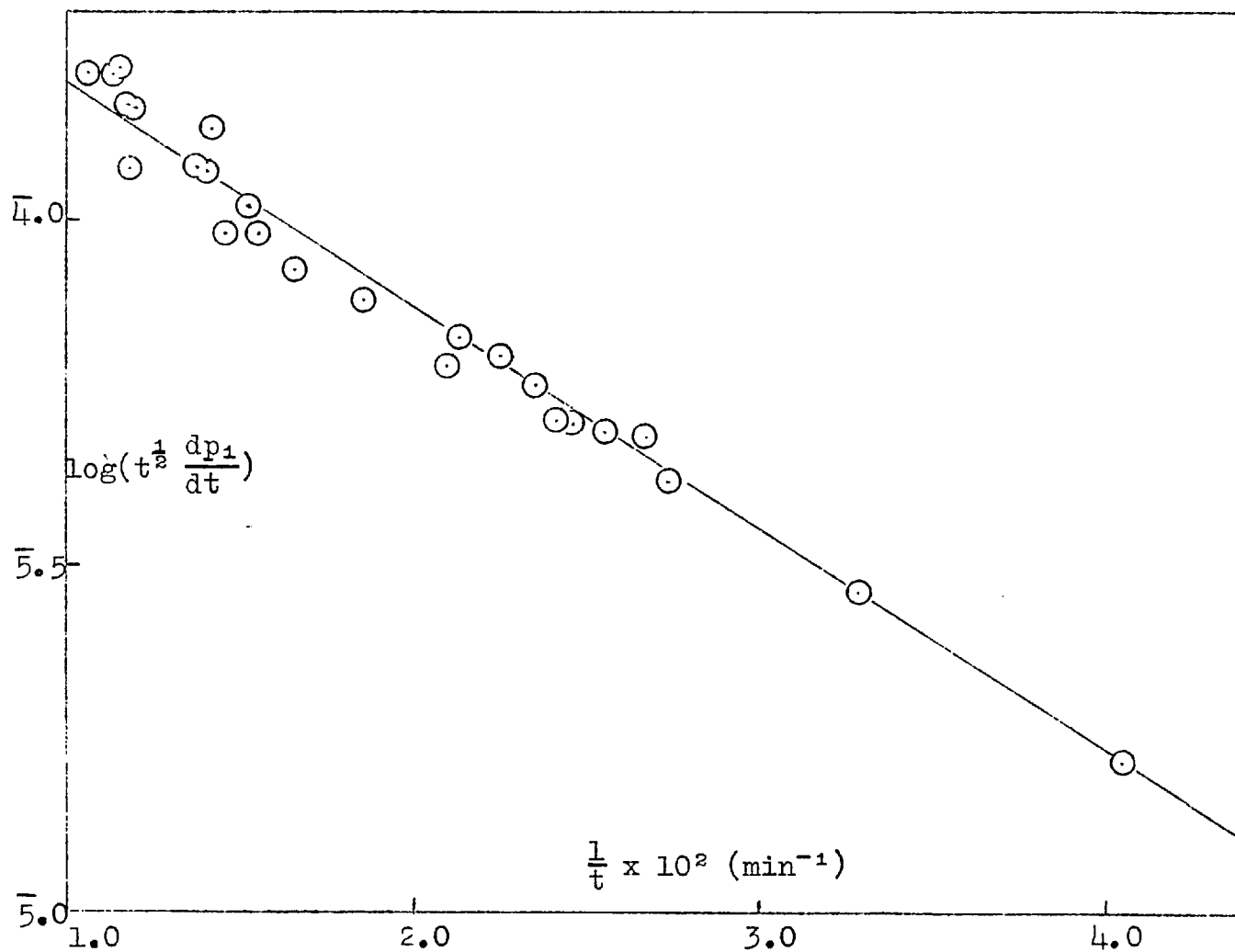


Fig. 4-2 The "early approximation" analysis for SiR-M:Ar at -78°C .

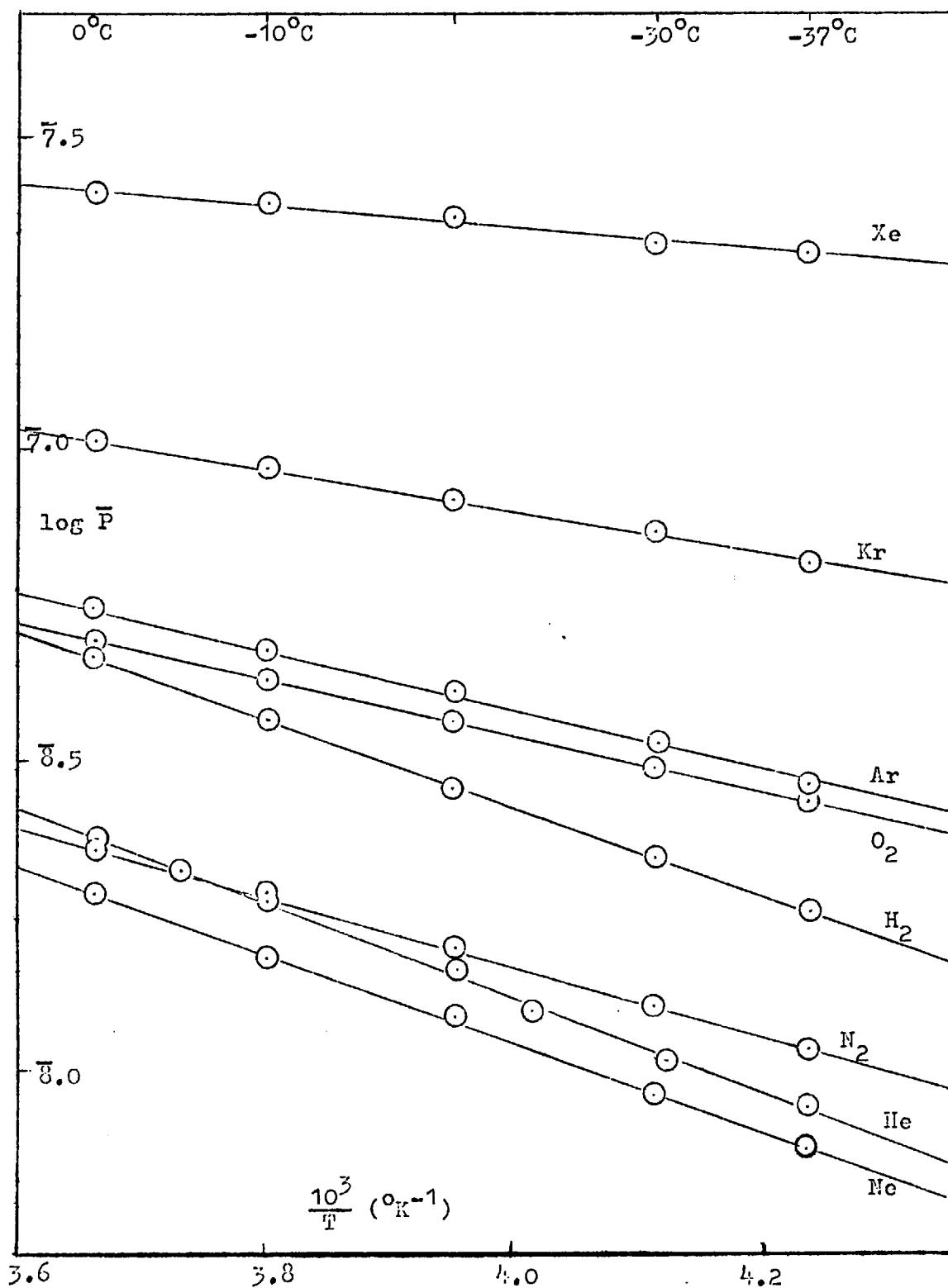


Fig.4-3 Plots of $\log(\text{permeability coeff.})$ vs. reciprocal Kelvin temp.

for the plane sheet membrane, SiR-I.

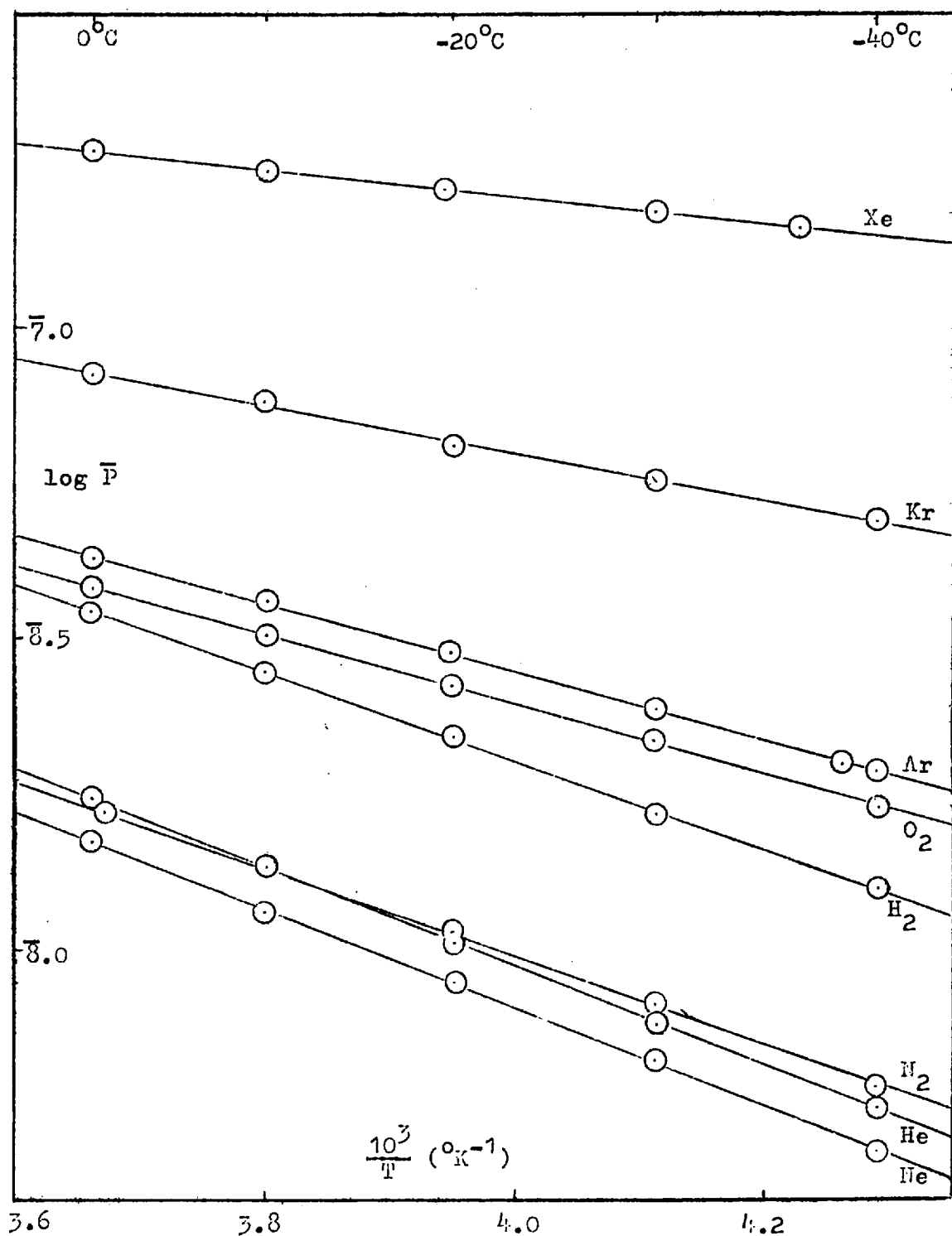


Fig.4-4 for the hollow cylindrical membrane SiR-M
Plots of $\log(\text{permeability coeff.})$ vs. reciprocal Kelvin temp.

those of Bearman, then the order becomes:

$$\bar{P}(\text{N}_2) < \bar{P}(\text{Ne}) < \bar{P}(\text{O}_2) < \bar{P}(\text{Ar}) < \bar{P}(\text{He}) < \bar{P}(\text{H}_2) < \bar{P}(\text{Kr}) < \bar{P}(\text{Xe}).$$

It appears therefore that He and H₂ are more permeable than Ar and O₂ in natural rubber, whereas the reverse is true for silicone rubber. In Table 4.19 are listed the permeability data of natural rubber determined by Bearman⁹⁸ and by van Amerongen⁵ as compared with those of silicone rubbers measured in this work. The ratio $\bar{P}(\text{silicone rubber})/\bar{P}(\text{natural rubber})$ serves only as a guide because of differing filler contents. Also since values of $\bar{P}(\text{natural rubber})$ are at higher temperatures than those of $\bar{P}(\text{silicone rubber})$, the ratios stated are the lower limit only. The much higher permeability of silicone rubber as compared to natural rubber is also found by Raman⁹⁶ who showed that the permeability of silicone rubber to isomeric C₄- and C₅-paraffin is 25 to 40 times larger than those of natural rubber.

TABLE 4-19 Permeability of natural rubber and silicone rubber to gases.

Gas	$\bar{P} \times 10^8$ (nat. rubber)	$\bar{P} \times 10^8$ (SiR-I at 0°C)	$\bar{P} \times 10^8$ (SiR-M at 0°C)	$\frac{\bar{P}(\text{SiR-I})}{\bar{P}(\text{nat.})}$	$\frac{\bar{P}(\text{SiR-M})}{\bar{P}(\text{nat.})}$
He	0.443(34°C)	2.332	1.766	5.26	3.99
Ne	0.113(34.5°C)	1.914	1.48 ₄	16.94	13.13
Ar	0.289(34.5°C)	5.51	4.27 ₄	19.06	14.79
Kr	0.637(34.5°C)	10.30	8.40	16.16	13.19
Xe	0.967(34.5°C)	25.51	19.15	26.38	19.80
H ₂	0.312(25°C)	4.64	3.507	14.87	11.24
N ₂	0.492(25°C)	2.27	1.711	4.61	3.48
O ₂	0.081(25°C)	4.89	3.848	60.37	47.51

The sequence of the transient-state diffusion coefficients for both SiR-I and SiR-M between -10°C and -40°C is

$$D_L(\text{Xe}) < D_L(\text{Kr}) < D_L(\text{N}_2) < D_L(\text{Ar}) < D_L(\text{O}_2) < D_L(\text{Ne}) < D_L(\text{H}_2) < D_L(\text{He})$$

with some uncertainty in the placing of H_2 and He (see Fig. 4.5 and Fig. 4.6). The sequence of the magnitudes of the collision diameters⁹⁹ of the gases is

$$\text{He}(2.18\text{\AA}) < \text{Ne}(2.60) < \text{H}_2(2.72) < \text{O}_2(3.62) < \text{Ar}(3.66) < \text{N}_2(3.78) \\ < \text{Kr}(4.16) < \text{Xe}(4.92\text{\AA}).$$

It is then seen that the sequence of values of D_L is quite closely paralleled by the dimension of the penetrant, but that the values of $\bar{P}$ are not so directly influenced. The explanation lies in the composite nature of $\bar{P}$, remembering that $\bar{P} = D_L \sigma_D$.

In the case of the hollow cylindrical membrane (SiR-M) the experimental temperature was further lowered below $\sim -40^{\circ}\text{C}$. Investigations using H_2 , Ne , Ar and H_2 as probes between -55°C and -78°C revealed a sharp change in the morphology of the silicone elastomer as detected by the sudden drop in the flow rate of the gas as the temperature was lowered from -48°C to -55°C . This is attributed to the crystallization of the silicone elastomer. Thus at -55°C and below, the amorphous phase of the membrane through which diffusion process takes place is substantially reduced, whilst the effective path length for the penetrant to traverse from one face of the membrane to the other is increased. This crystallization phenomenon agrees with the findings of Warrick et al.⁵⁷ and of Warrick⁵⁸ who, by means of X-ray and physical methods of measurement, showed that a relatively large amount of crystalline material forms

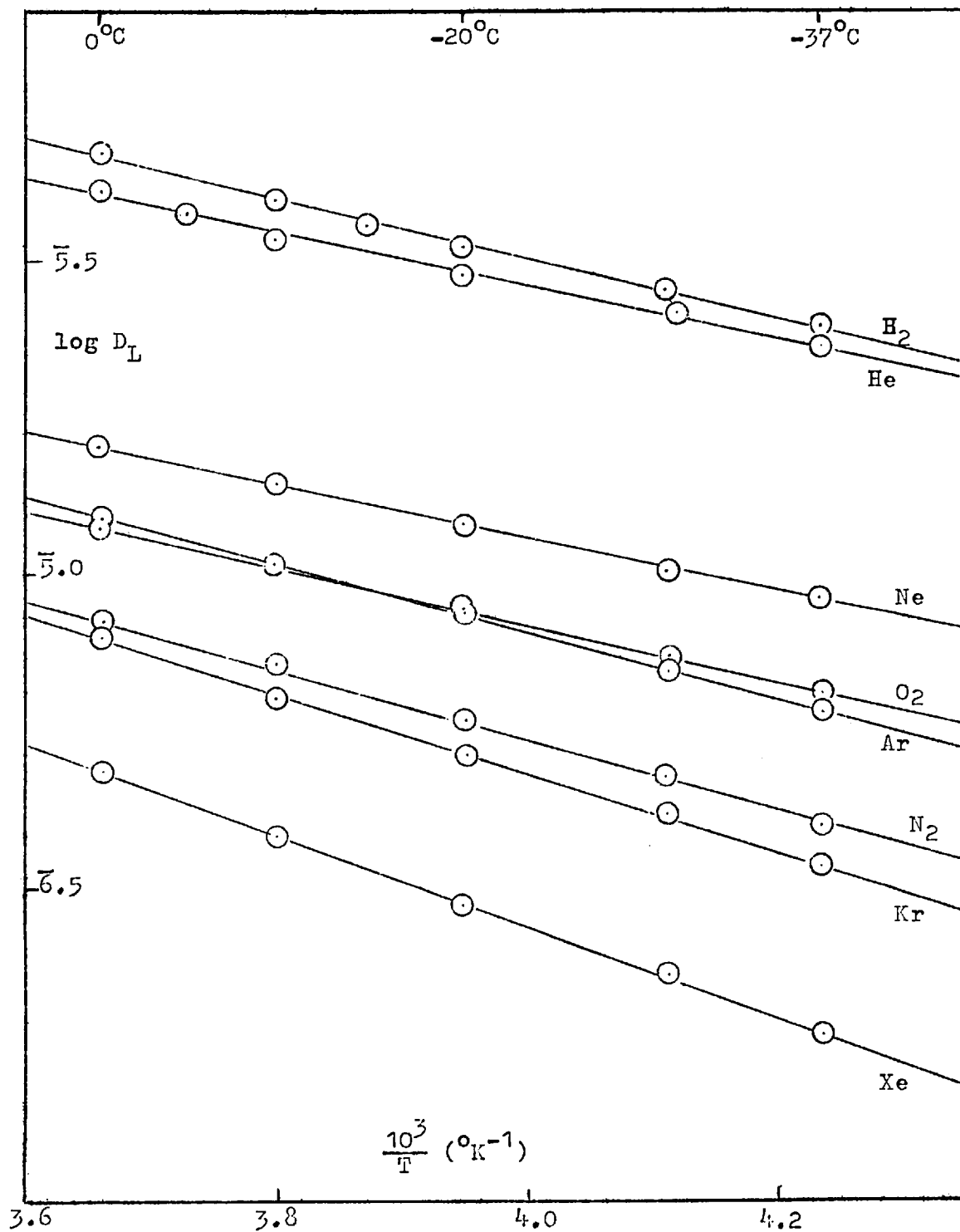


Fig.4-5 for the plane sheet membrane SiR-I.
 { transient state }
 Plots of $\log(\text{diffusion coeff.})$ vs reciprocal Kelvin temp.

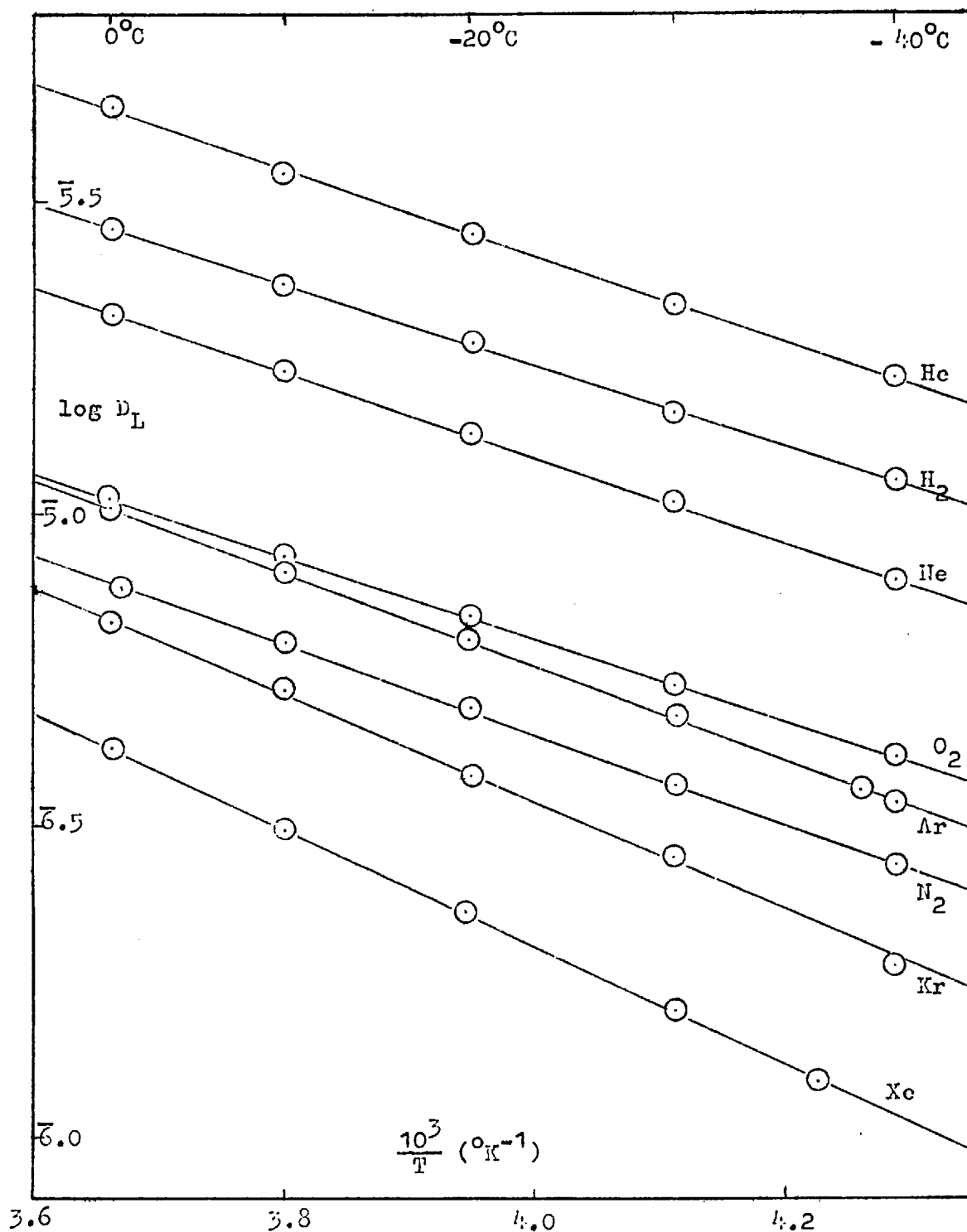


Fig. 4-6 for the hollow cylindrical membrane SiR-M.
 Plots of $\log(\text{transient state diffusion coeff.})$ vs reciprocal Kelvin temp.

within the narrow temperature range of -50°C to -60°C . The crystalline fraction at -60°C was reported to be 0.42.

