



HAL
open science

Transport Properties of Gases in Polymers: Experimental Methods

B. Flaconneche, J. Martin, M. H. Klopffer

► **To cite this version:**

B. Flaconneche, J. Martin, M. H. Klopffer. Transport Properties of Gases in Polymers: Experimental Methods. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, 2001, 56 (3), pp.245-259. 10.2516/ogst:2001022 . hal-02053928

HAL Id: hal-02053928

<https://ifp.hal.science/hal-02053928>

Submitted on 1 Mar 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Transport Properties of Gases in Polymers: Experimental Methods

B. Flaconnèche¹, J. Martin¹ and M.H. Klopffer¹

¹ Institut français du pétrole, Division Chimie et Physico-Chimie appliquées, Département Matériaux,
1 et 4, avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France
e-mail: bruno.flaconneche@ifp.fr - joseph.martin@ifp.fr - m-helene.klopffer@ifp.fr

Résumé — Méthodes de mesure des coefficients de transport de gaz dans les polymères — La perméabilité aux gaz des polymères est une propriété inhérente à leur structure, qui résulte de la solubilisation des fluides dans la matière, puis de la diffusion de ces produits à travers la matrice polymère. L'aptitude d'un gaz à pouvoir traverser plus ou moins rapidement un matériau peut être mise à profit dans de nombreux domaines industriels. Des polymères très peu perméables sont par exemple recherchés dans des domaines aussi divers que la production pétrolière, l'emballage alimentaire ou le domaine automobile. Dans les applications pétrolières, la fonction principale des polymères est d'assurer l'étanchéité des structures telles que les conduites. Dans ce cas, les matériaux sont au contact de gaz à haute température et sous forte pression et les informations concernant les coefficients de transport dans ces conditions extrêmes ne sont généralement pas disponibles dans la littérature. C'est pourquoi certains appareillages susceptibles de donner accès à ces valeurs ont été développés. Après quelques rappels théoriques des méthodes de calcul pour l'obtention des coefficients de transport et une brève revue bibliographique des différentes techniques expérimentales existantes, les différents montages expérimentaux étudiés sont décrits précisément.

Mots-clés : perméabilité, diffusion, solubilité, polymères, gaz, méthodes expérimentales.

Abstract — Transport Properties of Gases in Polymers: Experimental Methods — The permeability of gases in polymers is a property inherent to their structure, which results, firstly, from the absorption of fluids by the material, then, from the diffusion of these products through the polymer matrix. The capacity of a gas to cross more or less fast a material can be used in numerous industrial domains. For example, polymers of low permeability are looked for in domains as different as the oil production, the food packaging or the automotive industry. For oil applications, the main function of polymers is to ensure the leakproof of pipes for example. In that case, materials are in contact of gas at high temperature and high pressure. As the information concerning the gases transport coefficients in these extreme conditions was not available in literature, devices able to give access to these properties were developed. In this paper, the methods for obtaining the transport coefficients and a brief bibliographical review of the various existing experimental techniques are presented. Then, the various experimental devices developed are described in detail.

Keywords: permeability, diffusion, solubility, polymers, gas, experimental methods.

LIST OF NOTATIONS

Characteristics of Polymers

LDPE Low density polyethylene
MDPE Medium density polyethylene

Gases Transport Coefficients

LP Low pressure
HP High pressure
STP Standard conditions of temperature (273 K) and pressure (0.1013 MPa)
 P_e Permeability coefficient ($\text{cm}^3(\text{STP})/\text{cm}\cdot\text{s}\cdot\text{MPa}$)
 D Diffusion coefficient (cm^2/s)
 S Solubility coefficient ($\text{cm}^3(\text{STP})/\text{cm}^3\cdot\text{MPa}$)
 Θ Time lag (s)

Gases

He Helium
 N_2 Nitrogen
Ar Argon
 CH_4 Methane
 CO_2 Carbon dioxide
 H_2S Hydrogen sulphide

INTRODUCTION

The first observation of the permeation phenomenon goes back to 1829 when T. Graham noticed the inflation of a rubber structure in the presence of carbon dioxide [1, 2]. A more systematic study allowed J.K. Mitchell to note a more or less fast deflation of its rubber balloons according to the kind of gas with which they had been filled [1, 2]. As some authors told it, T. Graham published then an article that remains for them one of the starting points of the science of the transport phenomena in polymers [1, 2]. During this work, he built a device in which a gas crossed a membrane, accumulated in a volume under vacuum, and moved a column of mercury. He observed especially that:

- the permeation process began with the gas dissolution in the rubber then continued by the diffusion of all the species dissolved in the matrix;
- the permeation rates were independent of whether the diffusing gas accumulated in a vacuum volume or in a volume full of a gas other than the penetrant;
- the temperature increase had two competing effects on permeation rates: decrease of the solubility of the diffusing species and increase of the diffusion rate.

Since these initial observations, the gas permeation in a polymer material can be defined as the property of this

material to be penetrated and crossed by the gas molecules. Hence, the permeability corresponds to a gas flow through this material. It is generally admitted that this phenomenon decomposes into three successive stages:

- gas absorption (by chemical affinity or solubility) by the polymer from the side submitted to the highest pressure;
- gas diffusion inside the polymer matrix;
- gas desorption from the side at the lowest pressure.

Some qualities such as low density or good chemical resistance allow polymers to be widely used in domains as varied as the oil & gas industry (offshore flexible pipes), the automotive industry (tanks, pipes), the food packaging industry (barrier films), the separation industry (selective membranes) or, still, the medical domain. In some applications, the permeability is an advantage and this property is used especially to separate gases having different permeation rates or to control perfectly the medicine diffusion in the human body. In the other cases, this property is a drawback. In the field of the offshore flexible pipes, a corrosive gas, such as hydrogen sulphide, diffusing through layers of polymers can corrode the metal layers which assure the mechanical resistance of the structure. In every case, a best knowledge of the transport phenomena, that is to say the permeation, the diffusion and the solubility of gases in polymers, is essential for the choice and the design of the structures. Hence, numerous experimental techniques, adapted to the coefficient to be measured or to the investigated domain, have been developed to obtain these properties.

1 EVALUATION OF THE TRANSPORT COEFFICIENTS

The definition of the three transport coefficients (solubility, diffusion and permeability) requires some theoretical considerations. The flux, J , of the gas in a polymer matrix can be defined as the quantity of diffusing, Q , which crosses the membrane area, A , during the time t [3]:

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

By analogy with heat transfer by conduction, the transfer of matter by diffusion indicates that the flux J in every point of the membrane is proportional to the gradient of the gas concentration C . The first Fick's law expresses this result by the relation [3-10]:

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

D is called the diffusion coefficient and can be expressed in cm^2/s . By expressing the fact that the amount of gas by unity of membrane volume is equal to the increase of the gas concentration with regard to time, it is possible to write, in the case of unidirectional diffusion:

$$-\frac{dJ}{dx} = \frac{dC}{dt} \quad (3)$$

Combining Relations (2) and (3) and assuming that D is constant in the membrane leads to Fick's second law [3-10]:

$$\frac{dC}{dt} = -D \frac{d^2C}{dx^2} \quad (4)$$

When a polymer membrane, of thickness l , is exposed to a gas and when the diffusion coefficient is constant, the integration of Equation (2) gives:

$$J \int_0^l dx = -D \int_{C_1}^{C_2} dC \quad (5)$$

Then:

$$J = \frac{D(C_1 - C_2)}{l} \quad (6)$$

C_1 and C_2 are the gas concentrations in the membrane near both faces of the sample. They are supposed to be related to the partial pressures by Henry's law [3-10]:

$$C = S p \quad (7)$$

where p is the pressure and S the solubility coefficient which can be expressed in $\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{MPa}$. Then, by using Equation (7), Equation (6) becomes:

$$J = \frac{DS(p_1 - p_2)}{l} \quad (8)$$

By definition, the product DS , noted Pe , is the permeability coefficient. If D is given in cm^2/s and S , the ratio of the gas concentration in the polymer to the pressure, in $\text{cm}^3(\text{STP})/\text{cm}^3 \cdot \text{MPa}$, Pe can be expressed in $\text{cm}^3(\text{STP})/\text{cm} \cdot \text{s} \cdot \text{MPa}$.

