Transport Properties of Gases in Polymers: Bibliographic Review

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LIST OF THE USED NOTATIONS

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<thead>
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<th>Acronym</th>
<th>Substance</th>
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<tr>
<td>PE</td>
<td>Polyethylene</td>
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<tr>
<td>HDPE</td>
<td>High density polyethylene</td>
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<tr>
<td>LDPE</td>
<td>Low density polyethylene</td>
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<tr>
<td>PP</td>
<td>Polypropylene</td>
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<tr>
<td>PVF2</td>
<td>Polyvinylidene fluoride</td>
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<tr>
<td>PTFE</td>
<td>Poly(tetrafluoroethylene)</td>
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<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
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<td>PEN</td>
<td>Poly(ethylene naphthalate)</td>
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<tr>
<td>PC</td>
<td>Polycarbonate</td>
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<td>He</td>
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<td>N(_2)</td>
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<td>H(_2)</td>
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<td>O(_2)</td>
<td>Oxygen</td>
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<td>CH(_4)</td>
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<td>CO(_2)</td>
<td>Carbon dioxide</td>
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<tr>
<td>C(_2)H(_4)</td>
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<tr>
<td>C(_3)H(_8)</td>
<td>Propane</td>
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<tr>
<td>CH(_3)Cl</td>
<td>Methyl chloride</td>
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Résumé — Transport de molécules gazeuses dans les polymères : revue bibliographique — Après quelques rappels concernant les lois classiques des phénomènes de transport, cet article, purement bibliographique, présente les différents modèles théoriques proposés pour décrire le mécanisme de transport d’espèces chimiques dans les polymères par diffusion moléculaire. Il s’appuiera ensuite sur de nombreuses études menées antérieurement, pour montrer que la perméabilité des gaz (ou vapeurs organiques) dépend fortement de la structure du polymère (cristallinité, histoire thermomécanique), de la taille et de la nature du pénétrant ainsi que des conditions de température et de pression.

Mots-clés : polymère, gaz, perméabilité, diffusion, solubilité.

Abstract — Transport Properties of Gases in Polymers: Bibliographic Review — After some general considerations and basic equations on transport phenomena in polymers, this review, exclusively bibliographical, presents different concepts and theoretical models that have been proposed and developed to describe the transport mechanism of molecular species in polymers by diffusion. Based on numerous previous studies, it will show how the permeability of gases (or organic vapours) depends strongly on the polymer structure (degree of crystallinity, thermal and mechanical histories), on the penetrant size and nature as well as on the conditions of temperature and pressure.

Keywords: polymer, gas, permeability, diffusion, solubility.
INTRODUCTION

Polymer materials are often used because of their good barrier properties, for instance in a number of important practical applications such as food packaging, protective coatings, selective barriers for the separation of gases, etc. The improvement of their performances requires a better knowledge of the factors governing the transport properties of the small molecules through polymer membranes. At the molecular level, the complete understanding of the transport mechanism is still far from satisfactory.

Penetrant transport through a polymer membrane can be defined as the property of this material to be penetrated and crossed by the gases molecules. It is described by a solution-diffusion mechanism.

In a general way, the transport phenomena can be decomposed into five successive stages (Crank and Park, 1968) and are represented in Figure 1:
- diffusion through the limit layer of the side corresponding to the higher partial pressure (upstream side);
- absorption of the gas (by chemical affinity or by solubility) by the polymer;
- diffusion of the gas inside the membrane polymer;
- desorption of the gas at the side of lower partial pressure;
- diffusion through the limit layer of the downstream side.

Let us clarify that the polymer membrane is considered as a homogeneous, non-porous material at a given temperature. Generally, the formation of a limit layer of gas staying on each side of the membrane is not observed and the resistances associated to the steps 1 and 5 are negligible relatively to the others. Since the phenomena of concentration polariation are weak, the transport of a gas molecule through a homogeneous polymer matrix can be described as the following process: condensation and solution of the penetrant at one surface of the membrane, followed by diffusion, in a form of a liquid, through it under the influence of a concentration gradient (chemical potential) and finally evaporation at the other surface to the gaseous state (Naylor, 1989). The permeability coefficient is, by definition, the product of the solubility coefficient by the diffusion one. We are going now to describe more exactly these processes.

1 CLASSIC LAWS OF THE TRANSPORT PHENOMENA

1.1 The Diffusion Coefficient

The diffusion is the process by which a small molecule (organic liquids, vapours, gases, etc.) is transferred in the system due to random molecular motions. So, it is a kinetic term that reflects the penetrant mobility in the polymer phase.

1.1.1 Fick’s Laws of Diffusion

Let us consider a polymer membrane of thickness $l$, of surface $A$ submitted to a fluid and $Q$ the total amount of penetrant which has passed through this membrane during the time $t$. The quantity of penetrant, which crossed the polymer membrane during one unit of time and by unit of area, is $J$, the diffusive flux of a penetrant molecule, given by:

$$ J = \frac{Q}{At} \quad (1) $$

The Fick’s first law (Fick, 1855; Crank, 1975) establishes a linear relation between the flux of substance diffusing through a membrane and the concentration gradient between both sides of the membrane:

$$ J = -D \nabla C \quad (2) $$

where $D$ is called the diffusion coefficient (length$^2$/time, cm$^2$/s).

This first law is applicable in the steady state, reached when the concentration does not vary with time and the flux is constant. In the unidirectional case, when the diffusion occurred only in one direction $x$, the relation reduces to:

$$ J_x = -D \frac{\partial C}{\partial x} \quad (3) $$

This simplification is valid when the thickness of the considered membrane is much smaller than the other dimensions (for example, the diameter in the case of a
circular membrane). If this condition is not verified, the phenomena of diffusion in the other directions cannot be neglected any more.

In transient state, the transfer of matter by diffusion is different from zero and the penetrant concentration is a function of position and time. Fick’s second law of diffusion describes this non-steady state and is given by (in the unidirectional case):

$$\frac{\partial C(x,t)}{\partial t} = - \frac{\partial J_x}{\partial x} = \frac{\partial (D \nabla C)}{\partial x} = \frac{\partial D}{\partial x} \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2}$$

(4)

$C(x,t)$ is the local penetrant concentration at a position coordinate $x$ and at time $t$. This differential equation can be integrated, by taking into account the initial condition ($t = 0$) and boundary conditions ($x = 0, l$) (Crank, 1975), and constitutes the theoretical reference for numerous problems of common diffusion. The resolution of this equation gives the concentration profile in the diffusion zone at different intervals of time.

For numerous penetrant-polymer systems, and in defined conditions, $D$ can be considered as constant in all the membrane thickness, the previous equation reduces then to:

$$\frac{dC}{dt} = D \frac{d^2 C}{dx^2}$$

(5)

In most cases, $D$ is dependent on the sorbed penetrant concentration and is written as $D(C)$. Then, one can define a mean diffusion coefficient over the entire range of concentration (Crank and Park, 1968) by:

$$D = \frac{1}{C_M - C_v} \int_d^M D(C) \, dC$$

(6)

$$D = \frac{c_y}{c_v} \int_d^M D(C) \, dC$$

(6)

Apparent values of $D$ can be obtained by the “time lag” method developed by Barrer (1939). This analytical method consists in representing the quantity of penetrants which has crossed the sample during the time $t$, versus time (Flaconnèche et al., 2001).

In steady state, this amount is directly proportional to time. The intercept of the time axis with the extrapolated linear steady state portion of the curve is called the time lag, $\theta$. The coefficient $D$ can then be evaluated (Rogers, 1985) from this characteristic time. This time represents the time from which the steady state is reached. If $D$ is supposed independent of the concentration (case of a constant concentration gradient within the membrane), the diffusion coefficient is related to the time lag by the following relation (Comyn, 1985; Crank and Park, 1968):

$$D = \frac{j^2}{6\theta}$$

(7)

Qualitatively, this relation demonstrates that the transient state, which corresponds to the establishment of the concentration profile within the membrane, will be all the more long as $D$ will be small. From 1957, Frisch (1957) proposed expressions for the time lag, supposing that $D$ depends on the concentration (with an exponential or linear relation), but without explicitly solving the diffusion equation of Fick.

1.1.2 Mechanisms of Diffusion

To understand the mechanisms of diffusion on a microscopic level, it is important to study the polymer-solute interactions. The polymer structure is an important parameter to take into account because the transport phenomena in a glassy polymer differ totally from those in a rubbery polymer. The diffusion in a matrix polymer can be classified into three categories (Crank, 1975; Rogers, 1985; Aminabhavi and Aithal, 1988) which depend on the relative mobilities of the penetrant and polymer:

- the case I or Fickian: the diffusion process has a rate much smaller than that of the relaxation modes of the polymeric matrix. The sorption equilibrium is quickly reached, the boundary conditions are independent of time and do not depend on swelling kinetics;
- the case II, or non-Fickian behaviour, relates to a fast diffusion process compared with the simultaneous relaxation processes of the polymer. Here, the sorption phenomena are complicated by a strong dependence with the swelling kinetics. These deviations from the Fickian behaviour are generally found in the case of the sorption of organic vapours by solid polymers and can persist until $T_g + 15^\circ C$;
- the anomalous diffusion which refers to a process when the diffusion and the polymer relaxation rates are comparable. The sorption and the transport of molecules are affected by the presence of pre-existing microvoids in the matrix, the penetrant motion is influenced by the geometrical structure of the polymer.