It is observed that between -55°C and -78°C values of $\bar{P}$ and D_L increase in the same order as previously noted at the higher temperature range, i.e.

$$\begin{aligned}\bar{P}(\text{Ne}) < \bar{P}(\text{He}) < \bar{P}(\text{H}_2) < \bar{P}(\text{Ar}) \\ D_L(\text{Ar}) < D_L(\text{Ne}) < D_L(\text{H}_2) < D_L(\text{He}).\end{aligned}$$

4.2.2 Separation factor

As explained in Section 1.8, the separation factor, S , can in the steady state be estimated from the ratio of the individual permeabilities. In Tables 4.20 and 4.21 are listed the relative permeabilities of SiR-I, SiR-M and other membranes to inert and permanent gases at various temperatures. Although there is a definite improvement in the separation factor as the temperature is lowered, this improvement is not very striking. For instance, the separative factor for He and Ne as compared with Xe increases by about two-fold as the temperature decreases from 0° to -37°C . Table 4.20 also shows that for He:Xe pair, SiR-I at -37°C is, as a separation medium, approximately ten times better than natural rubber at $+34.5^{\circ}\text{C}$. In so far as the separation of the gases by means of silicone elastomers is concerned, it appears from this steady state investigation that no striking improvement is achieved by lowering the working temperature.

TABLE 4-20 Relative permeabilities of silicone and natural rubbers at the temperatures indicated.

T°C	Elastomer	Xe	He	Ne	Ar	Kr	H ₂	N ₂	O ₂
0	SiR-I	1	0.091	0.075	0.216	0.40	0.182	0.089	0.192
-30	SiR-I	1	0.048	0.042	0.154	0.338	0.102	0.059	0.142
-37	SiR-I	1	0.042	0.0364	0.14	0.32	0.088	0.053	0.13
0	SiR-M	1	0.092	0.077	0.223	0.439	0.183	0.087	0.201
-30	SiR-M	1	0.049	0.043	0.159	0.37	0.108	0.054	0.141
+34.5	Nat. rubber*	1	0.458	0.117	0.299	0.659			

* from ref. 98

TABLE 4-21 Relative permeabilities of various membranes at the temperatures indicated.

T°C	Membrane	H ₂	He	Ne	Ar	N ₂	O ₂
0	SiR-I	1	0.502	0.413	1.19	0.49	1.05
-30	SiR-I	1	0.467	0.416	1.51	-	-
0	SiR-M	1	0.504	0.423	1.22	0.49	1.10
-30	SiR-M	1	0.458	0.399	1.47	0.49	1.30
-55	SiR-M	1	0.49	0.395	1.29	-	-
-78	SiR-M	1	0.48	0.31	1.02	-	-
25	Nat. rubber* (vulcanised)	1	0.62	-	-	0.16	0.44
~20	Nat. rubber* (unvulcanised)	1	0.30	-	0.19	0.11	0.35
20	Neoprene* (vulcanised)	1	0.61	-	0.29	0.10	-
25	Butadiene rubber/	1	-	-	-	0.15	0.45
25	Buna S/	1	0.57	-	-	0.16	0.43
25	Methyl rubber/	1	0.85	-	-	0.028	0.12
25	Perbunan/	1	0.76	-	-	0.077	0.28
25	Neoprene G/	1	-	-	-	0.086	0.29

* from ref. 1

/ from ref. 4

4.2.3 Diffusion coefficients and the physical properties of the diffusing molecules

Diffusion of gas molecules in a high polymeric membrane depends, among other things, on the physical properties of the diffusing molecules of which the diameter, d , is an important example. While the diffusion coefficients have been shown to decrease with increasing d , a simple linear correlation is not however shown. In particular, it is noted that He and H_2 have, compared to other gases used, exceptionally high diffusion coefficients.

A linear relationship between $\log D$ and d^2 has been reported by Brandt¹⁰. Using the diffusion data obtained in this work, the correlation between $\log D_L$ and d^2 is shown in Fig. 4.7. Here again He and H_2 lie far above the lines.

The influence of the molecular weight of the penetrant upon the diffusion coefficient is also very striking. Eliminating the effect of molecular shape by considering the spherically shaped inert gases only, the manner in which D_L varies with the atomic weight of inert gases is shown in Fig. 4.8. The smoothness of the curve tempts one to see if D_L varies exponentially with the atomic weight. This, however, is not the case. According to the kinetic theory of gases,

$$D = \frac{1}{3} \lambda \bar{w} \quad (4.1)$$

where λ is the mean free path, and $\bar{w}$ is the root mean square velocity. At constant temperature λ and $\bar{w}$ are functions of the molecular weight, M , of the gases, e.g. $\bar{w} \propto M^{\frac{1}{2}}$ and $\lambda \propto M^{-\frac{2}{3}}$. Hence D is reduced to a

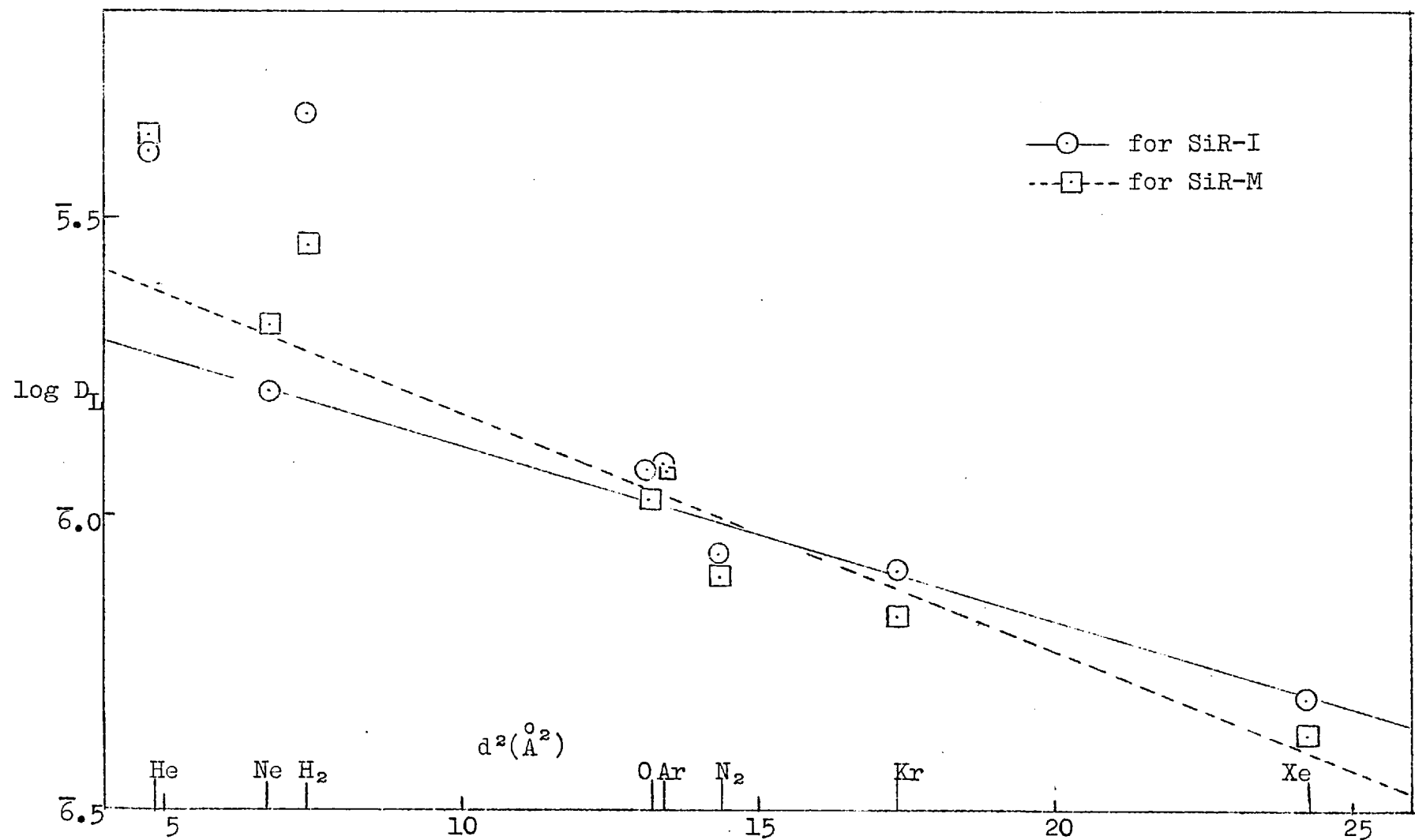
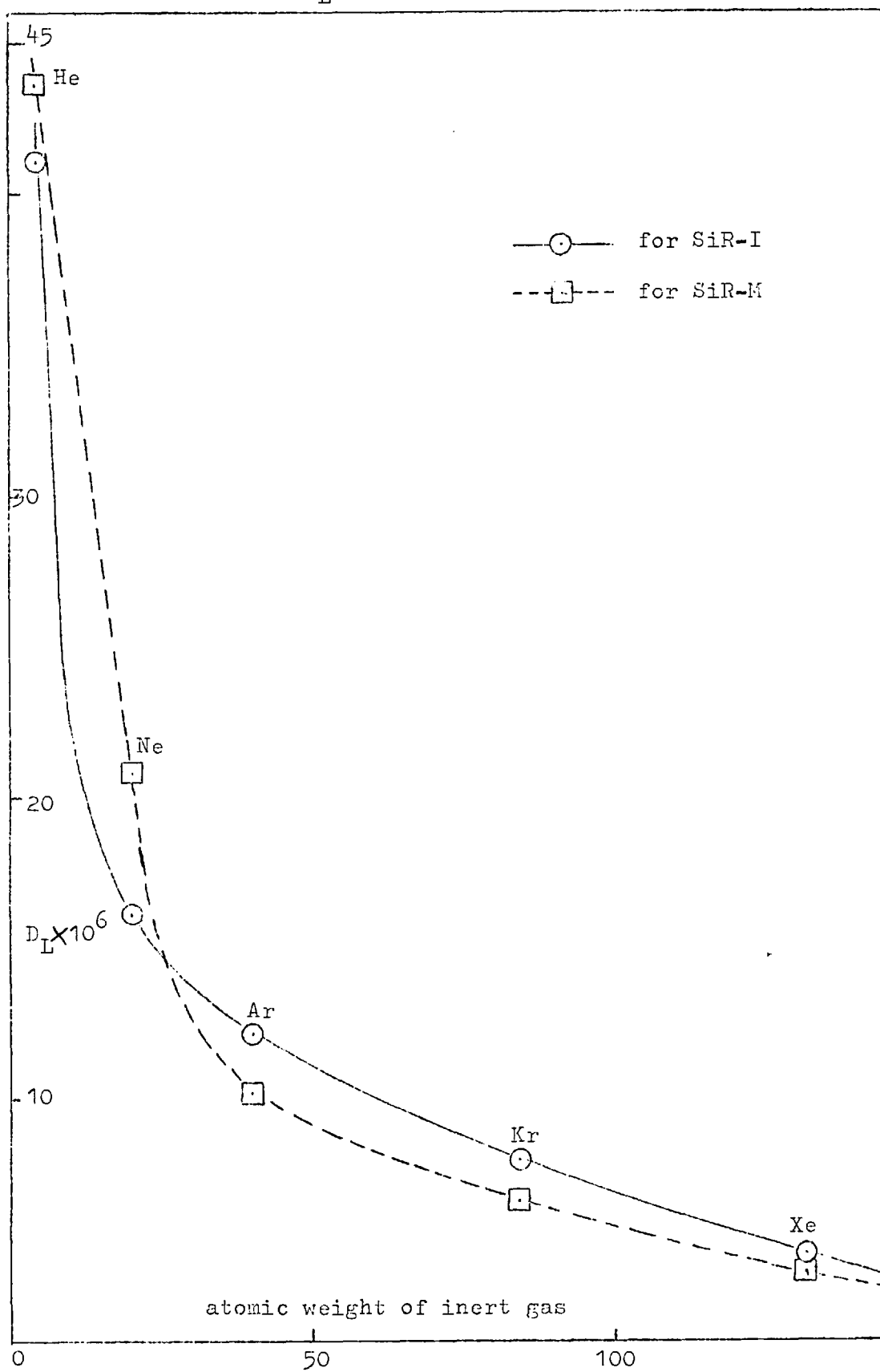


Fig. 4-7 Plots of $\log D_L$ (0°C) against the square of the collision diameter

Fig.4-8 Plots of D_L at 0°C vs the atomic weight of inert gas.

function of molecular weight. Also according to the Stokes-Einstein equation,

$$D = \frac{RT}{6\pi\eta rN} \quad (4.2)$$

where η is the viscosity of the medium, r is the mean radius of the gas molecule, and N is the Avogadro's number. Since r is related to the molecular weight M of the gas, eq. (4.2) may be written as

$$D = f(M) \quad (4.3)$$

To a first approximation, (4.3) may be written as

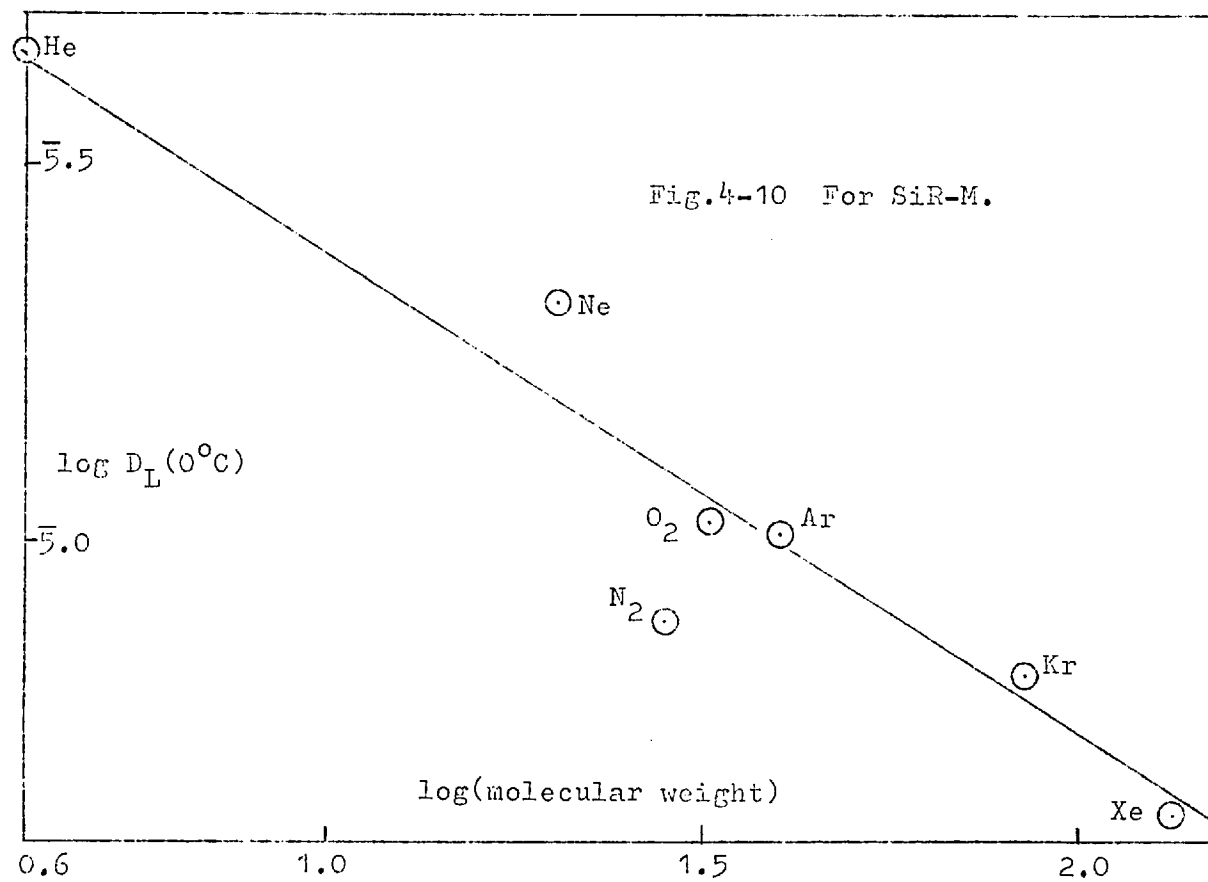
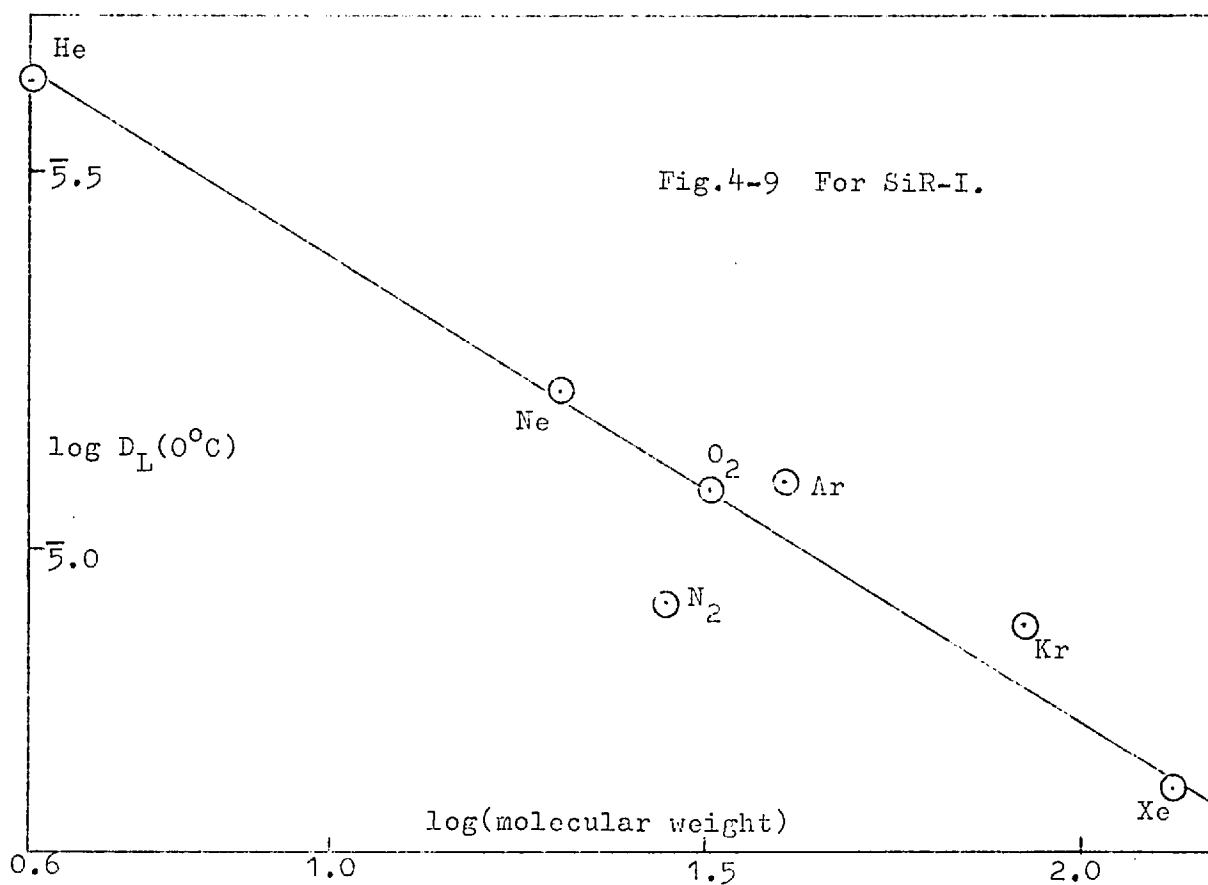
$$D = bM^a \quad (4.4)$$

where a and b are functions of both the membrane structure and temperature, and are constant for a particular membrane at a fixed temperature. Eq. (4.4) therefore indicates that $\log D$ must be a linear function of $\log M$. Fig. 4.9 and Fig. 4.10 show the resultant plots.

If the polarisability of the gas is used as a parameter in place of the atomic weight, the corresponding plots are found to be very similar.

4.2.4 Temperature coefficients of permeation and diffusion

It has been found in the present investigations that, for each gas-elastomer system, whether above or below the transition temperature, the plots of $\log \bar{P}$ vs $\frac{1}{T}$ and $\log D_L$ vs $\frac{1}{T}$ are virtually linear. These plots are shown in Figs. 4.3 to 4.6 (for all the gases used and for temperatures between 0°C and -40°C) and Figs. 4.11 to 4.13 (for He, Ne, Ar and H₂ covering



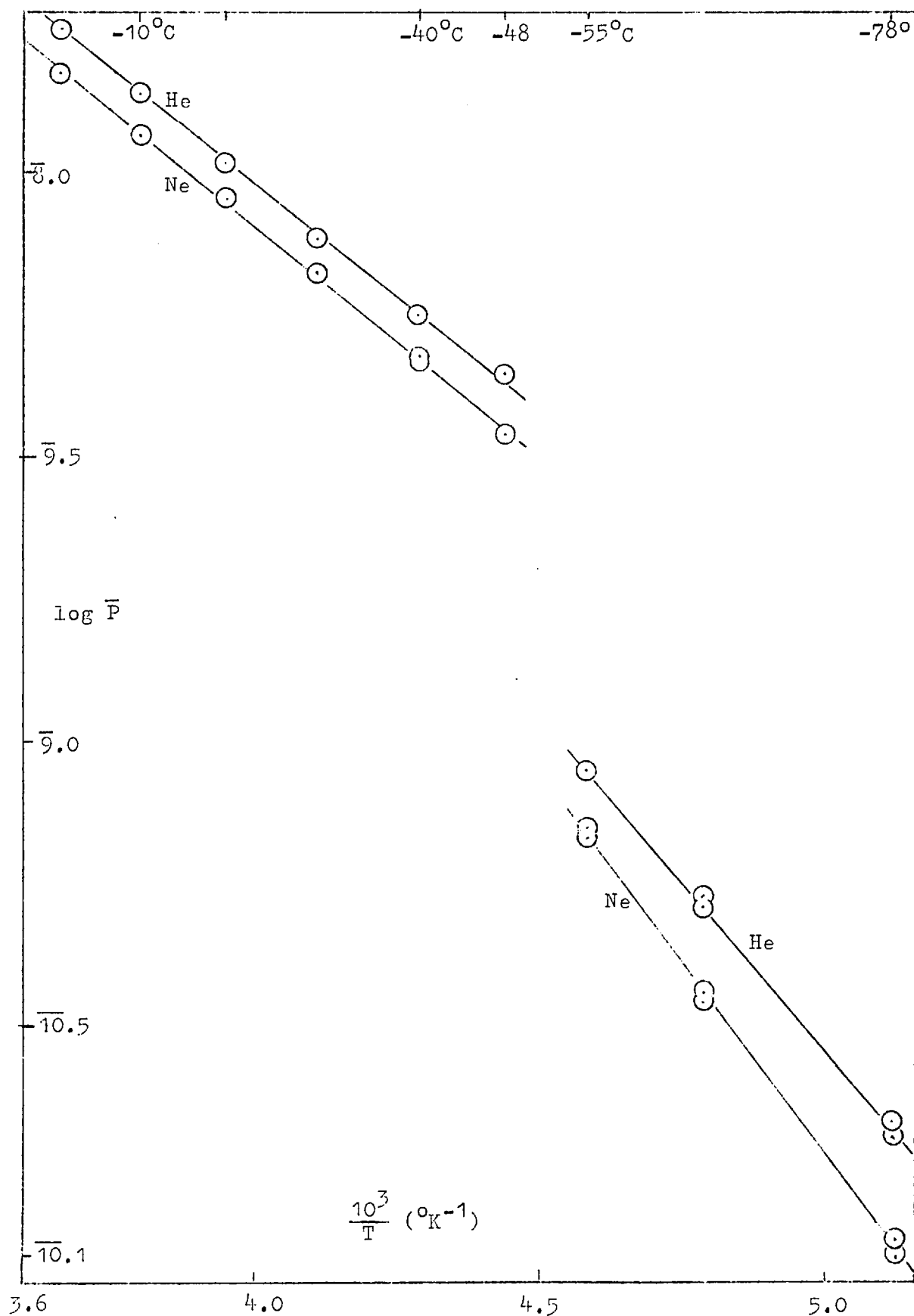


Fig.4-11 For SiR-M

Plots of log(permeability coefficient) vs reciprocal Kelvin temp.

