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DIFFUSION OF POLYMERS: A REVIEW

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The main thrust of this report is to provide a comprehensive literature review on diffusion in polymers.

The report starts with a description of diffusion processes, clearly identifying the terminology involved as well as the methods for measuring diffusion coefficients. The factors affecting diffusivities and the theories for predicting the dependence of diffusivity on concentration are also covered.

Finally, an experimental technique and a design for an experimental set-up are described.

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POLYMERS
DIFFUSION
PERMEATION

DIFFUSION IN POLYMERS: A REVIEW

by

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SUMMARY

The main thrust of this report is to provide a comprehensive literature review on diffusion in polymers.

The report starts out with a description of diffusion processes, clearly identifying the terminology involved as well as the methods for measuring diffusion coefficients. The factors affecting diffusivities and the theories for predicting the dependence of diffusivity on concentration are also covered.

Finally, an experimental technique and a design for an experimental set-up are described.

1. INTRODUCTION

The objectives of this work are (i) to obtain values of the diffusion coefficients for several penetrant-polymeric film systems, and (ii) to study the effect of various variables, e.g., temperature, penetrant size and nature of polymer used, on the diffusion coefficient.

The polymers used are in the form of films (or membranes) and the technique used is known as the desorption method.

The desorption method involves immersing the polymer films in a penetrant until equilibrium is reached at the temperature of the experiment. The surfaces of the film are dried quickly and carefully, then the film is suspended in an electrorecording balance which is then evacuated. The weight loss of the film is monitored against the time. This process is continued until equilibrium is reached. Subsequently, the data are utilized in calculating the diffusion coefficients according to the procedures which will be outlined later in this report.

The desorption method was employed by McCall (1957) in studying the desorption kinetics for a thin slab of polyethylene, where the mathematical treatment of the problem was presented. Following that, McCall et al. (1957) utilized that mathematical treatment in determining the diffusion coefficient for the polyethylene-water system and studying its desorption kinetics.

The mathematical treatment of McCall (1957), however, considered the two cases where (i) the diffusion coefficient is independent of concentration, and (ii) the simple case where the

diffusion coefficient is assumed to depend on concentration in an exponential manner.

Fels and Huang (1970) utilized Fujita's (1961) free volume theory expression to describe the dependence of the diffusion coefficient on concentration. They incorporated it into Fick's second law of diffusion. This yielded a differential equation, which they solved by using the 4th-order Runge-Kutta procedure.

However, the paper by Fels and Huang (1970) as well as the dissertation on which the work was based are full of errors to such an extent that it is very difficult for the reader to follow their solution. Moreover, the solution obtained is strongly influenced by the various assumptions they made. It is also subject to the accuracy of the Runge-Kutta procedure.

Asfour et al. (1986) corrected the several errors committed by Fels and Huang (1970) and provided a more reliable numerical technique to solve the non-linear partial differential equation. This allows the determination of the values of the free volume theory parameters, which in turn provides an expression for the dependence of diffusivity on concentration.

The work on this project covers three phases, viz., a complete literature survey on the subject, design and commissioning of the equipment required for this project, and finally collecting and analyzing the experimental diffusion data.

This report is concerned with the first two phases; viz., the literature survey and the design of the set-up. Work on the third phase, viz., collecting and analyzing the diffusion data is in progress.

The literature survey will cover the following:

- (i) description of the diffusion process,
- (ii) terminology used in diffusion,
- (iii) methods used in measuring diffusion coefficients,
- (iv) sorption features,
- (v) factors affecting diffusion of organic vapors in polymers,
- (vi) a brief account on Fujita's, (1961) free volume theory,
- (vii) description of the method of determining the diffusion coefficients of liquids in polymer films and the pertinent mathematical treatment.

2. REVIEW OF THE LITERATURE

2.1 Description of the Diffusion Process

Diffusion is a process by which matter is transported from one part of a system to another. The driving force of diffusion is still a controversial matter. Concentration gradient has long been used as the driving force behind any diffusional process; however, developing the diffusion equation using arguments based on thermodynamics of irreversible processes suggests that the chemical potential gradient is the true driving force of diffusion. Experimental evidence confirming that chemical potential gradient is the driving force of diffusion has been obtained, e.g., Cullinan and Lenczk (1969). However, Dankwerts (1971) argues that suggesting that using the gradient of chemical potential as a driving force of diffusion is inconsistent with the random nature of the process. Dullien (1979), indicated that Dankwerts' argument is equivalent to the proposition that the magnitude of the tendency for a non-ideal solution to reach equilibrium is simply proportional to the concentration gradients which is clearly in contradiction with experience as expressed in the basic principles of thermodynamics.

Diffusion can be described by Fick's first law which is given by:

$$\vec{F}_A^C = -D_F \nabla C_A \quad (1)$$

where F_A represents the flow of component A in moles per unit area per

unit time with respect to fixed co-ordinates. C_A is the concentration of component A, in moles per unit volume and D_F is known as the "Fickian diffusivity" and has the dimensions of area per unit time.

When diffusion is considered to take place in one direction, i.e., there is a concentration gradient only along the x-axis, then Equation (1) can be rewritten as follows:

$$F_A = -D_F \frac{d C_A}{dx} \quad (2)$$

Equations (1) and (2) are rigorous only in case of ideal systems, i.e., composition independent partial molar volumes. For systems showing a large volume change on mixing, the use of the aforementioned equations may result in significant errors in the value of the diffusion coefficients.

For cases where unsteady-state diffusion takes place, Fick's second law of diffusion may be used. Equation (3) gives Fick's second law for unidirectional diffusion.

$$\frac{\partial C_A}{\partial t} = D_F \frac{\partial^2 C_A}{\partial x^2} \quad (3)$$

In Equation (3), it was assumed that the diffusion coefficient does not depend on concentration. When the diffusion coefficient depends markedly on the concentration, then Equation (3) can be rewritten as follows:

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left(D_F \frac{\partial C_A}{\partial x} \right) \quad (4)$$

A complete definition of the diffusion coefficient, requires specifying both the units and the frame of reference.