The three main methods to obtain the coefficients Pe , D and S from experimental curves are presented in the following paragraphs. The first, based on techniques of transmission measurements, allows generally to calculate the permeability coefficient. The second, also based on tests by transmission, is called the method of "time lag". It provides the permeability coefficient and the diffusion coefficient. The latter is based on experimental techniques of sorption-desorption and allows to obtain the coefficients of solubility and diffusion.

1.1 Steady State

The simplest technique to determine the diffusion coefficient is based on Fick's first law (2). Let us consider the gas diffusion through a flat membrane of thickness l , both surfaces of which are respectively maintained to gas concentrations C_1 and C_2 . At the beginning of the experiment, the flux and the gas concentration in every point of the membrane vary with time. When the steady state is reached, Fick's first law expresses that the concentration varies

linearly from C_1 to C_2 in the membrane and that the gas flux is the same in every section of the membrane. Generally C_2 is maintained to 0 and the membrane thickness as well as the applied pressure are known. If the value of C_1 is known, the diffusion coefficient can be directly obtained by measurement of the diffusive flux [3-7].

In many systems, the surface concentrations are unknown, whereas the pressures p_1 and p_2 on each membrane face are known. The flux can be expressed by using Equation (8). In most of the methods of transmission measure, p_1 is highly greater than p_2 (generally maintained to 0). By considering, either the flux but the gas amount, Q , that crossed the polymer membrane of area A and of thickness l during the time t , the permeability coefficient may be written [4-10]:

$$Pe = \frac{Q l}{t A p_1} \quad (9)$$

1.2 Time Lag Method

When a gas pressure is applied to one of the membrane faces, before reaching the steady state, the flux and the concentration vary with time in every point inside the membrane. The gas amount, $Q(t)$, which crosses this membrane, during the time t , is given by the limited series development approaching the integration of Fick's second law (4) [5, 8, 10]:

$$\frac{Q(t)}{l C_1} = \frac{Dt}{l^2} - \frac{1}{6} - \frac{2}{\pi^2} \sum_1^{\infty} \frac{(-1)^n}{n^2} \exp\left(\frac{-D n^2 \pi^2 t}{l^2}\right) \quad (10)$$

When t tends towards the very long times, the steady state is reached and the exponential term becomes negligible. The curve representing $Q(t)$ versus time (Fig. 1) is then a straight line of expression:

$$Q(t) = \frac{DC_1}{l} \left(t - \frac{l^2}{6D} \right) \quad (11)$$

The intercept between this line and the x axis is equal to:

$$\Theta = \frac{l^2}{6D} \quad (12)$$

Θ is called the "time lag". According to Equation (12), it is possible to deduce the diffusion coefficient. In steady state, Equation (9) provides the permeability coefficient, and the solubility coefficient is then calculated by making the ratio of Pe over D .

More generally, when the coefficient depends on the gas concentration, it is possible, with some limitations, to determine the following inequality for a large number of (polymer-gas) systems [7-9]:

$$\frac{1}{6} \leq \frac{\Theta D}{l^2} \leq \frac{1}{2} \quad (13)$$

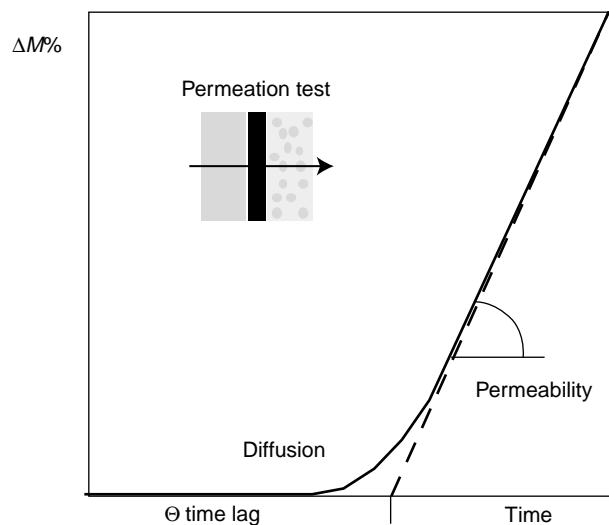


Figure 1
Theoretical curve of a permeation experiment.

This method has just been detailed in the case of unidirectional diffusion through a flat membrane. For particular initial conditions as well as for samples of different geometrical shapes (cylindrical, spherical), numerous adapted solutions were determined [6, 11-13].

1.3 Analysis of the Sorption-Desorption Tests

When a film or a membrane of polymer is immersed in a penetrant, the concentration, *C*, in the material is given, at

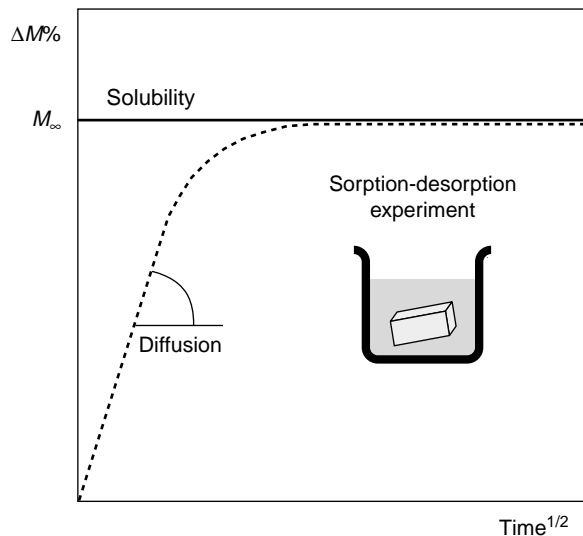


Figure 2
Theoretical curve of a sorption experiment.

time *t*, by the solution of the second Fick's equation (4). In the case of unidirectional diffusion, one obtains [8, 10, 14]:

$$\frac{C}{C_1} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{4l^2}\right) \cos\left(\frac{(2n+1)\pi x}{2l}\right) \tag{14}$$

In that case, the film thickness is equal to *2l*, and *C*₁, the gas concentration in contact with the faces of the film, is considered as immediately established. It is also necessary to note that this equation does not take into account the diffusion towards the edges of the membrane, as far as, in this system, the thickness of the film is very small compared to the other dimensions. Equation (14) can be integrated to obtain the mass of penetrant, *M(t)*, absorbed by the sample at time *t*, assuming that the temperature and the pressure are constant. If *D* is assumed to be constant, the following relation is obtained [5, 8-10, 14]:

$$\frac{M(t)}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{l^2}\right) \tag{15}$$

*M*_∞ is the mass of the diffusing species absorbed by the material at equilibrium. The volume of gas sorbed at equilibrium, *V*_∞ in cm³(STP), can be obtained from the value of *M*_∞ by the following relation:

$$V_{\infty} = \frac{M_{\infty} - M_i}{M_{\text{gaz}}} 22400 \tag{16}$$

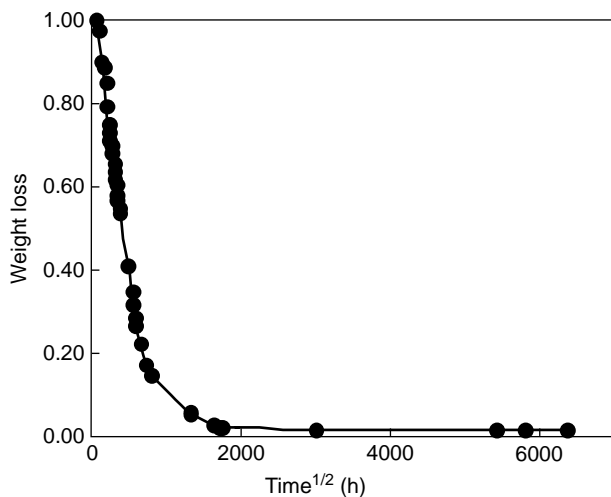


Figure 3
CO₂ desorption curve in LDPE at 22°C.

The constant 22 400 corresponds to the volume in cm^3 occupied by a mole of gas in the standard conditions of pressure and temperature. M_i is the initial mass of the sample and M_{gaz} is the molar mass of the studied gas. The solubility coefficient (in $\text{cm}^3(\text{STP})/\text{cm}^3\cdot\text{MPa}$) is easily obtained by:

$$S = \frac{V_{\infty}}{p V_{\text{pol}}} \quad (17)$$

where p is the applied gas pressure and V_{pol} the volume of the polymer membrane.