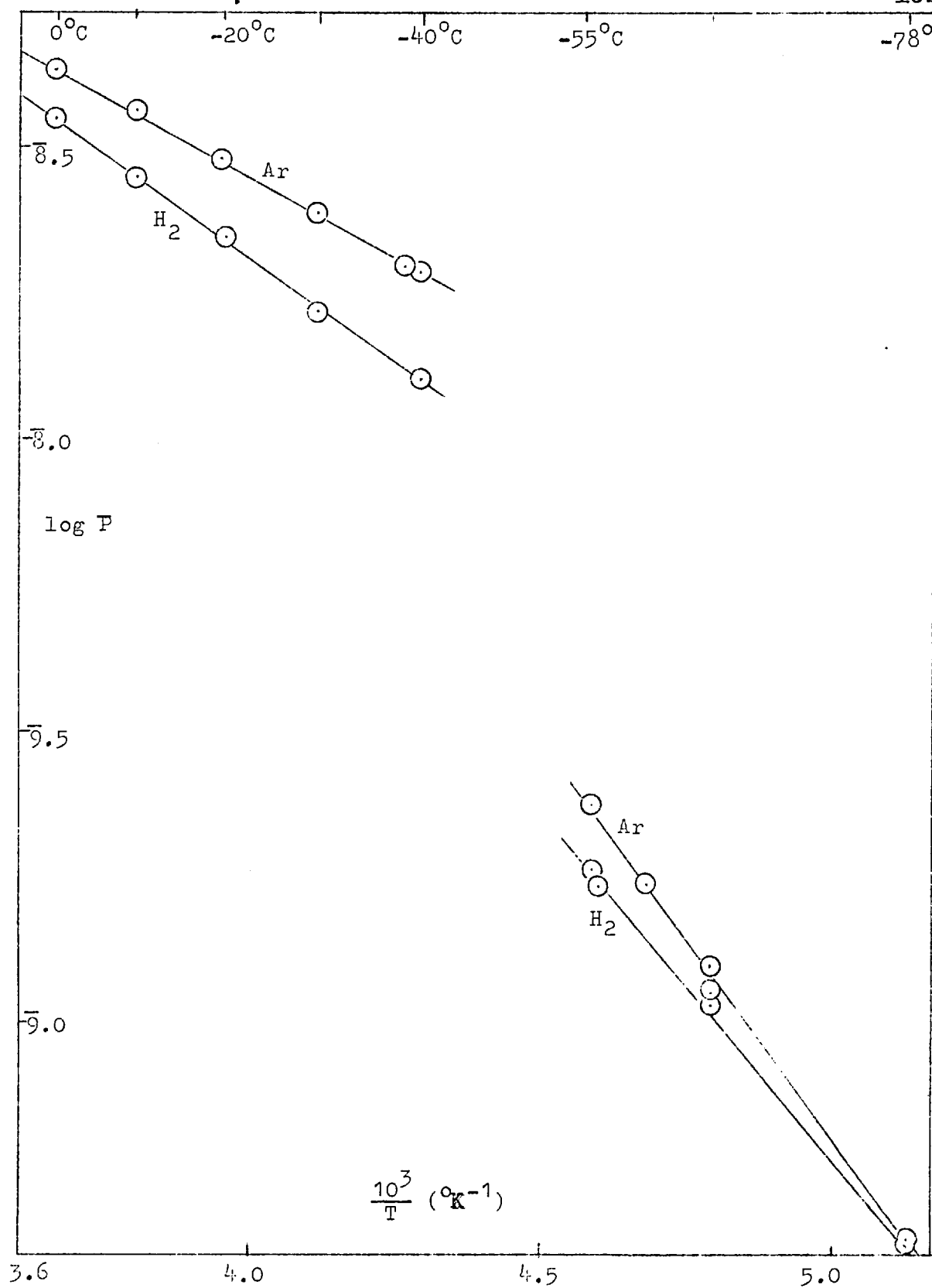
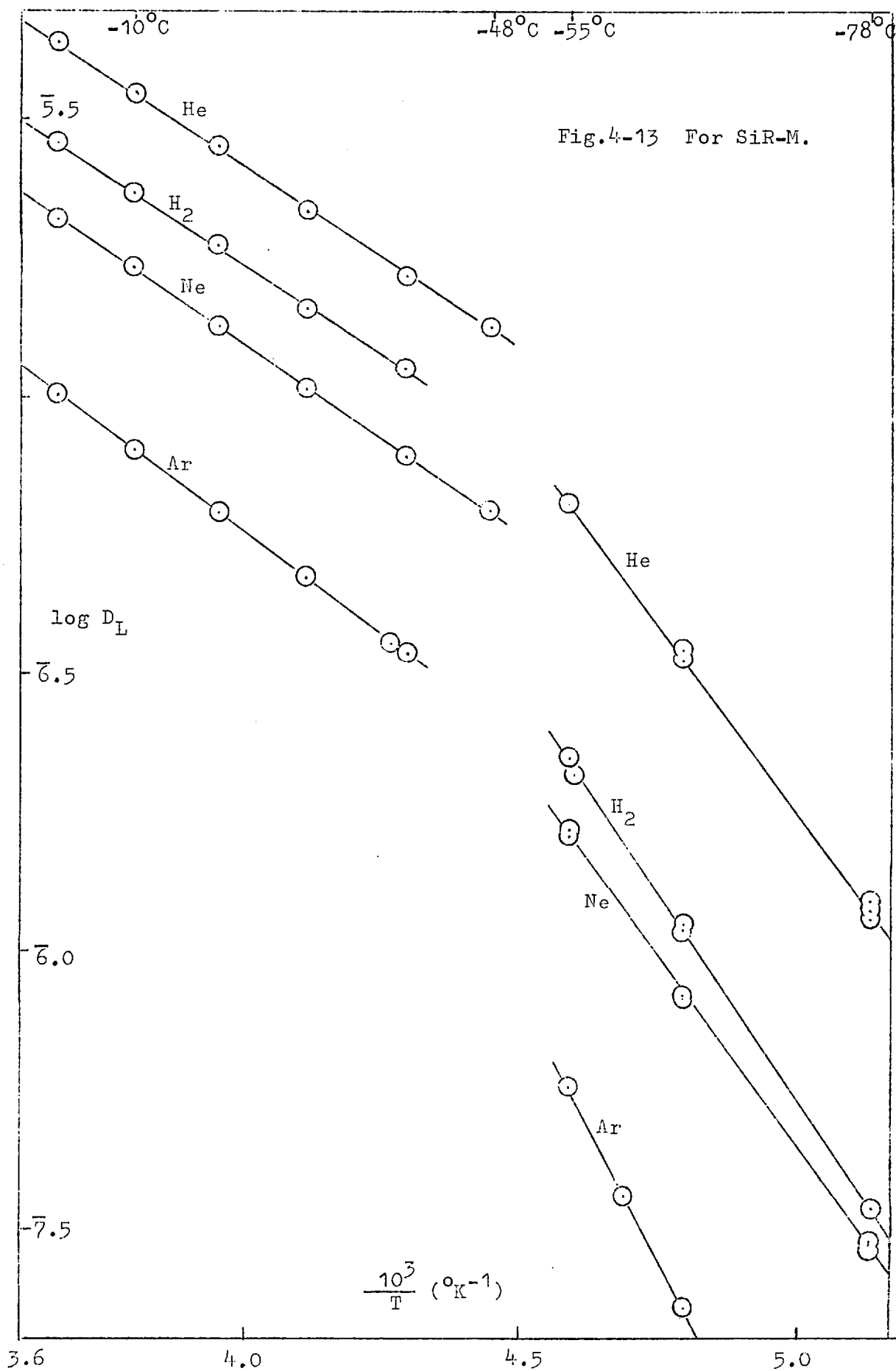


Fig. 4-12 For SiR-M

Plots of $\log(\text{permeability coefficient})$ vs reciprocal Kelvin temp.



a wider temperature range between 0°C and -78°C). It follows, therefore, that eq. (1.1) and eq. (1.3) are both obeyed within the temperature range investigated. However, above and below the transition temperature the magnitude of the apparent energy of activation for permeation (E_p) and for diffusion (E_D) are not equal. In Table 4.22, 4.23 and 4.24 are listed the values of E_p and E_D , together with their corresponding values of P_0 and D_0 , for SiR-I and SiR-M elastomers and the temperature range indicated. In accordance with eq. (1.1) and eq. (1.3), E_p and E_D have been deduced from the slopes, and P_0 and D_0 from the intercepts on the ordinate of the linear plots of $\log \bar{P}$ vs $\frac{1}{T}$ and $\log D_L$ vs $\frac{1}{T}$ respectively. To obtain the best averages, the slopes and the intercepts have been calculated statistically from the experimental data by the least squares method. (NOTE: Experimental data at -48°C for He and Ne were not included in the least squares calculations). It is seen that values of E_D (SiR-M) are consistently larger than those of E_D (SiR-I) - a consequence to be predicted owing to the enhanced mechanical strength of SiR-M imposed by the larger amount of the filler content.

The interesting feature of Tables 4.22 and 4.23 are the extremely low values of E_D and D_0 compared with those of any other membrane available so far. As a comparison, the energy of activation for self-diffusion of several polydimethylsiloxanes containing from 1 to 9 dimethylsiloxane groups has been found¹⁰⁰ to reach a limit of approximately 4000 cal/mole as the length of the chain is increased. The low values of E_D in silicone elastomers are undoubtedly the direct

TABLE 4-22 (SiR-I) The apparent energy of activation
for permeation and diffusion in cal/mole (0°C to -37°C)

Gas	E_p	$P_0 \times 10^6$	E_D	$D_0 \times 10^3$
He	3508	15.16	1905	1.32
Ne	3250	7.63	2002	0.64
Ar	2267	3.61	2471	1.17
Kr	1535	1.74	2913	1.70
Xe	776	1.08	3340	2.27
H ₂	3274	19.17	2222	2.79
N ₂	2609	2.80	2685	1.21
O ₂	2075	2.24	2162	0.64

TABLE 4-23 (SiR-M) The apparent energy of activation
for permeation and diffusion in cal/mole (0°C - -40°C)

Gas	E_p	$P_0 \times 10^6$	E_D	$D_0 \times 10^3$
He	3670	15.25	3091	12.94
Ne	3639	12.18	3131	6.70
Ar	2542	4.67	3459	5.96
Kr	1769	2.20	4052	11.88
Xe	1001	1.21	4355	12.88
H ₂	3274	14.67	2989	7.04
N ₂	3272	7.11	3330	3.59
O ₂	2597	4.63	3055	2.95

TABLE 4-24 (SiR-M) The apparent energy of activation
for permeation and diffusion in cal/mole (-55°C to -78°C)

Gas	E_p	$P_0 \times 10^6$	E_D	D_0
He	5457	264.4	6211	10.64
Ne	6137	958.5	6254	2.96
Ar	6309	4833	9158	851.6
H ₂	5298	365.9	6793	13.97

consequence of the relative ease of rotation about $\text{Si} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \end{smallmatrix} \text{Si}$ linkages and the relatively weak interaction forces that exist between neighbouring siloxane segments¹⁰¹.

For diffusion in rubber, the activation energy is close to the activation energy for viscous flow of the rubber²³. Since the activation energy for viscous-flow of silicone elastomer is about 4000 cal/mol, E_D values of this work also approach this magnitude as the penetrant size increases. For isomeric C_4 and C_5 paraffins diffusing in silicone rubber, this is particularly so ($E_D \sim 4000$ cal/mole); hence, diffusion can involve the movement of the polymer segments of the size contributing to viscous flow.

When E_D is plotted against the square of the collision diameter, d , of the gas atoms or molecules, the result shown in Fig. 4.14 is fairly linear, especially if only the inert gases are considered. According to Meares⁶ the unit diffusion step appears, therefore, to be governed by the energy required to separate the surrounding medium to give a space of sufficient cross-section for the diffusing molecule to pass, and not the energy required to produce a hole for the molecule to pass into.

In all gas-silicone elastomer systems, investigated in this work the values of E_p observed are positive; that is to say, the permeability coefficients $\bar{P}$ decrease with decreasing temperature, or $\frac{d\bar{P}}{dT} = +ve$. Contrary to this finding is the case of isomeric C_4 and C_5 paraffins permeating through silicone rubber.

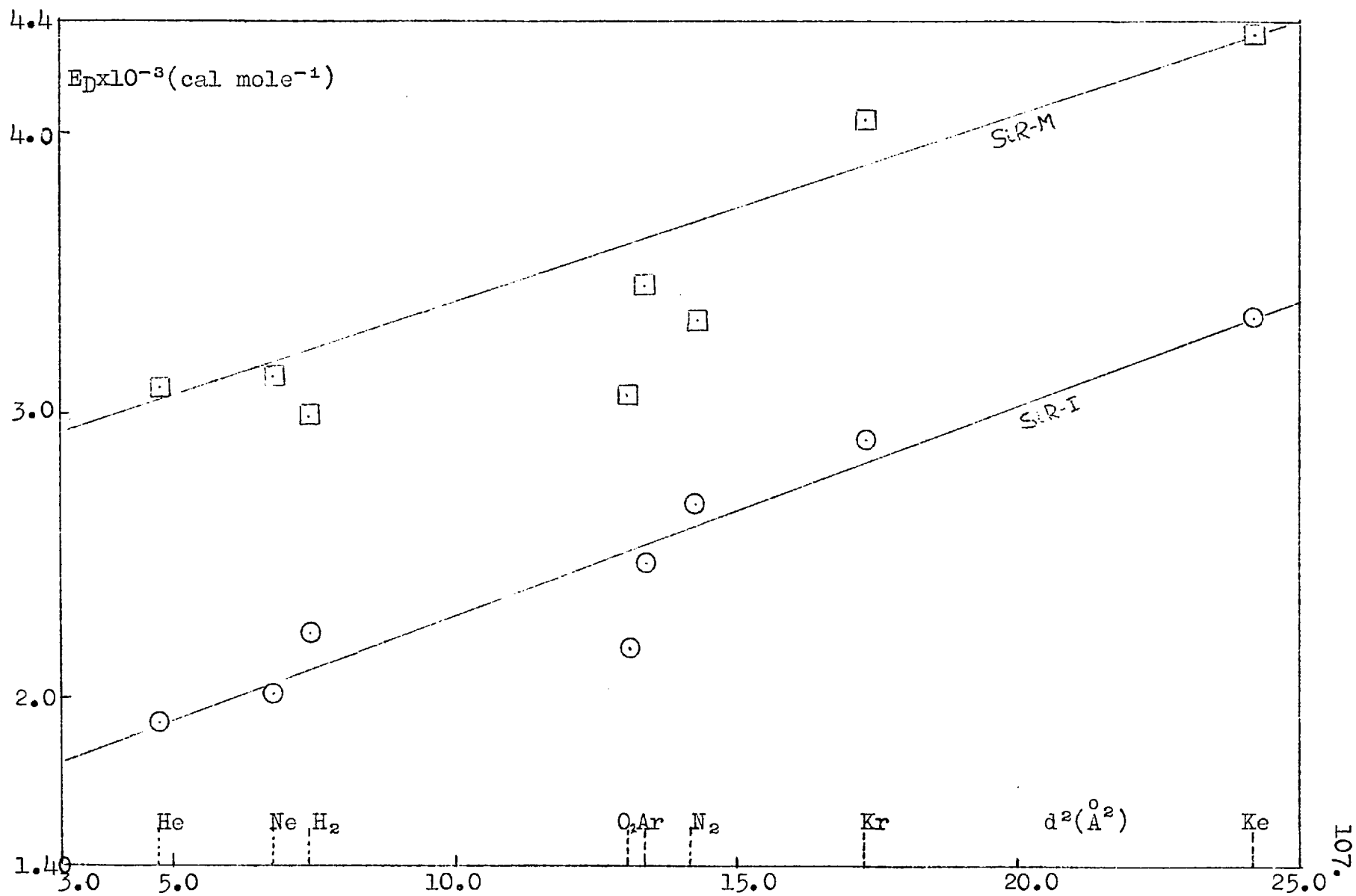


FIG. 4-14 Plots of E_D vs d^2 .

Here E_p is negative or $\frac{d\bar{P}}{dT} = -ve$. The explanation to this contrary behaviour lies in the relative magnitude of E_D (a positive quantity which is comparatively small for silicone elastomer) and of the partial molar heat of solution $\Delta\bar{H}^0$ (a negative or positive quantity depending on the properties of gas-elastomer system) as embodied in eq. (1.5), i.e. $E_p = E_D + \Delta\bar{H}^0$.

4.2.5 Interpretation of D_0

The magnitude of D_0 which appears in eq. (1.3) may, according to the zone theory of activation, be considered as a measure of the zone size. D_0 depends, among other factors, on E_D and the mean distance λ moved by the gas molecule in a unit diffusion process. Barrer and Skirrow²¹ have shown that D_0 increases with increasing degree of vulcanisation, this increase being reflected much more markedly for larger penetrant sizes.

Whilst the values of D_0 for natural rubber and most other polymers are large, those for silicone rubber are small and have magnitudes comparable to D_0 for diffusion in monomeric organic solvents (e.g. Table 4.25). This is not surprising for silicone rubber is noted for its weak intermolecular cohesion. The random motions of the siloxane molecules even at low temperatures are such as would normally be associated with the liquid state. Thus, diffusion of a small gas atom or molecule in silicone elastomer requires much smaller number of chain segments to be loosened for a successful unit diffusion process to take place.

Ottar¹⁰² has recently determined a number of self-diffusion coefficients D^* in monomeric organic liquids and liquid metals at various temperatures. His data permits one to calculate and deduce the activation energy for self-diffusion E_D and the constant D_0 . Values of E_D and D_0 so obtained are tabulated in Table 4.25.

TABLE 4.25

The energy of activation for self-diffusion E_D and the constant D_0 deduced from Ottar's data

Self-diffusion in:	E_D (cal/mole)	$D_0 \times 10^3$ (cm ² sec ⁻¹)
Benzene	2965	3.35
Methanol	3040	5.57
Ethanol	3703	9.47
Propanol	5003	34.89
Isopropanol	5780	121.3
n-Butanol	5167	28.33
Iso- ~~but~~ anol	6100	118.4
Mercury	1165	0.13
Indium	1401	0.16
Liq. sodium	2390	0.93
Liq. lead	3973	0.43

(a) According to the transition state theory

The expression for D , is, according to the transition state theory, given by eq. (2.44). Tables 4.26 and 4.27 show the values of the entropy of activation, $\Delta S^\ddagger$, associated with an Avogadro number of unit diffusion processes, together with the corresponding heat $\Delta H^\ddagger$ and free energy $\Delta G^\ddagger$ of activation. These data have been calculated from eq. (2.44),

assuming a value of $\lambda^2 = 10^{-15}(\text{cm}^2)$. In Table 4.28 are also listed, for SiR-I, values of $\Delta S^\ddagger$, $\Delta H^\ddagger$ and $\Delta G^\ddagger$ similarly calculated from the corrected values of D_0 given by Raman⁹⁶: (NOTE: D_0 values in his thesis have been miscalculated). It is seen from Tables 4.26, 4.27 and 4.28 that $\Delta S^\ddagger$ for silicone elastomers is consistently negative, whilst $\Delta S^\ddagger$ for natural rubber is positive (e.g. ref. 21), the latter indicating activation of a considerable zone of the medium accompanying diffusion. According to the discussion detailed in section 2.7 it is therefore likely that the gas diffusion process in silicone elastomer does not involve a considerable disturbance in the polymer matrix surrounding the penetrant in the formation of the transition state. A linear plot of $\Delta S^\ddagger$ vs E_D (or better $\Delta S^\ddagger$ vs $\frac{E_D}{T}$) was predicted by Barrer⁷⁹ for a process in which the activation energy is shared between a number of degrees of freedom in a zone of activation. For SiR-I, the plot is shown in Fig. 4.15 in which the line shown may be represented by

$$\Delta S^\ddagger = -10.15 + 0.523 \frac{E_D}{T}.$$

The corresponding equation for natural rubber was given by Barrer and Skirrow²¹ as

$$\Delta S^\ddagger = -4.6 + 0.65 \frac{E_D}{T}.$$

The significance of this relationship as well as the plausible explanation of the negative values of $\Delta S^\ddagger$ will be discussed later in section 4.2.6.