2.2 Terminology Used in Diffusion

2.2.1 The mutual diffusion coefficient, D^V

Considering the inter-diffusion of A and B in a closed system and assuming no net change of volume on mixing, one can write:

$$F_A = -D_A^V \frac{d c_A}{dx} \quad (5)$$

$$F_B = -D_B^V \frac{d c_B}{dx} \quad (6)$$

where c_A and c_B are the concentrations of A and B in mass units per unit volume of the mixture. The dimensions of D_A^V and D_B^V are area per unit time.

If the specific volumes of A and B are denoted by v_A and v_B , and if one envisages that A and B interdiffuse across a plane through which there is no net transfer of volume, then it follows from Equations (5) and (6) that:

$$v_A F_A = v_B F_B \quad (7)$$

or

$$v_A D_A^V \frac{d c_A}{dx} + v_B D_B^V \frac{d c_B}{dx} = 0 \quad (8)$$

Now, one can write:

$$v_A c_A + v_B c_B = 1 \quad (9)$$

which upon differentiation with respect to x , yields:

$$v_A \frac{d c_A}{dx} + v_B \frac{d c_B}{dx} = 0 \quad (10)$$

In order that Equations (8) and (10) be satisfied it follows that:

$$D_A^V \equiv D_B^V \quad (11)$$

Consequently, the behavior of a two component system, satisfying the condition of no volume change on mixing, may be described in terms of a single diffusion coefficient, which may vary with composition. Such single diffusion coefficient is referred to as the mutual diffusion coefficient.

2.2.2 Intrinsic diffusion coefficient, D_i

On the basis of his observations while studying diffusion in metal alloys, Darken (1949) argued that the use of diffusivities as commonly defined is inadequate for describing the diffusion phenomena. Darken (1949) proposed the use of two diffusivities in binary systems, one for each component.

Hartley and Crank (1949) extended Darken's treatment to liquid solutions. They assumed that due to the difference of the mass and size

of two interdiffusing species A and B, a hydrostatic pressure tends to build up in the region of the solution which contributes least to the volume rate of transfer. This pressure is relieved by a compensating mass flow of A and B together, that is of the whole solution.

On that basis Hartley and Crank (1949) argued that the overall rate of transfer of A across a volume fixed section may thus be expressed as the combined effect of a mass flow and a transfer due to pure diffusion. Since the amount of A transferred by the mass flow of the whole solution is proportional to the concentration of A, it follows that the diffusion coefficient D_A must necessarily be a function of the concentration of A. Consequently, Hartley and Crank (1949) argued that from the point of view of interpreting diffusion coefficients in terms of molecular motions, the mutual diffusion coefficient, D^V , thus appears to be unnecessarily complicated by the presence of mass flow. This prompted Hartley and Crank (1949) to define new diffusion coefficients; viz., D_A and D_B in terms of the rate of transfer of A and B, respectively, across a plane fixed so that no mass flow occurs through it.

Hartley and Crank (1949) provided the following relationship between the intrinsic diffusivities and mutual diffusivity

$$D^V = V_A C_A (D_B - D_A) + D_A \quad (12)$$

where C_A denotes the concentration of component A, and V_A is the constant volume used in the definition of concentration. If the molal volumes vary with composition, the coefficient D^V has no physical

significance but \mathcal{D}_A and \mathcal{D}_B can still be defined in terms of the rates of transfer of A and B, respectively across a plane which moves so that there is no bulk flow of A and B together through it (Crank, 1979).

The foregoing discussion implies that there are two diffusion coefficients, one for each component, which in case of diffusion is not meaningful. This is because, in diffusion, for a two-component system there is only one coefficient. However, Crank and Park (1968), indicated that, in several instances, diffusion measurements have been evaluated in terms of intrinsic diffusion coefficients.

When volume change on mixing accompany diffusion in a certain system, it is usual to select a suitable frame of reference so that the diffusion of component B with respect to that frame of reference is zero. This permits denoting the diffusivity of component A as D_A . Such diffusion coefficient can be related to the mutual diffusion coefficient by (Crank and Park, 1968):

$$D_A^B = D^v \phi_B^2 \quad (13)$$

where ϕ_B is the volume fraction of component B.

The value of D^v or D_A^B must be known in order to evaluate \mathcal{D}_A and \mathcal{D}_B separately.

For diffusion in solvent-polymer systems, the intrinsic diffusion coefficient for the polymer is very small compared with that of the solvent. In fact, the intrinsic diffusion coefficient of the polymer, \mathcal{D}_B can be assumed zero. Consequently, Equation (12) can be rewritten as follows:

$$D^V = D_A(1 - v_A C_A) = D_A \phi_B \quad (14)$$

using Equation (13)

$$D_A^B = D_A \phi_B^3 \quad (15)$$

where ϕ_B is the volume fraction of the polymer. In deriving Equation (15) it is assumed that diffusion takes place perpendicular to the polymer film. This may be a good assumption at the initial stages of sorption, however, at the latter stages relaxation stresses in the polymer film can cause expansion in the plane of the polymer film. Moreover, it is unlikely that swelling can be either strictly unidirectional or isotropic. Consequently, Garret (1965) suggested the use of the following equation:

$$D_A = \frac{D_A^B}{\phi_B^{7/3}} \quad (16)$$

2.2.3 Thermodynamic diffusion coefficient, D^*

As indicated earlier, concentration has long been used as the driving force behind any diffusional process. Developing the diffusion equation using irreversible thermodynamical arguments suggested using the chemical potential gradient as the driving force of diffusion rather than using concentration gradient. Therefore, the mutual diffusion coefficient defined by Equations (5) and (6) should be corrected. It has been shown (e.g., Dullien, 1960) that usually:

$$D_A^* = D_A^V / \beta' \quad (17)$$

$$D_B^* = D_B^V / \beta' \quad (18)$$

where

$$\beta' = \frac{d \ln a_i}{d \ln x_i}$$

where a_i and x_i are the activity and the mole fraction of component i , respectively. β' is generally called the thermodynamic correction factor.

Ghai et al. (1973), pointed out that the use of the thermodynamic correction factor, β' , results, in most of the cases, in "overcorrection" for the composition dependence of the diffusion coefficient. In other words, it changes a positive deviation from linear dependence of the diffusion coefficient on composition to a negative one, and vice-versa. In fact it was shown, for several systems, by Asfour (1979) and by Dullien and Asfour (1985) that $\ln D^*$ deviates from linearity more strongly and more often than $\ln D^V$.