These deviations from the Fickian behaviour will not be discussed in more details. However, it is important to underline that when a polymer is highly plasticized by a penetrant, the coefficients of diffusion and solubility may become a function of the concentration and of time, consequently, the problem to be solved is then non-Fickian (Stern and Trohalaki, 1990; Stern, 1994). To have an idea of the involved mechanism of transport, a common practice consists in adjusting the sorption results (Crank and Park, 1968; Aminabhavi and Aithal, 1988) by a law of the type:

$$\frac{M_t}{M_\infty} = k t^n$$

(8)

where $M_t$ and $M_\infty$ represent respectively the mass uptake of the penetrant at time $t$ and at long times, that is when the
equilibrium is reached, \( k \) is a constant. The value of \( n \) informs about the type of transport mechanism. A value of \( n = 0.5 \) indicates a Fickian diffusion whereas \( n = 1 \) relates to the case II. Intermediate values of \( n \) suggest a combination of these two mechanisms. On the other hand, the discrepancies between the experimental sorption and desorption curves are representative of different kinetics and then, of a concentration-dependent diffusion coefficient (Crank, 1975; Brolly et al., 1996a, 1996b).

1.2 The Solubility Coefficient

At a given temperature, the local concentration \( C \) of the gas dissolved in the polymer can be related to the pressure by the following relation:

\[
C = S(C)p
\]

(9)

where \( S(C) \) is the solubility coefficient (which may be a function of \( C \) or \( p \)). This coefficient which has a thermodynamic origin, depends on the polymer-penetrant interactions as well as on the gas condensibility. For low pressures and ideal gas, Henry’s law is obtained (Stannett, 1968):

\[
C = k_D p
\]

(10)

where \( k_D \) is the proportionality constant of Henry’s law. In fact, it is the solubility coefficient when there is no concentration dependence.

In practice, for the permeation of simple gases of low molecular weight in rubbery polymers (that is at temperatures above their glass transition temperature), and under relatively moderate pressures, the diffusion mechanism is Fickian and the departures from Henry’s law for the sorption are negligible (Flaconnèche, 1995). However, in the most general case, \( S \) is a function of the temperature, the pressure or the concentration. The various expressions of \( S \) corresponding to the different sorption modes will be detailed in Section 2. Attention may be paid to the used units:

– the concentration \( C \) is expressed in \( \text{cm}^3 \text{ (STP)/cm}^3 \text{ polymer} \). In a more explicit way, it is the concentration of the sorbed gas (calculated in the Standard Conditions of Temperature and Pressure, i.e. 273 K and 1 atm = 1.013*10^5 Pa) by the polymer which is subjected to a pressure \( p \) of the penetrant;

– the solubility coefficient \( S \) is given in \( \text{cm}^3 \text{ (STP)/cm}^3 \cdot \text{MPa} \).

1.3 The Permeability

Figure 2 represents a plane homogeneous membrane of thickness \( l \) such as \( p_M \) and \( p_V \) are the partial pressures at the two sides of the membrane \( (p_M > p_V) \). When Henry’s law is satisfied, the diffusive flux in steady state is given by:

\[
J = DS \left( \frac{p_M - p_V}{l} \right)
\]

(11)

The product \( DS \) is called, by definition, the permeability coefficient:

\[
Pe = DS
\]

(12)

The coefficient of permeability appears as the product of a kinetic factor \( (D) \) which reflects the dynamics of the penetrant-polymer system and of a thermodynamic term \( (S) \) which depends on the penetrant-polymer interactions. So, this coefficient represents the ease with which the gas crosses the membrane when this one is submitted to a pressure gradient.

In the absolutely general case where no hypothesis is done on the dependence of the coefficients of diffusion and solubility on the gas concentration in the polymer, the definite transport coefficients are in fact mean transport coefficients. The diffusion coefficient is then given by Equation (6) and the following relation is obtained for the solubility (Crank and Park, 1968; Crank, 1975; Rogers, 1985; Stern, 1994):

\[
\bar{S} = \frac{C_M - C_V}{p_M - p_V}
\]

(13)

The mean permeability coefficient of the gas through the polymer is defined by (Crank and Park, 1968; Crank, 1975; Rogers, 1985):

\[
\overline{Pe} = \overline{D \bar{S}}
\]

(14)

This definition will remain valid independently of the models used to express the dependence of \( D \) and \( S \). In a very general way, \( Pe \) depends on the polymer nature, the gas, the upstream and downstream pressures and the temperature. Besides, in the case of binary gas mixtures, this coefficient depends on the partial pressures of each gas (even in terms of fugacity) that is on the mixture composition. This point will
not be discussed here. However, the study of the transport mechanisms also requires information about the evolution of $D$ and $S$ with these parameters (Costello and Koros, 1993; Dhingra and Marand, 1998; Thundyil et al., 1999). The dimension of the permeability coefficient is: volume of gas (STP)/(length·time·pressure) or: cm$^3$ gas (STP)/(cm·s·MPa). In the permeation experiments, one measures $Pe$ by applying a downstream pressure close to zero (Flaconnèche, 1995), then $p_M = p_v \ll C_v \ll 0$. The mean solubility coefficient will be reduced so, with a good approximation, to the gas solubility on the upstream side of the membrane:

$$S \equiv \frac{C_M}{p_M} = \frac{C_x}{p}$$

$C_x$ being the maximal concentration of the mobile species on the upstream surface of the membrane under a pressure $p$.

## 2 Sorption Modes

The sorption is the term generally used to describe the dissolution of the penetrant in the matrix polymer (Crank and Park, 1968; Rogers, 1985; Naylor, 1989). This term includes the absorption, the adsorption, as well as the trapping in microvoids or the clustering of aggregates. It should be noted that in the same polymer membrane, diffusing molecules may be sorbed according to different sorption modes. Besides, the distribution of the penetrant according to these various modes may change with the temperature, the sorbed concentration, the swelling behaviour of the matrix, time, etc.

The quantity of solute molecules dispersed in the matrix polymer at equilibrium and their sorption mode, in given conditions, are governed by the thermodynamics of the polymer-penetrant system, in particular by the nature and the force of the interactions. Figure 3 presents the five classic cases of sorption. As for Table 1, it indicates for each model the nature of the dominant interactions. The case of binary gas mixtures, which will not be discussed here, is even more complex because it is necessary, furthermore, to take into account the non-idealities associated to the behaviour of the gas phase as also the effects of competition between both components. These features may lead to strong differences if compared to the solubility values estimated for pure gases (Chern et al., 1983; Costello and Koros, 1993; Thundyil et al., 1999).

### 2.1 Henry’s Law Sorption

The case I, the simplest, was presented in Section 1.2: the gas is considered as ideal and it exists a linear relation between the penetrant concentration in the membrane and its partial pressure:

$$C = k_D p$$

The constant $k_D$ is in fact $S$, the solubility coefficient of the gas in the polymer, independent of the concentration at a

![Figure 3](https://example.com/figure3.png)

Typical isotherm plots of sorbed concentration versus vapour pressure.
given temperature. The gas is here randomly dispersed in the matrix so that neither polymer-penetrant nor penetrant-penetrant pairs are preferred. This mode is observed essentially for low pressures when the penetrant-penetrant and the penetrant-polymer interactions are weak in front of the polymer-polymer interactions.

2.2 Langmuir-Mode Sorption

The case II corresponds to a predominance of the penetrant-polymer interactions. Diffusing molecules occupy specific sites in the polymer, for example, pre-existing microvoids or high-area inorganic fillers. When all the sites are occupied, a small quantity of diffusing molecules may solubilise. The penetrant concentration is then given by:

\[ C_H = \frac{C_H'bp}{1 + bp} \]  

where \( C_H' \) is a “hole saturation” constant and \( b \) is a “hole affinity” constant.

2.3 Dual-Mode Sorption

This dual mode was proposed to describe curves observed in the case of sorption of low-activity gases in glassy polymers. It postulates the existence of two populations of diffusing molecules. This situation corresponds to the combination of the two previous modes and will be detailed in Section 3.1.1. Nevertheless, this model is valid for moderate pressures, in the absence of strong interactions. It cannot describe the sorption phenomena when there is some swelling or plasticization of the matrix by the sorbed molecules.

2.4 Flory-Huggins Mode

The interactions between the diffusing molecules are stronger than the penetrant-polymer interactions and the solubility coefficient increases continuously with pressure. Two physical interpretations of this behaviour are possible: first of all, a plasticization of the polymer by the sorbed molecules or the association of clusters in the case of water-hydrophobic all, a plasticization of the polymer by the sorbed molecules.

\[ \chi \]

represents the enthalpic interaction parameter between the component in the mixture, defined as the vapour pressure of the gas \( p \) divided by the saturation vapour pressure \( p^0 \) at the experimental temperature, \( \phi \) is the volume fraction of the permeant in the polymer and \( \chi \) the enthalpic interaction parameter between the polymer and the solute.

2.5 BET Mode

This last case corresponds to the combination of the Langmuir and Flory-Huggins modes. In practice, it can be representative of the sorption of water in highly hydrophilic polymers (Hernandez and Gavara, 1994; Hernandez et al., 1992): initially, the water molecules are strongly sorbed in specific sites corresponding to polar groups, then at higher pressures, the clustering process may occur.