According to Equation (15), the value of t/l^2 for which the ratio $M(t)/M_{\infty}$ is equal to 1/2 is expressed by the following equation [9]:

$$\left(\frac{t}{l^2}\right)_{\frac{1}{2}} = \frac{1}{D} \left[\frac{-1}{\pi^2} \ln \left\{ \frac{\pi^2}{16} - \frac{1}{9} \left(\frac{\pi^2}{16} \right)^9 \right\} \right] \quad (18)$$

This is equivalent to the next relation (19), which gives the coefficient of diffusion [5, 8-10, 14]:

$$D = \frac{0.04919}{\left(\frac{t}{l^2}\right)_{\frac{1}{2}}} \quad (19)$$

In Figures 2 and 3, a theoretical curve of gas sorption in a polymer matrix and an experimental test of CO_2 desorption in a low-density polyethylene are respectively plotted.

2 EXPERIMENTAL TECHNIQUES

A large number of measurement methods of polymer permeability to gases or vapours can be found in the literature [2, 15-17]. Nevertheless, most of the experimental techniques used for studying the gases diffusion in polymers involve one of these three modes of transport:

- sorption-desorption;
- permeation through a membrane into a closed chamber (constant volume);
- permeation through a membrane into a flowing stream (constant pressure).

2.1 Sorption-Desorption

This kind of experiments consists in recording the weight variation (uptake or loss) of a polymer sample, with time, either directly by gravimetric methods, or indirectly by pressure or volume measurements, for example. The sorption measurement allows to directly obtain the solubility coefficient and to calculate, assuming some hypotheses, an apparent diffusion coefficient. These techniques should be very sensitive, because the absorbed quantities are often very small. They must also be able to operate in high-pressure and

high-temperature conditions corresponding to industrial realities. They are generally recommended for experiments performed at high pressure and are not efficient for studies of rapid processes [2].

Among the various experimental approaches, gravimetric techniques seem to be the most intuitive. The principle is to quantify the weight variation of a polymer sample submitted to a gas, with an electronic balance for example. Introduced into a high-pressure (HP) cell, this balance allows to obtain tests at a pressure of 6 MPa and temperatures of about 80°C [18, 19]. Some evolutions of this technique allow to perform measurements at a pressure of 12 MPa and a temperature up to 350°C with a resolution of $10 \mu\text{g}$, for an initial weight of polymer sample of about 1 g [20, 21]. By installing an electromagnetic coupling to transmit the sample weight to an external balance, it is possible to obtain a system called “magnetic suspension balance” [22]. By this method, a pressure of 45 MPa and a temperature of 250°C can be reached, for a weight of sample of 25 g, with a resolution of about $10 \mu\text{g}$. One of the advantages of this kind of device is the separation of the saturation system from the balance, avoiding a deterioration of the balance by aggressive gases.

A second approach is based on oscillation techniques. This kind of method is called “indirect” because the sample weight is deduced from the resonance characteristics of a support. The main method is the quartz crystal microbalance. A polymer film is deposited on a piezoelectric crystal. Under the influence of an alternating current, this crystal undergoes a deformation that becomes maximal at the frequency of resonance. This frequency depends on the mass of the support: an increase of the polymer mass entails a reduction of the crystal resonance frequency [23, 24]. The useful pressures with this kind of device are about 15 MPa, while the temperatures of measure should be lower than the glass transition temperature (T_g), for the amorphous polymers, and included between T_g and T_f (melting temperature) for thermoplastics. The advantage of these microbalances is to give quickly precise results. Nevertheless, the polymer is in the form of thin film and the adsorption phenomena (with regard to the absorption), which is not always representative of the industrial applications, is favoured. A second technique called “oscillating arm” allows to link the gas mass absorbed by the polymer, in the form of a block connected to the arm, with the oscillation frequency of this arm [25]. This method allows to reach high pressures and to use rather heavy samples of polymer. Then, it seems less limited than the quartz crystal microbalance. Some authors also tried to couple this oscillation approach with a gravimetric measure, what allowed them to obtain simultaneously the weight variation and the swelling of the sample [26].

The volumetric techniques or PVT (pressure-volume-temperature) are the oldest and the most used for the determination of the solubility coefficient. They are based on

a matter balance of the fluid before and after its absorption by the polymer. A sample of the polymer is introduced into a HP cell under vacuum. The gas is compressed in a neighbouring cell. The quantity of available fluid is estimated by using an equation of state. Then, both cells are connected and the equilibrium is reached when the pressure stabilises. This measure is difficult because it is necessary to know perfectly the volume of the cells and of the polymer sample, and also, the tests duration [27, 28]. Some methods were tested to determine the PVT relations of polymers during injection moulding [29].

Some less usual techniques, such as inverse gas chromatography (IGC) or freeze-purge-desorption [30], can also be used. In the first case, the polymer constitutes the steady phase of the chromatography column. The retention times of the fluids used are in direct relation with the retention volume, and consequently, with the absorbed quantity in the steady phase. The test temperatures can be very high but the limitation of this kind of measurement is the weak pressure supported by the columns.

2.2 Reception into a Closed Receiving Chamber

The principle of this kind of measurement is to determine, in function of time, the gas amount crossing a polymer membrane and accumulating in a closed receiving chamber. The upper pressure is generally maintained constant and highly greater than the downstream pressure, to obtain a pressure difference almost constant. In most of the cases, the permeation curve approaches asymptotically a straight line for long times, and the transport coefficients can be then determined by the time lag method. Techniques based on this principle allow to measure small permeation rates. They are strongly advised when diffusing or vapours easy to condense, the chemical species of which are very difficult to analyse continuously, are used.

By gravimetric methods, the gas amount crossing a polymer membrane to accumulate in a cell is determined in function of time by continuous or discontinuous weighing. It is clear that the interruption of the permeation phenomenon by cell manipulations can entail important errors. This test is generally used for condensable vapours and polymers, the permeability of which is high. For slow permeation rates and for time lag determination, it is better to use manometric or volumetric methods.

By using the volumetric methods, the quantification of the gas volume crossing the polymer sample is made by movement of a fluid in a capillary tube. This measure is less and less used and often reserved for the very fast phenomena of permeation. These methods turn out less sensitive than pressure measurements and, hence, are rarely used for precise determination of the time lag.

With the manometric methods, which are the most used systems for permeability determination, the pressure change, entailed by the gas accumulation in a receiving chamber, is continually recorded [31-33]. By knowing the reception volume as well as the operating conditions, it is possible to link the pressure measured to the quantity of accumulated gas. From there, it is easy to obtain the transport coefficients by the calculations described in the first part. The design of the devices allows to reach temperatures of about 200-300°C and pressures up to 100 MPa.

In the case of “analytical methods”, the receiving chamber contains a gas different from that to analyse. Some parameters, directly proportional to the gas quantity which has passed through the polymer sample, can be evaluated by various techniques [34]: infrared spectroscopy, ultraviolet (UV) spectroscopy, mass spectroscopy, radio tracers or thermal conductivity.

2.3 Reception into a Flowing Stream

In this last scenario, the studied diffusing species cross the polymer membrane to reach an opened volume swept away by a gas stream. This gas serves for pulling the penetrant towards an appropriate detector measuring the present penetrant proportion.

Various kinds of detectors can be used such as detectors of UV beams, gas analysers (oxygen detectors), thermal conductivity or, still, mass spectrometer.

This kind of measurement is advantageous because it can be applied to membranes susceptible to tear under high pressures (food packaging) [35]. The obtained results are generally of much better quality for high-permeability samples.

An extension of this kind of technique is the study of gas mixture permeability. Indeed, the industrial applications need materials able to support not a pure gas but rather gas mixtures. By using gas chromatography or mass spectrometry, each gas having crossed the polymer membrane can be quantified. Then, it is possible to determine the intrinsic transport coefficients of each of the gases constituting the initial mixture. It is also possible to detect the presence of particular affinities of a polymer for a gas. This technique is very useful in the field of the selective membranes, based mainly on the analysis by gas chromatography. It allows to determine the permeability coefficient of numerous polymers to binary gas mixtures, such as CH₄-CO₂ [36-40].