2.3 Methods for the Measurement of Diffusion Coefficients

Several methods are reported in the literature for the experimental study of diffusion in polymer films. A comprehensive review of these methods has been published by Crank (1979). A brief account on each of these methods is in order.

2.3.1 Permeation methods

In these methods one surface of the polymer membrane is brought in contact with penetrant vapour at constant pressure. The other surface is kept at a lower vapour pressure. The quantity of the penetrant vapour permeating through the membrane is measured as a function of time. The diffusion coefficient can be obtained from either of the two following methods:

(i) Steady state flux method

In this technique the flux, F , of the diffusing substance is obtained when one surface of the polymer membrane is kept at a fixed pressure P_1 and the other surface at a lower pressure P_2 . At steady state:

$$F = -D \frac{dc}{dx} = \frac{D(C_1 - C_2)}{\ell} \quad (19)$$

when the surface concentrations are not known, then

$$F = \frac{P(p_1 - p_2)}{\ell} \quad (20)$$

where P is the permeability coefficient. D and P can be related to each other when the solubility is known:

$$D = \frac{P}{S} \quad (21)$$

(ii) Time lag method

If one surface of the polymer film is brought in contact

with a gas or vapour at a fixed vapour pressure, some time is required before the penetrant appears on the evacuated side of the film. A quantitative measure of this time is related to the diffusion coefficient by:

$$D = \frac{\ell^2}{6L} \quad (22)$$

where ℓ is the thickness of the polymer film and L is the time lag which is obtained by extrapolating the linear part of the pressure versus time curve of the steady state experiment.

2.3.2 Radiotracer method

This method provides useful information about the molecular mobility in diffusion without any overall gradient of chemical composition. If the diffusant is applied at the lower surface of the polymer film then the D can be calculated using the following equation:

$$\ln(A_{\infty} - A_t) = \text{const.} - \pi^2 D t / \ell^2 \quad (23)$$

where A_t is the β particle count at any time t and A_{∞} is the β particle count after a time long enough to achieve uniform concentration of the diffusant throughout the polymer.

2.3.3 Determination of concentration distance curves method

In this method the experimental problem consists of the determination of some concentration indicating physical properties as a function of distance from an initially sharp boundary between the polymer and the penetrant. A refractive index technique has been developed by Crank and Robinson (1951), and a number of systems have been studied using this method. This technique has been applied subsequently by Hays and Park, (1955) and Park and Said (1985).

This method requires a polymer sample, 1 mm thick, to be clamped between silvered optically flat glass plates and immersed in the liquid penetrant. The penetrant diffuses into the edge of the polymer sheet. The concentration differences produced result in the formation of Fabry-Perot fringes which are recorded by photomicrography and are used to calculate the concentration distance curves. It should, however, be pointed out that this method has not been widely used since the same data can be obtained by the simpler permeation methods.

2.3.4 Sorption kinetics

Various methods have been developed for measuring the uptake of penetrant vapours as a function of time. These methods begin with the direct weighing of the polymer sample after being exposed to vapours. Later on a quartz spring was used and nowadays the electronic microbalance is being increasingly used.

Alternatively the volume of the vapours sorbed can be measured directly. In some cases when the sorption is fast, the temperature of the polymer sample increases with time due to the heat of condensation

of the vapours. Then sorption may be controlled by the rate of loss of heat. A technique using air blasts, has been employed to overcome this difficulty.

A relationship between the diffusion coefficient and initial rate of vapour sorption in a polymer can be obtained from Fick's second law of diffusion (Crank, 1956):

$$D = \frac{\ell^2 \pi}{16} \left(\frac{M_t / M_\infty}{t^{1/2}} \right)^2 \quad (24)$$

where D is the diffusion coefficient, ℓ is the thickness of the polymer sheet and M_t and M_∞ are the amount of vapour sorbed at time t and at equilibrium, respectively. The value of D can be deduced from the observation of the initial gradient on the graph of M_t / M_∞ versus $t^{1/2}$.

For a concentration dependent diffusion coefficient, the method of interval sorption is adopted where a series of sorption curves are produced for a range of concentrations. The initial gradients of each sorption curve yields a mean value of diffusion coefficient. Calculations have shown that for any one experiment D provides a reasonable approximation to:

$$\frac{1}{C_o} \int_0^{C_o} D \, dC \quad (25)$$

By deducing values of D for each experiment and using the approximate relationship:

$$\bar{D} = \frac{1}{C_o} \int_0^{C_o} D \, dC \quad (26)$$

a graph of DC_0 as a function of C_0 can be drawn and numerical or graphical differentiation with respect to C_0 gives a first approximation to the relationship between D and C . In many cases this first approximation is sufficiently accurate. Alternatively correction curves showing the difference between $1/C_0 \int_0^C D dC$ and \bar{D}/D_0 can be used thus avoiding the need for a second approximation (Crank, 1956). Here, D_0 is the value of D at zero penetrant concentration.

The method can be applied to combined sorption and desorption data. If D_s is calculated from the initial gradient for sorption and \bar{D}_d from the gradient of desorption then $1/2(D_s + D_d)$ is a better approximation to $\frac{1}{C_0} \int_0^C D dC$ than either \bar{D}_s or D_d .

During the later stages of diffusion the graph of $\ln(M_\infty - M_t)$ against time approaches a straight line whose slope is given by:

$$\frac{d}{dt} [\ln(M_\infty - M_t)] = -D_0 \pi^2 / \lambda \quad (27)$$

The final concentration during desorption tends to be zero. For constant D , both sorption and desorption experiments should yield the same value, otherwise sorption will yield $D(C_0)$ and desorption D_0 .

2.4 Sorption Features

2.4.1 General

Polymers at temperatures above their glass transition temperature are in a rubbery state. At such a state polymers respond quickly to changes. Sorption in that case is known as "Fickian" sorption.

When a polymer is in a glassy state, i.e., below its glass transition temperature, the properties of such a polymer also tend to be time dependent. However, it should be noted here that in this case the time scale is quite different. Sorption and desorption of penetrant molecules result in structural changes as well as internal stresses which are believed to cause anomalous or non-Fickian behavior.

The following classification according to the relative rates of diffusion and polymer relaxation has been proposed by Alfrey et al.