3 THEORIES OF GAS DIFFUSION AND MODELS

Numerous theoretical models have been previously proposed (Crank and Park, 1968; Comyn, 1985; Aminabhavi and Aithal, 1988; Stern and Trohalaki, 1990; Stern, 1994) to describe the transport mechanism of species in polymers by diffusion at a molecular level. Such models supply expressions of the coefficients of diffusion and permeability from statistical mechanical considerations (free volume theory) and energetic or structural considerations. The formulation of these coefficients is complicated by the fact that the transport phenomena are due to different mechanisms in rubbery and glassy polymers, i.e., at temperatures respectively above or below their glass transition temperature. Besides, parameters such as the degree of crystallinity of the polymer, its swelling by the sorbed molecules as well as its thermal history (Crank and Park, 1968; Comyn, 1985) are significant.

3.1 Glassy Polymers (\( T < T_g \))

The transport mechanisms in polymers at a molecular level are not completely understood when \( T < T_g \). All the models proposed in the literature are phenomenological and contain one or several adjustable parameters which should be determined experimentally and are suitable only to a limited number of systems (Stern, 1994).

A polymer in the glassy state has a specific volume \( V_s \) bigger than the specific volume of equilibrium \( V_r \). This difference, due to the non-equilibrium character of the glassy state, is at the origin of the non-linearity of the sorption isotherms (Barrer et al., 1958) that is the dependence of the solubility coefficient on pressure. On the other hand, when a polymer is exposed to a vapour, the gas molecules dissolved in the matrix may change the polymer microstructure. This process can lead to a decrease of \( T_g \) and an increase of the specific volume \( V_s \) that is a plasticization effect (Zhang and Handa, 1998). In some extreme cases, for high pressure, the opposite effect may be observed: the \( T_s \) matrix will raise, contrary to \( V_r \), due to a compression of the polymer, thereby a reduction of its segmental motions. The phenomena are much more complex in the glassy polymers. To describe the solution and the diffusion of molecules in glassy polymers,
we shall detail the dual-mode sorption model, the most usually used (Barrer et al., 1958), then the gas-polymer matrix model (Sefcik et al., 1983; Raucher and Sefcik, 1983a).

### 3.1.1 Dual-Mode Sorption Model

This model, initially proposed by Barrer et al. (1958) to explain the dependence on concentration of the solubility coefficient found for the glassy polymers, was then extended by Koros and Paul for the diffusion coefficient (Paul and Koros, 1976; Koros et al., 1976).

This model postulates that there are two distinct populations of diffusing molecules (with local equilibrium between them): molecules dissolved in the polymer by an ordinary dissolution process with a concentration \( C_D \) and a second population corresponding to trapped molecules by adsorption on specific sites (micropores or holes) with a concentration \( C_H \). Generally, one thinks that these holes are generated by the slow relaxation processes associated to the glass transition or by the unrelaxed volume frozen during the glass transition (Stastna and De Kee, 1995). The relative proportions of the penetrant in every state depend on the total concentration. Besides, one supposes that at the equilibrium pressure \( p \), the concentration of the dissolved molecules in the polymer by an ordinary mechanism dissolution, \( C_D \), obeys Henry’s law (Eq. (10)), and, that the concentration of molecules sorbed in a limited number of pre-existing microcavities is given by the equation of Langmuir:

\[
C_H = \frac{C_H' b p}{1 + b p}
\]

where \( C_H' \), called a “Langmuir saturation” constant, is directly related to the global volume of specific sites, that is a measure of the concentration in “holes”, and \( b \) is a constant, characterising the affinity for these sites (see Section 2.2).

The total concentration is then given by:

\[
C = C_D + C_H = k_D p + \frac{C_H' b p}{1 + b p}
\]

which can be written as a function of Henry’s concentration:

\[
C = C_D \left(1 + \frac{K}{1 + \alpha C_D}\right)
\]

with:

\[K = \frac{C_H' b}{k_D}\] and: \[\alpha = \frac{b}{k_D}\]

In this model, the solubility coefficient has for expression:

\[
S = \frac{C}{p} = k_D + \frac{C_H' b}{1 + b p}
\]

It may be noticed that \( S \) decreases when the pressure increases.

Initially, it was assumed that the population of Langmuir was completely immobilised and did not participate in the transport (Vieth and Sladek, 1965; Raucher and Sefcik, 1983a) what implied a constant permeability coefficient. Experimentally, permeability measurements have shown evidence of a decrease of the permeability coefficient with the upstream gas pressure: let us quote, for instance, the case of \( CO_2 \) in polycarbonate at \( 35^\circ C \) (Koros et al., 1976). Petropoulos (1970) and, later, Paul and Koros (1976) supposed that the population of Langmuir had a partial mobility compared with the other population, i.e., the molecules trapped in “holes” were not completely immobilised. The approaches of these authors differ by the fact that Petropoulos (1970) considered that the driving force, responsible for the substance transport, is due to a chemical potential gradient whereas Paul and Koros (1976) developed a model with partial immobilisation but based on a concentration gradient. These latter ones were able to obtain expressions for the coefficients of diffusion, permeability and time lag (Koros et al., 1976).

It is so supposed that every population has its own constant diffusion coefficient: \( D_H \) for the dissolved molecules and \( D_H \) for the others (\( D_H \) is generally weaker than \( D_D \) because the diffusional jumps in the environment of Henry’s population are easier). Besides, it is based on the assumption that gases do not interact with the matrix (in particular, there is no swelling): the various constants \( k_D', D_H \) and \( D_H \) are independent of the pressure and concentration. In the hypothesis where the fluxes of both species are independent, the total flux of diffusing molecules through the polymer is (Paul and Koros, 1976; Aminabhavi and Aithal, 1988):

\[
J = J_D + J_H = -\frac{\partial}{\partial x} (D_D C_D + D_H C_H)
\]

\[
= -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x}
\]

It is possible to show that, from a mathematical point of view, the previous equation is equivalent to the following one:

\[
J = -D_{\text{eff}} \frac{\partial C_D}{\partial x}
\]

where \( D_{\text{eff}} \) is an effective diffusion coefficient, dependent on the concentration (or the upstream pressure) given by (Paul and Koros, 1976; Koros et al., 1976):

\[
D_{\text{eff}} = D(C) = D_D \left[1 + \frac{K (D_H / D_D)}{(1 + \alpha C_D)^2}\right]^{1/2}
\]

Often one defines: \( D_H / D_D = F \leq 1 \).
This model can be expressed in a different way, by giving a physical meaning to the parameter \( F \). Indeed, the authors (Paul and Koros, 1976; Koros et al., 1976) considered that the population of diffusing molecules is divided into two categories:

- all the species dissolved by ordinary dissolution plus a fraction \( F \) of the molecules trapped in microcavities are fully mobile and have a diffusion coefficient \( D_p \). It represents a concentration \( C_p + F C_{ip} \);
- a fraction \( (1-F) \) of the latter species is totally immobilised representing a concentration \((1-F)C_{ip}\).

Hence, the permeability coefficient is expressed as follows:

\[
Pe = k_p D_D \left( 1 + \frac{FK}{1 + bp} \right)
\]

and the time lag is given by:

\[
\theta = \frac{f^2}{6D_D} \left[ 1 + f(K, F, b, p) \right]
\]

where \( f \) is a complex analytical function of the listed parameters. When the population of Langmuir is little numerous or with no mobility \((F = 0)\), the extreme case of Henry’s model is found.

The influence of the pressure on the coefficients of solubility, permeability and on the time lag in the glassy polymer-gas systems is expressed via the distribution of the gas molecules between the two sorption modes. Although \( k_p \), \( D_H \) and \( D_D \) are supposed to be constant, the effective coefficients of solubility and diffusion change with the pressure in the same way as the report \( C_p/C_{ip} \) which evolves continuously with \( p \) (Eq. (18)). When strong interactions take place between the polymer and the penetrant (plasticizer which modifies the polymer state), this model is modified by introducing an exponential dependence of \( D \) with concentration (Stern and Saxena, 1980; Aminabhavi and Aithal, 1988). This model was generalised by Fredrickson and Helfand (1985) by taking into account the coupling between both diffusing species, that is a possible exchange between the two populations (from Henry to Langmuir mode for example). The dual-mode sorption model has represented in a satisfactory way the solubility and the gases transport in glassy polymers, polar or not (Aminabhavi and Aithal, 1988; Urugami et al., 1986) but there are some major drawbacks. The nature and the distribution of microcavities are not really known; they are described by free volume pockets of lower density. From a macroscopic point of view, we can mention that certain authors observed the existence of two different populations, by experiments of nuclear magnetic resonance of carbon 13 \(^{13}\text{C}-\text{NMR} \) carried out on CO\(_2\) sorbed in polycarbonate (Cain et al., 1991) or polystyrene (Bandis et al., 1993).

### 3.1.2 Gas-Polymer Matrix Model

This second model expressing the dependence on concentration of sorption and gases transport phenomena in glassy polymers was developed by Sefcik and Raucher (Raucher and Sefcik, 1983a, 1983b; Sefcik et al., 1983). It is based on the assumption that there is only one population of penetrant but that there is an interaction between the solute and the polymer matrix. The presence of these sorbed molecules can then perturb the structural properties and the dynamics of the polymer and thereby the transport characteristics of the system. Let us underline here that, in all the molecular approaches (see below Section 3.2.1) expressing the dependence of \( D \) on the temperature (of Arrhenius type, see below Section 4), the common idea is that the activation energy of the diffusion represents the energy necessary for the separation of macromolecular chains by cooperative motions of sufficient amplitude to allow the penetrant to execute its diffusional jump.