(b) According to the zone theory

Assuming values of $\nu = 2.5 \times 10^{12} (\text{sec}^{-1})$, $\lambda^2 = 10^{-15} (\text{cm}^2)$ and $\rho_f = \frac{1}{8}$, attempts were made to

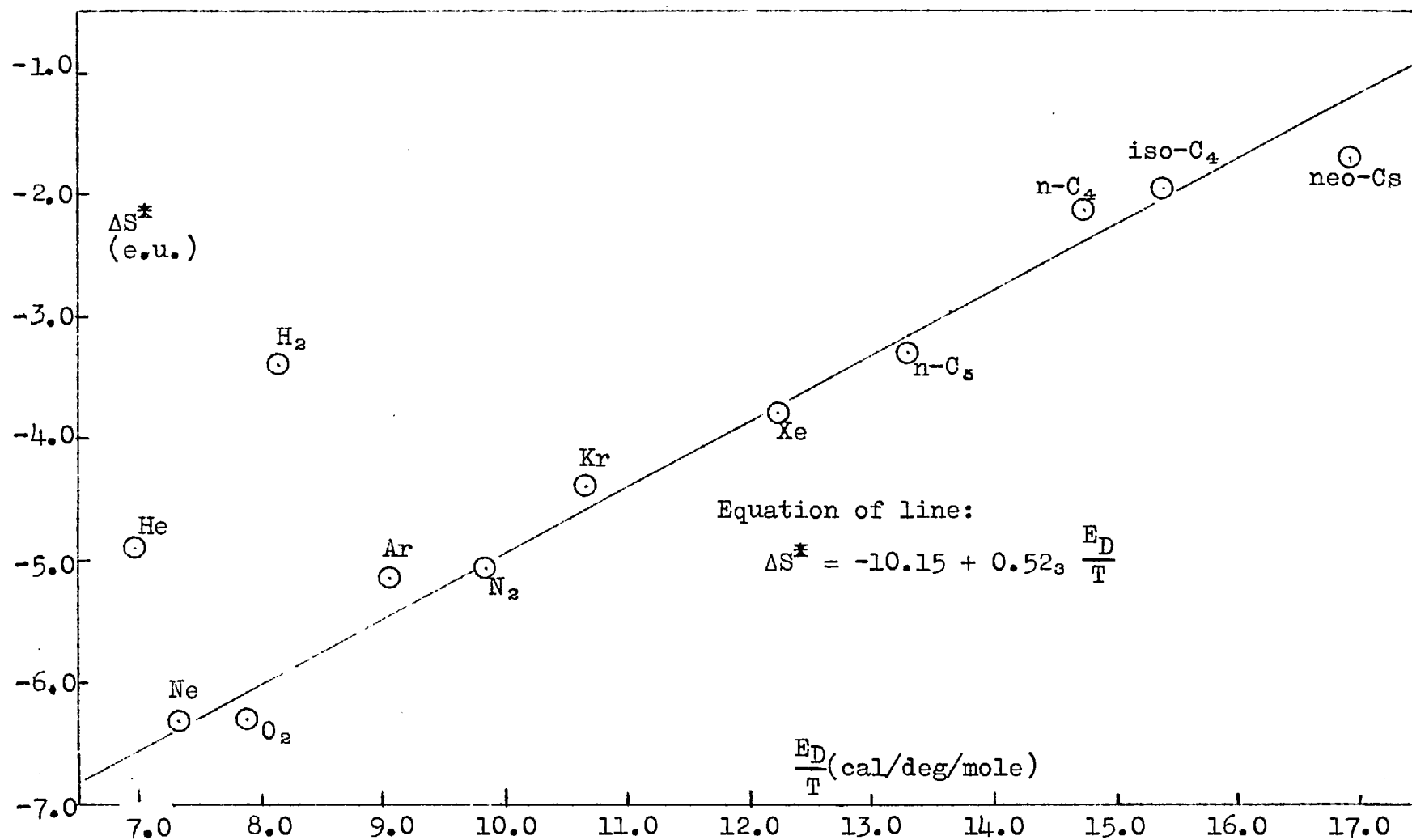


FIG. 4-15. Plot of ΔS^* vs $\frac{E_D}{T}$ (for SiR-I, $T = 273.16^\circ\text{K}$).

TABLE 4.26 (SiR-I) Entropy, enthalpy and free energy of activation at 273.16°K according to the Transition State Theory.

Gas	$\Delta S^\ddagger$ (e.u.)	$\Delta H^\ddagger$ (cal/mole)	$\Delta G^\ddagger$ (cal/mole)
He	-4.89	1362	2698
Ne	-6.33	1459	3188
Ar	-5.14	1928	3332
Kr	-4.39	2370	3569
Xe	-3.82	2797	3840
H ₂	-3.40	1679	2609
N ₂	-5.07	2142	3527
O ₂	-6.32	1619	3347
n-C ₄ H ₁₀	-4.91	2840	4182

TABLE 4.27 (SiR-M) Entropy, enthalpy and free energy of activation at 273.16°K according to the Transition State Theory.

Gas	$\Delta S^\ddagger$ (e.u.)	$\Delta H^\ddagger$ (cal/mole)	$\Delta G^\ddagger$ (cal/mole)
He	-0.36	2548	2647
Ne	-1.66	2588	3042
Ar	-1.90	2916	3434
Kr	-0.53	3509	3653
Xe	-0.37	3812	3912
H ₂	-1.57	2446	2874
N ₂	-2.90	2787	3580
O ₂	-3.29	2512	3412

TABLE 4.28 (SiR-I) Entropy, enthalpy and free energy of activation at 273.16°K according to the Transition State Theory - recalculated from Raman's data.⁹⁸

	E_D (cal/mole)	$D_0 \times 10^3$	$\Delta S^\ddagger$ (e.u.)	$\Delta H^\ddagger$ (cal/mole)	$\Delta G^\ddagger$ (cal/mole)
n-butane	4032	5.30	-2.13	3489	4071
iso-butane	4209	5.82	-1.94	3666	4197
n-pentane	3632	2.25	-3.83	3089	4136
neo-pentane	4632	6.06	-1.72	4089	4560

deduce the number of degrees of freedom f among which the total activation energy is shared in any zone by means of eq. (2.52) and the method explained therein. The values of f so obtained (with $T = 273.16^\circ\text{K}$) are shown in Table 4.29. f so calculated is very sensitive to the value of the product $\rho_f v \lambda^2$. An interpretation of the analogous problem of viscous flow⁷⁶

TABLE 4-29 The number of degrees of freedom f sharing in the diffusion process.

Gas	f	
	SiR-I	SiR-M
He	-	-
Ne	-	-
Ar	3(2.7)	8
Kr	3(3.2)	9
Xe	3(3.3)	8
H ₂	-	-
N ₂	-	5
O ₂	-	5
n-butane	5	
iso-butane	5	
n-pentane	3	
neo-pentane	4	

suggested values of ρ_f of $\frac{1}{6}$ to about 10^{-3} , so that the range in $\rho_f v \lambda^2$ may be appreciable. The dashes in Table 4.29 indicate that f is so small that the experimental value of $\log D_0$ fails to give a satisfactory value of f for the values of $\rho_f v \lambda^2$ assumed. Again the indication is that, in contrast to the diffusion of gas in natural rubber, only a small zone of activation is required in order for a unit diffusion process to take place. Moreover, for the smallest gases (H₂ and He), the mechanism of the diffusion process in silicone rubber may be partially interstitial in character.

4.2.6 Functional relationship

The linear relationship between $\log D_0$ or $\Delta S^\ddagger$ vs. E_D has been demonstrated^{4,6,76,79} for a number of diffusion systems. The fulfilment of this condition which is valid for viscous flow in liquids and diffusion in elastomers is evidence for the existence of internal mobility in the system concerned. Barrer^{2,76} pointed out, however, that the most general relationship is between $\log D_0$ and $\frac{E_D}{T}$ (see also section 2.6). The validity of this relationship (for $T = 273.16^\circ\text{K}$) is shown in Fig. 4.16 (representing data of Raman⁹⁶ and this work), Fig. 4.17 (representing Ottar's¹⁰² data of self-diffusion in monomeric organic solvents and in liquid metals) and Fig. 4.18 (from combination of the above data with those given by Barrer for gas-elastomer system² and liquid-liquid system⁷⁵). The equations of the lines are respectively

$$\begin{aligned}\log D_0 &= -4.07 + 0.12 \frac{E_D}{T} \quad (\text{Fig. 4.16, SiR-I}) \\ \log D_0 &= -3.77 + 0.125 \frac{E_D}{T} \quad (\text{Fig. 4.17, Organic solvents}) \\ \log D_0 &= -4.73 + 0.19 \frac{E_D}{T} \quad (\text{Fig. 4.17, Liq. Hg, In, Na}) \\ \log D_0 &= -4.20 + 0.138 \frac{E_D}{T} \quad (\text{Fig. 4.18, above data + lit.data}).\end{aligned}$$

Close observation seems to indicate that for gas diffusion in elastomers points representing He and H₂ lie consistently above the general line shown in Fig. 4.16 and in Fig. 4.18.

For a substantial group of diffusion coefficients in elastomers, Barrer and Skirrow²¹ found

$$\log D_0 = -3.6 + 0.14 \frac{E_D}{T},$$

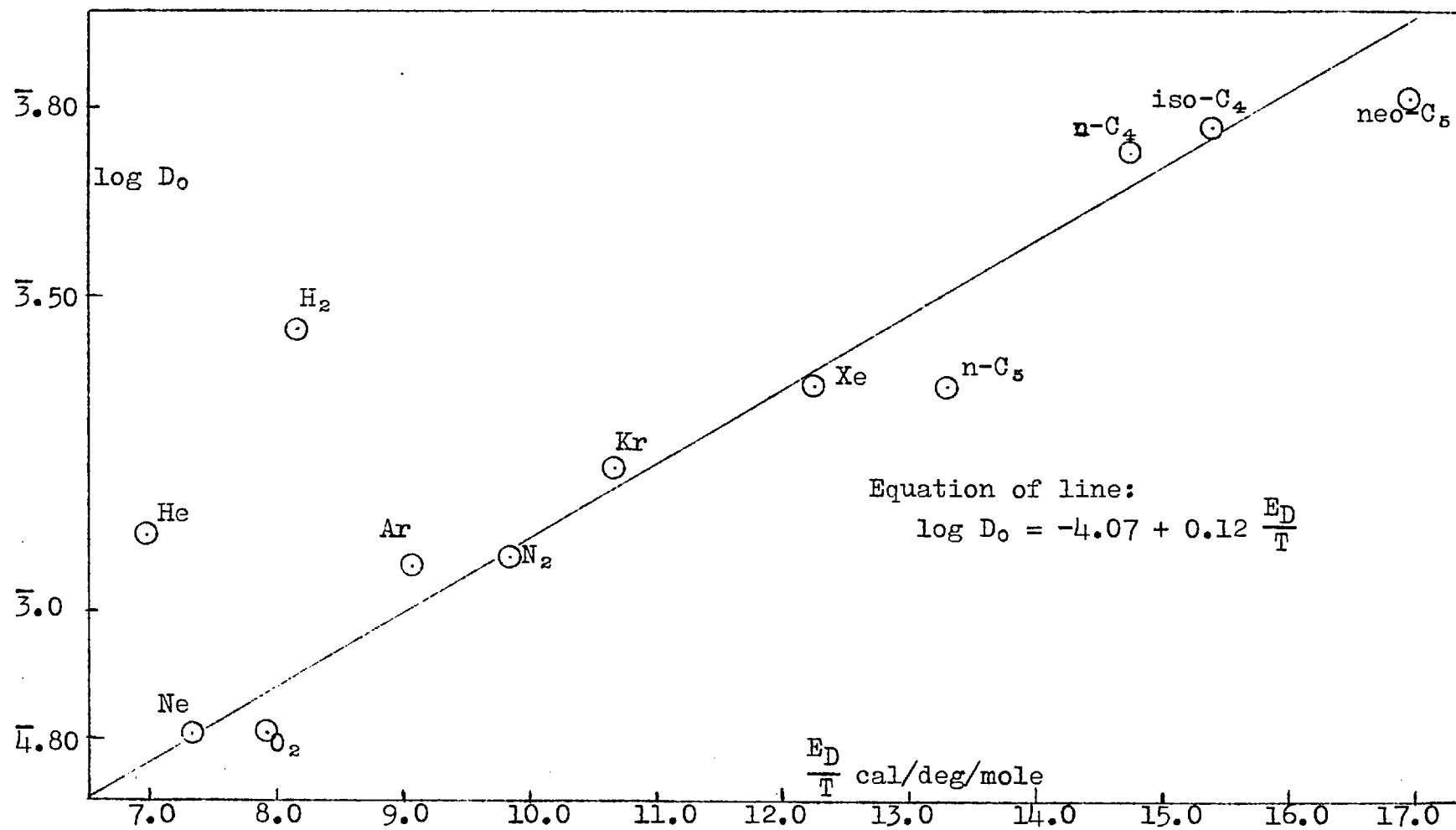


Fig. 4-16. Plot of $\log D_0$ vs. $\frac{E_D}{T}$ (for SiR-I at 273.16°K)

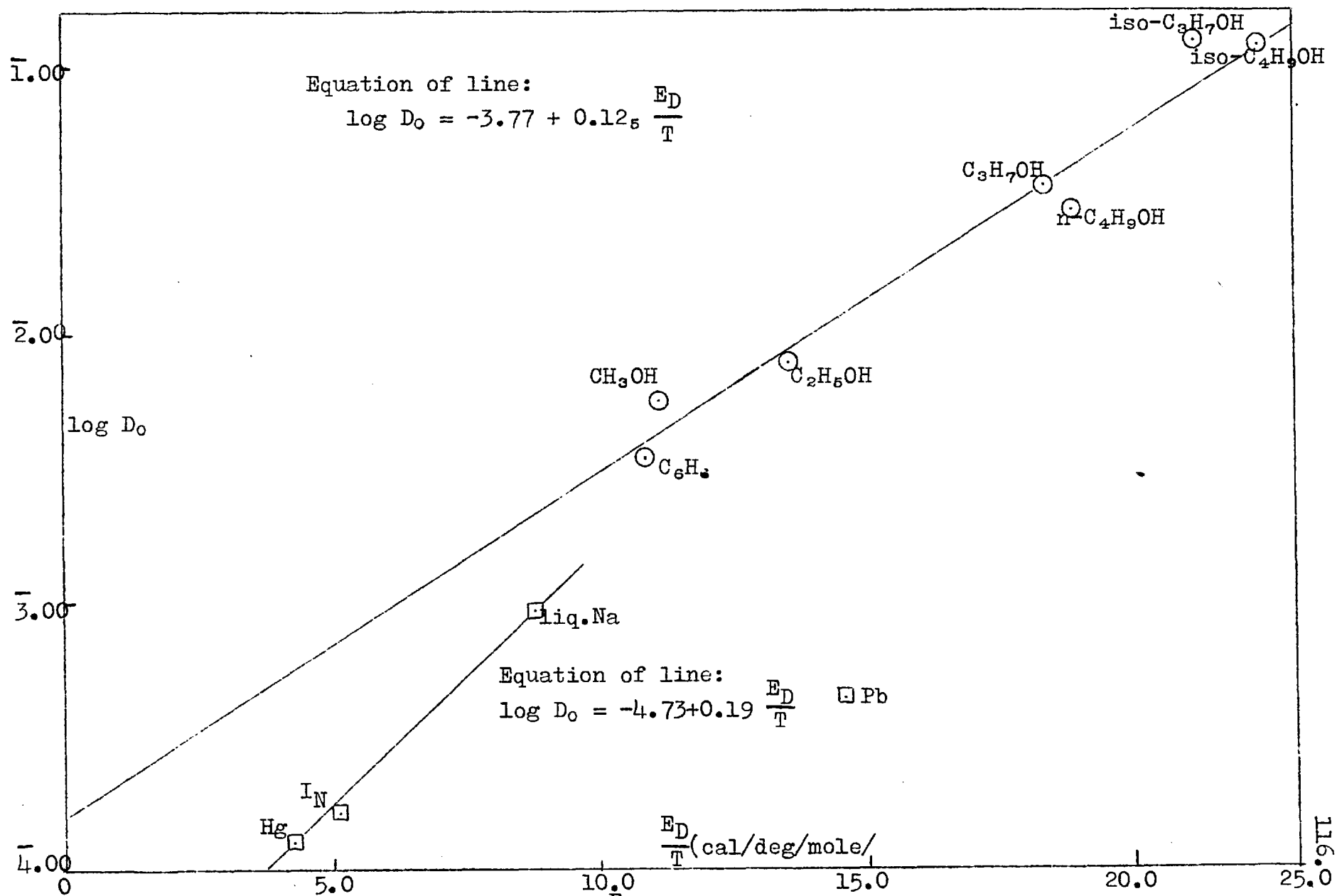
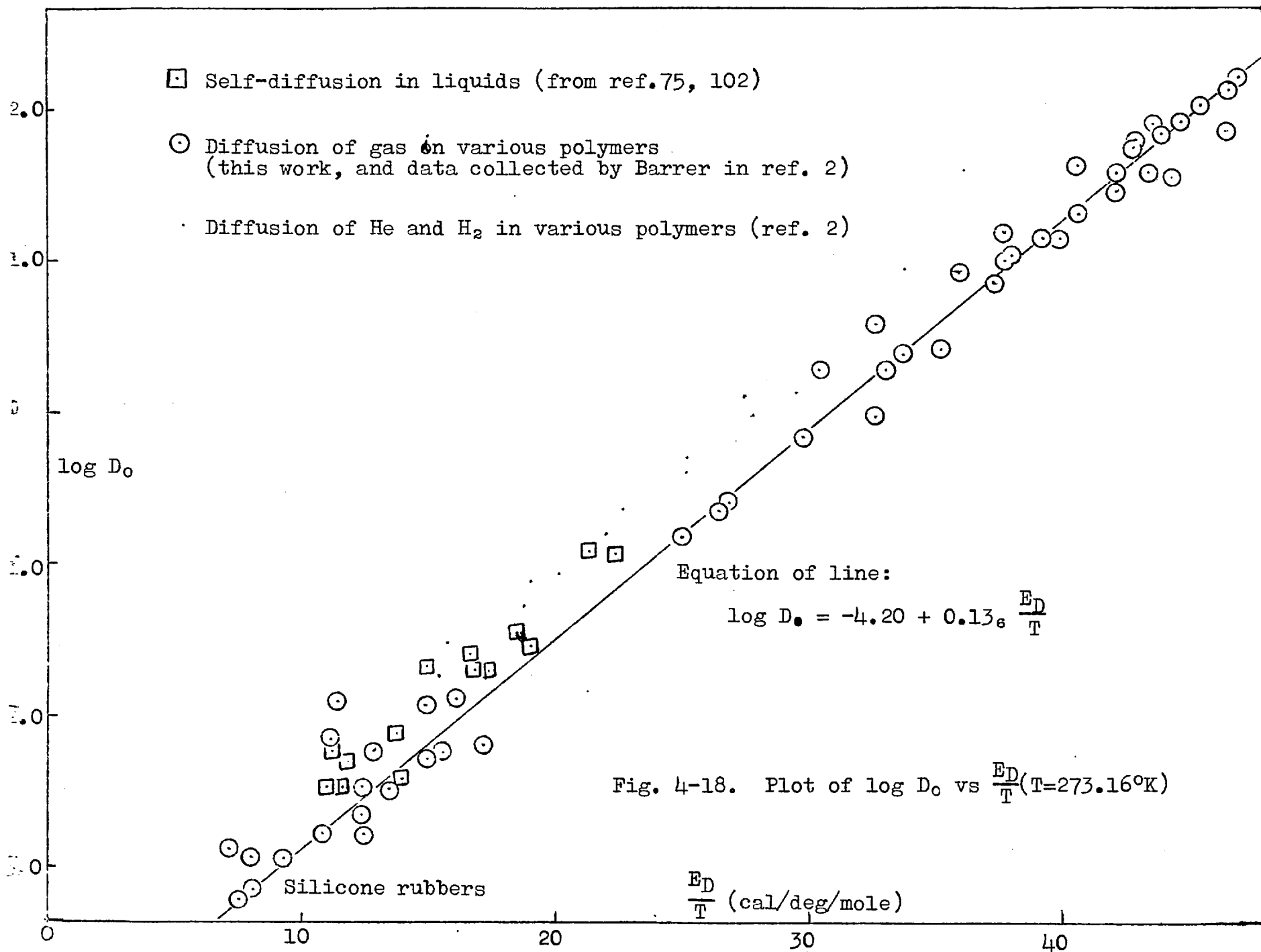


Fig. 4-17. Plot of $\log D_0$ vs. $\frac{E_D}{T}$



while Barrer ⁷⁶ found for viscous flow in many different kinds of molecular and atomic fluids, including liquid metals,

$$\log \phi_0 = 2.43 + 0.17 \frac{E\phi}{T}.$$

Here ϕ is the fluidity, and is given approximately by the expression $\phi = \phi_0 \exp - \frac{E\phi}{RT}$. It is seen that the slopes in all the plots of $\log D_0$ vs. $\frac{E_D}{T}$ are less than 0.22, which is the maximum value to be expected only if the range in $\log D$ or $\log \phi$ is completely negligible compared with that in $0.22 \frac{E_D}{T}$ (see section 2.6). However, this assumption would not be quite correct, and so the apparent slopes of the mean straight lines in the plots of $\log D_0$ vs. $\frac{E_D}{T}$ are rather less than 0.22.

It was pointed out by Raman⁹⁶ that data of $\log D_0$ for silicone rubbers do not, within the limit of experimental error, lie on the average line shown in Fig. 4.18, thus indicating the failure of the zone theory. Since the interpretation of the above functional relationship is a very natural one the only exception to this general rule in the case of silicone rubber seems rather suspicious. Indeed it was found that the values of D_0 have been miscalculated. Recalculated data of D_0 (Table 4.28) show that they do obey the functional relationships of $\log D_0$ vs. $\frac{E_D}{T}$ (Fig. 4.16 and Fig. 4.18) and ΔS^* vs. $\frac{E_D}{T}$ (Fig. 4.15).

When the relationship between ΔS^* and D_0 as expressed by eq. (2.44) is used, the equation of the line

$$\log D_0 = -4.07 + 0.12 \frac{E_D}{T} \quad (\text{Fig. 4.16 for SiR-I})$$

as predicted by the zone theory, becomes approximately equivalent to

$$\Delta S^* = -10.15 + 0.52 \frac{E_D}{T} \quad (\text{Fig. 4.15 for SiR-I}).$$

Thus, while D_0 is a measure of the zone size according to the zone theory, the magnitude of $\Delta S^\ddagger$ provides a comparable measure in terms of the transition state theory. Remembering that D_0 is given by eq. (2.48),

$$\text{i.e. } D_0 = \rho_f v \lambda^2 \left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} \exp(1-f)$$

where ρ_f has the form $\sum \left(\frac{1}{m}\right)^p$ (see section 2.8), it is not difficult to see, therefore, that $\Delta S^\ddagger$ is made up of two contributions: (i) a positive quantity which depends on $\frac{E_D}{T}$ and is a function of the zone size corresponding with an accumulation of the energy of activation through many degrees of freedom, which gives rise to the term $\left(\frac{E}{RT}\right)^{f-1} \frac{1}{(f-1)!} \exp(1-f)$ of eq. (2.48), and (ii) a negative quantity to allow for the possible need for synchronised movements of the diffusing molecules and of the neighbouring polymer segments in order for diffusion process to take place. Since this is an improbable event, the process occurs with a decrease in entropy, giving rise to the term ρ_f or $\sum \left(\frac{1}{m}\right)^p$ in eq. (2.48). If the two entropy terms corresponding to (i) and (ii) above are denoted by $\Delta S_f^\ddagger$ and $\Delta S_{\text{coop}}^\ddagger$ respectively, then

$$\Delta S^\ddagger = \Delta S_{\text{coop}}^\ddagger + \Delta S_f^\ddagger$$

In the case of many polymers, e.g. natural rubber, $\frac{E_D}{T}$ will be relatively large and therefore the larger $\Delta S_f^\ddagger$ will result in a positive total $\Delta S^\ddagger$. However, in the case of unassociated monomeric liquids, and in silicone elastomers, $\frac{E_D}{T}$ is much smaller so that the contribution to the negative entropy as given by $\Delta S_{\text{coop}}^\ddagger$ can become the governing factor. As a result

the total entropy of activation, ΔS^* , can then be negative. This explains the values of ΔS^* for silicone elastomer as shown in section 4.2.5(a), Tables 4.26, 4.27 and 4.28.