(1966):

- (i) Fickian diffusion (known as Case I diffusion), in which the rate of diffusion is much lower than that of relaxation,
- (ii) Case II diffusion, where diffusion is very rapid compared with the relaxation processes, and
- (iii) non-Fickian or anomalous diffusion which occurs when the diffusion and relaxation rates are comparable.

A brief account of the characteristics of each of the above cases is in order.

(1) Fickian or Case I diffusion

When a plot of fractional uptake M_t/M_∞ versus $t^{1/2}$ is prepared, the following characteristics are observed in case of Fickian diffusion:

- a. in the initial stages, the plot is linear,
- b. when the relationship ceases to be linear, a curve become concave towards the abscissa, is obtained,

c. when the diffusion coefficient increases with concentration, desorption is always slower than sorption

(ii) Case II diffusion

In some cases it has been noticed that the sorption plots of weight gain versus time are linear (Alfrey et al. 1966; Hopfenberg et al., 1966) and the transport is entirely controlled by the polymer relaxation and is known as Case II diffusion. It is characterized by a sharp front moving into the polymer at constant velocity. This sharp boundary separates the outer swollen shell, essentially at equilibrium concentration, from an unpenetrated glassy core. Surface compression in the swollen gel will be balanced by the biaxial tension in the unpenetrated core of the specimen and a stress gradient is expected at the front. These internal stresses tend to extend the glassy core and increase the area of the sheet. It has also been suggested that solvent crazing and some form of stress crazing accompanies the Case II sorption process, provided sufficient large swelling stresses are generated at the boundary between the swollen polymer (Hopfenberg et al. 1970). Recently, results of the internal stresses, generated during the swelling and the desorption process has been reported (Thomas and Windle, 1981) and subsequently a theory has been proposed in terms of the

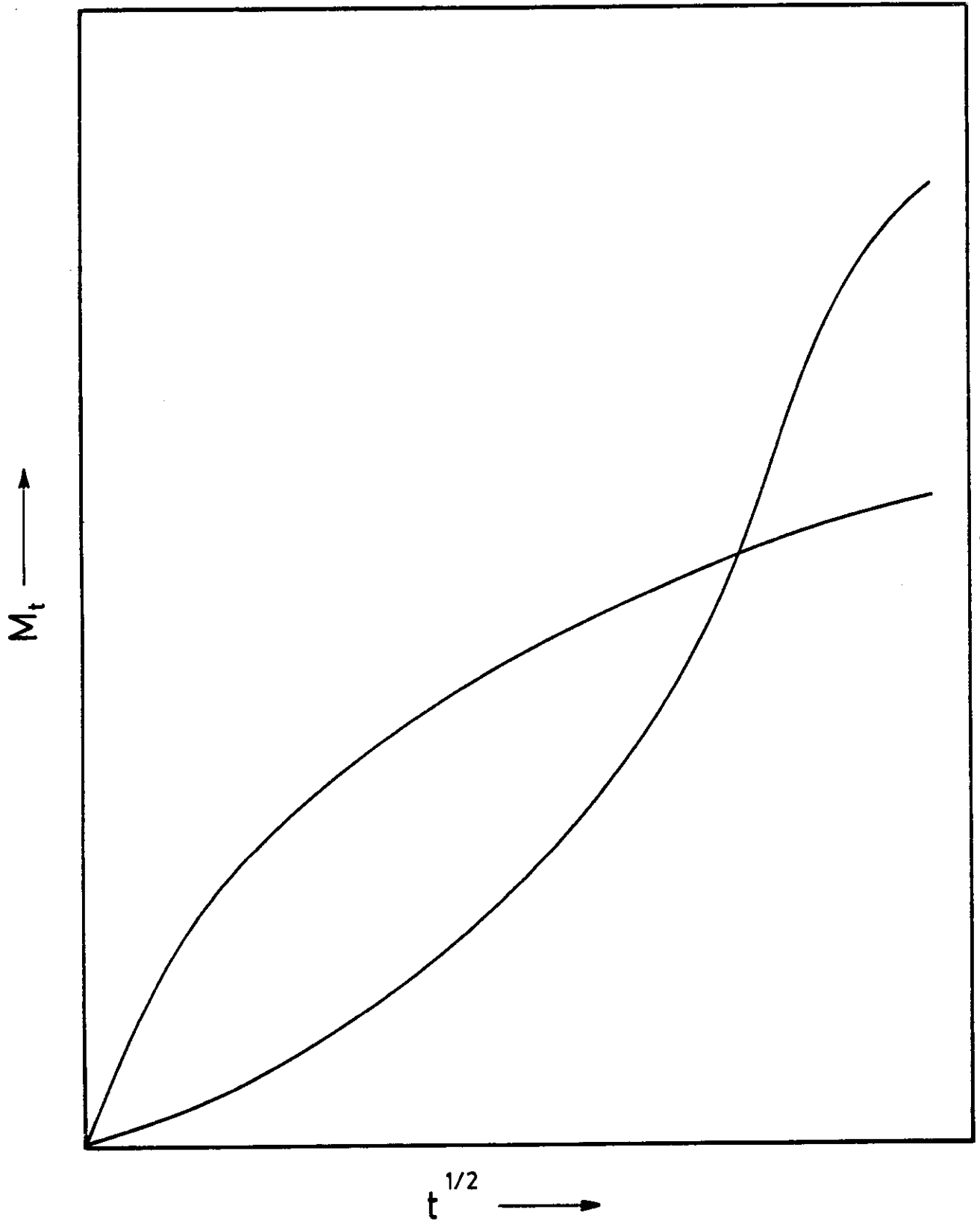


Figure 1 : Sigmoid Curve

diffusivity of the penetrant and the viscous flow rate of the polymer (Thomas and Windle, 1982).

The kinetic parameters of the limiting relaxation and diffusion controlling mechanisms were obtained from the initial and final behaviour of liquid n-hexane sorption in glassy polystyrene (Nicholas and De Notaristefano, 1984) and it has been reported that the overall solvent penetration process becomes diffusion controlled at high temperatures and at high values of the penetrant swollen shell.