This model supposes that the interactions between the sorbed molecules and the matrix facilitate the penetrant jumps between chains and that the variations of the diffusion coefficient are a direct result of the modification of the main-chain motions (increase of the frequency of the cooperative motions (Pace and Datyner, 1979c)). In fact, it is proposed that the presence of the penetrant will reduce the intermolecular forces between the polymer chains, resulting in a decrease of the activation energy necessary for the separation of chains. The increase of the penetrant concentration leads, via an enhanced segmental mobility of the chains, to a higher diffusion coefficient and a lower solubility coefficient. From a mathematical viewpoint, this theory proposes the following relation to express the interaction between the penetrant and the polymer:

\[
S = S_0 \exp(-\alpha' \kappa)
\]

with:

\[
\kappa = \frac{T_s(0) - T_s(C)}{T}
\]

\( S_0 \) is the solubility value to zero concentration, \( \alpha' \) a constant, \( T_s(0) \) and \( T_s(C) \) are respectively the glass transition temperature of the pure polymer and that of the polymer-gas system. If one supposes a linear diminution of \( T_s \) with concentration (Raucher and Sefcik, 1983a), Equation (26) becomes:

\[
S = S_0 \exp(-\alpha C)
\]

This equation can be written as (after a limited development):

\[
S(C) = \frac{S_0}{1 + \alpha C}
\]
α being a new constant. This theory was extended to include
the diffusion coefficient $D$. One supposes that $D$ increases
with the frequency of the cooperative main-chain motions
(Pace and Datyner, 1979a). The following expressions are then obtained:

$$D = D_0(1 + \beta^*\kappa)\exp(\beta^*\kappa)$$

(30)

Or, by supposing that a linear relation exists between $\kappa$ and $C$:

$$D = D_0(1 + \beta C)\exp(\beta C)$$

(31)

$S_0$ and $D_0$ are the transport coefficients in the limit of zero
concentration, they have not really a physical meaning but
they describe rather well the system behaviour if there were no
change induced in the polymer matrix. Experimentally, $D$
varies during the experiment. Then, it is better to talk about an
effective diffusion coefficient. Besides, if the term $\beta C$ is small,
the previous equation becomes (Raucher and Sefcik, 1983b):

$$\bar{D} = D_0 \exp(\beta C)$$

(32)

In the previous equation, and in the two following ones,
what the authors have called $C$ is in fact the concentration on
the upstream side of the membrane, which corresponds to $C_{\infty}$. The following expression is thus obtained for the
permeability coefficient:

$$Pe = D_0 S_0 \exp[(\beta - \alpha) C]$$

(33)

Concerning the time lag, Raucher and Sefcik (1983b)
proposed:

$$\theta = \frac{l^2}{6D_0} \frac{10 + 25\beta C + 16(\beta C)^2}{10(1 + \beta C)^3}$$

(34)

These same authors (Sefcik et al., 1983; Sefcik and
Schaefer, 1983) have studied the transport of $H_2$ and $CO_2$
in PVC plasticized (with various contents of plasticizers)
at room temperature (under relatively low pressures: until
0.4 MPa). Their $^{13}$C-NMR experiments have shown an
evolution of the characteristic times of the cooperative main-
chain motions similar to that of the effective diffusion
coefficients of gases (calculated from time lag values). More
exactly, they have shown that a matrix modification
(plasticization or antiplasticization effect) has an influence
on the gas diffusion coefficients.

### 3.1.3 Comparison of these Two Models

Different research teams were interested in these two models
to report their results. The opinions are shared as for their
validity.

Raucher and Sefcik (1983a, 1983b), as underlined earlier,
obtained a relationship between the effective diffusion
coefficients and the frequency of the cooperative main-chain
motions of the polymer, what shows the importance of the
molecular motions in the determination of the transport
parameters. Then, the diffusion coefficient depends on
concentration, what is incompatible with the initial
assumptions of the dual-mode sorption model considering
that $D_H$ and $D_H$ are constant. On the other hand, they studied
the CO$_2$-polycarbonate system at 35°C, the pressure varying
from 0 to 2 MPa (Raucher and Sefcik, 1983b). They analysed
the results of sorption and permeation by using these two
models. The time lag values deduced from the gas-polymer
matrix model are in good agreement with the experimental
results on all the range of studied pressure, contrary to the
dual-mode sorption model. According to them, the dual-
mode sorption model is based on a correct mathematical
description but on invalid physical assumptions, which are
the existence of two different populations of diffusing
molecules and the absence of gas-polymer interactions. Also,
let us quote Brolly et al. (1996a, 1996b) who determined
experimentally the effective coefficients of solubility and
diffusion of CO$_2$ in PET and in PEN, at room temperature,
the pressure varying from 0.0125 to 0.5 MPa. These authors
used the finite difference modelling for obtaining the
parameters relative to the two models and so the variations of
the effective diffusion coefficient with the penetrant
concentration. They were not able to conclude as for the
validity of one of those models. Indeed, the dual-mode
sorption model seemed more successful to report their results
but, on the other hand, they observed a single population of
CO$_2$ molecules by infrared spectroscopy and additional
experiments proved that the sorbed CO$_2$ interacted with the
polymer.

### 3.2 Rubbery Polymers ($T > T_g$)

To describe the diffusion of small molecules in polymers
above their glass transition temperature, a certain number of
molecular models and theories derived from the free volume
theory were proposed (Crank and Park 1968; Comyn, 1985).
The models are based upon analysis of the relative mobility
of the diffusing molecules and of polymer chains by taking
into account relevant intermolecular forces. This second type
of approach does not offer a precise description of the
phenomenon but relates, thanks to statistical mechanical
considerations, the diffusion coefficient to the free volume
of the system. These models developed for rubbery polymers
were, in some cases, applied to glassy polymers (Stern and

#### 3.2.1 Molecular Models

A certain number of formulations are based on energy
considerations, let us describe them briefly. Barrer (1937)
was the first one to show that the diffusion of molecules in
polymers was a thermally activated process. Then, various
theories were developed to explain this Arrhenius behaviour.
with temperature (Kumins and Kwei, 1968). In these approaches, the diffusing molecule moves from a position to the other one when a sufficient amount of activation energy is available for the system (the solute plus the surrounding chains). In other words, the energy for diffusion is postulated to arise from the need to separate the polymer matrix sufficiently to allow the permeant molecule to make a unit diffusional jump.

The first molecular models were relatively simple (Fig. 4) but they were able to predict only the diffusion activation energy and not the diffusion coefficients. These models sometimes required adjustable parameters (Rogers, 1985; Aminabhavi and Aithal, 1988; Stern and Trohalaki, 1990) whose physical meaning was not always well defined (structure, volume, energy).

In the Activated Zone Theory of Barrer (1957), this activation energy is said distributed between the various degrees of freedom of the system. The important idea is that the cooperative segmental motions of the polymer participate in the diffusion process. Brandt (1959) suggested afterwards to define the activation energy from considerations on the molecular structure of the polymer. In this theory, a molecular model is formulated where the activation energy is decomposed into two terms: \( E_D = E_i + E_b \). The first term characterises the intermolecular energy \( E_i \) required to overcome the attractive forces between chains and create a “hole” in the polymer structure for the penetrant. The second term represents the intramolecular energy \( E_b \) used to bend the neighbouring chains of the penetrant. These two terms depend mainly on the penetrant diameter \( \sigma_p \left( E_i \propto \sigma_p^1; E_b \propto \sigma_p^2 \right) \), the chain length involved in diffusion, the length of an elementary jump, etc. The thermal energy is not considered here. This theory has been applied successfully for the diffusion of different molecules (CO\(_2\), CH\(_3\)Cl, CHF\(_3\) and SF\(_6\)) in PTFE (Brandt and Anysas, 1963), and for simple gases through PE (Michaels and Bixler, 1961b). It allowed to show that the evolution of \( E_D \) with \( \sigma_p^2 \) was not strictly linear.

DiBenedetto and Paul (DiBenedetto, 1963; DiBenedetto and Paul, 1964) developed two different approaches, one based on statistical mechanics (fluctuations theory) applied to diffusion in glassy polymers, and the other on the molecular theory for transport in rubbery zones. In this last approach, the activation energy of the diffusion is equal to the potential energy difference between the “normal” dissolved state and the “activated” state in which the cylindrical cavity allowing the penetrant to move is present (Fig. 4). This variation of the interaction energy between macromolecules is defined by a 6-12 Lennard-Jones potential.

More recently, Pace and Datyner (1979a, 1979b, 1979c, 1980) proposed a diffusion theory, which incorporated both DiBenedetto and Paul’s model and Brandt’s theory. They suggested that the transport process could be due to two separate mechanisms: diffusion along the chain direction and perpendicular jumps to the main-chain direction. It is these latter jumps across chains that control the time scale of the transport phenomenon and define the activation energy of diffusion. A good agreement between their model’s predictions and the experimental results, for amorphous or semicrystalline polymers, is obtained to express the dependence of the activation energy on the penetrant diameter. They have also extended their model to the diffusion of more complex molecules such as organic solvents, dying agents (Pace and Datyner, 1979b).

\[ \text{Figure 4} \]
First molecular models for diffusion in rubbery polymers.
The recent development of techniques of microstructure numerical simulation makes possible the modelling of transport phenomena in polymers, especially by application of Monte-Carlo simulation techniques, molecular dynamics (MD), Brownian motions. In recent studies, MD simulations allowed to estimate rather precisely the diffusion coefficients in rubbery polymers, for example, for CH₄ in PE (Pant and Boyd, 1992), for He and CH₄ in PDMS (Sok and Berendsen, 1992). The transport of diffusing molecules in glassy polymers is much more complex because such polymers are not in a state of true thermodynamic equilibrium considering the scale of diffusion measurements. Besides, the diffusion coefficients in such matrices are smaller, of several orders of magnitude, what requires much longer calculation times (Gusev and Suter, 1992; Gusev et al., 1994). An important and useful concept, appeared in the early sixties, to understand the permeation mechanisms in the amorphous polymers, is the fractional free volume. Cohen and Turnbull (1959) considered the diffusion of hard spheres in a liquid as the result of a redistribution of the free volume inside the liquid with no energy variation associated. Besides, in 1953, Bueche gave an analysis of the segmental mobility in polymers which was based on the theory of free volume fluctuations (Bueche, 1953; Slater, 1939).