Tentatively, if $\Delta S_{\text{coop.}}^*$ can be regarded as a constant (A) irrespective of the molecular dimension of the penetrant, then

$$\begin{aligned}\Delta S^* &= \Delta S_{\text{coop.}}^* + \Delta S_f^* \\ &= A + B \frac{E_D}{T}\end{aligned}$$

where B is a constant, and $\Delta S_f^* = B \frac{E_D}{T}$. Since Fig. 4-15 indicates that from the present investigations $\Delta S^* = -10.15 + 0.523 \frac{E_D}{T}$, it follows that $A (= \Delta S_{\text{coop.}}^*)$ and B can be deduced. Hence

$$\Delta S_{\text{coop.}}^* = R \ln \rho_f = R \ln \sum \left(\frac{1}{m} \right)^p = -10.15$$

$$\text{and so, } \rho_f \text{ or } \sum \left(\frac{1}{m} \right)^p = \frac{1}{166}.$$

In natural rubber²¹, $\Delta S^* = -4.6 + 0.65 \frac{E_D}{T}$, so that $\rho_f = \frac{1}{10}$. These values of ρ_f in silicone and natural rubber serve therefore to indicate the approximate magnitudes which this factor ρ_f can assume.

4.3 EQUILIBRIUM PHENOMENA

4.3.1 The solubility coefficients

Plane sheet membrane (SiR-I): The dynamic solubility coefficients, σ_D , for SiR-I at temperatures between 0°C and -37.4°C are listed in section 4.1.1 (Tables 4.1 to 4.9). These tables also include data of $\bar{P}$ and D_L from which values of σ_D were deduced. In Table 4.10A are presented the static solubility coefficients, σ_s , of n-butane at various temperatures between 0°C and -63°C. These data of σ_{sv} have been deduced from the slopes of the plots of $\frac{v_s}{V}$ against p_s (Fig. 4-19), for which the experimental data are given in Table 4.10.

Hollow cylindrical membrane (SiR-M): The dynamic solubility coefficients, σ_D , for SiR-M are tabulated in section 4.1.2 (Tables 4.11 to 4.18). These solubility coefficients have been measured at temperatures between 0°C and -40°C. In the case of He, Ne, Ar and H₂, determinations of σ_D over a wider temperature range between 0°C and -78°C were also made. The sudden drop in the magnitude of σ_D as the temperature is lowered from -48°C to -55°C can partly be attributed to the reduction in the volume fraction of the amorphous phase of the silicone elastomer as a result of crystallization. As more crystalline particles are formed, i.e. as the amount of the amorphous phase is further reduced, when the temperature is lowered below -55°C, σ_D should decrease proportionally if the role of the filler particles is unaltered and the membrane can be considered as a three-phase model for the analysis of gas sorption and diffusion. The

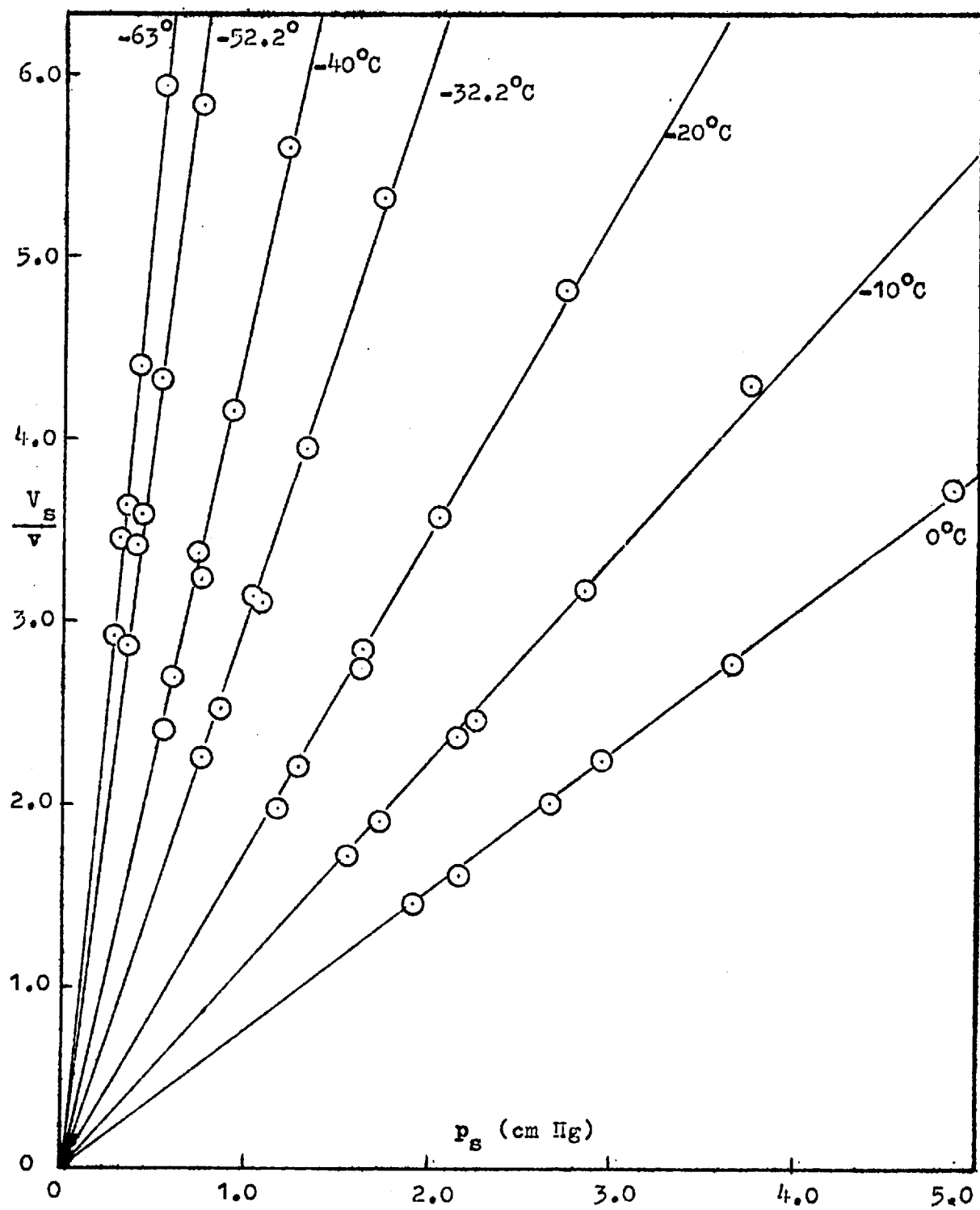


Fig. 4.19 Static solubility measurement for SiR-I:n-butane

anomalous behaviour of the temperature coefficients of σ_D in the temperature range between -55°C and -78°C (see section 4.3.4) seems to bring into question the validity of the dynamic method employed to determine the correct values of the solubility coefficients below the transition temperature. The dynamically derived solubility coefficients would be correct if the static and dynamic methods of solubility measurements yield the same results. The observed values of σ_D at temperatures between -55° and -78°C as deduced from $\sigma_D = (\bar{P}/D_L)^{1/6}$ may be regarded as the apparent dynamic solubility coefficients. Moreover, the possibility of "gap" formation within the membrane, as well as the possibility of sorption of the gas by the filler particles, as crystallization proceeds, may not be completely ruled out.

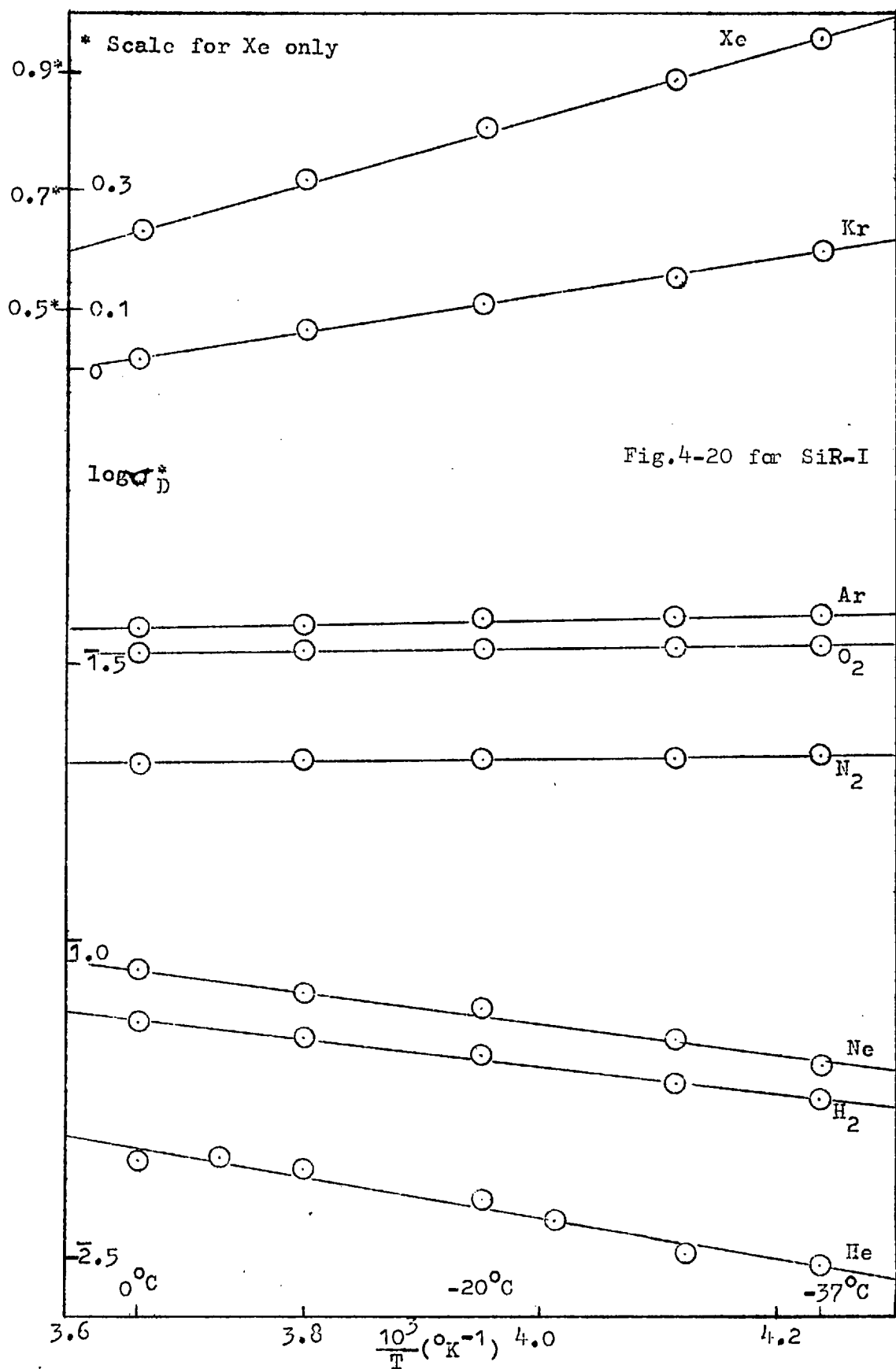
Above the transition temperature, the magnitudes of σ_D for both SiR-I and SiR-M increase in the following order (see Fig. 4.20 and Fig. 4.21) except in the case of SiR-I where $\sigma_D(\text{H}_2) < \sigma_D(\text{Ne})$:

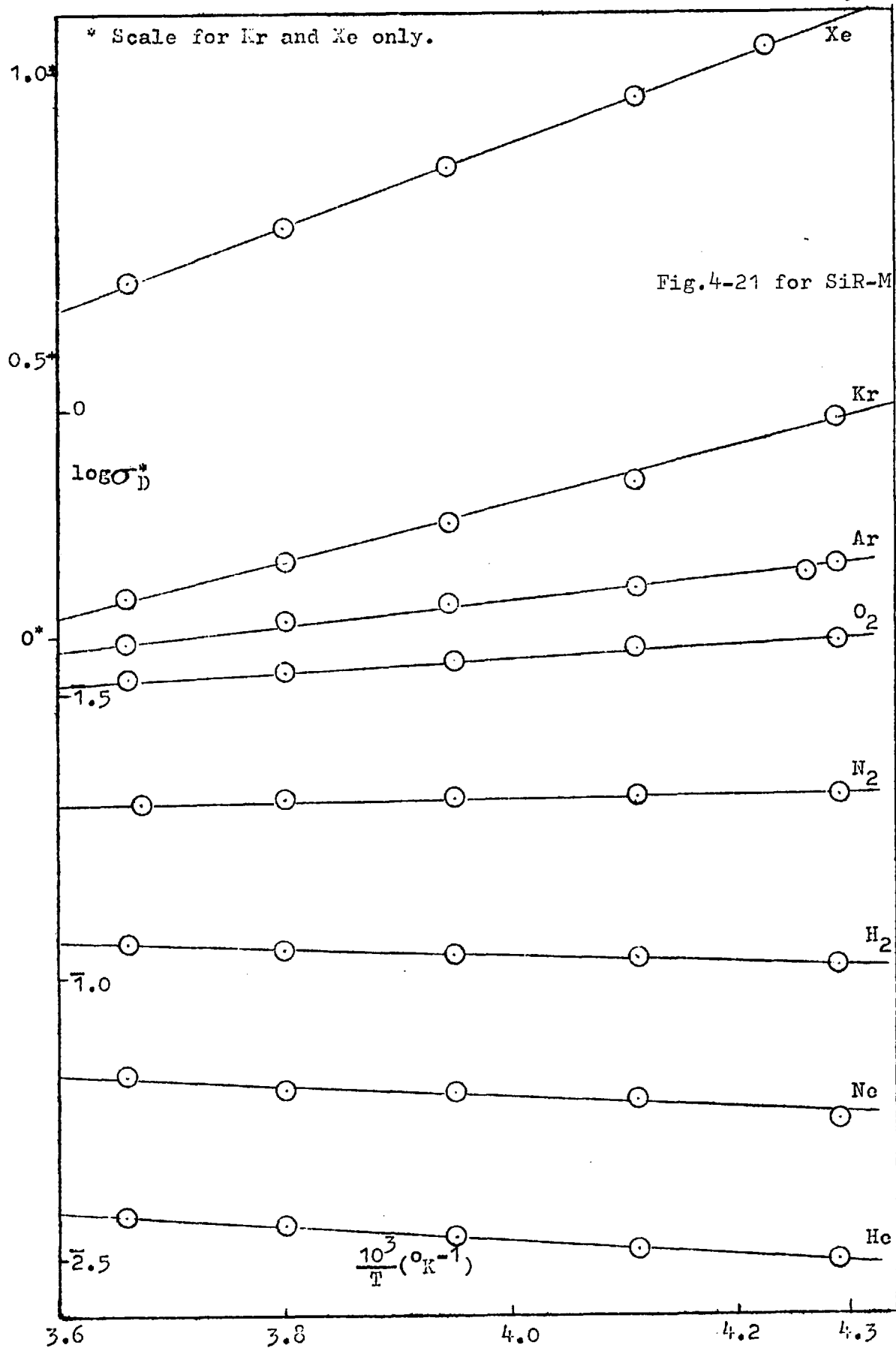
$$\sigma_D(\text{He}) < \sigma_D(\text{Ne}) < \sigma_D(\text{H}_2) < \sigma_D(\text{N}_2) < \sigma_D(\text{O}_2) < \sigma_D(\text{Ar}) < \sigma_D(\text{Kr}) < \sigma_D(\text{Xe}).$$

This is in agreement with the solubilities of these gases in various organic solvents¹⁰³.

4.3.2 Solubility of a gas in relation to its critical and boiling temperatures

The solubility of a gas is related to its tendency to condense, of which its critical temperature, T_c , or its boiling temperature, T_b , is a measure. van Amerongen⁵, Gee⁹⁷, and Barrer and Skirrow²¹ have shown that there is a linear relationship between the





logarithm of the solubility coefficient (at a constant temperature, for a given elastomer) and T_c or T_b of the gas. This is supported, within the limit of accuracy, by Fig. 4.22 (for SiR-I) and Fig. 4.24 (for SiR-M) for solubility data at 0°C . The best line passing through the experimental points is represented by

$$\text{for SiR-I} \quad \log \sigma_D^*(0^\circ\text{C}) = -1.39 + 0.0066T_c \quad (4.5)$$

$$\log \sigma_D^*(0^\circ\text{C}) = -1.41 + 0.0116T_b \quad (4.6)$$

$$\text{for SiR-M} \quad \log \sigma_D^*(0^\circ\text{C}) = -1.42 + 0.0068T_c \quad (4.7)$$

$$\log \sigma_D^*(0^\circ\text{C}) = -1.48 + 0.0125T_b \quad (4.8)$$

(NOTE: The best line will henceforth be used to represent the statistical line calculated by the least square method). It follows, therefore, that once the slope and the intercept of these plots have been determined for a given elastomer, it should be possible to predict the solubility of another gas merely from a knowledge of its critical and boiling temperatures.

The corresponding equations relating the logarithm of solubility coefficients and the critical and boiling temperatures have been given by various authors as follows:

$$\text{van Amerongen}^5: \log \sigma_D^*(25^\circ\text{C}) = -2.1 + 0.0074T_c \quad (4.9)$$

$$\log \sigma_D^*(25^\circ\text{C}) = -2.1 + 0.0123T_b \quad (4.10)$$

for the solution of gases at 25°C in vulcanised natural rubber;

$$\text{Aitken and} \quad \log \sigma_S^* = -2.47 + 0.0093T_c \quad (4.11)$$

$$\text{Barrer}^{22}: \log \sigma_S^* = -2.27 + 0.012T_b \quad (4.12)$$

for the solution of N_2 , isomeric C_4 and C_5 paraffins;

Barrer and Skirrow²¹: $\log \sigma_D(50^\circ\text{C}) = -2.0 + 0.007T_c$ (4.13)

for the solution of N_2 , normal C_1 to C_8 paraffins.

Comparison of eqs. (4.5), (4.7), (4.9), (4.11) and (4.13) shows that the slopes of the lines are substantially equivalent. This is also true for the slopes of eqs. (4.6), (4.8), (4.10) and (4.12).

Considering the process of solution of the gas in elastomer as made up of the condensation of the gas followed by mixing of the gas with the elastomer, Gee⁹⁷ arrived at the following equation relating the solubility coefficient and the boiling temperature:

$$-2.303 \log \sigma = 4.5 + \chi_1 - 10 \frac{T_b}{T} \quad (4.14)$$

where χ_1 is the interaction parameter, and T is the experimental temperature. The value of χ_1 is relatively unimportant for gases. So by putting $\chi_1 = 0$ and $T = 273.16^\circ\text{K}$ or 298.16°K , eq. (4.14) becomes

$$\log \sigma(0^\circ\text{C}) = -1.95 + 0.0159T_b \quad (4.15)$$

$$\log \sigma(25^\circ\text{C}) = -1.95 + 0.0146T_b \quad (4.15a)$$

If $T_b = 0.6T_c$ (Guldberg-Guye rule), eq. (4.15) and eq. (4.15a) are reduced respectively to:

$$\log \sigma(0^\circ\text{C}) = -1.95 + 0.0095T_c \quad (4.16)$$

$$\log \sigma(25^\circ\text{C}) = -1.95 + 0.0088T_c \quad (4.16a)$$

In spite of the simplicity of the analysis, it is seen that Gee's equations compare reasonably with those observed. It appears, therefore, that the plot of $\log \sigma$ vs. T_c or T_b is virtually linear, and the magnitude of the slopes is nearly equivalent whether in silicone elastomer or in natural rubber.

The solubility data at 0°C of inert gases in water have been given (e.g. ref. 104, p. 392). Converting these data into units used in the present work, the following relationships are obtained for comparison:

$$\log \sigma(0^\circ\text{C}) = -2.05 + 0.0049T_c \quad (4.17)$$

$$\log \sigma(0^\circ\text{C}) = -2.07 + 0.0087T_b \quad (4.18)$$

4.3.3 Solubility of a gas in relation to its force constant

The Lennard-Jones 6-12 force constant $\frac{\epsilon}{k}$ is related to the critical temperature, b.p., m.p. and other properties of the gas. Like the critical and boiling temperatures mentioned in section 4.3.2, $\frac{\epsilon}{k}$ can also be used to correlate the solubility data of gases in elastomers¹² or in organic solvents^{103,105}.

In Fig. 4.23 (for SiR-I) and Fig. 4.25 (for SiR-M) are plotted $\log \sigma_D^* (0^\circ\text{C})$ against $\frac{\epsilon}{k}$ from the solubility data at 0°C of gases in silicone elastomers. The values of $\frac{\epsilon}{k}$ are those used by Jolley and Hildebrand¹⁰⁵. To facilitate comparison with other solubility data of gases in elastomers as well as in monomeric organic solvents, Fig. 4.26 is also presented. Thus an analogy may be drawn between a low molecular weight liquid and a high polymeric elastomer with respect to the thermodynamic properties.