(iii) Non-Fickian or anomalous diffusion

Crank (1979) indicated that if the amount sorbed at time t is denoted by $K t^n$, where K and n are constants, then Case I systems are characterized by $n = 1/2$ and Case II systems by $n = 1$. Non-Fickian systems lie between Case I and Case II, i.e., n takes a value between $1/2$ and 1 or changes sigmoidally from one to the other.

Sigmoid curves of the shape of Figure 1 have been reported for many systems by Park (1968). The sorption curves show a point of inflexion at about 50% sorption. Also, it appears from such curves that the initial rate of desorption exceeds that of sorption. However, the rate of desorption soon slows down and the curves cross.

2.5 Factors Affecting Diffusion of Vapours and Liquids in Polymers

The diffusion of vapours and liquids in polymers has features similar to those of gases, e.g., the temperature dependence, nature of the diffusant and the polymer are similar. However, due to the high solubility of vapours in polymers and the swelling, of polymers, the changes in diffusion coefficients are quite different.

(i) Temperature

Diffusion in polymers is regarded as an activated process. The dependence of the diffusion coefficient can be expressed by an Arrhenius type relationship:

$$D = D^0 \exp[-E_d/RT] \quad (28)$$

The relationship between $\ln D$ and $1/T$ has been reported to be linear for many polymer penetrant systems, but it is only true for a limited temperature range and a decrease in E_d with increasing temperature has been observed for a number of systems. The dependence of E_d on T has been interpreted by a Transition State Theory, which predicts that the curved plots of E_d vs $1/T$ are due to the decrease in activation energy and activation entropy (Amerongen, 1950). It suggests that the energy required to create a hole of suitable size to accommodate the diffusing molecule, is almost the same as E_d . Alternatively, The Zone Theory assumes that the co-operative movement in several degrees of freedom is

required in a zone of a polymer before a unit diffusion step can occur (Barren, 1960). This suggests that the motion of several polymer segments is involved in the diffusion step.

Increasing the penetrant concentration also decreases the activation energy, E_d , values which can be related to the plasticization effect of the penetrant. Recently, the increase in diffusivity values with temperature has also been discussed under the Free Volume Theory (Duda et al., 1982).

(ii) Diffusant

Diffusion coefficients have been found to decrease with the increasing size of the penetrant molecule. For small molecules the decrease in diffusivity is accompanied by an increase in the activation energy of diffusion, but after a critical size has been reached, the activation energy no longer increases (Kokes and Long, 1953). This suggests that after this critical size, the unit step involved in diffusion is the same as for the viscous flow situation. When the diffusing molecule is large its shape has a considerable effect on the diffusion rate. Studies on diffusion of n-hexadecane and DDT in plasticized PVC show that the larger but more flexible molecule of n-hexadecane diffuses more quickly than the smaller but rigid molecule of DDT (Park and Saleem, 1984).

(iii) Nature of the polymer

a. Chemical structure

The free volume theory is based on the availability of local free volume in the polymer, which is related to the flexibility of the polymer chains and the cohesive energy of the polymer. It was found that due to its unsaturated backbone, polybutadiene had a higher diffusion coefficient than hydrogenated polybutadiene (Michaels and Bixter, 1961). The introduction of methyl groups decreases the chain flexibility and results in a lower diffusivity value (Amerongen, 1950). Recent studies on the water low density polyethylene system (McCall and Douglass, 1984) suggest that solubility and diffusivity depend on the state of oxidation of the polymer. The oxygen groups act as traps to bind water molecules. Hydroxyl, hydroperoxide and carboxylic acid groups form the strongest traps. Ketones are weaker and ester groups exhibit negligible trapping.

b. Crosslinking

In some studies, it has been demonstrated that as the crosslinking increases, the diffusivity decreases and the activation energy increases (Atikmand and Barrer, 1955), suggesting that there is a tendency of the diffusion medium at high crosslinking to act as a molecular sieve. However, a smaller decrease for

large molecules was also reported, contrary to the above mentioned claim (Mears, 1957). DeCandia et al. (1982) report no change in diffusivity for crosslinked and uncrosslinked LDPE.

(iv) Glass transition temperature, T_g

In the study of sorption in polyvinyl alcohol (Mears, 1957) it was noticed for the first time that the slope of the Arrhenius plot changes on passing through T_g . This was attributed to increased segmental mobility of the polymer molecules above T_g . No changes were found in the slope of the Arrhenius-type plot for some gases (Stannet, 1966) which indicate the possibility that some polymers have a mean hole size which leads to transition effects with large penetrant molecules only. For many polymer vapour systems the sorption is Fickian above the glass transition temperature. Also, it has been reported in many cases that the diffusivity increases with the lowering of the glass transition temperature (Saleem, 1977), whereas non-Fickian sorption is observed below the glass transition temperature as explained earlier.

(v) Plasticizer

It is believed that the addition of a plasticizer decreases the cohesive forces between the polymer chains resulting in an increase in the segmental

mobility, which results in an increase in the rate of diffusion and a decrease in activation energy. A thorough study on the diffusion of various vapours in plasticized PVC confirms this behaviour (Saleem, 1977). It also reveals the effect of the chemical nature of the plasticizer on diffusion (Park and Saleem, 1984).

It has also been observed in the diffusion of gases in polyvinyl chloride plasticized with tricresyl phosphate that the diffusion coefficient first decreased up to 15% concentration, acting as an antiplasticizer by reducing the co-operative main chain molecular motion of polyvinyl chloride. However, beyond that limit of concentration the diffusivity was found to increase with increasing the concentration of plasticizer (Sefcik et al. 1983).

(vi)

Polymer morphology

The diffusivity of vapours in polymers is dependent on polymer morphology. In the case of polybutadiene it was found that the diffusivity drops suddenly after a 75% trans content in the polymer. At this stage, there is an onset of crystallinity which increases from zero to 80% on moving from 75 to 100% trans content (Brown et al. 1973). Studies on methylene chloride polyether ketone also show that the sorption of methylene chloride decreases with

increasing crystallinity of the polymer (Stober et al., 1984), whereas the rate of desorption is found to be independent of crystallinity.

Thermal history, annealing, drawing and quenching of the polymer also affect the sorption rates.