### 3.2.2 Free Volume Theory

(In the following of this article, the index 1 refers to the diffusing molecule and the index 2 to the polymer.)

As we underlined it, a certain number of theories derived from the free volume were advanced to study the diffusion in polymers. One of the most promising and earliest free volume models was developed by Fujita. Fujita (Fujita et al., 1960; Fujita and Kishimoto, 1961) suggested the molecular transport to be due to a redistribution of free volume and not due to a thermal activation. The basic idea of this theory is that a diffusing molecule can only move from one position to another when, in its neighbourhood, the local free volume exceeds a certain critical value. The dependence of diffusion when, in its neighbourhood, the local free volume exceeds a certain critical value. The dependence of diffusion coefficient in terms of the interaction parameter and fractional free volume:

\[ D_T = \frac{RT A_d \exp\left(-\frac{B_d}{f}\right)}{f} = RT m_d \quad (36) \]

The various parameters appearing in this equation are:

- \( m_d \): the mobility of the diffusing molecule relative to the polymer
- \( A_d \): a parameter which depends on the penetrant size and shape
- \( B_d \): a characteristic parameter of the available free volume fraction

and \( f \), the fractional free volume of the system is given by:

\[ f = \phi_1 f_1 + \phi_2 f_2 \quad (37) \]

where \( \phi \), and \( f \) are respectively the volume fraction and the free volume fraction of the component \( i \). \( D_T \) is in fact the thermodynamic diffusion coefficient of the penetrant defined by (Comyn, 1985):

\[ D_T = D \frac{\partial \ln C}{\partial \ln a} \quad (38) \]

\( C \) and \( a \) are respectively the penetrant concentration and activity. Equation (36) is sometimes expressed by:

\[ D_T = A \exp\left(-\frac{b v^*}{f}\right) \quad (39) \]

where \( v^* \) is a critical volume related to the penetrant size, \( A \) and \( b \) are constants of the considered system.

Generally, \( S \) is only a function of penetrant-polymer interactions but experimentally, an evolution of the solubility with \( f \) was found (Maeda and Paul, 1985). In 1975, from thermodynamic considerations (entropy of mixture and Flory-Huggins equation), Peterlin (1975) proposed the following expression for the solubility coefficient in terms of the interaction parameter and fractional free volume:

\[ S = \frac{f}{f_1 p_l^0 \exp(1 + \chi_1)} \quad (40) \]

where \( \chi_1 \) is the Flory-Huggins interaction parameter, \( p_l^0 \) is the liquid-vapour equilibrium pressure of the gas at temperature \( T \) (saturated vapour pressure). Assuming that \( \phi_1 \) is very small, it is then reasonable to replace \( f \) by \( f_2 \). Then the previous expression becomes:

\[ S = \frac{f_2}{f_1 p_l^0 \exp(1 + \chi_1)} = k f_2 \quad (41) \]

with \( k \), constant for the considered system.
As for the diffusion coefficient, after modification of Equation (36), Peterlin (1975) proposed:

$$D = D(0) \exp (\alpha_d C)$$

(42)

where $D(0)$ represents the limit of the diffusion coefficient to zero concentration and is written as:

$$D(0) = RTA_d \exp \left( -\frac{B_d}{\phi_2 f_2} \right)$$

(43)

and:

$$\alpha_d = \frac{B_d f_3}{(\phi_2 f_2)^2}$$

(44)

Brown et al. (1973) found that $D(0)$ decreased with the penetrant size of the diffusing molecule in various polybutadienes. Nevertheless, it is worth noting that $D$ depends more strongly on $f$ than $S$.

This model has been applied successfully to a certain number of organic vapour-rubbery polymer systems in which $D$ exhibits a strong concentration dependence. However, Fujita et al. (1960) considered it inappropriate for the diffusion of small molecules like water in rubbery polymers, which is largely independent of the concentration. Kulkarni and Stern (1983) studied the diffusion of CO$_2$, CH$_4$, C$_2$H$_4$ and C$_3$H$_8$ in PE ($\phi_a = 0.552$) at 5$^\circ$, 20$^\circ$ and 35$^\circ$C for pressures reaching 4 MPa. They wanted to test the ability of Fujita’s model to describe the diffusion of small non-polar molecules in polymers. A correction was brought to the model to raise its limitation. Indeed, it is important to underline that the free volume fraction depends on three thermodynamic variables (Frisch, 1970; Stern et al., 1972; Kulkarni and Stern, 1983): the temperature $T$, the hydrostatic pressure $p$ applied to the system which is in fact the penetrant pressure; and the penetrant concentration which can be expressed as a volume fraction:

$$f(T, p, C) = f_{\text{ref}}(T_{\text{ref}}, p_{\text{ref}}, 0) + \alpha(T - T_{\text{ref}}) - \beta(p - p_{\text{ref}}) + \gamma C$$

(45)

The first term of this equation represents the fractional free volume of the system in a reference state, which is the pure polymer at $T_{\text{ref}}$ and at $p_{\text{ref}}$.

The second term characterises the increase of $f$ due to the thermal dilation with $\alpha$, the thermal expansion coefficient of the free volume.

The third term shows how the free volume decreases during a hydrostatic compression, $\beta$ being the compressibility ($\beta = \chi_l - \chi_g$, the coefficients $\chi$ are the compressibilities of the liquid and glassy states).

The last term is a measure of the penetrant effectiveness in increasing the free volume, $\gamma$ being a coefficient of concentration.

These three parameters ($\alpha$, $\beta$, $\gamma$) are characteristics of the considered system. Often, the chosen reference state is the pure polymer at its glass transition temperature and under 0.1 MPa, $f_g(T, 1, 0)$, which corresponds to an iso-free-volume state whatever the polymer. With such modifications taking into account the gas pressure effect, Stern et al. (1983a, 1986) have shown that Fujita’s model was able to apply to small non-polar molecules in polymers. They assigned the differences observed in the case of water to its hydrogen-bonding nature rather than to a failure of the model. The validity of this model (Stern et al., 1983a, 1986) has been also tested for the permeation of other small molecules (Ar, SF$_6$, CF$_4$ and C$_2$H$_2$F$_2$ until 1.5 MPa) in PE from 5$^\circ$ to 50$^\circ$C and for binary gas mixtures (Stern et al., 1983b; Koros et al., 1981).

Vrentas and Duda (1977) used another model also based on free volume, while making use of the thermodynamic theory of Flory as well as on the entanglement theory of Bueche (1962) (friction coefficient idea). This model is relevant at temperatures above and below the glass transition temperature. A mutual polymer/solvent diffusion coefficient is calculated as a function of the solvent concentration, but it requires values of at least ten parameters. All these phenomenological models of transport based on the free volume idea are a little bit outdated because of the development of the numerical techniques such as MD simulation.

A topic of some controversy was the study of the free volume effect on the temperature dependence of $D$. Indeed Fujita’s model does not predict an Arrhenius type behaviour for the temperature influence on the diffusion coefficient but a WLF (Williams-Landel-Ferry) type relation (Ferry, 1980; Aminabhavi and Athital, 1988).

**Semicrystalline Polymers**

Due to their morphology, the case of semicrystalline polymers is particular and will be detailed in the paragraph dedicated to the influence of the polymer crystallinity on the transport coefficients (see below Section 7.1).

By assuming that a semicrystalline polymer can be represented by a two-phase mixture of crystallites and amorphous polymer, the model predicts $f_{a'}$, the free volume fraction of the amorphous phase. Indeed, studies have shown that the sorption and diffusion phenomena took place exclusively in the amorphous phase of the polymer and not in its crystalline zones (Michaels and Parker, 1959; Michaels and Bixler, 1961a, 1961b). The previous equations (39) and (41) can thus be written as (Michaels and Bixler, 1961a, 1961b; Kulkarni and Stern, 1983):

$$S_{a'} = kf_{a'}$$

(46)

$$D_{Ta} = A\exp \left( \frac{-bv^*}{f_{a'}} \right)$$

(47)
where:
- \( \Delta H_{\text{cond}} \) is the molar heat of condensation, this term is always negative and small for gases (Crank and Park, 1968);
- \( \Delta H_1 \) is the partial molar heat of mixing. This is a small and positive term, which can be estimated from the cohesive energy densities of the penetrant and the polymer by using Hildebrand’s theory (Hildebrand and Scott, 1950):

\[
\Delta H_1 = V_1 (\delta_1 - \delta_2)^2 \phi_2^2
\]  

The parameters of solubility \( \delta_1 \) and \( \delta_2 \) are the square roots of the cohesive energy densities of the penetrant and the polymer, \( V_1 \) is the partial molar volume of the penetrant and \( \phi_2 \) the volume fraction of the polymer in the mixture.