3 SPECIFIC DEVICES DEVELOPED

In the oil environment, one of the main functions of polymers concerns the leakproof (inner sheath of offshore flexible

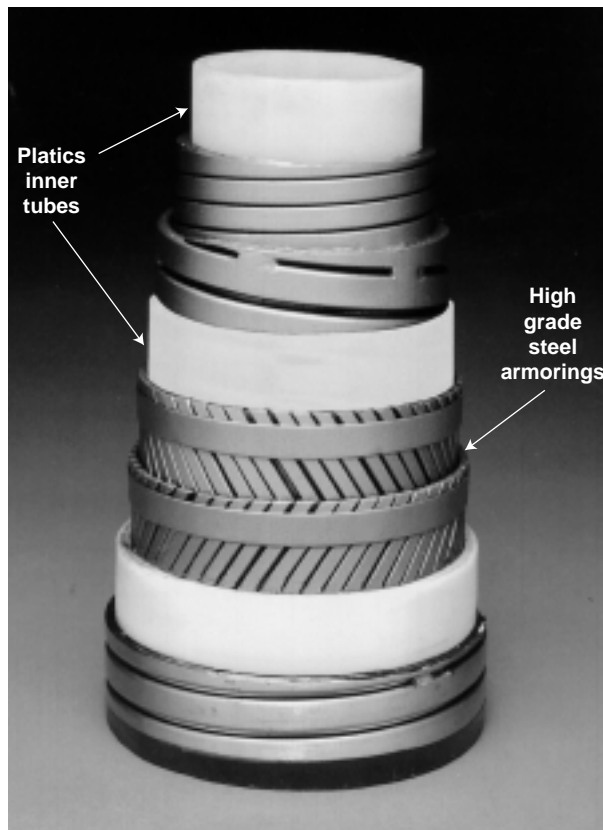


Figure 4
Cutaway view of an offshore oil & gas flexible pipe.

pipes, “O” rings, gas or fuel tanks, selective membranes). In that case and mainly for the flexible pipes for petroleum transport (*Fig. 4*), the materials are in contact with gases at high temperature and high pressure. It is essential to understand some phenomena such as blistering of flexible pipe inner sheaths (gas absorption in the polymer followed by an explosive decompression), or corrosion of the metal armorings of flexible pipes (diffusion of corrosive gases through polymer sheaths). The information relative to this domain concerns the very high pressures and is generally not available in the literature. Then, devices were developed to determine the gases transport coefficients for polymers.

Two devices based on a continuous measure of the pressure accumulation in a closed receiving chamber were developed. The acquisition system of each device is completely automatic. The first device is dedicated to the measurements of the so-called “medium pressure” permeability. It allows measures at gas pressures ranging from 1 to 14 MPa. The second device, named “high pressure”, is equipped with a compressor, which can perform tests for pressures going up to 100 MPa.

3.1 Gases Permeability at Medium Pressures

3.1.1 Description and Operating Principle

The medium-pressure cell of permeation, a simplified plan of which is presented in Figure 5, is constituted by the following elements:

- a gas supply system:
 - system of studied gas selection;
 - for reasons of safety in the laboratory, the gas to be tested is stored in a tank of 2 litres of gas under pressure;
 - a pressure gauge for the supply of the measurement system;
- a permeation cell:
 - a cell body useful to the location of the polymer membrane and to the gas inlet;
 - a cell hat allowing to close and to ensure the leakproof of the apparatus;
 - O rings;
 - a sintered stainless steel disc preventing the membranes deformations, to avoid tearing of the polymer that would entail the deterioration of the pressure sensor;
 - a system of temperature control allowing the adjustment and the reading of the temperature;
 - a two-threshold pressure sensor, allowing the measure of the pressure accumulated in the closed receiving chamber, but also to pilot the opening and the lock of the quick opening valve;
 - an electropneumatic quick opening valve to purge the closed volume;

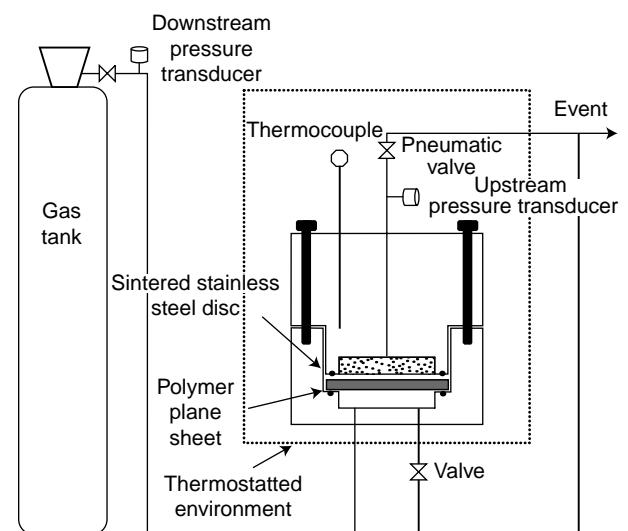


Figure 5
Schematic of the medium-pressure gas permeation cell.

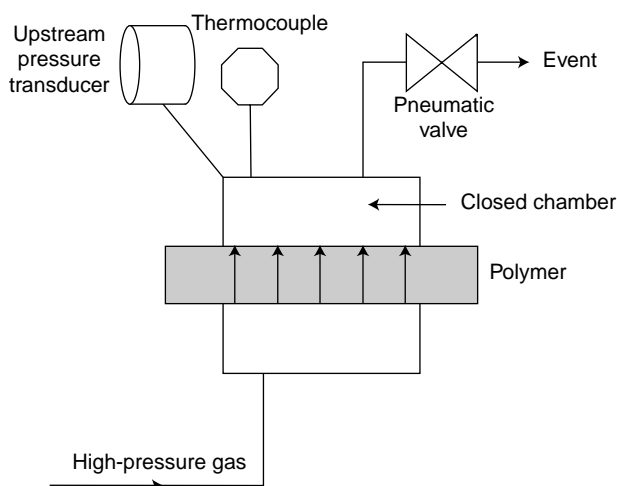


Figure 6

Working procedure of the permeation cells (HP and MP).

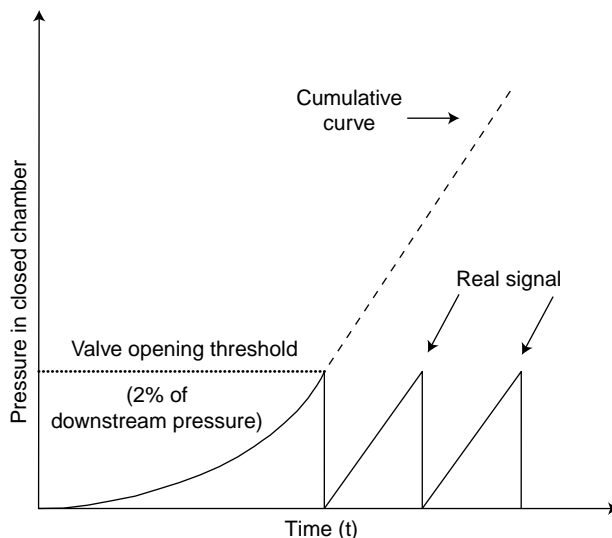


Figure 7

Theoretical recording of a real signal and cumulative curve.

– a data acquisition system:

- an electronic acquisition card for the reading and the transfer of the analogical signals from various sensors;
- a data acquisition software to record and store the experimental data in files;
- a microcomputer for the data processing and the storage of the results.

The cell allows the continuous measure of the signal even for long duration tests. Indeed, for very small permeation rates, the regulation of the acquisition frequency can be of several points per minute to some points a day, for duration going from some hours to some weeks. The usable gases are CH_4 , CO_2 , He, N_2 , Ar. Pressure ranges from 1 to 14 MPa (except for the CO_2 supplied pressure, which is limited to 5 MPa) and temperature can vary from 30° to 140°C . The membranes can be made up of thermoplastics, composites or rubbers. The membrane thickness is between 0.5 and 6 mm.

Then, the gas amount crossing a polymer membrane is determined from the pressure variation due to the gas accumulation in a closed receiving chamber (Fig. 6). The closed volume pressure is relaxed every time it reaches a value of some percents of the applied pressure. By knowing the pressure increase in function of time and the number of decompressions, the global experimental curve is reconstituted (Fig. 7).