Uniplaner oriented films show faster sorption (Drechsel et al. 1953). Similar results were obtained for Polystyrene samples with various draw ratios (Nicolois et al. 1979). In the case of LDPE toluene system it was observed that the diffusion behaviour of the oriented samples was non-Fickian (Bischoff and Eyerer, 1984). The annealing of these samples resulted in a decay of the orientation and consequently a change in the diffusion mechanism. It reduces the strain of the molecules and their influence is reduced. It is interesting to note that it has been suggested that the transport properties appear to be extremely sensitive probes for detecting small variations in the micromorphology (De Candia et al. 1980).

(vii) Concentration dependence

At low concentrations the concentration dependence of diffusion coefficients can be expressed as follows (Park, 1950):

$$D = D_0 e^{\alpha C} \quad (29)$$

where D_0 is the diffusion coefficient at zero concentration, C is concentration and a is a constant which gives a useful measure of the concentration dependence. This dependence varies with the nature of the polymer and penetrant. Good solvents are expected to loosen the polymer structure resulting in greater mobility. Thus, it is reported that as the polymer penetrant interaction parameter increases, the concentration dependence also increases (Kokes and Long, 1953).

For a history dependent diffusion coefficient in the glassy state, the diffusion coefficient D_i resulting from the rapid change in concentration is given by:

$$D_i = D_0 e^{aC} \quad (30)$$

At constant concentration, it is assumed that the diffusion coefficient changes with time until a final value of equilibrium diffusivity, D_e , is reached:

$$D_e = D_0 e^{bC} \quad (31)$$

Where b is a larger constant than a .

The time dependence results from an increase in free volume. It is assumed that the rate of increase of diffusivity obeys a first order law:

$$\left(\frac{\partial D}{\partial t}\right) = \alpha(D_e - D) \quad (32)$$

where the rate constant α is also a function of concentration.

$$\alpha = \alpha_0 e^{\sigma C} \quad (33)$$

The overall differential equation relating D to C and t is then given by:

$$\left(\frac{\partial D}{\partial t}\right) = \left(\frac{\partial D}{\partial C}\right) \left(\frac{\partial C}{\partial t}\right) + \alpha(D_e - D) \quad (34)$$

By trial and error calculations, it is possible to obtain a , b , α , α_0 and D_0 giving a reasonable fit to sorption and desorption curves (Crank, 1953).

A brief review of the free volume theory which predicts the dependence of diffusion coefficients on concentration will follow.

2.6 Theories Predicting the Dependence of Diffusivity on Concentration

2.6.1 General

It should be recognized by now that the diffusion coefficient is dependent on concentration. Assuming that diffusivity is either independent of concentration or changes linearly (as an approximation) with concentration is both unrealistic and inconsistent with experimental evidence. However, the prediction of the dependence of

diffusivity on concentration has been a persistent problem. Such a problem is caused by our almost complete ignorance of the nature of the intermolecular forces which determine the interaction among different molecules and hence affect diffusivities. In addition, especially in the case of liquid diffusion, our very little knowledge about the structure of liquids makes it impossible, at this stage, to formulate theories which can rigorously predict the dependence of diffusion coefficients on concentration. In fact, until now the true mechanism of the diffusion processes remains an unrevealed mystery. In addition, as indicated by Tyrrell (1969), there is "a deceptive simplicity" about the phenomenological description of the process as well as confusion about definitions which are not wholly absent even from the modern literature.

A number of theories such as Bueche's theory (1957), the theory of Cohen and Turnbull (1959), Barrer's Zone Theory (1957), Brandi's theory (1959), and the Fujita's Free Volume Theory (1961) have been put forward to describe the dependence of diffusion coefficients on concentration in polymers. The Free Volume Theory due to Fujita (1961) appears to be the most successful and most widely used for describing diffusional behaviour of organic penetrants in amorphous polymers.

2.6.2 The Free Volume Theory

The Free Volume Theory was developed by Fujita (1961). According to this theory, the diffusion of a penetrant molecule in an amorphous polymer is only possible when the local free volume in the region of the penetrant molecule exceeds a certain critical value. The

magnitude of such a local critical free volume depends on the size of the diffusant and is determined by the total free volume present in the system. In this theory, the thermodynamic diffusion coefficient, D^* , is related to the fractional free volume of the system, f_v , by the expression:

$$D^* = A RT \exp\left[-\frac{B}{f_v}\right] \quad (35)$$

where A and B are constants which depend on the molecular size of the diffusant and on the polymer. The constant B increases with increasing the molecular size of the penetrant, hence, it leads to a decrease in the diffusion coefficient.

The dependence on concentration, temperature, and on the glass transition temperature, T_g , results from the dependence of the fractional free volume, f_v , on these quantities. If the free volumes are assumed to be additive, then:

$$f_v = f_o + \beta'' \phi \quad (36)$$

where f_o is the fractional free volume of the pure polymer, β'' is a parameter representing the contribution of the penetrant to the free volume and ϕ is the volume fraction of the penetrant.

At zero penetrant concentration, Equation (35) can be rewritten as follows:

$$D_o = A RT \exp\left[-\frac{B}{f_o}\right] \quad (37)$$

The dependence of the fractional free volume on the glass transition temperature, T_g , and the temperature, T , can be deduced from the Williams, Landel and Ferry (1955) relationship:

$$f_o = f_g + \Delta\alpha(T - T_g) \quad (38)$$

where f_g and $\Delta\alpha$ have the following universal values for amorphous polymers:

$$\begin{aligned} f_g &= 0.025 \\ \Delta\alpha &= 4.8 \times 10^{-4} \end{aligned}$$

The Free Volume Theory has achieved some success, however, it does not correctly predict the dependence of the mutual diffusion coefficient, D^V , of small penetrant molecules in amorphous polymers on temperature and concentration.