For gases well above their critical temperature (such as \( \text{H}_2, \text{N}_2, \text{O}_2 \) at room temperature), \( \Delta H_{\text{cond}} \) is very weak and, so, \( \Delta H_1 \) is governed by \( \Delta H_1 \). As the interactions are negligible, this term will be positive and \( S \) will increase with \( T \) (Comyn, 1985). For more condensable gases and vapours (e.g., \( \text{CO}_2, \text{SO}_2, \text{NH}_3 \) and hydrocarbons), \( \Delta H_1 \) is negative due to the \( \Delta H_{\text{cond}} \)’s strong contribution and, for a given system, a decrease of the solubility will be observed with a temperature increase. This expresses the fact that the penetrant has more and more difficulties in condensing in the polymer when the temperature is raised. It is worth noting that by using the above relation, a positive value for \( \Delta H_1 \) (endothermic solution) is always obtained. However, if one considers polymer-gas systems in which the molecular interactions are particularly energetic, \( \Delta H_1 \)’s value can become negative (exothermic solution) and cannot be calculated any more by means of this formula.

The activation energy represents physically the energy level that a molecule should reach to make a jump between one position and another one; it is always a positive quantity. As a consequence, \( D \) is an increasing function of the increased temperature. This effect may be expressed in terms of an increase in free volume directly related to the bulk expansion of the polymer due to the increased segmental motions and hence, the diffusion process of molecules is facilitated. Then, the value of the activation energy is all the more high as the cohesive forces between chains are strong. On the other hand, for a given polymer, the activation energy \( E_p \) increases with the penetrant size (it needs more space), and reaches an asymptotic limit when the penetrant mobility becomes comparable to that of the polymer segments (Naylor, 1989; Van Amerongen, 1950). Experimentally, this theory was verified on numerous penetrant-polymer systems (Van Amerongen, 1951) and the determined activation energies are included between 10 and 100 kJ/mol. The pre-exponential factor \( D_0 \) has an entropic character (Van Krevelen, 1990; Stannett, 1968) and takes into account the length jump and increases with the penetrant size. However, for a given polymer and at a fixed temperature, the diffusion
coefficient always decreases with the diffusing molecule size. Finally, it was established that \( D_0 \) verified the following empirical relation (Van Krevelen, 1990; Rogers, 1985):

\[
\ln D_0 = a E_D + b
\]

with \( a \) and \( b \), coefficients depending on the considered penetrant type for a given polymer. The activation energy is independent of temperature only over a small range of temperatures. Van Amerongen (1950) showed clearly that, on a wide range of temperatures (from 20° to 100°C), the activation energy is a function of the temperature and is in agreement with the Activated Zone Theory of Barrer. When \( T \) increases, the chains entropy grows (so \( D_0 \)), the activated zone size is larger and the chains mobility is enhanced, therefore \( D_0 \) increases. Rogers (1985) considered that the energy is the sum of two terms:

\[
E_D = E_D (C \to 0) - \gamma RT
\]

\( E_D (C \to 0) \) represents a measure of the apparent activation energy for diffusion in a polymer matrix which is otherwise unaffected by the presence of the penetrant in terms of segmental motions. The second term characterises the amount by which the apparent activation energy is reduced by the sorption of the penetrant (plasticization). It is important to underline that generally, the diffusion of small, non-reactive molecules with the polymer leads to lower values of activation energy at \( T < T_g \) than at \( T > T_g \). However, recently, Tonge et al. (2001) studied PMMA in a range of temperatures near the glass transition temperature above and below. They did not observe this jump for \( E_D \) in the vicinity of \( T_g \), but on the other hand, \( D_0 \) varied sharply. To summarise, the factors that have an influence on the activation energy are the rigidity of the polymer backbone, the cohesion energy of the polymer and the penetrant size (Weinkauf and Paul, 1990). The variation of the diffusion coefficient with temperature being dominant with regard to that of the solubility (Koros and Paul, 1978), the permeability coefficient increases as the temperature grows.

5 INFLUENCE OF CONCENTRATION

For systems in which the solubility essentially obeys Henry’s law (hydrocarbons in elastomers), the dependence of the diffusion coefficient on the sorbed penetrant concentration has been empirically represented, at a given temperature, by equations of the form (Prager and Long, 1951; Barrer, 1957; Frisch, 1957; Crank, 1953, 1975; Crank and Park, 1968):

Linear model: \( D(C) = D(0) (1 + \beta C) \) (57)

And when the dependence is more pronounced:

Exponential model: \( D(C) = D(0) e^{\beta C} \) (58)

\( D(0) \) being the limit of \( D \) when \( C \) tends towards zero and \( \beta \), a constant parameter at a fixed \( T \), characterising this dependence. In the case where \( \beta = 0 \), the model corresponding to a constant \( D \) value is obtained. At the Institut français du pétrole (IFP), these various models were also considered (Benjelloun-Dabaghi et al., 2001).

For systems in which the sorption curves do not follow exactly Henry’s law but rather an isotherm of Flory-Huggins type (high-soluble gases in rubbery polymers), the following expression for \( S \) was proposed (Suwandi and Stern, 1973; Rogers, 1985; Naito et al., 1996):

\[
S(C) = S(0) e^{\sigma C}
\]

with \( S(0) \), the limit value of the solubility when the concentration is close to zero, which is in fact the Henry’s law coefficient \( k_D^* \), a characteristic parameter at a given temperature. \( \sigma \) is a constant relating to polymer-penetrant interactions.

The concentration dependence of \( D \) can be represented by:

\[
D(C) = D(0) e^{[\beta C/(1+\sigma C)]}
\]

Fujita et al. (1960) proposed a similar relation from considerations based on the free volume theory. Concerning the solubility coefficient, speaking about its dependence on concentration or on pressure is equivalent because one has the general relation:

\[
C = S(C)p
\]

By assuming a solubility dependence given by Equation (59), the concentration is then written as (Naito et al., 1996):

\[
C = \left[ k_D \exp(\sigma C) \right] p \Rightarrow \frac{k_D p}{1 - \sigma k_D p}
\]

This equation can be expressed in an equivalent way in terms of solubility:

\[
S(p) = \frac{k_D}{1 - \sigma k_D p}
\]

\( \sigma \) is a constant relating to the interaction parameter \( \chi \) and to the partial molar volume of the dissolved gas. It depends on temperature as well as \( k_D^* \).

6 INFLUENCE OF PRESSURE

The effect of pressure on gas diffusion through rubbery polymers was studied to develop membranes useful for the separation of gases (Stern et al., 1972). It seemed that the evolutions of the permeability coefficient with pressure depend on the diffusing molecule type. Indeed, for organic vapours or very soluble gases such as CO2, Pe increases whilst it decreases for little soluble gases such as He, N2. These results were analysed (Stern et al., 1972, 1986) on the
basis of the free volume theory for diffusion. They concluded that the pressure influence could be explained as the result of two opposing phenomena: one related to the hydrostatic pressure and the other due to the diffusing molecule concentration within the matrix, each of these effects leading to a different evolution of Pe.

6.1 Diffusion Coefficient

When the pressure on the upstream side of the membrane is increased, two opposite effects may occur:
- a hydrostatic pressure increase leads to an increase of the polymer density, via polymer compaction, thereby reducing the free volume inside the polymer;
- the pressure increase corresponds to an increase of the penetrant concentration in the membrane. These diffusing molecules can plasticize the macromolecular chains, which means a more important available free volume.

The first one of these two mechanisms tends to retard the diffusion process by reducing the segmental motions whereas the second enhances it.

Naito et al. (1991, 1993, 1996) have investigated the pressure effect (up to 10 MPa) on the permeability of some pure gases (with various molecular sizes and solubilities) in rubbery polymers such as PE, PP, poly(ethylene-co-vinyl acetate) and polybutadienes. To describe simultaneously both opposite effects related to pressure, they proposed, at a given temperature, the following model:

\[ D(C, p) = D(00) \exp(\beta h p + \alpha C) \] (63)

In this relation:
- \( D(00) \) is the diffusion coefficient at \( C = 0 \) and \( p = 0 \);
- the term \( \exp(\beta h p) \) represents the hydrostatic pressure effect, \( \beta h \) being a negative term because it expresses the drop of \( D \);
- the term \( \exp(\alpha C) \) characterises the increase of dissolved molecules in the polymer resulting from the plasticization, and hence, the more important available free volume.

This model turns out to be valid for pressures that never exceed 10 MPa. Besides, the authors showed that, according to the kinetic theory for diffusion in liquids, the coefficient \( \beta h \) is related to the activation volume \( V^* \) of the diffusion process, by means of the following relation (Naito et al., 1991):

\[ V^* = -RT \beta h \] (64)

with \( R \) the gas constant.

This relation is valid when the compressibility of the amorphous fraction of the polymer (the rubbery state is comparable to a liquid) is assumed to be negligible.

\( V^* \) being dependent on the molecular size of the penetrants, the following relation is proposed (Naito et al., 1993):

\[ \beta h = -A \bar{d}^n \] (65)

\( \bar{d} \) is the average molecular diameter of the gas, \( A \) a constant and \( n \) a constant between 2 and 3 (for LDPE and PP). As for \( \alpha \), it is proportional to the partial molar volume and then, to the penetrant diameter.

The mean solubility coefficient is described using a simplified form of the Flory-Huggins equation (Suwandi and Stern, 1973):

\[ \bar{S} = S(00) \exp(\sigma C_\infty) \] (66)

where \( S(00) \) represents the solubility value when \( C \) and \( p \) tend both towards 0 (Henry’s constant).