It is seen that the correlation is fairly good, except in many cases H_2 , and to a lesser extent He and Ne, tend to lie above the average line. This phenomenon is also observed by Hildebrand et al^{103,105} in their extensive survey of the solubilities of gases

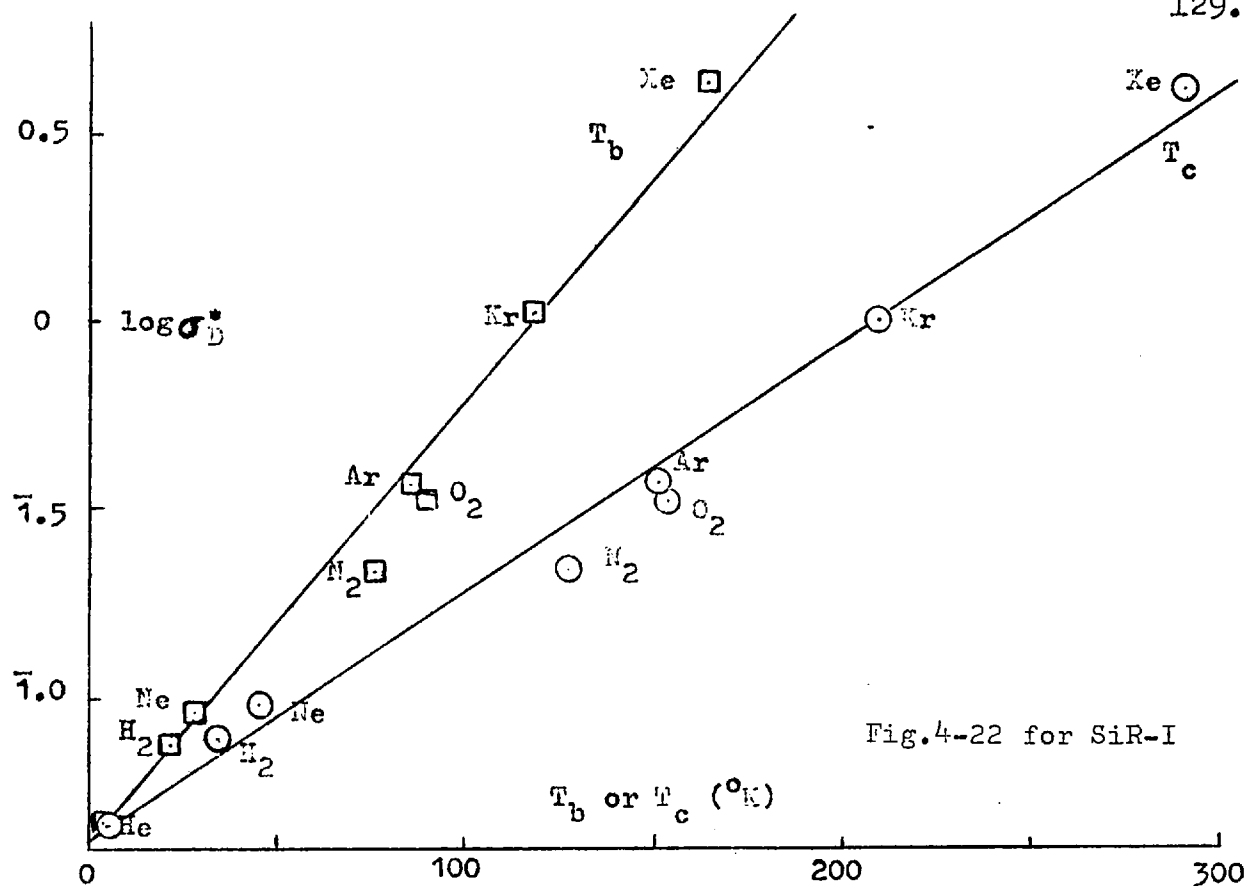


Fig.4-22 for SiR-I

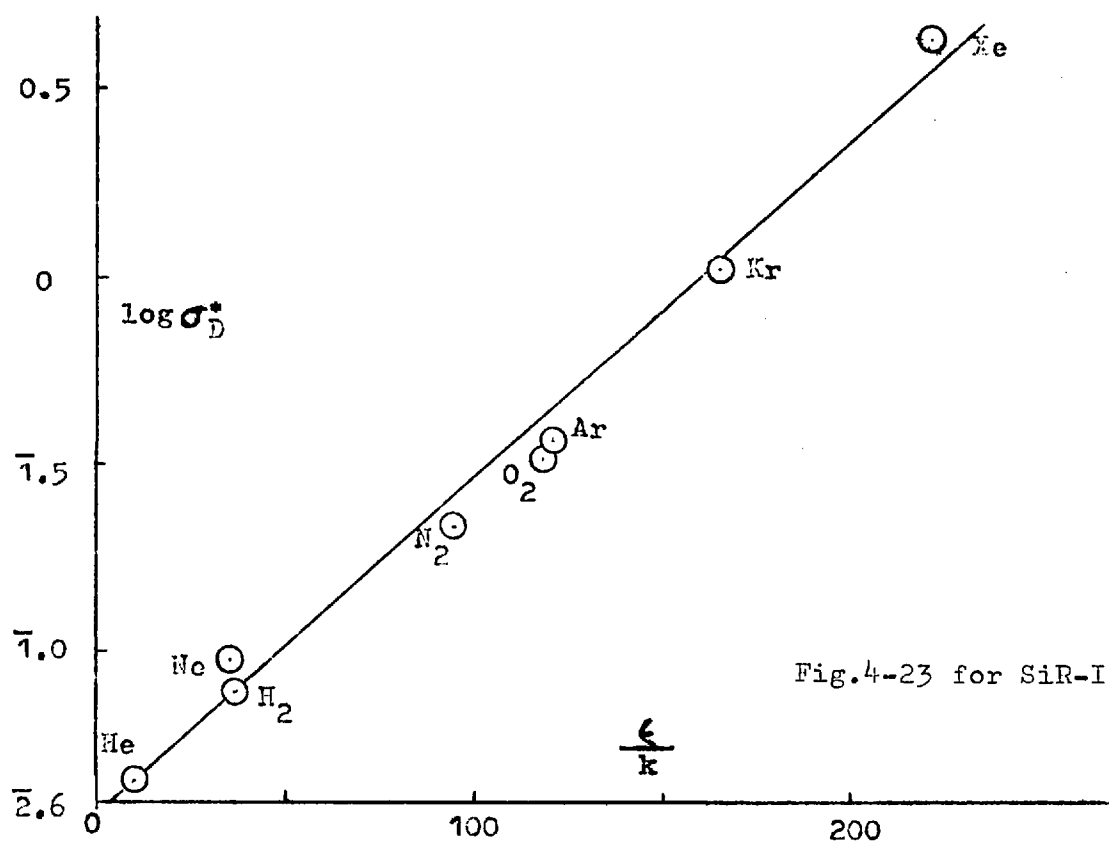


Fig.4-23 for SiR-I

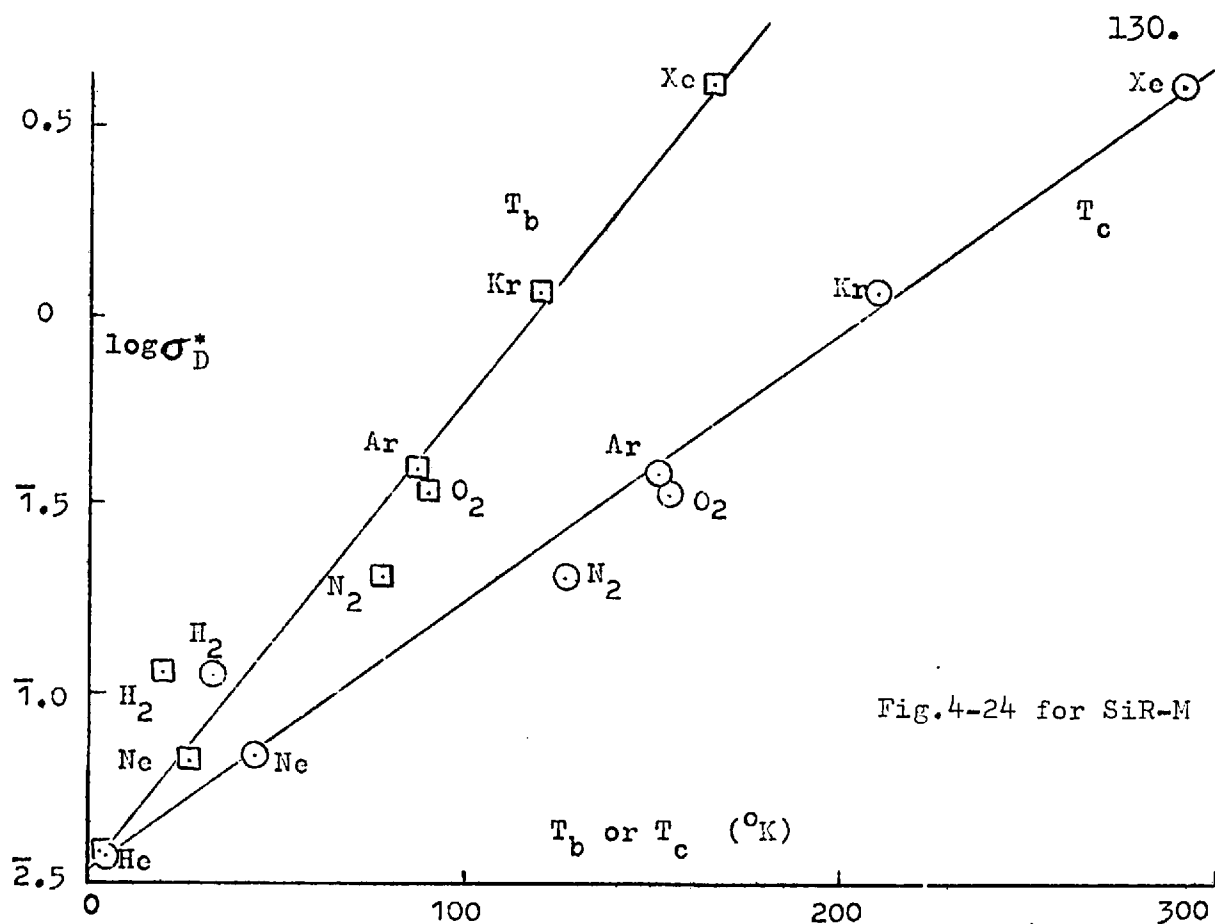


Fig.4-24 for SiR-M

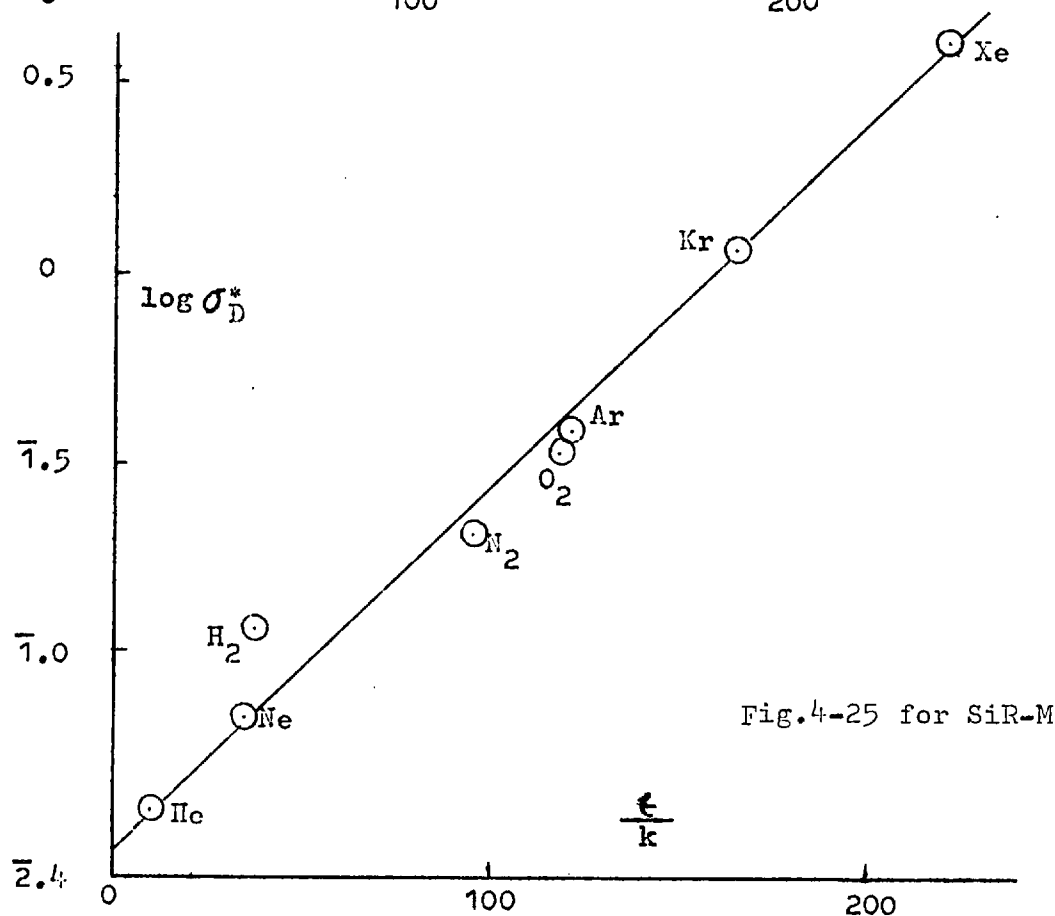


Fig.4-25 for SiR-M

in low molecular weight organic solvents. The best line for SiR-I and SiR-M may be represented by

$$\text{for SiR-I: } \log \sigma_D^*(0^\circ\text{C}) = 0.0089 \frac{\epsilon}{k} - 1.44 \quad (4.19)$$

$$\text{for SiR-M: } \log \sigma_D^*(0^\circ\text{C}) = 0.0092 \frac{\epsilon}{k} - 1.48 \quad (4.20)$$

while Michaels and Bixler¹² gave the following relation for gases dissolving in amorphous polyethylene,

$$\log \sigma_D^*(25^\circ\text{C}) = 0.0095 \frac{\epsilon}{k} - 2.20 \quad (4.21)$$

It appears that the plot of $\log \sigma$ vs. $\frac{\epsilon}{k}$ is virtually linear for both in monomeric liquids or in certain polymers. The fact that these lines (Fig. 4.26) are more or less parallel to one another lends further support to the analogy between the solution process in elastomers and in low molecular weight non-polar organic solvents. The reason for the sequence of the lines is not completely understood, although it may partly be related to the solubility parameters of the elastomers or the solvents.

Michaels and Bixler¹² claimed that the force constant $\frac{\epsilon}{k}$ is a more fundamental parameter than the critical or boiling temperature. By equating the chemical potential of the gas in equilibrium with the polymer to the chemical potential of the dissolved gas, they arrived at the following expression relating the solubility coefficient and $\frac{\epsilon}{k}$:

$$\log(\sigma^* \bar{V}) = 0.0113 \frac{\epsilon}{k} - \frac{1 + \chi_1}{2.302} \quad (4.22)$$

where $\bar{V}$ is the partial molar volume and χ_1 is the interaction parameter. Since it is difficult to estimate $\bar{V}$ and χ_1 accurately, it has further been

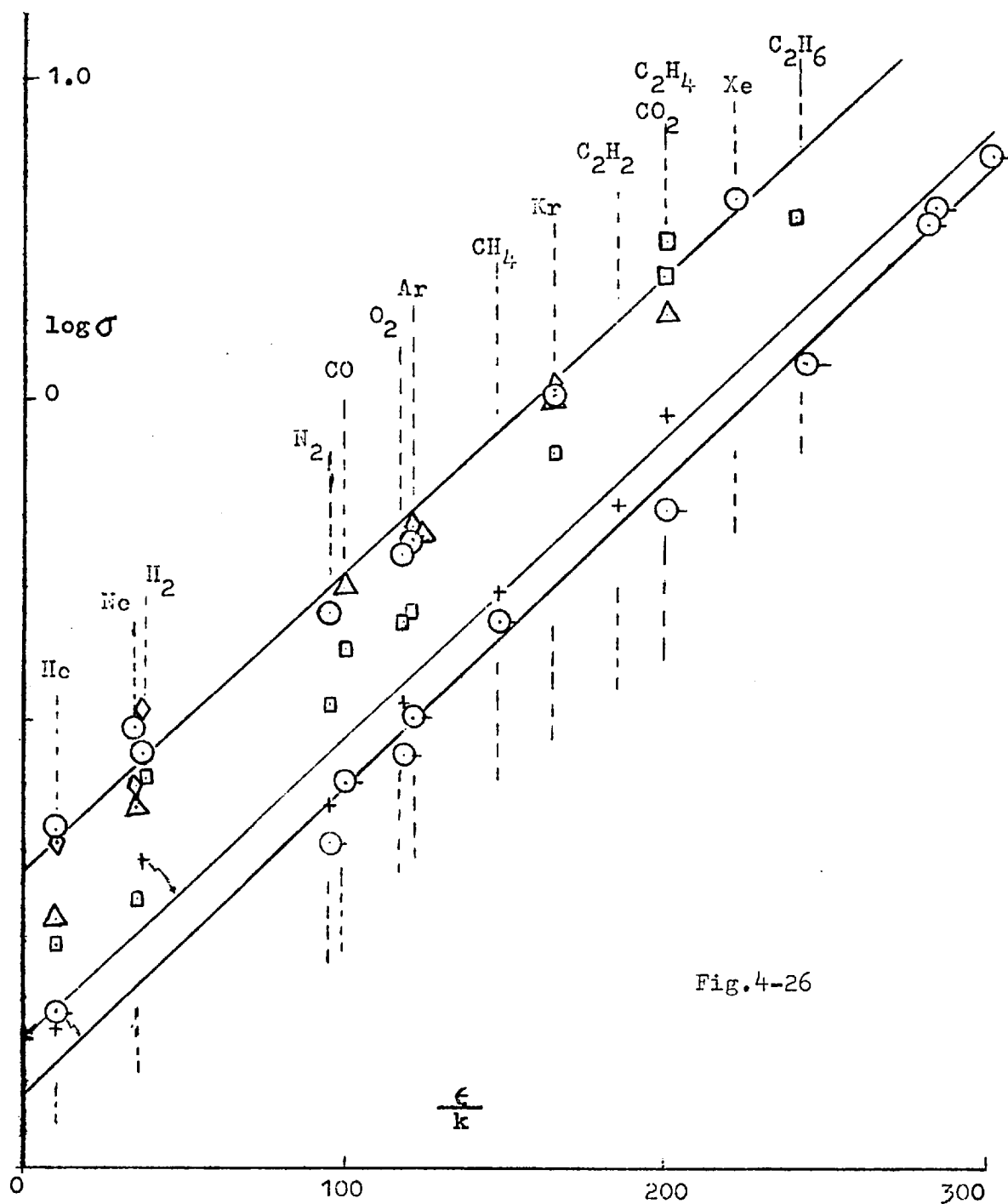


Fig.4-26

- Note: ○ solubility in silicone elastomer. (present work)
 + solubility in natural rubber. (ref. 5)
 ⊖ solubility in amorphous polyethylene. (ref. 12)
 ◻ solubility in benzene. (ref. 105)
 Δ solubility in n-heptane. (ref. 105)
 ◊ solubility in 2,2,4-Trimethylpentane. (ref. 105)

(σ in the ordinate refers to σ_D^* for SiR-I and for natural rubber, σ_D^* and σ_S^* for polyethylene and σ_S^* for monomeric liquids).

assumed that $\log \bar{V}$ and χ_1 are proportional to $\frac{\epsilon}{k}$. The validity of this assumption is shown by the linear plot of $\log \sigma^*$ vs. $\frac{\epsilon}{k}$. Moreover, the observed slope is 0.0095 (eq. 4.21) for gas-polyethylene system at 25°C, and 0.0089 (eq. 4.19) or 0.0092 (eq. 4.20) for gas-silicone elastomer system at 0°C, as compared to the theoretical slope of 0.0113 (eq. 4.22).

4.3.4 Temperature dependence of the solubility coefficients

When the static solubility coefficients σ_s of n-butane were plotted against the reciprocal of the experimental temperatures (0°C to -63°C), Fig. 4.27 was obtained. It is clearly shown that as crystallization sets in the slope of the line changes.

The plots of $\log \sigma_D^*$ vs. $\frac{1}{T}$ at temperatures between 0°C and -40°C have been shown in Fig. 4-20 (for SiR-I) and in Fig. 4-21 (for SiR-M). Within the limit of experimental error, these plots are virtually linear, thus obeying the solubility law expressed by eq. (1.4). From the statistical slopes and intercepts of these plots the apparent heats of solution ($\Delta \bar{H}^0$) and the constant σ_0 were deduced and presented in Table 4.30. (NOTE: $\Delta \bar{H}^0$ for n-butane was deduced from the static solubility coefficients σ_s . All σ_0 data are statistical intercepts on the ordinate when σ_D^* is expressed in cc NTP/cc at 1 cm Hg, not at 76 cm Hg). It is noted that the most incondensable gases, like H₂, He and Ne, generally exhibit heat absorption (positive $\Delta \bar{H}^0$). The solubility coefficients of these gases decrease with decreasing temperatures.

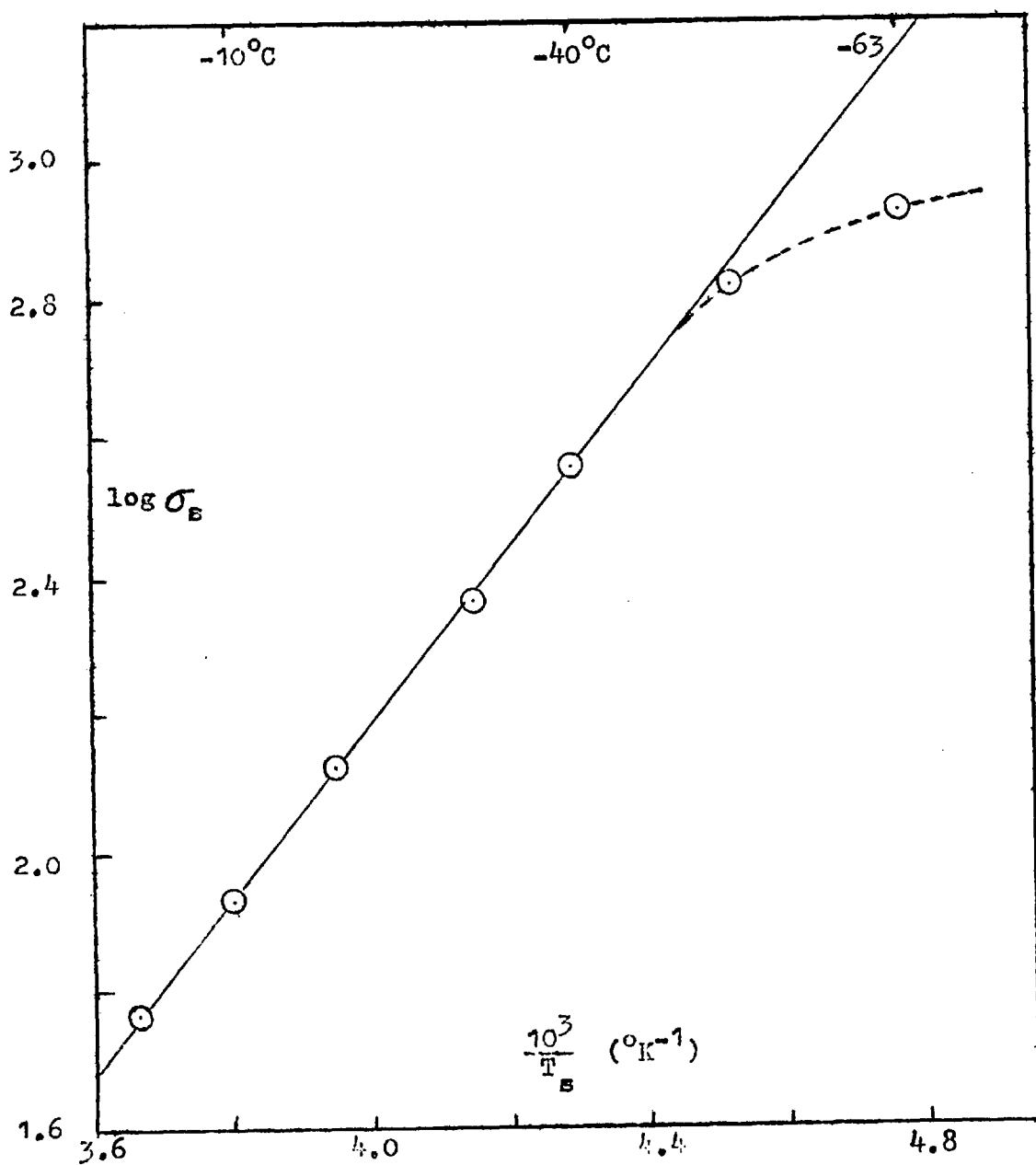


Fig. 4-27 for SiR-I : n-butane
 static
 Plot of $\log(\text{solubility coefficient})$ vs reciprocal temperature

TABLE 4.30 Heats of solution ($\Delta\bar{H}^0$) and the constant σ_0 (0°C to -40°C)

Gas	SiR-I		SiR-M	
	$\Delta\bar{H}^0$ (cal/mole)	$\sigma_0 \times 10^4$	$\Delta\bar{H}^0$ (cal/mole)	$\sigma_0 \times 10^4$
He	1590	119	581	14.5
Ne	1248	126	510	22.3
Ar	-207	33	-918	9.6
Kr	-1378	11	-2283	2.3
Xe	-2564	5	-3355	1.2
H ₂	1049	72	285	25.5
N ₂	-76	25	-61	24.0
O ₂	-86	37	-456	19.2
n-C ₄ H ₁₀	-5778	0.2		

Over a wider temperature range (0°C to -78°C), the temperature dependence of σ_D^* (SiR-M) for He, Ne, Ar and H₂ is shown in Figs. 4.28 to 4.31. It is seen that the sudden drop in σ_D^* as the temperature is lowered from -48° or -40°C to -55°C is accompanied by a change to a more negative apparent heat of solution as the temperature falls below -55°C . For He, Ne and H₂ the change is from positive $\Delta\bar{H}^0$ (0° to -40°C) to negative $\Delta\bar{H}^0$ (-55° to -78°C), and for Ar from negative $\Delta\bar{H}^0$ to a more negative $\Delta\bar{H}^0$. The best average values of $\Delta\bar{H}^0$ and σ_0 for SiR-M between -55° to -78°C are given in Table 4.31.