Recently, Vrentas and Duda and co-workers addressed the problems associated with the application of the Free Volume Theory to small penetrant molecules in a series of publications (1977, 1979, 1985a and 1985b). They proposed the following expression:

$$D^V = D_{01}(1-\phi_1)^2(1-2\chi\phi_1) \exp\left[-\gamma \frac{(\omega_1 V_1^* + \omega_2 \zeta V_2^*)}{V_{FH}}\right] \quad (39)$$

where γ is an "overlap" factor ranging from 0.5 to 1, ω_i is the mass

fraction of component i , V_i^* is the specific local critical free volume required for the unit diffusion step of component i , V_{FH} is the average hole free volume per gram of mixture, ϕ_1 is the volume fraction of the solvent, χ is the Flory-Huggins interaction parameter. D_{01} is a pre-exponential factor which depends on the temperature according to the following Arrhenius type expression:

$$D_{01} = D_0 e^{-(E_d/RT)} \quad (40)$$

The quantity ζ given in Equation (39) is defined by the following equation:

$$\zeta = \frac{V_1^* M_1}{V_2^* M_j} \quad (41)$$

where M_1 is the molecular weight of the solvent and M_j is the molecular weight of the "jumping" unit of the polymer.

Ju et al. (1981) tested Equation (39) using experimental data on poly(vinyl acetate), poly(methyl methacrylate), and polystyrene with chloroform, toluene, tetrahydrofuran, methanol and carbon disulphide. They concluded that Equation (39) provided an accurate description of diffusion in concentrated polymer solutions.

3. EXPERIMENTAL

3.1 Mathematical Description of the Physical System

The physical system employed in this investigation consists of a very thin rectangular polymer film which is suspended inside an electrorecording microbalance. The film is saturated with the penetrant under investigation. As soon as vacuum is turned on, it is assumed that the surface concentration of the penetrant drops instantaneously to zero. The polymer film under consideration extends from $-l$ to $+l$ in the x -direction.

Since unsteady-state diffusion is being considered here, Fick's second law should be employed:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left[D \frac{\partial C}{\partial x} \right] \quad (42)$$

with the following conditions:

(i) due to symmetry $\frac{\partial C}{\partial x} = 0$ at $x = 0$ and at all t

(ii) $C = 0$ at $x = \pm l$ and $t > 0$

(iii) $C = C_0$ at $t = 0$ and all x

The solution to Equation (42), using the separation of variables technique leads to the following expression:

$$C = [A \cos(\lambda x) + B \sin(\lambda x)] \exp - [\lambda^2 D t] \quad (43)$$

Application of the boundary and initial conditions mentioned earlier, combined with the orthogonality property of cosine functions leads to the following relations for λ and C :

$$\lambda = (2n+1) \frac{\pi}{2l} \quad (44)$$

$$C = \sum_{n=0}^{\infty} \left\{ \frac{4C_0 (-1)^n}{(2n+1)\pi} \cos\left[(2n+1) \frac{\pi x}{2l}\right] \exp\left[-\left(2n+1) \frac{\pi}{2l}\right]^2 D t\right. \right. \quad (45)$$

The quantity of liquid remaining in the polymer film per unit area, Q_t , is given by:

$$Q_t = 2 \int_t^{\infty} D \frac{\partial C}{\partial x} \Big|_{x=l} dt = \sum_{n=0}^{\infty} \left\{ \frac{4C_0}{l \left[\left(2n+1) \frac{\pi}{2l} \right]^2} \right\} \exp\left[-\left(2n+1) \frac{\pi}{2l}\right]^2 D t\right. \quad (46)$$

Since this series converges very rapidly, one can proceed using only one term. This term represents the system in the later stages of desorption where $D = D_0$.

$$Q_t \approx \left(\frac{16C_0 l}{\pi^2} \right) \exp \left[- \left(\frac{\pi}{2l} \right)^2 D_0 t \right] \quad (47)$$

Initially, the amount of liquid contained in the polymer film is denoted by Q_0 ; where

$$Q_0 \approx \frac{16C_0 l}{\pi^2} \quad (48)$$

If M_0 , M_t , and M_∞ denote the weights of the dry film and the liquid contained in the film per unit area at times 0, t , and ∞ , respectively, then

$$Q_t = M_t - M_\infty \quad (49)$$

$$Q_0 = M_0 - M_\infty \quad (50)$$

From the ratio of Equations (47) and (48) one obtains a linear plot of $\ln(M_t - M_\infty)$ versus t whose slope allows one to determine D_0 .

3.2 Design of the Experimental Apparatus

The experimental apparatus employed in this study consists of a CAHN 2000 electrorecording balance, a vacuum system, an HP 3421A data acquisition system, a Sargent-Welch temperature controller (Model ST) and a Unitron 2200 (Apple II plus compatible) microcomputer with printer.

A schematic layout of this apparatus is shown in Figure 2. The Cahn 2000 electrorecording microbalance consists of a control unit and a weighing unit, A. This weighing unit is enclosed by a glass vacuum bottle, B, having a vacuum outlet and three hangdown glass tubes, C, D and E. The polymer film F and counterweight stirrup G are suspended on the balance beam by means of hangdown wires and metal loops attached to the beam. The glass tube C, enclosing the polymer sample had a glass jacket, through which water at constant temperature (± 0.01 °C) is