This implies that the mean permeability coefficient is written as (Naito et al., 1996):

\[ \bar{Pe} = D(00) k D \exp \left[ \beta h p + \left( \frac{\sigma + \alpha}{2} k D \right) p \right] \] (67)

The model proposed in the modelling article (Benjelloun-Dabaghi et al., 2001) represents a generalisation of this Naito’s model (Eq. (63)) (Naito et al., 1996) for the highest pressures (greater than 20 MPa). The following general expression (Benjelloun-Dabaghi et al., 2001) is suggested to describe the dependence of \( D \) on the concentration, pressure and temperature:

\[ D(T,C,p) = D_{00}(T,p) e^{BC} = D_{000}(p) e^{-\frac{E_D}{RT}} e^{BC} \] (68)

The term \( D_{00}(p) \) representing the pressure effect on the diffusion coefficient is given by:

\[ D_{000}(p) = D_{000}^* \exp \left[ \beta h^L p + \beta h^Q p^2 \right] \] (69)

\( \beta h^L \) and \( \beta h^Q \) are coefficients (linear and quadratic) relative to the pressure dependence, of respective dimensions MPa\(^{-1}\) and MPa\(^{-2}\). The validity of the proposed model is studied for the PVDF-CO\(_2\) system in Benjelloun-Dabaghi et al. (2001).

6.2 Solubility Coefficient

For low pressures (lower than 10 MPa) in the presence of a slightly condensable gas, generally, the solubility depends neither on the gas concentration in the polymer, nor on the hydrostatic pressure applied to the membrane (Crank and Park, 1968; Comyn, 1985) but only on temperature (see Henry’s law, Eq. (9)). For higher pressures, one can however observe strong anomalies with regard to the behaviour envisaged by this simple law. In that case, it can be necessary to express the equation involving the solubility and the concentration in terms of the fugacity \( f \), and not pressure, to take into account the gas molecules compressibility:

\[ C = S(T) f \] (70)

This relationship allows to describe the penetrant concentration in the polymer for higher hydrostatic pressures,
by taking into account the non-idealities induced by the pressure itself in the gas phase. Nevertheless, when the gas concentration inside the polymer reaches higher values, this relation is no longer valid. It is suitable to use a new thermodynamic model which manages to describe exactly the phenomena related to the influence of the gas concentration on the solubility $S(T, C)$.

## 7 Parameters Affecting the Transport Properties

### 7.1 Crystallinity

Most of the existing models are based on the two-phase model proposed and developed by Michaels et al. (Michaels and Parker, 1959; Michaels and Bixler, 1961a, 1961b). Indeed, for isotropic HDPE with spherulitic structures, Michaels et al. (Michaels and Parker, 1959; Michaels and Bixler, 1961a, 1961b) have shown that the sorption and diffusion took place exclusively in the amorphous regions. The crystalline zones act as excluded volumes for the sorption process and are impermeable barriers for the diffusion process. Moreover, their existence does not seem to influence the sorption mode in the amorphous phase. The dispersed crystalline phase presents a resistance to the permeant passage. More exactly, these crystalline zones have two effects on the gases diffusion. On one hand, they increase the effective path length of diffusion, and, on the other hand, they seem to reduce the polymer chains mobility in the amorphous phase (because chain ends are trapped in the neighbouring crystalline lamellae) and, then, lead to a higher activation energy of diffusion. To account for these effects, Michaels et al. introduced a “tortuosity factor” $\tau$ and a “chain immobilisation factor” $\beta$.

They proposed the following expressions for the coefficients of solubility and diffusion:

$$ S = S^* \phi_a \quad (71) $$

$$ D = D^* \frac{\beta \tau}{\phi_a} \quad (72) $$

where $S^*$ and $D^*$ are the coefficients of solubility and diffusion in an amorphous, hypothetically, completely relaxed state (i.e. a completely amorphous polymer), and $\phi_a$ the volume fraction of the amorphous phase. $\beta$, the factor relating to chain immobilisation, reflects the hindrance of the crystalline zones on the amorphous; indeed the crystallites have a crosslinking or “anchoring” action which tends to immobilise amorphous chains. The tortuosity factor, $\tau$, characterises the more tortuous pathway that a diffusing molecule must take in a semicrystalline polymer to pass round impenetrable crystalline zones. It is a geometrical term which depends on the crystallites anisotropy degree, the degree of crystallinity and hence, the thermal history. For a constant volume fraction of amorphous phase, $\beta$ is correlated to temperature by an exponential relation (as $D^*$ and $S^*$) whereas $\tau$ is constant. $\beta$ and $D^*$ are both supposed to depend on the penetrant diameter. Michaels et al. showed that the nature of the amorphous phase remains essentially unperturbed despite the existence of the crystalline regions and that it is possible to write:

$$ S^* = S_a \quad (73) $$

where $S_a$ is the solubility coefficient in the amorphous component. This relation was confirmed over a wide range of crystallinity in the case of PE. However, it was not completely respected for PET (Michaels and Bixler, 1961a; Michaels et al., 1963a) where the solubility was lower than that predicted by Equations (71) and (73). Michaels et al. proposed that crystallisation tended to occur in the denser amorphous zones, which become then less accessible to diffusing molecules.

More recent studies of Puléo (1988), followed by other authors (Mogri and Paul, 2001; Weinkauf and Paul, 1990), have shown that certain crystalline structures will permit small molecules sorption and their diffusion. For example, a great amount of gas was sorbed in crystals of poly(4-methyl-1-pentene). These results can be explained by a more open structure of these crystals with a density not very different from that of the amorphous phase. Recently, it was also shown that molecules could penetrate into crystals of $\delta$ form in syndiotactic polystyrene (Guadagno et al., 1998; Manfredi et al., 1997). Concerning the diffusion coefficient, Michaels and Bixler (1961b) proposed:

$$ D^* = D_a \quad (74) $$

A power relationship has been suggested to relate the tortuosity factor to the amorphous volume fraction:

$$ \tau = \phi_a^{-n} \quad (75) $$

with $1 < n < 2$ for unoriented polymers. By taking $\beta = 1$, this leads to the expression below for $D$:

$$ D = D_a \phi_a^n \quad (76) $$

While considering the amorphous chains are restrained in mobility by their ends fixed in the adjacent crystals, Peterlin (1975) proposed slightly different expressions for the coefficients of diffusion and permeability:

$$ D = \frac{\Psi}{B} D_a \quad (77) $$

where $\Psi$ is the “detour ratio”, introduced by Klute (1959), describing the detour that the penetrant should make to avoid
the impermeable crystalline zones (0 < Ψ < 1), B, the
“blocking factor”, underlines that the amorphous regions
included between two crystalline zones are sometimes too
narrow and prevent the passage of the penetrant (B > 1).

It follows for the permeability coefficient:

\[ Pe = \frac{\Psi \phi_a}{B} Pe_a \]  

(78)

where \( \phi_a \) is the amorphous volume fraction and \( Pe_a \) the
permeability coefficient in the completely amorphous polymer. One of the limitations in the understanding of the transport mechanisms in the semicrystalline polymers is that \( D^*, S^* \) cannot be measured directly. In fact, few studies were
dedicated to polymers in a completely amorphous state so as
to become independent of the crystallinity aspect and, then,
to strictly determine the amorphous phase properties (at
\( T > T_f \) for instance, or by using a similar but amorphous polymer). However, certain evidence has shown that the crystalline phase affects the amorphous phase nature (Michaels and Bixler, 1961b; Budzien et al., 1998). Recently, Budzien et al. (1998) predicted, by using Flory-Huggins theory, gas solubilities that are approximately a factor of 2 higher than found with the extrapolation of Michaels and Bixler (1961b) for the amorphous PE (\( \phi_a = 100\% \)). Budzien et al. (1998) assigned this difference to the oversimplified aspect of the two-phase model, which neglects completely the contribution of the crystalline phase for the sorption. Indeed, the size and shape of crystallites, their spatial
distribution, the crystalline morphology (which depends on the molecular weight, polydispersity index, processing conditions), the degree of crystallinity and the presence of short ramifications are so many factors that are determined by the thermal and mechanical past treatment of the polymer and that will have an important influence on the transport processes. However, all the correlations are not completely established (Vittoria, 1995; Hedenqvist et al., 1996). A certain number of papers treated also of factors affecting the permeability of PE films (Krohn and Jordy, 1996; Krohn et al., 1997). These films are very used in the packaging field as barriers to gases, flavours or odours to maintain product
quality and provide shelf-life. The barrier properties of these films (of thickness between 10 and 90 \( \mu \)m) to water vapour and oxygen gas are important parameters. Some authors obtained the following relation (Alter, 1962; Klute, 1959) between permeability and polymer density \( \rho \):

\[ Pe = K (1 - \rho) \]  

(79)

where \( K \) and \( n \) are constants, \( n \) being close to 2. They
observed a significant increase of the permeability as the film
thickness is reduced. This was attributed to the existence of a
limit thickness below which the barrier properties of the film
are almost undefined (Talwar, 1973). This author suggested the idea that, during the fast cooling of a film, it appears near

7.2 Effect of Orientation

Uniaxial drawing of a polymer changes the amorphous chains “morphology” and their spatial distribution, leading
to an increase of the amorphous phase density and hence, a
reduction of its fractional free volume (Peterlin, 1975; Weinkauf and Paul, 1990). In the case of semicrystalline
polymers, this is coupled with a tortuosity modification. Then, it is not surprising that the permeation parameters
may be affected. However, the various authors do not always propose the same interpretations. For example,
Peterlin (1975) observed drastic reductions in sorption and
diffusion of organic vapours in HDPE at high draw ratio,
with an increase of the diffusion activation energy. These changes are attributed to modifications of the amorphous chains mobility or the fractional free volume with the drawing. Whereas Holden et al. (1985) reported similar changes for the permeation of He and \( O_2 \) in highly stretched PE but no considerable variation of the vacuum energies. Wang and Porter (1984) attributed this reduction of transport parameters with the draw ratio to an increase of the orientation and degree of crystallinity. The tortuosity factor is also affected. Sha and Harrison (1992) stretched HDPE in the presence of \( CO_2 \) at a sufficiently high draw ratio, to modify the morphology and obtained the transformation of the spherulitic structure to a microfibrillar one. They observed a very important drop of the permeability that they related to the variations of the amorphous phase density, therefore to the fractional free volume estimated for the amorphous phase, \( f_a \). For them, the evolutions of \( f_a \) are responsible for the transport parameters variations of the drawn samples. Recently, McGonigle et al. (2001) performed permeation experiments of various gases (\( N_2, Ar, He, CO_2, O_2 \)) in biaxially drawn films of PET and PEN. They observed a decrease of the barrier properties (\( S \) and \( D \)) with the draw ratio. They assigned this behaviour as resulting from the morphology modification (variation of the crystallinity degree, reorientation effect, disentanglement and alignment of the chains, higher degree of packing) and from the decrease of the free volume fraction of the amorphous phase (reduced segmental mobility).