3.1.2 Set-up of the Apparatus

To make sure to limit at most the main sources of potential errors resulting from the apparatus, it was necessary to measure accurately the closed volume and to verify the homogeneity of the temperature in the whole system. The evaluation of the closed volume was performed by

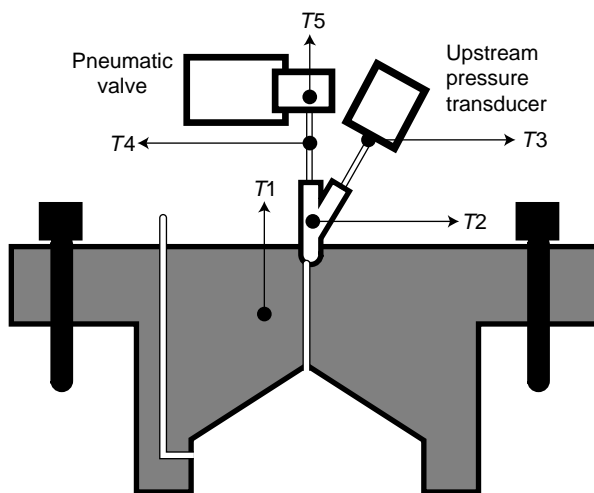


Figure 8

Checking of the permeation cell's temperature homogeneity.

volumetry at room temperature. The measurement average led to a volume of $13.6 \pm 0.1 \text{ cm}^3$. It was also verified that the whole closed volume was at a uniform temperature, by recording five temperatures on the cell (Fig. 8). This avoided corrections in the calculation of the transport coefficients.

The available diffusion area in the device can be considered in two ways:

- the surface bounded by the O ring centre (55 mm);
- the surface of the polymer directly in contact with the gas (40 mm).

To determine the correct value for the transport coefficient calculations, tests were performed on low-density

polyethylene membranes (Dow 300) in contact with helium at 5 MPa. The experimental conditions as well as the obtained results are given in Table 1.

TABLE 1
Comparison between helium flows through LDPE plane sheets
(\varnothing 70 mm and \varnothing 52 mm)

Polymer	Temp. (°C)	\varnothing (mm)	l (mm)	Flow (cm ³ /h)	Time lag (min)
LDPE	50	70	4	0.501 \pm 0.3	23 \pm 4
LDPE	50	70	4	0.524 \pm 0.3	25 \pm 4
LDPE	50	52	4	0.495 \pm 0.3	25 \pm 0.3
LDPE	50	52	4	0.520 \pm 0.3	26 \pm 0.3

The presence of the O ring did not seem necessary for thermoplastics, such as polyethylene. According to the obtained results, the leakproof was effective at the levels of the metal of the cell and the polymer membrane. Indeed, the gas flows were identical for the membranes of diameter 52 mm and those of diameter 70 mm. In an identical way, the time lag values were equal whatever the sample geometry. This tended to prove that the diffusion in the masked part of the membrane (> 40 mm) did not really influence the results. Then, the value of the permeation area was taken equal to that calculated from the polymer membrane diameter in direct contact with the gas (40 mm), that is 12.57 cm².

In a second series of tests, it was proved that the diffusing species accumulation until a pressure equal to 8% of the applied pressure had no influence on the permeability coefficients (Table 2). P_e values were calculated with an average Δp corrected according to the tolerated percentage of accumulation. For all the other measurements, it was decided to tolerate an accumulation of 2% of the applied pressure.

TABLE 2
Pressure accumulation in closed receiving chamber effect on permeability of LDPE to helium

% accumulation	Permeability (10 ⁻⁷ cm ³ (STP)/cm-s-MPa)
0.5	19.0 \pm 1.5
1	18.9 \pm 1.5
8	19.0 \pm 1.5

3.1.3 Data Processing

The data acquisition was performed through a card, of type Labcard PCL-818 from *Advantech*, configured for the simultaneous recording of sixteen analogical ways. It transferred the analogical signals from the various sensors

(thermocouples and pressure sensors) used for the measurements on the PC microcomputer. A data acquisition program was developed on the software Labtech Notebook™. It allows to show and to record in real time all the signals but also to calculate the global experimental curve. The data processing of the experimental files is based on the time lag method to obtain the transport coefficients. The data processing is performed by means of software implemented in C++ language. This software allows to get back the experimental data, to perform all the calculations of the transport coefficients (permeability, diffusion and solubility) and to edit a test report recapitulating the operating conditions (polymer, gas, pressure, temperature, etc.), the obtained coefficients (permeability, diffusion, solubility, time lag) and the experimental curve.

3.2 Permeability to Gases at High Pressure

3.2.1 Description of the Equipment

A HP cell of permeability, based on the time lag method, was developed to perform measures at pressures up to 100 MPa, a maximal temperature of 200°C and for membrane thickness ranging from 1 to 20 mm. With this cell, the use of corrosive gases such as H₂S is possible.

The test consists in recording the pressure rise in a closed receiving chamber according to time. In order to avoid the perturbation of the difference of pressure upstream and downstream the polymer membrane, a purge valve opens automatically when the pressure in the closed volume reaches a threshold value.

The installation includes: a compression unit, a HP module, a permeation cell, a low-pressure (LP) module, a heating system and a control system.

The compression unit is constituted by the gas supply and a compressor. The gas can be pure or in mixture. The compressor is a pneumatic compressor, Maximator DLE 75-2 marketed by *Autoclave Engineers Europe*. The pressure of suction of this compressor cannot be lower than 10 MPa. This imposes the use of a first stage of compression for gas supply at lower pressure, in the case of pure CO₂, pure H₂S or mixtures with high contents in one of these two gases. The membrane compressor works between 0 and 10 MPa. The maximal pressure of expulsion of Maximator DLE 75-2 is 120 MPa.

The HP module is located between the compressor and the HP permeability cell (Fig. 9). It consists in two HP valves, gas inlet pipes, gas outlet pipes, departure of the gas, as well as a spiral pipe, of the same nature, located just under the permeation cell and serving as a HP tank. The global volume of HP gas is about 410 cm³. A pressure sensor, placed near this tank, measures continuously the value of the high pressure p_c (order pressure).

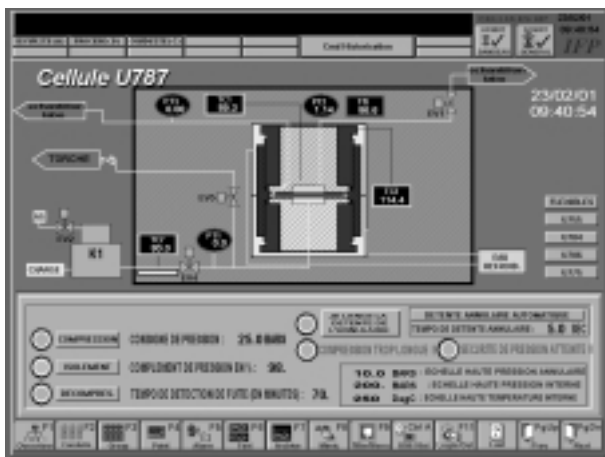


Figure 9
Schematic of the HP permeation cell.

The HP permeation cell is conceived on the same principle as the medium-pressure permeation cell. It is made of steel and constituted by an autoclave body and two corks. The maximum service pressure of the group is 120 MPa at a temperature of 200°C. The lower cork, fixed permanently to the autoclave body, is connected to the HP spiral reservoir. The polymer membrane to be tested can have a thickness included between 1 and 20 mm and a diameter included between 60 and 80 mm. A metallic ring of centring confines the membrane. This avoids membrane radial extrusion when it is submitted to high pressures and temperatures. A cylindrical room, 40 mm in diameter, is manufactured in the base of the upper cork. A sintered stainless steel disc, perfectly permeable to gases, the function of which is to collect the loads applied on the membrane, is inserted in this room. Two O rings assure the leakproof on both membrane faces. In the same way, the leakproof between the two corks and the autoclave body is also assured by two other O rings. A pressure sensor, connected to the leak channel manufactured in the upper cork, allows to verify the quality of the leakproof by measuring a possible rise of the pressure p_f (leak pressure) in the volume surrounding the membrane.

The LP module is connected to the exit of the canal manufactured in the upper cork of the permeation cell. A break disc protects the assembly in case of loss of leakproof of the HP cell or if the polymer membrane breaks. A pressure sensor allows to follow the pressure rise p_m (pressure of measure) in the volume downstream to the membrane (V_m , volume of measure), due to the gas diffusion through the membrane. A thermocouple indicates the temperature T_m (temperature of measure) of the gas near the pressure sensor. An automatic valve serves to lower the pressure p_m to the atmospheric pressure when it reaches a threshold value p_{ms} . The global volume (V_m) of the LP assembly downstream to the membrane is about 7 cm³.