TABLE 4.31 The apparent heat of solutions ($\Delta\bar{H}^0$) and σ_0 (-55°C to -78°C)

Gas	He	Ne	Ar	H ₂
$\Delta\bar{H}^0$ (cal/mole)	-753	-118	-2848	-1429
$\sigma_0 \times 10^4$	0.34	3.95	6.95	0.34

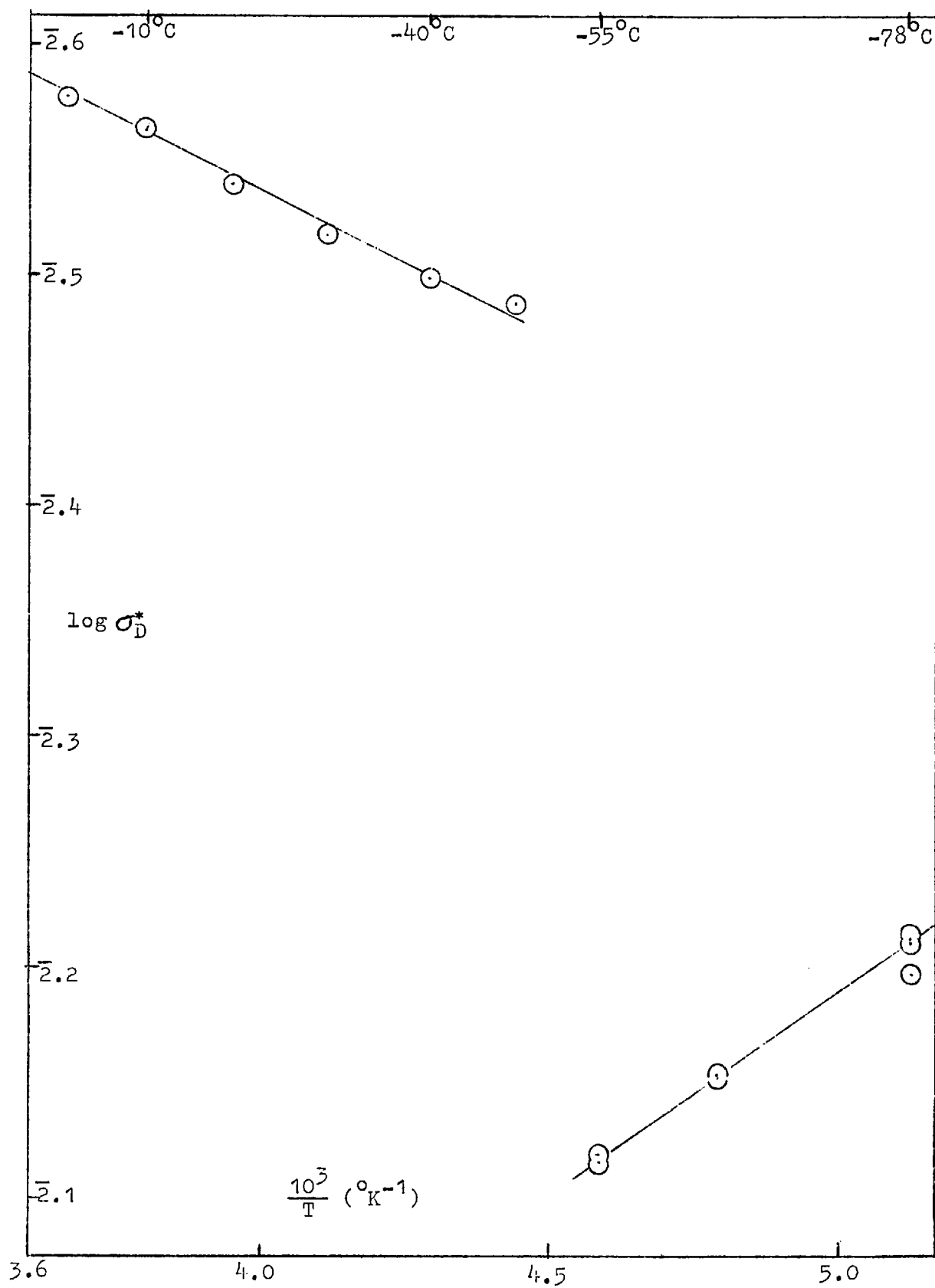


Fig. 4-28 for SiR-M : He system.

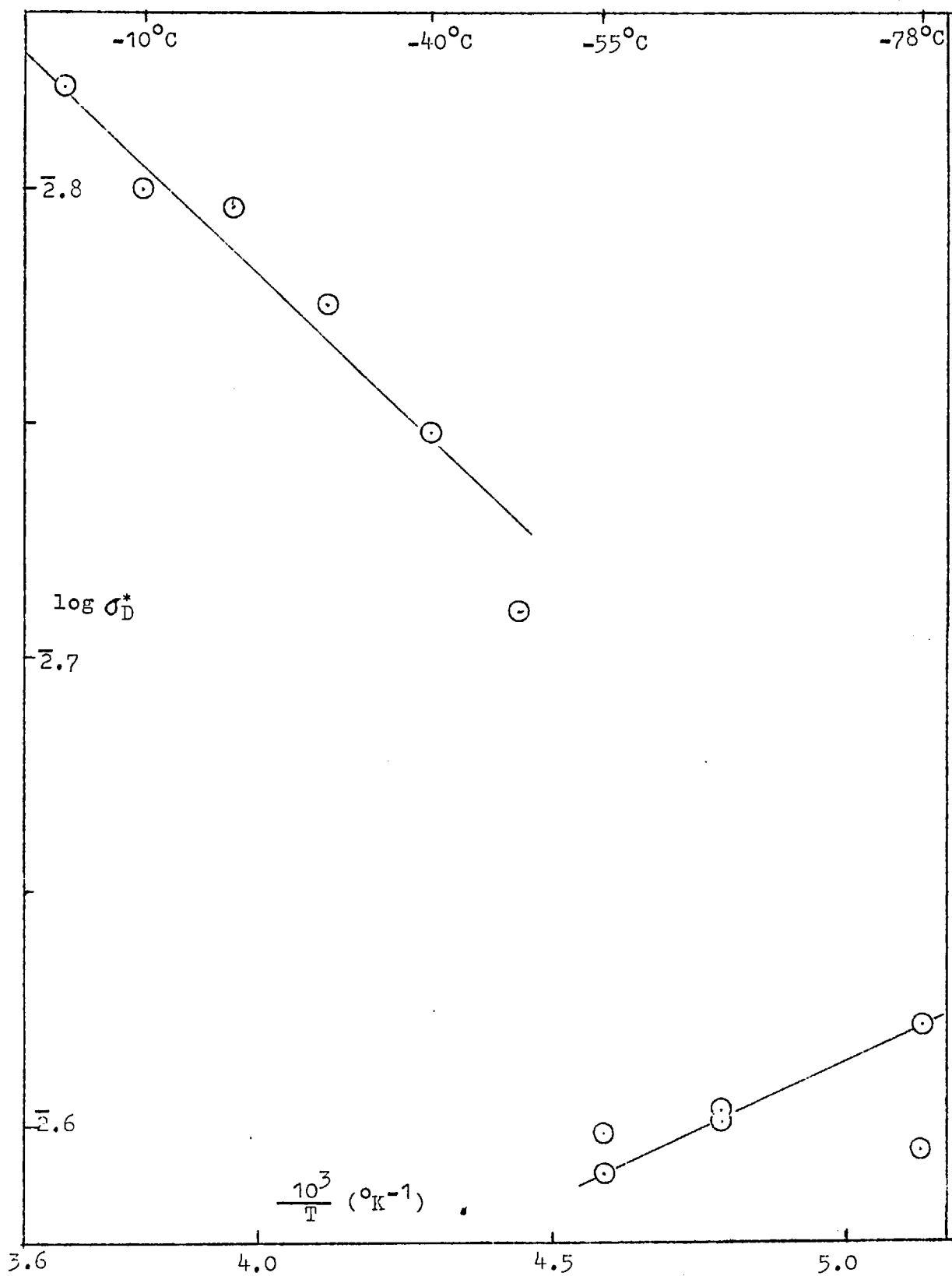


Fig.4-29 for SiR-M : Ne system.

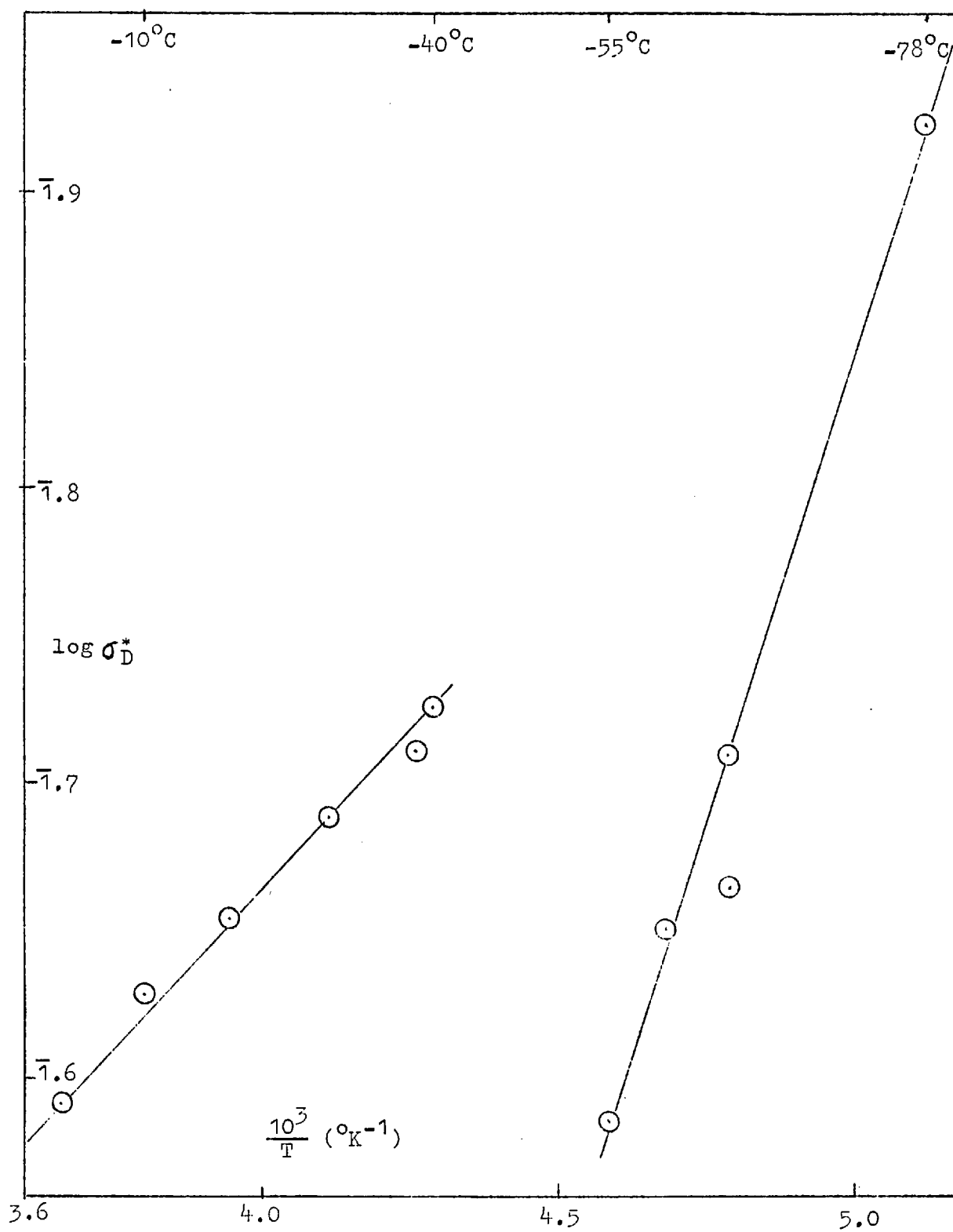
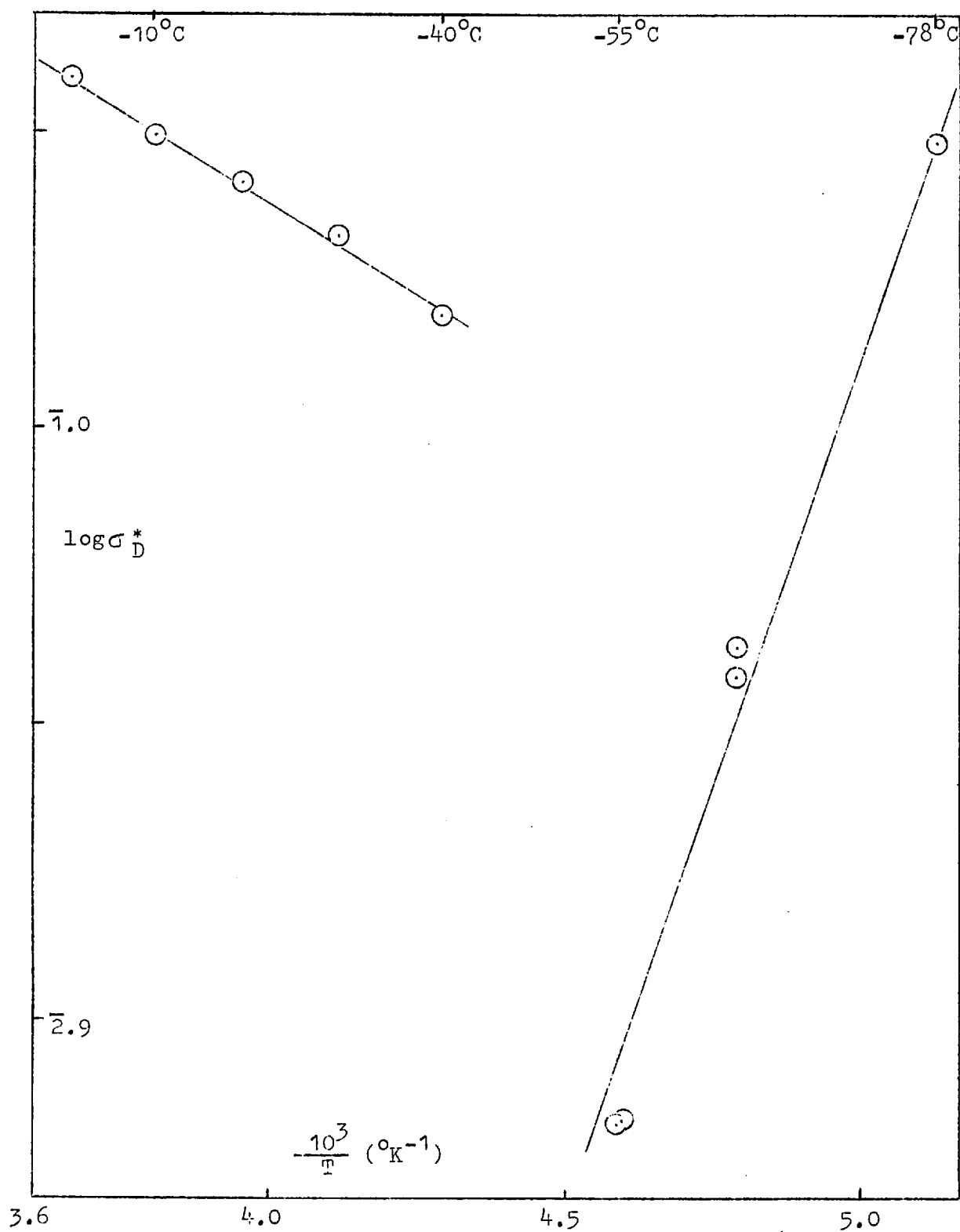


Fig.4-30 for SiR-M : Ar system.

Fig.4-31 for SiR-M : H₂ system.

This abnormal behaviour in the crystallization region is rather difficult to explain in view of the extreme heterogeneity of the membrane which is composed of filler plus crystalline particles embedded in the basic silicone polymer. The more negative values (heat evolved) of the heat of solution seems to suggest that filled silicone rubber at temperatures below its first transition temperature contains more than the equilibrium number of holes for the same rubber above the transition, if any. Since the heat of solution is the sum of the work required to create a hole (positive contribution) to accommodate the solute particle and the interaction energy between this particle and the surrounding polymer (negative contribution), it appears that in the crystallization region dissolved gas molecules are merely accommodated in the holes already present in the polymer bulk structure.

4.3.5 Free energy, heat and entropy of solution

A knowledge of the equilibrium state of the dissolved gas molecules is important in understanding the diffusion process. For a perfect gas solution obeying Henry's law, the standard partial molar free energy ($\Delta\bar{G}^0$), heat ($\Delta\bar{H}^0$), and entropy ($\Delta\bar{S}^0$) of solution may be deduced from the plots of $\log \sigma_D^*$ vs. $\frac{1}{T}$ according to the following relationships:

$$\Delta\bar{G}^0 = -RT \ln \sigma_D^* \quad (4.23)$$

$$\Delta\bar{H}^0 = RT^2 \frac{\partial \ln \sigma_D^*}{\partial T} \quad (4.24)$$

$$\text{and } \Delta\bar{S}^0 = R \ln \sigma_D^* + RT \frac{\partial \ln \sigma_D^*}{\partial T} \quad (4.25)$$

or simply from

$$\Delta\bar{S}^0 = (\Delta\bar{H}^0 - \Delta\bar{G}^0)/T \quad (4.26)$$

The chosen standard states are, for the gas phase, a pressure of 1 atm. and the experimental temperature; and for the solution phase a sorbed gas concentration of 1 cm³ (NTP) per cm³ of elastomer. Values of $\Delta\bar{G}^0$, $\Delta\bar{H}^0$ and $\Delta\bar{S}^0$ so calculated at $T = 273.16^\circ\text{K}$ are tabulated in Table 4.32. It is observed that $\Delta\bar{H}^0$ and $\Delta\bar{S}^0$ values for SiR-M are consistently more negative than the corresponding values for SiR-I.

The solubilities, expressed in terms of Ostwald solubility coefficients, of He, Ne, Ar and Kr in the saturated normal hydrocarbons and other organic solvents have been determined by Clever et al¹⁰⁶ at temperatures between 15°C and 41.8°C. In Table 4.33 are listed the equivalence of their solubility coefficients expressed in unit of the present work (i.e. the Bunsen solubility coefficient) as deduced from the relation:

$$\text{Ostwald coefficient} = \text{Bunsen coefficient} \times \left(\frac{T}{273}\right).$$

For comparison, the free energy, heat and entropy of solution were calculated and presented in Table 4.33 (for heptane and octane only). From the solubility data (at approximately 25°C and 35°C) of Thomsen et al¹⁰⁷, values of $\Delta\bar{G}^0$, $\Delta\bar{H}^0$ and $\Delta\bar{S}^0$ for permanent gases dissolving in heptane, octane and nonane were also calculated and collected in Table 4.34. Examination of Tables 4.32 to 4.34 reveals that $\Delta\bar{H}^0$ are distinctly positive for He, Ne and H₂, zero or nearly so for N₂ and O₂, and negative for Ar, Kr and Xe irrespective of the nature of the solvent - elastomer or organic liquid.

In the solution of gas in solvent, Frank and Evans¹⁰⁸ proposed, as a first approximation, that the dissolved gas takes on the properties of the solvent.

TABLE 4.32 Free energy, heat and entropy of solution at 273.16°K.

Gas	SiR-I			SiR-M		
	$\Delta\bar{G}^0$	$\Delta\bar{H}^0$	$\Delta\bar{S}^0$	$\Delta\bar{G}^0$	$\Delta\bar{H}^0$	$\Delta\bar{S}^0$
He	1674	1590	-0.31	1779	581	-4.39
Ne	1273	1248	-0.09	1472	510	-3.52
Ar	551	-207	-2.78	510	-918	-5.22
Kr	-17	-1378	-4.98	-88	-2283	-8.04
Xe	-783	-2564	-6.52	-780	-3355	-9.43
H ₂	1381	1049	-1.22	1176	285	-3.26
N ₂	834	-76	-3.33	862	-61	-3.38
O ₂	603	-86	-2.52	588	-456	-3.82
n-C ₄ H ₁₀	-2266	-5778	-12.85			

TABLE 4.33 Free energy, heat and entropy of solution at 25°C calculated from solubility data of Clever et al¹⁰⁶.

Gas	Solvent	$\sigma^{\#}(25^{\circ}\text{C})$	$\Delta\bar{G}^0$	$\Delta\bar{H}^0$	$\Delta\bar{S}^0$
He	Heptane	3.784×10^{-2}	1940	1614	-1.09
Ne	"	5.286×10^{-2}	1742	1218	-1.76
Ar	"	3.802×10^{-1}	573	-484	-3.55
Kr	"	± 1.096	-54	-1584	-5.5
He	Octane	3.225×10^{-2}	2035	1808	-0.76
Ne	"	$\pm 4.907 \times 10^{-2}$	1786	1525	-0.88
Ar	"	3.362×10^{-1}	646	-445	-3.66
Kr	"	± 0.974	15.6	-1400	-4.75

* at 25.2°C

TABLE 4.34 $\Delta\bar{G}^0$, $\Delta\bar{H}^0$ and $\Delta\bar{S}^0$ at 25°C calculated from solubility data of Thomsen et al¹⁰⁷.

Gas	Solvent	$\sigma^{\#}(25^{\circ}\text{C})$	$\Delta\bar{G}^0$	$\Delta\bar{H}^0$	$\Delta\bar{S}^0$
H ₂	Nonane	8.64×10^{-2}	1451	582	-2.92
N ₂	Heptane	2.06×10^{-1}	936	0	-3.14
O ₂	"	3.30×10^{-1}	657	0	-2.20
N ₂	Octane	1.79×10^{-1}	1019	0	-3.42
O ₂	"	2.86×10^{-1}	742	0	-2.49

Thus the entropy of solution of the gas would be equal to the entropy of condensation of the pure solvent. Frank and Evans pointed out, however, that the experimental entropy is usually much more positive than that just mentioned because (i) the gas in solution does not have the same free volume as the solvent, and (ii) there is a solvent reaction in which the dissolved gas loosens forces between neighbouring solvent molecules resulting in an increased partial molar entropy of the solute. The observed values of $\Delta\bar{S}^0$ in SiR-I and SiR-M and those in normal hydrocarbons are shown in Tables 4.32 to 4.34 for comparison.