7.3 Effect of Crosslinking

This effect was studied through experiments carried out with
elastomers of varying degrees of vulcanization (Stannett,
1968). It was observed that when the degree of crosslinking increases, the diffusion coefficient decreases and that the greater the magnitude of the change, the larger the penetrant molecule. The pre-exponential term $D_0$ and the activation energy $E_D$ both increase with the increasing crosslinking level but the polymer chains mobility is reduced, thus the combination of these effects leads to a drop of $D$. This is well understood with the free volume notions. In a similar way, in PE, the activation energy of diffusion increases with the degree of branching (Michaels and Parker, 1959).

### 7.4 Effect of Other Parameters

Many of these aspects have already been mentioned above.

#### 7.4.1 Nature of the Gas

**Diffusion Coefficient**

The nature and the size of the gas molecules which cross the membrane are parameters that play an important role in the determination of the diffusion coefficients. These characteristics can be taken into account by means of the Lennard-Jones parameters of the gas molecule, namely, the collision diameter $r$, and the characteristic interaction energy between molecules. Although numerous attempts were made (Griskey, 1977), it is practically impossible to find a model of general validity which could describe the dependence of $D$ on these parameters, because of the complexity of the phenomena to be envisaged. Numerous correlations suggested that $D$ is proportional to $r^n$. According to the authors, the constant $n$ may take different values but there is no evident relation with the penetrant diameter (Michaels and Bixler, 1961b; Griskey, 1977; Raucher and Sefcik, 1983b; Pace and Datyner, 1980). Moreover, the molecule anisotropy (spherical or elongated molecule) has a noticeable effect too (Stannett, 1968). Let us remind that the activation energy of diffusion represents the energy necessary for the separation of the polymer chains by cooperative motions of sufficient amplitude to allow the penetrant to undergo its diffusional jump (Pace and Datyner, 1979a, 1979b, 1979c). It is then clear that for big molecules, requiring larger holes to diffuse, the activation energy as well as the pre-exponential term $D_0$ will be higher. Besides, these two terms are related by a logarithmic relation (Comyn, 1985; Stannett, 1968). This results in every case in a decrease of the diffusion coefficient with the increasing penetrant size. Figure 5 represents the evolution of $\log D_0$ according to $E_D$, divided by the average temperature of measurement (Koros, 1990) for a whole series of polymer-gas systems. A lower activation energy is indeed found in the glassy polymers.

**Solubility Coefficient**

In the case of weak polymer-solute interactions, the solubility is controlled by the ease of the gas to condense (Stannett, 1968). A certain number of relations were proposed to describe the evolution of the logarithm of $S$ with various parameters such as the critical gas temperature (Van Amerongen, 1950; Suwandi and Stern, 1973; Stern et al., 1969), the boiling temperature or the Lennard-Jones parameters (Gee, 1947; Michaels and Bixler, 1961a; Van Krevlen, 1990; Flacconnèche et al., 2001). All these parameters, except in the presence of specific polymer-gas interactions, will raise with the penetrant size. Consequently, the solubility is an increasing function of the diffusing molecule size (Naylor, 1989).

#### 7.4.2 Nature of the Polymer

It is difficult to correlate the diffusivity of gases with the nature of the polymer because, unfortunately, it is impossible to change one feature of the polymer without affecting the others (Crank and Park, 1968). Indeed, the diffusion rate depends on the number and the distribution of pre-existing microvoids, and also on the ease of hole formation. This is reflected by some various parameters that, moreover, may be linked together. It is rather difficult to list them all, nevertheless let us quote the degree of chains packing, the segmental chain mobility, the polymer cohesive energy (*i.e.* chain stiffness), without forgetting also the thermal expansion coefficient, the glass transition temperature, the crystallinity, the addition of plasticizers or reinforcing fillers, etc. Certain studies showed the important role of the chain flexibility. Indeed, polymers with insaturations present higher diffusion coefficients (Van...
Amerongen, 1950) because they have a much more flexible chain. The introduction of lateral methyls in elastomers decreases the value of $D$ because the flexibility falls too (increase of the cohesive energy between chains). On the other hand, side-chain groups may provoke steric hindrances. The introduction of polar side-chains causes an increase of the energies of cohesion and of diffusion activation, thus resulting in a lower diffusion coefficient value. In fact, the chain flexibility and the cohesive energy between macromolecules influence directly the glass transition temperature. The value of the diffusion activation energy is all the more important as the existing cohesive forces between chains are strong and as the gas molecule dimensions are also large. The average molecular weight of the polymer seems to have no influence on $S$, $D$ and $Pe$, excepted for the very low values where the chain ends have a significant influence on the free volume.

### 7.4.3 Effect of the Glass Transition

We have already mentioned the effect of the $T_g$ value on the activation energy of diffusion (Crank and Park, 1968). Generally, in the same family of polymers, when $T_g$ increases, $E_D$ increases and $D$ decreases. Various polymers were studied over a wide range of temperatures including the glass transition temperature. It was obtained by different research teams (Michaelis et al., 1963b; Meares, 1954) that the evolution of log $D$ according to $1/T$ (Arrhenius’s plot) presented two zones separated by the glass transition and characterised by different activation energies. For $T < T_g$, the realised diffusional jump is small and corresponds to a weak $E_D$. When $T > T_g$, the chain segmental mobility is much more important, it allows to enlarge the activated zone and $E_D$ raises. These changes are directly correlated to the variation of the thermal expansion coefficient at $T_g$ and also to the penetrant size considering the size of its available space.

### 7.4.4 Effect of Plasticizers

In a general way (Stannett, 1968), the incorporation of plasticizers in polymers appears to have a relatively complex influence on the permeability while tending to increase it. Plasticizers may operate by their mechanical action by separating the macromolecular chains, leading thus to a decline of the intermolecular attractive forces. They increase so the mobility of these chains and facilitate the diffusion of the sorbed molecules by lowering the activation energy. By inserting between the macromolecular chains, these additives also lower the glass transition temperature of the polymer by modifying the local segmental motions and therefore have an indirect action on the transport parameters (Sefcik et al., 1983). These plasticizing molecules also possess their own diffusion coefficient that depends on their physical state (solid or liquid). Their influence is all the more marked as their affinity with the diffusing molecule is important.

### CONCLUSION

Numerous studies were dedicated to the transport of different molecules in polymers. Nevertheless, numerous questions remain about the complete understanding of the transport mechanism at the molecular level, the nature of the interactions involved. In the case of small molecules in rubbery polymers, the phenomena are rather simple and the diffusion is Fickian. The sorption phenomena as well as the influence of different parameters are relatively well known and can be summarised in Table 2 (Frisch, 1980). On the other hand, concerning the transport of more complex molecules, or systems, where the times associated to the molecular diffusion and the relaxation times of the polymer are in the same order of magnitude, the classic Fick’s laws do not apply any more and the transport mechanisms are far from being completely clear. An interesting case, which we suggest to approach in the future, concerns the study of the

### TABLE 2

<table>
<thead>
<tr>
<th>$T$ value compared to a characteristic temperature of the system</th>
<th>Gases with $T &gt; T_g$</th>
<th>More condensables gases or vapours $(T &lt; T_c)$</th>
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</thead>
<tbody>
<tr>
<td>$T &gt; T_g$</td>
<td>Rubbery polymers</td>
<td>Fickian diffusion</td>
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<td></td>
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<td>constant $D$: $D_0$</td>
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<td>constant $E_D$</td>
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<tr>
<td></td>
<td></td>
<td>Henry’s mode sorption</td>
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<tr>
<td></td>
<td></td>
<td>$S$ constant, increases slightly with $T$</td>
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<tr>
<td></td>
<td></td>
<td>$Pe$ decreases slightly with pressure (hydrostatic pressure effect)</td>
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<tr>
<td>$T &lt; T_g$</td>
<td>Glassy polymers</td>
<td>Dual mode sorption $S(p)$</td>
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<td>$E_D$ shows often breaks at or near $T_g$</td>
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permeability of binary gas mixtures through a polymer membrane under moderate pressures. Indeed, competitive effects between both types of molecules within the matrix polymer may appear and lead to differences compared with a simple additive law of mixture. The case of the high pressures was also rarely treated in literature. Finally, the study of the evolution of the transport coefficients when the polymer is under a mechanical stress could bring major information about the coupling effect between the physical and mechanical phenomena.

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