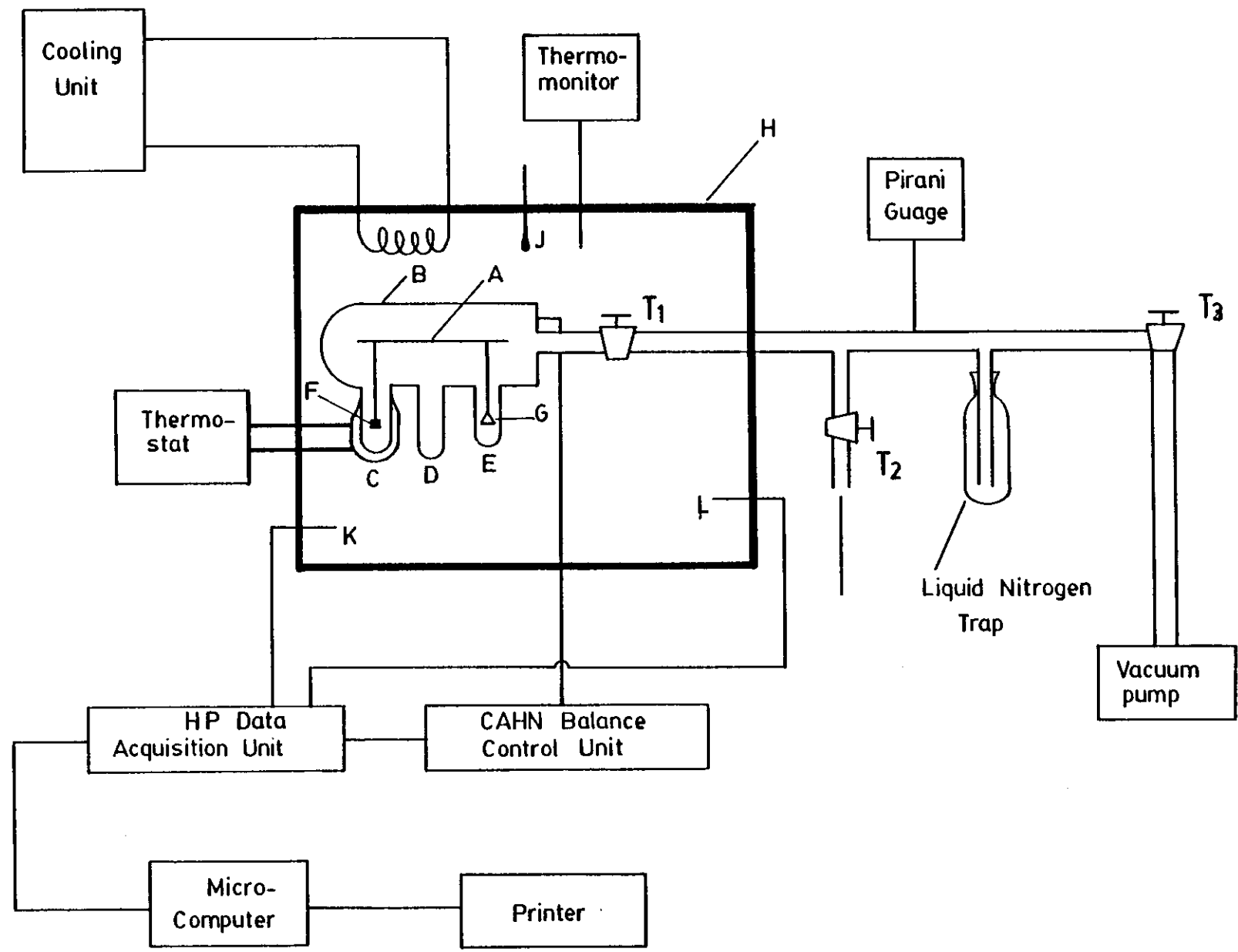


Figure 2 : A Schematic Diagram of the Experimental Set-up

circulated from a thermostat. In order to avoid condensation the whole weighing unit was fitted inside a metallic box, H. The temperature of this box is controlled by a Sargent-Welch Thermomonitor and an RMT cooling unit. The weighing unit is connected to the glass vacuum line through a cap. The vacuum line consists of a vacuum pump, liquid nitrogen trap, Pirani gauge and three taps T_1 , T_2 and T_3 . The weighing unit is evacuated by an opening tap T_1 , whereas tap T_2 is a vent and tap T_3 connects the system to the vacuum pump.

A precision mercury thermometer J and two thermocouples enable one to read the temperature at various points of the chamber. Normally, a variation of ± 0.3 °C is observed.

The data acquisition equipment consists of an HP 3421A data acquisition unit, a microcomputer and a printer. A 10 mv analog output from the electrobalance is fed to the data acquisition unit where it is digitized and sent to the microcomputer. The two thermocouples K and L are connected to the data acquisition unit.

The printer provides a hard copy of the weight averaged over a selected time interval and the temperatures read by the thermocouples K and L averaged over the same selected time interval.

3.3 Experimental Procedure

Rectangular specimens of the polymer film with a hole at the top are cut. The size and hence the weight of the sample depends on the system under consideration. Care was taken to have a sample weight which could enable us to operate below the 100 mg range limit of the microbalance. Each of these samples are then immersed in a test tube

containing the penetrant under investigation. This tube is already kept in a water basin at constant temperature. The sorption experiment is continued until sorption equilibrium is attained. The time required for this equilibrium depends on the polymer penetrant system; in most of the cases it did not exceed 24 hours. The equilibrium uptake of the penetrant is checked by periodically weighing the polymer film on a Mettler balance.

To start the desorption experiment the desorption chamber water circulating thermostat is set at the required temperature, and the electrobalance is calibrated according to the procedure described by the manufacturer.

Once sorption is complete the polymer film is removed from the liquid, and is sandwiched between two filter papers. This ensures the removal of the excess liquid from the surface of the polymer film, and thus a reproducible initial surface concentration of the penetrant can be achieved. The film is then suspended on the balance. The time between the removal of the film from the liquid up to the suspending of the film on the balance should not exceed 10 to 15 seconds. The balance is immediately opened to the vacuum system at a pressure of 0.01 mm Hg and desorption kinetics are followed by monitoring the weight loss with time on the microcomputer.

Reproducibility of results is checked by conducting duplicate runs.

4. NOMENCLATURE

A	=	Free Volume Theory Pre-exponential Factor or β Particle Count
B	=	Free Volume Theory Constant
C	=	Concentration; moles/unit volume
c	=	concentration; mass/unit volume
D	=	Diffusion Coefficient; m^2/s
E	=	Activation Energy; kJ/mol
F	=	Flux; moles/unit area x unit time
f	=	fractional Free Volume
L	=	Time Lag
ℓ	=	Film Thickness; m or mm
M	=	Mass; kg or gm
P	=	Permeability Coefficient
R	=	Universal Gas Constant
s	=	Solubility
T	=	Temperature; K
t	=	Time; seconds
V	=	Molar Volume; $m^3/kmol$ or L/kmol
v	=	Specific Volume; m^2/kg or L/gm

Superscripts

*	=	Thermodynamic
C	=	Co-ordinate-Fixed Frame of Reference
v	=	Volume-Fixed Frame of Reference

Subscripts

- 0, ∞ = Initial and at infinite time, respectively
- A, B = Components in a Mixture
- d = Diffusion
- e = Equilibrium
- g = Glass Transition
- i = Intrinsic or Component i
- t = Time

Greek Letters

- α = Thermal Expansion Coefficient or Constant
- β' = Thermodynamic Correction Factor
- β'' = Parameter Representing the Contribution of Penetrant to the Free Volume
- ϕ = Volume Fraction of Penetrant
- ζ = Quantity Defined by Equation (41)

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