The installation temperature is regulated by electrical heating. Two heating zones have been created. For the HP part, electrical resistances have been placed inside the frame hermetically closed by isolated steel sheets. For the LP part, heating clamps, that can be dismantled, have been placed on the upper part of the upper cork of the permeation cell. The pressure sensor, p_m , and the purge gate cannot work at high temperature. Then, they were slightly deported and placed over the heating clamps. The whole assembly is insulated. Finally, the regulation system allows to regulate T_m . Then, the output flow Q can be calculated from the formula:

$$Q = p_m \cdot V_m \cdot \frac{273}{T_m} \quad (20)$$

For safety, the HP permeation equipment is placed in a cell located in an explosion-protected zone.

The control system (monitoring and data acquisition of the HP cell) is a *Eurotherm Tacticien T3500* system which allows, from a computer located in a control room, to:

- monitor the set in pressure and the decompression of the HP apparatus;
- regulate and control the temperatures and the order pressures;
- create history files of the tests;
- manage the alarms of the system and the gas leak detection;
- transfer the data at the end of the test for processing.

An example of the synoptic of T3500 monitoring is given in Figure 9 and an example of acquisition and storing of the data is presented in Figure 10.

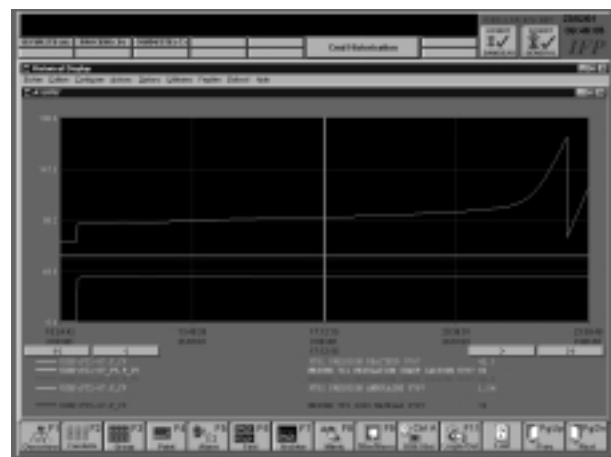


Figure 10
Acquisition and storage of data for a HP gas permeation experiment.

The information collected by all the sensors is transmitted to the control room. A command cupboard controls the whole system of measurement and allows to:

- activate at distance the operations of compression and decompression of the facilities;
- regulate the heating of the HP cell;
- activate the purge of the volume V_m ;
- record continuously the following parameters: p_m , T_m , p_p , T_a (the room temperature), p_c .

3.2.2 Operating Procedure

The permeation test procedure consists of the following stages:

- the polymer sample is cut in plane sheets obtained by compression moulding by single-screw extrusion. It is then weighed in the air and in an ethanol bath in order to determine its mass and its volume;
- the membrane thickness is measured in its middle by using a calliper square;
- the membrane is set in the metallic ring of centring. For each test, the O rings located on both faces of the membrane, as well as the sintered stainless steel disc, are changed;
- the upper cork is screwed on the HP cell and the LP assembly is connected;
- the leakproof of the LP module is checked;
- when the temperature of order is reached and when T_m in the downstream volume is stabilised (at least after 6 h), the rise in pressure is started. The initial time of the test corresponds to the time at which the temperature and the pressure of order are reached. At this moment, the volume V_m is purged;
- when the steady state is reached (after at least three times the time lag) the test is stopped: the HP module is decompressed and the heating is disconnected;
- when the measure cell is cold ($\leq 40^\circ\text{C}$), the LP module and the upper cork of the HP cell are dismantled and the membrane is recovered. The mass and the final volume of the membrane are then determined by a double weighing in the air and in the ethanol bath;
- the data processing allows to reconstruct the curves of pressure rise and of the volume V_m , according to time, and to calculate, by using the time lag method, the coefficients of permeability, diffusion and solubility. The various weights, the curve of pressure rise, the results of the calculations and the different observations on test progress are grouped together in a test file.

3.3 Permeability to Gas Mixtures

The offshore flexible pipes are not generally in contact of a single gas but rather submitted to mixtures of gases constituted mainly of methane and also of carbon dioxide and

of hydrogen sulphide. It is essential to possess some experimental equipment allowing to follow the transport kinetics of each of the gases in the mixture. Besides, this equipment should reveal possible gas-gas or gas-polymer interactions.

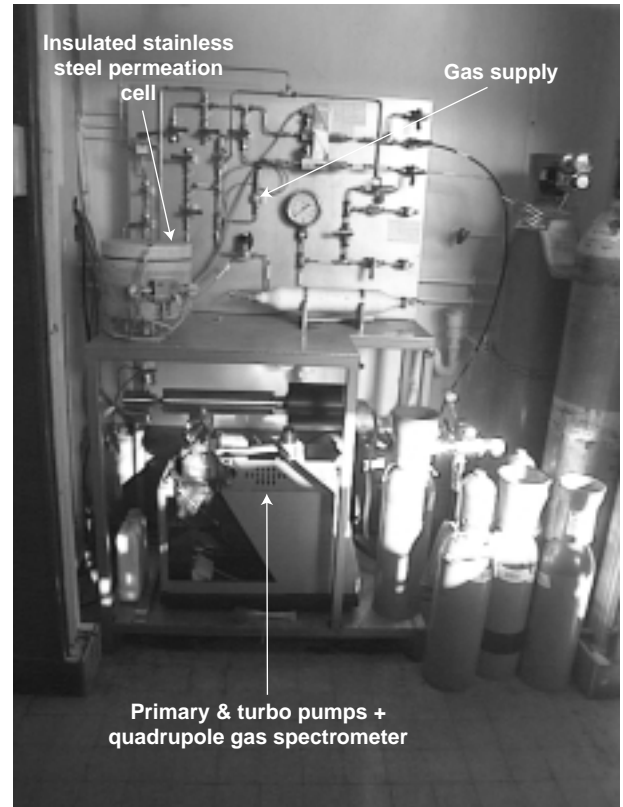


Figure 11
Photography of the mixed-gases permeation apparatus.

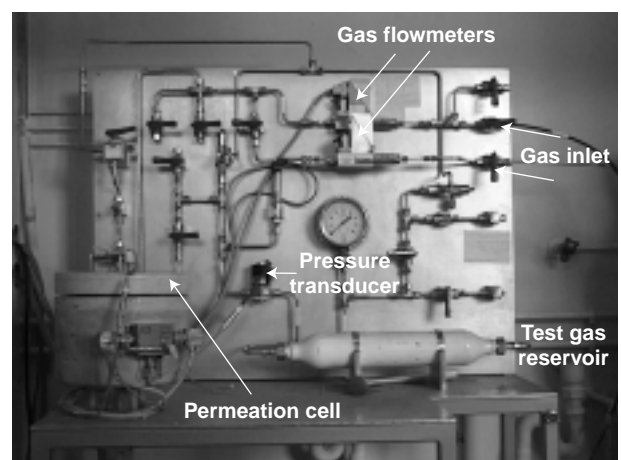


Figure 12
Photography of the gas supply system and the permeation cell.

3.3.1 Experimental Device

Figure 11 presents a general picture of the experimental device set-up to measure the permeability of polymers to gas mixtures. This equipment is constituted by three different parts:

- a gas supply system (*Fig. 12*) which serves for generating a continuous flow of gas (molar mixture of vector gas + internal standard (95% nitrogen-5% argon)) downstream to the membrane and to bring the studied gas mixture (molar mixture of methane-carbon dioxide) upstream to the polymer sample. This system consists of:
 - gases tanks and suitable manometer regulators (vector, mixtures to be analysed, standard);
 - electronic flowmeters for the regulation of the vector gas supply (60-600 cm³(STP)/h) and of the standard gas (6-60 cm³(STP)/h);
 - a reserve (ballast tank of 1 litre) and a system of pressure regulation of the studied gas mixture for the supply of the permeation cell;
 - a system of purge of all the present gases at the end of the test;
- a permeation cell (*Fig. 12*) identical to the medium-pressure cell but with a maximal reduction of the reception volume (≈ 2 cm³) swept by the vector gas. The aim is here to minimise the potential errors on the time lag calculation;
- a system of detection and data analysis (*Fig. 13*):
 - primary and secondary pumps allowing to assure a vacuum of 10^{-8} to 10^{-11} MPa in the mass spectrometer;
 - a high-precision leak valve to limit the gas supplying of the spectrometer;

- a mass spectrometer with quadrupole gas analyser (Quartz 100D from *VG Scientific*), detection by Faraday cup or electron multiplier;
- a microcomputer for the acquisition, treatment and storing of the signal.