4.3.6 Correlations of the heats of solution

(a) Heat of solution and the force constant ($\frac{\epsilon}{k}$):

It has been shown in section 4.3.3 that there exists a linear correlation between $\log \sigma_D^*$ and $\frac{\epsilon}{k}$ of the gas. If the thermodynamic model used in deriving the correlation of $\log \sigma_D^*$ vs. $\frac{\epsilon}{k}$ is more than fortuitously satisfactory, there should be a similar correlation for the heats of solution. The total heat effect, and thus the heat of solution associated with taking one mole of gas from the gas phase in equilibrium with the elastomer into solution in the polymer should include only the heat of condensation and the heat of solution or mixing. For the ideal model presented, Michaels and Bixler¹² gave the following relation between the heat of solution and the force constant:

$$\Delta\bar{H}^0 = 0.59\chi_1 - 0.0156 \frac{\epsilon}{k} \quad (4.27)$$

Fig. 4.32 is the result of using eq. (4.27) as a basis of correlation. The statistical line passing through the rather scattered experimental points is represented by:

$$\Delta \bar{H}^{\circ} = 1.88 - 0.0193 \frac{\epsilon}{k} \quad (\text{for SiR-I}) \quad (4.28)$$

$$\text{and } \Delta \bar{H}^{\circ} = 1.19 - 0.0190 \frac{\epsilon}{k} \quad (\text{for SiR-M}) \quad (4.29)$$

For polyethylene, the regression line was given by Michaels and Bixler¹² as

$$\Delta \bar{H}^{\circ} = 1.75 - 0.0164 \frac{\epsilon}{k} \quad (4.30)$$

It is seen that the agreement between the predicted (eq. 4.27) and the observed (eq. 4.28 and 4.29) slopes is not as good as that found in gas-polyethylene systems (eq. 4.30).

(b) Comparison between the heats of dilution evaluated from the observed heat of solution and from Hildebrand's equation

The process of solution of a gas below its critical temperature in an elastomer may be considered as made up of the condensation of the gas followed by mixing the condensed gas with the elastomer^{5,21,97}. Consequently, the heat of solution $\Delta \bar{H}^{\circ}$ may be divided into two terms:

$$\Delta \bar{H}^{\circ} = -\lambda_v + \Delta \bar{H}_1 \quad (4.31)$$

where λ_v is the molar heat of vaporisation, and $\Delta \bar{H}_1$ is the heat of ^{di}solution or the partial molar heat of mixing of the liquified gas with the polymer. Since $\Delta \bar{H}_1$ is also given by Hildebrand's equation (eq. 2.73) the value of $\Delta \bar{H}_1$ evaluated from the observed value of $\Delta \bar{H}^{\circ}$ through eq. (4.31) can be compared with the

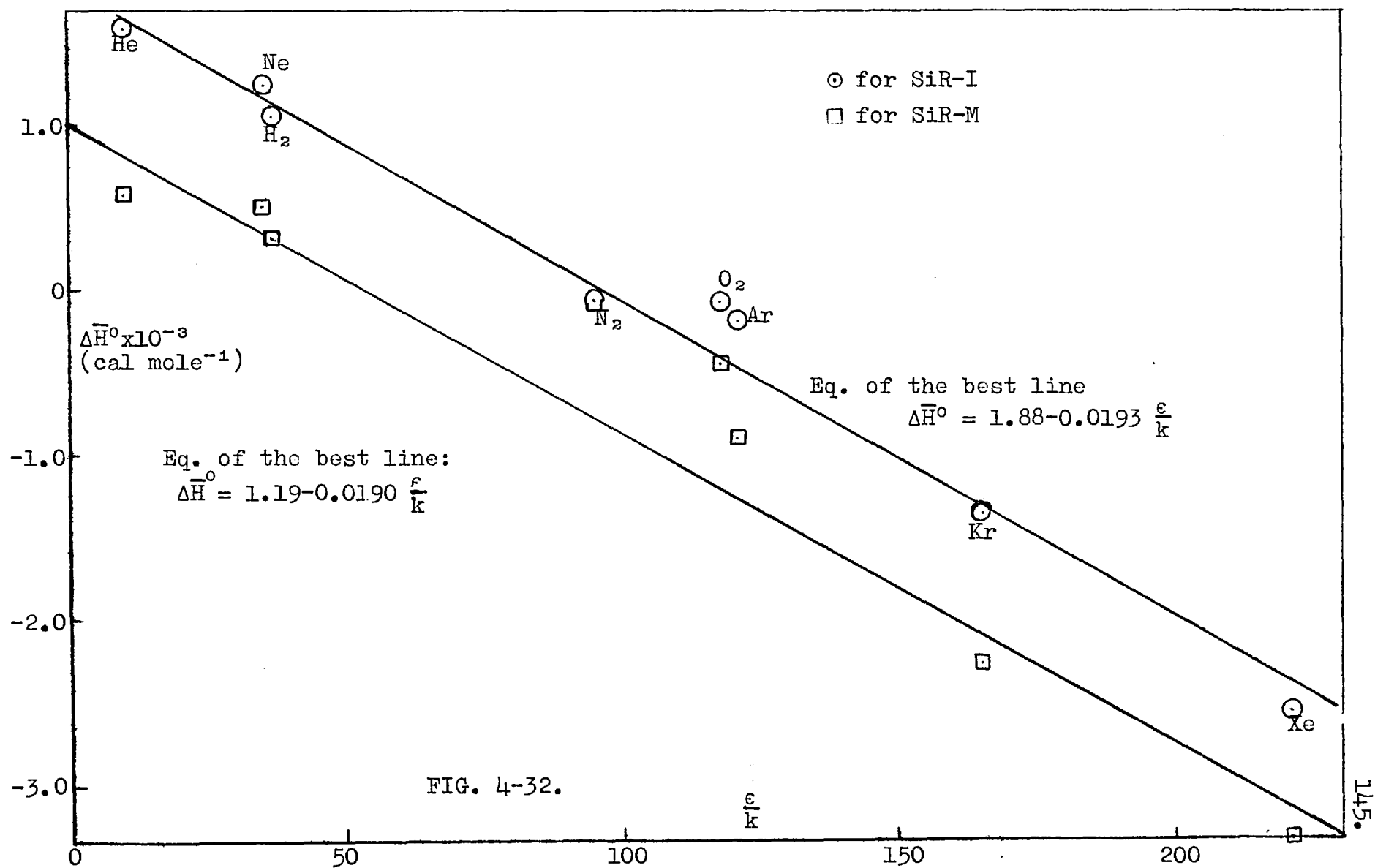


FIG. 4-32.

theoretical value calculated from eq. (2.73), assuming $v_2=1$ and the solubility parameter of silicone rubber $\delta_2 = \left(\frac{E_2}{V_2}\right)^{\frac{1}{2}} = 7.301^{109}$. The results are tabulated in Table 4.35. A certain degree of agreement was shown for n-butane and to a lesser extent for Xe and Kr. A wide deviation is noted for He, Ne, Ar, H₂, N₂ and O₂. These latter gases are at the temperature of the experiment (0°C to -40°C) which is far above their critical temperatures, T_c , making the hypothetical condensation process physically unreal. Note that as T_c increases the agreement between theoretical and experimental heats of dilution becomes closer. The heat of vaporisation (λ_v or E_1) of the gas is very sensitive to temperatures. It decreases with increasing temperature and hence it is difficult to establish its value for a gas at the experimental temperature, particularly when gases like He, Ne, Ar, H₂, N₂ and O₂ are concerned. It can be positively asserted, however, that the heats of vaporisation of these gases are lower at the experimental temperature than those stated in Table 4.35, which refers to the n.b.p. So far as He, and perhaps H₂ and Ne are concerned, there is therefore no necessity to take much account of the heat of vaporisation.

$\Delta\bar{H}_1$ data evaluated from eq. (2.73) are also open to criticism. The CED, $\left(\frac{E_1}{V_1}\right)$, or the solubility parameter, δ_1 , of the gas has been calculated at the n.b.p.; but it decreases with increasing temperature owing to decreasing E_1 and increasing V_1 . Thus, a lower value of δ_1 for He, Ne, Ar, H₂, N₂ and O₂ would reduce the difference between the theoretical and experimental values of $\Delta\bar{H}_1$.

TABLE 4.35 Comparison of the theoretical and observed heats of dilution.

Gas	E_1 or λ_v (cal/g mole)	V_1 (cm ³)	$\left(\frac{E_1}{V_1}\right)^{\frac{1}{2}} = \delta_1$	$\Delta\bar{H}^0$ (cal/mole)		$\Delta\bar{H}_1$ (cal/mole)		
				SiR-I	SiR-M	$(\delta_1 - \delta_2)^2 V_1 v_2^2$ (eq. 2.73)	$\Delta\bar{H}^0 + \lambda_v$ (eq. 4.31)	
							SiR-I	SiR-M
He	19.4	32.05	0.778 (0.67)	1590	581	1363.7	1609	600
Ne	414	16.72	4.976	1248	510	90.4	1688	924
Ar	1557.5	28.54	7.388	-207	-918	0.22	1350	639.5
Kr	2158	34.73	7.883	-1378	-2283	11.8	780	-125
Xe	3020	42.95	8.385	-2564	-3355	50	456	-335
H ₂	217.7	28.8	2.75 (2.5)	1049	285	596.5	1267	503
N ₂	1333.6	34.59	6.21 (5.9)	-76	-61	41.2	1258	1273
O ₂	1628.8	28.07	7.62 (7.4)	-86	-456	2.82	1543	1173
n-C ₄ H ₁₀	5318	96	7.443	-5545		1.94	-227	

NOTE: E_1 or λ_v is the latent heat of vaporization of liq. gas at n.b.p. (except n-C₄H₁₀ at 0°C). Inert gas data are taken from Cook¹⁰⁴; perm. gas data from ref.110.

V_1 is the molar volume of the liq. gas calculated from $V_1 = \text{atomic (or molecular) wt} / \text{density of liq. gas at n.b.p.}$ (except n-C₄H₁₀ value which is obtained from Hildebrand and Scott⁹², p. 436).

$\left(\frac{E_1}{V_1}\right)^{\frac{1}{2}} = \delta_1$ is the solubility parameter of the gas: in brackets are data of van Amerongen⁵. Hildebrand and Scott's value of δ_1 for n-C₄H₁₀ is 7.1 and this gives 3.75 for $\Delta\bar{H}_1$.

$\Delta\bar{H}^0$ is the observed apparent heat of solution.

$\Delta\bar{H}_1$ is the heat of dilution of the liq. gas with the elastomers. Theoretical data are in column 7, and experimental data in columns 8 and 9.

(c) Relationship between the heat and entropy of solution

An empirical linear relation between the heats and the entropies of condensation of pure non-associated liquids and of dilute solutions have been demonstrated by Bell¹¹¹ and by Barclay and Butler¹¹². This relation may well be represented by a linear equation of the type $\Delta\bar{S}^0 = a + b\Delta\bar{H}^0$, where a and b are constants. Moreover, Barclay and Butler¹¹² have shown that there is a value of a and one of b which give a line from which no normal substance, pure liquid or solute deviates very greatly. The value of b , i.e. the slope of $\Delta\bar{S}^0$ vs. $\Delta\bar{H}^0$ plot, was given by Barclay and Butler¹¹² as 0.0011, whilst an alternative slope re-evaluated from extended data by Frank¹¹³ is 0.00124. The latter slope is also supported by data of Clever et al¹⁰⁶ for the solution of inert gases in *n*-paraffins and in some of their methyl derivatives. In the present work, involving inert and permanent gases, the corresponding statistical slope was found to be 0.00154 for SiR-I and 0.00157 for SiR-M. Aitken and Barrer²² gave the slope as 0.0019 for solution of isomeric C_4 and C_5 hydrocarbons in natural rubber.

4.3.7 The free energy, heat and entropy of dilution

In Table 4.36 are presented the experimental values of the free energy of dilution $\Delta\bar{G}_1$, at various temperatures, and in Table 4.37 the free energy, heat $\Delta\bar{H}_1$ and entropy $\Delta\bar{S}_1$ of dilution calculated at 273.16°K. Since theoretical data of these thermodynamic quantities can also be calculated in terms of the theory

TABLE 4.36 Variation of the free energy of dilution with temperature.

T(°K)	SiR-I:Xe	SiR-I:n-butane	SiR-M:Xe
	$\Delta\bar{G}_1$	$\Delta\bar{G}_1$	$\Delta\bar{G}_1$
273.16	-2513	-1556	-2510
263.16	-2415	-1474	-2424
253.16	-2289	-1429	-2338 (253.56°K)
243.16	-2174	-1376	-2253
236.16	-2093	-1330	-2196 (236.56°K)

TABLE 4.37 Free energy, heat and entropy of dilution at 273.16°K.

System	$\Delta\bar{G}_1$ (cal/mole)	$\Delta\bar{H}_1$ (cal/mole)	$\Delta\bar{S}_1$ (e.u.)
SiR-I:Xe	-2513	573	11.55
SiR-I:n-butane	-1556	0	5.7
SiR-M:Xe	-2510	-170	8.65

TABLE 4.38 Theoretical heat and entropy of dilution together with the interaction parameter χ_1 at 273.16°K.

System	$\Delta\bar{H}_1$ (cal/mole) (eq. 2.73)	$\Delta\bar{S}_1$ (e.u.) (eq. 2.61)	χ_1 (eq. 2.70)
SiR-I:Xe	50	8.57	-0.32
SiR-I:n-butane	1.94	6.22	+0.27
SiR-M:Xe	50	8.57	-0.31 ₆

of the monomer-polymer mixture, comparison between the experimental and theoretical data serves to verify the validity of the theoretical model.

The values of $\Delta\bar{G}_1$, $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ were respectively deduced from eq. (2.53), (2.54) and (2.55). These data refer to the transfer at 273.16°K of liquid monomer to monomer-polymer mixture with a weight fraction w_1 of the sorbate equal to 0.01. This weight fraction has been used since it lies in the Henry's law region of sorption. w_1 refers to unit weight of an unfilled silicone elastomer. The p_1/p_1^0 ratio for sorbate is given by

$$\frac{p_1}{p_1^0} = \frac{0.01 \times 22400 \times \rho_2}{\sigma M p_1^0} \quad (4.32)$$

where p_1 is the experimental equilibrium gas phase pressure for $w_1=0.01$; p_1^0 is the saturated vapour pressure of the sorbate at the experimental temperatures, interpolated values of which were taken from Cook¹⁰⁴ for Xe and from Timmermans¹¹⁴ for n-butane; σ is the value of σ_D^* at the temperature indicated; M is the molecular or atomic weight of the sorbate; and ρ_2 is the density of pure silicone gum ($\rho_2=0.98$ g/cc). Data for $\Delta\bar{G}_1$, $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ for other gases are not given, because at the temperature of the experiment, these gases are above their critical temperatures.

It is seen that the values of $\Delta\bar{S}_1$ are positive and large, whilst those of $\Delta\bar{H}_1$ are small and close to zero. This is to be expected from the theory of monomer-polymer mixtures.

In order to compare the observed values of $\Delta\bar{S}_1$ with those calculated from the theory of the polymer solution (eq. 2.61), the weight fraction w_1 of the sorbate was converted to its volume fraction v_1 by the relation

$$v_1 = \frac{w_1 \rho_2}{\rho_1(\text{liq})} \quad (4.33)$$

where $\rho_1(\text{liq})$ is the density of the liquified sorbate, and ρ_2 is the density of pure silicone gum. The density of liq. Xe at 0°C is 1.982 (g/cc) taken from the interpolated data of Cook¹⁰⁵ (p.360), while that of n-butane at 0°C is taken from the Handbook¹¹⁰ and has a value of 0.601 (g/cc). Since $v_1 = (1-v_2)$, the entropy of dilution, $\Delta\bar{S}_1$, can then be calculated from eq. (2.61). Values of $\Delta\bar{S}_1$ calculated in this way are presented in Table 4.38. Table 4.38 also includes data of the heat of dilution, $\Delta\bar{H}_1$, calculated from Hildebrand's expression (eq. 2.73) assuming $v_2=1$ and of the interaction parameter χ_1 calculated from Flory-Huggin's equation (eq. 2.70) with $\frac{1}{x} = 0$.

4.3.8 Statistical treatment of the solubility of gases

As explained in section 2.10.1, the best test for Barrer's sorption isotherm for negligible interaction energy (eq. 2.80) is to determine the value of $\bar{v}$ for which experimental and calculated v_1 agree. In Table 4.39 are presented, accordingly, the observed mean vibration frequency, $\bar{v}$, which gives agreement with the observed solubility for $z=4$, $z=6$ and $T=273.16^\circ\text{K}$. The results are consistent among themselves

as indicated by the values of $\bar{v}$ which tend to decrease with increasing atomic or molecular weight of the sorbate. Fig. 4.33 shows the manner in which $\bar{v}$ varies with the atomic weight of inert gas. This behaviour has been noted by Barrer and Skirrow²¹ and by Barrer⁹⁴ who also found that the values of $\bar{v}$ tend to be constant for the same gas in different elastomers.

TABLE 4.39 Test of isotherm (eq. 2.80) for inert and permanent gases in silicone elastomers.

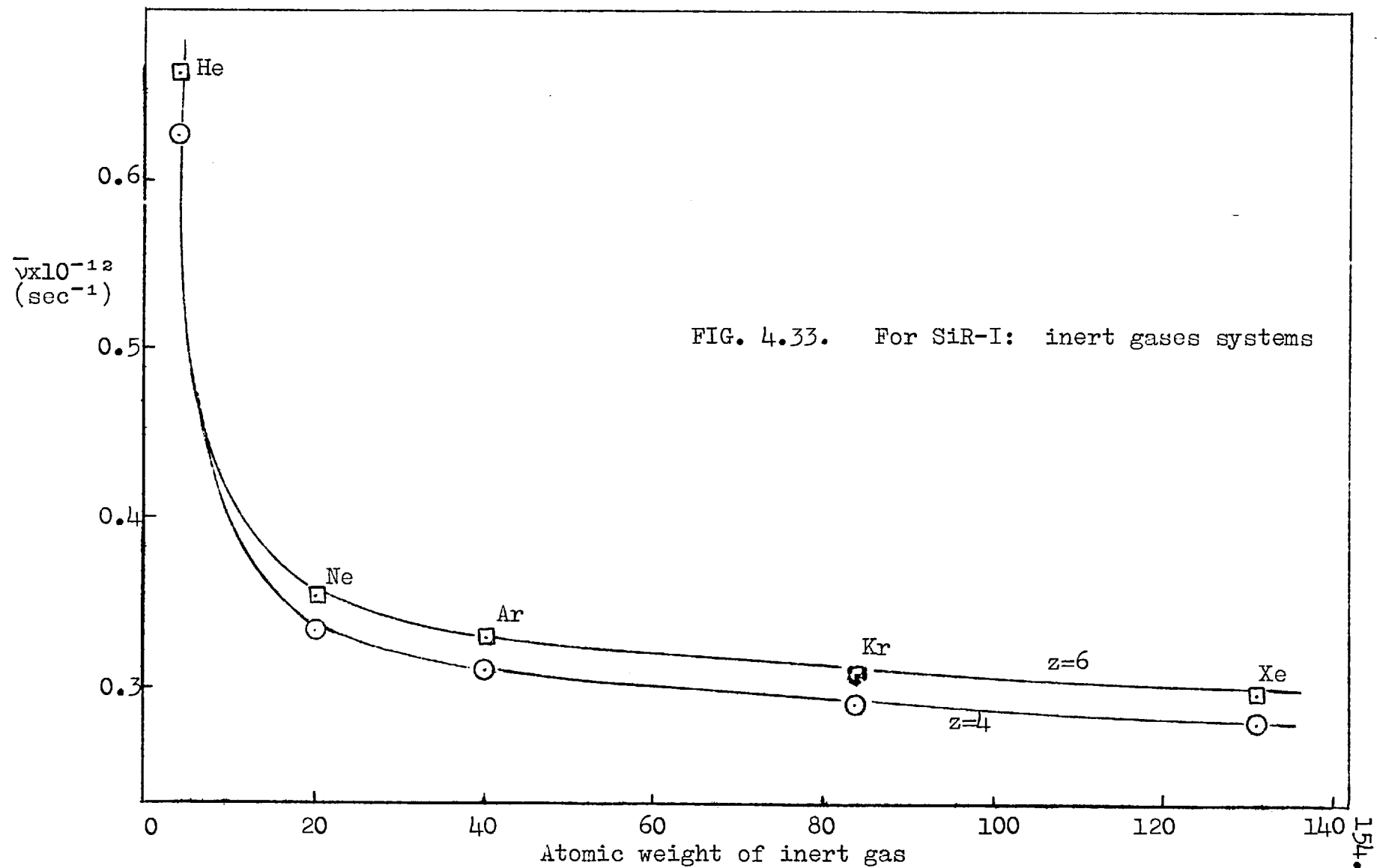
	Gas	v_1	$z=4$	$z=6$
			$\bar{v} \times 10^{12} (\text{sec}^{-1})$	$\bar{v} \times 10^{12} (\text{sec}^{-1})$
SiR-I	He	6.54×10^{-5}	0.63	0.66
	Ne	7.15×10^{-5}	0.33	0.35
	Ar	0.46×10^{-3}	0.31	0.33
	Kr	1.60×10^{-3}	0.29	0.31
	Xe	8.12×10^{-3}	0.28	0.30
	H ₂	0.10×10^{-3}	1.06	1.13
	N ₂	0.33×10^{-3}	0.38	0.40
	O ₂	0.41×10^{-3}	0.335	0.35
SiR-M	He	5.39×10^{-5}	1.24	1.31
	Ne	4.95×10^{-5}	0.59	0.63
	Ar	0.50×10^{-3}	0.47	0.50
	Kr	1.82×10^{-3}	0.49	0.51
	Xe	8.08×10^{-3}	0.46	0.48
	H ₂	0.15×10^{-3}	1.50	1.59
	N ₂	0.32×10^{-3}	0.39	0.41
	O ₂	0.42×10^{-3}	0.42	0.44

NOTE: $\bar{v}$ has been calculated from eq. (2.80), where the volume fraction of the sorbate is deduced from: $v_1 = \frac{\sigma_D(0^\circ\text{C}) \times \text{mol.vol.}}{22400}$ (see Table 4.35 for values of mol.vol.).

$p = 76 \text{ cm Hg}$; $T = 273.16^\circ\text{K}$; $v_2 = 1$.

ΔH is the heat of solution and is equivalent to $\Delta \bar{H}^\circ$ given in Table 4.30.

$\frac{1}{kT}$ which appears on the r.h.s. of eq. (2.80) is equal to 3.52×10^{17} ; since by expressing the pressure, p , in cm of Hg, the Boltzman constant k in $p = n_1 kT$ has a value given by: $k = 1.04 \times 10^{-20}$.



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