3.3.2 Operating Procedure

The system principle is based on gas permeation through a polymer membrane in a flowing stream of vector gas and detection by mass spectrometry. To perform a test, the following operating mode is followed:

- set-up of the membrane in the cell;
- regulation of the flow of vector gas + internal standard;
- setting of the leak valve of the spectrometer supply;
- waiting for the signal stabilisation on the mass spectrometer;
- supply of the cell, at regulated pressure, with the gas mixture;
- measurement with acquisition and computer storage of the signal;
- test stop, purge of the system, dismantling of the cell;
- data processing.

The mass spectrometer allows to put in evidence, by the appearance of peaks of intensity proportional to the flow, the presence of each of the various chemical species. Here, gases to be detected are:

- nitrogen: vector gas;
- argon: internal standard gas;
- methane and carbon dioxide: gas mixture to be studied.

For semicrystalline polymers such as polyamides or poly(vinylidene fluoride), the waited flows during a test are very small, about some tenths of cm³/h. As the mass spectrometer used cannot directly perform quantitative analyses, it is necessary to set up a preliminary calibration curve for each component of the gas mixture in the range of very small flows. This calibration allows to relate the ratio of the peaks intensity over the intensity of the internal standard gas (Ar) peak to the real flows of CH₄ and CO₂. To do it, perfectly determined flows of vector gas (mixture molar 95% N₂ + 5% Ar) and of standard gas (mixture molar 94% N₂ + 4% Ar + 1% CH₄ + 1% CO₂) are directly injected in the mass spectrometer.

Generally, the cracking of gases in the mass spectrometer gives, for every gas, a major peak corresponding to the gas molar mass and one or several minor peaks resulting from fragments of the main molecule. Some overlapping peaks appear then and, so, it is necessary to choose peaks corresponding to each gas studied, in a unique way. Table 3 gives the position of the major peaks as well as their intensity for each of the gases used in this equipment.

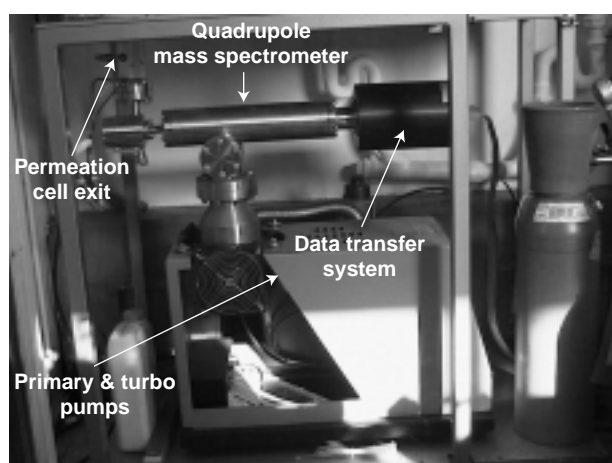


Figure 13

Photography of the detection system (pumps, mass spectrometer and data transfer).

TABLE 3
Intensity (%) and mass peak for several gases

Gas	Major peak		Minor peak (1)		Minor peak (2)	
	Mass	Intensity	Mass	Intensity	Mass	Intensity
Nitrogen	28	100%	14	5%	29	1%
Argon	40	100%	20	16%	36	1%
Methane	16	100%	15	85%	14	16%
CO ₂	44	100%	16	9%	28	8%

The values of this table report an overlapping of peaks 28 and 14 of the nitrogen with those of the other gases. This justifies the use of argon as the internal standard, the major peak (40) of which does not overlap with the other peaks. On the other hand, working on ratios of peaks, and not on absolute values, allows to avoid small variations entailed by possible fluctuations in the operating conditions (room temperature, flow of vector gas, etc.). The major peak of CO₂ is also isolated while that of methane overlaps with a peak arising from CO₂. Then, for the quantitative analyses, it has been chosen to base the calculations used for the determination of the transport coefficients on the following peaks:

- argon: peak 40 (major, intensity 100%);
- carbon dioxide: peak 44 (major, intensity 100%);
- methane: peak 15 (minor (1), intensity 85%).

The experimental curves so obtained represent the flow of each gas of the mixture, through a polymer membrane, according to time (Fig. 14). Then, by performing the curve of the gas amount accumulated according to time, a graphic representation is obtained, which can easily be analysed by the time lag method (Fig. 15).

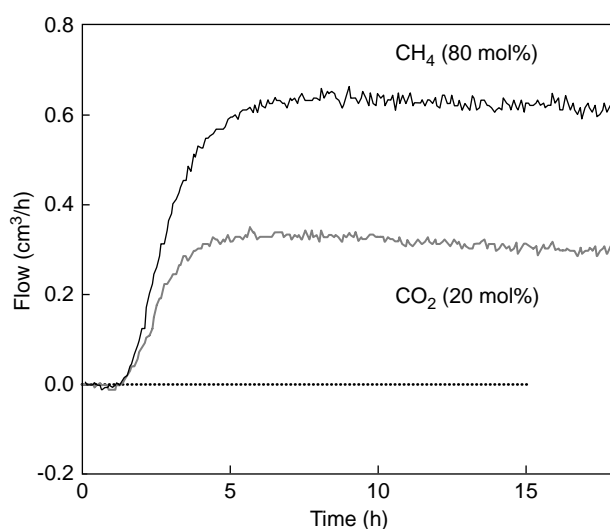


Figure 14
Mixed-gases (80% CH₄-20% CO₂) permeation curve in MDPE at 80°C.

CONCLUSIONS

Due to the increase of the constraints linked to environment safeguard, greenhouse effect, motor pollution, the decrease of the emanations of polluting and toxic products in the atmosphere become a crucial problem. In the field of polymers, this reduction needs a better knowledge of the fluid transport phenomena in these materials. Although a number of equipment was developed, as described in the bibliographical part, they remain generally dedicated to particular applications. So, these experimental techniques use material samples (thin films, pellets, very small masses, etc.) and operating conditions (low pressure and temperature, single gas, etc.) which are often little representative of the industrial necessities.

In the oil domain, especially that of the flexible pipes for hydrocarbon transport, some specific apparatus have been developed to perform permeation tests at high pressures (1 to 100 MPa) and high temperatures (40° in 200°C) on polymer samples of relatively high thickness (0.5 to 6 mm) in the presence of gas such as CH₄, CO₂ or H₂S.

Thanks to these devices, the objectives which it is possible to reach now are:

- the acquisition of experimental data essential for the design of industrial components;
- the quantification of the influence of some parameters on the transport coefficients, such as the presence of additives in polymers (plasticizers, fillers, etc.), the dependence of the diffusion coefficient on the concentration, or, still, the effect of very high pressures;
- the development of the knowledge about gas mixtures transport phenomena to get closer to industrial situations.

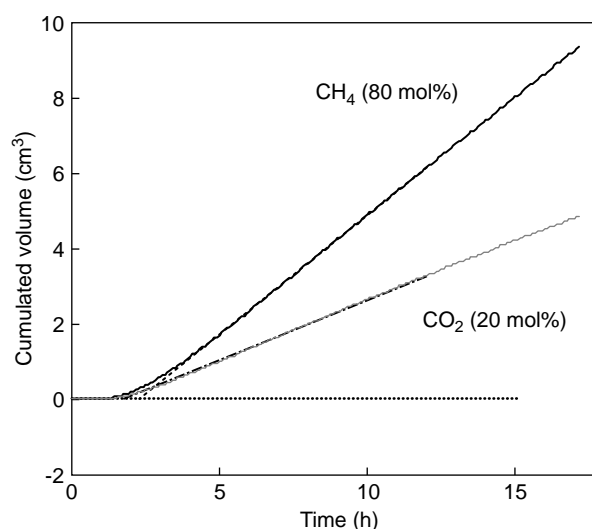


Figure 15
Mixed-gases (80% CH₄-20% CO₂) cumulated volume versus time for MDPE at 80°C.

All these data should turn out very useful for the development of models adapted to the description of gas transport phenomena in polymers.

REFERENCES

- Stern, S.A (1994) Polymers for Gas Separations. *J. Memb. Sci.*, **94**, 1-65, Academic Press, New York.
- Felder, R.M. and Huvard, G.S. (1980) Permeation, Diffusion, and Sorption of Vapors, in *Methods of Experimental Physics*, **16C**, 315-377, Academic Press, New York.
- Rogers, C.E. (1985) Permeations of Gases and Vapours in Polymers, in *Polymer Permeability*, Comyn, J. (ed.), Elsevier Applied Science, 11-73.
- Koros, W.J. and Hellums, M.W. (1985) Transport Properties, in *Encyclopedia of Polymer Science and Technology*, **Sup**, John Wiley & Sons, 725-802.
- Stancel, A.F. (1971) Diffusion through Polymers, in *Polymers Science and Materials*, Wiley Interscience, 247-274.
- Crank, J. (1975) *The Mathematics of Diffusion*, 2nd ed., Clarendon Press, Oxford.
- Crank, J. and Park, G.S. (1968) *Diffusion in Polymers*, Academic Press.
- Neogi, P. (1996) Transport Phenomena in Polymer Membranes, in *Diffusion in Polymers*, Marcel Dekker Inc., New York, 173-210.
- Naylor, T.V. (1989) Permeation Properties, in *Comprehensive Polymer Science*, **2**, 643-668, Pergamon Press.
- Rogers, C.E. (1964) Permeability and Chemical Resistance, in *Engineering Design for Plastics*, Baer, E. (ed.), Reinhold, New York, 609-688.
- Ash, R. and Barrie, J.A. (1986) Time Lag in Diffusion. *J. Appl. Polym. Sci.*, **31**, 1209-1218.
- Rutherford, S.W. (2001) Polymer Permeability and Time Lag at High Concentrations of Sorbate. *J. Memb. Sci.*, **31**, 101-107.
- Ash, R. (1996) Transient-State Transport in some Finite Systems. Part III: Some Historical and Hitherto Largely-Unexplored Aspects of Time-Lag Theory. *J. Memb. Sci.*, **117**, 79-108.
- Comyn, J. (1985) Introduction to Polymer Permeability and the Mathematic of Diffusion, in *Polymer Permeability*, Comyn, J. (ed.), Elsevier Applied Science, 1-11.
- Lomax, M.L. (1979) Permeability Review, in *Rapra Members Report No. 33*.
- Brown, R.P. (1981) Permeability, in *Handbook of Plastics Tests Methods*, 2nd ed., G. Godwin Limited, 378-394.
- Stannet, V. and Yasuda, H. (1965) The Measurement of Gas and Vapor Permeation and Diffusion in Polymers, in *Testing of Polymers*, Interscience Publishers, 393-418.
- Kamiya, Y., Mizoguchi, K., Naito, Y. and Hirose, T. (1986) Gas Sorption in Poly(vinyl benzoate). *J. Polym. Sci. Part B: Polym. Phys.*, **24**, 535-547.
- Kamiya, Y., Hirose, T., Mizoguchi, K. and Naito, Y. (1986) Gravimetric Study of High-Pressure Sorption of Gases in Polymers. *J. Polym. Sci. Part B: Polym. Phys.*, **24**, 1525-1539.
- Lee, J.G. and Flumerfelt, R.W. (1995) Nitrogen Solubilities in Low-Density Polyethylene at High Temperatures and High Pressures. *J. Appl. Polym. Sci.*, **58**, 2213-2219.
- Wong, B., Zhang, Z. and Handa, Y.P. (1998) High-Precision Gravimetric Technique for Determining the Solubility and Diffusivity of Gases in Polymers. *J. Polym. Sci. Part B: Polym. Phys.*, **36**, 2025-2032.
- Chaudhary, B.I. and Johns, A.I. (1998) Solubilities of Nitrogen, Isobutane and Carbon Dioxide in Polyethylene. *J. of Cell Plast.*, **34**, 312-328.
- Wang, N.H., Takishima, S. and Matsuoka, H. (1994) Measurement and Correlation of Solubility of a High Pressure Gas in a Polymer by Piezoelectric Quartz Sorption-CO₂ + PVAc and CO₂ + PBMA Systems. *Int. Chem. Eng.*, **34**, 255-262.
- Miura, K., Otake, K., Kurosawa, S., Sako, T., Sugeta, T., Nakane, T., Sato, M., Tsuji, T., Hiaki, T. and Hongo, M. (1998) Solubility and Adsorption of High Pressure Carbon Dioxide to Poly(styrene). *Fluid Phase Equilibria*, **144**, 181-189.
- Briscoe, B.J., Lorge, O., Wajs, A. and Dang, P. (1998) Carbon Dioxide-Poly(vinylidene fluoride) Interactions at High Pressure. *J. Polym. Sci. Part B: Polym. Phys.*, **36**, 2435-2447.
- Keller, J.U., Rave, H. and Staudt, R. (1999) Measurement of Gas Absorption in a Swelling Polymeric Material by a Combined Gravimetric-Dynamic Method. *Macromol. Chem. Phys.*, **200**, 2269-2275.
- Hilic, S. (2000) Mise au point d'une technique couplée, détecteur de fil vibrant et méthode PVT, pour la mesure simultanée du gonflement d'un polymère lors de l'absorption d'un fluide supercritique et de la solubilité du fluide dans le polymère. *PhD Thesis*, University of Clermont-Ferrand, France.
- Rodgers, P.A. (1993) Pressure-Volume-Temperature Relationships for Poly(vinylidene fluoride) and Polyamide-11. *J. Appl. Polym. Sci.*, **50**, 2075-2083.
- Chiu, C.P., Liu, K.A. and Wei, J.H. (1995) A Method for Measuring PVT Relationships of Thermoplastics Using an Injection Molding Machine. *Polym. Eng. Sci.*, **35**, 1505-1510.
- Togawa, J., Horiuchi, J.I., Kanno, T. and Kobayashi, M. (2001) Freeze-Purged-Desorption Method for Quantitative Evaluation of CO₂-Solubility in Polymeric Films. *J. Memb. Sci.*, **182**, 125-128.
- Naito, Y., Mizoguchi, K., Terada, K. and Kamiya, Y. (1991) The Effect of Pressure on Gas Permeation through Semicrystalline Polymers above the Glass Transition Temperature. *J. Polym. Sci. Part B: Polym. Phys.*, **29**, 457-462.
- Fitch, M.W., Koros, W.J., Nolen, R.L. and Carnes, J.R. (1993) Permeation of Several Gases through Elastomers, with Emphasis on the Deuterium/Hydrogen Pair. *J. Appl. Polym. Sci.*, **47**, 1033-1046.
- Naito, Y., Kamiya, Y., Terade, K., Mizoguchi, K. and Wang, J.S. (1996) Pressure Dependence of Gas Permeability in a Rubbery Polymer. *J. Appl. Polym. Sci.*, **61**, 945-950.
- Flaconèche, B. (1995) Perméabilité aux gaz de polymères semi-cristallins. *Thesis*, Conservatoire national des arts et métiers, Paris.
- Tokatli, K. and Özilgen, M. (1993) Temperature Effects on Permeation of Modified Atmosphere Gas Mixtures through a Low Density Polyethylene Package Film. *Polym. Inter.*, **30**, 109-113.

- 36 Costello, L.M. and Koros, W.J. (1993) Comparison of Pure and Mixed Gas CO₂ and CH₄ Permeabilities in Polycarbonate. *Ind. Eng. Chem. Res.*, **32**, 2277-2280.
- 37 Sada, E., Kumazawa, H. and Wang, J.S. (1992) Permeation of Binary Gas Mixture through Glassy Polymer Membranes with Concentration-Dependent Diffusivities. *J. Polym. Sci. Part B: Polym. Phys.*, **30**, 105-111.
- 38 Sada, E., Kumazawa, H., Xu, P. and Wang, S.T. (1990) Permeation of Mixed Gas in Glassy Polymer Membranes. *J. Appl. Polym. Sci.*, **40**, 1391-1399.
- 39 Chern, R.T., Koros, W.J., Yui, B., Hopfenberg, H.B. and Stannett, V.T. (1984) Selective Permeation of CO₂ and CH₄ through Kapton Polyimide: Effects of Penetrant Competition and Gas-Phase Nonideality. *J. Polym. Sci.: Polym. Phys. Ed.*, **22**, 1061-1084.
- 40 Stern, S.A., Mauze, G.R. and Frisch, H.L. (1983) Tests of a Free-Volume Model for the Permeation of Gas Mixtures through Polymer Membranes. CO₂-C₂H₄, CO₂-C₃H₈ and C₂H₄-C₃H₈ Mixtures in Polyethylene. *J. Polym. Sci.: Polym. Phys. Ed.*, **21**, 1275-1298.

Final manuscript received in April 2001